

THE STRUCTURE OF ATOMS – A BASIC QM TREATMENT

□ LEARNING OBJECTIVES

- The electronic structure of hydrogenic atoms: *Quantum Mechanical Model*
- To introduce the basic quantum mechanical principles of hydrogenic atomic structures, different types of quantum numbers, electron distributions, etc.

THE ELECTRONIC STRUCTURE OF HYDROGENIC ATOMS: *Quantum Mechanical Model*

Quantum Mechanics

- The main postulate of quantum mechanics establishes that the ***state of a quantum mechanical system*** is specified by a function called the ***wavefunction*** (ψ).
- The wavefunction is a ***function of*** the coordinates of the particle (the ***position***) and ***time***.
- The function: $|\psi(r)|^2 dV = \psi^*(r)\psi(r)dV$ is the ***probability*** that the particle lies in the volume element dV located at r .

Quantum Mechanics

□ Three additional postulates:

- Each **observable in classical mechanics** has an associated **operator in quantum mechanics**.
 - ✓ Examples of observables are *position, momentum, kinetic energy, total energy, angular momentum*, etc.
- An **operator** is defined to be a mathematical symbol that applied to a function gives a new function.
 - ✓ We have $\hat{A} f(x) = \phi(x)$, \hat{A} is an operator.
- Exceptionally the function $f(x)$ may be such that $\varphi(x)$ is proportional to $f(x)$; then we have $\hat{A} f(x) = \phi(x) = a f(x)$ where **a is some constant of proportionality**.
 - ✓ In this case $f(x)$ is called an **eigenfunction** of \hat{A} and **a** is the corresponding **eigenvalue**. ('eigen' in German means 'own' or 'inherent'.)
- The outcomes of any measurement of the observable associated with the operator \hat{A} are the eigenvalues **a** that satisfy the eigenvalue equation $\hat{A} f(x) = a f(x)$.
- The **average value** of the observable corresponding to \hat{A} is given by $\iiint_{-\infty}^{\infty} \psi^* \hat{A} \psi dV$ where dV is the differential of volume in the coordinates used to express ψ .

\hat{x} and $\hat{p} = -i\hbar\nabla$

they are called “fundamental operators”.

...Many operators are constructed from \hat{x} and \hat{p} ; for example, the Hamiltonian for a single particle:

$$H = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$$

where $\frac{\hat{p}^2}{2m}$ is the K.E. operator and \hat{V} is the P.E. operator.

Example: Consider the function $f(x,t) = e^{i(kx-\omega t)}$.

This represents a wave travelling in x direction.

Operate on $f(x)$ with the momentum operator:

$$\hat{p} f(x) = -i\hbar d/dx [f(x)] = (-i\hbar)(ik)e^{i(kx-\omega t)} = \hbar k f(x)$$

and since by the de Broglie relation $\hbar k$ is the momentum p of the particle, we have $\hat{p} f(x) = pf(x)$

Quantum mechanical operators for some physical observables.

Observable	symbol in classical physics	Operator in QM	Operation
Position	\mathbf{r}	$\hat{\mathbf{r}}$	multiply by \mathbf{r}
	p_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$
Momentum	p_y	\hat{p}_y	$-i\hbar \frac{\partial}{\partial y}$
	p_z	\hat{p}_z	$-i\hbar \frac{\partial}{\partial z}$
Kinetic Energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential Energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $\hat{V}(\mathbf{r})$
Total Energy	E	\hat{H}	$\hat{T} + \hat{V}$
Angular Momentum	l_x	\hat{l}_x	$-i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y})$
	l_y	\hat{l}_y	$-i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z})$
	l_z	\hat{l}_z	$-i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$

Table 11.3.1: Quantum mechanical operators for some physical observables.

THE ELECTRONIC STRUCTURE OF HYDROGENIC ATOMS: *Quantum Mechanical Model*

➤ *Quantum Mechanical Model* for a particle of mass m moving in one dimension (along x-axis) in a region where the potential energy is $V(x)$ the equation is given by the **Schrödinger equation which** takes the simple form:

➤
$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

where

- \hbar is the reduced Planck Constant where $\hbar=h/2\pi$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- E is the energy, a real number

- The term $d^2\psi(x)/dx^2$ can be thought of as a measure of how sharply the wavefunction $\psi(x)$ is curved.
- The **Schrödinger equation** is commonly written as
- $H \psi = E \psi$, where H is called the **hamiltonian** for the system.
- The Schrödinger equation is used to **calculate both the wavefunction ψ and the corresponding energy E** .
- The Schrödinger equation for *hydrogenic atom* is similar to the particle in one dimensional box, except in three dimensions.
- Consider a *hydrogenic atom (an atom or ion of arbitrary atomic number Z but having a single electron)*. Hydrogen itself is an example (with $Z = 1$).

- The potential energy $V(x)$ here is replaced by the Coulomb potential $V(r)$.
- The Coulomb potential energy of an electron in a hydrogenic atom of atomic number Z and therefore nuclear charge Ze is:

$$➤ V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

- ✓ where r is the distance of the electron from the nucleus and ϵ_0 is the vacuum permittivity.

- The *hamiltonian* for the entire atom, which consists of an electron and a nucleus of mass m_N , is therefore

$$\begin{aligned} \hat{H} &= \hat{E}_{k, \text{electron}} + \hat{E}_{k, \text{nucleus}} + \hat{V}(r) \\ &= -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \end{aligned}$$

Hamiltonian for a
hydrogenic atom

- The subscripts e and N on ∇^2 indicate differentiation with respect to the electron or nuclear coordinates.

The separation of variables

- Physical intuition suggests that the full Schrödinger equation ought to separate into two equations, one for the motion of the atom as a whole through space and the other for the motion of the electron relative to the nucleus.
- The Schrödinger equation for the internal motion of the electron relative to the nucleus is:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$
$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

Schrödinger
equation for a
hydrogenic atom

- where differentiation is now with respect to the coordinates of the electron relative to the nucleus. The quantity μ is called the **reduced mass**. The reduced mass is very similar to the electron mass because m_N , the mass of the nucleus, is much larger than the mass of an electron, so $1/\mu \approx 1/m_e$ and therefore $\mu \approx m_e$. In all except the most precise work, the reduced mass can be replaced by m_e .

- The variable r is the distance from the nucleus to the electron, or the magnitude of the blue vector r shown in Fig. 1.29 (and the red vector r shown in Fig. 5.1.)
- After rewriting the second derivatives in the Schrödinger equation in ***spherical coordinates*** (r, θ, ϕ), using the relationships in the caption of Figure 5.1, the equation looks impressively complicated, but it can be solved!
- The solution must be continuous in all three coordinates, and the radial portion must satisfy the boundary condition: $\psi \rightarrow 0$ as $r \rightarrow \infty$.
- This procedure leads to quantization of the energy and to equations for the associated wavefunctions just as we saw with the particle-in-a-box models.

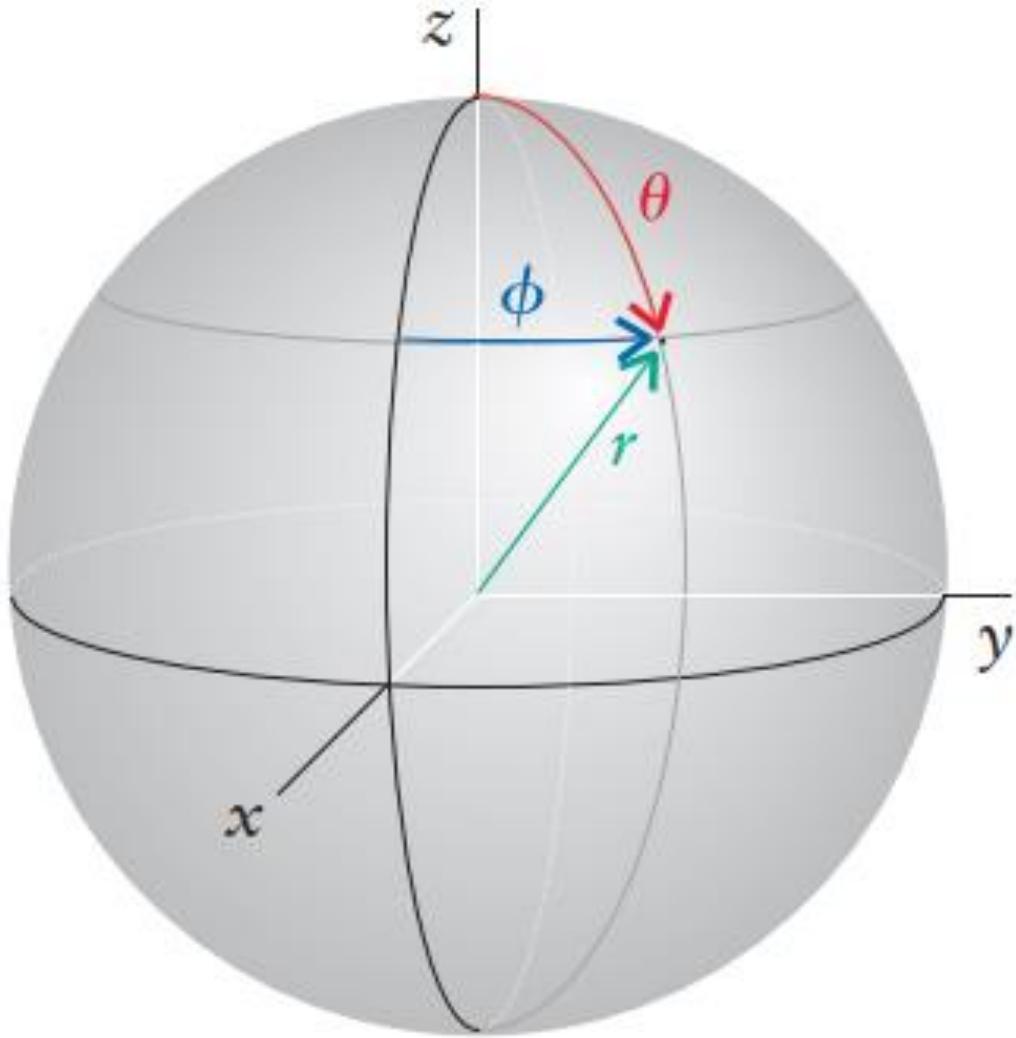


FIGURE 1.29 The spherical polar coordinates: r is the radius, which gives the distance from the center, θ is the *colatitude*, which gives the angle from the z -axis, and ϕ , the “longitude,” is the azimuth, which gives the angle from the x -axis.

Conventionally, θ is the angle from the z axis and ϕ is the angle from the x axis.

- Spherical coordinates are defined in Figure 5.1: r is the distance of the electron at P from the nucleus at O, and the angles θ and ϕ are similar to those used to locate points on the surface of the globe; θ is related to the latitude, and ϕ is related to the longitude.

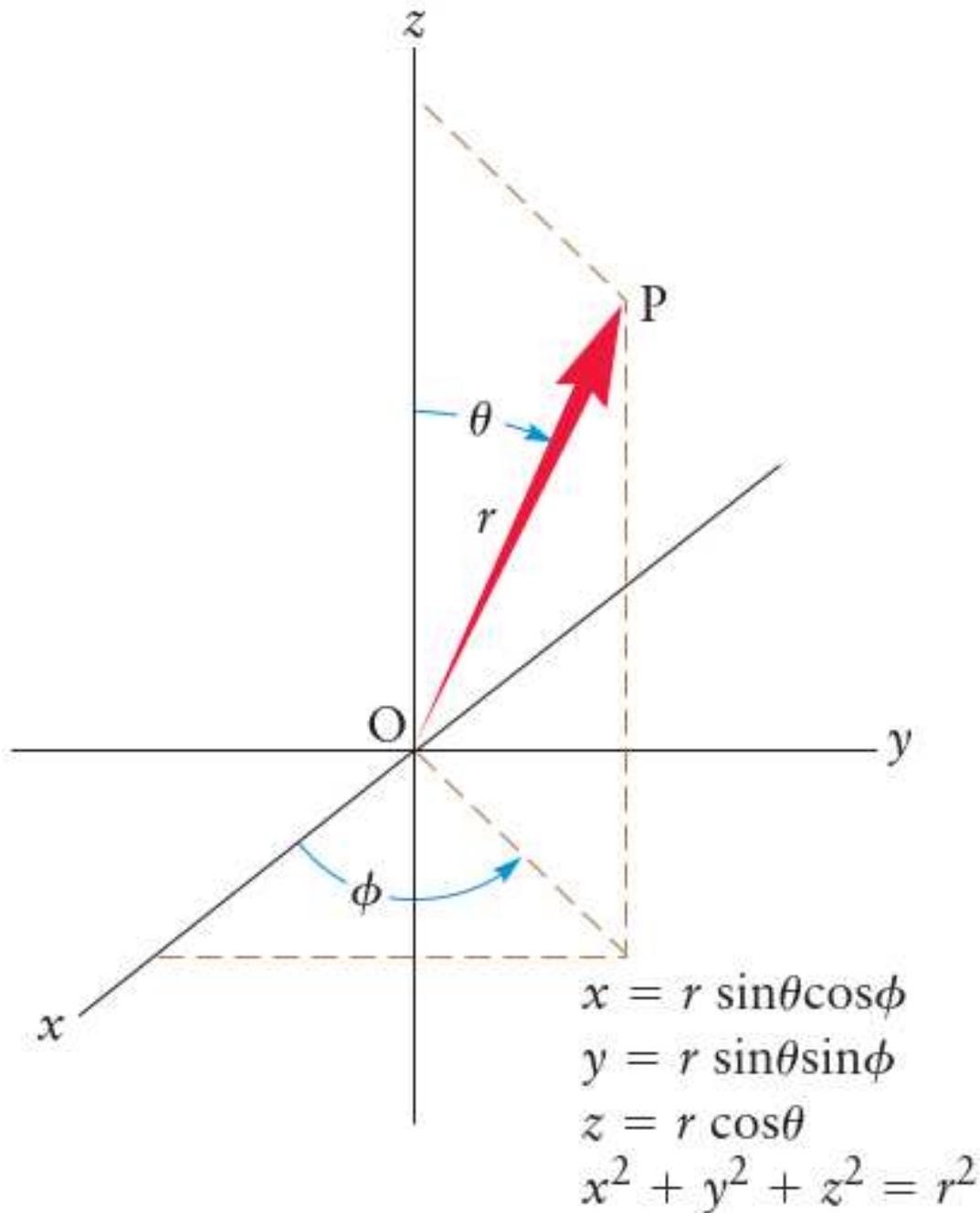


Figure 5.1 The relationship between spherical coordinates (r, θ, ϕ) and Cartesian coordinates (x, y, z) . Here, θ is the angle with respect to the Cartesian z -axis, which ranges from 0 to π , and ϕ is the azimuthal angle (the angle between the x -axis and the projection onto the x - y plane of the arrow from the origin to P), which ranges from 0 to 2π . Here, r is the distance of the electron from the nucleus at the origin, and ranges from 0 to ∞ .

- Each *wavefunction*, which in general varies from point to point, can be written as a function of the coordinates, $\psi(r, \theta, \phi)$.
- After substituting the polar coordinates for Cartesian coordinates and a very lengthy application of the chain rule, one gets the following Schrödinger eqn. in spherical polar coordinates:

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (4.2)$$

- Because the potential energy is *centrosymmetric* (independent of angle), the equation for the wavefunction is expected to be separable into radial and angular components.
- It turns out that *all the wavefunctions can be written as the product of a function that depends only on r and another function that depends only on the angles θ and φ*.

➤ That is,

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

- The function $R(r)$ is called the ***radial wavefunction***; it tells us how the wavefunction varies as we move away from the nucleus in any direction.
- The function $Y(\theta, \phi)$ is called the ***angular wavefunction***; it tells us how the wavefunction varies as the angles θ and ϕ change.
- Thus, the above equation can be separated into a radial part and an angular part, such that the wave function ψ can be taken as the product of a radial function R and an angular function Y , as shown in Equation (4.3).

- Multiplication of both sides of Equation (4.2) by $2mr^2$, followed by the method of separation of variables yields the slightly more manageable form of the Schrödinger equation for the hydrogen atom given in Equation (4.4), where β is the separation constant and we have incorporated \hbar in with β .

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (4.3)$$

$$\frac{1}{R(r)} \left[\frac{d}{dR} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right] = -Y(\theta, \phi) \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = \beta \quad (4.4)$$

- Neither of the differential equations in Equation (4.4) is particularly easy to solve.

- *Owing to the separation of variables, however, each solution will consist of two parts: a radial wavefunction $R(r)$ and an angular wavefunction $Y(\theta, \phi)$.*
- The *solutions to the angular part* are referred to as the *spherical harmonics*, a fairly common type of function in a wide variety of physical problems.
- So a particular orbital solution can be written as:
- $\Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$
- Where $n = 1, 2, 3, \dots$
 - $l = 0, 1, \dots, n-1$
 - $m_l = -l, \dots, -2, -1, 0, +1, +2, \dots, l$
- The radial wave function is only dependent on n and l , while the angular wavefunction is only dependent on l and m_l .

- These *three numbers* in the *solutions* are known as *three different quantum numbers* (Q.N.): n , l , and m_l .
- These quantum numbers arise naturally in the course of mathematics *because of the requirement that acceptable solutions are well-behaved functions*.
- This is in contrast to the older theory where the quantum numbers had to be added, apparently arbitrarily, to the classical description. The details of these calculations is too complicated to be discussed here.

- The three quantum numbers can only assume certain values.
- **1. PRINCIPAL QUANTUM NUMBER (n)** - Represents the **main energy level, or shell, occupied by an electron**. It is always a positive integer, that is $n = 1, 2, 3 \dots$
- **2. SECONDARY QUANTUM NUMBER (l ; Azimuthal (Orbital Angular Momentum Q.N.)** - Represents the energy sublevel, or **type of orbital**, occupied by the electron. The value of l depends on the value of n such that $l = 0, 1, \dots n-1$. This number is sometimes also called *azimuthal*, or *subsidiary*.
- **3. MAGNETIC QUANTUM NUMBER (m_l)** - Represents the number of possible orientations in 3-D space for each type of orbital. Since the type of orbital is determined by l , the value of m_l ranges between $-l$ and $+l$ such that $m_l = -l, \dots 0, \dots +l$.

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l \dots\dots$$

- The allowed values of the square of the angular momentum L and its z-projection are given by:

$$\text{Allowed values of } L^2 = \ell(\ell + 1) \frac{\hbar^2}{4\pi^2} \quad \ell = 0, 1, \dots, n - 1$$

$$\text{Allowed values of } L_z = m \frac{\hbar}{2\pi} \quad m = -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell$$

- For $n = 1$ (the ground state), the only allowed values for the angular momentum quantum numbers are ($\ell = 0, m = 0$). For $n = 2$, there are $n^2 = 4$ allowed sets of quantum numbers:

$$(\ell = 0, m = 0), (\ell = 1, m = 1), (\ell = 1, m = 0), (\ell = 1, m = -1)$$

- The orbitals of a shell with principal quantum number n therefore fall into **n subshells**, groups of orbitals that have the same value of l .
- Value of l 0 1 2 3.....
- Orbital type s p d f.....
- The labels come from the fact that spectroscopic lines were once classified as sharp, principal, diffuse, and fundamental.*next label...?*

- As its name suggests, l tells us the orbital angular momentum of the electron, a measure of the rate at which (in classical terms) the electron “circulates” round the nucleus:
- Orbital angular momentum = $\{l(l + 1)\}^{1/2} h/2\pi$
- An electron in an s-orbital (an “s-electron”), for which $l = 0$, has zero orbital angular momentum.
 - ✓ That means that we should imagine it not as circulating around the nucleus but simply as distributed evenly around it.
- An electron in a p-orbital ($l = 1$) has nonzero orbital angular momentum (of magnitude????); so, it can be thought of as circulating around the nucleus.
- An electron in a d-orbital ($l = 2$) has a higher orbital angular momentum, one in an f-orbital ($l = 3$) has an even higher angular momentum, and so on.

- The third quantum number required to specify an orbital is m_l , the magnetic quantum number, which distinguishes the individual orbitals within a subshell.
- This quantum number can take the values $m_l = l, (l - 1), \dots, 0, \dots, -l$.
- For example, when $l = 1$ (p-orbital), $m_l = 1, 0, -1$; so, there are three p-orbitals in a given shell.
- Alternatively, we can say that a subshell with $l = 1$ consists of three orbitals.
- The magnetic quantum number tells us the *orientation of the orbital motion of the electron*.
- Specifically, it tells us that the orbital angular momentum around an arbitrary axis is equal to $m_l \hbar / 2\pi$, the rest of the orbital motion (to make up the full amount of $\{l(l + 1)\}^{1/2}$) being around other axes.

- The equation does separate, and the two contributions to the wavefunction are solutions of two equations:

$$\nabla^2 Y = -l(l+1)Y$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right) + V_{\text{eff}} R = ER \quad \text{where} \quad V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

- The **first** Equation is the same as the *Schrödinger equation for a particle free to move at a constant radius around a central point*. The ***allowed solutions*** (*Angular wavefunctions*) are the spherical harmonics, and are **specified by the quantum numbers l and m_l** .
- The **second** Equation is called *the radial wave equation*. The radial wave equation describes the motion of a particle of mass μ in a one-dimensional region $0 \leq r < \infty$ where the potential energy is $V_{\text{eff}}(r)$.

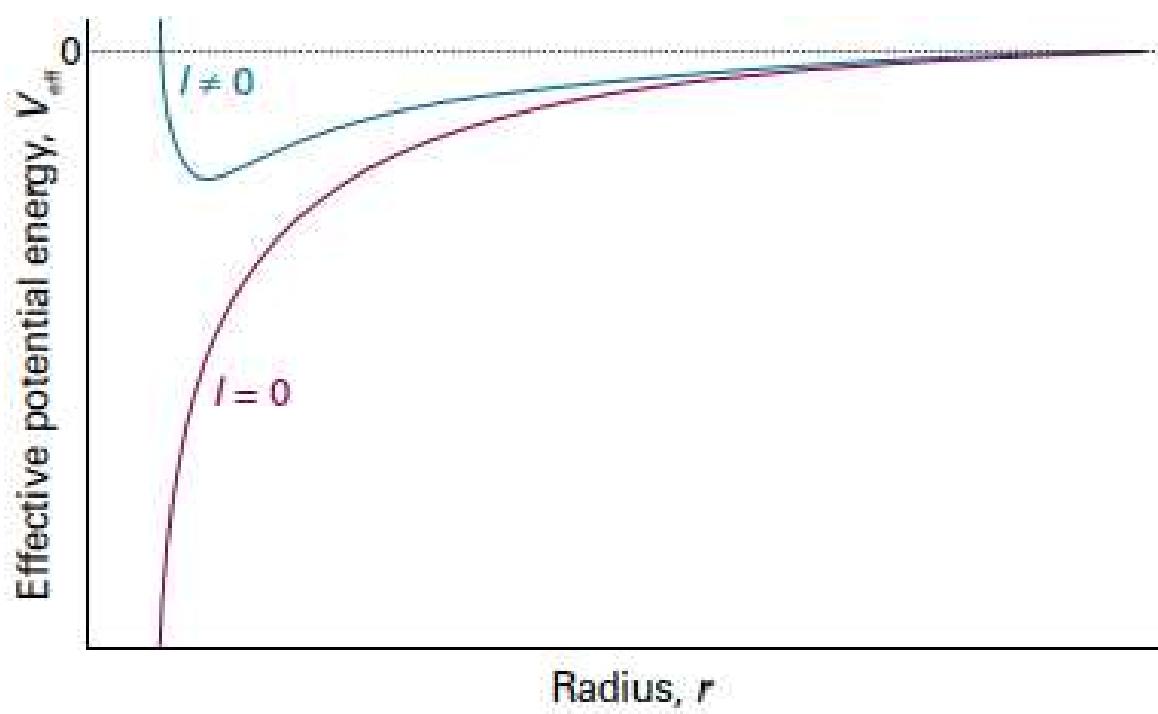
The radial solutions

- *Some features* of the shapes of the *radial wavefunctions* can be anticipated by examining the form of $V_{\text{eff}}(r)$.

$$V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

- The *first term* in the eqn. is the *Coulomb potential energy* of the electron in the field of the nucleus.
- The *second term* stems from what in classical physics would be called the *centrifugal force* arising from the angular momentum of the electron around the nucleus.
- When $l = 0$, the electron has **no angular momentum**, and the effective potential energy is *purely Coulombic*, and the *force exerted on the electron is attractive at all radii* (Fig. 8A.2).

- When $l \neq 0$, the centrifugal term gives a *positive contribution* to the effective potential energy, corresponding to *a repulsive force at all radii*.
- When *the electron is close to the nucleus ($r \approx 0$)*, *the positive contribution to the potential energy (which is proportional to $1/r^2$) dominates the Coulombic contribution (which is proportional to $1/r$)*, and the *net result* is an *effective repulsion of the electron from the nucleus*.
- The two effective potential energies, the one for $l = 0$ and the one for $l \neq 0$, are therefore qualitatively *very different close to the nucleus*.
- However, *they are similar at large distances* because the centrifugal contribution tends to zero more rapidly (as $1/r^2$) than the Coulombic contribution (as $1/r$).
- Therefore, the solutions with $l = 0$ and $l \neq 0$ are expected to be quite different near the nucleus but similar far away from it.



$$V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Figure 8A.2 The effective potential energy of an electron in the hydrogen atom.

- ✓ When the electron has ***zero orbital angular momentum*** ($l = 0$), the effective potential energy is the ***Coulombic potential energy***.
- ✓ When the electron has ***non-zero orbital angular momentum*** ($l \neq 0$), ***the centrifugal effect gives rise to a positive contribution which is very large close to the nucleus***.
- ✓ The $l = 0$ and $l \neq 0$ wavefunctions are therefore ***very different near the nucleus***.

- The *detailed solution* of the radial equation for the full range of radii shows how the form r^l close to the nucleus blends into the *exponentially decaying form at great distances*.
- It turns out that the two regions are bridged by a *polynomial* in r and that

$$R(r) = r^l L(r) e^{-r}$$

Dominant
 close to the Bridges the two
 nucleus ends of the function Dominant far
 from the nucleus

$$R(r) = \overbrace{r^l}^{\text{Dominant close to the nucleus}} \times \overbrace{(\text{polynomial in } r)}^{\text{Bridges the two ends of the function}} \times \overbrace{e^{-r}}^{\text{Dominant far from the nucleus}}$$

- The radial wavefunction therefore has the form:

$$R(r) = r^l L(r) e^{-r}$$

- ✓ with various constants and where $L(r)$ is the bridging polynomial.
- Close to the nucleus ($r \approx 0$) the polynomial is a constant and $e^{-r} \approx 1$, so $R(r) \propto r^l$; far from the nucleus the dominant term in the polynomial is proportional to r^{n-l-1} , where **n is an integer**, so regardless of the value of l , all the wavefunctions of a given value of n are proportional to $r^{n-1}e^{-r}$ and decay exponentially to zero in the same way (exponential functions e^{-x} always dominate simple powers, x^n).
- The detailed solution also shows that, for **the wavefunction to be acceptable, the value of n that appears in the polynomial can take only positive integral values, and specifically $n = 1, 2, \dots$**
- **This number** also determines the **allowed energies** through the expression as shown later.

- Two features of the radial wavefunction are important (physical interpretation):
 - Close to the nucleus the radial wavefunction is proportional to r^l , and *the higher the orbital angular momentum, the less likely it is that the electron will be found there* (Fig. 8A.3).
 - *Far from the nucleus all radial wavefunctions approach zero exponentially.*

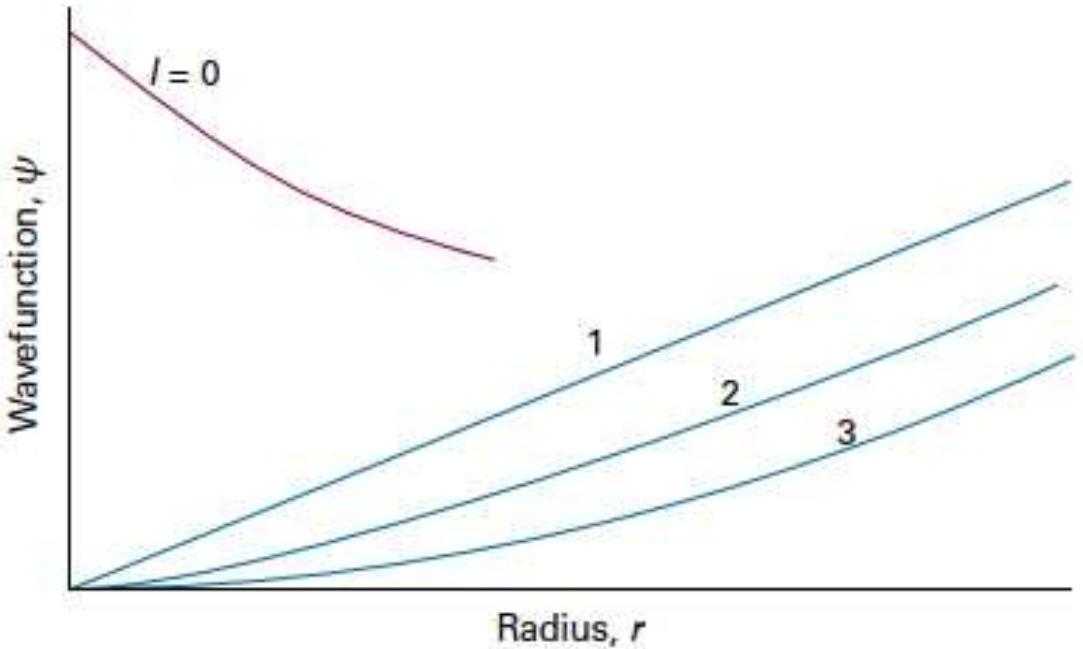


Figure 8A.3 Close to the nucleus, orbitals with $l = 1$ are proportional to r , orbitals with $l = 2$ are proportional to r^2 , and orbitals with $l = 3$ are proportional to r^3 . *Electrons are progressively excluded from the neighbourhood of the nucleus as l increases.* An orbital with $l = 0$ has a finite, non-zero value at the nucleus.

- The mathematical expressions for atomic orbitals—which are obtained as solutions of the Schrödinger equation—are more complicated than the sine functions for the particle in a box, but their essential features are straightforward.
- Moreover, we must never lose sight of *their interpretation*, that the ***square of a wavefunction tells us the probability density*** of an electron at each point.
- To visualize this probability density, imagine a cloud centered on the nucleus. The density of the cloud at each point represents the probability of finding an electron there.
- Denser regions of the cloud therefore represent locations where the electron is more likely to be found.

Hydrogen Atom

- The simplest case to consider is the hydrogen atom, with one positively charged proton in the nucleus and just one negatively charged electron orbiting around the nucleus.
- It is important to understand the orbitals of hydrogen, not only because hydrogen is an important element, but also because they serve as building blocks for understanding the orbitals of other atoms.

Atomic Orbitals and their energies

- We need to find the ***wavefunctions***.
 - ***Knowing the form of the wavefunctions allows us to go beyond the information provided by spectroscopy*** and determine not only the allowed energies of the electron in a hydrogen atom but also ***how the electron is distributed around the nucleus***.
 - ***The wavefunctions of electrons in atoms are called atomic orbitals.***
 - The name was chosen to suggest something less definite than an “orbit” of an electron around a nucleus and to take into account the wave nature of the electron.
- ## ***How many quantum numbers*** are needed to specify the wavefunction of an electron in a hydrogen atom?

- We need to know, as we describe in more detail immediately below, that *each wavefunction is labeled by three quantum numbers*: n is related to the *size and energy* of the orbital, l is related to its *shape*, and m_l is related to its *orientation in space*.
- We have already encountered n , the *principal quantum number*, which specifies the energy of the orbital in a one-electron atom.
- *In a one-electron atom, all atomic orbitals with the same value of the principal quantum number n have the same energy* and are said to belong to the same shell of the atom.
- The name “*shell*” reflects the fact that as n increases, the region of greatest probability density is like a nearly hollow shell of increasing radius.
- The higher the number of the shell, the further away from the nucleus are the electrons in that shell.

The Principal Quantum Number (n)

- An electron in an atom is like a particle in a box, in the sense that it is confined within the atom by the pull of the nucleus.
- We can therefore expect the electron's wavefunctions to obey certain boundary conditions, like the constraints we encountered when fitting a wave between the walls of a container.
- As we saw for a particle in a box, these ***constraints result in the quantization of energy and the existence of discrete energy levels.***
- Even at this early stage, we can expect the electron to be confined to certain energies, just as the spectroscopic observations require.

- To ***find the wavefunctions and energy levels*** of an electron in a hydrogen atom, we must solve the appropriate Schrödinger equation.
- The potential energy of an electron of charge $-e$ at a distance r from a nucleus of charge $+e$ (the “Coulomb” potential energy) is

$$V(r) = \frac{(-e)(+e)}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r}$$

- Solving the Schrödinger equation for a particle with this potential energy, Schrödinger found (1927) that the allowed energy levels for an electron in a hydrogen atom are:

$$E_n = -\frac{\hbar R}{n^2} \quad R = \frac{m_e e^4}{8\hbar^3 \epsilon_0^2} \quad n = 1, 2, \dots$$

- These energy levels have exactly the form suggested spectroscopically, but now we also have an expression for R in terms of more fundamental constants.
- When the fundamental constants are inserted into the expression for R , the value obtained is 3.29×10^{15} Hz, the same as the experimental value of the **Rydberg constant**.
- This agreement is a triumph for Schrödinger's theory and for quantum mechanics.
- The integer n , called the principal quantum number, indexes the individual energy levels. These are identical to the energy levels predicted by the Bohr theory.
- *Quantization arises because of the physical boundary conditions imposed on the solutions to the Schrödinger equation rather than from making arbitrary assumptions about the angular momentum.*

- A very similar expression applies to other one-electron ions, such as He^+ and even C^{5+} , with atomic number Z (They differ only in the charge $+Ze$ on the nucleus, and therefore in the magnitude of the attractive force experienced by the electron.):

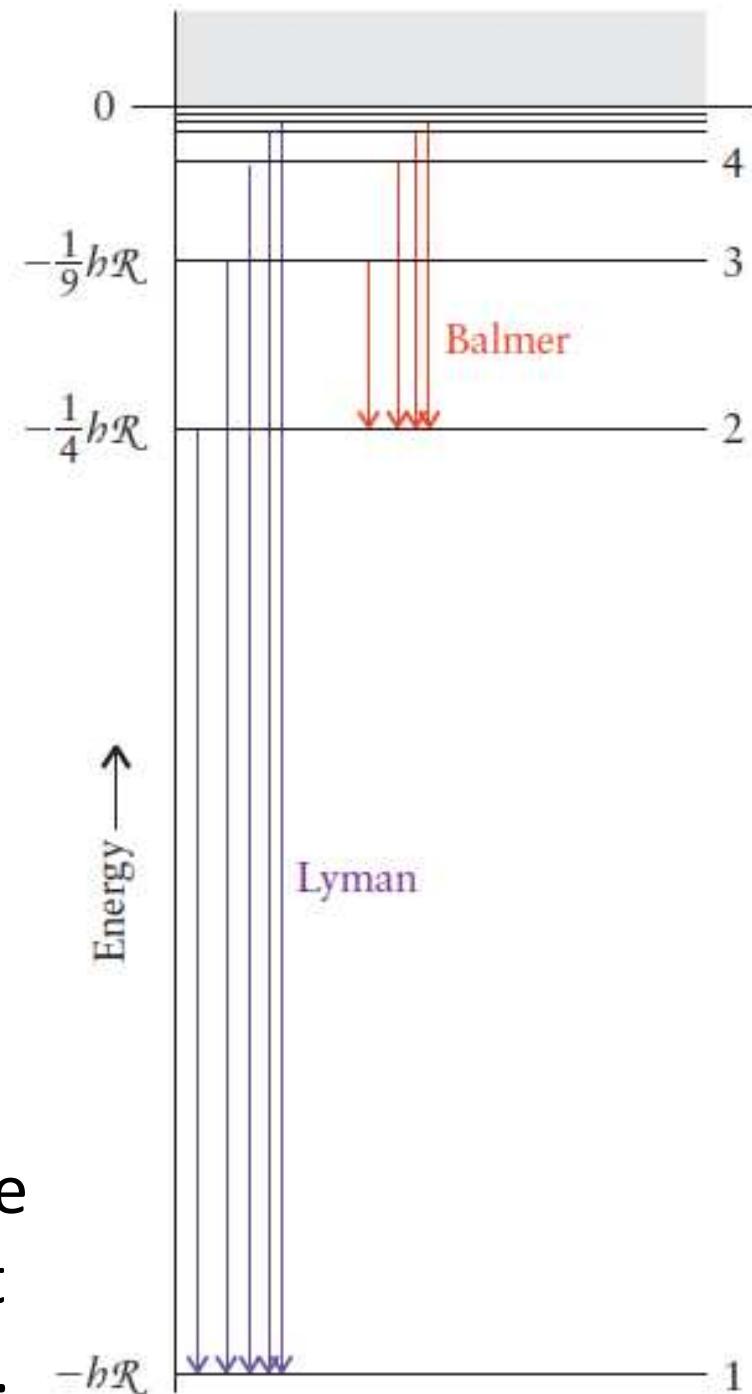
$$E_n = -\frac{Z^2 h \mathcal{R}}{n^2} \quad n = 1, 2, \dots$$

- What does this equation tell us?
 - ✓ All the ***energies are negative***, meaning that the electron has a lower energy in the atom than when it is far from the nucleus.
 - ✓ They refer to the **bound states** of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy).

- ✓ There are also solutions of the Schrödinger equation with *positive energies*. These solutions correspond to **unbound states** of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon.
- ✓ The energies of the ***unbound electron are not quantized*** and form the continuum states of the atom.
- Because **Z appears in the numerator**, we see that ***the greater the value of the nuclear charge the more tightly the electron is bound to a nucleus***.
- That **n appears in the denominator** shows that as *n* increases, the energy becomes less negative.

- Figure 1.28 shows the energy levels calculated.
- We see that they come closer together as n increases.
- Each level is labeled by the integer n , which is called the ***principal quantum number***, from $n = 1$ for the first (lowest, most negative) level, $n = 2$ for the second, continuing to infinity.
- The lowest energy possible for an electron in a hydrogen atom, $-hR$, is obtained when $n = 1$.
- ✓ This ***lowest energy state*** is called the ***ground state*** of the atom.

FIGURE 1.28 The permitted energy levels of a hydrogen atom as calculated above. The levels are labeled with the quantum number n , which ranges from 1 (for the lowest state) to infinity (for the separated proton and electron).



- A hydrogen atom is normally found in its ground state, with its electron in the level with $n = 1$.
- *When the bound electron is excited by absorbing a photon, its energy climbs up the ladder of levels as n increases.*
- *It reaches the top of the ladder, corresponding to $E = 0$ and freedom, when n reaches infinity.* At that point, the electron has left the atom. This process is called **ionization**.
- The difference in energy between the ground state and the ionized state is the energy required to remove an electron from the neutral atom in its ground state. The “**ionization energy**” itself, is the minimum energy needed to achieve ionization, with the electron removed from the orbital with $n = 1$ to a final state in which it has zero energy: *in this final state it is free of the nucleus and has zero kinetic energy.*
- **The energy levels of a hydrogen atom are defined by the principal quantum number, $n = 1, 2, \dots$** , and form a converging series, as shown in Fig. 1.28.

- The ***energy of a one-electron atom*** depends ***only*** on the ***principal quantum number n***, because the potential energy depends only on the radial distance.
- The Schrödinger equation also quantizes L^2 , the square magnitude of the angular momentum, as well as L_z , the projection of the angular momentum along the z-axis.
- Quantization of the square of the angular momentum as well as its projection along the z-axis requires ***two additional quantum numbers***.
- The ***angular momentum quantum number l***, may take on any integral value from 0 to $n - 1$, and the angular momentum projection quantum number m_l , may take on any integral value from $-l$ to l . The quantum number m_l is referred to as the ***magnetic quantum number*** because its value helps determine how the energy of the atom would shift when placed in an external magnetic field.

- Earlier, only the general form of the radial wavefunctions has been given. It is now time to show how they depend on various fundamental constants and the atomic number of the atom.
- For example, the *wavefunction corresponding to the ground state of the hydrogen atom* ($n = 1$) is

$$\psi(r, \theta, \phi) = \overbrace{\frac{2e^{-r/a_0}}{a_0^{3/2}}}^{\begin{matrix} R(r) \\ \text{---} \\ 2e^{-r/a_0} \end{matrix}} \times \overbrace{\frac{1}{2\pi^{1/2}}}^{\begin{matrix} Y(\theta, \phi) \\ \text{---} \\ 2\pi^{1/2} \end{matrix}} = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}} \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

- The quantity a_0 is called the **Bohr radius**; when the values of the fundamental constants are inserted, we find $a_0 = 52.9$ pm.
- What does this equation tell us?

❖ What does this equation tell us?

- The ***radial wavefunction $R(r)$ decays exponentially toward zero as r increases, which means that the probability density is highest close to the nucleus ($e^0 = 1$).***
- The Bohr radius tells us how sharply the wavefunction falls away with distance: when $r = a_0$, ψ has fallen to $1/e$ (37%) of its value at the nucleus.
- For this wavefunction, the ***angular wavefunction Y is a constant, independent of the angles***, which means that ***the wavefunction is the same in all directions.***
- We have seen the wavefunction for the ground state. What's about higher energy state wavefunctions?

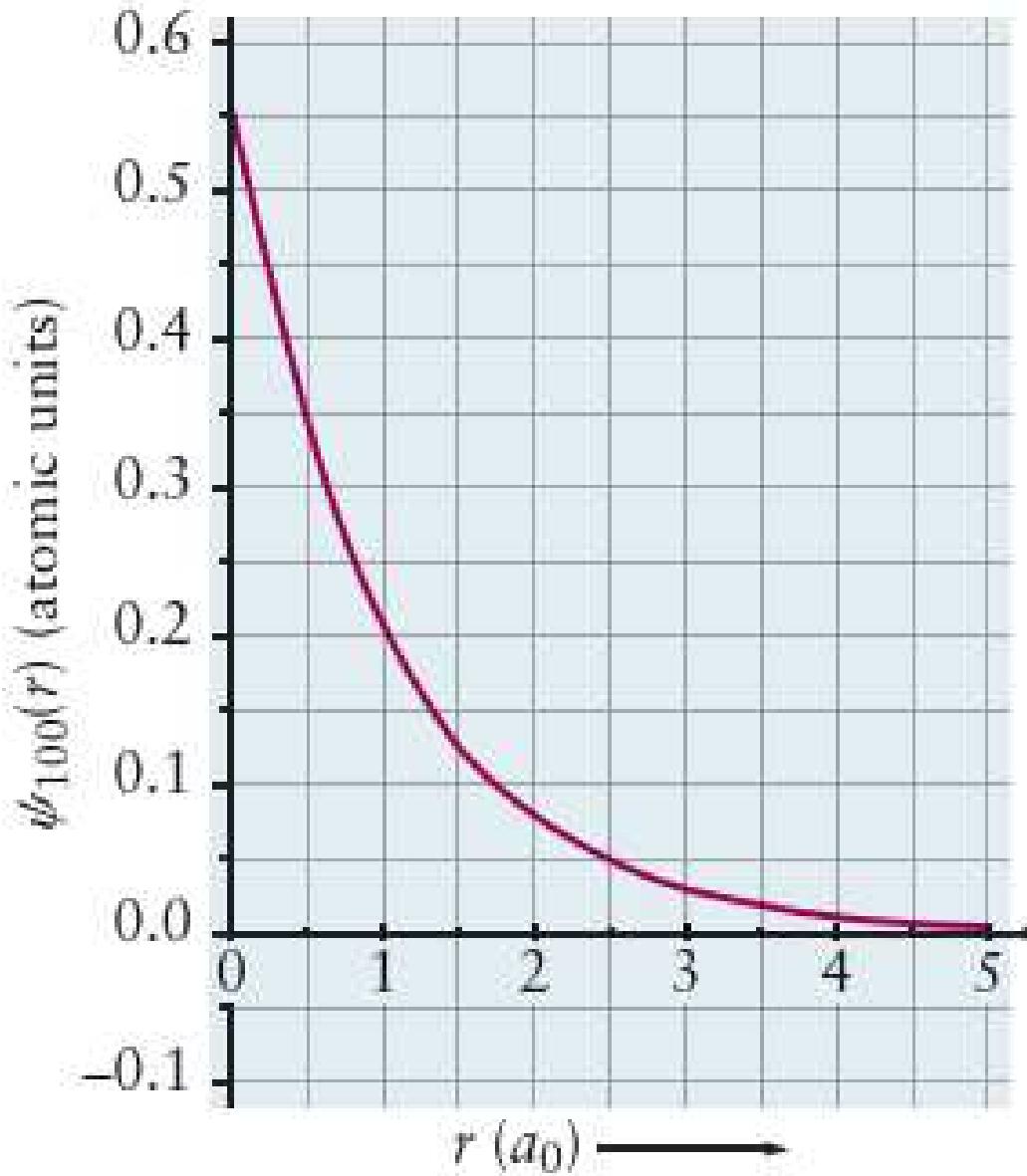


Figure 5.5 Plot of the hydrogen 1s orbital against distance from the nucleus.
The distance is measured in units of the Bohr radius a_0 .

- All the *higher energy levels have more than one wavefunction for each energy level.*
- One of the wavefunctions for the next higher energy level, with $n = 2$ and $E_2 = -(1/4) hR$, is

$$\psi(r, \theta, \phi) = \underbrace{\frac{1}{2\sqrt{6}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0}}_{R(r)} \times \underbrace{\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi}_{Y(\theta, \phi)}$$

$$= \frac{1}{4} \left(\frac{1}{2\pi a_0^5} \right)^{1/2} r e^{-r/2a_0} \sin \theta \cos \phi$$

- There are some more equations given below.

- ❖ The expressions for a number of other atomic orbitals are shown in Table 1.2a (for R) and Table 1.2b (for Y).

TABLE 1.2 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions			(b) Angular wavefunctions		
n	l	$R_{nl}(r)$	l	${}^n m_l$ [†]	$Y_{l,m_l}(\theta, \phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \sin\phi$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \sin\phi$
				zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \cos\phi$
				$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \cos 2\phi$
				z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2\theta - 1)$

* Note: In each case, $a_0 = 4\pi\epsilon_0^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

[†]In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l .

❖ What does this equation tell us?

- *The radial wave functions all show an exponential decay as the radius increases.*
- This wavefunction also falls exponentially toward zero as r increases.
- Notice, though, that the exponential function is multiplied by the factor r , so is zero at the nucleus (at $r = 0$) as well as far away from it.
- *The exponential decay is slower with increasing n because the denominator in the exponential term contains a factor of na_0 .*
- *Thus, the average radius (or size) of an orbital also increases with n .*
- We discuss the angular dependence shortly.

- For $n > 1$, the radial functions all have at least one radial node.
 - ✓ For the $2s$ orbital, for instance, which has the quantum numbers $n=2$, $l=0$, $m_l = 0$, the radial node occurs when $r = 2a_0/Z$ because this makes the second term in the parentheses zero ($a_0 = 52.9 \text{ pm}$, the Bohr radius).
- A **general rule** is that **there are $(n - l - 1)$ radial nodes** and **l angular nodes**. Thus, a $2s$ orbital has one radial node (no angular node), while a $2p$ orbital has no (zero) radial nodes but one angular node.
- ✓ For $n = 2$ and $l = 1$, there are 0 (zero) radial node and 1 angular node.

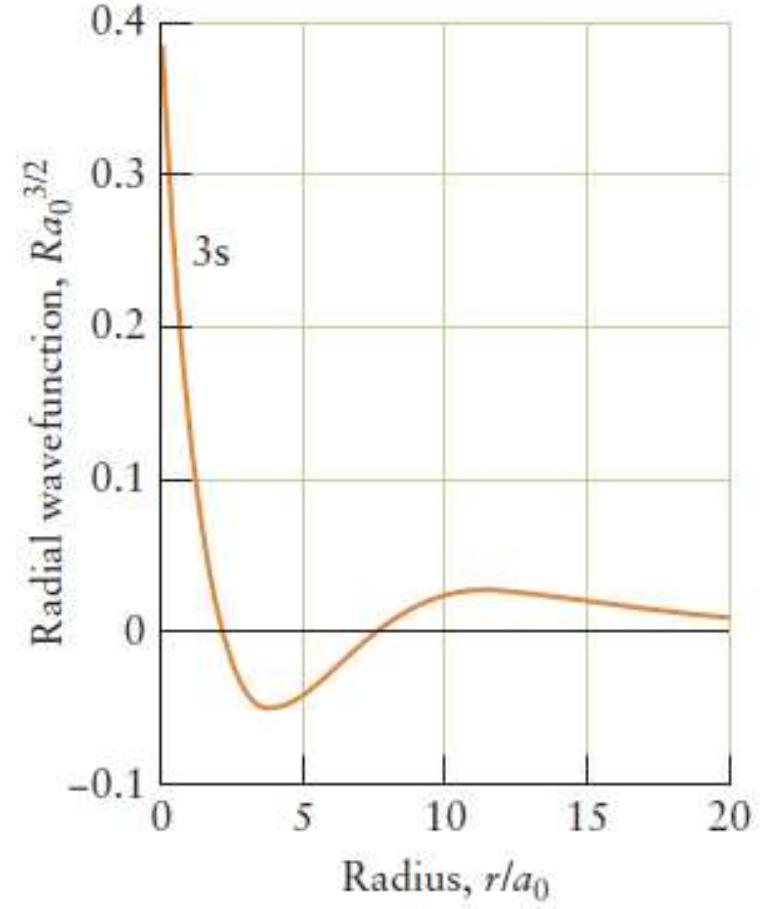
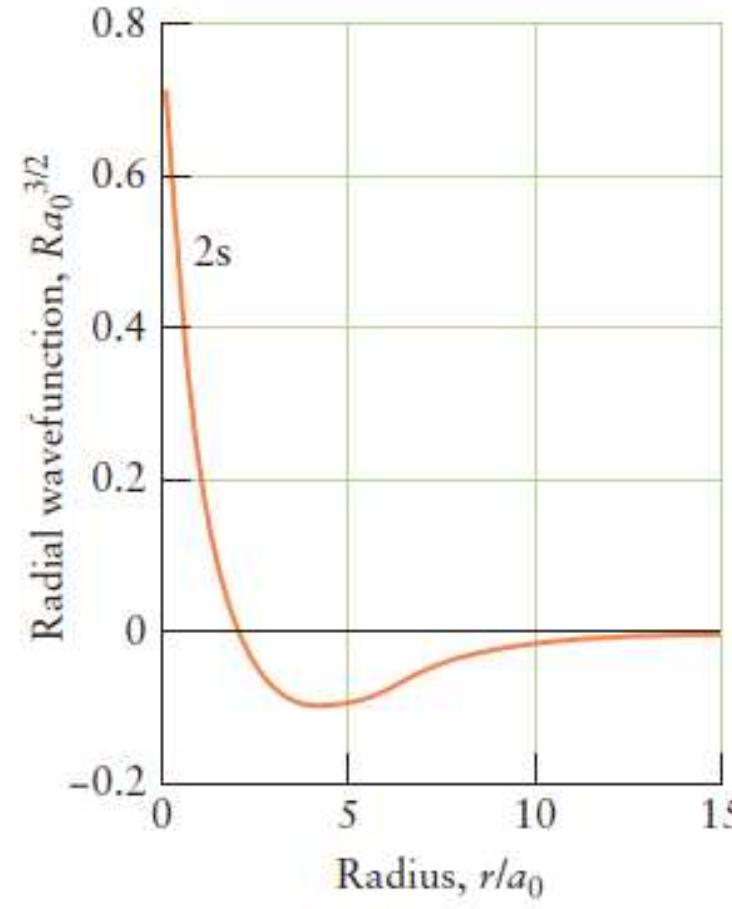
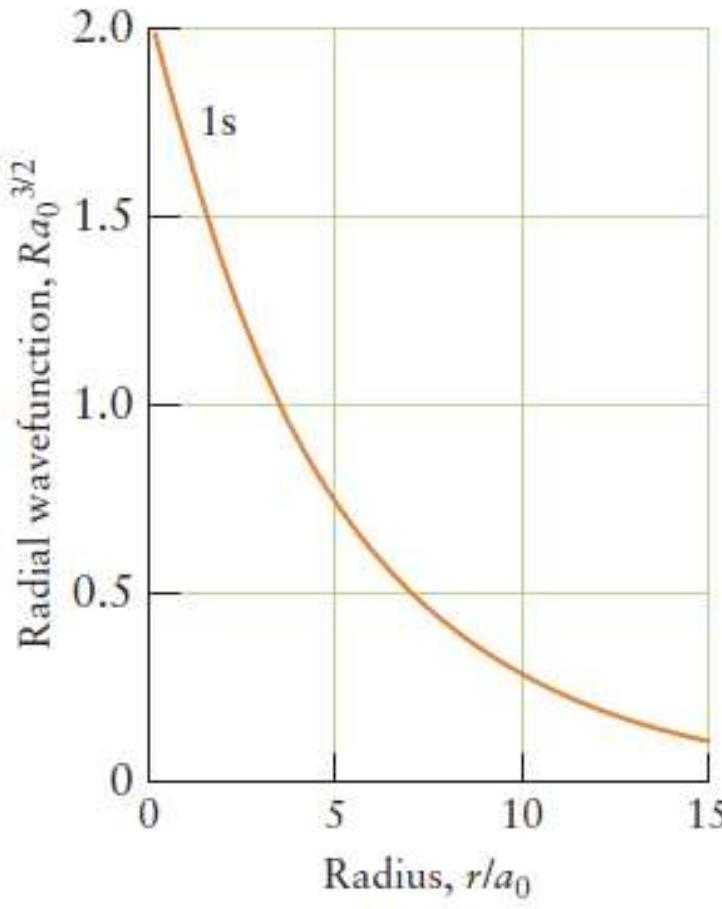


FIGURE 1.34 The radial wavefunctions of the first three s-orbitals of a hydrogen atom. Note that the number of radial nodes increases (as $n - 1$), as does the average distance of the electron from the nucleus. Because the probability density is given by 2 , all s-orbitals correspond to a nonzero probability density at the nucleus.

- The presence of the radial nodes is clearly indicated on the diagram.
- A second noteworthy feature is that the ***probability*** of the ***electron being close to the nucleus*** for a given value of n ***decreases*** in the order $s > p > d > f$.
- In other words, ***the s orbital “penetrates” the nucleus better than a p orbital having the same principal quantum number.***
- This fact is of ***utmost importance in the forthcoming section of shielding and influences a large number of an element’s chemical properties.***

- When the Schrödinger equation is solved in detail, it turns out that *three quantum numbers are needed to label each wavefunction* (because the atom is three-dimensional).
- The three quantum numbers are designated n , l , and m_l . However, it turns out that, for a hydrogen atom, wavefunctions with the ***same value of n all have the same energy (degenerate states: n^2)*** regardless of the values of the other two quantum numbers. (A set of equal energy levels is termed ***degenerate***.)
- $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < 5s = 5p = 5d = 5f < \dots$

- A more useful quantity than the *radial wave function* is the ***radial distribution function***, also called the ***radial probability function***.
- We use techniques to generate graphical representations of $(\psi_{nlm})^2$, where $|\psi_{nlm}|^2 dV$ is the probability of finding the electron in a small volume element dV .
- The ***radial distribution function is the probability that the electron will exist in a thin volume element dV at a distance r from the nucleus.***
- One way of visualizing this is to think of the volume element as a thin spherical shell, similar to one of the layers in an onion skin, existing at a distance r away from the nucleus.
- The volume element dV shown in Figure 4.2 represents a fraction of this “onion skin.”

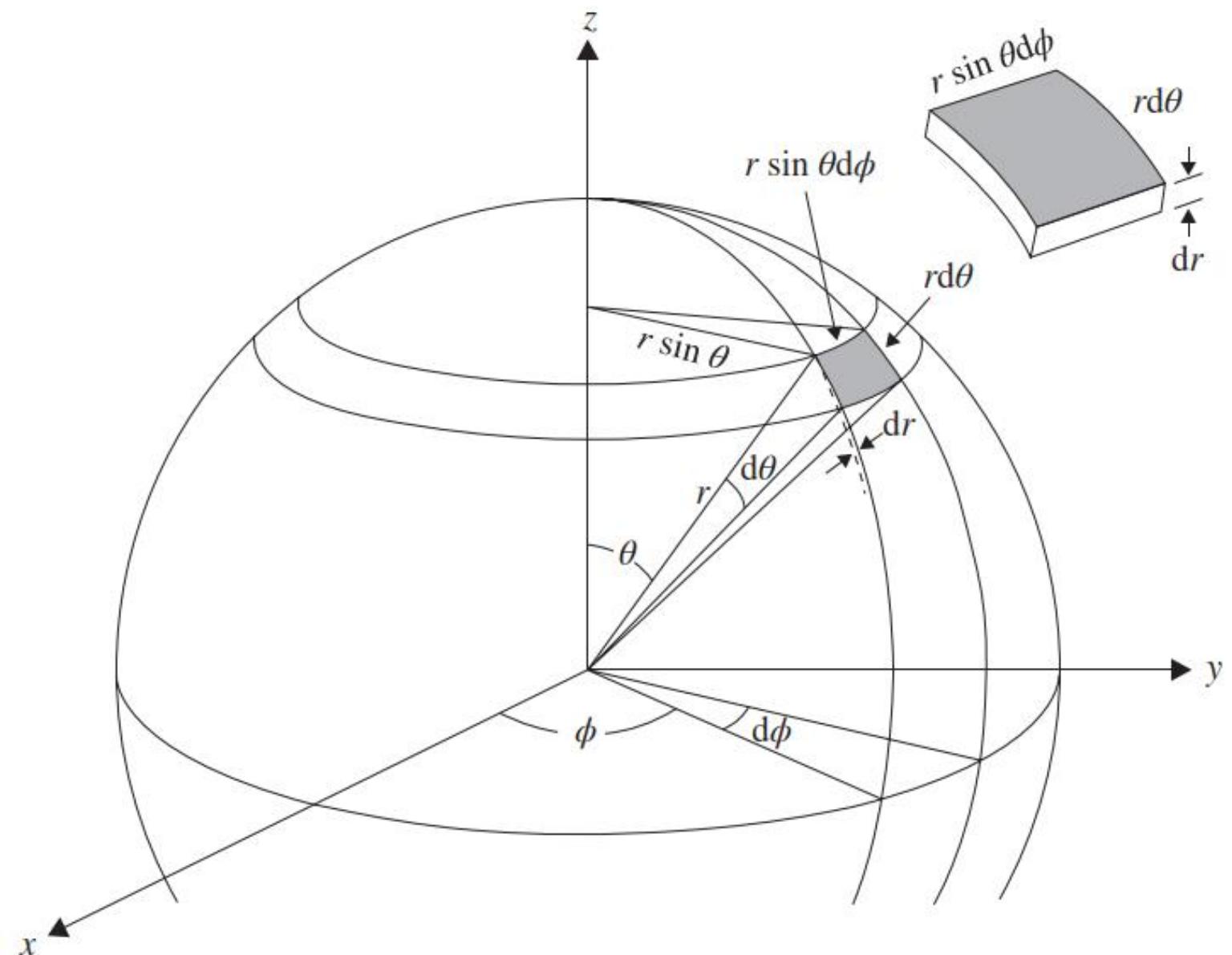


FIGURE 4.2.
Definition of the volume
element $d\tau$ in polar
coordinates:
 $d\tau = dV = r^2 \sin \theta dr d\theta d\phi$.

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McQuarrie, D. A.; Simon, J.
D. Physical Chemistry: A
Molecular Approach,
1997.]

- Because the probability of finding an electron in a given region of space goes as the square of the wavefunction (the Born interpretation), the radial distribution function is equal to $R(r)^2 dV$.
- The volume of a sphere is $V = (4/3)\pi r^3$, and therefore $dV/dr = 4\pi r^2$.
- Following substitution, the radial distribution function is defined as $4\pi r^2 R(r)^2 dr$.
- Plots of the radial distribution function for the first several types of orbitals in the hydrogen atom are shown in Figure 4.3.

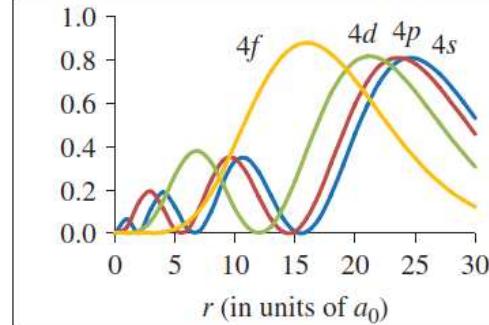
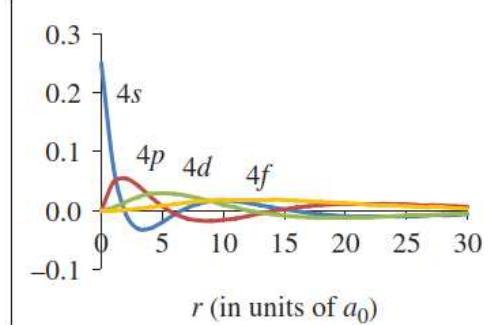
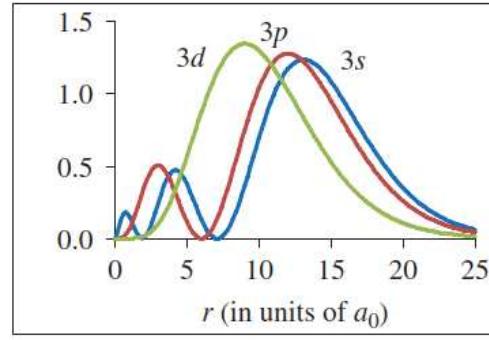
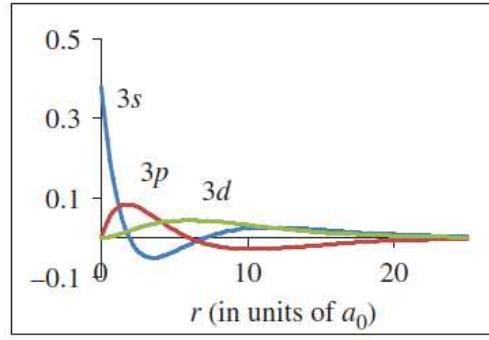
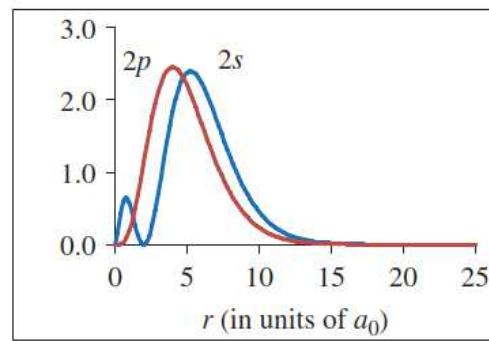
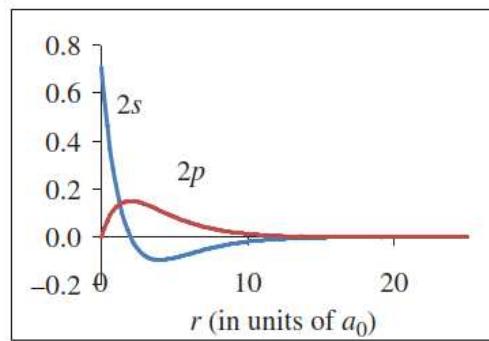
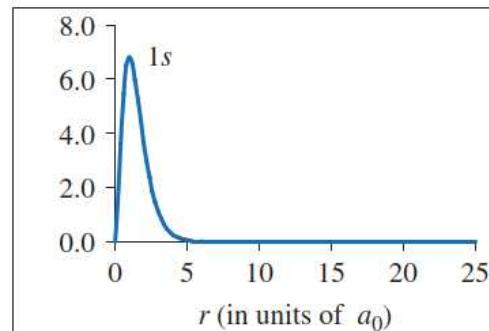
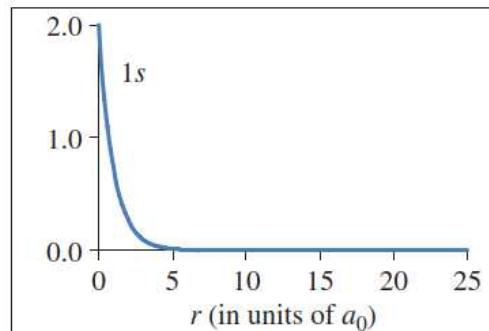


FIGURE 4.3
The radial function $R(r)$ (a) and
the *radial distribution function* (b)
for several types of orbitals in
the hydrogen atom. The y-scale
varies from one orbital to the
next.

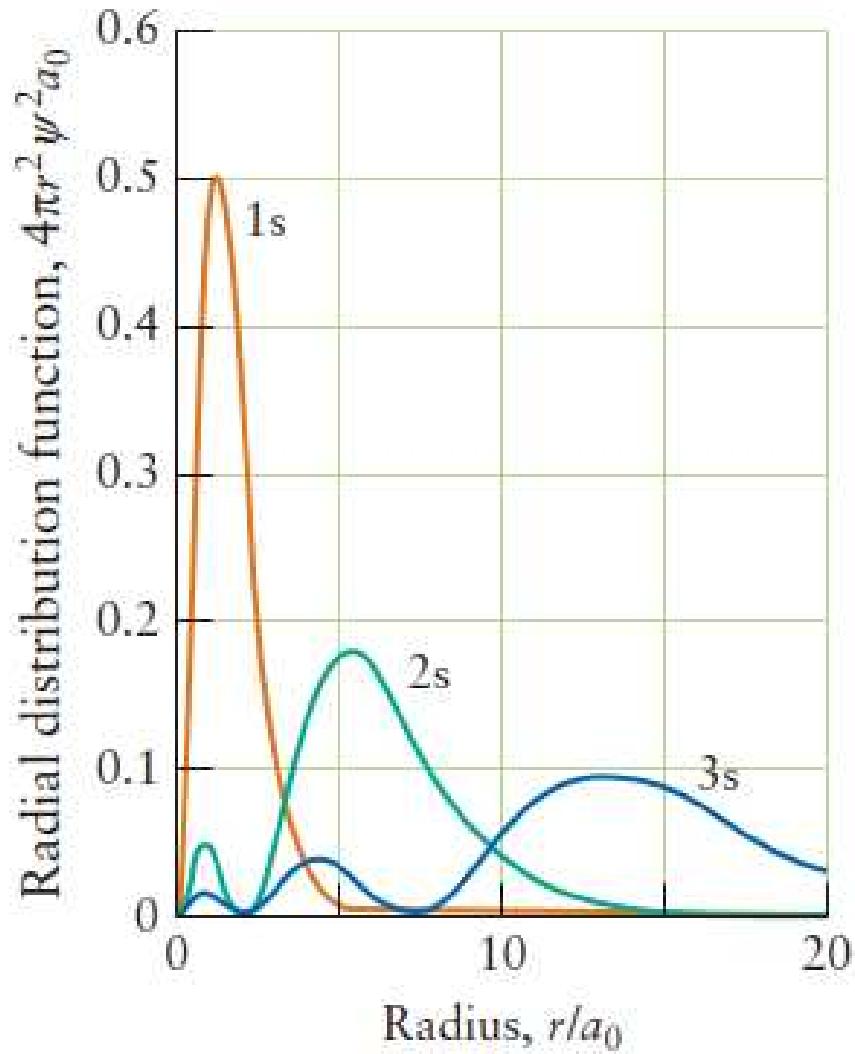


FIGURE 1.32 The radial distribution function tells us the probability density for finding an electron at a given radius summed over all directions. The graph shows the radial distribution function for the 1s-, 2s-, and 3s-orbitals in hydrogen. Note how the most probable radius (corresponding to the greatest maximum) increases as n increases.

Bohr Radius:

- ❖ Example 4-2. Show that the most probable radius for an electron in the 1s orbital of hydrogen is equal to the **Bohr radius**, a_0 .
- Solution:
 - ✓ The **most probable radius can be obtained from the highest peak in the radial distribution function**, because this function is a measure of the probability of finding an electron in a volume element at a certain distance from the nucleus.
 - ✓ Because the radial distribution function for a 1s orbital has a single peak, the radius at which this peak occurs can be calculated by taking the first derivative of the function with respect to r and setting it equal to zero.
 - ✓ For a 1s orbital, $R(r)$ and the first derivative of the radial probability function are

$$R(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$\begin{aligned}\frac{d(4\pi r^2 R^2)}{dr} &= \frac{d}{dr} \left[16\pi^2 \left(\frac{Z}{a_0} \right)^3 r^2 e^{-\frac{2Zr}{a_0}} \right] \\ &= 16\pi^2 \left(\frac{Z}{a_0} \right)^3 \left[2re^{-\frac{2Zr}{a_0}} - \frac{2Z}{a_0} r^2 e^{-\frac{2Zr}{a_0}} \right] = 0\end{aligned}$$

which implies that

$$\left[2r - \frac{2Z}{a_0} r^2 \right] = 0$$

Hence, $r = a_0/Z$. Because $Z = 1$ for H, $r = a_0 = 52.9 \text{ pm}$, the same result as in the Bohr model of the atom.

Radial Node:

Example 4-3. At what distance from the nucleus does the radial node in a 2s orbital occur?

Solution. The radial wave function for a 2s orbital is given here:

$$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right)^{3/2} e^{-\frac{Zr}{2a_0}}$$

Setting the middle term equal to zero, we find that $2 = \frac{Zr}{a_0}$ and hence $r = \frac{2a_0}{Z}$ = 106 pm.

Sizes and Shapes of Orbitals

- The sizes and shapes of the hydrogen atom orbitals are important in chemistry because they provide the foundations for the quantum description of chemical bonding and the molecular shapes to which it leads.
- Sizes and shapes of the orbitals are revealed by graphical analysis of the wave functions.

The Angular Wave Functions

- The *solutions to the angular part of the hydrogen atom* are known as the **spherical harmonics**.
- The angular wavefunctions $Y(\theta, \phi)$ depend on two variables and are therefore governed by the quantum numbers l and m_l .
- It is ***these quantum numbers that dictate the shape of the atomic orbitals.***
- Thus, for example, all of the s orbitals are spherical regardless of their principal quantum number and they each have the same angular dependence on θ and ϕ .
- Because $l = 0$ for s orbitals, m_l can only be zero; therefore, only one type of s orbital exists for any given value of n .

❖ ***s* Orbitals**

- Let's begin with the *s* orbital, corresponding to ψ_{nlm} with $l = 0$, (therefore, $m_l = 0$ as well).
- For all *s* orbitals, the angular part Y is a constant. Because ψ does not depend on either θ or φ , all *s* orbitals are *spherically symmetric* about the nucleus.
- This means that the value of the wave function for an *s* orbital (and therefore also the probability of finding the electron near some point in space) depends only on its distance, r , from the nucleus and not on its direction in space.
- There are several ways to visualize the ns orbitals with $n = 1, 2, 3, \dots$, and the probability density they describe.

- Figure 5.7 displays the relationships between the radial dependence of ψ and ψ^2 and the electron density representation for the 1s, 2s, and 3s orbitals.
- These schematic images display key features of these functions, but the radial dependence shown is not quantitative. The 2s and 3s orbitals have nodes, values of r at which the value of the wave function is 0, with lobes of positive phase and negative phase separated by the nodes. See Figure 5.7b.
- Figure 5.7c shows that ψ^2 passes through a local maximum value after r crosses each node, and then continues to fall off after the final node as r approaches very large values.
- From this behavior we generate the electron density representations in Figure 5.7a, in which the intensity of shading indicates the magnitude of the electron density in each region. The shading will be greatest at the local maximum values in ψ^2 and must fade to white at the nodes.

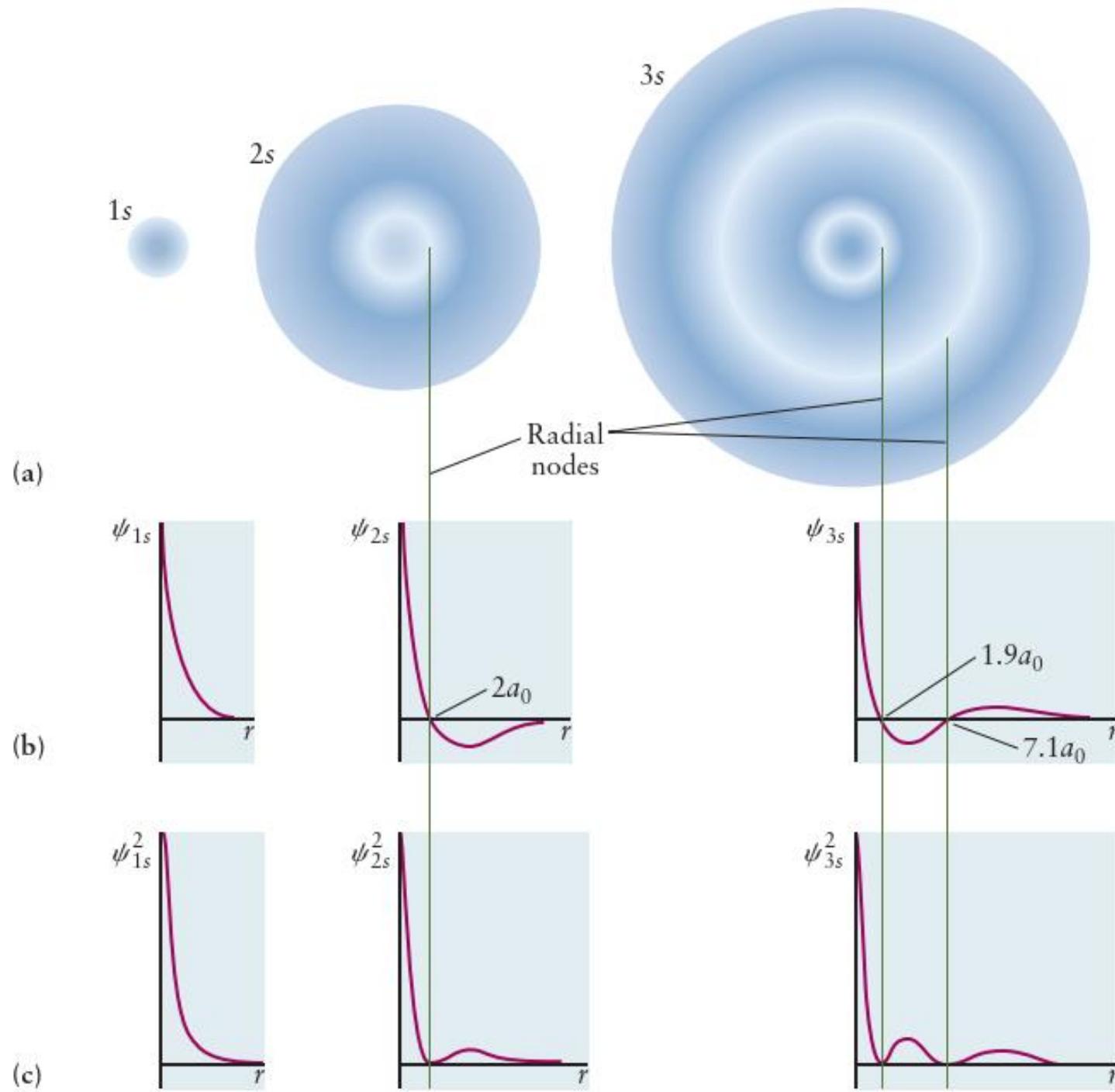


Figure 5.7 Qualitative representations of hydrogen s orbitals.

(a) An electron probability density representation of a hydrogen atom in its $1s$, $2s$, and $3s$ states. The spheres are cut off at a radius that encloses 90% of the probability density.

(b) The radial wave functions plotted against distance from the nucleus, r .

(c) Dependence of the probability density on the distance from the nucleus, given by the square of the wave function (prior to integrating over a thin spherical shell a distance r from the nucleus).

- A measure of the size of an orbital is the most probable distance of the electron from the nucleus in that orbital. The most probable location of the electron is progressively farther from the nucleus in ns orbitals for larger n .
- Nonetheless, ***there is a finite probability density for finding the electron at the nucleus*** in both 2s and 3s orbitals.
- ✓ This happens because electrons in s orbitals have no angular momentum ($l = 0$), and thus can approach the nucleus along the radial direction.
- The ability of electrons in s orbitals to “penetrate” close to the nucleus has important consequences in the structure of many-electron atoms and molecules (see later).

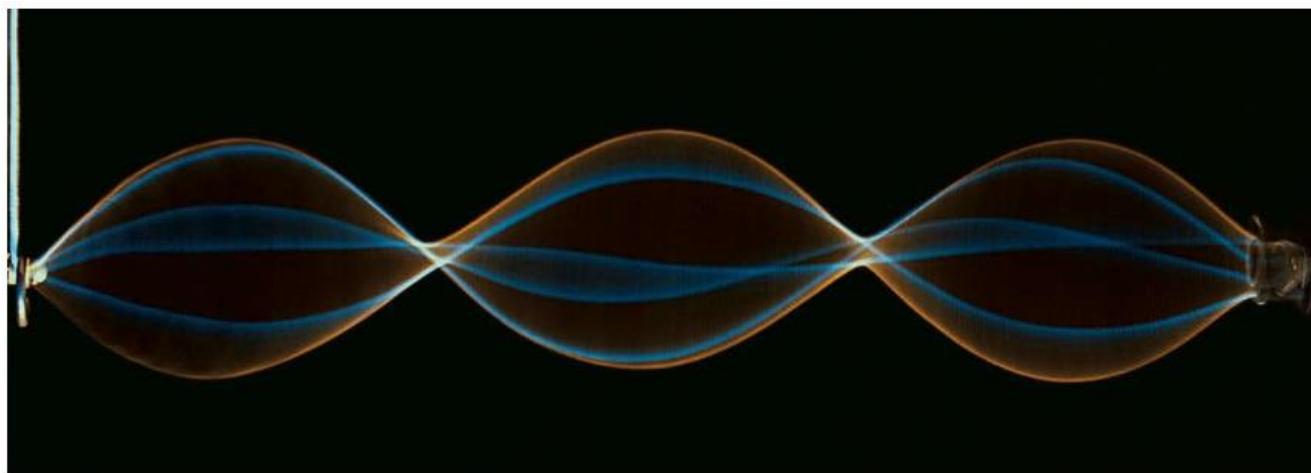
- Finally, note that an ns orbital has $n - 1$ radial nodes; a radial node is a spherical surface about the nucleus on which ψ and ψ^2 are 0.
- These spherical surfaces are the analogues of the nodal planes in the wave functions for a particle in a cubic box.
- The more the nodes in an orbital, the higher the energy of the corresponding quantum state of the atom. Just as for the particle in a box, the energies of orbitals increase as the number of nodes increases.
- Finally, we want to describe the ***size of the orbital***. What is meant by the size of an orbital? Strictly speaking, the wave function of an electron in an atom stretches out to infinity, so an atom has no clear boundary.
- ✓ We define the size of an atom as the extent of a “balloon skin” inside which 90% of the probability density of the electron is contained.

- Calculations show that spheres containing 90% of the probability density for an electron in the 1s, 2s, and 3s orbitals of the hydrogen atom have radii equal to 1.41 Å, 4.83 Å, and 10.29 Å, respectively.
- These results show that the size of an orbital increases with increasing quantum number n .
- A 3s orbital is larger than a 2s orbital, which, in turn, is larger than a 1s orbital.
- ✓ This is the quantum analog of the increase in radius of the Bohr orbits with increasing n .

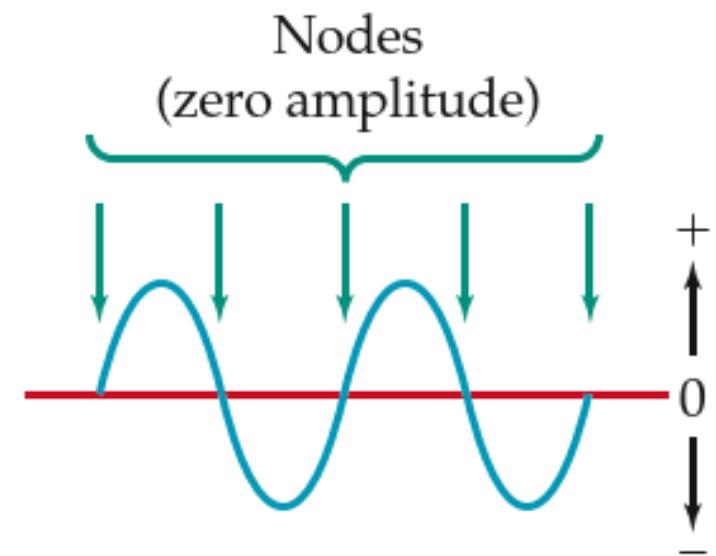
- Although all s orbitals are spherical, there are significant differences among the s orbitals in different shells.
- First, the size of the s orbital increases in successively higher shells, implying that an electron in an outer-shell s orbital is farther from the nucleus on average than an electron in an inner-shell s orbital and is therefore higher in energy.
- Second, the electron distribution in an outer-shell s orbital has more than one region of high probability. For example, *a 2s orbital is essentially a sphere within a sphere and has two regions of high probability, separated by a surface of zero electron probability* called a ***node***.
- Similarly, a 3s orbital has three regions of high probability and two spherical nodes.

- The concept of *an orbital node—a surface of zero electron probability separating regions of nonzero probability*—is difficult to grasp because it raises the question: How does an electron get from one region of the orbital to another if it can't be at the node?
- The question is misleading, though, because it assumes particle-like behavior for the electron rather than *the wavelike behavior that forms the basis of the quantum mechanical model*.
- In fact, nodes are an intrinsic property of all waves, from moving waves of water in the ocean to the stationary, or standing, wave generated by vibrating a rope or guitar string (Figure 2.11).

- A node simply corresponds to the zero-amplitude part of the wave. On either side of the node is a nonzero wave amplitude.
- Note that a wave has two phases—peaks above the zero line and troughs below—corresponding to different algebraic signs, + and -. Similarly, the different regions of 2s and 3s orbitals have different phases, + and -, as indicated in Figures.



When a rope is fixed at one end and vibrated rapidly at the other, a standing wave is generated.



The wave has two phases with different algebraic signs, + and -, separated by zero-amplitude regions, called *nodes*.

❖ *p* Orbitals

- Orbitals with angular quantum numbers different from 0 are not spherically symmetric.
- Interesting *angular effects arise from the quantization of angular momentum.*
- The angular wave function $Y_{lm}(\theta, \varphi)$ has separate lobes with positive and negative phase, with a node between them.
- There are $(2l + 1)$ projections of these angular momentum values along the z-axis.
- The three angular wave functions with $l = 1$, for which the allowed m values are -1, 0, and +1, lead to three orbitals (each called a *p* orbital) with the same shapes but different orientations in space.

- There are three different kinds of p orbitals because m_l can take values of -1 , 0 , or $+1$.
- The shapes of these orbitals are shown in Figure 4.4, where the orbital boundary indicates a 90% or greater probability of finding the electron in the enclosed region of space.

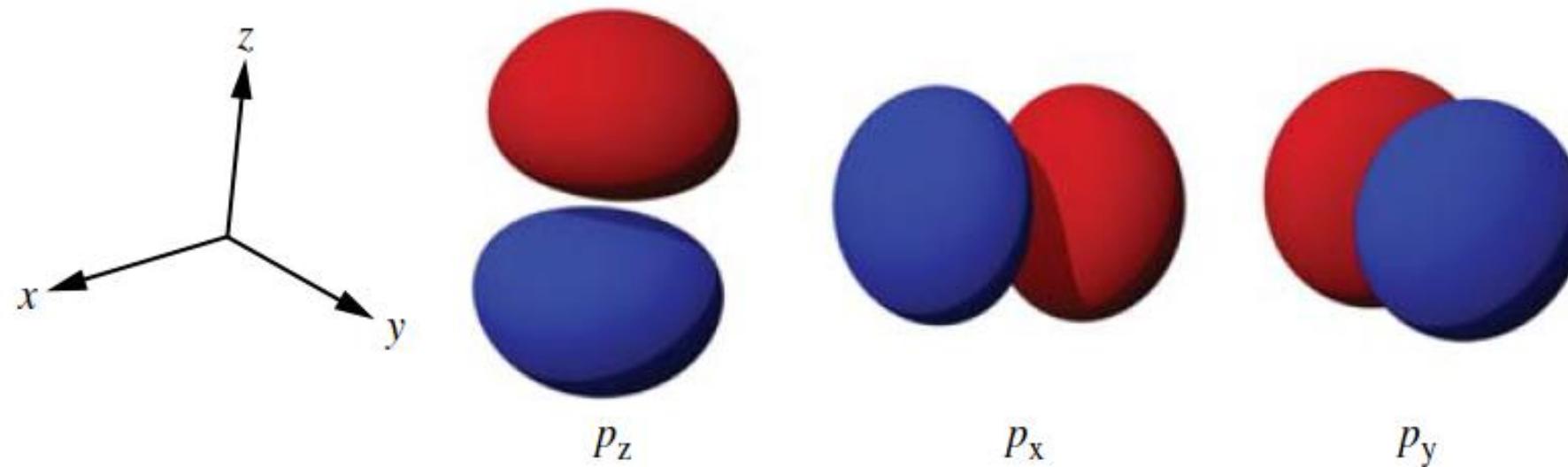


FIGURE 4.4. Shapes of the three p orbitals.

- If we consider the wave functions with $n = 2$ and $l = 1$, we have three wave functions,

$$\psi_{2,1,0} = R_{2,1}(r) Y_1^0(\theta, \phi) ,$$

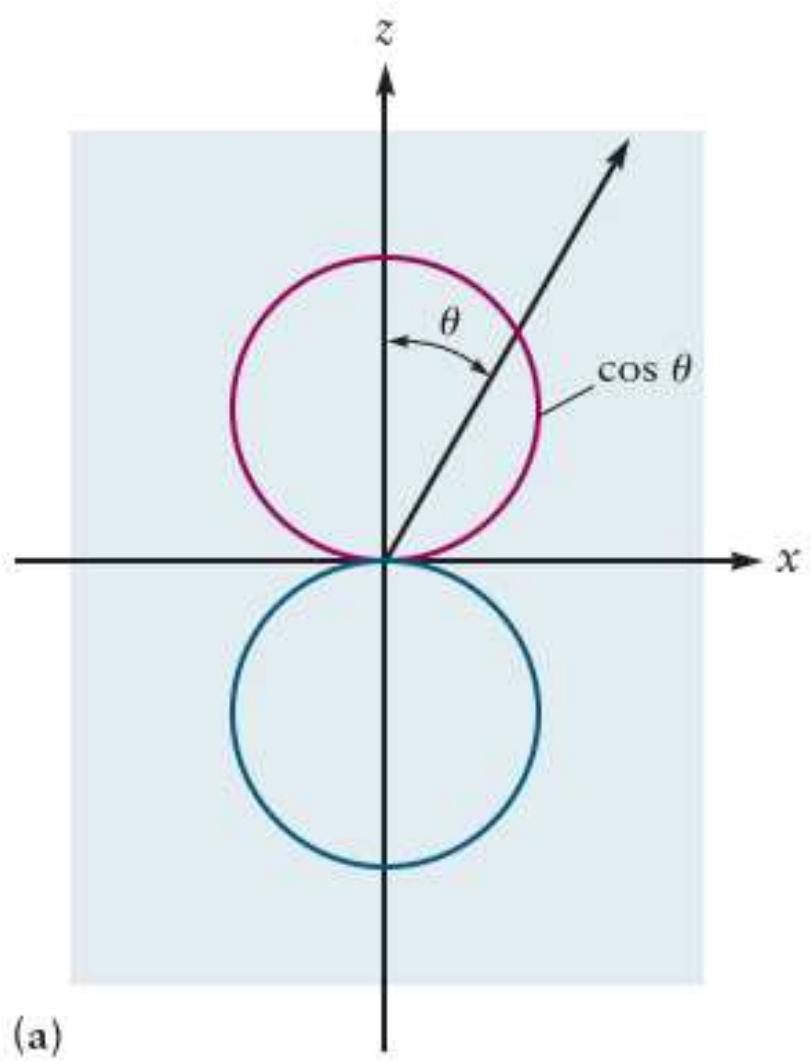
$$\psi_{2,1,1} = R_{2,1}(r) Y_1^1(\theta, \phi) ,$$

$$\psi_{2,1,-1} = R_{2,1}(r) Y_1^{-1}(\theta, \phi) .$$

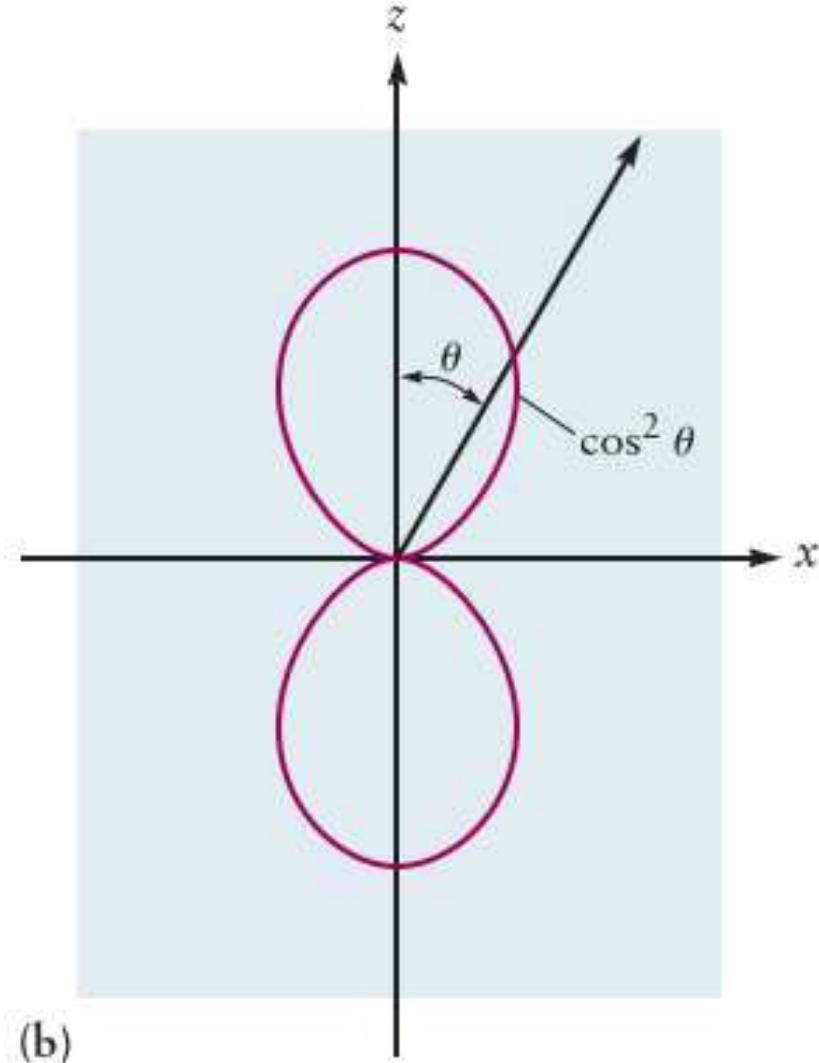
- When $m_l = 0$, the angular wavefunction is real, and the shape of the orbital consists of two lobes that lie along the z coordinate axis. Because its lobes lie along the z-axis, the p_0 orbital is also known as the p_z orbital.
- The angular wave functions $Y_{11}(\theta, \varphi)$ for $l = 1, m = 1$ and $Y_{1,-1}(\theta, \varphi)$ for $l = 1, m = -1$ do not have a simple geometrical interpretation.
- Notice that in general the Spherical Harmonics are complex functions. Often we are interested in the directionality of the wave function. Therefore, we construct linear combinations of Spherical Harmonics to represent orbitals (see later).

- The angular wave function $Y_{10}(\theta, \varphi)$ with the combination $l = 1, m = 0$ is called the angular portion of the p_0 orbital.
- When $m_l = 0$, the angular wavefunction is real, and the shape of the orbital consists of two lobes that lie along the z coordinate axis. Because its lobes lie along the z-axis, the p_0 orbital is also known as the p_z orbital.
- The wave function Y_{p_z} for the p_z orbital is proportional to $\cos \theta$. From the relation between spherical and Cartesian coordinates, you can see that $\cos \theta \propto z$; thus, the maximum probability density for this orbital (Figure 5.9b) is along the z-axis (where $\theta = 0$ or π).
- There is a node in the $x-y$ plane (where $\theta = \pi/2$, so $\cos \theta = 0$) (Fig. 5.9a). This nodal plane is called an **angular node**; the wave function changes sign across it.

- The p_z orbital therefore points along the z -axis, with its positive phase (red in Fig. 5.9a) on the side of the x - y plane where the z -axis is positive and negative phase (blue in Fig. 5.9a) on the side where the z -axis is negative.
- As a rule, every orbital will exhibit l angular nodal surfaces, which can be either planar or conical in shape.
- Thus, all three of the p orbitals will have a single angular nodal plane. Likewise, each d orbital will have two angular nodal surfaces and each f orbital will have three.



(a)



(b)

Figure 5.9 Two aspects of hydrogen p orbitals. (a) The angular wave function for the p_z orbital. The p_x and p_y orbitals are the same, but are oriented along the x - and y -axis, respectively. (b) The square of the angular wave function for the p_z orbital. Results for the p_x and p_y orbitals are the same, but are oriented along the x - and y -axis, respectively.

- Although the angular wave functions of orbitals having $|m_l| > 0$ all contain imaginary components in their exponential terms, the product Y^*Y is real and can therefore be plotted.
- The angular dependence of the 2p orbitals having $m_l = -1$ and $m_l = +1$ are identical.
- Both orbitals take on the shape of a donut with the z-axis passing through the center of the donut hole. The only difference between the two orbitals is that the electron is moving in opposite directions in each of them.

- The angular wave functions $Y_{11}(\theta, \varphi)$ for $l = 1, m = 1$ and $Y_{1,-1}(\theta, \varphi)$ for $l = 1, m = -1$ *do not have a simple geometrical interpretation.*
- Notice that in general the Spherical Harmonics are complex functions. Often we are interested in the directionality of the wave function. Therefore, we construct linear combinations of Spherical Harmonics to represent orbitals (see later). Thus, we represent the angular part separately from the radial part.
- Because of the requirement that all quantum mechanical operators be linear and Hermitian, any linear combination of two degenerate wave functions will also be an acceptable solution to the Schrödinger equation.
- Therefore, their sum and their difference, which are also allowed solutions of the Schrödinger equation for the hydrogen atom, do have simple interpretations.

- When the positive linear combination $\mathbf{Y}(1,1) + \mathbf{Y}(1,-1)$ is taken, where the numbers in parentheses refer to l and m_l , respectively, the equation for the familiar **p_y orbital is obtained** after normalization, as shown in Figure 4.5.
- When the negative linear combination $\mathbf{Y}(1,1) - \mathbf{Y}(1,-1)$ is taken, the equation for the **p_x orbital results** after normalization.
- This process is also known as the ***hybridization of atomic orbitals***.
- According to quantum theory, the hybrid orbitals must also be orthogonal to one another. These particular linear combinations ensure that all three p orbitals will have the same shape with their lobes pointing along the three orthogonal Cartesian axes.

- Therefore, we form two new angular wave functions:

$$2P_x = \frac{1}{\sqrt{2}} [Y_1^1 + Y_1^{-1}] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \cos(\phi),$$

$$2P_y = \frac{1}{\sqrt{2}} \left[\frac{Y_1^1 - Y_1^{-1}}{i} \right] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \sin(\phi).$$

- The resulting expressions for Yp_x and Yp_y are given in Table earlier.
- A comparison of these expressions with Figure shows that Yp_x lies along the x -axis and Yp_y lies along the y -axis, but otherwise have the same shape as Yp_z . They have nodes at the y - z and x - z planes, respectively.

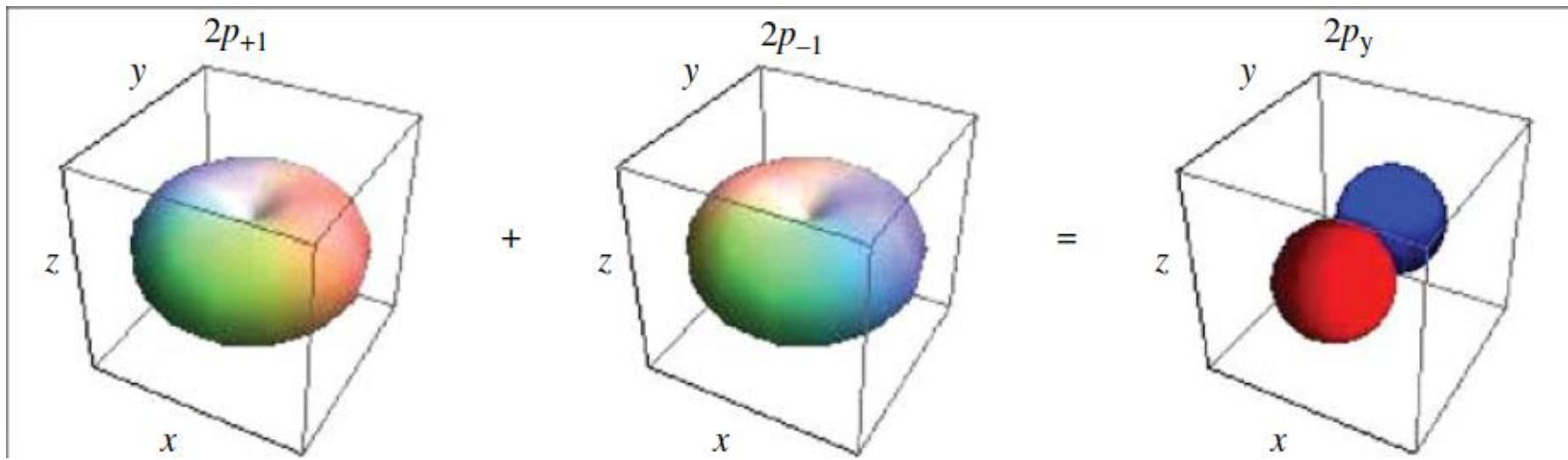
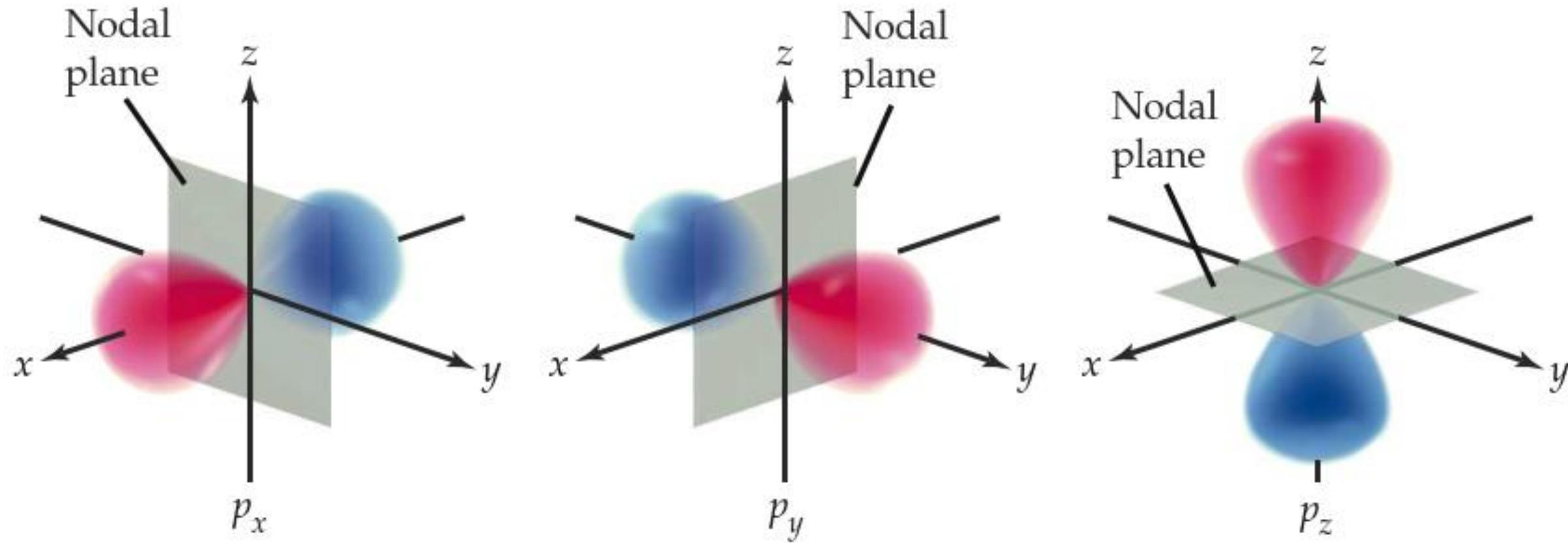


FIGURE 4.5. Illustration of how a linear combination of the $2p_{+1}$ and $2p_{-1}$ orbitals can be used to construct the more familiar $2p_y$ orbital. [Images by Lisa M. Goss. Used by permission.]

Each p orbital has two lobes of high electron probability separated by a nodal plane passing through the nucleus.



The **different colors** of the lobes represent different algebraic signs, analogous to the different phases of a wave.

- The five different kinds of d orbitals are shown in Figure 4.6.
- When $m_l = 0$, the d_z^2 orbital results.
- This orbital has two lobes of the same sign pointing along the z-axis, with a donut-shaped lobe of the opposite sign in the xy plane.
- Notice that there are two conical nodes, each beginning at the origin and pointing in a different direction along the z-axis.
- When $|m_l| = 1$, the product Y^*Y yields a probability function containing two donuts centered on the z-axis, where one lies above the xy plane and the other lies beneath it.

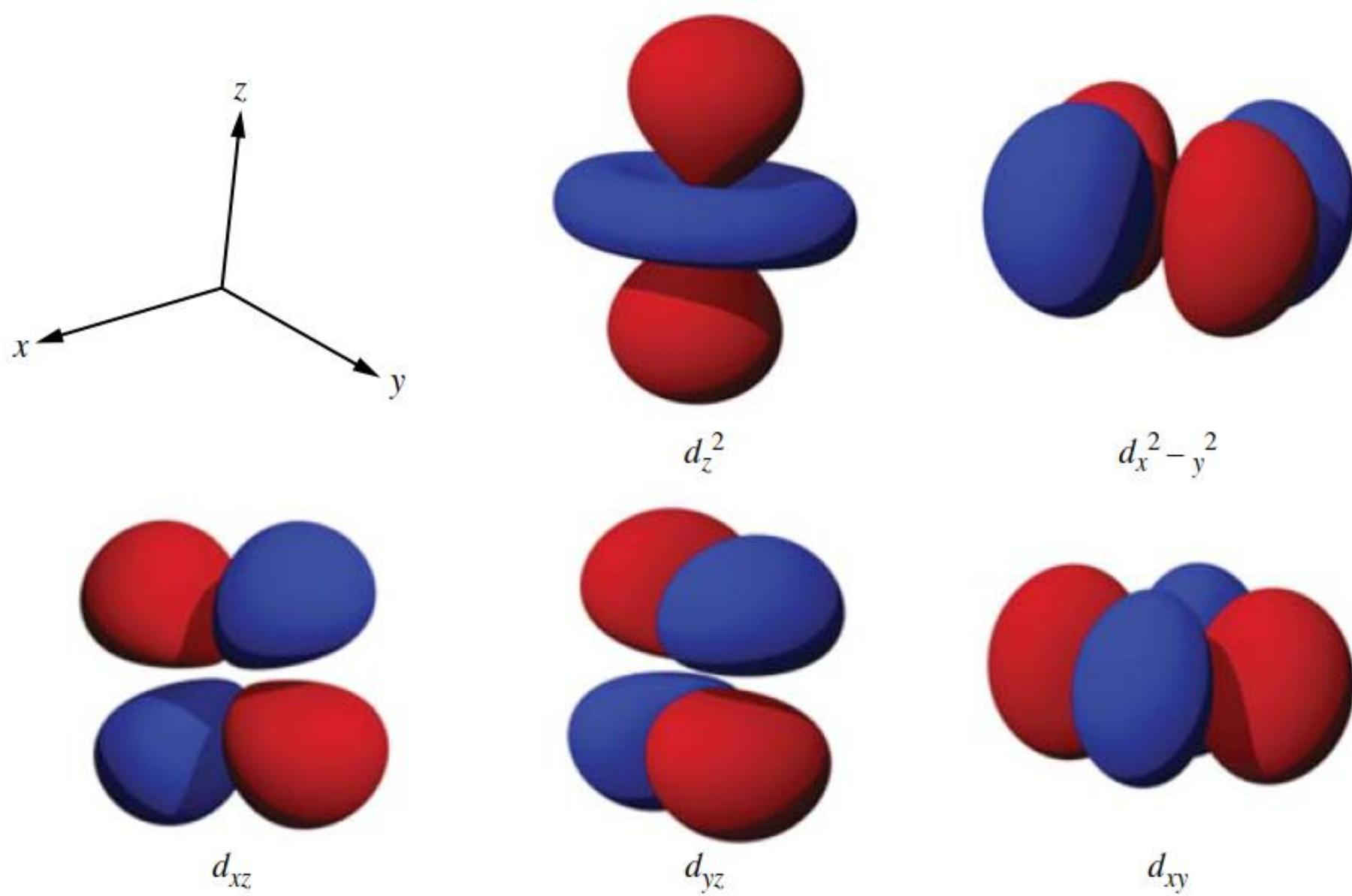


FIGURE 4.6. Shapes of the five *d* orbitals.

- When $|m_l| = 2$, the product Y^*Y looks similar to a single hollow donut lying in the xy plane, as shown in Figure 4.7.
- Taking the positive and negative linear combinations of $Y(2,1)$ with $Y(2,-1)$ yields the d_{xz} and the d_{yz} orbitals shown in Figure 4.6. Both of these orbitals contain four lobes (as in a four-leaf clover) of alternating sign of the wave function and lying in the xz and yz planes, respectively. Each of the four lobes lies between the coordinate axes.
- Likewise, linear combinations of the $Y(2,2)$ and $Y(2, -2)$ wave functions yield the d_{xy} and $d_{x^2-y^2}$ orbitals shown in Figure 4.6. Both orbitals lie in the xy plane and have the same alternating four-leaf clover shape. However, the d_{xy} orbital has its lobes pointing between the coordinate axes, while the $d_{x^2-y^2}$ orbital's lobes lie squarely on the coordinate axes.
- The names and shapes of the five d-orbitals are especially important in the field of coordination chemistry.

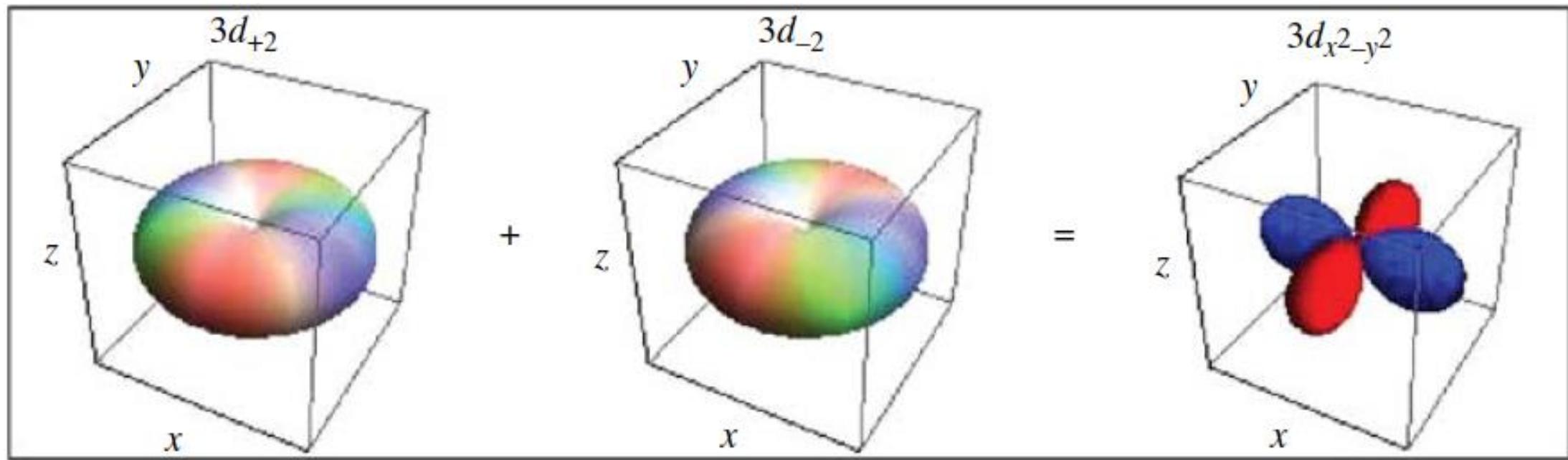
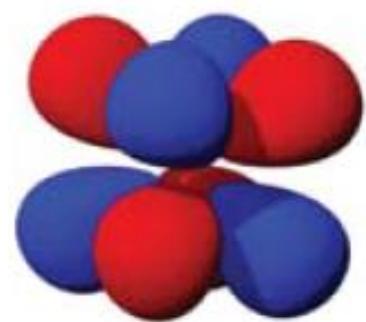
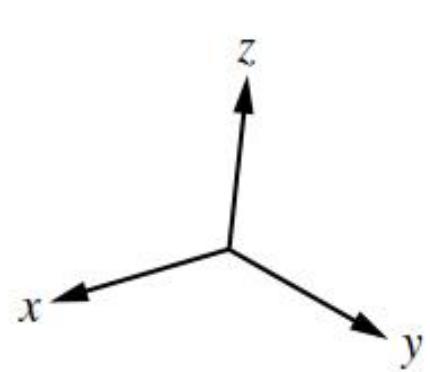
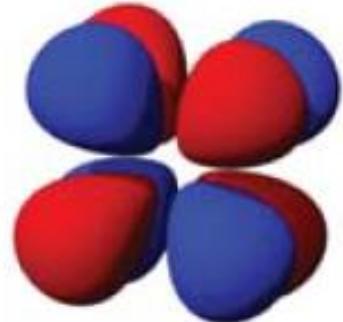


FIGURE 4.7. Illustration of how a linear combination of the $3d_{+2}$ and $3d_{-2}$ orbitals can be used to construct the more familiar $3d_{x^2-y^2}$ orbital. [Images by Lisa M. Goss. Used by permission.]

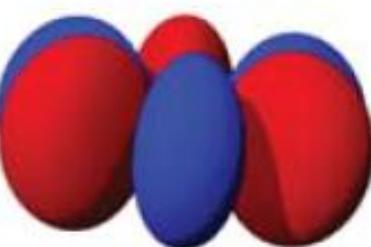
- The shapes of the seven *f* orbitals are shown in Figure 4.8.
- When $m_l = 0$, the f_z^3 orbital results, which has lobes of opposite sign along the z-axis and two donuts encircling that axis that also have opposite signs.
- For $|m_l| = 1$, the positive and negative linear combinations $Y(3,1) \pm Y(3,-1)$ yield the f_{xz}^2 and f_{yz}^2 orbitals, which have six lobes each lying in the xz and yz planes, respectively.
- For $|m_l| = 2$, the two hybrids are the f_{xyz} and $f_{z(x^2-y^2)}$ orbitals.
- Both of these orbitals have eight lobes forming a cubic shape, with the former lying between the x- and y-axes and the latter lying on the coordinate axes.
- Lastly, for $|m_l| = 3$, the hybrid orbitals are the $f_x(x^2-3y^2)$ and $f_y(3x^2-y^2)$ orbitals, which have six lobes each lying in the xy plane.
- The shapes of the seven *f*-orbitals are typically unimportant in chemical bonding and do not need to be memorized.



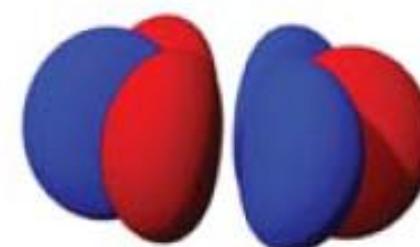
$$f_{xy}$$



$$f_z(x^2 - y^2)$$



$$f_x(x^2 - 3y^2)$$



$$f_y(3x^2 - y^2)$$

FIGURE 4.8. Shapes of the seven f orbitals, with $|m_f|$ increasing from left to right in the diagram.

- We summarize the important features of orbital shapes and sizes as follows:
 - 1. For a given value of l , an increase in n leads to an increase in the average distance of the electron from the nucleus, and therefore in the size of the orbital.
 - 2. An orbital with quantum numbers n and l , has **l angular nodes** and **$(n - l - 1)$ radial nodes**, giving a total of $(n - 1)$ nodes.
 - An angular node appears as a nodal plane in plots of p orbitals. The value of the radial or angular part of the wave function changes sign as you cross a radial or angular node respectively. For a one-electron atom or ion, the energy depends only on the number of nodes—that is, on n but not on l , or m . **The energy increases as the number of nodes increases.**
 - 3. As r approaches 0, $\psi(r, \theta, \varphi)$ vanishes for all orbitals except s orbitals; thus, only an electron in an s orbital can “***penetrate to the nucleus,***” that is, have a finite probability density right at the nucleus.

Several features common to all of the atomic orbitals are as follows:

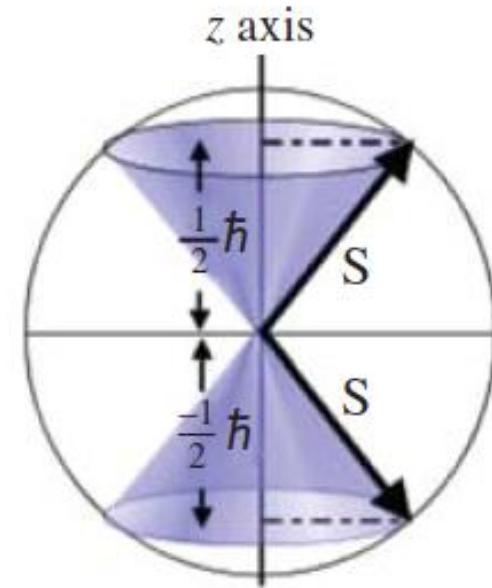
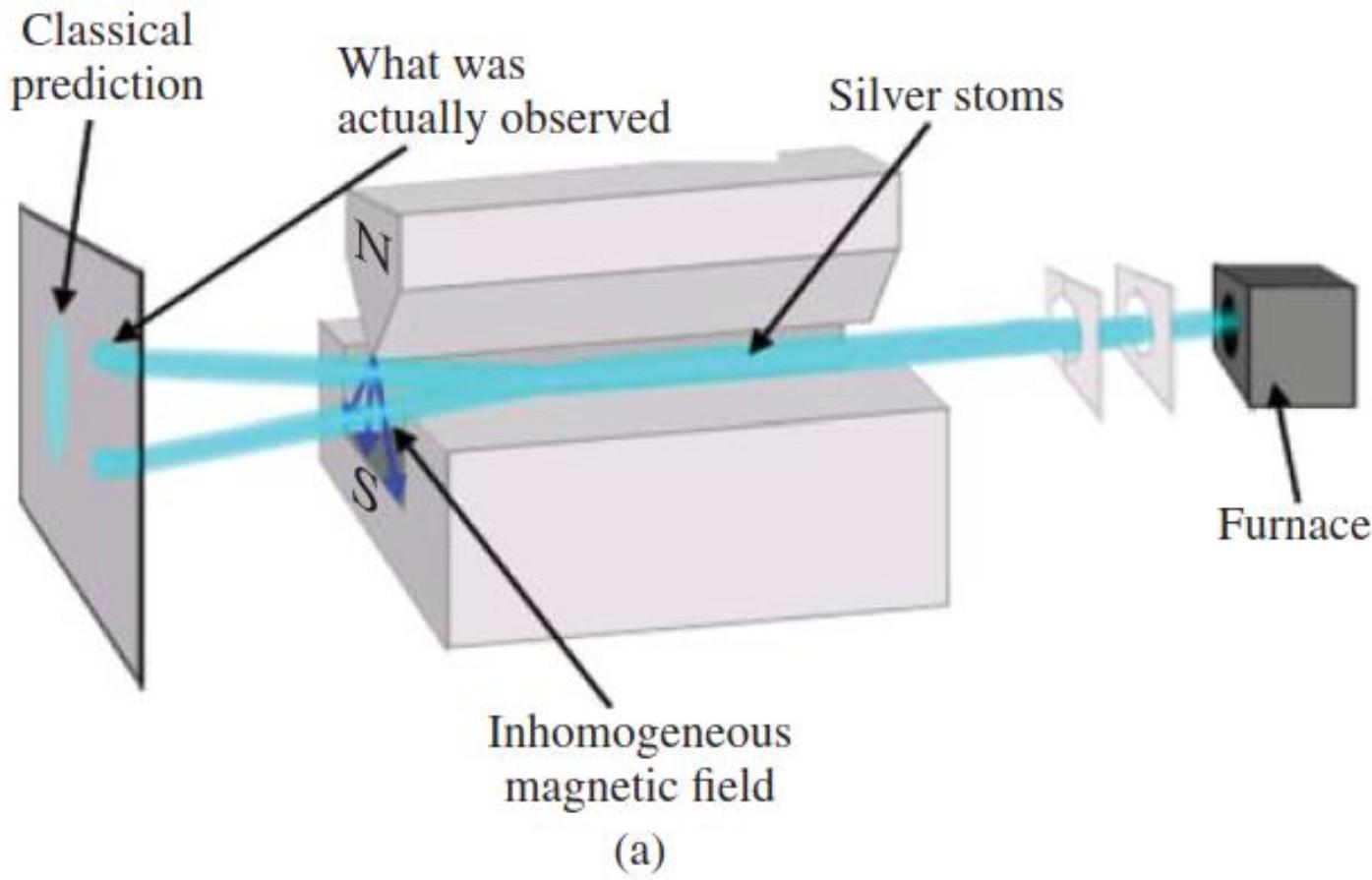
- • For any given value of l , the summation of the electron density probabilities for the complete set of orbitals will be a sphere. This is known as Unsöld's theorem. Thus, for example, the sum of the electron density for the $2p_x$, $2p_y$, and $2p_z$ orbitals is a sphere, as is the case for the lone $2s$ orbital.
- • The absolute value of m_l is the number of angular nodes that present themselves when the orbital is viewed from either direction along the z-axis.
- ✓ Thus, a p_z orbital ($m_l = 0$), when viewed from the “top” of the z-axis, will present with a positive lobe. The negative lobe that lies beneath this will not be observed from this vantage point.
- However, the p_x and p_y orbitals ($|m_l| = 1$) will each present one angular nodal plane when viewed along the z-axis.

- • The *symmetry of the atomic orbitals* with respect to *inversion* alternates in a regular pattern. The inversion operation means that if one takes any point (x, y, z) back through the origin an equal distance to point $(-x, -y, -z)$, the probability density will be identical in magnitude and sign. All *s* and *d* orbitals are symmetric (or *gerade*) with respect to inversion. All *p* and *f* orbitals are antisymmetric (or *ungerade*) with respect to inversion (they have the opposite sign). More generally, whenever *l* is odd, the atomic orbitals will be *gerade* and whenever *l* is even, they will be *ungerade*.
- • Both the number of nodal planes through the nucleus and the overall geometric complexity of the orbitals increase with the *l* quantum number of the subshell: An *s* orbital has one lobe and no nodal plane through the nucleus, a *p* orbital has two lobes and one nodal plane, and a *d* orbital has four lobes and two nodal planes. The seven *f* orbitals are more complex still, having eight lobes of maximum electron probability separated by three nodal planes through the nucleus.

ELECTRON SPIN AND THE PAULI PRINCIPLE

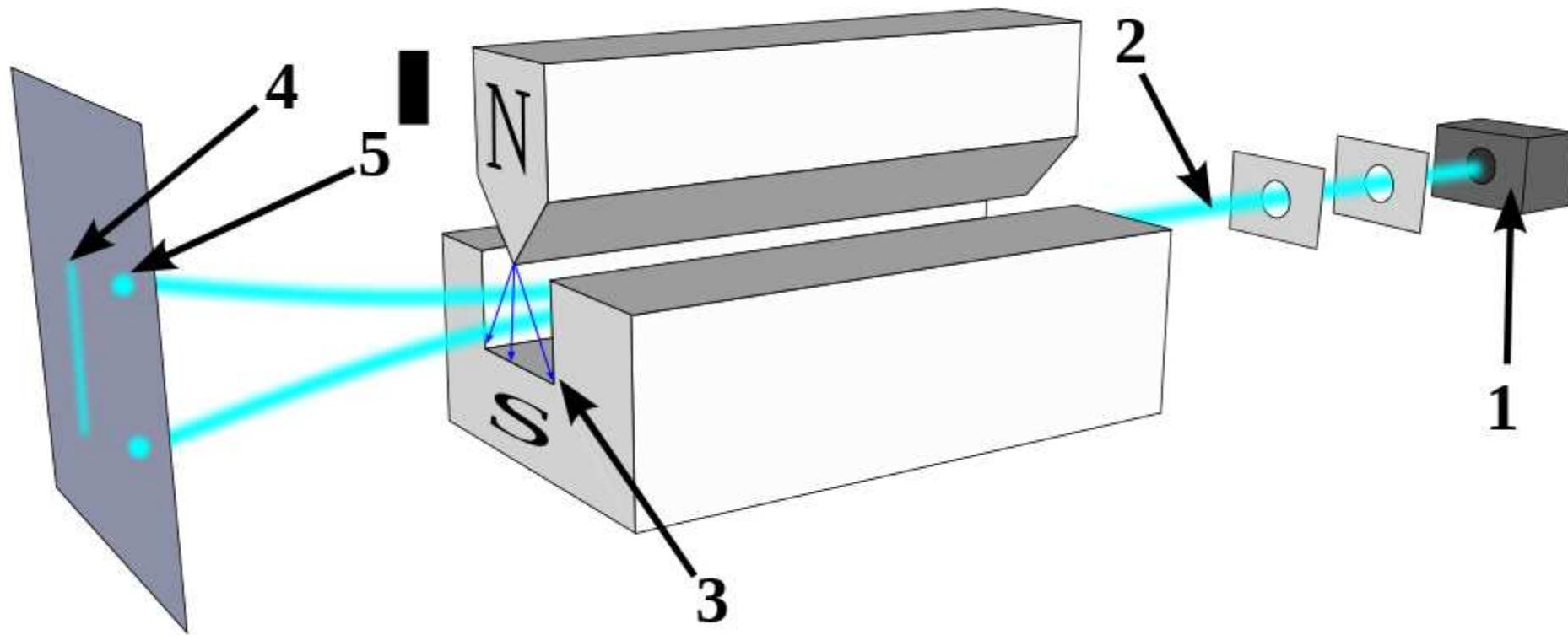
- Schrödinger's calculation of the energies of the hydrogen orbitals was a milestone in the development of modern atomic theory. Yet the observed spectral lines did not have exactly the frequencies he predicted.
- In 1925 (before Schrödinger's work but after Bohr had developed an earlier model of the atom), two Dutch–American physicists, Samuel Goudsmit and George Uhlenbeck, proposed an explanation for the tiny deviations that had been observed.
- They suggested that an electron behaves in some respects like a spinning sphere, something like a planet rotating on its axis. This property is called **spin**.

- The concept of *electron spin* was first postulated by Goudsmit and Uhlenbeck in 1925 in order to explain the fine structure (or splitting) of the line spectra of several of the alkali metals.
- The *Stern–Gerlach experiment*, depicted in Figure 4.13, provided the first experimental confirmation for the quantization of electron spin.
- In their 1922 experiment, Otto Stern and Walther Gerlach showed that a beam of silver atoms could be split into two beams by passing it through an inhomogeneous magnetic field.
- In addition to electrons, many nuclei also exhibit spin, forming the basis of nuclear magnetic resonance (NMR) and electron spin resonance (ESR) analytical techniques.



(b)

FIGURE 4.13. (a,b) Schematic diagram of the Stern–Gerlach experiment, showing how a beam of Ag atoms can be split by an inhomogeneous magnetic field into two different trajectories as a result of the different spin states they possess.



Ground-state Hydrogen atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin (which is based on the electron spin). (1) the hydrogen atom source, (2) collimated atomic beam, (3) inhomogeneous magnetic field, (4) the observed bifurcation of the beam (5) the predicted spread for a classical atom with no intrinsic electron spin.

- You may recall from classical physics that a small bar magnet will rotate to orient itself in the presence of an external magnetic field.
- If the magnetic field changes strength along a particular direction, then a force will be exerted on the bar magnet that will cause it to move in the direction of the changing field, and not just rotate to a new direction.
- If the *magnetic dipole moments of the silver atoms were randomly oriented* in space (as predicted by classical physics), then the *beam would be smeared out* at the detector to reflect *all possible orientations of the magnetic moment*.
- That the ***original beam is split into only two well-defined beams*** in this experiment ***demonstrates*** the unexpected fact that ***the orientation of the magnetic moment of the electron is quantized***.

We can use a magnetic field to inquire into the nature of the spin angular momentum as well. In fact, we have already discussed the pertinent experiment. The beam of hydrogen atoms was split into just two components in the atomic beam experiment. This means that the component of the electron's spin magnetic moment (and spin angular momentum) along a given axis may have only one of two possible values; the component may be aligned with the field and hence be attracted, or it may be opposed to the field and be repelled. The electron's spin magnetic moment has been detected in many different kinds of experiments and the results are remarkable in that only two components of constant magnitude are ever observed. The electron is always either repelled by the field or attracted to it. This implies that the magnitude of the spin angular momentum for a single electron may have ***only one possible value***. Since the number of possible values for the component of a given amount of angular momentum of any type in quantum mechanics is $(2l + 1)$, l must equal $\frac{1}{2}$ and only $\frac{1}{2}$ for the spin angular momentum, and the values of m for the electron spin, which assume values from a maximum of l to a minimum of $-l$ in steps of unity, must equal $+\frac{1}{2}$ and $-\frac{1}{2}$.

In this respect the spin angular momentum of the electron is quite different from its orbital angular momentum, which may have many possible values, as the value of l for the orbital motion is restricted only in that it must equal zero or an integer. It should be stressed that the splitting of the beam of hydrogen atoms into only two components is again evidence of quantization. If the atomic magnets (the hydrogen atoms) behaved according to classical mechanics, then the effect of the magnetic field would be simply to broaden the beam. The orientations of the atomic magnets would be random when they first entered the field of the magnet and classically the individual atomic magnets could be aligned at any and all angles with respect to the field, giving all possible components of the spin magnetic moment along the direction of the field. The inhomogeneous field would then exert a force proportional to the magnitude of the component, and the beam would broaden but not split.

Since the spin magnetic moment is an intrinsic property of the electron, even a beam of free electrons should be split into two components in a magnetic field. However, the charge possessed by the free electron also interacts with the magnetic field and the much smaller magnetic-magnetic interaction is masked by the usual deflection of a charge species in a magnetic field. By employing a neutral atom, the complications of the electronic charge may be avoided. The original experiment was performed on a beam of silver atoms by Stern and Gerlach in 1921. (We shall see shortly that the electrons in a silver atom do not possess any orbital angular momentum.)

- The result of this experiment is explained by introducing a fourth quantum number, m_s , which can take on two values, conventionally chosen to be +1/2 and -1/2 . For historical reasons, the fourth quantum number is referred to as the ***spin quantum number***. When $m_s = +1/2$, the electron spin is said to be “up,” and when $m_s = -1/2$, the spin is “down.”
- Schrödinger’s theory did not account for spin, but it emerged naturally when the British physicist Paul Dirac found a way (in 1928) to combine Einstein’s theory of relativity with Schrödinger’s approach.
- A *fourth quantum number*, called the ***spin quantum number***, is required when the relativistic effects of electronic motion are taken into consideration.
- In 1928, Paul Dirac developed a relativistic theory of quantum mechanics from which the concept of spin arose naturally.
- The inclusion of a *fourth variable (time)* required the *presence of a fourth quantum number*.

- According to Dirac's derivation, an electron possesses both orbital (L) and spin (S) angular momentum.
- The total angular momentum (J) is a linear combination of the two, as shown in Equation (4.13).

$$\hat{J} = \hat{L} + \hat{S} = -i\hbar \frac{\partial}{\partial \phi} \pm \frac{\hbar}{2} \quad (4.13)$$

- The spin angular momentum vector S can take values of $\pm m_s \hbar/2$, where m_s can take values of **+1/2** (α) or $-1/2$ (β), depending on whether it aligns **against** or with the external magnetic field, respectively.

- The usual classical picture of electron spin, where the electron can be considered as a top spinning on its axis either in the clockwise or the counterclockwise direction, is only useful as a conceptual tool. In actuality, *spin is strictly a quantum mechanical phenomenon* and it has no classical analogy.
- The spin quantum number arises from relativistic effects that are not included in the Schrödinger equation.
- For most practical purposes in chemistry, it is sufficient simply to solve the ordinary Schrödinger equation, and then associate with each electron a spin quantum number $m_s = +1/2$ or $-1/2$ which *does not affect the spatial probability distribution of the electron*.
- Including the **spin doubles the number of allowed quantum states with principal quantum number n , from n^2 to $2 n^2$.**
- This fact will assume considerable importance when considering the many-electron atoms in the next section.

Let us summarize what we have learned about this new property of the electron. Since an electron may exhibit a magnetic moment even when it does not possess orbital angular momentum, it must possess some internal motion. We call this motion the electron spin and treat it quantum mechanically as another kind of angular momentum. Experimentally, however, all we know is that the electron possesses an intrinsic magnetic moment. The remarkable feature of this intrinsic magnetic moment is that its magnitude and the number of components along a given axis are fixed. A given electron may exhibit only one of two possible components; it may be aligned with the field or against it. Experimentally, or theoretically, this is all we can know about the spin magnetic moment and the spin angular momentum. Hence only one quantum number is required to describe completely the spin properties of a single electron. We shall denote the value of this quantum number by \uparrow or \downarrow , the upwards-pointing arrow signifying that the component of the magnetic moment is aligned with the field and the downwards-pointing arrow that this component is opposed to the field.

A total of four quantum numbers is required to specify completely the state of an electron when it is bound to an atom. The quantum numbers n , l and m determine its energy, orbital angular momentum and its component of orbital angular momentum. The fourth quantum number, the spin quantum number, summarizes all that can be known about the spin angular momentum of the electron. This final quantum number may have only one of two possible values corresponding to the magnetic moment component being (a) aligned with the field or (b) opposed to it.

Effects of nuclear charge

- The basic shapes of orbitals are unchanged by changes in the nuclear charge, although their extensions into space depend inversely on the value of Z .
- Fig. 2.13 shows the radial density curve for the 1s orbital of *helium-like* species with different values of the nuclear charge.

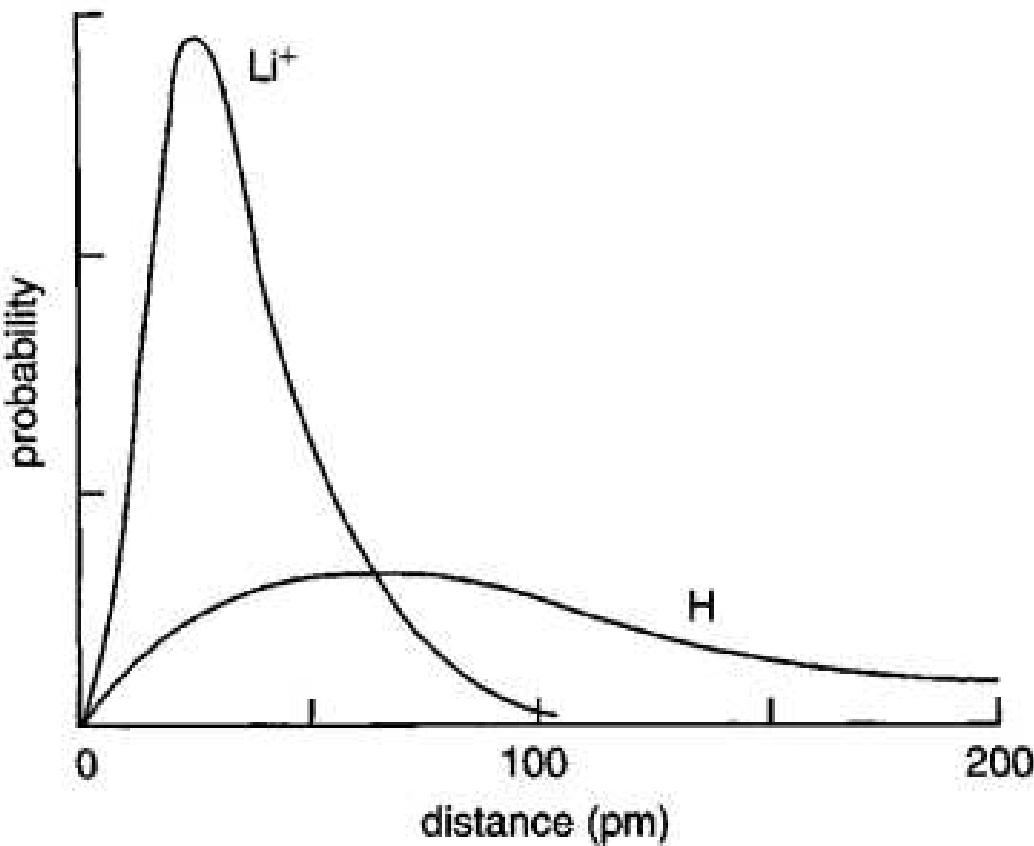


FIG. 2.13 Radial density curves for ions containing two electrons and with different nuclear charges.

This plot for isoelectronic ions illustrates the ***effect of increasing the nuclear charge*** from $Z = 1$ to $Z = 3$ on the spatial distribution of the electron probability density.

- The radius of the electron cloud around an atom is the resultant of this contraction of the charge cloud with increasing Z , and the fact that orbitals further and further out from the nucleus are being occupied as the atomic number rises.
- There is a general increase in atomic size as Z increases, but this change occurs in a very irregular manner (compare the plot of atomic radius against atomic number).
- The greatest jumps in radius come when the outermost electron starts to fill the s level of a new quantum shell and there are less sharp increases when any new level starts to be occupied and when spin-pairing occurs at p^4 and d^6 configurations.

POLYELECTRONIC ATOMS: MANY-ELECTRON ATOMS

- A neutral atom other than a hydrogen atom has more than one electron and is known as a many-electron atom.
- In the next sections, we build on what we have learned about the hydrogen atom to see how the presence of more than one electron affects the energies of atomic orbitals.
- The resulting electronic structures are the key to the periodic properties of the elements and the abilities of atoms to form chemical bonds. This material therefore underlies almost every aspect of chemistry.

❖ MANY-ELECTRON ATOMS: Orbital Energies

- The *electrons in a many-electron atom occupy orbitals like those of hydrogen.*
- However, ***the energies of these orbitals are not the same*** as those for a hydrogen atom.
- The *nucleus of a many-electron atom is more highly charged than the hydrogen nucleus, and the greater charge attracts electrons more strongly and hence lowers their energy.*
- However, ***the electrons also repel one another; this repulsion opposes the nuclear attraction and raises the energies of the orbitals.***

- In a helium atom, for instance, with two electrons, the charge of the nucleus is $2e$ and the total potential energy is given by three terms:

$$V = \underbrace{-\frac{2e^2}{4\pi\epsilon_0 r_1}}_{\text{Attraction of electron 1 to the nucleus}} - \underbrace{\frac{2e^2}{4\pi\epsilon_0 r_2}}_{\text{Attraction of electron 2 to the nucleus}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\text{Repulsion between the two electrons}}$$

- where r_1 is the distance of electron 1 from the nucleus, r_2 is the distance of electron 2 from the nucleus, and r_{12} is the distance between the two electrons.
- The two terms with negative signs (indicating that the potential energy falls as r_1 or r_2 decreases when either electron gets closer to the nucleus) represent the attractions between the nucleus and the two electrons. The term with a positive sign (indicating an increase in energy as r_{12} decreases) represents the repulsion between the two electrons.

- The Schrödinger equation based on this potential energy is impossibly difficult to solve exactly, but highly accurate numerical solutions can be obtained by using computers.
- The hydrogen atom, with one electron, has **no electron–electron repulsions** and all the orbitals of a given shell are ***degenerate***. For instance, the 2s-orbital and all three 2p-orbitals have the same energy.
- When dealing with many-electron atoms, we have to ***consider spin and electron-electron interaction***.
- By introducing the electron-electron interaction the hydron-like energy levels split reducing the degeneracy.
- In many-electron atoms, the results of spectroscopic experiments and calculations show that electron–electron repulsions cause the energy of a 2p-orbital to be higher than that of a 2s-orbital.

- Similarly, in the $n = 3$ shell, the three 3p-orbitals lie higher than the 3s-orbital, and the five 3d-orbitals lie higher still.
- ***How can we explain these energy differences?***
- As well as being attracted to the nucleus, each electron in a many-electron atom is repelled by the other electrons present.
- As a result, it is less tightly bound to the nucleus than it would be if those other electrons were absent.
- We say that each electron is ***shielded*** from the full attraction of the nucleus by the other electrons in the atom.
- The shielding effectively reduces the pull of the nucleus on an electron. The ***effective nuclear charge***, $Z_{\text{eff}}e$, experienced by the electron is always less than the actual nuclear charge, Ze , because the electron–electron repulsions work against the pull of the nucleus.

- A very *approximate form of the energy* of an electron in a many-electron atom is a version of hydrogen energy expression in which the true atomic number is replaced by the effective atomic number:

$$E_n = -\frac{Z_{\text{eff}}^2 h \mathcal{R}}{n^2}$$

$$V_n^{\text{eff}}(r) \approx -\frac{Z_{\text{eff}}(n)e^2}{r}$$

- Note that the other electrons do not “block” the influence of the nucleus; they simply provide additional repulsive coulombic interactions that partly counteract the pull of the nucleus.
- For example, the pull of the nucleus on an electron in the helium atom is less than its charge of $+2e$ would exert but greater than the net charge of $+e$ that we would expect if each electron balanced one positive charge exactly.

- An s-electron of any shell can be found very close to the nucleus (remember that ψ^2 for an s-orbital is nonzero at the nucleus), and so we say that it can penetrate through the inner shells.
- A p-electron penetrates much less because its orbital angular momentum prevents it from approaching close to the nucleus.
- We have seen that its wavefunction vanishes at the nucleus, and so there is zero probability density for finding a p-electron there.
- Because a p-electron penetrates less than an s-electron through the inner shells of the atom, it is more effectively shielded from the nucleus and hence experiences a smaller effective nuclear charge than an s-electron does.
- In other words, an s-electron is bound more tightly than a p-electron and has a slightly lower (more negative) energy.

- A *d*-electron is bound less tightly than a *p*-electron of the same shell because its orbital angular momentum is higher and it is therefore even less able to approach the nucleus closely.
- That is, *d*-electrons are higher in energy than *p*-electrons of the same shell, which are in turn higher in energy than *s*-electrons of that shell.
- ***The effects of penetration and shielding can be large.*** A 4*s*-electron generally has a much lower energy than that of a 4*p*- or 4*d*-electron; *it may even have lower energy than that of a 3*d*-electron of the same atom.*
- The precise ordering of orbitals depends on the number of electrons in the atom, as we shall see in the next section.
- ***In a many-electron atom, because of the effects of penetration and shielding, the order of energies of orbitals in a given shell is s < p < d < f.***

- Still each level is $(2l + 1)$ degenerate and each level can accommodate two electrons. But these electrons have to satisfy Pauli exclusion principle which stipulates that no two electrons can have the same quantum numbers n , l , m_l , and m_s .
- For example, we consider 22 electrons. These electrons are accommodated as:
- $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^4$:
- But the four d-electrons have several possibilities since the level is 5 fold degenerate.
- For multiple electrons we usually consider the total atoms spin, angular momentum and total angular momentum,

$$\vec{L} = \sum_{i=1}^n \vec{L}_i$$

$$\vec{S} = \sum_{i=1}^n \vec{S}_i$$

$$\vec{J} = \vec{L} + \vec{S},$$

with

$$|J| = \{|\vec{L} + \vec{S}|, |\vec{L} + \vec{S}| - 1, \dots, |\vec{L}| - |\vec{S}||\} .$$

With this definitions the atomic notation

$$^{2S+1}L_J$$

is used. In order to accommodate these electrons, we follow **Hund's rules**.

Hund's rules:

- 1) - The state with the largest value of total S is the most stable.
- 2) - If total S is the same, the largest total L is the most stable.
- 3) - If S and L are the same,
 - (a) *subshell less than half full* with the *smallest J* is the most stable.
 - (b) On the other hand, *subshell half or more than half full* with *largest J* is the most stable.

The Pauli Exclusion Principle

The consequences of the spin quantum number, when applied to the problem of the electronic structure of atoms, are not immediately obvious. The small magnitude of the electron's magnetic moment does not directly affect the energy of the electron to any significant degree. To see just how the spin of the electron does influence the problem, let us reconsider our atomic orbital model in the light of this new degree of freedom for the electron. In particular let us reconsider those instances in which our model failed to account for the observations.

- If a beam of helium atoms is passed through a magnetic field, no splitting and no deflection is observed. The helium atom, unlike the hydrogen atom is not magnetic.
- We could account for the absence of a magnetic moment for helium if we assumed that of the two electrons in the helium 1s orbital, one had its magnetic moment component up (\uparrow) and the other down (\downarrow).
- The two components would then cancel and there would be no resultant magnetic effect.
- Our complete description of the electronic configuration of the helium atom would be $1s^2(\uparrow\downarrow)$, i.e., both electrons have $n = 1$, $l = 0$, $m = 0$ and one has a spin (\uparrow) and the other a spin (\downarrow).

- You may wonder why the states of helium corresponding to the configurations $1s^2(\uparrow\uparrow)$ or $1s^2(\downarrow\downarrow)$ are not observed.
- These states should exhibit twice the magnetism possessed by a hydrogen atom.
- They are, however not found to occur.
- What about the excited states of the helium atom?
- An excited state results when one electron is raised in energy to an orbital with a higher n value.
- The electrons are thus in different orbitals.
- The spin assignments for an excited configuration can be made in more than one way and are such as to predict the occurrence of both magnetic and non-magnetic helium.
- For example, the configuration $1s^12s^1$ could be $1s^1(\uparrow)2s^1(\downarrow)$ and be nonmagnetic or it could equally well be $1s^1(\downarrow)2s^1(\downarrow)$ or $1s^1(\uparrow)2s^1(\uparrow)$ and be magnetic.

- Care must be exercised in the use of the abbreviated notation $1s^1(\uparrow)2s^1(\downarrow)$ to indicate the configuration and spin of a many-electron atom.
- In the present example, all we mean to imply is that the total component of the spin is zero. We do not imply that the electron in the $1s$ orbital necessarily has a spin "up" and that in the $2s$ orbital a spin "down."
- The situation could equally well be described by the notation $1s^1(\downarrow)2s^1(\uparrow)$.
- There is no experimental method by which we can distinguish between electrons in an atom, or, for that matter, determine any property of an individual electron in a many-electron system.
- Only the total magnetic moment, or total angular momentum, may be determined experimentally.
- ***Both*** the magnetic and non-magnetic forms are indeed found to occur for helium in an excited state.
- There are in fact two kinds of excited helium atoms, those which are ***non-magnetic*** and those which are ***magnetic***.

- If the two forms of helium possess different energies even though they have the same orbital configuration (we shall see why this should be so later) then we have an explanation for the previously noted discrepancy that helium exhibits twice the number of line spectra as does hydrogen.
- For every set of lines in the spectrum which arises from the transition of the electron from the configurations $1s^1(\uparrow)np^1(\downarrow)$ to the configuration $1s^1(\uparrow)2s^1(\downarrow)$ for example, there will be another set of lines due to transitions from $1s^1(\uparrow)np^1(\downarrow)$ to $1s^1(\uparrow)2s^1(\downarrow)$.
- The study of the magnetic properties of the ground and excited states of helium is sufficient to point out a general principle.
- For the ground state of helium, in which both electrons are in the same atomic orbital, ***only the non-magnetic form exists.***
- This would imply that when two electrons are in the same atomic orbital their spins must be paired, that is, one up (\uparrow) and one down (\downarrow).

- This is *an experimental fact* because helium is never found to be magnetic when it is in its electronic ground state.
- When the electrons are in different orbitals, then it is again an experimental fact that their spins may now be either paired ($\uparrow\downarrow$) or unpaired, e.g., ($\uparrow\uparrow$ or $\downarrow\downarrow$).
- Thus when two electrons are in the same orbital (i.e., they possess the same n , l and m values) their spins must be paired.
- When they are in different orbitals (one or more of their n , l and m values are different) then their spins may be paired or unpaired.
- We could generalize these observations by stating that "***no two electrons in the same atom may have all four quantum numbers the same.***"
- Stated in this way we see immediately that *any given orbital may hold no more than two electrons.*

- Since two electrons in the same orbital have the same values of n , l and m , they can differ only through their spin quantum number.
- However, the spin quantum number may have only one of two possible values, and these possibilities are given by (n, l, m, \uparrow) or (n, l, m, \downarrow) .
- We have indeed found the principle we were seeking, one which limits the occupation of an atomic orbital. This principle is known as the ***Pauli exclusion principle***.
- One form of it, suitable for use within the framework of the orbital approximation, is the statement given in quotation marks above.
- The Pauli principle cannot be derived from, nor is it predicted by, quantum mechanics.
- It is a law of nature which must be taken into account along with quantum mechanics if the properties of matter are to be correctly described.

- The concept of atomic orbitals, as derived from quantum mechanics, together with the Pauli exclusion principle which limits the occupation of a given orbital, provides an understanding of the electronic structure of many-electron atoms.
- We shall demonstrate this by "predicting" the existence of the periodic table.
- Calculations show that for the atoms from scandium to zinc the energies of the ***3d orbitals are always lower than the energy of the 4s orbital***, in spite of the greater penetration of a 4s electron.
- However, spectroscopic results show that ***Sc has the configuration [Ar]3d¹4s²***, not [Ar]3d³ or [Ar]3d²4s¹. It is due to the nature of electron–electron repulsions in 3d and 4s orbitals. Because the average distance of a 3d electron from the nucleus is less than that of a 4s electron, two 3d electrons are so close together that they repel each other more strongly than two 4s electrons do and 3d² and 3d³ configurations are ***disfavoured***.

- As a result, Sc has the configuration $[Ar]3d^14s^2$ rather than the two alternatives, for then the strong electron–electron repulsions in the 3d orbitals are minimized. The total energy of the atom is lower despite the cost of allowing electrons to populate the high energy 4s orbital. The electron configurations for scandium to zinc are of the form $[Ar]3d^n4s^2$, where $n = 1$ for scandium and $n = 10$ for zinc. Two notable exceptions, which are observed experimentally, are Cr, with electron configuration $[Ar]3d^54s^1$, and Cu, with electron configuration $[Ar]3d^{10}4s^1$.
- Half-filled and fully filled subshells have got extra stability. Therefore, one of the $4s^2$ electrons jumps to the $3d^4$ or $3d^9$ giving rise to $3d^54s^1$ and $3d^{10}4s^1$ configurations.

Electronic Basis for the Properties of the Elements

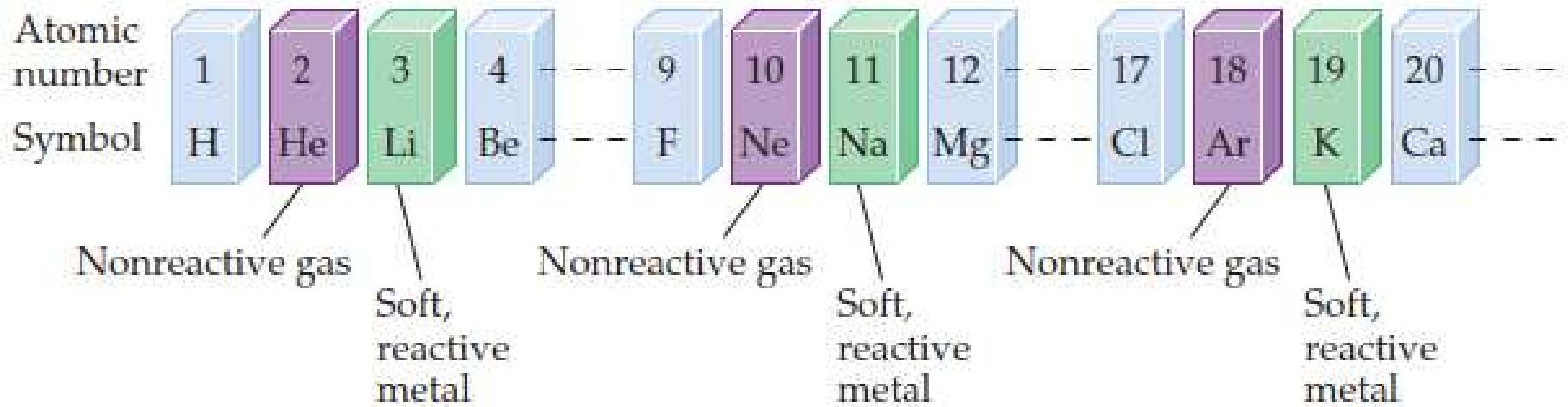
- We shall now present an interpretation of the physical and chemical properties of the elements based on the atomic orbital description of their electronic structures.
- Our discussion of the properties of the atoms will be a qualitative one, but it should be pointed out that many of the properties of atoms can now be accurately predicted by quantum mechanical calculations employing a very extended version of the atomic orbital concept.

Chemical Periodicity

- Many elements show strong similarities to one another.
- The elements lithium (Li), sodium (Na), and potassium (K) are:
 - ❖ all soft
 - ❖ very reactive metals....
- The elements helium (He), neon (Ne), and argon (Ar) are:
 - ❖ all nonreactive gases.
- If the elements are arranged in order of increasing *atomic number*, their chemical and physical properties show a repeating, or periodic, pattern.

Chemical Periodicity

- For example, each of the soft, reactive metals—lithium, sodium, and potassium—comes immediately after one of the nonreactive gases—helium, neon, and argon, respectively—as shown in Figure 2.13.



➤ If F is a reactive nonmetal, which other element or elements shown here are likely to be reactive nonmetals?

- Arranging elements by atomic number reveals a periodic pattern of properties.
- This pattern is the basis of the periodic table.

Electron Configurations and the Periodic Table

- As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table.
- Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order.
- As a result, the periodic table can be divided into “blocks” corresponding to the type of subshell that is being filled, as illustrated in Figure 6.9.1.

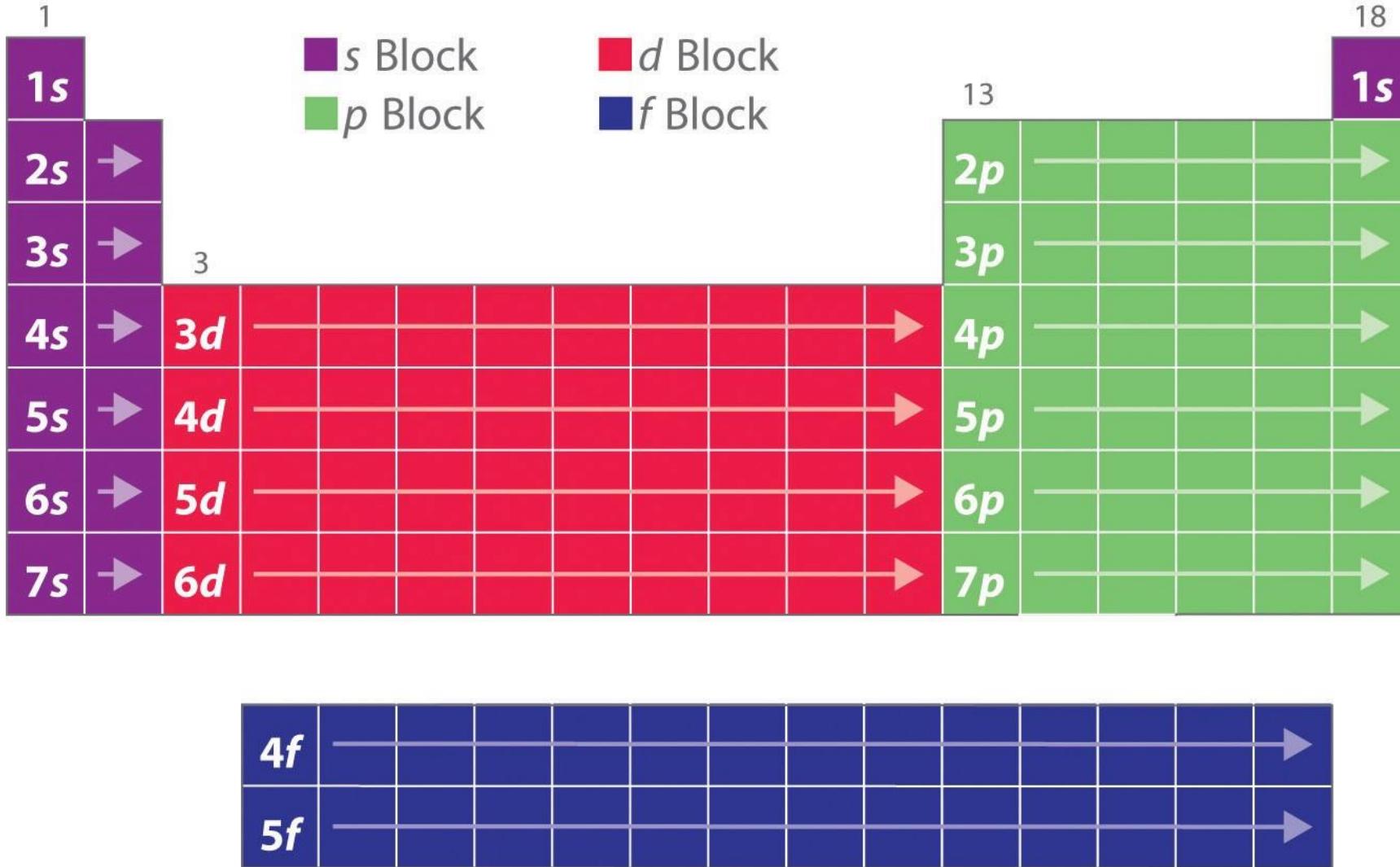
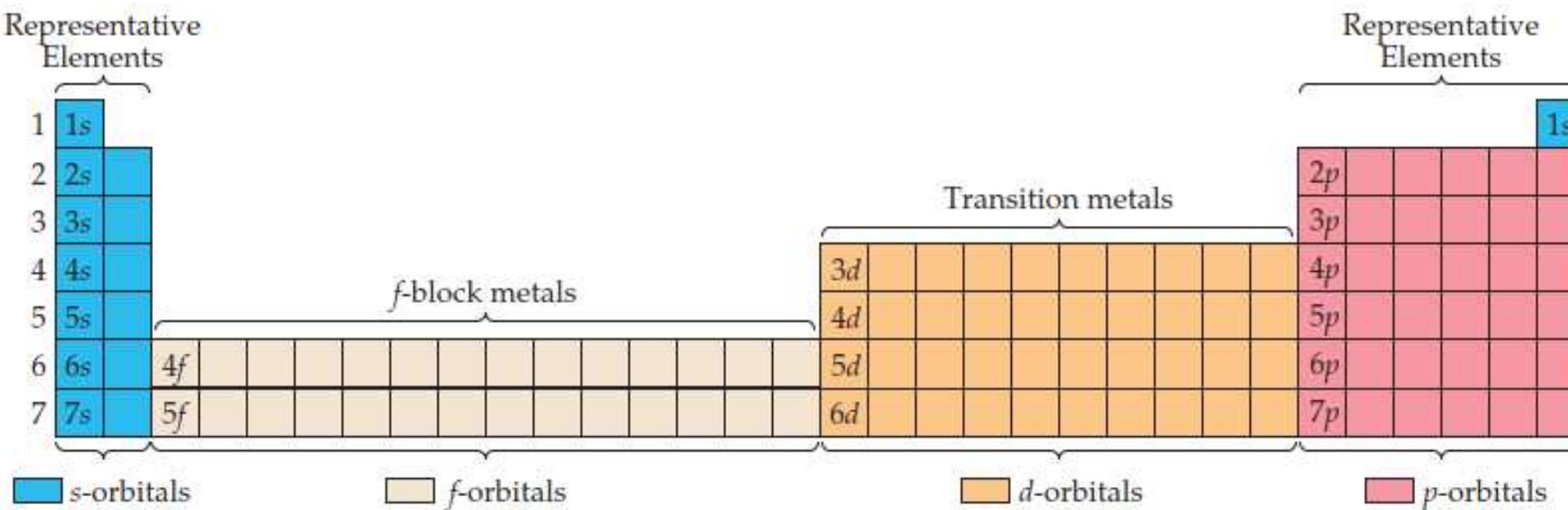


Figure 6.9.1: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element. The electron configurations of the elements are in Figure 6.9.2.

- For example, the two columns on the left, known as the *s* block, consisting of elements in which the *ns* orbitals are being filled.
- The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block.
- In between are the 10 columns of the *d* block, elements in which the $(n - 1)d$ orbitals are filled.
- At the bottom lie the 14 columns of the *f* block, elements in which the $(n - 2)f$ orbitals are filled.
- Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$.
- Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

☐ Regions of the long periodic table.



- ***p block***: where the valence p orbitals are being filled.
 - ❖ The s block and the p block elements together: ***representative elements***, sometimes called the ***main-group elements***.
- ***Transition metals***: the valence d orbitals are being filled and make up the d-block.
- ***f-block metals***: 14 columns in which the valence f orbitals are being filled and make up the f-block.

Periodic Table of Elements.

Periods — horizontal rows

The diagram illustrates the periodic table with several annotations:

- Elements arranged in order of increasing atomic number:** A callout box points to the first two columns (Groups 1A and 2A).
- Steplike line divides metals from nonmetals:** A callout box points to the transition metals and post-transition metals.
- containing elements with similar properties:** A callout box points to the second-period elements (Boron family) and the noble gases.

1A 1	1 H	2A 2																						8A 18
1																								2 He
2	3 Li	4 Be																						10 Ne
3	11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7																	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og						

Groups — vertical columns containing elements with similar properties

Steplike line divides metals from nonmetals

Elements arranged in order of increasing atomic number

		metals from nonmetals																	
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8			1B 9	2B 10		13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn		31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd		49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg		81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn		113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

- Metals
- Metalloids
- Nonmetals

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

The periodic table is the most significant tool that chemists use for organizing and remembering chemical facts.

- The color code of the Periodic Table shows that:
- ❖ except for hydrogen, all **the elements** on the *left* and in the *middle* of the table are **metallic elements, or metals.**
- ❖ All the metallic elements share ***characteristic properties***, such as luster and high electrical and heat conductivity, and all of them *except mercury (Hg) are solid at room temperature.*

- The metals are separated from the **nonmetallic elements**, or **nonmetals**, by a stepped line that runs from boron (B) to astatine (At).
- Nonmetals generally differ from metals in appearance and in other physical properties.
- At room temperature and pressure, some of the nonmetals are gaseous, some are solid, and one (Br) is liquid.
- Many of the elements that lie along the line that separates metals from nonmetals have properties that fall between those of metals and nonmetals. These elements are often referred to as **metalloids**.

- In the long form of the periodic table, families are labelled by both a number and by the letter A or B.
- Thus there is a IA family and a IB family.
- It will be noted that the elements in a B family all occur in the series of transition elements in which the *d* orbitals are being filled.
- In the A families, however, the *d* orbitals are either absent or are present as closed inner shells.
- For example, consider the electronic configurations of K (IA) and Cu (IB):



- Note that the most stable configuration for Cu is not [Ar] $3d^94s^2$ as expected. By transferring one of the 4s electrons to the 3d vacancy, the *d* subshell is filled and the electronic energy is lowered.
- The electron density distribution of the Cu atom is therefore a spherical one. Both K and Cu have one outer electron with a spherical charge distribution. They should have some properties in common, such as a tendency to lose one electron and form a positive ion.

- For this reason both families are labelled I.
- However, the shell underlying the outer electron in the K atom possesses a rare gas configuration, while in the Cu atom it is a set of filled *d* orbitals. This difference in electronic structure is sufficient to cause considerable differences in their chemistry, hence the further labels A and B.
- A rare gas configuration is always one of great stability, particularly when it occurs in a positive ion. (Recall that $I_2 = 47.3$ ev for sodium.) The species K^{+2} is never observed in solution chemistry, and could be produced in the gas phase only by an expenditure of energy far in excess of that observed in ordinary chemical reactions.
- The Cu^+ ion, on the other hand, very readily loses a second electron to form the Cu^{+2} ion. Indeed, Cu^{+2} is the more common ionic form of copper. Thus the d^{10} closed shell structure is more easily broken than a rare gas configuration, giving to Cu a variable valency of one or two.

- The order in which electrons are added to orbitals is read left to right beginning in the top-left corner.

1A 1	H $1s^1$	2A 2															8A 18		
Core	3 Li $2s^1$	4 Be $2s^2$															2 He $1s^2$		
[He]	11 Na $3s^1$	12 Mg $3s^2$	3B 3	4B 4	5B 5	6B 6	7B 7	8	9	10	8B	1B 11	2B 12	13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
[Ne]	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^23d^{10}$	32 Ge $4s^23d^{10}$	33 As $4s^23d^{10}$	34 Se $4s^23d^{10}$	35 Br $4p^5$	36 Kr $4s^23d^{10}$	
[Ar]	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^24d^3$	42 Mo $5s^14d^5$	43 Tc $5s^24d^5$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^24d^{10}$	50 Sn $5s^24d^{10}$	51 Sb $5s^24d^{10}$	52 Te $5s^24d^{10}$	53 I $5p^5$	54 Xe $5s^24d^{10}$	
[Kr]	55 Cs $6s^1$	56 Ba $6s^2$	71 Lu $6s^24f^{14}$	72 Hf $6s^24f^{14}$	73 Ta $6s^24f^{14}$	74 W $6s^24f^{14}$	75 Re $6s^24f^{14}$	76 Os $6s^24f^{14}$	77 Ir $6s^24f^{14}$	78 Pt $6s^14f^{14}$	79 Au $6s^24f^{14}$	80 Hg $6s^24f^{14}$	81 Tl $6s^24f^{14}$	82 Pb $6s^24f^{14}$	83 Bi $6s^24f^{14}$	84 Po $6s^24f^{14}$	85 At $6s^24f^{14}$	86 Rn $6s^24f^{14}$	
[Xe]	87 Fr $7s^1$	88 Ra $7s^2$	103 Lr $7s^25f^{14}$	104 Rf $7s^25f^{14}$	105 Db $7s^25f^{14}$	106 Sg $7s^25f^{14}$	107 Bh $7s^25f^{14}$	108 Hs $7s^25f^{14}$	109 Mt $7s^25f^{14}$	110 Ds $7s^25f^{14}$	111 Rg $7s^25f^{14}$	112 Cn $7s^25f^{14}$	113 Nh $7s^25f^{14}$	114 Fl $7s^25f^{14}$	115 Mc $7s^25f^{14}$	116 Lv $7s^25f^{14}$	117 Ts $7s^25f^{14}$	118 Og $7s^25f^{14}$	
[Xe]	Lanthanide series		57 La $6s^25d^1$	58 Ce $6s^24f^1$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^7$	65 Tb $6s^24f^8$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$			
[Rn]	Actinide series		89 Ac $7s^26d^1$	90 Th $7s^26d^2$	91 Pa $7s^25f^2$	92 U $7s^25f^3$	93 Np $7s^25f^4$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^7$	97 Bk $7s^25f^9$	98 Cf $7s^25f^{10}$	99 Es $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$			

- Elements in a group often *exhibit similarities in physical and chemical properties.* ... **WHY?**

- They have the same valence shell electronic configurations.....

- Many other *groups* in the periodic table also have *names*, listed in Table 2.3.

TABLE 2.3 Names of Some Groups in the Periodic Table

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens (pronounced kal'-ke-jens)	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

- Elements in a group often ***exhibit similarities in physical and chemical properties.***
- For example, the “**coinage metals**”—copper (Cu), silver (Ag), and gold (Au)—belong to group 11. These elements are less reactive than most metals, which is why they have been traditionally used throughout the world to make coins.

Penetration & Shielding

- *Penetration* and *shielding* are two underlying principles in determining the physical and chemical properties of elements. We can predict basic properties of elements by using shielding and penetration characteristics to assess basic trends.
- Electrons are negatively charged and are pulled pretty close to each other by their attraction to the positive charge of a nucleus. The electrons are attracted to the nucleus at the same time as electrons repel each other. The balance between attractive and repulsive forces results in ***shielding***. The orbital (*n*) and subshell (*m*) define how close an electron can approach the nucleus. The ability of an electron to get close to the nucleus is ***penetration***.
- In the simplest case, every electron in an atom would feel the same amount of "pull" from the nucleus. For example, in Li, all three electrons might "feel" the +3 charge from the nucleus. However, this is not the case when observing atomic behavior.

- When considering the core electrons (or the electrons closest to the nucleus), the nuclear charge "felt" by the electrons (Effective Nuclear Charge (Z_{eff})) is close to the actual nuclear charge.
- As you proceed from the core electrons to the outer valence electrons, Z_{eff} falls significantly.
- This is because of *shielding*, or simply the electrons closest to the nucleus decrease the amount of nuclear charge affecting the outer electrons.
- ✓ Shielding is caused by the combination of partial neutralization of nuclear charge by core electrons, and by electron-electron repulsion.
- The amount of charge felt by an electron depends on its distance from the nucleus. The closer an electron comes to the nucleus, or the more it *penetrates*, the stronger its attraction to the nucleus.
- Core electrons *penetrate* more and feel more of the nucleus than the other electrons.

- The amount of charge felt by an electron depends on its distance from the nucleus. The closer an electron comes to the nucleus, or the more it *penetrates*, the stronger its attraction to the nucleus. Core electrons *penetrate* more and feel more of the nucleus than the other electrons.

$$F_{\text{electron-nucleus}} = kZ e^2 / r^2$$

With Z is the charge of the nucleus (i.e., number of protons)

e is the charge of an electron or proton

r is the radius, or distance between the proton and the electron.

- Penetration and shielding result in an *Effective force* (F_{eff}) that holds the outer electrons to the atom, akin to Equation 2, but with Z_{eff} substituted for Z :

$$F_{\text{eff}} = k Z_{\text{eff}} e^2 / r^2$$

Orbital Penetration

- Penetration describes the proximity to which an electron can approach to the nucleus.
- In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom.
- Electrons in different orbitals have different wavefunctions and therefore different radial distributions and probabilities (defined by quantum numbers n and m , around the nucleus).
- In other words, penetration depends on the shell (n) and subshell (m). For example, we see that since a 2s electron has more electron density near the nucleus than a 2p electron, it is penetrating the nucleus of the atom more than the 2p electron.
- The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell.

- Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l): $s > p > d > f$
- And for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:
 - $1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f \dots$
- and the energy of an electron for each shell and subshell goes as follows...
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \dots$
- The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. If we imagine a dartboard that represents the circular shape of the s-orbital and if the darts landed in correlation to the probability to where an electron would be found, the greatest dart density would be at the 50 points region but most of the darts would be at the 30 point region. When considering the $1s$ -orbital, the spherical shell of 53 pm is represented by the 30 point ring.

- Electrons which experience *greater penetration* experience stronger attraction to the nucleus, *less shielding*, and therefore experience a larger *Effective Nuclear Charge* (Z_{eff}), but shield other electrons more effectively.

□ Shielding

- An atom (assuming its atomic number is greater than 2) has core electrons that are extremely attracted to the nucleus in the middle of the atom. However the number of protons in the nucleus are never equal to the number of core electrons (relatively) adjacent to the nucleus. The number of protons increase by one across the periodic table, but the number of core electrons change by periods.

- The first period has no core electrons, the second has 2, the third has 10, and etc. This number is not equal to the number of protons. So that means that the core electrons feel a stronger pull towards the nucleus than any other electron within the system. The valence electrons are farther out from the nucleus, so they experience a smaller force of attraction.
- Shielding refers to the core electrons repelling the outer rings and thus lowering the 1:1 ratio. Hence, the nucleus has "less grip" on the outer electrons and are shielded from them.
- Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.
- For example, Z_{eff} is calculated by subtracting the magnitude of shielding from the total nuclear charge.
- The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

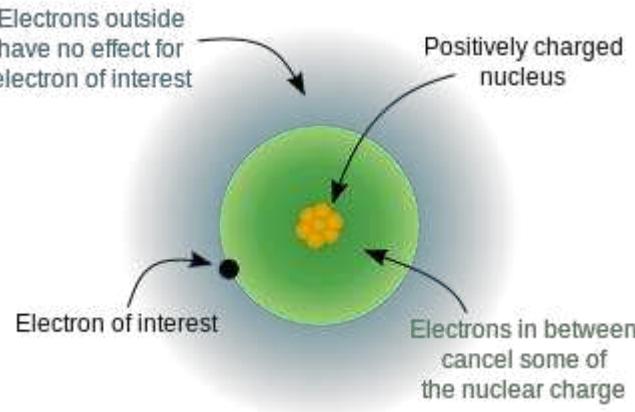


Figure 1: This image shows how inner electrons can shield outer electrons from the nuclear charge.
(CC BY-SA 3.0; from Wikipedia).

- Because the order of electron penetration from greatest to least is s , p , d , f ; the order of the amount of shielding done is also in the order s , p , d , f .
- Since the $2s$ electron has more density near the nucleus of an atom than a $2p$ electron, it is said to shield the $2p$ electron from the full effective charge of the nucleus. Therefore the $2p$ electron feels a lesser effect of the positively charged nucleus of the atom due to the shielding ability of the electrons closer to the nucleus than itself, (i.e. $2s$ electron).

- These electrons that are shielded from the full charge of the nucleus are said to experience an effective nuclear charge (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogen-like ions.
- The effective nuclear charge of an atom is given by the equation:
$$Z_{\text{eff}} = Z - S$$
 where Z is the atomic number (number of protons in nucleus) and S is the shielding constant.
- We can see from this equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases.
- Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus.
- This phenomena can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

Example 1: Fluorine, Neon, and Sodium

What is the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence) but the effective nuclear charge varies because each has a different atomic number A.

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

$$Z_{\text{eff}}(F^-) = 9 - 2 = 7+$$

$$Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$$

$$Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$$

So the sodium cation has the greatest effective nuclear charge, and thus the smallest radius.

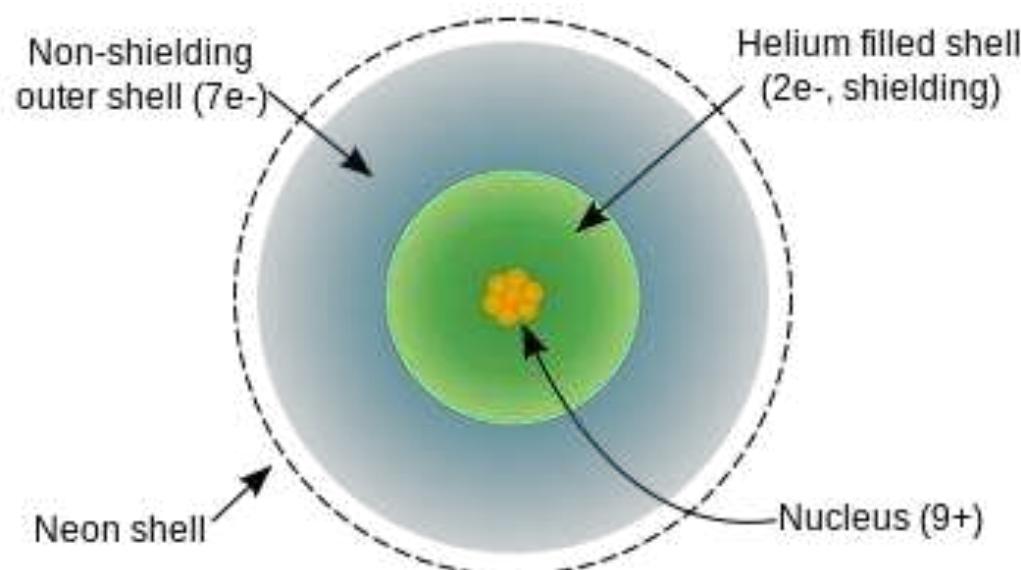


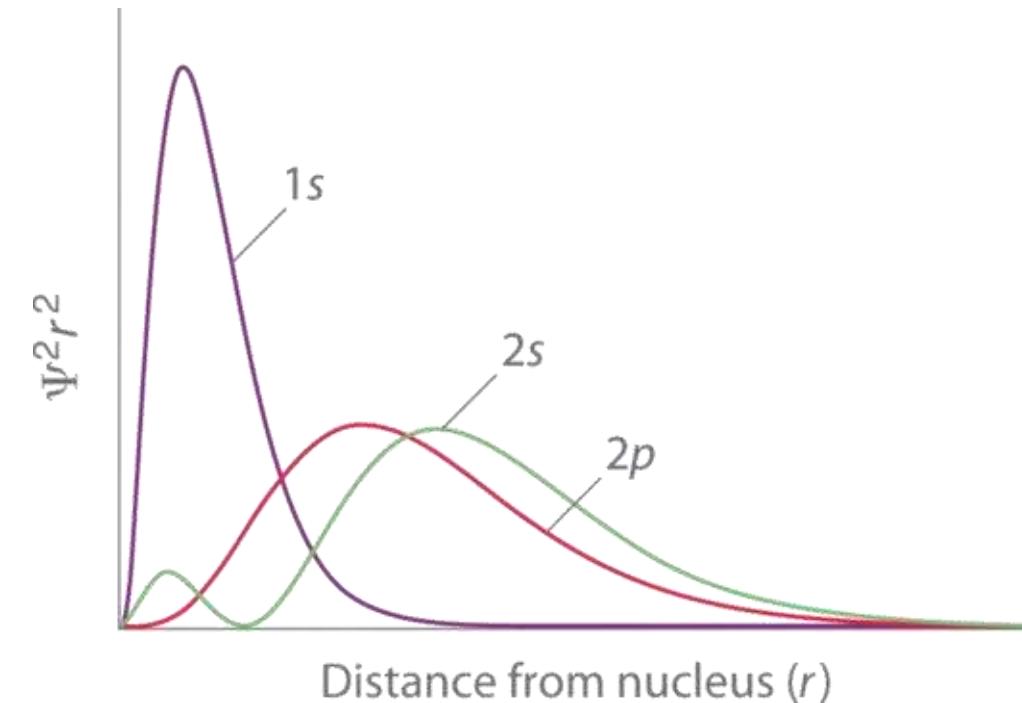
Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA- 3.0; Wikipedia).

Radial Distribution Graphs

A radial distribution function graph describes the distribution of orbitals with the effects of shielding (Figure 2). The small peak of the 2s orbital shows that the electrons in the 2s orbital are closest to the nucleus. Therefore, it is the electrons in the 2p orbital of Be that are being shielded from the nucleus, by the electrons in the 2s orbital.

The following is the radial distribution of the 1s and 2s orbitals. Notice the 1s orbital is shifted to the right, while the 2s orbital has a node.

Figure 2: Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.



Periodic Trends Due to Penetration and Shielding

- **Effective Nuclear Charge (Z_{eff}):** The effective nuclear charge *increases* from left to right and *increases* from top to bottom on the periodic table.
- **Atomic Radius:** The atomic radius decreases from left to right, and increases from top to bottom.
- **Ionization Energies:** The ionization energies increase from left to right, and decrease from top to bottom.
- **Electronegativity:** The electronegativity of the elements is highest near fluorine. In general, it increases from left to right and decreases from top to bottom.

Horizontal Variations

The experimental values of the atomic radii and the first and second ionization potentials of the elements (labelled as I_1 and I_2 respectively) in the third row of the periodic table are listed in Table 5-1. A study of these values will indicate the basic trends observed as the number of electrons is increased one at a time until all the orbitals with a given value of n are fully occupied.

Table 5-1: The Atomic Radii and Ionization Potentials* of Third Row Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Radius (Å)	1.86	1.60	1.48	1.17	1.0	1.06	0.97	
I_1 (ev)	5.14	7.64	5.98	8.15	11.0	10.4	13.0	15.8
I_2 (ev)	47.3	15.0	18.8	16.3	19.7	23.4	23.8	27.6

*The values for I_1 and I_2 are taken from C. E. Moore, *Atomic Energy Levels*, Vol. 1, N.B.S. Circular 467, Washington, D.C. (1949). I_2 is the energy required to remove an electron from the singly-charged ion, i.e., the energy required to ionize a second electron.

❖ Atomic radii

- The diameter of an atom is difficult to define precisely as the density distribution tails off at large distances. However, there is a limit as to how close two atoms can be pushed together in a solid material.
- We shall take one half of the distance between the nuclei of two atoms in an elemental solid as a rough measure of the atomic radius.
- Any consistent method of defining the radius leads to the same trend we see in Table 5-1.
- The size of the atom in general decreases as the number of electrons in the quantum shell is increased.
- This observation, which at first sight might appear surprising, finds a ready explanation through the concept of an ***effective nuclear charge***.

- The electric field and hence the attractive force exerted by the nucleus on an electron in the outer quantum shell is reduced because of the screening effect of the other electrons which are present in the atom.
- An outer electron does not penetrate to any great extent the tightly bound density distribution of the inner shell electrons.
- Consequently each inner electron (an electron with an n value less than the n value of the electron in question) reduces the value of the nuclear charge experienced by the outer electron by almost one unit.
- The remaining outer electrons on the other hand are, on the average, all at the same distance away from the nucleus as is the electron under consideration.
- Consequently each outer electron screens considerably less than one nuclear charge from the other outer electrons.
- Thus *the higher the ratio of outer shell to inner shell electrons, the larger will be the "effective nuclear charge" which is experienced by an electron in the outer shell.*

- All of the elements in a given row of the periodic table possess the same number of inner shell electrons. For example, the elements in the third row have the inner shell configuration of $1s^22s^22p^6$.
- As we move across the periodic table from left to right the nuclear charge increases, and each added electron is placed in the outer shell until a total of eight is reached and the quantum shell is full.
- *The number of outer shell electrons increases along a given period, but the number of inner shell electrons remains fixed.* Thus the effective nuclear charge increases from a minimum value for sodium, where the ratio of outer shell to inner shell electrons is 1:10, to a maximum value for argon where the same ratio is 8:10.
- The atomic radius undergoes a gradual decrease since the outer electrons become more tightly bound as the effective nuclear charge increases.

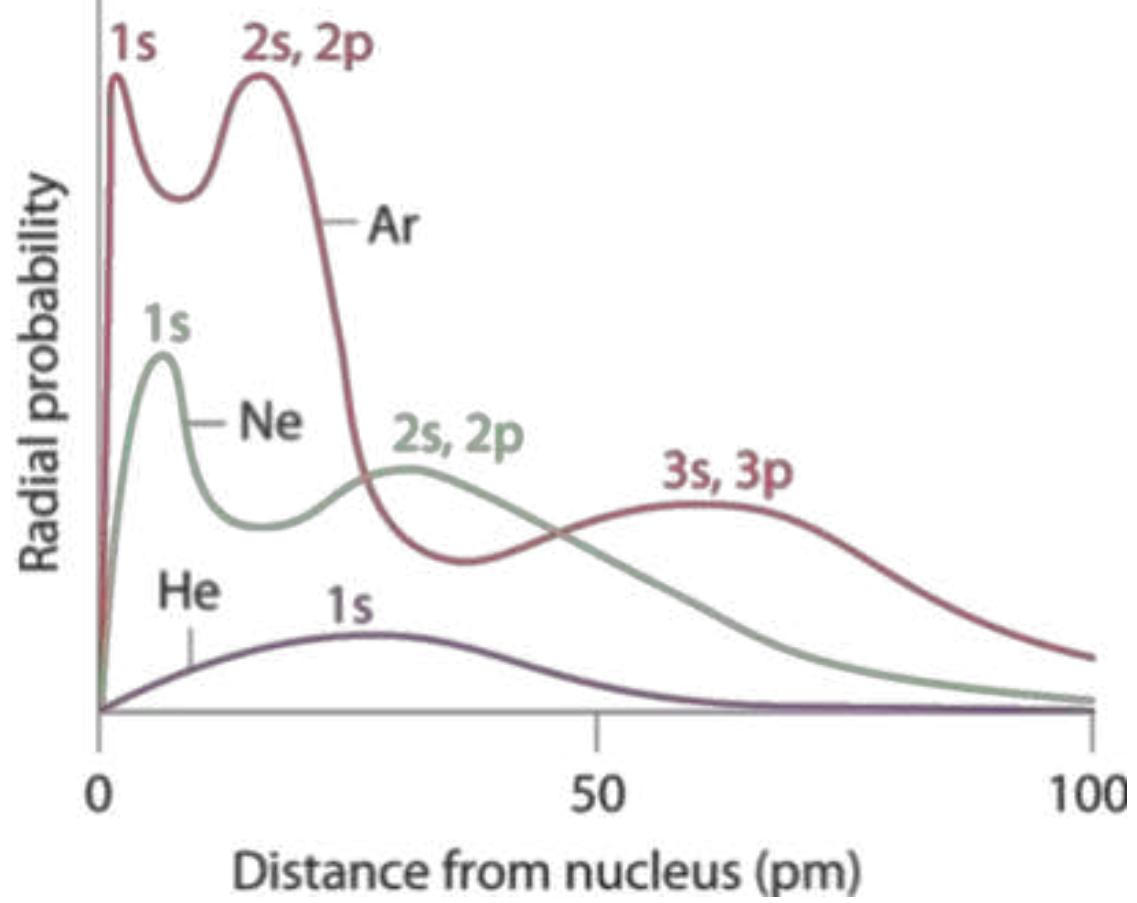


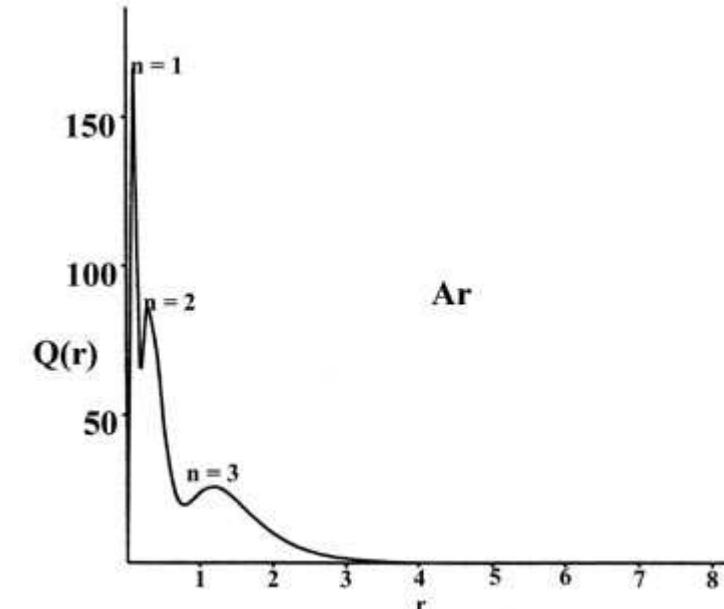
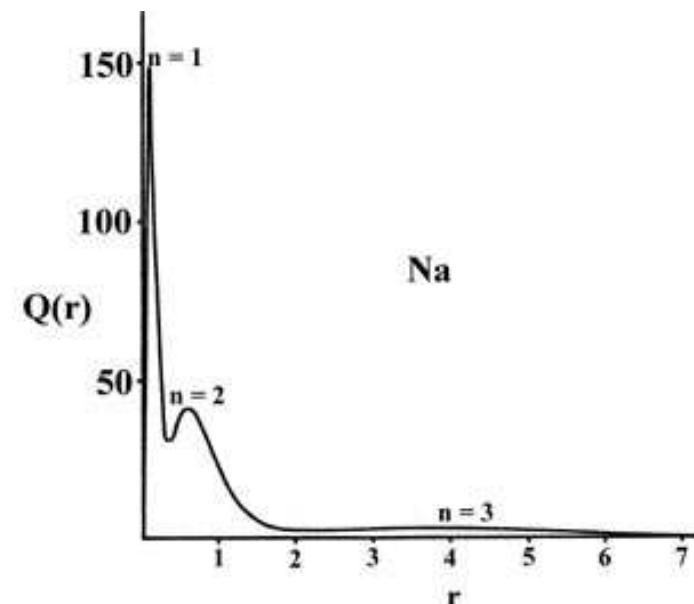
Figure 7.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈ 30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈ 8 pm, and the 2s and 2p electrons combine to form another maximum at ≈ 35 pm (the $n = 2$ shell). In Ar, the 1s electrons have a maximum at ≈ 2 pm, the 2s and 2p electrons combine to form a maximum at ≈ 18 pm, and the 3s and 3p electrons combine to form a maximum at ≈ 70 pm.

- Figure 7.3.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell.
- Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks.
- Argon, with filled $n = 1, 2$, and 3 principal shells, has three peaks.
- The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n . Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus.

- The energy of the $n = 1$ shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

- These features of the atomic density distributions are clearly evident in a graph of the radial distribution function, $Q(r)$. This function, it will be recalled, gives the number of electronic charges within a thin shell of space lying between two concentric spheres, one of radius r and the other with a radius only slightly larger. The radial distribution functions for atoms may be determined experimentally by X-ray or electron diffraction techniques.
- Plots of $Q(r)$ versus r for sodium and argon (Fig. 5-1), the first and last members of the third row of the periodic table, clearly reveal the persistence of a "shell structure" in the many-electron atoms.

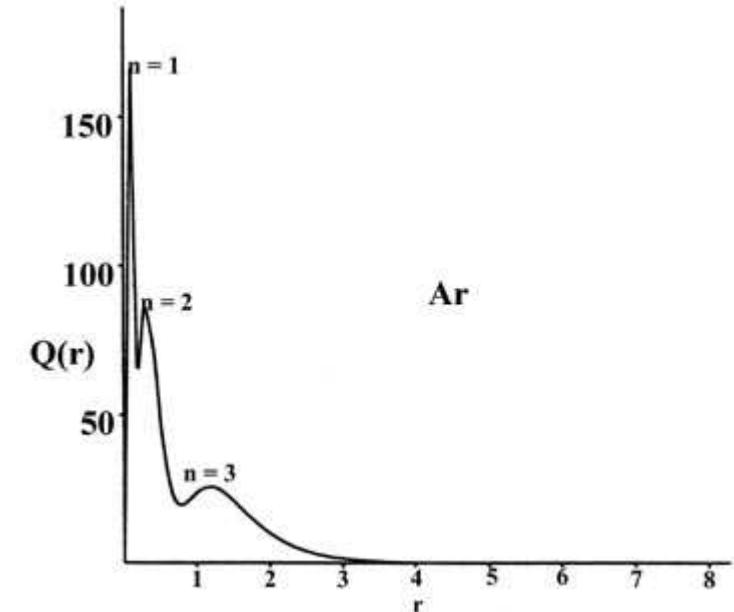
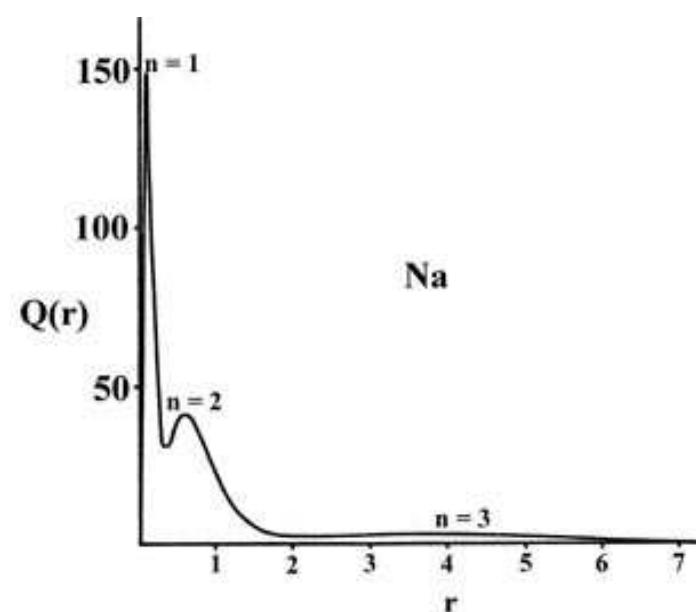
Fig. 5-1. The radial distribution functions $Q(r)$ for the Na and Ar atoms.



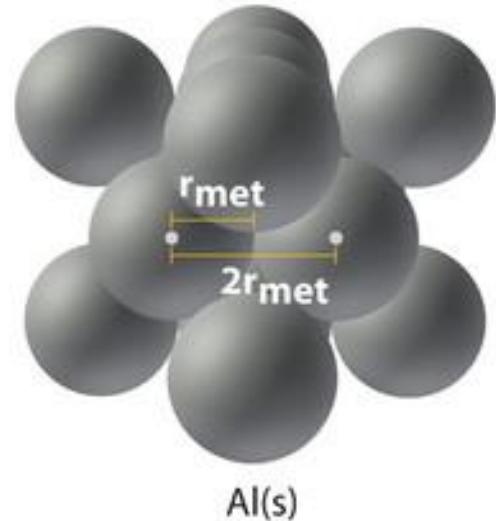
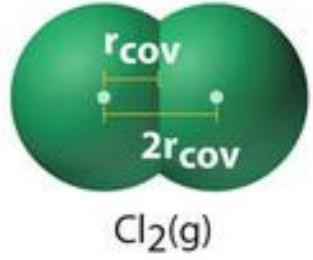
- There are three peaks in the density distribution corresponding to the presence of three principal quantum shells in the orbital model of the electronic structure of sodium and argon.
- The peak closest to the nucleus may be identified with the charge density in the $1s$ orbital, the middle peak with that in the $2s$ and $2p$ orbitals and the outer peak with the charge density in the $3s$ orbital in sodium and in the $3s$ and $3p$ orbitals in argon.
- The maxima in $Q(r)$ occur at smaller values of r for argon than for sodium as expected on the basis of a larger effective nuclear charge for argon than for sodium.
- Most of the $1s$ charge density is found within a very thin shell close to the nucleus in both cases as the inner shell density experiences the field of the full nuclear charge, $Z_{\text{Na}} = 11$ and $Z_{\text{Ar}} = 18$. The charge density in the $n = 2$ orbitals is confined to a shell which is narrower and closer to the nucleus in argon than in sodium. The electrons in this second shell experience a nuclear charge of approximately sixteen in argon but of only nine in sodium.

- The most dramatic effect of the difference in the effective nuclear charges of argon and sodium is evidenced by the appearance of the electron density in the valence shell.
- In sodium this shell is broad and diffuse as there are ten inner electrons shielding eleven nuclear charges.
- In argon where there are ten inner electrons to shield eighteen nuclear charges the valence shell is more contracted and it peaks at roughly one third of the corresponding distance in sodium. The valence shell density is clearly more tightly bound in argon than in sodium.

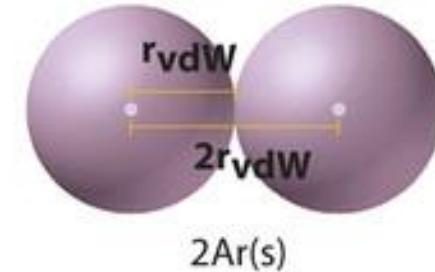
Fig. 5-1. The radial distribution functions $Q(r)$ for the Na and Ar atoms.



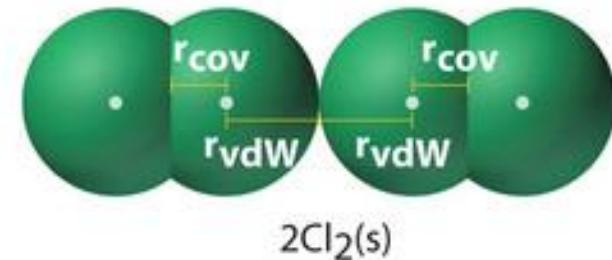
- Figure 7.3.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms.
- For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure 7.3.2a).
- Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ \AA} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.



(a) Covalent radius, r_{cov}



(c) van der Waals radius, r_{vdW}



(d) Covalent vs. vdW radii

Figure 7.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov} , is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2 . (b) The metallic atomic radius, r_{met} , is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW} , is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2 . The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

- In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.
- Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure 7.3.2b).

➤ For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure 7.3.2c). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $\text{Cl}_2(s)$ at low temperatures). These radii are generally not the same (Figure 7.3.2d).

- ***There is one exception*** to the trend of a decrease in diameter across a given row in that ***phosphorus has an atomic radius slightly smaller than that of sulphur*** which follows it in the table.
- ✓ The configuration of the outer electrons in phosphorus is $3s^23p^3$. Each of the p orbitals contains a single electron and according to Hund's rule all will have the same spin quantum number.
- ✓ *Electrons with identical spins have smaller electron-electron repulsion energies* than do electrons with paired spins, for reasons we have previously mentioned.
- ✓ Therefore, the larger the number of parallel spins in an atom, the smaller will be the average energy of repulsion between the electrons.
- Three is the maximum number of unpaired spins possible in any of the short periods as this corresponds to a half-filled set of p orbitals. The stabilizing effect of the decreased energy of repulsion between the electrons is comparable to the effect obtained by increasing the effective nuclear charge by approximately one. This can be seen by comparing phosphorus with sulphur.

- Sulphur has an increased nuclear charge but the added electron must be paired up with one of the electrons in the p orbitals. The number of unpaired electrons with parallel spins is thus reduced to two, the average energy of repulsion between the electrons is increased, and the ***sulphur atom is slightly larger than the phosphorus atom.***
- The decrease in energy which is obtained by maximizing the number of parallel spins is not sufficient to change the most stable outer configuration actually found for silicon, $3s^23p^2$, to that in which all four outer electrons have parallel spins, $3s^13p^3$. *This latter configuration could be obtained only by promoting an electron from a $3s$ orbital to a $3p$ orbital.* The $3s$ orbital is more stable than a $3p$ orbital because of the penetration effect, and the energy increase caused by the promotion of an electron from the $3s$ to a $3p$ orbital would not be offset by the energy decrease obtained by maximizing the number of parallel spins.
- It is interesting to note, however, that the reverse of this is true for some of the elements in the transition series.

- In these elements the $4s$ and $3d$ (or in general the ns and $(n - 1)d$) orbitals are the outer orbitals.
- The energy difference between an ns and an $(n - 1)d$ orbital is much less than that between an ns and an np orbital. *Thus the effect of maximizing the number of parallel spins can be overriding in these cases.*
- The outer electronic structure of vanadium is $4s^23d^3$. (Recall that there are five d orbitals and hence the configuration d^5 will represent five electrons with parallel spins.)
- We would expect the outer electronic configuration of the next element, chromium, to be $4s^23d^4$ with four parallel spins. Instead, the configuration is actually $4s^13d^5$ resulting in a total of six parallel spins and a reduction in the energy of repulsion between the electrons.

Vertical Relationships

- Table 5-2 lists the atomic radii and the ionization potentials of the elements found in the first column of the periodic table, the group I elements.

Table 5-2: Atomic Radii and Ionization Potentials of Group I Elements

Element	Li	Na	K	Rb	Cs
Radius (Å)	1.50	1.86	2.27	2.43	2.62
I_1 (ev)	5.4	5.1	4.3	4.2	3.9

- The average value of the distance between the electron and the nucleus increases as the value of the principal quantum number is increased.
- The increase in the atomic diameters down a given group in the periodic table is thus understandable. Each of the group I elements represents the beginning of a new quantum shell.
- There will be a very sharp decrease in the effective nuclear charge on passing from the preceding closed shell element to a member of group I, as the number of the inner shell electrons is increased by eight.
- This large sudden reduction in the effective nuclear charge and the fact that the electron, because of the Pauli exclusion principle, must enter a new quantum shell, causes the group I elements to be larger in size and much more readily ionized than the preceding noble gas elements. The decrease in the effective nuclear charge and the increase in the principal quantum number down a given family bring about a steady decrease in the observed ionization potentials. Thus the outer 6s electron in cesium is on the average, further from the nucleus than is the outer 2s electron in lithium. It is also more readily removed.

- So far we have considered the periodic variations in the energy required to remove an electron from an atom:
 $M \rightarrow M^+ + e^-$ **$I_1 = \text{a positive value}$**
- In some favourable cases it is possible to determine the energy released when an electron is added to an atom:
 $M + e^- \rightarrow M^-$ **$\Delta E = \text{a negative value}$**
- The magnitude of the energy released when an atom captures an extra electron is a measure of the atom's ***electron affinity***.
- It might at first seem surprising that a neutral atom may attract an extra electron. Indeed many elements do not have a detectable electron affinity. However, consider the outer electronic configuration of the group VII elements, the halogens:

ns^2np^5

- There is a single vacancy in the outer set of orbitals and the effective nuclear charge experienced by the valence electrons in a halogen atom is almost the maximum value possible for any given row.
- Because of the incomplete screening of the nuclear charge by the outer electrons, the remaining vacancy in the outer shell will, in effect, exert an attractive force on a free electron large enough to bind it to the atom.
- The electron affinities for the rare gas atoms will be effectively zero even though the effective nuclear charge is a maximum for this group of elements there are no vacancies in the outer set of orbitals in a rare gas atom and as a result of the Pauli principle, an extra electron would have to enter an orbital in the next quantum shell.
- The electron in this orbital will experience only a very small effective nuclear charge as all of the electrons originally present in the atom will be in inner shells with respect to it.

- Elements to the left of the periodic table, the alkali metals for example, do have vacancies in their outer quantum shell but their effective nuclear charges are very small in magnitude. Thus these elements do not exhibit a measurable electron affinity.
- The electron affinity increases across a given row of the periodic table and reaches a maximum value with the group VII elements. *This is a direct reflection of the variation in the effective nuclear charge.*
- The orbital vacancy in which the extra electron is placed is found at larger distances from the nucleus when the principal quantum number is increased. Thus the electron affinity should decrease down any given family of elements in the periodic table. For example, the electron affinities for the halogens **should** decrease in the order F > Cl > Br > I.
- The variation in the ionization potentials across a given row is reflected in the values shown in the atomic orbital energy level diagram for the elements from hydrogen through to neon

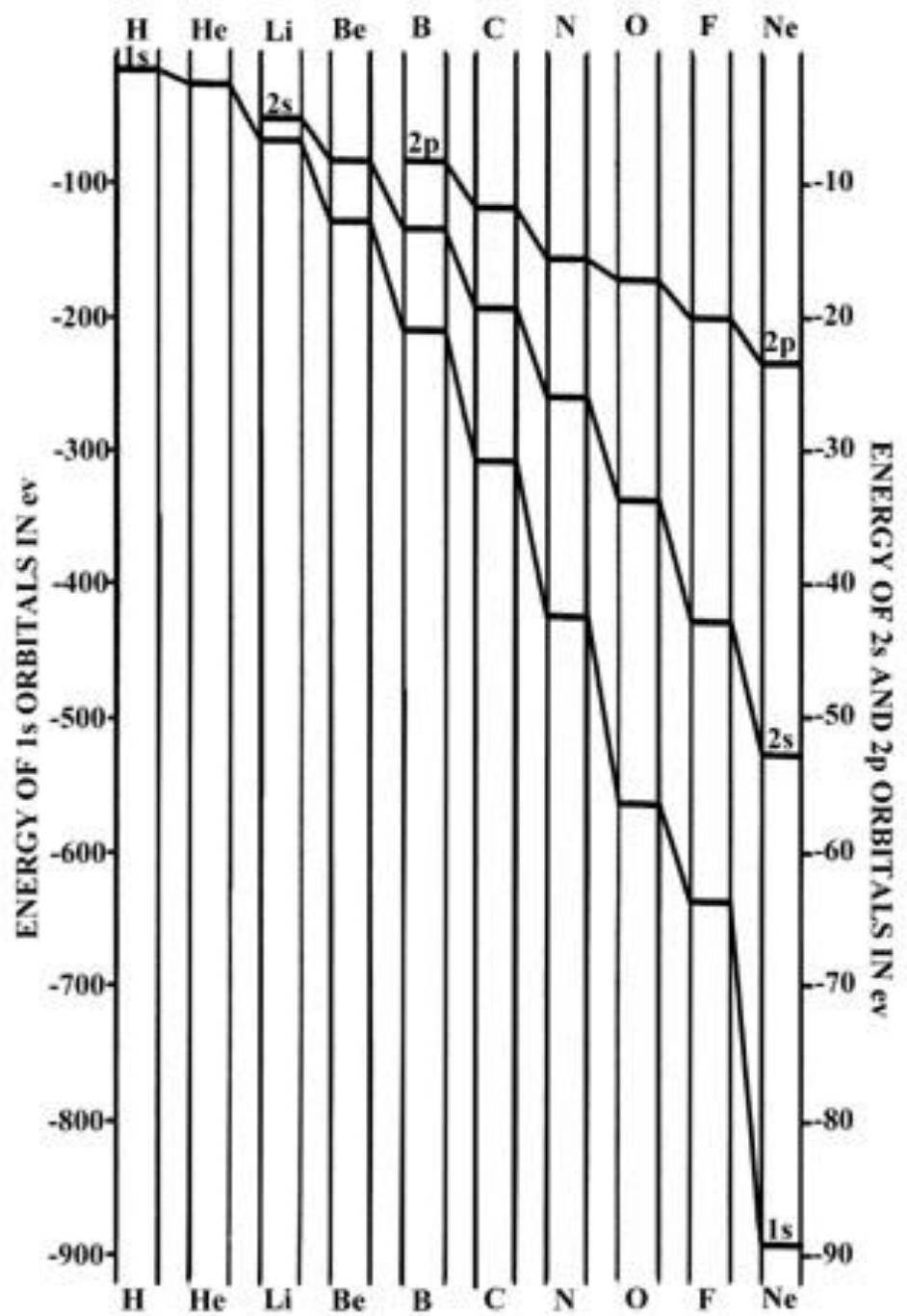


Fig. 5-3. An orbital energy level diagram for the elements H to Ne

- (Note that the energy scale used for the 1s orbital differs by a factor of ten from that for the 2s and 1p orbitals.)
- The orbital energies show a uniform decrease when the nuclear charge is increased, reflecting an increase in the binding of the electrons.
- The total energy of a many-electron atom is ***not*** simply the sum of the orbital energies. Summing the orbital energies does not take proper account of the repulsions between the electrons. The orbital energies do, however, provide ***approximate*** estimates of the ionization potentials.
- The ionization potential is the energy required to remove one electron from an atom, and an orbital energy is a measure of the binding of a ***single electron*** in a given orbital.
- Thus the ionization potential should be approximately equal to ***minus*** the orbital energy. For example, the ionization potential of lithium is 5.39 ev and the 2s orbital energy is -5.34 ev. Similarly I_1 , for neon is 21.56 ev and the 2p orbital energy is -23.14 ev.

- Shell structure is also evident in the ionization potentials and orbital energies of atoms.
- By exposing the atom to light of very short wavelength (in the X-ray region of the spectrum), it is possible to ionize one of the inner shell electrons, rather than a valence electron. That is, the energy of an X-ray photon is comparable to the binding energy of an inner shell electron.
- The resulting ion is in a very unstable configuration and after a very brief period of time an electron from the outer shell "falls" into the vacancy in the inner shell.
- In falling from an outer to an inner shell the binding of the electron is greatly increased and a photon is emitted.
- The energy of this photon should be *approximately* equal to the difference in energies of the outer shell and inner shell orbitals.
- For example, the photon emitted when neon loses an inner shell electron has an energy of 849 ev.

- The difference in energy between the $2p$ and $1s$ orbitals of neon is 869 ev. Photons with energies in this range occur in the X-ray region of the spectrum.
- It is apparent from the variation in the $1s$ orbital energies shown in Fig. 5-3 that the energies and hence the frequencies of the X-ray photons will increase as the nuclear charge is increased.
- It was from a study of the X-ray photons emitted by the elements that Moseley was first able to determine the nuclear charges (the atomic numbers) of the elements.

➤ Variation of the effective nuclear charge (Z_{eff}) for the outermost valence electron with atomic number

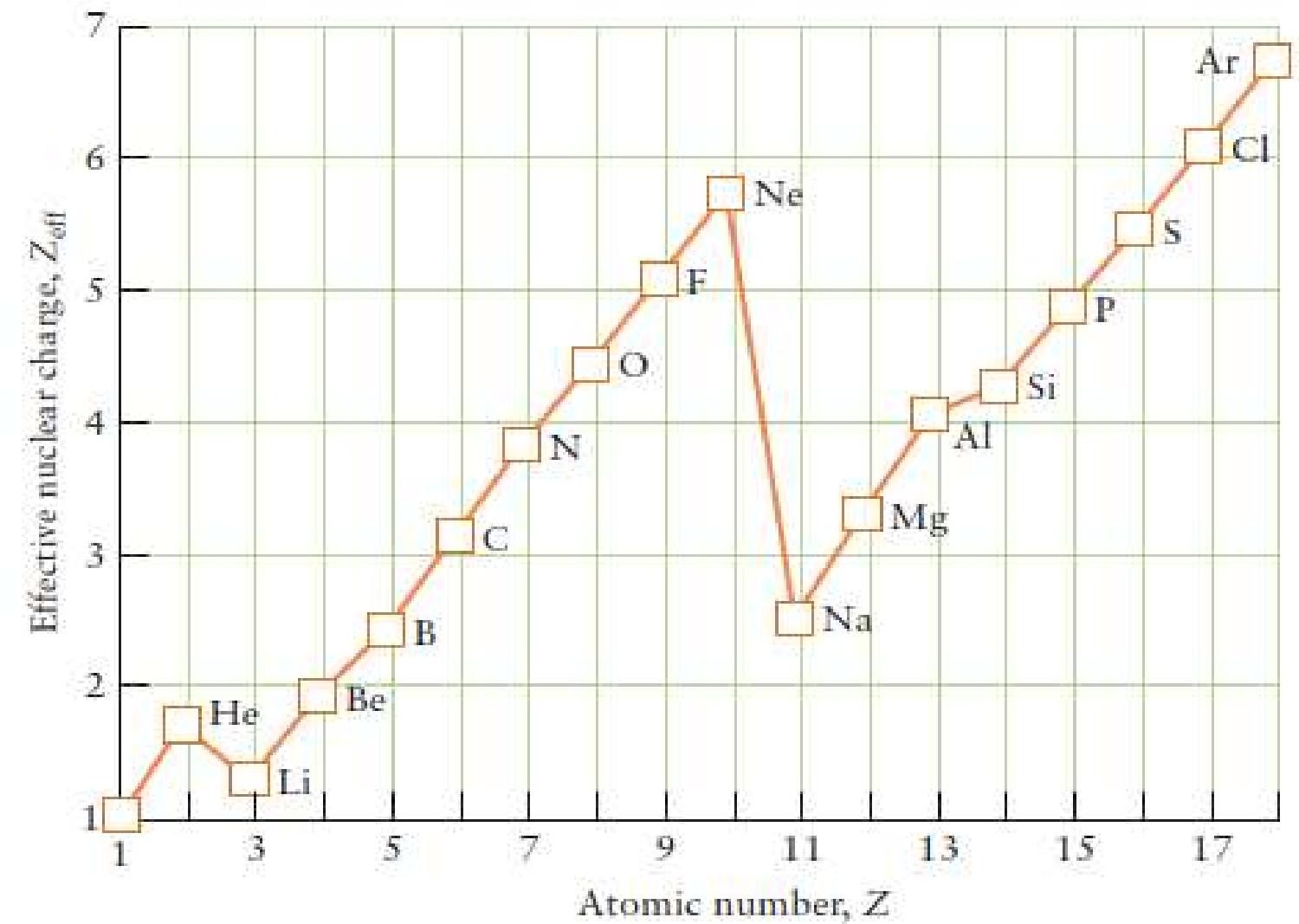


FIGURE 1.45 The variation of the effective nuclear charge for the outermost valence electron with atomic number. Notice that the effective nuclear charge increases from left to right across a period but drops when the outer electrons occupy a new shell. (The effective nuclear charge is actually $Z_{\text{eff}}e$, but Z_{eff} itself is commonly referred to as the charge.)

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 7.3.3).

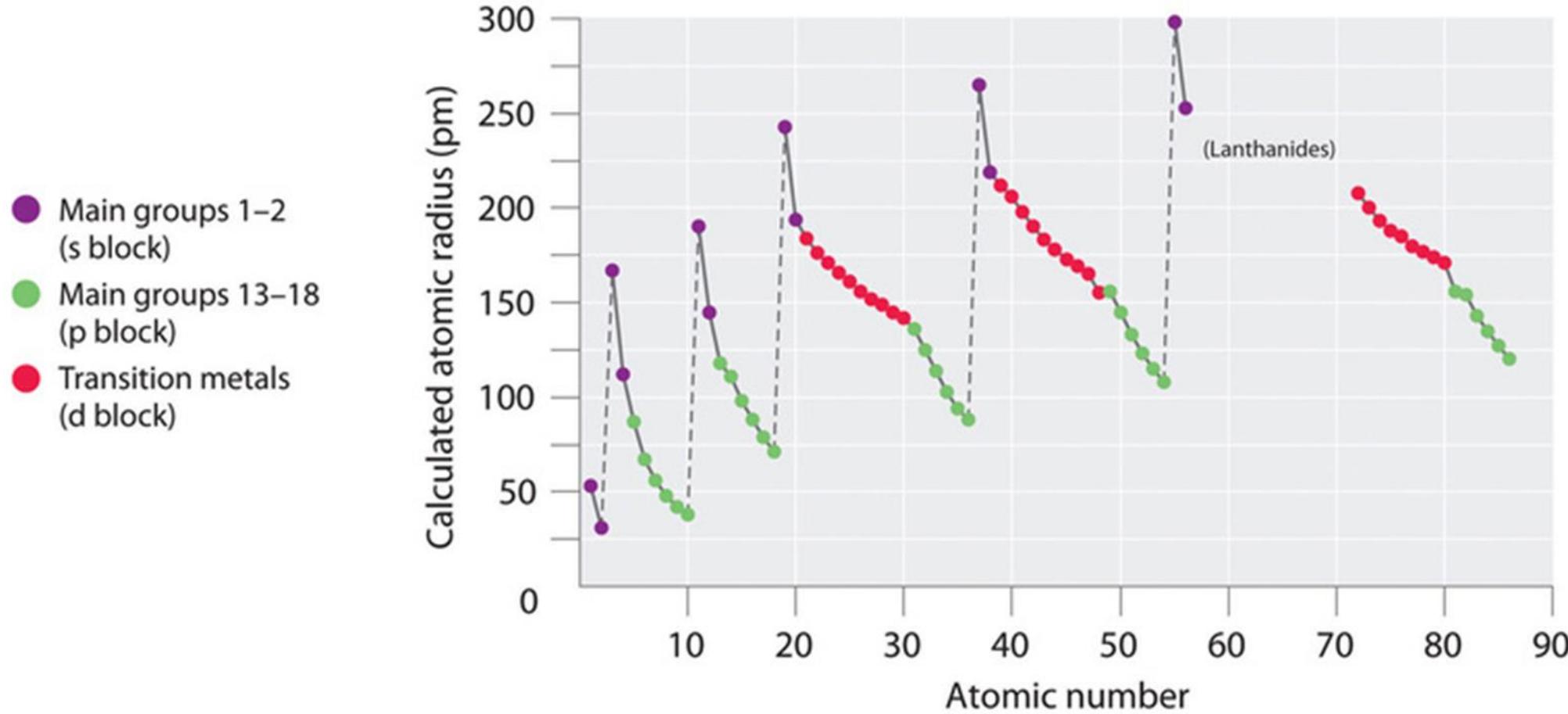


Figure 7.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 7.3.4).

Trends in atomic size result from differences in the effective nuclear charges (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always less than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

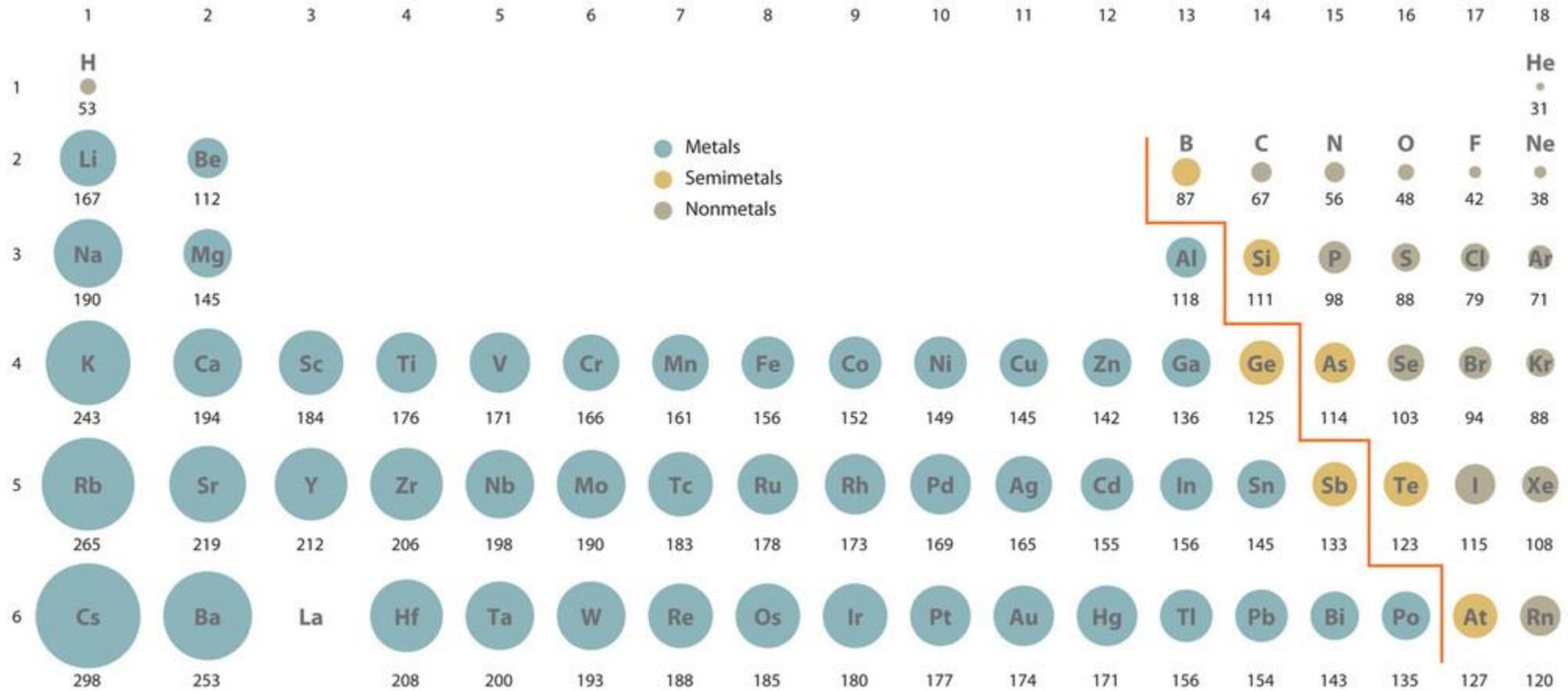


Figure 7.3.4 Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions.

Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

➤ Variation of atomic radii

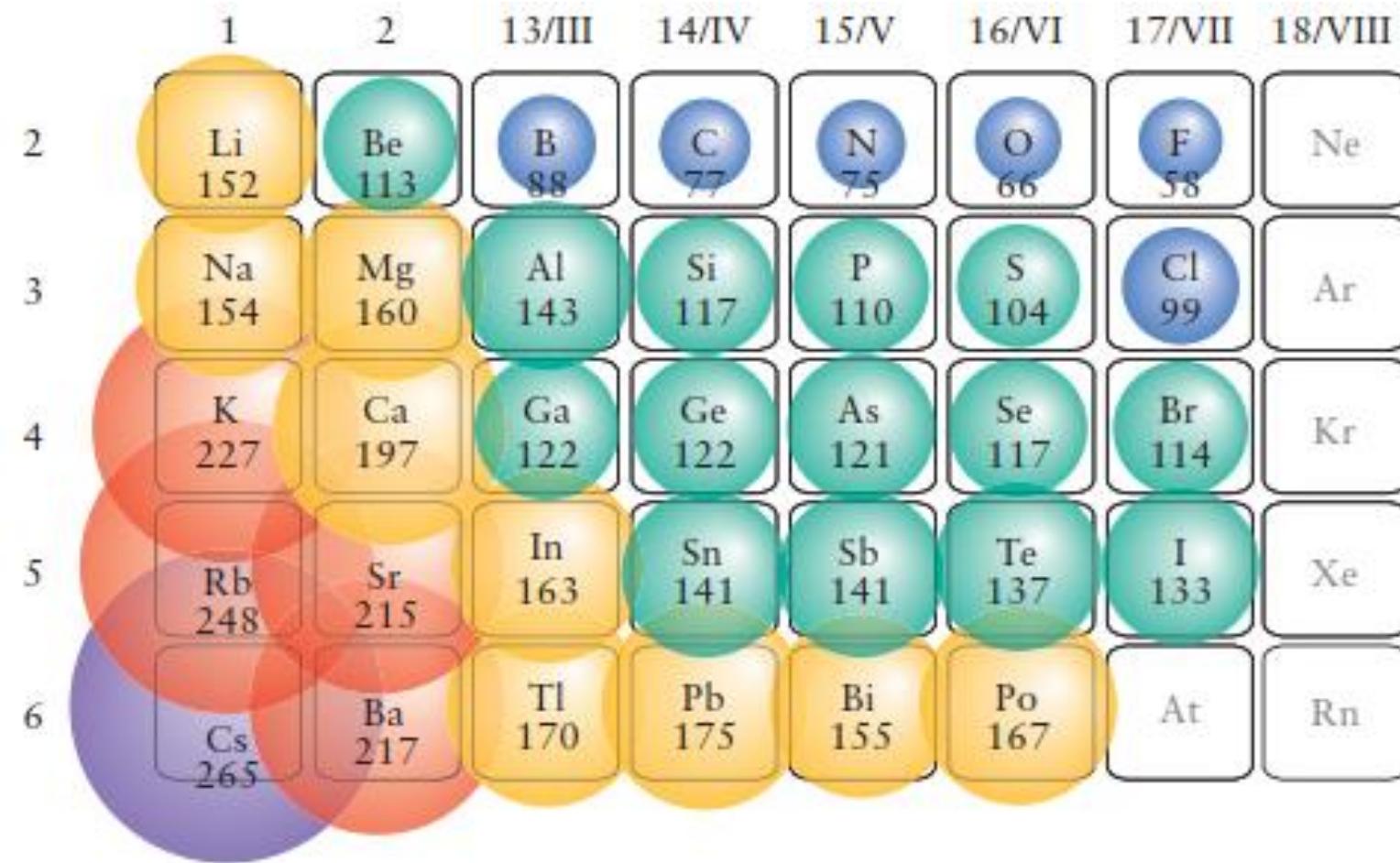


FIGURE 1.46 The **atomic radii** (in picometers) of the main-group elements.

The radii decrease from left to right in a period and increase down a group. The colors used here and in subsequent charts represent the general magnitude of the property.

- Atomic radii generally decrease from left to right across a period as the effective atomic charge increases, and they increase down a group as successive shells are occupied.

- The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s_2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10.
- Although electrons are being added to the 2s and 2p orbitals, electrons in the same principal shell are not very effective at shielding one another from the nuclear charge.
- Thus the single 2s electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of $Z_{\text{eff}} = +1.26$ for Li.)
- In contrast, the two 2s electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2s electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium.

- Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2s and 2p orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.
- The *increase in atomic size going down a column* is also due to *electron shielding*, but the situation is more complex because the principal quantum number n is not constant. *The size of the orbitals increases as n increases, provided the nuclear charge remains the same.*
- In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to ns orbitals with increasing values of n. However, *it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number n increases from 2 to 6, but the nuclear charge increases from +3 to +55!*

- As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the inner electrons.
- If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration.
- The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus.

- The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table.
- Irregularities can usually be explained by variations in effective nuclear charge.

□ **Ionic Radii and Isoelectronic Series**

- An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion).

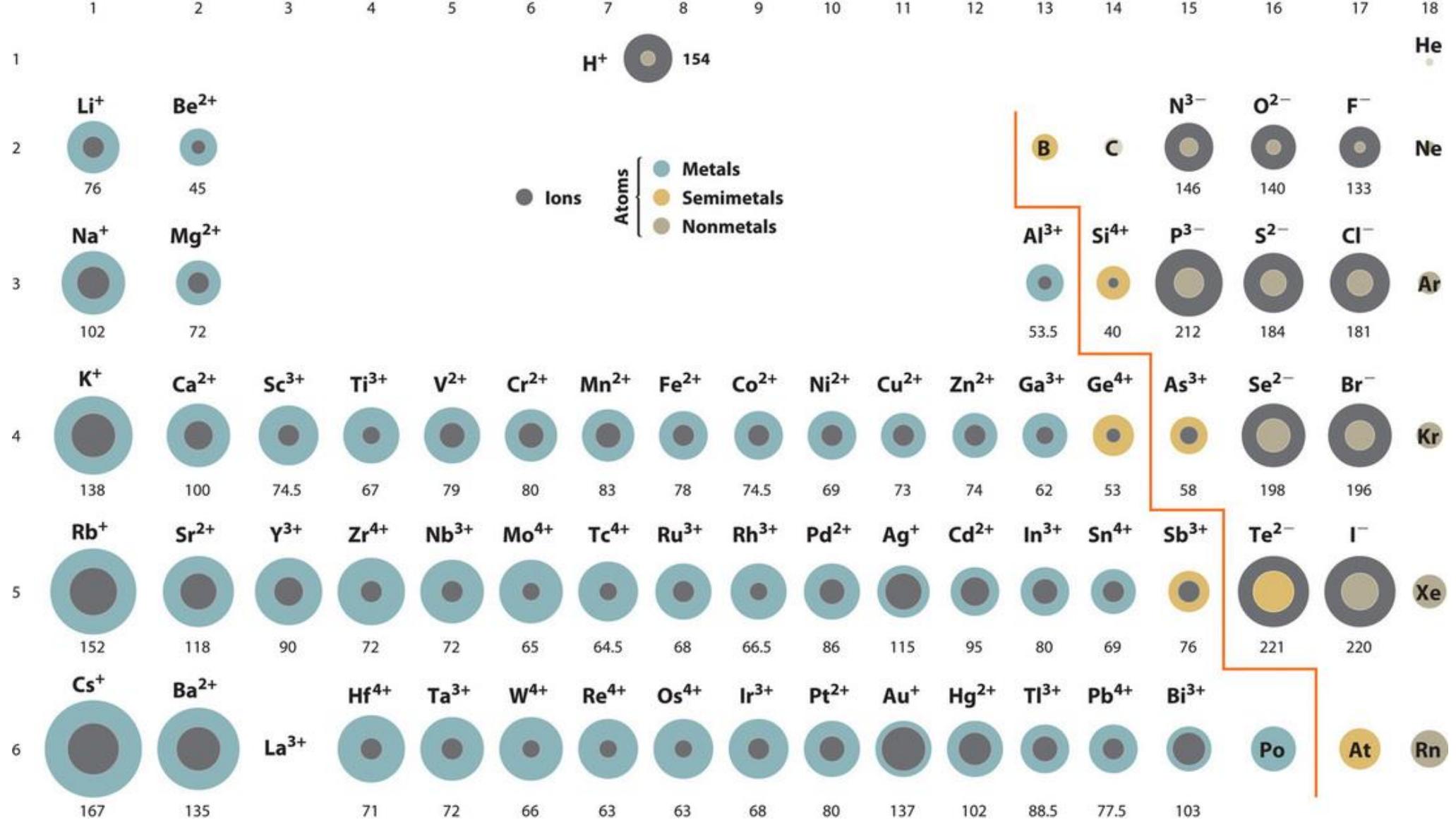


Figure 7.3.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the s-, p-, and d-Block Elements. Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Variation of ionic radii

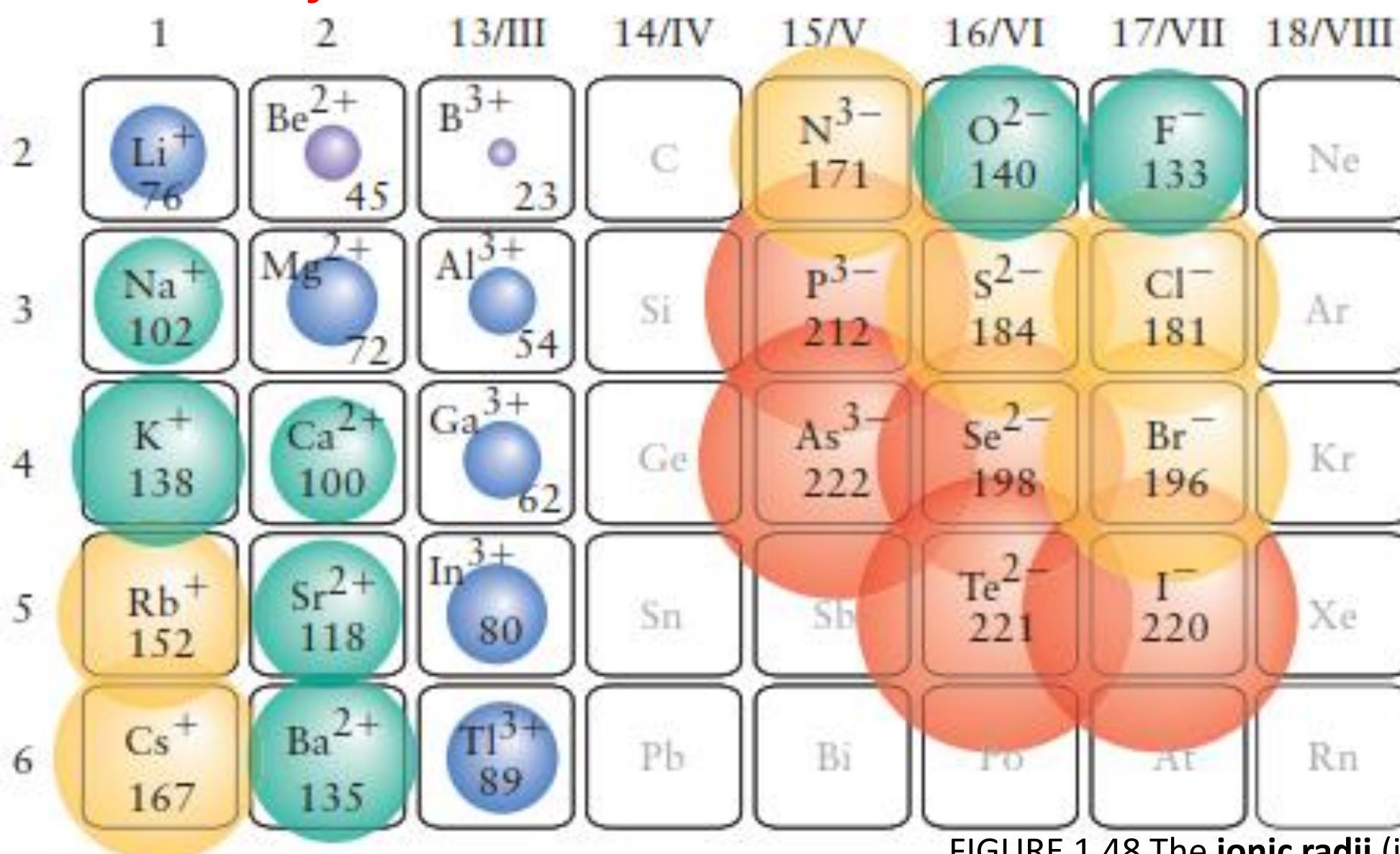


FIGURE 1.48 The **ionic radii** (in picometers) of the ions of the main-group elements. Note that cations are typically smaller than anions—in some cases, very much smaller.

➤ Variation of ionic radii

- ❖ Cations are smaller than their parent atoms while anions are larger.
- ❖ Ionic radii generally increase down a group and decrease from left to right across a period.

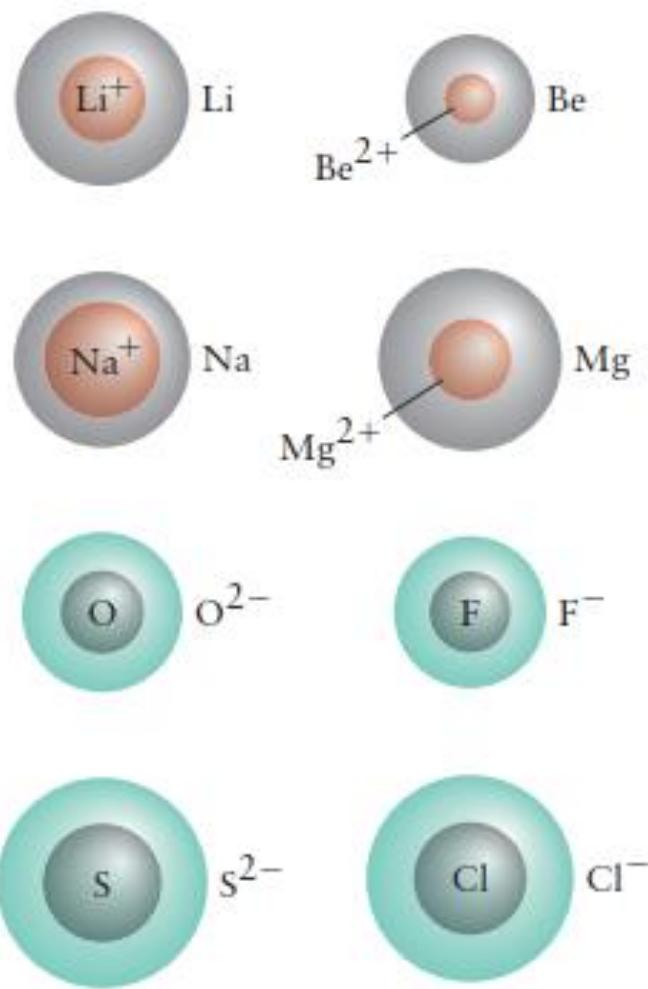
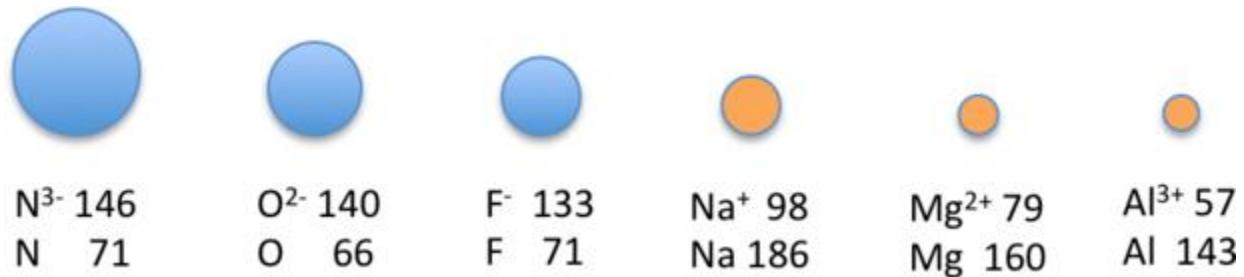


FIGURE 1.49 The relative sizes of some cations and anions compared with their parent atoms. Note that cations (pink) are smaller than their parent atoms (gray), whereas anions (green) are larger.

- All cations are smaller than their parent atoms, because the atom loses one or more electrons to form the cation and exposes its core, which is generally much smaller than the parent atom.
- ❖ For example, the atomic radius of Li, with the configuration $1s^22s^1$, is 152 pm, but the ionic radius of Li^+ , the bare helium-like $1s^2$ core of the parent atom, is only 76 pm.
- The anions are larger than their parent atoms. The reason can be traced to the increased number of electrons in the valence shell of the anion and the repulsive effects exerted by electrons on one another.
- The variation in the radii of anions shows the same diagonal trend as that for atoms and cations, with the smallest at the upper right of the periodic table, close to fluorine.

Isoelectronic series

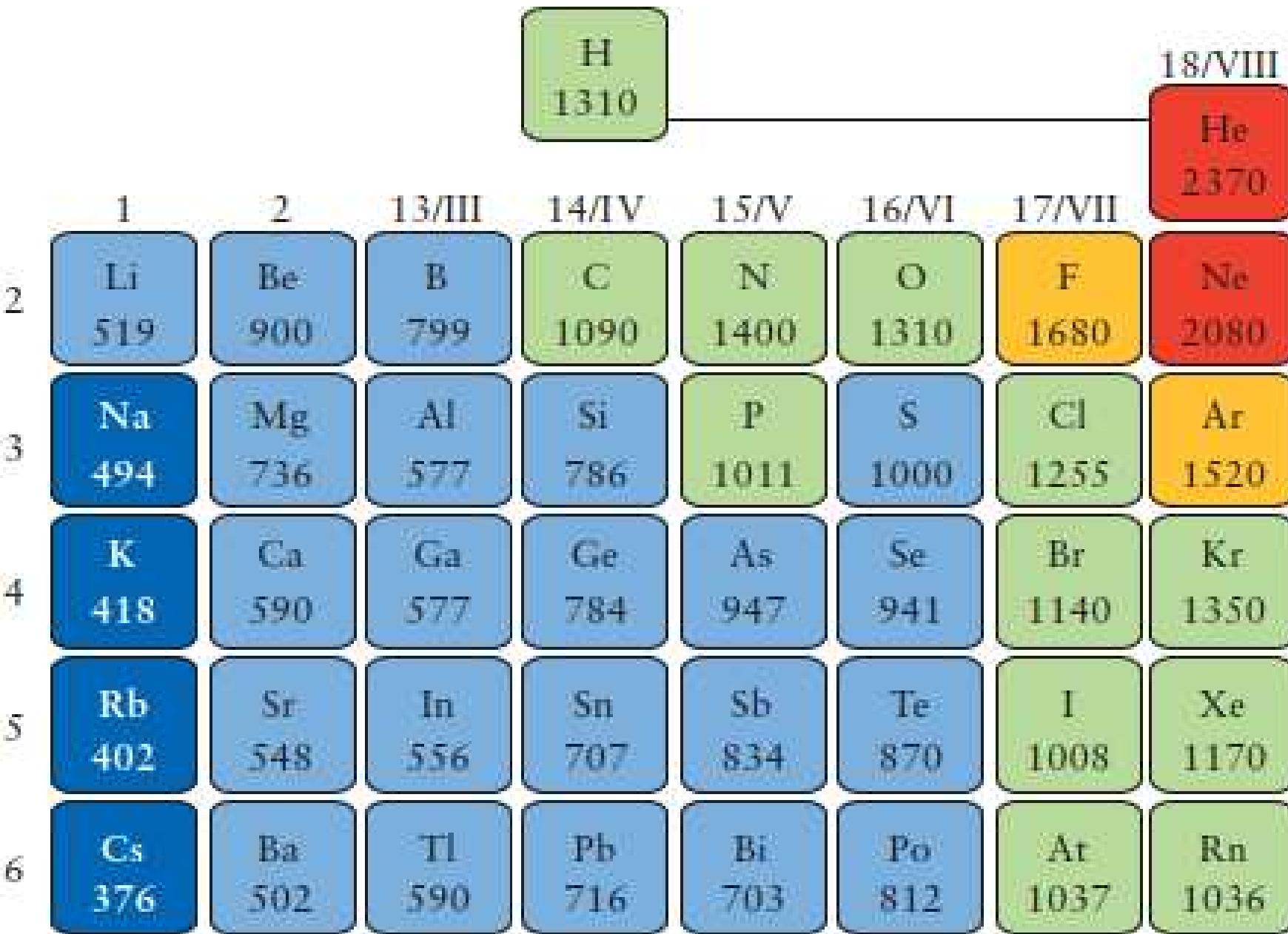
- Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table.
- Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an *isoelectronic series*.
- For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^22s^22p^6$) is shown below.



- The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+} . All six of the ions contain 10 electrons in the 1s, 2s, and 2p orbitals, but the nuclear charge varies from +7 (N) to +13 (Al).
- As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 7.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

- Atoms and ions with the same number of electrons are called **isoelectronic**.
- ❖ For example, Na^+ , F^- , and Mg^{2+} are isoelectronic. All three ions have the same electron configuration, $[\text{He}]2s^22p^6$, but *their radii differ because they have different nuclear charges* (see Fig. 1.48).
- ❖ *The Mg^{2+} ion has the largest nuclear charge*; so, it has the strongest attraction for the electrons and therefore the *smallest radius*.
- ❖ The *F^- ion has the lowest nuclear charge* of the three isoelectronic ions and, as a result, it has *the largest radius*.

□ Ionization Energy



❖ *In general, low values are found at the lower left of the table and high values are found at the upper right.*

FIGURE 1.50 The **first ionization energies** of the main-group elements, in kilojoules per mole.

The Ionization Potentials

- Reference to Table 5-1 indicates that in general the amount of energy required to remove one of the outer electrons increases as the effective nuclear charge increases.
- The increase in I_1 from approximately 5 eV for sodium to approximately 16 eV for argon dramatically illustrates the increase in the force which the nucleus exerts on the outer electrons as the nuclear charge and the number of *outer* electrons is increased.
- The effect of the half-filled set of *p* orbitals is again evident as I_1 is slightly larger for phosphorus than for sulphur.
- There is an apparent discrepancy in the value for I_1 observed for magnesium. The outer electronic configuration of magnesium is $3s^2$ and for aluminum is $3s^23p^1$. The value of 7.64 ev observed for magnesium is the energy required to remove a $3s$ electron, while the value quoted for aluminum is the energy required to remove a $3p$ electron.

- An *s* orbital is more stable than a *p* orbital because of its greater penetration of the inner core of electron density.
- Thus the penetration effect overrides the increase in the effective nuclear charge.
- We can test the validity of this explanation by comparing the energies required to remove a second electron (I_2) from the magnesium and aluminium atoms.
- The outer electronic configurations of the singly-charged magnesium and aluminum ions are $3s^1$ and $3s^2$. Thus a comparison of the second ionization potentials (I_2) will be free of the complication due to the penetration effect because we will be comparing the amount of energy required to remove an *s* electron in each case. The values in Table 5-1 indicate that the removal of an *s* electron requires more energy in aluminium than in magnesium, a result which is consistent with the greater effective nuclear charge for aluminium than for magnesium.
- What explanation can be given to the second ionization potential of sulfur being almost equal to that for chlorine?

➤ It is worthwhile noting the large value of the second ionization potential observed for sodium. The sodium ion has the electron configuration $1s^2 2s^2 2p^6$, i.e., there are no remaining outer electrons. The second ionization potential for sodium is, therefore, a measure of the amount of energy required to remove one of what were initially inner shell electrons in the neutral atom. The effective nuclear charge experienced by a $2p$ electron in the sodium ion will be very large indeed, because the number of inner shell electrons for an $n = 2$ electron is only two. That is, only the two electrons in the $1s$ orbital exert a large screening effect. Therefore, coupled to the fact that the ion bears a net positive charge, is the fact that the ratio of outer to inner shell electrons is 8:2, which is even more favourable than that obtained for argon. (Recall that in the neutral sodium atom the ratio is 1:10.) The value of I_2 , for sodium again emphasizes the electronic stability of a closed shell, a stability which is a direct reflection of the large value of the effective nuclear charge operative in such cases.

Ionization Energy

- *First ionization energies typically decrease down a group.*
- ❖ The *decrease down a group* can be explained by the finding that, *in successive periods, the outermost electron occupies a shell that is farther from the nucleus and is therefore less tightly bound.*
- ❖ Therefore, it takes less energy to remove an electron from a cesium atom, for instance, than from a sodium atom.

Ionization Energy

- ***First ionization energies generally increase across a period.***
- ❖ This trend can be traced to the increase in *effective nuclear charge* across a period.
- ❖ The small departures from this trend can be traced to repulsions between electrons, particularly electrons occupying the same orbital.
- ❖ For example, *the ionization energy of oxygen is slightly lower than that of nitrogen* because *in a nitrogen atom each p-orbital has one electron, but in oxygen the eighth electron is paired with an electron already occupying an orbital*. The repulsion between the two electrons in the same orbital raises their energy and makes one of them easier to remove from the atom than if the two electrons had been in different orbitals.

Ionization Energies of Transition Metals & Lanthanides

- As we noted, *the first ionization energies of the transition metals and the lanthanides change very little across each row.*
- Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements.
- The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations.
- Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons.
- As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

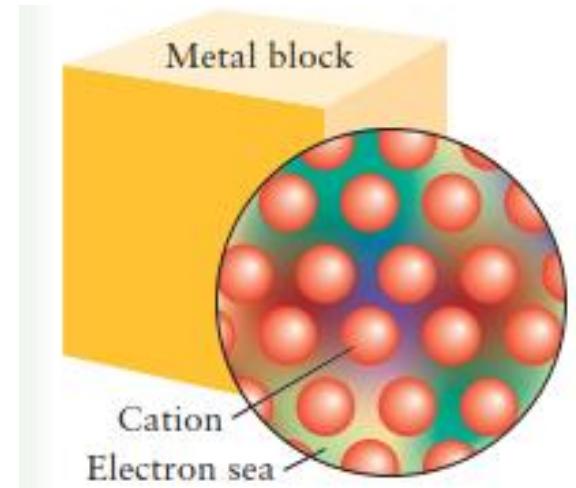
- That the ns electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order.
- In fact, the ns , the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the d orbitals are filled, the effective nuclear charge causes the $3d$ orbitals to be slightly lower in energy than the $4s$ orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the $4s$ electrons of titanium are lost before the $3d$ electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.
- Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Ionization Energy

- *The s- and p-block elements show a larger range of I_1 values than do the transition-metal elements.*
- Generally, the ionization energies of the *transition metals increase slowly* from left to right in a period.
- The f-block metals also show *only a small variation* in the values of I_1 .

□ The low ionization energies of elements at the lower left of the periodic table account for their **metallic character**. A *block of metal consists of a collection of cations of the element surrounded by a sea of valence electrons that the atoms have lost* (Fig. 1.53).

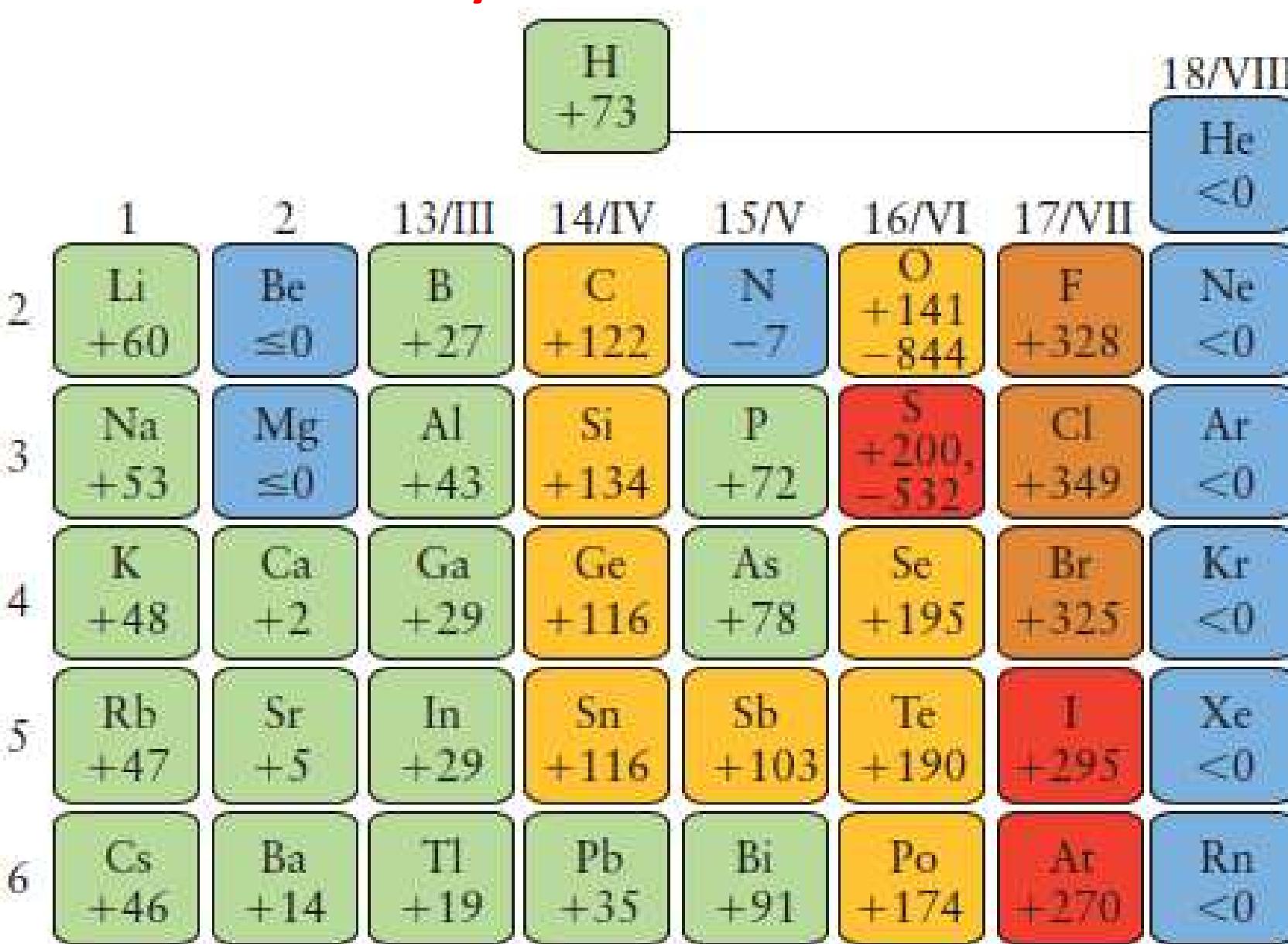
FIGURE 1.53 A block of metal consists of an array of cations (the spheres) surrounded by a sea of electrons. The charge of the electron sea cancels the charges of the cations. The electrons of the sea are mobile and can move past the cations quite easily and hence conduct an electric current.



➤ Only **elements with low ionization energies**—the members of the s-block, the d-block, the f-block, and the lower left of the p-block—can form **metallic solids**, because only **they can lose electrons easily**.

- Metals are found toward the lower left of the periodic table because these elements have low ionization energies and can readily lose their electrons.
- The elements at the upper right of the periodic table have high ionization energies; so, they do not readily lose electrons and are therefore not metals. —the nonmetals are found toward the upper right of the periodic table.
- The first ionization energy is highest for elements close to helium and is lowest for elements close to cesium.
- Second ionization energies are higher than first ionization energies (of the same element) and very much higher if the electron is to be removed from a closed shell.

□ Electron Affinity



➤ Where two values: first refers to the formation of a singly charged anion and the second is the additional energy needed to produce a doubly charged anion. The negative signs of the second values indicate that energy is required to add an electron to a singly charged anion.

FIGURE 1.54 The variation in electron affinity in kilojoules per mole of the main-group elements.

Electron Affinity

- The ***variation is less systematic than that for ionization energy***, but high values tend to be found close to fluorine (but not for the noble gases).
- Where two values are given, the first refers to the formation of a singly charged anion and the second is the additional energy needed to produce a doubly charged anion.
- The negative signs of the second values indicate that energy is required to add an electron to a singly charged anion.

Electron Affinity

- ❖ A Group 16/VI atom, such as O or S, has two vacancies in its valence-shell p-orbitals and can accommodate two additional electrons. The first electron affinity is positive because energy is released when an electron attaches to O or S. However, attachment of the second electron requires energy because of the repulsion by the negative charge already present in O⁻ or S⁻. Unlike that of a halide ion, however, the valence shell of the O⁻ anion has only seven electrons and thus can accommodate an additional electron.
- ✓ Therefore, we expect that less energy will be needed to make O²⁻ from O⁻ than to make F²⁻ from F⁻, where no such vacancy exists. In fact, 141 kJ·mol⁻¹ is released when the first electron adds to the neutral atom to form O⁻, but 844 kJ·mol⁻¹ must be supplied to add a second electron to form O²⁻; so, the total energy required **to make O²⁻ from O is -703 kJ·mol⁻¹.**
- ✓ **This energy can be achieved in chemical reactions/interactions, and O²⁻ ions are common in metal oxides.**

Predicting trends in electron affinity

- *The electron affinity of carbon is greater than that of nitrogen; indeed, the latter is negative.*

- *We expect more energy to be released when an electron enters the N atom, because an N atom is smaller than a C atom and its nucleus is more highly charged:* the effective nuclear charges for the outermost electrons of the neutral atoms are 3.8 for N and 3.1 for C. However, the opposite is observed.

- *Suggest a reason for this observation.*

- ✓ We must also consider the ***effective nuclear charges experienced by the valence electrons*** in the anions (Fig. 1.55). When C⁻ forms from C, the additional electron occupies an empty 2p-orbital. The *incoming electron is well separated from the other p-electrons*, and so *it experiences an effective nuclear charge close to 3.1*.
- ✓ When N⁻ forms from N, the additional electron must occupy a 2p-orbital that is already half full. The effective nuclear charge experienced by this electron is therefore much less than 3.8; so, energy is required to form N⁻, and the electron affinity of nitrogen is lower than that of carbon.

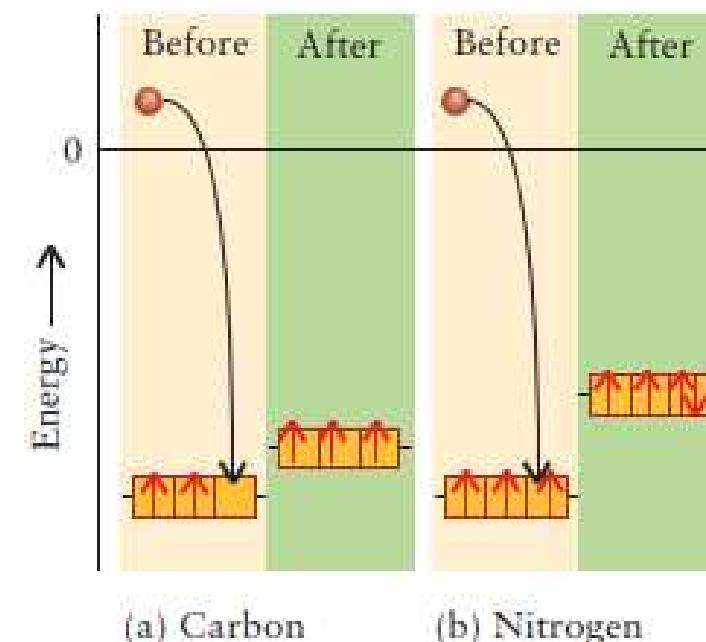


FIGURE 1.55 The energy changes taking place when an electron is added to a carbon atom and a nitrogen atom.

(a) A carbon atom can accommodate an additional electron in an empty p-orbital.

(b) When an electron is added to a nitrogen atom it must pair with an electron in a p-orbital. The incoming electron experiences so much repulsion from those already present in the nitrogen atom that the electron affinity of nitrogen is less than that of carbon and is in fact negative.

Polarizability

➤ For an isolated atom, the average distribution of electronic charge about the nucleus is spherical (Fig. 9-17a). This is not the case for an atom in the vicinity of another atom, molecule, or ion or in an externally applied electric field. For example, when an atom is placed in the electric field between two oppositely charged parallel plates (Fig. 9-17b), the position of the much heavier nucleus is left essentially unchanged but the electron cloud is distorted (shifted toward the positively charged plate). *Such an atom is said to be polarized.* For a polarized atom, the centers of positive and negative charges are displaced from each other. The magnitude of this displacement depends on how easily the electron cloud of the atom can be distorted.

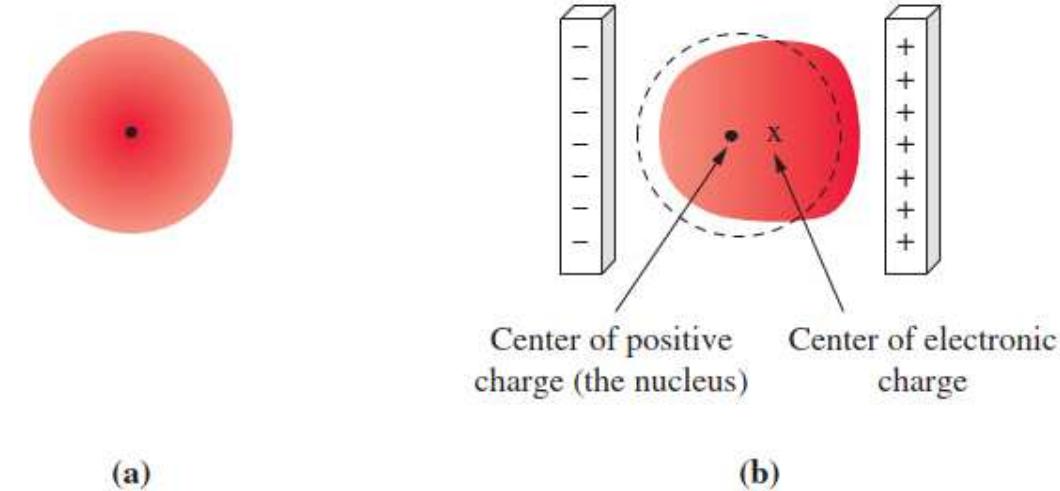


FIGURE 9-17 *Polarization of an atom*

(a) For an isolated atom, the distribution of electronic charge about the nucleus is spherical.

(b) *In an electric field, the distribution of electronic charge is nonspherical, and the centers of positive and negative charge no longer coincide. The atom is said to be polarized.*

Polarizability

- The *polarizability of an atom provides a measure of the extent to which its electron cloud can be distorted*, for example, by the application of an externally applied electric field or by the approach of another atom, molecule, or ion.
- It is often *expressed in units of volume*.
- The polarizability of an atom depends on how diffuse or spread out its electron cloud is, and in general.

Polarizability

➤ **Polarizability increases with the size of the atom.**

❖ Thus, polarizability **decreases from left to right across a period** and **increases from top to bottom within a group.**

❖ The polarizability of an atom is similar in magnitude to the atomic volume calculated from atomic radii, as suggested by Figure 9-18.

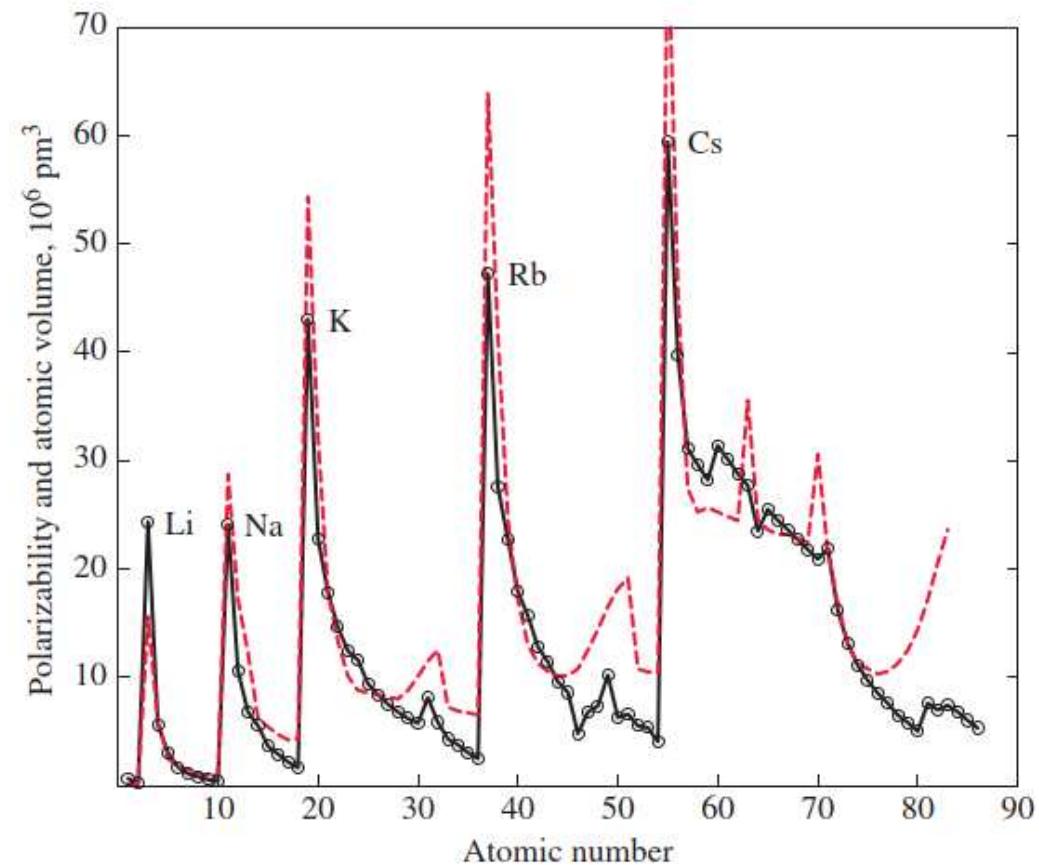


FIGURE 9-18
Polarizabilities and atomic volumes

The variation of polarizability with atomic number (solid black line) closely resembles that of atomic volume (dashed red line). The atomic volume is calculated as , where r is the atomic radius as defined in Figure 9-4. Both polarizability and atomic volume decrease from left to right across a period and increase from top to bottom in a group.

Polarizability

- ❖ Do all the electrons in an atom contribute equally to the polarizability?
 - No.
 - Quantum mechanical calculations on atoms reveal that the *loosely bound valence electrons contribute more to the polarizability than the tightly bound inner electrons*. This result is not totally unexpected because, as we have already learned, the valence electrons are, on average, farther from the nucleus and experience a smaller effective nuclear charge than do the inner electrons. Thus, *the valence electrons experience a greater shift in position than the inner electrons when an atom is placed in an externally applied electric field or is approached by another atom, molecule, or ion*.
 - We will see later that the polarizabilities of atoms, molecules, and ions enter into discussion of, for example, chemical bonding, intermolecular forces, phase changes, solvation, and chemical reactivity.

Some Chemical Implications

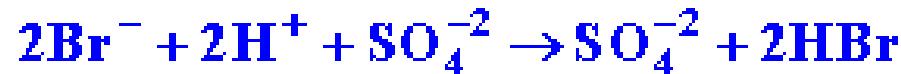
- A detailed study of the chemical implications of the orbital theory of electronic structure must await our discussion of the chemical bond. However, we can at this point correlate the gross chemical behaviour of the elements with the general results of the orbital theory.
- The effective nuclear charge is a minimum for the group I elements in any given row of the periodic table.
- Therefore, it requires less energy to remove an outer electron from one of these elements than from any other element in the periodic table.
- The strong reducing ability of these elements is readily accounted for.
- The variation in the relative reducing power of the elements across a given period or within a given group will be determined by the variation in the effective nuclear charge.

- The ability of the elements in a given row of the periodic table to act as reducing agents should undergo a continuous decrease from group I to group VII, since the effective nuclear charge increases across a given row.
- Similarly, the reducing ability should increase down a given column (group) in the table since the effective nuclear charge decreases as the principal quantum number is increased. Anticipating the fact that electrons can be transferred from one atom (the reducing agent) to another (the oxidizing agent) during a chemical reaction, we expect the elements to the left of the periodic table to exhibit a strong tendency to form positively charged ions.
- The ability of the elements to act as ***oxidizing agents*** should ***parallel directly*** the ***variations in the effective nuclear charge***.
- Thus the ***oxidizing ability should increase across a given row*** (from group I to group VII) and ***decrease down a given family***.

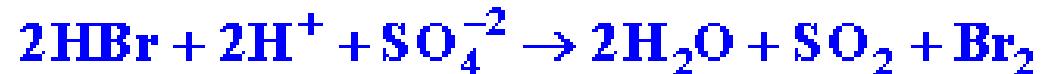
- These trends are, of course, just the opposite of those noted for the reducing ability.
- We can also relate the chemical terms "reducing ability" and "oxidizing ability" to the experimentally determined energy quantities, "ionization potential" and "electron affinity."
- The ***reducing ability should vary inversely with the ionization potential***, and the ***oxidizing ability should vary directly with the electron affinity***.
- The elements in groups VI and VII should exhibit a strong tendency for accepting electrons in chemical reactions to form negatively charged ions.
- Francium, which possesses a single outer electron in the 7s orbital, should be the strongest chemical reducing agent and fluorine, with an orbital vacancy in the 2p subshell, should be the strongest oxidizing agent.

- A great deal of chemistry can now be directly related to the electronic structure of the elements.
- For example, the reaction $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$ is explained chemically by stating that Cl_2 is a stronger oxidizing agent than Br_2 .
- The ***electronic interpretation*** is that the orbital vacancy in Cl is in a $3p$ orbital and closer to the nucleus than the $4p$ orbital vacancy in Br.
- Thus the effective nuclear charge which attracts the extra electron is larger for the Cl atom than for the Br atom.
- We could of course interpret this same reaction by stating that the ***Br⁻ ion is a stronger reducing agent than is the Cl⁻ ion.***
- In other words ***the extra electron in the Br⁻ ion is less tightly held than is the extra electron in the Cl⁻ ion.***
- The explanation in terms of the relative effective nuclear charges is the same as that given above.

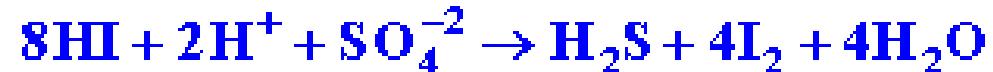
- The *decrease in the effective nuclear charge down the halogen family of elements leads to some interesting differences in their chemistry.*
- For example, hydrogen chloride may be prepared from sodium chloride and sulphuric acid: $2\text{Cl}^- + 2\text{H}^+ + \text{SO}_4^{2-} \rightarrow 2\text{HCl} + \text{SO}_4^{2-}$
- However, the *same* method ***cannot be employed*** in the preparation of ***hydrogen bromide*** or ***hydrogen iodide***. In the preparation of hydrogen bromide from sodium bromide,



- some of the HBr reacts further,



- and the *HBr is thus contaminated.*
- In preparation of hydrogen iodide, a further reaction again occurs:



- The last two reactions are clearly redox reactions in which ***the halide ions reduce the sulphur*** in the SO_4^{2-} anion ***to a lower oxidation state.***

- Since Cl has the *highest effective nuclear charge*, the **Cl⁻ ion should be the weakest reducing agent of the three halide ions.**
- Indeed, the Cl⁻ ion *is not a strong enough reducing agent* to change the oxidation state of S in SO₄⁻².
- The Br⁻ ion possesses an *intermediate value for the effective nuclear charge and thus it is a stronger reducing agent* than the Cl⁻ ion. The Br⁻ ion reduces the oxidation number of sulphur from (+6) to (+4).
- Since the I⁻ ion binds the extra electron least of all (the electron is in an $n = 5$ orbital and *the effective nuclear charge of iodine is the smallest of the three*), it should be **the strongest reducing agent of the three halide ions**. **The I⁻ ion in fact reduces the sulphur from (+6) to (-2)**.

A word about ***oxidation numbers*** and electron density distributions is appropriate at this point. An oxidation number does not, in general, represent the formal charge present on a species. Thus S is not S^{+6} in the SO_4^{-2} ion, nor is it S^{-2} in the H_2S molecule. However, the average electron density in the direct vicinity of the sulphur atom does increase on passing from SO_4^{-2} to H_2S . From their relative positions in the periodic table it is clear that oxygen will have a greater affinity for electrons than sulphur. Thus when sulphur is chemically bonded to oxygen the electron density in the vicinity of the sulphur atom is decreased over what it was in the free atom and increased in the region of each oxygen atom. Again it is clear from the relative positions of H and S in the periodic table that sulphur has a greater affinity for electrons than does hydrogen. Thus in the molecule H_2S , the electron density in the vicinity of the sulphur atom is increased over that found in the free atom. ***In changing the immediate chemical environment of the sulphur atom from that of four oxygen atoms to two hydrogen atoms, the electron density (i.e., the average number of electrons) in the vicinity of the sulphur atom has increased.*** The assignment of actual oxidation numbers is simply a bookkeeping device to keep track of the number of electrons, but ***the sign of the oxidation number does indicate the direction of the flow of electron density.*** Thus sulphur has a positive oxidation number when combined with oxygen (the sulphur atom has lost electron density) and a negative one when combined with hydrogen (the electron density around sulphur is now greater than in the sulphur atom).

The above are only a few examples of how a knowledge of the electronic structure of atoms may be used to understand and correlate a large amount of chemical information. It should be remembered, however, that chemistry is a study of very complex interactions and the few simple concepts advanced here cannot begin to account for the incredible variety of phenomena actually observed. Our discussion has been based solely on energy, and energy alone never determines completely the course of a reaction on a macroscopic level, i.e., when many molecules undergo the reaction. There are statistical factors, determined by the changes in the number of molecules and in the molecular dimensions, which must also be considered. Even so, the energy effect can often be overriding.

Diagonal Relationships

➤ A diagonal relationship is a similarity in properties between diagonal neighbors in the main groups of the periodic table (Fig. 1.58).

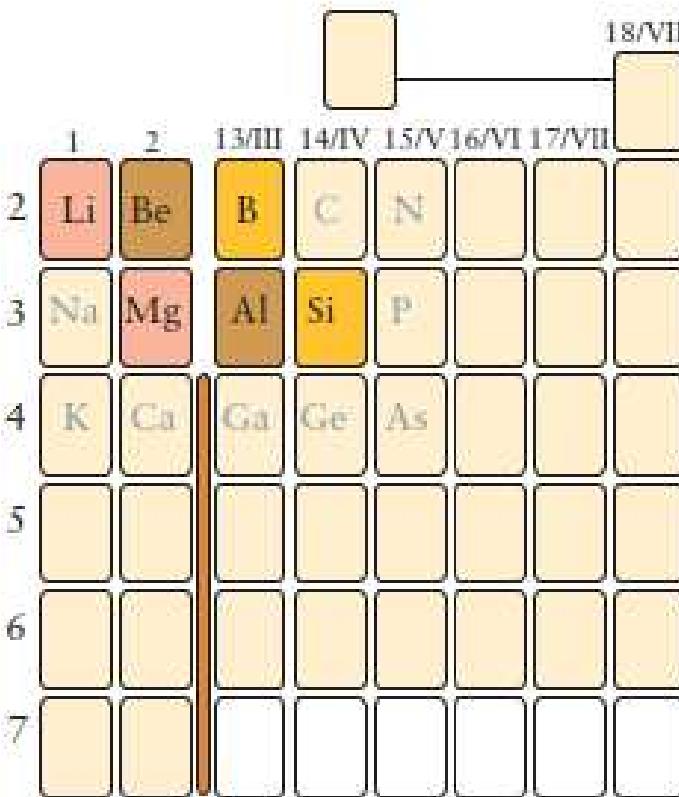


FIGURE 1.58 The pairs of elements represented by similarly colored boxes show a strong diagonal relationship to each other.

- A part of the ***reason for this similarity*** can be seen in Figs. 1.46 and 1.50 by concentrating on the colors that show the ***general trends in atomic radius and ionization energy***. The colored bands of similar values lie in diagonal stripes across the table.
- Because ***these characteristics affect the chemical properties of an element, it is not surprising to find that the elements within a diagonal band show similar chemical properties.***

Diagonal Relationships

- Diagonal relationships are helpful for making predictions about the properties of elements and their compounds.
- The diagonal band of metalloids dividing the metals from the nonmetals is one example of a diagonal relationship.
- So is the chemical similarity of lithium and magnesium and of beryllium and aluminum.
- ❖ For example, *both lithium and magnesium react directly with nitrogen to form nitrides.*
- ❖ Like *aluminum, beryllium reacts with both acids and bases.*

The Inert-Pair Effect

- One of the more *unusual periodic trends* is known as the **inert-pair effect**.
- *The inert-pair effect is the tendency to form ions two units lower in charge than expected from the group number; it is most pronounced for heavy elements in the p-block.*

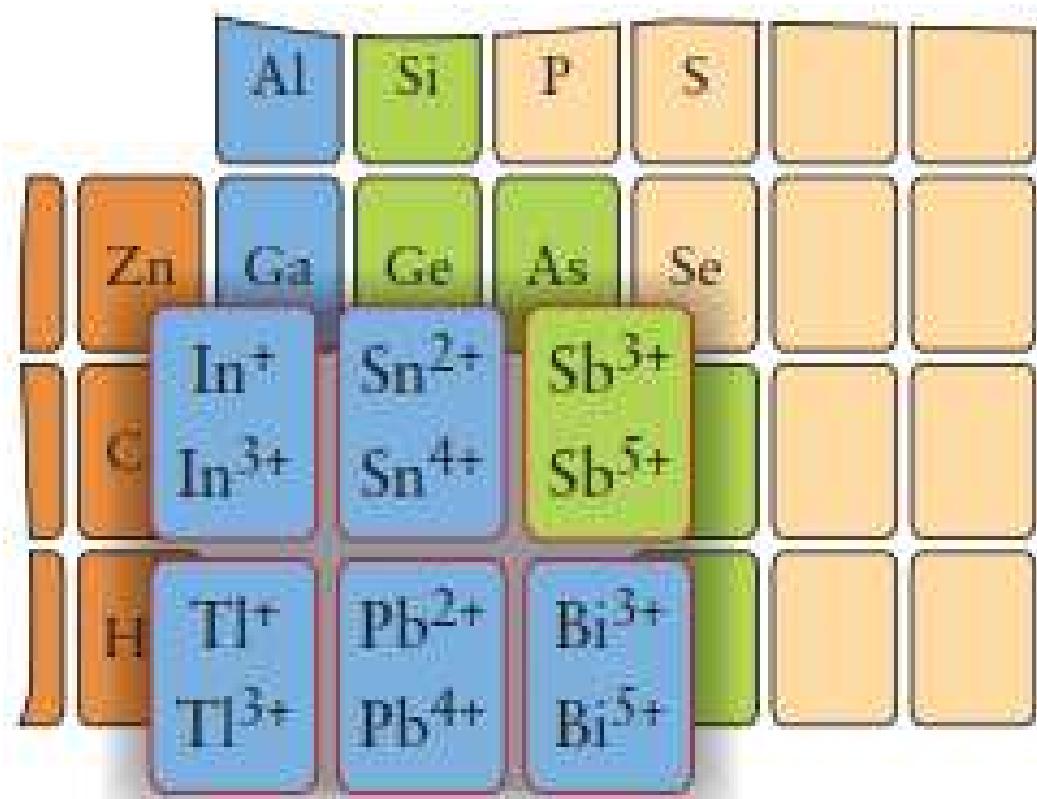


FIGURE 1.57 The typical ions formed by the heavy elements in Groups 13/III through 15/V show the influence of the inert pair—the tendency to form compounds in which the oxidation numbers differ by 2.

The Inert-Pair Effect

- The elements that immediately *follow the 4d and 5d transition series* are ***considerably less reactive than their group properties might have predicted***, and they also ***prefer oxidation states that are two lower than the usual group valence***.
- ❖ Consider, for example, the Group IIIA elements. The lighter elements, B, Al, and Ga take **only the +3 oxidation state** predicted by their group valence.
- ❖ However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states.
- The same trend is observed for the Group IVA elements. Again, the lighter elements C, Si, and Ge take the 4+ valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation state.
- The tendency to form ions two units lower in charge than expected from the group number is called the **inert-pair effect**.

The Inert-Pair Effect

- ❖ *An example of the inert-pair effect is found in Group 14/IV:* tin forms tin(IV) oxide when heated in air, but the heavier lead atom loses only its two p-electrons and forms lead(II) oxide. Tin(II) oxide can be prepared, but it is readily oxidized to tin(IV) oxide.
- Lead exhibits the inert-pair effect more strongly than tin.

Explanation:

- The relative stability of the lower oxidation states for the fifth and sixth series post-transition elements (In, Sn, Sb, Tl, Pb, Bi, and Po) **has been attributed to the** (i) **higher-than-expected ionization energies** for these seven elements and (ii) **weaker bond enthalpies**.

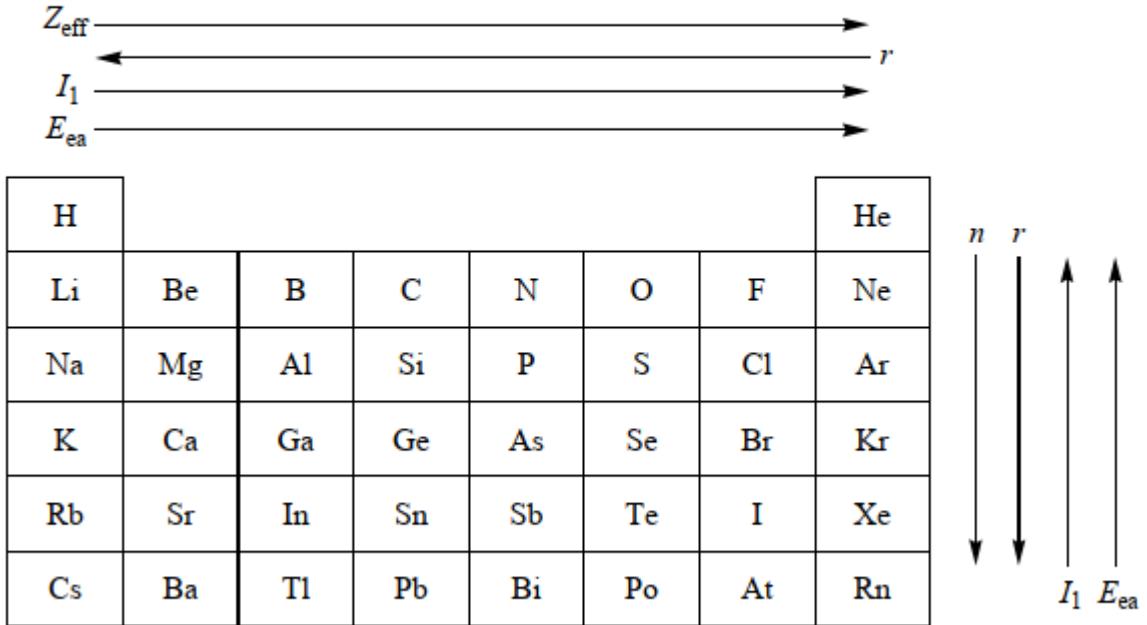
The Inert-Pair Effect: (i) *higher-than-expected ionization energies*

- *The larger-than-expected ionization energies for the post-transition series Group IIIA elements result from the fact that the valence s electrons are not shielded from the nucleus very effectively by the intervening d electrons.*
- As the two s electrons are both held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large.
- *Relativistic effects*, which are discussed in the following section, also contribute to the higher-than-expected ionization energies of the valence s electrons.
- Due to *higher-than-expected ionization energies*, it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners.

The Inert-Pair Effect: (ii) weaker bond enthalpies

- At the same time, *less energy is gained as a result of bond formation* because they also exhibit lower-than-predicted bond dissociation enthalpies.
- *Weaker bond enthalpies* are expected for the *heavier elements* as a result of the *diffuse nature of orbital overlap with increasing orbital size*.
- ***The end result*** is that these *elements prefer oxidation states that are two lower than their typical group valence*.
- The inert-pair effect is most pronounced among the heaviest members of a group, where the difference in energy between *s*- and *p*-electrons is greatest (Fig. 1.57).
- Even so, *the pair of s-electrons can be removed from the atom under sufficiently vigorous conditions*. An inert pair would be better called a “lazy pair” of electrons.

Main-Group Elements in the Periodic Table



Summary of trends in r , I_1 , and E_{ea}

- All depend on Z_{eff} and n of outer subshell electrons.
 - Recall that there are many exceptions to the general trends.
- Example: For electron affinity, the value for N is actually less than that for O.
- The diagram on the next page indicates the general behavior of the three properties (r , I_1 , and E_{ea}) with respect to both Z_{eff} and n (exceptions ignored, many in the case of electron affinity).

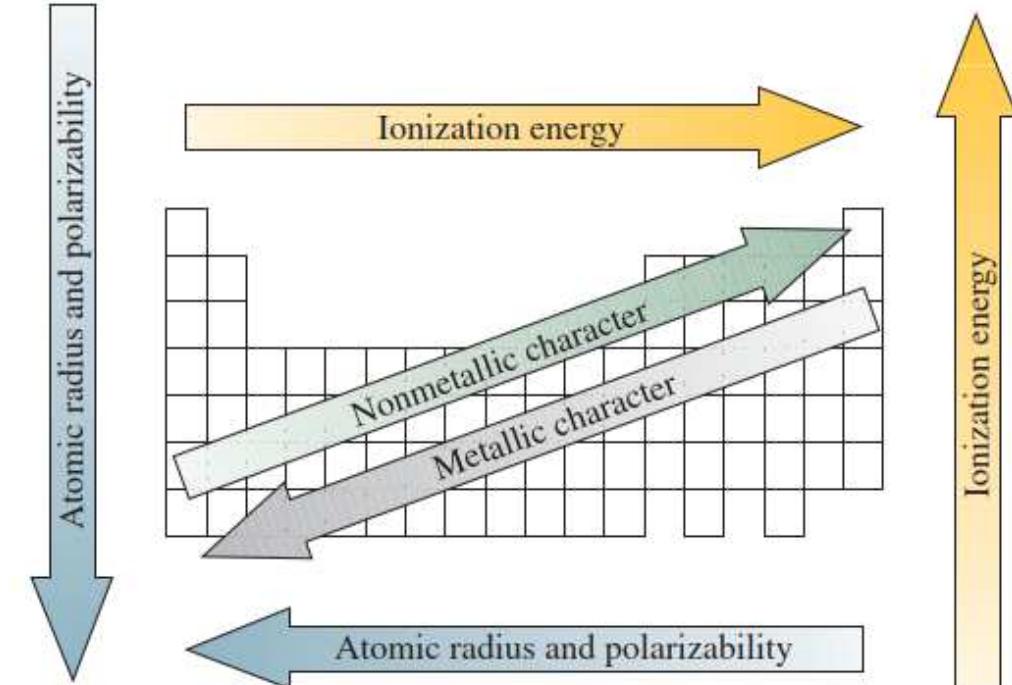


FIGURE 9-19

Atomic properties and the periodic table—a summary

Atomic radius refers to metallic radius for metals and covalent radius for nonmetals. Ionization energies refer to first ionization energy. Metallic character relates, generally, to the ability to lose electrons, and nonmetallic character to the ability to gain electrons.

Later, we will use our knowledge of the variation of ionization energy, electron affinity, and polarizability to explain various aspects of bonding. Figure 9-19 provides a useful summary.

❑ Trends in Relativistic Effects

❑ Why is mercury liquid at normal temperature and pressure?

❑ Why is *gold the least reactive of the coinage metals....?*

❑ Melting points: 3033, 2446, 1768, 1064, & -39°C.

76 Os	77 Ir	78 Pt	79 Au	80 Hg
----------	----------	----------	----------	----------

Why is mercury liquid at normal temperature and pressure?

76	77	78	79	80
Os	Ir	Pt	Au	Hg

melting points: 3033, 2446, 1768, 1064, & -39°C.

- A material's *melting point* has everything to do with the energy associated with the bonds between metal atoms.
- Metal is full of bonds between the atoms that make it up that determines its m.p.
- Most metal atoms readily share valence electrons with other atoms.
- Hg is liquid, basically it suggests that mercury atoms form weak bonds and is bad at sharing electrons. ...WHY...???

1A

1

1 H
$1s^1$

2A

2

3 Li
$2s^1$

3B

4B

5B

6B

7B

8

9

10

8B

1B

2B

11

12

13

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16

17

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□

Electronic Configurations

➤ Compare Gr. 2 (2A) with Gr. 12 (2B)

Core

[He]

[Ar]

[Kr]

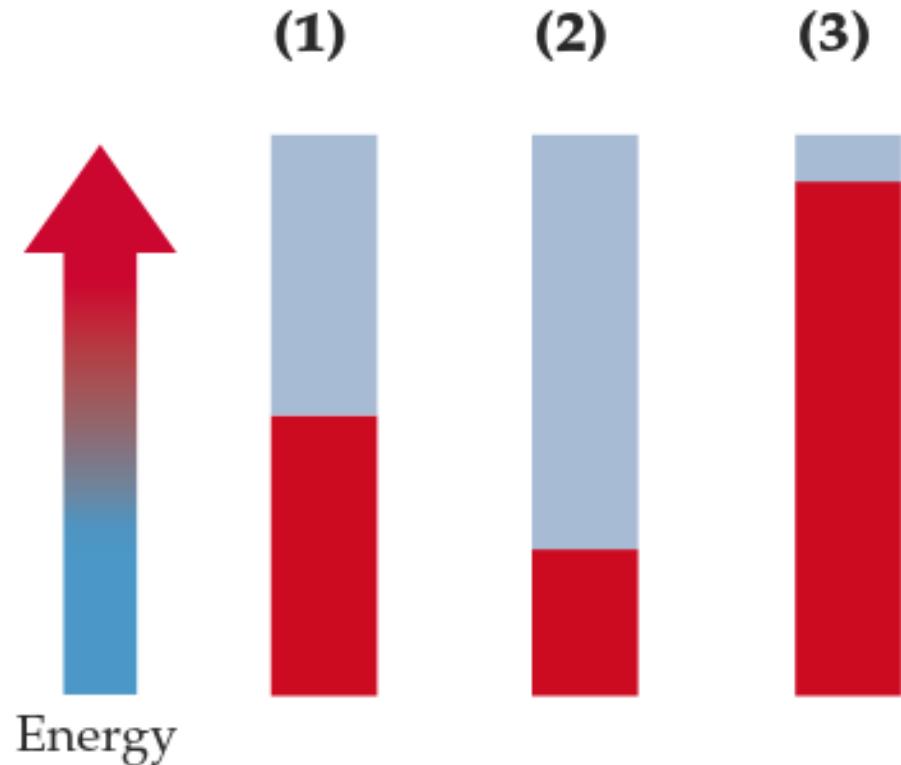
[Xe]

[Rn]

3
Li4
Be5
Na6
Mg7
Sc8
Ti9
V10
Cr11
Mn12
Fe13
Co14
Ni15
Cu16
Zn17
Ga18
Ge19
As20
Se21
Br22
Kr23
Rb24
Sr25
Y26
Zr27
Nb28
Mo29
Tc30
Ru31
Rh32
Pd33
Ag34
Cd35
In36
Sn37
Sb38
Te39
I40
Xe41
Cs42
Ba43
Lu44
Hf45
Ta46
W47
Re48
Os49
Ir50
Pt51
Au52
Hg53
Tl54
Pb55
Bi56
Po57
At58
Rn59
Fr60
Ra61
Lr62
Rf63
Db64
Sg65
Bh66
Hs67
Mt68
Ds69
Rg70
Cn71
Nh72
Fl73
Mc74
Lv75
Ts76
Og77
10378
10479
10580
10681
10782
10883
10984
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165140
166141
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Melting Point

- The following pictures show the electron populations of the composite s–d bands for three different transition metals (corresponding to 1, 2, & 3). The red color in the bands indicates occupied (bonding) MO band.



- (a) Which metal has the highest melting point?
- (b) Which metal has the lowest melting point?
- (c) What about their hardness?

- Both **hardness** and **melting point increase** as metal–metal bonding increases.
- They will depend on the **occupancy of the *bonding* and *antibonding* MOs**.
- The **melting point** and **hardness** of a metal is *expected to increase* as the *difference between the number of bonding and antibonding electrons increases*.
- Transition metals have *two ns* and *ten ($n - 1$)d* valence electrons.
- All the valence electrons will occupy a **composite s–d band**, which can **accommodate 12 electrons per metal atom**.
- Picture (1) Metal: Its s–d band is exactly **half-filled**, which corresponds to **six valence electrons (all are in bonding MOs)**. Its bonding MOs are completely filled and its antibonding MOs are completely vacant. Therefore, it has the **highest melting point**.

- Picture (2) Metal: Its s–d band is *one-fourth filled*, which corresponds to *three valence electrons (bonding)*.
- Picture (3) metal: Its s–d band is *eleven-twelfths filled*, which corresponds to 11 *valence electrons*. It has the **lowest melting point** because it has *six bonding electrons* and *five antibonding electrons* per atom, *an excess of only one bonding electron per atom*.
- Metal 1 is very hard because it has an excess of six bonding electrons per atom. Metal 3 is very soft because it has an excess of only one bonding electron per atom. Therefore, metals in order of increasing hardness: 3<2<1.

□ Melting points: 3033, 2446, 1768, 1064, & -39°C.

76 Os	77 Ir	78 Pt	79 Au	80 Hg
$6s^25d^6$	$6s^25d^7$	$6s^15d^9$	$6s^15d^{10}$	$6s^25d^{10}$

- Gold is also a *fairly soft metal*. Pure gold, which is 24 carats, is seldom used in the manufacture of jewelry because it is so soft that ordinary wear and tear will damage the metal. Instead, an alloy of 18k or 14k gold is generally used. A typical piece of 18k jewelry consists of 75.0% Au, 12.5% Ag, and 12.5% Cu, by mass. The presence of the other metals helps harden the alloy.

Why is mercury liquid at normal temperature and pressure?

-**Relativity** behind Mercury's liquidity and Gold's nobility.

(Reference: F Calvo et al, Angew. Chem., Int. Ed.. 2013.
DOI: 10.1002/anie.201302742)

- ✓ Trend in the contraction of 6s electron orbitals...

- ✓ An international team led by Peter Schwerdtfeger of Massey University Auckland in New Zealand used quantum mechanics to make calculations of *the heat capacity of the metal either including or excluding relativistic effects*.
- ✓ They showed that if they **ignored relativity** when making their calculations, *the predicted melting point of mercury was 82°C*. But if they **included relativistic effects** their answer closely matched the **experimental value of -39°C**.
- It was long **believed** that **valence electrons**, which are *important for chemical reactions, move rather slowly compared to the velocity of light ($v \ll c$) and should therefore not show significant effects coming from special relativity*.
- In contrast, the importance of **relativistic effects** for inner K- or L-shell electrons of heavy elements was long recognized.

RELATIVISTIC EFFECTS

- According to Einstein's theory of relativity, ***particles that are traveling at velocities approaching the speed of light are more massive than they are at rest***, as shown by Equation (5.37), where m_{rel} is the relativistic mass of the electron and m_0 is its rest mass.
- As a result of their ***relativistic heavier mass***, the accelerated electrons have a ***smaller average radius***, as indicated by Equation (5.38), which results from the derivation of the Bohr model of the atom:

$$m_{\text{rel}} = \frac{m_0}{\sqrt{1 - (v/c)^2}} \quad (5.37)$$

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e Z e^2} \quad (5.38)$$

- One basic consequence of the special theory of relativity is that *mass increases towards infinity as a body's velocity approaches c (speed of light)*, which is expressed mathematically as

$$m = m_0 / [1 - (v/c)^2]^{1/2},$$

where m is the corrected (relative) mass, m_0 is non-relativistic (rest) mass, and v is electron's speed.

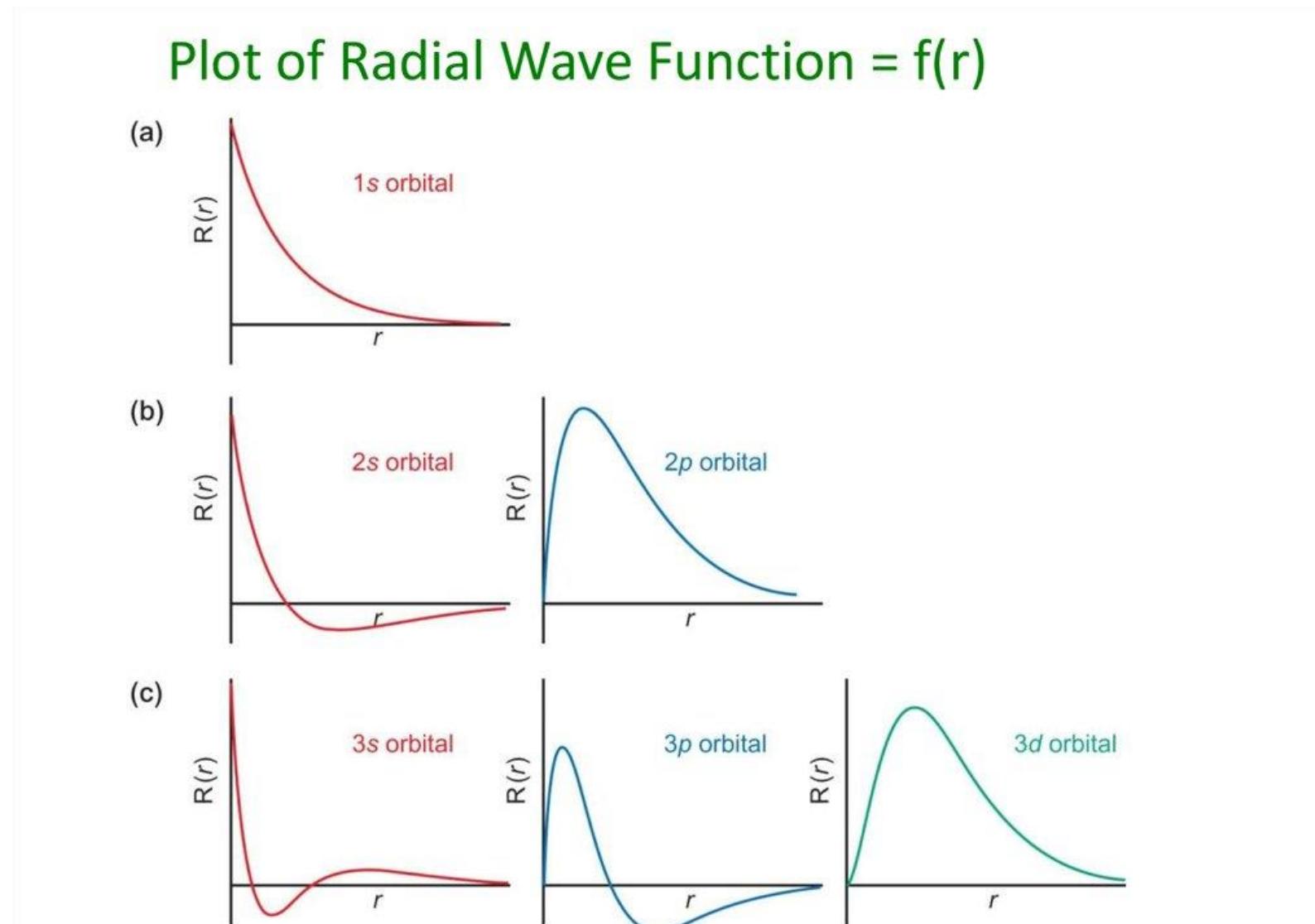
- For a given atom, *the average radial velocity of the 1s electrons is $V_r = Z$* , where Z is the atomic number. The expression v/c can therefore be calculated as $Z/137$ ($c = 137$ atomic units (a.u.)).
 - ❖ For example, in Hg, $Z = 80$ and v/c for the 1s electrons is $80/137 = 0.58$; that is, the 1s electrons have a radial velocity that is 58% of c .
- In fact, *the larger the nucleus gets, the greater the electrostatic attraction and the faster the electrons have to move to avoid falling into it.*

RELATIVISTIC EFFECTS

- *For most applications of chemistry, the effect of relativity on electronic motion can largely be ignored.WHY...???*
- For ***the smaller elements***, Schrödinger's ***nonrelativistic model*** is perfectly appropriate, as *the velocities of the electrons in the lighter elements rarely approach the speed of light.*
- However, ***the larger mass of the heavier elements exerts a stronger electrostatic pull on the inner-most electrons, sometimes accelerating them to speeds in excess of 10^8 m/s.***

RELATIVISTIC EFFECTS: *s, p, d, & f electrons*

❖ *s and p electrons penetrate the nucleus better than the d or f electrons do.*



RELATIVISTIC EFFECTS: *s, p, d, & f electrons*

- *Because the s and p electrons penetrate the nucleus better than the d or f electrons do, the s and p electrons are accelerated to a greater extent.*
- Thus, the *s and p orbitals effectively contract as relativistic effects become more prominent.*
- Furthermore, as the *s and p electrons migrate closer to the nucleus, this enhances their ability to shield the d and f electrons from experiencing the full attraction of the nucleus.*
- Thus, the *d and f orbitals expand as a result of relativity.*
- The *combined effect* is to *lower the energies of the s and p electrons*, as shown in Figure 5.12, while *raising the energy of the d and f electrons.*

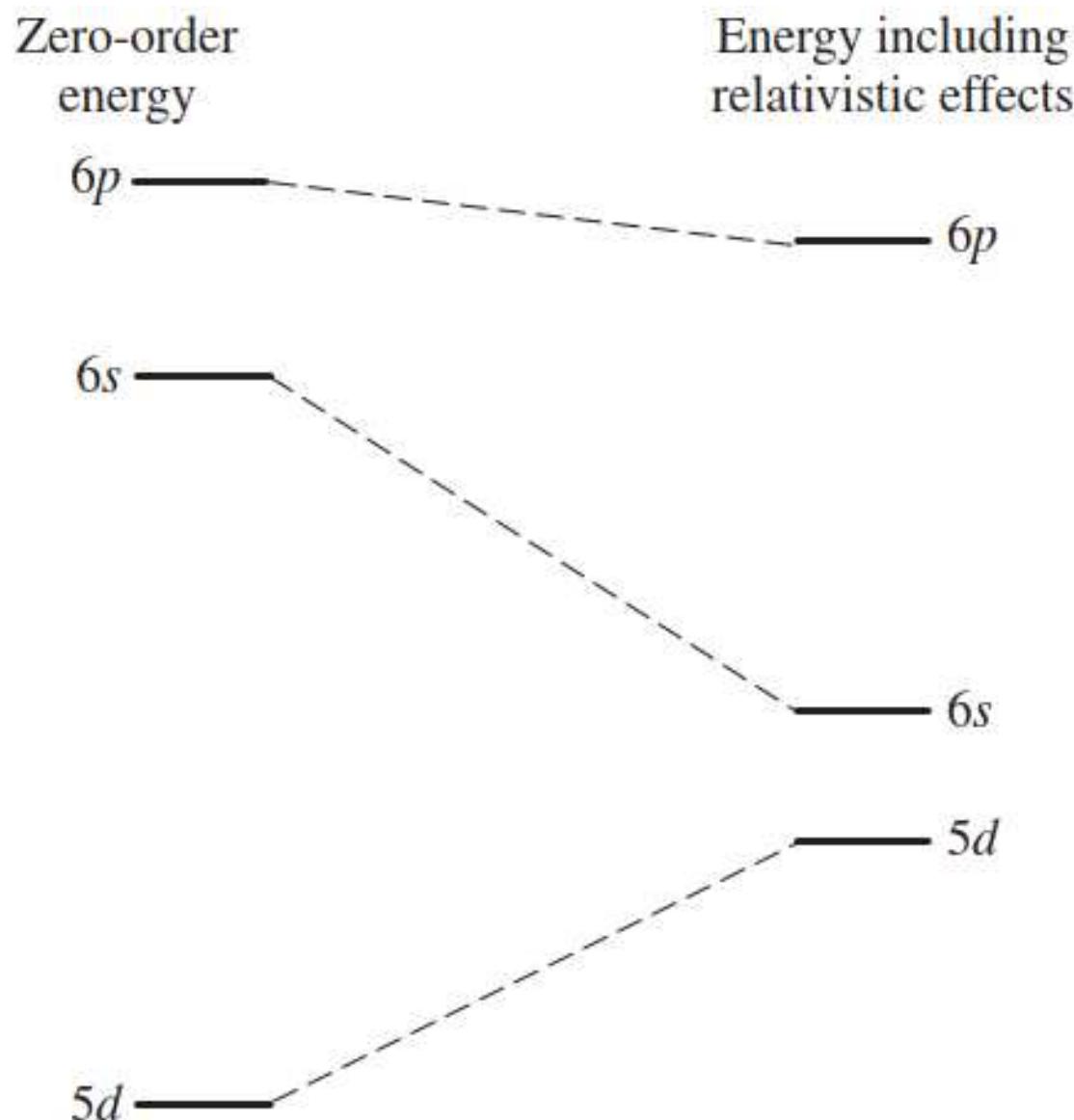


FIGURE 5.12 **Valence orbital energies** for Au and Hg in the absence of relativistic effects and with relativistic effects included.

Table 1

Relativistic effects: There are three major phenomena that result from relativistic effects

1. Direct

Contraction of s and p orbitals

The contraction is due to the relativistic mass increase as followed by the decrease of the Bohr radius. The contraction of the spherical $p_{1/2}$ subshell is comparable to the contraction of $s_{1/2}$. The $p_{3/2}$ subshell contracts much less.

2. Direct

Spin-orbit splitting

Instead of the orbital angular momentum l and the spin angular momentum s their vector sum $j = l + s$ is used (e.g., splitting of a p orbital to the $p_{1/2}$ ($|l-s|=1-\frac{1}{2}=\frac{1}{2}$) and $p_{3/2}$ ($|l+s|=1+\frac{1}{2}=3/2$) subshells).

3. Indirect

Expansion of d and f orbitals

The s and p orbitals contracting inside and outside the d and f orbitals screen the nuclear attraction of the latter thus leading to their radial expansion.

Relativistic effects are crucial to understanding the electronic structure of heavy elements.

□ There are three major phenomena that result from relativistic effects:

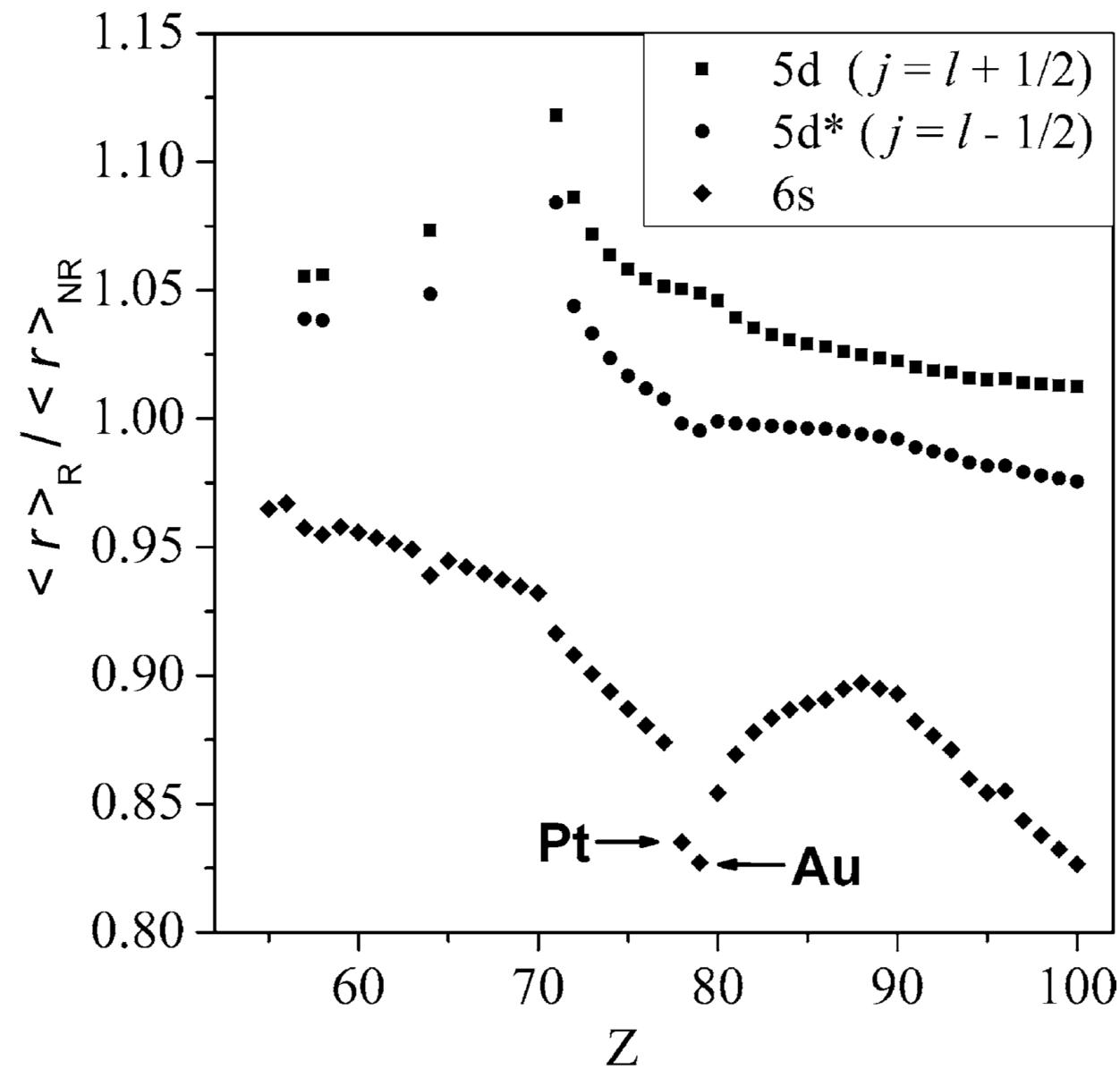
- The ***first*** can easily be rationalized by considering the equations above. In non-relativistic calculations, $c = \infty$ and v/c , therefore, approaches 0, so no mass correction need be applied to the particles under consideration.
- ✓ In situations in which c is considered to be 137 a.u., the mass of an electron will increase considerably. Because the Bohr radius of an electron orbiting a nucleus is inversely proportional to the mass of the electron, this ***increase in mass corresponds to a decrease in radius***. This relativistic contraction of the $1s$ orbital also applies to all other s and p orbitals. Thus, **the electrons are closer to the nucleus and have greater ionization energies**.
- ✓ Practically, this contraction is only significant for elements in which the $4f$ and $5d$ orbitals are filled (Figure 1).
- The ***second*** effect of a relativistic treatment is *spin-orbit coupling*, which accounts for the fine splitting in the atomic spectrum.
- The ***third*** manifestation of relativistic effects is *indirect*. Because of the relativistic contraction of all s orbitals, the nucleus becomes more screened resulting in a smaller effective nuclear charge, and therefore the higher angular momentum orbitals (the d and f orbitals) see a weaker nuclear attraction and expand.

- *The magnitude of the relativistic effect increases roughly as the square of the atomic number.*
- Thus, the *heavier elements experience considerably larger relativistic effects* than do the lighter ones.
- *For a number of elements heavier than Pt, the magnitude of the effect is even comparable to the strength of a chemical bond!*

Fig. 1. The relativistic contraction of the 6s orbital and expansion of the 5d and the 5d* orbitals for the elements with Z from 55 to 100 based on calculations by Desclaux (Ref. J.-P. Desclaux, At. Data Nucl. Data Tables 12 (1973) 311.)

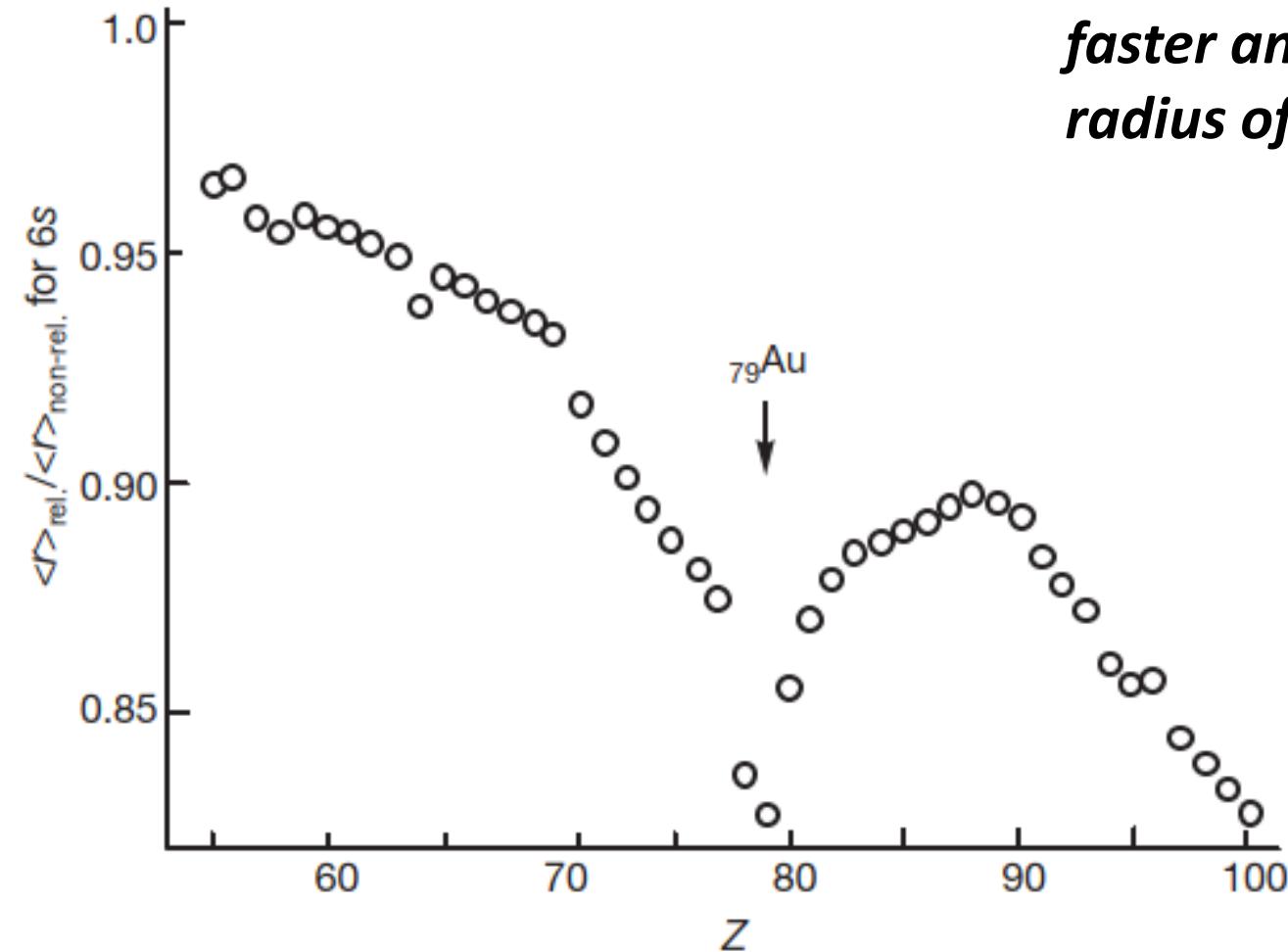
The graph of the 6s orbital contraction over the atomic number.

**Here also the 5d shell is included,
showing an orbital expansion due to an
indirect relativistic effect.**



➤ As you go down the periodic table the ***1s electrons get faster and faster, and therefore heavier, causing the radius of the atom to shrink.***

- ✓ In atoms of high nuclear charge (Z), as a consequence of a relativistic effect, the s electrons of an atom become more bound and their orbitals smaller than if this effect were absent. Simultaneously, the d (and f) electrons are less bound because of this effect, which scales roughly as Z^2 .
- ✓ Gold exhibits a large relativistic effect. ***This accounts for gold being more resistant to oxidation than silver. It also accounts for higher oxidation states being more accessible in gold than in silver.***



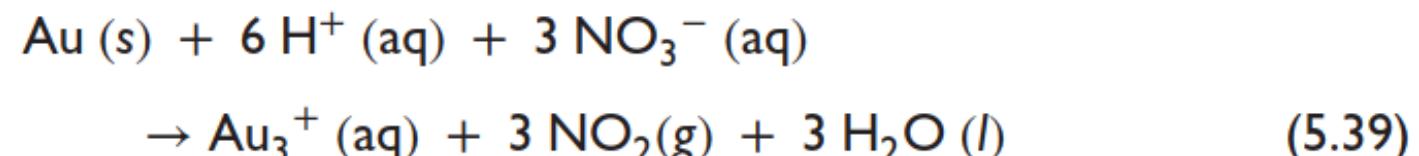
Calculated relativistic contraction of the 6s orbital. The relativistic and non-relativistic 6s orbital radii were determined computationally.

Notably, Pt, Au and Hg are markedly influenced.

- ❖ The *relativistic effect enhances the inert-pair effect* mentioned in the preceding section.
- *The smaller radius of the 6s orbital in Tl*, for instance, **causes the 6s electrons to be held more tightly** than they would have been in the absence of relativity and **raises their ionization energies**. Hence, Tl will commonly prefer the lower 1+ oxidation number over its 3+ state.
- ❖ However, unlike the inert-pair effect, any of the heavier elements can experience the relativistic effect.
- ✓ As an example, **gold is the least reactive of the coinage metals**. This explains why it was one of the first elements to be discovered by ancient Civilizations (about 10,000 years ago).
- ✓ *Gold exists in nature in its elemental form* and is only rarely found in minerals, such as calverite, AuTe_2 , and sylvanite, AuAgTe_4 . The electron configuration of Au is $[\text{Xe}] 4f^{14} 5d^{10} 6s^1$.

- As a result of *the relativistic effect in gold, the 6s electron has an unusually large ionization energy (890kJ/mol), compared with 746kJ/mol for Cu and 741kJ/mol for Ag*
- *and is extremely difficult to oxidize.*

- Hence, *gold will not rust in air, nor will it react with the oxidizing acid HNO₃.*
- In fact, in order to dissolve gold, a combination of one-part nitric acid with three-parts HCl must be employed. ***Nitric acid acts as the oxidizer, while the Cl⁻ ion helps to solubilize the gold as the complex ion AuCl₄⁻***, according to Equations (5.39) and (5.40). The mixture is known as **aqua regia** because it is the only acid that can dissolve the “royal” metals Au and Pt:



➤ As a result of *relativistic orbital contraction*, the atomic radius of Au is less than that expected on the basis of its periodic trends:

- Cu (135 pm),
- Ag (160 pm), and
- Au (135 pm).

➤ Because of the *small size of its half-filled 6s orbital*, the electron affinity (E.A.) of Au (223kJ/mol) is considerably larger

- than that for Ag (126kJ/mol) or
- Cu (118kJ/mol).

✓ The E.A. of Au is so large that gold exists as the Au⁻ anion in the compound cesium auride (CsAu).

- At the same time that the 6s orbital shrinks and is therefore stabilized by the relativistic effect, the 5d orbital expands and is destabilized.
- *Thus, the energy gap between the 5d and 6s orbitals is fairly small, and gold reflects light in the low-energy region of the visible spectrum. This is why gold has a distinctive yellowish color, unlike the silvery reflectance of most of the other metals.*

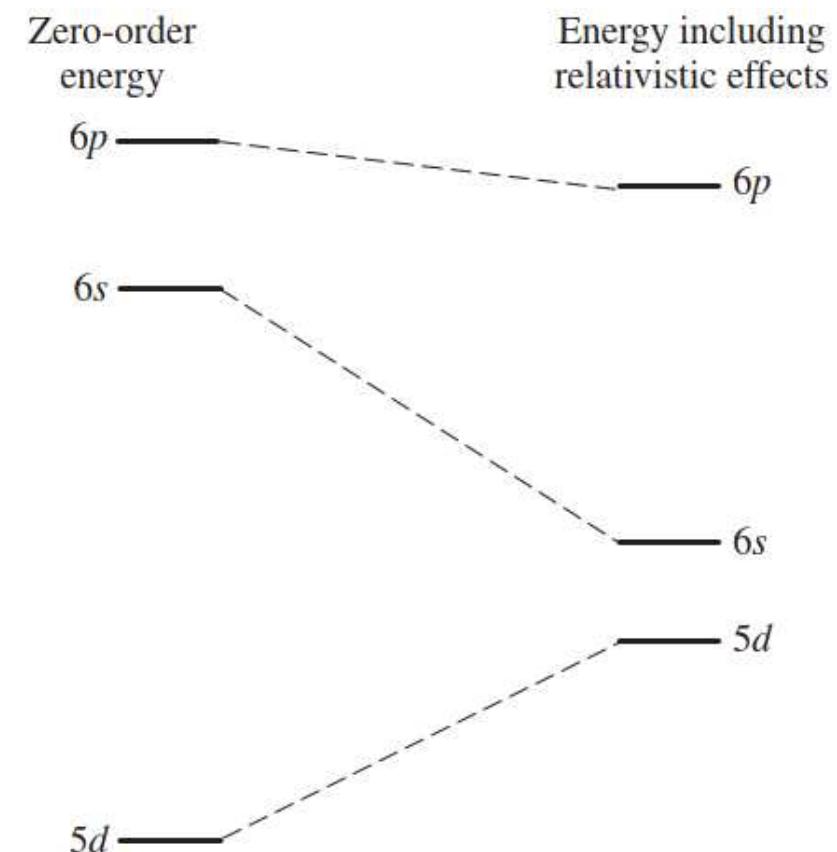


FIGURE 5.12 Valence orbital energies for Au in the absence of relativistic effects and with relativistic effects included.

- Among the experimental observations conventionally explained by relativistic effects is the **colour of Au**.
- ✓ In the 1960s, Pekka Pyykkö discovered that gold's color was the result of relativistic effects.
- ✓ *He showed that the relativistic effect causes the s electrons (and to a lesser extent, the p electrons) to be in smaller orbitals than if this effect were absent.*
- ✓ *Therefore, in the heavier elements, the s electrons are more strongly bound and shield the nuclear charge from the other electrons (especially d and f) more effectively than if the relativistic effects were absent. The d and f electrons are therefore less bound and occupy larger orbitals when relativistic effects are large.*
- ✓ *The raising of the Au 5d electron energies and the lowering of the valence 6s electron energies of gold means that the energy required to excite an electron from the 5d band to the Fermi level (largely 6s in character) lies in the visible rather than UV range of light. This accounts for the yellow color of gold.*

- ✓ *The golden colour is due to excitation of the 5d electrons to the Fermi level (6s), which occurs with a bandgap of 2.38 eV; blue visible light is therefore absorbed, while reflecting yellow and red light, and it is this that gives the metal its characteristic hue.*
- ✓ *In silver, by contrast, the bandgap is much larger, and no visible light is absorbed. The related absorption in silver (4d band to the Fermi level of ~5s character) is in the ultraviolet, at ~3.7 eV.*
- ✓ *Further calculations have subsequently shown the influence of relativity on the color and bond lengths of heavy metal compounds, as well as its importance in catalysis.*

- The unusual *differences between Au and Hg*, which are neighbors on the periodic table, *can also be ascribed to the relativistic energies* of the orbitals shown in Figure 5.12.
- Gold has a melting point of 1064°C, whereas Hg is a liquid at room temperature and has a melting point of –39°C.
- In many ways, *Au acts as a pseudo-halogen*, as evidenced by its ability to form the auride anion. *The low-lying 6s orbital in Au is singly occupied*. Therefore, like the halogens, gold can exist as the diatomic Au_2 .
- ✓ In fact, Au_2 has a *gas-phase bond dissociation energy (BDE) of 221 kJ/mol, which is even larger than that for I_2 (151 kJ/mol)* and only slightly smaller than that of Cl_2 (242 kJ/mol).

- **Mercury**, on the other hand, has two electrons in the low-lying 6s orbital ($4f^{14}5d^{10}6s^2$ electronic configuration) and it behaves as a **pseudo-noble gas**.
- ✓ By analogy with the noble gases, Hg(0) is fairly unreactive. Its unusually low melting point can be ascribed to the fact that Hg atoms can only aggregate together in the ***condensed phases as a result of weak van der Waals forces.***
- ✓ Mercury is unique among the transition metals because *it exists in the gas phase almost exclusively as monomeric Hg just like the noble gases do.*
- ✓ Mercury(0) cannot form a diatomic like Au(0) because its electrons are all paired.
- ✓ However, oxidation of Hg by one electron to form Hg(I), which is *isoelectronic with Au(0)*, leads to a **stable diatomic cation**, Hg_2^{2+} .

- In comparison with H, whose relativistic mass is 1.00003 times its rest mass and where its $1s$ electron has an average velocity of $0.0073c$, the relativistic mass of a $1s$ electron in Hg is 1.23 times its rest mass and its average velocity is $0.58c$, so that its size shrinks by a factor of nearly a quarter.
 - ***Because of the behavior of the valence electrons, mercury has a low melting point, is a poor electrical and thermal conductor and doesn't form diatomic mercury molecules in the gas phase.***
- Two other metals melt at slightly above room temperature, cesium at $28.4\text{ }^{\circ}\text{C}$ and gallium at $29.8\text{ }^{\circ}\text{C}$WHY....???

Periodicity in the Main-Group Elements

The physical and chemical properties of the main-group elements clearly display periodic character. We have seen it above for some properties.

The variations of metallic–nonmetallic character can be attributed in part to variations in the ionization energies of the corresponding atoms. *Elements with low ionization energy tend to be metallic, whereas those with high ionization energy tend to be nonmetallic.* As you saw in the previous section, ionization energy is a periodic property, so it is not surprising that the metallic–nonmetallic character of an element is similarly periodic.

The **basic–acidic behavior of the oxides of the elements is a good indicator of the metallic–nonmetallic character** of the elements. Oxides are classified as basic or acidic depending on their reactions with acids and bases. A basic oxide is an oxide that reacts with acids. **Most metal oxides are basic.** An acidic oxide is an oxide that reacts with bases. Most **nonmetal oxides are acidic** oxides. An **amphoteric oxide** is an oxide that has both basic and acidic properties.

In the following brief descriptions of the main-group elements, we will note the metallic–nonmetallic behavior of the elements, as well as the basic–acidic character of the oxides. **Although elements in a given group are expected to be similar, the degree of similarity does vary among the groups.** The alkali metals (Group 1A) show marked similarities, as do the halogens (Group 7A). On the other hand, the Group 4A elements range from a nonmetal (carbon) at the top of the column to a metal (lead) at the bottom. In either case, however, the changes from one element in a column to the next lower one are systematic, and the periodic table helps us to correlate these systematic changes.

Acid-Base Behavior of Oxides Metals are also distinguished from nonmetals by the acid-base behavior of their oxides in water:

- Most main-group metals transfer electrons to oxygen, so their oxides are ionic. In water, these oxides act as bases, producing OH^- ions from O^{2-} and reacting with acids.
- Nonmetals share electrons with oxygen, so nonmetal oxides are covalent. In water, these oxides act as acids, producing H^+ ions and reacting with bases.
- Some metals and many metalloids form oxides that are ***amphoteric***: they can act as acids or bases in water.

In Figure 8.16, the acid-base behavior of some common oxides of elements in Group 5A(15) and Period 3 is shown with a gradient from blue (basic) to red (acidic):

1. *As elements become more metallic down a group (larger size and smaller IE), their oxides become more basic.*
2. *As the elements become less metallic across a period (smaller size and higher IE), their oxides become more acidic.*

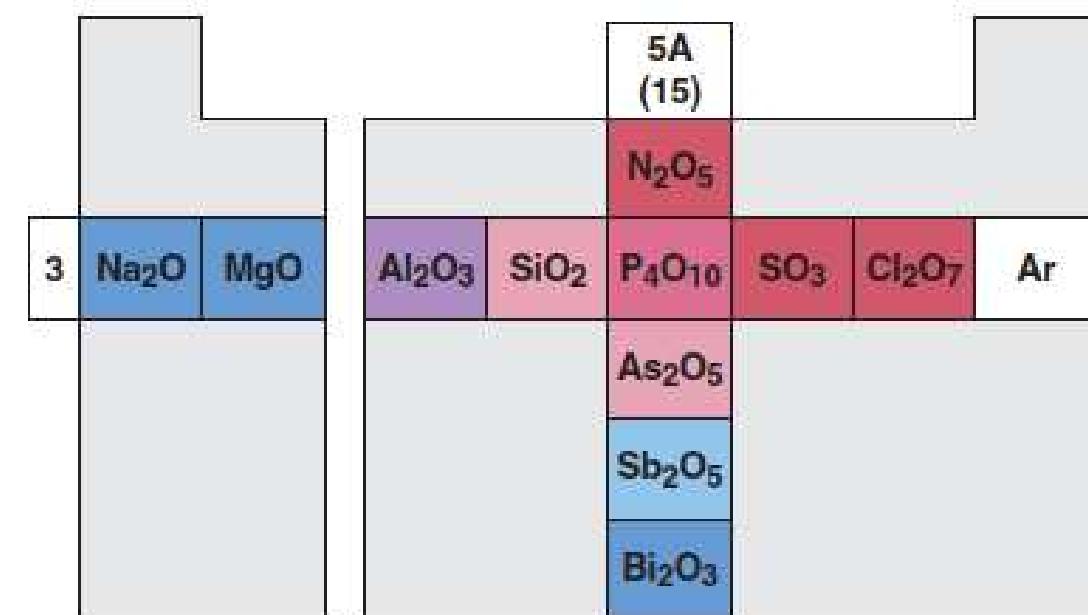


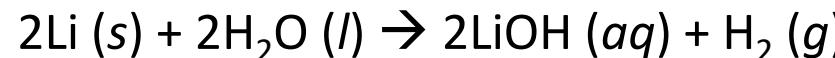
Figure 8.16 Acid-base behavior of some element oxides.

Hydrogen ($1s^1$)

Although the electron configuration of hydrogen would seem to place the element in Group 1A, its properties are quite different, and it seems best to consider this element as belonging in a group by itself. The element is a colorless gas composed of H_2 molecules. ***At very high pressures, however, hydrogen is believed to have metallic properties.***

Group 1A Elements, the Alkali Metals (ns^1)

The alkali metals are soft and reactive, with the reactivities increasing as you move down the column of elements. All of the metals react with water to produce hydrogen.



The vigor of the reaction increases from lithium (moderate) to rubidium (violent).

- All are reactive metals (except H); they form basic oxides (O^{2-}), peroxides (O_2^{2-}), or superoxides (O_2^-).
- *All alkali metals react, combine directly with hydrogen to form hydrides, MH. In hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as H^- , the hydride ion.*

Group 2A Elements, the Alkaline Earth Metals (ns^2)

The alkaline earth metals are also chemically reactive but much less so than the alkali metals. Reactivities increase going down the group. The alkaline earth metals form basic oxides with the general formula MO.

- *Compounds of s-block elements are ionic, except for beryllium.*

Group 3A Elements (ns^2np^1)

Groups 1A and 2A exhibit only slight increases in **metallic character down a column**, but **with Group 3A we see a significant increase**. The first Group 3A element, **boron**, is a **metalloid**. Other elements in this group—aluminum, gallium, indium, and thallium—are metals. (Gallium is a curious metal; it melts readily in the palm of the hand.)

The oxides in this group have the general formula M_2O_3 . Boron oxide, B_2O_3 , is an **acidic oxide**; aluminum oxide, Al_2O_3 , and gallium oxide, Ga_2O_3 , are **amphoteric oxides**. Indium oxide, In_2O_3 , and thallium oxide, Tl_2O_3 , are **basic**. *The change in the oxides from acidic to amphoteric to basic is indicative of an increase in metallic character of the elements.*

Group 4A Elements (ns^2np^2)

This group shows the **most distinct change in metallic character**. It begins with the **nonmetal carbon**, C, followed by the **metalloids** silicon, Si, and germanium, Ge, and then the **metals** tin (Sn), and lead (Pb). Both tin and lead were known to the ancients. All the elements in this group form oxides with the general formula RO_2 , which progress from acidic to amphoteric. Carbon dioxide, CO_2 , an acidic oxide, is a gas. (Carbon also forms the monoxide, CO.) Silicon dioxide, SiO_2 , an acidic oxide, exists as quartz and white sand (particles of quartz). Germanium dioxide, GeO_2 , is acidic, though less so than silicon dioxide. Tin dioxide, SnO_2 , an **amphoteric** oxide, is found as the mineral cassiterite, the principal ore of tin. Lead(IV) oxide, PbO_2 , is **amphoteric**. Lead has a more stable monoxide, PbO .



Figure... Oxides of some Group 4A elements
Powdered $Pb(II)O$ (yellow), $Pb(IV)O_2$ (dark brown), SnO_2 (white), and crystalline silicon dioxide (clear quartz).

Group 5A Elements (ns^2np^3)

The Group 5A elements also show the distinct transition from nonmetal (nitrogen, N, and phosphorus, P) to metalloid (arsenic, As, and antimony, Sb) to metal (bismuth, Bi). Nitrogen occurs as a colorless, odorless, relatively unreactive **gas** with N_2 molecules; white phosphorus is a white, waxy **solid** with P_4 molecules. Gray arsenic is a **brittle solid with metallic luster**; antimony is a brittle solid with a **silvery, metallic luster**. Bismuth is a **hard, lustrous metal** with a pinkish tinge.

The Group 5A elements form oxides with empirical formulas R_2O_3 and R_2O_5 . In some cases, the molecular formulas are twice these formulas—that is, R_4O_6 and R_4O_{10} . Nitrogen has the **acidic oxides** N_2O_3 and N_2O_5 , although it also has other, better-known oxides, such as NO. Phosphorus has the **acidic oxides** P_4O_6 and P_4O_{10} . Arsenic has the **acidic oxides** As_2O_3 and As_2O_5 ; antimony has the **amphoteric oxides** Sb_2O_3 and Sb_2O_5 ; and bismuth has the **basic oxide** Bi_2O_3 .

Group 6A Elements, the Chalcogens (ns^2np^4)

These elements, the chalcogens (pronounced kal'-ke-jens), show the transition from nonmetal (oxygen, O, sulfur, S, and selenium, Se) to metalloid (tellurium, Te) to metal (polonium, Po). Oxygen occurs as a colorless, odorless **gas** with O_2 molecules. It also has an allotrope, ozone, with molecular formula O_3 . Sulfur is a brittle, yellow **solid** with molecular formula S_8 . Tellurium is a shiny **gray, brittle solid**; polonium is a **silvery metal**.

Sulfur, selenium, and tellurium form oxides with the formulas RO_2 and RO_3 . (Sulfur burns in air to form sulfur dioxide). These oxides, except for TeO_2 , are **acidic**; TeO_2 is **amphoteric**. Polonium has an oxide PoO_2 , which is **amphoteric**, though more basic in character than TeO_2 .

Group 7A Elements, the Halogens (ns^2np^5)

The halogens are reactive nonmetals with the general molecular formula X_2 , where X symbolizes a halogen. Fluorine, F_2 , is a pale yellow **gas**; chlorine, Cl_2 , a pale greenish yellow **gas**; bromine, Br_2 , a reddish brown **liquid**; and iodine, I_2 , a bluish black **solid** that has a violet vapor. All isotopes of astatine have very short half-lives, and observable quantities of the element have not been prepared. Astatine might be expected to be a metalloid. Each halogen forms several compounds with oxygen; these are generally unstable, acidic oxides.

Group 8A Elements, the Noble Gases (ns^2np^6)

The Group 8A elements exist as gases consisting of uncombined atoms. For a long time these elements were thought to be chemically inert, because no compounds were known. Then, in the early 1960s, several compounds of xenon were prepared. Now compounds are also known for argon, krypton, and radon. These elements are known as the noble gases because of their relative unreactivity.

- **p-block elements**

→ Members are metals, metalloids, and nonmetals.

Metals: Group 13 (Al, Ga, In, Tl); Group 14 (Sn, Pb); Group 15 (Bi). Note: These metals have relatively low I_1 , but larger than those of the s block and d block.

Metalloids: Group 13 (B); Group 14 (Si, Ge); Group 15 (As, Sb); Group 16 (Te, Po). Note: *Metalloids have the physical appearance and properties of metals but behave chemically as nonmetals.*

Nonmetals: Group 14 (C); Group 15 (N, P); Group 16 (O, S, Se); Groups 17 & 18 (All). Notes: High Eea in Groups 13–17; these atoms tend to gain electrons to complete their subshells.

- **d-block elements (Groups 3–12)**

→ All are metals (most are transition metals), with properties intermediate to those of s-block and p-block metals.

→ The Chemistry of Transition Metal Elements depends upon their *d* orbital electrons. When a *transition metal atom ionizes, electrons from the ns orbital are removed first.*

Note: All Group 12 cations retain the filled d-subshell. For this reason, these elements (Zn, Cd, Hg) are *not classified as transition metals.* Recall that in this text *d-orbital electrons are considered to be valence electrons for all the d-block elements.*

- **Transition metals**

→ Form compounds with a variety of oxidation states (oxidation numbers)

→ Form alloys

→ Facilitate subtle changes in organisms

- **f -block elements (lanthanides and actinides)**

→ Rare on Earth

→ Lanthanides are incorporated in superconducting materials.

→ Lanthanides are used in electronic devices such as plasma TVs, disk drives, and mobile phones.

→ Actinides are all radioactive elements; most do not occur naturally on the Earth.

CHEMISTRY PUT TO WORK: Ionic Size and Lithium-Ion Batteries

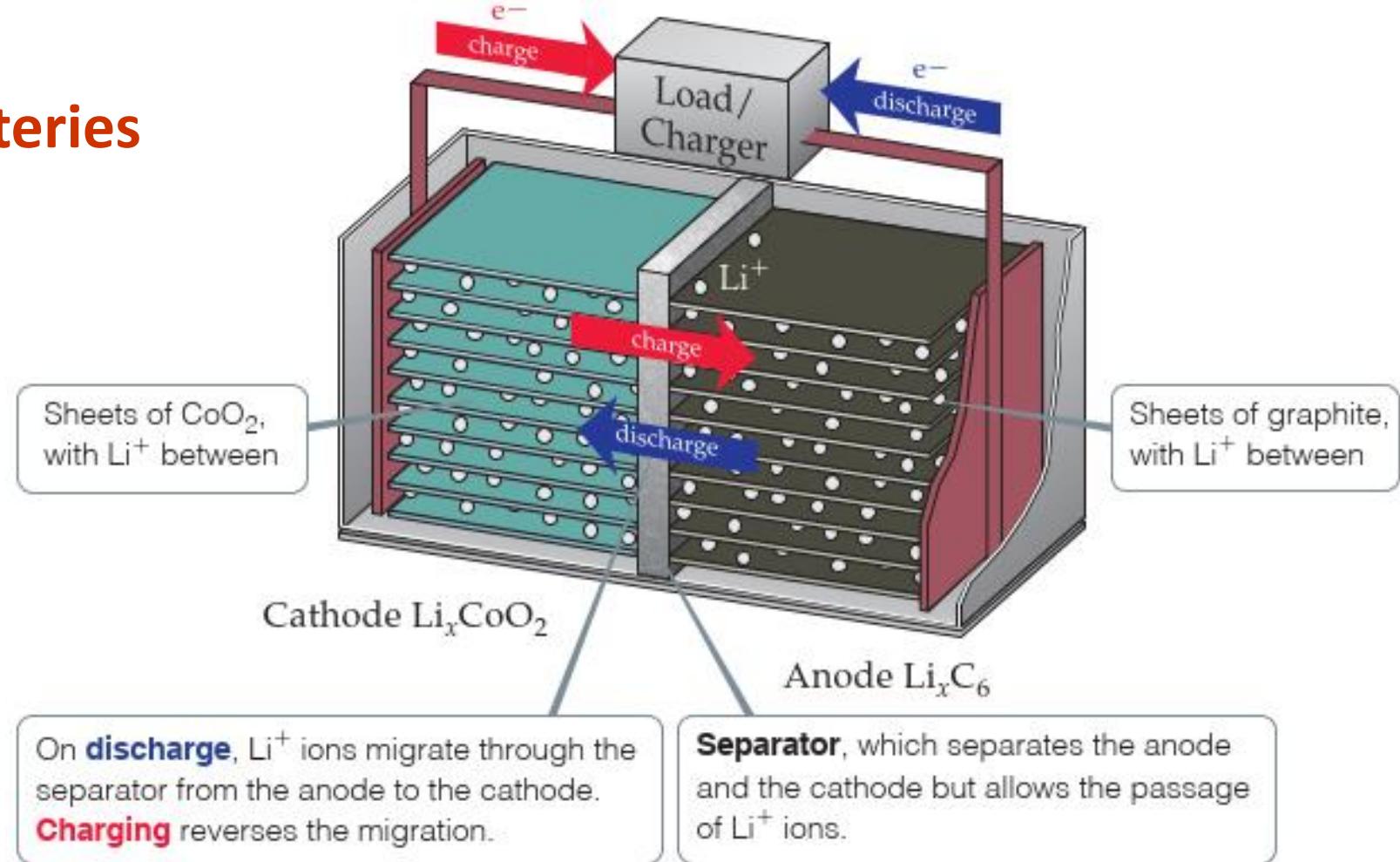


Figure 7.9 Schematic of a lithium-ion battery.

- “Lithium-ion” batteries have become the most common energy sources for modern electronic devices such as cell phones, Tabs, laptop computers, electric vehicles, smart watches and many other devices.
- It *relies in part on the small size of the lithium ion for their operation.*

CHEMISTRY PUT TO WORK: Ionic Size and Lithium-Ion Batteries

- A fully charged battery spontaneously produces an electric current and, therefore, power when its positive and negative electrodes are connected to an electrical load, such as a device to be powered. The positive electrode is called the anode, and the negative electrode is called the cathode.

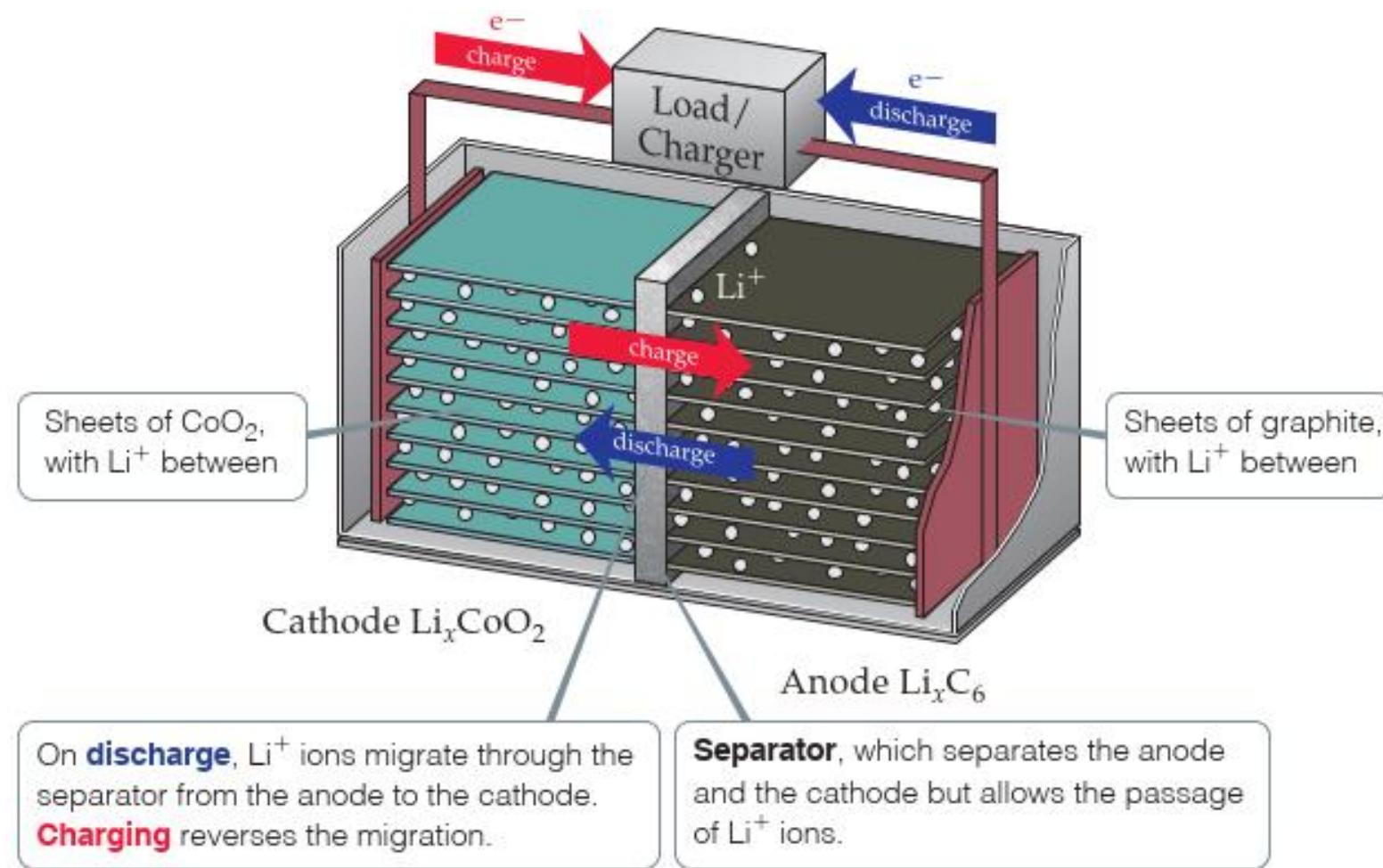


Figure 7.9 Schematic of a lithium-ion battery.

- **Ionic size plays a major role in determining the properties of devices that rely on movement of ions**, such as batteries.

☐ Lithium-Ion Batteries: *Construction and Working Principles*

- The *materials* used for the electrodes in lithium-ion batteries are *under intense development*. Currently, the ***anode material is graphite***, a form of carbon, and the ***cathode is a transition metal oxide***, often *lithium cobalt oxide*, LiCoO_2 (Figure 7.9).
- Between anode and cathode is a **separator**, a *porous solid material that allows the passage of lithium ions but not electrons*.

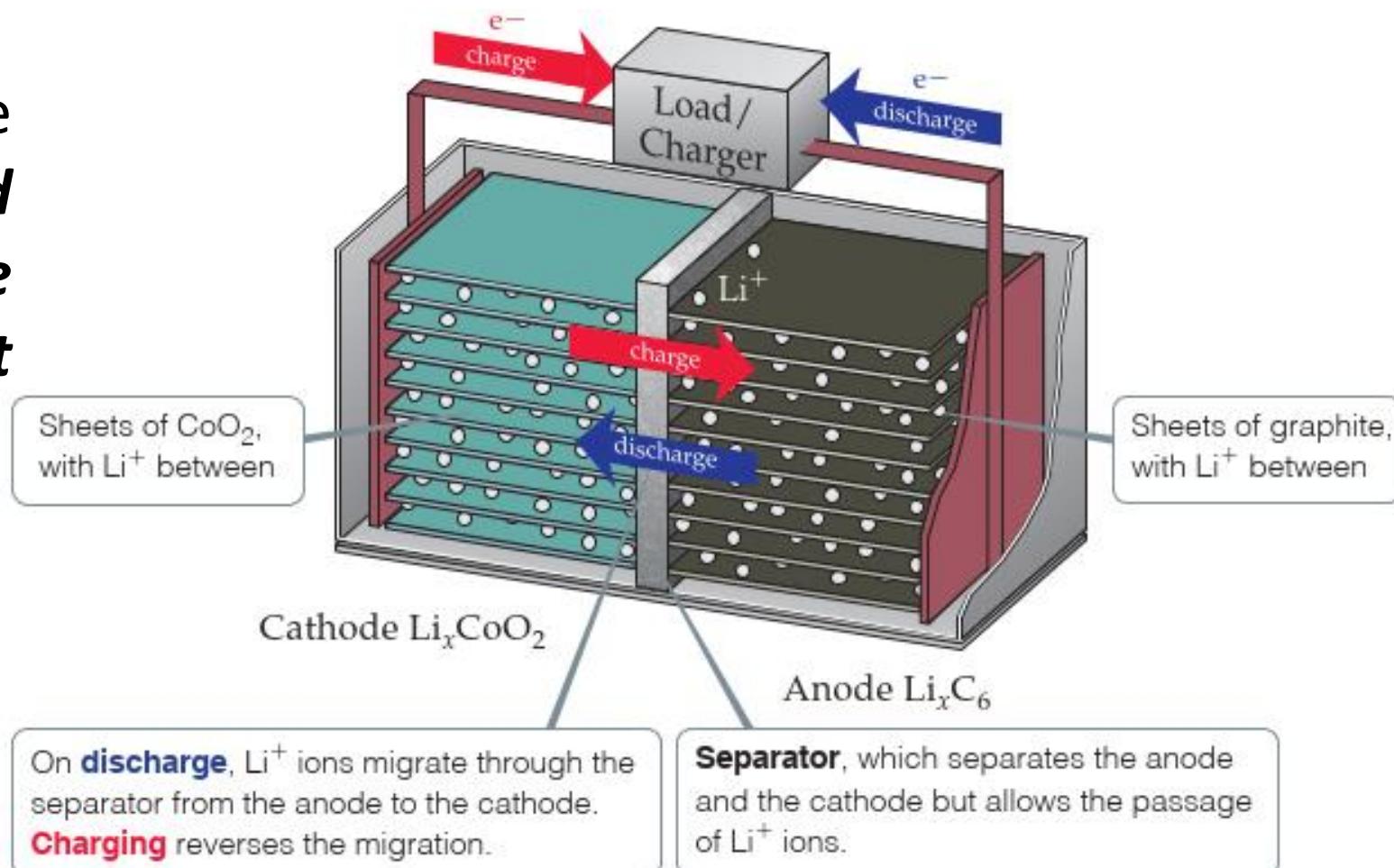


Figure 7.9 Schematic of a lithium-ion battery.

Lithium-Ion Batteries: *Construction and Working Principles*

- When the ***battery is being charged by an external source, lithium ions migrate through the separator from the cathode to the anode*** where they insert between the layers of carbon atoms.
- The ***ability of an ion to move*** through a solid increases as ***the size of the ion decreases*** and as ***the charge on the ion decreases***.
- Lithium ions are smaller than most other cations, and they carry only a 1+ charge, which ***allows them to migrate more readily than other ions can***.
- As an added bonus, ***lithium is one of the lightest elements***, which is attractive for use in electric vehicles.

- The working principle of lithium ion battery is shown in Figure 1.
- Lithium-ion battery is actually a kind of lithium-ion concentration difference battery.
- When charging, Li^+ is extracted from the positive electrode and inserted into the negative electrode through the electrolyte.
- The negative electrode is in a lithium-rich state.
- At the same time, the compensation charge of electrons is supplied from the external circuit to the carbon negative electrode to ensure the balance of charge.
- When discharging, the opposite is true. Li^+ is extracted from the negative electrode and inserted into the positive electrode material through the electrolyte, and the positive electrode is in a lithium-rich state.

The chemical expression of lithium ion battery is:

(+) LiCoO_2 | Electrolyte | Graphite (-)

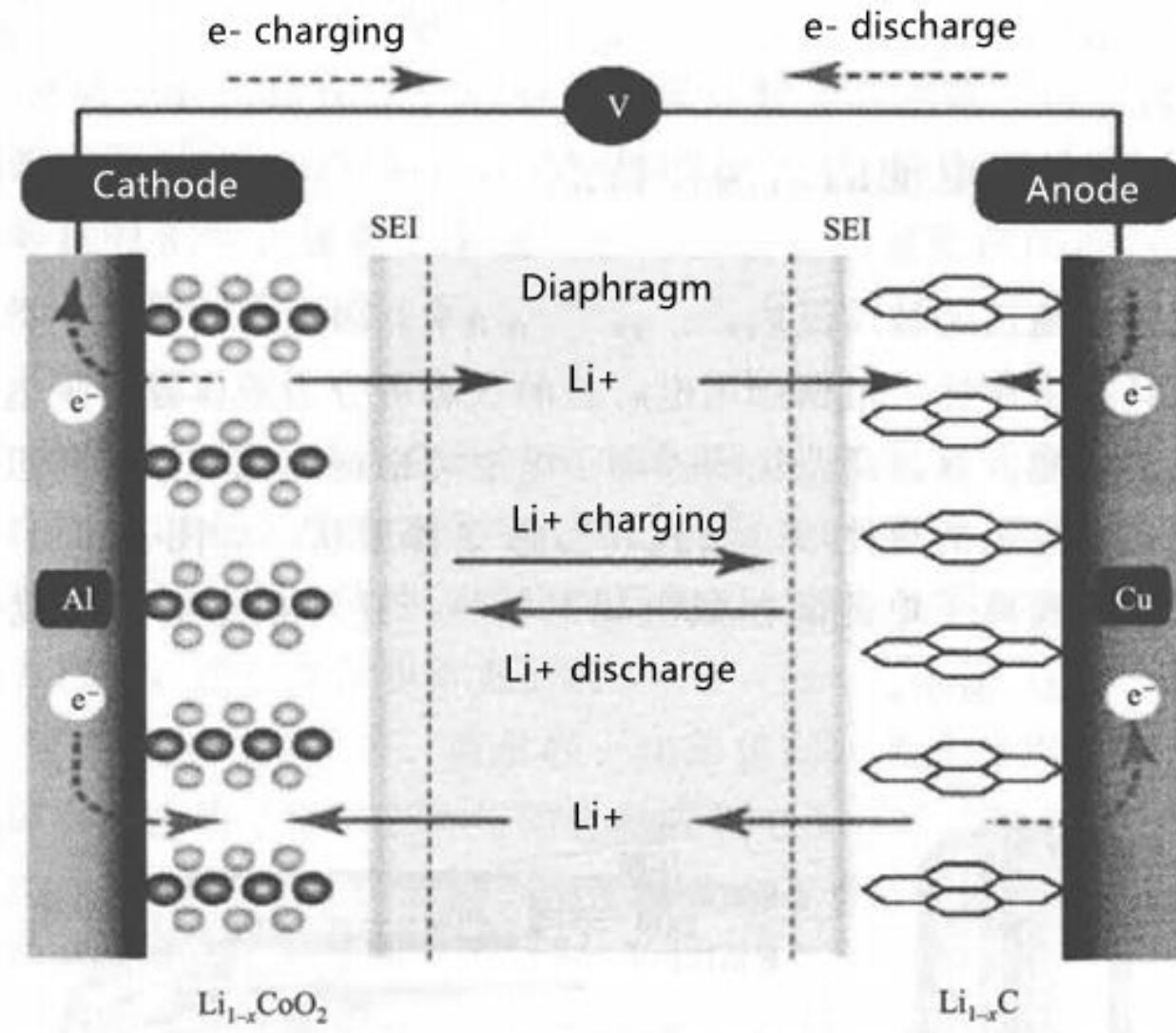
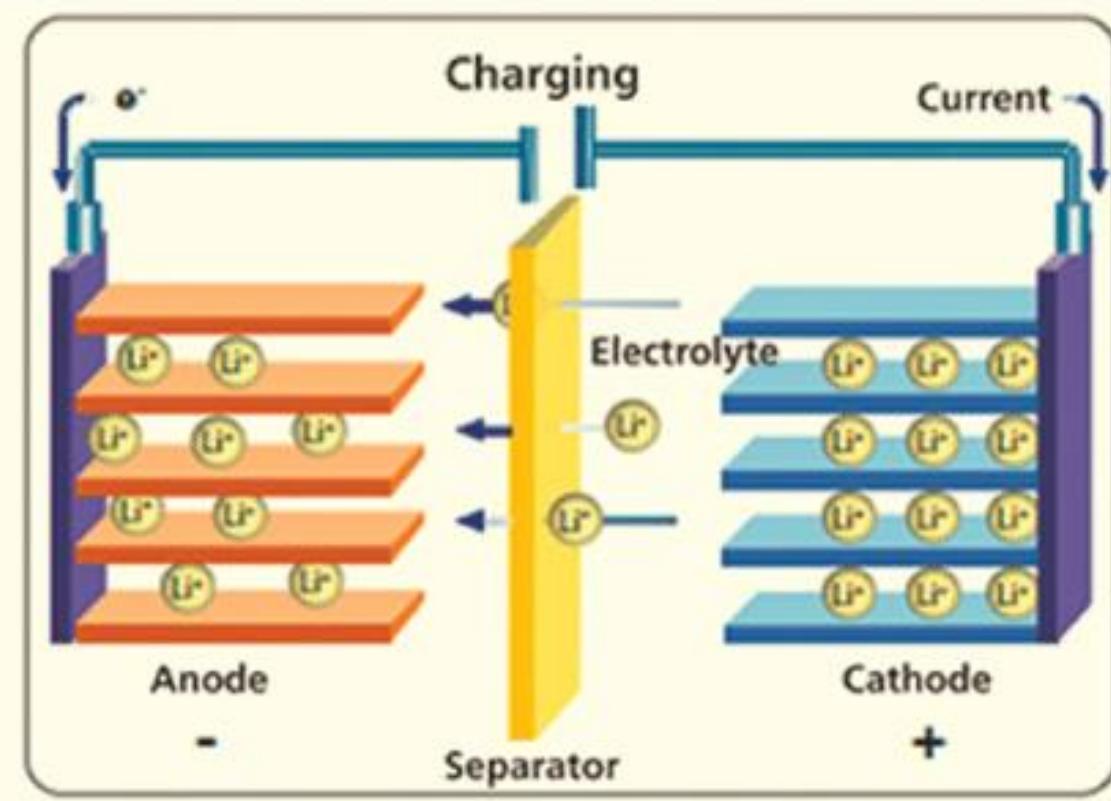
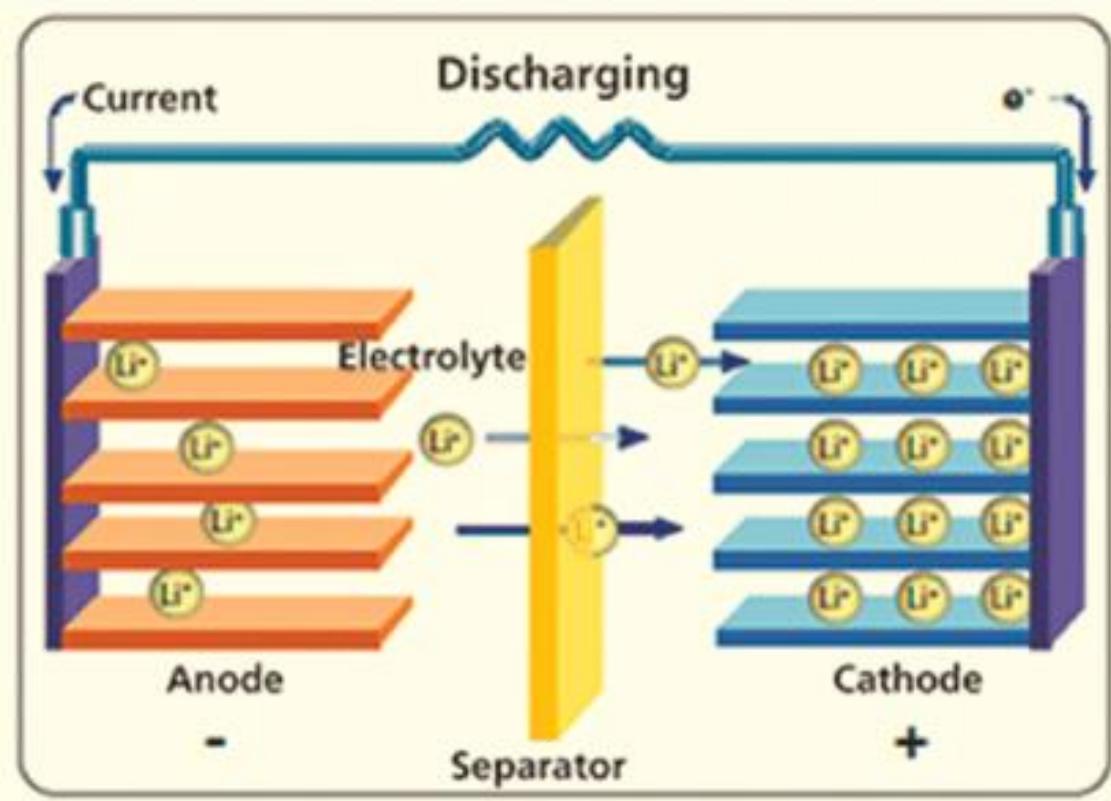


Figure 1: Working principle of lithium ion battery



Lithium-Ion Batteries: *Construction and Working Principles*

- When the **battery discharges**, the lithium ions move from anode to cathode. To maintain charge balance, electrons simultaneously migrate from anode to cathode through an external circuit, thereby producing electricity.
- At the cathode, lithium ions then *insert* in the oxide material. Again, the *small size* of lithium ions is an advantage.
- For every lithium ion that inserts into the lithium cobalt oxide cathode, a **Co⁴⁺ ion is reduced to a Co³⁺ ion by an electron** that has traveled through the external circuit.
- The ion migration and the changes in structure that result when lithium ions enter and leave the electrode materials are complicated.

Lithium-Ion Batteries:

- Furthermore, the ***operation of all batteries generate heat*** because *they are not perfectly efficient*.
- In the case of *Li-ion batteries*, the ***heating of the separator material (typically a polymer) has led to problems*** as the size of the batteries has been scaled larger to increase energy capacity. In a very small number of cases, overheating of Li-ion batteries has caused the *batteries to catch fire*.
- *New separator materials that allow for faster passage of lithium ions with less heat generation* are also under development.

Lithium-Ion Batteries

- Teams worldwide are also trying to *discover new cathode and anode materials* that will *easily accept and release lithium ions* without falling apart over many repeated cycles.
- Some research groups are looking at *using sodium ions instead of lithium ions* because *sodium is far more abundant than lithium*, although the larger size of sodium ions poses additional challenges.
- In the coming years, look for continued advances in battery technology based on alkali metal ions.

CHEMICAL BONDS

- The properties of a substance are determined *in part* by the chemical bonds that hold the atoms/ions together.
- ✓ For example, sodium (a silvery metal) reacts with chlorine (a pale greenish yellow gas) to produce sodium chloride (table salt, a white solid).
- ✓ The substances in this reaction are quite different, as are their chemical bonds. Sodium chloride, NaCl, consists of Na^+ and Cl^- ions held in a regular arrangement, or crystal, by ionic bonds.

❖ **What do we mean by the Chemical Bonds?**

❖ **What determines the type of bonding in each substance?**

❖ **How do you describe the bonding in various substances?**

- We shall briefly discuss these aspects here.

❖ What do we mean by Chemical Bonds?

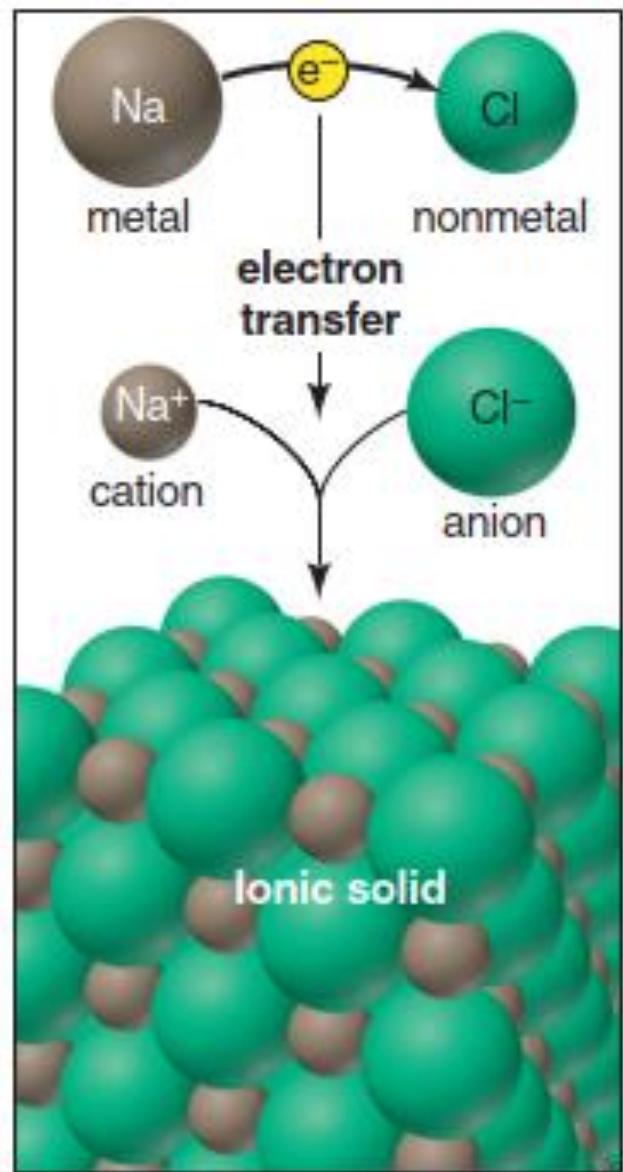
- A chemical bond is the link....in the form of the net force of attractions existing between atoms/ions in a substance.
- ✓ *When a chemical reaction occurs between atoms, some of their electrons are reorganized, resulting in a net attractive force—a chemical bond—between the atoms.*
- When **a chemical bond forms** between two atoms, the *resulting arrangement of the two nuclei and their electrons has a lower energy* than the total energy of the separate atoms.
- *The changes in energy responsible for the formation of bonds.*
- Therefore, bond formation depends on the electronic structures of atoms.

➤ If the **lowest energy can be achieved** by:

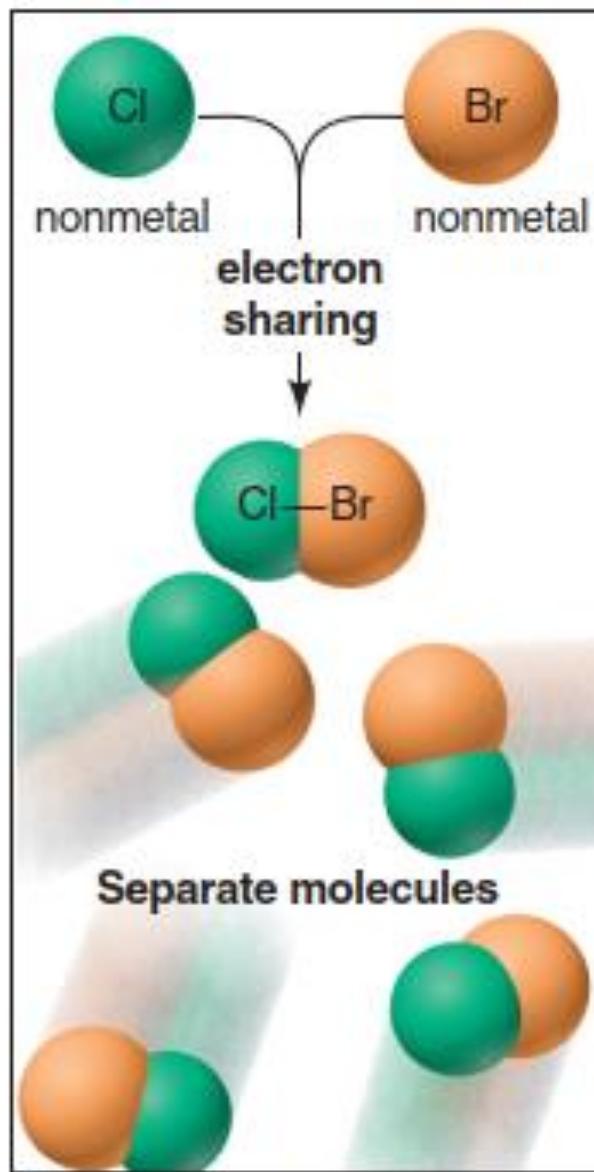
....the **complete transfer of one or more electrons** from each atom of one element to those of another, then ions form and the compound is held together by the **electrostatic attraction** between them. **Ionic bonding** results from the attractive force of oppositely charged ions.e.g., NaCl.

.... **sharing of electrons**, which are attracted to the positively charged cores of both atoms, thus linking them. This kind of linking of the atoms is called a **covalent bond** and discrete molecules are formed.e.g., Cl₂, CH₄.

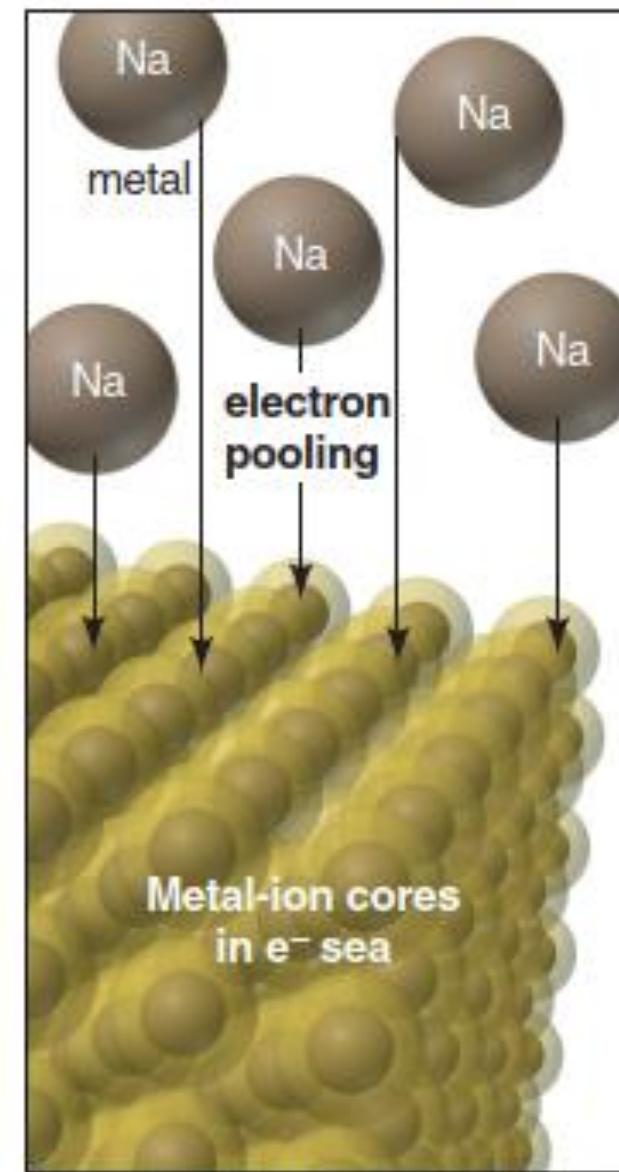
....A **third type of bond** is the **metallic bond**, in which **large numbers of cations are held together by a sea of electrons**. For example, a piece of copper consists of a stack of copper ions held together by a sea of valence electrons, each of which comes from one of the atoms in the sample. We consider the metallic bond in more detail in later. In this section we examine ionic and covalent bonds.e.g., Cu, Ag,



A Ionic bonding



B Covalent bonding



C Metallic bonding

Figure 9.2 Three models of chemical bonding.

➤ Chemists generally think of bonds as falling into these three broad categories—*Ionic, covalent, and metallic.*

□ What determines the type of bonding in each substance?

□ How do you describe the bonding in various substances?

➤ In this section, we will look at some simple, useful concepts of bonding that can help us answer these questions. We will be concerned with ionic and covalent bonds in particular.

What determines the type of bonding in each substance?

➤ **ATOMIC PROPERTIES AND CHEMICAL BONDS**

➤ **Types of Bonding:** Three Ways **Metals** and **Nonmetals** Combine

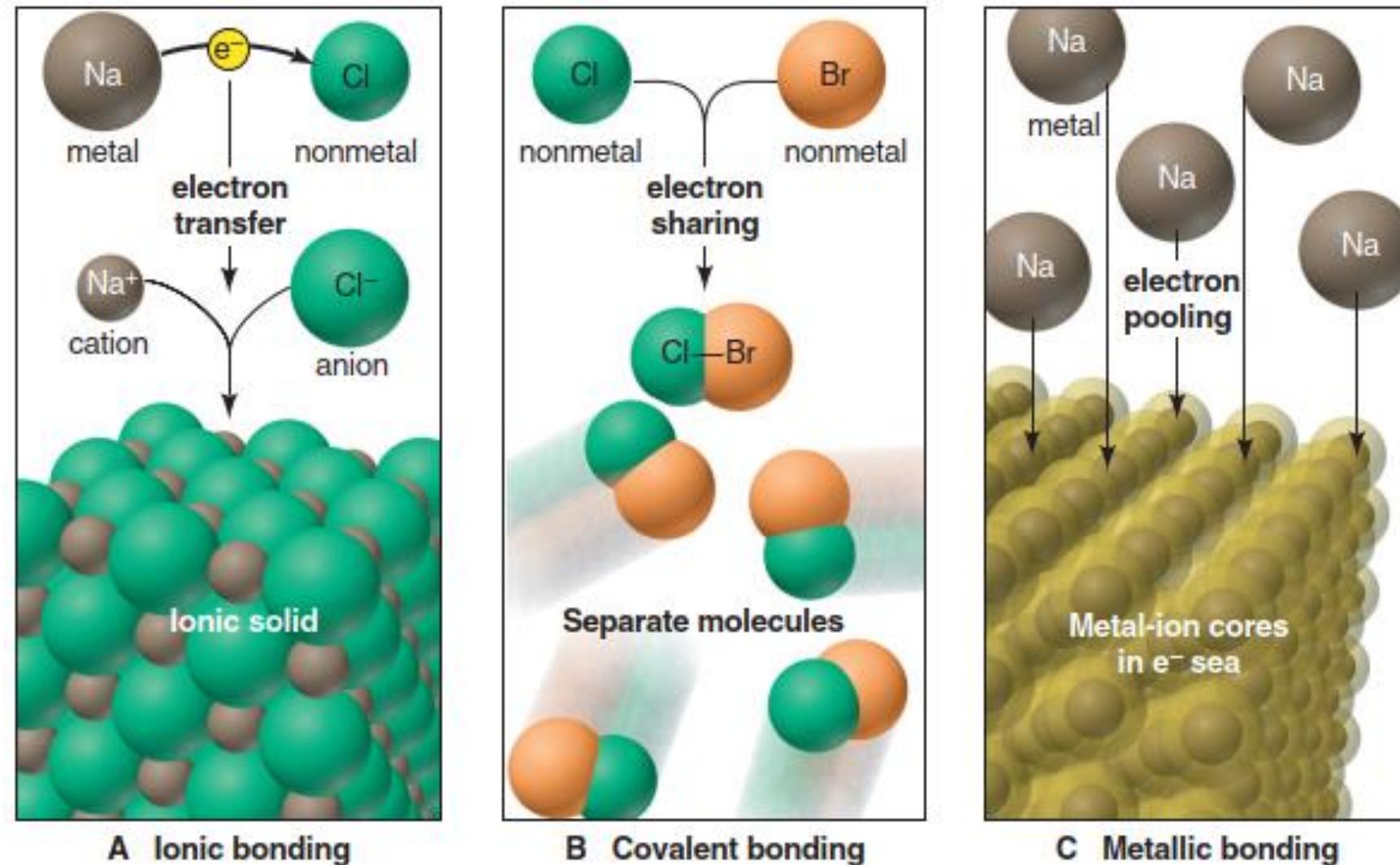


Figure 9.2 Three models of chemical bonding.

ATOMIC PROPERTIES AND CHEMICAL BONDS

□ Types of Bonding: Three Ways Metals and Nonmetals Combine

- In general, there is a gradation from atoms of more metallic elements to atoms of more nonmetallic elements across a period and up a group.
- Three types of bonding result from the three ways these two types of atoms can combine.

- 1. **Metal with nonmetal**: electron transfer and ionic bonding (Figure 9.2A). We observe **ionic bonding** between atoms with large differences in their tendencies to lose or gain electrons. Such differences occur between reactive metals [Groups 1A(1) and 2A(2)] and nonmetals [Group 7A(17) and the top of Group 6A(16)].
- ✓ A metal atom (*low IE*) loses its one or two valence electrons, and a nonmetal atom (*highly negative EA*) gains the electron(s).
 - ✓ Electron transfer from metal to nonmetal occurs, and each atom forms an ion with a noble gas electron configuration.
 - ✓ The electrostatic attractions between these positive and negative ions draw them into a three-dimensional array to form an ionic solid.
 - ✓ Note that the **chemical formula** of an ionic compound is the **empirical formula** because it gives the **cation-to-anion ratio**.

➤ 2. ***Nonmetal with nonmetal***: electron sharing and **covalent bonding**.

- ✓ When two atoms differ little, or not at all, in their tendencies to lose or gain electrons, we observe electron sharing and covalent bonding, which occurs most commonly between nonmetal atoms.
- ✓ Each atom holds onto its own electrons tightly (*high IE*) and attracts other electrons (*highly negative EA*).
- ✓ The nucleus of each atom attracts the valence electrons of the other, which draws the atoms together.
- ✓ The shared electron pair is typically localized between the two atoms, linking them in a covalent bond of a particular length and strength. In most cases, separate molecules result when atoms bond covalently. Note that the chemical formula of a covalent compound is the molecular formula because it gives the actual numbers of atoms in each molecule.

➤ 3. ***Metal with metal***: electron pooling and **metallic bonding**.

- ✓ Metal atoms are relatively large, and their few outer electrons are well shielded by filled inner levels (core electrons). Thus, they lose outer electrons easily (**low IE**) and do not gain them readily (slightly negative or positive EA). **These properties lead metal atoms to share their valence electrons, but not by covalent bonding.**
- ✓ In the simplest model of metallic bonding, the enormous number of atoms in a sample of a metal pool their valence electrons into a “sea” of electrons that “flows” between and around each metal-ion core (nucleus plus inner electrons), thereby attracting them and holding them together.
- ✓ Unlike the localized electrons in covalent bonding, ***electrons in metallic bonding are delocalized***, moving freely throughout the entire piece of metal.

- In the world of real substances, ***there are exceptions to these idealized models***, so you can't always predict bond type from positions of the elements in the periodic table.
- ✓ As just one example, when the metal ***beryllium*** [Group 2A(2)] ***combines with the nonmetal chlorine*** [Group 7A(17)], the ***bonding fits the covalent model*** better than the ionic model.
- ✓ Thus, just as we see gradations in atomic behavior within a group or period, we see a gradation in bonding from one type to another.

❖ Ionic Bonds

- The first explanation of chemical bonding was suggested by the properties of salts, substances now known to be ionic.
- Salts are generally crystalline solids that melt at high temperatures. Sodium chloride, for example, melts at 801°C.
- A molten salt (the liquid after melting) conducts an electric current.
- A salt dissolved in water gives a solution that also conducts an electric current.
- The electrical conductivity of the molten salt and the salt solution results from the motion of ions in the liquids.
- This suggests the possibility that ions exist in certain solids, held together by the attraction of opposite charges.

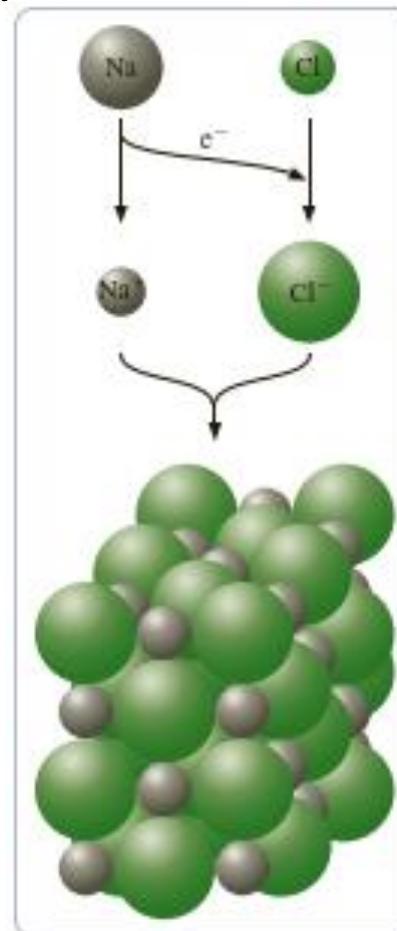
➤ Describing Ionic Bonds

➤ **An ionic bond is a chemical bond formed by the electrostatic attraction between positive and negative ions.**

➤ To understand why ionic bonding occurs, consider the transfer of a valence electron from a sodium atom (electron configuration $[\text{Ne}]3s^1$) to the valence shell of a chlorine atom ($[\text{Ne}]3s^23p^5$). You can represent the electron transfer by the following equation:



➤ According to the Lewis electron-dot symbol (in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element):



➤ As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration (ns^2np^6). The sodium atom has lost its 3s electron and has taken on the neon configuration, [Ne].

- The chlorine atom has accepted the electron into its 3p subshell and has taken on the argon configuration, [Ne]3s²3p⁶.
- ***Such noble-gas configurations and the corresponding ions are particularly stable.*** This stability of the ions ***accounts in part for the formation of the ionic solid NaCl.***
- Once a cation or anion forms, it attracts ions of opposite charge. Within the sodium chloride crystal, NaCl, every Na⁺ ion is surrounded by six Cl⁻ ions, and every Cl⁻ ion by six Na⁺ ions.

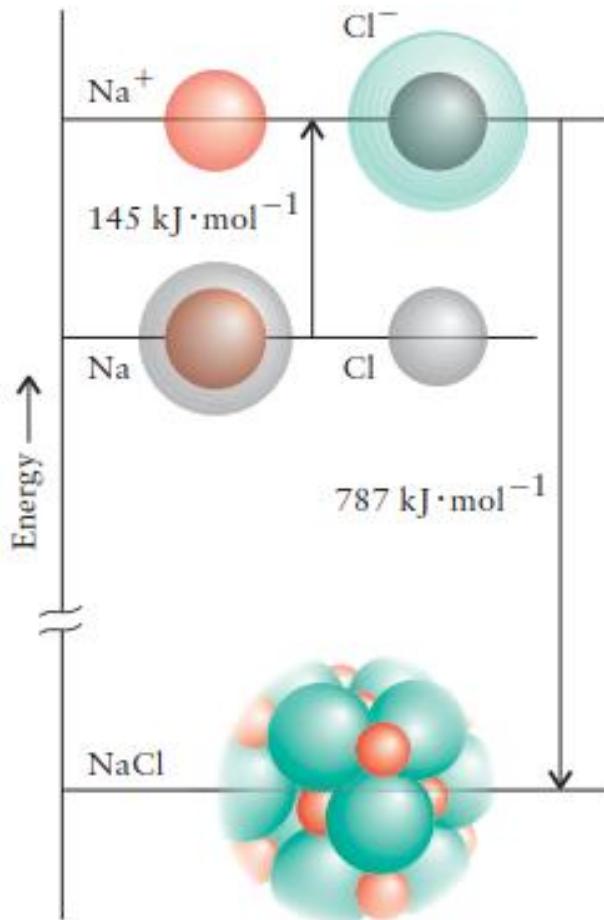


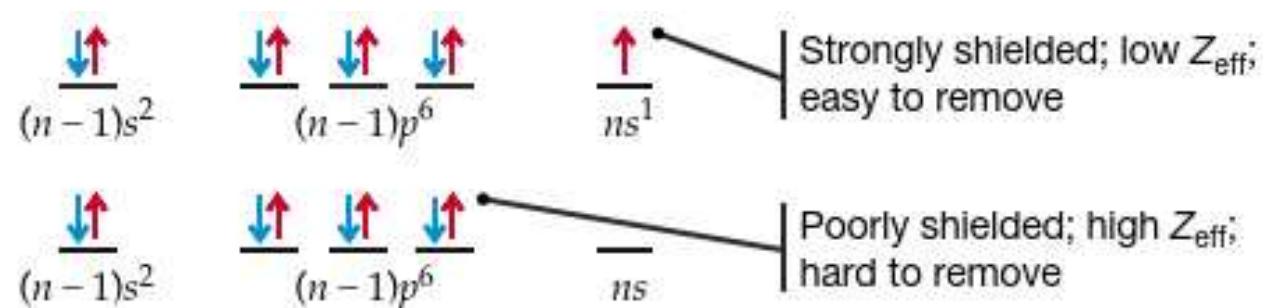
FIGURE... Energy is needed to produce cations and anions from neutral atoms: the ionization energy of the metal atoms is only ***partly*** recovered from the electron affinity of the nonmetal atoms.

The overall lowering of energy that drags the ionic solid into existence arises from the strong attraction between cations and anions of NaCl(s).

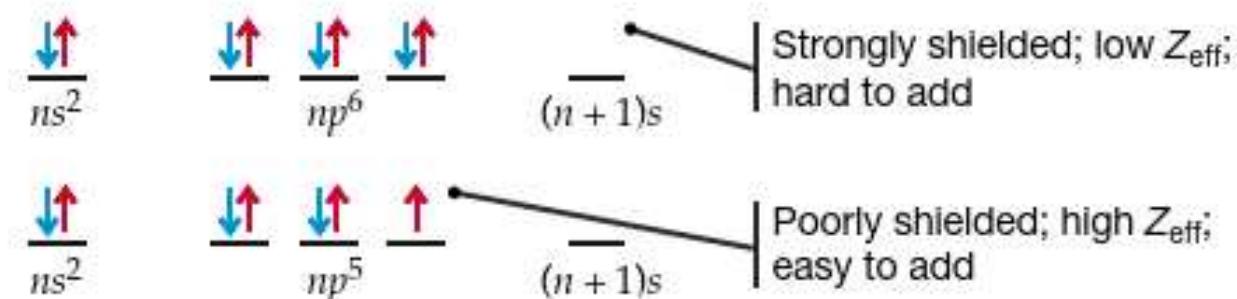
☐ THE OCTET RULE FOR MAIN-GROUP ATOMS

❖ What factors determine how many electrons an atom is likely to gain or lose?

- Electrons are most likely to be lost if they are held loosely in the first place—that is, if they feel a relatively low effective nuclear charge, Z_{eff} , and have relatively low ionization energies.
- *Valence-shell electrons in the group 1A, 2A, and 3A metals*, for instance, are shielded from the nucleus by core electrons, feel a low Z_{eff} , and are therefore lost relatively easily. Once the next lower noble-gas configuration is reached, though, loss of an additional electron suddenly becomes much more difficult because it must come from an inner shell, where it feels a much higher Z_{eff} .



- Conversely, ***electrons are most likely to be gained if they can be held tightly by a high Z_{eff}*** . Valence-shell electrons in the group 6A and 7A elements, for example, are poorly shielded, feel high values of Z_{eff} , and aren't lost easily.
- The ***high Z_{eff} thus makes possible the gain of one or more additional electrons into vacant valence-shell orbitals***.
- Once the noble-gas configuration is reached, though, lower-energy orbitals are ***no longer available***. Any additional electron would have to be placed in a higher-energy orbital, where it would feel only a low Z_{eff} .



- ✓ Taking electrons from a filled octet is difficult because they are tightly held by a high Z_{eff} ;
 - ✓ adding more electrons to a filled octet is difficult because, with s and p subshells full, no low-energy orbital is available.
- **Eight** is therefore the **optimum number** for **valence-shell electrons**.

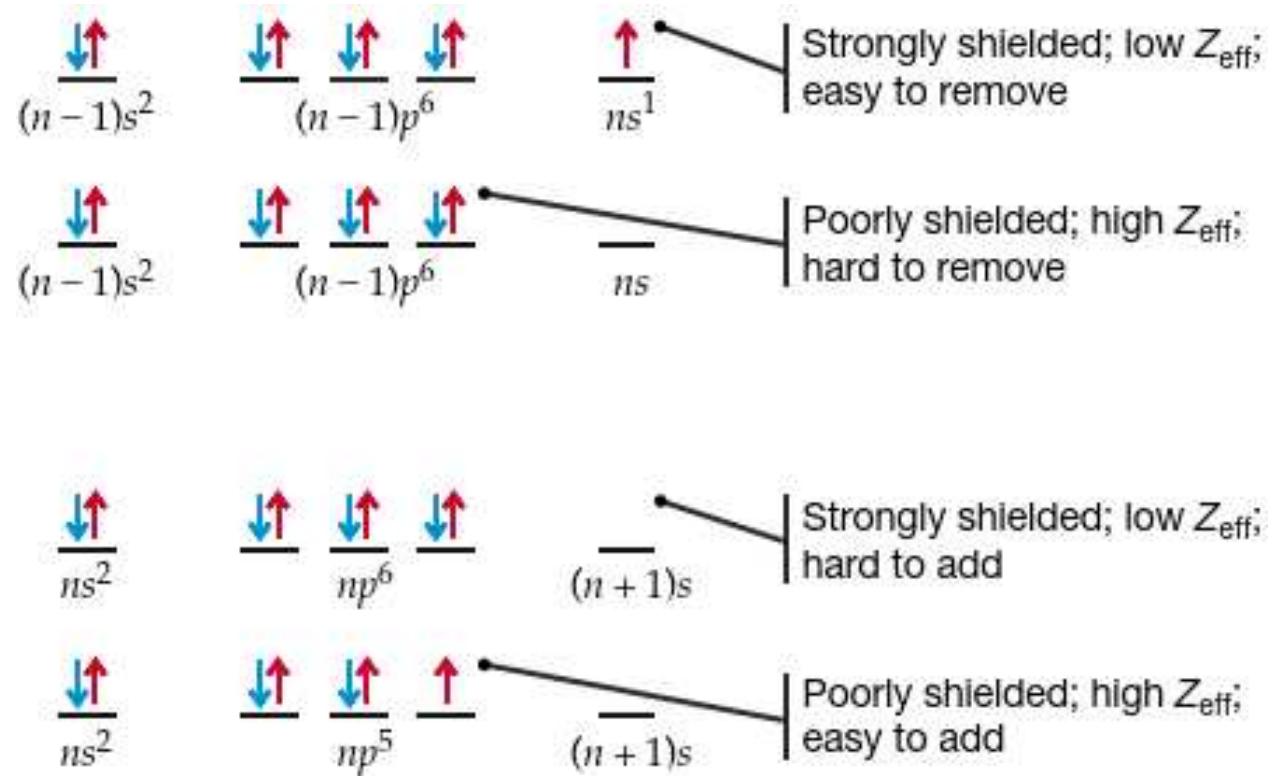


TABLE 6.2 Examples of Monatomic Ions and Their Nearest Noble Gases

Noble Gases		Metals Lose Valence Electrons			Nonmetals Gain Valence Electrons			Noble Gases
		1A (1)	2A (2)	3A (13)	5A (15)	6A (16)	7A (17)	
He		Li^+						
Ne		Na^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	F^-	Ne
Ar		K^+	Ca^{2+}		P^{3-}	S^{2-}	Cl^-	Ar
Kr		Rb^+	Sr^{2+}				Br^-	Kr
Xe		Cs^+	Ba^{2+}				I^-	Xe

❖ Octet Rule

- ✓ Main-group elements tend to undergo reactions that leave them with eight outer-shell electrons.
- ✓ That is, main-group elements react so that they attain a noble-gas electron configuration with filled *s* and *p* subshells in their valence electron shell.
- In the formation of either an ionic bond or a covalent bond, atoms of *main-group elements* lose, gain, or share valence electrons to acquire an octet of eight valence electrons. This tendency of atoms to attain a stable electron arrangement is known as the **octet rule**.
- *According to the octet rule of Lewis and Kossel, atoms tend to interact through electronic rearrangements that produce a noble gas electronic configuration for each atom involved in the interaction.*

- ✓ We have seen why the octet rule works or how the octet rule arises.
- The rule provides a key to our qualitative understanding of the ways in which atoms bond and form compounds.
- As we'll see later, ***there are exceptions to the octet rule.***
- ✓ A few elements achieve the ***stability of helium with two valence electrons.***
- ✓ Similarly, we do ***not*** use the octet rule with ***transition elements***, elements in the third and lower rows of the periodic table.
- Nevertheless, the rule is extremely useful for making predictions and for providing insights about chemical bonding.

Energetics of Ionic Bond Formation

- We have seen in a *qualitative way* how/why a sodium atom and a chlorine atom might be expected to form an ionic bond.
- It is instructive, however, to **look at the energy changes involved in ionic bond formation.**
- From this analysis, you can gain further understanding of why certain atoms bond ionically and others do not.
- *If atoms come to bond together, there should be a net decrease in energy, because the bonded state should be more stable and therefore at a lower energy level.*

- If atoms come to bond together, there should be a net decrease in energy, because the bonded state should be more stable and therefore at a lower energy level.**
- Consider again the formation of an ionic bond between a sodium atom and a chlorine atom.
- One can think of this as occurring in two steps:
 - ✓ (1) An electron is transferred between the two separate atoms to give ions.
 - ✓ (2) The ions then attract one another to form an ionic bond.
- The *first step requires removal of the 3s electron* from the sodium atom (**requires energy**, the first ionization energy of the sodium atom, +496 kJ/mol) and *the addition of this electron to the valence shell of the chlorine atom* (**releases energy**, -349 kJ/mol, which is the electron affinity of the chlorine atom).

- The *overall process* would be an *endothermic* process that requires $496 - 349 = 147 \text{ kJ/mol}$ (Figure 2.4).
- So, *the process requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom.*

$$\begin{array}{ll} E_i \text{ for Na} = +495.8 \text{ kJ/mol} & \text{(Unfavorable)} \\ E_{ea} \text{ for Cl} = -348.6 \text{ kJ/mol} & \text{(Favorable)} \\ \hline \Delta E & = +147.2 \text{ kJ/mol} \\ & \text{(Unfavorable)} \end{array}$$

- A gas of widely separated Na^+ and Cl^- ions has a higher energy than a gas of neutral Na and Cl atoms. *The formation of ions from the atoms is NOT in itself energetically favorable.....!!!! How does NaCl form then?*

➤ This endothermic process corresponds to *the formation of sodium and chloride ions that are infinitely far apart*—in other words, *the positive energy change assumes that the ions do not interact with each other, which is quite different from the situation in ionic solids.*

➤ When positive and negative ions bond together, however, more than enough energy is released to make the overall process favorable.

➤ Now consider what happens when gaseous Na^+ and Cl^- ions come together to form a crystalline solid. The process releases a lot of energy, and **experimentally** it is found that



➤ Therefore, the **net change in energy** for the overall process is $(145 - 787) \text{ kJ/mol} = -642 \text{ kJ/mol}$ (Fig. 2.4), a **huge decrease in energy**.

➤ We conclude that a solid composed of Na^+ and Cl^- ions has a lower energy than does a collection of widely separated Na and Cl atoms.

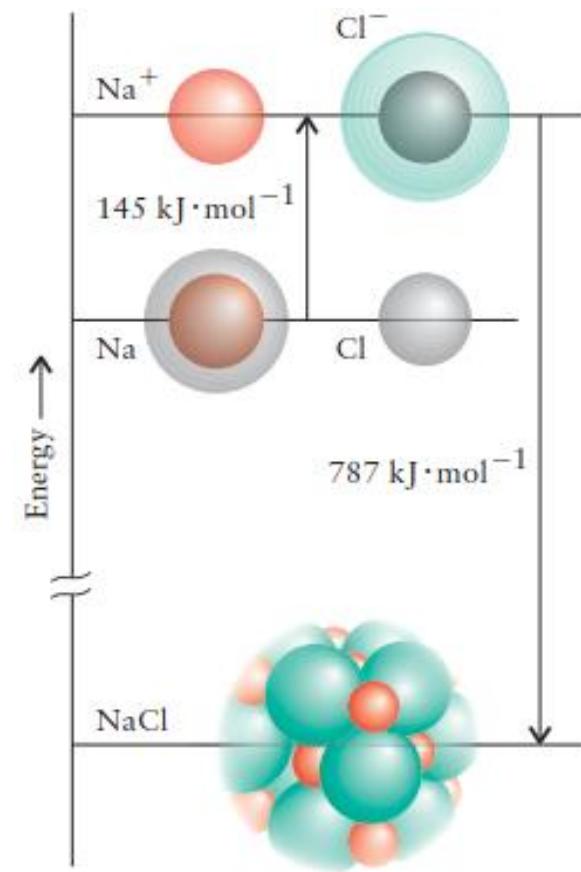
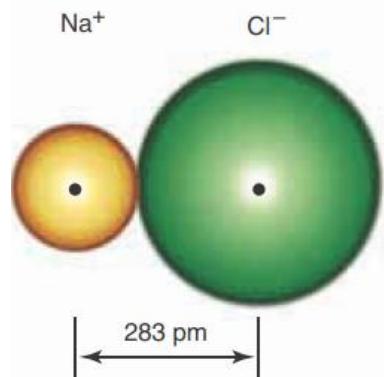


FIGURE 2.4... Energy is needed to produce cations and anions from neutral atoms: the ionization energy of the metal atoms is only partly recovered from the electron affinity of the nonmetal atoms. The overall lowering of energy that drags the ionic solid into existence arises from the strong attraction between cations and anions of $\text{NaCl}(\text{s})$.

- What *principally determines the energy released when ions bond* is ***the attraction of oppositely charged ions.***
- ✓ To see this, let's look first at ***the energy obtained when a Na^+ ion and a Cl^- ion come together*** to form ***an ion-pair molecule.***
- ✓ We will estimate this energy by making the simplifying assumption that the *ions are spheres*, just touching, with the distance between the nuclei of the ions equal to this distance in the NaCl crystal.
- ✓ From experiment, this distance is known to be 283 pm, or 2.83×10^{-10} m.
- ✓ To calculate the energy obtained when the ion spheres come together, we use Coulomb's law.

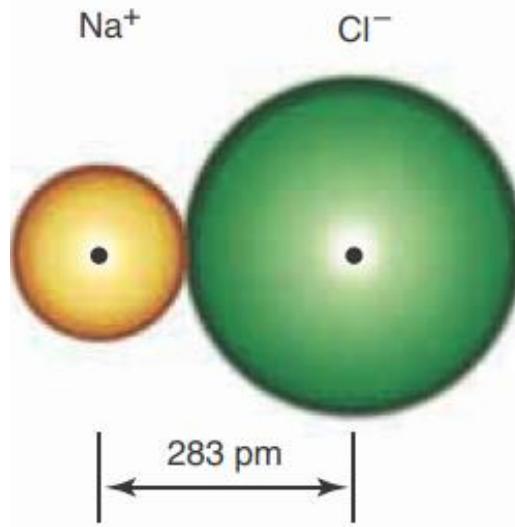
$$E = \frac{kQ_1 Q_2}{r}$$



✓ Coulomb's law states that the potential energy obtained in bringing two charges Q_1 and Q_2 , initially far apart, up to a distance r apart is directly proportional to the product of the charges and inversely proportional to the distance between them:

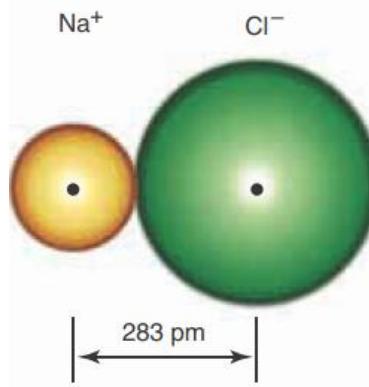
$$E = \frac{kQ_1Q_2}{r}$$

$$E = \frac{k(+z_1e)(-z_2e)}{r}$$



- ✓ Here k is a physical constant, equal to $8.99 \times 10^9 \text{ J.m/C}^2$ (C is the symbol for coulomb).
- ✓ Z_i is the charge number of the i -th ion. The charge on Na^+ is $+e$ and that on Cl^- is $-e$, where e equals $1.602 \times 10^{-19} \text{ C}$.

Figure 6.9 A solid-sphere representation of the ion pair $\text{Na}^+\text{Cl}^-(g)$. The sodium ion can be represented as a hard sphere of radius 102 pm and the chloride ion can be represented as a hard sphere of radius 181 pm. Because the two ions have opposite charges, they draw together until they touch, with a distance between their centers of $102 \text{ pm} + 181 \text{ pm} = 283 \text{ pm}$. They are bound together at this distance in an ionic bond. We call this value the equilibrium ion-pair separation distance.



- ✓ Thus, our estimate of the energy of attraction of Na^+ and Cl^- ions to form *an ion pair* is

$$E = \frac{-(8.99 \times 10^9 \text{ J} \cdot \text{m}/\text{C}^2) \times (1.602 \times 10^{-19} \text{ C})^2}{2.82 \times 10^{-10} \text{ m}} = -8.18 \times 10^{-19} \text{ J}$$

- ✓ *The minus sign means energy is released.* This energy is for the *formation of one ion pair*.
- ✓ To express this for **one mole** of Na^+Cl^- **ion pairs**, we multiply by Avogadro's number, 6.02×10^{23} . We obtain **-493 kJ/mol for the energy** when one mole of Na^+ and one mole of Cl^- come together to form Na^+Cl^- ion pairs.
- ✓ *What we see...??*

- What we see is that:
 - ✓ *the formation of ion pairs from sodium and chlorine atoms is energetically favorable* and
 - ✓ *the energy required for the formation of ionic bonds is supplied largely by the attraction between oppositely charged ions.*
- But it (-493 kJ/mol) does **not account for the -642 kJ/mol decrease of energy!**

THE FORMATION OF IONIC SOLIDS: *The Lattice Energy Contribution*

- A very important point to note is that an *ionic solid is not held together by the sum total of the attraction of the specific pairs of oppositely charged ions.*
- It is something more than that: all the cations interact to a greater or lesser extent with all the anions, all the cations repel each other, and all the anions repel each other. *An ionic bond is a “global” characteristic of the entire crystal.*
- *The maximum attraction of ions of opposite charge with the minimum repulsion of ions of the same charge is obtained with the formation of the crystalline solid.*
- This gives **additional stability** and additional energy is released. This is the negative of the *lattice energy* of NaCl.
- The additional energy (in going from ion pairs to the crystalline solid) equals -293 kJ/mol.

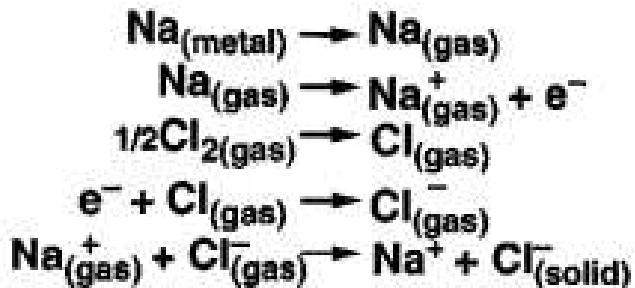
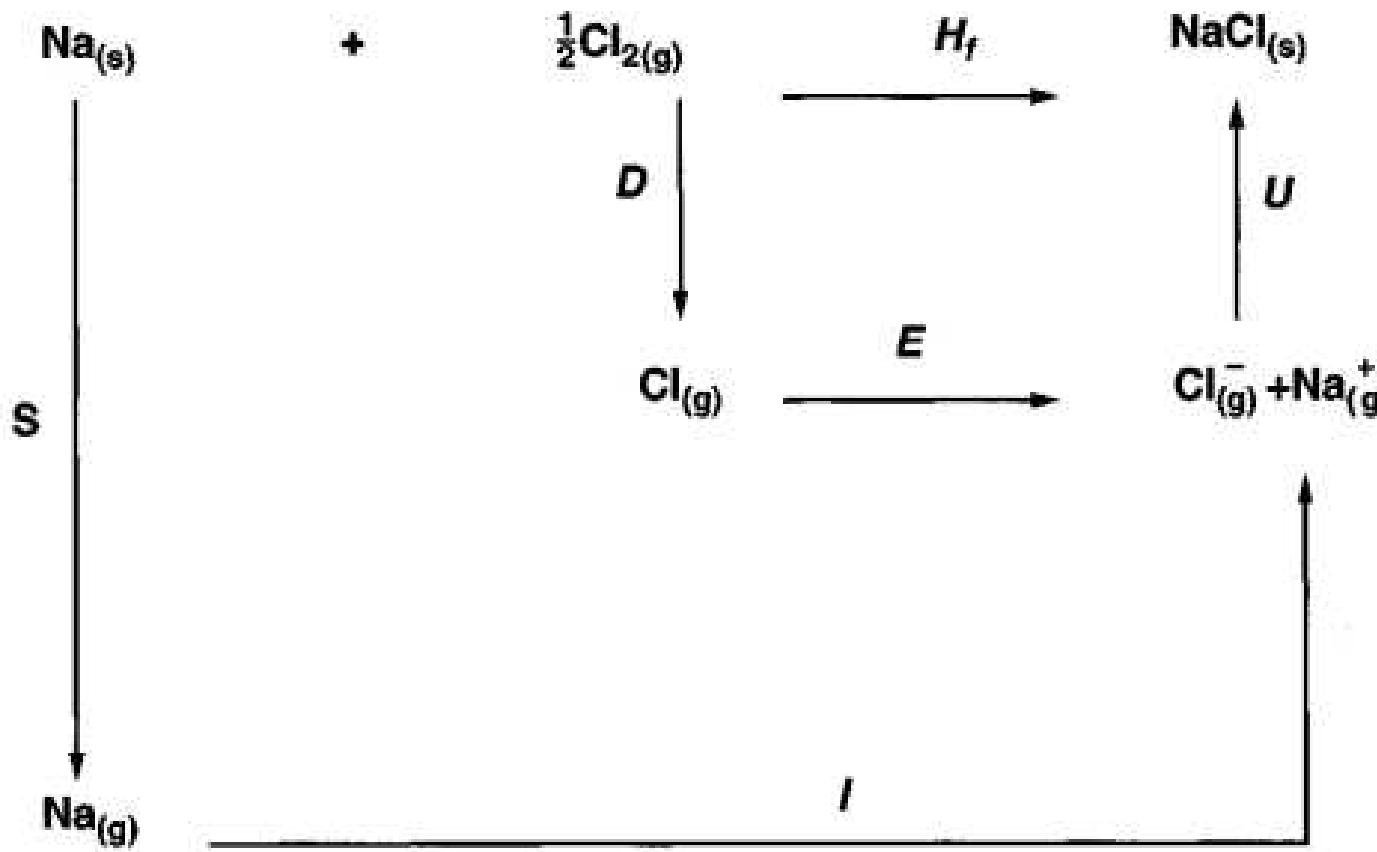
- **The lattice energy is the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.** For sodium chloride, the process is



- The distances between ions in the crystal are continuously enlarged until the ions are very far apart.
- **One can obtain an experimental value** for this process from thermodynamic data (see the **Born–Haber cycle** on the next page).
- The lattice energy for NaCl is 786 kJ/mol so that for the reverse process, when the ions come together to bond, the energy is –786 kJ/mol.
- Consequently, the net energy obtained when gaseous Na and Cl atoms form solid NaCl is $(-786 + 147)$ kJ/mol = –639 kJ/mol.
- The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

Calculation of Lattice Energies: The Born–Haber Cycle

- *Lattice energies cannot be determined directly by experiment.*
- However, this quantity can be indirectly determined from experiment by means of a thermochemical “cycle” originated by Max Born and Fritz Haber in 1919 and now called the **Born–Haber cycle**.
- The calculation involves envisioning the formation of an ionic compound as occurring in a series of well-defined steps.



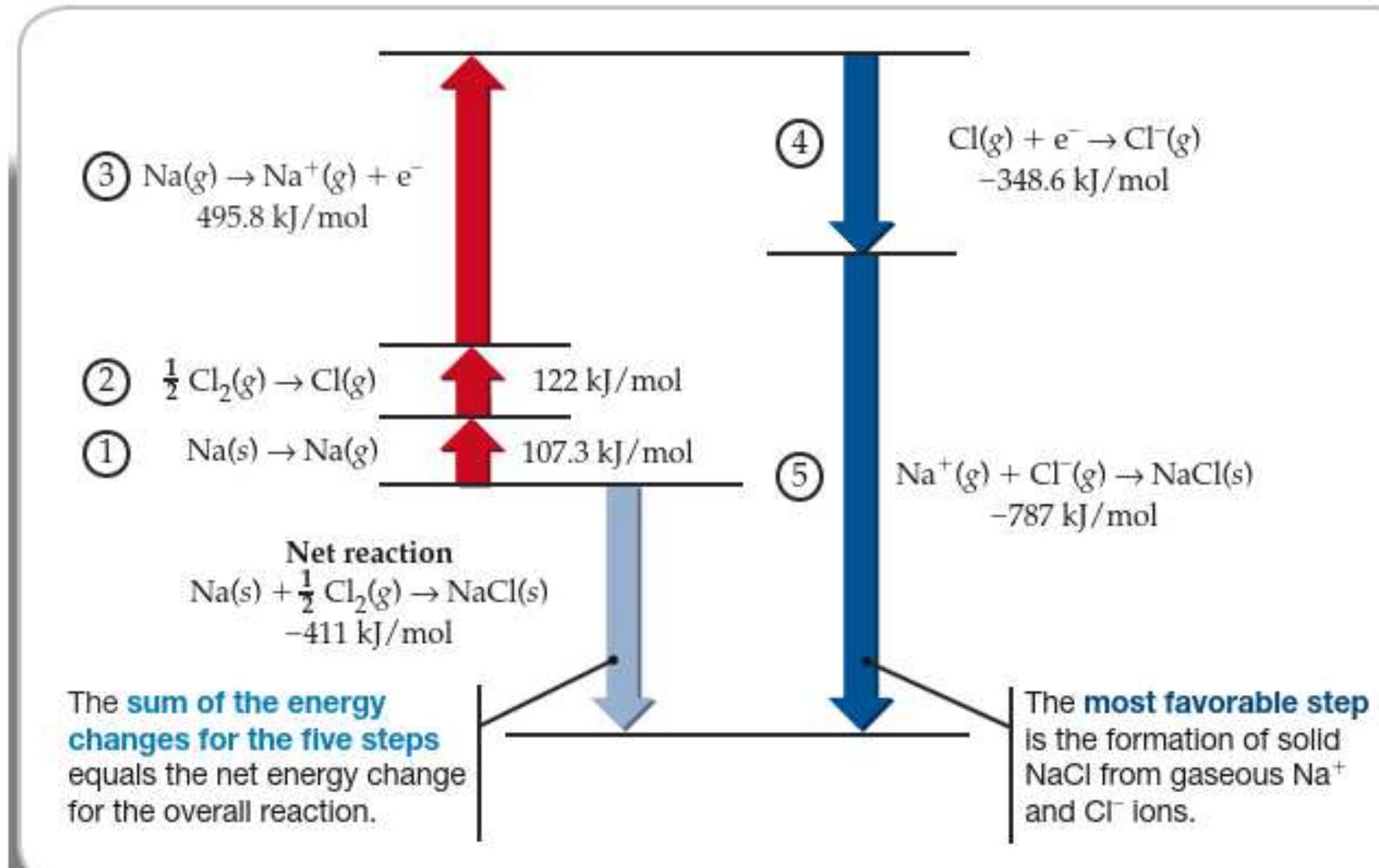
	energy changes	kJ mol^{-1}
heat of sublimation	$S + 109.0$	
ionization potential	$I + 495.9$	
$\frac{1}{2} \times$ heat of dissociation	$D + 120.9$	
electron affinity	$E - 349.2$	
lattice energy	$U - 764.4$	

FIG. 5. 5 Born-Haber cycle for the formation of sodium chloride

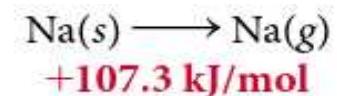
□ Calculation of Lattice Energies: The Born–Haber Cycle

- The thermochemical cycle is named after the German scientists Max Born (1882–1970) and Fritz Haber (1868–1934), who introduced it to analyze the factors contributing to the stability of ionic compounds.

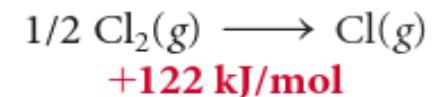
FIGURE 3.12. A Born–Haber cycle for the formation of $\text{NaCl}(s)$ from $\text{Na}(s)$ and $\text{Cl}_2(g)$.



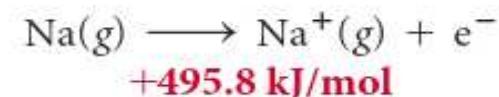
Step 1. Solid Na metal is converted into isolated, gaseous Na atoms, a process called sublimation. Because energy must be added to disrupt the forces holding atoms together in a solid, the heat of sublimation has a positive value: +107.3 kJ/mol for Na.



Step 2. Gaseous Cl_2 molecules are split into individual Cl atoms. Energy must be added to break molecules apart, and the energy required for bond breaking therefore has a positive value: +243 kJ/mol for Cl_2 (or 122 kJ/mol for $\frac{1}{2} \text{Cl}_2$).



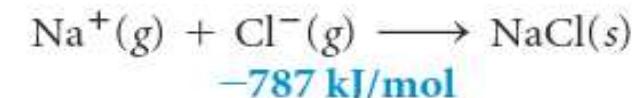
Step 3. Gaseous Na atoms from Step 1 are ionized into Na^+ plus electrons. The energy required is the first ionization energy of sodium (E_{i1}) and has a positive value: +495.8 kJ/mol.



Step 4. Cl^- ions are formed from Cl atoms by addition of an electron. The energy released is the electron affinity of chlorine (E_{ea}) and has a negative value: -348.6 kJ/mol.



Step 5. Lastly, solid NaCl is formed from Na^+ and Cl^- ions. The energy change is a measure of the overall electrostatic interactions between ions in the solid. It is the amount of energy released when isolated ions condense to form a solid, and it has a negative value: -787 kJ/mol for NaCl.



Net reaction:

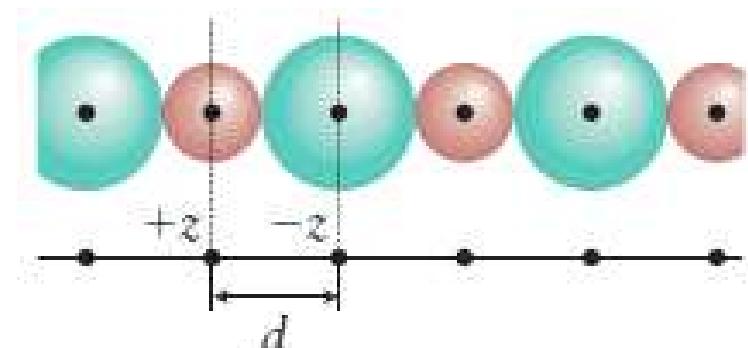


Net energy change:

-411 kJ/mol

Calculation of lattice energy

- **Using Coulomb's law for all these interactions, it is possible to calculate the energy of the entire crystal**, and such calculations have been done by chemists for many different types of crystals.
- **The resultant energy is called the lattice energy of the crystal.**
- In calculating **lattice energies**, we picture a crystal as made up of small **hard** (impenetrable) **spherical particles** situated at lattice positions, as depicted in Figure



- **In actuality**, the particles are not completely impenetrable and wiggle, or vibrate, a little bit about their equilibrium positions, but our hard-sphere model is perfectly adequate for such calculations.

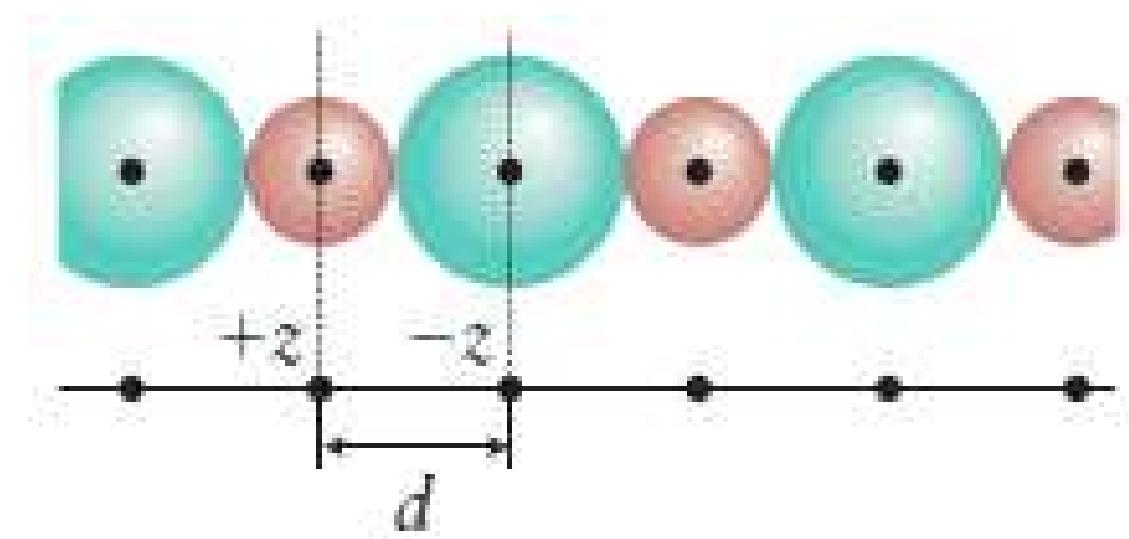
- Our starting point for understanding the interaction between ions in a solid is the expression for the Coulomb potential energy of the interaction of two individual ions:

$$E_{P,12} = \frac{(z_1 e) \times (z_2 e)}{4\pi\epsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r_{12}} \quad (1)^*$$

- ✓ In this expression, e is the fundamental charge (the absolute value of the charge of an electron), z_1 and z_2 are the charge numbers of the two ions, r_{12} is the distance between the centers of the ions, and ϵ_0 ("epsilon zero") is the vacuum permittivity.

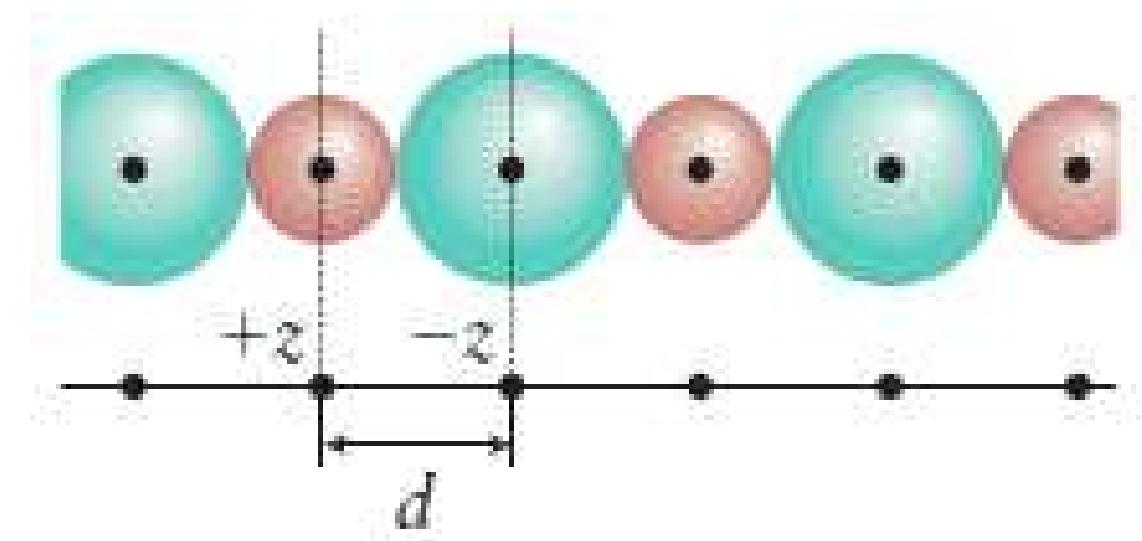
- Each ion in a solid experiences attractions from all the other oppositely charged ions and repulsions from all the other like-charged ions.
- The total potential energy is the sum of all these contributions.
- Each cation is surrounded by anions, and there is a large negative (energy-lowering) contribution from the attraction of the opposite charges.
- Beyond those nearest neighbors, there are cations that contribute a positive (repulsive, energy-raising) term to the total potential energy of the central cation.

FIGURE 2.6 The arrangement used to calculate the potential energy of an ion in a line of alternating cations (red spheres) and anions (green spheres). We concentrate on one ion, the “central” ion denoted by the vertical dotted line.



- There is also a negative contribution from the anions beyond those cations, a positive contribution from the cations beyond them, and so on, to the edge of the solid.
- These repulsions and attractions become progressively weaker as the distance from the central ion increases, but because the nearest neighbors of an ion give rise to a strong attraction, the net outcome of all these contributions is a lowering of energy.
- Our task is to assess how far the energy is lowered by using the Coulomb potential energy expression in Eq. 1.
- To calculate the electrostatic potential energy of an ionic solid we start with a simple model: **a single line of uniformly spaced alternating cations and anions, with d the distance between their centers, the sum of the ionic radii (Fig. 2.6).**

FIGURE 2.6 The arrangement used to calculate the potential energy of an ion in a line of alternating cations (red spheres) and anions (green spheres). We concentrate on one ion, the “central” ion denoted by the vertical dotted line.



- If the charge numbers of the ions have the same absolute value (+1 and -1, or +2 and -2, for instance), then $z_1 = +z$, $z_2 = -z$, and $z_1 z_2 = -z^2$.
- The potential energy of the central ion is calculated by summing all the Coulomb potential energy terms, *with negative terms representing attractions to oppositely charged ions and positive terms representing repulsions from like-charged ions*.
- with $d = r_{\text{cation}} + r_{\text{anion}}$ the distance between the centers of neighboring ions.

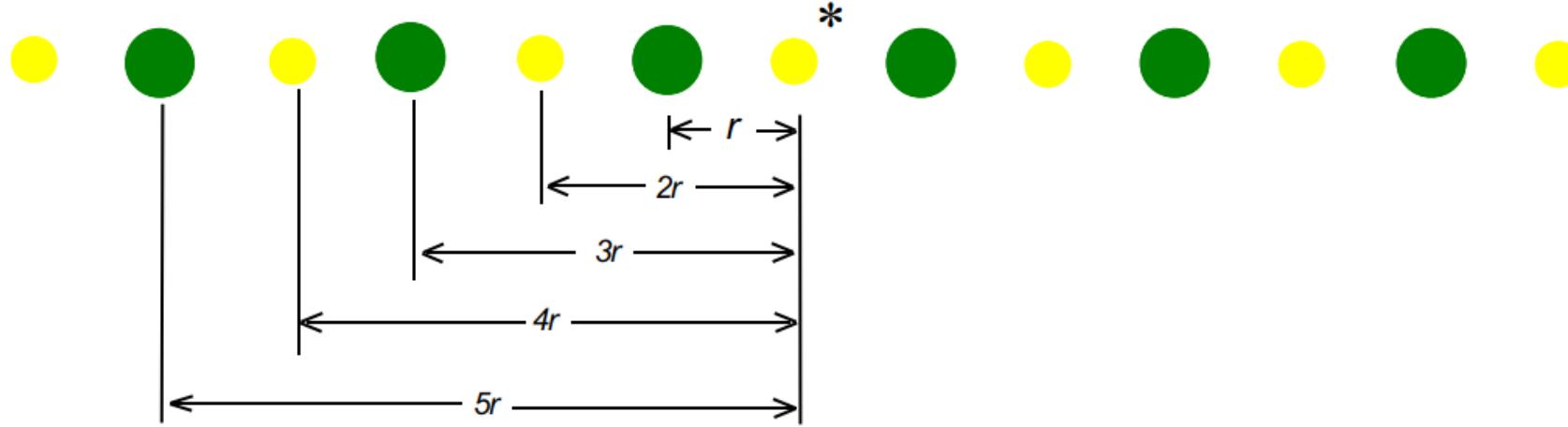


FIGURE 7.2 A “lattice” composed of a chain of alternating positive and negative ions.

- For the interaction arising from ions extending in a line to the right of the central ion, the total potential energy of the central ion is

$$E_p = \frac{1}{4\pi\epsilon_0} \times \left(-\frac{z^2 e^2}{d} + \frac{z^2 e^2}{2d} - \frac{z^2 e^2}{3d} + \frac{z^2 e^2}{4d} - \dots \right)$$

$$= \frac{z^2 e^2}{4\pi\epsilon_0 d} \times \overbrace{\left(-1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right)}^{-\ln 2}$$

$$= -\frac{z^2 e^2}{4\pi\epsilon_0 d} \times \ln 2$$

- Next, we multiply E_p by 2 to obtain the total energy arising from interactions with ions on each side of the ion.
- We then multiply by Avogadro's constant, N_A , to obtain the potential energy per mole of ions.

- We have found that the molar potential energy of a one-dimensional crystal in which cations and anions alternate along a line has the form

$$E_p = -2 \ln 2 \times \frac{z^2 N_A e^2}{4\pi\epsilon_0 d}$$

- The calculation can be *extended to three-dimensional arrays* of ions with different charge numbers z_A and z_B :

$$E_p = -A \times \frac{|z_A z_B| N_A e^2}{4\pi\epsilon_0 d}$$

- The factor A is a *positive numerical constant* called the **Madelung constant** (named after the German physicist Erwin Madelung); its *value depends on how the ions are arranged* (geometric arrangements) *in the crystal*. For a rock salt structure, $A = 1.748$.
- Table 15C.3 lists Madelung constants for other common structures.

Table 15C.3 Madelung constants

Structural type	<i>A</i>
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite (zinc blende)	1.638
Wurtzite	1.641

What does this equation tell us?

- Because the potential energy is negative, there is a net lowering of energy, which means that *the attraction between opposite charges overcomes the repulsion between like charges.*
- The potential energy is *strongly negative* when
 - ✓ *the ions are highly charged* (large values of z) and
 - ✓ *the separation between them is small* (small values of d), which is the case when the ions themselves are small.
- In all cases, the energy lowering that occurs when an ionic solid forms is greatest for *small, highly charged ions.*

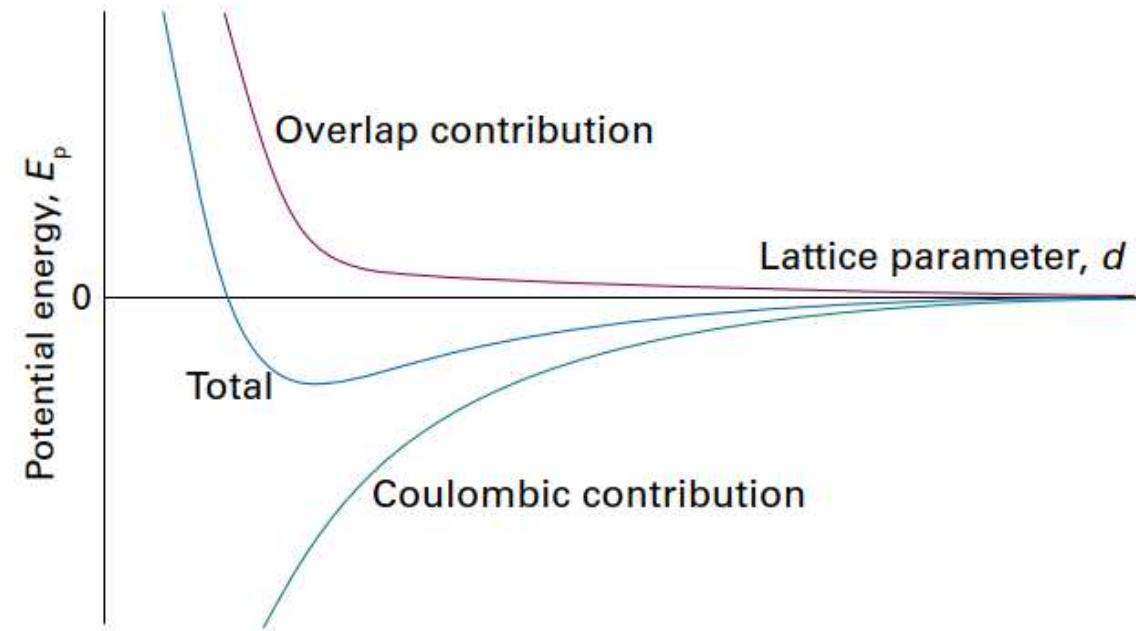
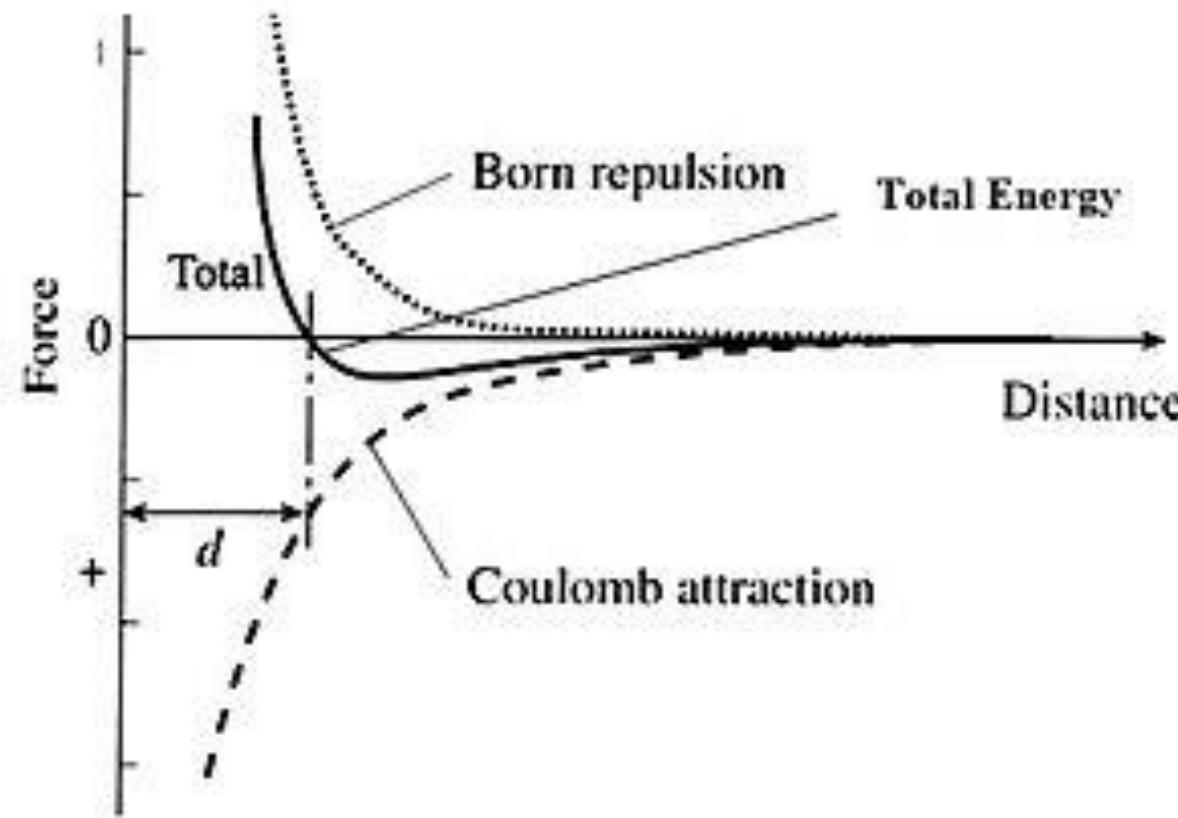
- ✓ For example, there is a strong interaction between the Mg^{2+} and the O^{2-} ions in magnesium oxide, ***MgO***, because the ions have high charges and small radii.
- ✓ This strong interaction is one reason why magnesium oxide survives at such high temperatures that it can be used for ***furnace linings***.
- ✓ It is an example of a “***refractory***” material, a substance that can withstand high temperatures.
- ✓ One of the *reasons why all ionic compounds are solids at room temperature is because of the large amount of energy that must be supplied to break up these extended crystal lattices*.
- The *potential energy becomes more and more negative as the separation d decreases*. However, a collection of ions *does not collapse to a point* because repulsive effects between neighbors become important as soon as they come into contact, and the energy quickly rises again.

- The Coulomb interaction is **not** the only contribution to the lattice energy.
- When atomic orbitals overlap to form bonding and antibonding molecular orbitals and both kinds of orbitals are full, there is an increase in energy because the antibonding orbital is raised in energy more than the bonding orbital is lowered.
- This positive contribution to the potential energy depends on the overlap of the atomic orbitals, and, because orbitals decay exponentially with distance, at large distances from the nucleus it is often modelled by writing

- ✓ To take the repulsion effects between close neighbors in an ionic solid into account it is commonly supposed that the repulsive contribution to the potential energy rises exponentially with decreasing separation.

$$E_{repulsion} = B \exp\left(\frac{-d}{d^*}\right)$$

- ✓ For example, in the Born approximation, B is a constant and d^* is a number with units of length, which is usually empirically determined from compressibility data.
- ✓ A typical value of d^* is 0.345 Å.
- ✓ The total energy of the ionic bond between two atoms is then calculated as the ***combination of net electrostatic and the closed-shell repulsion energies***, as shown in the figure at the right.



$$E_{repulsion} = B \exp\left(\frac{-d}{d^*}\right)$$

- This ***repulsion force is short range*** and is typically modeled as falling off exponentially or with a high power of the distance r between atoms.

□ Total lattice energy of a crystal....

- Having in hand a formula for the *electrostatic repulsion energy*, we can now add it to the Coulomb contribution to obtain an equation that gives us the total lattice energy.
- At the equilibrium bond distance, the forces on all the ions are zero, and we can use this fact to eliminate the constant B :

$$\left[\frac{dE}{dr} \right]_{r=r_0} = 0.$$

- The *energy at the minimum* is given by the **Born–Mayer** equation:

$$E_{p,\min} = -\frac{N_A |z_A z_B| e^2}{4\pi\epsilon_0 d} \left(1 - \frac{d^*}{d} \right) A \quad \text{Born–Mayer equation}$$

- Provided zero-point contributions to the energy are ignored, the negative of this potential energy can be identified with the lattice energy.

❖ ***What does this equation tell us?***

- As before, the *negative sign of this potential energy tells us that the ions have a lower potential energy* when they are present as a solid rather than widely separated as a gas.
- The *greatest stabilization is expected when the ions are highly charged* (so $|z_1 z_2|$ is large) and *small* (so d is small, but not smaller than d^*).
- The *energy released by the attraction between ions of unlike charge more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process.*
- *The strong attractions also cause most ionic materials to be hard and brittle with high melting points—for example, NaCl melts at 801 °C.*

➤ Table 6.6 lists the *calculated values of the lattice energy per formula unit for a number of ionic solids.*

➤ You can see that the agreement between the calculated and experimental values is quite good, which lends credence to the hard-sphere model of ionic crystals that we have used for our calculations.

TABLE 6.6 Calculated and experimental lattice energies of some selected ionic compounds

Compound	Calculated lattice energies/ aJ·formula unit ⁻¹	Measured lattice energies/ aJ·formula unit ⁻¹
NaF	-1.51	-1.54
NaCl	-1.28	-1.31
NaBr	-1.22	-1.25
KF	-1.34	-1.38
KCl	-1.16	-1.20
KBr	-1.11	-1.15
CaF ₂	-4.38	-4.40
CaCl ₂	-3.77	-3.77
Na ₂ O	-4.12	-4.11
K ₂ O	-3.72	-3.71
CaO	-5.67	-5.65

- Notice from Table 6.6 that the value of the lattice energy for NaCl(s), -1.28 aJ per formula unit, is about one and a half times the magnitude of the coulombic energy per NaCl(g) ion pair of -0.816 aJ that we calculated from simple electrostatic ion-pair attractions.
- Similarly, from Table 6.6 we see that the value of the lattice energy for CaO(s) is -5.67 aJ per formula unit, also about one and a half times the magnitude of the coulombic energy per CaO(g) ion pair of -3.85 aJ .
- *These higher energies result from considering the interactions of all the neighboring ions, next neighboring ions, and so forth, when calculating the lattice energy of an ionic crystal.*

➤ This relationship helps us explain the effects of ionic size and charge on trends in lattice energy:

1. **Effect of ionic size.** As we move *down a group*, ionic radii increase, so the electrostatic energy between cations and anions decreases; thus, lattice energies should decrease as well. Figure 9.7 shows that, for the alkali-metal halides, *lattice energy decreases down* the group whether we hold the cation constant (LiF to LiI) or the anion constant (LiF to RbF).
2. **Effect of ionic charge.** *Across a period, ionic charge changes.* For example, lithium fluoride and magnesium oxide have cations and anions of about equal radii ($\text{Li}^+ = 76 \text{ pm}$ and $\text{Mg}^{2+} = 72 \text{ pm}$; $\text{F}^- = 133 \text{ pm}$ and $\text{O}^{2-} = 140 \text{ pm}$). The major difference is between singly charged Li^+ and F^- ions and doubly charged Mg^{2+} and O^{2-} ions. The difference in the lattice energies of the two compounds is striking:

$$\Delta H_{\text{lattice}}^\circ \text{ of LiF} = 1050 \text{ kJ/mol}$$

and

$$\Delta H_{\text{lattice}}^\circ \text{ of MgO} = 3923 \text{ kJ/mol}$$

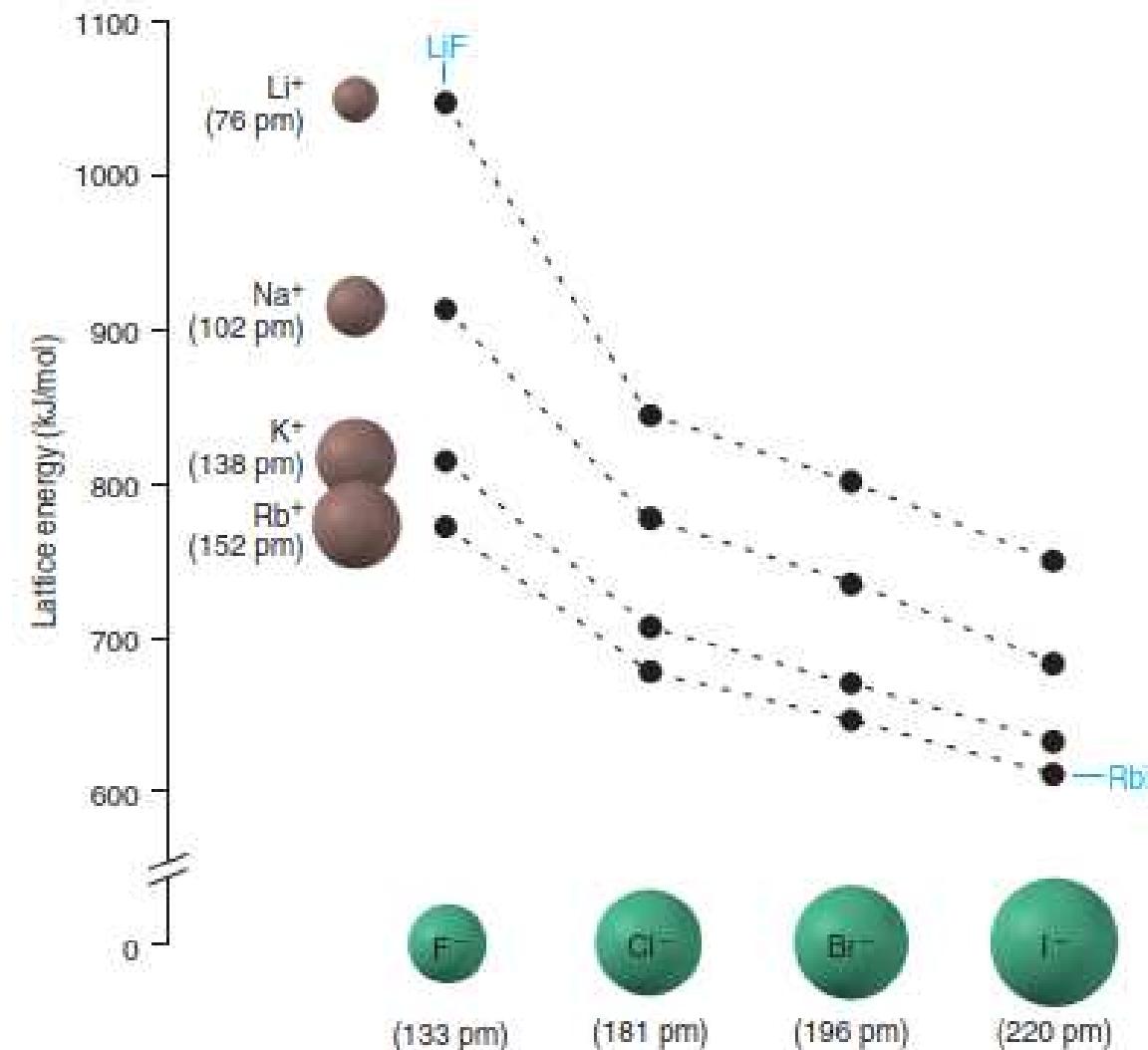
- This nearly four-fold increase in $\Delta H_{\text{lattice}}$ reflects the four-fold increase in the product of the charges (1×1 vs. 2×2) in the numerator in Equation.
 - ✓ The very large lattice energy of MgO more than compensates for the energy required to form the Mg^{2+} and O^{2-} ions.
 - ✓ In fact, *the lattice energy is the reason that compounds with 2+ cations and 2- anions even exist.*
- The **magnitude of the lattice energy of an ionic solid depends on **the charges** of the ions, their **sizes**, and their **arrangement in the solid**.**
- The attractive interaction between two oppositely charged ions increases as the magnitudes of their charges increase and as the distance between their centers decreases.

- Lattice energies are large when the distance between ions is small and when the charges z_1 and z_2 are large. A small distance means that the ions are close together, which implies that they have small ionic radii.
- Thus, *for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.*
- The variation in the magnitude of lattice energies depends more on ionic charge than on ionic radius because ionic radii vary over only a limited range compared to charges.
- Thus, if z_1 and z_2 are held constant, the largest lattice energies belong to compounds formed from the smallest ions, as listed in the following Table.

Periodic Trends in Lattice Energy

The lattice energy results from electrostatic interactions among ions, so its magnitude depends on ionic size, ionic charge, and ionic arrangement in the solid. Therefore, we expect to see periodic trends in lattice energy.

Figure 9.7 Trends in lattice energy. The lattice energies are shown for compounds formed from a given Group 1A(1) cation (left side) and one of the Group 7A(17) anions (bottom). LiF (smallest ions) has the highest lattice energy, and Rbl (largest ions) has the lowest.



➤ Note that the lattice energy for AlCl_3 (Table 12.4) is considerably larger than for MgCl_2 or NaCl , even though each cation has the same electron configuration. All three of the given factors support this observation (the ionic radii of six-coordinate Na^+ , Mg^{2+} , and Al^{3+} are 102, 72, and 54pm). When comparisons are made between the sodium halides, the decreasing lattice energy as one descends the halogens is a direct result of the periodic trend for the ionic radius of the halide, which increases down the group.

➤ Likewise, a comparison of the lattice energies of the alkali metal chlorides increases as the ionic radius of the cation decreases. The main differences between the lattice energies of the isoelectronic LiF and BeO are the increased charge and smaller ionic radius of the ions in the latter compound.

TABLE 12.4 Lattice energies for selected ionic solids.

Ionic Solid	U_0 , kJ/mol	Ionic Solid	U_0 , kJ/mol
NaF	-914	LiCl	-840
NaCl	-787	NaCl	-787
NaBr	-728	KCl	-701
NaI	-681	RbCl	-682
LiF	-1,036	CsCl	-630
BeO	-4,443	Al_2O_3	-15,916
MgCl_2	-2,526	Fe_2O_3	-14,774
AlCl_3	-5,492		

- The *more negative lattice energy* for Al_2O_3 compared to Fe_2O_3 results from **the smaller ionic radius of the Al^{3+} cation**. The Al^{3+} ion has an ionic radius of 54 pm, as compared with the 65 pm ionic radius of Fe^{3+} .
 - ✓ This example serves to illustrate the importance of the interionic separation term (d). A difference of less than 10 pm in the ionic radius causes Al_2O_3 to have a lattice energy that is >1100 kJ/mol more negative than that for Fe_2O_3 .
-
- In turn, the more negative lattice energy of Al_2O_3 is the **main thermodynamic driving force** for the **thermite reaction**, given by Equation (12.8).
 - The **thermite reaction**, which is a common chemical demonstration, is so exothermic (-851.5 kJ/mol) that it generates temperatures up to 3000°C (hot enough to produce molten iron). This reaction was used during the Civil War to repair torn-up railroad tracks.



☐ **Ionic solids typically have high melting points and are brittle. The coulombic interaction between ions in a solid is large when the ions are small and highly charged.**

➤ We can now see why nature has adopted an ionic solid, **calcium phosphate, for our skeletons**: the doubly charged small Ca^{2+} ions and the triply charged PO_4^{3-} ions attract one another very strongly and clump together tightly to form a rigid, insoluble solid (Fig. 2.8).

FIGURE 2.8 A micrograph of bone, which owes its rigidity to calcium phosphate.

The overlay shows part of the crystal structure of calcium phosphate. Phosphate ions are polyatomic ions; however, as shown in the inset, they are nearly spherical and fit into crystal structures in much the same way as monatomic ions of charge -3 .

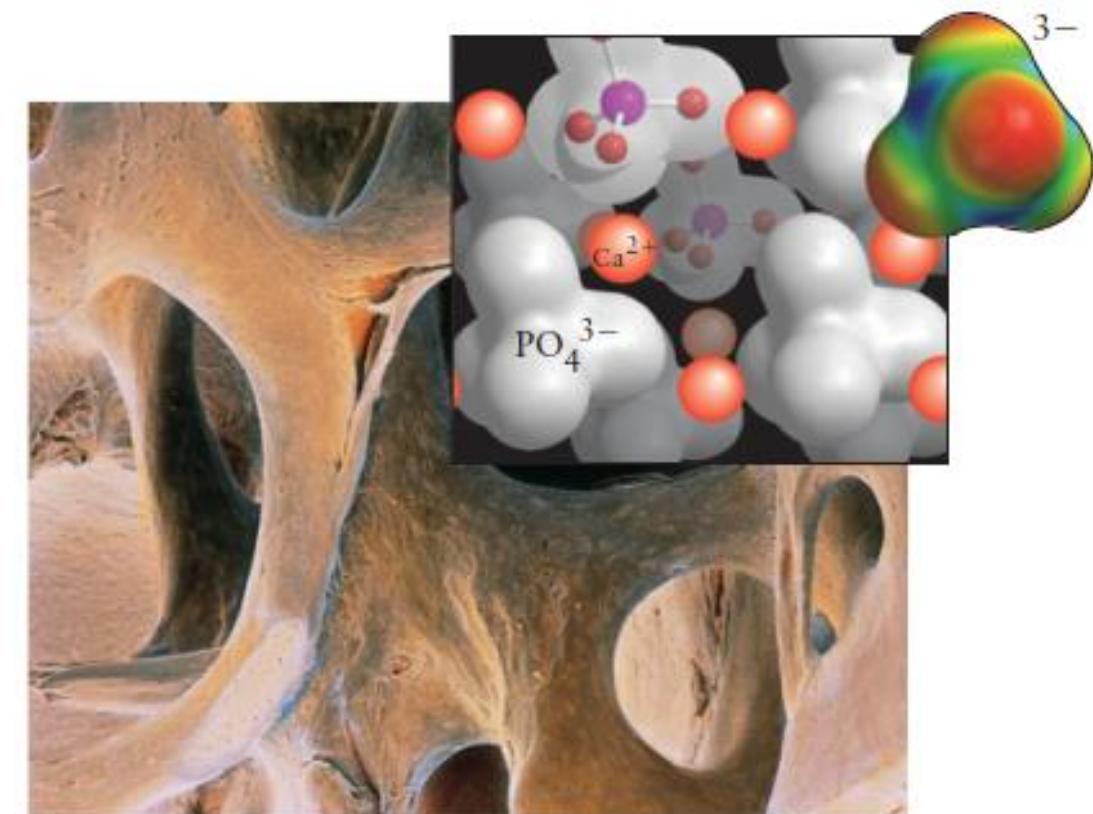


Table 8.1 lists the lattice energies for a number of ionic compounds. The large positive values indicate that the ions are strongly attracted to one another in ionic solids.

TABLE 8.1 Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2526
LiCl	834	SrCl ₂	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

- Table 9.1 lists the ***lattice energies and the melting points*** of several common ionic compounds.
- There is a *rough correlation* between lattice energy and melting point.
- The larger the lattice energy, the more stable the solid and the more tightly held the ions. It takes more energy to melt such a solid, and so the solid has a higher melting point than one with a smaller lattice energy.
- Note that MgCl₂, MgO, and CaO have unusually high lattice energies. The first of these ionic compounds has a doubly charged cation (Mg²⁺) and in the second and third compounds there is an interaction between two doubly charged species (Mg²⁺ or Ca²⁺ and O²⁻). The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations.

Table 9.1

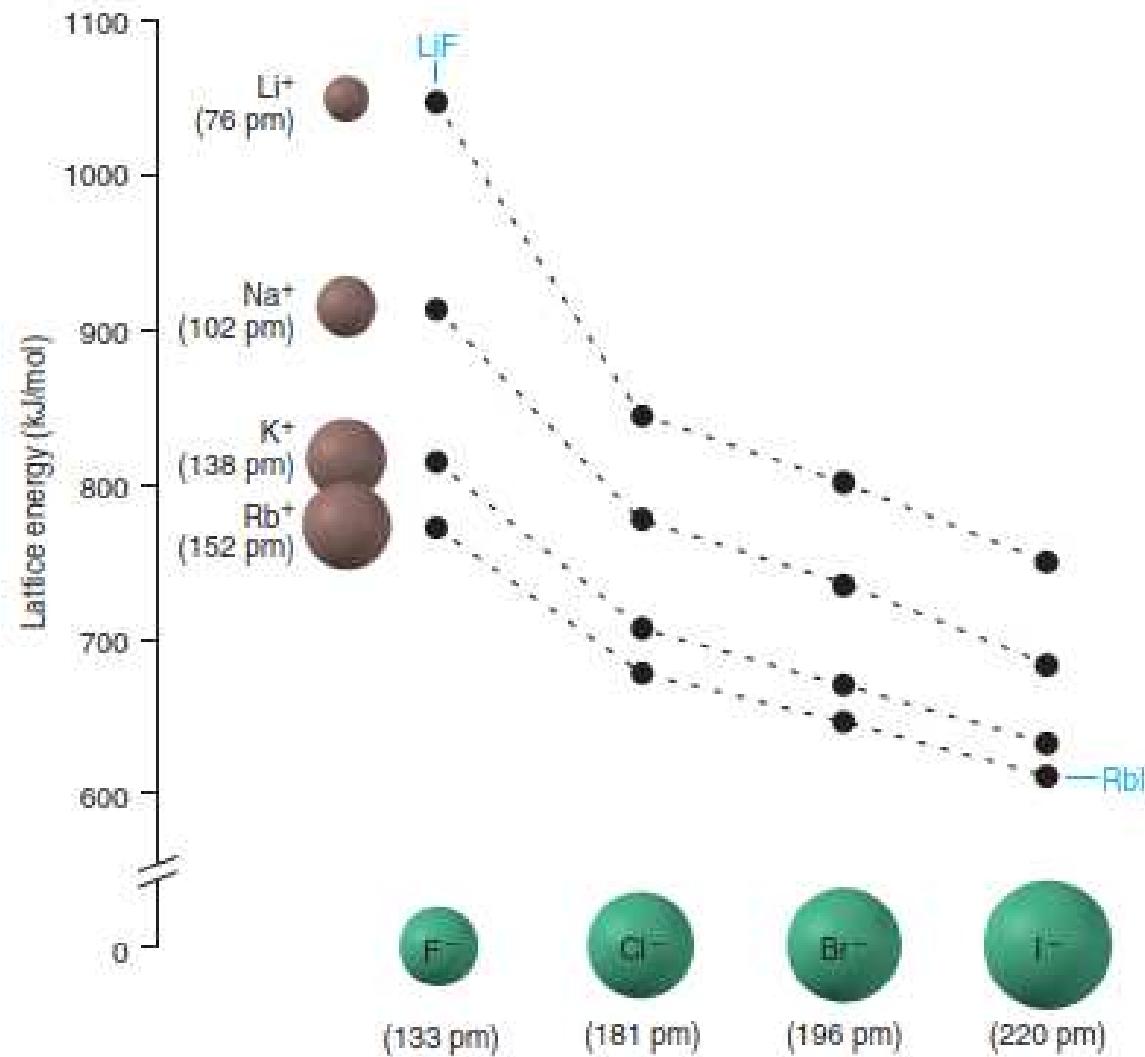
Lattice Energies and Melting Points of Some Ionic Compounds

	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
MgCl ₂	2527	714
MgO	3890	2800
CaO	3414	2580

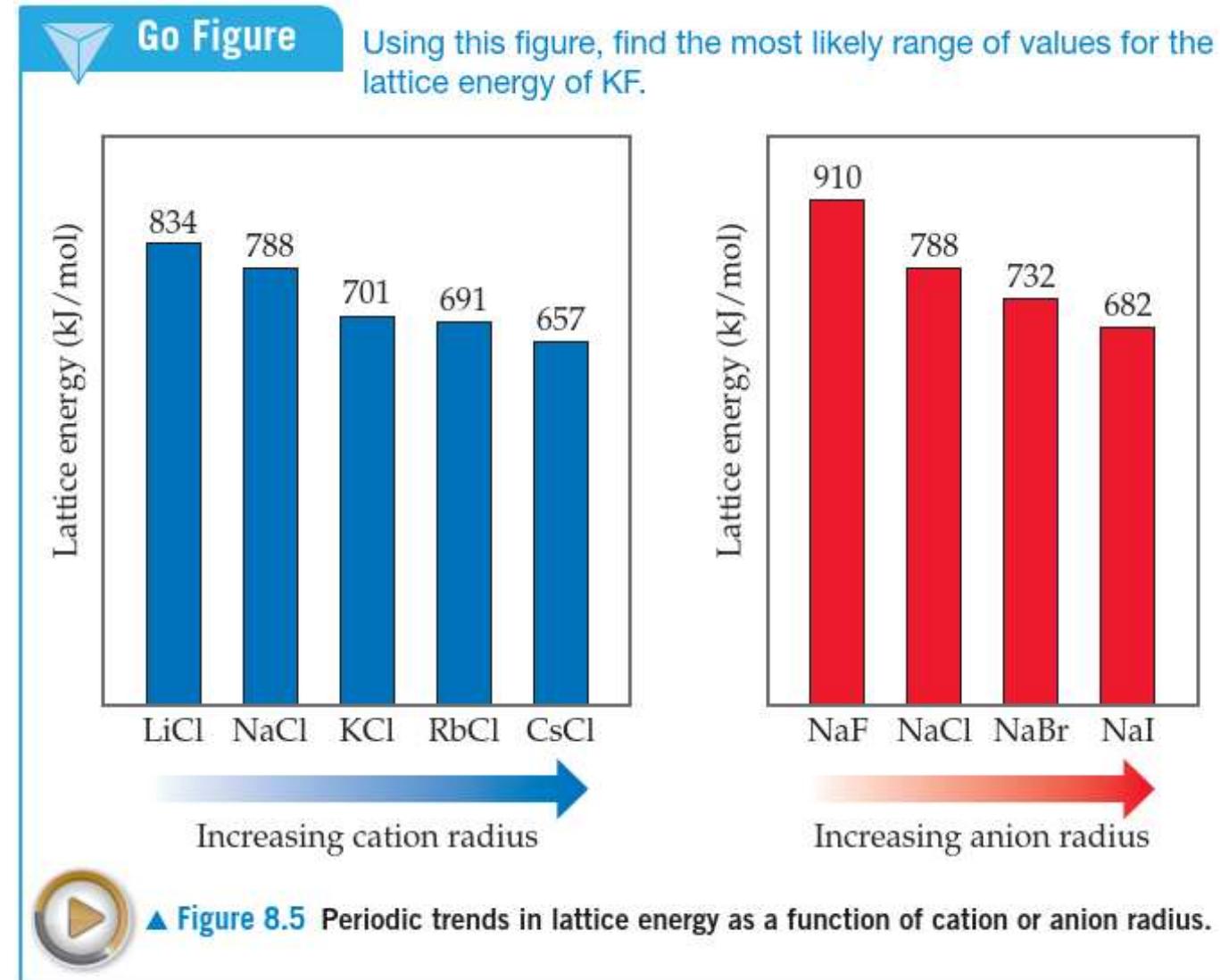
Periodic Trends in Lattice Energy

The lattice energy results from electrostatic interactions among ions, so its magnitude depends on ionic size, ionic charge, and ionic arrangement in the solid. Therefore, we expect to see periodic trends in lattice energy.

Figure 9.7 Trends in lattice energy. The lattice energies are shown for compounds formed from a given Group 1A(1) cation (left side) and one of the Group 7A(17) anions (bottom). LiF (smallest ions) has the highest lattice energy, and RbI (largest ions) has the lowest.



➤ Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius. In particular, because ionic radius increases as we go down a group of the periodic table, we find that, for a given type of ionic compound, lattice energy decreases as we go down a group. Figure 8.5 illustrates this trend for the alkali chlorides MCl ($M = Li, Na, K, Rb, Cs$) and the sodium halides NaX ($X = F, Cl, Br, I$).



How the Model Explains the Properties of Ionic Compounds?

➤ *The central role of any model is to explain the facts.* With atomic-level views, we can see how the ionic bonding model accounts for the properties of ionic solids:

1. Electrical conductivity. Ionic compounds typically do not conduct electricity in the solid state but do conduct when melted or dissolved. According to the model, the solid consists of fixed ions, but when it melts or dissolves, the ions can move and carry a current.

2. Thermal conductivity. Large amounts of energy are needed to free the ions from their fixed positions and separate them. Thus, we expect ionic compounds to have high melting points and much higher boiling points.

- ✓ In fact, the *interionic attraction is so strong that the vapor consists of ion pairs, gaseous ionic molecules*, rather than individual ions.
- ✓ In their normal state, as you know, ionic compounds are solid arrays of ions, and no separate molecules exist.

3. Physical behavior. As a typical ionic compound, a piece of rock salt (NaCl) is hard (does not dent), rigid (does not bend), and *brittle* (cracks without deforming).

- ✓ These *properties arise from the strong attractive forces* that hold the ions in specific positions. *Moving them out of position requires overcoming these forces*, so rock salt does not dent or bend.
- ✓ If enough force is applied, *ions of like charge are brought next to each other*, and repulsions between them crack the sample suddenly (Figure 9.8).

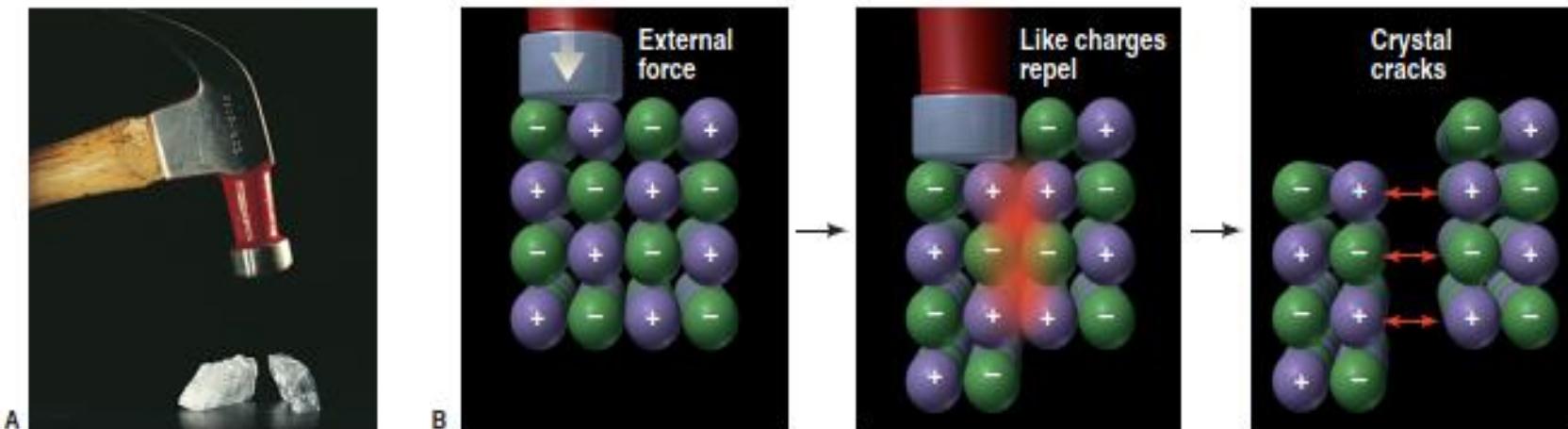


Figure 9.8 Why ionic compounds crack.
A, Ionic compounds crack when struck with enough force. B, When a force moves like charges near each other, repulsions cause a crack.

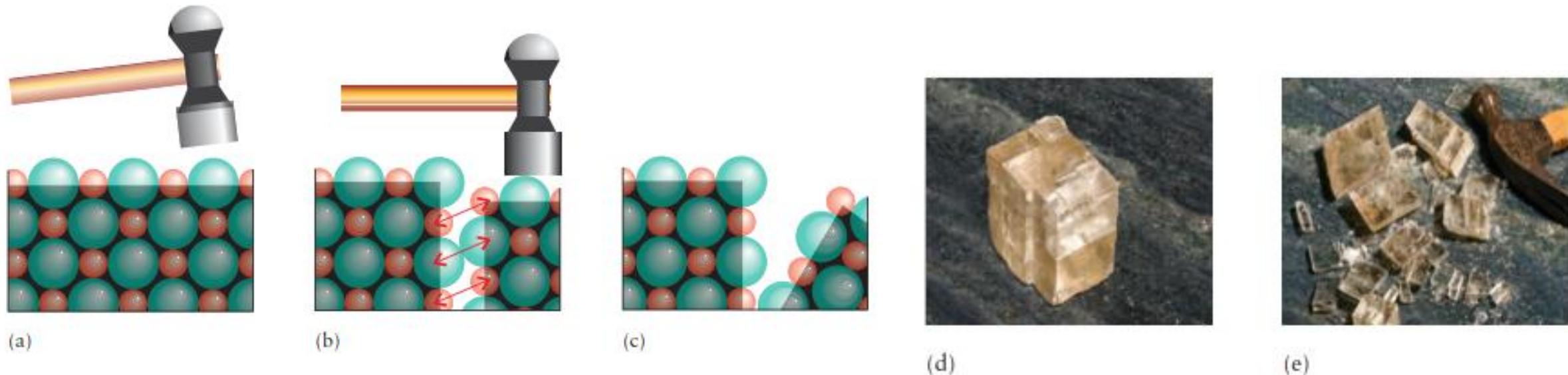


FIGURE 2.5 This sequence of images illustrates why ionic solids are brittle. (a) The original solid consists of an orderly array of cations and anions. (b) A hammer blow can push ions with like charges into adjacent positions; this proximity of like charges raises strong repulsive forces (as depicted by the double-headed arrows). (c) As the result of these repulsive forces, the solid breaks apart into fragments. (d) The smooth faces of this calcite crystal result from the regular arrangement of the calcium and carbonate ions. (e) The blow of a hammer has shattered the crystal, leaving flat, regular surfaces consisting of planes of ions. Compare this image with the result of striking a metallic crystal. The cationic cores in the electron sea are mobile.

- By assessing this interaction quantitatively, ***we can see what determines the lattice energy of the solid***, the difference in energy between the ions packed together in a solid and the ions widely separated as a gas. High lattice energy indicates that the ions interact strongly with one another to give a tightly bonded solid.
- The strong electrostatic interactions between charged ions account for the typical properties of ionic solids, such as their high melting points and their brittleness. A high temperature is required before the ions are able to move past one another to form a liquid.
- Ionic solids are brittle because of the same strong attractions and repulsions. We cannot just push a block of ions in one region of the crystal past the ions in a neighboring region: when we strike an ionic solid, ions with like charges come into contact and repel one another. The resulting repulsions cause it to shatter into fragments (Fig. 2.5).

CHEMICAL BONDS THEORY– COVALENT BONDING

Requirements of any satisfactory Theory of Chemical Bonding...

It should explain...

1. Why some **atoms combine to form molecules** whereas some do not. For example, H_2 stable; not He_2 .
2. Why atoms form molecules in **definite proportions** and **why there is saturation of valency**. For example, CH_4 is a stable molecule but not CH_3 , CH_2 ...
3. The 3-dimensional **shapes** of molecules, **bond angles**, **bond lengths**, and **bond energies**.

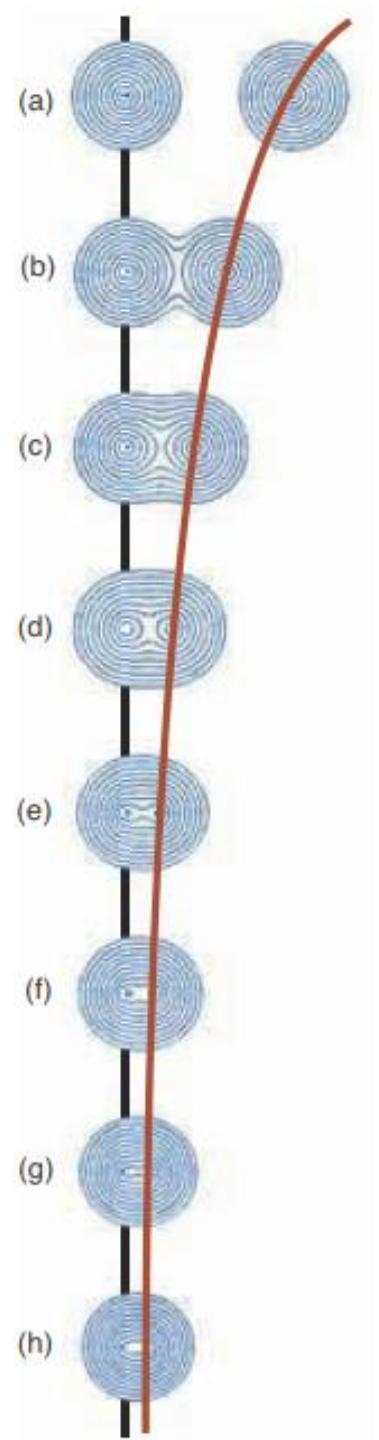
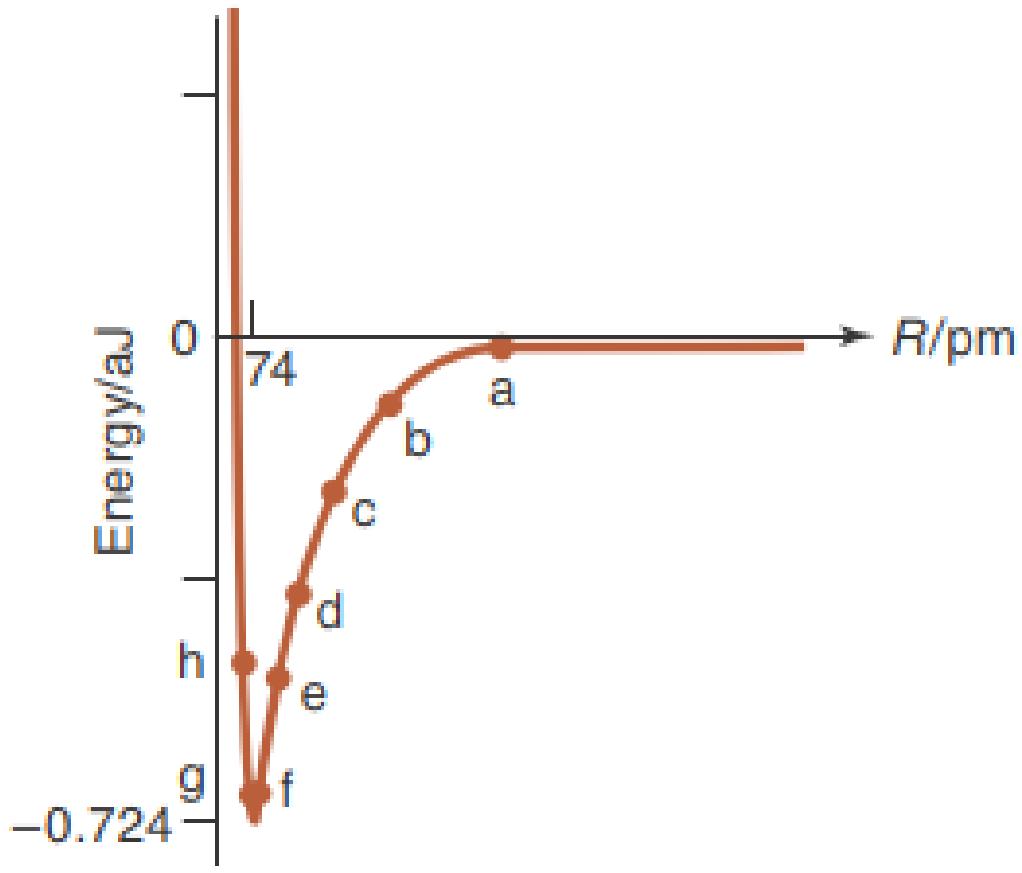
CHEMICAL BONDS THEORY– Covalent Bonding

- *Quantum mechanics* help to understand the *nature of chemical bonding* and *predict the structures* and *properties* of *small molecules*.
- ✓ However, for *large molecules* *approximate quantum mechanical* methods have been used and even then, *the calculations provide a lot of information* about the molecular structures and chemical properties.
- There are *two major approaches* to the calculation of molecular structure, *valence-bond theory (VB theory)* and *molecular orbital theory (MO theory)*.
- Almost all modern computational work makes use of MO theory.
- Valence-bond theory has left its imprint on the language of chemistry, and it is important to know the significance of terms that chemists use every day. Therefore, our discussion is organized as follows.
- First, we set out the concepts common to all levels of description.
- ✓ Then we present the basic ideas of MO theory.
- ✓ Next, we present the VB theory, which gives us a simple qualitative understanding of bond formation.

- Molecular orbital theory (MO theory)**
- The MO Theory applied to the Simplest Diatomic Molecules: H_2^+ and H_2**
- The basic procedures of molecular orbital methods**
 - The formalism that applies to the molecular orbital method will be illustrated by considering a hydrogen molecule, but a more detailed description of both H_2^+ and H_2 will be given in the next section.
 - To begin our description of diatomic molecules, let us imagine that two hydrogen atoms that are separated by a relatively large distance are being brought closer together.
 - As the atoms approach each other, there is an attraction between them that gets greater as the distance between them becomes shorter.
 - Eventually, the atoms reach a distance of separation that represents the most favorable (minimum energy) distance, the bond length in the H_2 molecule (74 pm).

Figure 9.1 Electron density contour diagrams of two hydrogen atoms as a function of their separation (right side). At large separations, as in (a), the two orbitals appear simply as those of two separate atoms. **As the atoms come together, the two separate atomic orbitals combine into one molecular orbital encompassing both nuclei**, as in (b) through (h). The lower left part of the figure shows the energy of two hydrogen atoms as a function of their separation R . The labels (a) through (h) correspond to those in the right part of the figure.

- ✓ At large distances, the two hydrogen atoms do not interact, so their interaction energy is zero.
- ✓ As the *two atoms come together*, they *attract* each other, and so their *interaction energy becomes negative*.
- ✓ When they are less than 74 pm apart, the interaction energy increases, and *they repel each other*.
- ✓ The **bond length** of a H_2 molecule is the distance *at which the energy is a minimum*, that is, 74 pm.
- ✓ The energy at this distance is -0.724 aJ , which is the energy required to dissociate the H_2 molecule into two separate hydrogen atoms.



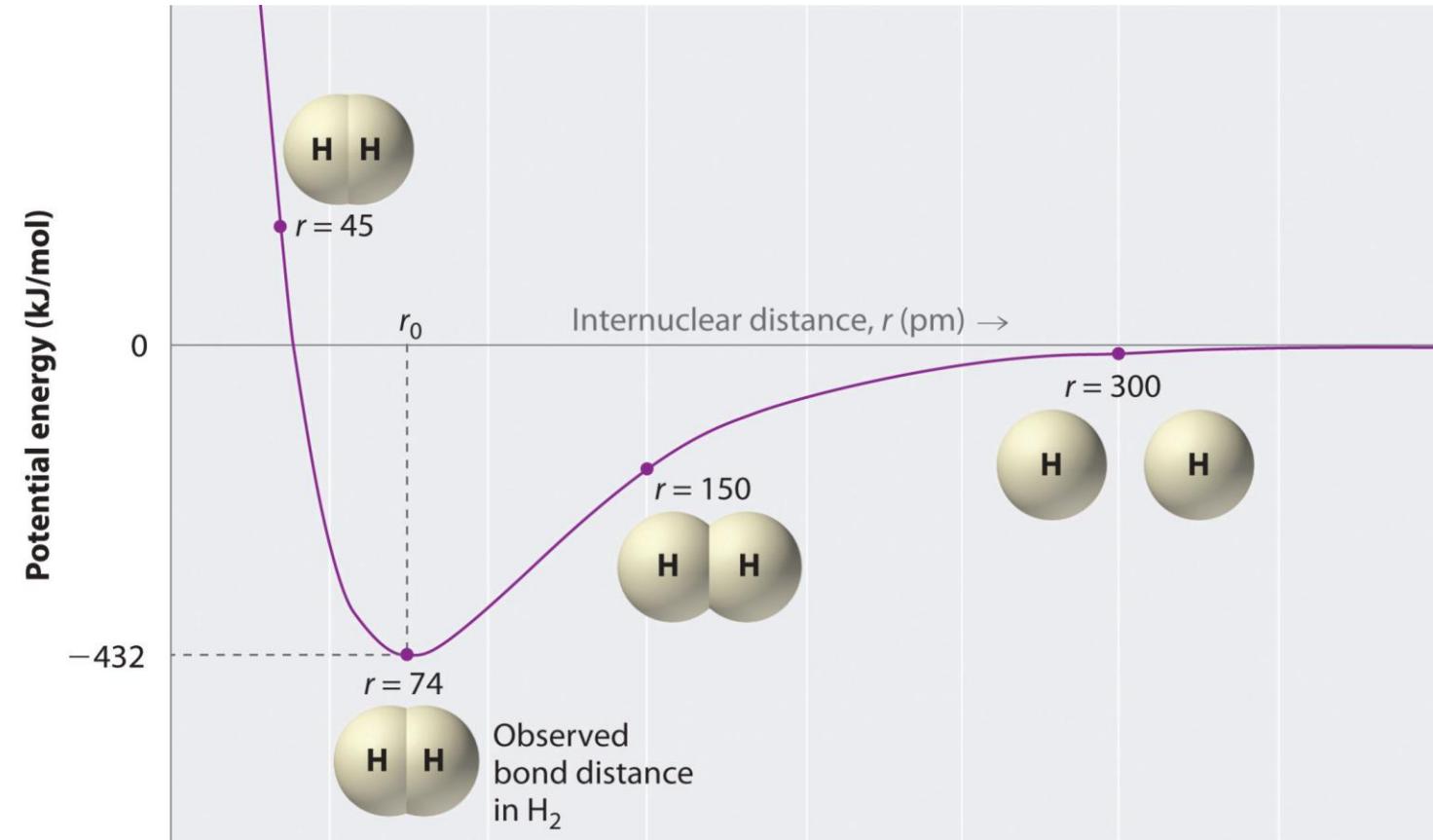
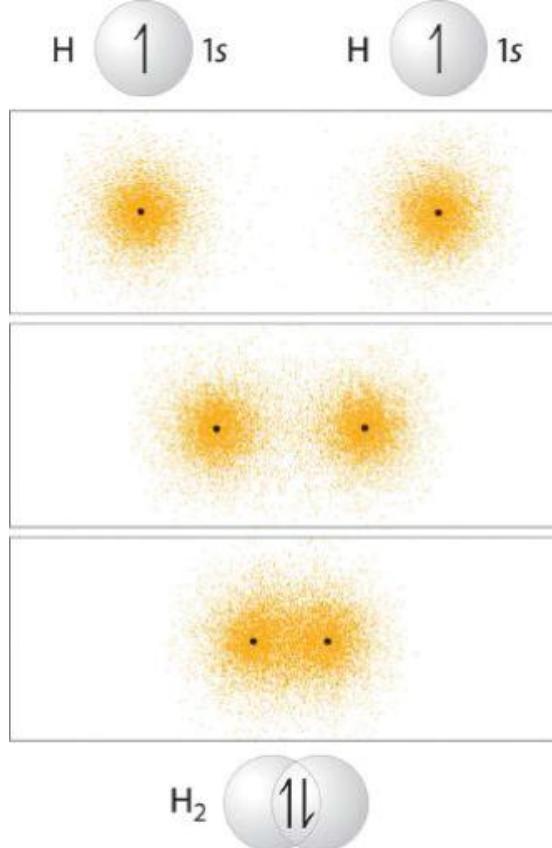
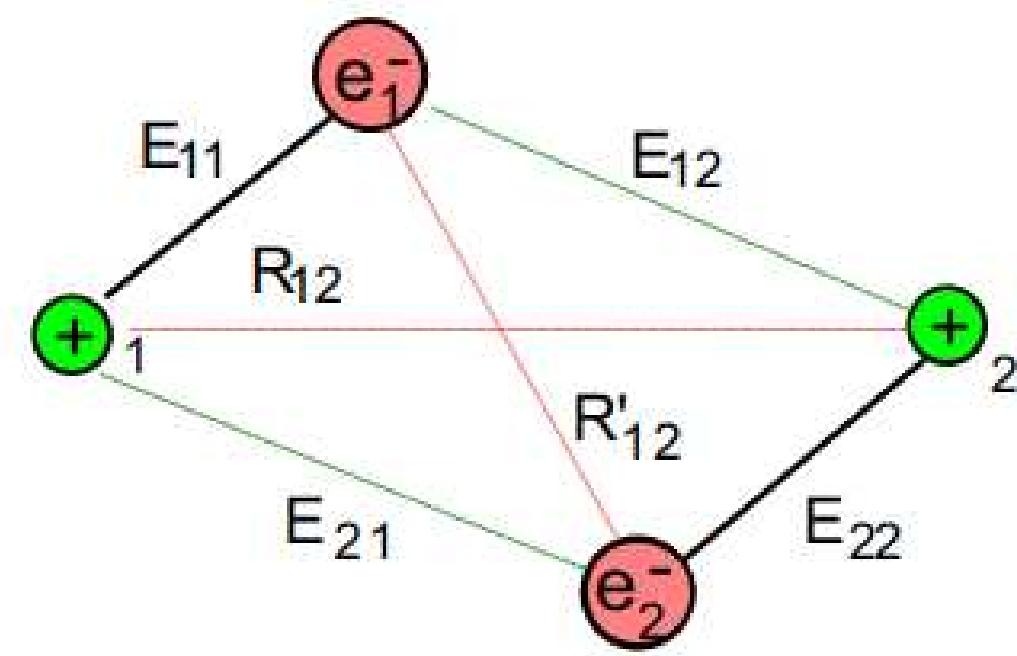


Figure : A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

- As the distance between the atoms decreases, the nuclei begin to repel each other as do the two electrons.
- However, there are forces of attraction between the nucleus in atom 1 and the electron in atom 2 and between the nucleus in atom 2 and the electron in atom 1. We can illustrate the interactions involved as shown in Fig. 3.1.

FIGURE 3.1 Interactions within a hydrogen molecule. The quantities represented as R are the repulsions and those as E are the attraction energies. The subscripts indicate the nuclei and electrons involved.



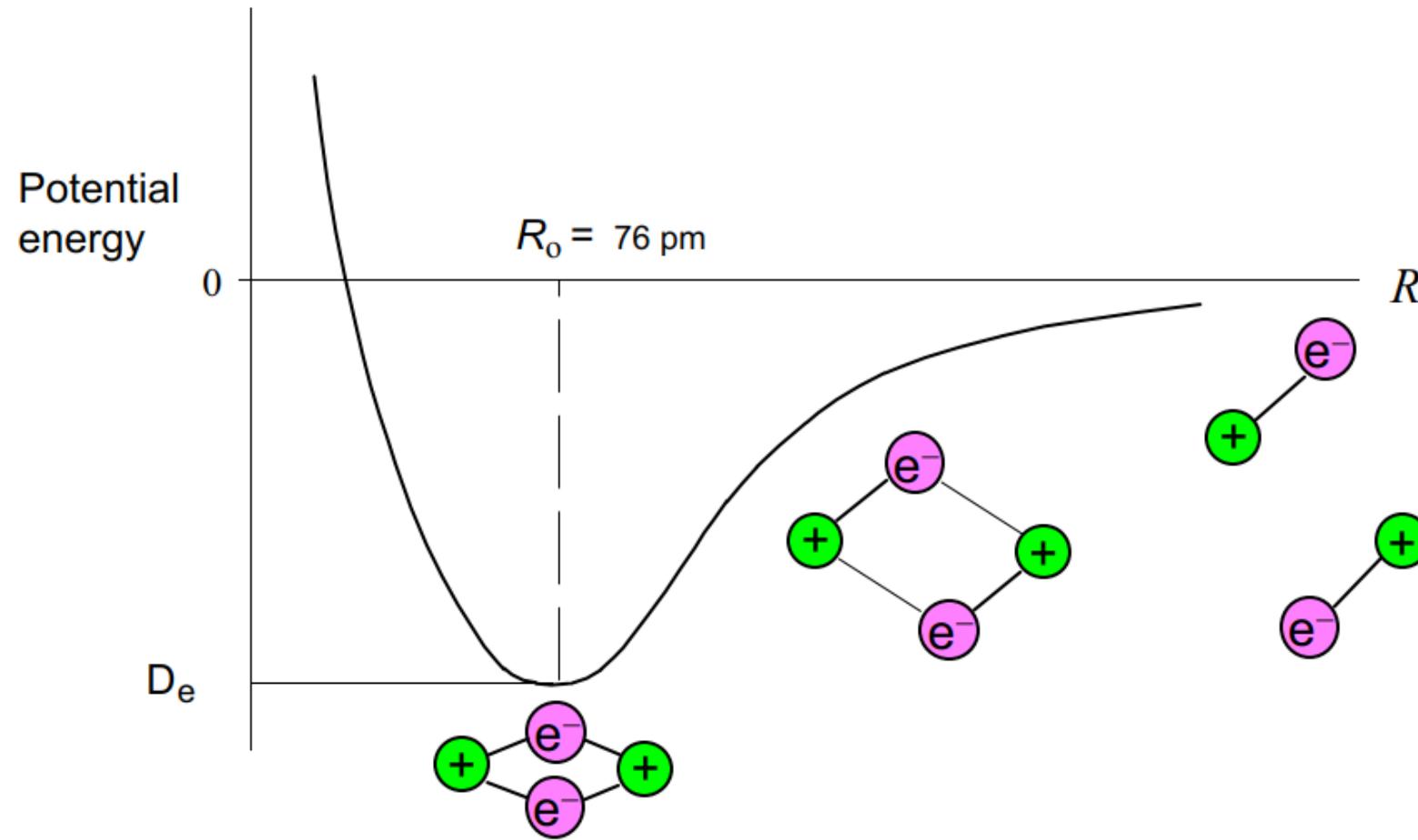


FIGURE 3.2 A greatly simplified representation of the interaction of two hydrogen atoms that form a molecule as they come together.

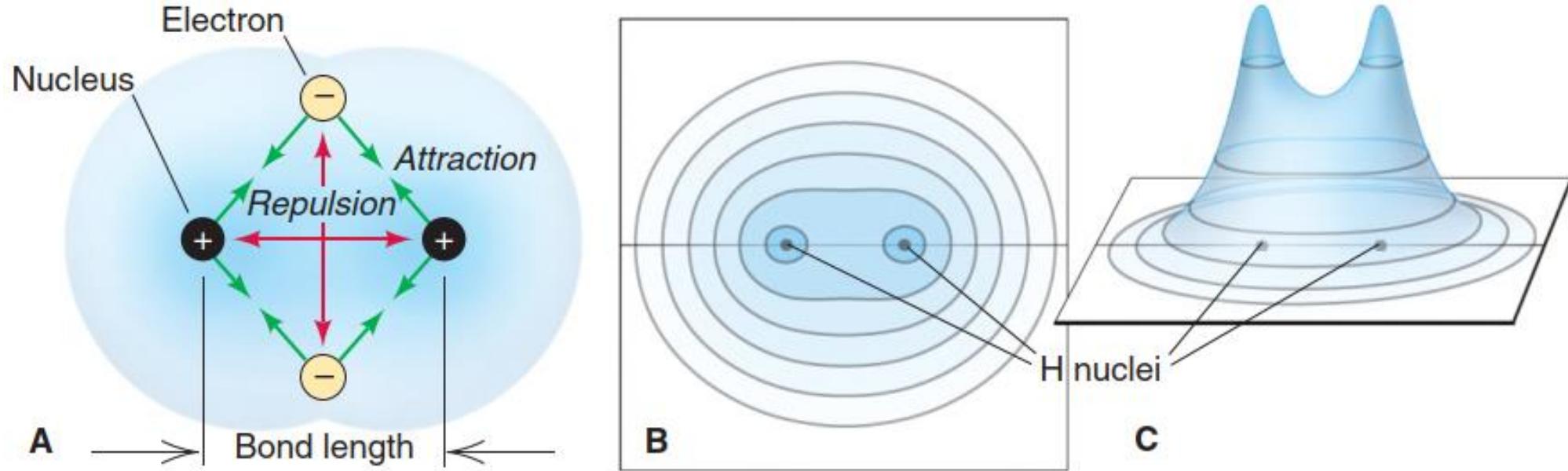


Figure 9.11 Distribution of electron density in H_2 .

(A): At some ***distance (bond length), attractions balance repulsions.*** Electron density (blue shading) is high around and between the nuclei.

(B): Electron density doubles with each concentric curve.

(C): The highest regions of electron density are shown as peaks.

- Figure 9.1 shows *contour diagrams of the ground state electron density of a H₂ molecule as a function of the separation of the nuclei of the two hydrogen atoms.*
- We see that *at large separations the two atoms hardly interact, so the electron density is just that of two electrons, each in a 1s orbital about each of the two hydrogen atoms.*
- *As the separation decreases, however, the two 1s orbitals overlap and combine into one orbital that is distributed around both nuclei.* Such an orbital is called a **molecular orbital** because it extends over both nuclei in the molecule.
- Throughout this section, we shall build molecular orbitals by combining atomic orbitals on different atoms.
- *When electrons occupy these orbitals, the buildup of electron density between the nuclei results in a covalent bond.*

- Note how the detailed quantum theoretical results shown in Figure 9.1 correspond to the Lewis formula; both approaches picture a covalent bond as the sharing of an electron pair between two nuclei.
- The *lower (left) part of Figure 9.1 shows the **energies that correspond to the electron densities**.*
- Notice that *interaction energies are negative for any distances at which the atoms attract each other.*
- These *negative values mean that the energy of a H–H bond is less than that of two separated hydrogen atoms*, which in turn *means that a H_2 molecule is more stable than two isolated hydrogen atoms under these conditions.*
- The graph shows that, for a H_2 molecule, the interaction energy has a minimum at the internuclear separation $R = 74 \text{ pm}$. This value of R is the predicted length of a H_2 bond and is in excellent agreement with the experimental value.

- We know that for each atom the ionization potential is 13.6 eV, the bond energy for the H_2 molecule is 4.51 eV (432 kJ mol^{-1}), and the bond length is 76 pm. Keep in mind that bond energy is expressed as the energy necessary to break the bond and is therefore a positive quantity. If the bond forms, energy equivalent to the bond energy is released, so it is a negative quantity.
- The fact that the nuclei do not get closer together ***does not mean*** that the forces of attraction and repulsion are equal.
- The minimum distance is that distance where the total energy (attraction and repulsion) is most favorable.
- Because the molecule has some vibrational energy, the internuclear distance is not constant, but the equilibrium distance is R_o .
- Fig. 3.2 shows how the energy of interaction between two hydrogen atoms varies with internuclear distance.

MO Theory: Molecular orbital and energy

- Let's look at the approach of quantum theory.
- To describe the hydrogen molecule by quantum mechanical methods, a wave function is taken as the starting point for application of the methods that allows the calculation of values for the dynamical variables.
- It is with a *wave function* that we must again begin our treatment of the H_2 molecule by the molecular orbital method.
- However, what *wave function* do we need?
- We need a wave function for the H_2 molecule, and that ***wave function is constructed from the atomic wave functions.***
- All *modern work builds approximations to the true molecular orbital by formulating models based on linear combinations of the atomic orbitals* on the atoms in the molecule.
- A given MO, Ψ , can thus be written as a **linear combination of the atomic orbitals** (AOs) on individual atoms in the molecule. This is called the **LCAO-MO model**. The justification for this assumption is that the linear combination of AOs is the simplest wave function we can write that leads to the electron delocalization over the molecule.

- One of the techniques used to construct molecular wave functions is known as the **linear combination of atomic orbitals (LCAO)**.
- The linear combination of atomic orbitals can be written mathematically as
- $\Psi = \sum a_i \phi_i$
- In this equation, ψ is the molecular wave function, ϕ is an atomic wave function, and a is a weighting coefficient, which gives the relative weight in the “mix” of the atomic wave functions. The summation is over i , the number of atomic wave functions (number of atoms) being combined.
- If a diatomic molecule is being described, there are only two atoms involved so the equation becomes
- $\Psi = a_1 \phi_1 + a_2 \phi_2$
- Although the combination has been written as a sum, the difference is also an acceptable linear combination.
- The weighting coefficients are variables that must be determined.

- ❑ Generally, when *choosing atomic orbitals for linear combination*, three pre-requisites need to be fulfilled:
 - The *energies of the two atomic orbitals need to be at a comparable level.*
 - Both atomic orbitals need to be able to *produce sufficient overlap.*
 - The *two atomic orbitals need to have the same symmetry with respect to the interatomic axis.*
- A *molecule must have as many molecular orbitals as there are atomic orbitals.*

- In quantum Mechanics, it was shown that to ***calculate the average value for a dynamical variable a whose operator is α*** , it is necessary to make use of the relationship

$$\langle a \rangle = \frac{\int \psi^* \alpha \psi d\tau}{\int \psi^* \psi d\tau} \quad (3.3)$$

- If the property we wish to *determine* is the ***energy (E)***, this equation becomes

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (3.4)$$

- Where \hat{H} is the Hamiltonian operator, the operator for total energy.
- The expression shown in Eq. (3.2) is substituted for ψ in the equation above which gives

$$E = \frac{\int (a_1 \phi_1^* + a_2 \phi_2^*) \hat{H} (a_1 \phi_1 + a_2 \phi_2) d\tau}{\int (a_1 \phi_1^* + a_2 \phi_2^*)(a_1 \phi_1 + a_2 \phi_2) d\tau} \quad (3.5)$$

- When the multiplications are carried out and the constants are removed from the integrals we obtain

$$E = \frac{a_1^2 \int \phi_1^* \hat{H} \phi_1 d\tau + 2a_1 a_2 \int \phi_1^* \hat{H} \phi_2 d\tau + a_2^2 \int \phi_2^* \hat{H} \phi_2 d\tau}{a_1^2 \int \phi_1^* \phi_1 d\tau + 2a_1 a_2 \int \phi_1^* \phi_2 d\tau + a_2^2 \int \phi_2^* \phi_2 d\tau} \quad (3.6)$$

- In writing this equation, it was assumed that

$$\int \phi_1^* \hat{H} \phi_2 d\tau = \int \phi_2^* \hat{H} \phi_1 d\tau \quad (3.7)$$

- and that

$$\int \phi_1^* \phi_2 d\tau = \int \phi_2^* \phi_1 d\tau \quad (3.8)$$

- These assumptions are valid for a diatomic molecule composed of identical atoms (homo-nuclear diatomic) because ϕ_1 and ϕ_2 are identical and real in this case.

- In working with the quantities in equations such as Eq. (3.6), certain elements are frequently encountered. For simplicity, the definitions that will be adopted are as follows:

$$H_{11} = \int \phi_1^* \hat{H} \phi_1 d\tau \quad (3.9)$$

$$H_{12} = \int \phi_1^* \hat{H} \phi_2 d\tau \quad (3.10)$$

- Because \hat{H} is the operator for total energy, H_{11} represents the binding energy of an electron in atom 1 to its nucleus. If the subscripts on the wave functions are both 2, the binding energy of electron 2 to its nucleus is indicated.
- Because the electron is restricted to only one nucleus (nucleus i , in this case), H_{ii} is said to consist of atomic integrals.
- Such integrals (H_{ii}) represent the ***energy of an electrostatic interaction***, so they are known as ***Coulomb integrals*** (α). (The symbol H_{ij} is a shorthand notation for the integrals involving \hat{H} and the AOs i and j as follows: $H_{ij} = \int \varphi_i^* \hat{H} \varphi_j d\tau$.)

- Because the electron is assigned to both nuclei in H_{ij} , or can exchange from one nucleus to the other (in contrast to H_{AA} , where the electron is restricted to one nucleus), integrals of the type (H_{ij}) shown in Eq. (3.10) indicate *the energy of the interaction of the electron in atom 1 with the nucleus in atom 2*. Therefore, they are known as **exchange (or bond) integrals (β)**. Since \hat{H} is Hermitian and the functions in these integrals are real, we conclude that $H_{AB} = H_{BA}$. The integral H_{AB} is also called a **resonance integral**.
- The **exchange integrals** represent the interaction of nucleus 1 with electron 2 and the interaction of nucleus 2 with electron 1.
- *Interactions of this type must be related to the distance separating the nuclei, so the value of an exchange integral can be expressed in terms of the distance separating the atomic nuclei.*
- As a result of the Hamiltonian being an operator for energy, both types of integrals represent energies.
- Furthermore, because these integrals represent favorable interactions, they are both negative (representing attractions) in sign.

- Because the integral shown in Eq. (3.9) represents the energy with which electron 1 is bound to nucleus 1, it is simply the ***binding energy of the electron in atom 1***.
- The ***binding energy of an electron is the reverse*** (with respect to sign) ***of the ionization potential***. Therefore, *it is customary to represent these Coulomb integrals in terms of the ionization potentials by reversing the sign*. Although it will not be shown here, the validity of this approximation lies in a principle known as ***Koopmans' theorem***. The valence state ionization potential (VSIP) is generally used to give the value of the Coulomb integral. This assumes that the orbitals are identical in the ion and the neutral atom. However, this relationship is not strictly correct.
- Suppose an electron is being removed from a carbon atom that has a configuration of $2p^2$.
- With there being two electrons in a set of three orbitals, there are 15 microstates that represent the possible permutations in placing the electrons in the orbitals. There is an exchange energy that is associated with this configuration because of the interchangeability of the electrons in the orbitals, and we say that the electrons are correlated. When one electron is removed, the single electron remaining in the $2p$ orbitals has a different exchange energy so the measured ionization potential also has associated with it other energy terms related to the difference in exchange energy. Such energies are small compared to the ionization potential, so the VSIP energies are normally used to represent the Coulomb integrals.

- In addition to the *integrals that represent energies*, there are ***integrals of a type in which no operator occurs***. These are represented as

$$S_{11} = \int \phi_1^* \phi_1 d\tau \quad (3.11)$$

$$S_{12} = \int \phi_1^* \phi_2 d\tau \quad (3.12)$$

- If the subscripts are identical, orbitals on the same atom are indicated, and *if the atomic wave functions are normalized*, the value of such an integral is 1.
- As a result, we can write

$$S_{11} = \int \phi_1^* \phi_1 d\tau = S_{22} = \int \phi_2^* \phi_2 d\tau = 1 \quad (3.13)$$

- On the other hand, the integrals of the type

$$S_{12} = \int \phi_1^* \phi_2 d\tau = S_{21} = \int \phi_2^* \phi_1 d\tau \quad (3.14)$$

- involves the product of an atomic orbital situated on nucleus 1 and one situated on nucleus 2, where the two nuclei are separated by a distance R , as in Figures 10.10 & 12.1.
- This product is significant only for regions where the two atomic orbitals have a large overlap. Integrals of this type are known as **overlap integrals**, and in a general way, they represent the **effectiveness with which the orbitals overlap in a region of space**.
- Consequently, S_{ij} is called an **overlap integral** that gives the extent of overlap and is an abbreviation for $S_{ij} = \int \varphi_i^* \varphi_j d\tau$.
- The overlap is a new concept that was not encountered in atomic systems.

- If the two atoms are separated by a large distance, the overlap integral approaches 0. However, if the atoms are closer together, there is some overlap of the orbitals and $S > 0$. If the atoms were forced together in such a way that the two nuclei coincided (internuclear distance is 0), we would expect $S = 1$ because the orbitals would be congruent
- Clearly, the value of an overlap integral such as those shown in Eq. (3.14) must be somewhere between 0 and 1, and it must be a function of the internuclear distance. With the exchange integrals and overlap integrals both being functions of the internuclear distance, it should be possible to express one in terms of the other. We will return to this point later.

- The meaning of S is indicated pictorially in Figure 12.1. In words, ***it is a measure of the degree to which both of the AOs have nonzero values in the same region.*** S can have values between 0 and 1 and decreases as the distance between the two nuclei increases. It has the value zero for widely separated atoms and 1 for superimposed atoms. As we will see later, *in order to have chemical bond formation it is necessary that $S > 0$.*
- Thus, we see that $0 \leq S(R) \leq 1$.

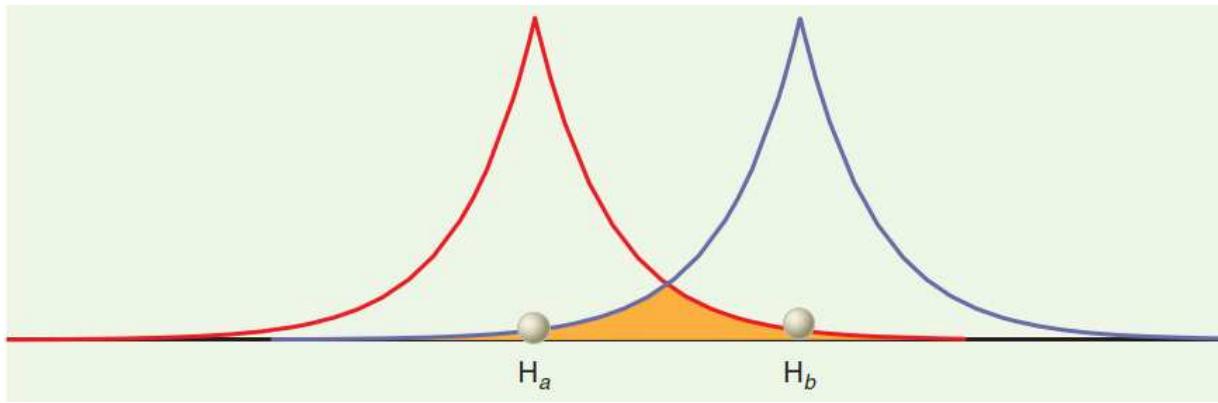


FIGURE 12.1

The amplitude of two 1s atomic orbitals is shown along an axis connecting the atoms. The overlap is appreciable only for regions in which the amplitude of both AOs is significantly different from zero. Such a region is shown schematically in orange. In reality, the overlap occurs in three-dimensional space.

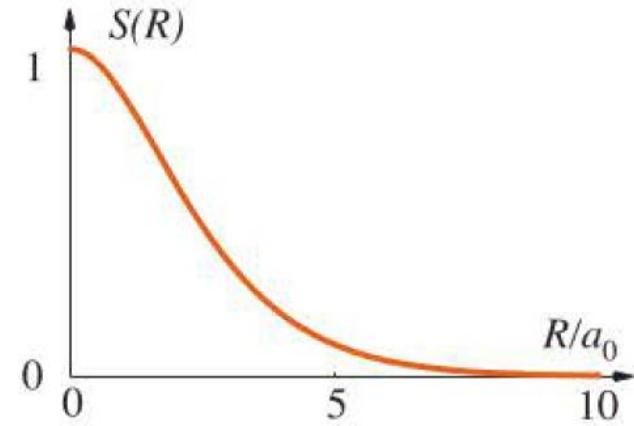


FIGURE 10.10

The overlap integral $S(R)$, for two hydrogen-atom 1s orbitals, plotted versus the internuclear separation in atomic units.

- **The Overlap Integral Is a Quantitative Measure of the Overlap of Atomic Orbitals Situated on Different Atoms.** For H_2^+ at its equilibrium bond length, $S \approx 0.59$.

- The appearance of Eq. (3.6) can be simplified greatly by using the notation described above. When the substitutions are made, the result is

$$E = \frac{a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 + 2a_1 a_2 S_{12} + a_2^2} \quad (3.15)$$

- in which we have assumed that S_{11} and S_{22} are both equal to 1 because of the atomic wave functions being normalized.
- We now seek to find values of the weighting coefficients that make the energy a minimum. To find a minimum in the energy expression, we take the partial derivatives with respect to a_1 and a_2 and set them equal to 0.

$$\left(\frac{\partial E}{\partial a_1} \right)_{a_2} = 0 \quad \left(\frac{\partial E}{\partial a_2} \right)_{a_1} = 0 \quad (3.16)$$

- When the differentiations are carried out with respect to a_1 and a_2 in turn while keeping the other constant, we obtain two equations that after simplification can be written as

$$a_1(H_{11} - E) + a_2(H_{12} - S_{12}E) = 0 \quad (3.17)$$

$$a_1(H_{21} - S_{21}E) + a_2(H_{22} - E) = 0 \quad (3.18)$$

- These equations are known as the *secular equations*, and in them the weighting coefficients a_1 and a_2 are the unknowns.
- These equations constitute a pair of linear equations that can be written in the form

$$ax + by = 0 \quad \text{and} \quad cx + dy = 0 \quad (3.19)$$

- It can be shown that a nontrivial solution for a pair of linear equations requires that the determinant of the coefficients must be equal to 0. This means that

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - E \end{vmatrix} = 0 \quad (3.20)$$

- The molecule being described is a homonuclear diatomic, so $H_{12} = H_{21}$ and $S_{12} = S_{21}$.
- If we represent S_{12} and S_{21} by S and let $H_{11} = H_{22}$, the expansion of the determinant yields

$$(H_{11} - E)^2 - (H_{12} - SE)^2 = 0 \quad (3.21)$$

- By equating the two terms on the left-hand side of Eq. (3.21), taking the square root gives

$$H_{11} - E = \pm(H_{12} - SE) \quad (3.22)$$

- from which we find two values for E (denoted as E_b and E_a).

- Two values for E are denoted as E_b and E_a :

$$E_b = \frac{H_{11} + H_{12}}{1 + S} \quad \text{and} \quad E_a = \frac{H_{11} - H_{12}}{1 - S} \quad (3.23)$$

- The energy state labeled E_b is known as the ***bonding or symmetric state***, whereas that designated as E_a is called the ***antibonding or asymmetric state***.
- Quantitative calculations show that near the equilibrium distance $R = R_e$, H_{12} is negative and $|H_{12}| > |H_{11}|$. Since H_{12} is negative and $S > 0$, therefore E_b represents the state of lower energy ($E_b < E_a$).
- The bonding and antibonding states are “split” below and above the energy state of the electron in an atom, not below and above an energy of 0.
- However, the ***antibonding state is raised a greater amount than the bonding state is lowered relative to the atomic orbital energy***. This can be seen from the relationships shown in Eq. (3.23) because in the first case the denominator is $(1 + S)$, but in the other it is $(1 - S)$.

- Fig. 3.3 shows the qualitative energy diagram for the bonding and antibonding molecular orbitals relative to the 1s atomic orbital.

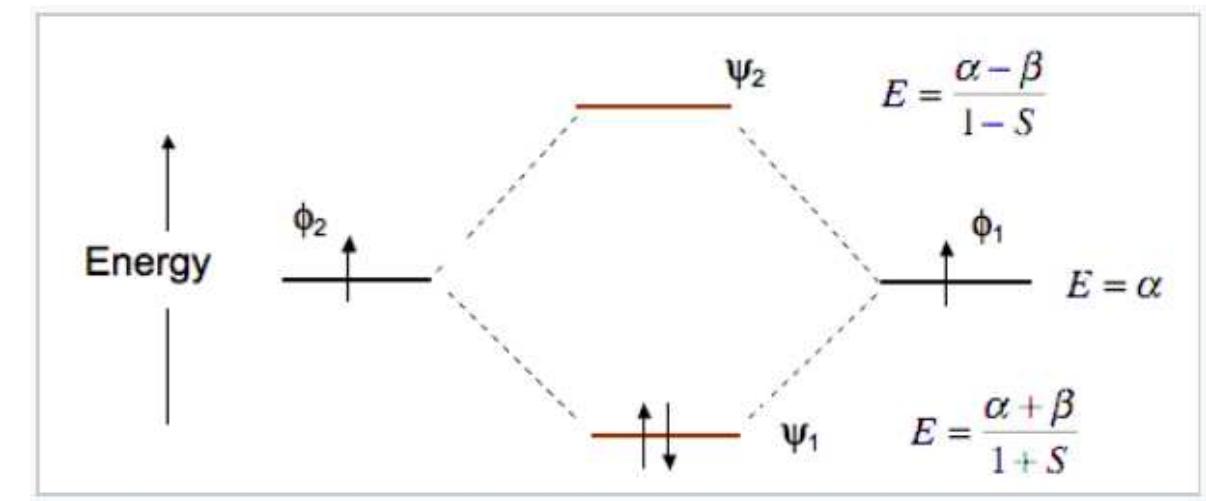
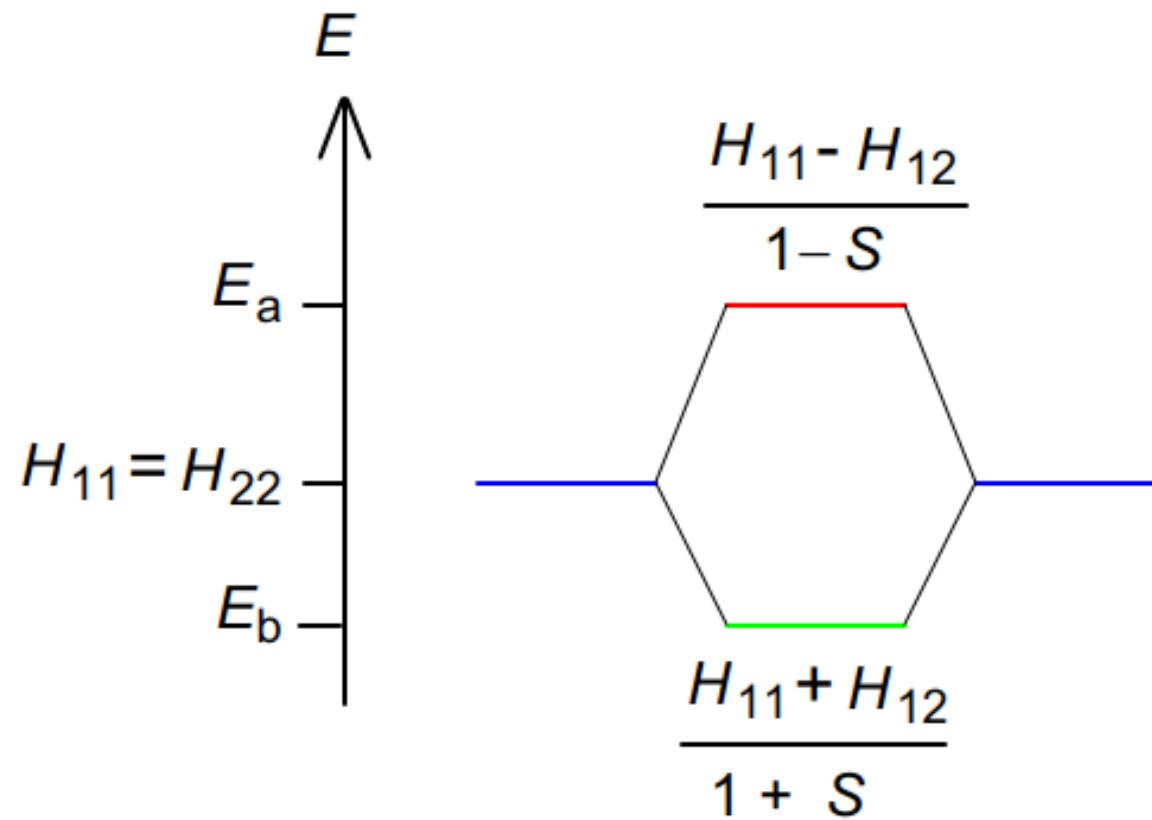


Figure 2.2.6 : Molecular orbital energy diagram for the H_2 molecule

FIGURE 3.3 Combination of two s orbitals to produce *bonding* and *antibonding* orbitals.

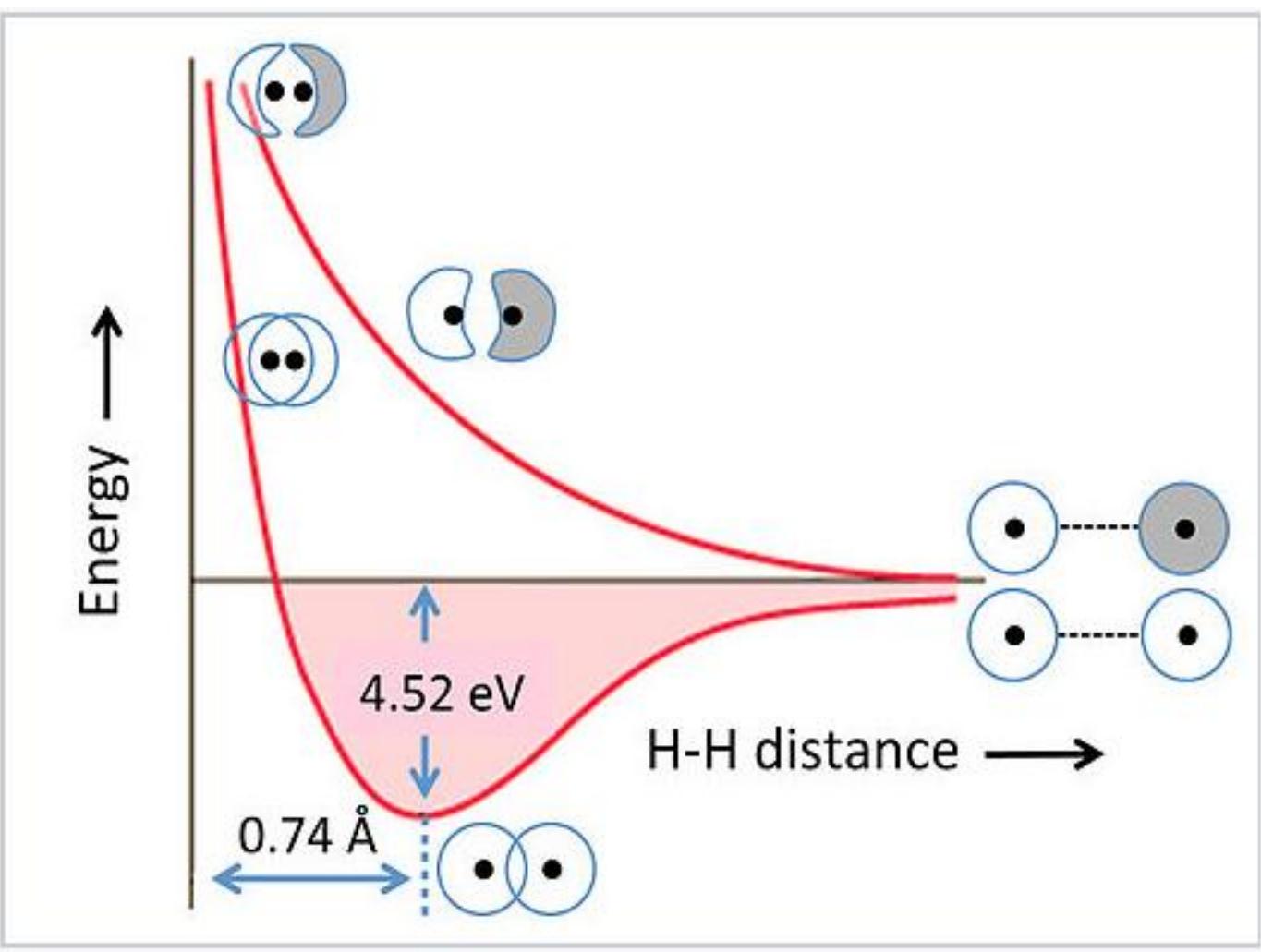


Figure 2.2.5 : Energy *as a function of internuclear distance* for the bonding and antibonding orbitals of the H₂ molecule

Figure 12.2 **summarizes** the following results of this discussion **pictorially** in a molecular orbital energy diagram using H_2 as an example:

- Two **localized** AOs combine to form two **delocalized** MOs provided that S_{AB} is nonzero. This is the case if there are regions in space in which the amplitudes of both AOs are nonzero.
 - The energy of one MO is lowered and the energy of the other MO is raised relative to the AO energy. The amount by which the MO energy differs from the AO energy depends on H_{AB} and S_{AB} .
 - Because $S_{AB} > 0$, $(1 + S_{AB}) > (1 - S_{AB})$ and ε_2 is raised relative to the AO energy more than ε_1 is lowered.
 - The AO coefficients have the same sign (in-phase) in the lower energy MO and the opposite sign (out-of-phase) in the higher energy MO.
- In a molecular orbital energy diagram, *the energy of the orbital* rather than the total energy of the molecule is displayed. For this reason, the appropriate energy operator in calculating the MO energy is \hat{H}_{el} rather than total \hat{H} .

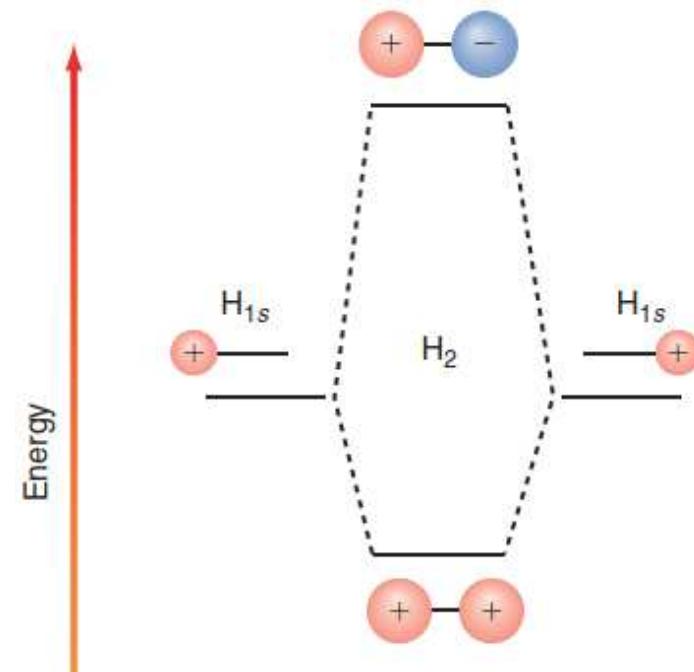


FIGURE 12.2

Molecular orbital energy diagram for a qualitative description of bonding in H_2 . The atomic orbitals are shown to the left and right, and the molecular orbitals are shown in the middle. Dashed lines connect the MO with the AOs from which it was constructed. Shaded circles have a diameter proportional to the coefficients c_A and c_B . Red and blue shading signifies positive and negative signs of the AO coefficients, respectively. Interchanging red and blue does not generate a different MO.

- Fig. 3.4 shows a *more correctly scaled* energy level diagram that results for the hydrogen molecule. Note that the energy for the 1s atomic orbital of a hydrogen atom is at $-1312 \text{ kJ mol}^{-1}$ because the ionization potential is 1312 kJ mol^{-1} (13.6 eV). Note also that the bonding molecular orbital has an energy of $-1528 \text{ kJ mol}^{-1}$, which is lower than that of the 1s atomic state.

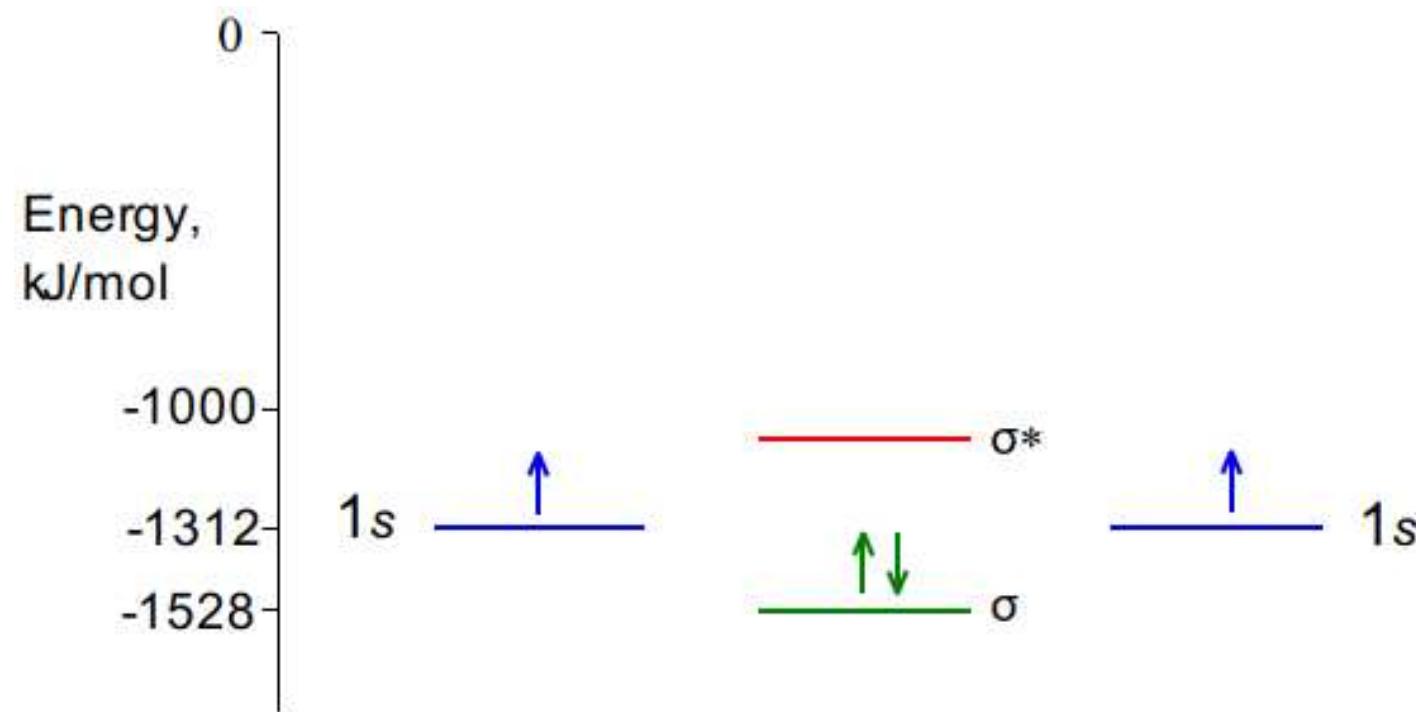


FIGURE 3.4 The energy level diagram for the H_2 molecule.

- If a hydrogen molecule is separated into the two constituent atoms, the result ***is equivalent to taking the two electrons in the bonding molecular orbital and placing them back in the atomic orbitals.***
- Because there are two electrons, that energy would be $2(1528 - 1312) = 432 \text{ kJ.mol}^{-1}$, the bond energy of the H_2 molecule.
- From the molecular orbital diagram, it can be seen that although the energy of the antibonding state is higher than that of the hydrogen atom, it is still very ***negative***.
- ***An energy of 0 does not result*** because even when the atoms are completely separated the energy of the system is the sum of the binding energies in the atoms which is $2 (-1312) \text{ kJ.mol}^{-1}$.

- If we let A represent the normalization constant, the condition for normalization is that

$$1 = \int A^2(\phi_1 + \phi_2)d\tau = A^2 \left[\int \phi_1^2 d\tau + \int \phi_2^2 d\tau + 2 \int \phi_1 \phi_2 d\tau \right] \quad (3.26)$$

- The first and second integrals on the right-hand side of this equation evaluates to 1 because the atomic wave functions are assumed to be normalized.
- Therefore, the right-hand side of the equation reduces to

$$1 = A^2[1 + 1 + 2S] \quad (3.27)$$

- and we find that the normalization constant is given by

$$A = \frac{1}{\sqrt{2 + 2S}} \quad (3.28)$$

- and the wave functions can be represented as shown in Eqs. (3.24) and (3.25).

- If we substitute the values for the energy as shown in Eq. (3.23) into the secular equations, we find that
- $a_1 = a_2$ (for the symmetric state) and $a_1 = -a_2$ (for the antisymmetric state).
- When these relationships between the weighting coefficients are used, it is found that

$$\psi_b = a_1\phi_1 + a_2\phi_2 = \frac{1}{\sqrt{2+2S}}(\phi_1 + \phi_2) \quad (3.24) \quad \text{or } \psi_b = \frac{1s_1 + 1s_2}{\sqrt{2(1+S)}}$$

$$\psi_a = a_1\phi_1 - a_2\phi_2 = \frac{1}{\sqrt{2-2S}}(\phi_1 - \phi_2) \quad (3.25) \quad \text{or } \psi_a = \frac{1s_1 - 1s_2}{\sqrt{2(1-S)}}$$

➤ The normalized trial function corresponding to the energy E_b is therefore

$$\Psi_b = \frac{1s_A + 1s_B}{\sqrt{2(1 + S_{AB})}}$$

➤ The normalized trial function corresponding to the energy E_a is

$$\Psi_a = \frac{1s_A - 1s_B}{\sqrt{2(1 - S_{AB})}}$$

$$E_+(R) = \frac{H_{AA}(R) + H_{AB}(R)}{1 + S(R)} \quad E_-(R) = \frac{H_{AA}(R) - H_{AB}(R)}{1 - S(R)},$$

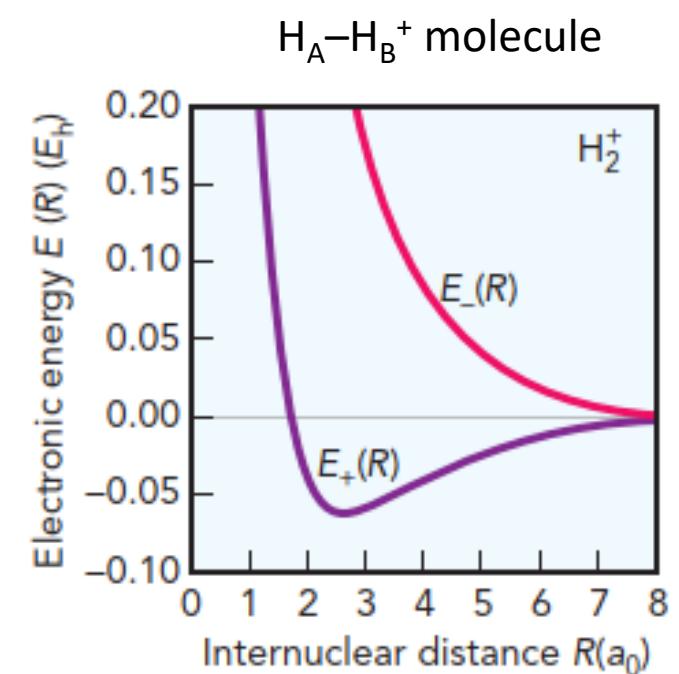


Figure 5.10 The electronic energy functions $E_+(R)$ and $E_-(R)$ for H_2^+ .

- Although we have dealt with a diatomic molecule consisting of two hydrogen atoms, the procedure is exactly the same if the molecule is Li_2 except that the atomic wave functions are 2s wave functions and the energies involved are those appropriate to lithium atoms. The VSIP for lithium is only $513 \text{ kJ}\cdot\text{mol}^{-1}$ rather than 1312 kJ mol^{-1} as it is for hydrogen.
- *When performing molecular orbital calculations, overlap and exchange integrals must be evaluated.*
- With modern computing techniques, overlap integrals are most often evaluated as part of the calculation.
- The wave functions are of the Slater type, and the overlap integrals can be evaluated for varying bond lengths and angles.

MOT: Hamiltonian (H) of the Simplest Diatomic Molecules: H_2^+ and H_2

- As a *first step* in setting up the Schrödinger equation for H_2^+ and H_2 molecules, the nuclei are fixed at some given separation.
- *Then* the electrons are included, and the equation is solved to give the wave functions and energies that describe the two electrons.
- The *wavefunction* that corresponds to the lowest energy, the *ground state wavefunction*, can be used to compute *contour diagrams*, much like the maps used to show peaks and valleys in hilly terrain. These diagrams show the distribution of electron density around the two nuclei.
- For simplicity, let's consider the simplest neutral molecule, H_2 . The Schrödinger equation for a H_2 , like that for a hydrogen atom, gives a set of wave functions, or orbitals, and their corresponding energies. As noted earlier, these orbitals extend over both nuclei in H_2 and therefore are called **molecular orbitals (MOs)**.

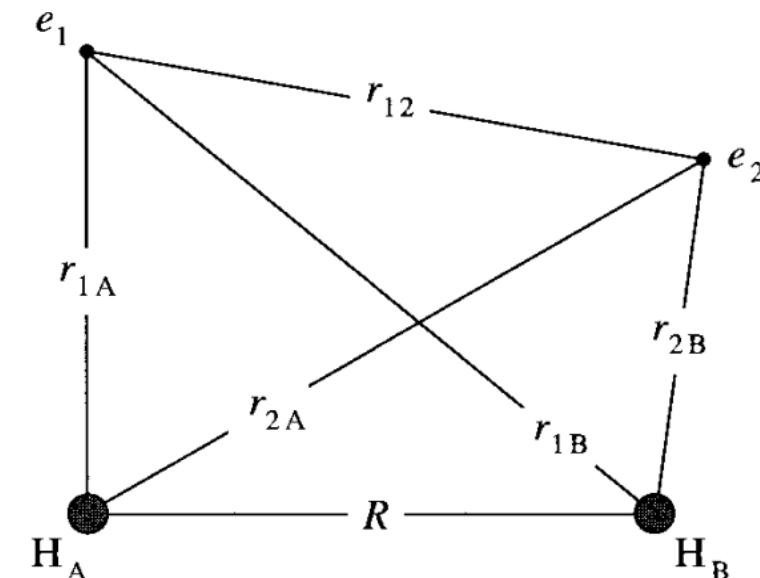
- The Hamiltonian operator for a hydrogen molecule (H_2) is given by

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.1)$$

- In Equation 9.1, the subscripts A and B refer to the nuclei of the individual atoms, the *subscripts 1 and 2 refer to the individual electrons*, and the various distances r_{1A} , r_{1B} , etc. are as illustrated in Figure 9.1.

FIGURE 9.1

Definition of the distances between the nuclei and the electrons involved in the ***Hamiltonian operator for a hydrogen molecule***.



- In these expressions e is the magnitude of the charge on the protons and the electrons, m_e and M are the masses of the electron and proton respectively and ϵ_0 is the vacuum permittivity.
- The symbol ∇^2 , which is spoken ‘del squared’ (Laplacian), is defined by:

$$\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

- The first two terms of the Hamiltonian operator in Equation 9.1 correspond to the kinetic energy of the two nuclei; the next two terms represent the kinetic energy of the two electrons; the four ensuing negative terms describe the contributions to the potential energy that arise from the attraction between the nuclei and the electrons; and the final two positive terms account for electron-electron and nuclear-nuclear repulsion, respectively.

- The total Hamiltonian operator is therefore the sum of ten terms, and we immediately recognize that it is unlikely that a solution of Schrödinger's eigenvalue-eigenfunction equation can be found, even for this, the simplest of molecules.
 - Therefore, if the theory is to be applicable, some way or ways, of **simplifying the problem** must be found.
- The Born-Oppenheimer (BO) Approximation**.....Separates the Nuclear and Electronic motions and simplifies Schrodinger Equation for Molecules
- All theories of molecular structure adopt the **Born-Oppenheimer (BO) approximation**.
 - In this approximation, it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move around them.

- The *nuclei can be thought of as being fixed at arbitrary locations* so that the *Schrodinger equation can be solved for the electrons alone.*
- The *approximation is quite good for molecules in their electronic ground states.*
- Since electrons are much lighter than nuclei, electrons move much faster than nuclei in a molecule, for calculations suggest that (in classical terms) *the nuclei in H₂ move through only about 1 pm while the electron speeds through 1000 pm.*
- ✓ Because of the large difference between the masses of the nuclei and the electrons, we can reasonably view the nuclei as fixed in position relative to the motion of the electrons.
- ✓ *Under such an approximation, the kinetic energy terms of the nuclei (the first two terms in the Hamiltonian operator, Equation 9.1) can be treated separately.*
- This approximation of neglecting the nuclear motion is called the *Born-Oppenheimer approximation.*

- Although the Born-Oppenheimer approximation will lead to approximate values of the energies and wave functions, it can be systematically corrected using perturbation theory. For most practical purposes, however, these corrections are on the order of the mass ratio ($\sim 10^{-3}$), and so the Born-Oppenheimer approximation is a very good approximation.
- The Hamiltonian operator for a hydrogen molecule (H_2) is given by

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.1)$$

➤ Neglecting the nuclear kinetic energy terms in Equation 9.1 gives the Hamiltonian operator for the motion of the electrons around the two nuclei fixed at an internuclear separation:

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \quad (9.2)$$

➤ As usual, we will express *all our equations in atomic units* and so Equation 9.2 becomes:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (9.3)$$

➤ Because the nuclei are considered to be fixed, the quantity R in Equation 9.2 is treated as a parameter; the energy we will calculate using the above Hamiltonian operator will depend upon R .

- By invoking the Born-Oppenheimer approximation, the energies and wavefunctions of a diatomic molecule **can be obtained by selecting an internuclear separation and then solving the Schrodinger equation for the electrons**. Then the calculation can be repeated at a different internuclear separation, and so on. **If a stable molecule is to be formed, there must be a decrease in energy as we move towards smaller values of R** and this process will continue until the mutual repulsion of the nuclei and of the electrons begins to make itself felt and the energy begins to rise again; normally quite steeply.
- In this way it is possible to explore **how the energy of the molecule varies with bond length** and obtain a **molecular potential energy curve**, a graph showing how the molecular energy depends on the internuclear separation (Fig. 1). The graph is called a **potential energy curve** because the nuclei are stationary and contribute no kinetic energy.
- Once the curve has been calculated, **two important parameters can be identified**: the **equilibrium bond length**, R_e , the internuclear separation at the minimum of the curve, and D_e **the depth of the minimum below the energy of the infinitely widely separated and stationary atoms**.
- Similar considerations apply to **polyatomic molecules**, where **bond angles** may be varied as well as **bond lengths**.

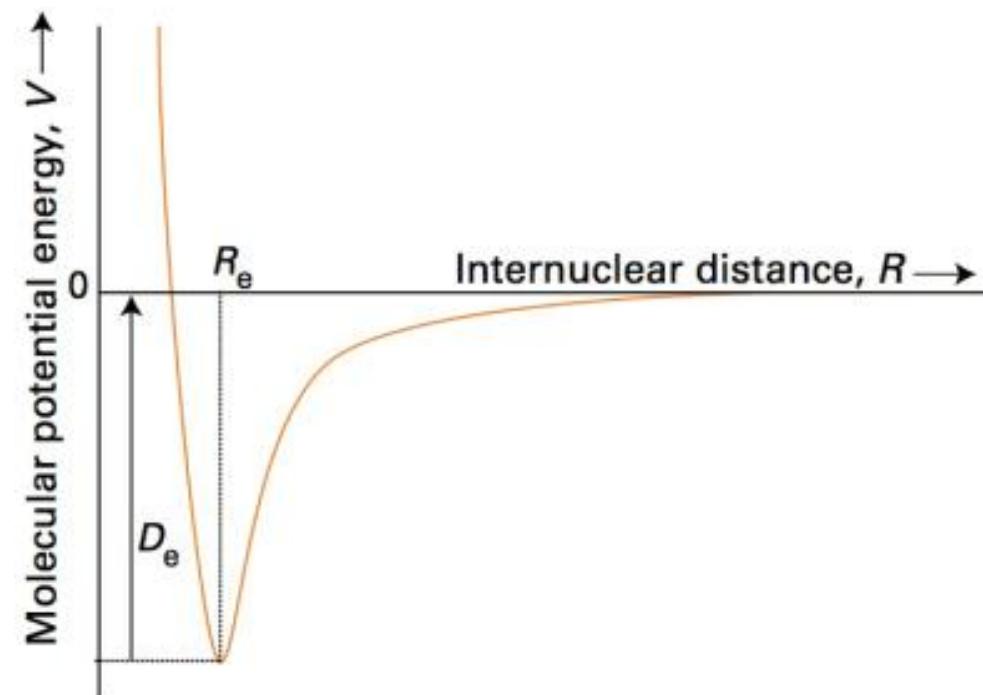


Fig. 1 A molecular potential energy curve. The equilibrium bond length R_e , corresponds to the energy minimum D_e .

This distance is known as the equilibrium internuclear distance, R_e , and is found experimentally to be 74.1 pm.

The corresponding experimental energy is 4.747 eV (7.6056×10^{-19} J) below the energy of the two, non-interacting hydrogen atoms.

This is the energy which we shall seek to calculate by determining the difference between the electronic energy of two independent hydrogen atoms and that of the hydrogen (H–H) molecule with a bond length of R_e . The symbol for this energy difference is D_e .

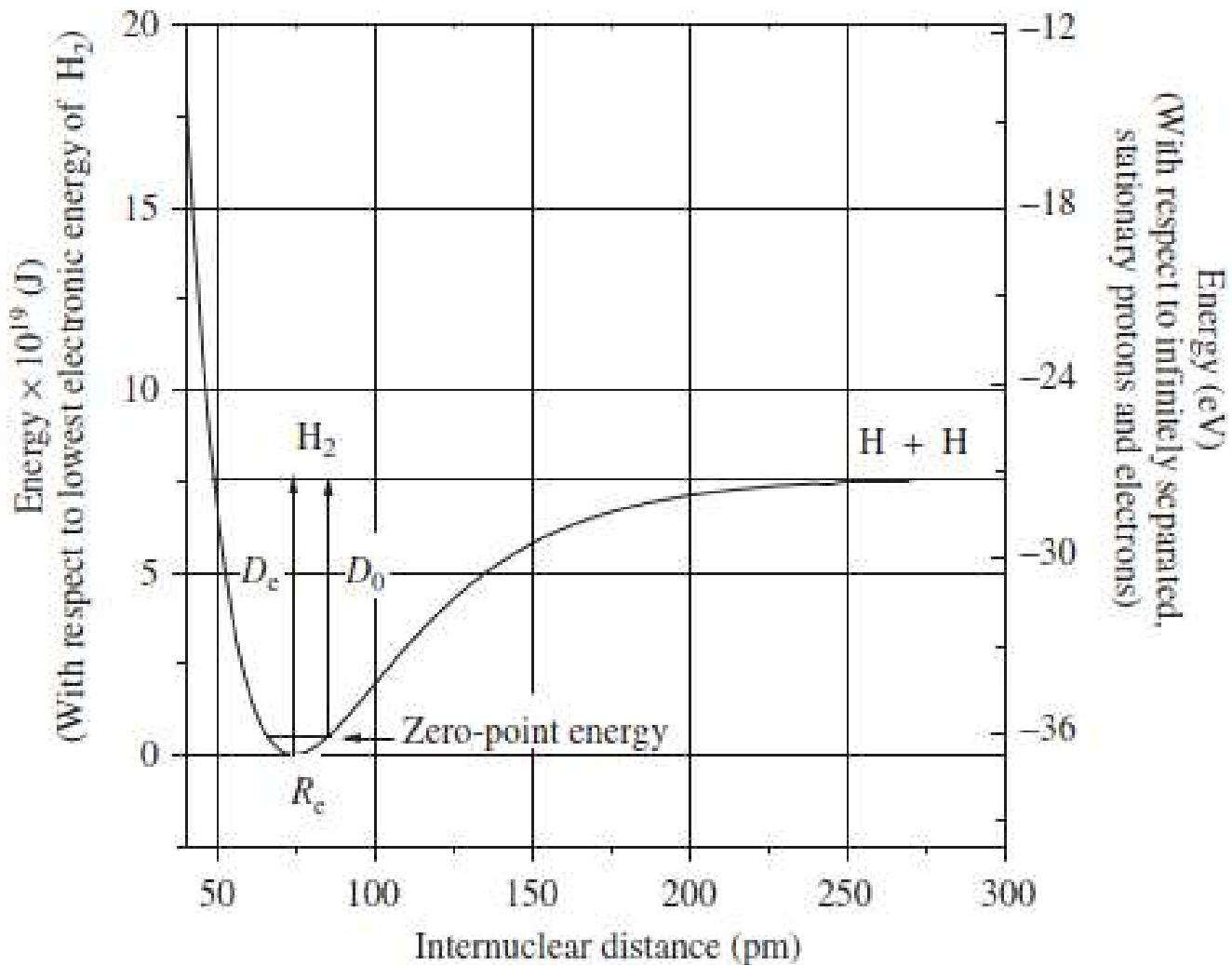
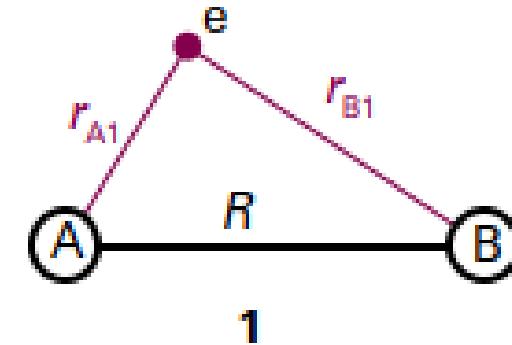


Figure 6.3 The hydrogen molecule: energy versus internuclear distance

❖ The Case of the Simplest Diatomic Species: Hydrogen Molecular Ion H_2^+ (one-electron system)

The Hamiltonian for the single electron in H_2^+ is
.....?????.....



where r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. In the expression for V , the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei.

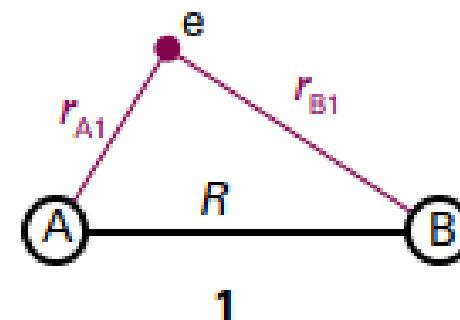
The Simplest Diatomic Species: Hydrogen Molecular Ion H_2^+ (one-electron system)

A one-electron system that applies to homonuclear diatomic molecules is the hydrogen molecular ion, H_2^+ , which consists of two protons and one electron. The H_2^+ ion can be produced experimentally by using $\text{H}_2(\text{g})$ in a discharge tube. It is a stable species, with a bond length of 106 pm and a bond energy of 0.423 aJ.

The Schrödinger equation for a H_2^+ ion, like that for a hydrogen atom, is relatively easy to solve, and we obtain a set of wave functions, or orbitals, and their corresponding energies. As noted earlier, these orbitals extend over both nuclei in H_2^+ and therefore are called **molecular orbitals**. As it was done with the various hydrogen atomic orbitals to build up the electronic structures of more complicated atoms, in the same way, we will now use the various H_2^+ molecular orbitals to build up the electronic structures of more complicated diatomic molecules.

The Hamiltonian for the single electron in H_2^+ is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 + V \quad V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R} \right)$$



where r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. In the expression for V , the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei. The collection of fundamental constant $e^2/4\pi\epsilon_0$ occurs widely throughout this section and is denoted j_0 .

Molecular-Orbital Theory: H_2^+ Is the Prototypical Species

- *The one-electron wavefunctions obtained by solving the Schrödinger equation $\hat{H}\psi = E\psi$ are called **molecular orbitals**.*
- A molecular orbital ψ gives, through the value of $|\psi|^2$, the distribution of the electron in the molecule. A molecular orbital extends over the molecule like how electrons in an atom occupy atomic orbitals.
- For molecules, the Schrodinger equation for the one-electron molecular ion H_2^+ is solved, and the resulting orbitals are used to construct the wave functions for more complicated molecules.
- We should emphasize at this point that H_2^+ is a stable species that has been well studied spectroscopically. It has a bond length of 106 pm ($2.00a_0$) and a binding energy of 268 $\text{kJ}\cdot\text{mol}^{-1}$ ($0.103E_h$).

- Because H_2^+ is a one-electron species, the Schrodinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation.
- Nevertheless, the solutions are not easy to use, and their mathematical form does not give much physical insight as to how and why bonding occurs.
- Instead, it is more useful to solve H_2^+ approximately and use the resultant approximate molecular orbitals to build molecular wave functions.
- Although this approach may seem a crude way to proceed (after all, the problem can be solved exactly), it provides good physical insight into the nature of chemical bonds in molecules and yields results in good agreement with experimental observations. Furthermore, this approach can be systematically improved to give any desired degree of accuracy.

❖ The construction of molecular orbitals of H₂

- A molecular orbital is a one-electron wavefunction that spreads throughout the molecule.
- The mathematical forms of such orbitals are highly complicated, even for such a simple species as H₂⁺, and they are unknown in general. All *modern work builds approximations to the true molecular orbital by formulating models based on linear combinations of the atomic orbitals on the atoms in the molecule.*
- According to the general principles of quantum mechanics, *if there are several possible outcomes, then the overall wavefunction is a superposition - a linear combination of the wavefunctions that represent the individual outcomes.*

- In H_2^+ , there are two possible outcomes: an electron may be found either in an atomic orbital φ_A centred on A or in an atomic orbital φ_B centred on B.
- When we add two wavefunctions to get a new wavefunction, we can vary their relative phase.
- The two functions can be given the same phase ($\varphi_A + \varphi_B$) or opposite phases ($\varphi_A - \varphi_B$).
- To write these two options formally, we have, therefore, the two possible (unnormalized) wavefunctions for molecular orbitals are

$$\Psi_{\pm} = c_A \varphi_A \pm c_B \varphi_B \quad \text{where } c_A \text{ and } c_B \text{ are numerical coefficients.}$$

- The AOs are the **basis functions** for the MO. However, such a small basis set is inadequate for quantitative calculations, and in solving the computational problems, one need to use much larger basis sets.

- The *squares of the coefficients give the relative proportions of the atomic orbitals contributing to the molecular orbital.*
- ✓ In a homonuclear diatomic molecule (such as H₂, O₂, or Cl₂) an electron can be found with equal probability in orbital A or orbital B, so the squares of the coefficients must be equal, which implies that $c_B = \pm c_A$.
- ✓ Note that before we can discuss a probability density associated with these molecular orbitals, so Ψ_{\pm} must be normalized.
- ✓ Next by using the approximate MO in terms of the atomic orbitals, *one needs to minimize the MO energy with respect to the values of the AO coefficients c_A and c_B .*

Bonding orbitals

According to the Born interpretation, ***the probability density of the electron at each point in H_2^+ is proportional to the square modulus of its wavefunction at that point.*** The probability density corresponding to the (real) wavefunction ψ_+ is

$$\psi_+^2 \propto \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

Bonding probability
density (9B.3)

This probability density is plotted in Fig. 9B.4. An important feature becomes apparent in the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn. 9B.3, the total probability density is proportional to the sum of:

- ψ_A^2 , the probability density if the electron were confined to atom A;
- ψ_B^2 , the probability density if the electron were confined to atom B;
- $2\psi_A\psi_B$, an extra contribution to the density from both atomic orbitals.

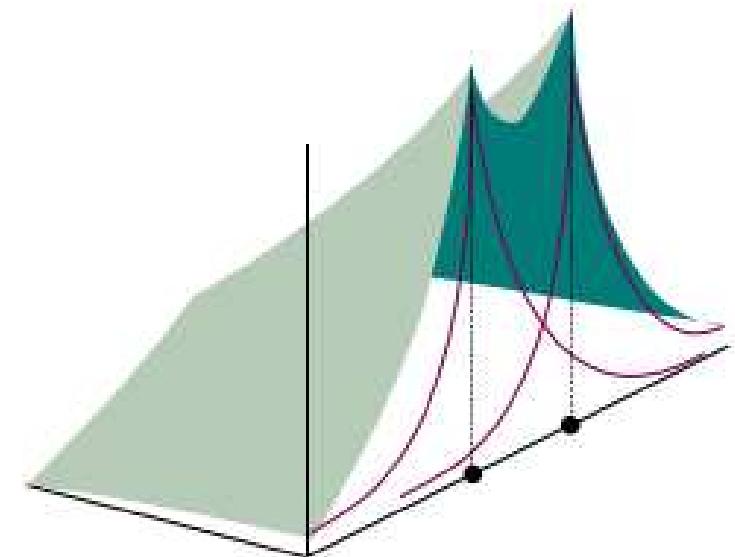


Figure 9B.4 The electron density calculated by forming the square of the wavefunction used to construct Fig. 9B.2. Note the accumulation of electron density in the internuclear region.

□ The last contribution, **the *overlap density***, is crucial because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the *constructive interference of the two atomic orbitals*: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atom. This observation is summarized as:

- Bonds form as a result of the build-up of electron density where atomic orbitals overlap and interfere constructively.
- ✓ All descriptions of bonding recognize the buildup of electron density in the region between the two nuclei at the expense of the regions beyond the nuclei.

$$\Psi_+^2 \propto \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$

Bonding probability
density

(9B.3)

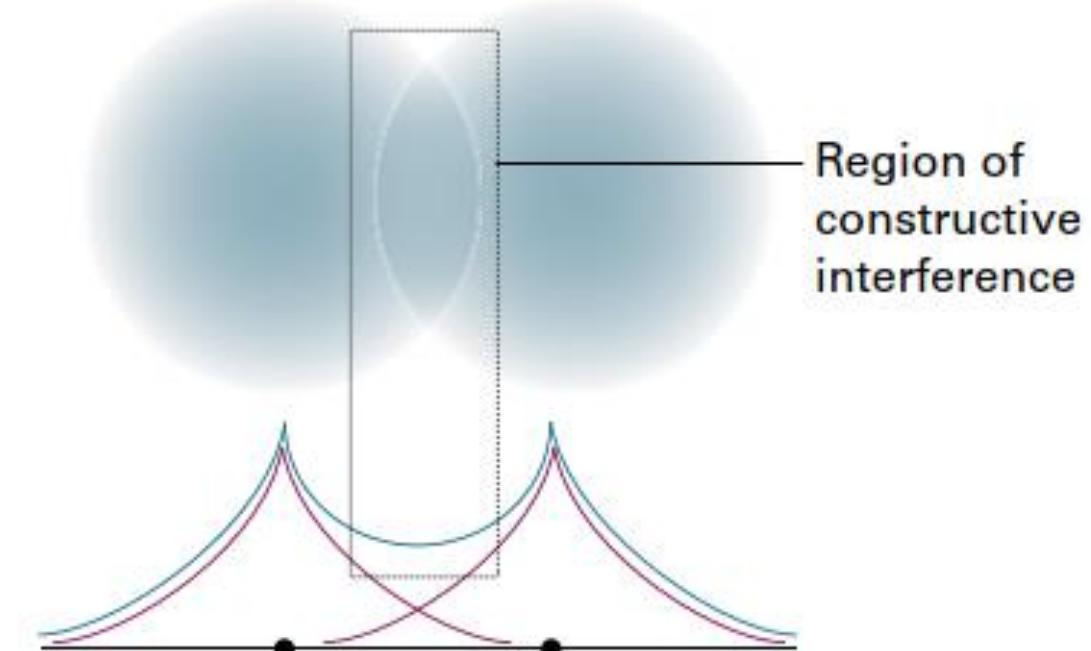


Figure 9B.7 A representation of the constructive interference (blue line) that occurs when two H_{1s} orbitals overlap and form a bonding σ orbital.

- The conventional explanation of this observation is based on the notion that *the accumulation of electron density between the nuclei* puts the electron in a position where it interacts strongly with both nuclei. Hence, *the energy of the molecule is lower than that of the separate atoms*, where each electron can interact strongly with only one nucleus.
- This conventional explanation, however, has been called into question, because shifting an electron away from a nucleus into the internuclear region raises its potential energy. The modern (and still controversial) explanation does not emerge from the simple LCAO treatment given here.
- ✓ It seems that, at the same time as the electron shifts into the internuclear region, the atomic orbitals shrink. This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wave function is changed, but the change in kinetic energy is dominated by the change in potential energy.
- Throughout the following discussion the strength of chemical bonds is ascribed to the accumulation of electron density in the internuclear region. In molecules more complicated than H_2^+ the true source of energy lowering may be this accumulation of electron density or some indirect but related effect.

Antibonding orbitals

The linear combination ψ_- has higher energy than ψ_+ , and for now, it is labeled σ^* because it is also a σ orbital. This orbital has a nodal plane perpendicular to the internuclear axis and passes through the mid-point of the bond where ψ_A and ψ_B cancel exactly (Figs. 9B.8 and 9B.9).

The probability density is

$$\psi_-^2 \propto \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

Antibonding
probability density

(9B.6)

There is a reduction in probability density between the nuclei due to the term $-2\psi_A\psi_B$ (Fig. 9B.10); in physical terms, *there is destructive interference where the two atomic orbitals overlap.*

- The σ^* orbital is an example of an antibonding orbital, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated

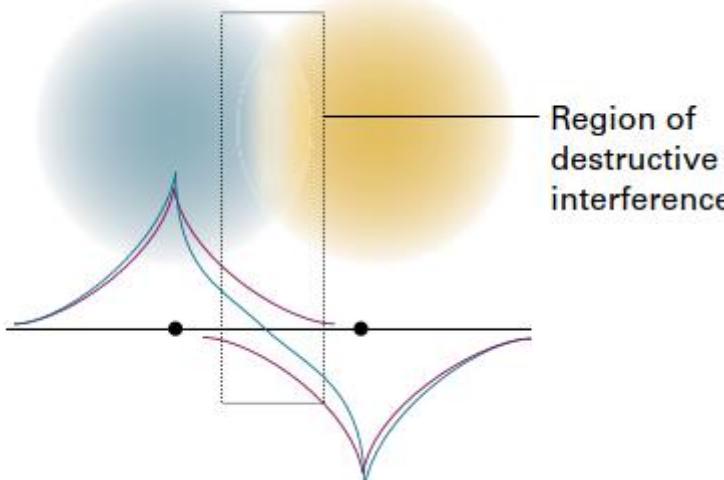
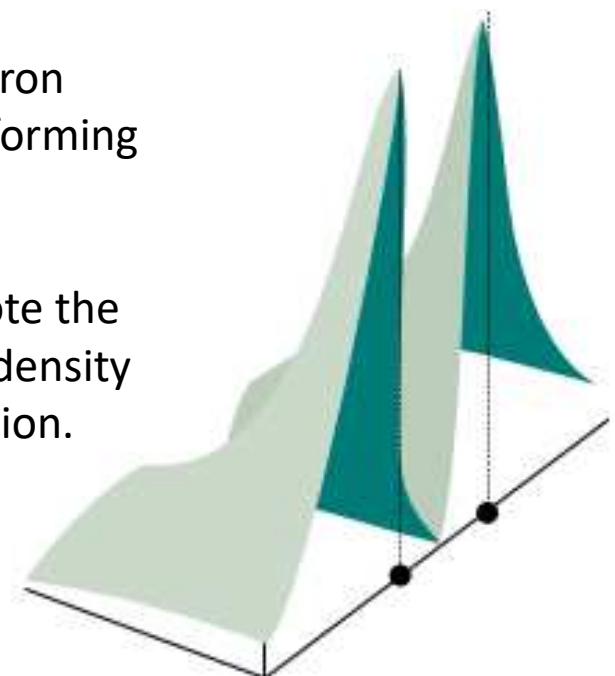


Figure 9B.8 A representation of the destructive interference that occurs when two H_{1s} orbitals overlap and form an antibonding σ orbital.

Figure 9B.10 The electron density calculated by forming the square of the wavefunction used to construct Fig. 9B.9. Note the reduction of electron density in the internuclear region.



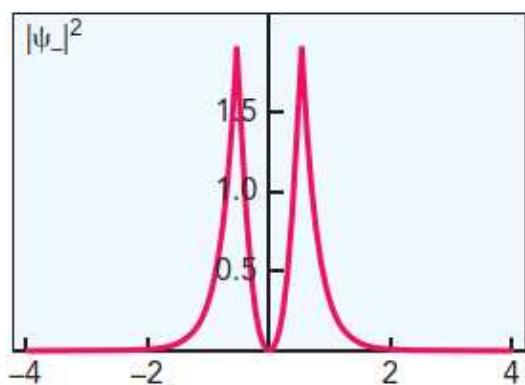
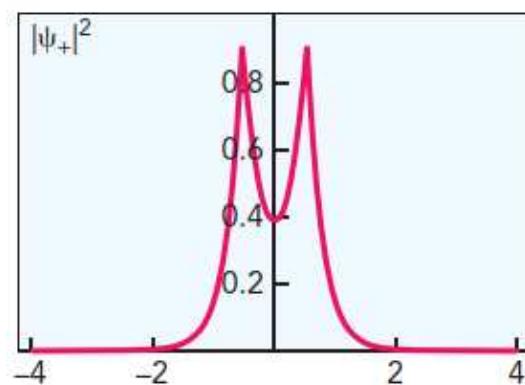
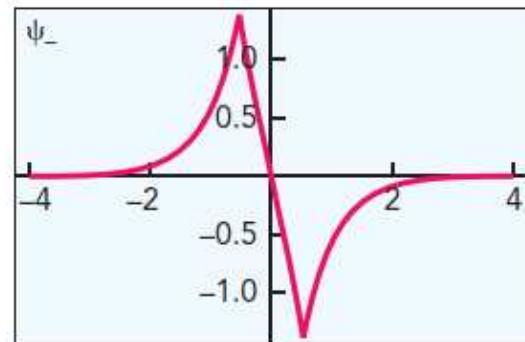
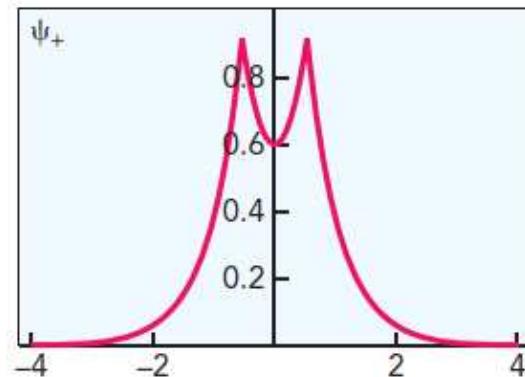


Figure 5.8. The ψ_+ and ψ_- wavefunctions and probability densities, graphed as functions of z .

The key feature for us here is that in the ψ_- orbital, the density goes to zero at the midpoint between the two nuclei. This is expected for a wavelike electron: with enough energy, it should be able to oscillate with a node in the middle. But this node reduces the electron charge in the binding region, causing the orbital to have the net impact of weakening the bond between the two nuclei.

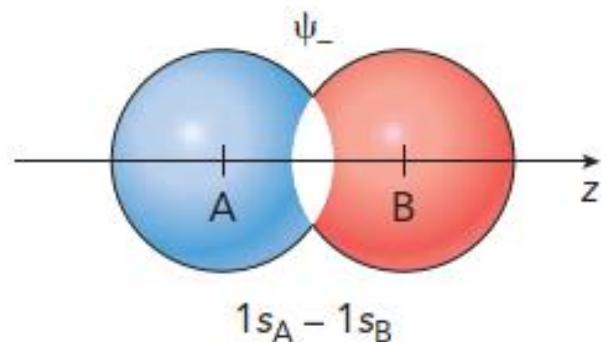
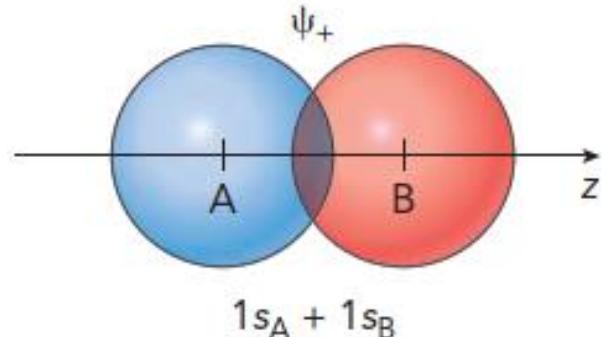


Figure 5.7 The ψ_+ and ψ_- MOs. We combine the two spherically symmetric 1s orbitals on nuclei A and B to get the simplest molecular orbitals.

Orbital notation

For homonuclear diatomic molecules (molecules consisting of two atoms of the same element, such as N₂), it proves helpful to label a molecular *orbital according to its inversion symmetry, the behaviour of the wavefunction when it is inverted through the centre* (more formally, the centre of inversion, Topic 10A) of the molecule. Thus, *any point on the bonding σ orbital that is projected through the centre of the molecule and out an equal distance on the other side leads to an identical value (and sign) of the wavefunction* (Fig. 9B.12).

- ✓ This so-called **gerade** symmetry (from the German word for ‘even’) is denoted by a subscript **g**, as in σ_g . The same procedure applied to the antibonding σ^* orbital results in the same amplitude but *opposite sign of the wavefunction*. This **ungerade** symmetry (‘odd symmetry’) is denoted by a subscript **u**, as in σ_u .
- ✓ The inversion symmetry classification is *not applicable to heteronuclear diatomic molecules* (diatomic molecules formed by atoms from two different elements, such as CO) because these molecules do not have a centre of inversion.

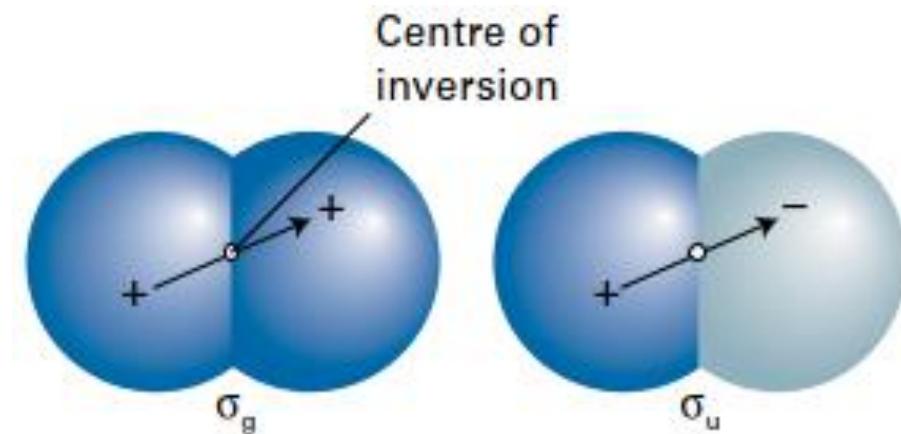
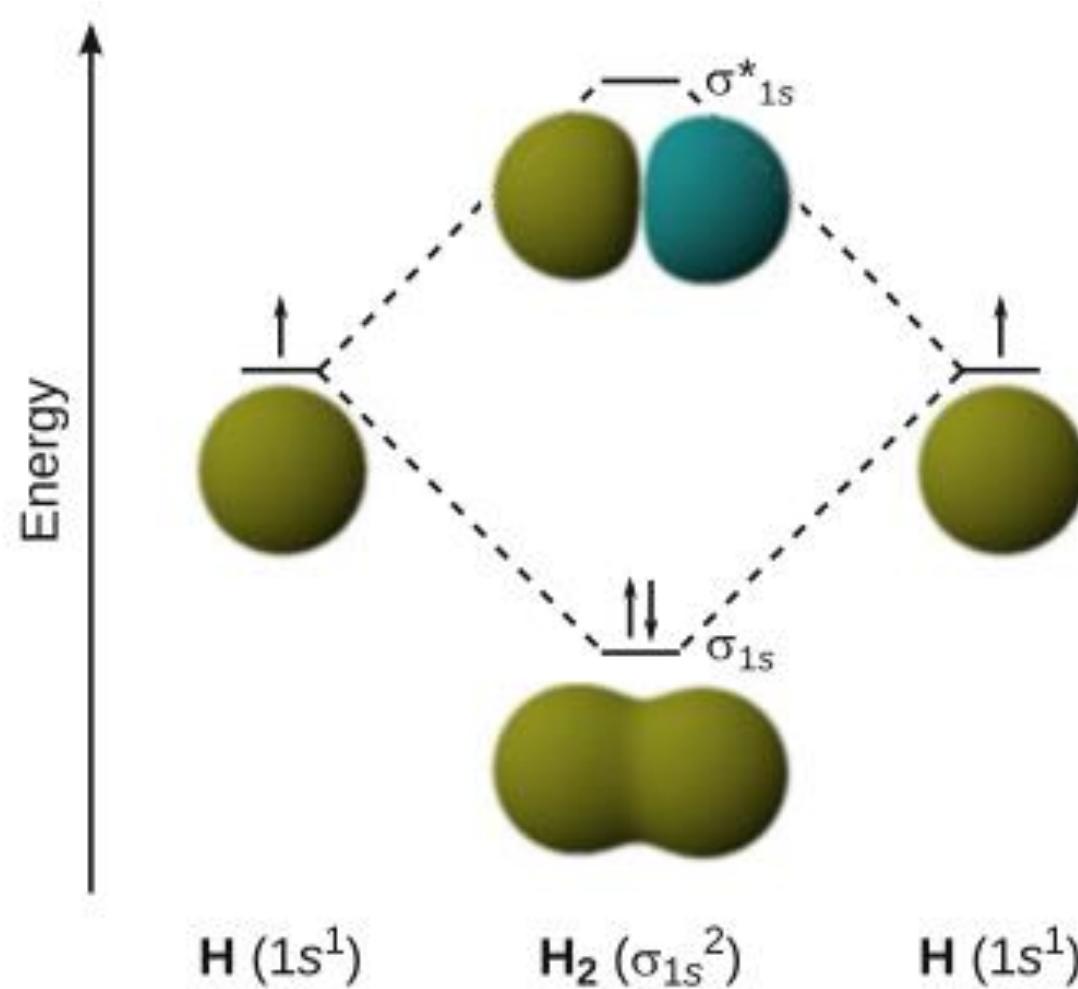


Figure 9B.12 The parity of an orbital is even (**g**) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (**u**) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the **g, u** classification is irrelevant.

Fig. 11.3 Linear combination of the two 1s orbitals in hydrogen leads to bonding and anti-bonding molecular orbitals of H_2



When 1s orbitals are combined (added or subtracted), a **bonding orbital of lower energy** (an orbital which, if occupied, helps to bind two atoms together) and **an antibonding orbital of higher energy** (which, if occupied, weakens the bond) are formed.

A **molecular orbital that has cylindrical symmetry around the internuclear axis**, such as the one being discussed, is called a **σ orbital** because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis. An electron that occupies a σ orbital is called a σ electron, and if that is the only electron present in the molecule (as in the ground state of H_2^+), then the configuration of the molecule is σ^1 .

The most important conclusions that can be drawn from this figure are that σ_{1s} describes a stable molecule because the energy has a well-defined minimum at $R=R_e$ and that σ_{1s}^* does not describe a bound state of H and H^+ because for all R, which makes the molecule unstable with respect to dissociation. Therefore, we conclude that only a molecule described by σ_{1s} molecular orbital is a stable molecule. The ψ_g and ψ_u wave functions are referred to as **bonding and antibonding molecular orbitals**, respectively, to emphasize their relationship to the chemical bond.

Calculations on H_2^+ give $R_e = 2.49a_0 = 132 \text{ pm}$ and $hcD_e = 1.76 \text{ eV}$ (171 kJ mol^{-1}); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

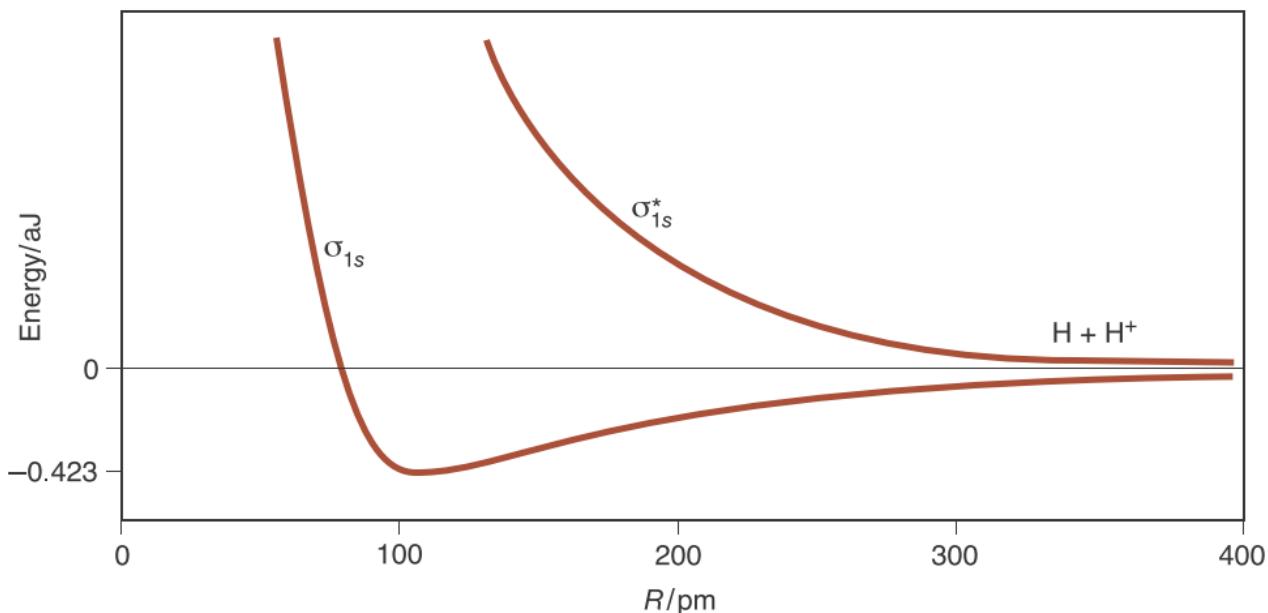
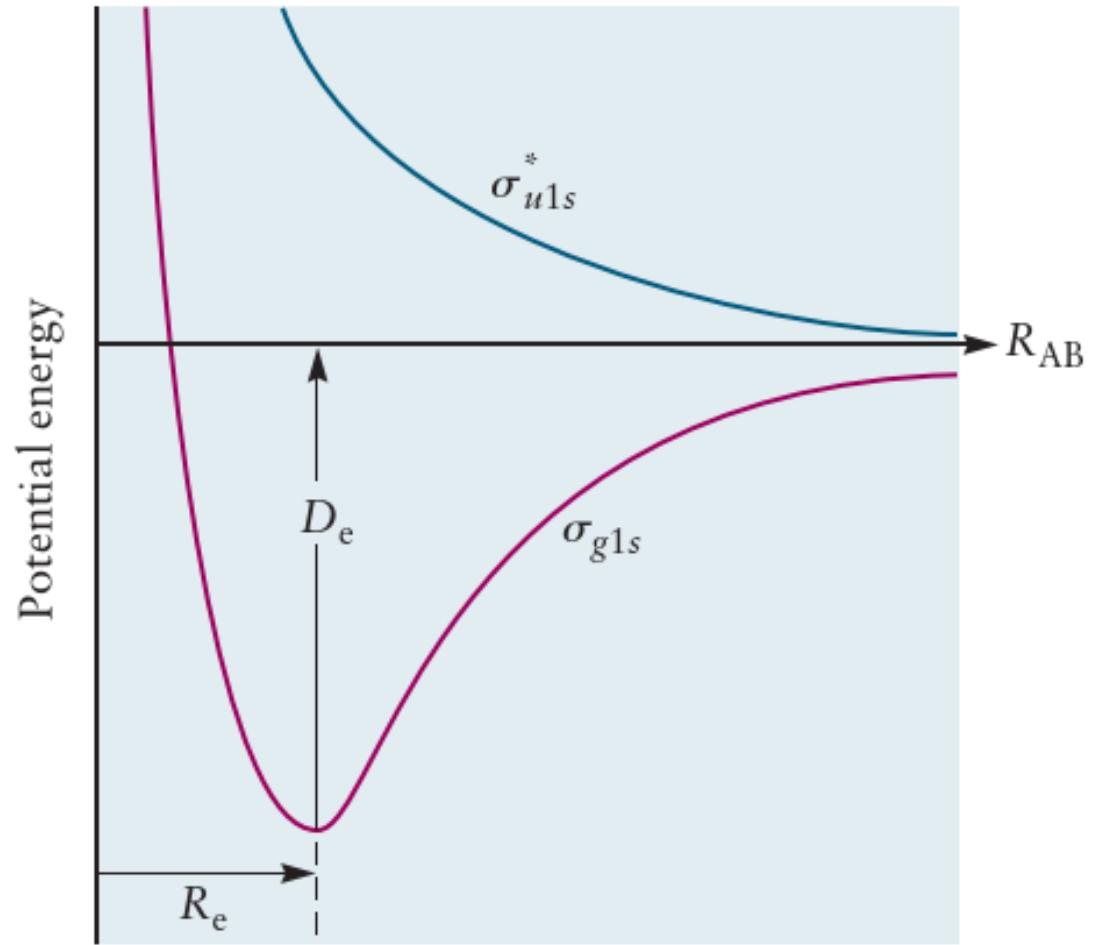


Figure 9.4 Potential energy of the σ_{1s} bonding molecular orbital and σ_{1s}^* antibonding molecular orbital for H_2^+ as a function of the internuclear separation between the two hydrogen nuclei. The minimum in the lower curve represents the equilibrium nuclear separation or average bond length of the molecular ion (106 pm). This energy minimum depicts the formation of a stable bond. In contrast, the energy of the σ_{1s}^* orbital (upper curve) is always above that of the separated atoms, making this an antibonding orbital.

FIGURE 6.9 Effective potential energy of the protons in H_2^+ when the electron is in a σ_{g1s} (bonding) and σ_{g1s}^* (antibonding) molecular orbital, shown as a function of internuclear separation R_{AB} in the LCAO approximation.



The energy-level diagram within the LCAO approximation is given by a correlation diagram (Fig. 6.11), which shows that two 1s atomic orbitals have been combined to give a σ_{g1s} MO with energy lower than the atomic orbitals and a σ^*_{u1s} MO with higher energy than the atomic orbitals. This diagram is a purely qualitative representation of the same information contained in Figure 6.9. The actual energy level values will depend on the distance between the fixed nuclei (as shown in Figure 6.9) and must be determined from calculations.

Even without the results shown in Figure 6.9, we would know that an electron in an antibonding orbital has higher energy than one in a bonding orbital because the antibonding orbital has a node.

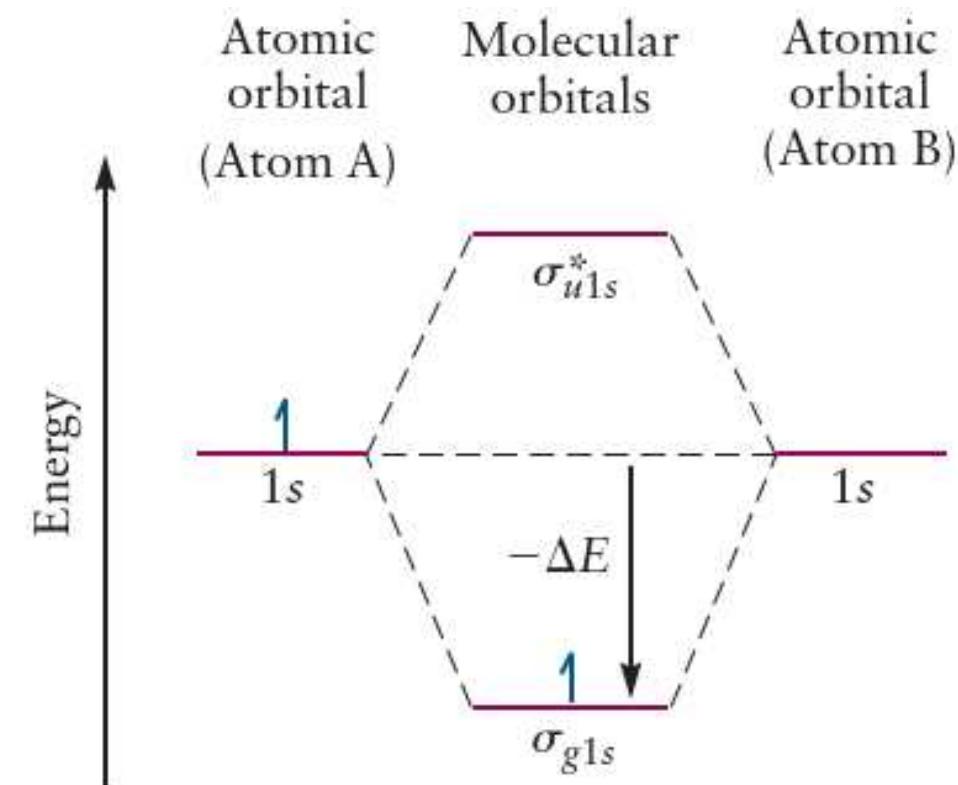
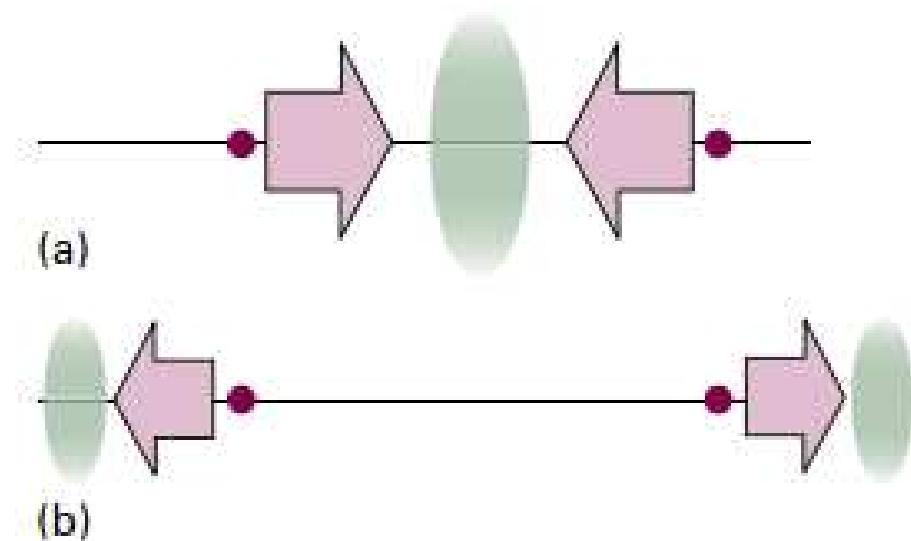


FIGURE 6.11 Correlation diagram for H_2^+ in the linear combination of atomic orbitals (LCAO) approximation. The bonding orbital is stabilized relative to the noninteracting system.
 $E_{1s} + (-\Delta E) = E_{\sigma g1s}$ so ΔE is a positive number.

□ The variation of $E\sigma^*$ with R shows the destabilizing effect of an antibonding electron. The effect is partly due to the fact that an *antibonding electron is excluded from the internuclear region* and hence is distributed largely outside the bonding region. In effect, whereas **a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart** (Fig. 9B.11). The illustration also shows another feature drawn on later: $|E\sigma^* - EH_{1s}| > |E\sigma - EH_{1s}|$, which indicates that the antibonding orbital is more antibonding than the bonding orbital is bonding. *This important conclusion stems in part from the presence of the nucleus–nucleus repulsion (j_0/R): this contribution raises the energy of both molecular orbitals.*

Figure 9B.11 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.



- The basic principles dealing with the molecular orbital description of the bonding in diatomic molecules have been presented in the previous section. Atomic orbitals other than ns orbitals can also interact to form molecular orbitals. Because individual p , d , and f orbitals are not spherically symmetrical, however, we need to define a coordinate system, so we know which lobes are interacting in three-dimensional space.
- Recall that for each np subshell, for example, there are np_x , np_y , and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.
- Just as with ns orbitals, we can form molecular orbitals from np orbitals by taking their mathematical sum and difference.
- When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np atomic orbitals in part (a) in Figure 10.7.5, it is the mathematical *difference* of their wave functions that results in *constructive interference*, which in turn increases the electron probability density between the two atoms.

- The difference therefore corresponds to a molecular orbital called a **bonding molecular orbital** because, just as with the σ orbitals discussed previously, it is *symmetrical about the internuclear axis* (in this case, the z-axis):
$$\sigma_{npz} = n_{pz}(A) - n_{pz}(B)$$
- The other possible combination of the two np orbitals is the mathematical sum:
$$\sigma_{npz} = n_{pz}(A) + n_{pz}(B)$$
- In this combination, shown in part (b) in Figure 10.7.5, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive interference* of the two waves and creating a node between the two atoms. Hence this is an **antibonding molecular orbital**. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a σ_{npz} antibonding molecular orbital.
- Whenever orbitals combine, the bonding combination is always lower in energy (more stable) than the atomic orbitals from which it was derived, and the antibonding combination is higher in energy (less stable).

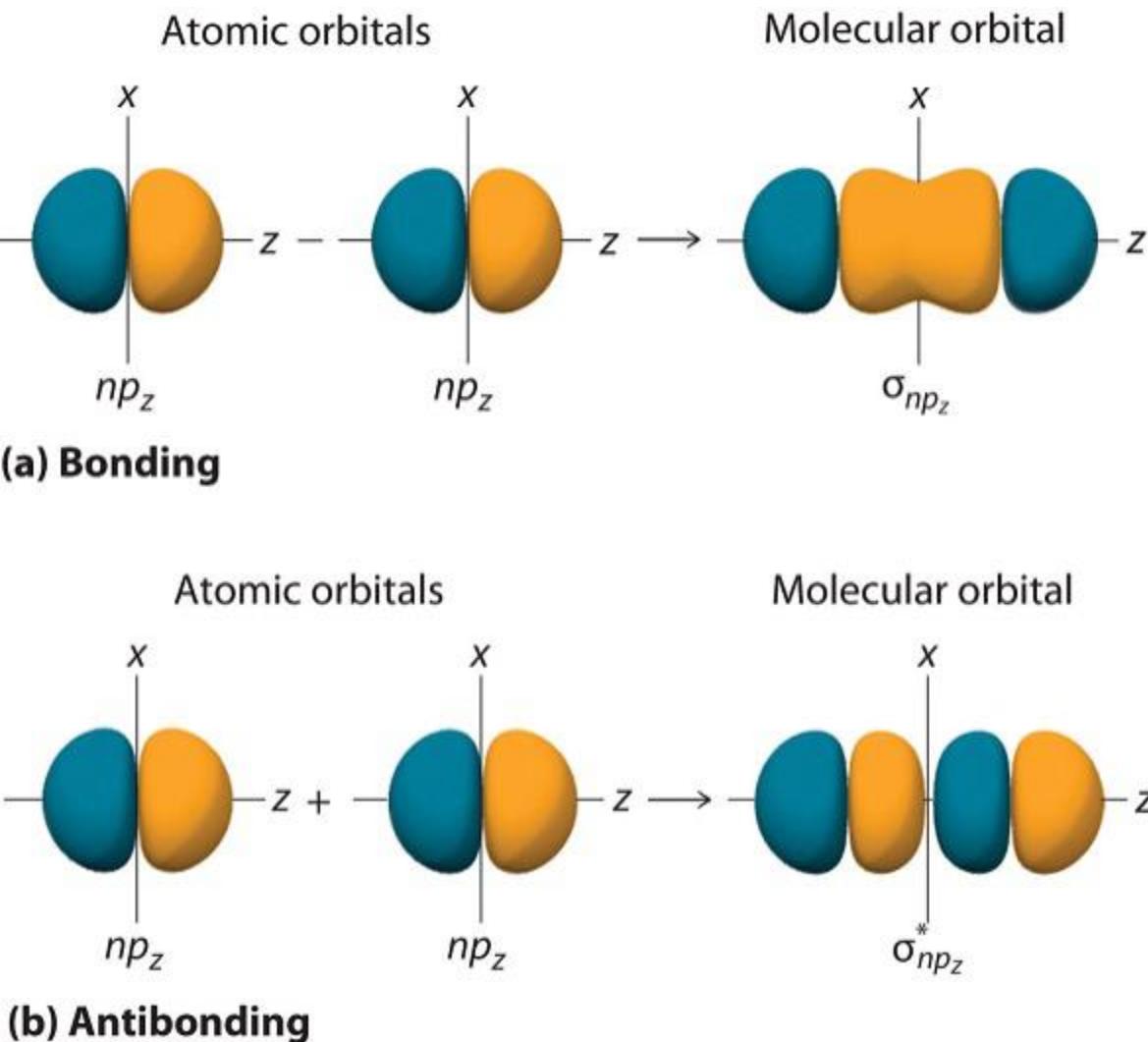


Figure 10.7.5 Formation of Molecular Orbitals from np Atomic Orbitals on Adjacent Atoms.

- (a) By convention, in a linear molecule or ion, the z -axis always corresponds to the internuclear axis, with $+z$ to the right. As a result, the signs of the lobes of the np atomic orbitals on the two atoms alternate $- + - +$, from left to right. *In this case, the σ (bonding) molecular orbital corresponds to the mathematical difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei.
- (b) In contrast, the σ^* (antibonding) molecular orbital corresponds to the *mathematical sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

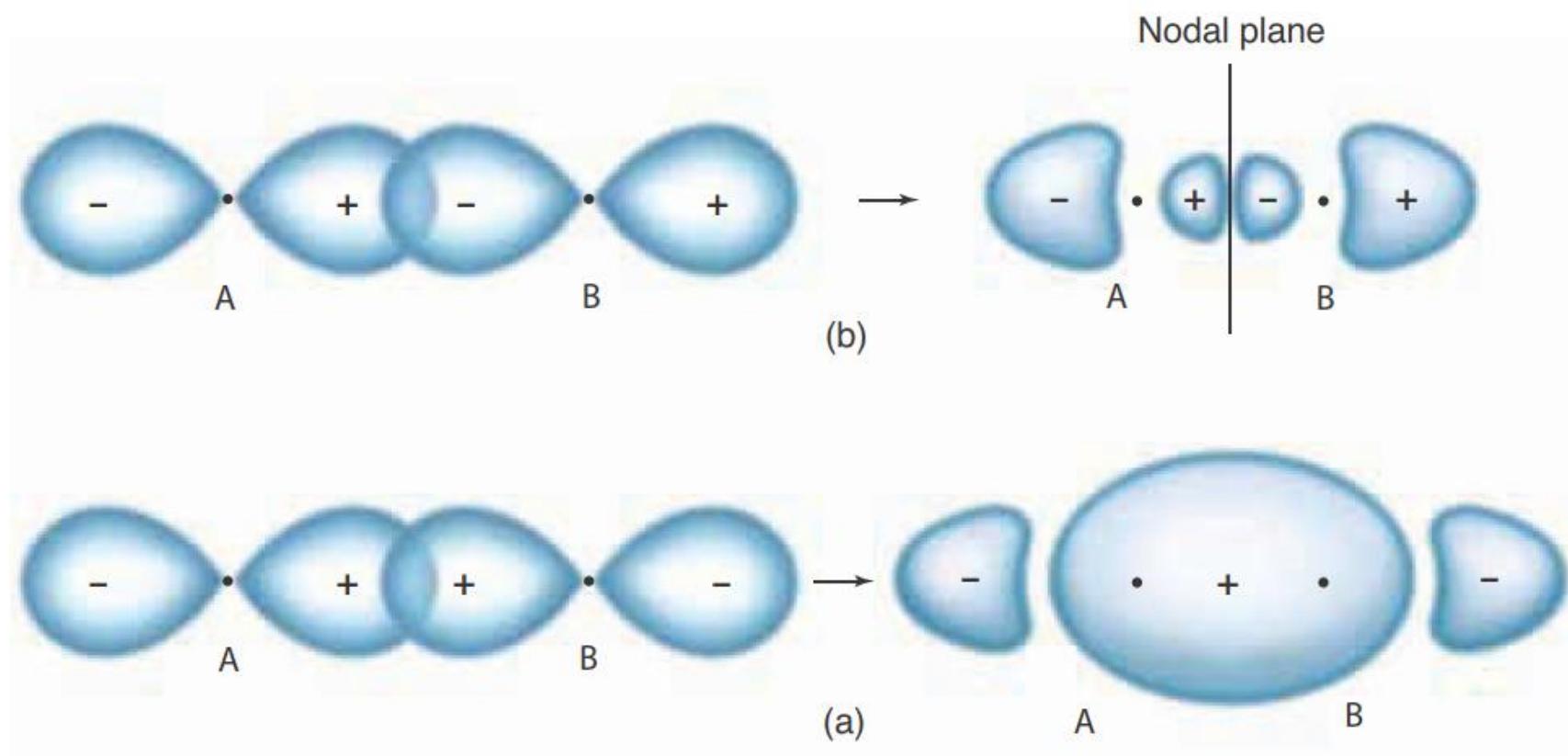


Figure 9.7 The combination of 2p orbitals that lie along the internuclear (z) axis. One lobe of a p orbital has a positive sign and the other a negative sign, as indicated in the figure. In (a), the $2p_z$ orbitals are combined such that the lobes having the same sign overlap, resulting in a bonding σ_{2p_z} orbital. In (b), they are combined such that lobes of different signs overlap, resulting in an antibonding $\sigma^*_{2p_z}$ orbital.

- The remaining p orbitals on each of the two atoms, np_x and np_y , do not point directly toward each other. Instead, they are perpendicular to the internuclear axis.
- The two p orbitals have their lobes extending either above/below or in front/behind of the internuclear axis.
- Overlap of those p orbitals therefore leads to electron density between the two atoms above/below or in front/behind of the inter-nuclear axis. Such orbitals are called π orbitals. As before, constructive and destructive interference is possible, giving rise to two molecular orbitals upon interaction, π and π^* .
- If we arbitrarily label the axes as shown in Figure 10.7.6, we see that we have two pairs of np orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane.
- Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other.

- These interactions are *side-to-side* rather than the head-to-head interactions characteristic of σ orbitals.
- Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference.
- The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals).
- The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π^*) orbital.

- An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel np atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.
 - $\pi_{np_x} = np_x(A) + np_x(B)$
 - $\pi_{np_x}^* = np_x(A) - np_x(B)$
- The two np_y orbitals can also combine using side-to-side interactions to produce a bonding molecular orbital and an antibonding molecular orbital. Because the np and np atomic orbitals interact in the same way (side-to-side) and have the same energy, the bonding and molecular orbitals are a degenerate pair, as are the antibonding and molecular orbitals.
- Notably, the π/π^* orbitals do not possess rotational symmetry, as the sign of those orbitals changes when rotating 180° around the inter-nuclear axis.

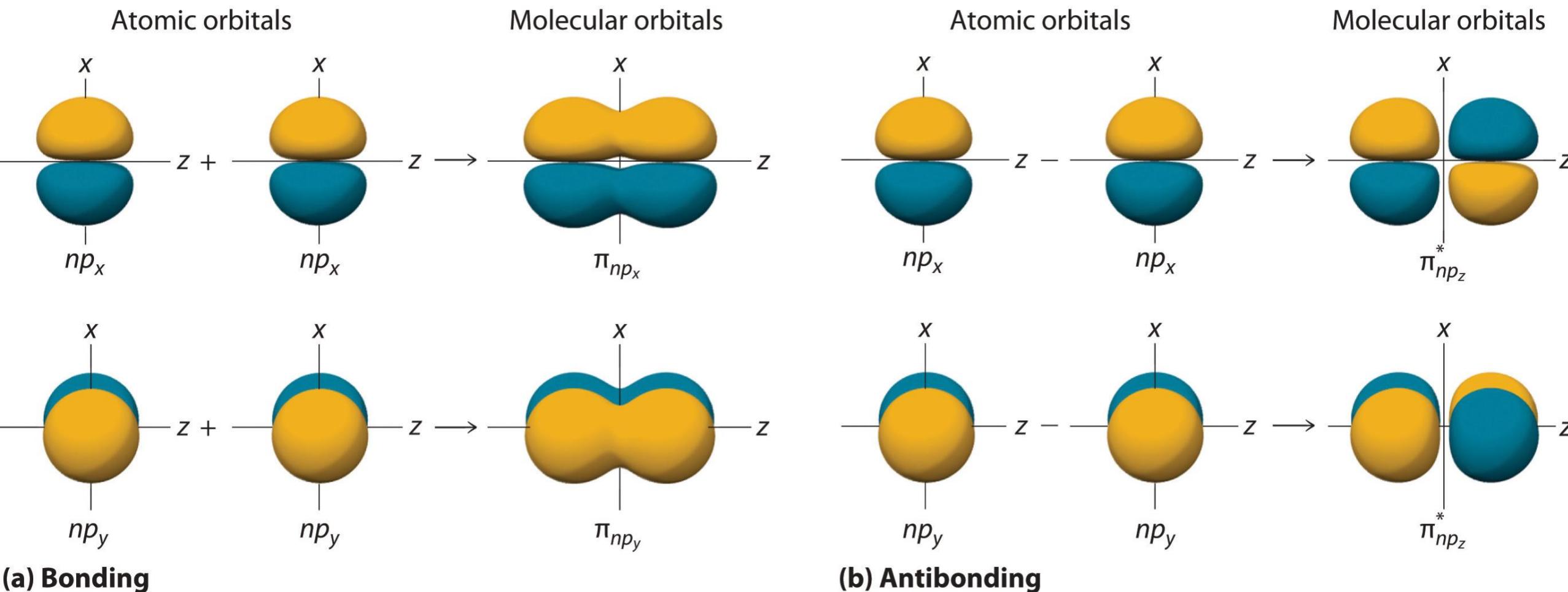


Figure 10.7.6: Formation of π Molecular Orbitals from np and np Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the np and the np atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

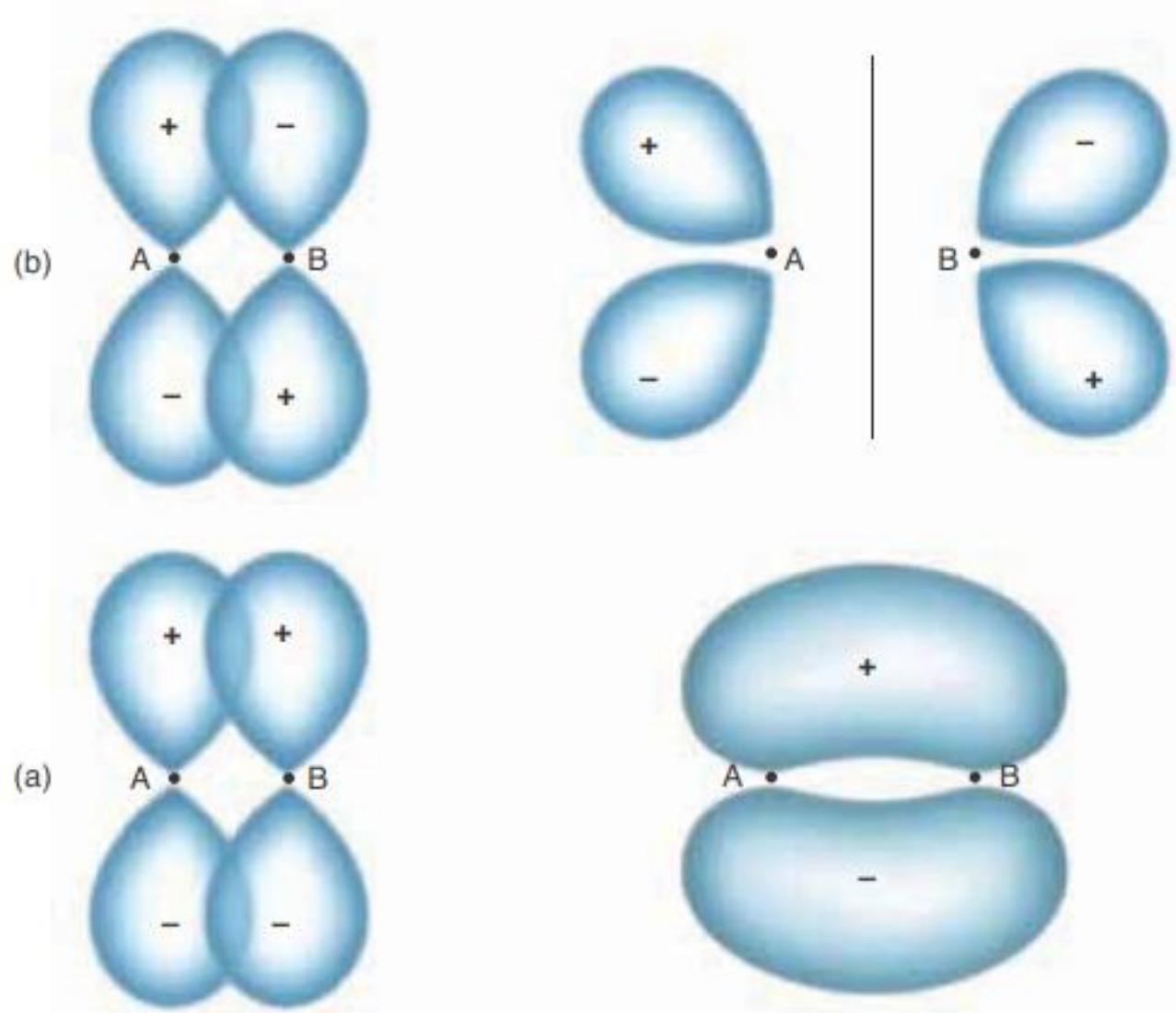


Figure 9.8 The combination of 2p orbitals that lie perpendicular to the internuclear axis. In (a), the p_y orbitals are combined such that lobes of the same sign overlap, resulting in a bonding π_{2py} orbital. In (b), the p_y orbitals are combined such that lobes of opposite sign overlap, resulting in an antibonding π^*_{2py} orbital. There is a similar picture for the p_z orbitals.

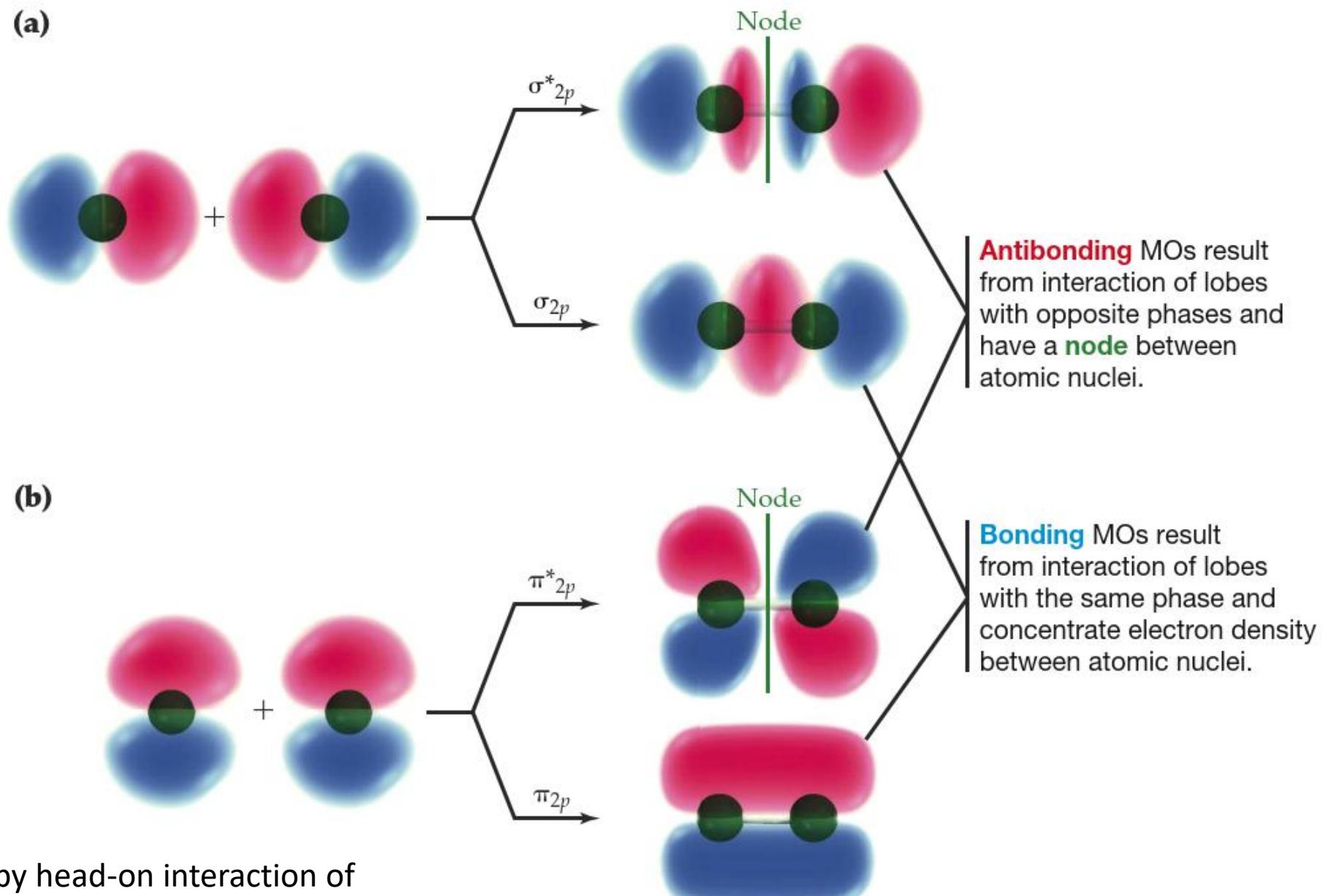


FIGURE 5.13

Formation of (a) σ_{2p} and σ^*_{2p} MOs by head-on interaction of two p atomic orbitals, and (b) π_{2p} and π^*_{2p} MOs by sideways interaction of two p orbitals.

- Figure 10.7.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three np atomic orbitals each.
- There are six degenerate p atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding.
- The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond.
- Conversely, the antibonding molecular orbitals are higher in energy, as shown.
- ***The energy difference between the σ and σ^* molecular orbitals is significantly greater*** than the difference between the two π and π^* sets.
- ✓ The ***reason for this is that the atomic orbital overlap and thus the strength of the interaction is greater for a σ bond*** than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

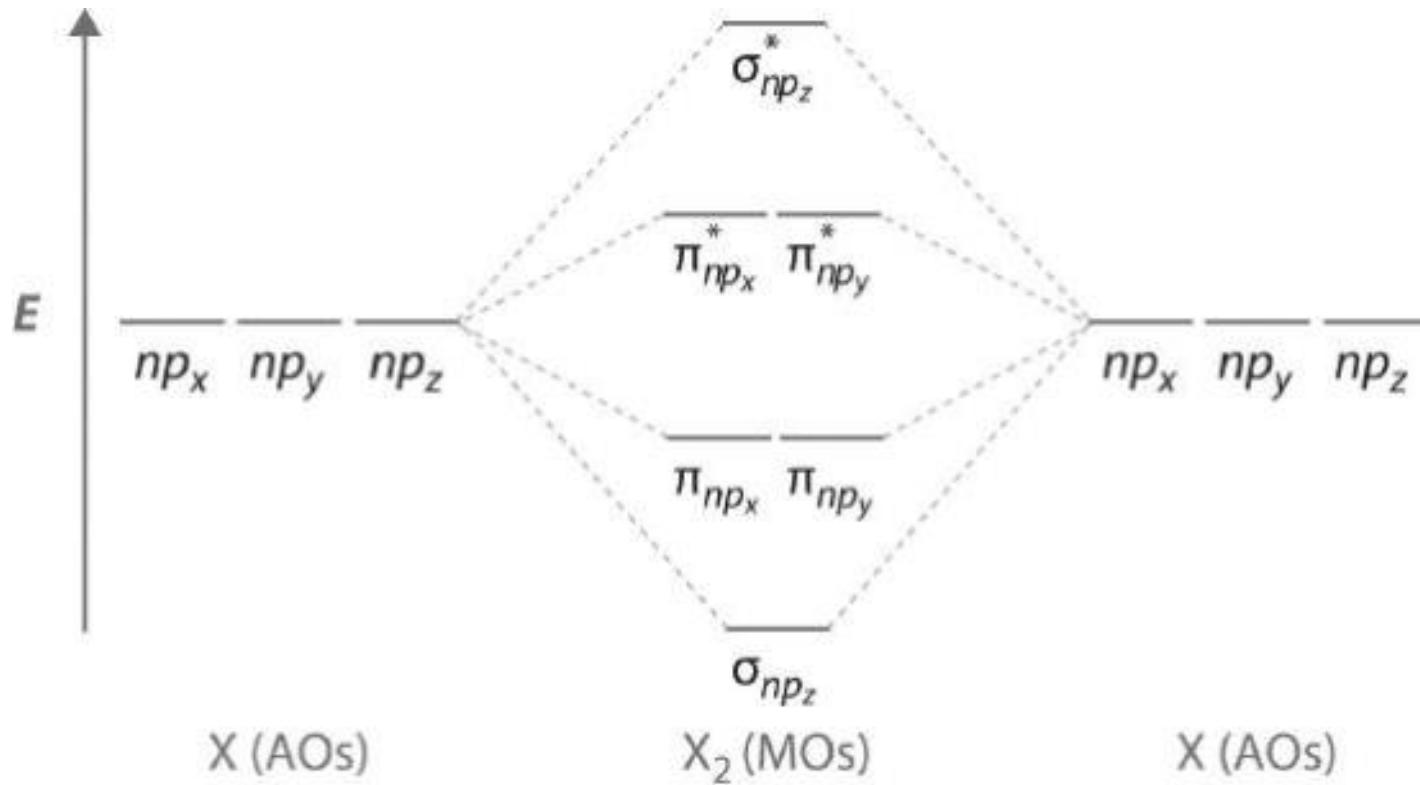
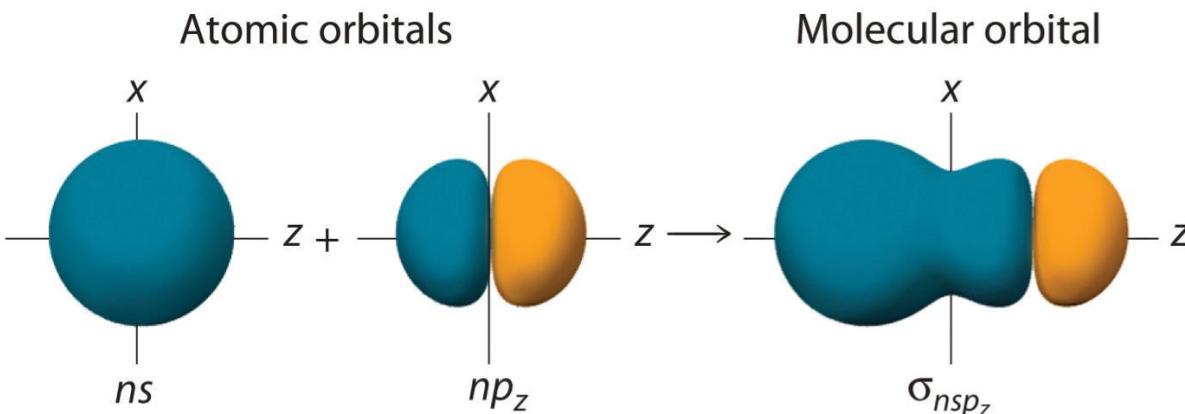
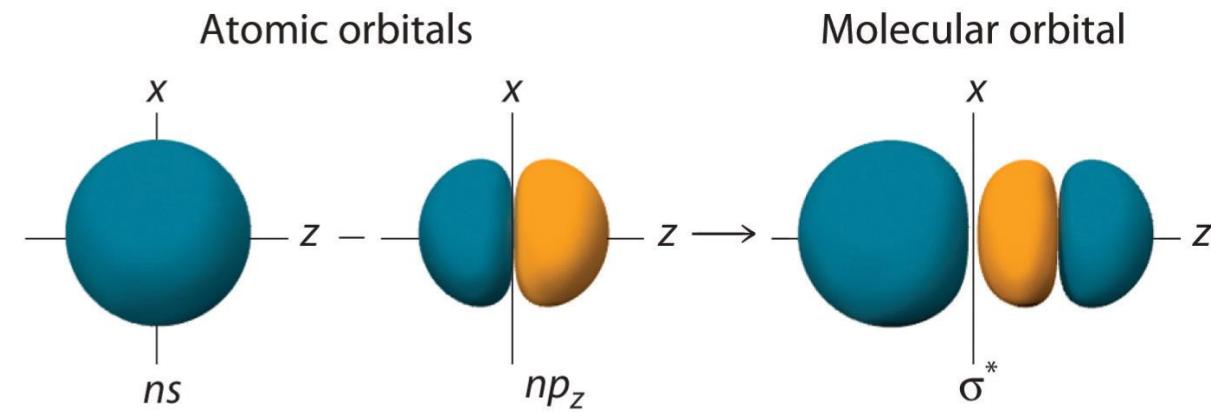


Figure 10.7.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_z , np_x , and np_y Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ^* molecular orbitals is greater than the energy difference between the π and π^* orbitals.

- Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an ns atomic orbital on one atom with an np_z atomic orbital on another.
- As shown in Figure 10.7.8, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ^* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.



(a) Bonding



(b) Antibonding

Figure 10.7.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np Atomic Orbital on an Adjacent Atom.

- (a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei.
- (b) The mathematical difference results in a σ^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

- The essential idea is that orbital lobes of the same sign can lead to favorable overlap (the overlap integral has a value > 0).
- This can occur between orbitals of different types in several ways.
- Fig. 3.6 shows a few types of orbital overlap that lead to bonding.
- Figure 3.7 shows types of orbital interactions that do not lead to bond formation.

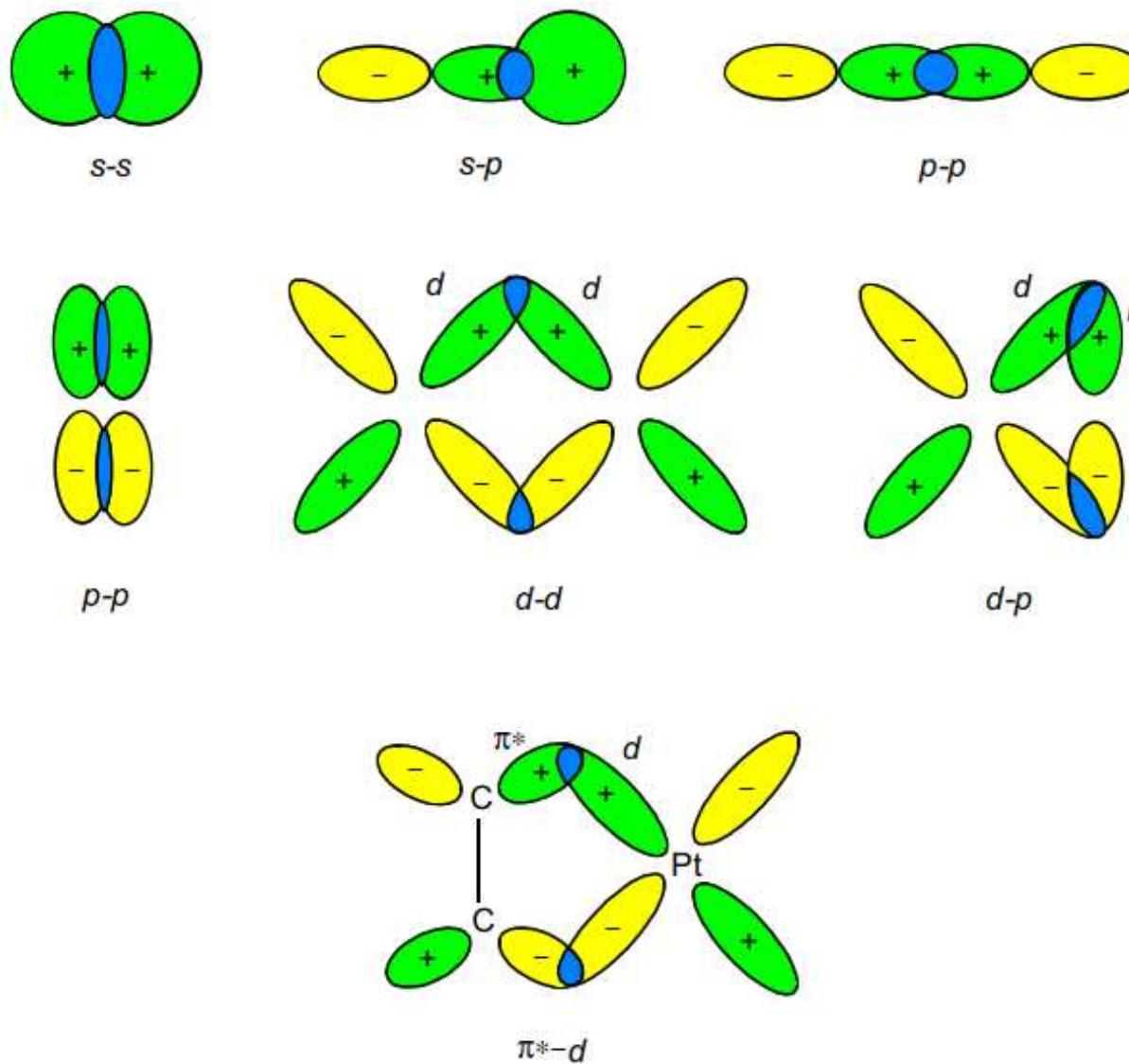
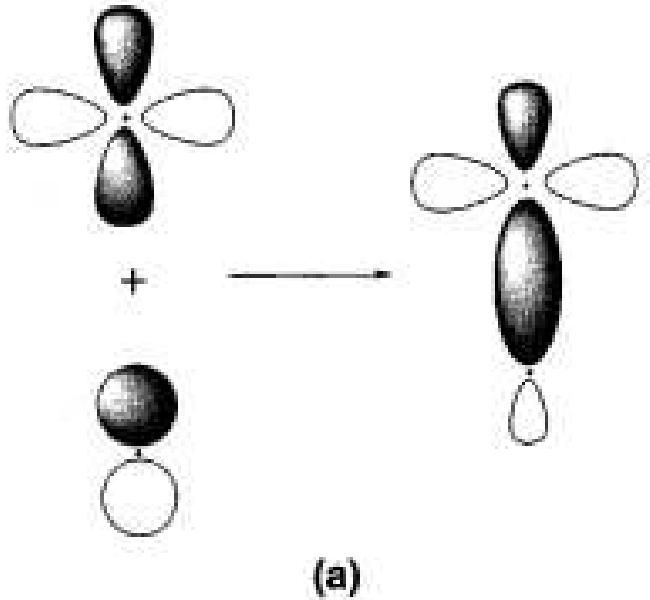
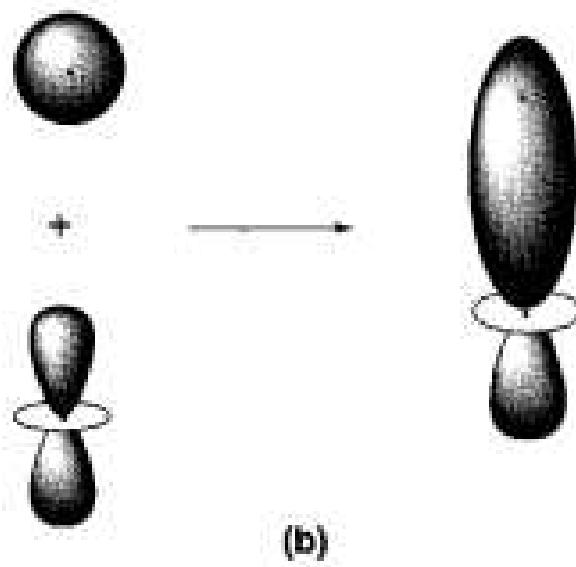


FIGURE 3.6 Some types of orbital overlap that lead to energetically favorable interactions (overlap integral > 0).



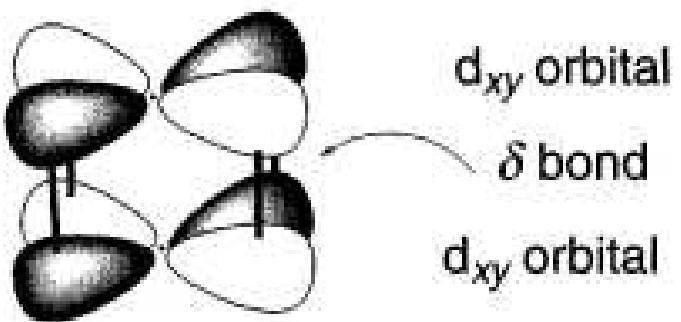
(a)



(b)



(c)



(d)

FIG. 3.1 4 Molecular orbitals involving d orbitals. These diagrams indicate the formation of σ , π and δ bonds, involving d orbitals. (a) σ bond between p_y and $d_{x^2-y^2}$, (b) σ bond between s and d_z^2 , (c) π bond between p_y and d_{xy} , (d) δ bond between two d_{xy} orbitals.

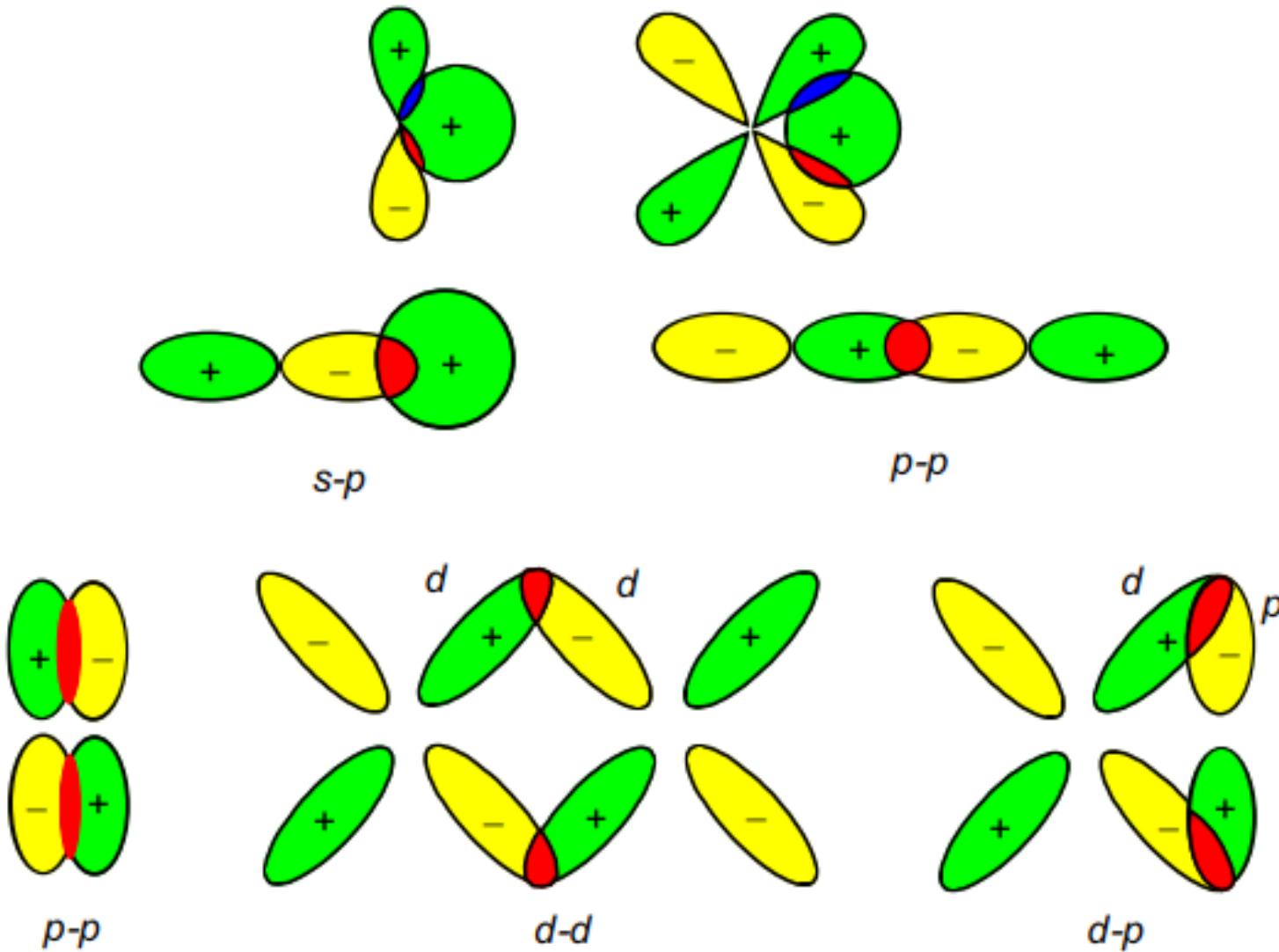


FIGURE 3.7 Patterns of orbital overlap that **do not** lead to bonds.

The Electronic Structure of Many-Electron Molecules

- Once the MO energy levels have been calculated, a molecular configuration is obtained by putting two electrons in each MO, in order of increasing orbital energy, until all electrons have been accommodated.
- If the degeneracy of an energy level is greater than one, Hund's first rule is followed, and the electrons are placed in the MOs in such a way that the total number of unpaired electrons is maximized.
- Recall that the order of the energies of the orbitals for multielectron atoms does not follow the order of the energies of the hydrogen atomic orbitals.
- ✓ For instance, the energy of the 4s orbital is less than that of the 3d orbitals for multielectron atoms. A similar thing happens when we use the H_2^+ molecular orbitals that we have constructed from the combination of hydrogen atomic orbitals.

- ✓ The ordering of the molecular orbitals depends on Z (Z is the atomic number or number of protons in an atom). *For $Z > 7$, the σ_{2p} and π_{2p} orbitals interchange energies so that the energy of the σ_{2p} orbital is less than that of the π_{2p} orbitals.*
- The ordering of the energies of the molecular orbitals that we use to write electron configuration of the second-row homonuclear diatomic molecules Li_2 through Ne_2 is shown in Figure 9.11.
- ✓ Observe that the order of the σ_{2p} and π_{2p} orbitals changes in going from N_2 to O_2 molecules.

➤ The relative order of σ - and π orbitals arising from linear combination of 2p orbitals is shown below.

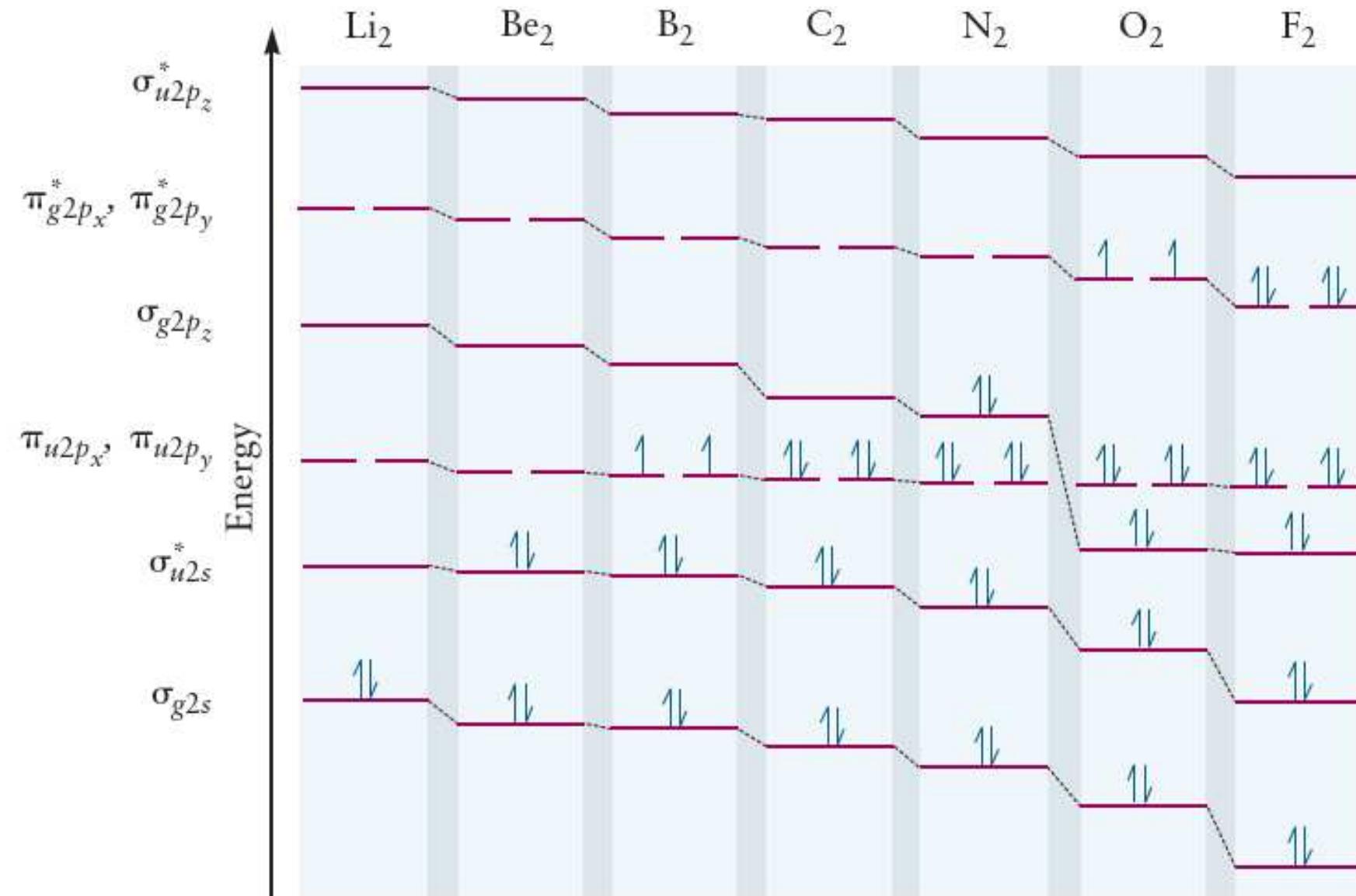


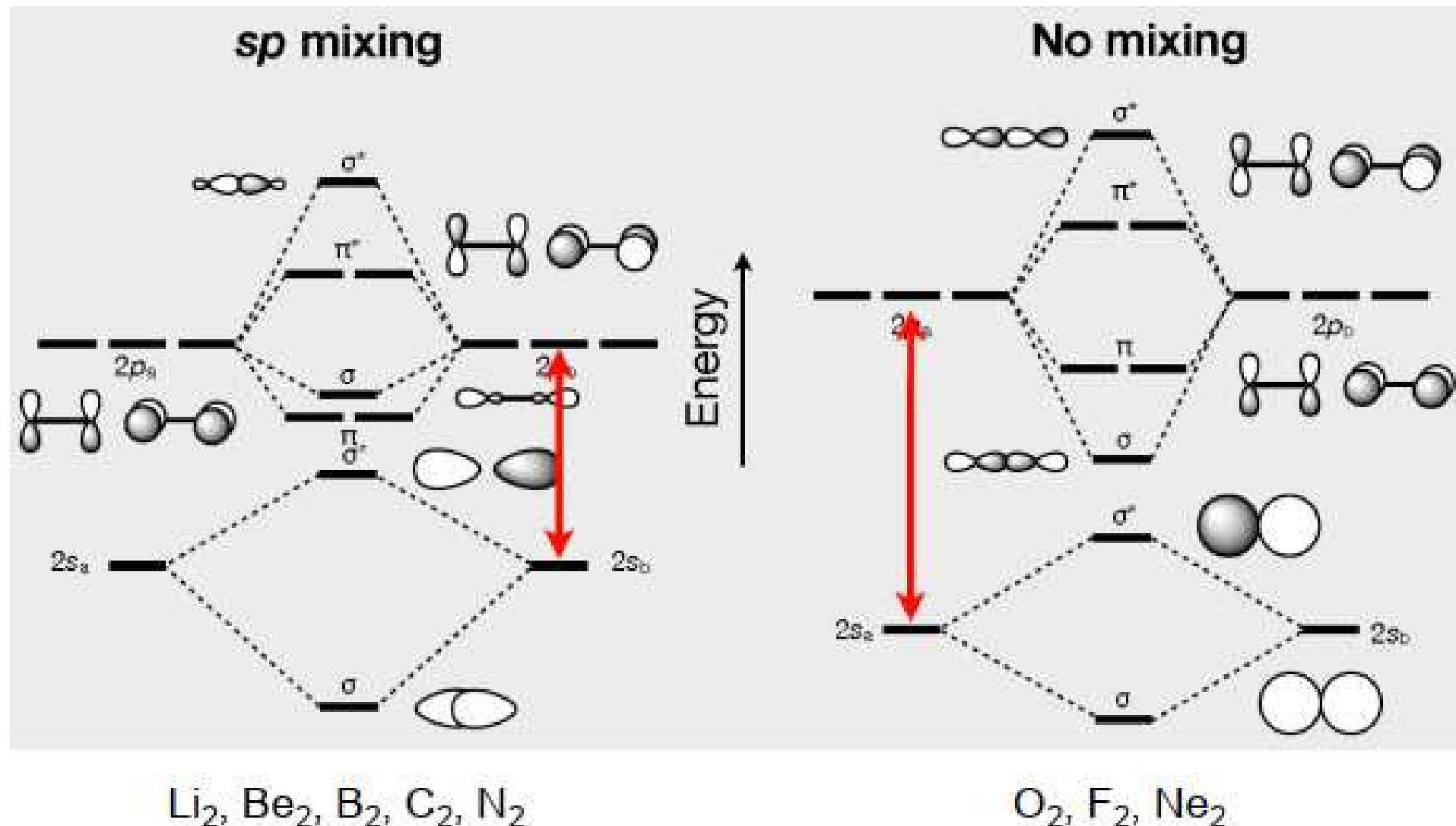
Figure 9.11 The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li_2 through F_2 . Notice that for O_2 through Ne_2 the energy of the $\sigma_g 2p_z$ orbital is below that of the $\pi_u 2p$ orbitals.

Spectroscopic evidence shows that in O_2 (and in F_2) the $\sigma_g 2p_z$ MO is lower in energy than the $\pi_u 2p$ MO.

➤ Note: As Electronegativity increases, the MO energy decreases.

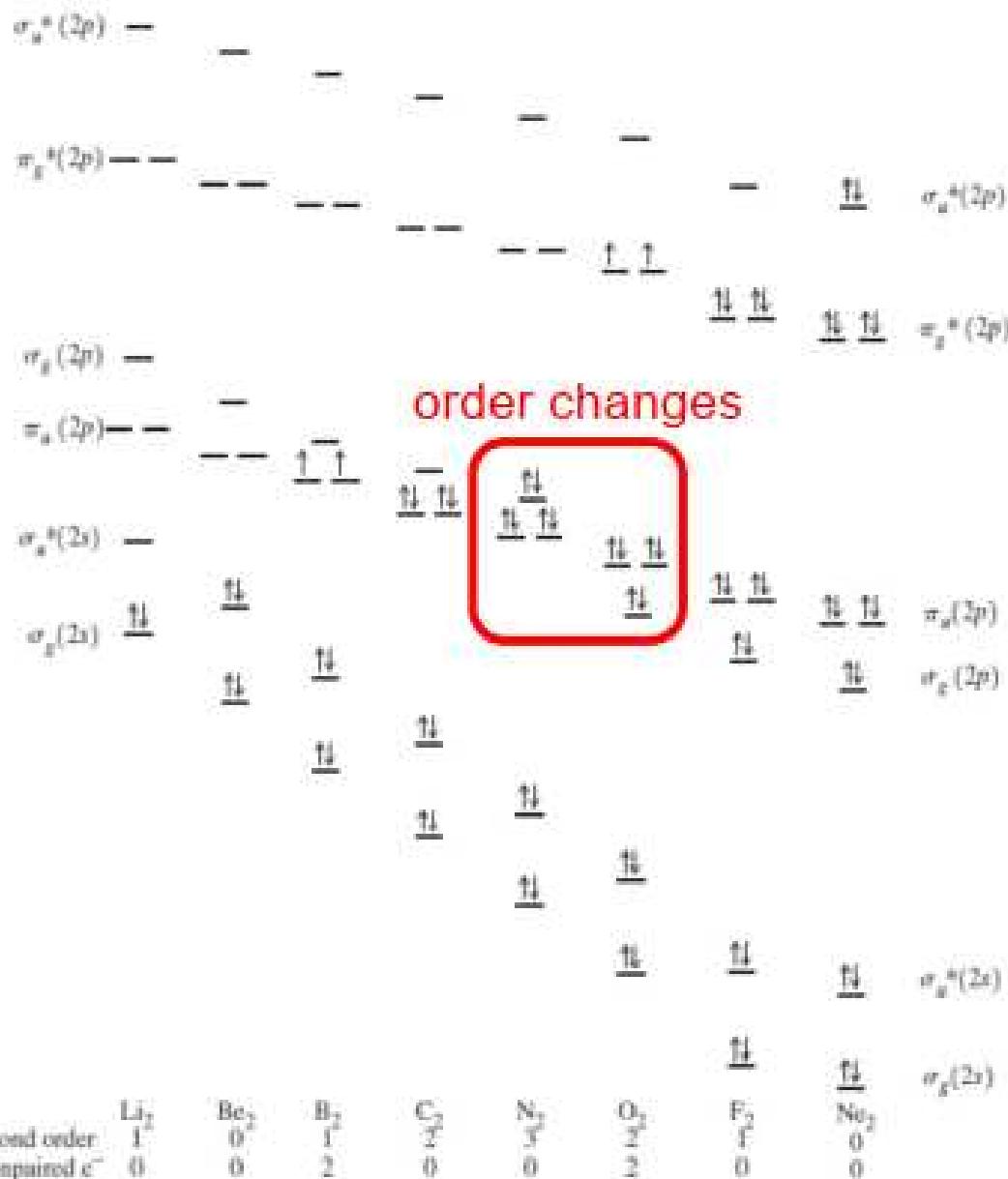
MOs of Homonuclear Diatomic Molecules: **Orbital Mixing**

- ❖ The MO picture of homonuclear diatomic molecules depends on the amount of ***sp* mixing**.



Orbital Mixing

The size of the effect depends on the 2s-2p energy difference.



small $Z_{\text{eff}} =$
small energy
difference =
large sp mixing

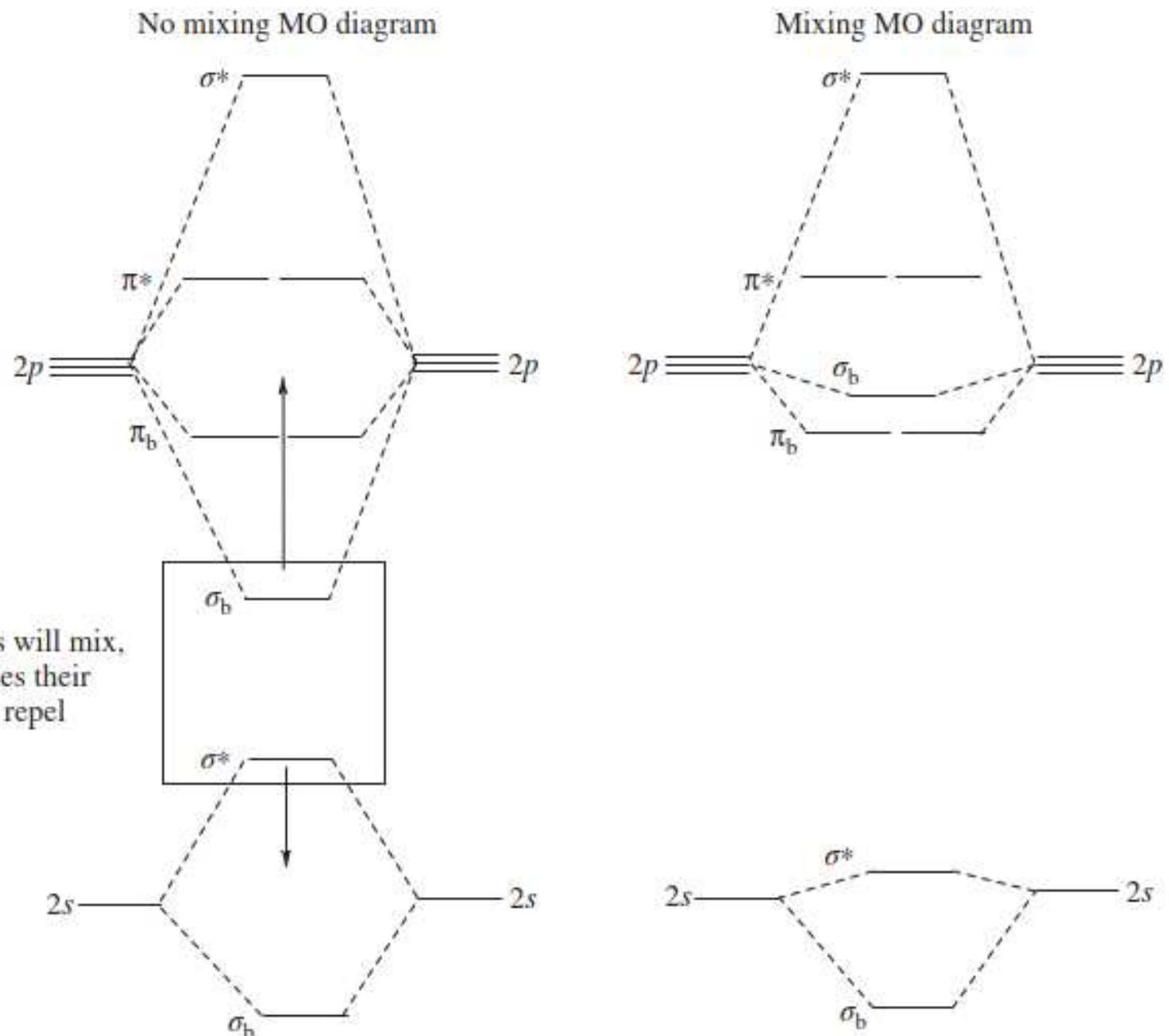
large $Z_{\text{eff}} =$
large energy
difference =
small sp mixing

☐ Orbital Mixing

- The MOs derived from the 2s and $2p_z$ AOs *both have sigma symmetry*, they can “mix” with each other.
- In other words, all four AOs will form linear combinations to make the four sigma MOs.
- *For the lowest energy σ_b MO, the coefficients for the 2s wavefunctions will be significantly larger than those for the $2p_z$ wavefunctions in the linear combination trial function because the 2s orbitals lie closest in energy on the MO diagram to the lowest energy σ_b MO.*
- Likewise, for the highest energy σ^* MO, the coefficients for the $2p_z$ wavefunctions will be much greater than those for the 2s wavefunctions.

- However, for the σ^* and σ_b MOs that are intermediate in energy on the MO diagram (and close in energy to each other), the coefficients for all four atomic orbital basis functions will be similar.
- This MO concept of mixing is therefore very similar to the VB concept of hybridization.
- ***Whenever two MOs have the same symmetry and similar energies, the electrons occupying those orbitals will lie in similar regions of space and will therefore repel one another.***
- This causes the two intermediate sigma MOs on the MO diagram to repel each other, as shown in Figure 10.26.
- The result of the mixing is the modified MO diagram shown below.

Orbital Mixing



Orbitals of similar but unequal energies can interact if they have the same symmetry. The 2s and 2p_z orbitals form MOs with the same sigma symmetry (σ_g and σ_u). s-p mixing causes the σ_g and σ_u MOs to be pushed apart in energy:

FIGURE 10.26
Whenever two MOs have the same symmetry and similar energies, they will mix with each other; in extreme cases, this can lead to the MO diagram shown at right.

Molecular Orbital theory Predicts the Electron Configurations of Diatomic Molecules

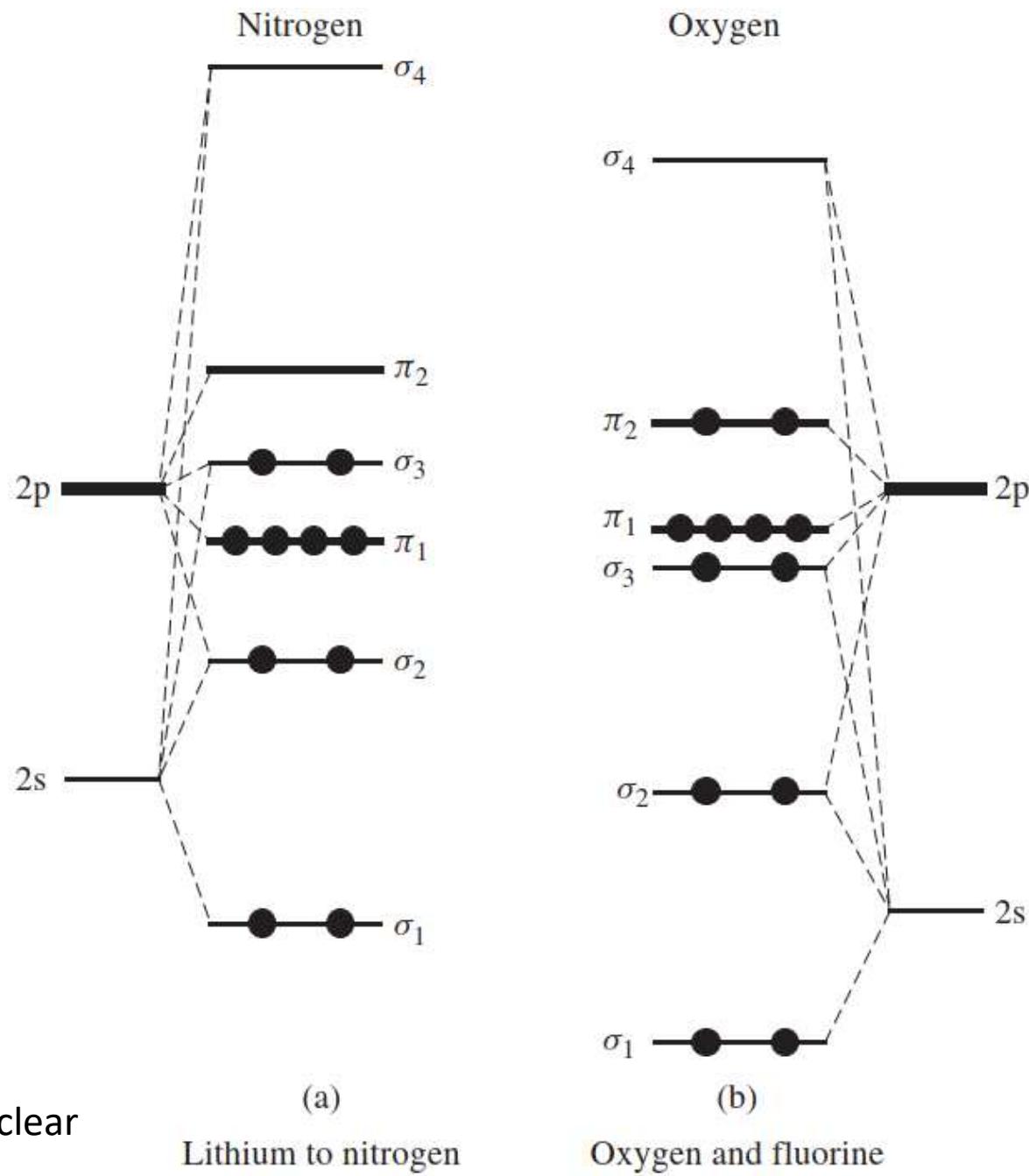
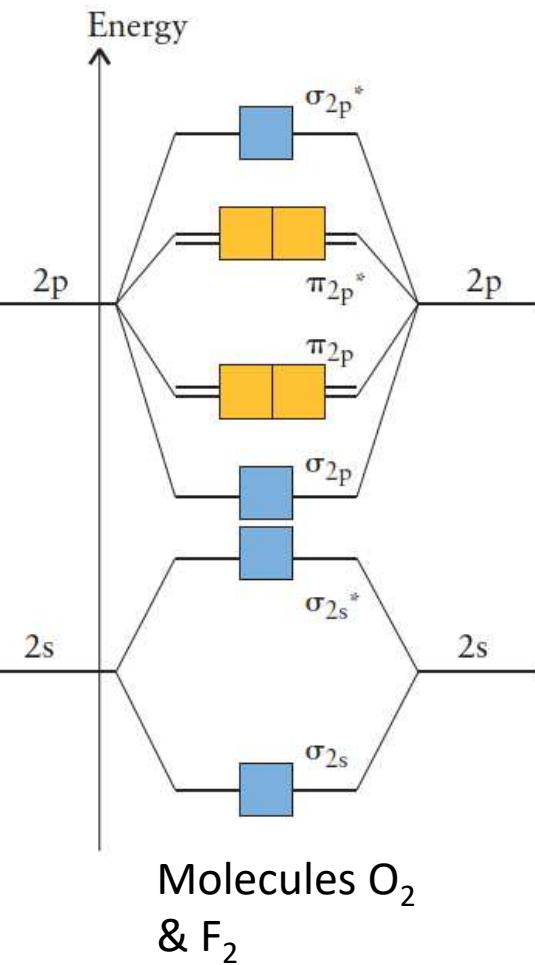
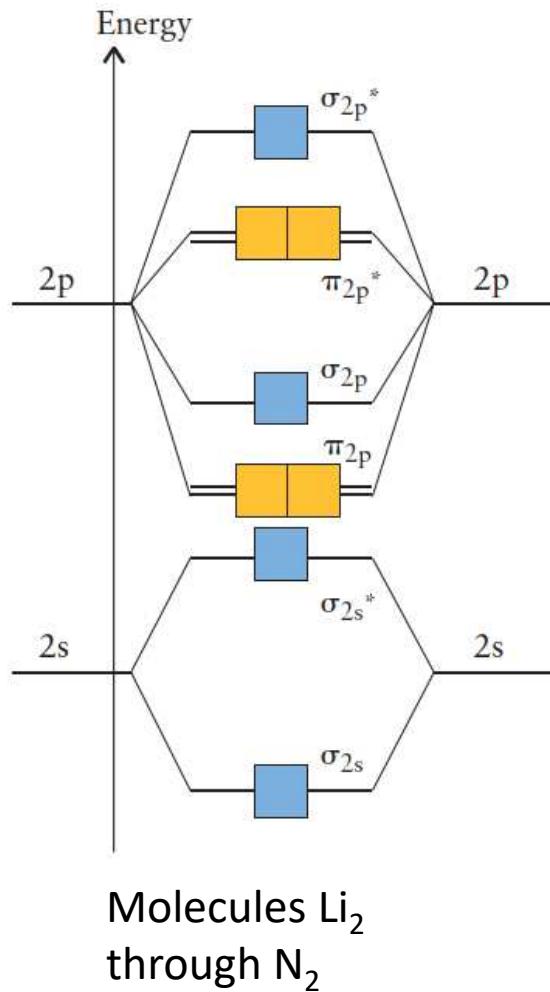


Figure 6.9 Molecular orbital energy-level schemes for homonuclear diatomic molecules of the first row of the periodic table.

- To make our theory more quantitative, we can define a quantity called bond order by the equation:

$$\text{bond order} = \frac{\left(\begin{array}{c} \text{number of} \\ \text{electrons in} \\ \text{bonding orbitals} \end{array} \right) - \left(\begin{array}{c} \text{number of} \\ \text{electrons in} \\ \text{antibonding orbitals} \end{array} \right)}{2} \quad (9.1)$$

- A bond order of $\frac{1}{2}$ indicates a one-electron bond (one-half of an electron pair); a bond order of 1 indicates a single bond (one pair of electrons); a bond order of 2 indicates a double bond (two pairs of electrons); and so on.

Table 9.1 summarizes the properties of the molecular species, H_2^+ , H_2 , He_2^+ , and He_2 .

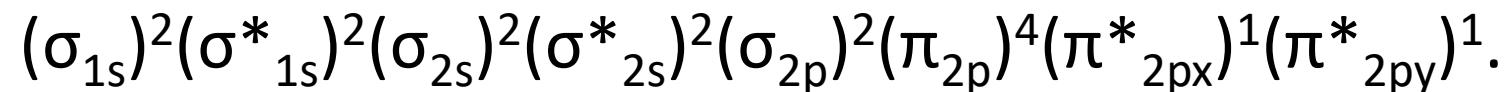
TABLE 9.1 Molecular properties of H_2^+ , H_2 , He_2^+ , and He_2

Species	Number of electrons	Ground state configuration	Bond order	Bond length/pm	Bond energy/aJ
H_2^+	1	$(\sigma_{1s})^1$	$\frac{1}{2}$	106	0.423
H_2	2	$(\sigma_{1s})^2$	1	74	0.724
He_2^+	3	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	108	0.400
He_2	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

- ❖ *Bonding MOs produce charge buildup between the nuclei, whereas antibonding MOs produce charge depletion between the nuclei. Hence removal of an electron from a bonding MO usually decreases D_e (dissociation energy), whereas the removal of an electron from an antibonding MO increases D_e .*
- ❖ Note that **as R_e decreases, the energies of bonding MOs decrease**, while the energies of antibonding MOs increase.
- ✓ For example, the highest filled MO in N_2 is bonding, and in going from the ground state of N_2 to that of N_2^+ the dissociation energy decreases (and the bond length increases).
- ✓ In contrast, the highest filled MO of O_2 is antibonding, and in going from O_2 to O_2^+ the dissociation energy increases (and R_e decreases).
- The designation of bonding or antibonding is not relevant to the effect of the electrons on the total energy of the molecule. Energy is always required to ionize a stable molecule, no matter which electron is removed. Hence *both bonding and antibonding electrons in a stable molecule decrease the total molecular energy.*

- One of the *most impressive aspects of molecular orbital theory is its ability to predict that oxygen molecules are paramagnetic*. This property means that oxygen is weakly attracted to a region between the poles of a magnet.
- Most substances are **diamagnetic**, meaning that they are slightly repelled by a magnetic field.
- Let's see how the paramagnetism of O₂(g) is related to its electron structure.
- The **Lewis formula** of an O₂ molecule does not account for the paramagnetism of O₂(g). According to the octet rule, we should write the Lewis formula of an O₂ molecule as ::, but this formula **implies incorrectly** that *all the electrons are paired*.
- The oxygen molecule is **an exception to the utility of Lewis formulas**, whereas the more fundamental molecular orbital theory is able to account successfully for the distribution of the electrons in molecular oxygen.

- Each oxygen atom has eight electrons; thus, an O₂ molecule has a total of 16 electrons.
- When the 16 electrons are placed according to the molecular orbital diagram given in Figure 9.11, the last two go into the π*_{2p} orbitals. As in the atomic case, we apply Hund's rule.
- Because the two π*_{2p} orbitals have the same energy (degenerate), we place one electron in each π*_{2p} orbital such that the two electrons have unpaired spins, as shown in Figure 9.11.
- The ground state electron configuration of an O₂ molecule is:



- According to Hund's rule, each π*_{2p} orbital is occupied by one electron and the spins are unpaired, we get a ***triplet term***. By Hund's rule this is the ground term.

- Therefore, *an oxygen molecule has a net electron spin and so acts like a tiny magnet*. Thus, O₂(g) is attracted into a region between the poles of a magnet.
 - This explanation of the paramagnetism of O₂ was one of the early triumphs of MO theory.
-
- The amount of oxygen in air can be monitored by measuring its paramagnetism. *Because oxygen is the only major component of air that is paramagnetic*, the measured *paramagnetism of air is directly proportional to the amount of oxygen present*.
 - Linus Pauling developed a method using the paramagnetism of oxygen to monitor oxygen levels in submarines and airplanes in World War II. A similar method is still used by physicians to *monitor the oxygen content in blood during anesthesia*.

- Note, the bond order for the O_2 molecule is $(8 - 4)/2 = 2$, and we say that a bond order of 2 is equivalent to a double bond.
- If an electron is removed from an oxygen molecule, the species O_2^+ results, and the electron removed comes from the highest occupied orbital, which is a π^* (antibonding) orbital. The bond order for O_2^+ is $(8 - 3)/2 = 2.5$, which is higher than that of the O_2 molecule; removing the one electron actually gives us a more stable species. *Because of this, it is not at all unreasonable to expect there to be some reactions in which an oxygen molecule reacts by losing an electron to form O_2^+ , the dioxygenyl cation.*
- Of course, such a reaction would require the reaction of oxygen with a very strong oxidizing agent. One such oxidizing agent is PtF_6^- , which contains platinum in the +6 oxidation state.
- The reaction with oxygen can be written as
 - $\text{PtF}_6^- + \text{O}_2 \rightarrow \text{O}_2^+ + \text{PtF}_6^-$.

- This constitutes a very good test of our model of bonding and antibonding orbitals. Although this reaction shows the formation of O_2^+ , in the same way, it is also possible to add one electron to the O_2 molecule to produce O_2^- , the superoxide ion, or two electrons to form O_2^{2-} , the peroxide ion.
- Adding an electron to O_2 results in a weakening of the bond, as evidenced by the lower bond energy of O_2^- . The bond energy in this ion is not known, but the length of the bond is greater, and this is indicative of a lower bond energy. These two dioxygen ions, by the way, are highly reactive and can be observed only in the gas phase.
- In each case, the electrons are added to the antibonding π^* orbitals, which reduces the bond order from the value of 2 in the O_2 molecule.
- For O_2^- the bond order is 1.5, but it is only 1 for O_2^{2-} , the peroxide ion.
- The O–O bond energy in the peroxide ion has a strength of only $142\text{ kJ}\cdot\text{mol}^{-1}$ and, as expected, most peroxides are very reactive compounds.
- The superoxide ion is produced by the reaction: $K + O_2 \rightarrow KO_2$

Heteronuclear Diatomic Molecules

- Molecular orbital theory can also be applied to **heteronuclear diatomic molecules** (diatomic molecules in which the two atoms are different).
- A heteronuclear diatomic molecule is a diatomic molecule formed from atoms of two different elements; two examples are CO and HCl. Heteronuclear diatomic ions, such as CN^- , are also important in chemistry.
- *In order to sketch the one-electron MO diagrams for heteronuclear diatomics, some understanding of the relative energies of the combining AOs must be known* in advance in order to determine which AOs are close enough in energy to form linear combinations where the MO wavefunction is not simply that of a single AO.
- *The ordinary energy-level scheme can be used if the atomic numbers of the two atoms in the molecule differ by only one or two atomic numbers.*

➤ The ground state electron configurations of the following three species are:



with bond orders of $\frac{1}{2}$, 3, and $\frac{1}{2}$, respectively. Thus, we predict that a CO molecule has the shortest bond, which is correct.

Homonuclear	$1\sigma_g$	$1\sigma_u^*$	$2\sigma_g$	$2\sigma_u^*$	$1\pi_u$	$3\sigma_g$	$1\pi_g^*$	$3\sigma_u^*$
Heteronuclear	1σ	2σ	3σ	4σ	1π	5σ	2π	6σ

Polar bonds and MOT

- In a heteronuclear species **the electron distribution in the covalent bond between the atoms is not symmetrical** between the atoms because it is energetically favorable for a bonding electron pair to be found closer to one atom rather than the other. This imbalance results in a **polar bond**, which is a covalent bond in which the electron pair is shared unequally by the two atoms.
- Molecular orbital theory takes polar bonds into their stride. A polar bond consists of two electrons in an orbital of the form $\Psi = c_A \Psi_A + c_B \Psi_B$ A general LCAO (1) with c_B^2 **not** equal to c_A^2 .
- If $c_B^2 > c_A^2$, the electrons have a greater probability of being found on B than on A and the molecule is polar in the sense $\delta^+A-\delta^-B$.
- A nonpolar bond, a covalent bond in which the electron pair is shared equally between the two atoms and *there are zero partial charges on each atom*, has $c_B^2 = c_A^2$.
- A pure ionic bond, in which one atom has obtained virtually sole possession of the electron pair (as in Cs^+F^- , to a first approximation), has one coefficient zero (so that A^+B^- would have $c_A^2 = 0$ and $c_B^2 = 1$).

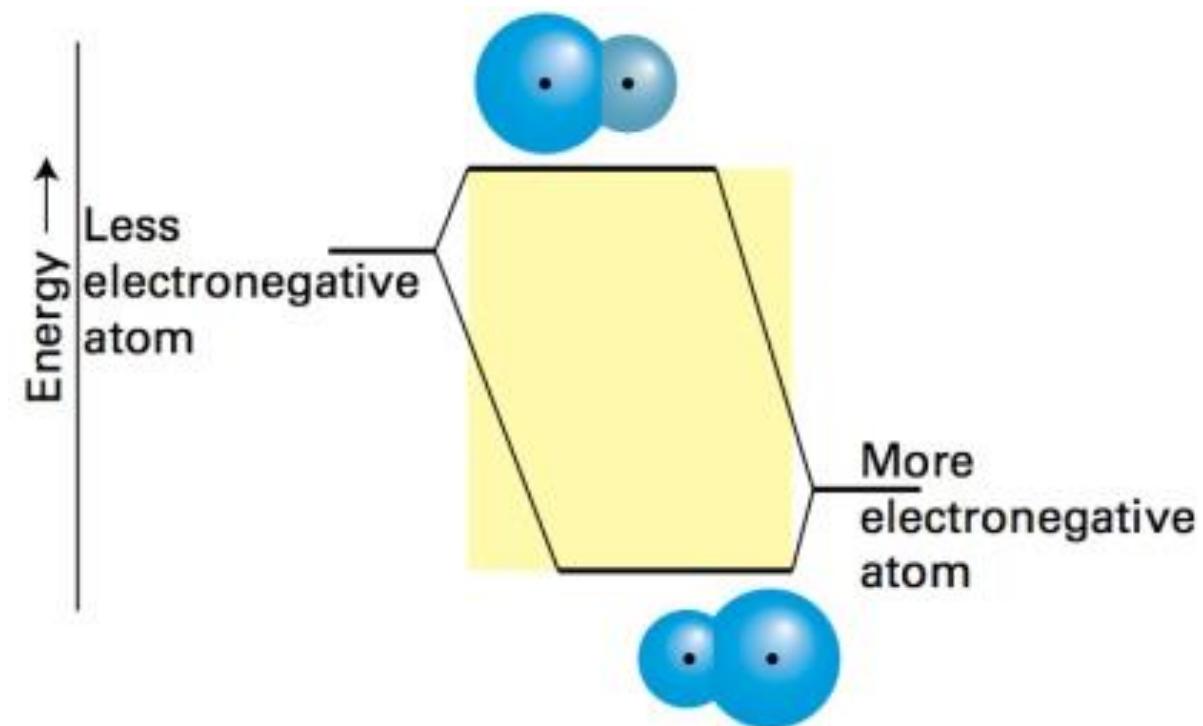
□ It will be familiar from introductory chemistry that the unequal sharing of electrons is related to the **electronegativity**, χ (chi), of an element, its power to draw electrons to itself when it is part of a compound. ***A general feature of molecular orbitals between dissimilar atoms is that the atomic orbital with the higher electronegativity makes the larger contribution to the lower energy molecular orbital.*** The opposite is true of the orbital with higher energy (the antibonding orbital), for which the principal contribution comes from the atomic orbital with higher energy (the less electronegative atom):

- ✓ Bonding orbitals: for $\chi_A > \chi_B, c_A^2 > c_B^2$
- ✓ Anti bonding orbitals: for $\chi_A > \chi_B, c_A^2 < c_B^2$

Figure 1 shows a schematic representation of this point.

Fig. 1 A schematic representation of the relative contributions to bonding and anti bonding molecular orbitals of atoms of different electronegativities. In the bonding orbital, the more electronegative atom makes the greater contribution (represented by the larger sphere), and the electrons of the bond are more likely to be found on that atom. The opposite is true of an antibonding orbital. A part of the reason why an antibonding orbital is of high energy is that the electrons that occupy it are likely to be found on the less electronegative atom.

➤ A MO energy-level diagram is skewed toward the more electronegative atom.

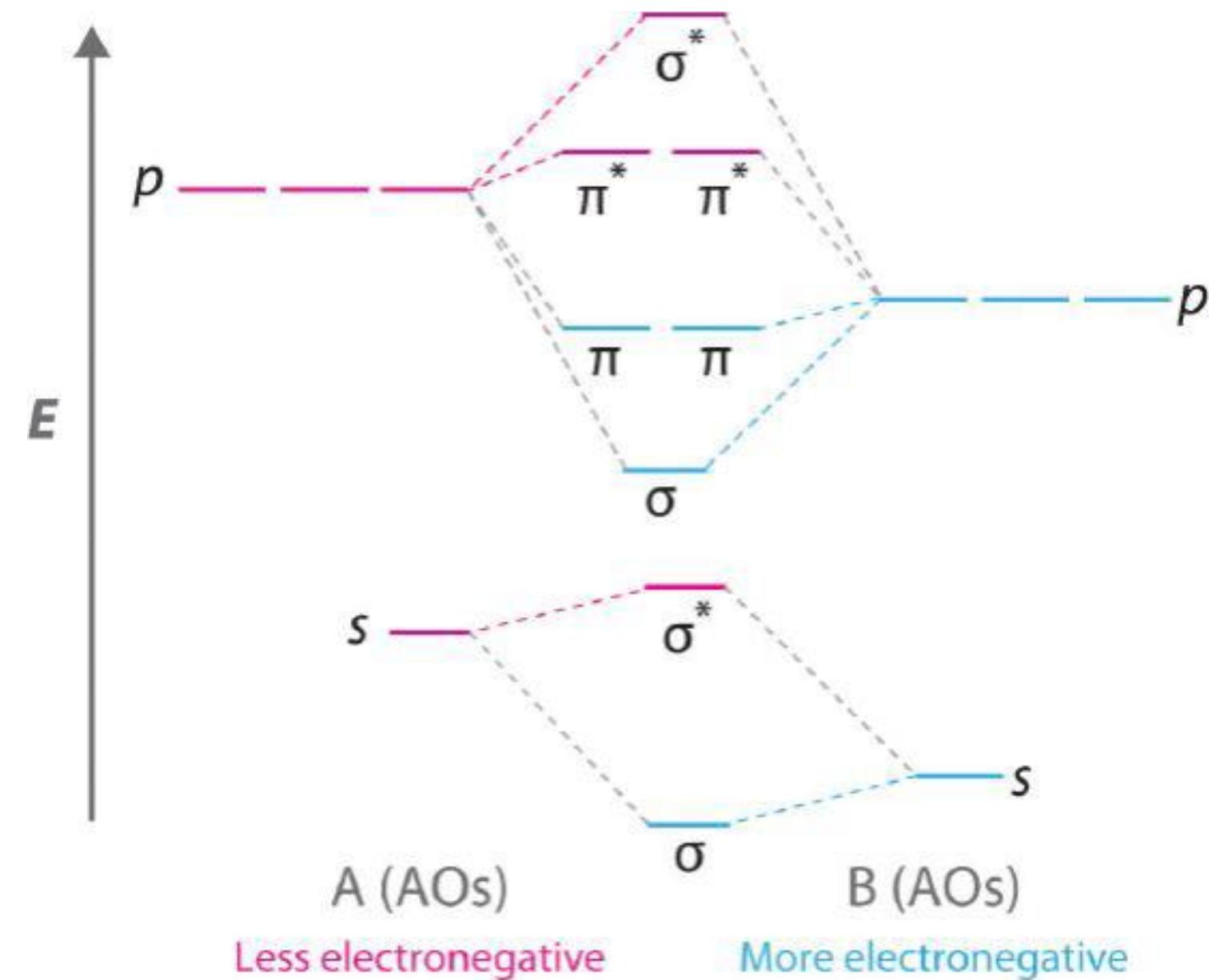


- A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

Figure 10.8.4: Molecular Orbital Energy-Level Diagram for a *Heteronuclear Diatomic Molecule AB*, where $\chi_B > \chi_A$.

The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom.

Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. *On average, they are closer to the B atom, resulting in a polar covalent bond.*

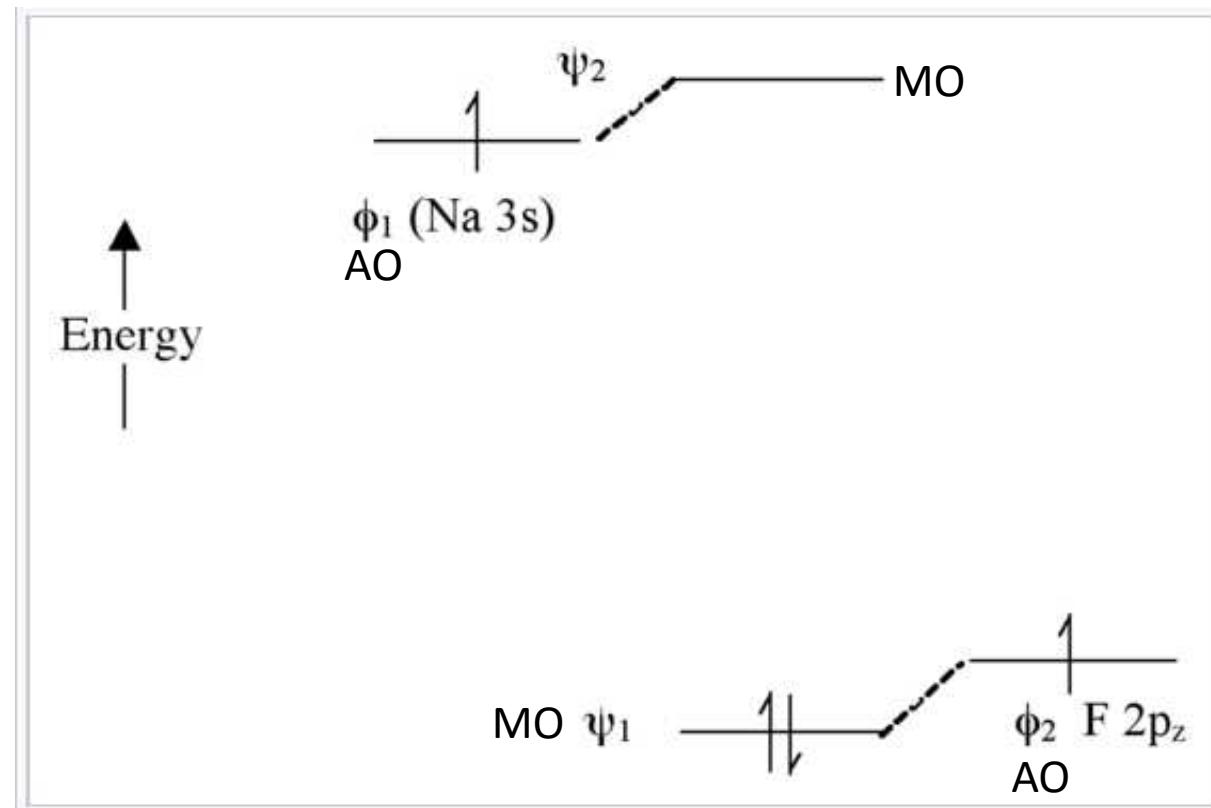


Extreme case - Ionic bonding (NaF):

In this case, there is not much mixing between the AO's because their energies are far apart (Fig. 2.2.8). ***The two bonding electrons are localized on the F atom*** so that we can write the molecule as Na^+F^- .

Note that if we were to ***excite an electron*** from ψ_1 MO to ψ_2 MO using light, the resulting electronic configuration would be $(\psi^1\psi^1)$ and we would be Na^0F^0 . ***This is called a charge transfer transition.***

Figure 2.2.8 : Molecular orbital energy diagram illustrating ionic bonding in the NaF molecule



- In NaCl, the **sodium 3s orbital** (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals.
- The chlorine 3s and 3p_z orbitals *have compatible symmetry*, yet only the **3p_z** orbital (-13.8 eV) is **close enough** in energy to interact with the Na 3s; still, the *energy difference is large enough to make bonding weak*.
- The Na 3s orbital combines with Cl 3p_z to form the molecular orbitals labeled 4σ and 4σ* in Figure 5.3.2.1. The **4σ orbital is weakly bonding, but is very close** in energy to the **Cl 3p_z orbital**, and is **mostly Cl-like in character**.
- Notice that ***all σ orbitals look very much like either s or p orbitals centered on the Cl atom***, while the 4σ* orbital is **centered almost entirely on Na**.
- The ***lack of molecular orbitals that are distributed over both atoms at once is consistent with a lack of significant covalent bond character*** in NaCl.
- The ***bonding here is characterized by the transfer of one electron from Na to Cl and is almost entirely electrostatic***.
- Bonding that is mostly electrostatic in character is non-directional, unlike true covalent bonding.

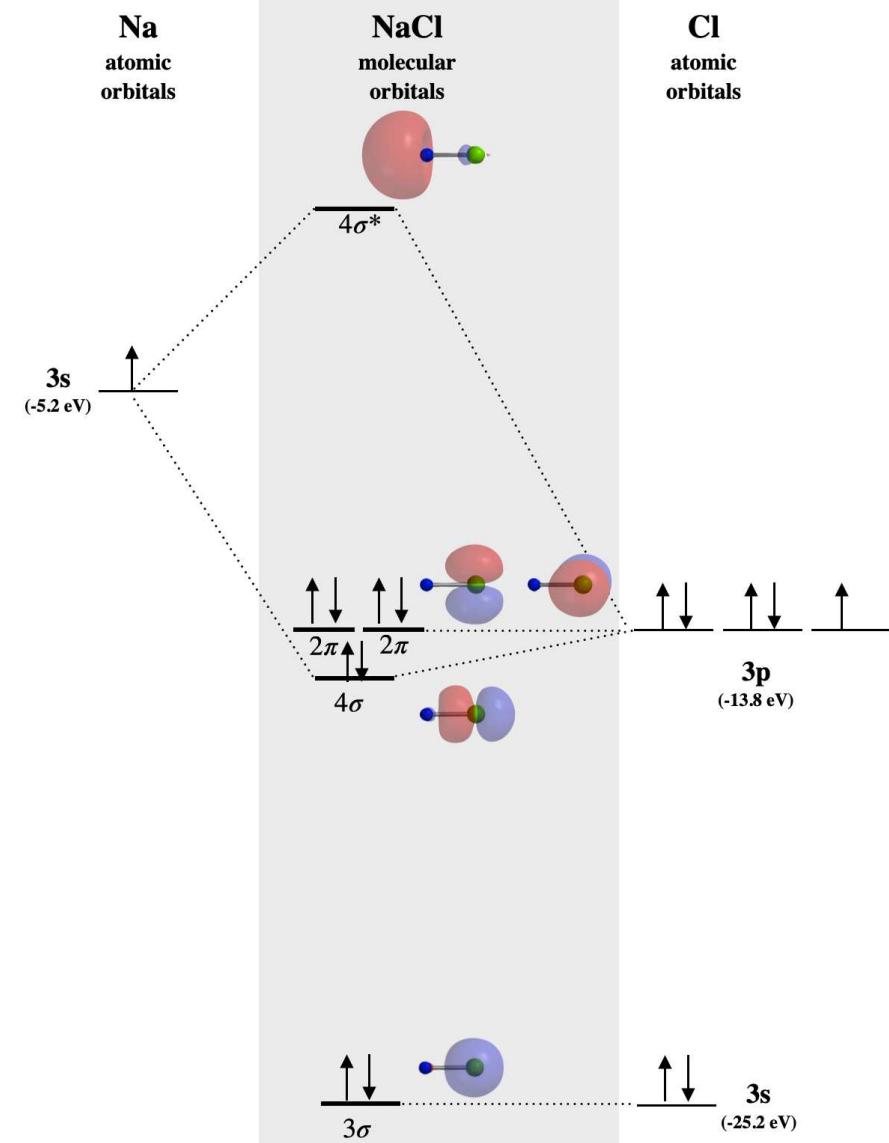
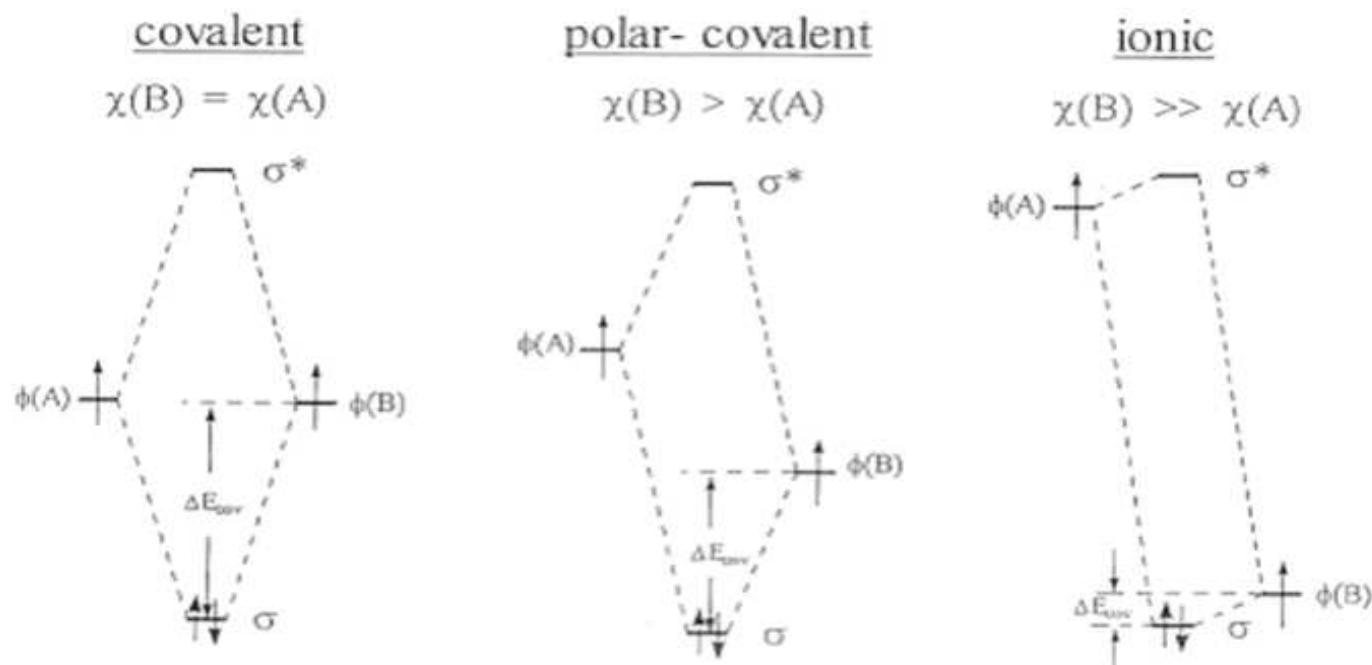


Figure 5.3.2.1: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

MO Description of A-B Covalent, Polar-Covalent, and Ionic Bonds

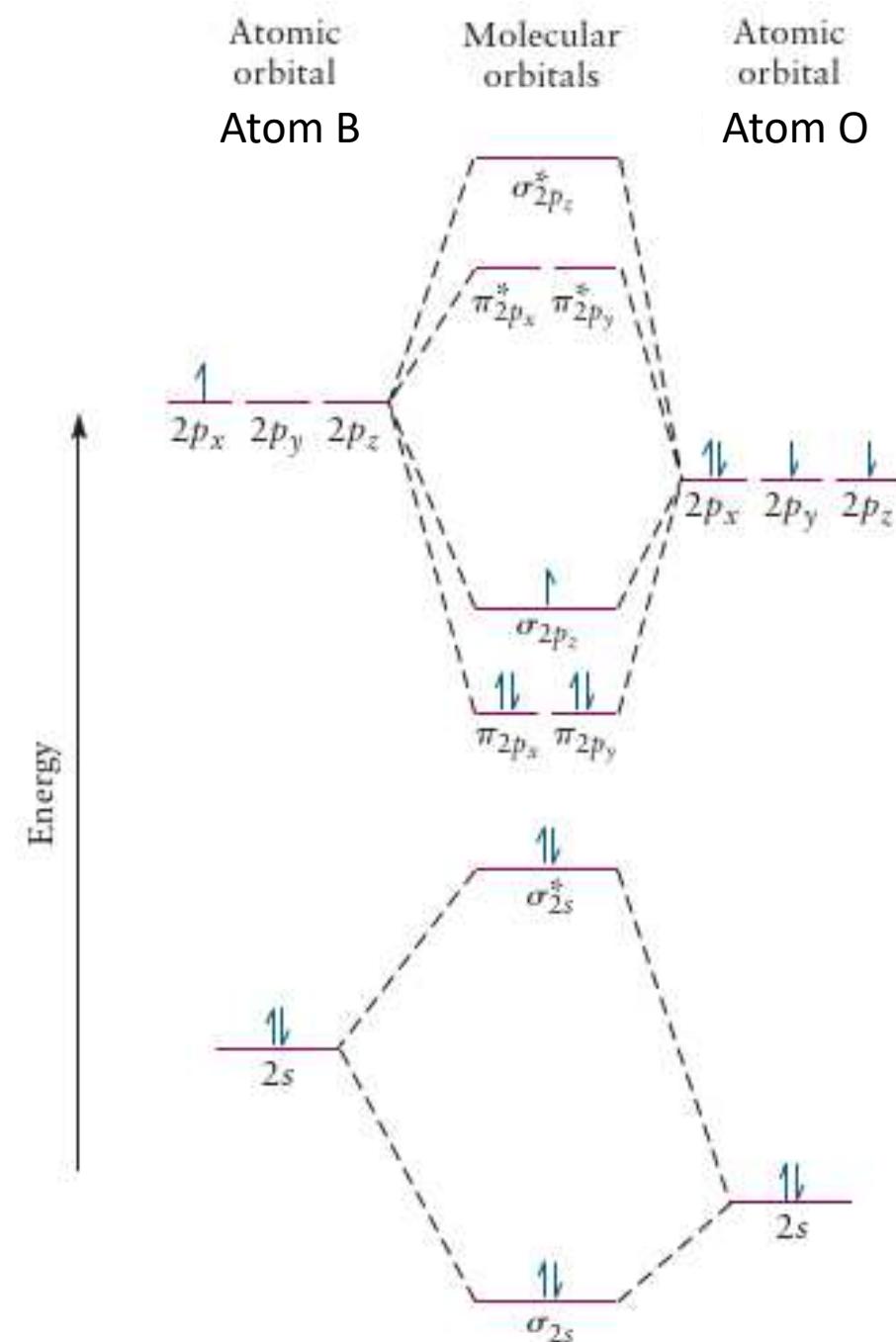


Key Features:

- 1) The diatomic MO's are: $\psi_b(\sigma) = a\phi(A) + b\phi(B)$
 $\psi_a(\sigma^*) = b\phi(A) - a\phi(B)$
- 2) Since each AO *must be fully utilized*, ($a^2 + b^2 = 1$),
 - i) If $\chi(B) = \chi(A)$, then $b = a$
 - ii) If $\chi(B) > \chi(A)$, then $b > a$
 - iii) If $\chi(B) \gg \chi(A)$, then $b \sim 1$, and:
 $\psi_b(\sigma) \sim \phi(B)$, $\psi_a(\sigma^*) \sim \phi(A)$

- To illustrate the differences between homonuclear and heteronuclear diatomic molecules, first we consider **boron monoxide (BO)** molecule.

FIGURE 6.21 Correlation diagram for heteronuclear diatomic molecule, **boron monoxide (BO)**. The atomic orbitals for the more electronegative atom (O) are displaced downward because they have lower energies than those for B. The orbital filling shown is that for BO.



- Next we consider HF molecule to illustrate the differences between homonuclear and heteronuclear diatomic molecules.
- This molecule illustrates the case in which the valence electrons on the combining atoms occupy different electron shells: the 1s AO on H and the 2s and 2p AOs on F. The energies of the valence electrons in the 2s and 2p atomic orbitals on fluorine are $-1.477 E_h$ and $-0.684E_h$, respectively. The energy of the valence electron in the 1s atomic orbital on hydrogen is $-0.500E_h$.
- *Because the 2p atomic orbitals on fluorine are the closest in energy to the 1s orbital on hydrogen, a first approximation to the molecular orbital would be to consider linear combinations of these two different types of atomic orbitals.*

➤ But which 2p atomic orbital should be used? Defining the z-axis as the internuclear axis, Figure 9.18 shows the overlap of the fluorine 2p_z and 2p_x orbitals with the hydrogen 1s orbital.

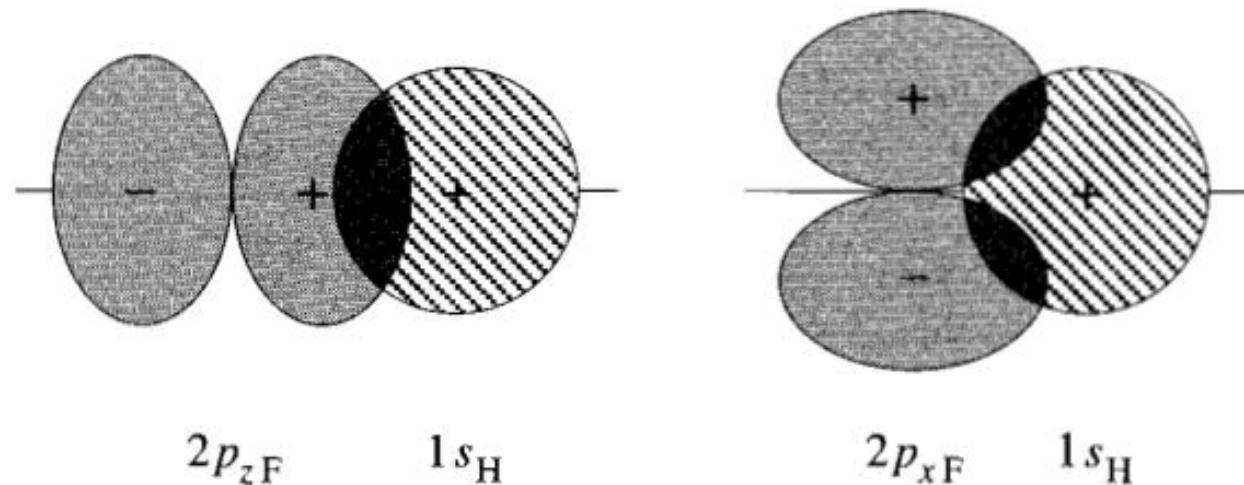


FIGURE 9.18

The overlap of the fluorine 2p_z and 2p_x atomic orbitals with the hydrogen 1s atomic orbital. Because of the change in sign of the 2p_x wave function, the net overlap between the 2p_x and hydrogen 1s is zero for all internuclear distance. A set of two molecular orbitals result from the overlap of the fluorine 2p_z atomic orbital and the hydrogen 1s atomic orbital. The bonding σ orbital, σ_b , is the one shown.

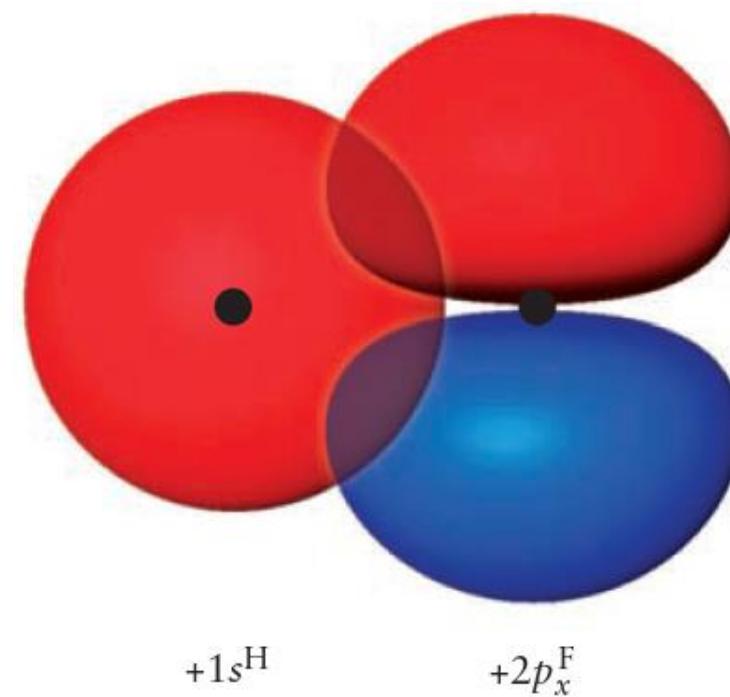


FIGURE 6.22 The H 1s and F 2p_x (or 2p_y) orbitals have no net overlap in HF.

- The fluorine $2p_y$ atomic orbital overlaps the hydrogen 1s atomic orbital in a similar manner as the $2p_x$ orbital except that it is directed along the y-axis instead of the x-axis.
- *The hydrogen 1s and fluorine $2p_z$ orbitals overlap constructively, so we can use linear combinations of these two orbitals.* However, because of the change in sign of the wave function for the $2p_x$ ($2p_y$) atomic orbital with respect to the y-z plane (x-z plane) and the constant sign of the hydrogen 1s atomic orbital, the net overlap between the $2p_x$ ($2p_y$) on fluorine and the 1s on hydrogen is zero for all internuclear distances.
- Thus, a first approximation to the molecular orbital would be the linear combinations of the fluorine $2p_z$ and hydrogen 1s atomic orbitals.
- The molecular orbitals are symmetric about the internuclear axis, so both are σ molecular orbitals (one bonding, σ_b , and one antibonding, σ_a).
- Figure 2.21 shows the molecular-orbital energy-level diagram for HF. (The $1s_F$ orbital is not shown.)

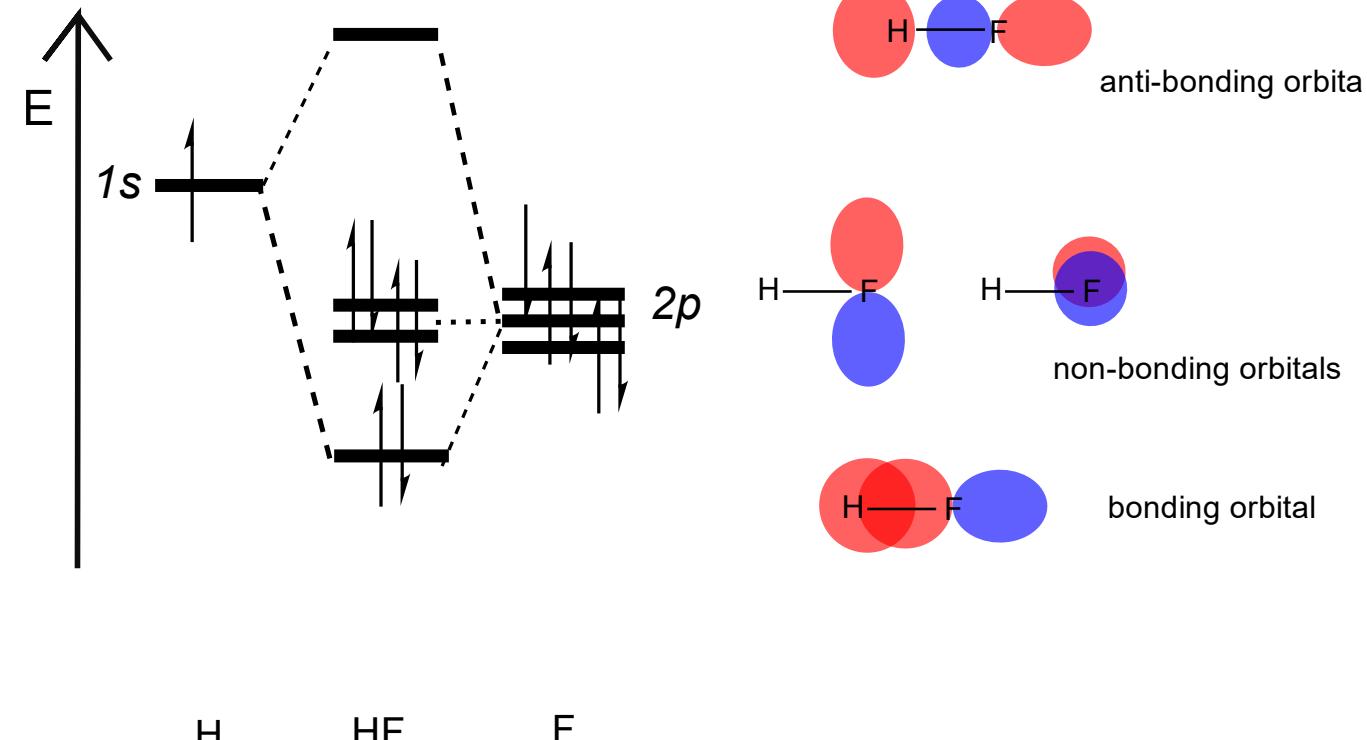
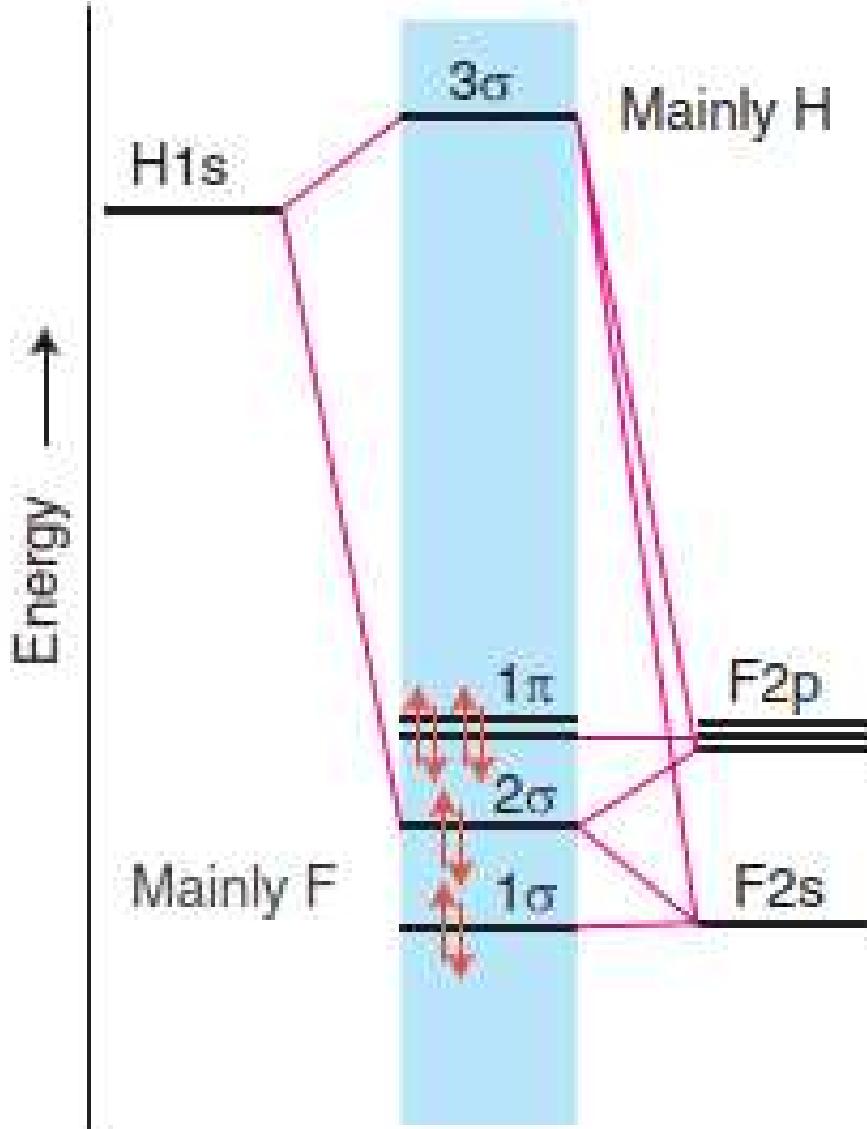


Figure 2.21* The molecular orbital energy-level diagram for HF. The relative positions of the atomic orbitals reflect the ionization energies of the atoms. The fluorine 1s orbital is not shown. Note that the $2p_{x_F}$ and $2p_{y_F}$ orbitals are nonbonding orbitals.

- The ***eight valence electrons*** occupy the four lowest energy orbitals in accord with the Pauli Exclusion Principle, so the ground-state valence electron configuration of HF is $(2s_F)^2(\sigma_b)^2(2p_{xF})^2(2p_{yF})^2$.
- The $2s_F$, $2p_{xF}$ and $2p_{yF}$ orbitals are ***non-bonding orbitals*** (*almost no change in energy w.r.t. AOs*), so the **bond order** of HF is one.

The calculated molecular orbital energy diagram for HF is shown in Figure 12.22. The AOs on the two atoms that give rise to the MOs are shown on the right side of the diagram, with the size of the orbital proportional to its coefficient in the MO. Numerical calculations show that the 1s electrons are almost completely localized on the F atom.

The 1π electrons are completely localized on the F atom because the $2p_x$ and $2p_y$ orbitals on F have a zero net overlap with the 1s orbital on H. [Electrons in MOs localized on a single atom are referred to as *nonbonding electrons*.](#) The mixing of 2s and 2p AOs in the 3σ and $4\sigma^*$ MOs changes the electron distribution in the HF molecule somewhat when compared with a homonuclear diatomic molecule. *The 3σ MO has less bonding character and the $4\sigma^*$ MO has less antibonding character.* Note that the total bond order is approximately one because the 2σ MO is largely localized on the F atom, the 3σ MO is not totally bonding, and the 1π MOs are completely localized on the F atom. The MO energy diagram depicts the MOs in terms of their constituent AOs.

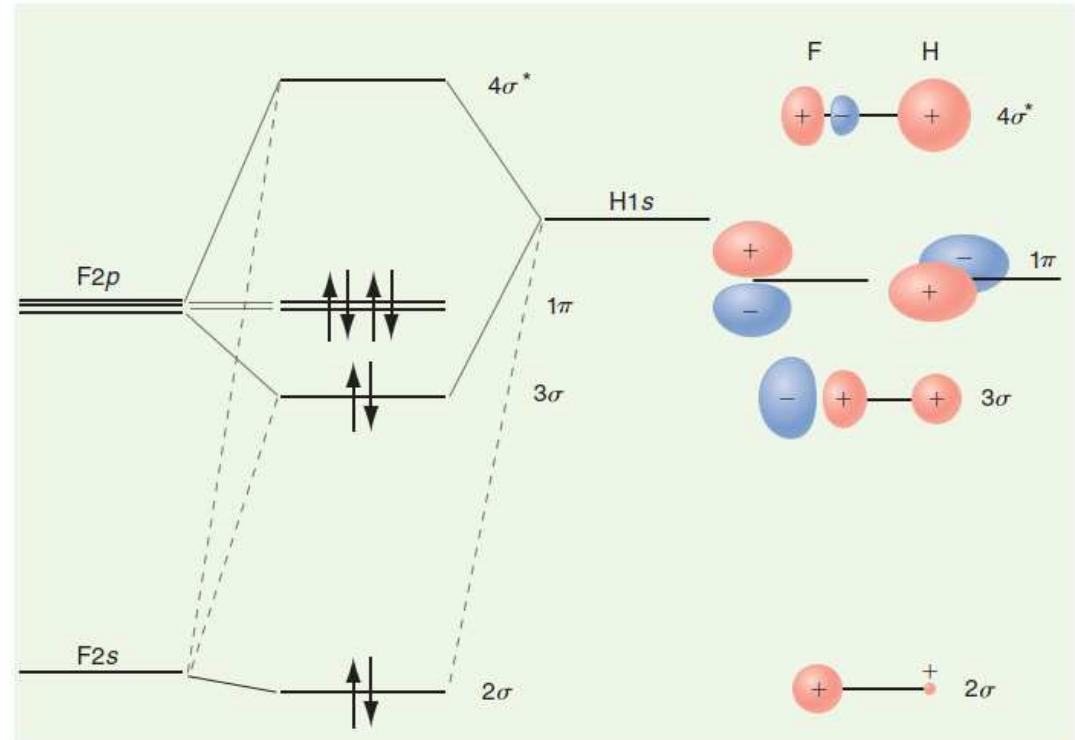


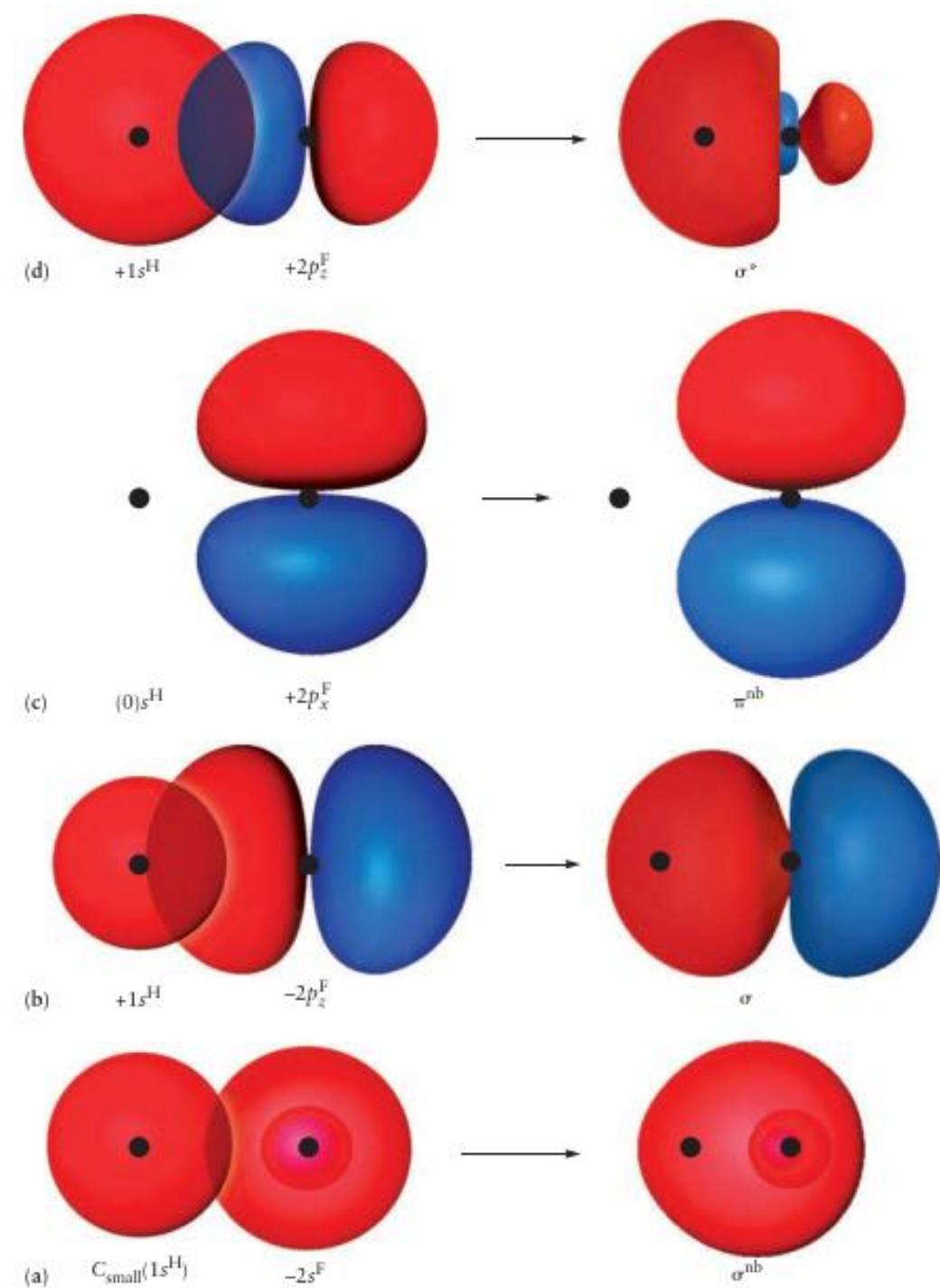
FIGURE 12.22 Schematic energy diagram (Correlation diagram) showing the relationship between the atomic and molecular orbital energy levels for the valence electrons in HF. The degenerate p and π orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown as solid lines. Lesser contributions are shown as dashed lines. The MOs are depicted to the right of the figure. We assign the 1s electrons on F to the 1σ MO, which is localized on the F atom.
The 2s, $2p_x$, and $2p_y$ atomic orbitals of fluorine do not mix with the 1s atomic orbital of hydrogen, and therefore remain *nonbonding*.

FIGURE 6.23 Overlap of atomic orbitals in HF.
(Note: in the correlation diagram in Figure 6.24 it is assumed that lowest energy orbital is a nonbonding one that looks identical to a 2s orbital on the F atom, with no contribution from the H 1s orbital.)

In the graphical depiction of this orbital in (a) in this figure, a small coefficient multiplies the H 1s orbital in this linear combination; the overlap is negligible.)

(Courtesy of Mr. Hatem

Helal and Professor William A. Goddard III,
California Institute of Technology, and Dr. Kelly
P. Gaither, University of Texas at Austin.)



- ✓ As expected, in the σ bonding orbital the electron density is much greater on the more electronegative fluorine than on the hydrogen.
- ✓ However, in the σ^* antibonding orbital, this **polarity is reversed**. *The estimated dipole moment is smaller in the excited state than in the ground state.*

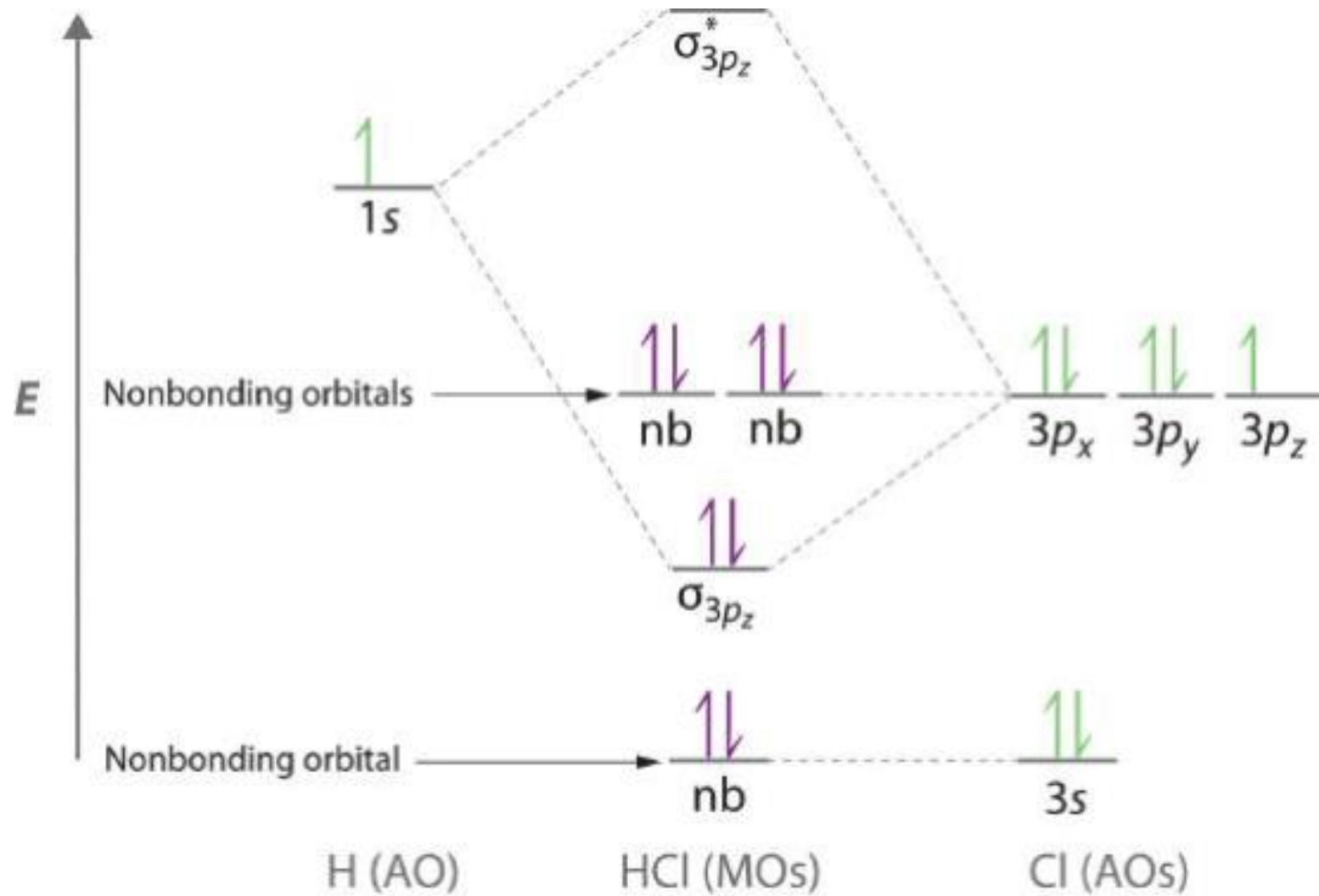
Nonbonding Molecular Orbitals: Lone pairs of electrons

- Molecular orbital theory is also able to explain ***the presence of lone pairs of electrons.***
- Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom.
- Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 10.8.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine.

- Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital.
- The $3p_x$ and $3p_y$ atomic orbitals have ***no net overlap*** with the 1s orbital on hydrogen, so they are *not involved in bonding*.
- Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change (significantly) when HCl forms, they are called ***nonbonding molecular orbitals***.
- A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons.
- By definition, electrons in ***nonbonding orbitals have no effect on bond order***, so they are not counted in the calculation of bond order.
- Thus, the predicted bond order of HCl is $(2 - 0) \div 2 = 1$.

- Because the σ bonding molecular orbital is closer in energy to the Cl 3p than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A **molecular orbital approach** to bonding can therefore be used to **describe the polarization of the H–Cl bond** to give $\text{H}^{\delta+}\text{—Cl}^{\delta-}$.

Figure 10.8.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the 3p orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.



- An **energy-level diagram for O–H** calculated for the experimentally observed O–H bond length of 97.0 pm is shown in Figure 6.10.
- On the far right of the figure, the *coefficients of the AOs, i.e., C_1 , C_2 and C_3 , for each σ MO are shown. They tell us how each AO contributes to each MO and the signs also show the bonding or antibonding nature of the MO.*
- *Immediately beneath each coefficient its square is entered* because it is the square of the wave function which gives the electron density and the second row of figures therefore reveals how the electrons are distributed in that particular MO; if it contains any.

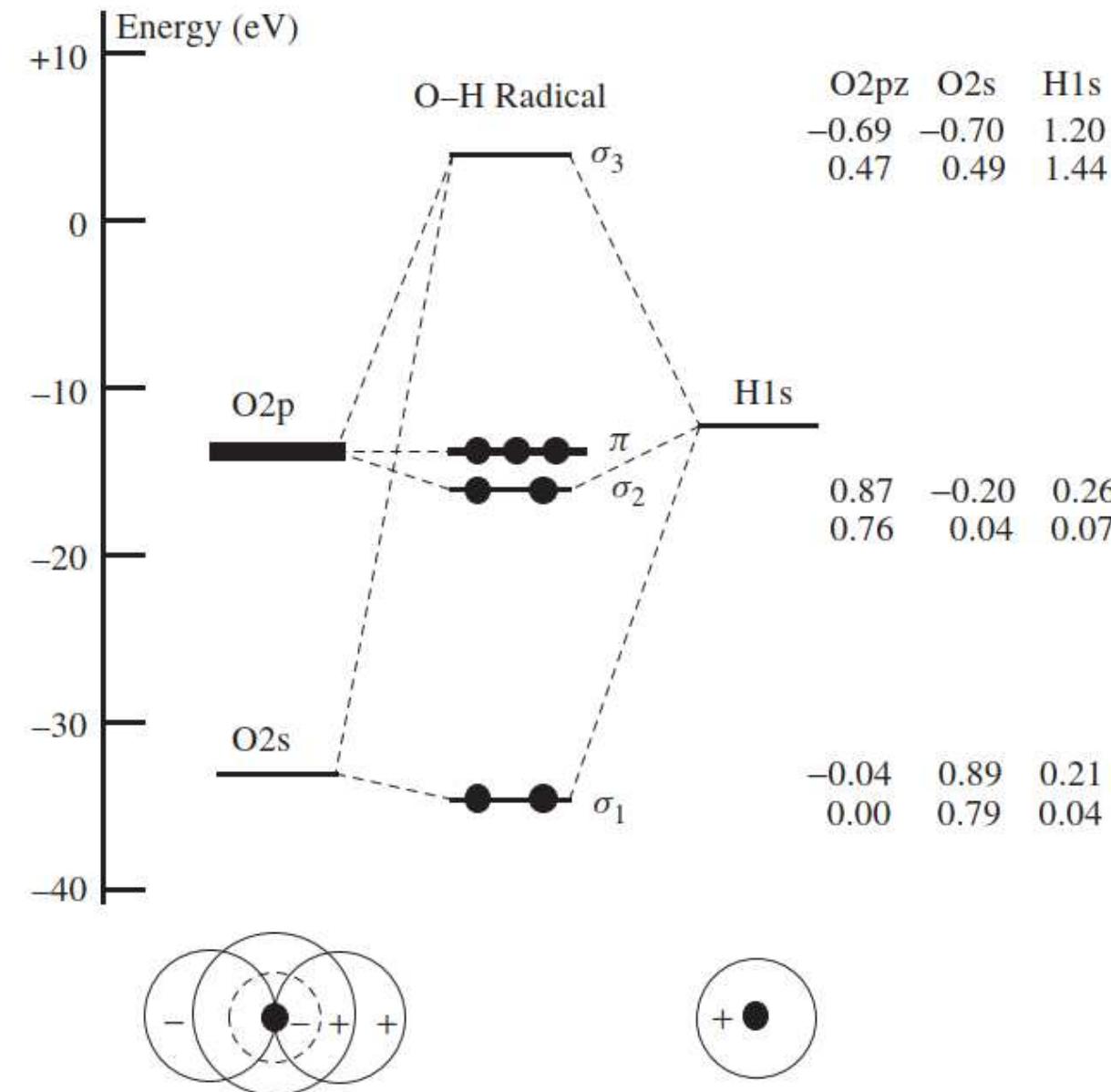


Figure 6.10 A molecular orbital energy-level scheme for the OH radical.

❖ Energy-level diagram for O–H Radical

- The positive lobe of the oxygen $2p_z$ orbital is directed towards the hydrogen atom.
- On the right of the diagram the 1s AO of hydrogen is shown at an energy of -13.60 eV . On the left of the diagram, the 2s and 2p AOs of the oxygen atom are plotted at -32.30 eV and -14.80 eV respectively.
- The oxygen 1s AO is not involved in the bonding and does not feature in the diagram.
- In the center of the figure, the calculated energy levels of O–H are shown at -33.39 eV , -15.85 eV , -14.80 eV (doubly degenerate) and $+6.62\text{ eV}$.
- The dots indicate the filling of the available MOs with electrons.

- On the far right of the figure, *the coefficients of the AOs, i.e., C_1 , C_2 and C_3 , for each σ MO are shown.* They tell us how each AO contributes to each MO and the signs also show the bonding or antibonding nature of the MO.
 - *Immediately beneath each coefficient its square is entered* because it is the square of the wave function which gives the electron density and the second row of figures therefore reveals how the electrons are distributed in that particular MO; if it contains any.
 - Let us first consider the MO of lowest energy; σ_1 , $E = -33.39$ eV. The major contributor with a coefficient of +0.889 is the oxygen 2s AO and hydrogen 1s also plays a part with a coefficient of +0.212. The contribution of oxygen 2pz is too small to concern us. Note that the orbital is bonding, because the two AO contributors overlap in phase, and of σ type.
- ✓ We place **two of our seven electrons** in this MO.

- The MO next in energy (σ_2 , $E = -15.85$ eV) involves the same three AOs but the oxygen $2p_z$ now plays by far the most important role.
- Note that the oxygen $2s$ – hydrogen $1s$ overlap is antibonding while the oxygen $2p_z$ – hydrogen $1s$ overlap is bonding. The last is by far the greater and dominates so that the MO is bonding *in total*.
- ✓ It is important to observe that, *where many AOs are involved, both bonding and antibonding interactions can be found within the same MO.*
- The next two MOs, the degenerate pair of π symmetry at $E = -14.80$ eV, are non-bonding MOs.
- ✓ The π -type oxygen $2p_x$ and oxygen $2p_y$ AOs have zero overlap with the σ -type hydrogen $1s$ AO and there is no interaction between them. Consequently, these two oxygen $2p$ AOs are found in the molecule with an unchanged energy of -14.80 eV. *Their AO coefficients are each 1.0.*

- Since seven electrons are available to fill the MOs of O–H (the oxygen 1s electrons being omitted from the diagram), the last three electrons must be placed in these two orbitals, of which one will be only half-full.
- ***The unpaired electron makes the O–H radical paramagnetic and very reactive.***
- ***The highest MO (σ_3) is very high in energy ($E = +6.62$ eV) and strongly antibonding in all its overlaps. If electrons find their way into this MO, by absorbing light, for example, the molecule becomes even more reactive.***

❖ ***CHARGE DISTRIBUTION: Mulliken population analysis***

A further piece of interesting information can be obtained from the results of an MO calculation. From the atomic orbital coefficients for each occupied MO and the calculated overlap integrals the distribution of the electrons throughout the molecule may be calculated. In the present example of ***the O–H radical it is found that the seven valence electrons are distributed such that 6.48 of them are on the oxygen atom*** and 0.52 on the hydrogen. Thus, the hydrogen carries a partial positive charge of approximately $+e/2$ and the oxygen a partial negative charge of $-e/2$, where e is the charge on the proton.

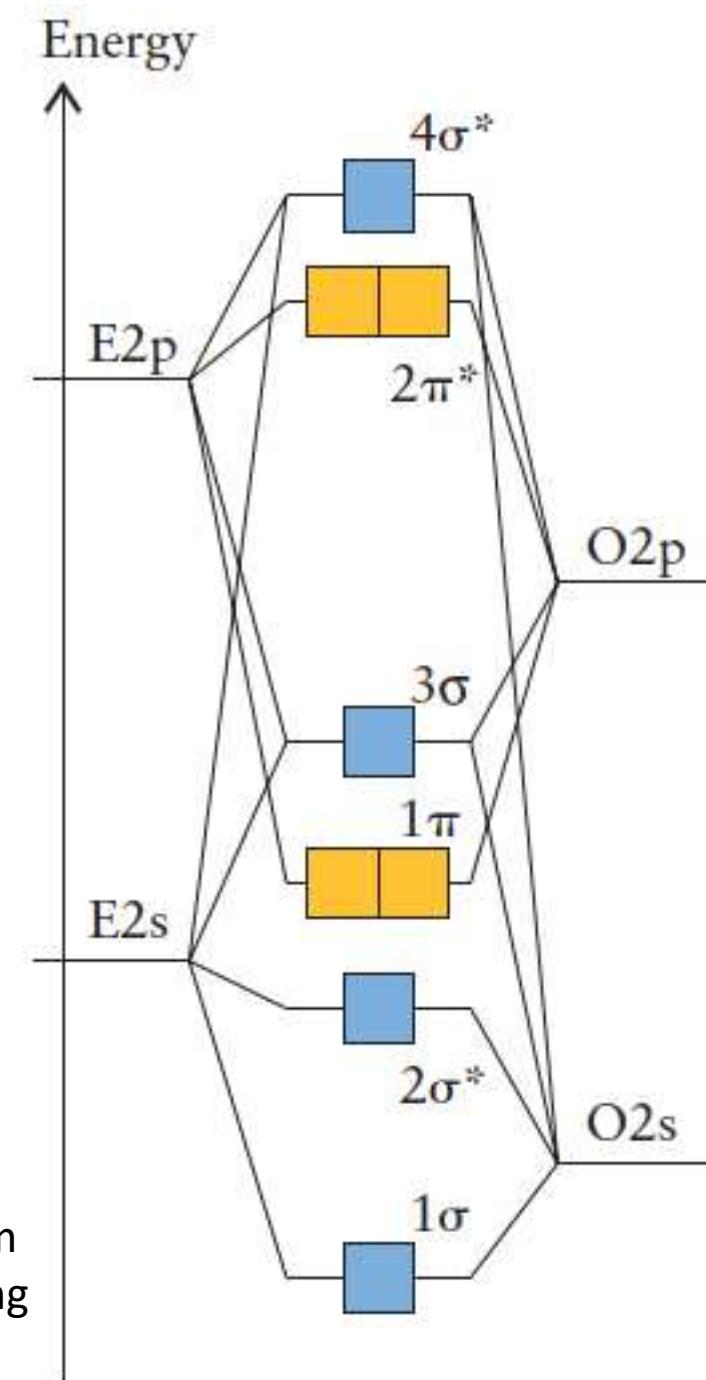
This type of analysis of the distribution of the electrons within the molecule is usually termed ***Mulliken population analysis***, after R.S. Mulliken who first introduced the idea.

□ The molecular orbital energy-level diagrams of **heteronuclear** diatomic molecules are ***much harder to predict qualitatively***, and ***we have to calculate each one explicitly because the atomic orbitals contribute differently to each one.***

- Figure 3.35 shows the calculated scheme typically found for **CO** and **NO**. We can use this diagram to state the electron configuration by using the same procedure as for homonuclear diatomic molecules.
- Write the configuration of the ground state of the **cyanide ion**, **CN⁻**, assuming that its molecular orbital energy-level diagram is the same as that for **CO**.
- ✓ Calculate the bond order.
- ✓ Could you suggest whether the negative charge is on C or N.....??

FIGURE 3.35 The molecular orbital schemes typical of those calculated for a diatomic oxide molecule, *EO* (where *E* = **C** for **CO** and *E* = **N** for **NO**).

- Note that the σ -orbitals are formed from mixtures of *s*- and p_z -orbitals on both atoms; accordingly, we label them simply 1σ , 2σ , etc. in order of increasing energy.



❖ MO Diagram of CO

- The MO diagram for the CO molecule is shown in Figure 10.28. *Using the periodic trend that the energies of the 2s and 2p orbitals decrease across the second period, the relative energies of the C and O AOs can be placed on the extreme left and right of the one-electron MO diagram. The C AOs lie at higher energies than those of the O AOs.*
- Because CO is isolectronic with N_2 , which undergoes orbital mixing, it is likely that the MO diagram for CO will also exhibit mixing. This result is borne out by the PES (photoelectron spectroscopy) data for CO.
- Because of the relative energies of the C and O AOs, a CO bonding MO, closer in energy to O, has a greater contribution from the O AO, while a CO *antibonding MO, closer in energy to C, has a greater contribution from the C AO.*

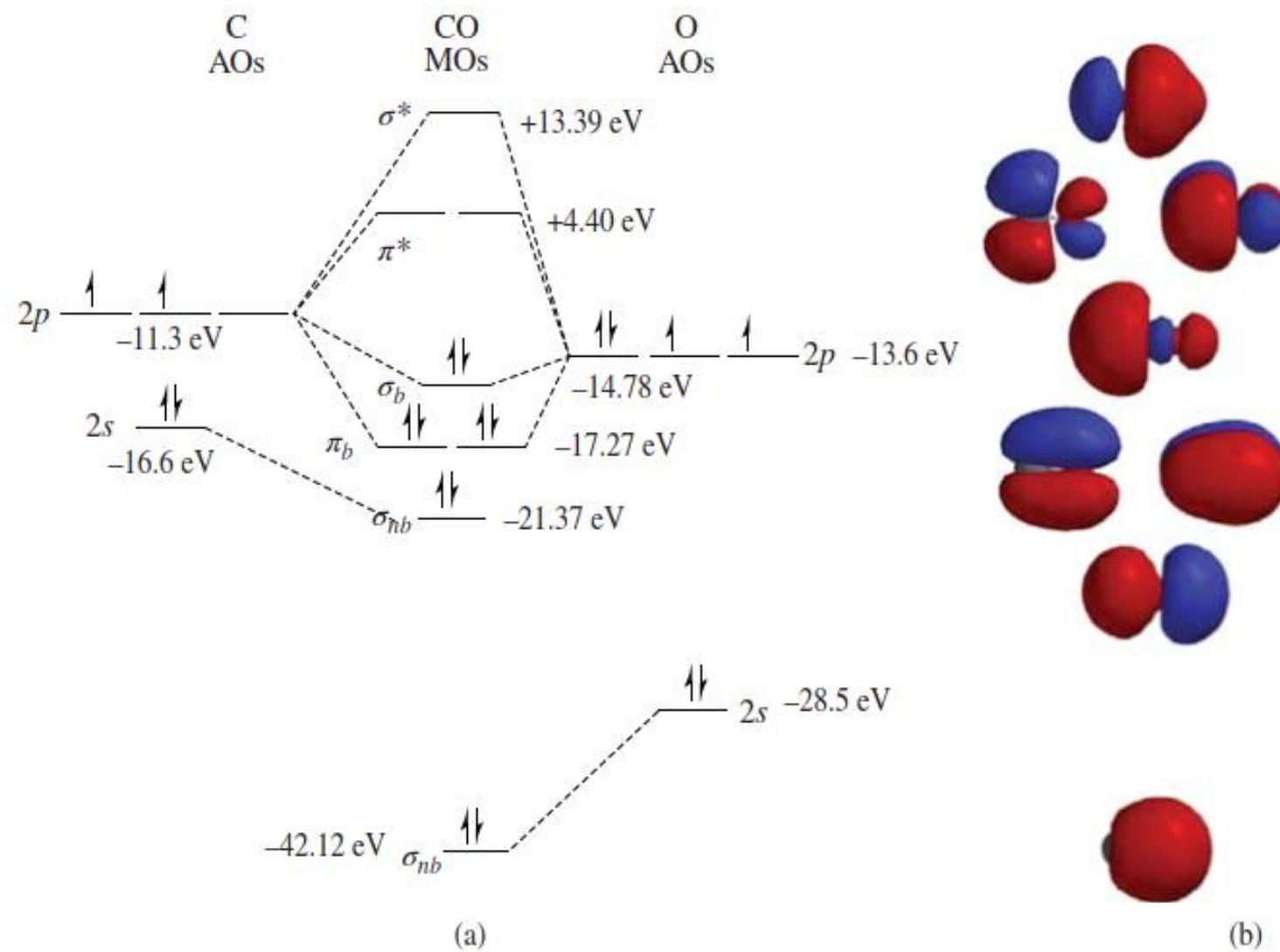
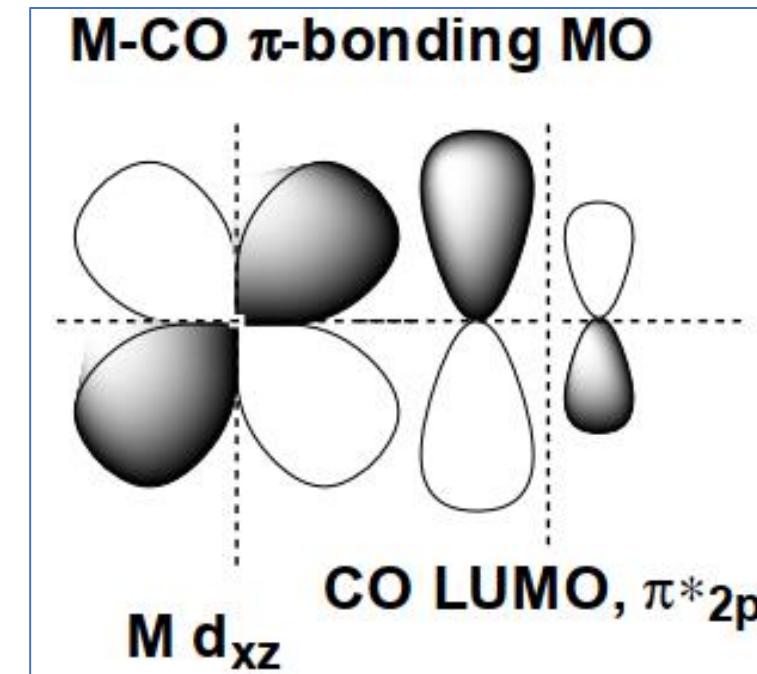


FIGURE 10.28
(a) One-electron molecular orbital diagram for CO, showing the calculated shapes of the MOs of CO (b). The energies and the shapes of the MOs were calculated using Wavefunction's Spartan Student Edition version 5.0.

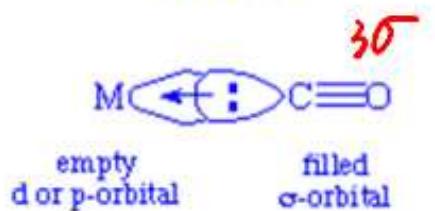
- In the heteronuclear molecule, the percentage contribution of AO character in the σ_b ($2p_z$) and π_b MOs is larger for the O atom than it is for the C atom because the energies of these MOs are closer to AOs derived from O than from C. *This is reflected in the shapes of these MOs*, which show more electron density on the O atom than on the C atom.
- It is also consistent with the expected polarity of the bond, where the bonding electrons are drawn closer to the O atom as a result of its larger electronegativity.
- Thus, **MOT can also explain the relative polarity** of bonds in heteronuclear diatomics.
- Furthermore, the **Lewis structure of CO has a lone pair of electrons on C and a second lone pair on O**.

- The lowest energy MO on the diagram is a sigma MO that is much closer in energy to the 2s AO on oxygen than it is to the 2s AO on C. Therefore, the weighting coefficient in the LCAO-MO method will consist predominantly of O character. *Because the composition of this MO is almost identical to its corresponding AO, the character of the resulting MO is nonbonding (nb).*
- The same is true for the second lowest MO, which consists largely of C character(recall that the 2s and 2p AOs mix in C, a fact reflected in the shape of this MO).
- ***These nonbonding MOs can be used to indicate the two lone pairs in the CO molecule***—one lies on the O atom and the other on the C atom.
- ***Nonbonding MOs are not counted in the determination of the bond order. Thus, the overall bond order for CO is 3, consistent with its Lewis structure.***

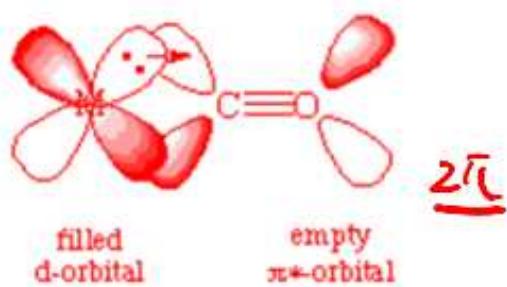
- The lowest *unoccupied molecular orbital (LUMO)* is 2π , which is largely *a doubly degenerate orbital of $2p$ character on carbon*.
- This combination of *a lone pair orbital on C* and *a pair of empty π orbitals* also largely on C is at the root of *the importance of carbon monoxide in d-block chemistry*, because it enables it to form an extensive series of carbonyl complexes by *a combination of electron pair donation* (overlapping with empty M d-orbitals) and *electron acceptance into the 2π orbitals*.



σ bond:



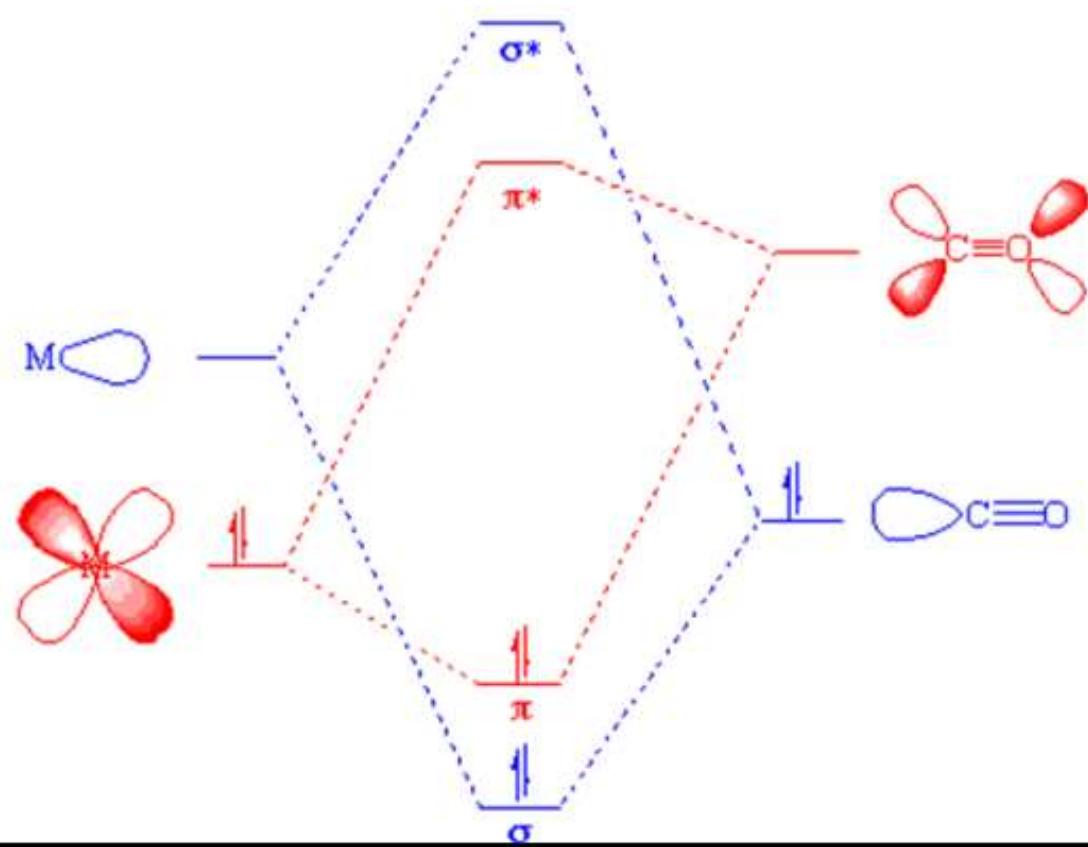
π backbond:



L_nM

$L_nM(CO)$

CO



Dipole Moment

- The considerations earlier assumed that the linear combination of atomic orbitals occurs between two atoms of the same element, which results in formation of homonuclear diatomic molecules. This manifests itself in the fact that the two interacting atomic orbitals possess the same energy. Moreover, at the level of the quantum mechanical wave function, this results in equality of the two coefficients c_1 and c_2 (Eq. 11.12) or $\lambda = \pm 1$ (Eq. 11.13).
 - $\Psi = c_1 \Psi_1 + c_2 \Psi_2$ (Eqn. 11:12)
 - This approach is called the linear combination of atomic orbitals (LCAO) and can alternatively be formulated as:
 - $\Psi = \Psi_1 + \lambda \Psi_2$, (Eqn. 11:13)
 - where λ is a measure of the polarity of the molecular orbital.

- Whereas the same methodology can be applied to hetero-nuclear diatomic molecules, we appreciate that the two atoms no longer belong to the same element, hence the energies of the interacting atomic orbitals are no longer equal.
- Similarly, the weighting coefficients c_1 and c_2 are not the same, and $\lambda \neq \pm 1$.
- As mentioned in Sect. 11.3.2, the coefficient λ is a measure of the polarity of the molecular orbital, and if its value deviates from 1, the bond possesses a ***permanent electric dipole momentum*** (i.e., a bond moment).
- This is a result of one atom in the molecule attracting electrons more strongly than the other, leading to a formal partial negative charge on one atom and a formal positive charge on the other.
- In general, a dipole moment μ arises from a charge separation in space, and is thus defined as

$$\mu = Q \cdot r, \quad (11.15)$$

- where Q is the separated charge (e.g., $1 \text{ e} = 1.602 \times 10^{-19} \text{ C}$) and r the distance between the positive and negative centers.
- Since such separations happen at the scale of a chemical bond, the dipole moment is measured in multiples of $3.338 \times 10^{-30} \text{ C m}$ which is called the *debye*:

$$[\mu] = 3.338 \cdot 10^{-30} \text{ C m} = 1 \text{ D}$$

- and leads to the dipole moment for the charge separation due to one electron displaced by $1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$ of

$$\mu = 1.602 \cdot 10^{-19} \text{ C} \cdot 10^{-10} \text{ m} = 1.602 \cdot 10^{-29} \text{ C m} = 4.8 \text{ D.}$$

- When assessing the ***overall dipole moment*** of a molecule, one considers the individual bond moments as vectors (i.e. they have a value/length and a direction) and estimates the overall dipole moment by vector addition.

- Every polar covalent bond contains an ionic character due to the displacement of shared electron clouds towards the atom with high electronegativity.
 - The percentage of ionic character in a covalent bond is obtained using the formula,
- % ionic character = (μ (observed) / μ (theoretical)) *100**
- where, μ = Dipole moment in Debye.
 - ❖ Calculate the percentage ionic and covalent character in HF molecules having bond distance = 0.92Å and dipole moment=1.78D?

Ans: Given, μ (observed) = 1.78D = 1.78×10^{-18} esu.cm (1D = 10^{-18} esu.cm)
 $r = 0.92\text{\AA} = 0.92 \times 10^{-8}$ cm

We know, % ionic character = (μ (observed)/ μ (theoretical))*100

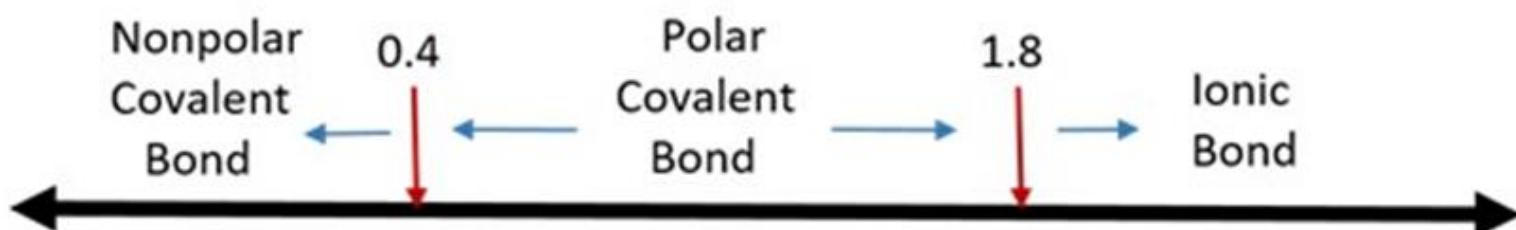
Also, μ (theoretical) = Q*r = 4.8×10^{-10} esu*0.92*10⁻⁸cm, (where Q= charge of electron).

Now, % ionic character = $(1.78 \times 10^{-18}\text{esu.cm}) / (4.8 \times 10^{-10}\text{esu} \times 0.92 \times 10^{-8}\text{cm}) = 0.403 = 40.3\%$

Ionic character = 40.3%

Hence, Covalent character = $100 - 40.3 = 59.3\%$.

Electronegativity Difference



Examples:



$$2.5 - 2.1 = 0.4$$

$$3.5 - 2.5 = 1.0$$

$$3.0 - 0.9 = 2.1$$

Dipole Moment of Ionic Compounds

The electronegativity difference between Na and Cl of 2.1 suggests that NaCl forms an ionic bond. If the bonding in crystalline NaCl was 100% ionic, the charge on the sodium atom was +1·e, and the charge on the chlorine –1·e. With an inter-nuclear distance of 2.36 Å, this results in a dipole moment of $\mu = 11.34 \text{ D}$. The experimental value of the dipole moment can be obtained by microwave spectroscopy and yields $\mu = 9.001 \text{ D}$. The ratio of the experimental and theoretical dipole moments

$$\frac{\mu_{\text{exp}}}{\mu_{\text{theor}}} = \frac{9.001 \text{ D}}{11.34 \text{ D}} = 0.794$$

indicates that the bonding between sodium and chlorine in the ionic solid is ~80% ionic.

Polyatomic Molecules

- Molecular orbital theory can be used to discuss in a uniform manner the electronic structures of triatomic molecules, finite groups of atoms, and the almost infinite arrays of atoms in solids.
- In each case the molecular orbitals resemble those of diatomic molecules, the only important difference being that the orbitals are built from a more extensive basis set of atomic orbitals.
- As remarked earlier, a key point to bear in mind is that from N atomic orbitals it is possible to construct N molecular orbitals.
- We have seen that the general structure of molecular orbital energy-level diagrams can be derived by grouping the orbitals into different sets, the σ and π orbitals, according to their shapes.
- The same procedure is used in the discussion of the molecular orbitals of polyatomic molecules. However, because their shapes are more complex than diatomic molecules, we need a more powerful approach.
- The discussion of polyatomic molecules are therefore carried out in two stages. First, we use intuitive ideas about molecular shape to construct molecular orbitals, as is done here. Also, one discusses the shapes of molecules and the use of their symmetry characteristics to construct molecular orbitals and account for other properties.

(a) Polyatomic molecular orbitals

Key points: Molecular orbitals are formed from linear combinations of atomic orbitals of the same symmetry; their energies can be determined experimentally from gas-phase photoelectron spectra and interpreted in terms of the pattern of orbital overlap.

- The features that have been introduced in connection with diatomic molecules are present in all polyatomic molecules. In each case, we write the molecular orbital of a given symmetry (such as the σ orbitals of a linear molecule) as a sum of all the atomic orbitals that can overlap to form orbitals of that symmetry:

$$\Psi = \sum_i c_i \chi_i \quad (2.8)$$

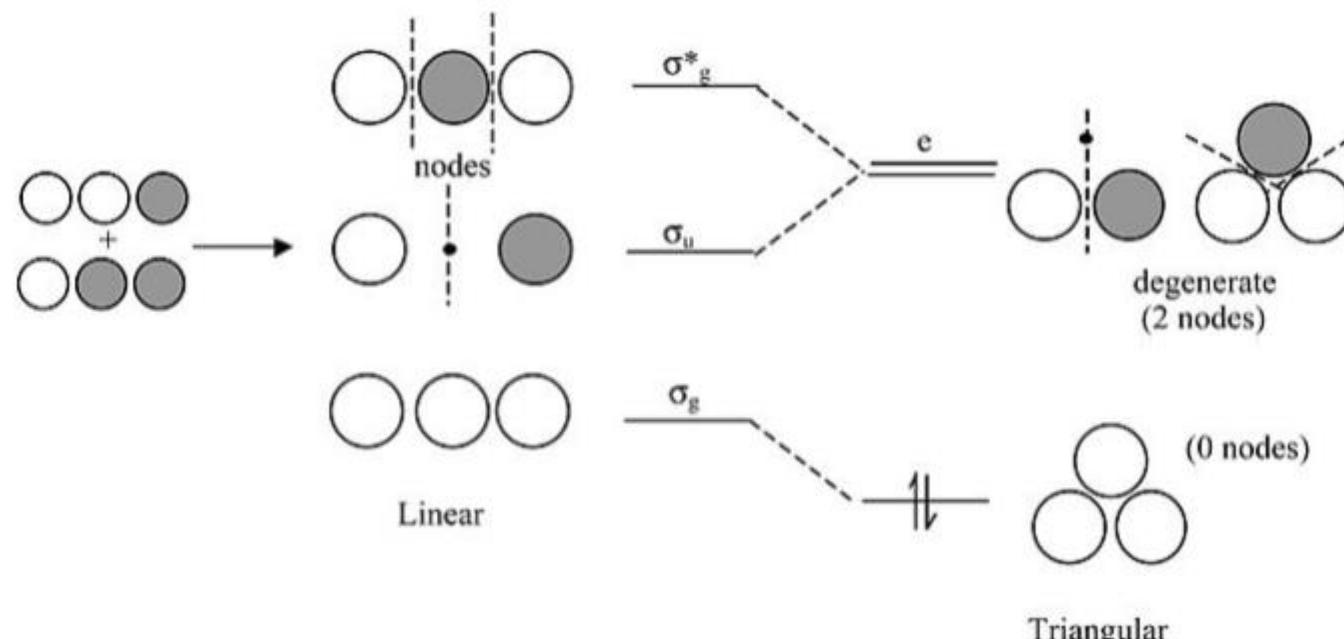
In this linear combination, the χ_i are atomic orbitals (usually the valence orbitals of each atom in the molecule) and the index i runs over all the atomic orbitals that have the appropriate symmetry.

➤ From N atomic orbitals we can construct N molecular orbitals. Then,

- The greater the number of nodes in a molecular orbital, the greater the antibonding character and the higher the orbital energy.
- Orbitals constructed from lower energy atomic orbitals lie lower in energy (so atomic s orbitals typically produce lower energy molecular orbitals than atomic p orbitals of the same shell).
- Interactions between nonnearest-neighbor atoms are weakly bonding (lower the energy slightly) if the orbital lobes on these atoms have the same sign (and interfere constructively). They are weakly antibonding if the signs are opposite (and interfere destructively).

❖ Three-Center Bonding

- Many (but not all) of the problems we will solve with MO theory derive from the MO diagram of the H molecule, which is a case of two-center bonding. The rest we will solve by analogy to the H_3^+ ion, which introduces the concept of three-center bonding.
- We can draw the H_3^+ ion (and also H_3 and H_3^-) in either a **linear** or **triangular** geometry.



Walsh correlation diagram for H_3^+

❖ A few important points about this diagram:

- For the linear form of the ion, the highest and lowest MO's are symmetric with respect to the inversion center in the molecule. Note that the central 1s orbital has g symmetry, so by symmetry, it has zero overlap with the u combination of the two 1s orbitals on the ends. This makes the σ orbital a nonbonding orbital.
- In the triangular form of the molecule, the orbitals that derive from σ and σ^* become degenerate (i.e., they have identically the same energy by symmetry).
- The *term symbol “e” means doubly degenerate.*
- We will see later that *“t” means triply degenerate.*
- Note that we drop the “g” and “u” for the triangular orbitals because a triangle does not have an inversion center.
- *The triangular form is most stable* because the two electrons in H_3^+ have lower energy in the lowest orbital. *Bending the molecule creates a third bonding interaction* between the 1s orbitals on the ends.

❖ Delocalized, or multi-centred, σ orbitals

- Instead of constructing a set of two-centre bonds we could describe a polyatomic species by constructing orbitals centred over all the atoms of the molecule. A full discussion is beyond our scope, but the general approach may be illustrated.
- Consider first a very simple example, the BeH_2 monomer. The orbital combinations are shown in Fig. 4.17.
- The beryllium 2s orbital combines, in phase, with the s orbitals on hydrogens A and B to form the 3-centre orbital, ψ_1 .
- The electron probability density in this orbital, ψ_1^2 , will be concentrated in the regions of highest field between the nuclei, and will experience more attraction than in the isolated atoms. Thus, ψ_1 is bonding.

- Similarly, ψ_2 , formed by the combination s (on A) + p_z- s (on B), is bonding. The corresponding out-of-phase combinations ψ_1^* and ψ_2^* are clearly anti-bonding.
- Since both the p_x and p_y orbitals on beryllium have nodes in the plane of the two hydrogens, no combinations between these and the hydrogen s orbitals are possible.
- Thus, we can draw up a qualitative energy level diagram, Fig. 4.18.
- Notice, firstly, that six atomic orbitals (4 on Be, 1 on each H) give six BeH₂ orbitals (ψ_1 , ψ_1^* , ψ_2 , ψ_2^* together with p_x and p_y).
- Secondly, the four electrons are placed in the two bonding levels giving two bonds holding the three atoms together. This is equivalent to two Be—H single bonds, but the bonding electrons are spread over all three atoms.
- Finally, the energy separation of ψ_1 and ψ_2 reflects approximately the separation of the beryllium 2s and 2p atomic levels.

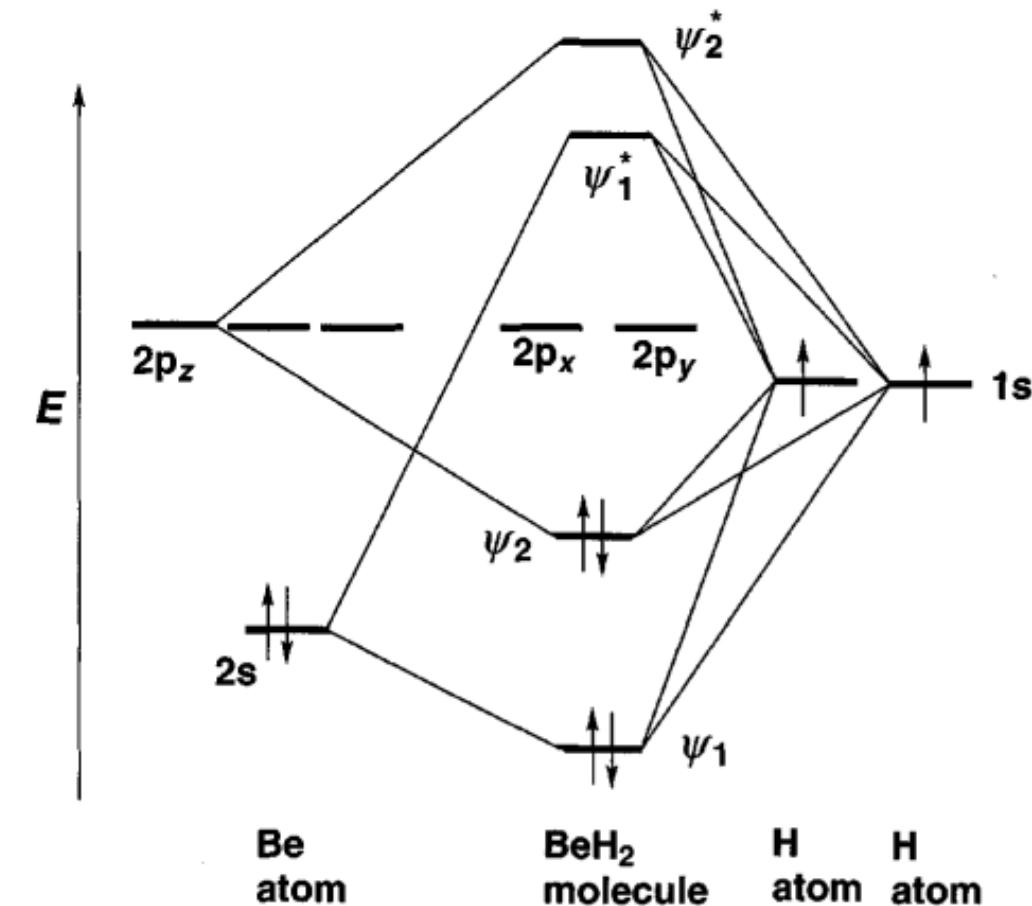
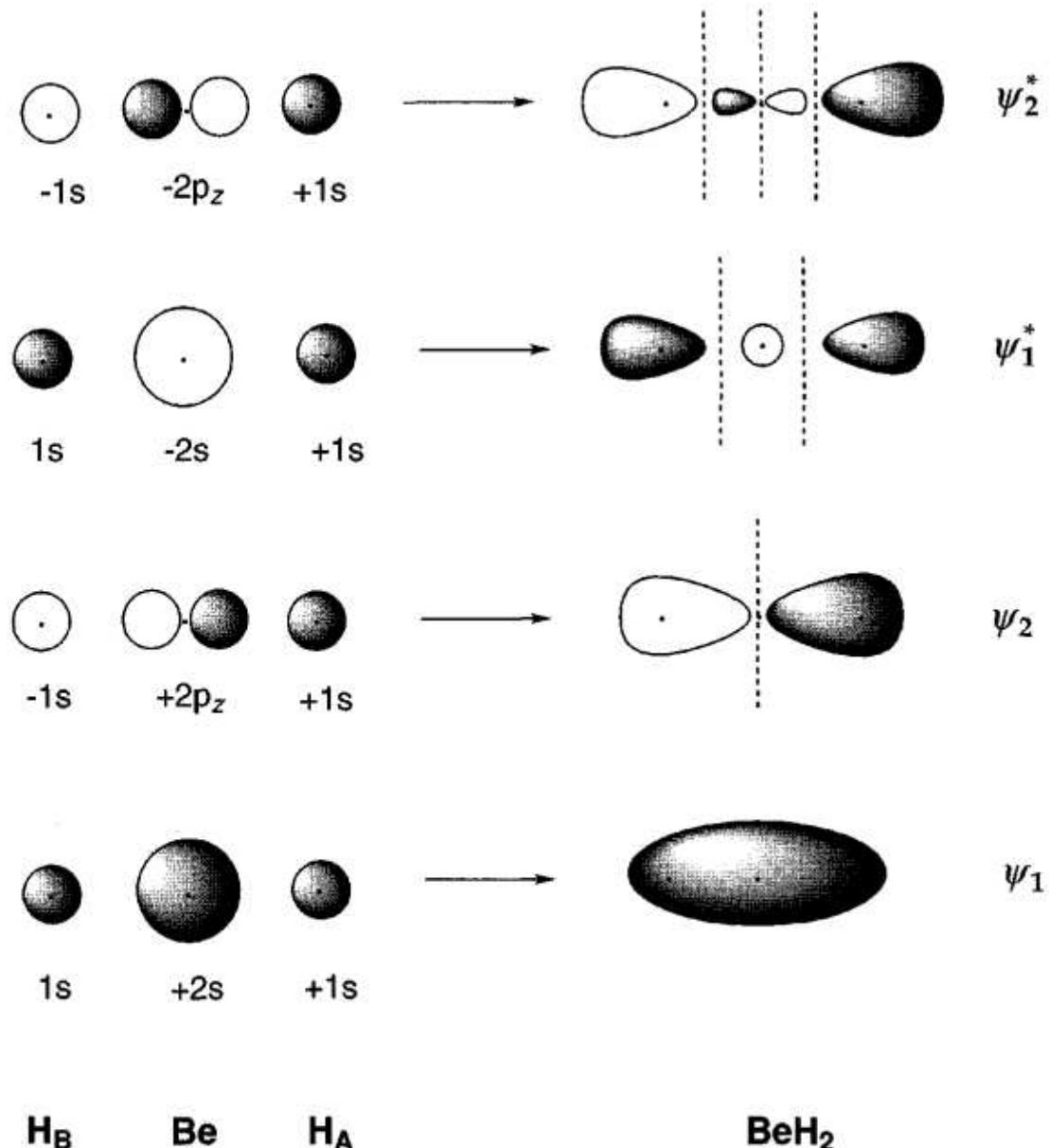
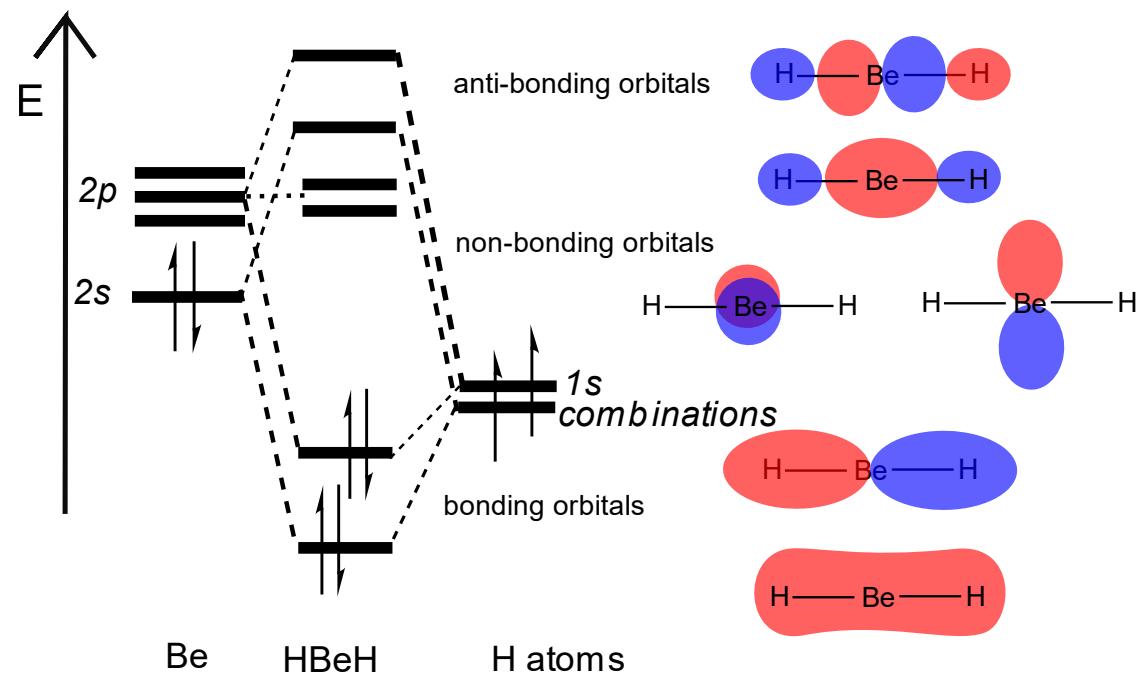
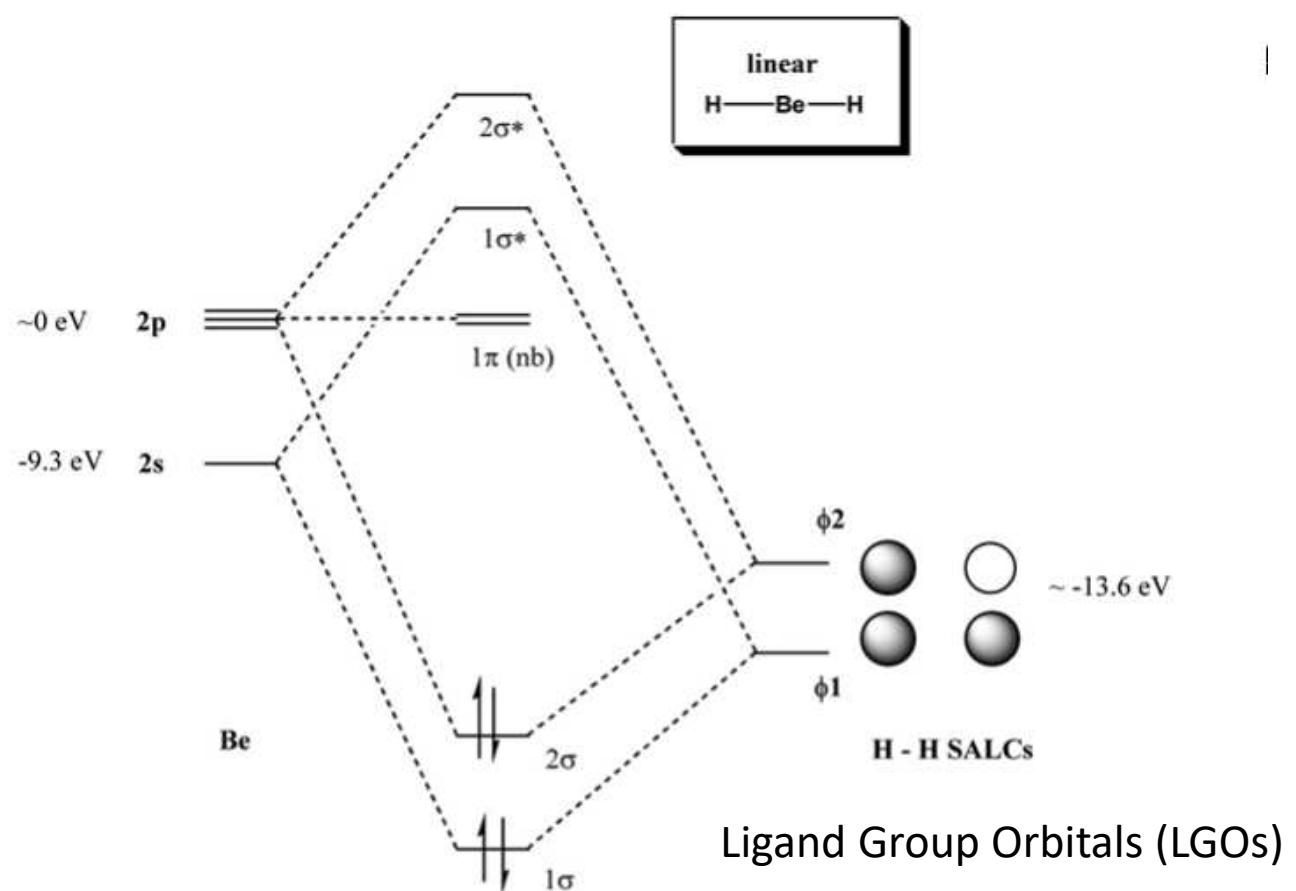
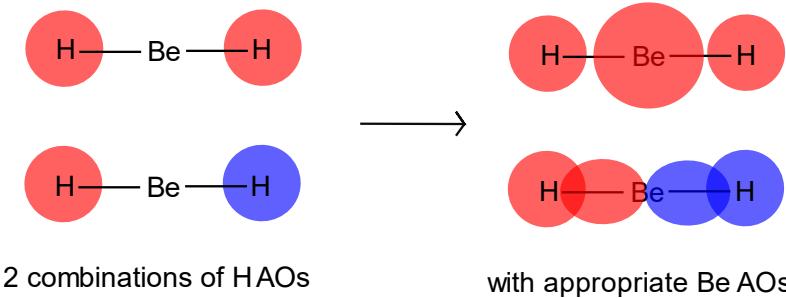


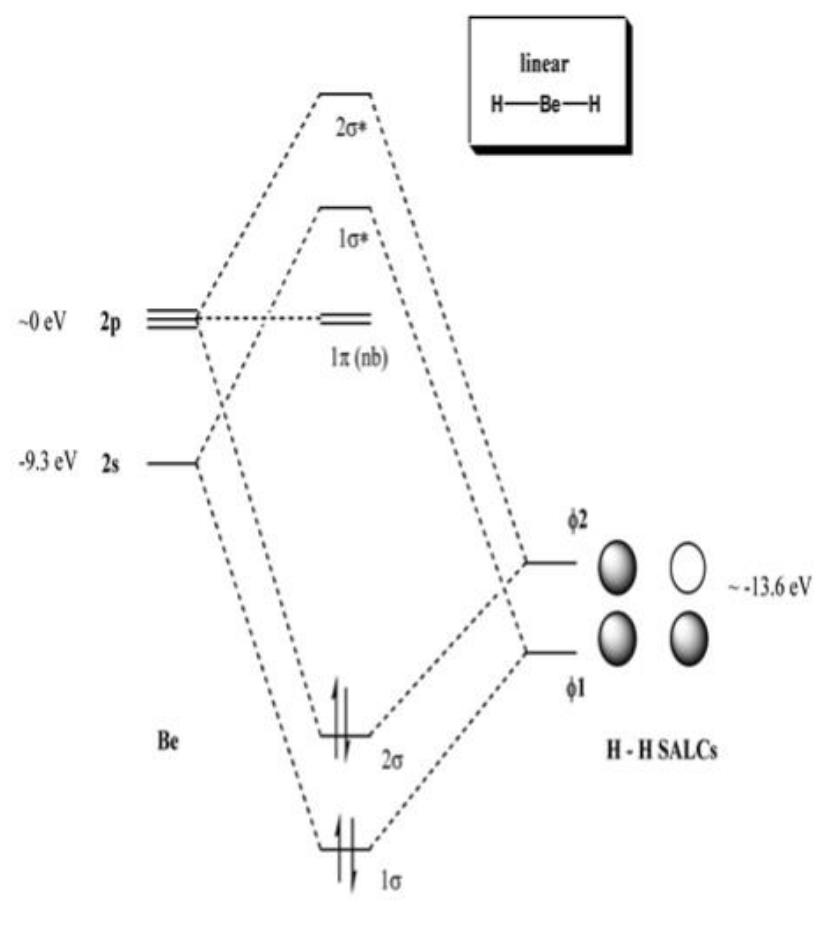
FIG. 4.18 Schematic energy level diagram for BeH_2 . Note that the z axis is the H-Be-H axis (*linear molecule*). The p_x and p_y orbitals on Be are not involved in molecular orbital formation and are simply repeated in the BeH_2 column of the diagram

FIG. 4.17 Formation of molecular orbitals in BeH_2 (schematic). Nodal planes are indicated by dotted lines

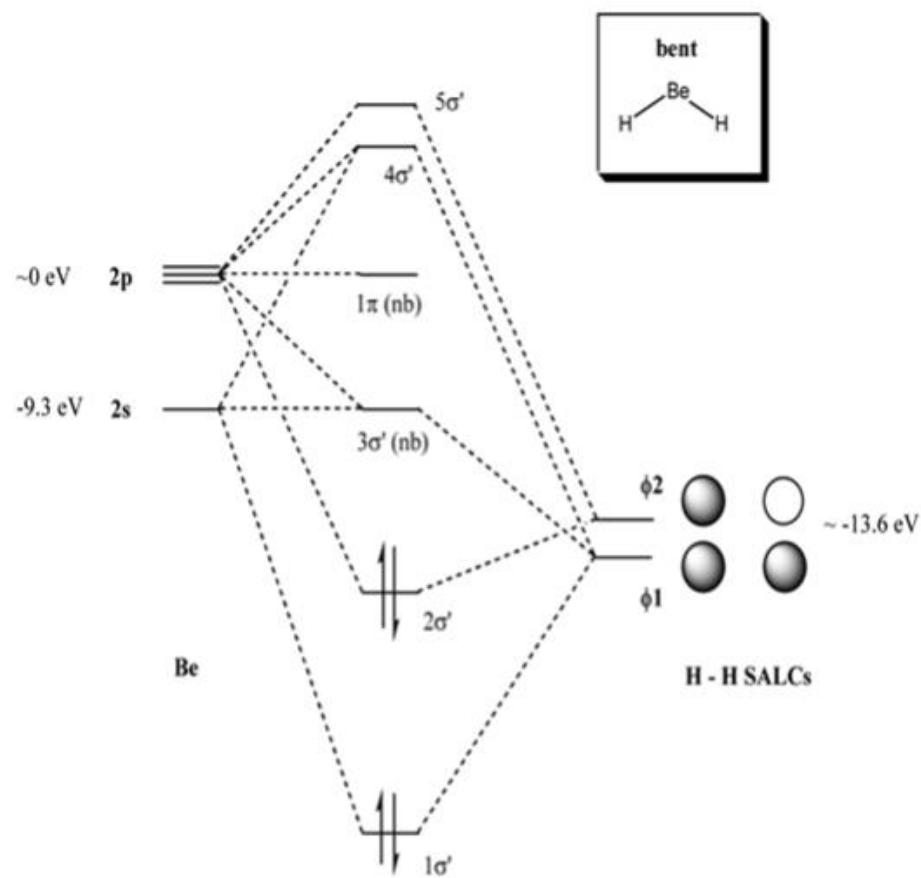


allowed overlaps: Symmetry adopted

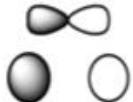




allowed overlaps:



allowed overlaps:



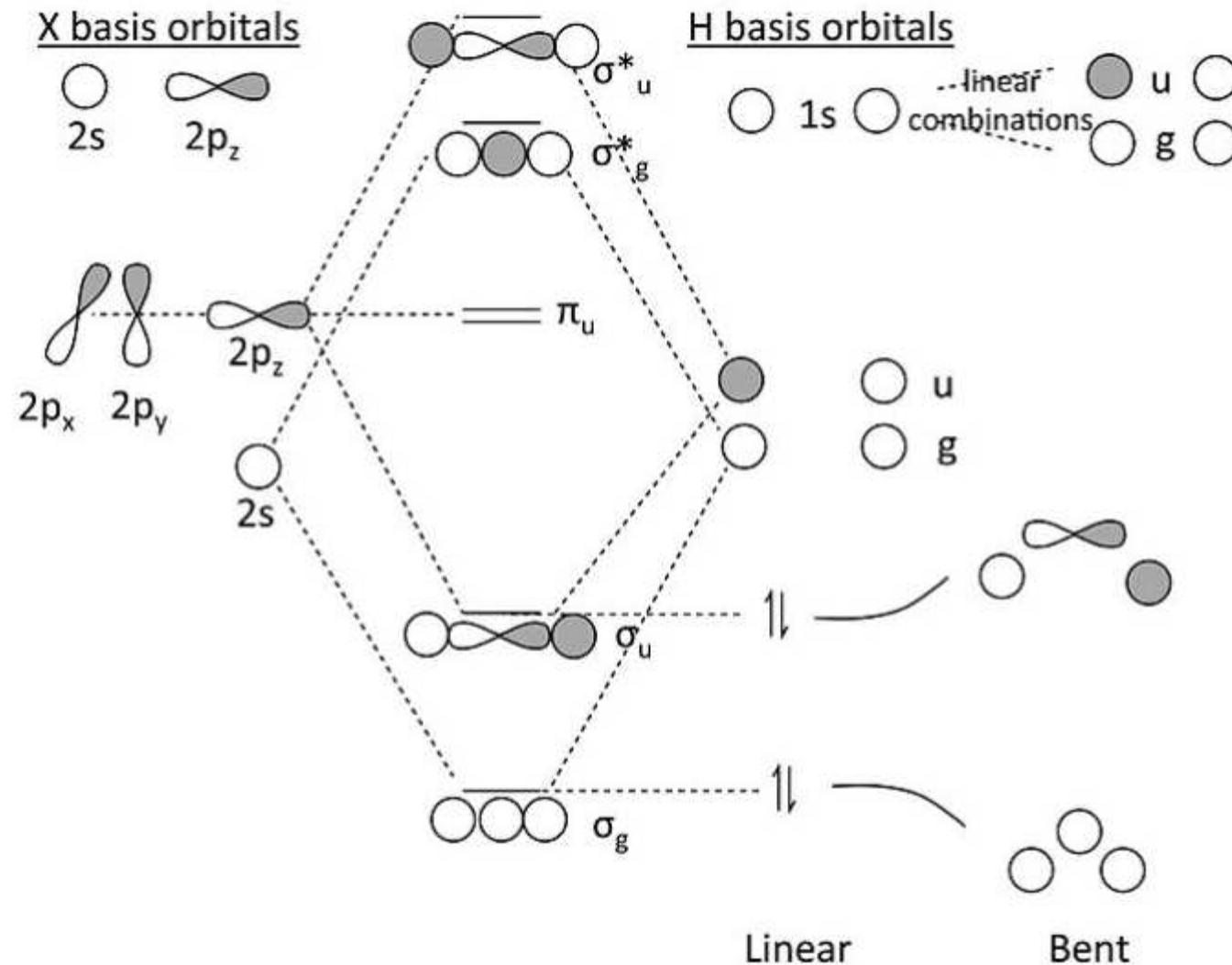
MO diagram for XH (X = Be, B, C...):

In the linear form of the molecule, which has inversion symmetry, the 2s and 2p orbitals of the X atom factor into three symmetry classes:

$$2s = \sigma_g$$

$$2p_z = \sigma_u$$

$$2p_x, 2p_y = \pi_u$$

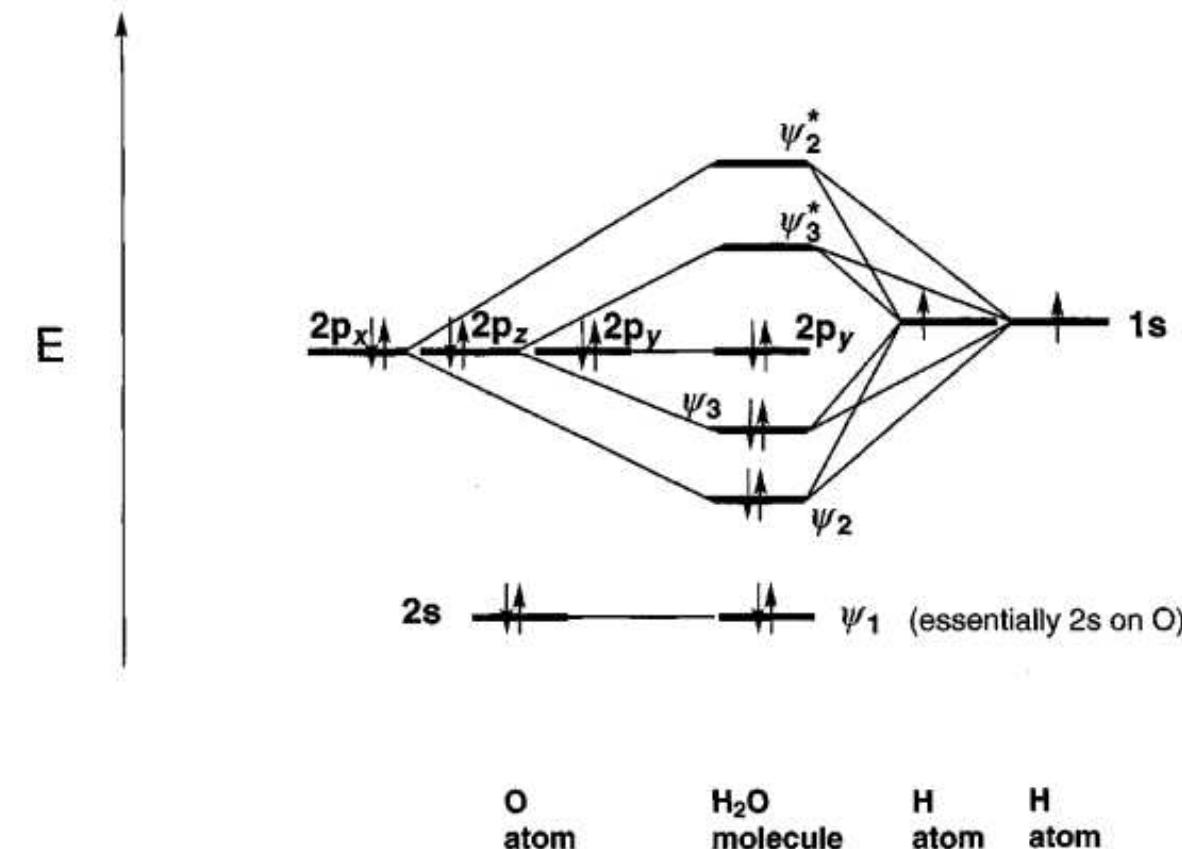


We can see that the two H 1s orbitals make two linear combinations, one with σ_g symmetry and one with σ_u symmetry. They look like the bonding and antibonding MO's of the H₂ molecule.

The π orbitals must be non-bonding because there is no combination of the H 1s orbitals that has π_u symmetry.

❖ For a second example, we can compare the water molecule, H_2O , with BeH_2 . Let us take the change in two steps. If we replace Be by an atom of higher nuclear charge, such as O, the electrons will be more tightly bound and the energy levels of the 2s and 2p orbitals will move down in the diagram relative to the hydrogen 1s orbitals. In terms of Fig. 4.17, the 2s orbital would be smaller and the overlaps in would be less. Thus, the energy level diagram for a hypothetical linear OH_2 molecule would have ψ_1 and 2s at about the same level and the oxygen 2p would give the closest match to the hydrogen orbitals.

FIG. 4.20 Energy level diagram for H_2O (schematic). Compare with Fig. 4.18 for BeH_2 . The nonlinear shape allows overlap with both the p orbitals in the plane of the molecule. As the oxygen s orbital is very tightly bound, ψ_1 is essentially nonbonding.



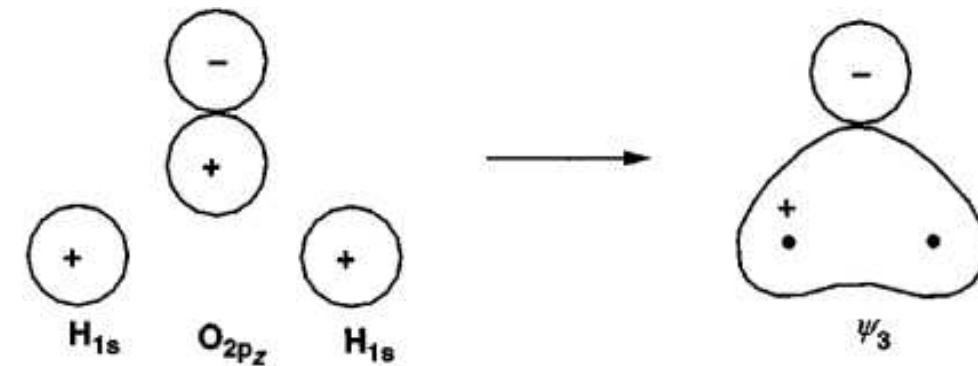
Now the Question....

Why is Water Bent???

If we now bend the H_2O molecule, we have to change the alignment of z since the unique direction is now the bisector of the HOH angle. Let us take *the plane of the molecule as xz* and thus, the x axis is in-plane at right angles to z (i.e., in the position of the z axis of BeH_2) and the *y axis is perpendicular to the plane*. While this change to sustain the 'z as unique direction' convention may seem pedantic, it avoids confusion when symmetry is introduced more formally in detailed treatments.

With this change, the three-centre orbital in the bent molecule corresponding to Ψ_2 in Fig. 4.17 (i) uses the p_x orbital on O in place of p_z and (ii) is a less effective overlap since the hydrogens have moved down. In compensation, the hydrogens can also overlap on the other in-plane oxygen orbital, p_z , as indicated in Fig. 4.19.

FIG. 4.19 Bonding orbital from in-phase overlap of $2p_z$ orbital on O with H 1s orbitals



- Now let's consider what happens to these molecular orbitals as the molecule bends.
- Surely the energies and the molecular orbitals depend upon the shape of the molecule.
- For example, for a linear AH_2 molecule there is no net overlap between the 1s orbitals on the hydrogen atoms and the $2p_x$ and $2p_y$ orbitals on the central atom (Figure 10.11).
- For a bent molecule, however, this is no longer the case. If the molecule bends in the y-z plane, a net overlap (of bonding character) results with the $2p_y$ orbital, as shown in Figure 10.11.
- The net overlap between the 1s orbitals on the hydrogen atoms and the $2p_x$ orbital on the central atom is still zero, however.
- Because there is a net overlap of the 1s orbitals with only one of the 2p orbitals, the degeneracy of the π orbitals is lifted upon bending. What was once a nonbonding orbital of the linear molecule becomes a bonding orbital in the bent molecule.

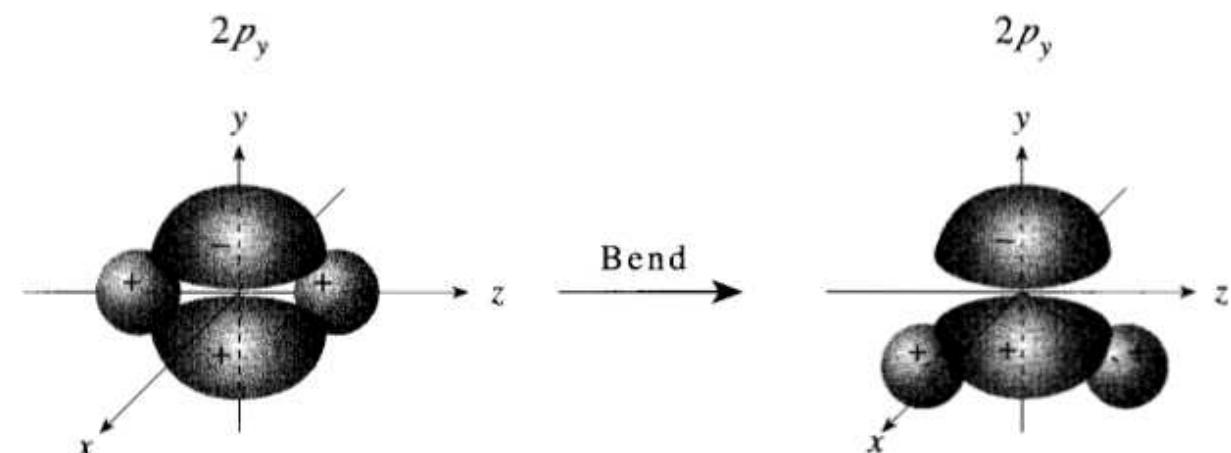


FIGURE 10.11

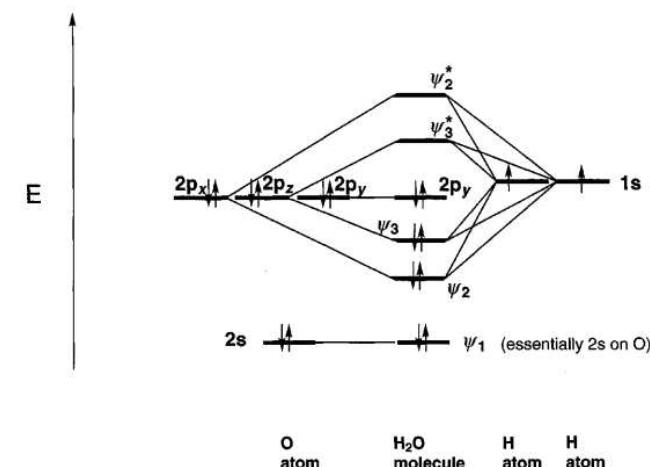
The net overlap of hydrogen 1s orbitals with a central atom $2p_y$ orbital is zero for a linear molecule. If the molecule is bent, however, a nonzero net orbital overlap of the $2p_y$ orbital on the central A atom with the 1s orbitals on the two hydrogen atoms results.

Combining all these ideas, we can describe the interactions in the V-shaped H₂O molecule thus:

- (1) because of the increased nuclear charge, the overlap of the oxygen 2s orbital with the hydrogen 1s orbitals is minor so that the ψ_1 orbital in water is essentially the oxygen 2s orbital and makes only a minor contribution to the bonding.
- (2) the orbital corresponding to ψ_2 in Fig. 4.17 now involves, by convention, the oxygen 2p_x orbital and is less strongly bonding as the overlap is less. Correspondingly, the antibonding combination ψ_2^* is less destabilized.
- (3) a new interaction involving the second in-plane orbital on oxygen provides a bonding combination ψ_3 shown in Fig. 4.19, and the corresponding out-of-phase antibonding combination ψ_3^* .

Thus, the energy level diagram for water is that of Fig. 4.20. The eight valency electrons fill the two bonding orbitals and the two nonbonding orbitals. Thus, there are two bonds and two nonbonding pairs.

FIG. 4.20 Energy level diagram for H₂O (schematic). Compare with Fig. 4.18 for BeH₂. The nonlinear shape allows overlap with both the p orbitals in the plane of the molecule. As the oxygen s orbital is very tightly bound, ψ_1 is essentially nonbonding.



- One of the strengths of VSEPR theory was that it could correctly predict the geometries of most small molecules.
- **We now show how MO theory is also capable of predicting molecular geometry.**
- Let us begin this process by considering the class of molecules having the formula AH_2 , where A can represent any element.
- There are ***two limiting geometries having this molecular formula:*** linear ($D_{\infty h}$) and bent (C_{2v}).
- The one-electron MO diagrams for these two limiting cases were shown in Figure 10.29 and Example 10-7.
- In 1953, A. D. Walsh made a plot of the “***orbital binding energies***” as a function of the bond angle.
- *The total energy for a molecule will then be the sum of its orbital binding energies.*
- ***Whichever configuration has the lowest overall energy will dictate the molecule's geometry.***
- The molecular geometry will therefore depend on which orbitals are occupied.

- Today, the energies of the MOs are used in place of orbital binding energies.
- The Walsh diagram for AH_2 is nothing more than a correlation diagram, where each MO in the $D_{\infty h}$ point group has a corresponding MO in the C_{2v} point group.
- For each pair of corresponding MOs, a consideration of ***the degree of orbital overlap can be used to determine if the energy of that orbital is lower in the linear or in the bent geometry.***
- Thus, a plot of the relative orbital energies can be made as a function of the bond angle.
- Whether the geometry of a molecule is linear or bent (at a particular angle) depends on which structure is lowest in energy, that can be determined using the ***Walsh correlation diagram.***

- The molecular orbitals for a bent triatomic molecule will be represented by different linear combinations of the atomic orbitals from those found for a linear structure.
- By solving for the energy as a function of all bond angles between a linear geometry and a 90° geometry, we can determine how the molecular orbitals for the linear molecule evolve into those characteristic of the 90° geometry.
- A plot of the energy of a molecular orbital as a function of a systematic change in molecular geometry is called a **Walsh correlation diagram**.
- Figure 10.12 (*Ref. McQuarrie's book*) shows the Walsh correlation diagram for a triatomic molecule, AH₂, for which the energies of all six of the molecular orbitals are plotted as a function of bond angle.
- Note that the labels designating the orbitals for the 90° geometry are different from those used for the linear molecule.
- By their definitions, the σ and π designations can be used to describe only a linear molecule.
- The labels for a bent molecule, a₁, b₁ and b₂, reflect specific symmetry properties of the molecule.
- Here we will use them simply as a short-hand notation for the molecular orbitals of the bent molecule.

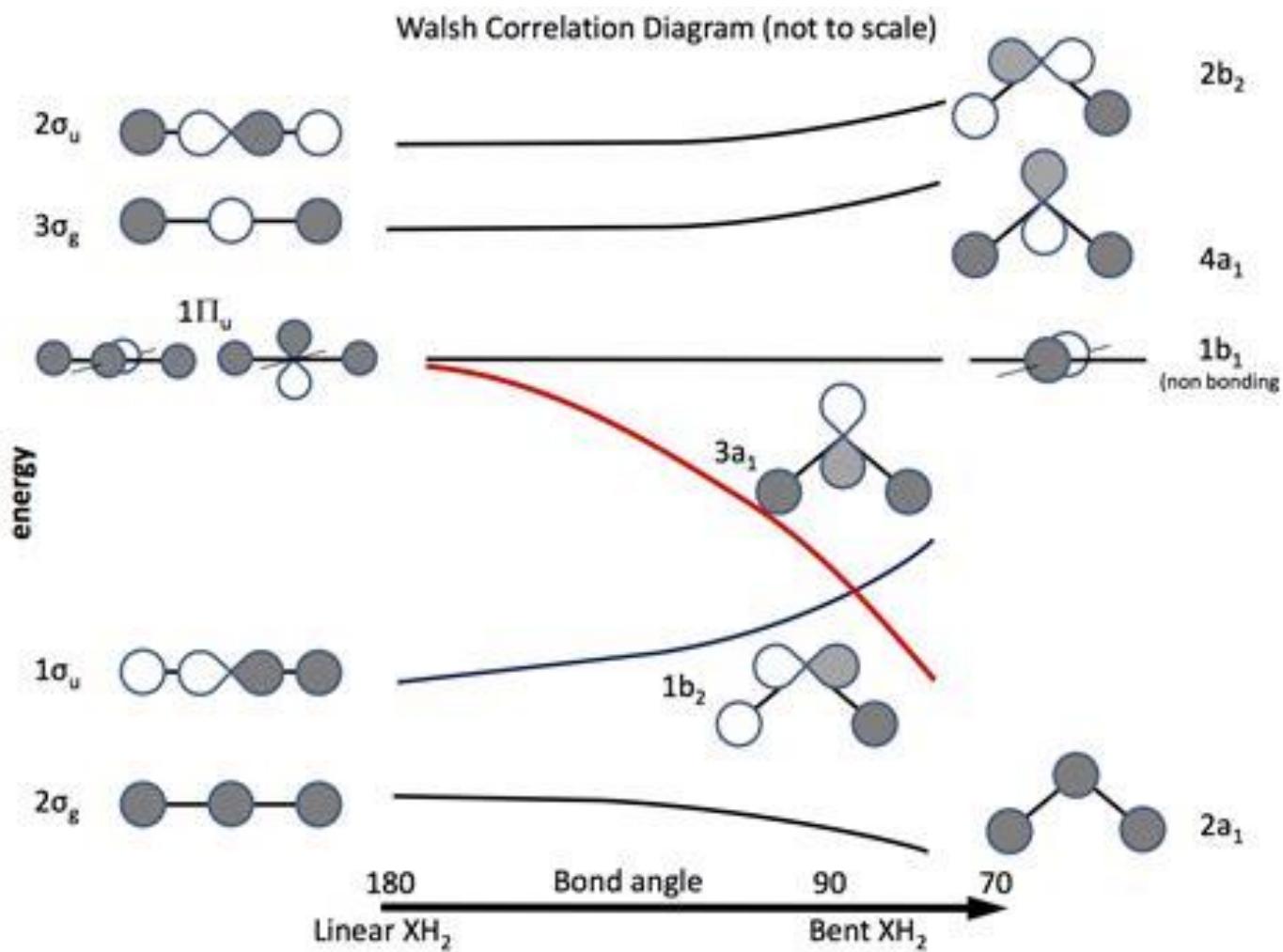
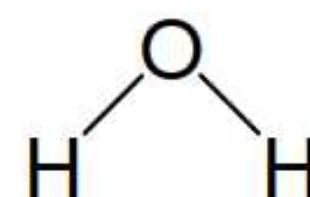
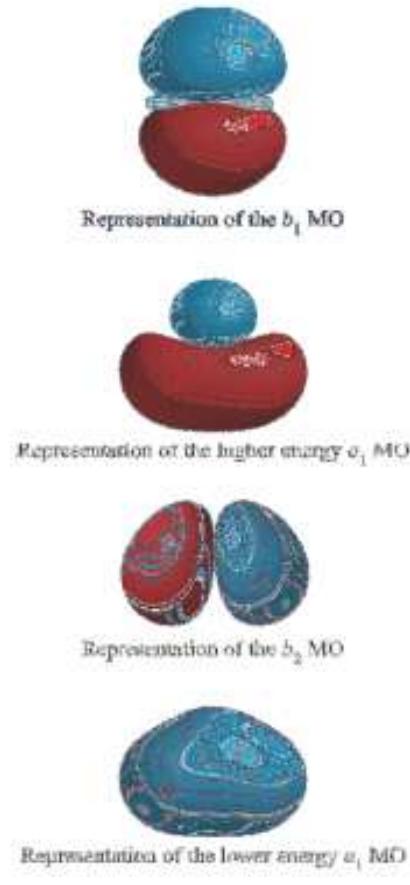
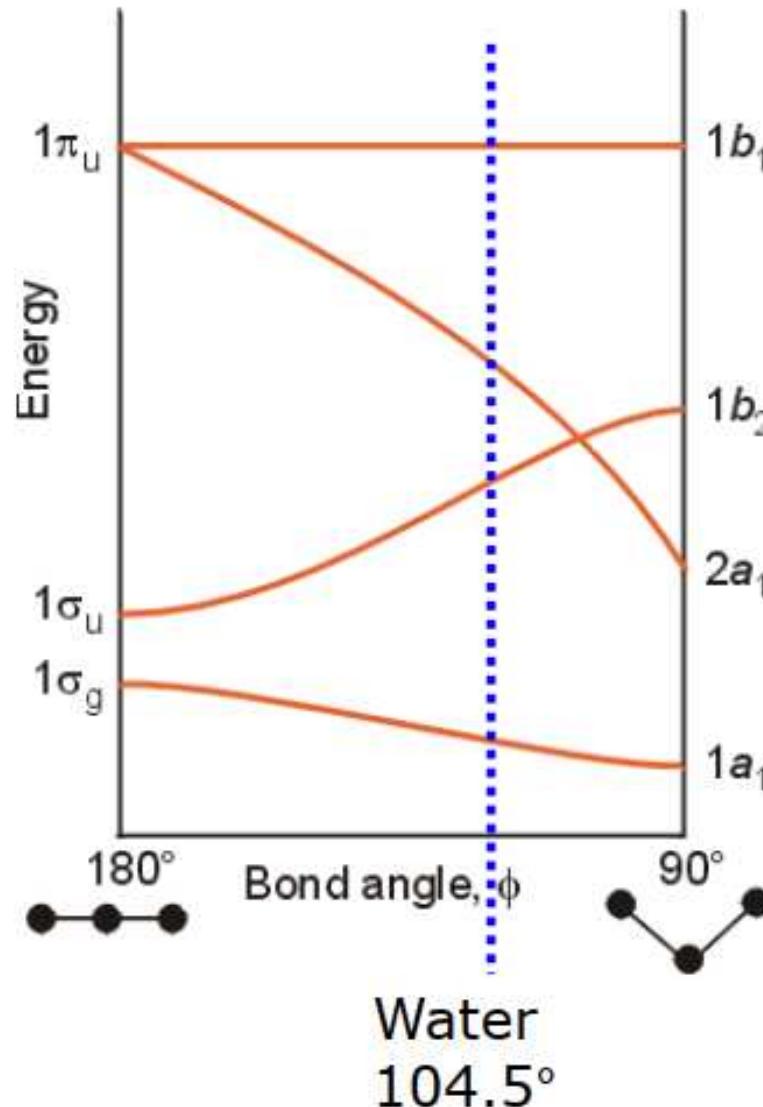
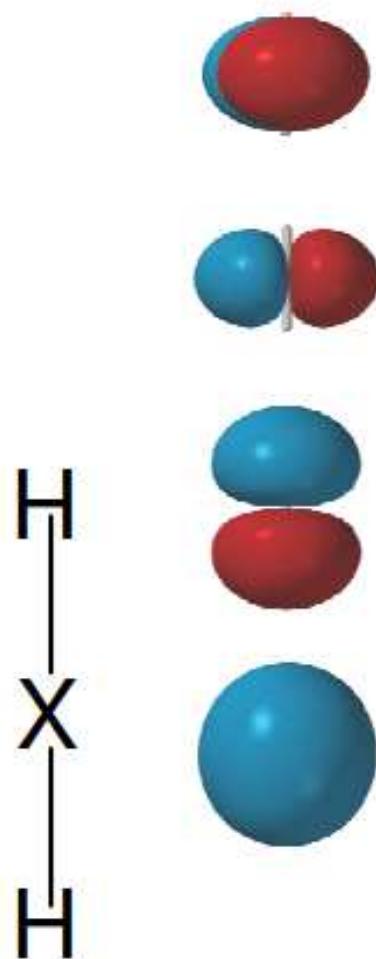


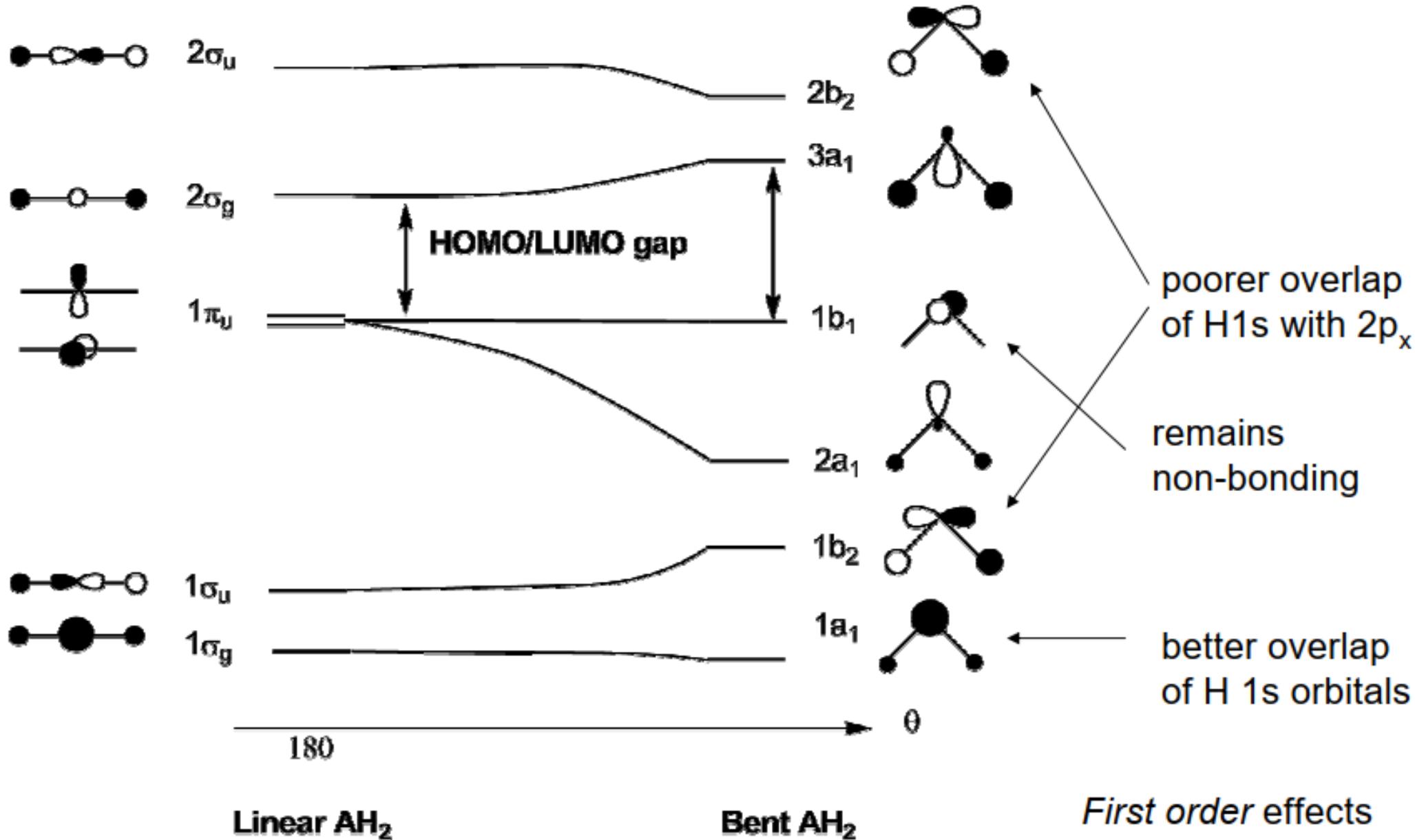
FIGURE 10.12 The Walsh correlation diagram for the *valence electrons* of an AH_2 molecule. The left side of the diagram gives the energy ordering of the molecular orbitals for an H-A-H bond angle of 180° (linear). The right side gives the energy ordering of the molecular orbitals for an H-A-H bond angle of 90° . The solid lines tell us how the energies of the molecular orbitals depend upon H-A-H bond angles between 90° and 180° (linear).

- Bending lifts the degeneracy of the $1\pi_u$ orbitals in the linear structure, stabilizing the $3a_1$ (see Figure 10.12), and not affecting the energy of the $1b_1$ orbital. For large bending angles, the energy of the $3a_1$ orbital drops below that of the $1b_2$ orbital.

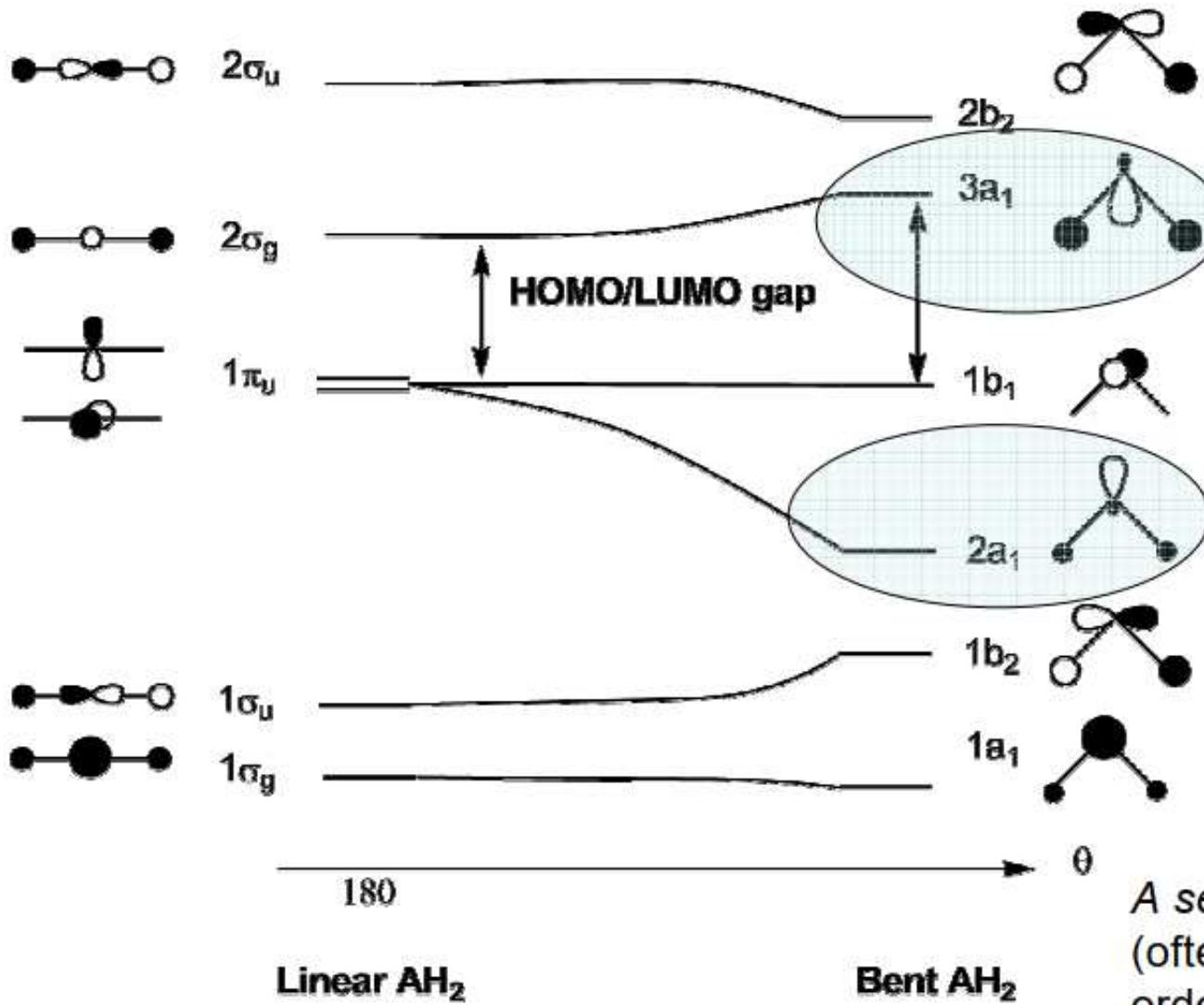
Molecular Orbital Theory – Walsh diagram



Walsh diagram



Walsh diagram

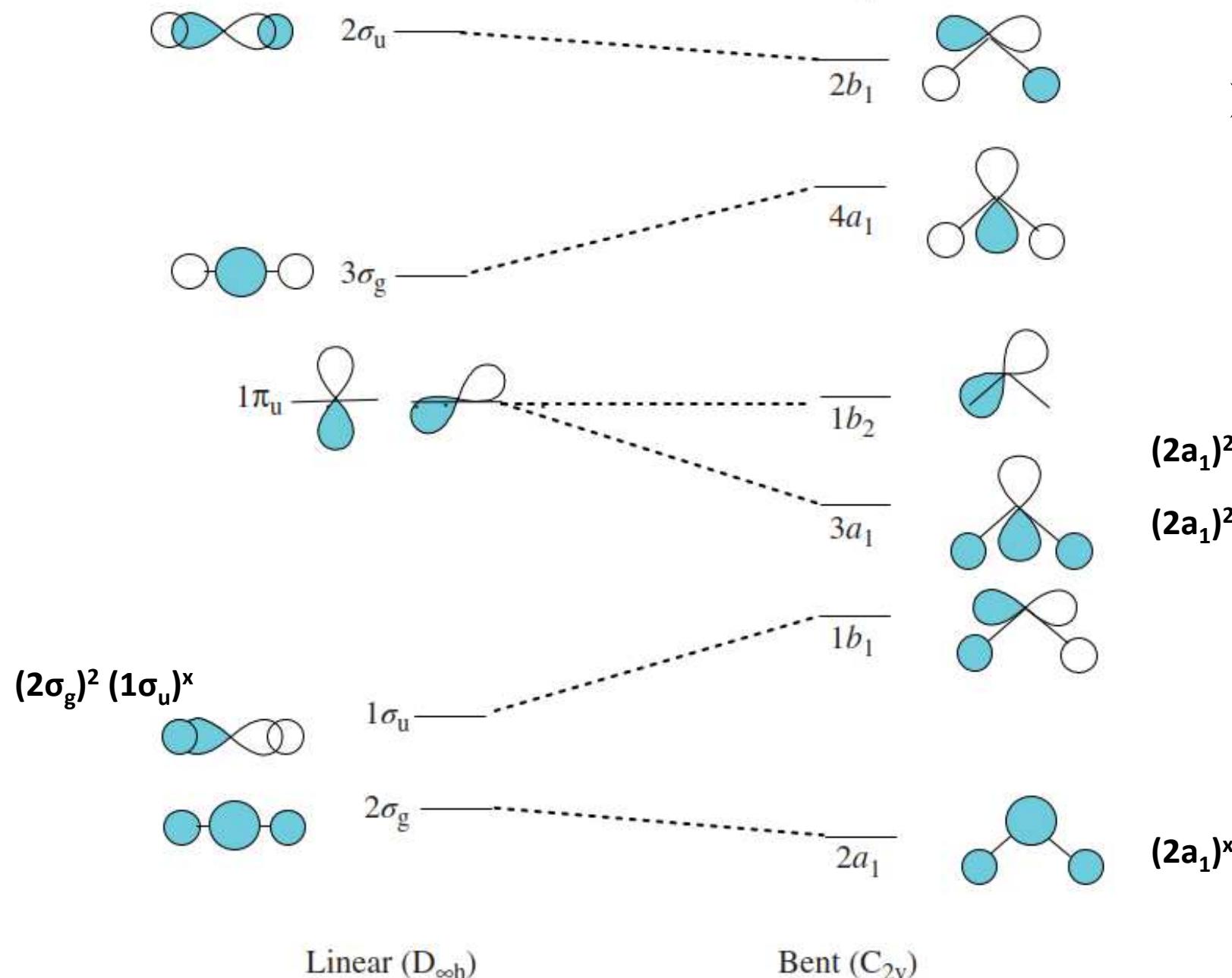


mixing can occur
between 2 orbitals
because they both
transform
as a_1 in the lower
symmetry

A second order effect
(often called a second
order Jahn Teller distortion)

$$\propto \frac{1}{\Delta E}$$

➤ The MOs for the Walsh diagram for AH_2 molecules are shown in Figure 10.30.



➤ note a combination of first and second order Jahn-Teller effects

$$(2a_1)^2 (1b_1)^2 (3a_1)^2 1b_2^x$$

$$(2a_1)^2 (1b_1)^2 (3a_1)^x$$

$$(2a_1)^x$$

- The $2a_1$ MO in the bent configuration is lower in energy than the corresponding $2\sigma_g$ MO in the linear geometry because of the increased orbital overlap between the ligands as the bond angle decreases from 180° .
- Thus, any AH_2 molecule having 1–2 valence electrons will prefer to populate the $2a_1$ MO in the bent molecular geometry.
- ✓ The H_3^+ ion, whose structure has been determined to form an equilateral triangle, is an example of a two-electron AH_2 molecule.
- A consideration of the next highest level of MOs in each geometry shows that there is considerably more overlap in the $1\sigma_u$ MO of the linear geometry (where the $2p_z$ orbital interacts directly with the 2H SALC (symmetry-adapted linear combination)) than in the $1b_1$ MO of the bent geometry (where the $2p_z$ orbital and the SALC are at an angle to one another).
- ✓ Thus, any AH_2 molecule having 3–4 valence electrons will prefer the linear molecular geometry.
- ✓ We have already encountered one such example in BeH_2 , which has four valence electrons. Lithium dihydride (which has three valence electrons) is another example.

- Moving up the MO diagram to the third set of corresponding MOs, the $1\pi_{ux}$ MO in $D_{\infty h}$ is nonbonding, while the corresponding $3a_1$ MO in C_{2v} is bonding.
- ✓ Thus, any AH_2 molecule having **5–6 valence electrons** will favor the **bent** molecular geometry, as is the case for BH_2 , which has five valence electrons and an equilibrium bond angle of 131° .
- Moving up to the fourth energy level, the $1\pi_{uy}$ MO in $D_{\infty h}$ is nonbonding, while the corresponding $1b_2$ MO in C_{2v} is also nonbonding. Thus, these two orbitals have the same energy. Any AH_2 molecule having **7–8 total valence electrons** will prefer the **bent molecular geometry**, because it is the **overall orbital energy that matters**.
- ✓ The **water molecule, which has eight valence electrons**, has a **bent molecular geometry** (104.5°).

- Continuing up the MO diagram to the fifth energy level, the $3\sigma_g$ MO in $D_{\infty h}$ is less antibonding than the $4a_1$ MO in C_{2v} .
- ✓ Thus, any AH_2 species containing 9–10 valence electrons will prefer a linear geometry.
- Finally, the $2\sigma_u$ MO in $D_{\infty h}$ is more antibonding than the $2b_2$ MO in C_{2v} , so that 11- to 12-electron AH_2 molecules would prefer to be bent. Because of the population of antibonding MOs at these higher levels, very few such species actually exist.
- *Walsh diagrams are extremely accurate in the prediction of molecular geometries.* A summary of the results for AH_2 molecules is provided in Table 10.9.

Walsh's Rules:

- An AH_2 molecule will be Linear if it contains 3 or 4 valence electrons. e.g. BeH_2 , BH_2^+
- Bent if it contains 1,2, or 5–8 valence electrons. e.g. BH_2 , CH_2 , NH_2 , H_2O , H_2S .

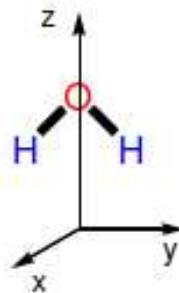
TABLE 10.9 Predicted molecular geometries of AH_2 molecules using Walsh diagrams as a function of the total number of valence electrons in the molecule.

Number of Valence e ⁻	Predicted Geometry
1–2	Bent
3–4	Linear
5–8	Bent
9–10	Linear
11–12	Bent

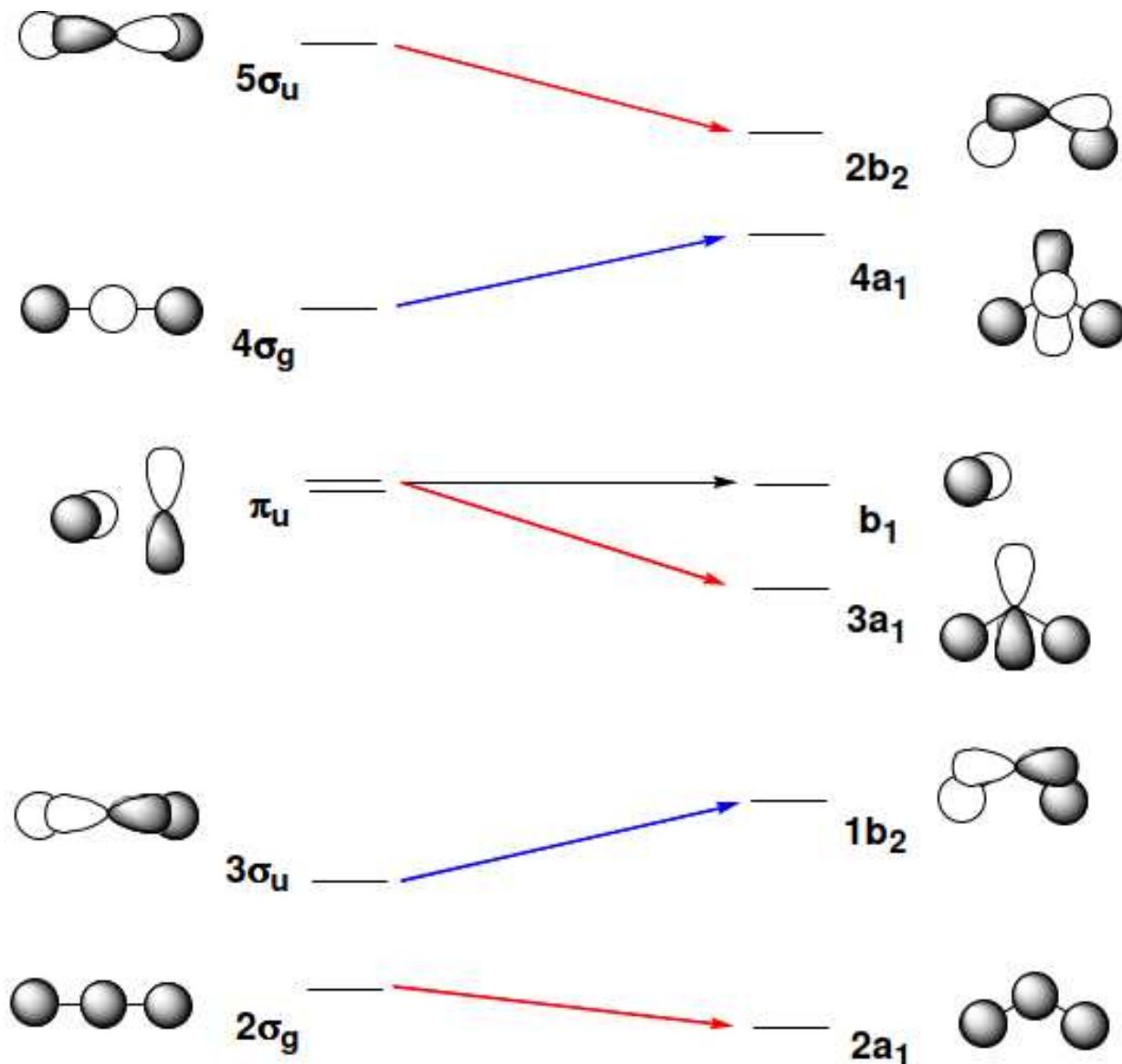
- ✓ For a linear structure, this would correspond to the electron configuration of $(2\sigma_g)^2 (1\sigma_u)^2$.
 - ✓ A bent structure would have an electron configuration of $(2a_1)^2 (1b_2)^2$ or $(2a_1)^2 (3a_1)^2$, depending on the bond angle.
 - ✓ Because bending destabilizes the energy of the lowest two molecular orbitals, the electron configuration $(2\sigma_g)^2 (1\sigma_u)^2$ is lower in energy than either $(2a_1)^2 (1b_2)^2$ or $(2a_1)^2 (3a_1)^2$.
 - ✓ The Walsh correlation diagram correctly predicts that BeH_2 is linear.
- Recall: a molecule adopts the structure that best stabilizes the HOMO.
- ✓ If the HOMO is unperturbed by the structural change under consideration, then the occupied MO lying closest to it governs the geometric preference.

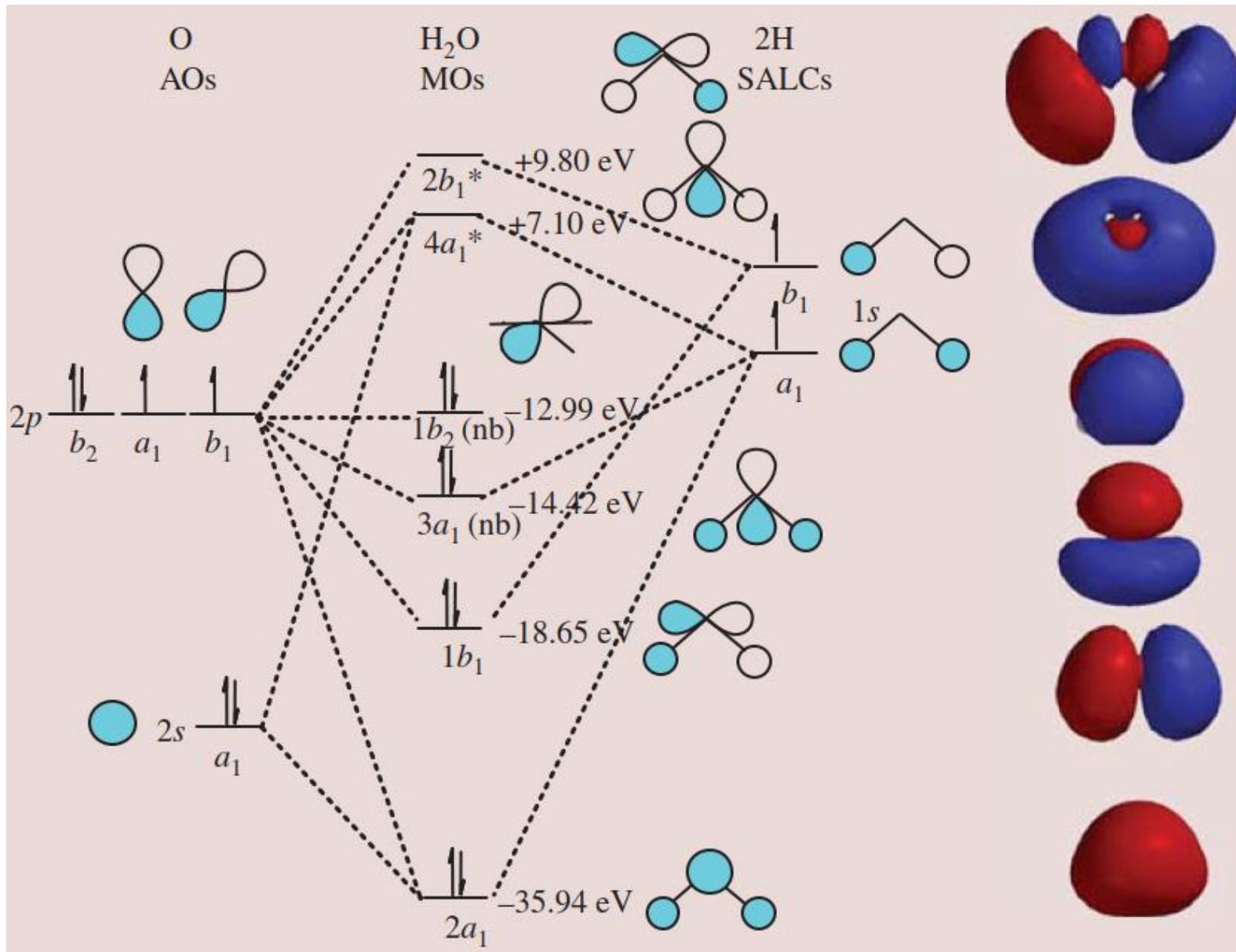
MO theory and molecular geometry (Walsh diagrams)

- Correlate changes in energy of MO's between species AB_x of high and lower symmetry, such as BeH_2 and H_2O .

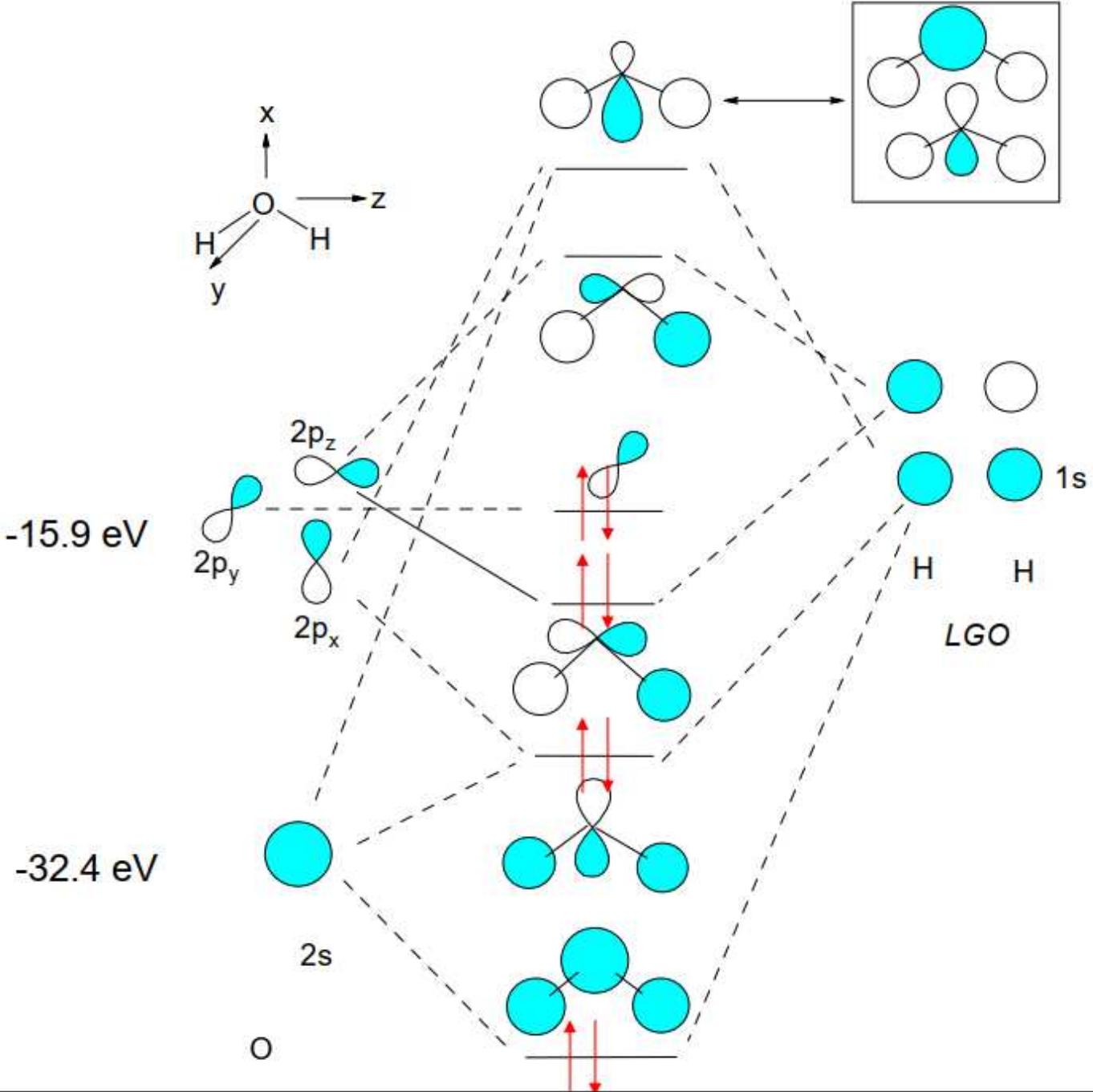


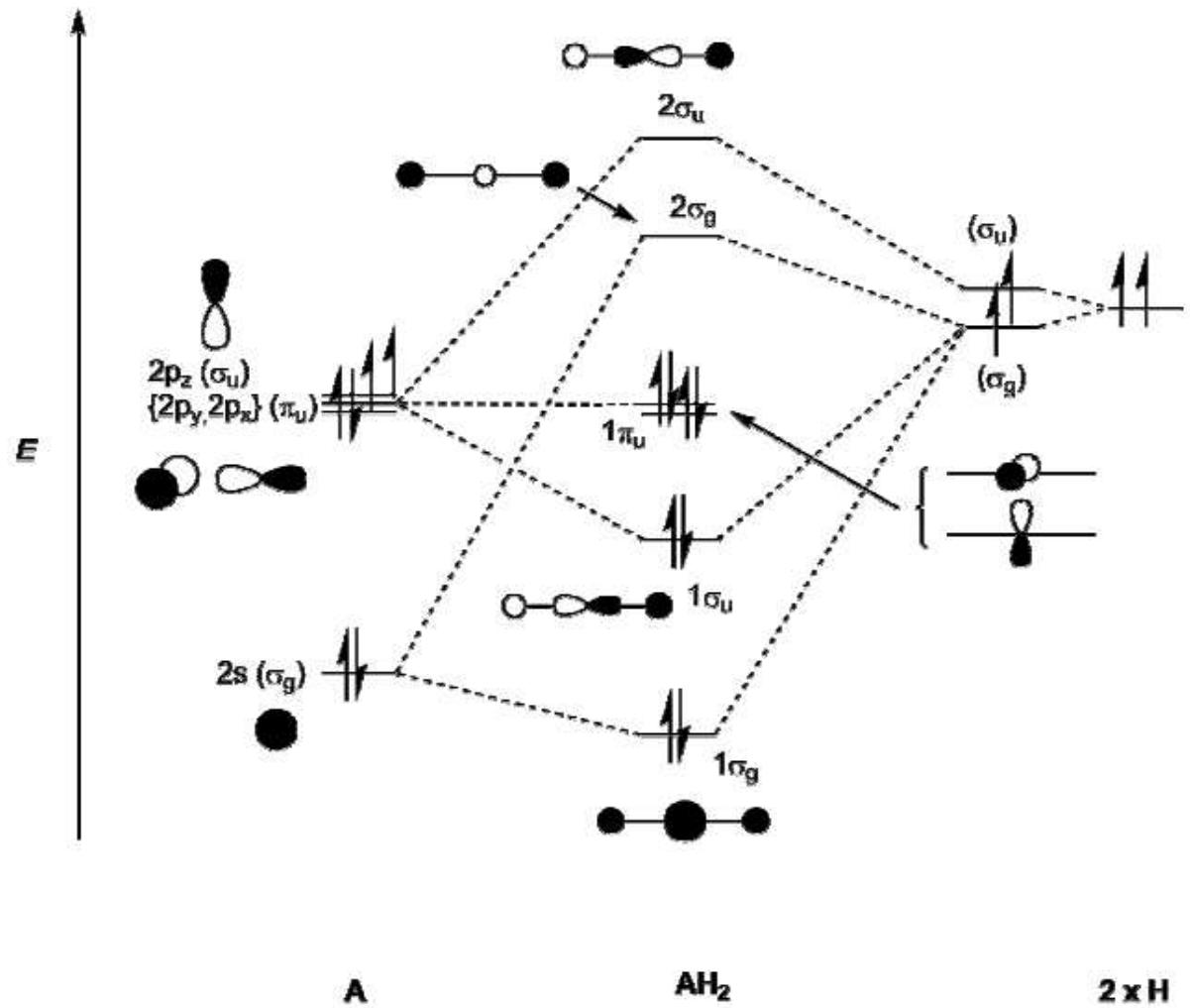
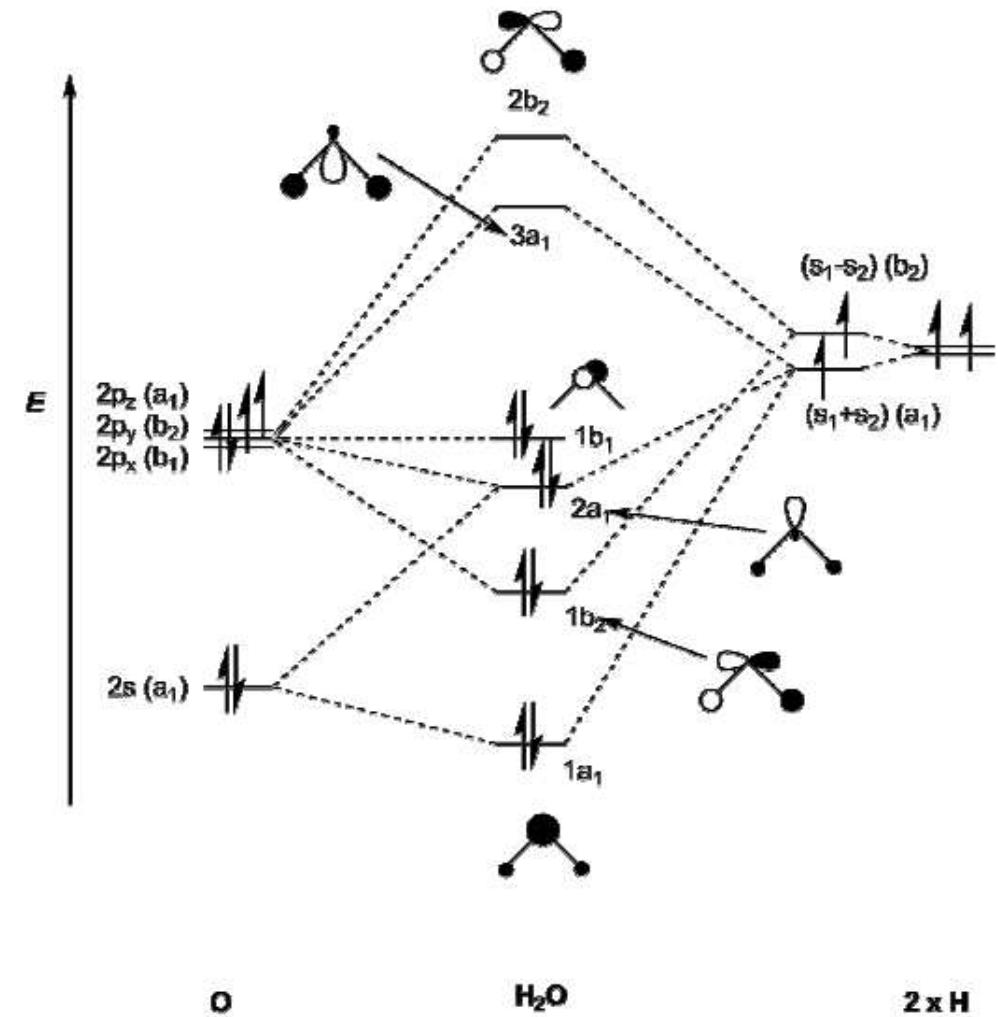
BeH_2	$2\sigma_g^2 3\sigma_u^2$	linear
BH_2	$2a_1^2 1b_2^2 3a_1^1$, 131°
CH_2	$2a_1^2 1b_2^2 3a_1^2$, 102°
NH_2	$2a_1^2 1b_2^2 3a_1^2 1b_1^1$, 103°
OH_2	$2a_1^2 1b_2^2 3a_1^2 1b_1^2$, 105°
FH_2^+	$2a_1^2 1b_2^2 3a_1^2 1b_1^2$, 113°





Example 10.7 The H_2O molecule is bent and belongs to the C_{2v} point group.



$D_{\infty h}$  C_{2v} 

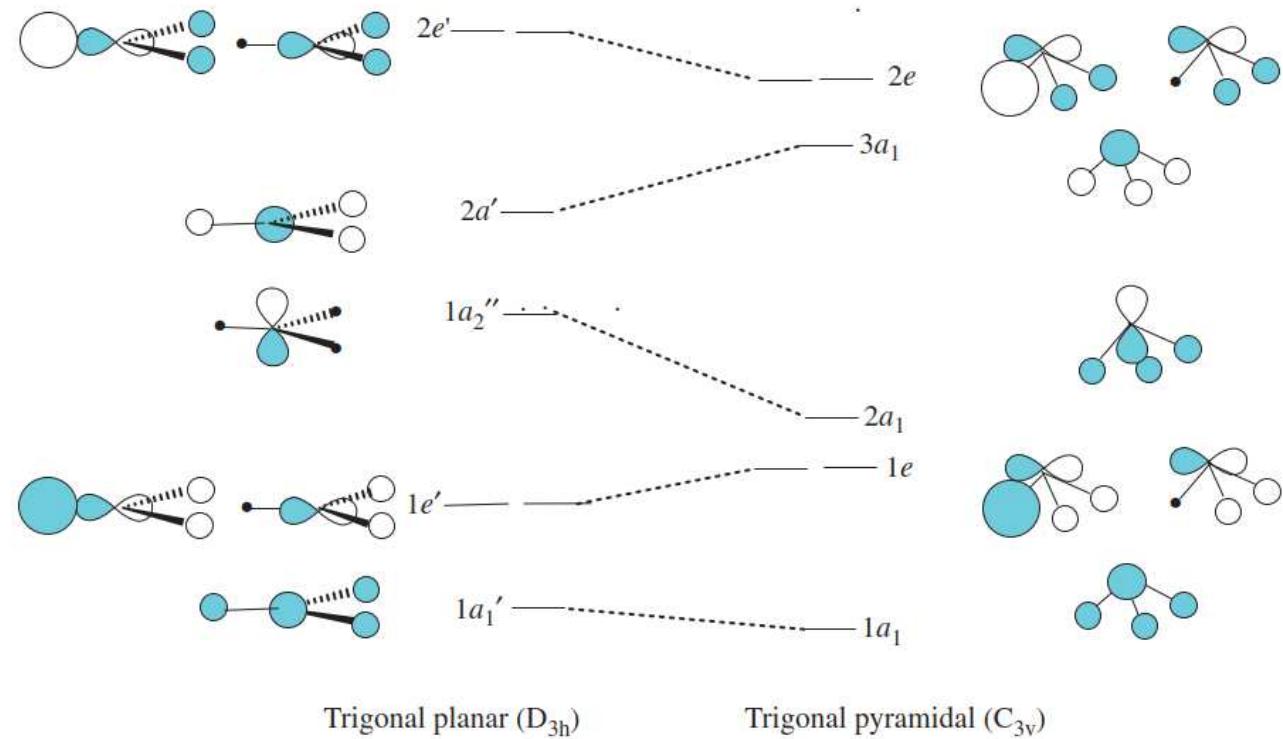
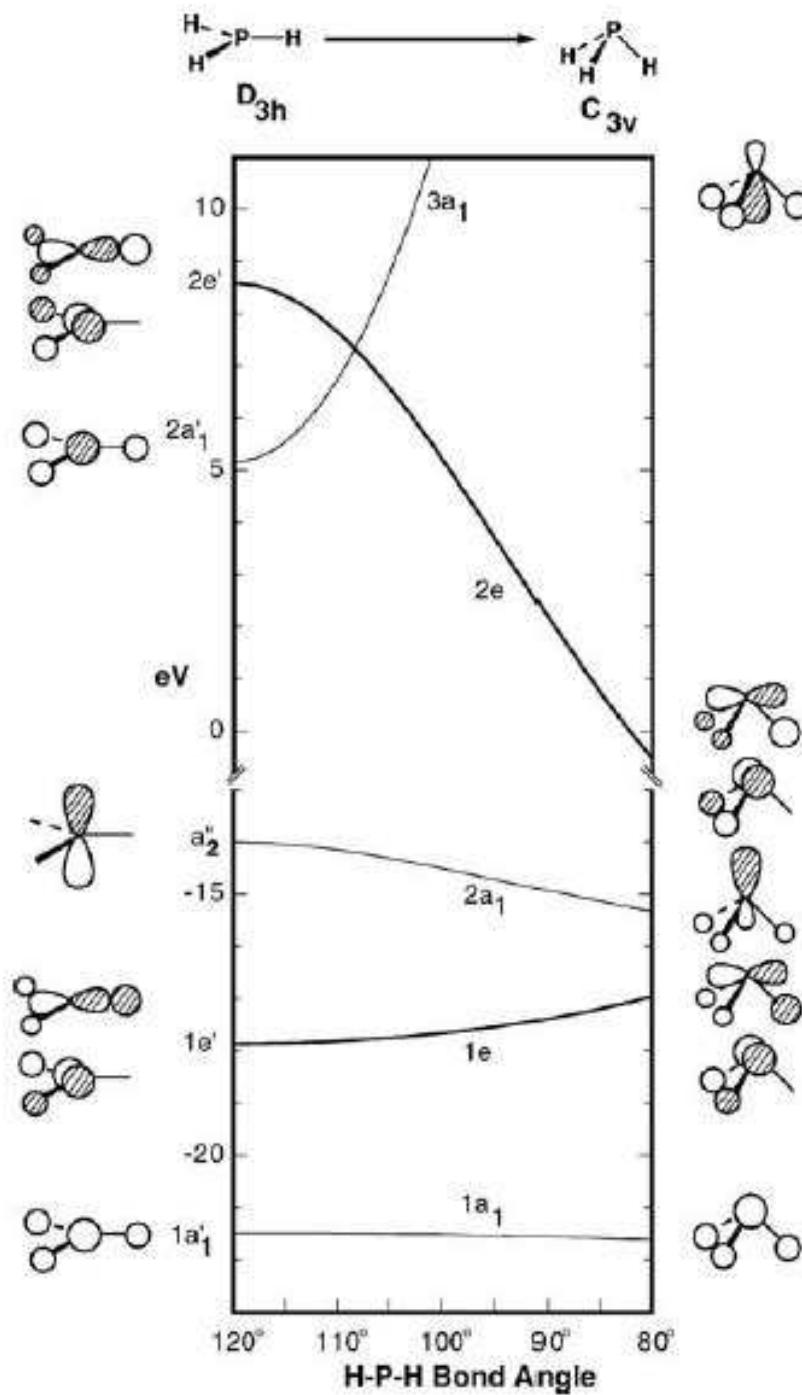


FIGURE 10.31 Walsh diagram for AH_3 molecules.

TABLE 10.10 Predicted molecular geometries of AH_3 molecules using Walsh diagrams as a function of the total number of valence electrons in the molecule.

Number of Valence e^-	Predicted Geometry
1–2	Trigonal pyramidal
3–6	Trigonal planar
7–8	Trigonal pyramidal
9–10	Trigonal planar
11–14	Trigonal pyramidal

Walsh's Rules:

- An AH_3 molecule will be *pyramidal* if it contains 1,2 or 8 valence electrons. e.g. NH_3 .
- *planar* if it contains 3-6 valence electrons. e.g. BH_3 , NH_3^+ .

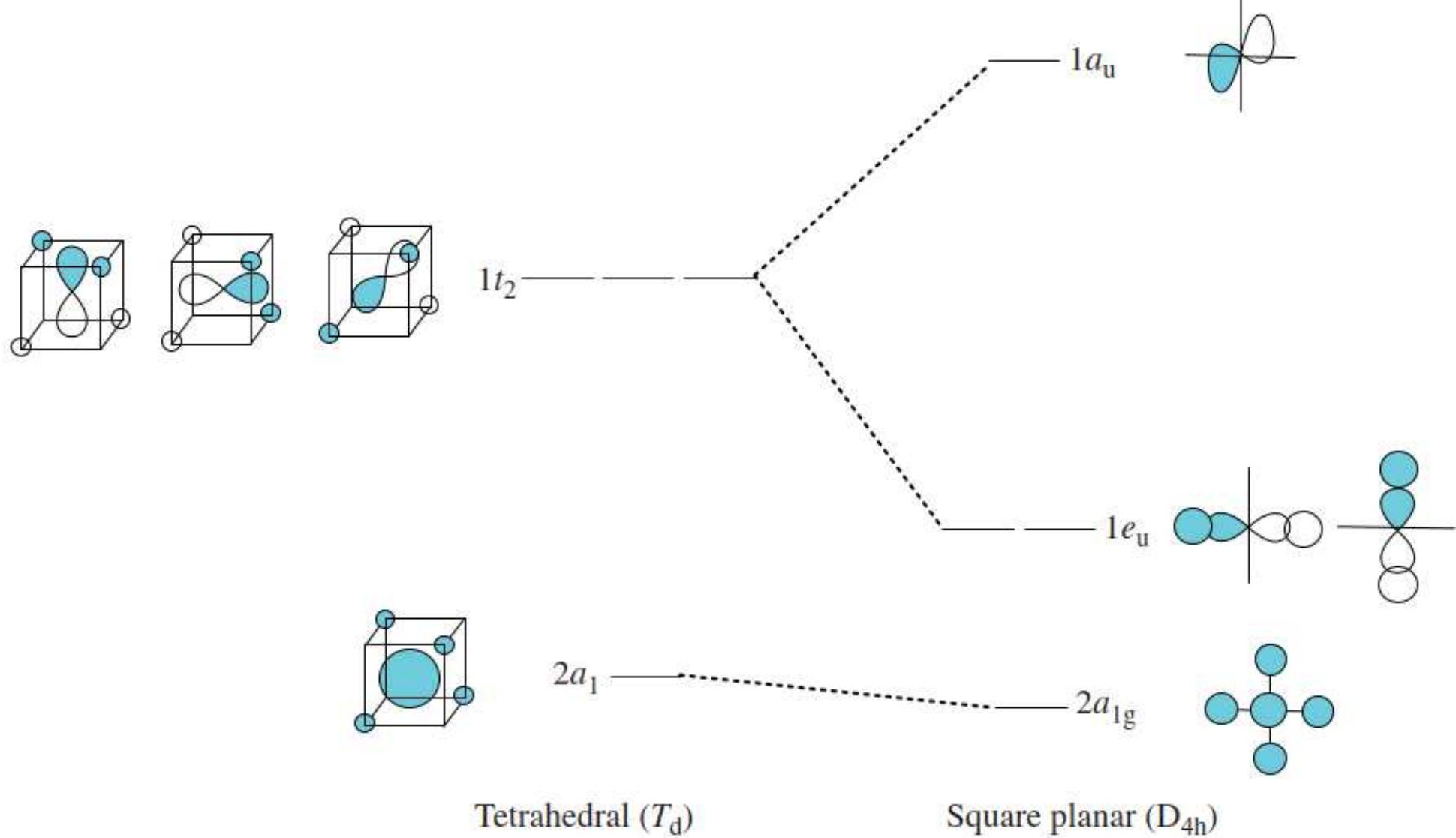


FIGURE 10.35 Partial Walsh diagram for AH_4 molecules.

TABLE 10.12 Predicted molecular geometries of AH_4 molecules as a function of the total number of valence electrons in the molecule using the partial Walsh diagram shown in Figure 10.34.

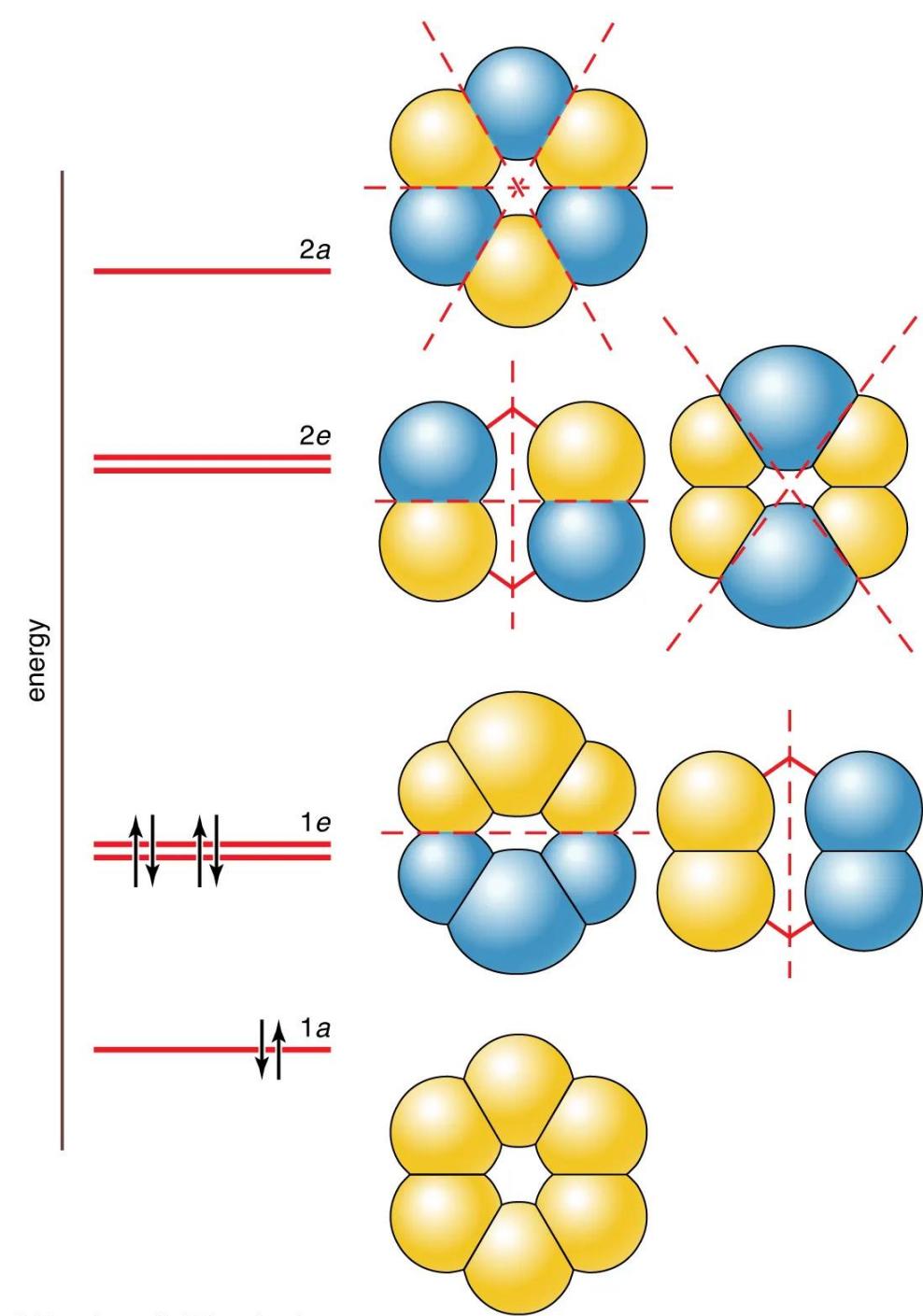
Number of Valence e^-	Predicted Geometry
1–6	Square planar
7–8	Tetrahedral

A qualitative Walsh diagram for AH_4 molecules is shown in Figure 10.35. Only the lower energy MOs in the $T_d \rightarrow D_{4h}$ transition are shown in the figure. Table 10.12 lists the predicted molecular geometries for AH_4 molecules as a function of the total number of valence electrons. Thus, the **eight-electron species** BH_4^- , CH_4 , and NH_4^+ are **tetrahedral**, while the **six-electron species** LiH_4^- , BeH_4 , and BH_4^+ are **square planar**.

It is not always strictly appropriate to use the notation σ and π in polyatomic molecules because these labels apply to a linear molecule. However, it is often convenient to continue to use the notation when concentrating on the local form of an orbital—its shape relative to the internuclear axis between two neighbouring atoms (this is an example of how the language of valence bond theory survives in MO theory). The correct procedure for labelling orbitals in polyatomic molecules according to their symmetry. For our present purposes all we need know of this more appropriate procedure is the following:

- a, b denote a nondegenerate orbital
- e denotes a doubly degenerate orbital (two orbitals of the same energy)
- t denotes a triply degenerate orbital (three orbitals of the same energy).

Subscripts and superscripts are sometimes added to these letters, as in a_1 , b_1 , e_g , and t_2 because it is sometimes necessary to distinguish different a, b, e, and t orbitals according to a more detailed analysis of their symmetries.



benzene

Figure 15: The six π molecular orbitals of a benzene molecule and their relative energies. Only the three lowest-energy orbitals are occupied in benzene. The bonding and antibonding character of these orbitals is distributed around the ring of carbon atoms. The dashed lines represent nodal planes, and the shading reflects the two possible phases of the orbitals. Constructive interference, resulting in an area of high electron density, occurs between like phases; destructive interference, resulting in a nodal plane, occurs between unlike phases.

(b) Hypervalence in the context of molecular orbitals

Key point: The delocalization of molecular orbitals means that an electron pair can contribute to the bonding of more than two atoms.

- In valence bond theory, to explain **hypervalence** we use *d* orbitals to allow the valence shell of an atom to accommodate more than eight electrons. *Molecular orbital theory explains it rather more elegantly.*
- We consider SF₆, which has six S—F bonds and hence 12 electrons involved in forming bonds and is therefore hypervalent.
- The simple basis set of atomic orbitals that are used to construct the *molecular orbitals consists of the valence shell s and p orbitals of the sulfur atom and one p orbital of each of the six F atoms and pointing towards the sulfur atom. We use the F2p orbitals rather than the F2s orbitals because they match the sulfur orbitals more closely in energy.* From these 10 atomic orbitals it is possible to construct 10 molecular orbitals.
- Calculations indicate that four of the orbitals are bonding and four are antibonding; the two remaining orbitals are nonbonding (Fig. 2.31).

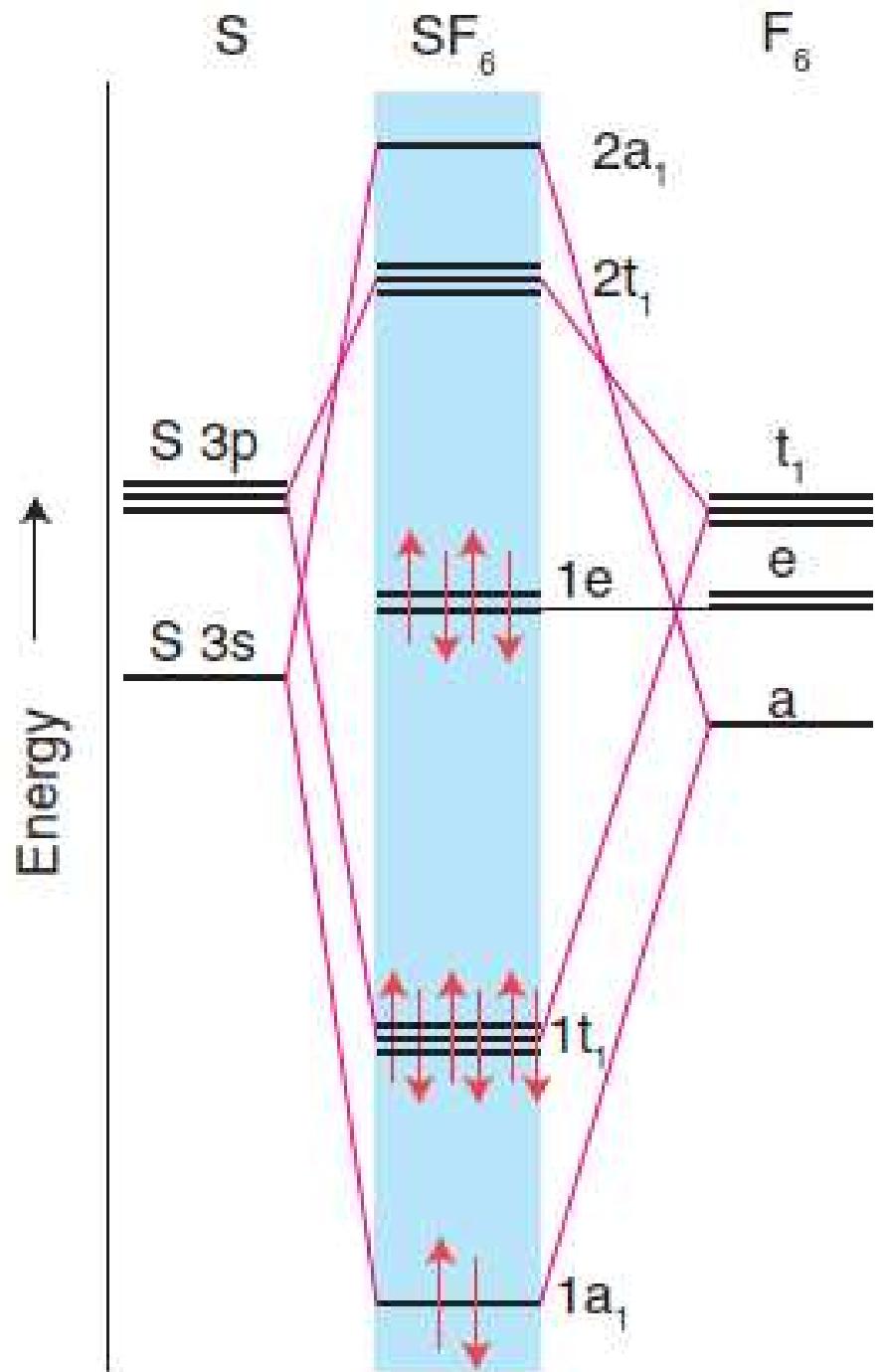


Figure 2.31 A schematic molecular orbital energy-level diagram for SF_6 .

There are 12 electrons to accommodate. The first two enter $1a_1$ and the next six enter $1t_1$. The remaining four fill the nonbonding pair of orbitals, resulting in the configuration: $1a_1^2 1t_1^6 1e^4$.

As we see, none of the antibonding orbitals ($2a_1$ and $2t_1$) is occupied.

Molecular orbital theory, therefore, accounts for the formation of SF_6 , with four bonding orbitals and two nonbonding orbitals occupied, and does not need to invoke $S3d$ orbitals and octet expansion.

This does not mean that d orbitals cannot participate in the bonding, but it does show that they are not necessary for bonding six F atoms to the central sulfur atom.

The limitation of valence bond theory is the assumption that each atomic orbital on the central atom can participate in the formation of only one bond. Molecular orbital theory takes hypervalence in its stride by having available plenty of orbitals, not all of which are antibonding. Therefore, *the question of when hypervalence can occur appears to depend on factors other than d-orbital availability, such as the ability of small atoms to pack around a large atom.*

(c) Localization

Key point: Localized and delocalized descriptions of bonds are mathematically equivalent, but one description may be more suitable for a particular property, as summarized in Table 2.5.

Table 2.5 suggests when it is appropriate to select a *delocalized description or a localized description*. In general, *a delocalized description is needed for dealing with global properties of the entire molecule*. Such properties include electronic spectra (UV and visible transitions), photoionization spectra, ionization and electron attachment energies, and reduction potentials.

In contrast, a localized description is most appropriate for dealing with properties of a fragment of a total molecule. Such properties include bond strength, bond length, bond force constant, and some aspects of reactions (such as acid–base character): in these aspects the localized description is more appropriate because it focuses attention on the distribution of electrons in and around a particular bond.

Table 2.5 A general indication of the properties for which localized and delocalized descriptions are appropriate

Localized appropriate	Delocalized appropriate
Bond strengths	Electronic spectra
Force constants	Photoionization
Bond lengths	Electron attachment
Brønsted acidity*	Magnetism
VSEPR description	Standard potentials†

A striking feature of the VB approach to chemical bonding is its accord with chemical instinct, as it identifies something that can be called ‘an A—B bond’. Both OH bonds in H_2O , for instance, are treated as localized, equivalent structures because each one consists of an electron pair shared between O and H.

This feature appears to be absent from MO theory because molecular orbitals are delocalized and the electrons that occupy them bind all the atoms together, not just a specific pair of neighbouring atoms.

The concept of an A—B bond as existing independently of other bonds in the molecule, and of being transferable from one molecule to another, seems to have been lost. However, we shall now show that the molecular orbital description is mathematically almost equivalent to the overall electron distribution as described by individual bonds. The demonstration hinges on the fact that linear combinations of molecular orbitals can be formed that result in the same overall electron distribution, but the individual orbitals are distinctly different.

Consider the H₂O molecule. The two occupied bonding orbitals of the delocalized description, 1a₁ and 1b₂, are shown in Fig. 2.32. If we form the sum 1a₁ + 1b₂, the negative half of 1b₂ cancels half the 1a₁ orbital almost completely, leaving a localized orbital between O and the other H. Likewise, when we form the difference 1a₁ - 1b₂, the other half of the 1a₁ orbital is cancelled almost completely, so leaving a localized orbital between the other pair of atoms. Therefore, by taking sums and differences of delocalized orbitals, localized orbitals are created (and vice versa). Because these are two equivalent ways of describing the same overall electron population, one description cannot be said to be better than the other.

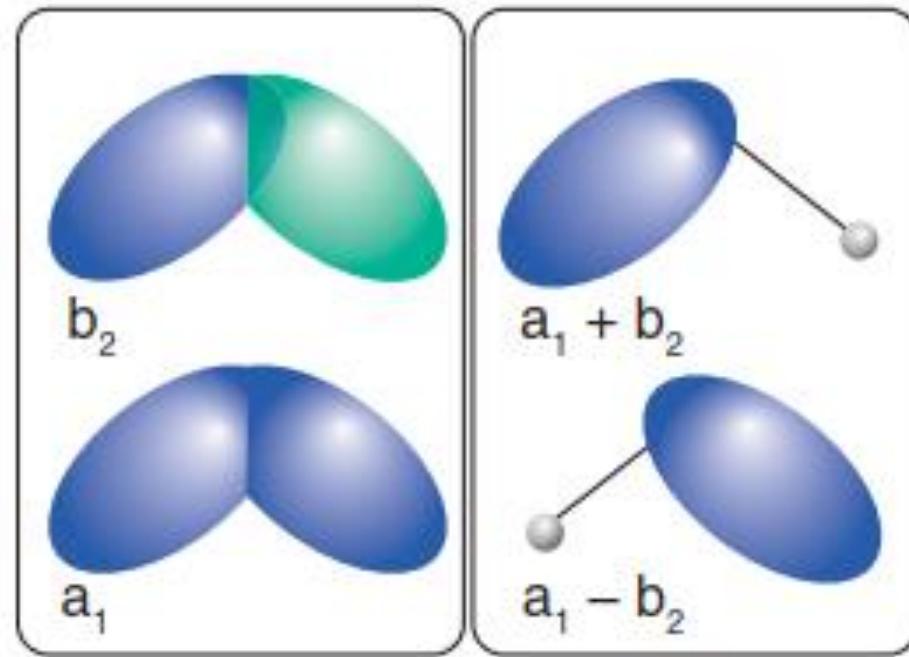


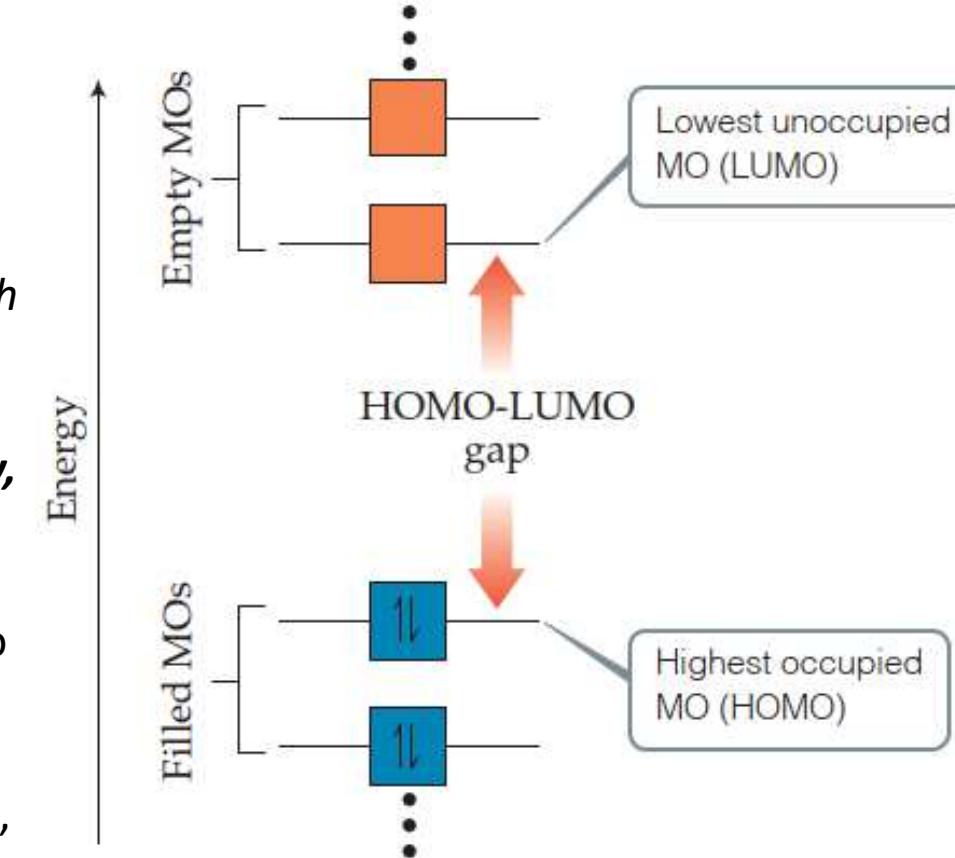
Figure 2.32 The two occupied 1a₁ and 1b₂ orbitals of the H₂O molecule and their sum 1a₁+1b₂ and difference 1a₁-1b₂. In each case we form an almost fully localized orbital between a pair of atoms.

❖CHEMISTRY PUT TO WORK: Orbitals and Energy

- Asked to identify the **major technological challenge for the twenty-first century, you might say “energy,”** reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. *One of the most remarkable sources of clean energy is the Sun, which sends enough energy to power the world for millions of years.* Our challenge is to capture enough of this energy in a form that allows us to use it as needed.
- **Photovoltaic solar cells convert the light from the Sun into usable electricity,** and the development of more efficient solar cells is one way to address Earth’s future energy needs.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun, especially from the visible portion of the spectrum, to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of visible light by chemicals. It is helpful to think of this process in the context of molecular orbital theory: **Light excites an electron from a filled molecular orbital to an empty one at higher energy.** Because MOs have definite energies, only light of the proper wavelengths can excite electrons.

In discussing light absorption by molecules, we can focus on the two **frontier MOs** shown in Figure 9.47. The highest occupied molecular orbital (**HOMO**) is the MO of highest energy that has electrons in it. The lowest unoccupied molecular orbital (**LUMO**) is the MO of lowest energy that does not have electrons in it. In CO, for example, the HOMO is the σ_b MO and the LUMO is the 2π MO.



▲ Figure 9.47 Definitions of the highest occupied and lowest unoccupied molecular orbitals. The energy difference between these is the HOMO-LUMO gap.

- The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the minimum energy needed to excite an electron in the molecule.
- Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to the higher level.
- The minimum energy needed to excite an electron from the HOMO to the LUMO in N₂ corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. As a result, N₂ cannot absorb visible light and is therefore colorless.
- The magnitude of the energy gap between filled and empty electronic states is critical for solar energy conversion. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy.
- Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However, TiO₂ is white and absorbs only a small amount of the Sun's radiant energy.
- Scientists are working to make solar cells in which TiO₂ is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum. If the HOMO of these molecules is higher in energy than the HOMO of TiO₂, the excited electrons will flow from the molecules into the TiO₂, thereby generating electricity when the device is illuminated with light and connected to an external circuit.
- Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world's energy portfolio.

Photoelectron Spectra (PES) Support the Existence of Atomic and Molecular Orbitals

- The idea of atomic orbitals and molecular orbitals is rather abstract and sometimes appears far removed from reality.
- The energies of orbitals are calculated today by solving the Schrödinger equation with computer software. The commercial software available is now so sophisticated that this approach can be as easy as typing in the name of the molecule or drawing it on screen. But these values are theoretical. How do we determine orbital energies experimentally?
- It so happens, however, that the electron configurations of molecules can be demonstrated experimentally. The approach used is very similar to the photoelectric effect.
- If high energy electromagnetic radiation is directed into a gas, electrons are ejected from the molecules in the gas.
- *The energy required to eject an electron from a molecule, called the ionization energy, is a direct measure of how strongly bound the electron is within the molecule.* The ionization energy of an electron within a molecule depends upon the molecular orbital the electron occupies; ***the lower the energy of the molecular orbital, the more energy needed to remove, or ionize, an electron from that molecular orbital.***
- *The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules is called photoelectron spectroscopy (PES).*

Photoelectron Spectra (PES) Support the Existence of Molecular Orbitals

Photoelectron spectroscopy is an instrumental technique that enables the measurement of **orbital energies** in atoms and molecules. In this technique gas phase atoms or molecules are ionized by high-energy radiation. For a molecule (M), the process is as follows:



A photon with sufficient energy ($h\nu$) can cause an electron to be ejected from the atom or molecule. If the photon has energy that is above the threshold required for ionization, the excess energy is imparted as kinetic energy to the ejected electron. The ionization energy (**orbital energy**), the energy of the absorbed photon, and the kinetic energy of the ejected electron are related by the equation.

$$IE = h\nu - KE(\text{electron})$$

We know ν , the frequency of the radiation being used to bombard the molecules; so, if we could measure the kinetic energy of the ejected electron, KE , we could solve this expression to find the orbital energy.

The kinetic energy of an ejected electron depends on its speed, V , because $KE = mV^2/2$. A photoelectron spectrometer acts like a mass spectrometer in that it measures V for electrons just as a mass spectrometer can measure V for ions. In this method, the electrons pass through a region of electric or magnetic field, which deflects their path. As the strength of the field is changed, the paths of the electrons change, too, until they fall on a detector and generate a signal. From the strength of the field required to obtain a signal, we can work out the speed (and hence the kinetic energy) of electrons ejected from a given orbital and so obtain the energy of the orbital from which they came.

A photoelectron spectrometer contains a source of high-frequency, short-wavelength radiation.

Ultraviolet radiation is used (for XPS) most often for molecules, but x-rays are used (for ESCA) to explore orbitals buried deeply inside solids. Photons in both frequency ranges have so much energy that they can eject electrons from the molecular orbitals they occupy.

Photoelectron spectroscopy may be used to study orbital energies of either core or valence electrons.

Ionization of a core electron requires x-ray radiation (ESCA, *electron spectroscopy for chemical analysis*) whereas *ionization of valence electrons (which are responsible for bonding in molecules) requires lower energy ultraviolet (UV) radiation.*

Helium gas is the most common UV radiation source used for the photoelectron spectroscopy of molecules. When electronically excited, He atoms emit nearly monochromatic (single wavelength) radiation at a wavelength of 58.4 nm. The energy of these photons is above the threshold required to eject electrons from many valence shell molecular orbitals.

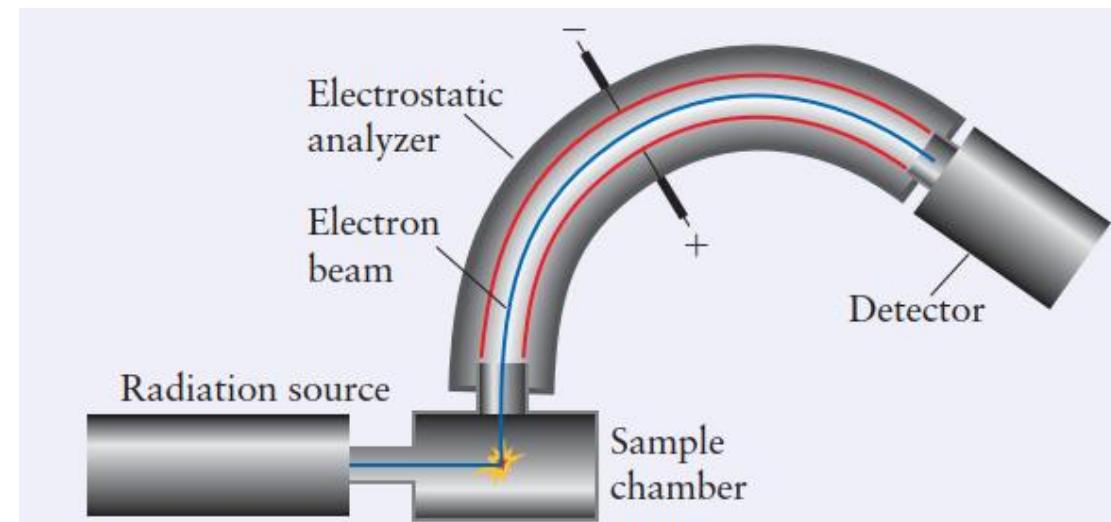
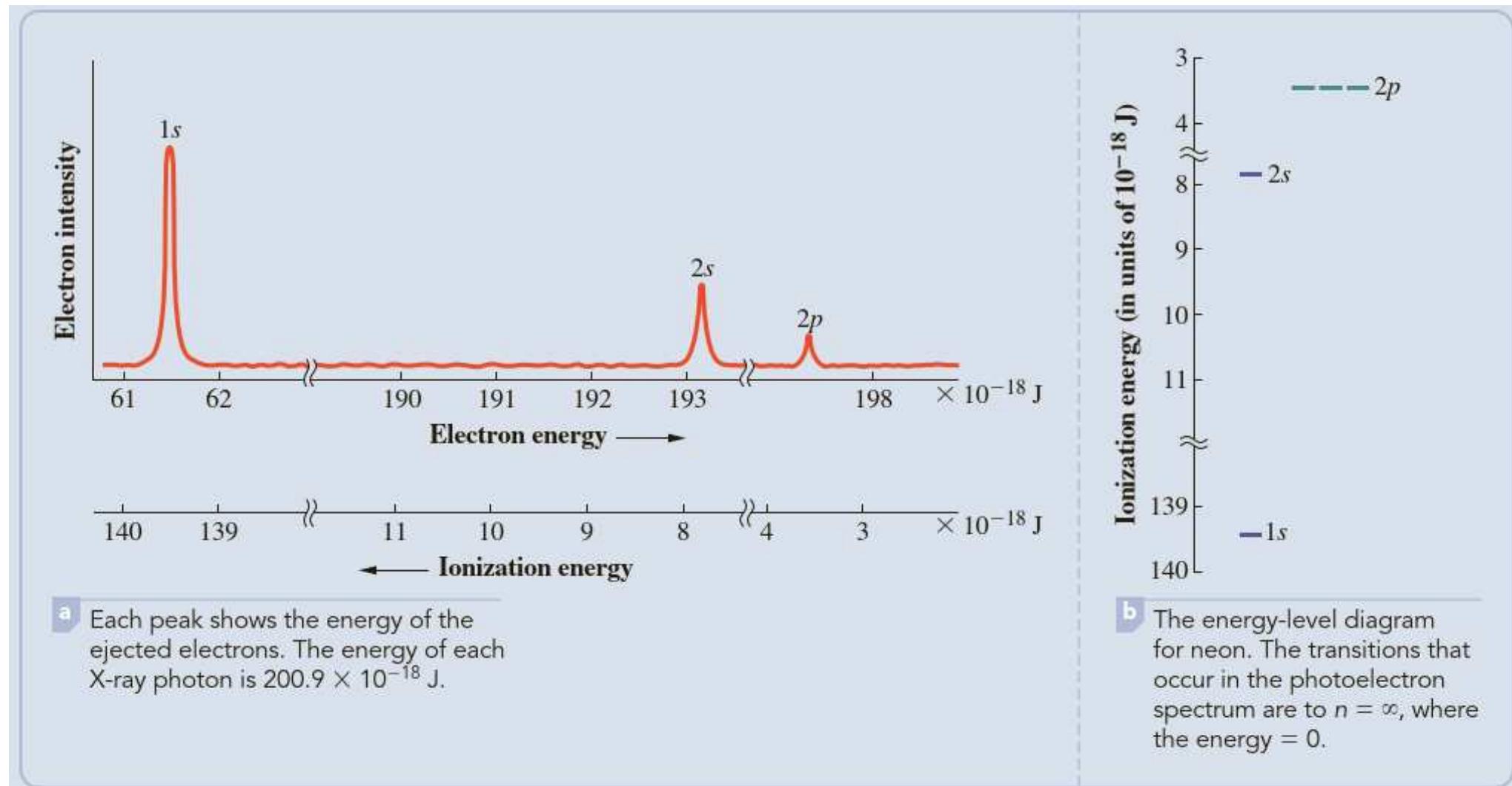


Diagram of a photoelectron spectrometer.

If you look at the electrons ejected from neon, you find that they have kinetic energies related to the ionization energies from all possible orbitals (1s, 2s, and 2p) in the atom. *When you scan the various kinetic energies of ejected electrons, you see a spectrum with peaks corresponding to the different occupied orbitals* (see Figure 8.11a). These ionization energies are approximately equal to the positive values of the orbital energies (Figure 8.11b), so *this spectrum provides direct experimental verification of the discrete energy levels associated with the electrons of the atom/molecule.*

Figure 8.11. X-ray photoelectron spectrum of neon



A photoelectron spectrum of N_2 is shown in Figure 9.16. According to Figure 9.13, the ground-state configuration of N_2 is $\text{KK}(\sigma_g^1 2s)^2 (\sigma_u^1 2s)^2 (\pi_u^1 2p_x)^2 (\pi_u^1 2p_y)^2 (\sigma_g^1 2p_z)^2$.

The peaks in the photoelectron spectrum correspond to the energies of occupied molecular orbitals. *Photoelectron spectra provide striking experimental support for the molecular-orbital picture being developed here.*

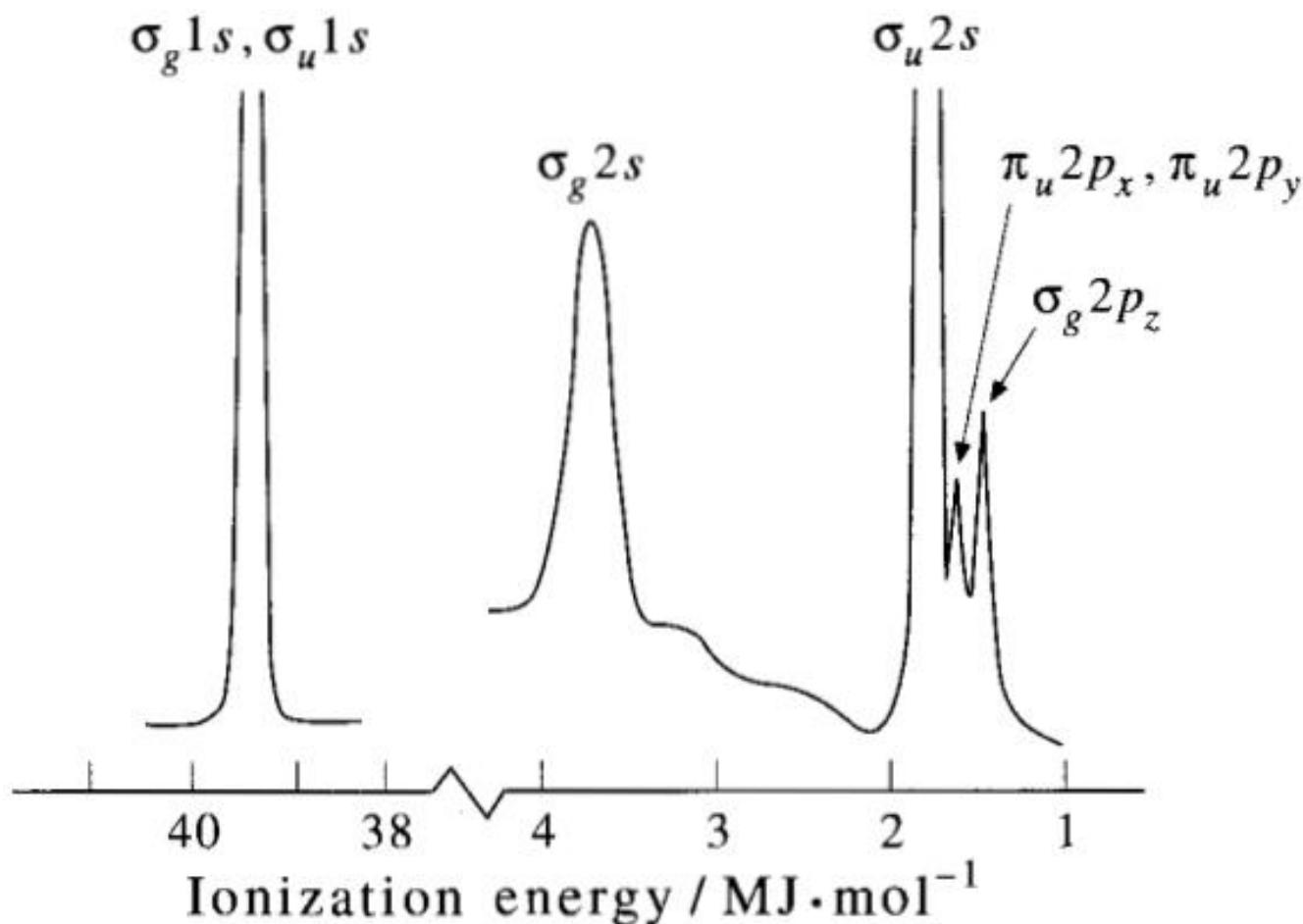


FIGURE 9.16
The photoelectron spectrum of N_2 . The peaks in this plot are caused by electrons being ejected from various molecular orbitals.

In photoelectron spectroscopy (PES), we illuminate a sample with high-frequency radiation (ultraviolet or X-ray) and measure the kinetic energy of the photoelectrons emitted from the sample.

We used PES to confirm the shell structure of the atom predicted by quantum mechanics. For molecules, PES confirms the MO description of bonding and measures the energy, ε , for individual MOs. *The bridge between PES results and MO theory is Koopmans's approximation.* These three tools are used together to study the electronic structure of molecules in all branches of chemistry.

As a concrete example, suppose we illuminate a diatomic gaseous sample with He(I) radiation, which has energy of 21.22 eV and a wavelength of 58.43 nm, and we measure the kinetic energy of the emitted photoelectrons with an energy analyzer. The resulting PES spectrum shows a series of peaks, each of which we label with an index i . We subtract the measured kinetic energy from the photon energy, which is fixed in our experiment. Thus, by conservation of energy, we are measuring the *ionization energy*, IE_i , required to liberate those electrons that contribute to peak i . **Koopmans's theorem states that the measured ionization energy is the negative of the energy of the orbital from which the photoelectrons were emitted: $IE_i = -\varepsilon_i$.** (Recall that IE_i is positive because it must be provided to the system, and that ε_i is negative because it measures the amount by which the molecular orbital is stabilized relative to the cation plus a free electron.) Koopmans's theorem is only an approximation, because it assumes that the ion produced during photoemission has the same orbital energies as the parent neutral molecule. In addition to the relaxation of the resulting ion as observed for atoms, some of the energy provided by the photon can be used to excite vibrational states in the molecular ion, which requires an amount of energy, $E_i^{(vib)}$. Now the energy conservation equation is

$$h\nu_{\text{photon}} - \frac{1}{2} m_e v^2 = -\varepsilon_i + E_i^{(vib)} = IE_i$$

As a result of the vibrational excitation, the peak i in the spectrum is actually a series of narrower peaks; the separation between adjacent peaks depends on the vibrational frequency of the diatomic ion. The result illustrated in Figure C6.1 shows the PES of hydrogen.

The peak near 15.5 eV corresponds to the ionization energy for removing electrons with no vibrational excitation of the resulting molecular ion. As the energy increases along the axis toward 18 eV, the amount of vibrational excitation of the H_2^+ ion increases, and the spacing between vibrational levels becomes smaller. The H_2^+ ion is approaching its dissociation limit.

These vibrational “**fine-structure**” peaks on the PES data at first appear to be a nuisance, but in fact, they greatly aid in relating experimental data to particular MOs. **The connection is made through the concept of bond order** introduced in Section 6.4.

Case A: If the **photoelectron is removed from a bonding MO**, the bond order of the positive ion will be smaller than the bond order of the parent molecule.

Consequently, **the bond in the molecular ion will be less stiff**, and **its vibrational frequency** (determined directly from the PES fine structure) will be **lower** than that of the parent molecule (determined by vibrational spectroscopy).

Case B: If the photoelectron is **emitted from an antibonding orbital**, the bond order of the positive ion will be larger than the bond order of the parent molecule. The bond in the diatomic molecular ion will be **stiffer** and will show a **higher vibrational frequency**.

Case C: If the photoelectron is emitted from a nonbonding orbital, there is no change in the bond order, and consequently little or no change in the vibrational frequency.

Here, the PES spectrum for the orbital will show few vibrational peaks, because the disturbance to the bond during photoemission is quite small. By contrast, the spectrum in *Case A* will show several vibrational fine structure peaks because removal of a bonding electron is a major disturbance that starts many vibrations of the bond. *Case B* is intermediate, with fewer vibrational subpeaks, because removing an antibonding electron disturbs the bond, but less so than in Case A.

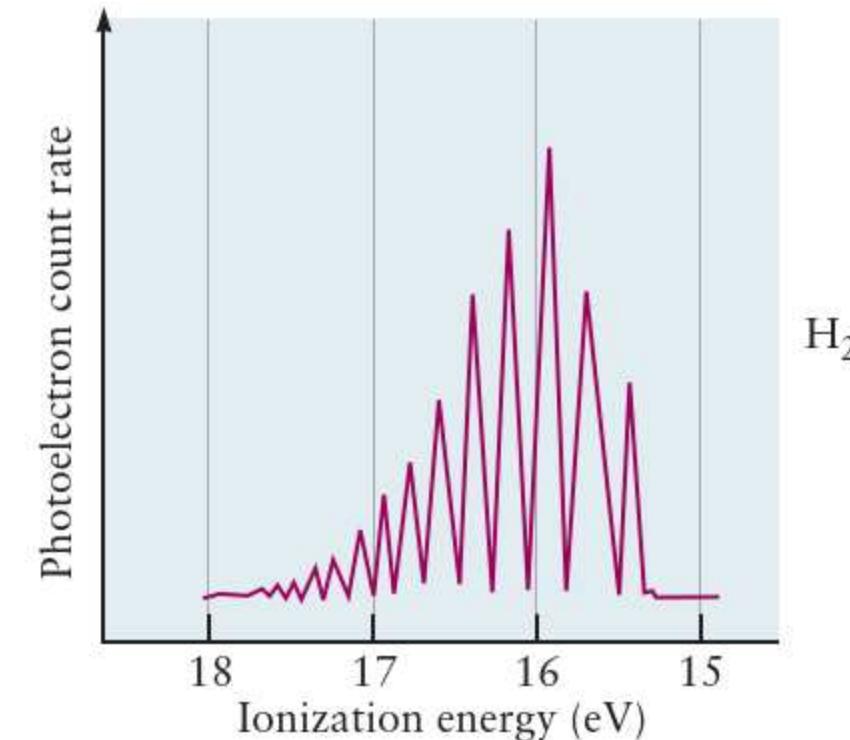


Figure c6.1 The photoelectron spectrum of H_2 shows a series of peaks corresponding to the vibrational excitation of H_2^+ .

The photoelectron spectra for N₂ and O₂ are shown in Figures C6.2 and C6.3. The experimental peaks have been assigned to orbitals by slightly more complex versions of the arguments used previously. Note that for N₂, the energy for the σ_{g2p_z} MO is lower than that for π_{u2px} and π_{u2py} whereas the order is switched for O₂, as indicated in Figure 6.17, Table 6.3, and the related text. This switch is due to interaction between the 2s and 2p AOs.

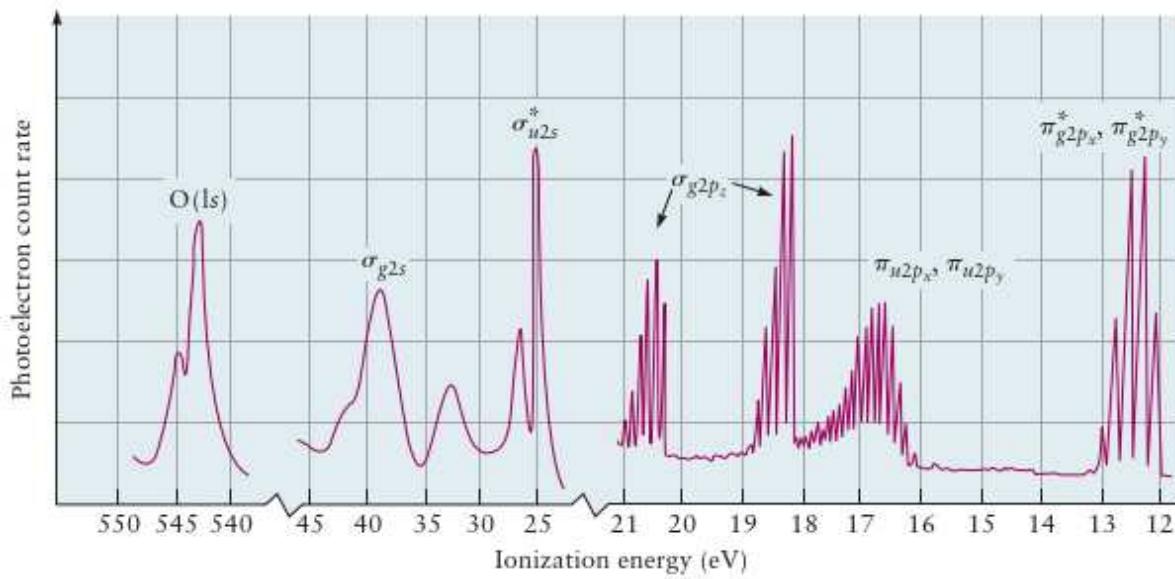


FIGURE c6.3 The photoelectron spectrum for O₂ shows valence electrons in the occupied molecular orbitals and the O(1s) core electrons.

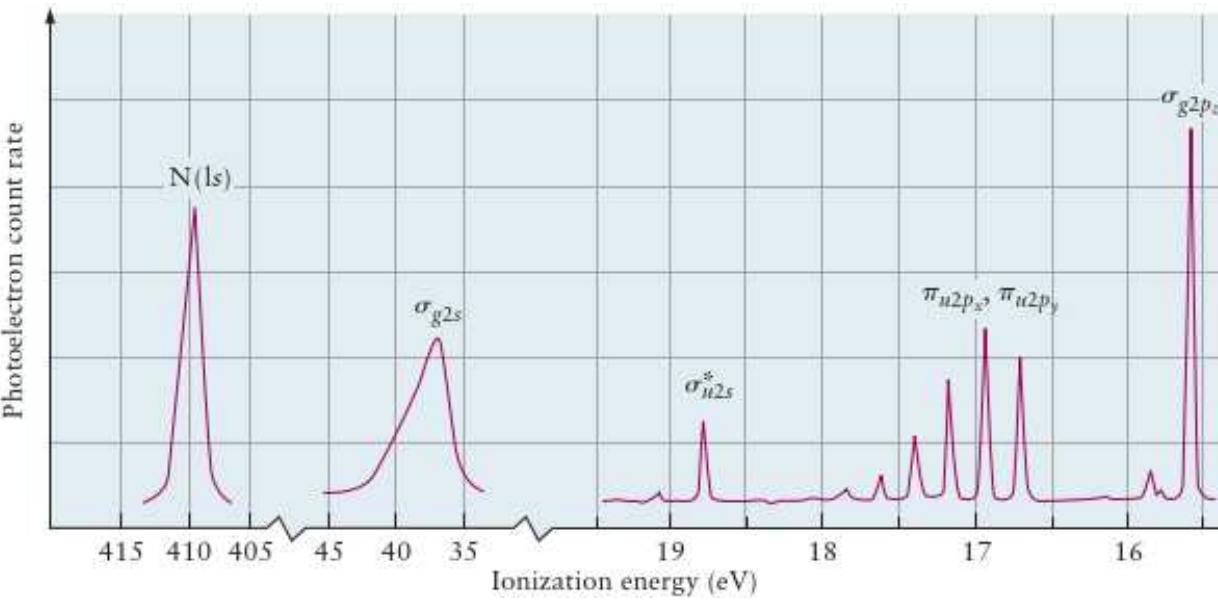
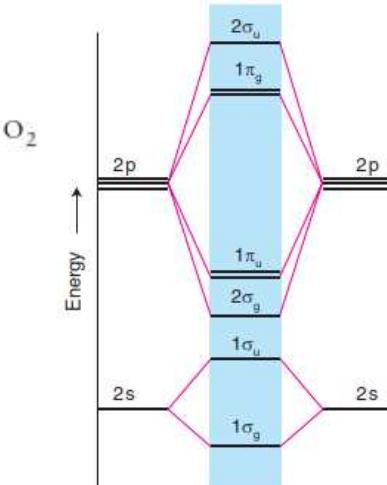


FIGURE c6.2 The photoelectron spectrum for N₂ shows the valence electrons in the occupied molecular orbitals and the N(1s) core electrons.



MO energy-level diagram for N₂ and F₂.

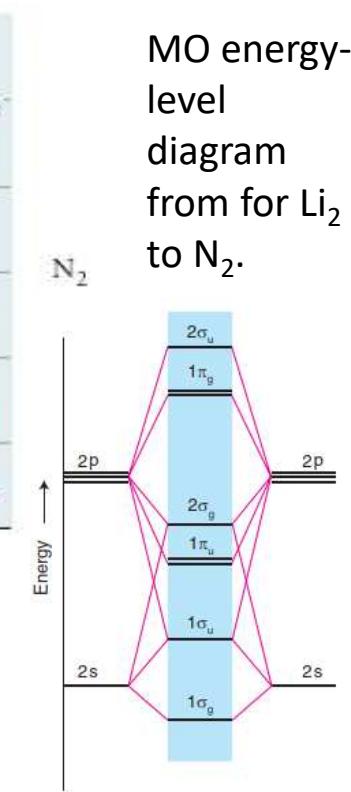
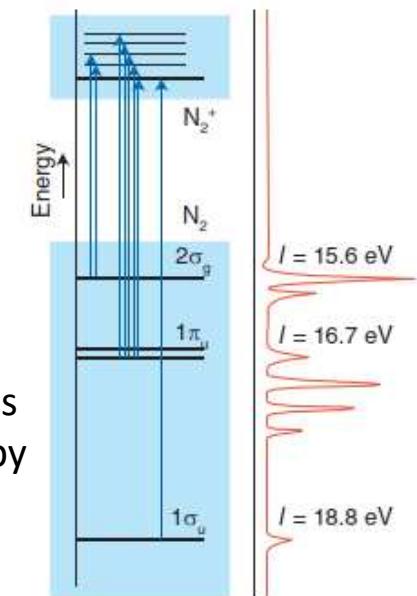
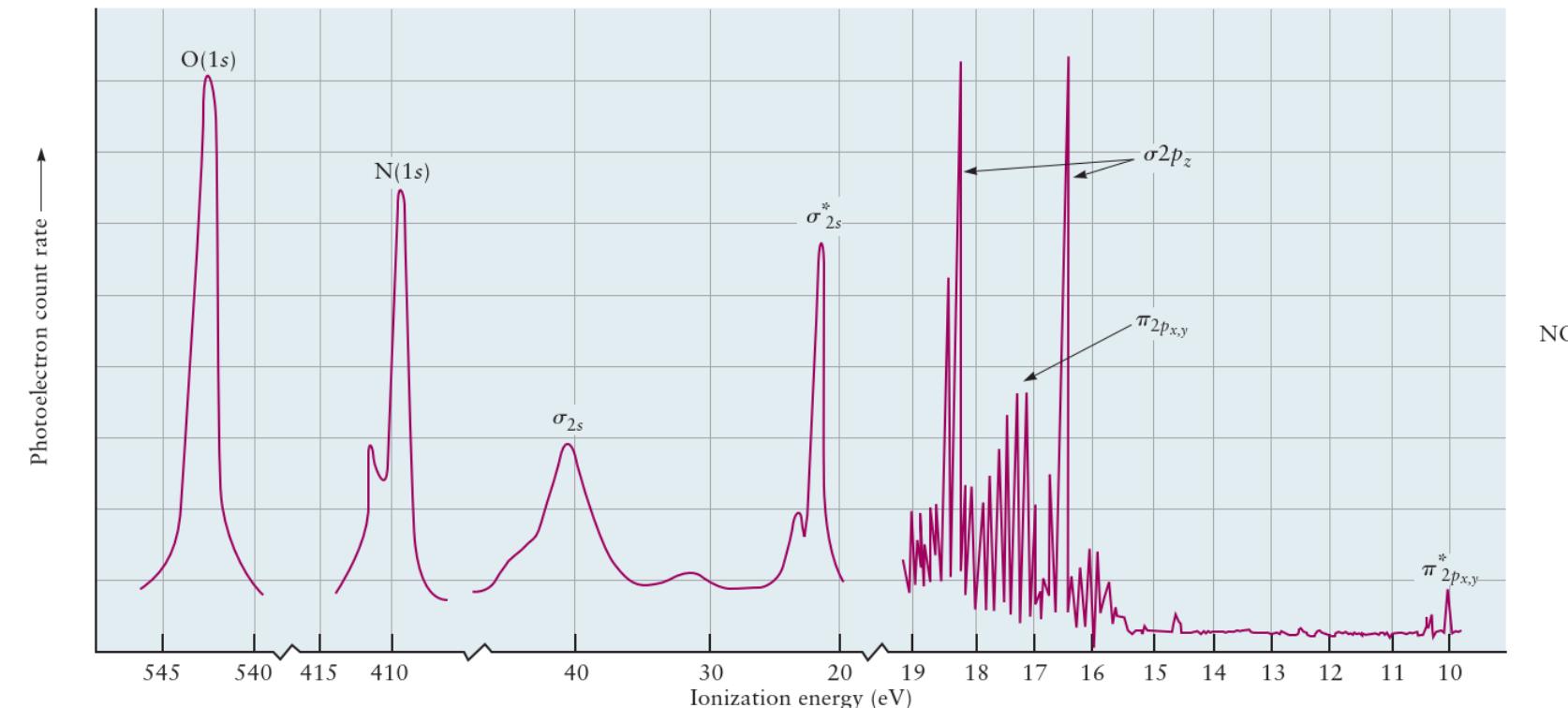


Figure 2.11 The UV photoelectron spectrum of N₂. The fine structure in the spectrum arises from excitation of vibrations in the cation formed by photoejection of an electron.



- The photoelectron spectrum for NO is shown in Figure C6.4. The orbital assignments are based on the arguments summarized above. Note that the 1s core levels for both N and O appear at the same orbital energies as they do in their respective elemental gases, N₂ and O₂.
- This experimental result demonstrates clearly that the core levels do not participate in chemical bond formation and can be neglected in the MO analysis of bond formation.
- These examples show that photoelectron spectroscopy is useful in testing theoretical models for bonding because it directly measures ionization energies that can be correlated with theoretical orbital energies through Koopmans's theorem. These methods are readily extended to polyatomic molecules



NO

FIGURE C6.4 The photoelectron spectrum for NO.

FIGURE c6.4 The photoelectron spectrum for NO.

The figure shows the valence shell photoelectron spectrum for N_2 molecules. The molecular orbital diagram indicates that N_2 has four types of filled orbitals: σ_{2s} , σ^*_{2s} , π_{2p} , and σ_{2p} . The photoelectron spectrum detects three groupings of ejected electrons with average ionization energies of 15.6 eV, 16.7 eV, and 18.6 eV (where **1 electron volt = $1.60218 \times 10^{-19} \text{ J}$**). These electrons are ejected from the σ^*_{2s} , π_{2p} , and σ_{2p} orbitals, respectively. A fourth peak is not seen because the energy required to remove an electron from the σ_{2s} orbital is higher than that of the photons emitted by the excited helium atoms.

The extra peaks, most obvious around 17–18 eV, are associated with ionization from the π orbital. They result from coupling of the ionization energy and the energy resulting from molecular vibrations.

QUESTIONS:

1. Photoelectron spectroscopy is similar to the photoelectric effect. However, in the photoelectric effect, electrons are ejected when light strikes the surface of a(n)
2. Using the accompanying figure regarding N_2 , state which molecular orbital (σ^*2s , $\pi2p$, or $\sigma2p$) has an ionization energy of 15.6 eV.
3. The N_2^+ ions that are formed when electrons with ionization energies of 15.6 eV and 16.7 eV are ejected have longer bond lengths than the ion when an electron with an ionization energy of 18.6 eV is created. Why?

Figure 9.17 presents the photoelectron spectrum of CO. The energies of the molecular orbitals are revealed nicely by these data. In addition, the photoelectron spectrum exhibits peaks characteristic of the atomic 1s orbitals on carbon and oxygen. Notice the high binding energy of the 1s atomic orbitals. This energy is a result of their being close to the nuclei and these data further verify that the 1s electrons do not play a significant role in the bonding of these molecules.

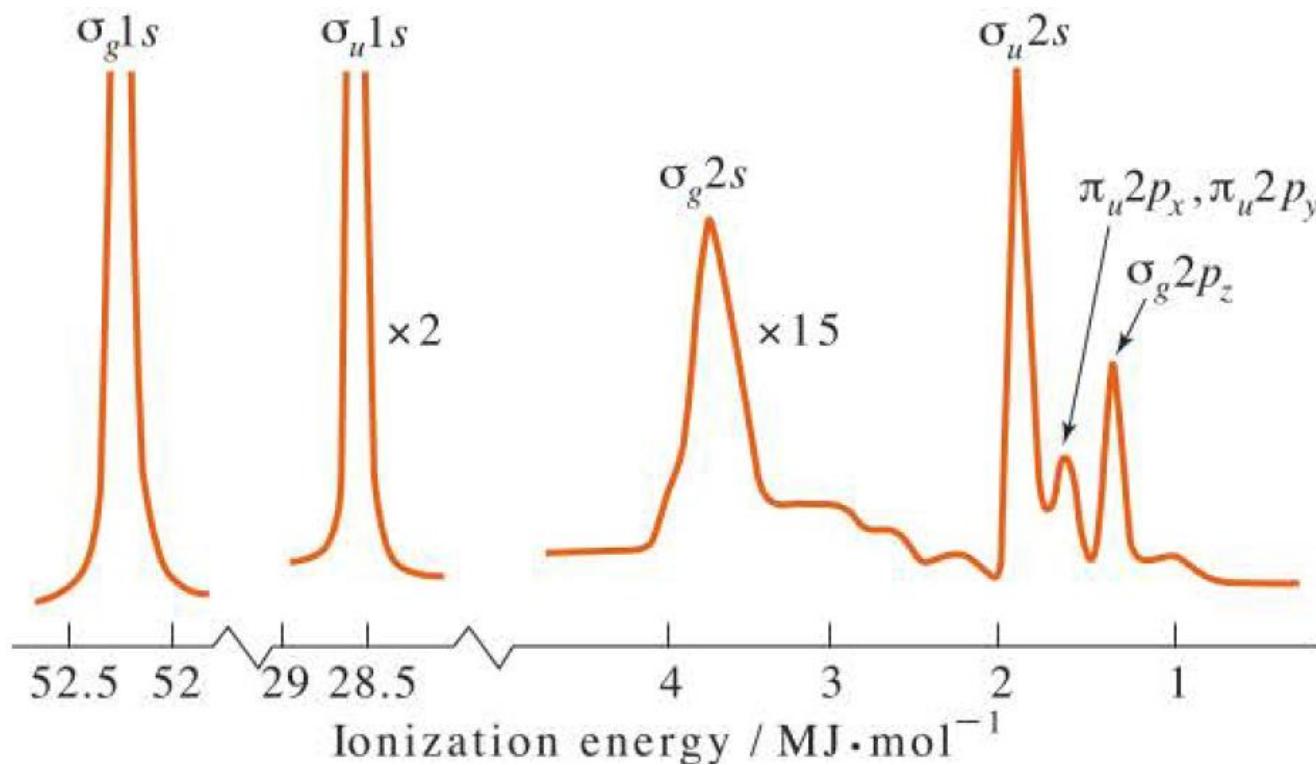


FIGURE 9.17
The photoelectron spectrum of CO. The energies associated with various molecular orbitals are identified. The $\sigma 1s$ and $\sigma 1s^*$ orbitals are essentially the 1s electrons of the oxygen and carbon atoms, respectively. The relatively large ionization energies of these electrons indicate that they are held tightly by the nuclei and play no role in bonding.

Bond length. A covalent bond has a bond length, the distance between the nuclei of two bonded atoms. The bond length is the distance between the nuclei at the point of minimum energy (bottom of the well). Like bond energies, these values are average bond lengths for a bond in different substances. Bond length is related to the sum of the radii of the bonded atoms. In fact, most atomic radii are calculated from measured bond lengths. Bond lengths for a series of similar bonds, as in the halogens, increase with atomic size (Figure 9.12).

The order, energy, and length of a covalent bond are interrelated. Two nuclei are more strongly attracted to two shared pairs than to one, so double-bonded atoms are drawn closer together and are more difficult to pull apart than single-bonded atoms: **for a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy.** Thus, as Table 9.3 shows, for a given pair of atoms, a shorter bond is a stronger bond.

Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

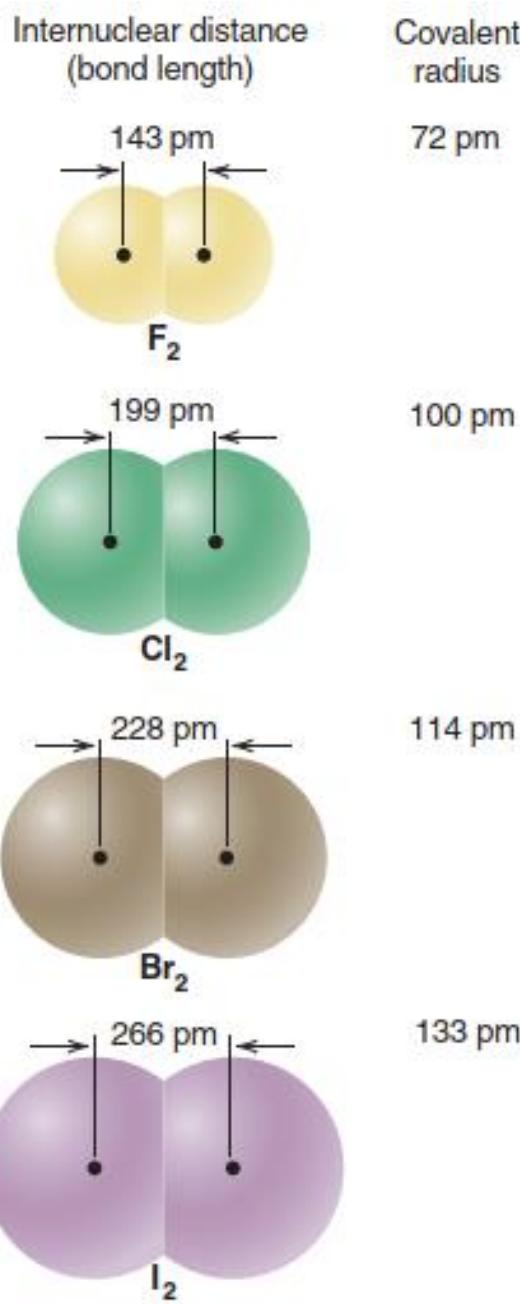


Figure 9.12 Bond length and covalent radius.

In some cases, we can see a ***relation among atomic size, bond length, and bond energy*** by varying one of the atoms in a single bond while holding the other constant:

- ***Variation within a group.*** The trend in carbon-halogen single bond lengths, C—I > C—Br > C—Cl, parallels the trend in atomic size, I > Br > Cl, and is opposite to the trend in bond energy, C—Cl > C—Br > C—I.
- ***Variation within a period.*** Looking again at single bonds involving carbon, the trend in bond lengths, C—N > C—O > C—F, is opposite to the trend in bond energy, C—F > C—O > C—N.

HOW DO WE KNOW . . . THE LENGTH OF A CHEMICAL BOND?

Why do you need to know?

Rotational spectroscopy provides very precise details of **bond lengths** and **bond angles** of molecules in the gas phase. Transitions between rotational levels also contribute to vibrational and electronic spectra and are used in the investigation of gas-phase reactions such as those taking place in the atmosphere.

- Analysis of rotational spectra yields the bond lengths and bond angles of molecules in the gas phase.

Very little energy is needed to change the state of rotation of a molecule, so the electromagnetic radiation emitted or absorbed lies in the microwave region, with wavelengths of the order of 0.1-1 cm and frequencies close to 10 GHz. The *rotational spectroscopy* of gas-phase samples is therefore also known as *microwave spectroscopy*. Gaseous samples are essential for rotational (microwave) spectroscopy, for in that phase molecules rotate freely.

The rotational energy levels of molecules:

The rotational states of molecules are based on a model system called a *rigid rotor*, a body that is not distorted by the stress of rotation. The simplest type of rigid rotor is called a linear rotor, and corresponds to a linear molecule, such as HCl, CO₂, or HCCH, that is supposed not to be able to bend or stretch under the stress of rotation. As shown in the following Justification, the energies of a linear rotor are

$$E_J = \hbar B J(J + 1)$$
$$J = 0, 1, 2, \dots$$

Rotational energy levels
[linear rotor] (1)

where J is the rotational quantum number. The constant B (a frequency, with the units hertz, Hz, with 1 Hz denoting 1 cycle per second; expressed as a wavenumber, with B/c , where c is the speed of light) is called the rotational constant of the molecule, and is defined as

$$B = \frac{\hbar}{4\pi I}$$

Rotational constant (2)

where I is the moment of inertia of the molecule.

The moment of inertia of a molecule is the mass of each atom multiplied by the square of its perpendicular distance from the axis of rotation (Fig. 1):

$$I = \sum_i m_i r_i^2$$

Moment of inertia (3)

Moments of inertia*

1. Diatomic molecules



$$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$$

Here R is the bond length.

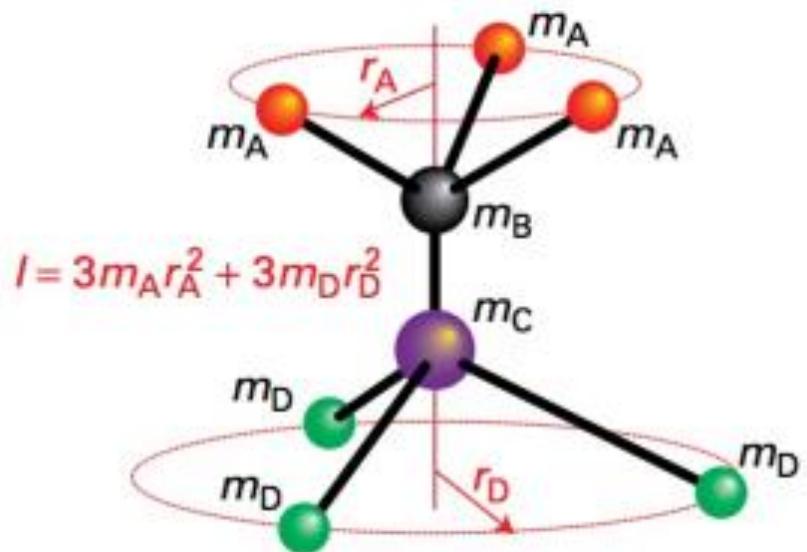


Fig. 1 The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the center of mass lies on an axis passing through the Band C atoms, and the perpendicular distances are measured from this axis.

Using IR Spectroscopy to Study Covalent Compounds

Infrared spectroscopy and Vibrations of Chemical Bonds:

Chemists often study the types of covalent bonds in a molecule using a technique called infrared (IR) spectroscopy. The bonds in all molecules, whether in a gas, a liquid, or a solid, undergo continual vibrations. We can think of any covalent bond between two atoms, say, the C—C bond in ethane ($\text{H}_3\text{C}—\text{CH}_3$), as a spring that is continually stretching, twisting, and bending.

Each motion occurs at a particular frequency, which depends on the “stiffness” of the spring (the bond energy), the type of motion, and the masses of the atoms. The frequencies of these vibrational motions correspond to the wavelengths of photons that lie within the IR region of the electromagnetic spectrum. Thus, the energies of these motions are quantized. And, just as an atom can absorb a photon of a particular energy and attain a different electron energy level, a molecule can absorb an IR photon of a particular energy and attain a different vibrational energy level.

Each kind of bond (C—C, C=C, C—O, etc.) absorbs a characteristic range of IR wavelengths and quantity of radiation, which depends on the molecule’s overall structure. The absorptions by all the bonds in a given molecule create a unique pattern that appears as downward pointing peaks of varying depth and sharpness. Thus, each compound has a characteristic IR spectrum that can be used to identify it, much like a fingerprint is used to identify a person. As an example, consider the compounds 2-butanol and diethyl ether. These compounds have the same molecular formula ($\text{C}_4\text{H}_{10}\text{O}$) but different structural formulas and, therefore, are constitutional (structural) isomers. Figure 9.15 shows that they have very different IR spectra.

Infrared spectroscopy and Vibrations of Chemical Bonds:

A chemical bond acts like a stiff spring connecting nuclei. As a result, the nuclei in a molecule vibrate, rather than maintaining fixed positions relative to each other.

Nuclear vibration is depicted in Figure 9.23, which shows a spring model of HCl.

This vibration of molecules is revealed in their absorption of infrared radiation. (An instrument for observing the absorption of infrared radiation is shown in Figure 9.24.)

The frequency of radiation absorbed equals the frequencies of nuclear vibrations. For example, the H-Cl bond vibrates at a frequency of 8.652×10^{13} vibrations per second. If radiation of this frequency falls on the molecule, it absorbs the radiation, which is in the infrared region, and begins vibrating more strongly.

The infrared absorption spectrum of a molecule of even moderate size can have a rather complicated appearance. Figure 9.25 shows the infrared (IR) spectrum of ethyl butyrate, a compound present in pineapple flavor. The complicated appearance of the IR spectrum is actually an advantage. Two different compounds are unlikely to have exactly the same IR spectrum. Therefore, the IR spectrum can act as a compound's "fingerprint."

The IR spectrum of a compound can also yield structural information. Suppose you would like to obtain the structural formula of ethyl butyrate. The molecular formula, determined from combustion analysis, is $C_6H_{12}O_2$. Important information about this structure can be obtained from Figure 9.25.

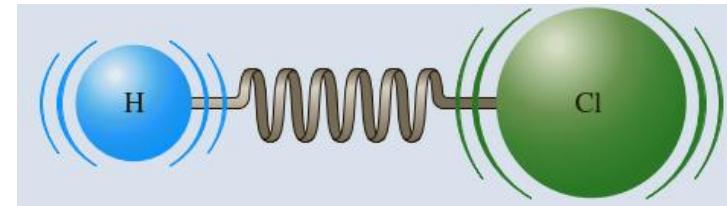


Figure 9.23. Vibration of the HCl molecule The vibrating molecule is represented here by a spring model. The atoms in the molecule vibrate; that is, they move constantly back and forth.



Courtesy of Thermoscientific

Figure 9.24. A Fourier transform infrared (FTIR) spectrometer A Fourier transform instrument collects data over a broad range simultaneously, using Fourier transform mathematics to obtain an infrared spectrum. The instrument shown is a Nicolet iS 50 FT-IR Spectrometer.

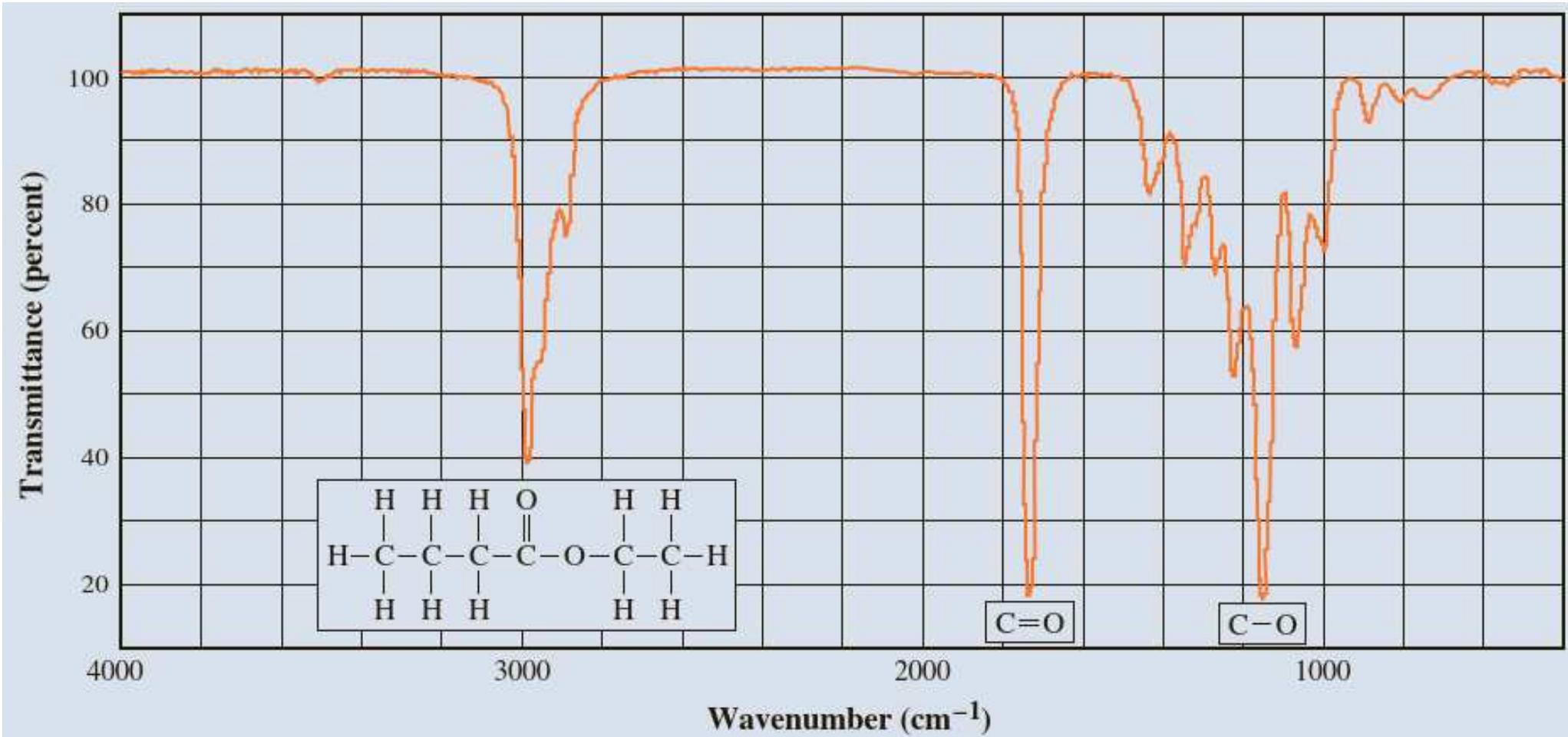


Figure 9.25 ▲

Infrared spectrum of ethyl butyrate (gas phase) Note the peaks corresponding to vibrations of $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bonds. The molecular structure is shown at the bottom left. (From NIST Mass Spec Data Center, S.E. Stein, director, “IR and Mass Spectra” in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Eds. W.G. Mallard and P.J. Linstrom, February 2000, National Institute of Standards and Technology, Gaithersburg, MD, 20899 [<http://webbook.nist.gov>]. © 1991, 1994, 1996, 1997, 1998, 1999, 2000. Copyright by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved.)

You first need to be able to read such a spectrum. Instead of plotting an IR spectrum in frequency units (since the frequencies are very large), you usually would give the frequencies in wavenumbers, which are proportional to frequency. To get the wavenumber, you divide the frequency by the speed of light expressed in centimeters per second. For example, HCl absorbs at $(8.652 \times 10^{13} \text{ s}^{-1})/(2.998 \times 10^{10} \text{ cm/s}) = 2886 \text{ cm}^{-1}$ (wavenumbers).

Wavenumber, or sometimes wavelength, is plotted along the horizontal axis.

Percent transmittance – that is, the percent of radiation that passes through a sample – is plotted on the vertical axis. When a molecule absorbs radiation of a given frequency or wavenumber, this is seen in the spectrum as an inverted spike (peak) at that wavenumber. Certain structural features of molecules appear as absorption peaks in definite regions of the infrared spectrum. For example, the absorption peak at 1730 cm^{-1} is characteristic of the C=O bond. With some knowledge of where various bonds absorb, one can identify other peaks, including that of C – O at 1180 cm^{-1} . (Generally, the IR peak for an A–B bond occurs at lower wavenumber than for an A=B bond.) The IR spectrum does not reveal the complete structure, but it provides important clues. Data from other instruments, such as the mass spectrometer, give additional clues.

Vibrational spectroscopy confines itself to that narrow region of the electromagnetic spectrum where the absorption of a photon has sufficient energy to cause the nuclei of the excited molecule to vibrate. For all practical purposes, this implies a wavelength in the range 2.5–50 μm (or 200–4000 cm^{-1} in wavenumbers) with corresponding energies of 2.4–48 kJ/mol.

The only circumstances under which IR transition will be allowed are when the absorption of IR radiation causes a change in the molecule's permanent dipole moment.

Although it might seem natural to assume that the vibrations in molecules involve completely random gyrations of all the atoms in the molecule, the actual vibrational motions of the atoms are always a superposition (or linear combination) of certain fundamental vibrations known as the normal modes of vibration. As mentioned previously, there are a total of $3N-6$ (or $3N-5$ if the molecule is linear) normal modes of vibration, and it is the different types and symmetries of these normal modes with which we shall be concerned. Each normal mode of vibration occurs at one of the natural frequencies of the molecule in much the same way as a tuning fork vibrates at a natural frequency. A more rigorous definition is that a normal mode of vibration is one in which “each atom is displaced from its equilibrium position by an amount that corresponds to its maximum amplitude and that when they are allowed to relax they will all undergo a motion at the same frequency so that they will simultaneously pass through the equilibrium configuration.”

A diatomic molecule will have only a single vibrational mode and it will be a stretching mode that lies along the internuclear axis, as shown in Figure 9.23. One can consider the two nuclei in the A-X bond to be attached by an imaginary spring that allows them to simultaneously stretch to their maximum amplitude, pass back through their equilibrium bond length, and then contract to some minimum distance in sync with one another.

The vibrational quantum number can take only nonnegative, integral values: $v = 0, 1, 2, \dots$

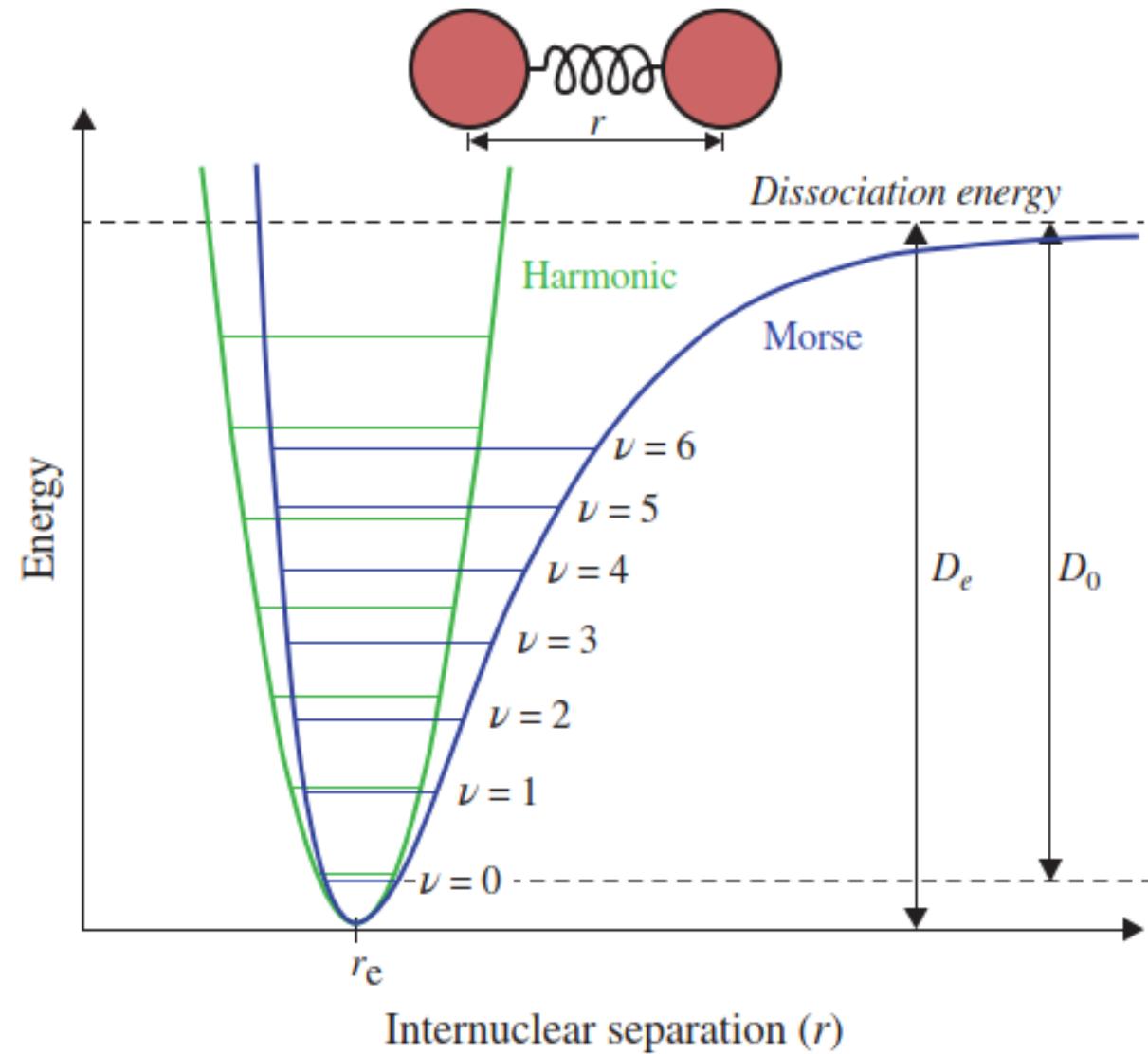
Notice that the molecule has a zero-point energy even at 0 K and that the vibrational levels are evenly spaced for a harmonic oscillator. The transition from the $v = 0$ level to the $v = 1$ level is known as the *fundamental frequency*, whereas transitions from $v = 0$ to higher levels are known as the *overtones*.

$$E_v = \left(v + \frac{1}{2}\right) h\omega \quad (9.5)$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (9.6)$$

$$\mu = \frac{m(A) m(X)}{m(A) + m(X)} \quad (9.7)$$

FIGURE 9.5
A comparison of the Morse potential (blue) and the harmonic oscillator potential (green), showing the effects of anharmonicity of the potential energy curve, where D_e is the depth of the well. [© Mark M Samoza/CCC-BY-SA_3.0/GFDL /Wikimedia Commons; reproduced from http://en.wikipedia.org/wiki/Morse_potential.]



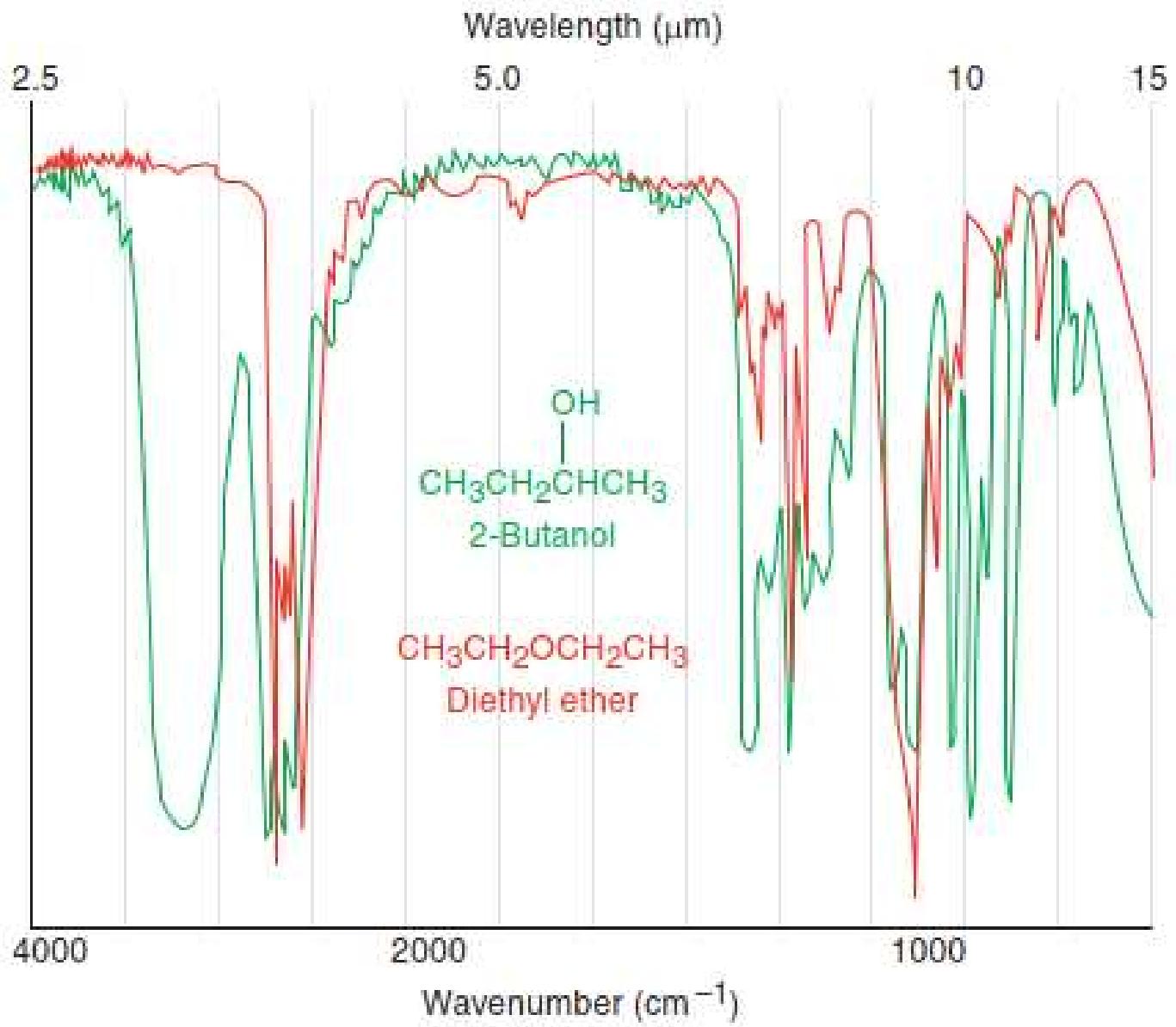
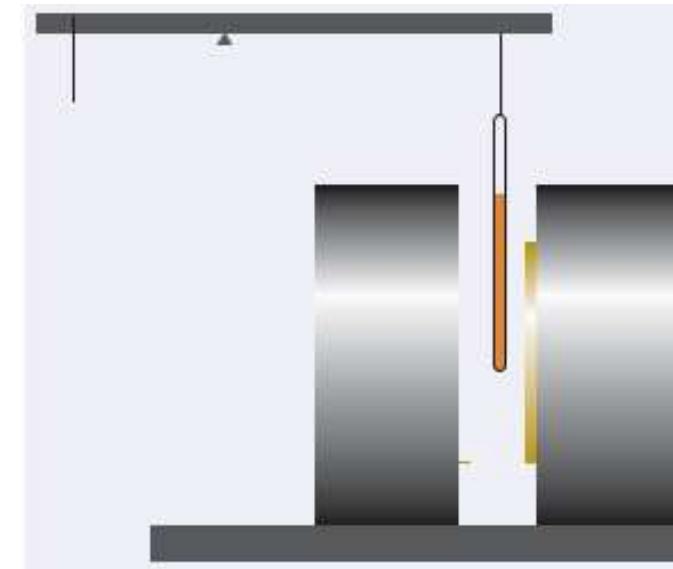


Figure 9.15 The infrared spectra of 2-butanol (green) and diethyl ether (red).

HOW DO WE KNOW . . . THAT ELECTRONS ARE NOT PAIRED?

Most common materials are diamagnetic. The tendency of a diamagnetic substance to move out of a magnetic field can be detected by hanging a long, thin sample from the pan of a balance and letting it lie between the poles of an electromagnet.

This arrangement, which was once the primary technique used to measure the magnetic properties of samples, is called a **Gouy balance**. When the electromagnet is turned on, a diamagnetic sample tends to move upward, out of the field, so it appears to weigh less than in the absence of the field. The diamagnetism arises from the effect of the magnetic field on the electrons in the molecule: the field forces the electrons to circulate through the nuclear framework. Because electrons are charged particles, this circulation corresponds to an electric current circulating within the molecule. That current gives rise to its own magnetic field, which opposes the applied field. The sample tends to move out of the field so as to minimize this opposing field.



A Gouy balance is used to observe the magnetic character of a sample by detecting the extent to which it is drawn into (paramagnetic substances) or driven out of (diamagnetic substances) a magnetic field.

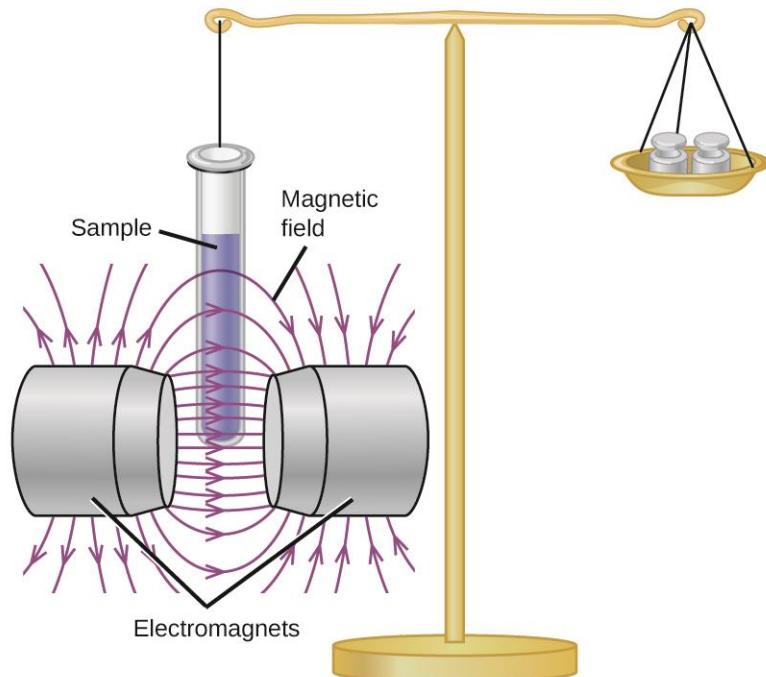


Figure 8.4.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

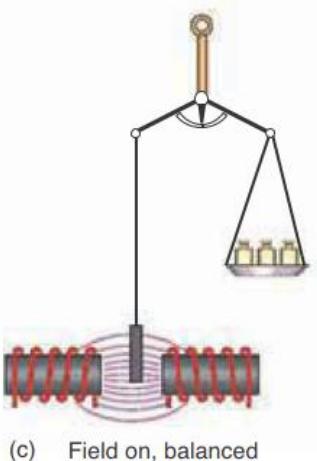
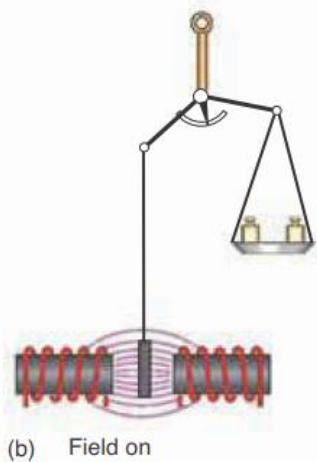
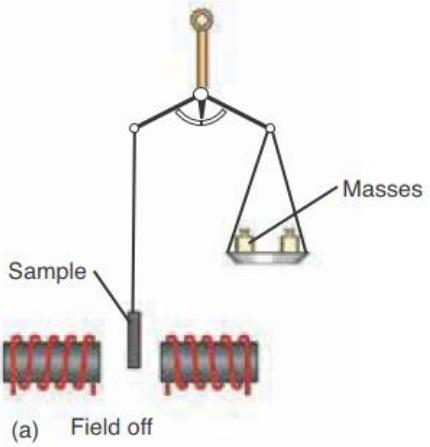
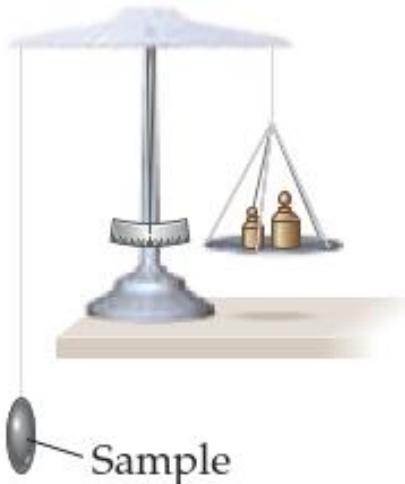
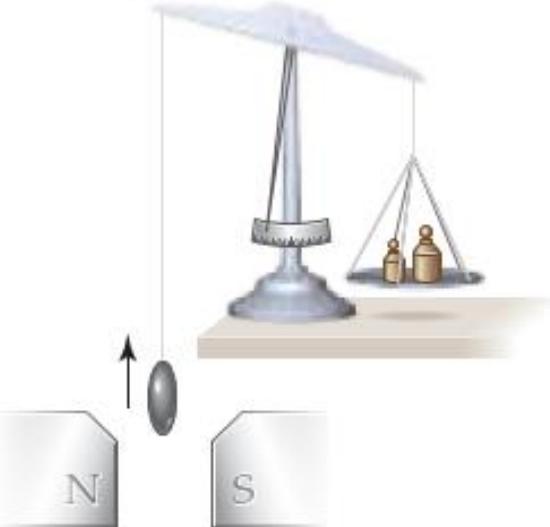


Figure 6.7 One method for determining the electronic configuration of transition metal ions is to use a magnetic field. Because unpaired electrons act like tiny magnets, the number of unpaired electrons in a transition metal ion can be determined by weighing the sample in a magnetic field. If the sample contains unpaired electrons, the magnetic attractive force on the sample makes it appear heavier. The number of unpaired electrons in the sample and the electron configuration can be calculated from the apparent mass gain when the field is on. Masses are added to the balance pan until balance is restored with the field on.

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

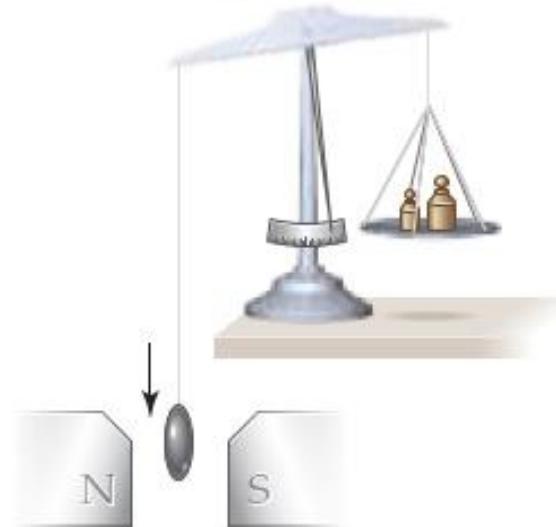


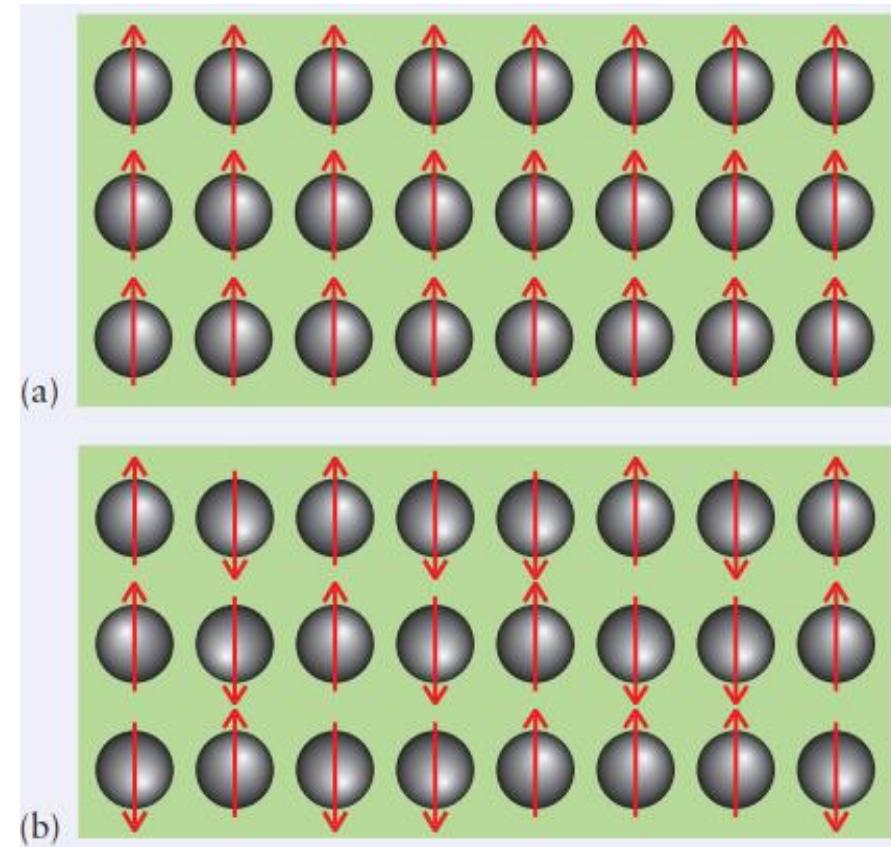
Figure 9.44 Determining the magnetic properties of a sample.

Compounds with unpaired electrons are paramagnetic. They tend to move into a magnetic field and can be identified because they seem to weigh more in a Gouy balance when a magnetic field is applied than when it is absent. *Paramagnetism arises from the electron spins, which behave like tiny bar magnets that tend to line up with the applied field.* The more that can line up in this way, the greater the lowering of energy and the heavier the sample appears to weigh.

Oxygen is a paramagnetic substance because it has two unpaired electrons: this property is used to detect the concentration of oxygen in incubators. *All radicals are paramagnetic.*

Many compounds of the d-block elements are paramagnetic because they have various numbers of unpaired d-electrons.

The modern approach to measuring magnetic properties is to use a *superconducting quantum interference device (a SQUID)*, which is highly sensitive to small magnetic fields and can make very precise measurements on small samples.



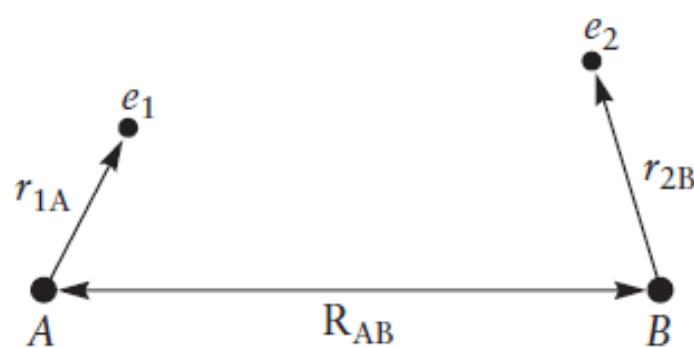
(a) In a magnetic field, the spins of electrons in both paramagnetic and ferromagnetic substances are aligned. (b) The spins of electrons in a paramagnetic substance return to a random orientation after an applied magnetic field is removed. However, the spins of electrons in a ferromagnetic substance remain aligned after a magnetic field is removed.

Electron Pair Bond and Valence Bond Theory (VBT): The Orbital Overlap Model of Bonding

- The characteristics (bond length, bond energy, polarity, etc.) of specific chemical bonds such as O—H, C—C, and C—H do not differ much from molecule to molecule.
- If the bonding electrons are spread out over the entire molecule, as described by the LCAO model, then why should the properties of a bond be nearly independent of the nature of the rest of the molecule?
- Would some other model that associates electrons directly with the bond provide a better description of chemical bonds?
- The **valence bond (VB) theory** was developed to provide a quantum explanation and justification for the Lewis electron pair model in which the chemical bond is described as a *pair of electrons localized between two atoms*.
- The valence bond theory constructs a wave function for each individual chemical bond by assuming that each participating atom arrives with at least one unpaired electron in an AO. The **VB wave function** for the bond is a **product of two one-electron AO wave functions**, each describing an electron localized on one of the atoms. The **spins of the electrons must be paired** to satisfy the Pauli exclusion principle.

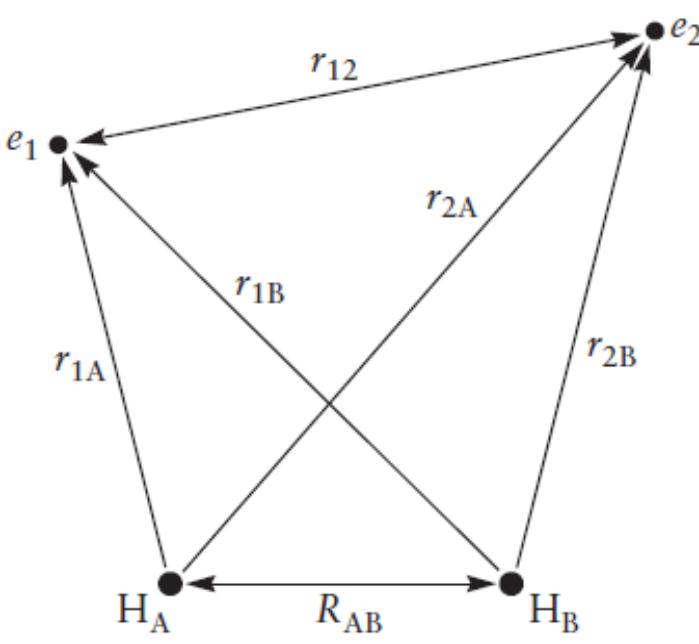
- The VB description for H₂ was developed by the German physicists Walter Heitler and Fritz London in 1927, just one year after Schrödinger introduced wave mechanics to explain the structure of the H atom. The American physicist John C. Slater also made important contributions to developing the VB method. Establishing the VB method as one of the cornerstones of modern structural chemistry awaited the pioneering work of the American chemist Linus Pauling, who used it to describe structure and bonding in polyatomic molecules, starting in 1931.
- VB theory predates LCAO theory, and until modern computer calculations became available in the 1960s, VB theory was more widely used than LCAO because it could describe molecular structure without performing detailed calculations. VB theory is still very popular today for the same reason.
- This section presents a qualitative version of VB theory, which easily describes the structure and geometry of bonds in polyatomic molecules by hand-drawn sketches. Because of this ease, qualitative VB theory is a very useful complement to qualitative LCAO theory. It is widely used in organic and inorganic chemistry and in biochemistry.
- Later, we compare VB and LCAO methods and see when one is preferable to the other. In some cases, we see it is beneficial to use the two methods together.

❖ Single Bonds



(a)

- Consider that the hydrogen molecule, described by the Lewis structure H:H, is formed by combining two hydrogen atoms each with the electron configuration H: (1s)¹. The two atoms approach one another and begin to interact as shown in Figures 6.25 & 9.1.



(b)

- FIGURE 6.25** Two hydrogen atoms approach one another. The protons are separated by the distance R_{AB} .
- (a) At large values of R_{AB} each electron interacts only with the proton to which it is bound.
 - (b) As the atoms approach closer, both electrons interact with both protons. The distance of electron 1 (e_1) from nuclei A and B is given by r_{1A} , r_{1B} ; the distance of electron 2 (e_2) from nuclei A and B is given by r_{2A} , r_{2B} ; the distance between the electrons is given by r_{12} .

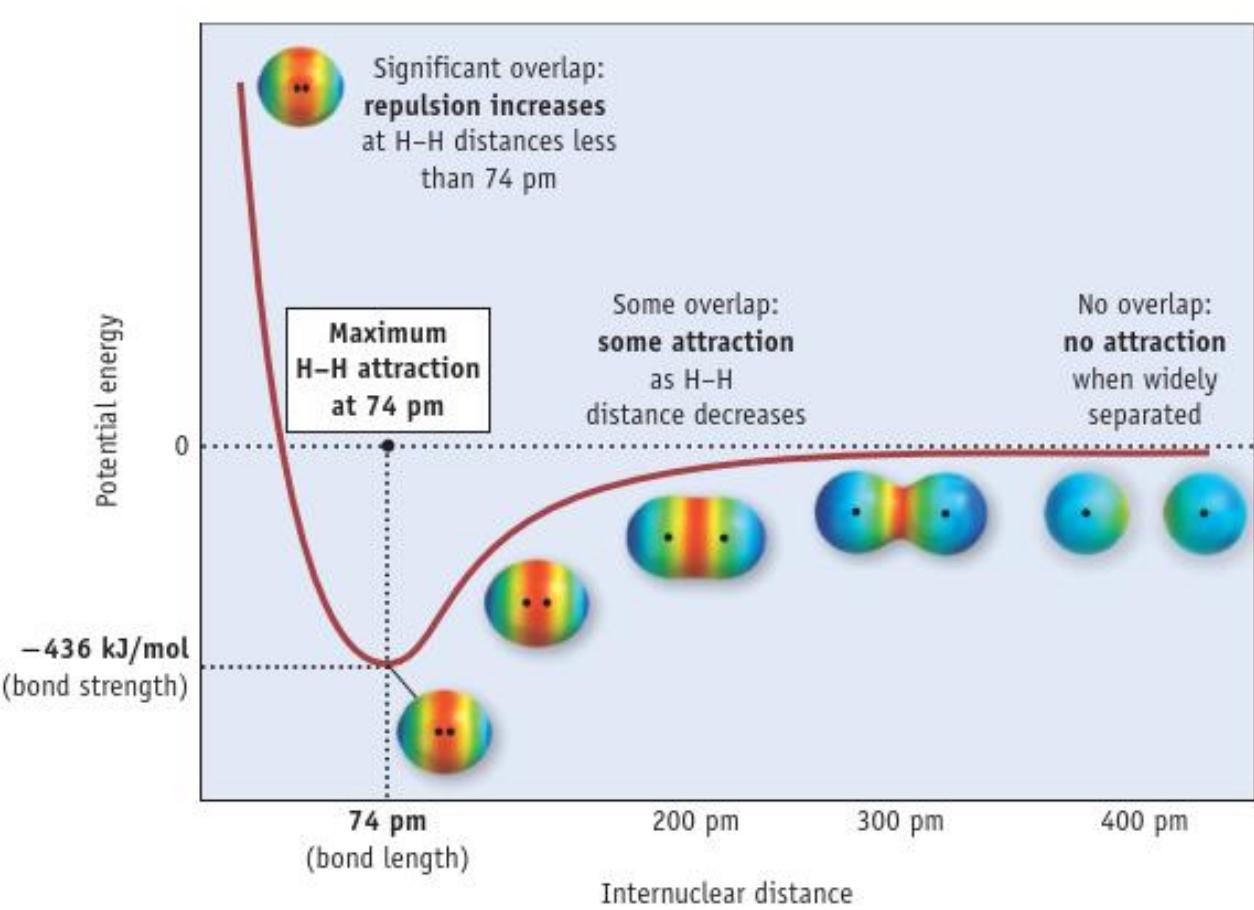


FIGURE 9.1 Potential energy change during H–H bond formation from isolated hydrogen atoms.

The red color in the orbital pictures reflects the increase in electron density between the H atoms as the distance decreases.

➤ Widely separated, the two atoms do not interact. If the atoms move closer together, however, *the electron on one atom is attracted to the positive charge of the nucleus of the other atom*. As illustrated in Figure 9.1, this distorts the electron clouds of the two atoms, drawing the electrons toward the region of space between the atoms *where the two orbitals overlap*. Because of *the attractive forces between the nuclei and electrons, the potential energy of the system decreases*.

- At a distance of 74 pm between the H atoms, the potential energy reaches a minimum. Decreasing the distance between the H atoms further, however, results in a rapid increase in the potential energy due to repulsions between the nuclei of the two atoms and between the electrons of the atoms.
- A system is stable when the potential energy is lowest. Based on the analysis described here, this is predicted to occur when the two hydrogen atoms are 74 pm apart. Significantly, 74 pm also corresponds to the experimentally measured bond distance in the H_2 molecule.
- In the H_2 molecule, the two electrons, one from each atom and with opposite spins, pair up to form the bond. There is a net stabilization, representing the extent to which the energies of the two electrons are lowered from their value in the free atoms.

- The protons are separated by the distance R_{AB} . At very large separations, each electron is bound to its own proton, and is located by coordinate r_{1A} or r_{2B} . At very large distances, the atoms are independent of each other, and the wave function describing the pair of them is

$$\varphi^A(r_{1A})\varphi^B(r_{2B})$$

- This result is a consequence of the form of the Schrödinger equation. *If two objects are independent*, their total energy is the sum of the individual energies, and *the wave function for the two of them is the product of the individual wave functions*.
- As the atoms approach closer together so that bond formation is a possibility, it is reasonable to propose an *approximate* wave function for the two of them would take the form

$$\psi^{el}(r_{1A}, r_{2B}; R_{AB}) = c(R_{AB})\varphi^A(r_{1A})\varphi^B(r_{2B})$$

in which the coefficient $c(R_{AB})$ compensates for the fact that the product form is strictly valid only at very large values of R_{AB} .

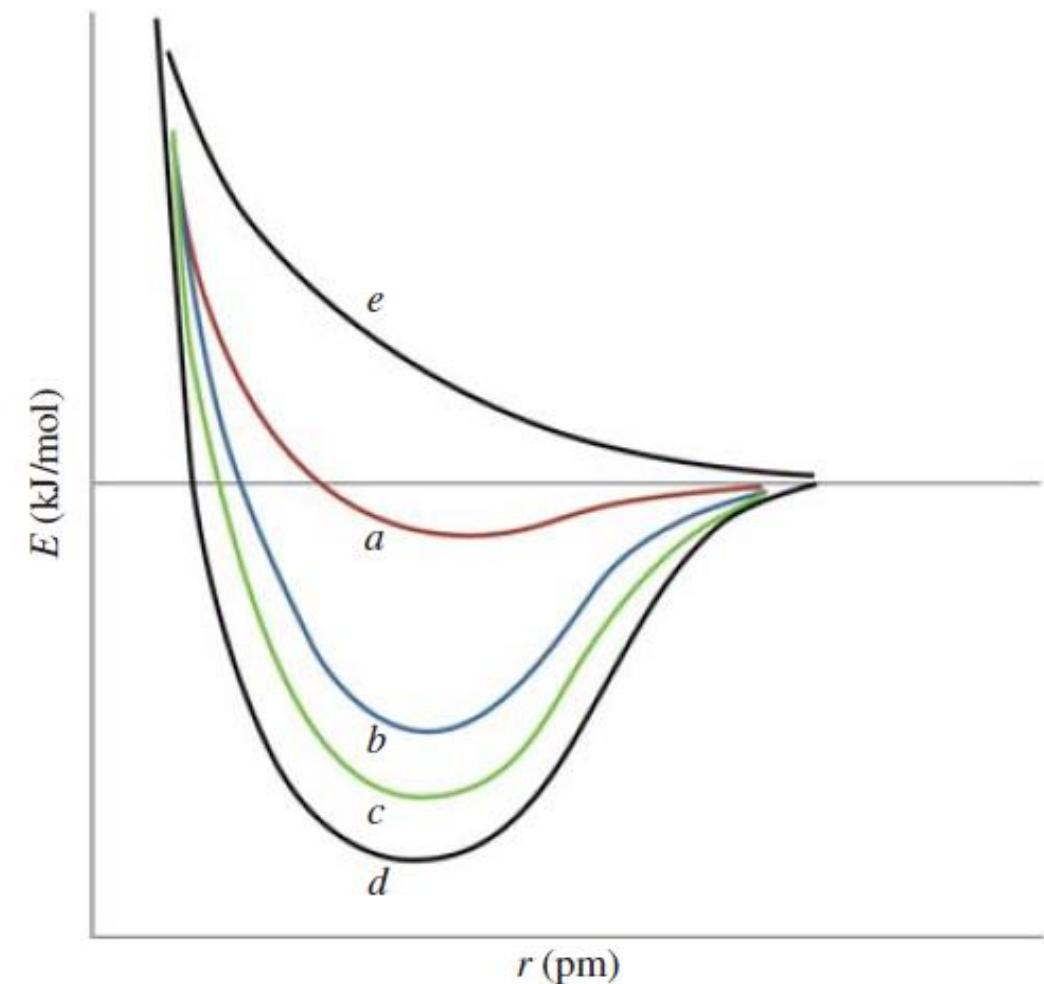
➤ Curve (a) represents the energy for the isolated H atoms, given by the total wavefunction shown in Equation (10.1), where the subscripts A and B refer to the two H nuclei and the numbers 1 and 2 refer to imaginary labels placed on the two electrons. It has a minimum value at 90 pm and only 25 kJ/mol.

➤ $\psi(H_2) = \psi^A(1)\psi^B(2)$ (10.1)

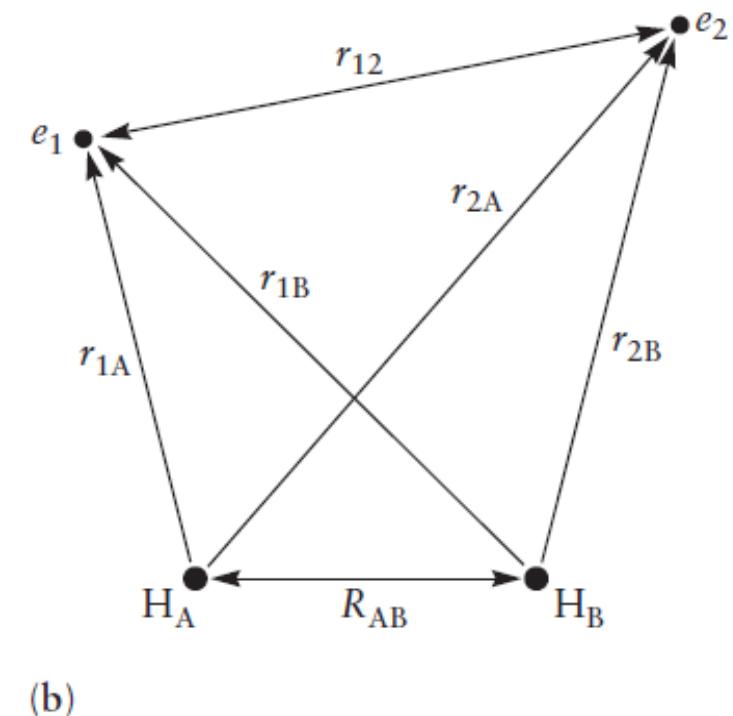
➤ The potential energy diagram shown in Figure 10.1 shows that *amendments to the VB model is essential* for the hydrogen molecule.

FIGURE 10.1

Artist's rendering of the theoretical potential energy curves (a)–(c) constructed using the data given by Equations (10.1)–(10.3), along with the experimentally observed attractive potential (d) for the H_2 molecule. Curve (e) is the experimental repulsive term. [Blatt Communications.]



- The ***valence bond wave function can be improved*** further by taking into consideration the ***other contributions***.
- For example, as the atoms begin to interact strongly, we cannot determine whether electron 1 arrived with proton A and electron 2 with proton B, or vice versa, because the electrons are indistinguishable.
- We assign electron 1 to proton A and electron 2 to proton B in the first product form, and in the second product we switch each electron to the other proton.
- The wave functions representing such states will be
 - $1s_A(1)1s_B(2)$ and $1s_A(2)1s_B(1)$.



- To allow for both possibilities we propose ***a wave function that is a sum of two of the product forms*** just discussed.
- The result is

$$\psi^{el}(r_{1A}, r_{2B}; R_{AB}) = c_1(R_{AB})\varphi_A(r_{1A})\varphi_B(r_{2B}) + c_2(R_{AB})\varphi_A(r_{2A})\varphi_B(r_{1B})$$

- Symmetry requires that $c_1 = c_2$ and $c_1 = -c_2$ be equally valid choices. We label these combinations *gerade (g)* and *ungerade (u)* respectively to show how each behaves under inversion symmetry.

$$\psi_g^{el} = c_1(R_{AB})[\varphi_A(r_{1A})\varphi_B(r_{2B}) + \varphi^A\varphi_A(r_{2A})\varphi_B(r_{1B})]$$

$$\psi_u^{el} = c_1(R_{AB})[\varphi_A(r_{1A})\varphi_B(r_{2B}) - \varphi^A\varphi_A(r_{2A})\varphi_B(r_{1B})]$$

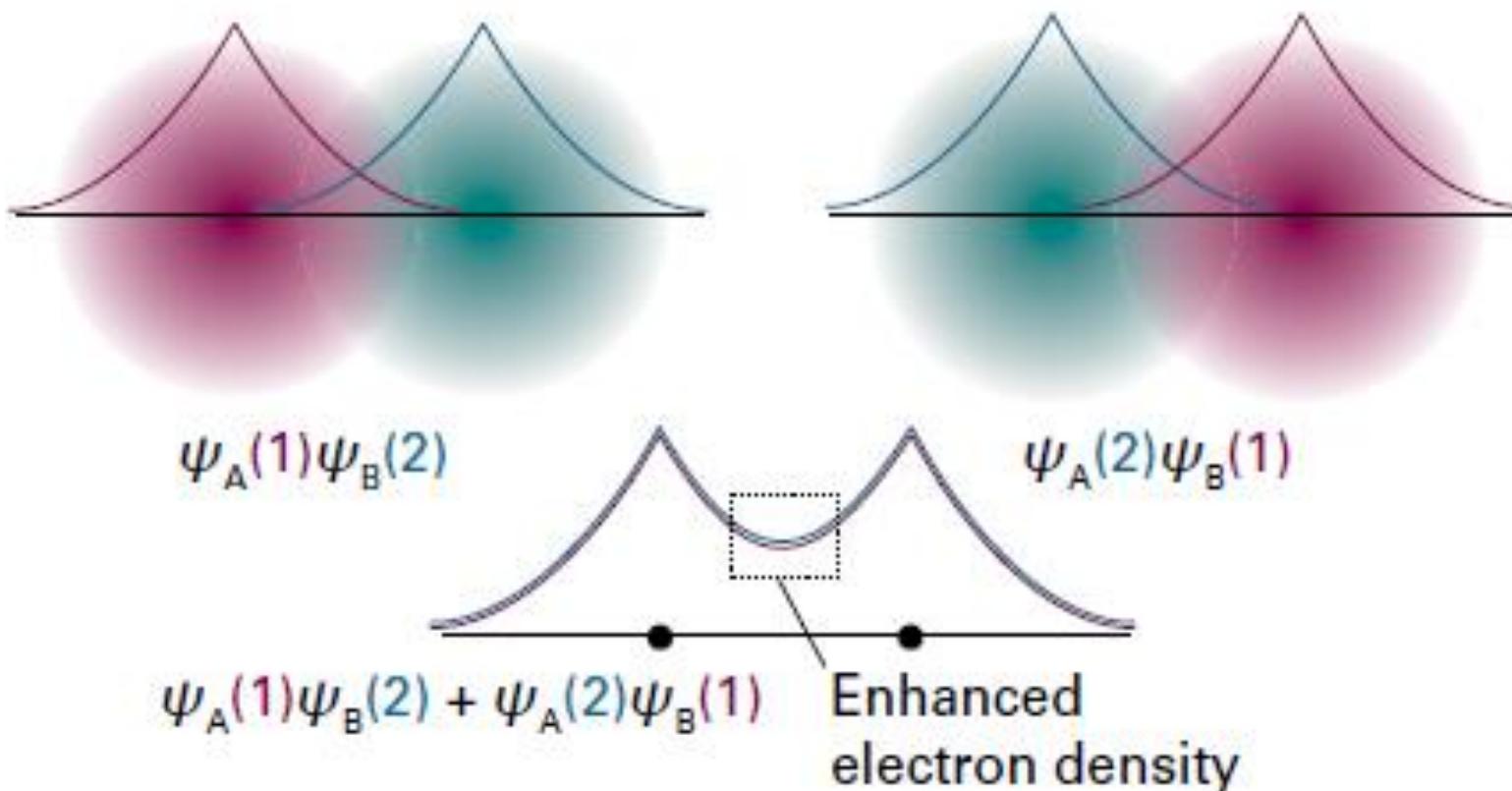


Figure 9A.1 It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The atomic orbital for electron 1 is represented by the purple shading, and that of electron 2 is represented by the green shading. The left illustration represents $\psi_A(1)\psi_B(2)$ and the right illustration represents the contribution $\psi_A(2)\psi_B(1)$. When the two contributions are superimposed, there is interference between the purple contributions and between the green contributions, resulting in an enhanced (two-electron) density in the internuclear region.

- The first equation is *symmetric* and the second is *antisymmetric* with respect to the *interchange of electrons*.
- *We must check both cases to determine whether they describe bond formation, using our familiar criteria of increased electron density between the nuclei and energy reduced below that of the separated atoms.*
- It requires some care to calculate the electron density for ψ_g^{el} and ψ_u^{el} . Unlike the one-electron wave functions we have seen earlier, these are examples of *two-electron functions*, which depend explicitly on the positions of both electrons.
- Their squares give the probability density for finding electron 1 at r_1 and electron 2 at r_2 . To calculate the probability density for finding electron 1 at r_1 , no matter where electron 2 is located, we must square the function and then average over all possible locations for electron 2. Similarly, we calculate the probability density for finding electron 2 at r_2 regardless of the location of electron 1. Adding these results together gives the total electron density at each point in space, as a function of the internuclear distance R_{AB} .
- The results for ψ_g^{el} and ψ_u^{el} are shown in Figure 6.26a.

- The wave function ψ_g^{el} shows increased electron density between the nuclei, whereas ψ_u^{el} shows reduced electron density between the nuclei.
- The shape of the electron density in three dimensions is more conveniently obtained from computer calculations using a quantitative version of the VB method.
- Figure 6.26b shows a three-dimensional isosurface of the electron density for H_2 calculated from ψ_g^{el} .

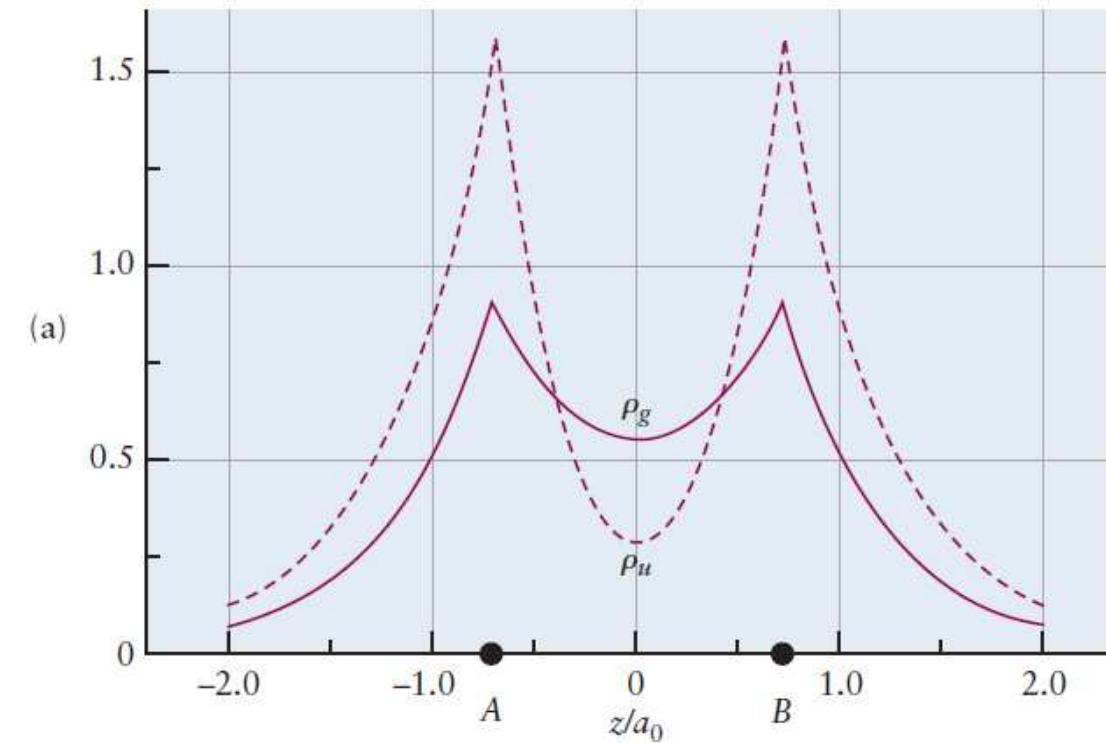
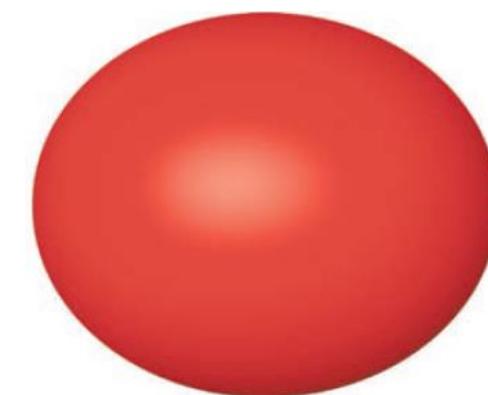


FIGURE 6.26 The electron density for the ψ_g^{el} and ψ_u^{el} wave functions in the simple valence bond model for H_2 .

(a) The electron density ρ_g for ψ_g^{el} and ρ_u for ψ_u^{el} calculated analytically as described in the text.

(b)



(b) Three-dimensional isosurface of the electron density for the ψ_g^{el} wave function obtained by computer calculations. (Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)

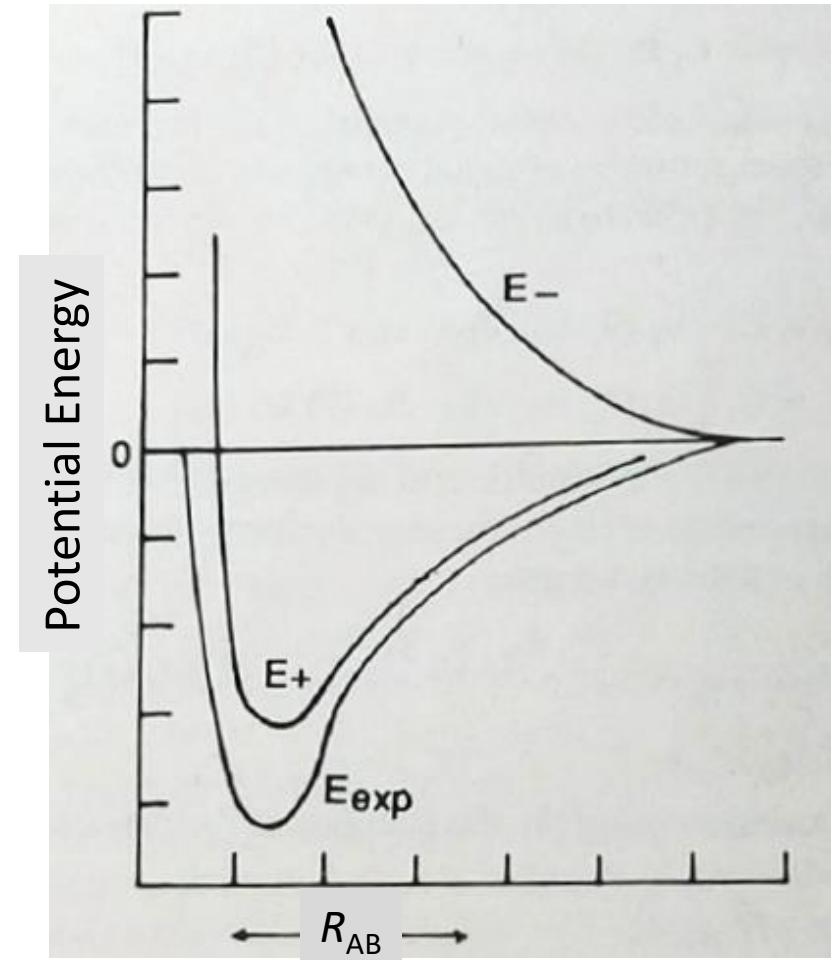
- Therefore, we conclude that the correct wave function to describe an electron-pair bond in H₂ by the VB method is

$$\psi_g^{el} = c_1(R_{AB})[1s^A(1)1s^B(2) + 1s^A(2)1s^B(1)]$$

$$\psi_u^{el} = c_1(R_{AB})[1s^A(1)1s^B(2) - 1s^A(2)1s^B(1)]$$

- It is a straightforward exercise in quantum mechanics—although beyond our scope—to calculate the energy of the hydrogen molecule as a function of R_{AB} when the electrons are described by ψ_g^{el} and ψ_u^{el} .
- The results give the effective potential energy curve for each value of R_{AB}.
- The two calculated effective potential energy curves (Fig. 5.9...below) are qualitatively similar to those in MO theory.
- They show that ψ_g^{el} describes a state with lower energy than that of the separated atoms, whereas ψ_u^{el} describes a state whose energy is higher than that of the separated atoms for all values of R_{AB}.

Fig. 5.9 Potential energy curve for the hydrogen molecule showing antisymmetric (E_- for ψ_u^{el}), symmetric state (E_+ for ψ_g^{el}) and the experimental curve (E_{exp}).



- *There is discrepancy* between the calculated (E_+) and experimental (E_{exp}) potential energy curves for the hydrogen molecule.

- The ***valence bond wave function can be improved*** further by taking into consideration the ***ionic contribution***, because there is a finite probability of finding the electrons near the same nucleus. The possibility of an ionic contribution to the bonding, where both of the electrons reside either on nucleus A or on nucleus B, will give the wave functions representing such states

$$\psi(H_2) = 1sA(1)1sA(2) + 1sB(1)1sB(2) \quad (10.2)$$

- The complete molecular wave function then becomes

$$\psi_{VB}^{el} = c_1 1sA(1)1sB(2) + c_2 1sA(2)1sB(1) + c_3 1sA(1)1sA(2) + c_4 1sB(1)1sB(2)$$

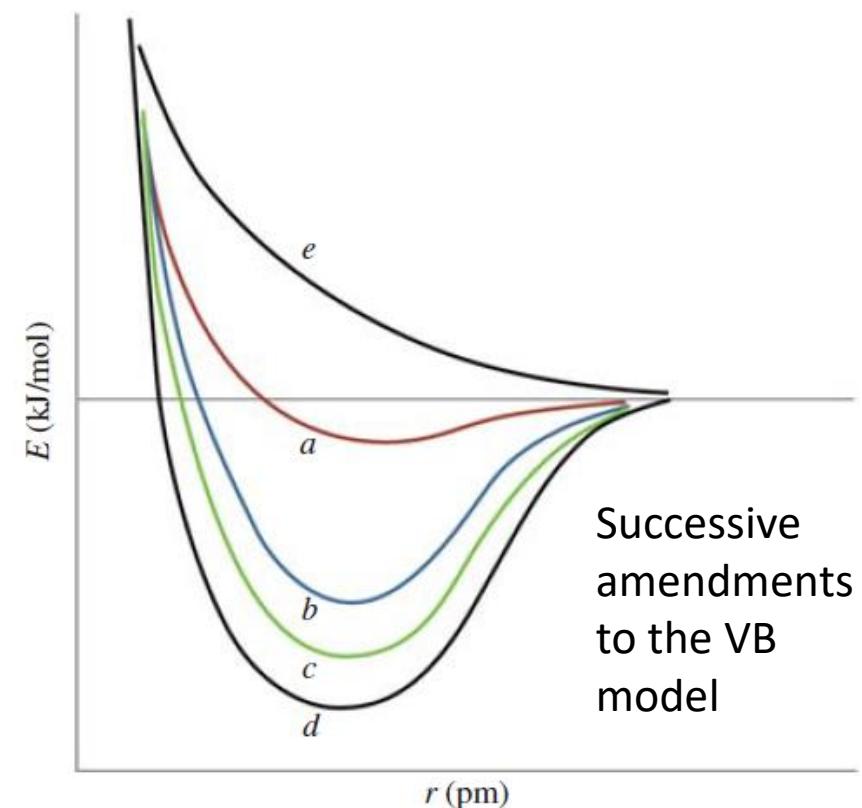
- The probability of an ionic contribution in H_2 , where there is no difference in electronegativity between the two H atoms is very small, and so a weighting factor λ is included as a coefficient in Equation (10.3) in front of each of the ionic terms (where $\lambda \ll 1$). The minimum now occurs at 74.6 pm and 397 kJ/mol.

$$\psi(H_2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) + \lambda\psi_A(1)\psi_A(2) + \lambda\psi_B(1)\psi_B(2) \quad (10.3)$$

- After application of these corrections to the VB model, the theoretical curve (c) closely matches that of the experimental curve for the H_2 molecule when the two electrons have opposite spin, as shown in Figure 10.1 by curve (d), the attractive term.
- This minimum occurs at 74 pm and 432 kJ/mol.
- Curve (e) at the top of the diagram corresponds with the experimental values for two electrons in the H_2 molecule having identical spins, or the repulsive term.
- A correction for the shielding of one electron from experiencing the full strength of either nuclear attraction by the presence of the other electron improves the curve, leading to a minimum at 74 pm and 365 kJ/mol.

FIGURE 10.1

Artist's rendering of the theoretical potential energy curves (a)–(c) constructed using the data given by Equations (10.1)–(10.3), along with the experimentally observed attractive potential (d) for the H_2 molecule. Curve (e) is the experimental repulsive term. [Blatt Communications.]



- The potential energy diagram shown in Figure 10.1 shows *how successive amendments to the VB model led to a more precise record of the potential energy curve* for the hydrogen molecule.

- Now let's consider the **formation of F_2** , represented by its Lewis diagram, from two F atoms each with electron configuration F: $(1s)^2(2s)^2(2p_x)^2(2p_y)^2(2p_z)^1$.
- Suppose the two atoms labeled A and B approach each other along the z-axis so that their $2p_z$ orbitals with the same phase point toward each other. As the atoms draw close, these two orbitals can overlap to form a single bond with two electrons. Reasoning as we did above for H_2 , we write the VB wave function for the electron pair bond in F_2 (neglecting ionic contributions) as

$$\psi_g^{\text{bond}} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

- The electron density obtained from this wave function is represented by the three-dimensional isosurface shown in Figure 6.27. It gives the probability density for locating two electrons in the F_2 molecule with internuclear separation R_{AB} . Comparing this surface with the one shown in Figure 6.26b clearly reveals the influence of its parentage in $2p$ AOs.
- This wave function gives ***no information on the eight pairs of electrons remaining in their atomic orbitals on atoms A and B***, six pairs of which are shown as unshared pairs in the Lewis diagram for F_2 (Fig. 6.28).

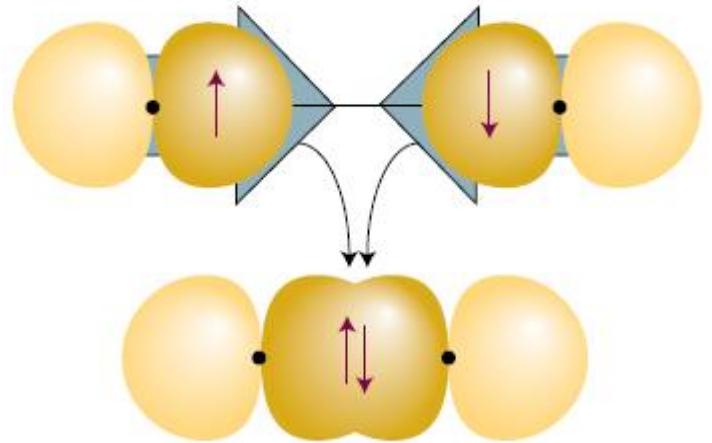


Figure 9A.2 The orbital overlap and spin pairing between electrons in two collinear p orbitals that results in the formation of a σ bond.

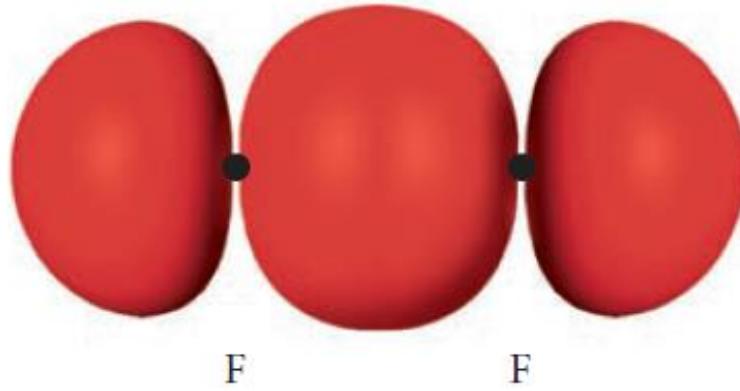


FIGURE 6.27 Isosurface representation of the electron density in the $F_2 \sigma$ bond formed from a pair of electrons initially localized in a $2p_z$ orbital on each F atom.

(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)



FIGURE 6.28 Lewis diagram for F_2 .

- The VB model also describes bond formation in **heteronuclear diatomics**.
- We can combine the features of the two preceding examples to describe HF, which has one shared pair in a single bond produced by overlap of H 1s and F 2p_z.
- To write a wave function for the electron pair bond, one might begin with

$$\psi^{\text{bond}} = C_1[2p_z^F(1)1s^H(2)] + C_2[2p_z^F(2)1s^H(1)]$$

- However, C₁ and C₂ are equal and should be omitted. The electron density isosurface is depicted in Figure 6.29.

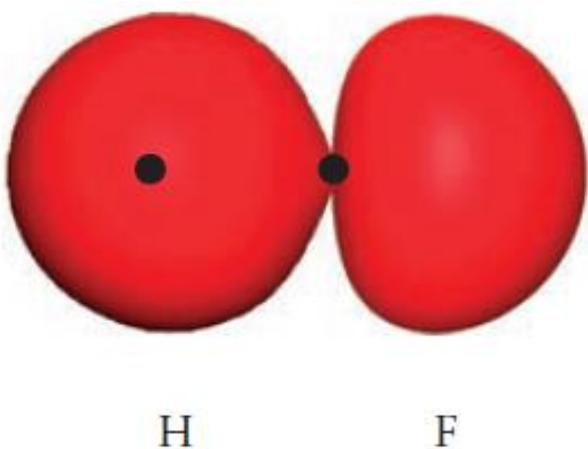


FIGURE 6.29 Isosurface representation of the electron density in the HF σ bond formed from a pair of electrons initially localized in a 1s orbital on H and in a 2p_z orbital on F.
(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)

- The bond pair wave functions were specially constructed to describe two electrons localized between two atoms as a single chemical bond between the atoms.
 - These wave functions should **not** be called **MOs**, because they are not single-electron functions and they are not delocalized over the entire molecule.
 - The corresponding single bonds, shown in Figures 6.26, 6.27, and 6.29 are examples of a **sigma (σ) bond**, because *their electron density is cylindrically symmetric about the bond axis*. Because of this symmetry it is said to have *zero angular momentum about the bond axis*.
 - Finally, electrons are not placed in these bonds by the aufbau principle. Rather, each bond is formed by overlap of two AOs, each of which is already half-filled with one electron.
 - The electrons in the two participating AOs must have opposite spin, so the bond corresponds to an electron pair with opposite, or “paired” spins.
- At its core, *the valence bond model states that chemical bonds form as a result of the overlap of the valence AOs on two different nuclei* such that both nuclei can share a pair of electrons.
- By sharing the pair of electrons, the atom assumes a more stable configuration with two electrons surrounding it (so that it has an electron configuration analogous to the noble gas atom, often achieving a full octet).

- A chemist's picture of a covalent bond is one in which the ***spins of two electrons pair as the atomic orbitals overlap***. It can be shown that the origin of the role of spin is that the wavefunction in eqn 9A.2 can be formed only by two spin-paired electrons.

$$\Psi(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$$

A valence-bond
wavefunction

(9A.2)

❖ Establishing the origin of electron pairs in VB theory

- The Pauli principle requires the overall wavefunction of two electrons, *the wavefunction including spin*, to change the sign when the labels of the electrons are interchanged. The Pauli principle requires that $\Psi(2,1) = -\Psi(1,2)$.
- The overall VB wavefunction for two electrons is: $\Psi(1,2) = \{\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\}\sigma(1,2)$ where σ represents the spin component of the wavefunction. When the labels 1 and 2 are interchanged, this wavefunction becomes

$$\Psi(2,1) = \{\psi_A(2)\psi_B(1) + \psi_A(1)\psi_B(2)\}\sigma(2,1) = \{\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\}\sigma(2,1)$$

- The Pauli principle requires that $\Psi(2,1) = -\Psi(1,2)$, which is satisfied only if $\sigma(2,1) = -\sigma(1,2)$.

$$^1\Psi = \overbrace{\frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2))}^{\textbf{Symmetric} \times \textbf{Antisymmetric}} \begin{matrix} M_S \\ 0 \end{matrix}$$

$$^3\Psi = \overbrace{\frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))}^{\textbf{Antisymmetric} \times \textbf{Symmetric}} \left\{ \begin{matrix} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{matrix} \right\} \begin{matrix} 1 \\ 0 \\ -1 \end{matrix}$$

- The combination of two spins that has this property is
- $\sigma(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$
- which corresponds to paired electron spins.
- Therefore, the state of lower energy (and hence the formation of a chemical bond) is achieved if the electron spins are paired.
- Spin pairing is not an end in itself: it is a means of achieving a wavefunction, and the probability distribution it implies, that corresponds to a low energy.

❖ Multiple Bonds

- To see how the VB method describes multiple bonds, let's examine N₂. Suppose two nitrogen atoms with electron configuration N: (1s)²(2s)²(2p_x)¹(2p_y)¹(2p_z)¹ approach one another along the z-axis.
- The two 2p_z orbitals can overlap and form a σ bond whose wave function is

$$\psi_{\sigma}^{\text{bond}} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

- The 2p_x orbitals and the 2p_y orbitals on the two atoms do not approach head-on in this configuration, but rather *side-to-side*. Therefore, the positive lobes of the 2p_x orbitals can overlap laterally, as can the negative lobes. Together they form a **pi (π) bond**, which has a node through the plane containing the bond axis with amplitude above and below the plane.
- Similarly, the 2p_y orbitals on the two atoms can overlap to form a second π bond, the π_y bond in the y-z plane.
- The wave functions for the π_x and π_y bonds are

$$\psi_{\pi_x}^{\text{bond}}(1,2) = C_1[2p_x^A(1)2p_x^B(2)] + C_1[2p_x^A(2)2p_x^B(1)]$$

$$\psi_{\pi_y}^{\text{bond}}(1,2) = C_1[2p_y^A(1)2p_y^B(2) + 2p_y^A(2)2p_y^B(1)]$$

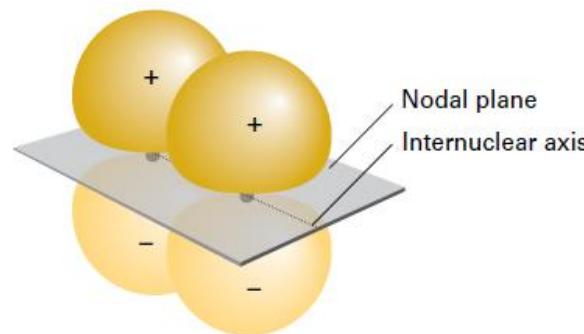


Figure 9A.3 A π bond results from orbital overlap and spin pairing between electrons in p orbitals with their axes perpendicular to the internuclear axis. The bond has two lobes of electron density separated by a nodal plane.

- Again, the two spins in each bond are opposite.
- The three bonds in N_2 are shown as isosurfaces of electron density in Figure 6.31.

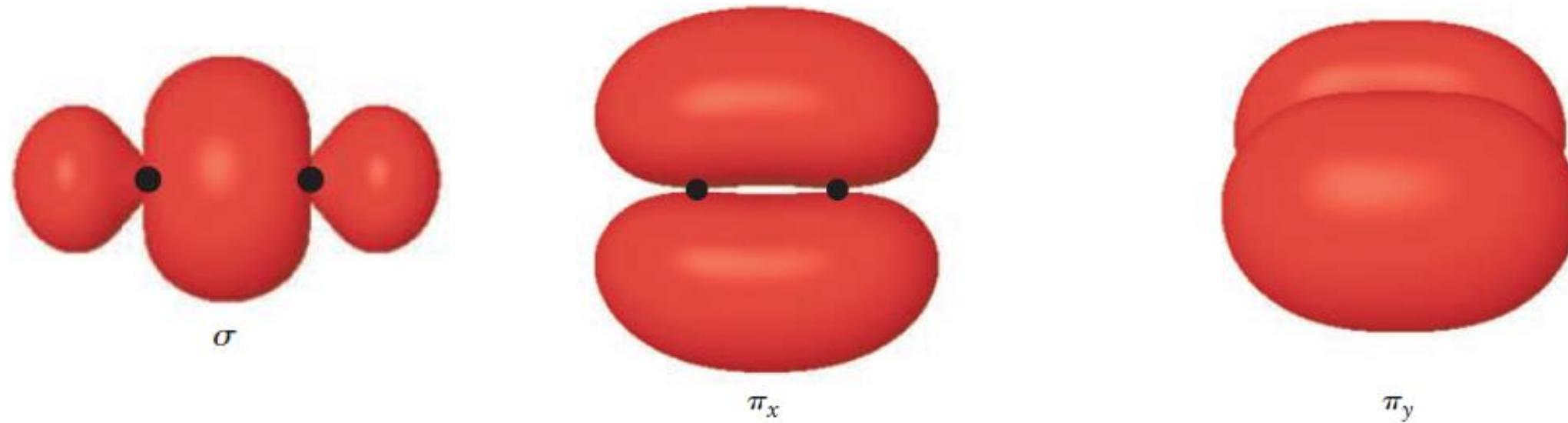


FIGURE 6.31 Isosurface representation of the electron densities in the σ bond and the two π bonds for nitrogen obtained by computer calculations.
(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)

❖ Polyatomic Molecules

- Describing the three-dimensional structure of polyatomic molecules requires that we include bond angles as well as bond lengths. Let's test the VB approximation on the second-period hydrides, whose structures to see how well it describes bond angles and molecular shapes.
- Beryllium hydride, BeH_2 , has four valence electrons, two from Be and one each from the two H atoms, all of which appear in the Lewis diagram in Figure 6.32.



Figure 6.32 Lewis diagram for BeH_2 .

- In VSEPR theory, the steric number is 2, so the molecule is predicted to be linear, and this prediction is verified by experiment. The electron configuration of the central atom is Be: $(1s)^2(2s)^2$. There are no unpaired electrons to overlap with H(1s) orbitals, so the VB model fails to predict the formation of BeH_2 .
- Boron hydride, BH_3 (Fig. 6.33), has six valence electrons corresponding to steric number 3 and a trigonal planar structure. With the electron configuration B: $(1s)^2(2s)^2(2p)^1$ on the central atom, the VB model cannot account for the formation of BH_3 and, in fact, predicts that *BH is the stable molecule, which does not agree with experiment.*

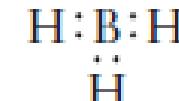


Figure 6.33 Lewis diagram for BH_3 .

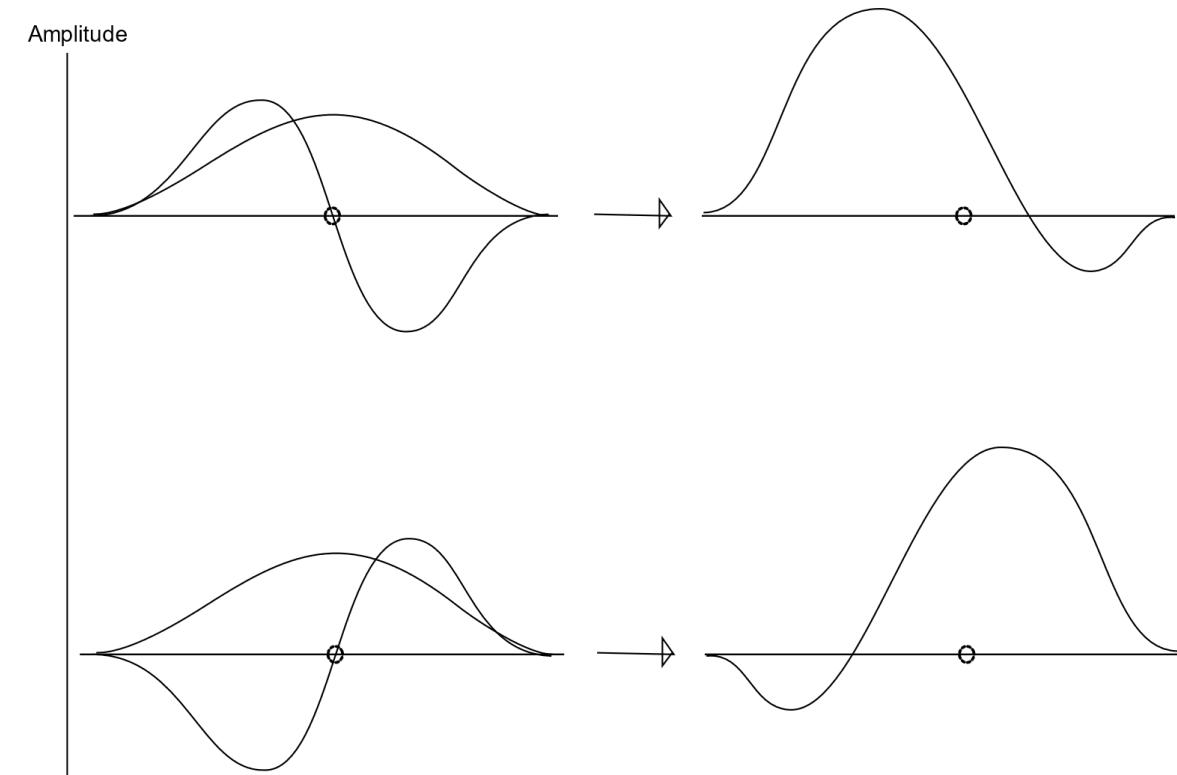
- ❑ Methane, CH_4 , has steric number 4, and VSEPR predicts a tetrahedral structure, which is confirmed by experiment.
 - ✓ Starting with the electron configuration C: $(1s)^2(2s)^2(2p)^2$, the VB model cannot account for the formation of CH_4 and predicts that CH_2 would be the stable hydride, which is again contrary to the experimental results.
-
- ❑ Ammonia, NH_3 , has steric number 4 with three shared pairs and one unshared pair on the N atom. VSEPR predicts a trigonal pyramid structure, as a subcase of tetrahedral structure, with angles slightly less than 109.5° due to repulsion between the unshared pair and the three bonding pairs. Experiment verifies this structure with angles of 107° .
 - ✓ The electron configuration N: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$ would permit the formation of three σ bonds by overlap of H($1s$) orbitals with each of the $2p$ orbitals on N.
 - ✓ Because these $2p$ orbitals are all *mutually perpendicular*, VB predicts a trigonal pyramid but one with bond angles of 90° .

- These examples show that the **VB model does not accurately describe bonding in the second-period hydrides**. It predicts the wrong valence for atoms in Groups IIA through IVA, and the wrong structure for atoms in Groups VA and VIA. Clearly, the model had to be improved.
- Linus Pauling gave the answer in 1931 by introducing the concepts of ***promotion*** and ***hybridization***.
- Atoms such as Be, B, and C can have the correct valence for bonding by promotion of valence electrons from the ground state to excited states at higher energy. For example,
- Be: $(1s)^2(2s)^2 \rightarrow$ Be: $(1s)^2(2s)^1(2p)^1$ and
- C: $(1s)^2(2s)^2(2p)^2 \rightarrow$ C: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$ are ready to form BeH_2 and CH_4 , respectively.
- These excited states are known from spectroscopy. The C excited state lies about 8.26 eV (190 kcal mol⁻¹) above the ground state; *promoting an electron to create the excited state clearly requires energy*.
- Pauling ***argued*** that this *investment would be repaid by the energy released when the C-H bonds of methane form* (about 100 kcal mol⁻¹ for each bond).

- Even though the *valence* is correct after *promotion*, the *structure would still be wrong*.
- Beryllium hydride would have two different kinds of bonds, and methane would have three identical bonds formed by overlap of H(1s) with the C(2p) orbitals and a different bond formed by H(1s) and C(2s).
- Pauling proposed that new atomic orbitals with the proper symmetry for bond formation could be formed by ***hybridization*** of 2s and 2p orbitals after promotion.
- ✓ The Be(2s) and Be($2p_z$) orbitals would combine to form *two equivalent hybrid atomic orbitals oriented 180° apart*.
- ✓ The C(2s) would hybridize with the three C(2p) orbitals to give four equivalent new atomic orbitals arranged as a tetrahedron around the C atom.
- Pauling's achievements made it possible to describe polyatomic molecules by VB theory, and *hybridization has provided the vocabulary and structural concepts* for many of the fields of inorganic chemistry, organic chemistry, and biochemistry.

- We can build hybrid orbitals using wave interference.
- First, let's think about a molecule like BeF_2 (in the gas phase, where it is a molecule and not an ionic solid). This molecule is predicted to be linear, so how do we put the 4 bonding electrons into 2 orbitals pointed in the right direction? We can imagine taking the Be 2s orbital and 2p_z orbital, and combining them in 2 ways, adding and subtracting. This gives us 2 new orbitals. (Any time you combine orbitals, you get as many out as you put in.) This is first shown using "1-D" waves, where the x-axis is radius and the y-axis is Ψ . It's important to think about the phases of the orbitals during this combination and think about constructive and destructive interference.

The **formation of sp hybrid orbitals**, illustrated with approximate 1-D waves, showing Ψ vs radius. The small circle shows the position of the nucleus. We add the 2 waves on the left to get the total wave on the right.



Rules for orbital hybridization:

1. Add and subtract atomic orbitals to get hybrid orbitals.
 2. We get the same number of orbitals out as we put in.
 3. The energy of a hybrid orbital is the weighted average of the atomic orbitals that make it up.
 4. The coefficients are determined by the constraints that the hybrid orbitals must be *orthogonal* and *normalized*.
- When both orbitals are ***normalized***: $\int \psi_1^2 d\tau = \int \psi_2^2 d\tau = 1$ and ***orthogonal***: $\int \psi_1 \psi_2 d\tau = 0$.

❖ Orbital Hybridization for Polyatomic Molecules

- Pauling developed the method of hybrid orbitals to describe the bonding in molecules containing second-period atoms with steric numbers 2, 3, and 4.
- We will use the lower-case Greek letter “chi” χ to represent hybrid orbitals.

❖ Orbital Hybridization for Polyatomic Molecules

□ *sp* Hybridization

- Let's discuss these hybridization schemes in sequence, starting with BeH_2 . In each case we will learn how to construct the hybrid orbitals and how to use them to describe the bonds and the three-dimensional structure of polyatomic molecules.
- Because the BeH_2 molecule is known to be linear, we need two new atomic orbitals oriented 180° apart on the Be atom, each of which can overlap with one H atom.
- We can generate these new atomic orbitals in the following way. Let's define the z-axis of the coordinate system to lie along the H—Be—H bonds and place the Be nucleus at the origin. We mix the $2s$ and $2p_z$ orbitals of Be to form two new orbitals on the Be atom. The linear combinations that correspond to Figure 6.37b (with the z-axis pointing to the right), are

$$\chi_1(r) = \frac{1}{\sqrt{2}} [-2s - 2p_z]$$

$$\chi_2(r) = \frac{1}{\sqrt{2}} [-2s + 2p_z]$$

- Here we have simply added and subtracted the $2s$ and $2p_z$ orbitals; we leave it as an exercise for the interested student to show that both orbitals are ***normalized*** (i.e., $\int \psi_1^2 d\tau = \int \psi_2^2 d\tau = 1$) and ***orthogonal*** (i.e., $\int \psi_1 \psi_2 d\tau = 0$).

- ✓ The coefficient $1/\sqrt{2}$ is a normalization constant.
- ✓ We call these *sp hybrid atomic orbitals because they are formed as the sum or difference of one s orbital and one p orbital*.
- ✓ Like the familiar s and p orbitals, **a hybrid atomic orbital is a one-electron wave function** that is defined at every point in space.
- ✓ The value of the wave function at each point is the sum or difference of the original AOs combined to form the hybrid.
- ✓ Its square at each point in three-dimensional space gives the probability density for finding the electron at that point, when the electron is in the hybrid orbital.

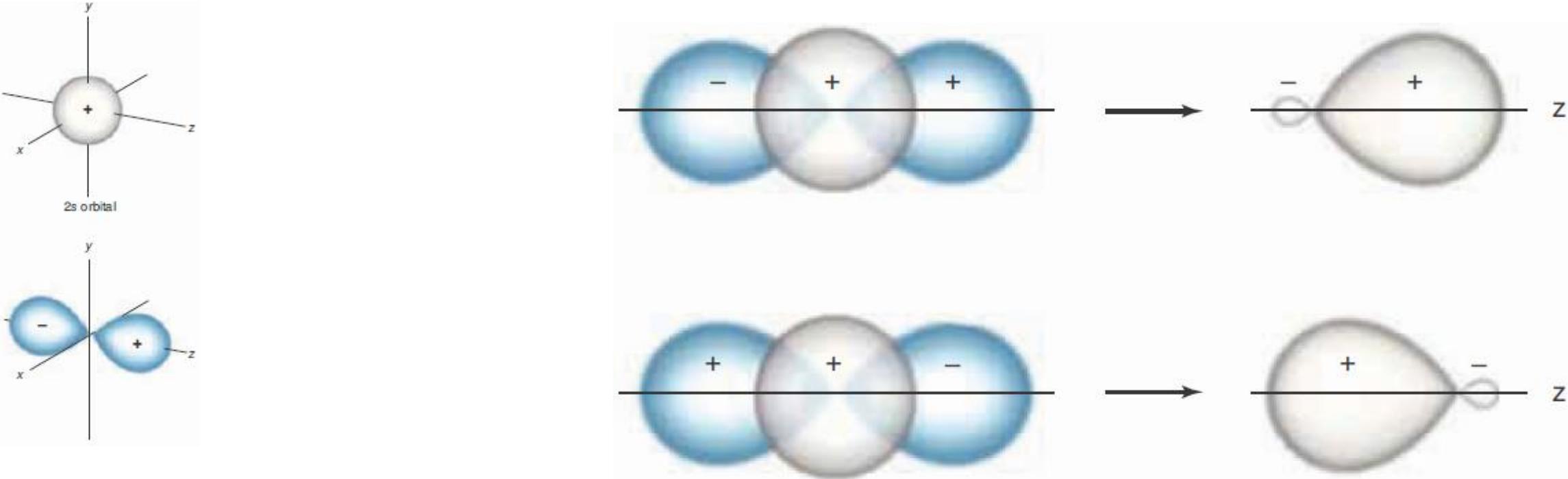


Figure 9.16 The formation of two *sp* hybrid orbitals from a *2s* and a *2p* atomic orbital oriented along the bonding axis. The two resulting *sp* orbitals are 180° apart.

Addition and subtraction of the *2s* and *2p* atomic orbitals may be illustrated by reversing the signs on the *2p* orbital, as shown here. The *2s* and *2p* orbitals reinforce each other in regions where they have values with the same sign and partially cancel each other in regions where they have values of opposite sign.

Consequently, each *sp* orbital consists of a large lobe of positive value and a small lobe of negative value. For simplicity, we often shall omit the little lobes of negative value.

- The formation, shapes, and orientation of the sp hybrid orbitals—and their participation in chemical bonds—are shown in Figure 6.37.
- ✓ The first column shows the standard orbitals on the Be atom before hybridization, and the second shows the hybrid atomic orbitals on Be resulting from the linear combination of the Be 2s and 2pz atomic orbitals.
- ✓ The hybrid atomic orbital shown on the top of the second column is the one with large electron density pointing in the negative z direction. It is the one that will have substantial overlap with the H atom coming in from the left as you form H-Be-H.
- ✓ As the two hydrogen atoms approach the Be atom from opposite directions along the z-axis, each shares its electron with the nearest hybrid orbital to form a localized s bond (see Fig. 6.37c). The result is a pair of localized σ bonds, one on each side of the Be atom.

- ✓ The third column in Figure 6.37 illustrates these two σ bonds by locating the Be and H nuclei at distances apart equal to the experimental bond length of BeH_2 , and placing an sp hybrid on the Be atom and a 1s AO on the H atom in order to show where these orbitals overlap.
- ✓ Since the advent of the VB method, chemists have used qualitative sketches similar to this third column to show the location, shape, and orientation of the σ bonds.
- ✓ With modern computational methods, detailed representations of the electron density can be obtained from the wave functions for the two bonding pairs.
- ✓ The fourth column in Figure 6.37 shows the electron density in the s bonds of BeH_2 calculated in this way.

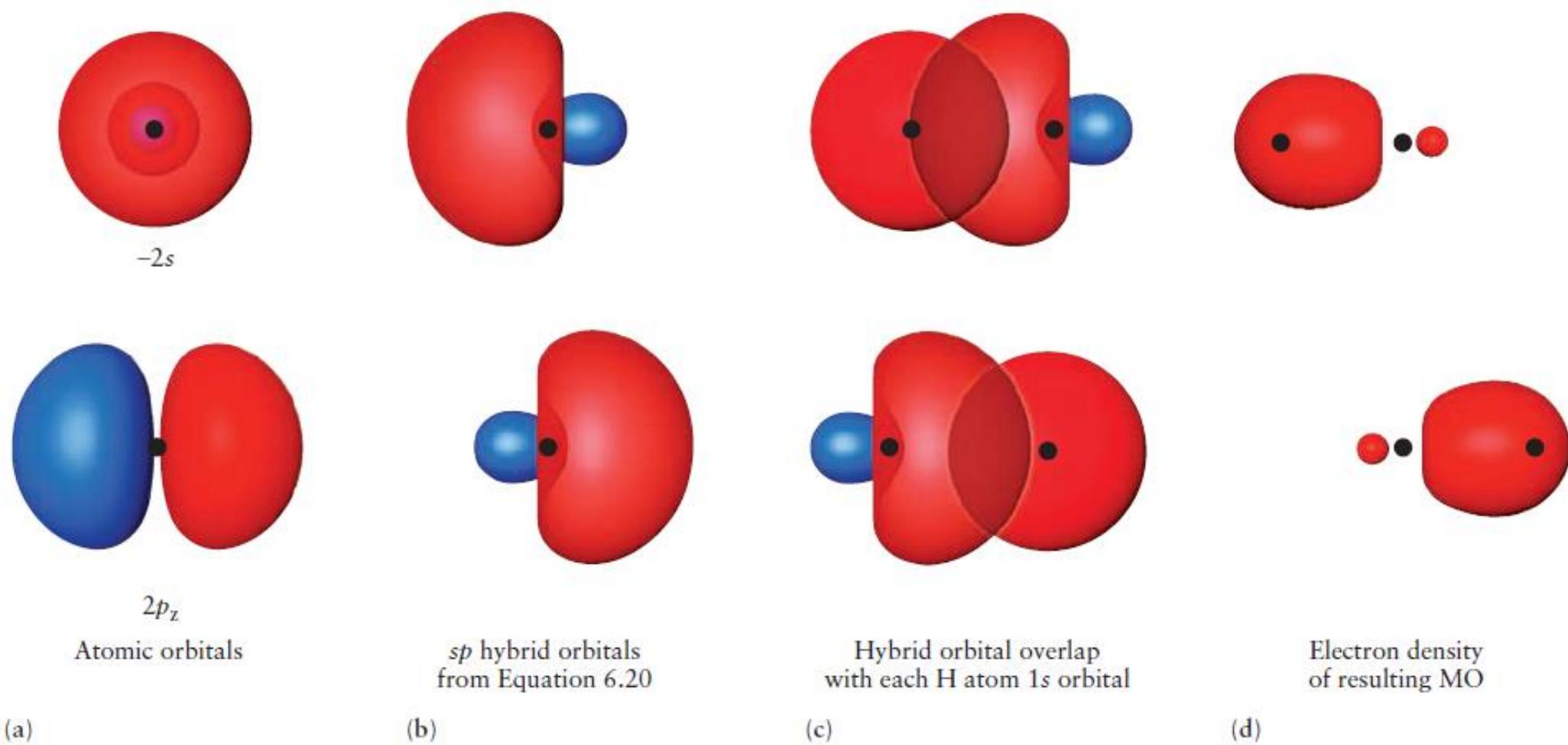
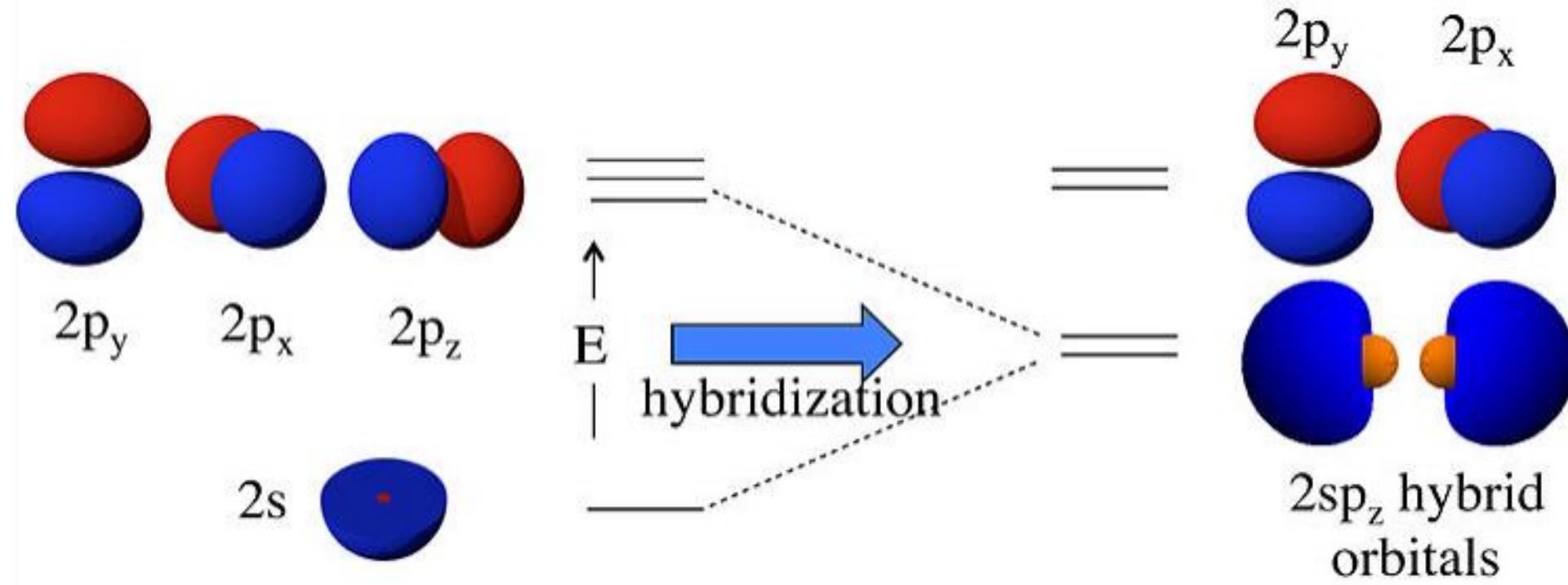


FIGURE 6.37 Formation, shapes, and bonding of the sp hybrid orbitals in the BeH_2 molecule.

- The $-2s$ and $2p_z$ orbitals of the Be atom.
- The two sp hybrid orbitals formed from the $2s$ and $2p_z$ orbitals on the beryllium atom.
- The two σ bonds that form from the overlap of the sp hybrid orbitals with the hydrogen 1s orbitals, making two single bonds in the BeH_2 molecule.
- Electron density in the two σ bonds obtained by computer calculations.

(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, University of Texas at Austin.)

- ✓ sp hybridization explains how an atom can have a pair of σ bonds at an angle of 180° apart and therefore be part of a linear molecule.
- ✓ This result is broadly applicable and can be combined with other aspects of molecular structure.
- ✓ Later in this section, we shall see that atoms *having more than two valence electrons can form linear molecules through sp hybridization and at the same time can also form multiple bonds through linear combinations of the two p orbitals not used in making the sp hybrid AOs with orbitals on other atoms.*



- The formation of *sp* hybrid orbitals results from combining the *2s* orbital and one *2p* orbital on a single atom..
- Linear combinations of the *2s* and *2p_z* atomic orbitals make two *2sp_z* hybrids. The *2p_x* and *2p_y* orbitals are unchanged.
- Because each hybrid is built from one *s* orbital and one *p* orbital, it is called an ***sp* hybrid orbital**.

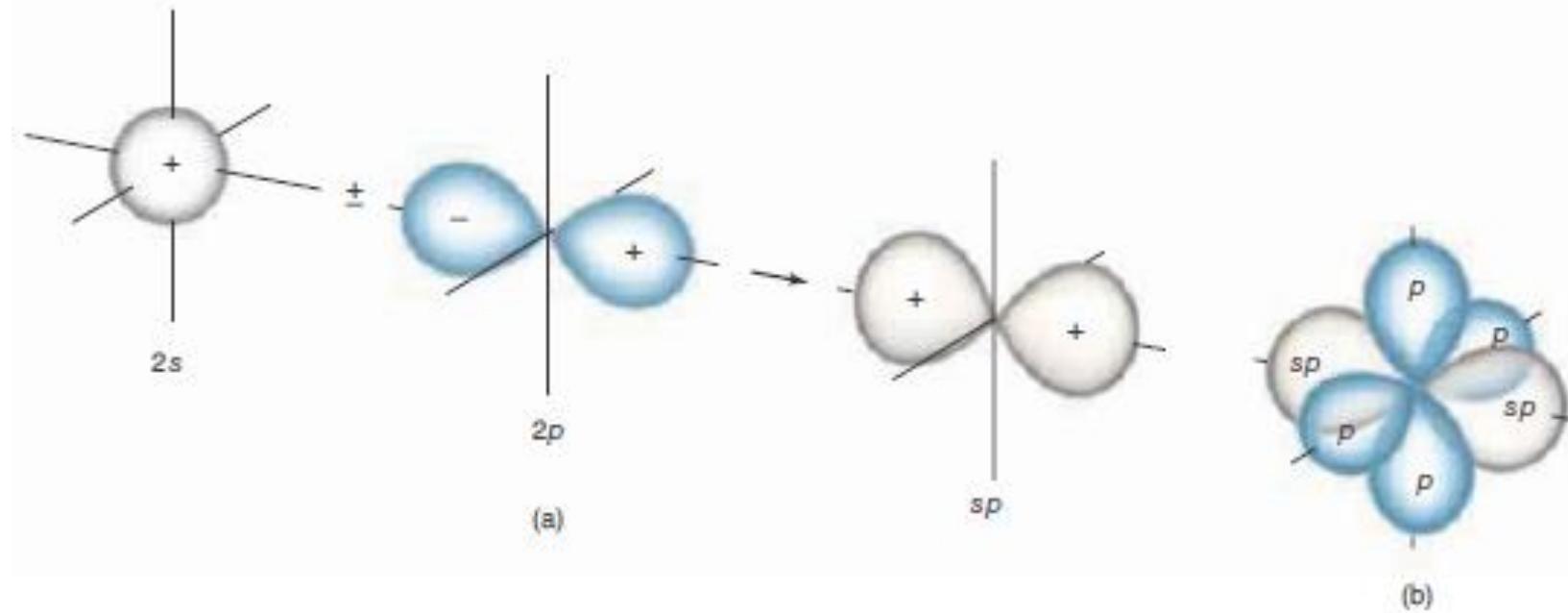


Figure 9.17 The formation of *sp* hybrid orbitals results from combining the *2s* orbital and one *2p* orbital on a single atom.

The two *sp* orbitals are equivalent and are 180° apart.

In (a), for simplicity, only the *2p* orbital that is combined with the *2s* orbital is shown.

In (b), all the orbitals are shown.

The two *2p* orbitals that are not combined with the *2s* orbital are perpendicular to each other and to the line formed by the *sp* hybrid orbitals. The little lobes of negative sign cannot be seen in this figure.

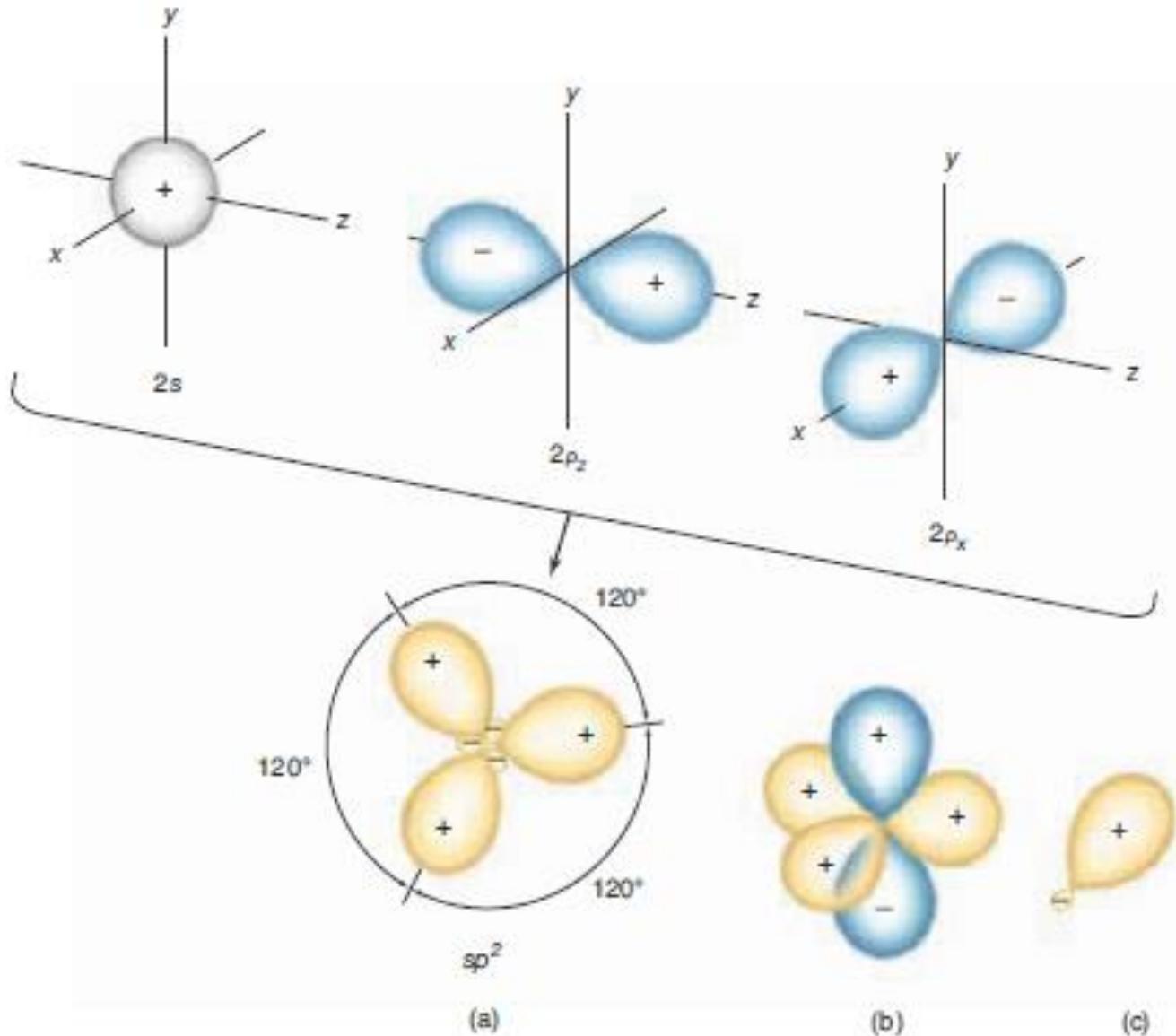


Figure 9.20 The formation of sp^2 hybrid orbitals by combining the 2s orbital and two 2p orbitals on a single atom.

- (a) The three sp^2 orbitals formed are equivalent, lie in a plane, and are 120° apart. For simplicity, only the two 2p orbitals that are combined with the 2s orbital are shown.
- (b) The 2p orbital that is not combined with the 2s orbital is perpendicular to the plane formed by the three sp^2 orbitals. The relatively small negative value regions of the sp^2 hybrid orbitals are omitted.
- (c) A single complete sp^2 hybrid orbital.

➤ Because each hybrid is built from one s orbital and two p orbitals, it is called an **sp^2 hybrid orbital**.

*sp*³ hybrid orbitals

The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$

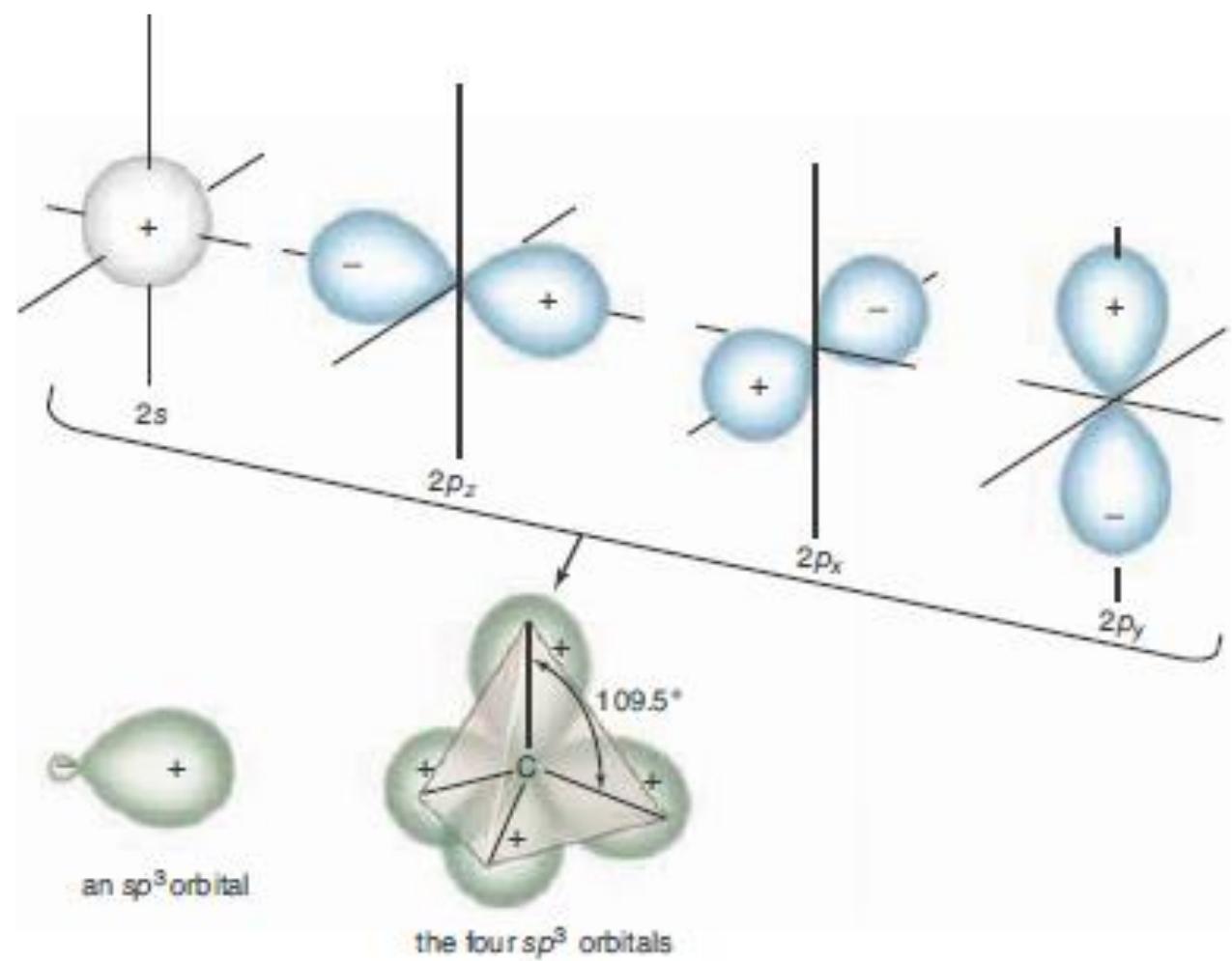
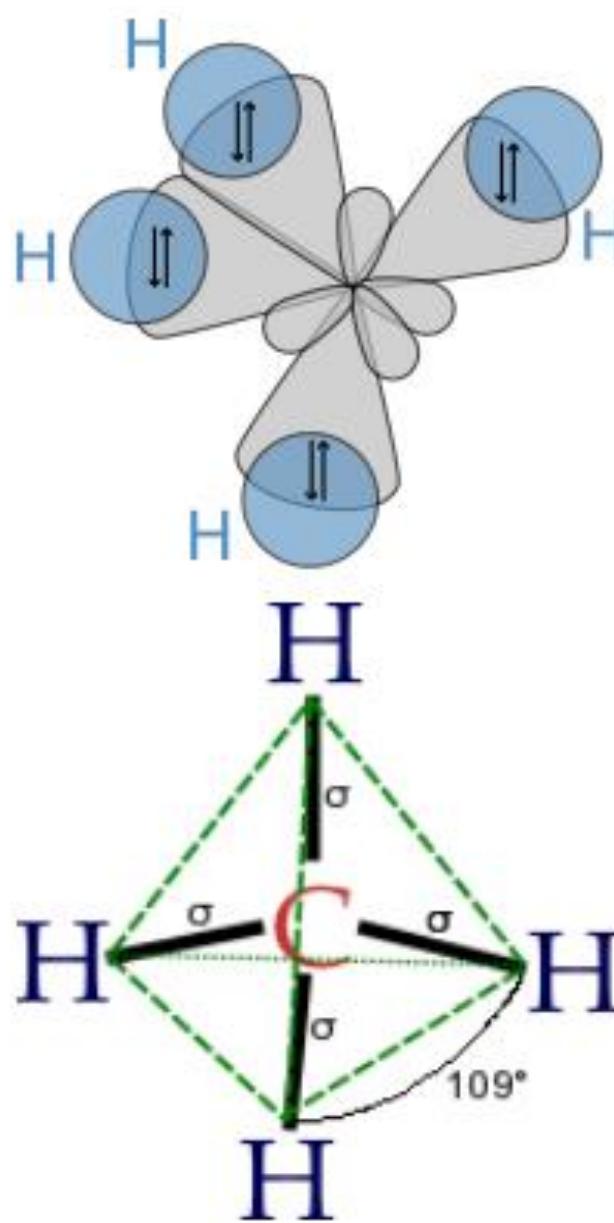


Figure 9.22 The 2s and three 2p orbitals on an atom can be combined to form four sp^3 hybrid orbitals that are all equivalent and point toward the vertices of a tetrahedron. The angle between sp^3 orbitals is the tetrahedral bond angle, 109.5°. The small negative value regions of the sp^3 orbitals are omitted from the tetrahedral figure to simplify the figure. A single sp^3 orbital is shown to the left of the set of four sp^3 orbitals.

sp^3 hybrid orbitals and CH_4



- As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the appropriate direction.
- A **hybrid orbital has enhanced amplitude in the internuclear region**, which arises from the constructive interference between the s orbital and the positive lobes of the p orbitals.
- ✓ As a result, ***the bond strength is greater than for a bond formed from an s or p orbital alone***. This *increased bond strength is another factor that helps to repay the promotion energy*.
- The hybridization of N atomic orbitals always results in the formation of N hybrid orbitals, which *may either form bonds or may contain lone pairs of electrons*, pairs of electrons that do not participate directly in bond formation (but may influence the shape of the molecule).

NOTE:

- All ***spⁿ-hybridized orbitals are more directional*** than s or p AOs are by themselves.
- ✓ ***Increased directionality implies increased orbital overlap.***
- ✓ This is at least part of the reason that it is worth *paying the price of electron promotion* in the first place—***the increased overlap will gain more energy back when the hybrid orbitals on the central atom overlap with the ligand orbitals to form bonds.***
- The ***amount of overlap in spⁿ hybrid orbitals increases with the percent s-character.***
- The ***more s-character in the hybrid orbital, the lower the overall energy of that orbital will be and the larger the size of the “big” lobe of the spⁿ hybrid.***
- ✓ Thus, *sp* orbitals have greater overlap with the ligand orbitals than do *sp²* or *sp³* orbitals.

Angle between two hybrid orbitals

- All these types of hybrid orbitals have strong directional characteristics and the *angle between two hybrid orbitals is calculated by using the following relation.*
- For sp^n hybridized orbitals ($n = 1-3$), the relationship between the **bond angle (θ)** and the **decimal percent s-character (S)** is given by Equation (10.8).

$$\cos \theta = \frac{S}{S-1} \quad (10.8)$$

- The angle between the axes of the sp^3 hybrid orbitals is the tetrahedral angle, $\arccos(-1/3) = 109.47^\circ$.
- Calculate the **bond angle (θ)** for (pure) sp^2 hybridized orbitals.
- What is the p-character of the (pure) sp^2 hybridized orbitals?
- For hybrids that also contain some *d-orbital character*, the relationship between the bond angle and directionality of the hybrid orbitals is somewhat more complex and is not discussed here.

- In sp^2 hybrid orbitals where the fraction of s character is $1/3$, this becomes $\cos \theta = (1/3)/[(1/3) - 1] = -0.5$ for which $\theta = 120^\circ$.
- Fig. 4.4 shows the relationship between the calculated bond angles and the fraction of s character in the hybrid orbitals.

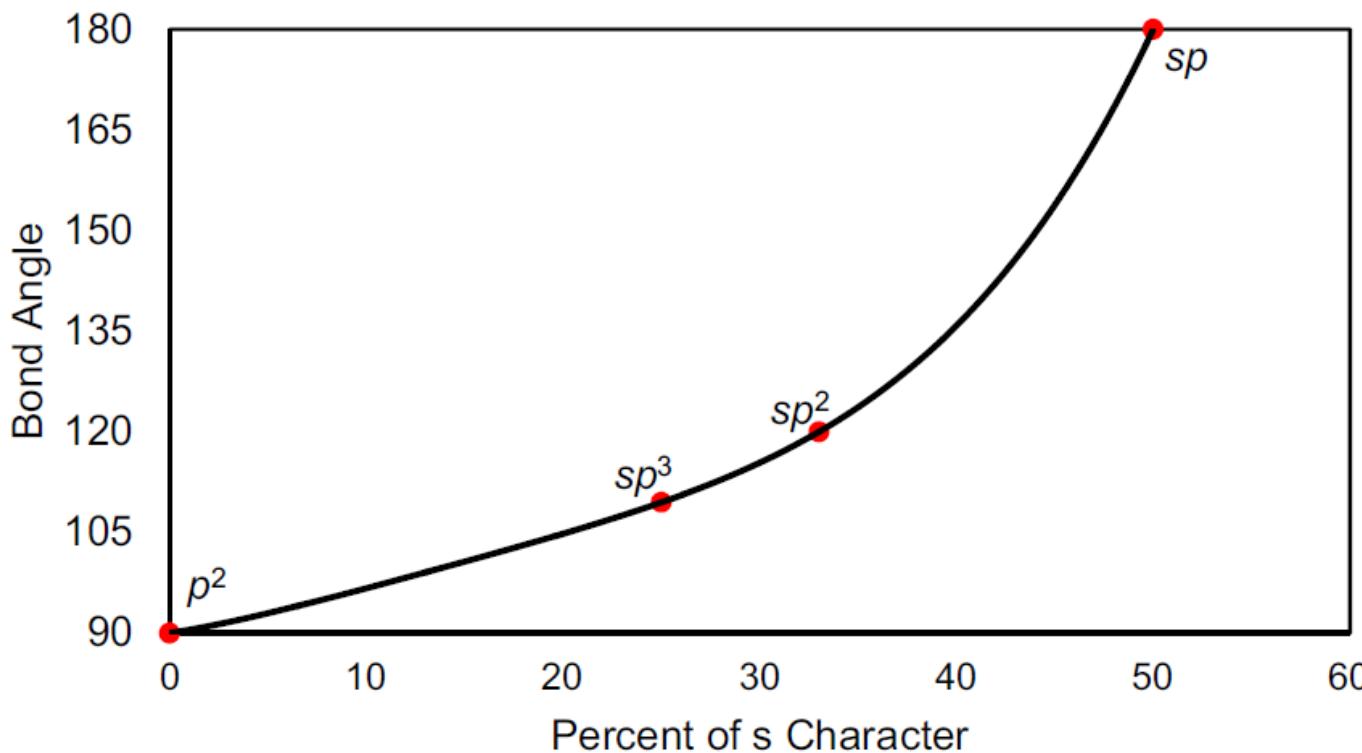


FIGURE 4.4 Variation in bond angle in hybrid orbitals with percent s character in sp^n ($n = 1-3$).

- Although the hybrid orbitals that can be constructed for s and p orbitals are designated as sp, sp^2 , and sp^3 , such hybridization may not always be this simple. In simple molecules such as BeF_2 , BF_3 , and CH_4 the bond angles conform to the expected angles of 180° , 120° , and $109^\circ 28'$, respectively.
- However, in the cases of H_2S and PH_3 the bond angles deviate to such an extent that it is unreasonable to expect hybrid bonding orbitals of sp^3 with the effect of unshared pairs causing the large deviation in bond angles.
- By making use of the relationship, it is possible to show that in PH_3 and H_2S the fraction of s character is only 5.4% and 3.7%, respectively.
- Partial hybridization can thus be invoked to explain the bond angles in hydrides of elements in the third long row.
- For H_2Se and H_3As , the bond angles are even closer to 90° , indicating that the bonding involves essentially pure p orbitals on the central atom.
- *Electron distribution in s orbitals is much more diffuse than in sp^n hybrids or p orbitals alone.*
- As a consequence, the **unshared pair of electrons** in PH_3 has **much less** attraction for H^+ , meaning that it is much less basic than NH_3 .

❖ Hybridization and Lone Pairs and Basicity

- In H_2O , the experimental H—O—H bond angle is 104.5° .
- Application of Equation (10.8) yields a value of $S = 0.20$.
- ✓ Thus, the two O—H bonding orbitals can be considered to have 20% s-character and 80% p-character.
- ✓ Because the overall hybridization in water was sp^3 , this result implies that the two lone pairs in H_2O have 30% s-character (because $2 * 20\% + 2 * 30\% = 100\%$) and 70% p-character (because $2 * 80\%$ (2-bonds) and $2 * 70\%$ (2-lone pairs) = 300%) so that the overall hybridization still averages to sp^3 .
- ✓ In water, two of the valence electrons on the oxygen atom are involved in the bonds with hydrogen atoms while four remain as two sets of lone pair electrons on the oxygen atom. We expect the pair of bonding orbitals to be equivalent and the pair of orbitals for the lone pairs to be equivalent, but there is no reason to expect the bonding orbitals to be equivalent to the lone pair orbitals.

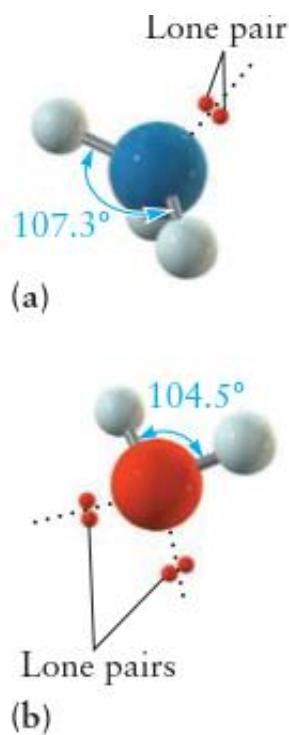


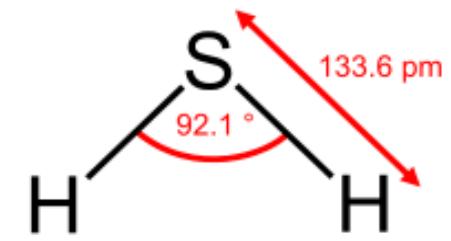
FIGURE 6.41 (a)
Ammonia (NH_3)
has a pyramidal
structure (b)
Water (H_2O) has
a bent structure
(both has bond
angles less than
 109.5°).

- ✓ Different Hybrid Orbitals are used for the Bonding Electrons and the Lone Pair Electrons in water.
- ✓ The ground-state electron configuration of an oxygen atom is $1s^2 2s^2 2p_x^2 p_y^1 2p_z^1$. Because the $2p_y$ and $2p_z$ orbitals contain only one electron, they can form chemical bonds with the hydrogen 1s electron.
- ✓ This model predicts, however, that the bond angle in water is 90° , compared with the observed bond angle of 104.5° .
- ✓ Even though the oxygen atom contains the needed electrons in half-filled atomic orbitals to account for the number of chemical bonds in water, the geometry of the molecule necessitates the consideration of hybrid orbitals on the central oxygen molecule. The bond angle in water (104°) is between that predicted using sp^2 hybrid orbitals (120°) and 2p orbitals (90°).
- ✓ Sometimes, it has been explained from sp^2 form of the hybrid orbitals on the oxygen atom is given by
$$\Psi = c_1 2s + c_2 2p_y + c_3 2p_z \quad (10.11)$$
- ✓ One needs to determine the coefficients c_1 , c_2 , and c_3 such that two orthogonal orbitals are directed at an angle of 104° . (Ref. McQuarrie's Book: page# 379)

- The experimental bond angle in NH_3 is 107.2° . Application of Equation (10.8) yields 23% s-character and 77% p-character in each of the three N–H single bonds.
- Because $3 \times (23.3\%) = 69\%$, the ***lone pair*** in ammonia has approximately ***31% s-character***.
- ✓ As a result, the lone pair in NH_3 will have ***slightly greater*** s-character than will the lone pair in H_2O (H_2O lone pair has ***30% s-character***).
- ✓ The ***greater basicity of NH_3 relative to H_2O*** can at least ***in part*** be attributed to the fact that the ***lone pair in ammonia will have a greater amount of overlap with the 1s-orbital*** on a proton than will a lone pair on water.
- The general conclusion is that sp^3 hybridization with a lone pair in one of the hybrid AOs explains the trigonal pyramid structure for AX_3 molecules, as a subcase of tetrahedral structure.
- ✓ Examples include the hydrides and halides of the Group V elements N, P, As, Sb, and Bi, all of which have the trigonal pyramid structure with bond angles ranging from 107° to 92° .
- ✓ *Additional effects must be considered to explain the range of bond angle values in this group of molecules.*

- Similarly, sp^3 hybridization with lone pairs in two of the hybrid AOs explains the bent or angular structure for AX_2 molecules, as a subcase of tetrahedral structure. Other examples besides water are H_2S , OF_2 , and SF_2 . Again, additional effects must be considered to explain the range of bond angle values in this group of molecules.
- Interestingly, the bond angles in PH_3 , H_2S and H_2Se are close to 90° , suggesting that P, S, and Se ***primarily use their p-orbitals*** in bonding to H in these molecules.
- Although the energy difference between s and p orbitals stays roughly constant going down the periodic table, why does hybridization occur when the central atom is oxygen or nitrogen but not when it is S or P?
- The ***answer*** lies in the fact that there are two major results of hybridization of orbitals.
- The first is that the orbitals are directed in space at different angles than are the unhybridized atomic orbitals. We have already seen the types of structures that result and how less repulsion results. However, the other result of hybridization is that the orbitals are changed in size. The hybridization of 3s and 3p orbitals on sulfur or phosphorus would produce more favorable bond angles with regard to repulsion, but *the overlap between those orbitals and the hydrogen 1s orbitals is less effective*.

- The hydrogen orbital can overlap better with a smaller unhybridized p orbital on sulfur or phosphorus. The result is that the orbitals used by the central atom have a very slight degree of hybridization but closely resemble pure p orbitals.
- Despite the fact that the energy difference between s and p orbitals stays roughly constant going down the periodic table, but the **bond energy decreases as the valence electrons get farther away from the nucleus.**
- For these heavier elements, **the bonding energy is not enough to offset the energy needed to promote the s electrons to s-p hybrid orbitals.**
- In compounds of elements in the 3rd, 4th, and 5th rows of the periodic table, there thus is a ***decreasing tendency to use s-p orbital hybrids in bonding.***
- Based on this analysis, we would expect that H_2Se and AsH_3 would have bond angles that deviate even more from the tetrahedral bond angle. In accord with this, the bond angles for these molecules are 91.0° and 91.8° , respectively, indicating that the bonding orbitals on the central atoms are nearly pure p orbitals. The hydrogen compounds of the heavier members of Groups V and VI have bond angles that are even closer to right angles (H_2Te , 90° ; SbH_3 , 91.3°).



π bond formation: Multiple bonding in a molecule

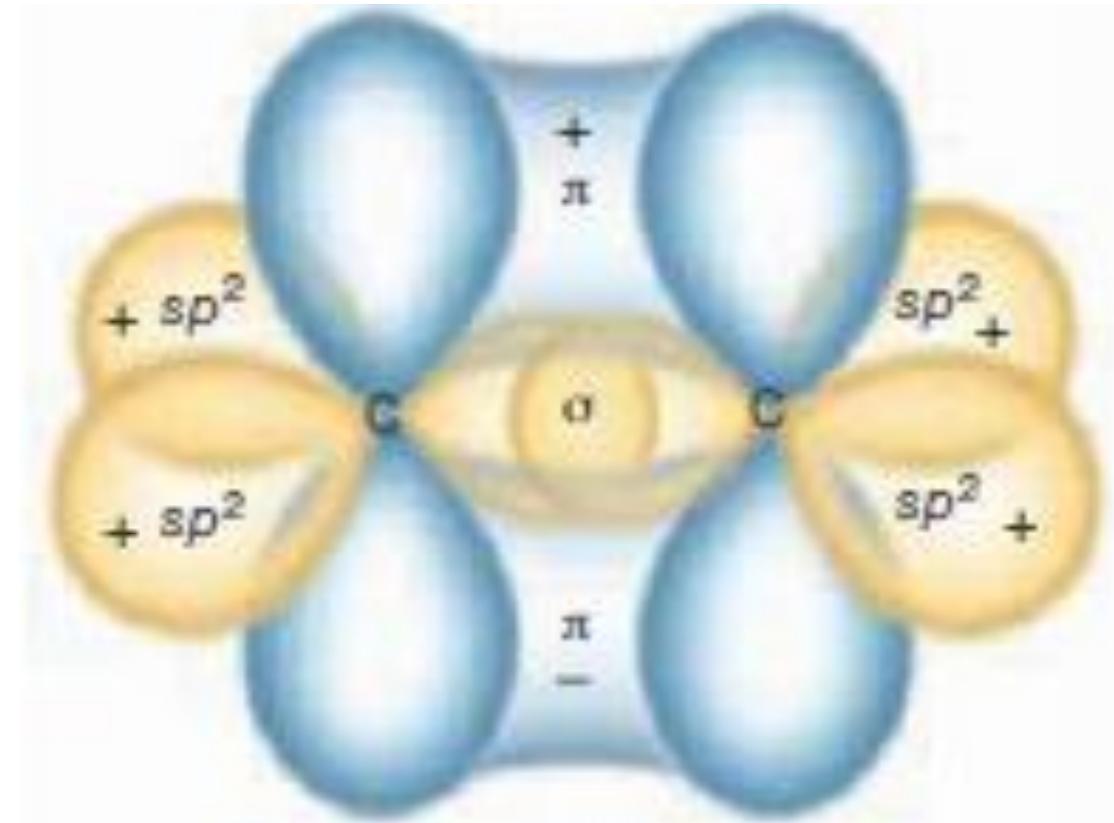


Figure 9.34 A double bond in an ethylene molecule consists of a σ bond and a π bond. The σ bond results from the combination of two sp^2 orbitals, one from each carbon atom. The π bond results from the combination (lateral overlap) of two $2p$ orbitals, one from each carbon atom. The π orbital maintains the σ -bond framework in a planar shape and prevents rotation about the double bond.

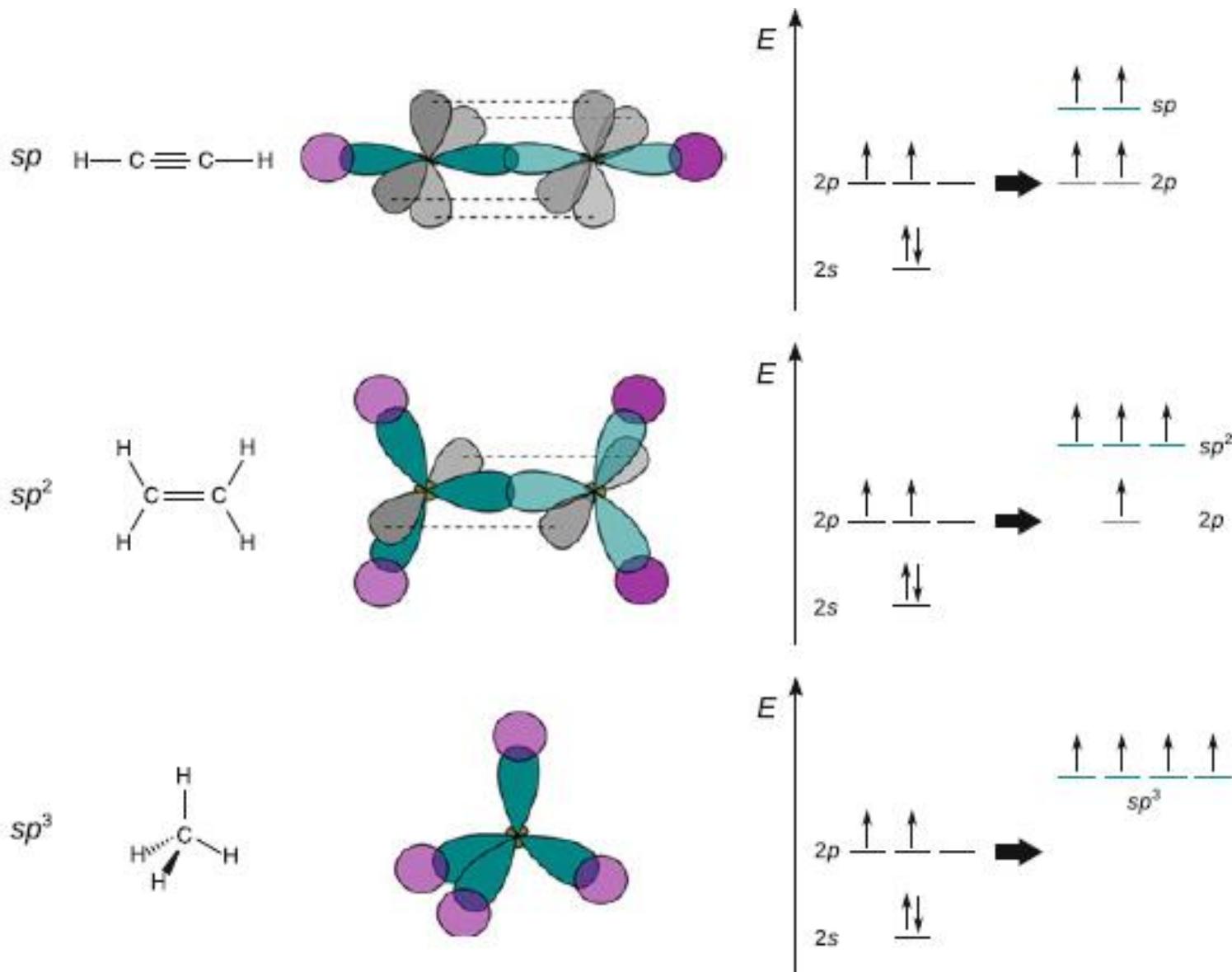


Fig. 11.14 Schematic illustration of bond formation in acetylene, ethylene and methane. The hybrid atomic orbitals of carbon are colored turquoise, the 2p orbitals grey and the 1s orbitals of hydrogen are colored magenta.

- Hybrid orbitals of different compositions are used to match different molecular geometries and to provide a basis for their VB description. For example, sp^2 hybridization is used to reproduce the electron distribution needed for trigonal-planar species, such as on B in BF_3 and N in NO_3^- , and sp hybridization reproduces a linear distribution.
- The lobes of the **sp^3 hybrid** orbitals point towards the vertices of a tetrahedron (or alternate corners of a cube), consistent with the tetrahedral bond angle in CH_4 and the nearly tetrahedral angles in NH_3 and H_2O . Similarly, we can show that we can construct the trigonal bipyramidal electronic shape by making sp and sp^2 hybrids, and the octahedral geometry from three sets of sp hybrids. ***The picture that emerges from this is that the atomic orbitals can hybridize as required by the shape that best minimizes electron pair repulsions.***
- Table 3.2 gives the hybrids needed to match the geometries of a variety of electron distributions and **includes hybridization schemes that include d orbitals, thus accounting for hypervalence.**

TABLE 3.2 Hybridization and Molecular Shape*

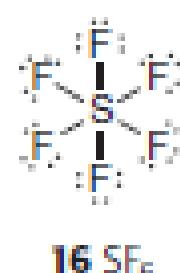
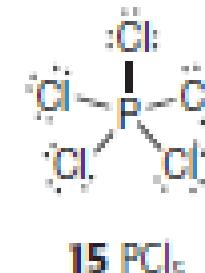
Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

*Other combinations of s-, p-, and d-orbitals can give rise to the same or different shapes, but the combinations in the table are the most common.

Hypervalence

Key point: Hypervalence and octet expansion occur for elements following Period 2.

- The elements of Period 2, Li through Ne, obey the octet rule quite well, but elements of later periods show deviations from it. For example, the bonding in PCl_5 requires the P atom to have 10 electrons in its valence shell, one pair for each P-Cl bond (15). Similarly, in SF_6 the S atom must have 12 electrons if each F atom is to be bound to the central S atom by an electron pair (16). Species of this kind, which in terms of Lewis structures demand the presence of more than an octet of electrons around at least one atom, are called **hypervalent**.
- One explanation of hypervalence invokes the availability of low-lying unfilled d orbitals, which can accommodate the additional electrons.
- According to this explanation, a P atom can accommodate more than eight electrons if it uses its vacant 3d orbitals. In PCl_5 , with its five pairs of bonding electrons, at least one 3d orbital must be used in addition to the four 3s and 3p orbitals of the valence shell.
- The rarity of hypervalence in Period 2 is then ascribed to the absence of 2d orbitals. However, the real reason for the **rarity of hyper valence in Period 2 may be the geometrical difficulty of packing** more than four atoms around a small central atom and may in fact have little to do with the availability of d orbitals.
- The molecular orbital theory of bonding describes the bonding in hypervalent compounds without invoking participation of d orbitals.



Resonance

- Another term introduced into chemistry by *VB theory* is **resonance**, the superposition of the wavefunctions representing different electron distributions in the same nuclear framework.
- To understand what this means, consider the VB description of a purely covalently bonded HCl molecule, which could be written as $\Psi_{\text{H-Cl}} = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)$, with Ψ_A now a H1s orbital and Ψ_B a Cl3p orbital.
- This description allows electron 1 to be on the H atom when electron 2 is on the Cl atom, and vice versa, but it does not allow for the possibility that both electrons are on the Cl atom ($\Psi_{\text{H}^+\text{Cl}^-} = \Psi_B(1)\Psi_B(2)$, representing the ionic form H^+Cl^-) or both are on the H atom ($\Psi_{\text{H}^-\text{Cl}^+} = \Psi_A(1)\Psi_A(2)$, representing the much less likely ionic form H^-Cl^+).
- A *better description of the wavefunction for the molecule is as a superposition of the covalent and ionic descriptions*, written as (with a slightly simplified notation, and ignoring the less likely H^-Cl^+ possibility) $\Psi_{\text{HCl}} = \Psi_{\text{H-Cl}} + \lambda \Psi_{\text{H}^+\text{Cl}^-}$ with λ (lambda) some numerical coefficient.
- In general, $\Psi = \Psi_{\text{covalent}} + \lambda \Psi_{\text{ionic}}$ (9A.3)
where Ψ_{covalent} is the two-electron wavefunction for the purely covalent form of the bond and Ψ_{ionic} is the two-electron wavefunction for the ionic form of the bond.
- In this case, where one structure is pure covalent and the other pure ionic, it is called **ionic-covalent resonance**.

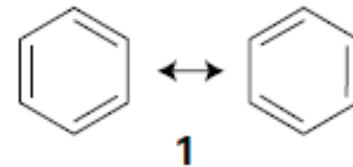
- The interpretation of the (un-normalized) wavefunction, which is called a **resonance hybrid**, is that if the molecule is inspected, then the probability that it would be found with an ionic structure is proportional to λ^2 .
 - ✓ If $\lambda^2 \ll 1$, the covalent description is dominant.
 - ✓ If $\lambda^2 \gg 1$, the ionic description is dominant.
- **Resonance** is not a flickering between the contributing states: it *is a blending of their characteristics*.
- *It is only a mathematical device for achieving a closer approximation to the true wavefunction* of the molecule than that represented by any single contributing electronic structure alone.
- A systematic way of calculating the value of λ is provided by the **variation principle**:
 - If an arbitrary wavefunction is used to calculate the energy, then the value calculated is never less than the true energy. The *arbitrary wavefunction* is called the **trial wavefunction**.
- The principle implies that if the *energy*, the expectation value of the hamiltonian, is calculated for various trial wavefunctions with *different values of the parameter λ* , then *the best value of λ is the one that results in the lowest energy*. The ionic contribution to the resonance is then proportional to λ^2 .

- Consider a bond described by eqn 9A.3. If the lowest energy is reached when $\lambda = 0.1$, then the best description of the bond in the molecule is a resonance structure described by the wavefunction $\Psi = \Psi_{\text{covalent}} + 0.1\Psi_{\text{ionic}}$.
- ✓ This wavefunction implies that the probabilities of finding the molecule in its covalent and ionic forms are in the ratio 100:1 (because $0.1^2 = 0.01$).
- Resonance plays an important role in the VB description of polyatomic molecules. One of the most famous examples of resonance is in the VB description of benzene, where the wavefunction of the molecule is written as a superposition of the many-electron wavefunctions of the two covalent Kekulé structures:

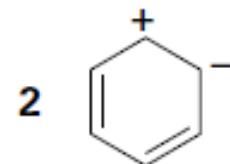


- The two contributing structures have identical energies, so they contribute equally to the superposition.

- The effect of resonance (which is represented by a double-headed arrow (**1**)), in this case, is to distribute double-bond character around the ring and to make the lengths and strengths of all the carbon–carbon bonds identical.



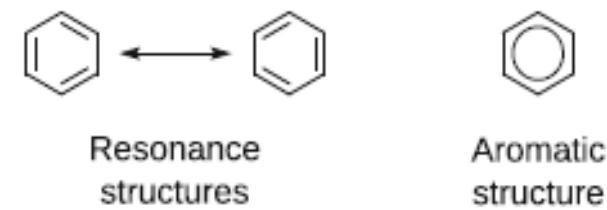
- *The wavefunction is improved by allowing resonance because it allows the electrons to adjust into a distribution of lower energy.* This lowering is called the **resonance stabilization** of the molecule and, in the context of VB theory, is largely responsible for the unusual stability of aromatic rings.
- *Resonance always lowers the energy, and the lowering is greatest when the contributing structures have similar energies.*
- The wavefunction of benzene is improved still further, and the calculated energy of the molecule is lowered still further, if ionic–covalent resonance is also considered, by allowing a small admixture of ionic structures, such as (**2**).



Resonance Structures and Electron Delocalization

- Both the molecular orbital (MO) theory and the valence bond (VB) theory are useful approaches to describe chemical bonding. One aspect of the VB method that is very appealing to many chemists is the fact that it allows depiction of molecules in connectivity diagrams which remains the by far most frequently used method to denote molecular structures.
- However, it is often impossible to denote the properties of particular molecules with a single structure.
- The most prominent example is certainly benzene (C_6H_6) for which a cyclic structure was first proposed by Kekulé in 1865. A ring structure can be accomplished with $6 \times 4 = 24$ carbon valence electrons, if one assumes three alternating double bonds (see Fig. 11.15).
- Such a structure would require that there are two types of C–C bond lengths in the ring: 1.54 Å for a single, and 1.33 Å for a double bond. In contrast, the experimentally determined C–C bond length in benzene is 1.40 Å.
- We realize that the assignment of the C–C double bond in the ring is entirely arbitrary and can formally suggest a second structure where the double bonds are localized differently.
- More realistically, though, the molecule resonates between the two depicted structures which depict two possible extremes. The possible extreme structures are those we can depict with localized bonds and are called resonance structures. In the depiction of such structures, a double-headed arrow is used to indicate that the structure(s) shown are indeed resonance structures.
- Resonance structures arise when the valence bond method is used to describe molecules; this is typically the case when constructing connectivity diagrams such as in Fig. 11.15.

Fig. 11.15 Depiction of resonance and aromatic structures of benzene



- In benzene, the C atoms and their attached H atoms all lie in the same plane, with the C atoms forming a hexagonal ring.
- To describe the bonding in the Kekule structures of benzene in terms of VB theory, we need hybrid orbitals that match the 120° bond angles of the hexagonal ring. Therefore, we take each carbon atom to be sp^2 hybridized, as in ethene (Fig. 3.20). The three hybrid orbitals each have one electron, with the fourth valence electron in an unhybridized 2p-orbital perpendicular to the plane of the hybrids. The sp^2 hybrid orbitals on each carbon atom overlap with those of their neighbors, which results in six σ -bonds between them. The remaining sp^2 hybrid orbital on each carbon atom overlaps with a hydrogen 1s-orbital, resulting in six carbon–hydrogen bonds. Finally, the side-by-side overlap of the 2p-orbitals on each C atom results in a π -bond between each carbon atom and one of its neighbors (Fig. 3.21). The resulting pattern of π -bonds matches either of the two Kekule structures, and the overall structure is a resonance hybrid of the two. This resonance ensures that the electrons in the π -bonds are spread around the entire ring (Fig. 3.22).

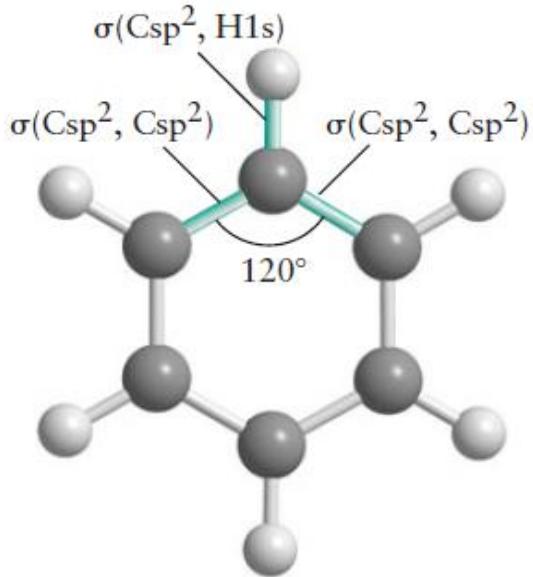


FIGURE 3.20 The framework of σ -bonds in benzene: each carbon atom is sp^2 hybridized, and the array of hybrid orbitals matches the bond angles (of 120°) in the hexagonal molecule. The bonds around only one carbon atom are labeled; all the others are the same.

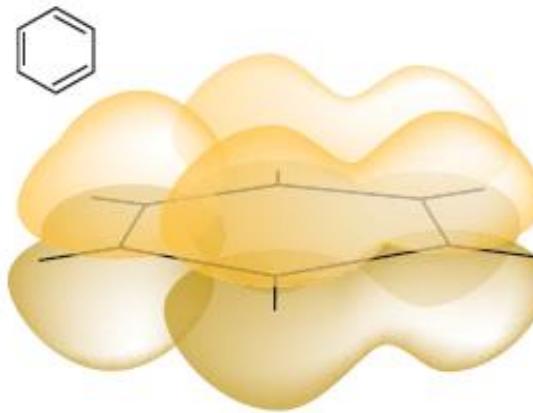


FIGURE 3.21 Unhybridized carbon 2p-orbitals can form a π -bond with either of their immediate neighbors. Two arrangements are possible, each one corresponding to a different Kekulé structure. One Kekulé structure and the corresponding π -bonds are shown here.

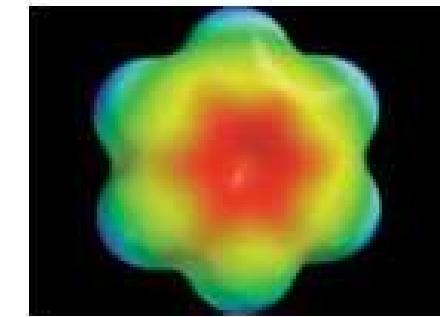
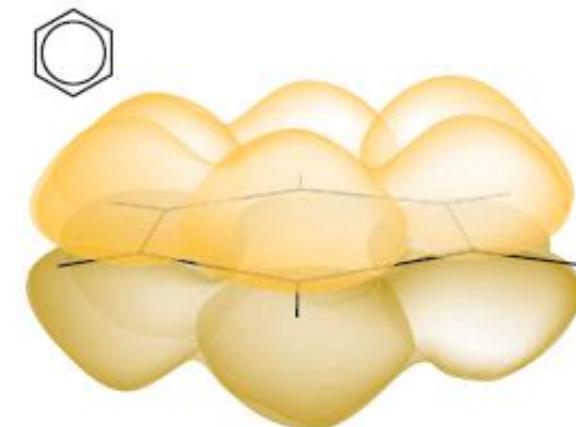
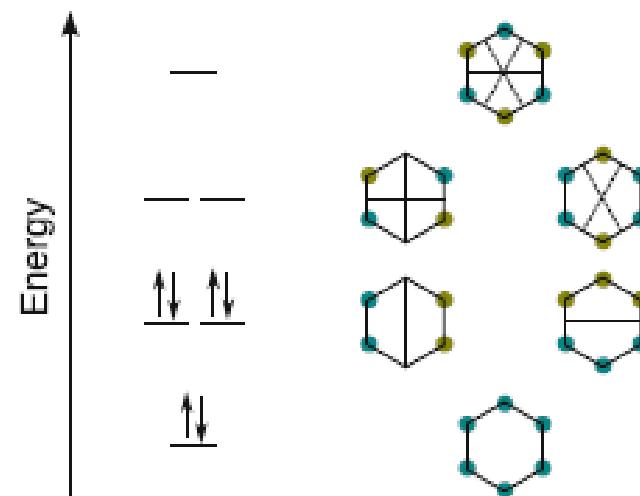


FIGURE 3.22 As a result of resonance between two structures like the one shown in Fig. 3.21 (corresponding to resonance of the two Kekulé structures), the π -electrons form a double doughnut-shaped cloud above and below the plane of the ring.

- An alternative explanation for phenomena such as aromaticity is provided by the molecular orbital (MO) theory. Focusing on the π electron system, we need to consider the six p_z orbitals which need to be combined in accordance with the linear combination of atomic orbitals.
- Therefore, six different linear combinations of the wave functions of the six p_z orbitals have to be generated. This results in three bonding and three anti-bonding molecular orbitals.
- The phase distribution in the different molecular orbitals are indicated in Fig. 11.16 by colours and the boundaries define the nodal planes. The (bonding) MO with the lowest energy shows that these electrons are delocalized over the entire ring. With increasing energy, the number of nodal planes increase and thus the compartmentalization of the orbitals. Electrons populating the higher energy MOs are therefore increasingly localized.

Fig. 11.16 The molecular orbitals and schematic representation of wave functions of the π system of benzene



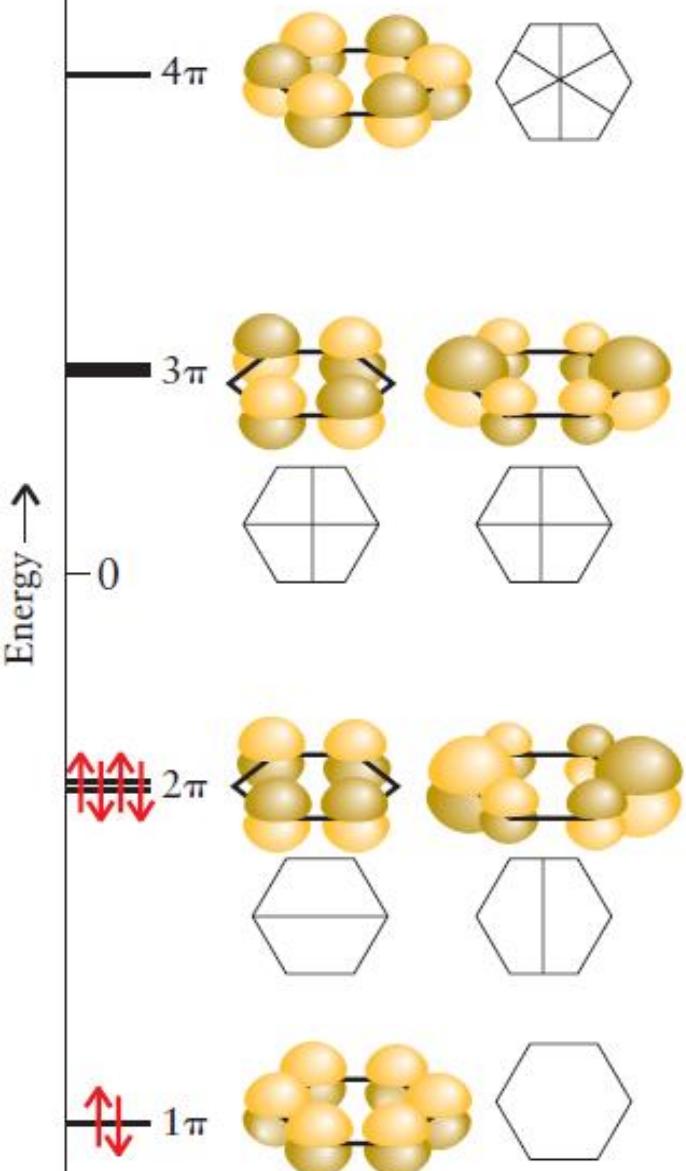


FIGURE 3.37 The six π -orbitals of benzene; locations of nodes are shown with line drawings. Note that the orbitals range from fully bonding (no internuclear nodes) to fully antibonding (six internuclear nodes). The zero of energy corresponds to the total energy of the separated atoms. The three orbitals with negative energies have net bonding character.

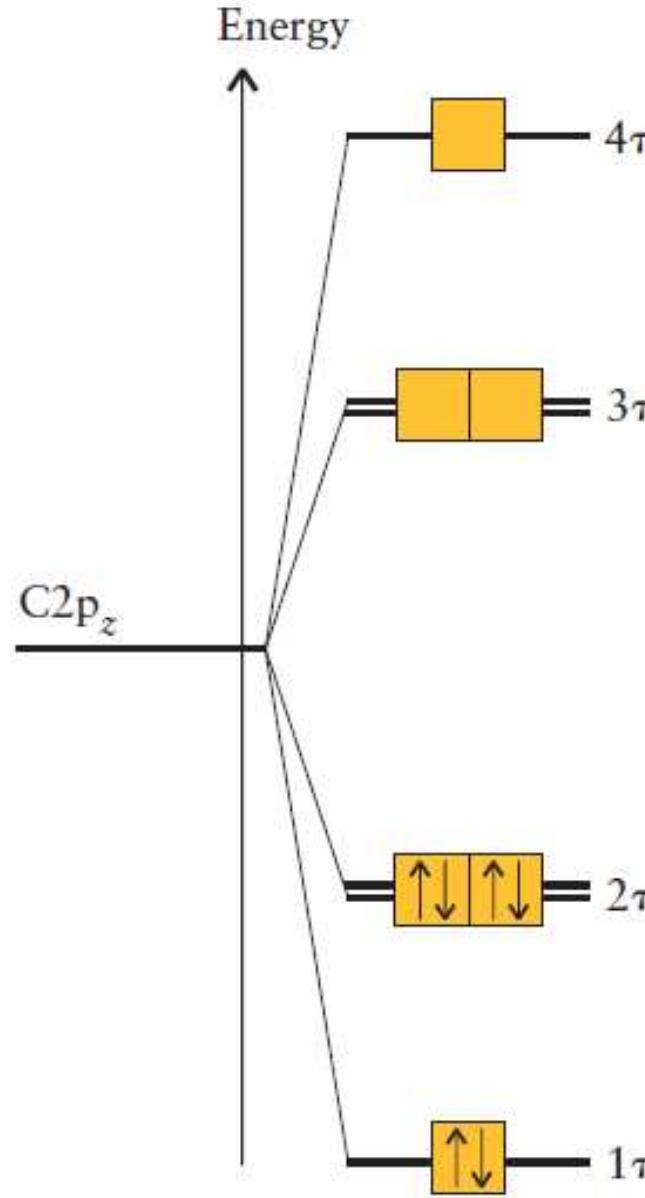
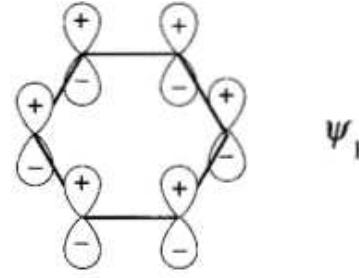
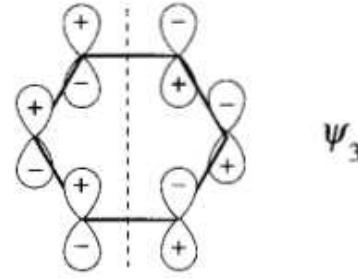
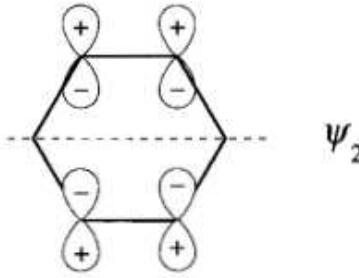
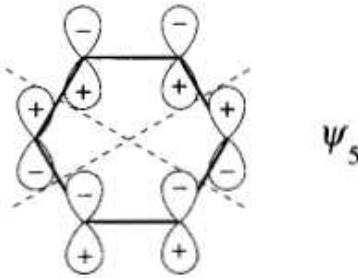
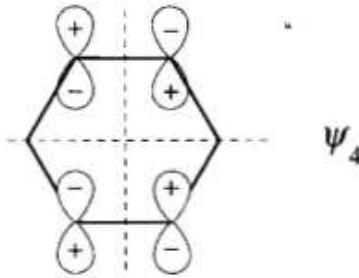
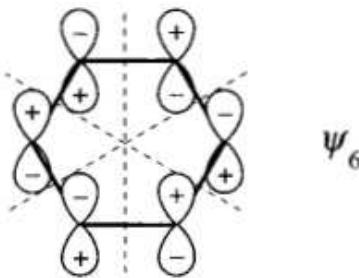


FIGURE 3.38 The molecular orbital energy-level diagram for the π -orbitals of benzene. In the ground state of the molecule, only the net bonding orbitals are occupied.

➤ The π molecular orbitals for benzene and the nodal planes.



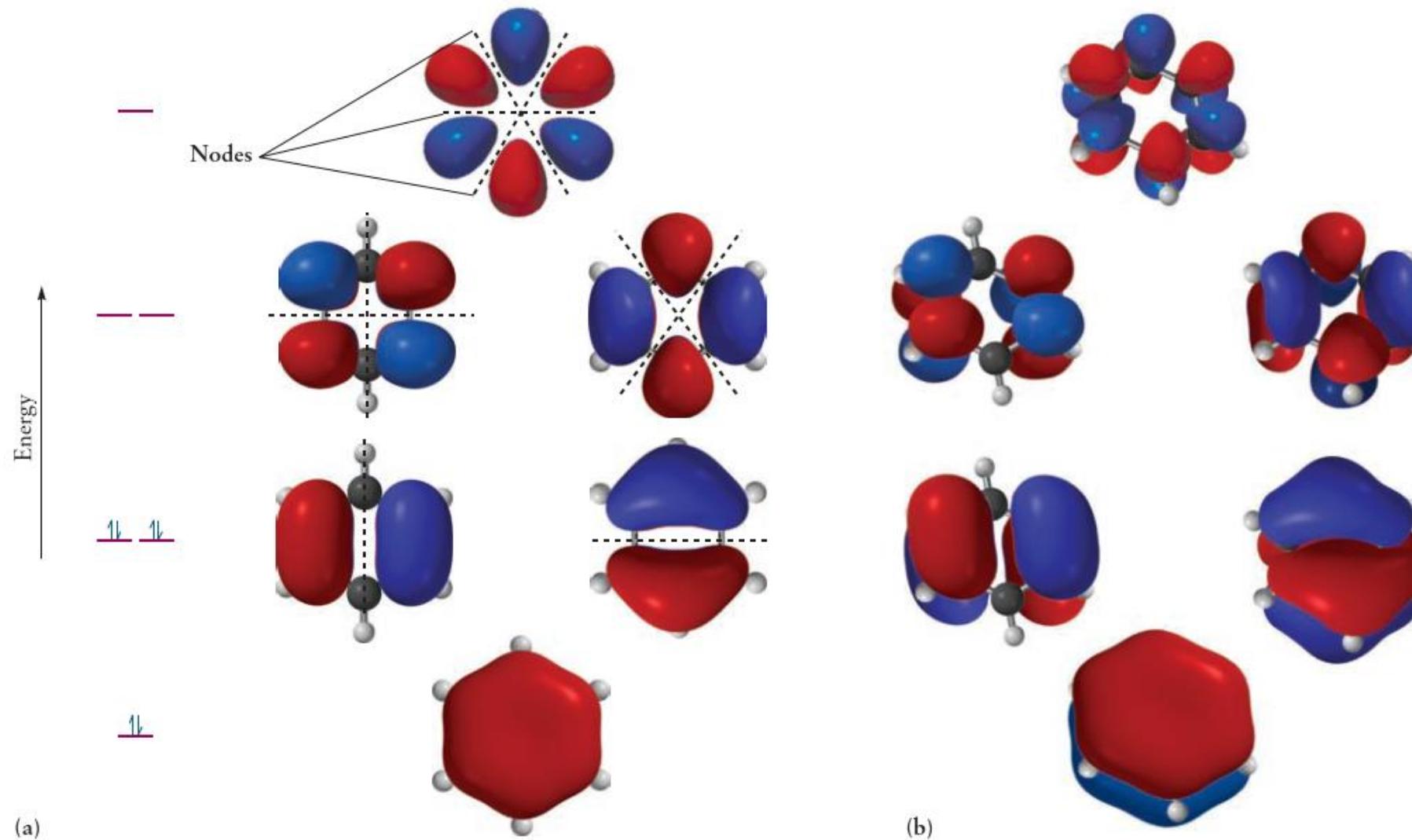


Figure 6.54 The six π molecular orbitals for benzene. In the view from the top in (a) you can more easily see the nodal planes indicated in dashed lines. In the view from the side in (b), you can see how each molecular orbital results from a linear combination of six $2p_z$ atomic orbitals oriented perpendicular to the plane of the molecule. Only the three lowest energy orbitals are occupied in molecules of benzene in the ground state.

- Finally, we show the de-localized p orbitals of benzene in Figure 6.54. You can easily tell from the perspective view in Figure 6.54(b) what particular linear combination of the six 2p orbitals perpendicular to the plane of the molecule were used to make each delocalized π orbital.
- The six π MOs are characterized by their energies and by the number of nodal planes perpendicular to the molecular plane.
- The lowest energy MO has no such nodal planes, the next highest energy orbitals are a degenerate pair with one nodal plane, the next highest in energy are also degenerate with two nodal planes, and the highest energy orbital has three nodal planes.
- The C_6H_6 molecule has *30 valence electrons*, of which *24 occupy σ bonding orbitals* formed from a linear combination of two sp^2 hybrids (for each C–C bond) or a linear combination of an sp^2 hybrid with an H 1s AO (for each C–H bond).
- When the six remaining valence electrons are placed in the three lowest energy π orbitals, the resulting electron distribution is the same in all six carbon–carbon bonds.
- As a result, benzene has six carbon–carbon bonds of equal length whose properties are intermediate between those of single and double bonds.

Bonding in Coordination Compounds

- The theories of chemical bonding that we discussed earlier do not help much in explaining the characteristic colors and magnetic properties of complex ions.
- A satisfactory theory of bonding in coordination compounds must account for properties such as color and magnetism, as well as stereochemistry and bond strength.
- No single theory as yet does all this for us. Rather, several different approaches have been applied to transition metal complexes.
- A theory that provides an explanation of these properties is **crystal field theory (CFT)**.
- In 1929, J. Becquerel proposed that the central metal ion in a transition-metal complex was *subject to an electrostatic field originating from the surrounding ligands*.
- In transition metal ions, we need to focus on how the electrons in the **d orbitals** of a metal ion are affected when they are in a complex.
- In the same year, Hans Albrecht Bethe used symmetry and group theory to place Becquerel's idea on the firm theoretical foundation we now call CF theory.

- Just three years later, in 1932, John Hasbrouck Van Vleck (1899–1980) demonstrated the power of the new theory when he interpreted the paramagnetism of the first-row transition-metal complexes and the rare earths with good quantitative accuracy.
- Van Vleck and his co-workers made many other seminal contributions to the development of the theory and its applications over the following decade.
- A ***valence bond approach*** to the problem was introduced in the 1940s by Linus Pauling, but it *proved less successful* than the CF theory in the interpretation of electronic spectra.
- With the growth of the molecular orbital (MO) theory in the second half of the 20th century, the time appeared ripe to tackle the most obvious shortcoming of the CF theory.
- The *interaction between ligand and central metal ion is clearly more than a purely electrostatic one*; there is also a significant element of covalency which should be amenable to a MO treatment. The range of theories which grew from this seed carries the collective name of ***ligand field theory***.
- *Modifications of the simple crystal field theory that take into account such factors as the partial covalency of the metal–ligand bond are called ligand field theory*. This term is often used to signify both the purely electrostatic crystal field theory and its modifications.

Table 20.1 Electron Configurations and Other Properties of the First-Row Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configuration									
M	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$
M^{2+}	—	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9
Ionization energy (kJ/mol)									
First	631	658	650	652	717	759	760	736	745
Second	1235	1309	1413	1591	1509	1561	1645	1751	1958
Third	2389	2650	2828	2986	3250	2956	3231	3393	3578
Radius (pm)									
M	162	147	134	130	135	126	125	124	128
M^{2+}	—	90	88	85	80	77	75	69	72
M^{3+}	81	77	74	64	66	60	64	—	—
Standard reduction potential (V)*									
	-2.08	-1.63	-1.2	-0.74	-1.18	-0.44	-0.28	-0.25	0.34

*The half-reaction is $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ (except for Sc and Cr, where the ions are Sc^{3+} and Cr^{3+} , respectively).

Valence bond (VB) model

- Valence bond (VB) model is a localized bonding model for covalent bonds.
- Because the coordinate covalent bond is simply a sub-set of covalent bonding, it might be reasonable to begin a discussion of the bonding in coordination compounds by employing a VB approach.
- Because most coordination compounds have the octahedral geometry, we begin with the *σ-bonding formed using the six bond vectors depicted in Figure 16.2.*

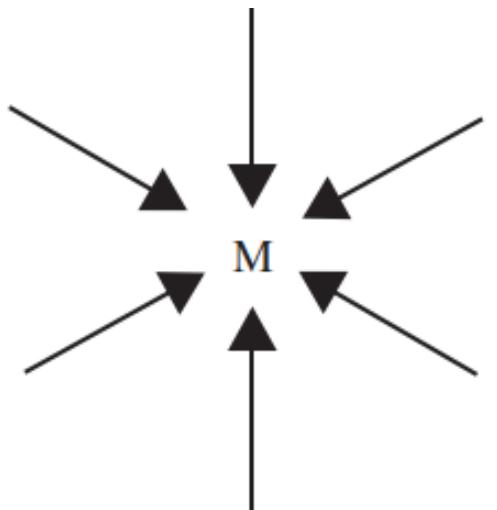
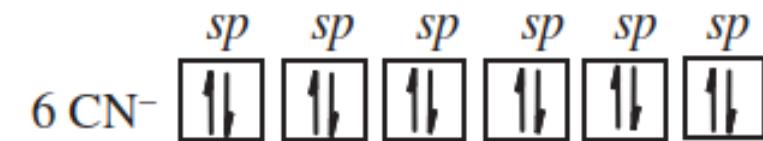
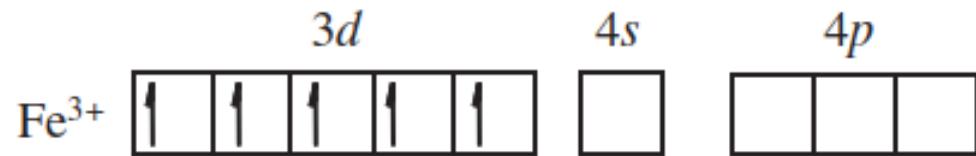


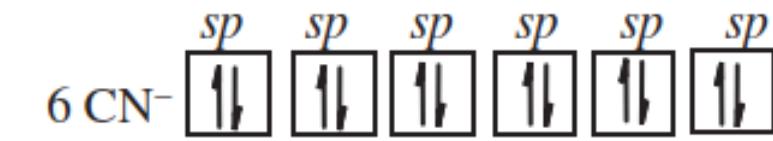
FIGURE 16.2 Bond vector basis set for the hybridization of a metal ion (M) in an octahedral coordination geometry.

- *The hybridization of an octahedral coordination compound is d^2sp^3 .* The results match our chemical intuition because the ligands in an octahedral coordination geometry lie along the x, y, and z coordinate axes.
- Thus, *the six σ -donating ligands will have maximum overlap with the three p-orbitals*, which also lie along the coordinate axes; the $d_{x^2-y^2}$ orbital, which has its lobes along the x and y axes; the d_{z^2} orbital, which has its larger lobe lying along the z axis and the donut region in the xy plane; and, of course, the spherically symmetric s-orbital.
- The VB development for $[\text{Fe}(\text{CN})_6]^{3-}$ is shown in Figure 16.3.
- Each of the empty d^2sp^3 hybrid orbitals on the Fe^{3+} ion can accept a pair of electrons from one of the sp hybrid orbitals on the CN^- ligands to form the six Fe–CN coordinate covalent bonds.

FIGURE 16.3

Valence bond treatment for the $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

Pairing
(costs some energy)



Hybridization
(no energy cost)

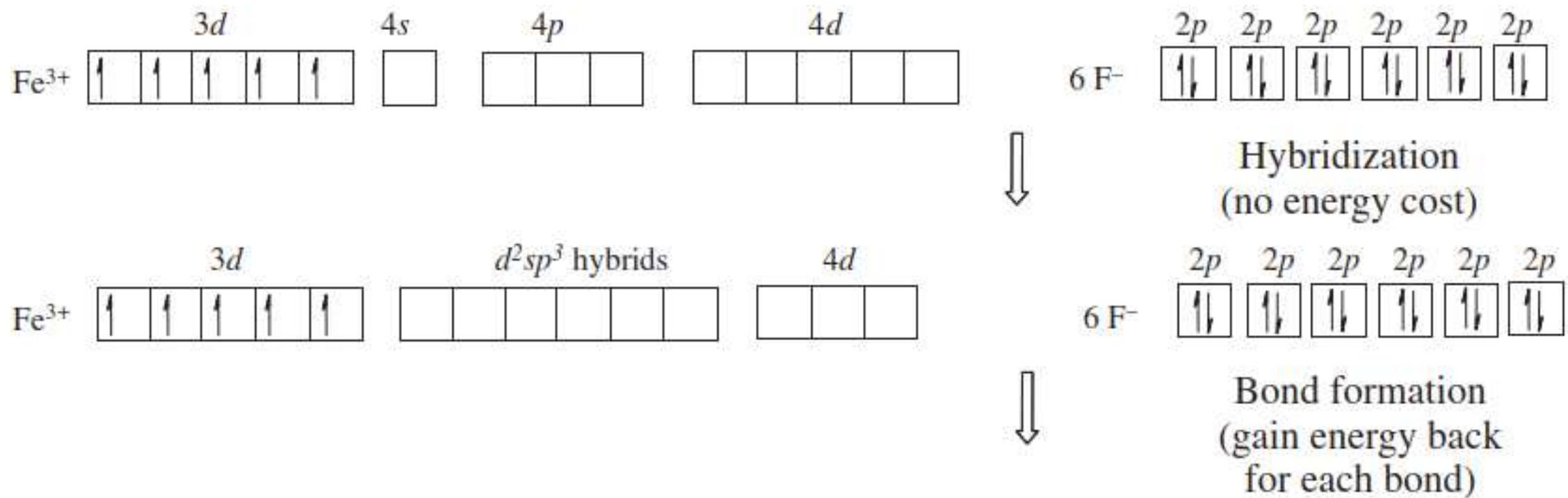


Bond formation
(gain energy back
for each bond)

➤ How many unpaired electrons are there in the complex ion?

- The calculated magnetic moment value 1.73 BM of the ferricyanide ion *is in reasonable agreement with the experimental value 2.20 BM.*
- ***One problem*** with the VB model is that *not every Fe³⁺ coordination compound has the same magnetic properties.*
- For example, *the experimental magnetic moment of [FeF₆]³⁻ (5.85BM) is more consistent with five unpaired electrons than it is with one electron.*
- The ***only way to rationalize*** the magnetic behavior of [FeF₆]³⁻ is to use the VB development shown in Figure 16.4, where the 3d electrons remain unpaired and *the much higher lying 4d orbitals are used in the construction of the six d²sp³ hybrids (sp³d²).*
- Clearly, this is ***not*** a very satisfying model.

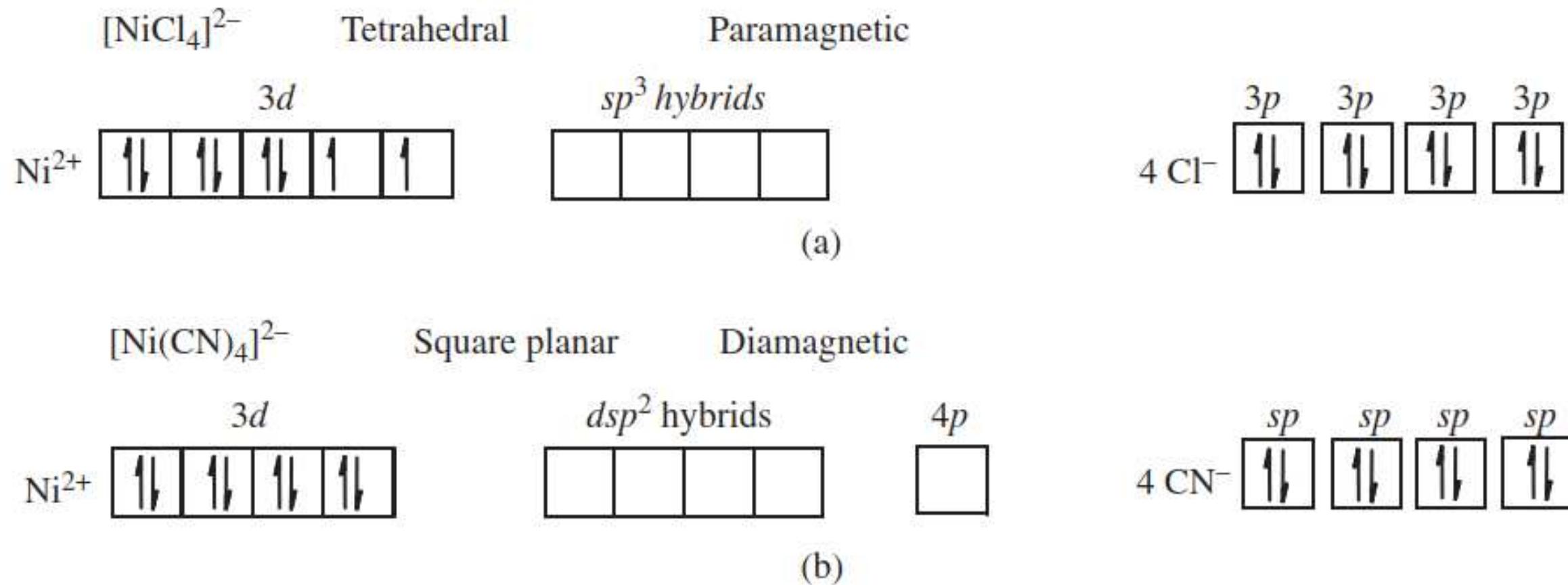
FIGURE 16.4 Valence bond treatment for the $[\text{FeF}_6]^{3-}$ ion.



➤ How many unpaired electrons are there in the complex ion?

- Another shortcoming of the VB model is its **inability to predict the geometry** of **four-coordinate** compounds.
- ✓ For example, the $[\text{NiCl}_4]^{2-}$ ion is **tetrahedral** and **paramagnetic**, while the isoelectronic $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ ions are **square planar** and **diamagnetic**.
- The VB treatment for the two different cases is shown in Figure 16.5.
- As we know, tetrahedral compounds are sp^3 hybridized, while square planar (D_{4h}) compounds are $d_{x^2-y^2}\text{sp}^2$ hybridized.
- Another obvious problem with the VB model is that *it fails to explain the diverse colors, electronic spectra, and photoelectron spectroscopy* of coordination compounds.
- Thus, the *VB theory is of little use in coordination chemistry*, and it is included here only for historical purposes.

FIGURE 16.5 Valence bond treatment for $[\text{NiCl}_4]^{2-}$ (a) and $[\text{Ni}(\text{CN})_4]^{2-}$ (b).



➤ How many unpaired electrons are there in the complex ions?

CRYSTAL FIELD THEORY

- The VB model of chemical bonding developed is incapable of explaining the magnetic properties of coordination compounds, the preference of some metals for square planar over tetrahedral coordination, and the rich electronic spectra of coordination compounds.
- As a result of its many shortcomings, an alternative model called *crystal field theory* (CFT) was proposed by the physicist Hans Bethe in 1929.
- Originally developed to explain the electronic transitions in colored minerals, CFT takes a completely electrostatic (ionic) approach.
- According to this model, the metal ion can be represented as a sphere of positive charge at the center of the coordination compound (or occupying one of the cationic sites in a crystalline lattice), while the ligands behave as negative point charges distributed around the metal ion with the appropriate coordination geometry.

- The ***crystal field theory focuses on the repulsions*** between ***ligand electrons*** and ***d electrons*** of the central ion.
- The interaction of a free metal ion in the gas phase with a sphere of negative charge causes the energy of the *d*-orbitals to increase as a result of the smaller value of *r*.
- All five of the *d* orbitals are **alike in energy** when in an **isolated atom or ion**, but they are **unlike in their spatial orientations**.
- ✓ One of them, is directed along the *z* axis, and another, has lobes along the *x* and *y* axes.
- ✓ The remaining three have lobes extending into regions between the perpendicular *x*, *y*, and *z* axes.

- According to the **crystal-field model**, the energies of the d-orbitals are a function of the ***relative positions of the ligands and the d-orbitals*** as shown in Figure 1.

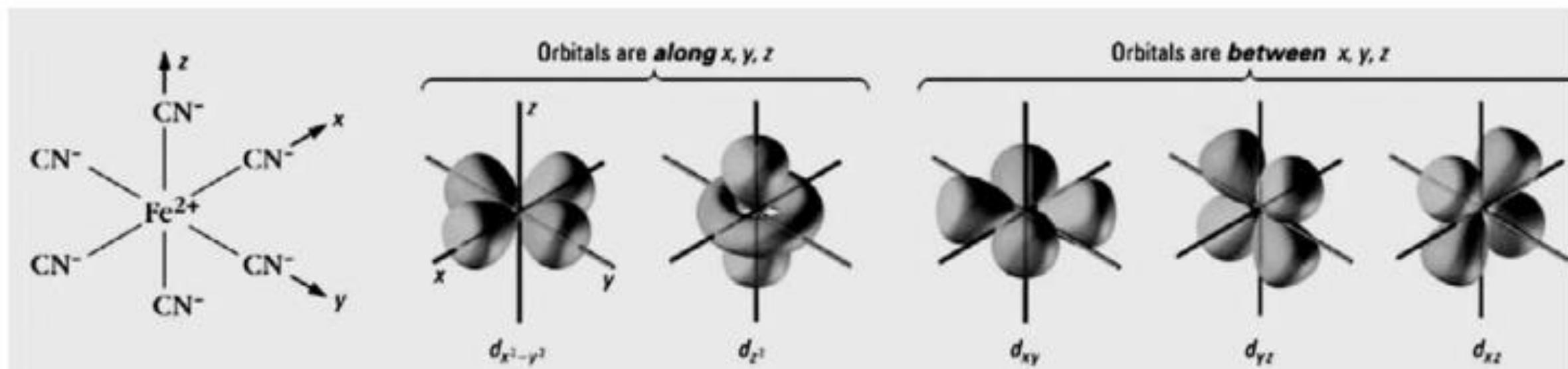


Fig. 1. The spatial arrangement of d-orbitals of an Fe^{2+} ion.

- In the presence of ligands, because repulsions exist between ligand electrons and d electrons, the ***d-orbital energy levels of the central metal ion are raised***.
- As we will soon see, however, they are not all raised to the same extent.

- Let us first consider the case for the *most common coordination geometry of octahedral*.
- The crystal field (CF) treatment of the problem is developed in Figure 16.6, which shows what happens to the energies of the degenerate set of *d*-orbitals when an imaginary sphere of negative charge is introduced to a positively charged transition metal cation in the gas phase.
- In the first step, the energies of all the *d*-orbitals are raised as the distance separating the charges (*r*) in the denominator of Coulomb's law decreases.
- In the next step, the sphere of negative charge is divided by six and placed into specific sites around the metal ion in the positions where the ligands lie. *For octahedral coordination, these negative point charges lie along the positive and negative directions of the three Cartesian axes.*
- ✓ *Since the value of r has not changed in this second step (it simply involved a redistribution of the negative charge), the overall energy of the d-orbitals remains unchanged by this second perturbation. However, the degeneracy of the orbitals is removed, as some of the orbitals lie closer to the negative point charges than others.*
- When the orbitals are filled with electrons, the repulsion between electrons in the *d*-orbitals and the negative point charges representing the ligands in the crystal will cause some of the orbitals to be raised in energy.

Six co-ordinate octahedral complexes

- The five d orbitals of transition metal cations are degenerate and have equal energy.

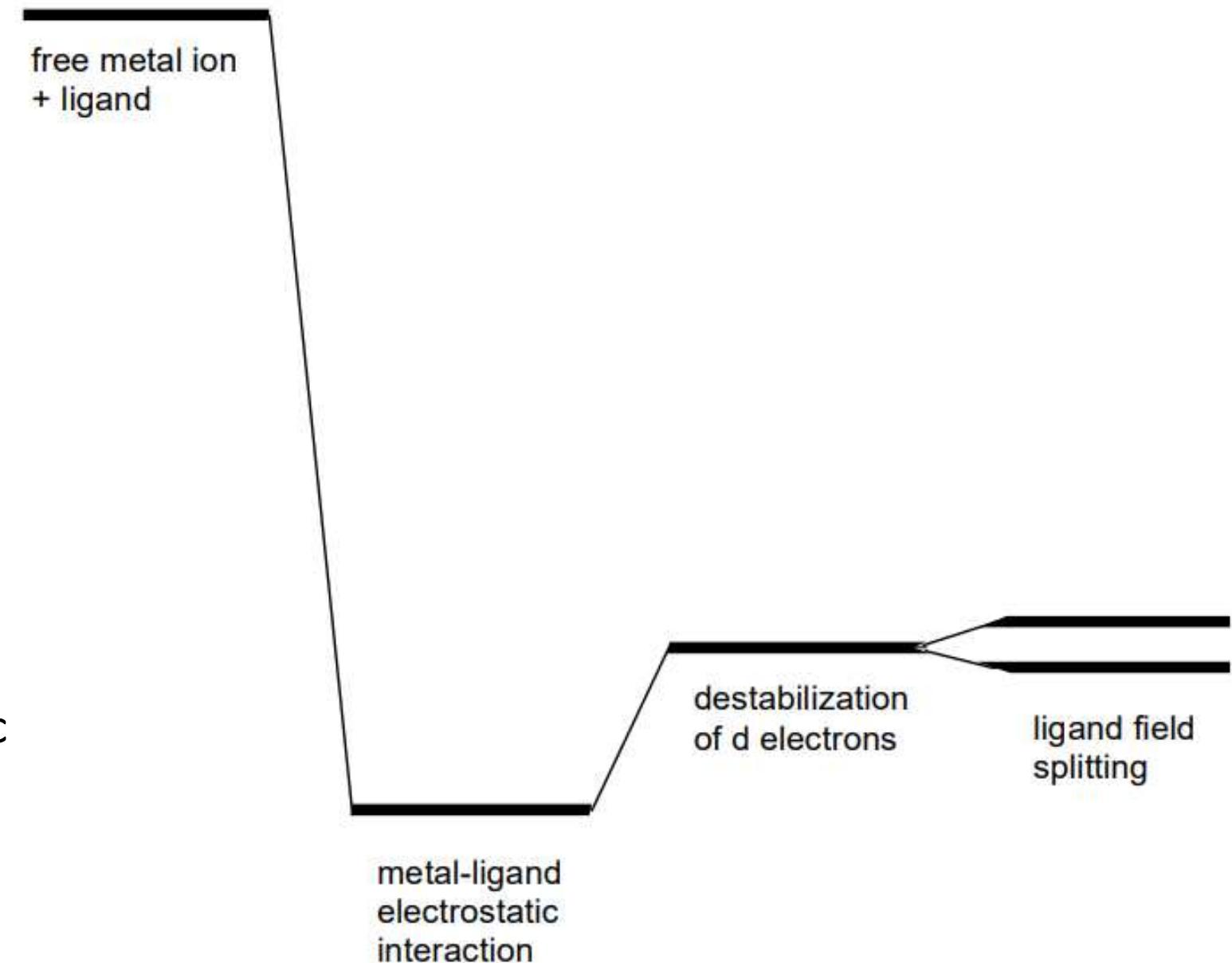


Figure 6.2.4: Change of electronic energy upon complex formation.

➤ According to the **crystal-field model**, the energies of the d-orbitals are a function of the ***relative positions of the ligands and the d-orbitals*** as shown in Figure 1.

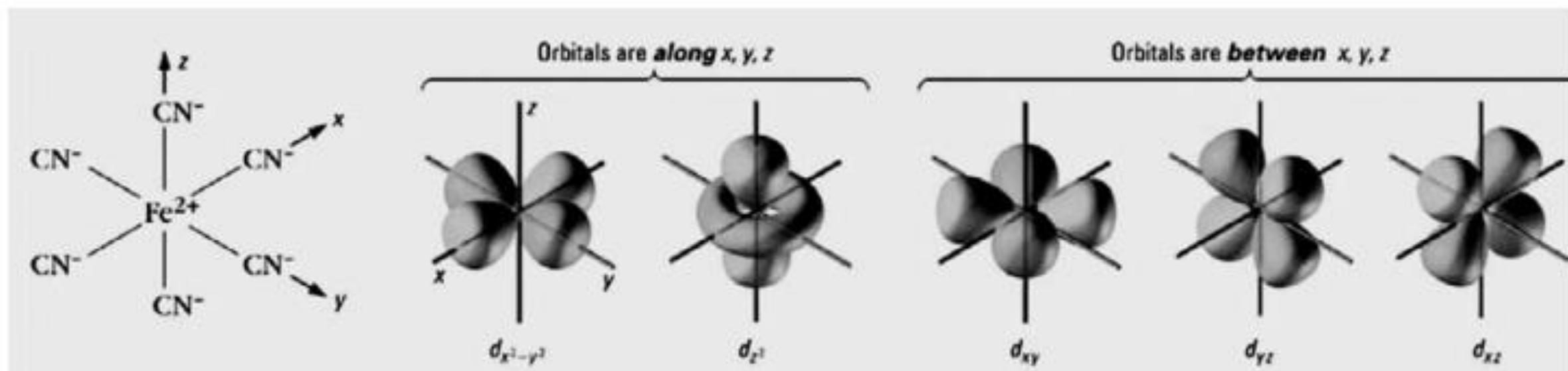


Fig. 1. The spatial arrangement of d-orbitals of an Fe^{2+} ion and the octahedral configuration of 6 CN^- ligands. The ligands are aligned along the x , y , and z axes and interact *most strongly* with electrons in the 2 orbitals that also are aligned along the axes and *not so strongly* with electrons in the 3 orbitals that are aligned between the axes.

- ❖ Which orbitals experience a direct head-on interaction with the ligands that also lie along the axes?
- ❖ Which orbitals do not experience a direct head-on interaction with the ligands?

☐ Splitting of d Orbitals in an Octahedral Field of Ligands

- The crystal field model explains that the ***properties of complexes result from the splitting of d-orbital energies***, which arises from electrostatic attractions between the metal cation and the negative charge of the ligands. This *negative charge is either partial, as in a polar covalent ligand like NH₃, or full, as in an anionic ligand like Cl⁻*.
- Picture six ligands approaching a metal ion along the mutually perpendicular x, y, and z axes, which form an octahedral arrangement (Figure 22.16A).
- Let's follow the orientation of ligand and orbital and how the approach affects orbital energies.

Figure 22.16 The five d orbitals in an octahedral field of ligands. Orange balls: Ligands.

A: Ligands approach along the x, y, and z axes.

B and C: The $d_{x^2-y^2}$ and d_{z^2} orbitals point directly at some of the ligands.

D to F: The d_{xy} , d_{xz} , and d_{yz} orbitals point between the ligands.

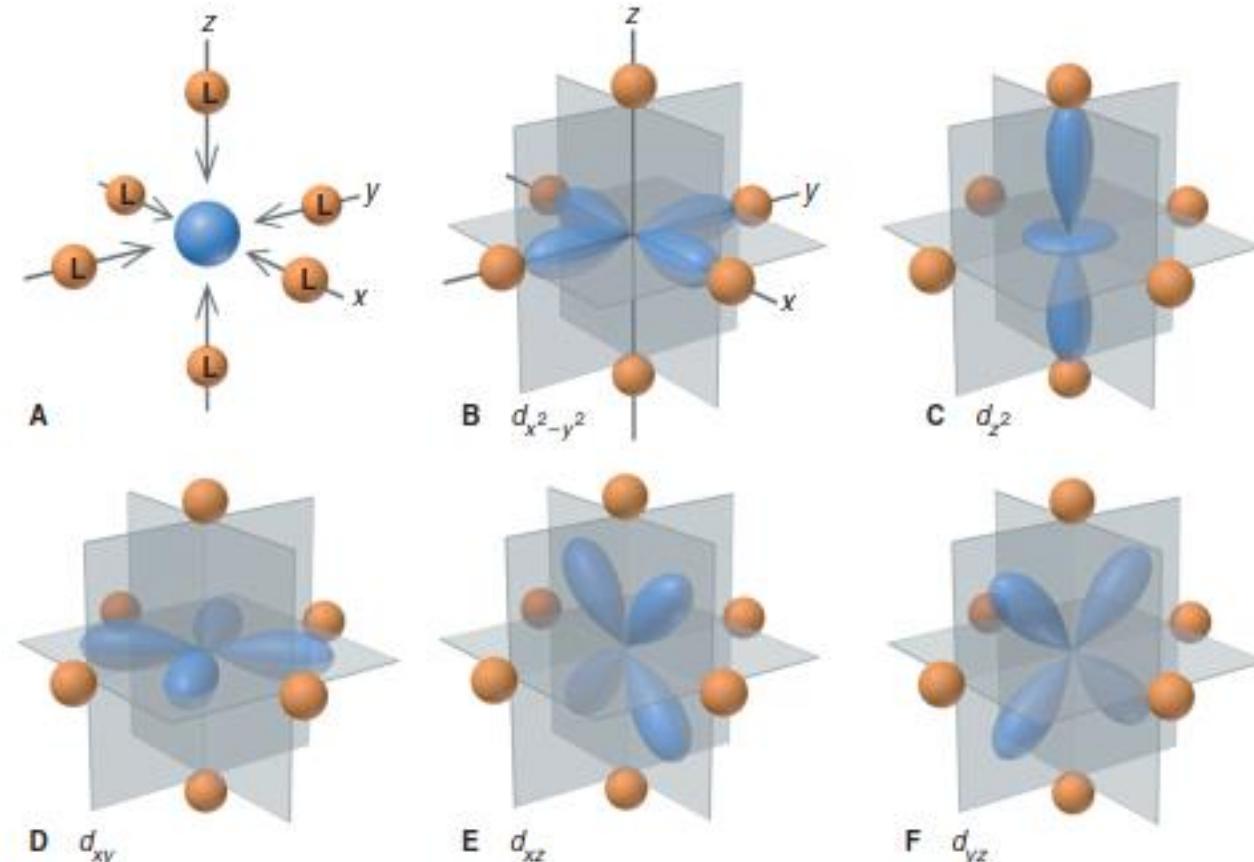


Figure 22.22.

The five d orbitals. The d_{z^2} orbital has a dumbbell shape with a collar; the other orbitals have cloverleaf shapes. In an isolated atom, these orbitals have the same energy. However, in an octahedral complex, the orbitals split into two sets, with the d_{z^2} and $d_{x^2-y^2}$ orbitals having higher energy than the other three. Note that the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals point toward the ligands (represented here by negative charges), whereas the lobes of the other orbitals point between ligands. The repulsion is greater in the case of the d_{z^2} and $d_{x^2-y^2}$ orbitals.

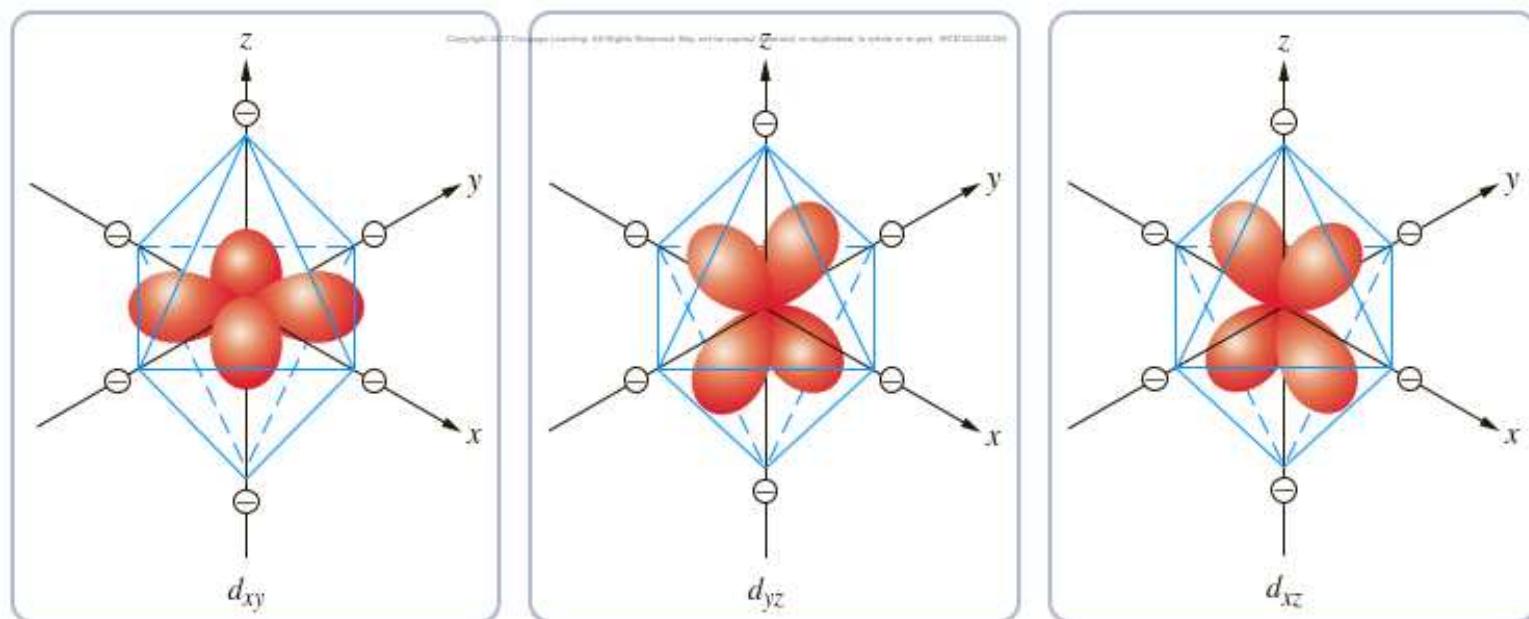
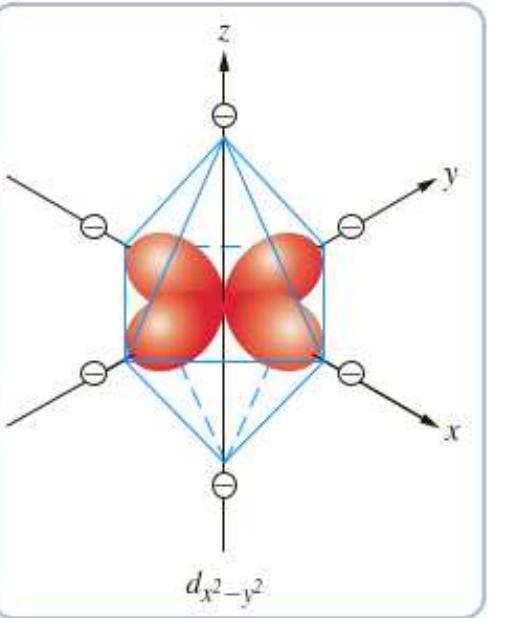
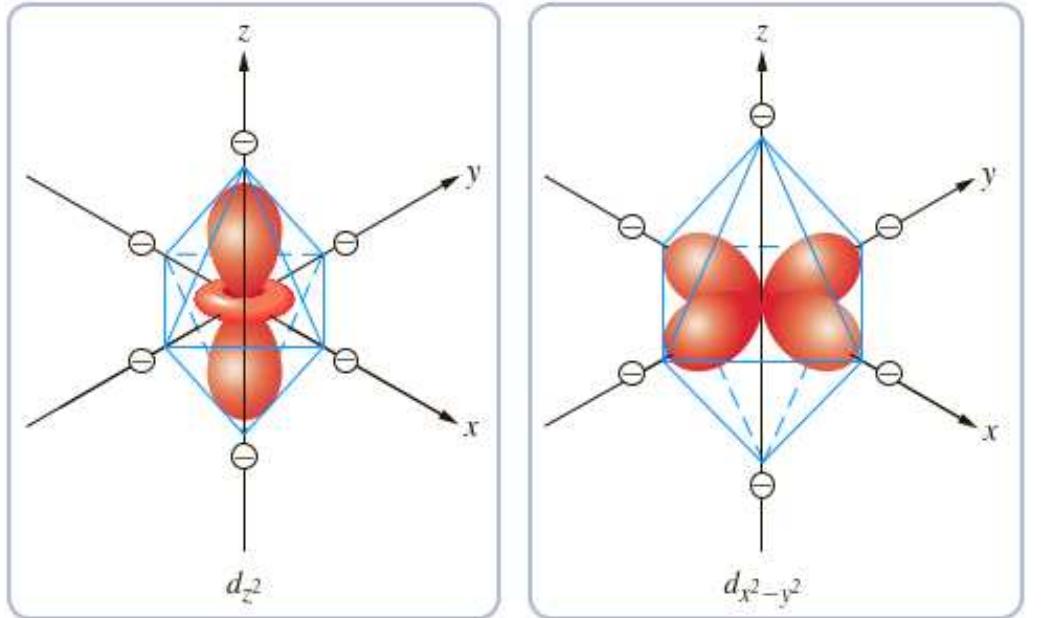
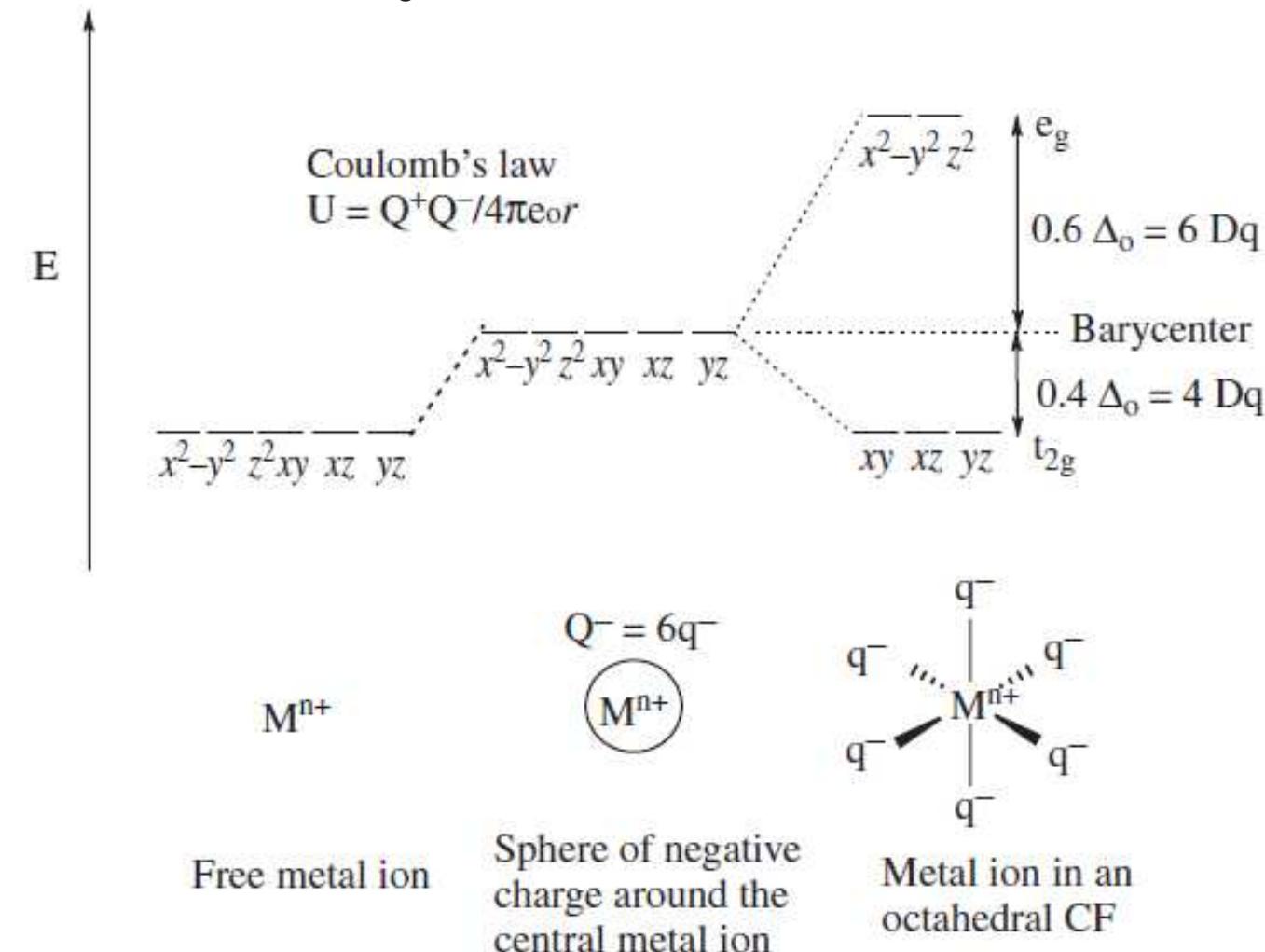


FIGURE 16.6 The interaction of a free metal ion in the gas phase with a sphere of negative charge causes the energy of the d-orbitals to increase as a result of the smaller value of r .

Redistribution of the negative charge in an octahedral CF causes some of the orbitals to be raised with respect to the barycenter, while others are stabilized.

- The splitting between the two energy levels is defined as Δ_o or 10 Dq.
- According to group theory, the d_{xy} , d_{xz} , and d_{yz} orbitals are triply degenerate in an octahedral CF and have their lobes pointed between the coordinate axes and away from the negative point charges. Thus, the d-orbitals will split into two different sets in an octahedral CF.
- Group theory tells us that the higher lying, doubly degenerate set of orbitals has e_g symmetry, while the lower lying, triply degenerate set is t_{2g} .



- Redistribution of the negative charge in an octahedral CF causes some of the orbitals to be raised with respect to the barycenter, while others are stabilized.
- The splitting between the two energy levels is defined as Δ_o or $10 Dq$.
- Because the $d_{x^2-y^2}$ and d_{z^2} orbitals have lobes that point directly at the negative point charges as shown in Figure 22.16, they will be raised in energy as a result of electron-electron repulsions.
- Because the total energy of the d -orbitals must remain unchanged by this second step, the energies of the remaining three d -orbitals must be lowered relative to the *barycenter*.

Splitting of d-orbital energies in an octahedral field of ligands

- In the isolated ion, the d orbitals have different orientations but equal energies. An energy diagram shows that the five d orbitals are most stable in the free ion and their average energy is raised in the ligand field.
- As ligands approach, their electron pairs repel electrons in the five d orbitals of the metal ion.
- But, in the negative field of ligands, the d electrons are **repelled unequally** because of their different orbital orientations and **the orbital energies split**, with two d orbitals higher in energy and three lower (Figure 22.17):
 - *The two higher energy orbitals are e_g orbitals, and they arise from the $d_{x^2 - y^2}$ and d_{z^2} (experience stronger repulsions).*
 - *The three lower energy orbitals are t_{2g} orbitals, and they arise from the d_{xy} , d_{xz} , and d_{yz} (experience less strong repulsions).*

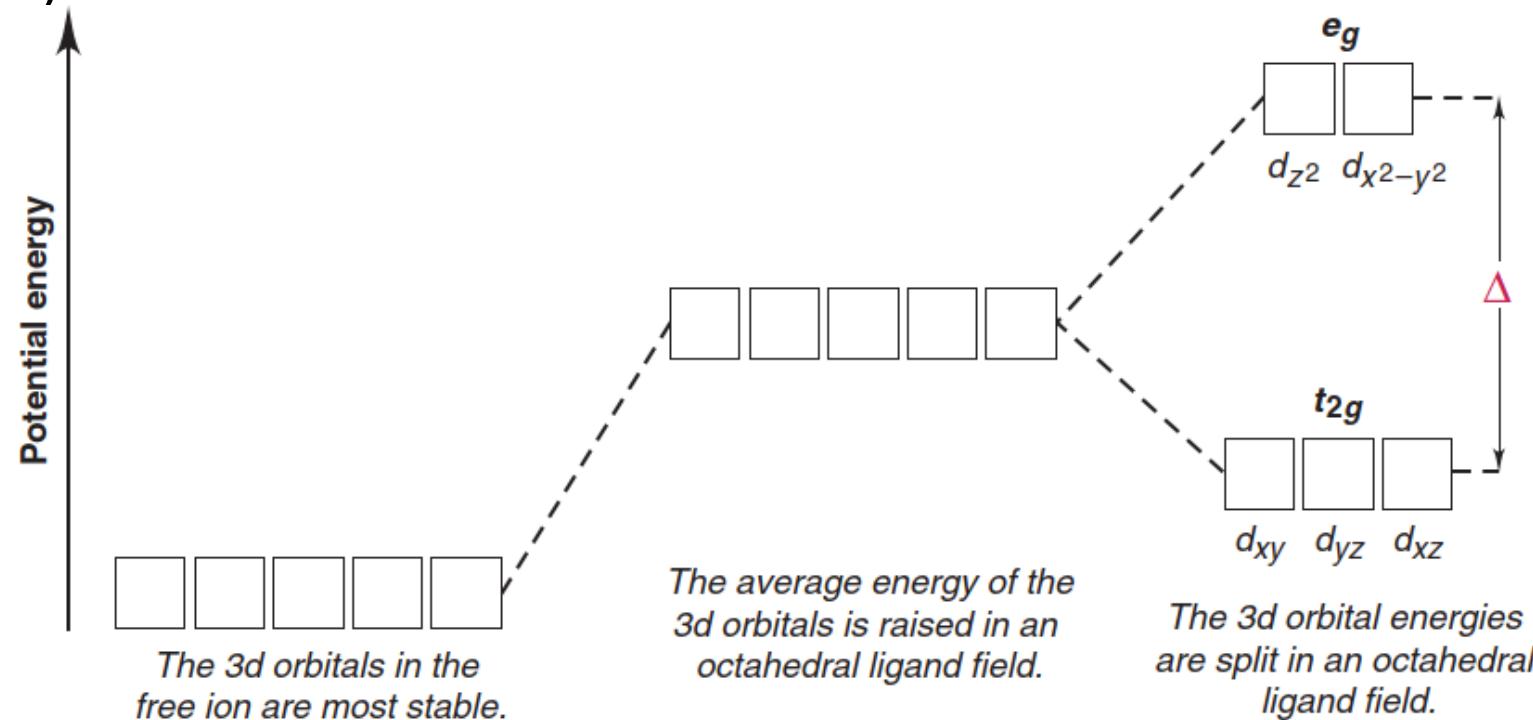


Figure 22.17 Splitting of d-orbital energies in an octahedral field of ligands.

Crystal field splitting energy (Δ)

- The splitting of orbital energies is called the *crystal field effect*, and the energy difference between e_g and t_{2g} orbitals is the **crystal field splitting energy (Δ)**.
- *Different ligands create crystal fields of different strength:*
 - **Strong-field ligands** lead to a *larger splitting energy* (larger Δ).
 - **Weak-field ligands** lead to a *smaller splitting energy* (smaller Δ).
- ✓ For instance, H_2O is a *weak-field ligand*, and CN^- is a *strong-field ligand* (Figure 22.18). Note the different orbital occupancies; we discuss the reason for these differences shortly.

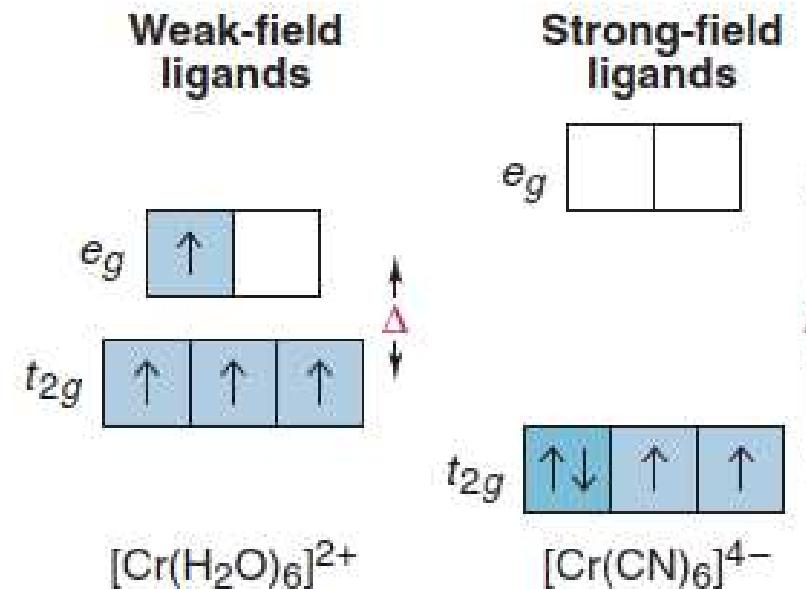


Figure 22.18 The effect of ligands and splitting energy orbital occupancy.

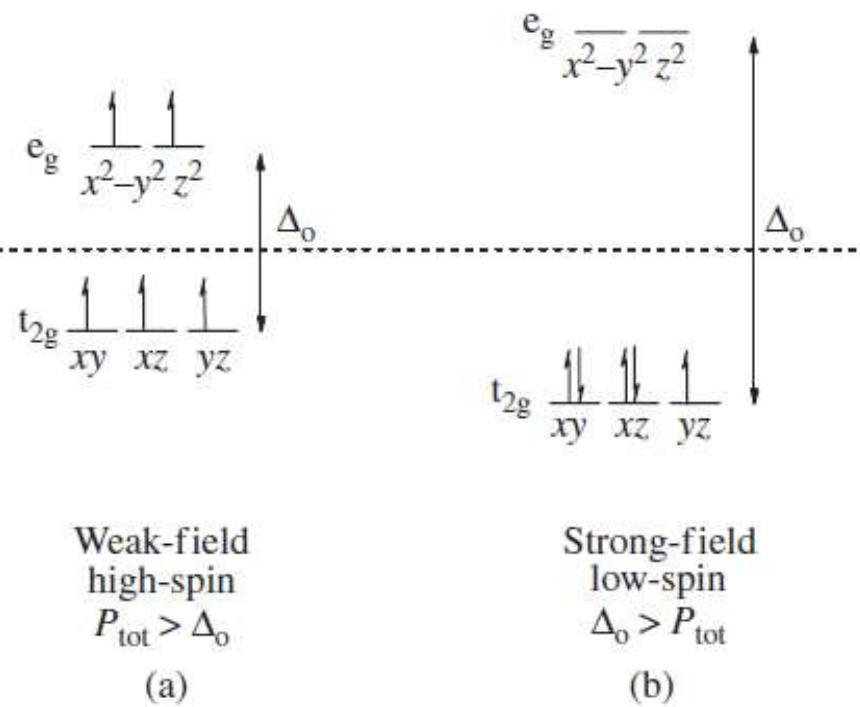
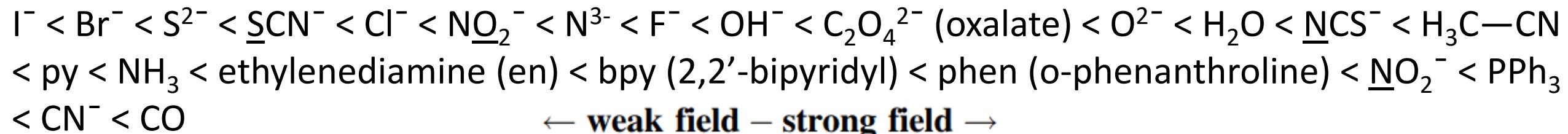


FIGURE 16.8

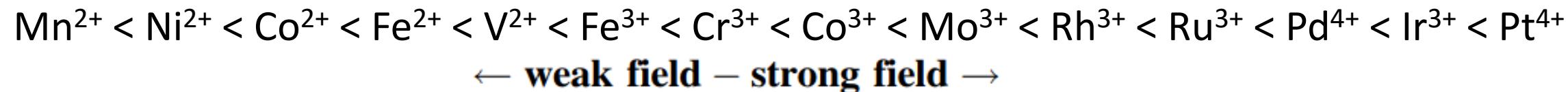
The relative energies of the five d -orbitals (a) in a weak CF and (b) in a strong CF. The dashed line represents the barycenter.

- As the valence d -electrons fill the empty orbitals in Figure according to the Aufbau principle, they will first populate the lower-lying t_{2g} set, going in with their spins paired according to Hund's rule.
- *Because the degenerate orbitals are indistinguishable, there is only one way to write the electron configurations for $d^1 - d^3$.*
- For the $d^4 - d^7$ electron configurations, however, there are two possible ways for the valence electrons in a metal to occupy the t_{2g} and e_g sets of orbitals.
- ✓ If the magnitude of $\Delta_o > P_{\text{tot}}$ (where P_{tot} is the total pairing energy), *then the electrons will pair up first in a strong-field, low-spin (LS) configuration*, as shown in Figure here (16.18 (a)).
- ✓ If $P_{\text{tot}} > \Delta_o$, on the other hand, it will be easier for the electrons to *fill the upper e_g level before they pair up*, leading to the *weak-field, high-spin (HS) configuration* shown in Figure 16.8(b).

□ Importantly, the **magnitude** of Δ , which can be *measured spectroscopically* (for d-d transitions), depends on **the identity and charge of the metal ion**, as well as **the type of ligand**. By characterizing a range of different ligands, a **spectrochemical series** can be established which lists the ligands in the order of increasing Δ :



➤ Given the same geometry of coordination and identical ligands, the crystal field splitting Δ for different *metals* increases in the following order (approximately):



The *value of Δ_0 increases with an increasing oxidation state of the central metal ion* (compare the two entries for Fe and Co) and *increases down a group* (compare, for instance, the locations of Co, Rh, and Ir). The *variation with oxidation state reflects the smaller size of more highly charged ions and the consequently shorter metal-ligand distances and stronger interaction energies*. The *increase down a group reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands*.

Low-Spin and High-Spin Complexes

- The *magnitude of the crystal field splitting Δ can affect the electronic configuration*, and thus *the magnetic properties of a complex*; in particular, if there are several electrons populating the d orbitals, such as for example in Fe^{3+} .
- As illustrated in Fig. 11.11, electrons are filled into the orbitals according to the principles we have established before. One electron is added to each of the degenerate orbitals until each orbital has one electron with the same spin. In an octahedral complex, this works straightforwardly up to the third electron.
- *The fourth electron could either be placed as a paired electron in the lower set of d orbitals (**low-spin complex**) or as an unpaired electron in the energetically higher set of d orbitals (**high-spin complex**).*

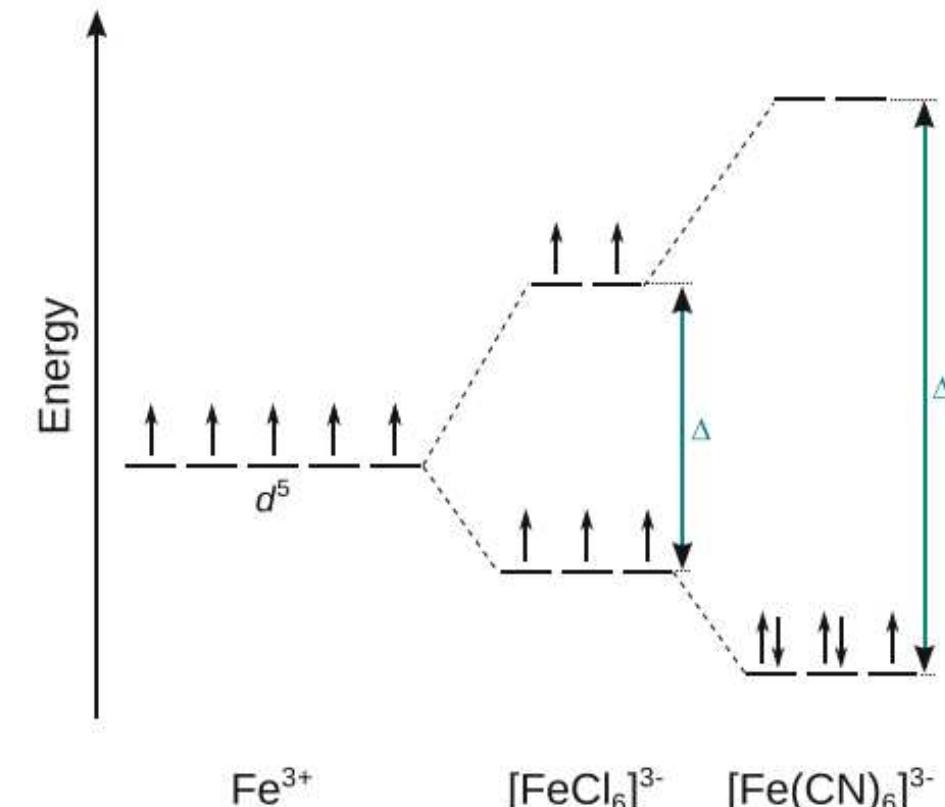


Fig. 11.11 Comparison of crystal field splitting for two Fe^{3+} complexes.

- Whether the **first or the second** scenario happens **depends on the magnitude of crystal field splitting Δ and the pairing energy.**
- Therefore, *high-spin complexes are typically found with metals/ligands at the weak-field end of the spectrochemical series* (such as e.g. $[\text{FeCl}_6]^{3-}$); vice versa, **low-spin complexes** are expected in complexes that comprise **metals and ligands at the high-field end** of the spectrochemical series (such as e.g. $[\text{Fe}(\text{CN})_6]^{3-}$).
- Since the formation of either a high-spin or a low-spin complex affects the pairing of electrons, the **crystal field splitting has repercussions in the magnetic properties** of a complex.
- Importantly, *with octahedral geometry, the options of forming either low-spin or high-spin complexes only exist for systems with 4–7 electrons in the d orbitals* (d^4 , d^5 , d^6 , d^7 complexes). For d^1 , d^2 d^3 and d^8 , d^9 , d^{10} complexes, there is only one possible electron configuration.

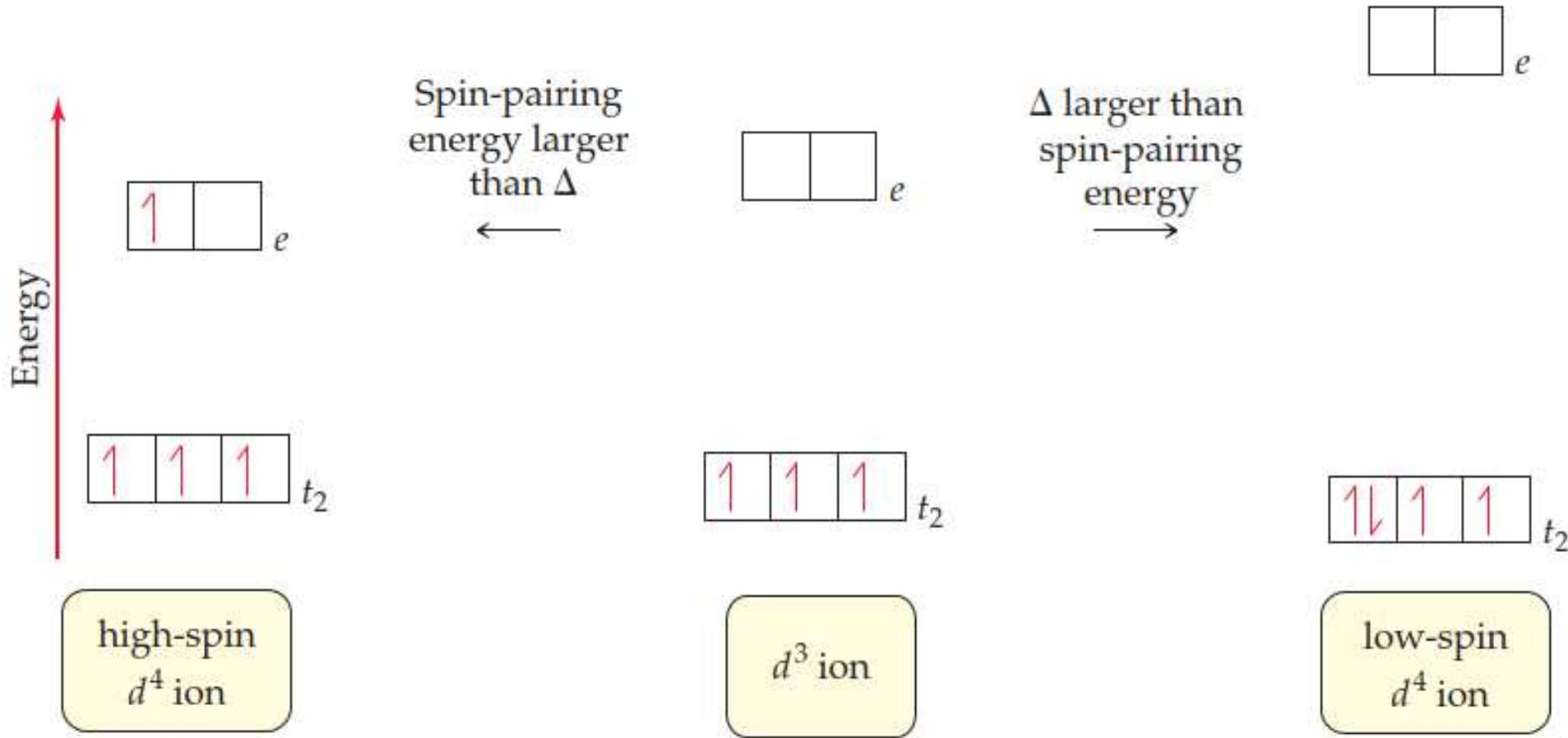


Figure 23.31 Two possibilities for adding a fourth electron to a d^3 octahedral complex. Whether the fourth electron goes into a t_2 orbital or into an e orbital depends on the relative energies of the crystal-field splitting energy and the spin-pairing energy.

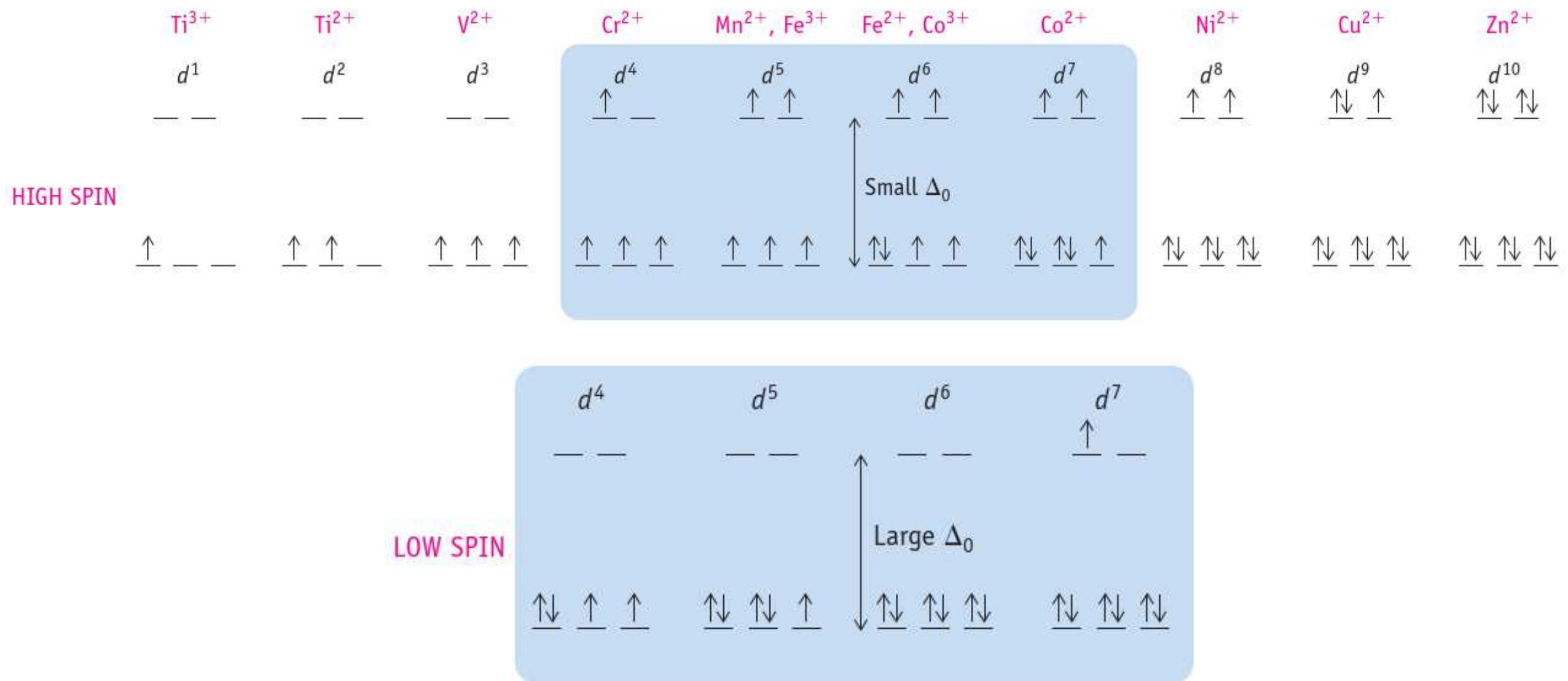


Figure 22.24 High- and low-spin octahedral complexes. d-Orbital occupancy for octahedral complexes of metal ions. Only the d^4 through d^7 cases have both high- and low-spin configurations.

Splitting of d-orbital energies in Tetrahedral complexes: Coordination number four

- Four-coordinate tetrahedral complexes are second only in abundance to octahedral complexes for the 3d metals.
- The same kind of arguments based on crystal-field theory can be applied to these species as we used for octahedral complexes.
- In the tetrahedral arrangement, no orbital points directly at a ligand in the tetrahedral case, but the d_{xy} type lies closer to the ligand than $d_{x^2-y^2}$ or d_{z^2} .
- Fig. 22.24 shows that the distances are as half the side of a cube compared with half the face diagonal.
- Consideration of the spatial arrangement of the orbitals shows that: the e orbitals point between the positions of the ligands and their partial negative charges, whereas the t_2 orbitals point more directly towards the ligands (Fig. 20.9).
- A tetrahedral crystal field splits d orbitals into two sets but with the *two e orbitals* (the $d_{x^2-y^2}$ and the d_{z^2}) *lower in energy* than the three t_2 orbitals (the d_{xy} , the d_{yz} , and the d_{zx}) (Fig. 20.8).
- Thus, *e orbitals lie below the t_2 orbitals.*

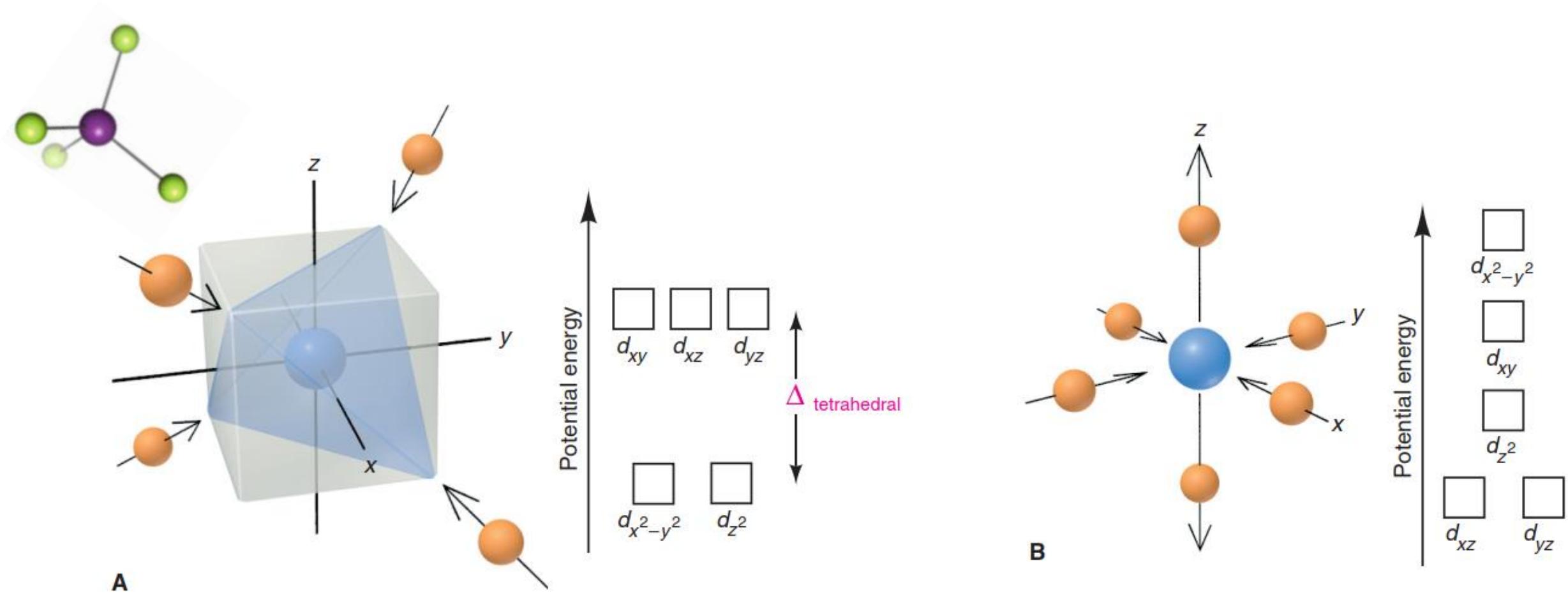


Figure 22.24 Splitting of d-orbital energies in 4 coordination complexes.

A: The pattern of splitting by a **tetrahedral field of ligands** is the opposite of the octahedral pattern.

B: Splitting by a **square planar field of ligands** decreases the energies of d_{xz} , d_{yz} , and especially d_{z^2} orbitals relative to the octahedral pattern.

□ Splitting of d-orbital energies in Tetrahedral complexes: Coordination number four

Key points: In a tetrahedral complex, the e orbitals lie below the t₂ orbitals; only the *high-spin* case need be considered.

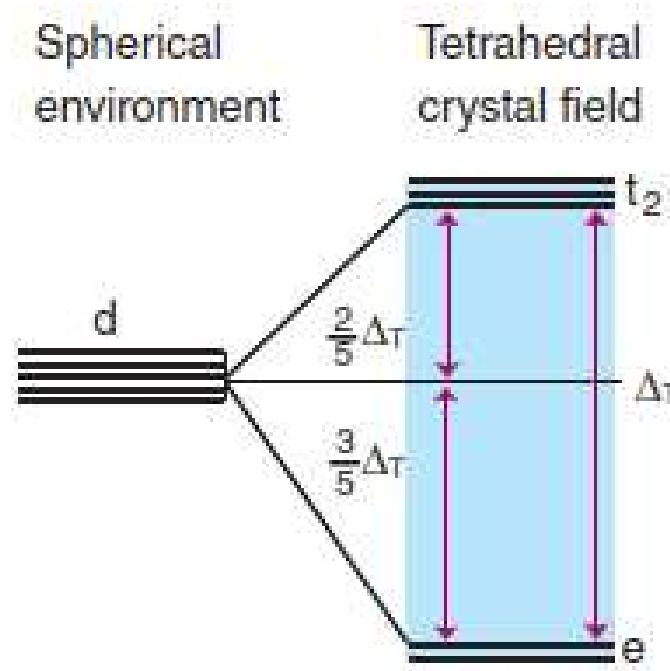


Figure 20.8 The orbital energy-level diagram used in the application of the building-up principle in a crystal-field analysis of a tetrahedral complex.

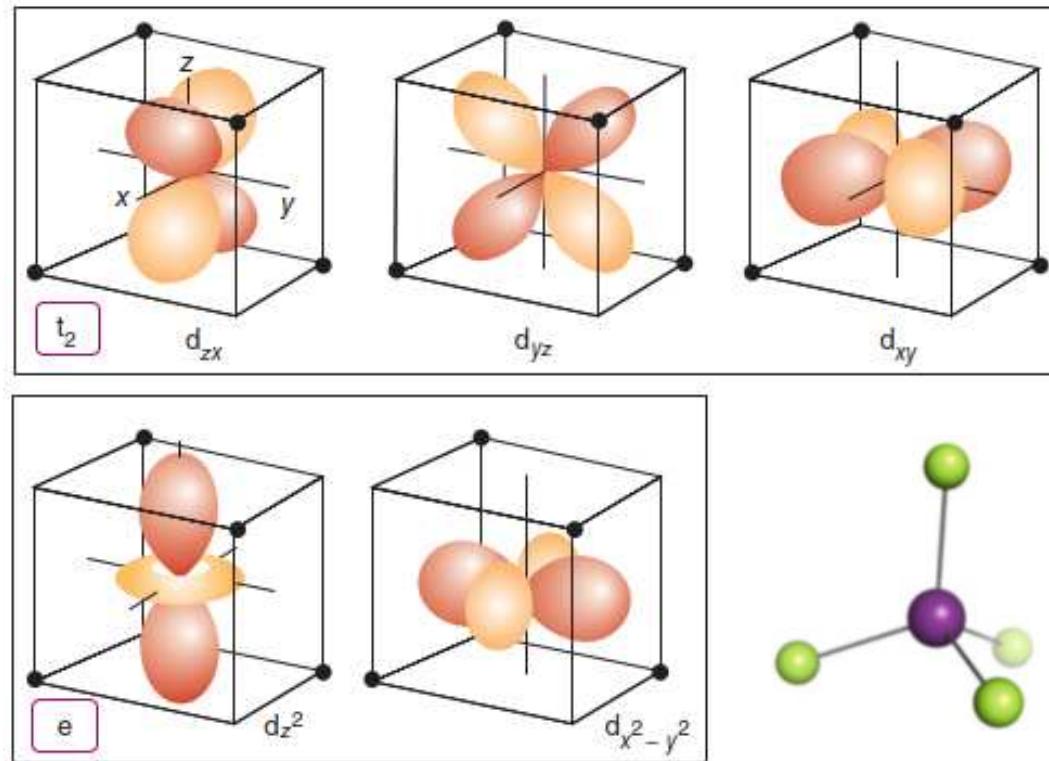


Figure 20.9. The effect of a tetrahedral crystal field on a set of d orbitals is to split them into two sets; the e pair (which point less directly at the ligands) lie lower in energy than the t₂ triplet.

- Because there is **no center of inversion** in a tetrahedral complex, the orbital designation does not include the parity label *g* or *u*.
- A second difference is that the ligand-field splitting parameter in a tetrahedral complex, Δ_T , is less than Δ_O , as should be expected for complexes with **fewer ligands, none of which is oriented directly at the d orbitals** (in fact, $\Delta_T \approx \frac{4}{9} \Delta_O$).
- The lack of direct interaction between orbitals and ligands in the tetrahedral configuration reduces the magnitude of the crystal field splitting by a geometrical factor equal to $2/3$, and the fact that there are only four ligands instead of six ($4/6$) reduces the ligand field by another $2/3$. The total splitting in the tetrahedral case is thus approximately $2/3 \times 2/3 = 4/9$ of the octahedral splitting.
- The pairing energy is invariably more unfavorable than Δ_T , and normally only high-spin tetrahedral complexes are encountered.
- In theory, alternative electron configurations are possible for the cases d^3 , d^4 , d^5 and d^6 in the tetrahedral field but the gain in CFSE (crystal field stabilization energy) is reduced by the smaller size of the splitting, and the loss of exchange energy is never counterbalanced. Thus, all tetrahedral complexes are **high spin**.

□ Calculation of Crystal (Ligand)-field stabilization energies (CFSE or LFSE)

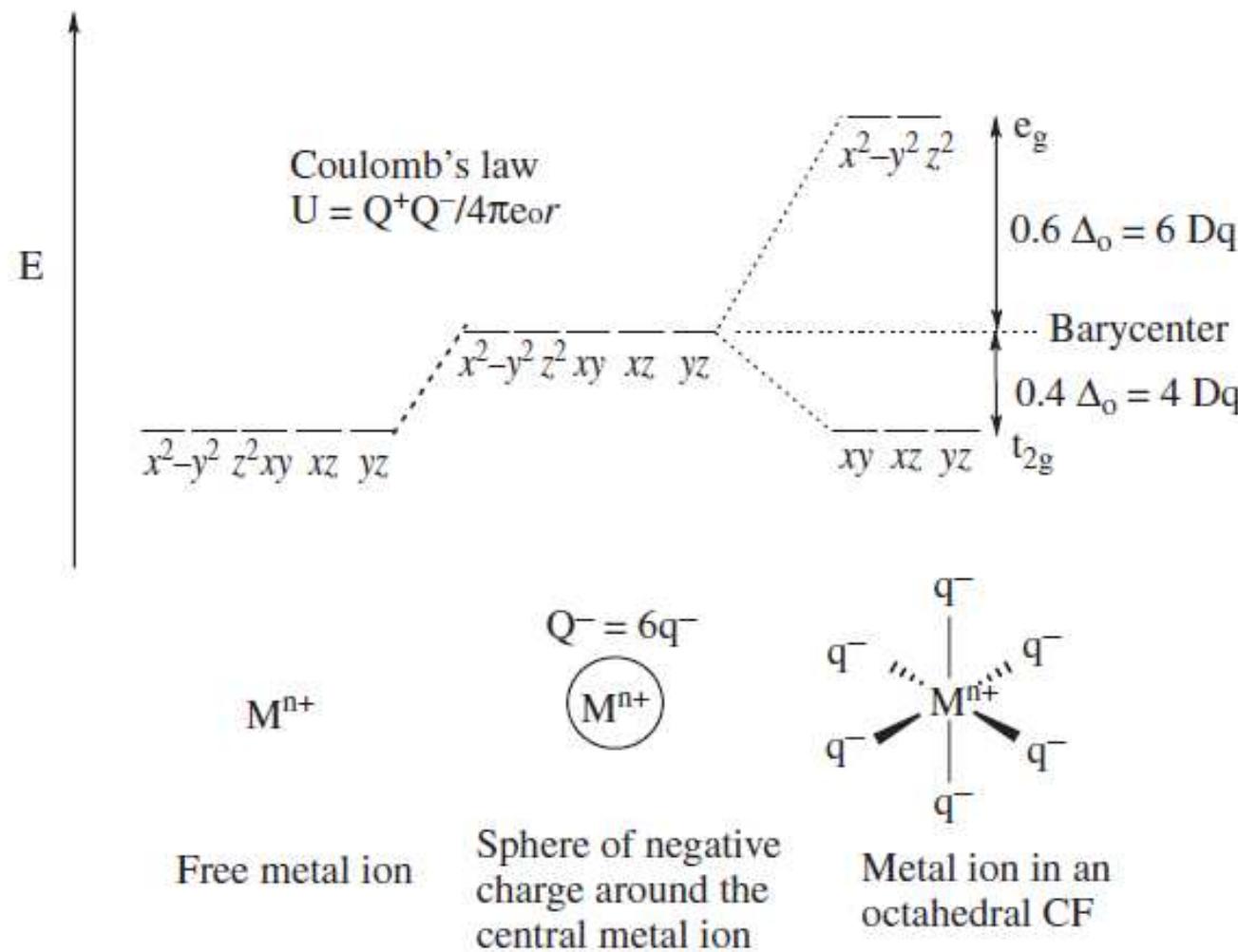


FIGURE 16.6

The interaction of a free metal ion in the gas phase with a sphere of negative charge causes the energy of the d -orbitals to increase as a result of the smaller value of r . Redistribution of the negative charge in an octahedral CF causes some of the orbitals to be raised with respect to the barycenter, while others are stabilized. The splitting between the two energy levels is defined as Δ_o or $10 Dq$.

□ Calculation of Crystal (Ligand)-field stabilization energies (CFSE or LFSE)

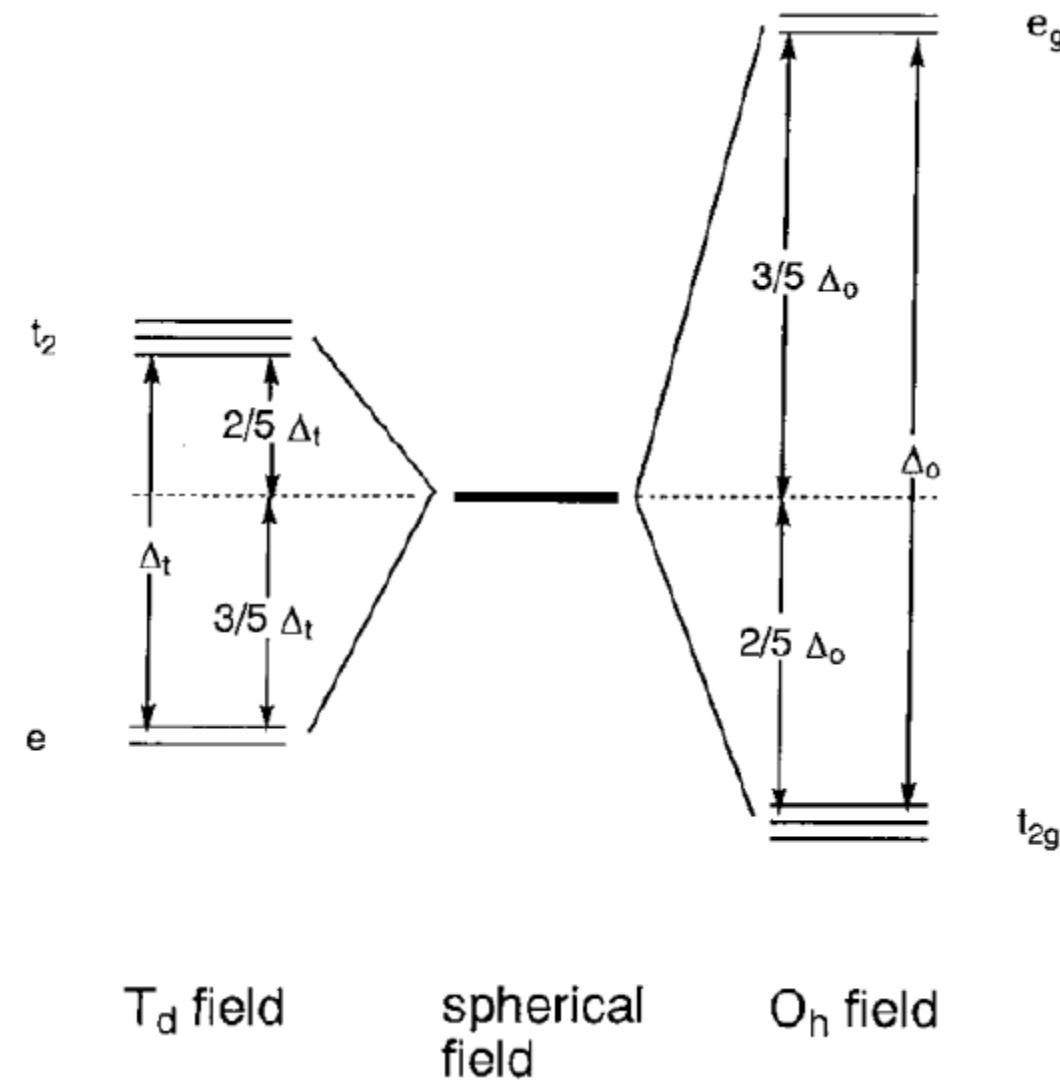


Figure 6.2.6: Ligand field splitting in tetrahedral and octahedral complexes.

- If the energy difference between the t_{2g} and e_g levels is defined as Δ_o or 10 Dq, then the e_g set will be raised by $0.6\Delta_o$ (6 Dq) and the t_{2g} set will be lowered by $0.4\Delta_o$ (4 Dq) relative to the barycenter.
- Thus, six of the electrons in the d^{10} electron configuration would be stabilized by 4Dq each (for a total stabilization of 24Dq) and the other four electrons would be destabilized by 6Dq each (for a total destabilization of 24 Dq). Overall, the energy of the 10 electrons occupying the d -orbitals in an octahedral CF would be identical to that of the barycenter.
- It is this splitting of the d -orbitals by the CF that causes the coordination compounds to be colored. If the light of the appropriate wavelength is shone on the molecule, an electron from the lower lying t_{2g} set can be photochemically excited to an empty orbital in the e_g set, causing an electronic absorption in the visible region.

- Transition metal ions have 0 to 10 d electrons and when the split d orbitals are filled from a lower energy level, the electron configuration $t_{2g}^x e_g^y$ corresponding to each ion is obtained.
- With the zero energy level chosen as the average energy level, the energy of the electron configuration relative to zero energy becomes
 - $LFSE = (-0.4x + 0.6y)\Delta_0$
- This value is called the **ligand field stabilization energy (LFSE)** or **crystal field stabilization energy (CFSE)**.
- The electron configuration with a smaller value (taking the minus sign into consideration) is more stable.
- LFSE is an important parameter to explain some properties of d-block transition metal complexes.

- A condition other than the orbital energy level is required to explain the filling of electrons being populated into the split t_{2g} and e_g orbitals.
- Two electrons can occupy an orbital with anti-parallel spins but a strong electrostatic repulsion occurs between two electrons in the same orbital. This repulsive interaction is called **pairing energy, P**.
- When the number of d electrons is less than three, the pairing energy is minimized by loading the electrons in the t_{2g} orbital with parallel spins. Namely, the electron configurations arising are t_{2g}^1 , t_{2g}^2 , or t_{2g}^3 .
- Two possibilities arise when the fourth electron occupies either of the t_{2g} or e_g orbitals. The lower energy orbital t_{2g} is favorable but occupation of the same orbital gives rise to **pairing energy, P**. The total energy becomes
 - $-0.4\Delta_o \times 4 + P = -1.6\Delta_o + P$
 - If the fourth electron occupies the energetically unfavorable e_g orbital, the total energy becomes
 - $-0.4\Delta_o \times 3 + 0.6\Delta_o = -0.6\Delta_o$

- The choice of the electron configuration depends on which of the above values is larger. Therefore, if $\Delta_o > P$, t_{2g}^4 is favored and this is called the strong field case or the **low spin** electron configuration.
- If $\Delta_o < P$, $t_{2g}^3e_g^1$ is favored and this is called the weak field case or the **high spin** electron configuration.
- A similar choice is required for d^5 , d^6 , and d^7 octahedral complexes, and in the strong field case, t_{2g}^5 , t_{2g}^6 , or $t_{2g}^6e_g^1$ configurations are favored, whereas, in the weak field case, $t_{2g}^3e_g^2$, $t_{2g}^4e_g^2$, or $t_{2g}^5e_g^2$ configurations are favored.
- The ligand field splitting parameter Δ_o is decided by the nature of the ligands and metal, whereas *the pairing energy, P, is almost constant* and shows only a slight dependence on the identity of the metal.

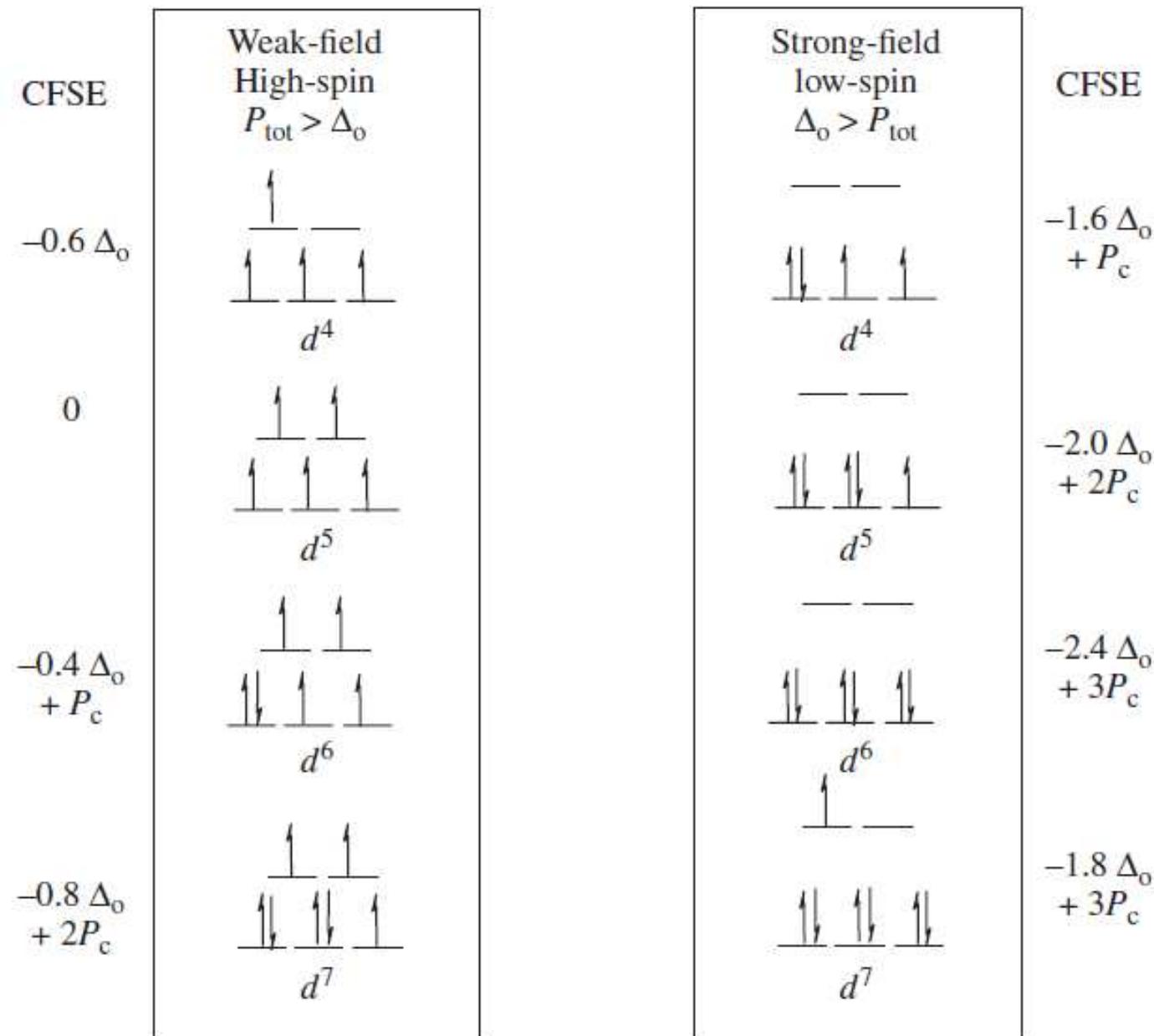
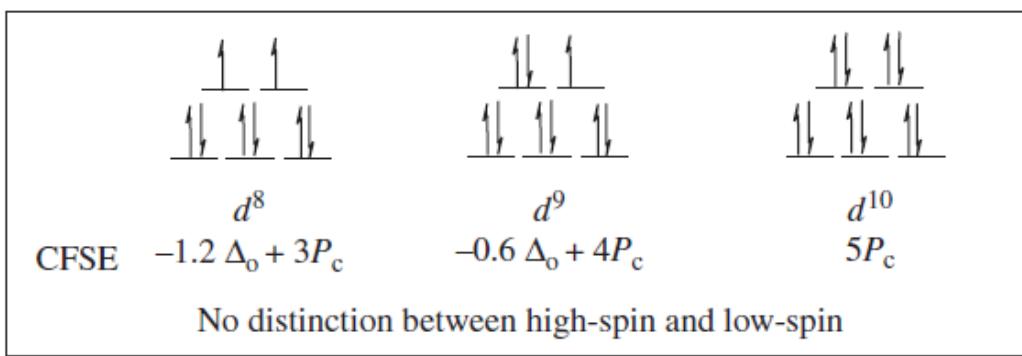
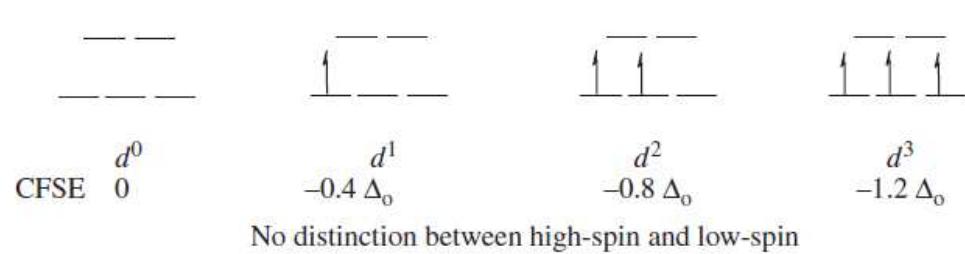


FIGURE 16.9
Crystal field splitting diagram for the different d^n configurations in an octahedral CF and their crystal field splitting energy. P_c = Coulomb pairing energies.

- Ligand-field stabilization energies can be calculated in the same way as for octahedral complexes. Since tetrahedral complexes are always high-spin, there is never any need to consider the *pairing energy* in the LFSE, and the only differences compared with octahedral complexes are the order of occupation (e before t_2) and the **contribution of each orbital to the total energy** ($- \frac{3}{5} \Delta_T$ for an electron in e orbital and $+ \frac{2}{5} \Delta_T$ for a t_2 orbital).
- The CFSE values for these high-spin configurations are given in Table 13.10.

Number of <i>d</i> electrons	Electronic configuration			CFSE	
	<i>e</i>	<i>t</i> ₂		(as ΔE_{tetr}) (assuming $\Delta E_{\text{tetr}} = 4/9 \Delta E_{\text{oct}}$)	(as ΔE_{oct})
1	↑			$-3/5$	-0.27
2	↑	↑		$-6/5$	-0.53
3	↑	↑	↑	$-6/5 + 2/5$	-0.36
4	↑	↑	↑	$-6/5 + 4/5$	-0.18
5	↑	↑	↑	$-6/5 + 6/5$	0.00
6	↑↓	↑	↑	$-9/5 + 6/5$	-0.27
7	↑↓	↑↓	↑	$-12/5 + 6/5$	-0.53
8	↑↓	↑↓	↑↓	$-12/5 + 8/5$	-0.36
9	↑↓	↑↓	↑↓	$-12/5 + 10/5$	-0.18
10	↑↓	↑↓	↑↓	$-12/5 + 12/5$	0.00

TABLE 13.10 CFSE values in a tetrahedral field

Table 20.4 lists the configurations of tetrahedral d^n complexes together with the calculated values of the LFSE, and Table 20.5 lists some experimental values of Δ_T for a number of complexes.

Table 20.4 Ligand-field stabilization energies for tetrahedral complexes*

d^n	Config.	N	LFSE/ Δ_T
d^0		0	0
d^1	e^1	1	-0.6
d^2	e^2	2	-1.2
d^3	$e^2t_2^1$	3	-0.8
d^4	$e^2t_2^2$	4	-0.4
d^5	$e^2t_2^3$	5	0
d^6	$e^3t_2^3$	4	-0.6
d^7	$e^4t_2^3$	3	-1.2
d^8	$e^4t_2^4$	2	-0.8
d^9	$e^4t_2^5$	1	-0.4
d^{10}	$e^4t_2^6$	0	0

* N is the number of unpaired electrons.

Table 20.5 Values of Δ_T for representative tetrahedral complexes

Complex	Δ_T/cm^{-1}
$[\text{VCl}_4]$	9010
$[\text{CoCl}_4]^{2-}$	3300
$[\text{CoBr}_4]^{2-}$	2900
$[\text{CoI}_4]^{2-}$	2700
$[\text{Co}(\text{NCS})_4]^{2-}$	4700

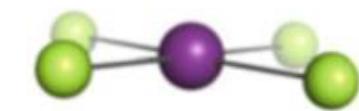
- It will be seen that *the CFSE in an octahedral configuration is always greater than that in the corresponding tetrahedral configuration*, **except in the cases of d^0 , d^5 and d^{10}** where both values are zero.
- The configurations with the next smallest CFSE loss in the tetrahedral field compared to the octahedral field are d^1 and d^6 if the octahedral state is high spin.
- *The adoption of 4-coordination rather than 6-coordination is expected, in general, to be accompanied by loss of energy of formation* as only four interactions occur instead of six.
- In addition, *there is commonly a loss of CFSE as well*.

Table 6.2.2. Ligand field stabilization energy (LFSE)

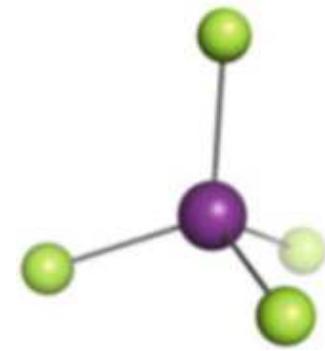
		Octahedral				Tetrahedral	
		<i>Strong field (LS)</i>		<i>Weak field (HS)</i>			
d^n	Example	n	Δ_o	n	Δ_o	n	Δ_t
d^1	Ti^{3+}	1	0.4	1	0.4	1	0.6
d^2	V^{3+}	2	0.8	2	0.8	2	1.2
d^3	Cr^{3+}, V^{2+}	3	1.2	3	1.2	3	0.8
d^4	Cr^{2+}, Mn^{3+}	2	1.6	4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0	5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4	4	0.4	4	0.6
d^7	Co^{2+}	1	1.8	3	0.8	3	1.2
d^8	Ni^{2+}	2	1.2	2	1.2	2	0.8
d^9	Cu^{2+}	1	0.6	1	0.6	1	0.4
d^{10}	Cu^{1+}	0	0	0	0	0	0

Tetrahedral and Square-planar configurations: 4-coordination complexes

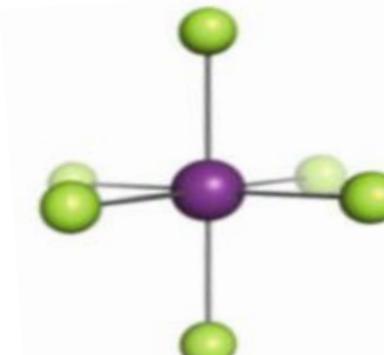
- Other than octahedral, two configurations that are common among the elements of the first transition series are the tetrahedral and square-planar configurations, both involving 4-coordination.
- The **square-planar configuration** may be considered as derived from the octahedral one by removing the ligands on the z-axis.
- An elongation of the M-L distances on the z-axis can lead to an **intermediate case** corresponds to elongation of the metal-ligand distances on the z-axis, to **unsymmetric substitution** on the z-axis in a complex such as MX_4Z_2 , (both of which are **tetragonal distortions**) or to the case of the 5-coordinated **square pyramidal configuration**.
- An elongation of the M-L distances on the z-axis leads to a decrease of the interaction between the ligand field and those metal orbitals with components in the z direction.



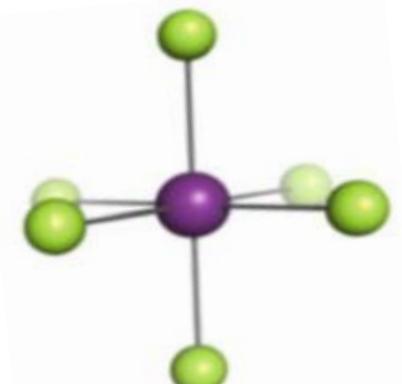
Square-planar



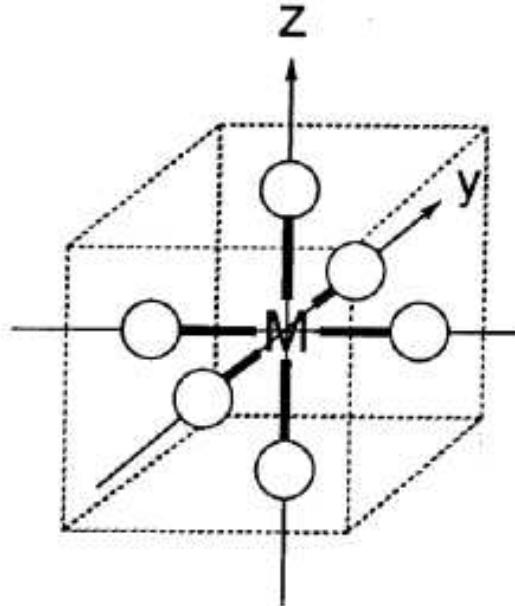
Tetrahedral



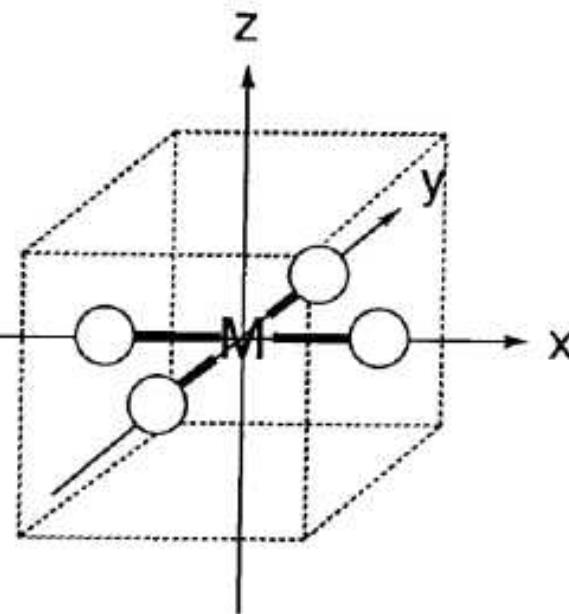
Octahedral



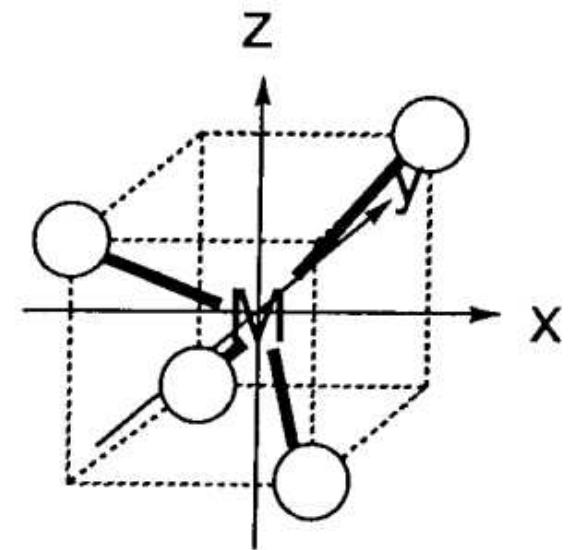
Z-axis elongated
Octahedral



octahedral coordination



square planar coordination



tetrahedral coordination

Figure 6.2.5: Ligand positions in the Cartesian coordinate with a metal ion at the origin.

- The energy levels therefore split as indicated in Fig. 13.8a with the d_{z^2} level and the d_{xz} and d_{yz} levels falling below the others.
- The $d_{x^2-y^2}$ and d_{xy} levels rise slightly as the metal-ligand distances in the xy plane shorten a little because of the decrease in repulsion from the z ligands.
- If the z ligands are removed completely to give the ***square-planar configuration***, the energy level diagram of Fig. 13.8b results. Here, the d_{z^2} and d_{xy} levels have crossed over. Notice that, as the configuration in the xy plane is similar to that in the octahedron, the energy separation between $d_{x^2-y^2}$ and d_{xy} remains practically the same as the octahedral ΔE .

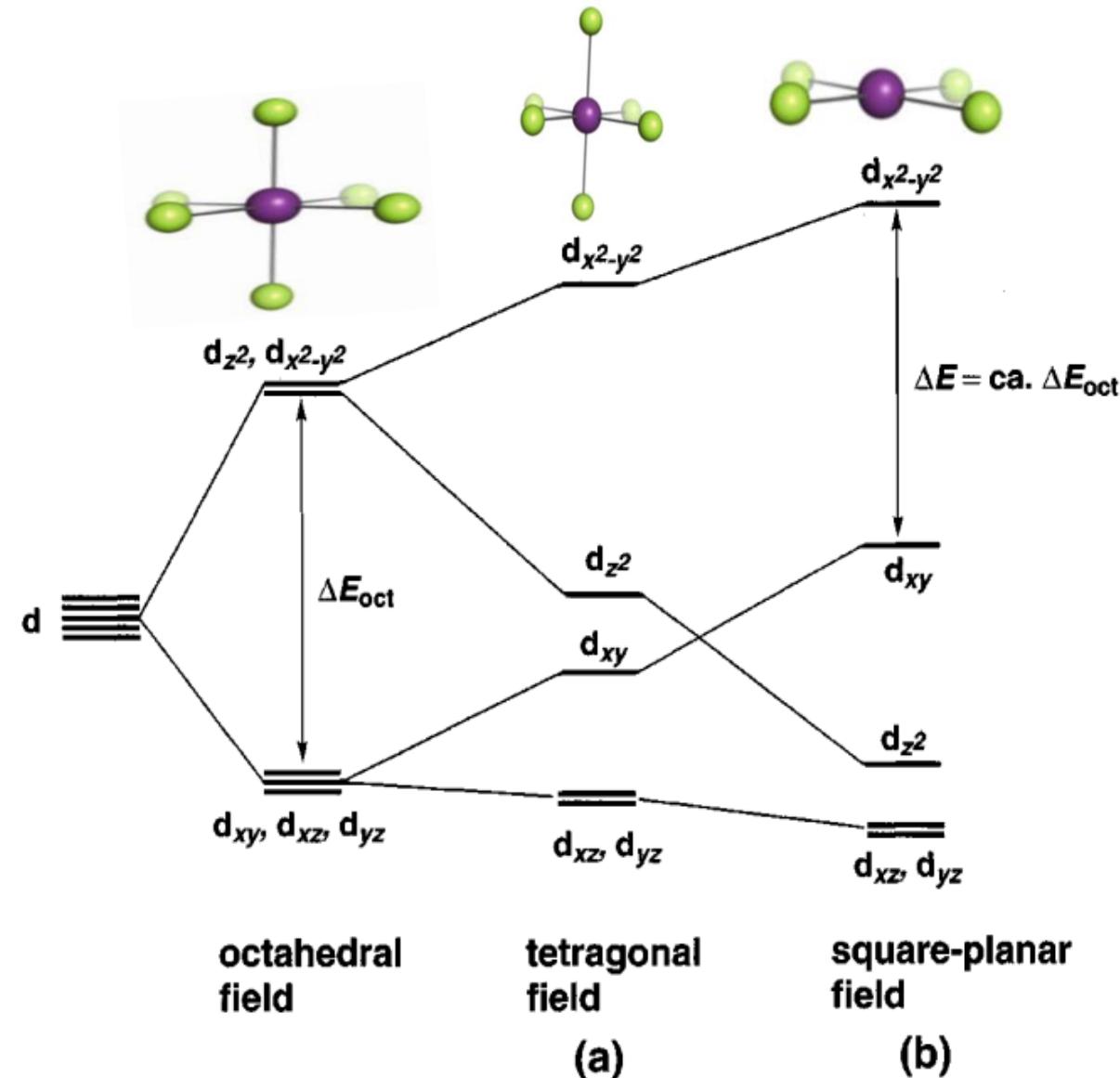
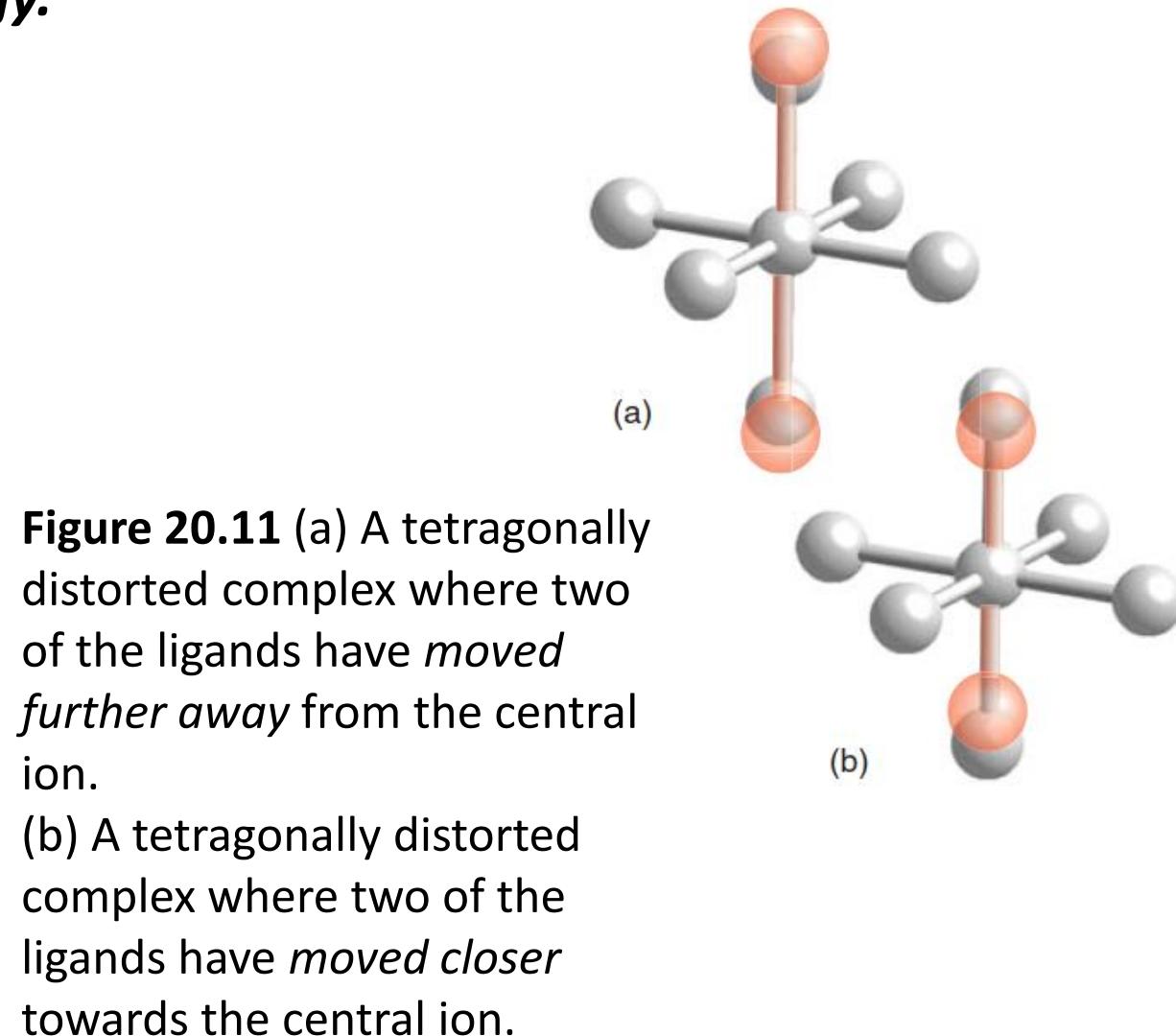


FIG. 13.8 Effect on orbital energies of removing ligands on the z axis, starting from an octahedron:
(a) the tetragonal field with nonequivalent z ligands, (b) the square-planar field with no z ligands

Tetragonally distorted complexes: the Jahn–Teller effect

Key points: A tetragonal distortion can be expected when the ground electronic configuration of a complex is **orbitally degenerate** and **asymmetrically filled**; the complex will distort so as to remove the degeneracy and achieve lower energy.

- Six-coordinate ***d⁹* complexes of copper(II)** usually depart considerably from octahedral geometry and show pronounced tetragonal distortions (Fig. 20.11).
- High-spin d⁴ (for instance, Cr²⁺ and Mn³⁺) and low-spin d⁷ six-coordinate complexes (for instance, Ni³⁺) may show a similar distortion, but *complexes of these ions are less common*, and the distortions are less pronounced than those in copper(II)).



- These distortions are manifestations of the **Jahn-Teller effect**: if the ground electronic configuration of a **nonlinear** complex is **orbitally degenerate** and **asymmetrically filled**, then the complex distorts so as to remove the degeneracy and achieve a lower energy.

- The physical origin of the effect is quite easy to identify. Thus, a **tetragonal distortion of a regular octahedron**, corresponding to extension along the z-axis and compression on the x- and y-axes, **lowers the energy** of the $e_g(d_{z^2})$ orbital and increases the energy of the $e_g(d_{x^2-y^2})$ orbital (Fig. 20.12).

- For example, in a d^9 complex (with a configuration that would be $t_{2g}^6 e_g^3$ in O_h), such a distortion leaves two electrons in the d_{z^2} orbital with a lower energy and one in the $d_{x^2-y^2}$ orbital with a higher energy.

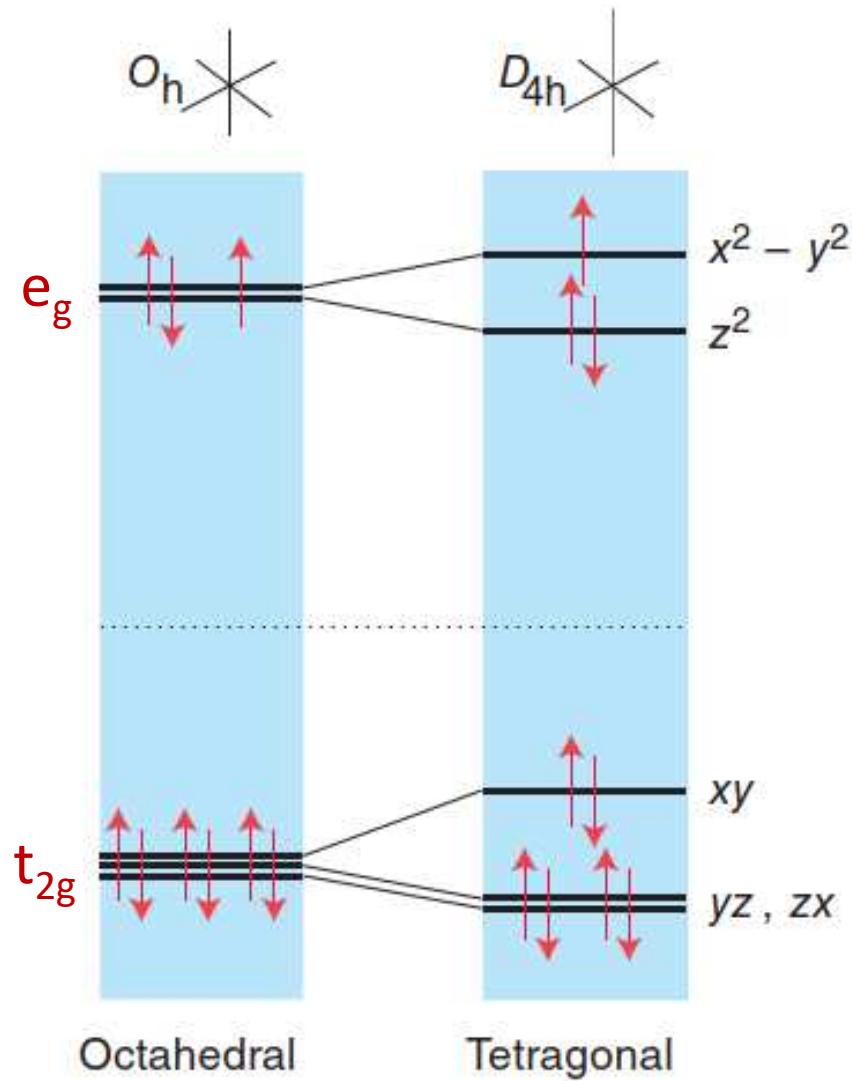


Figure 20.12 The effect of tetragonal distortions (compression along x and y and extension along z) on the energies of d orbitals. The orbital occupation is for a d^9 complex.

- They have a d⁹ configurations and the e_g orbitals in the octahedral structure are occupied by three electrons.
- If the e_g orbitals split and two electrons occupy the lower orbital and one electron the upper orbital, **the system gains energy of a half of the energy difference, δ , of two split orbitals**. Therefore, a tetragonal distortion in the z axis becomes favorable with respect to Octahedral.
- Therefore, if **one or three electrons occupy the e_g orbitals (as in high-spin d⁴, low-spin d⁷, and d⁹ complexes)** a **tetragonal distortion may be energetically advantageous**.

□ Which d^n electron configurations would show a Jahn–Teller effect?

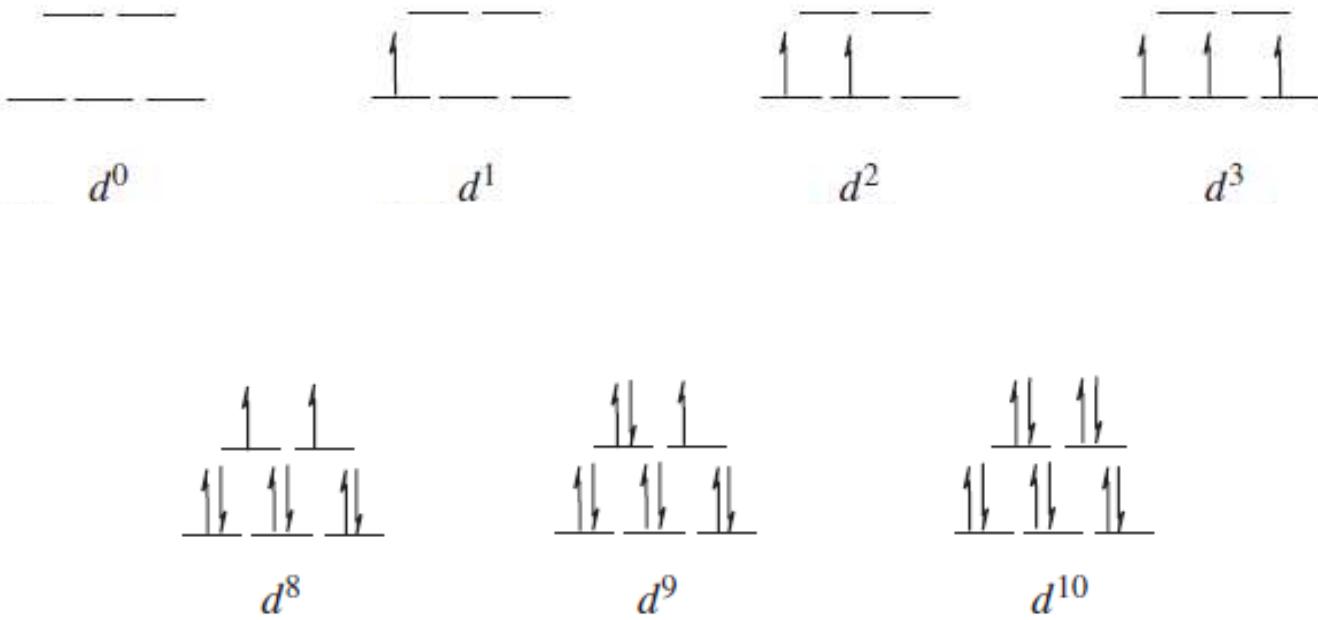
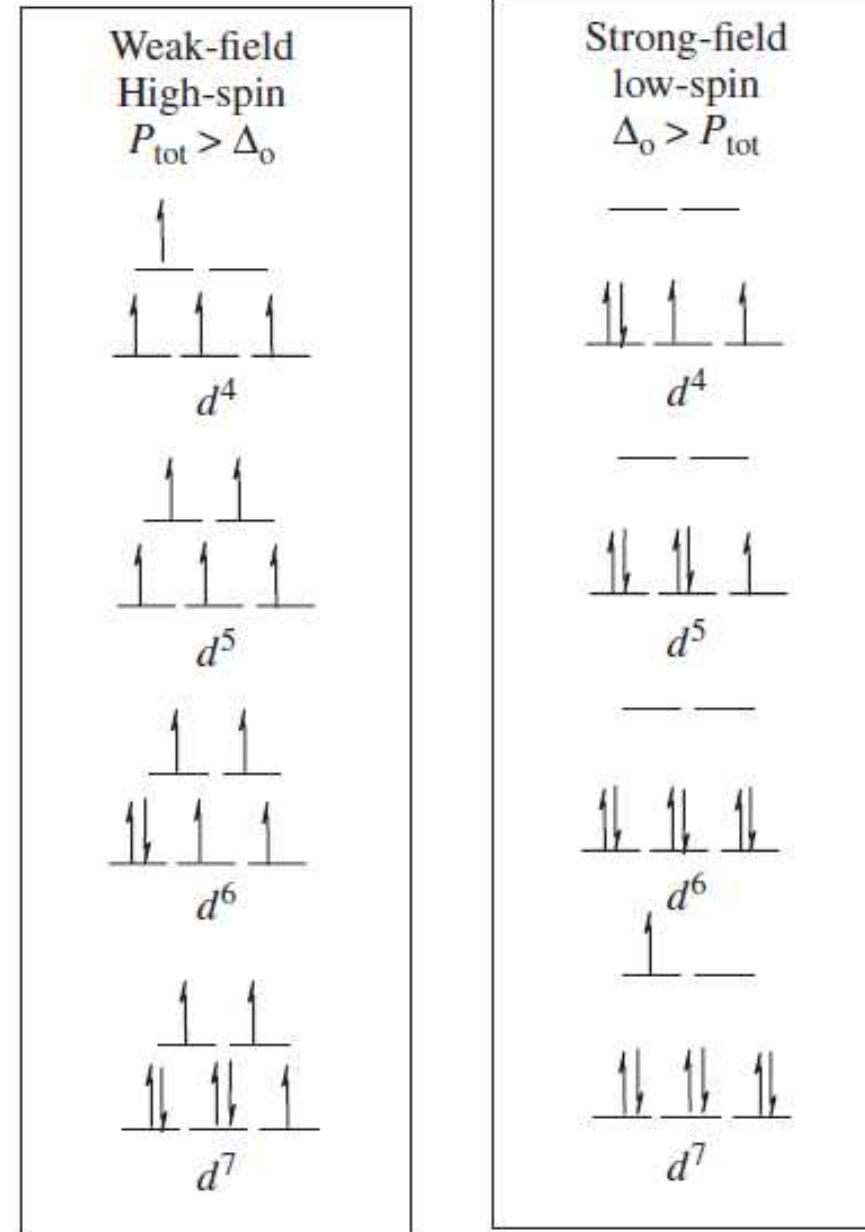


FIGURE.....

Crystal field splitting diagram for the different d^n configurations in an **octahedral CF**



□ Which d^n electron configurations would show a Jahn–Teller effect?

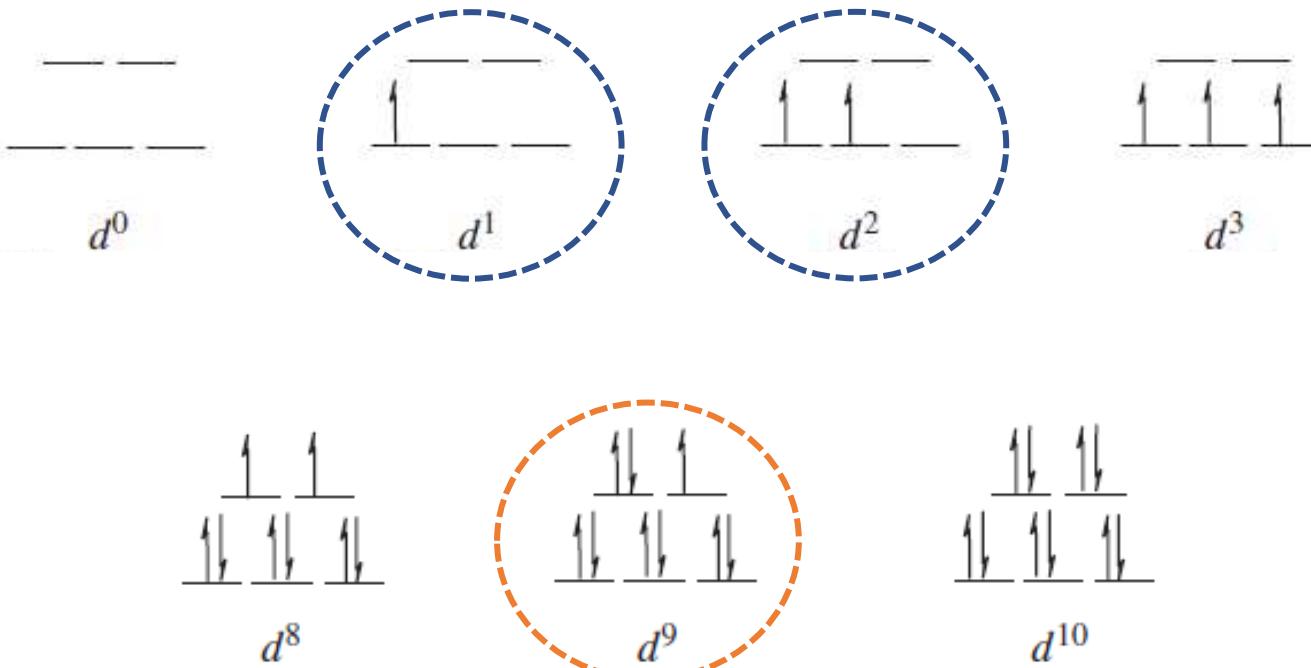
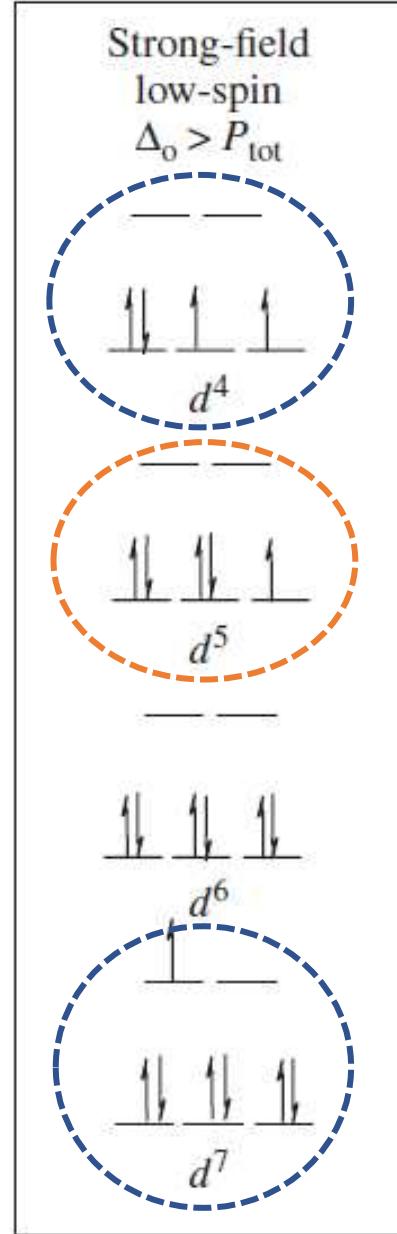
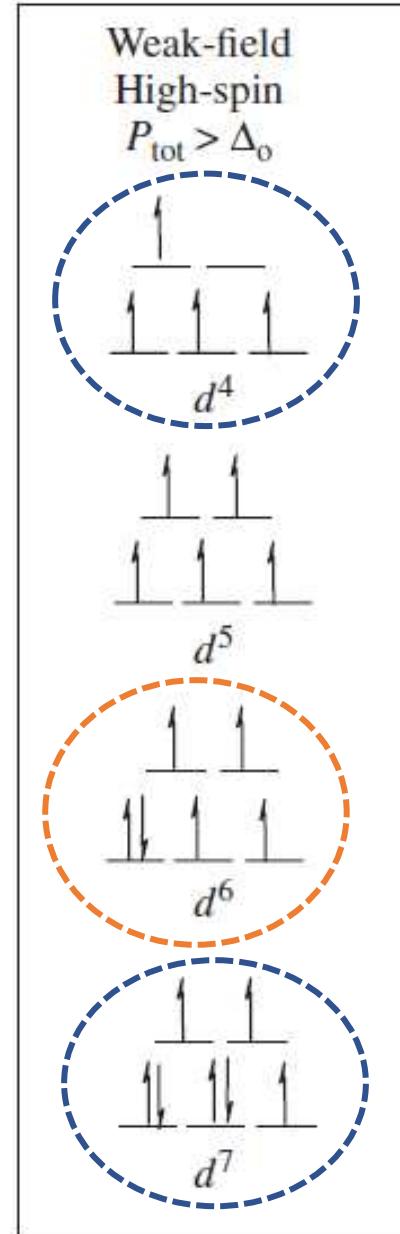


FIGURE.....

Crystal field splitting diagram for the different d^n configurations in an octahedral CF.



Which d^n electron configurations would show a Jahn–Teller effect?

Number of <i>d</i> electrons	<i>Electronic configuration</i>	
	<i>e</i>	<i>t</i> ₂
1	↑	
2	↑	↑
3	↑	↑
4	↑	↑
5	↑	↑
6	↑↓	↑
7	↑↓	↑↓
8	↑↓	↑↓
9	↑↓	↑↓
10	↑↓	↑↓

FIGURE.....

Crystal field splitting diagram for the different d^n configurations in a **tetrahedral** CF.

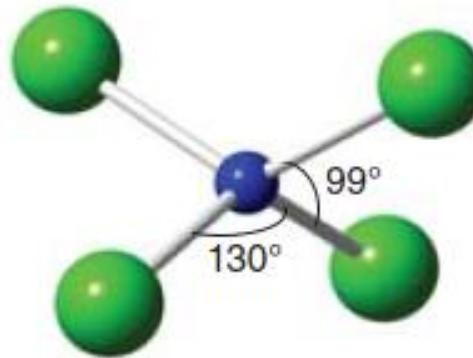
Which d^n electron configurations would show a Jahn–Teller effect?

Number of d electrons	Electronic configuration		
	e	t_2	
1	↑		
2	↑	↑	
3	↑	↑	
4	↑	↑	
5	↑	↑	
6	↑↓	↑	
7	↑↓	↑↓	
8	↑↓	↑↓	
9	↑↓	↑↓	
10	↑↓	↑↓	

FIGURE.....

Crystal field splitting diagram for the different d^n configurations in a **tetrahedral CF**.

- A Jahn–Teller effect is possible for other electron configurations of octahedral complexes (the d^1 , d^2 , low-spin d^4 and d^5 , high-spin d^6 , and d^7 configurations) and for tetrahedral complexes (the d^1 , d^3 , d^4 , d^6 , d^8 , and d^9 configurations).
- However, as neither the t_{2g} orbitals in an octahedral complex nor any of the d orbitals in a tetrahedral complex point directly at the ligands, **the effect is normally much smaller**, as is any measurable distortion. Tetrahedral Cu^{2+} compounds often show a slightly ‘flattened’ tetrahedral geometry as seen for the $[\text{CuCl}_4]^{2-}$ anion in Cs_2CuCl_4 .



The flattened $[\text{CuCl}_4]^{2-}$ anion

❖ Two Types of Distortions:

- The Jahn–Teller effect identifies an unstable geometry (**a nonlinear complex with an orbitally degenerate ground state**); however, *it does not predict the preferred distortion*.
- For instance, with an octahedral complex, *instead of axial elongation and equatorial compression*, the degeneracy can **also** be removed by axial compression and equatorial elongation.
- Which distortion occurs in practice is **a matter of energetics, not symmetry**.
- However, because *axial elongation weakens two bonds, but equatorial elongation weakens four*, **axial elongation is more common than axial compression**.

❖ Two Types of Distortions:

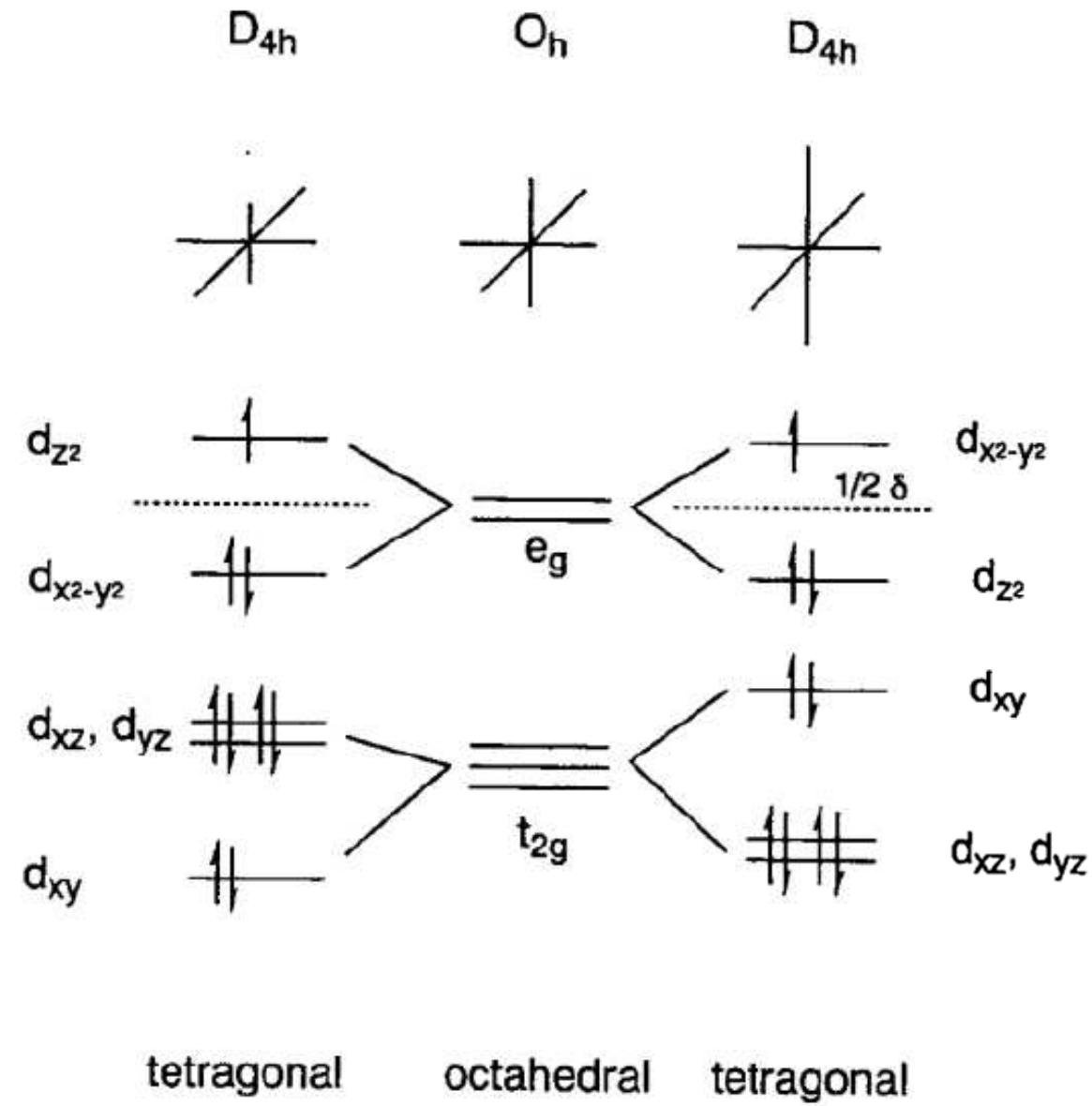
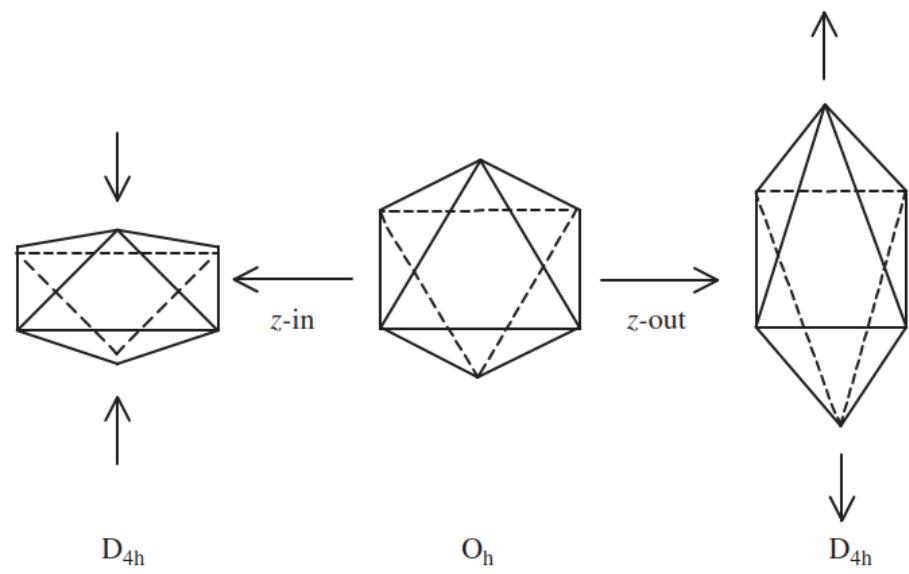


Figure 6.2.8: Jahn-Teller splitting in a Cu^{2+} ion.

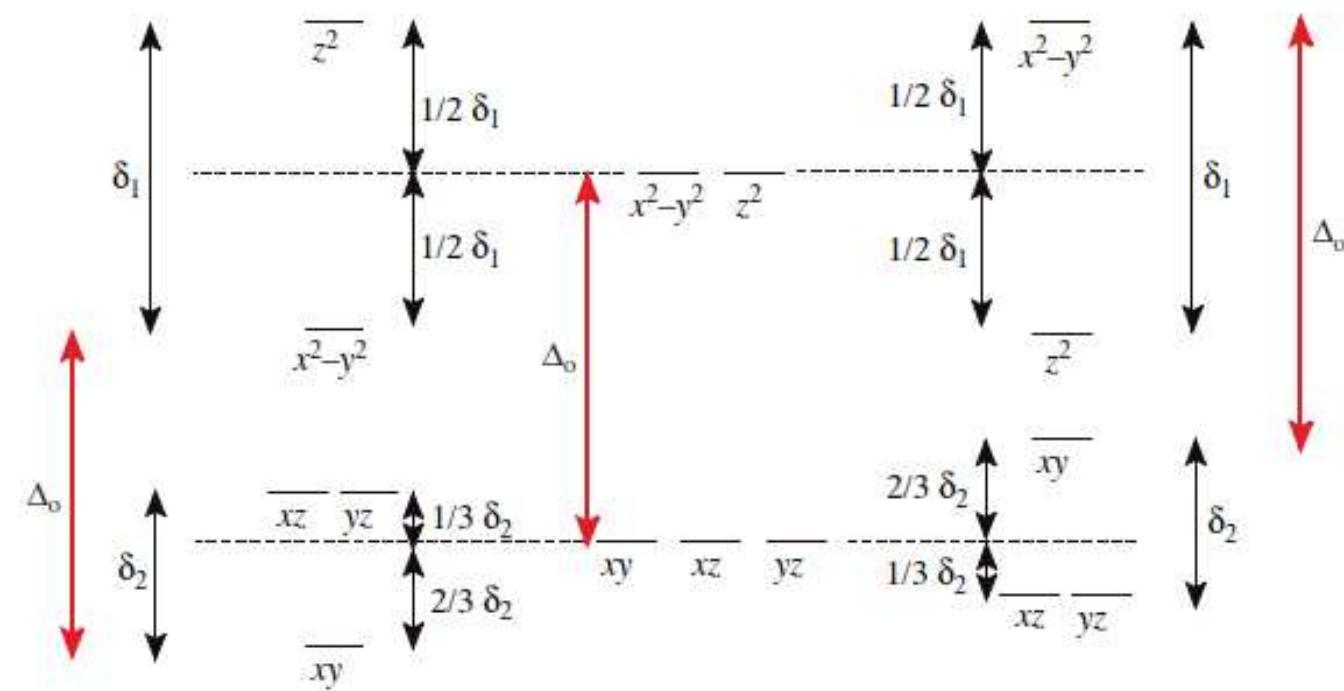
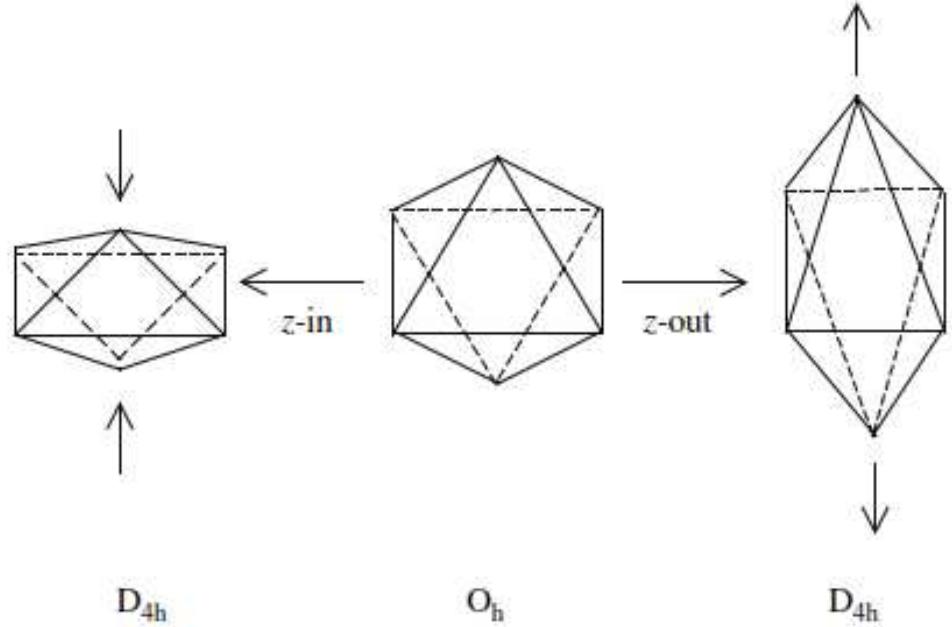


FIGURE 16.50 Tetragonal distortions from O_h symmetry and their effects on the energies of the d-orbitals. The “z-out” tetragonal distortion is shown on the right and the “z-in” tetragonal distortion is shown on the left.

- Splitting of terms observed in the electronic transitions of coordination compounds that we shall see later.
- For instance, splitting of the terms for a $d^1 [TiCl_6]^{3-}$ ion as it undergoes a tetragonal distortion from octahedral symmetry, illustrating the ***two observed spin-allowed transitions*** for the complex.
- Other forms of experimental verification of the Jahn–Teller effect include the ESR spectra of coordination compounds, X-ray crystallographic data showing different M–L bond lengths, and thermodynamic data.
- As an example, consider ***the stepwise formation constants*** in Table 16.28 for $[Cu(NH_3)_6]^{2+}$, which has the d^9 electron configuration. As expected, the stability constants decrease with increasing n because there is less positive charge on the metal as it becomes more saturated with ligands. However, there is an abrupt drop in the stability of the Cu(II) compounds between $n= 4$ and $n=5$. The reason that it is ***so difficult to add the fifth and sixth NH_3 ligands*** to Cu^{2+} is that the octahedral complex undergoes a “z-out” tetragonal distortion, which significantly weakens the two bonds along the z-axis.

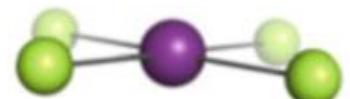
TABLE 16.28 Stepwise formation constants for $[\text{Cu}(\text{NH}_3)_n]^{2+}$.

K_1	2×10^4	K_4	2×10^2
K_2	4×10^3	K_5	3×10^{-1}
K_3	1×10^3	K_6	Very small

- A *Jahn–Teller distortion can hop from one orientation to another* and give rise to the *dynamic Jahn–Teller effect*.
- ✓ For example, below 20 K the EPR spectrum of $[\text{Cu}(\text{OH}_2)_6]^{2+}$ shows a static distortion (more precisely, one that is effectively stationary on the timescale of the resonance experiment). However, above 20 K the distortion disappears because it hops more rapidly than the timescale of the EPR observation.

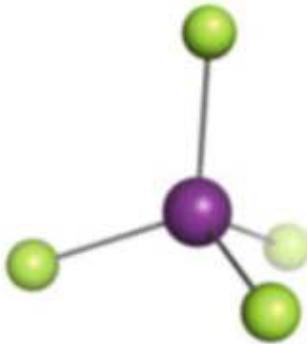
Coordination number four: Square Planar Complex

➤ Which of the following geometries is the **less sterically demanding arrangement?**

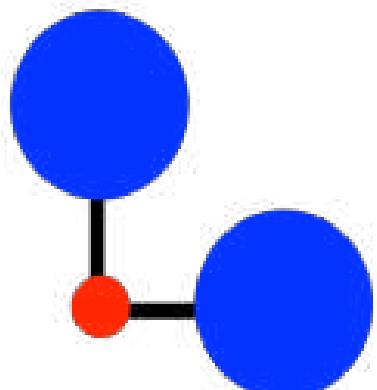


Square-planar

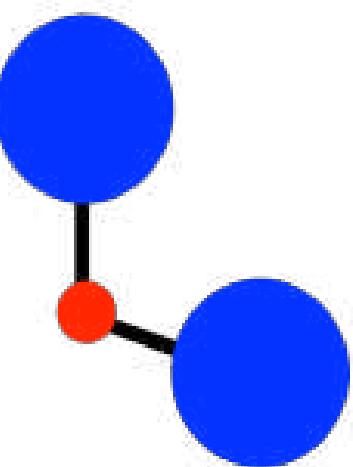
vs.



Tetrahedral



square planar
90°



tetrahedral
109°

- In a tetrahedron, all the ligands are 109.5° from each other.
- In a square planar geometry, the ligands are only 90° from each other.
- Tetrahedral geometry is always less crowded than square planar, so that factor always provides a bias toward tetrahedral geometry.
- As a result, we might expect *square planar geometry to occur only when steric is heavily outweighed by ligand field stabilization energy.*

□ Square-planar complexes : Coordination number four

- Although a *tetrahedral arrangement of four ligands is the least sterically demanding arrangement, some complexes exist with four ligands in an apparently higher-energy square-planar arrangement.*
- If only electrostatic interactions are considered, a square-planar arrangement of ligands gives the d-orbital splitting shown in Fig. 20.10 , with $d_{x^2-y^2}$ raised above all the others.
- This arrangement may become **energetically favorable when there are eight d electrons, and the crystal field is strong enough to favor the low-spin $d_{yz}^2 d_{zx}^2 d_{z^2}^2 d_{xy}^2$ configuration.**
- **In this configuration the electronic stabilization energy can more than compensate for any unfavorable steric interactions.**

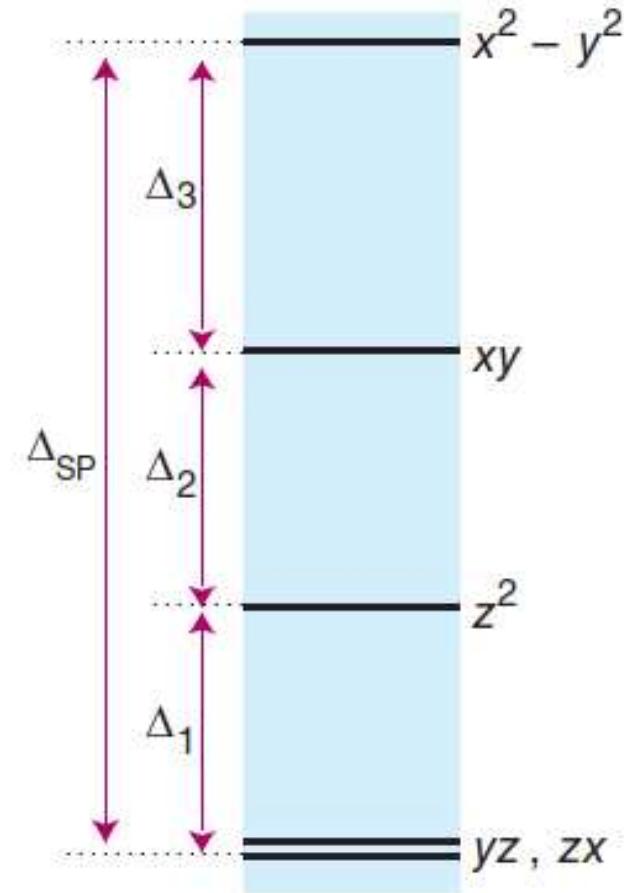
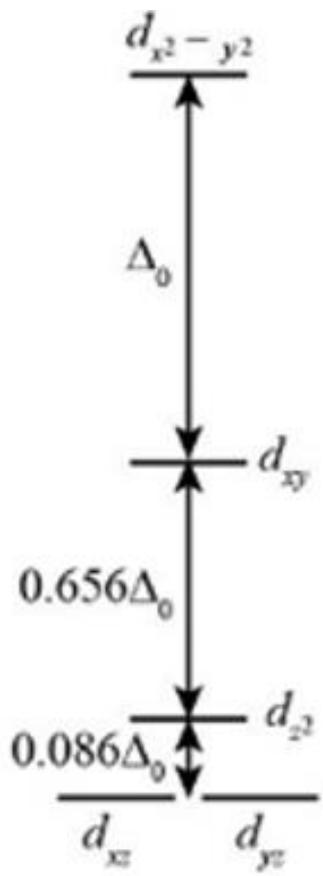
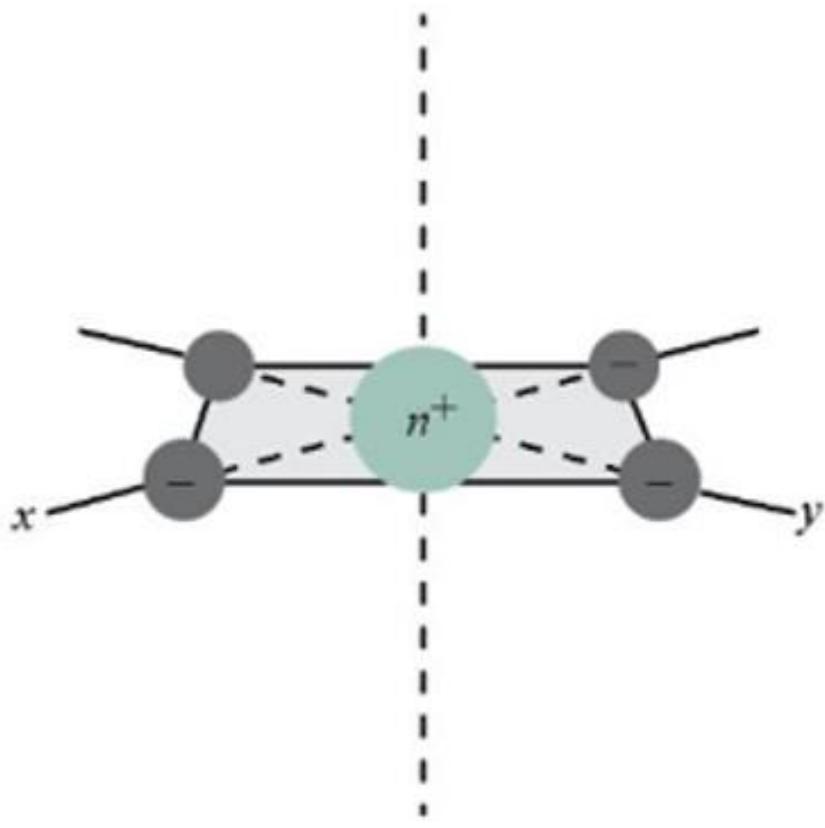


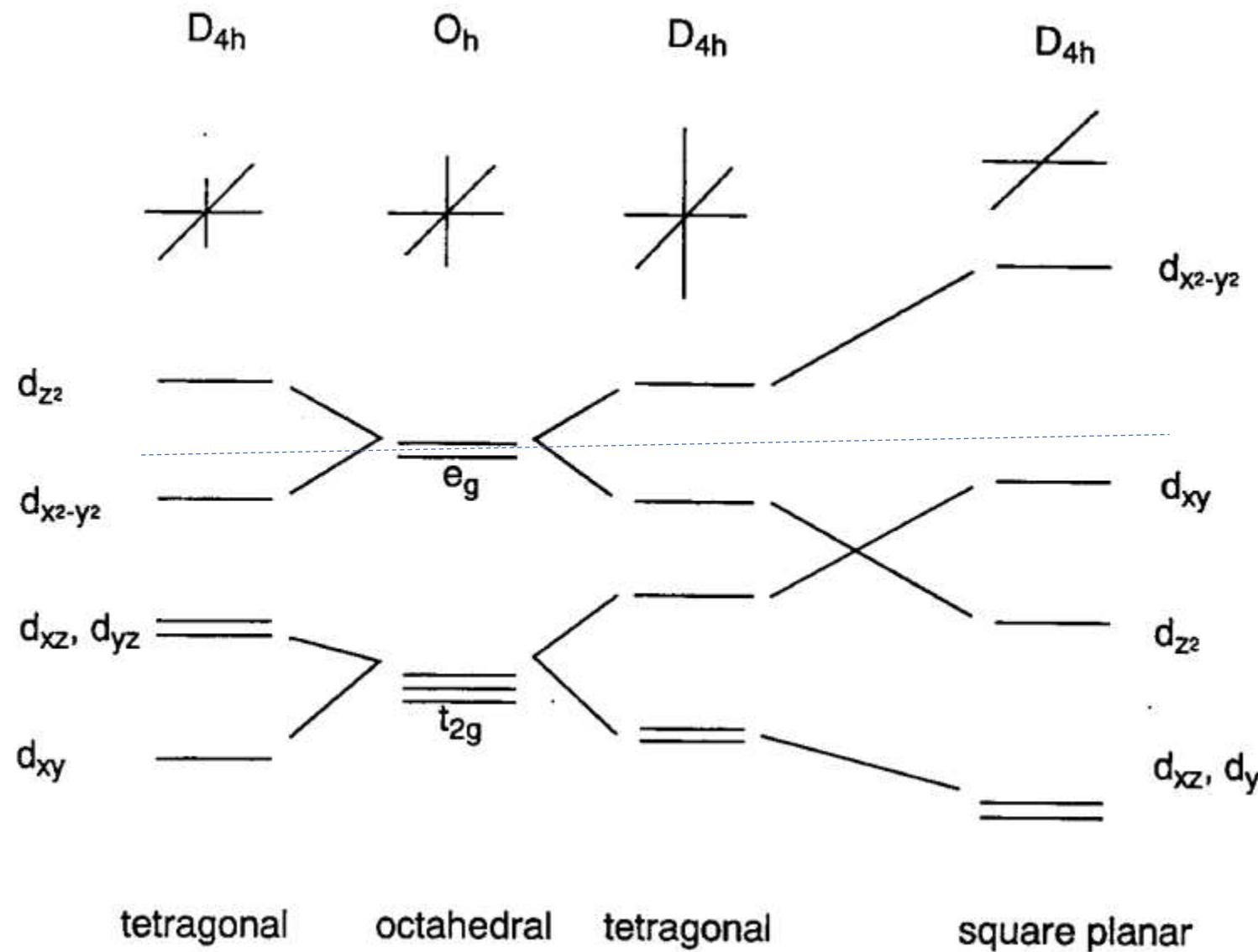
Figure 20.10 The orbital splitting parameters for a square-planar complex.

- Complexes with four ligands in a plane containing the central metal are termed square planar complexes.
- It is easier to understand the electronic energy levels of the d orbitals in square planar complexes by starting from those for hexacoordinate octahedral complexes.
- Placing the six ligands along the Cartesian axes, the two ligands on the z-axis are gradually removed from the central metal, and finally, only four ligands are left on the xy plane.
- The interaction of the two z-coordinate ligands with the d_{z^2} , d_{xz} , and d_{yz} orbitals becomes smaller, and the energy levels of these ligands lower.
- On the other hand, the remaining four ligands approach the metal, and the $d_{x^2-y^2}$ and d_{xy} energy levels rise as a result of the removal of the two ligands.
- This results in the order of the energy levels of five d orbitals being d_{xz} , $d_{yz} < d_{z^2} < d_{xy} \ll d_{x^2-y^2}$ (Figure 6.2.7).
- Rh^+ , Ir^+ , Pd^{2+} , Pt^{2+} , and Au^{3+} complexes with a d^8 configuration tend to form square planar structures because eight electrons occupy the lower orbitals leaving the highest $d_{x^2-y^2}$ orbital empty.



Splitting of the degenerate d-orbitals due to a square planar ligand field

Figure 6.2.7: Change of the orbital energy from octahedral to square planar complexes.



Square-planar complexes : Coordination number four

Key points: A d^8 configuration, *coupled with a strong crystal field*, favors the formation of square-planar complexes.

- *This tendency is enhanced with the 4d and 5d metals because of their larger size and the greater ease of electron pairing.*
- Thus, many square-planar complexes are found for complexes of the **large** $4d^8$ and $5d^8$ Rh(I), Ir(I), Pt(II), Pd(II), and Au(III) ions, in which *unfavorable steric constraints have less effect, and there is a large ligand-field splitting associated with the 4d- and 5d-series metals.*
- One should note that **pairing energies** for the 4d- and 5d-series metals *tend to be lower* than for the 3d-series metals, and *this difference provides a further factor* that favors the formation of low-spin square-planar complexes with these metals.

- The d⁸ metal ions, such as [PdCl₄]²⁻, form square planar complex.
- By contrast, small 3d-series metal complexes such as [NiX₄]²⁻, with X a halide, are *generally tetrahedral* because the ligand-field splitting parameter is generally quite small and *will not compensate sufficiently for the unfavorable steric interactions*.
- However, only *when the ligand is high in the spectrochemical series is the LFSE large enough to result in the formation of a square-planar complex*, as, for example, with [Ni(CN)₄]²⁻.
- In the *square planar case, only low-spin complexes* have been found.
- *Square-planar complexes are low spin and usually diamagnetic* because the four pairs of d electrons fill the four lowest-energy orbitals.

Octahedral vs. tetrahedral (vs. square planar) coordination

Key points: Consideration of the CFSE (LFSE) predicts that

- ✓ **d³ and d⁸ ions strongly prefer an octahedral geometry over a tetrahedral one;**
 - ✓ *for other configurations the preference is less pronounced;*
 - ✓ *CFSE has no bearing on the geometry of d⁰, high-spin d⁵, and d¹⁰ ions.*
- An octahedral complex has six M–L bonding interactions and, *in the absence of significant steric and electronic effects*, this arrangement will have a lower energy than a tetrahedral complex with just four M–L bonding interactions.
- We can now complete the discussion by considering the electronic effects that favor an octahedral complex over a tetrahedral one.
- These considerations, and the data for the CFSE values, allow a prediction of the most probable cases in which 4-coordination will be found for transition elements of the first series.
- The geometry of complexes of ions with d⁰, d⁵, and d¹⁰ configurations will not be affected by the number of *d* electrons, as there is no LFSE for these species.

- Figure 20.13 illustrates the variation of the LFSE (CFSE) for tetrahedral and high-spin octahedral complexes for all electronic configurations.
- It is apparent that, in terms of LFSE, ***octahedral geometries are strongly preferred over tetrahedral for d³ and d⁸ complexes***: chromium(III) (d^3) and nickel(II) (d^8) do indeed show an exceptional preference for octahedral geometries.
- *Similarly, d⁴ and d⁹ configurations show a preference for octahedral complexes (for example Mn(III) and Cu(II); note that the Jahn–Teller effect enhances this preference),*
- ✓ whereas *tetrahedral complexes of d¹, d², d⁶, and d⁷ ions will not be too disfavored*; thus V(II) (d^2) and Co(II) (d^7) form tetrahedral complexes ($[MX_4]^{2-}$) with chloride, bromide, and iodide ligands.

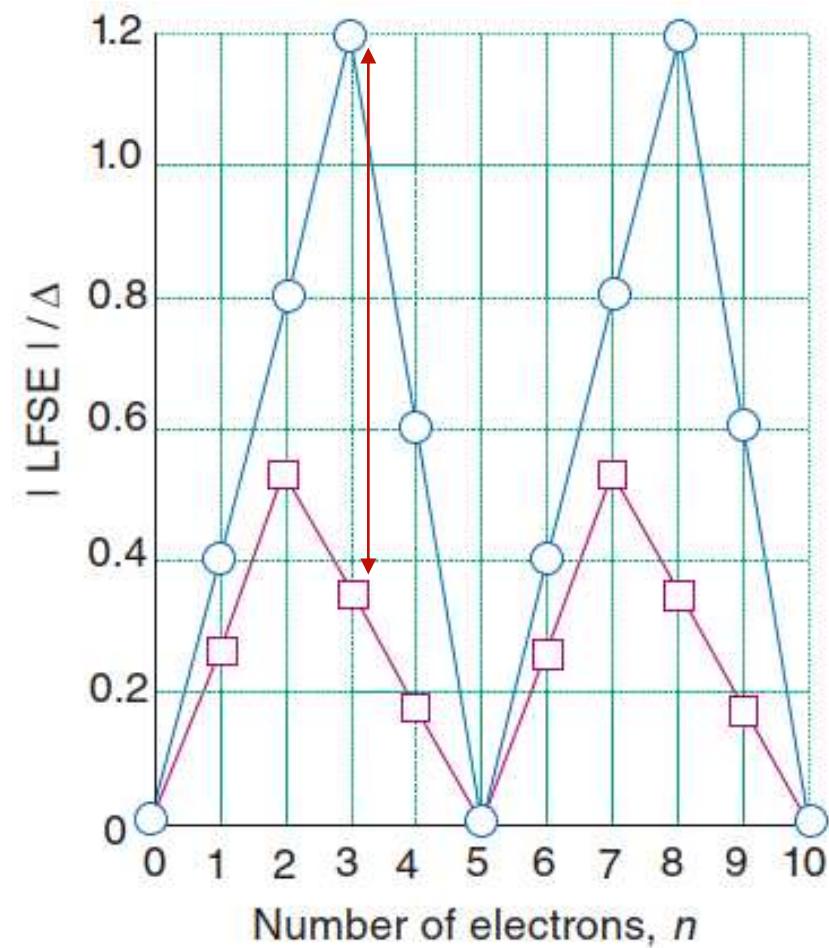


Figure 20.13 The ligand-field stabilization energy for d^n complexes in octahedral (high-spin, circles) and tetrahedral (squares) complexes. The LFSE is shown in terms of Δ_0 , by applying the relation $\Delta_T = \frac{4}{9} \Delta_0$.

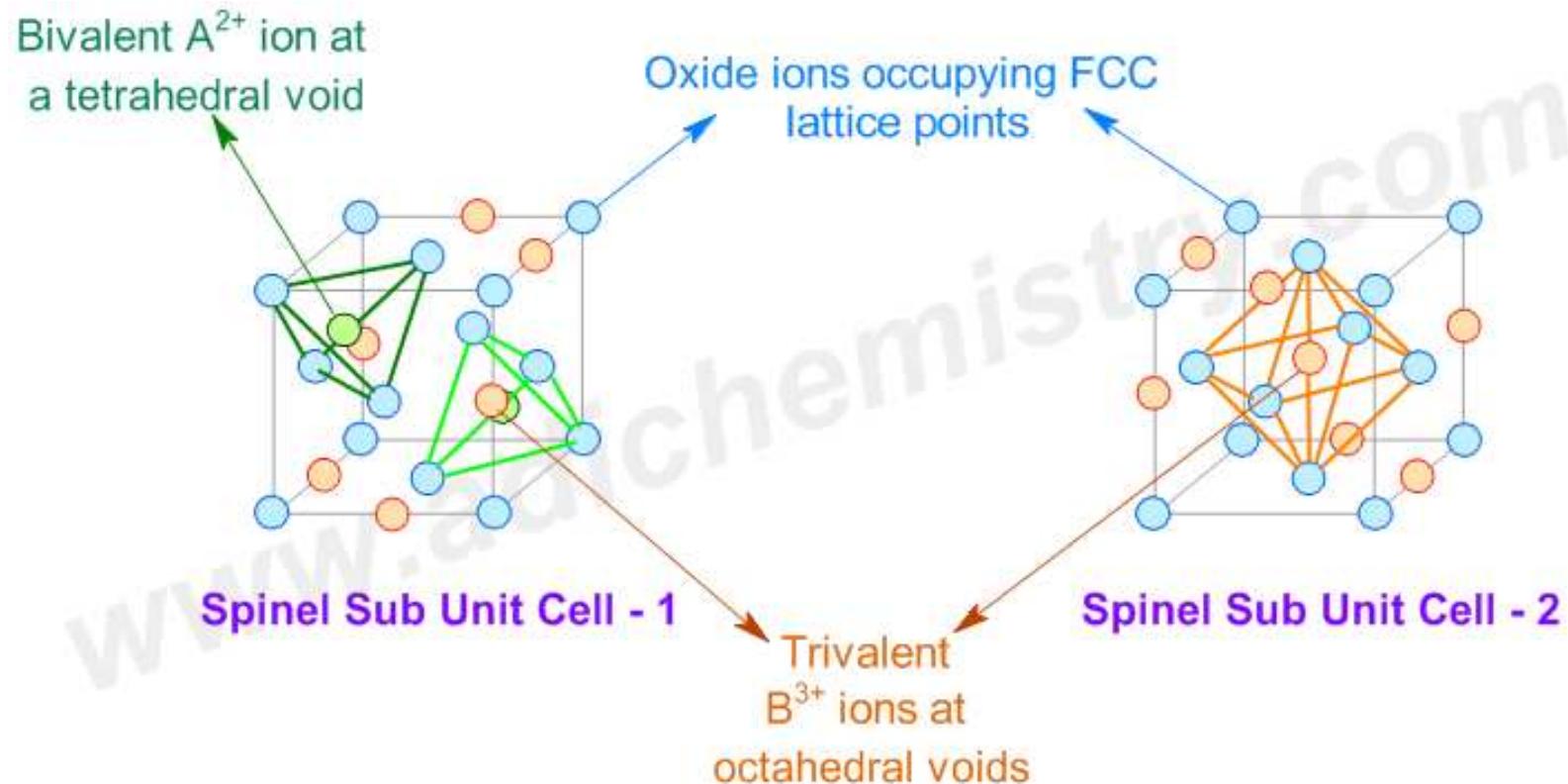
- The tetrahedral configuration is expected to be unfavorable compared with the octahedral one, *except in the case of large ligands with low positions in the spectrochemical series, or in the ions with 0, (1), 5, (6) or 10 d electrons.*
- The **larger ligands** will experience steric hindrance to formation of 6-coordinated complexes and the interactions will also be reduced due to the increased metal-ligand distances.
- The **low position in the spectrochemical series** ensures that any loss of CFSE is not too serious due to the low intrinsic value of ΔE (similarly, *a low charge on the transition metal ion affects the ΔE value so divalent ions should form tetrahedral complexes more readily than trivalent ones, and a fortiori for lower charges*).
- Finally, the d configurations listed are those with the lowest CFSE differences. In practice, *tetrahedral complexes are typically formed by the halides (except fluoride) and related ligands.*

- Because the size of the d-orbital splitting, and hence the LFSE, depends on the ligand, it follows that a preference for octahedral coordination will be least pronounced for weak-field ligands.
- With strong-field ligands, low-spin complexes might be preferred and, although the situation is complicated by the pairing energy, the LFSE of a low-spin octahedral complex will be greater than that of a high-spin complex. **There will thus be a correspondingly greater preference for octahedral over tetrahedral coordination when the octahedral complex is low-spin.**
- *This preference for octahedral over tetrahedral coordination* plays an important role *in the solid state* by influencing *the structures that are adopted by d-metal compounds*.
- *This influence is demonstrated by the ways in which the different metal ions A and B in spinels* (of formula AB_2O_4) *occupy the octahedral or tetrahedral sites.*

❖ Mixed metal oxides

- Spinel, MgAl_2O_4 , has a structure in which Mg^{2+} occupy 1/8 of the tetrahedral cavities and Al^{3+} 1/2 of the octahedral cavities of a ccp array of oxygen atoms.
- Among the oxides of composition $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$ (A^{2+} are Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, and B^{3+} are Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni, and Rh), those in which the *tetrahedral holes are occupied by A^{2+}* are called **normal spinels** (or by B^{3+} are called **inverse spinels**, respectively).
- Spinel itself has a normal spinel-type structure.
- MgFe_2O_4 and Fe_3O_4 have inverse spinel-type structures.
- *Crystal field stabilization energies differ depending on whether the crystal field of the oxygen atoms is a regular tetrahedron or octahedron.*
- Therefore, *when the metal component is a transition metal, the energy difference is one of the factors to determine which of A^{2+} or B^{3+} is favorable to fill the tetrahedral cavities.*

➤ A **normal spinel** can be represented as: $(A^{II})^{tet}(B^{III})_2^{oct}O_4$, where: A^{II} = a divalent cation (like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn) and B^{III} = a trivalent cation (like Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni) and X (a weak-field ligand) = O, S, Se, etc.



- A ***normal spinel*** structure is assumed if both divalent and trivalent metals are **nontransition metals** since **no CFSE** is involved.
- Usually d³ & d⁸ ions have strongest preference for octahedral geometry.
- There is a tendency of formation of ***inverse spinel structure*** in some cases (not all the cases) which contain transition metal ions. This is because, the transition metal ion **may get extra stability (LFSE) in octahedral geometry**, and prefers octahedral voids over tetrahedral ones. That means, if A^{II} has d³ or d⁸ configuration and the B^{III} ion has configuration other than these, then the **spinel is inverted**.
- An ***inverse spinel*** can be represented as: (B^{III})^{tet}(A^{II})^{oct}(B^{III})^{oct}O₄
- Examples of ***Inverse spinels***: Fe₃O₄ (ferrite), CoFe₂O₄, NiFe₂O₄, etc.
- The above ***inverse spinels*** can also be written as:

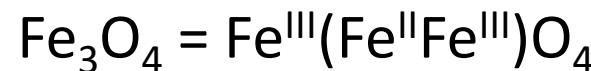


Table 6.2.2. Ligand field stabilization energy (LFSE)

		Octahedral				Tetrahedral	
		<i>Strong field (LS)</i>		<i>Weak field (HS)</i>			
d^n	Example	n	Δ_o	n	Δ_o	n	Δ_t
d^1	Ti^{3+}	1	0.4	1	0.4	1	0.6
d^2	V^{3+}	2	0.8	2	0.8	2	1.2
d^3	Cr^{3+}, V^{2+}	3	1.2	3	1.2	3	0.8
d^4	Cr^{2+}, Mn^{3+}	2	1.6	4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0	5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4	4	0.4	4	0.6
d^7	Co^{2+}	1	1.8	3	0.8	3	1.2
d^8	Ni^{2+}	2	1.2	2	1.2	2	0.8
d^9	Cu^{2+}	1	0.6	1	0.6	1	0.4
d^{10}	Cu^{1+}	0	0	0	0	0	0

Rules:

1. If both A^{+2} and B^{+3} are non-transition metals, then spinel will be NORMAL.
2. If A^{+2} is non-transition metal and B^{+3} is transition metal (with $d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$) then spinel will be NORMAL.
3. If A is transition metal with ($d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$) and B is also transition metal with ($d^0 d^5$ and d^{10}) system, then spinel will be INVERSE.

A^{II}	B^{III}	Structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	Non transition metal	Spinel structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Spinel structure
A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Non transition metal or transition meta with d^0 or d^5 or d^{10} configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

- The case of the square-planar configuration is rather different. Because the bond distances in the xy plane are essentially the same in octahedral and square-planar configurations, steric effects are negligible and the increase in attractions due to *forming six bonds rather than four will normally overwhelmingly favor* the regular octahedral complex.
- ***Changes in CFSE for low numbers of d electrons either favor the octahedral case or are small.*** Consider, however, the case of d^8 . In an octahedral complex, there are two electrons in the e_g level, while the square-planar configuration allows these to be paired in the d_{xy} orbital (Fig. 13.10) with a gain in CFSE of about $2\Delta E_{\text{oct}}$. (*This is only approximate* as the lower levels in the square-planar case do not match the octahedral t_{2g} levels, but they are quite close.)
- This is offset by a reduction in exchange energy from the 13K of the octahedral case to 12K for two sets of four electrons. However, ***if ΔE is sufficiently large, it is possible for the gain in CFSE to overbalance the loss in bonding interactions and the small loss in exchange energy.***
- It is found that *square-planar complexes are indeed formed by d^8 ions with ligands to the right of the spectrochemical series*: for example, Ni^{2+} forms a square-planar cyanide complex, $\text{Ni}(\text{CN})_4^{2-}$, while its hydrate or ammine are octahedral, e.g., $\text{Ni}(\text{NH}_3)_6^{2+}$. The larger ΔE values of heavier elements or of more highly charged elements extend the scope of formation of square complexes. Thus, all complexes, even halides, of platinum (II) and gold (III) (both d^8) are square-planar.

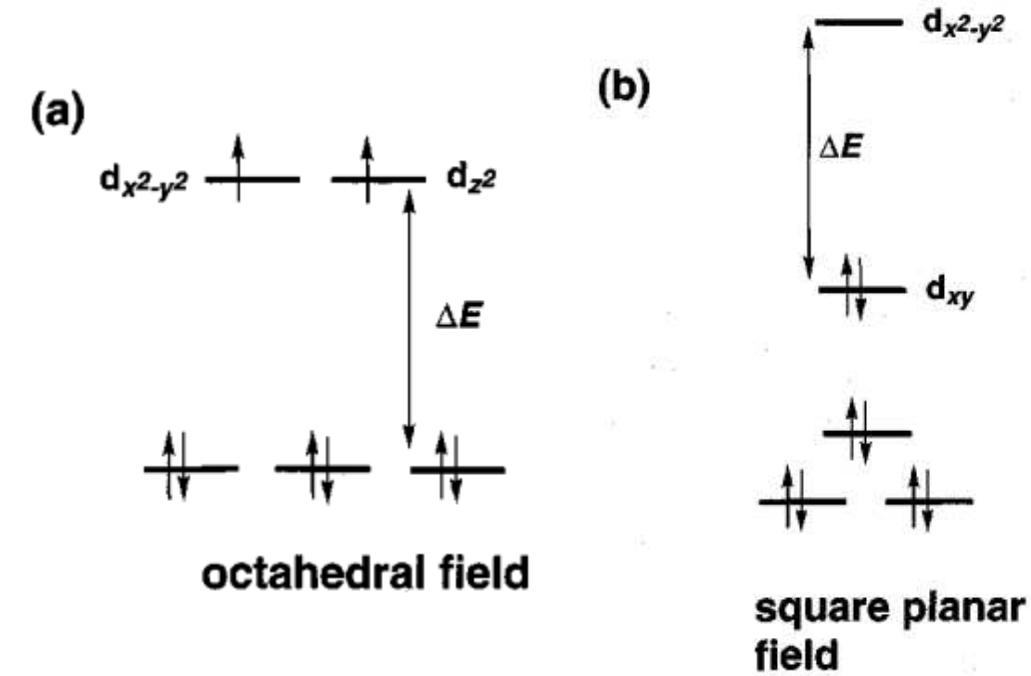


FIG. 13.10 The configuration of electrons in a d complex: (a) octahedral and (b) square-planar.

- Steric interactions favor a tetrahedral geometry for four-coordinate compounds (as per valence-shell electron-pair repulsion (VSEPR) theory), but square planar geometry can occur for electronic reasons, which happens most often with a LS d^8 electron configuration.
- The reason for this is because there is such a large separation between the b_{1g} and b_{2g} MOs. If the complex is LS d^8 , it will have an extremely favorable CFSE of $-24.56\Delta_o$. Thus, square planar compounds are often always LS.

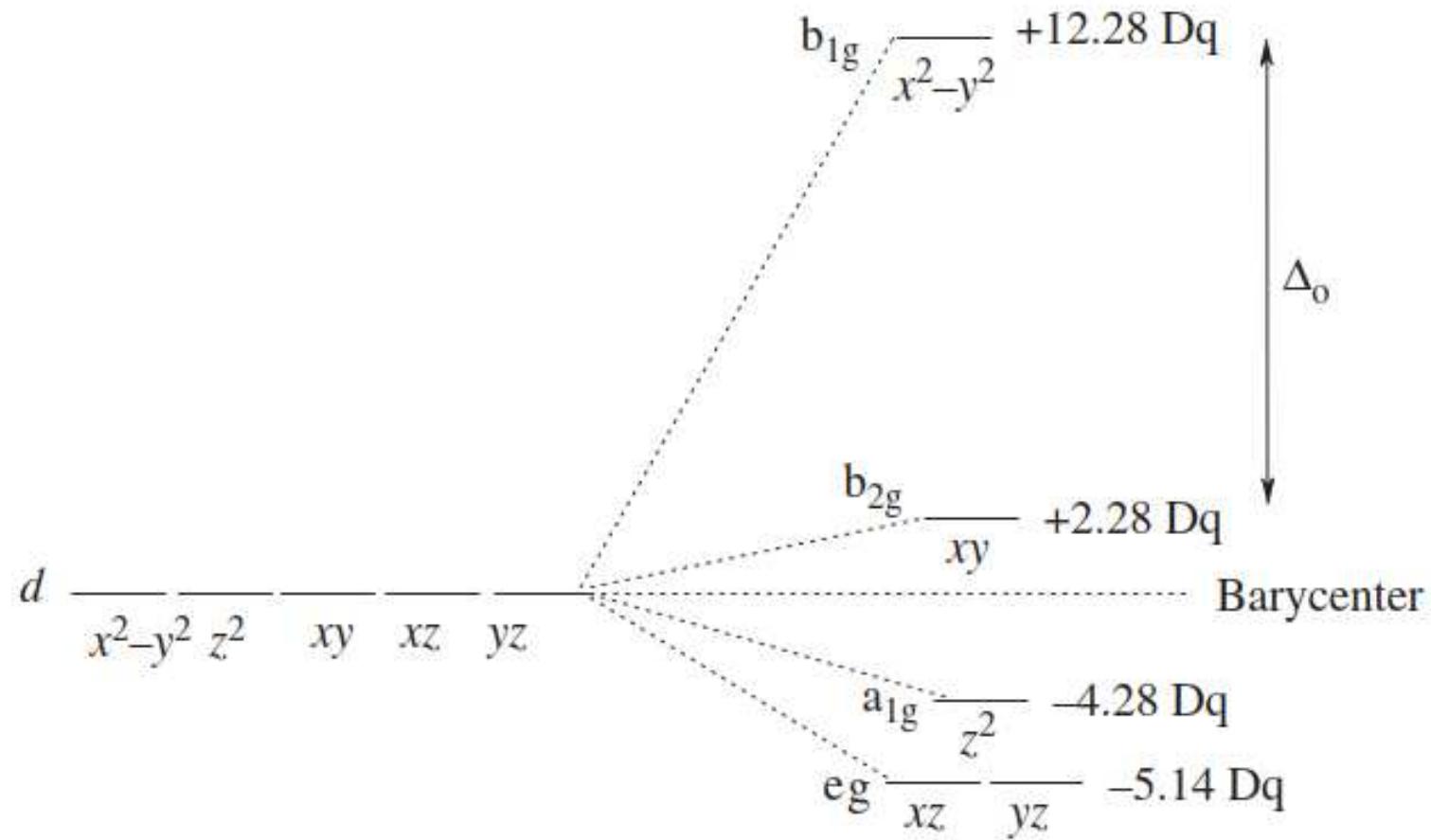


FIGURE 16.15 Crystal field splitting pattern for the square planar geometry.

- This extra CFSE found in square-planar complexes of d^8 elements also occurs for the d^7 and d^9 configurations. However, the CFSE gain is only Δ_o .

TABLE 13.11 Species forming square-planar complexes

<i>d electron configuration</i>	<i>Species</i>		<i>Approx. CFSE</i>	<i>Unpaired electrons</i>
d^8	Ni(II)	Pd(II)	$2\Delta E_{\text{oct}}$	0
		Rh(I)	ΔE_{oct}	
		Au(III)		
d^9	Cu(II)	Ag(II)	ΔE_{oct}	1 (in $d_{x^2-y^2}$)
d^7	Co(II)		ΔE_{oct}	1 (in d_{xy})
d^6	Fe(II)		$\frac{1}{2}\Delta E_{\text{oct}}$	2
d^4	Cr(II)		$\frac{1}{2}\Delta E_{\text{oct}}$	4

The Cr(II) spin corresponds to one electron in each of the four stable orbitals, and the Fe(II) value indicates two filled and two half-filled orbitals. The CFSE are with respect to the octahedral configuration, those for d^4 and d^6 being for the weak field configuration.

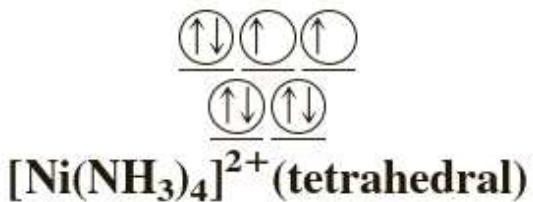
- Table 13.11 lists the species which typically form square-planar complexes.
- While such *square complexes of the first-row elements are comparatively rare*, those formed by heavy transition elements are the majority of the representatives of these oxidation states, especially for the d⁸ configurations.
- *In configurations other than d⁸, the CFSE gain relative to octahedral is small, and most of these configurations are distorted in the octahedral case*, so it is often difficult to decide what has happened. *For example, copper(II) compounds often show four short bonds in a square plane with two longer ones, or even three sets of pairs of bonds with different lengths.*
- The distortion mentioned in the last paragraph arises whenever the d_{z²} and d_{x²-y²} orbitals are unequally occupied. If, for example, there is *one electron in the d_{z²} orbital*, ligands on the z axis are more shielded from the nuclear field than are ligands on the x and y axes. *The ligand-metal distances in the z direction are therefore shorter than those in the xy plane.* If the electron is, instead, in the d_{x²-y²} orbital the four distances in the xy plane are shorter. Such distortions, which are less simple than described here, are one manifestation of *the Jahn-Teller theorem, which states that if a system has unequally occupied, degenerate energy levels it will distort as to raise the degeneracy.* Cases where distortions are expected are d⁴ high spin, d⁷ low spin and d⁹. *Distortions involving t_{2g} levels are normally too small to be detected.*

- Describe the d-electron distributions of the complexes $[\text{Ni}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$, according to crystal field theory. The tetraamminenickel(II) ion is *paramagnetic*, and the tetracyanonickelate(II) ion is *diamagnetic*.

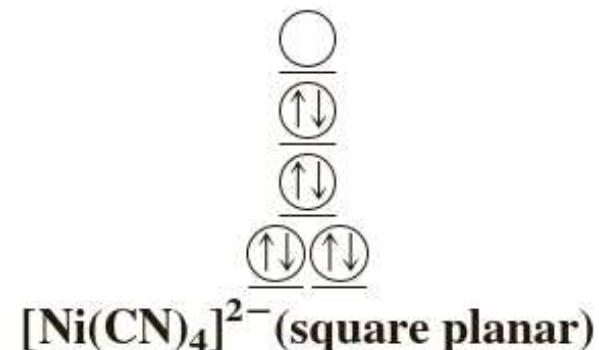
- Describe the d-electron distributions of the complexes $[\text{Ni}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$, according to crystal field theory. The tetraamminenickel(II) ion is *paramagnetic*, and the tetracyanonickelate(II) ion is *diamagnetic*.

....The complex ions given in the problem are 4 C.N.: ***either tetrahedral or square planar.***

- **The tetrahedral field to give high-spin complexes and the square planar field to give low-spin complexes.** Therefore, the geometry of the $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ion, which is paramagnetic (8 electrons are **NOT** paired), is probably tetrahedral. The distribution of d electrons in the Ni^{2+} ion (configuration d^8) is:



The geometry of $[\text{Ni}(\text{CN})_4]^{2-}$, which is diamagnetic (all 8 electrons are **paired**), is probably square planar; the distribution of d electrons is:



CFT Evidences/Applications

One of the earliest thermodynamic studies in support of CFT was published by Don McClure in 1959. McClure showed that the absolute magnitudes of the lattice enthalpies of the divalent metal halides from the first transition series depended on the CFSE of the metal ion, as shown in Figure 16.10.

- In general, *the lattice enthalpy increases across the series as a result of the decreasing size of the ionic radius that accompanies the increase in the effective nuclear charge.*
- However, *the actual lattice enthalpies do not fit to a smooth, linear progression across the row.* Instead, there are distinct peaks and valleys in the experimental data.
- ***Those d^n configurations having the smallest deviation from the expected linear trend occur for the d^0 , d^5 , and d^{10} electron configurations,*** each of which has a CFSE= 0 (ignoring the pairing energy). Some ***of the larger deviations from the linear progression (which correspond to more stable lattice enthalpies)*** occur for the d^3 and d^8 electron configurations, which (not coincidentally) happen to have the largest CFSEs ($-1.2\Delta_o$).

$$\text{CFSE} = [(-0.4) * (\text{no. of electrons in } t_{2g})] + [(0.6) * (\text{no. of electrons in } e_g)]$$

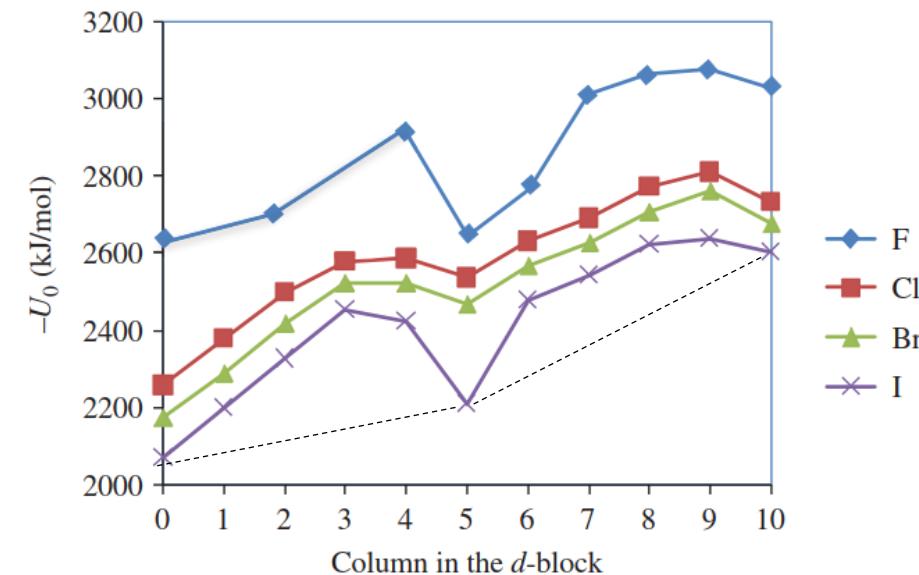


FIGURE 16.10. The absolute value of the magnitude of the lattice enthalpies (kJ/mol) for the divalent metal halides of the first transition series. [Data were obtained from <http://www.webelements.com> (accessed March 29, 2014)]. Thermochemical data were chosen over calculated values whenever they were known.]

- Other evidence for CFT comes from the **enthalpies of hydration** for the divalent metal ions of the first transition series. Again, a linear trend is expected, *the general trend to greater hydration enthalpy (more exothermic hydration) on crossing the period from left to right*. The experimental data are shown by the solid blue line in Figs. 16.11 and 20.7.
- The largest deviations from the expected trend occur for those d^n electron configurations having the greatest CFSE, namely d^3 and d^8 . If the CFSE is subtracted from the experimental enthalpy of hydration, the expected linear trend is observed, as shown by the solid red line.

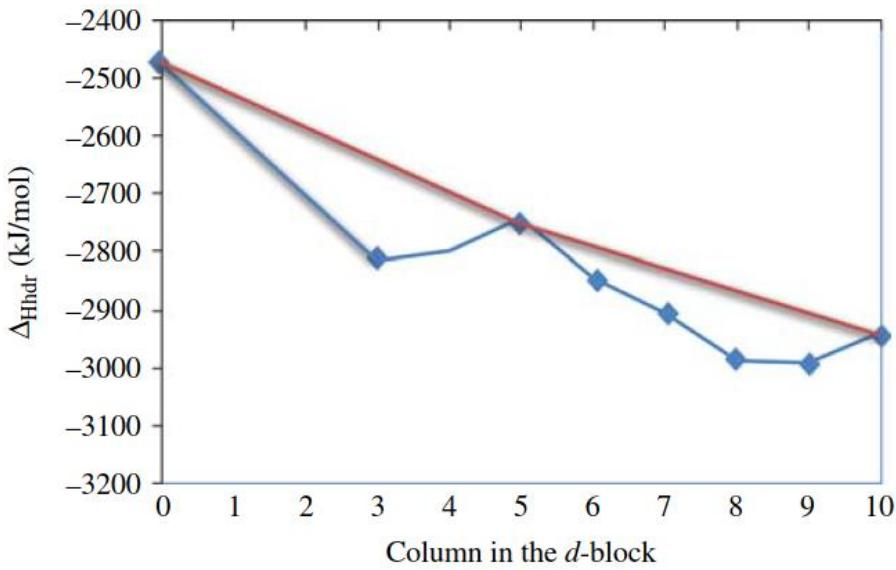


FIGURE 16.11

Hydration enthalpies for the first row divalent transition metals as a function of d^n electron count.

The blue line represents the experimental data, while the red line approximates the experimental values minus the CFSE.

The hydration enthalpy for the $2+$ ions is the enthalpy change for the reaction: $M^{2+} (g) + 6 H_2O \rightarrow [M(H_2O)_6]^{2+}$

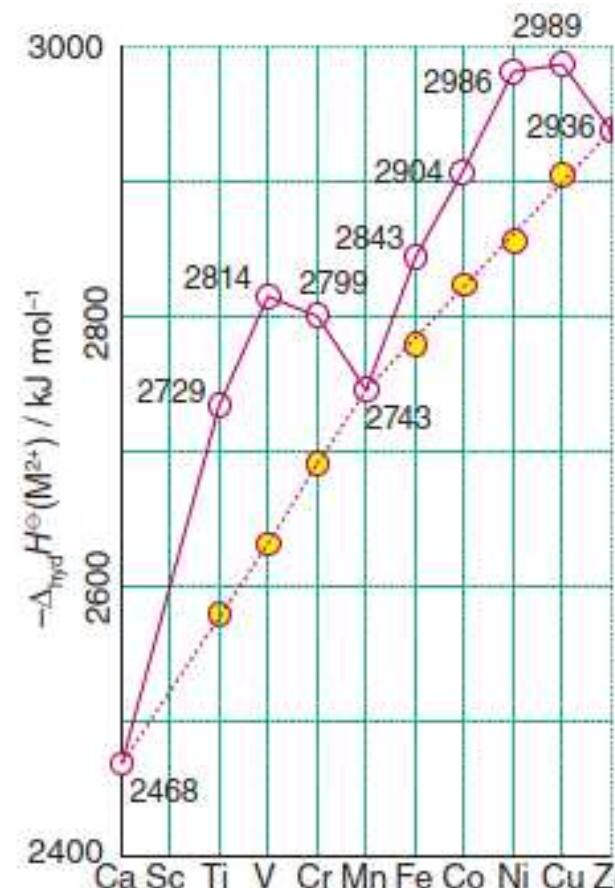
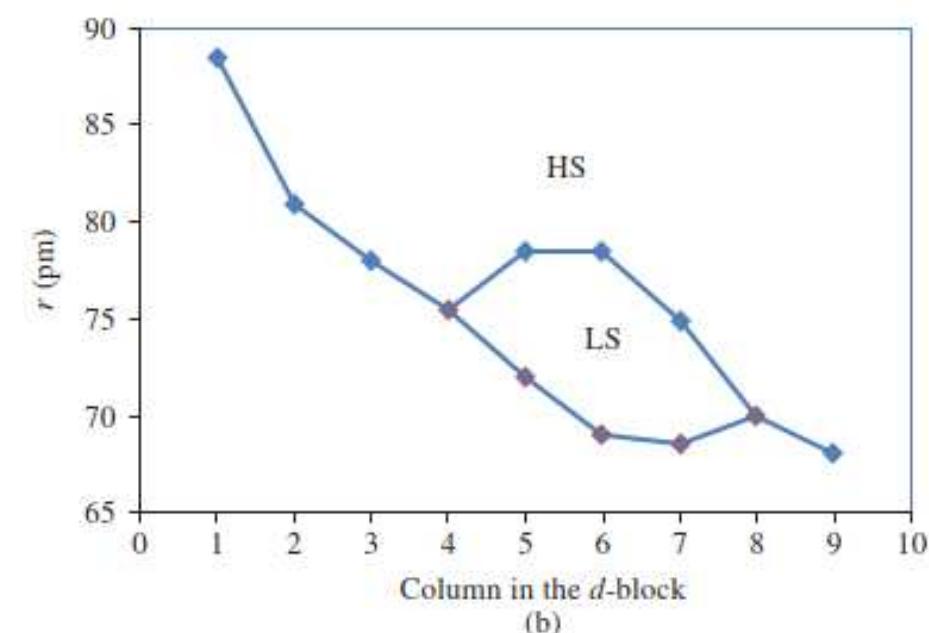
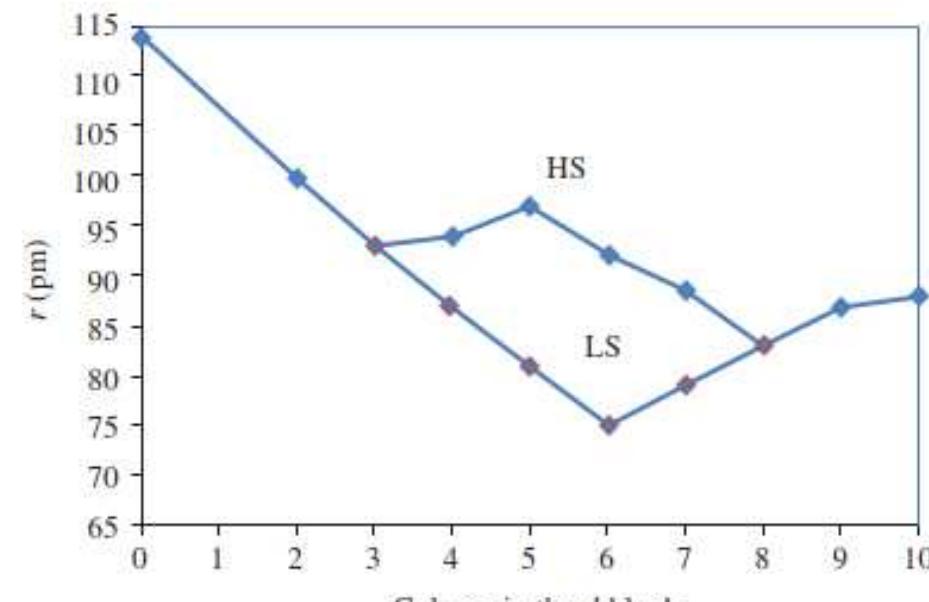


Figure 20.7 The hydration enthalpy of M^{2+} ions of the first row of the d block. The straight dotted lines show the trend when the crystal-field stabilization energy has been subtracted from the observed values.

Note the general trend to greater hydration enthalpy (more exothermic hydration) on crossing the period from left to right.

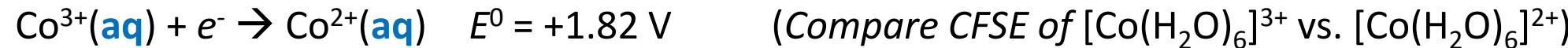
- With the advent of reliable X-ray crystallographic data, the **ionic radii** of the divalent and trivalent metal ions of the first transition series were reported by Shannon and Prewitt. In the case of coordination compounds having **LS** electron configurations, the **ionic radius decreases across the series as the t_{2g} set is filled until the d^6 electron configuration is reached**, as shown in Figure 16.12.
- The decrease across the row occurs (in part) because the **low-lying t_{2g} orbitals are somewhat bonding in nature**. Then, from d^7 to d^{10} , there is a gradual increase in the ionic radius as the higher lying, antibonding e_g set of orbitals is occupied. For the corresponding HS compounds, the radius decreases across the series until it reaches the d^3 configuration, where the t_{2g} orbitals are half-filled. The fourth and fifth electrons then occupy the antibonding e_g set and the ionic radius increases. It gradually decreases for d^6 – d^8 as the electrons again fill the more bonding t_{2g} level before finally increasing for d^9 and d^{10} as the e_g level is further occupied.

FIGURE 16.12. Ionic radii for divalent (a) and trivalent (b) first-row transition metal ions.
[Data were obtained from <http://www.webelements.com> (accessed March 29, 2014).]

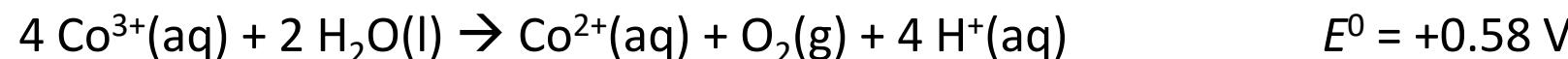


❖ Stabilization of Oxidation States

The standard electrode potential for the reduction of Co(III) to Co(II) is



This large positive value suggests that Co^{3+} (aq) is a strong oxidizing agent, strong enough to oxidize water to O_2 (g)



Yet one of the complex ions, $[\text{Co}(\text{NH}_3)_6]^{3+}$, is stable in water solution, even though it contains cobalt in the +3 oxidation state. But $[\text{Co}(\text{NH}_3)_6]^{2+}$ is easily oxidized to Co(III) complex. On the other hand, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is a stable complex.

This phenomenon can be explained as follows:

- Co^{2+} is a d^7 electron system whereas Co^{3+} is a d^6 one.
- **H_2O is a weak field ligand, and we expect a high spin (HS) complex** with it. The HS d-electron configuration for d^7 and d^6 are, respectively: $t_{2g}^5e_g^2$ and $t_{2g}^4e_g^2$. The crystal field stabilization energy (CFSE) is higher for $t_{2g}^5e_g^2$ configuration, i.e., d^7 and hence Co^{2+} is preferred for the ligand, H_2O .
- On the other hand, **NH_3 is a strong field ligand, and we expect a low spin (LS) complex** with it. The LS d-electron configurations for d^7 and d^6 are: $t_{2g}^6e_g^1$ and t_{2g}^6 respectively. The crystal field stabilization energy (CFSE) is higher for the t_{2g}^6 configuration, i.e., d^6 and hence Co^{3+} is preferred for the ligand, NH_3 .
- **The ability of a strong electron-pair donor** (strong Lewis base) to stabilize high oxidation states in the way that NH_3 does in Co(III) complexes and O^{2-} in Mn(VII) complexes (such as MnO_4^-) affords a means of attaining certain oxidation states that might otherwise be difficult or impossible to attain.

MAGNETIC MEASUREMENTS

Key points: *Magnetic measurements are used to determine the number of unpaired spins in a complex* and hence to identify its ground-state configuration. A spin-only calculation may fail for low-spin d⁵ and for high-spin 3d⁶ and 3d⁷ complexes.

The experimental distinction between high-spin and low-spin octahedral complexes is based on the determination of their magnetic properties. Compounds are classified as diamagnetic if they are repelled by a magnetic field and paramagnetic if they are attracted by a magnetic field. The two classes are distinguished experimentally by magnetometry. The *magnitude of the paramagnetism of a complex is commonly reported in terms of the magnetic dipole moment* it possesses: the higher the magnetic dipole moment of the complex, the greater the paramagnetism of the sample.

In a free atom or ion, both the orbital and the spin angular momenta give rise to a magnetic moment and contribute to the paramagnetism. The following formula for the magnetic moment (μ) of a molecule in Bohr magnetons is:

$$\mu_{\text{total}} = -[\{L(L + 1)\} + 4\{S(S + 1)\}]^{1/2} \mu_B$$

When *the atom or ion is part of a complex, any orbital angular momentum is normally quenched, or suppressed*, as a result of the interactions of the electrons with their nonspherical environment. However, if any electrons are unpaired, *the net electron spin angular momentum survives* and gives rise to **spin-only paramagnetism**, which is characteristic of many d-metal complexes. The spin-only magnetic moment, μ , of a complex with total spin quantum number S is:

$$\mu = 2\{S(S + 1)\}^{\frac{1}{2}} \mu_B \quad (20.1)$$

where μ_B is the Bohr magneton, $\mu_B = e\hbar/2m_e$ with the value 9.274×10^{-24} J T⁻¹. Because **S = N/2**, where *N is the number of unpaired electrons*, each with spin $s = 1/2$,

$$\mu = \{N(N + 2)\}^{\frac{1}{2}} \mu_B \quad (20.2)$$

- Based on Hund's rule, electrons occupy orbitals of equal energy one at a time. When all lower energy orbitals are half-filled,
- The next electron can enter a half-filled orbital and pair up by overcoming a repulsive pairing energy (E_{pairing}).
- The next electron can enter an empty, higher energy orbital by overcoming Δ (crystal field splitting energy).
- Thus, the relative sizes of E_{pairing} and Δ determine the occupancy of d orbitals, which determines the number of unpaired electrons and, thus, the magnetic behavior of the ion.
- A measurement of the magnetic moment of a d-block complex can usually be interpreted in terms of the number of unpaired electrons it contains, and hence it is possible to tell whether a complex is high or low spin by examining its magnetic behavior.
- For example, magnetic measurements on a d⁶ complex easily distinguish between a high-spin t_{2g}⁴ e_g² (N = 4, S = 2, $\mu = 4.90\mu_B$) configuration and a low-spin t_{2g}⁶ (N = 0, S = 0, $\mu = 0$) configuration.
- ✓ The high-spin complex [Fe(H₂O)₆]²⁺ has four unpaired electrons and is paramagnetic (*attracted by a magnet*), whereas the low-spin [Fe(CN)₆]⁴⁻ complex has no unpaired electrons and is diamagnetic (*repelled by a magnet*).

❖ **Test:** The magnetic moment of the complex $[\text{Mn}(\text{NCS})_6]^{4-}$ is $6.06 \mu_\text{B}$. What is its d-electron configuration?

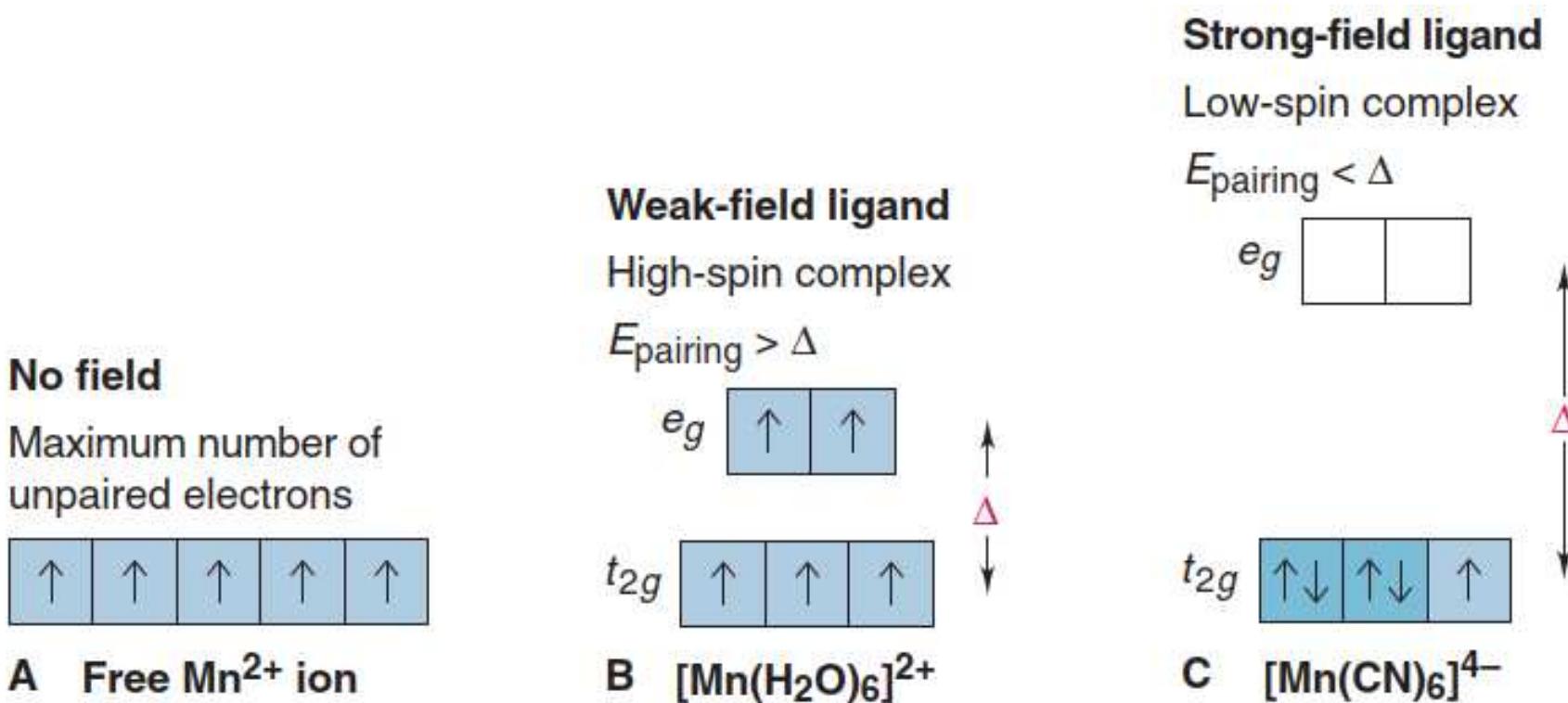


Figure 22.22 High-spin and low-spin octahedral complex ions of Mn^{2+} . A: Free Mn^{2+} has five unpaired electrons. B: Bonded to a weak-field ligand, Mn^{2+} still has five unpaired electrons (high-spin complex). C: Bonded to a strong-field ligand, Mn^{2+} has one unpaired electron (low-spin complex).

- The spin-only magnetic moments for some electron configurations are listed in Table 20.3 and compared there with experimental values for a number of 3d complexes.
- For most 3d complexes (and some 4d complexes), experimental values lie reasonably close to spin-only predictions, so it becomes possible to identify correctly the number of unpaired electrons and assign the ground-state configuration.
- For instance, $[\text{Fe}(\text{OH}_2)_6]^{3-}$ is paramagnetic with a magnetic moment of $5.9\mu_B$. As shown in Table 20.3, this value is consistent with there being five unpaired electrons ($N = 5$ and $S = 5/2$), which implies a high-spin $t_{2g}^3 e_g^2$ configuration.

Table 20.3 Calculated spin-only magnetic moments

Ion	Electron configuration	S	μ/μ_B Calculated	Experimental
Ti ³⁺	t_{2g}^1	$\frac{1}{2}$	1.73	1.7–1.8
V ³⁺	t_{2g}^2	1	2.83	2.7–2.9
Cr ³⁺	t_{2g}^3	$\frac{3}{2}$	3.87	3.8
Mn ³⁺	$t_{2g}^3 e_g^1$	2	4.90	4.8–4.9
Fe ³⁺	$t_{2g}^3 e_g^2$	$\frac{5}{2}$	5.92	5.9

Table 7.3 Calculated magnetic moments, in Bohr magnetons, of the ground states of some free transition-metal ions and the experimental magnetic moments for the octahedrally co-ordinated ions in their high-spin configurations

Ion	S	L	n	n'	μ_S	μ_{total}	μ_{exp}
Ti ³⁺	$\frac{1}{2}$	2	1	1	1.73	3.00	1.7 – 1.8 [†]
V ⁴⁺	$\frac{1}{2}$	2	1	1	1.73	3.00	1.7 – 1.8 [†]
V ³⁺	1	3	2	2	2.83	4.47	2.6 – 2.8 [†]
Cr ³⁺	$\frac{3}{2}$	3	3	3	3.87	5.20	3.7 – 3.9
Cr ²⁺	2	2	4	4	4.90	5.48	4.7 – 4.9
Mn ³⁺	2	2	4	4	4.90	5.48	4.9 – 5.0
Mn ²⁺	$\frac{5}{2}$	0	5	5	5.92	5.92	5.6 – 6.1
Fe ³⁺	$\frac{5}{2}$	0	5	5	5.92	5.92	5.7 – 6.0
Fe ²⁺	2	2	6	4	4.90	5.48	5.1 – 5.5 [†]
Co ³⁺	2	2	6	4	4.90	5.48	ca. 5.4 [†]
Co ²⁺	$\frac{3}{2}$	3	7	3	3.87	5.20	4.1 – 5.2 [†]
Ni ²⁺	1	3	8	2	2.83	4.47	2.8 – 3.5
Cu ²⁺	$\frac{1}{2}$	2	9	1	1.73	3.00	1.7 – 2.2

[†]The configurations marked † are those for which there can be an orbital contribution to the magnetic moment, see text. n = number of d electrons, n' = number unpaired.

H.L. Schläfer and G. Gliemann, *Basic Principles of Ligand Field Theory*. © 1969, John Wiley & Sons Ltd; reprinted with permission.

Q. Predict the number of unpaired spins in the $[\text{Cr}(\text{en})_3]^{2+}$ ion. Calculate magnetic moment.

Strategy The magnetic properties of a complex ion depend on the *strength of the ligands*. Strong-field ligands cause a high degree of splitting among the d orbital energy levels, resulting in low-spin complexes. Weak-field ligands, which cause a small degree of splitting among the d orbital energy levels, result in high-spin complexes.

Solution

The electron configuration of Cr^{2+} is $[\text{Ar}]3\text{d}^4$. Because *en is a strong-field ligand*, we expect $[\text{Cr}(\text{en})_3]^{2+}$ to be a low-spin complex. All four electrons will be placed in the lower-energy d orbitals (d_{xy}^2 , d_{yz}^1 , and d_{xz}^1) and there will be *two unpaired spins*.

- The *complex ion is diamagnetic*. Use *ideas from the crystal field theory to speculate on its probable structure*.

- The interpretation of magnetic measurements is sometimes less straightforward than the above examples might suggest.
- ✓ For example, the potassium salt of $[\text{Fe}(\text{CN})_6]^{3-}$ has $\mu = 2.3\mu_B$, which is between the spin-only values for one and two unpaired electrons ($1.7\mu_B$ and $2.8\mu_B$, respectively). In this case, the spin-only assumption has failed because the orbital contribution to the magnetic moment is substantial.

□ Optical Properties of Coordination Complexes

❖ A *solution of CuSO_4* (in fact, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$) appears *blue*. Why?

What Is Color?

White light consists of all wavelengths (λ) in the visible range and can be dispersed into colors of a narrower wavelength range.

Objects appear colored in white light because they absorb only certain wavelengths: an opaque object reflects the other wavelengths, and a clear one transmits them. If an object absorbs all visible wavelengths, it appears black; if it reflects all, it appears white.

Each color has a complementary color; for example, green and red are complementary colors. Figure 22.15 shows these relationships on an artist's color wheel in which complementary colors are wedges opposite each other. *A mixture of complementary colors absorbs all visible wavelengths and appears black.*

An object has a particular color for one of two reasons:

- It **reflects** (or **transmits**) light of that color. Thus, if an object absorbs all wavelengths except green, the reflected (or transmitted) light is seen as green.
- It **absorbs** light of the *complementary color*. Thus, if the object absorbs only red, the complement of green, the remaining mixture of reflected (or transmitted) wavelengths is also seen as green.

❖ A solution of $CuSO_4$ appears blue to us. Why?

❖ Consider the hydrated cupric ion, $[Cu(H_2O)_6]^{2+}$, which *absorbs light in the orange region of the spectrum so that a solution of $CuSO_4$ appears blue to us.*

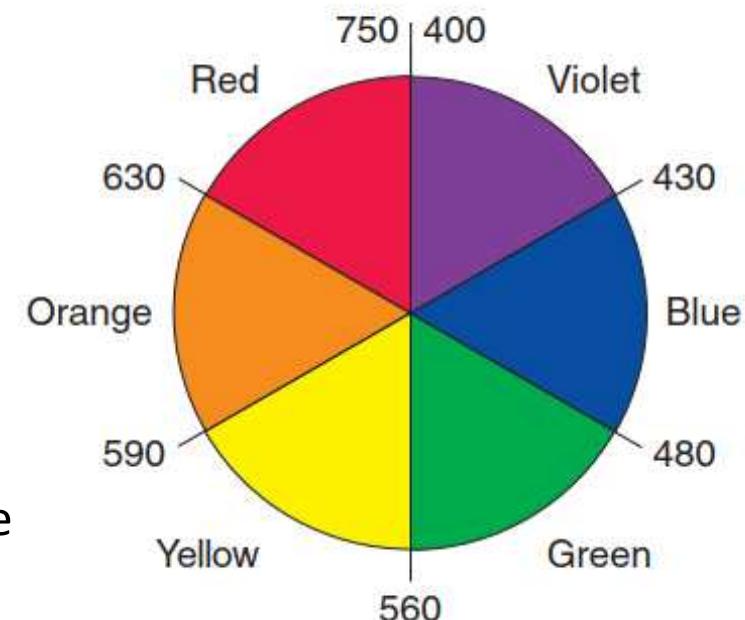


Figure 22.15 An artist's wheel. Colors, with approximate wavelength ranges (in nm), are shown as wedges.

Table 22.9 lists the color absorbed and the resulting color observed.

Table 22.9 Relation Between Absorbed and Observed Colors

Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

Optical Properties of Coordination Complexes

❖ THE ELECTRONIC SPECTROSCOPY OF TRANSITION-METAL COMPLEXES

- No account of the theory of the transition-metal ions would be complete without some reference to their electronic spectroscopy.
- But this is a vast and complicated subject which is well treated in a number of specialist volumes and here we can only draw attention to a few significant points.
- We have been drawn into consideration of electronic spectra because *spectral data provide the most direct way of determining the crystal field splitting, Δ , (d-orbital splitting) energy, the essential parameters of the CF model.*
- A d-to-d ($d \rightarrow d$) transition must occur for a transition metal complex to show color. Therefore, *ions with d^0 or d^{10} electron configurations are usually colorless.*
- ✓ Compare the colors of aq. CuSO_4 and aq. ZnSO_4 . Explain the origin of the difference.

❖ Explaining the Colors of Transition Metal Complexes:

- The color of a coordination compound is determined by Δ of its complex ion. When the ion absorbs radiant energy, electrons can move from the lower energy level to the higher energy level (say, t_{2g} to e_g). Recall that the ***difference between two energy levels is equal to the energy (and inversely related to the wavelength) of the absorbed photon:***

$$\Delta E_{\text{electron}} = E_{\text{photon}} = h\nu = hc/\lambda$$

- Consider the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion, which appears **purple** in aqueous solution (Figure 22.19, see below).
- Hydrated Ti^{3+} has its ***one d electron*** in one of the three lower energy t_{2g} orbitals.
- The energy difference (Δ) between the t_{2g} and e_g orbitals in this ion corresponds to photons between the green and yellow range. When white light shines on the solution, these colors of light are absorbed, and the electron jumps to one of the e_g orbitals.
- Red, blue, and violet light are transmitted, so the solution appears purple.

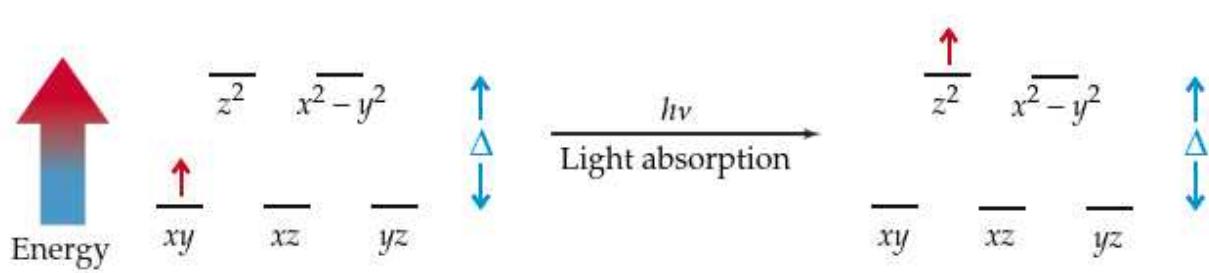
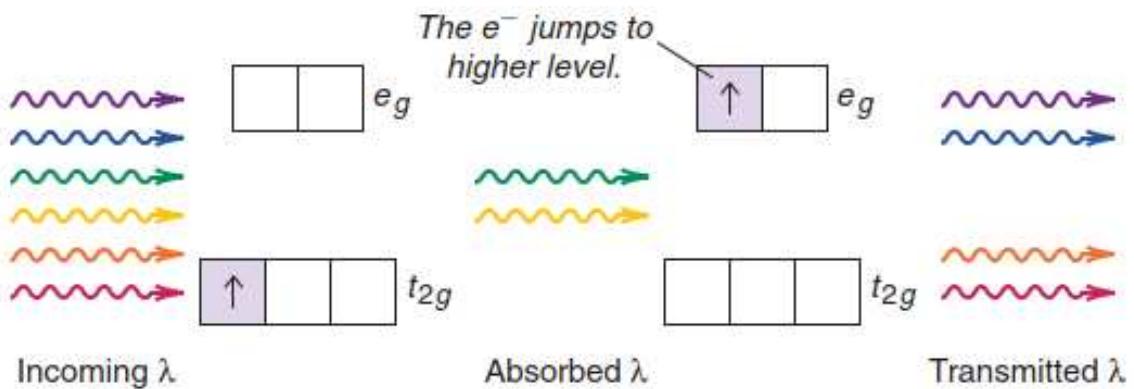
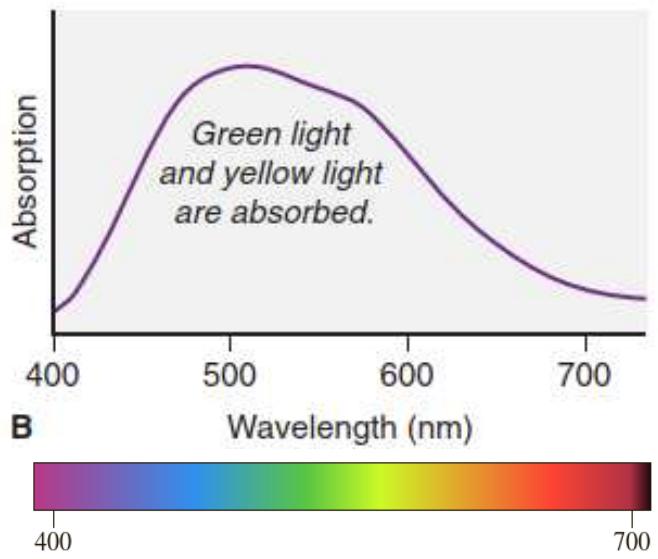


Figure 22.19 The color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

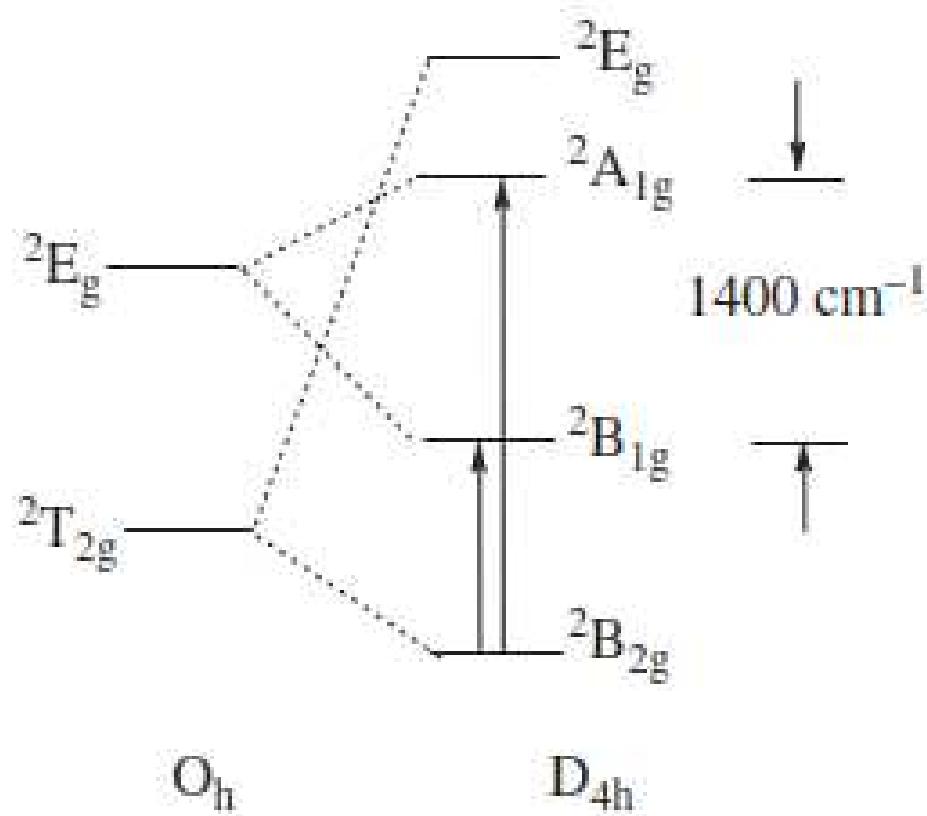
A: The hydrated Ti^{3+} ion shows purple color.

B: An absorption spectrum shows that **green light** and **yellow light** are absorbed and other wavelengths are transmitted.

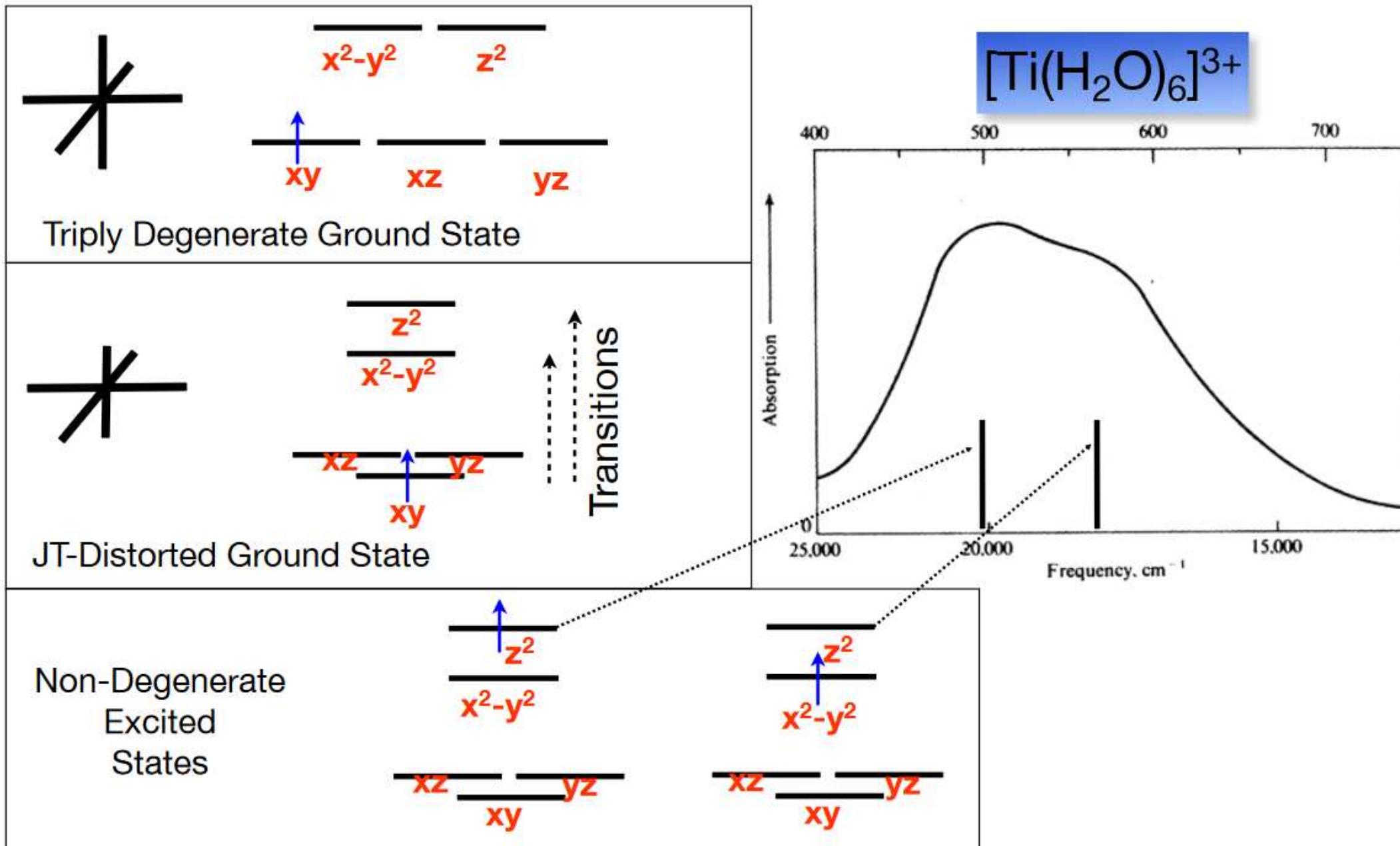
C: The process of photon absorption. An orbital diagram depicts the light colors absorbed when the d electron jumps to the higher level when the energy of the incoming photon is equal to the crystal field splitting. The **maximum absorption peak** in the visible region occurs at $\sim 498 \text{ nm}$.

- The electronic spectrum of this d¹ coordination compound is ***expected*** to have ***a single LF transition*** in the absence of Jahn–Teller splitting.
- In fact, the spectrum of the [TiCl₆]³⁻ ion consists of ***two closely spaced peaks*** separated by approximately 1400cm⁻¹.
- As a result of the tetragonal distortion, the symmetry of the complex is lowered from O_h to D_{4h}.
- The separation of these peaks by 1400cm⁻¹ implies that the magnitude of δ_2 is also 1400cm⁻¹.

FIGURE 16.51. Splitting of the terms for a d¹ [TiCl₆]³⁻ ion as it undergoes a tetragonal distortion from octahedral symmetry, illustrating the two observed spin-allowed transitions for the complex.
(Note: not drawn to scale.)



The Jahn-Teller Effect: An Example



- The best way to measure crystal field splitting is to use spectroscopy to determine the wavelength at which light is absorbed. The $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion provides a straightforward example, because Ti^{3+} has only one 3d electron (Figure 20.14). The $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion absorbs light in the visible region of the spectrum (Figure 20.15). The wavelength corresponding to maximum absorption is 498 nm [Figure 20.14(b)]. This information enables us to calculate the crystal field splitting as follows. We start by writing:

$$\Delta = h\nu$$

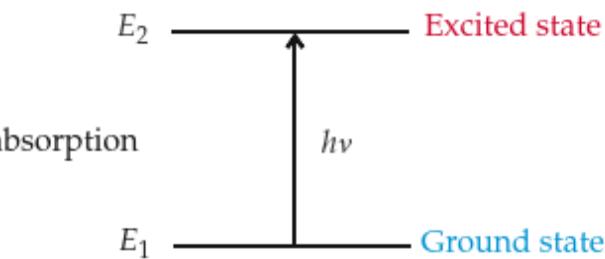
(20.1)

Also

$$\nu = \frac{c}{\lambda}$$

where c is the speed of light and λ is the wavelength. Therefore,

$$\begin{aligned}\Delta &= \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(498 \text{ nm})(1 \times 10^{-9} \text{ m}/1 \text{ nm})} \\ &= 3.99 \times 10^{-19} \text{ J}\end{aligned}$$



Equation (7.3) shows that $E = hc/\lambda$.

This is the energy required to excite *one* $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion. To express this energy difference in the more convenient units of kilojoules per mole, we write

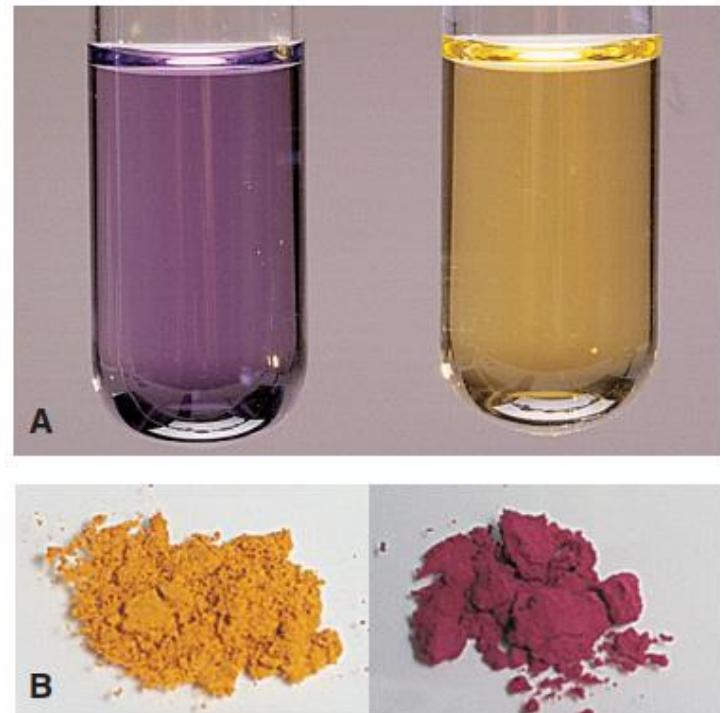
$$\begin{aligned}\Delta &= (3.99 \times 10^{-19} \text{ J/ion})(6.02 \times 10^{23} \text{ ions/mol}) \\ &= 240,000 \text{ J/mol} \\ &= 240 \text{ kJ/mol}\end{aligned}$$

- Absorption spectra can show the wavelengths absorbed by: (1) a metal ion with different ligands and (2) different metal ions with the same ligand.
- Such data allow us to relate the energy of the absorbed light to Δ and make two key observations:
 - **For a given ligand, color depends on the oxidation state of the metal ion.** In Figure 22.20A, aqueous $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (left) is violet and $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (right) is yellow.
 - **For a given metal ion, color depends on the ligand.** A single ligand substitution can affect the wavelengths absorbed and, thus, the color (Figure 22.20B).

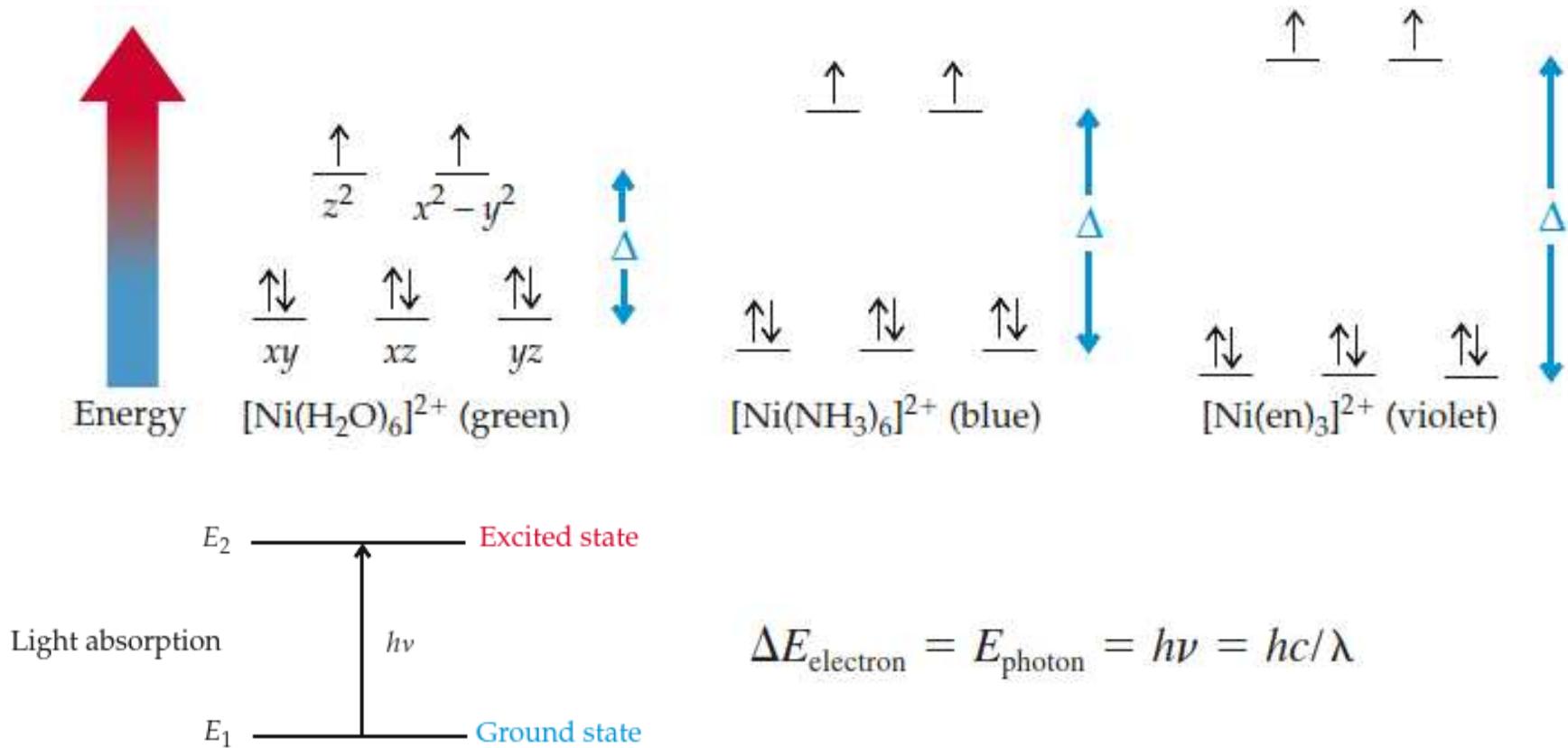
Figure 22.20 Effects of *oxidation state* and *ligand* on color.

A: Solutions of two hydrated vanadium ions: O.N. of V is +2 (left); O.N. of V is +3 (right).

B: A change in one *ligand can influence the color*. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is yellow (left), and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ is purple (right).



➤ The absorption spectra of different complexes indicate that the *size of the crystal field splitting depends on the nature of the ligands*. For example, Δ for Ni^{2+} ($[\text{Ar}] \ 3\text{d}^8$) complexes increases as the ligand varies from H_2O to NH_3 to ethylenediamine (en). Accordingly, the electronic transitions shift to higher energy (shorter wavelength) as the ligand varies from H_2O to NH_3 to en, thus accounting for the observed variation in color (Figure 20.24):



Δ increases, shorter wavelengths (higher energies)

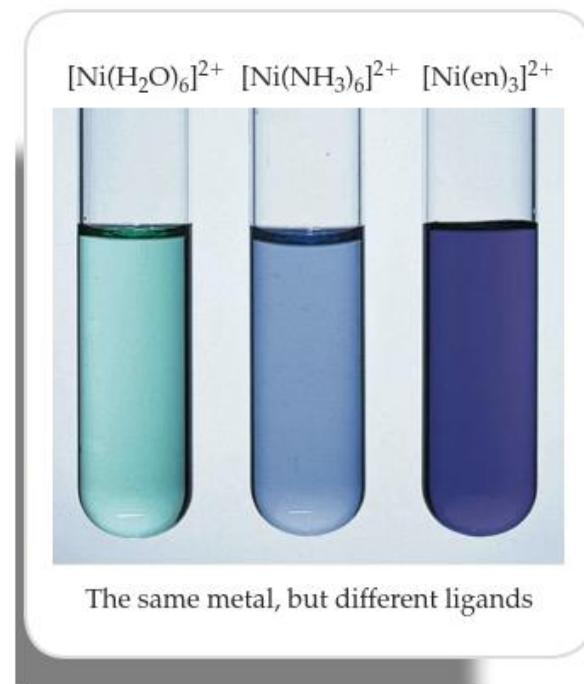


FIGURE 20.24

Aqueous solutions that contain $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, and $[\text{Ni}(\text{en})_3]^{2+}$.

The Spectrochemical Series:

- The fact that *color depends on the ligand allows us to create a spectrochemical series*, which ranks the ability of a ligand to split d-orbital energies (Figure 22.21). Using this series, we can predict the relative magnitude of Δ for a series of octahedral complexes of a given metal ion.
- ✓ Although we cannot predict the actual color of a given complex, we can determine whether a complex will absorb longer or shorter wavelengths than other complexes in the series.

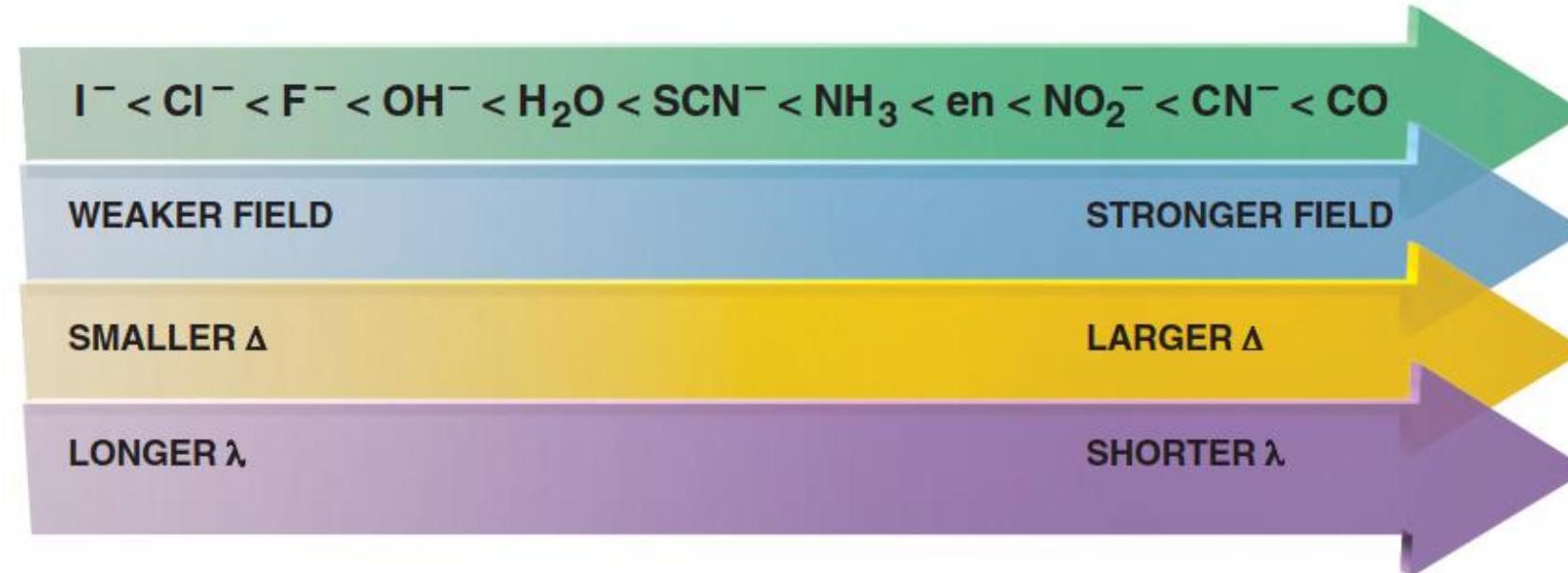


Figure 22.21 The spectrochemical series. As Δ increases, shorter wavelengths (higher energies) of light must be absorbed to excite electrons. For reference, water is a weak-field ligand.

Ranking Crystal Field Splitting Energies (Δ) for Complex Ions of a Metal

Problem Rank $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Ti}(\text{CN})_6]^{3-}$, and $[\text{Ti}(\text{NH}_3)_6]^{3+}$ in terms of Δ and of the energy of visible light absorbed.

Plan The formulas show that Ti has an oxidation state of +3 in the three ions. From Figure 22.21, we rank the ligands by crystal field strength: the stronger the ligand, the greater the splitting, and the higher the energy of light absorbed.

Solution The ligand field strength is in the order $\text{CN}^- > \text{NH}_3 > \text{H}_2\text{O}$, so the relative size of Δ and energy of light absorbed is



FOLLOW-UP PROBLEM 22.4 Which complex ion absorbs visible light of higher energy, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{V}(\text{NH}_3)_6]^{3+}$?

❖ REVIEW OF CONCEPTS

The Cr^{3+} ion forms octahedral complexes with two neutral ligands X and Y. The color of $[\text{CrX}_6]^{3+}$ is blue while that of $[\text{CrY}_6]^{3+}$ is yellow. Which is a stronger field ligand?

Q. The color of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ is violet whereas that of $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is yellow. Explain this difference in color.

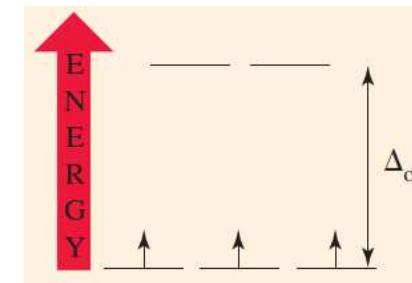
....Both chromium(III) complexes are octahedral, and the electron configuration of Cr^{3+} is $[\text{Ar}]d^3$. From these facts, we can construct the energy-level diagram shown here. The three unpaired electrons go into the three lower-energy d orbitals. When a photon of light is absorbed, an electron is promoted from a d orbital of lower energy to a d orbital of higher energy. The quantity of energy required for this promotion depends on the energy level separation, Δ_o .

According to the spectrochemical series, NH_3 produces a greater splitting of the d energy level than does H_2O .

We should expect $[\text{Cr}(\text{NH}_3)_6]^{3+}$ to absorb light of a shorter wavelength (higher energy) than does $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

Thus, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ absorbs in the violet region of the spectrum, and the transmitted light is yellow.

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ absorbs in the yellow region of the spectrum, and the transmitted light is violet.



If we measure the wavelength, λ , of the photon absorbed, we can then calculate the splitting energy, $\Delta_o = hc/\lambda$. Stronger field ligands increase the magnitude of Δ_o therefore, shorter wavelengths of light are absorbed and longer wavelengths are transmitted.

PRACTICE Example: The color of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is pink, whereas that of tetrahedral $[\text{CoCl}_4]^{2-}$ is blue. Explain this difference in color.

❖ Charge-Transfer Color

The CF model is concerned solely with the energies of the d-electron states but the intense colors of many transition-metal complexes, e.g., the purple color of $[\text{MnO}_4]^-$ and the blood red of $[\text{Fe}(\text{CNS})_6]^{3-}$, arise **not from** $\text{d} \rightarrow \text{d}$ transitions, which as we have seen above are normally very weak, but from ***charge-transfer transitions in which electrons are transferred from the ligands to the metal (LMCT)***.

$[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ shows a strong absorption at 522 nm due to the reverse process, a ***metal-to-ligand charge transfer (MLCT)***.

Transitions of this type are further evidence of covalency and require a molecular orbital treatment for their quantitative understanding.



KMnO_4



K_2CrO_4



KClO_4

Figure 23.35 The colors of compounds can arise from charge-transfer transitions. KMnO_4 and K_2CrO_4 are colored due to ligand-to-metal charge-transfer transitions in their anions. Higher energy ultraviolet photons are needed to excite the charge-transfer transition in the perchlorate ion, therefore KClO_4 is white.

- You have probably seen many colorful transition-metal compounds, including those shown in Figure 23.35. Many of these compounds are colored because of d-d transitions.
- Some colored complexes, however, including the violet permanganate ion, MnO_4^- , and the yellow chromate ion, CrO_4^{2-} , derive their color from a different type of excitation involving the d orbitals.
- A complex may absorb radiation as a result of the ***transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa***. This mode of chromophore activity is shown by the permanganate ion, MnO_4^- , and accounts for its intense violet color. In this oxoanion, the electron migrates from an orbital that is largely confined to the O atom ligands to an orbital that is largely confined to the Mn atom. It is therefore an example of a **ligand-to-metal charge-transfer transition (LMCT)**.
- The reverse migration, a **metal-to-ligand charge-transfer transition (MLCT)**, can also occur. An example is the transfer of a d electron into the antibonding π orbitals of an aromatic ligand. The resulting excited state may have a very long lifetime if the electron is extensively delocalized over several aromatic rings, and such species can participate in photochemically induced redox reactions.

- The permanganate ion strongly absorbs visible light (which arises from strong absorption within the range of 420–700 nm), with maximum absorption at 565 nm. Because violet is complementary to yellow, this strong absorption in the yellow portion of the visible spectrum is responsible for the violet color of salts and solutions of the ion.
- ✓ What is happening during this absorption of light?
- ✓ The MnO_4^- ion is a complex of Mn(VII). Because **Mn(VII)** has a $[\text{Ar}]3\text{d}^0$ electron configuration, the absorption cannot be due to a d-d transition because **there are no d electrons to excite!**
- ✓ That does not mean, however, that the d orbitals are not involved in the transition. The excitation in the MnO_4^- ion is due to a **charge-transfer transition, in which an electron on one oxygen ligand is excited into a vacant d orbital on the Mn ion** (Figure 23.36).
- ✓ In essence, an electron is transferred from a ligand to the metal, so this transition is called a **ligand-to-metal charge-transfer (LMCT) transition**.
- ✓ An LMCT transition is also responsible for the color of the CrO_4^{2-} , which contains the Cr(VI) ion with an $[\text{Ar}]3\text{d}^0$ electron configuration.

- Also shown in Figure 23.35 is a salt of the perchlorate ion (ClO_4^-). Like MnO_4^- , ClO_4^- is tetrahedral and has its central atom in the +7 oxidation state. However, because the Cl atom ***does not have low-lying d orbitals***, exciting an electron from O to Cl requires a more energetic photon than does it does in MnO_4^- . The first absorption for ClO_4^- is in the ultraviolet portion of the spectrum, so no visible light is absorbed and the salt appears white.

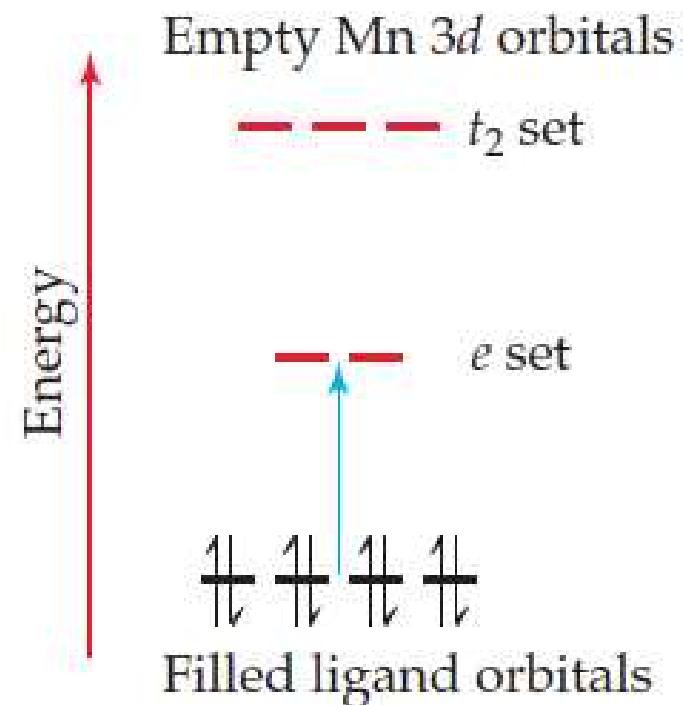


Figure 23.36 Ligand-to-metal charge-transfer transition in MnO_4^- . As shown by the blue arrow, an electron is excited from a nonbonding orbital on O into one of the empty d orbitals on Mn.

- Other complexes exhibit charge-transfer excitations in which an electron from the metal atom is excited to an empty orbital on a ligand. Such an excitation is called a **metal-to-ligand charge-transfer (MLCT)** transition.
 - Lastly, **metal-to-metal charge-transfer (MMCT)** bands occur between metal-centered orbitals on two different metals within the same complex, such as those in Prussian blue. In the case of mixed-valence compounds, one of the metals must be in a low oxidation state so that it can act as an electron donor, while the other metal exists in a high oxidation state and acts as the electron acceptor.
- ✓ Prussian blue is a coordination compound containing both iron(II) and iron(III) linked together by cyanide ligands ($\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$).
- ***Charge-transfer transitions are generally more intense than d-d transitions.***
 - Many metal-containing pigments used for oil painting, such as cadmium yellow (CdS), chrome yellow (PbCrO_4), and red ochre (Fe_2O_3), have intense colors because of ***charge-transfer transitions***.

- **Spectroscopic selection rules** say that *transitions between states of the same parity (such as d → d) are strictly forbidden; the Laporte rule.*
- ✓ The fact that these $d \rightarrow d$ bands, though rather weak, are indeed observed is due to the loss of parity which can arise in either a static or a dynamic manner. *If the ligand environment is not strictly octahedral*, e.g., because of a slight static distortion, then the center of symmetry of the complex as a whole may be lost, and with it the definitive even parity of the d orbitals and states.
- ✓ A $d \rightarrow d$ transition may then become weakly allowed, frequently because the lowered symmetry allows p and d orbitals to mix. This is particularly true of *tetrahedral complexes*.
- ✓ *The tetrahedron has no center of symmetry and the $d \rightarrow d$ transitions of tetrahedral complexes are invariably more intense than those of their octahedral counterparts.*
- ✓ The *loss of symmetry* need not be permanent and static; *vibrations* can have the same effect of making a transition partially allowed.
- ✓ Further, allowed transitions occur between states of the same multiplicity, say, singlet to singlet or triplet to triplet. *$d \rightarrow d$ transitions which involve a change of multiplicity, say, triplet to singlet, are doubly forbidden* and are very weak indeed. But as *spin-orbit coupling* grows in the 4d and 5d series of metals, and especially in the rare earths, nominally spin-forbidden transitions gain in intensity because of the loss of a clearly defined multiplicity for each state.

The **Laporte selection rule** for centrosymmetric molecules (those with a center of inversion) and atoms states that:
The only allowed transitions are transitions that are accompanied by a change of parity.
That is, $u \rightarrow g$ and $g \rightarrow u$ transitions are allowed, but $g \rightarrow g$ and $u \rightarrow u$ transitions are **forbidden**.

According to the Laporte rule (Section 11.3), d-d transitions are parity-forbidden in octahedral complexes because they are $g \rightarrow g$ transitions (more specifically $e_g - t_{2g}$ transitions). However, d-d transitions become **weakly allowed** as vibronic transitions as a result of coupling to asymmetrical vibrations such as that shown in Fig. 11.7.

In charge-transfer transitions the **electron moves through a considerable distance** (the transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa), which means that the **transition dipole moment may be large** and the **absorption is correspondingly intense**.

The **intensities of charge-transfer transitions are proportional to the square of the transition dipole moment**, in the usual way. We can think of the transition moment as a measure of the distance moved by the electron as it migrates from metal to ligand or vice versa, with a large distance of migration corresponding to a large transition dipole moment and therefore a high intensity of absorption.

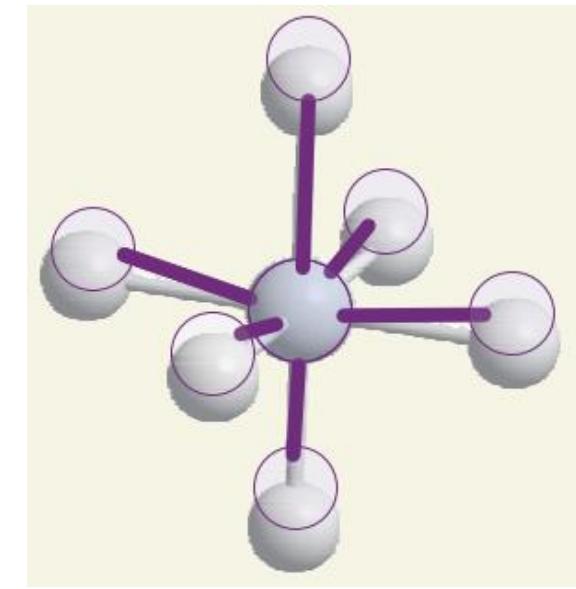


Fig. 11.7 A d-d transition is parity-forbidden because it corresponds to a $g-g$ transition. However, a vibration of the molecule can destroy the inversion symmetry of the molecule and the g,u classification no longer applies. The removal of the centre of symmetry gives rise to a vibronically allowed transition.

One can thus only expect absorption or emission of light by molecules that possess a dipole momentum. Typically, these will be permanent dipoles, but in some applications dipoles may also be induced in molecules that have no permanent dipole momentum.

Chromophores are the light absorbing moieties within a molecule. Due to differences in electronegativity between individual atoms, they possess a spatial distribution of electric charge. This results in a dipole momentum $\vec{\mu}_0$ (ground state), such as for example the permanent dipole momentum of a carboxylic acid or an amide group.

When light is absorbed by the chromophore, the distribution of electric charge is altered and the dipole momentum changes accordingly ($\vec{\mu}_1$; excited state). The transition dipole momentum $\vec{\mu}_{01}$ is the vector difference between the dipole momentum of the chromophore in the ground and the excited state. ***This transition dipole momentum is a measure for transition probability***, and its dipole strength, D_{01} , is defined as the squared length of the transition dipole momentum vector:

$$D_{01} = |\vec{\mu}_{01}|^2$$

The strength of this transition dipole momentum is directly related to the probability with which a transition occurs, i.e. the strength of an absorption band.

Spectroscopic data can thus be analyzed to obtain numerical values for a transition dipole momentum which connects the absorption spectrum to the quantum mechanical wave function of a molecule.

☐ Ligand Field Theory: Why?

- Properties such as the absorption of visible light due to d-d-transitions and magnetic susceptibility of metal complexes can be macroscopically observed, and the crystal field theory delivers predictions that are in good agreement with macroscopic observations for some complexes.
- Crystal-field theory provides a simple conceptual model that can be used to interpret magnetic, spectroscopic, and thermochemical data by using empirical values of Δ_0 .
- Crystal field theory is based on a very primitive model of bonding. For example, *the theory treats ligands as point charges or dipoles, but ligands are not point charges*: they are actual molecules or ions.
- The theory ***does not take into account the overlap of ligand and metal-atom orbitals. It only considers the electrostatic interactions between metal and ligands and ignores any covalent character of metal-ligand bonds.***
- *You may have noticed that the ligand orbitals are not actually featured in the discussion. Further, the theory leaves several questions unanswered.*

- *The crystal-field theory cannot account for the ligand spectrochemical series.*
- Why, for instance, is the electrically neutral molecule CO a strong-field ligand but the negatively charged ion Cl⁻ a weak-field ligand?
- To improve the model of bonding in complexes, chemists have turned to *molecular orbital theory*.
- **Ligand field theory** describes bonding in complexes in terms of molecular orbitals built from the metal atom d-orbitals and ligand orbitals.
- In contrast to crystal field theory, which models the structure of the complex in terms of point charges, **ligand field theory assumes, more realistically, that ligands are attached to the central metal atom or ion by covalent bonds.**
- As we shall see, much of the work that we have done in connection with crystal field theory can be transferred into ligand field theory: ***the principal difference is the origin of the ligand field splitting.***
- **Ligand-field theory**, which is an application of **molecular orbital theory** that concentrates on the d orbitals of the central metal atom, provides a more substantial framework for understanding the origins of Δ_0 .

- The ligand field theory overcomes several defects by taking into account **covalent contributions** of metal-ligand interactions.
- To describe the electronic structure of a complex, first we set up molecular orbitals from the available atomic orbitals in the complex, just as we would for a molecule.
- The ***d* orbitals that do not extend into the direction of the coordinated ligands** are now deemed to not take part in bond formation and thus called **non-bonding orbitals**.
- Accordingly, their energy does not change as compared to the set of degenerate *d* orbitals in the free metal ion.
- Notice that the **t_{2g} -orbitals** on the metal atom have no partners among the ligands in octahedral environment. There are simply no ligand orbitals to match them. Therefore, these three orbitals are **nonbonding orbitals** in the complex.

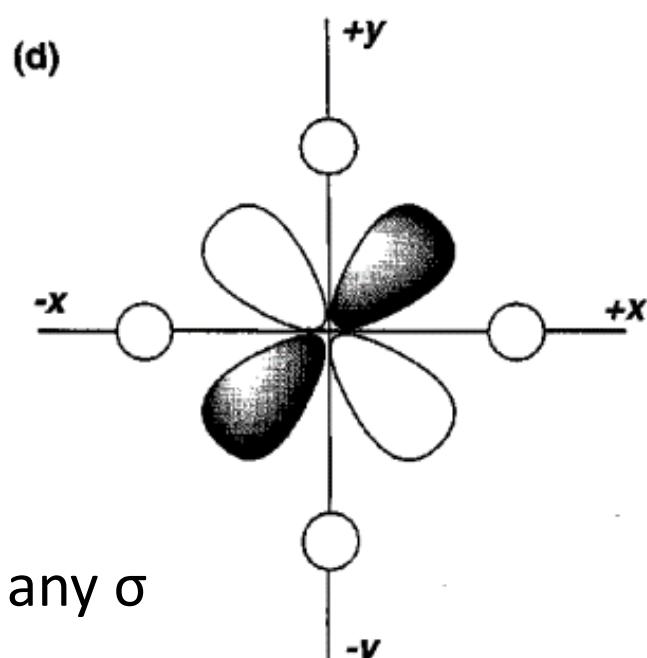


FIG. 13. 6 Fig. (d) shows how the d_{xy} orbital is wrongly aligned to form any σ bond; the other two t_{2g} orbitals are similarly nonbonding.

- The strategy for describing the molecular orbitals of a d-metal complex follows procedures similar to those described earlier for bonding in polyatomic molecules: the valence orbitals on the metal and ligand are used to form *symmetry-adapted* linear combinations (SALCs) and then the relative energies of the molecular orbitals are estimated by using empirical energy and overlap considerations. These relative energies can be verified and positioned more precisely by comparison with experimental data (particularly UV-visible absorption and photoelectron spectroscopy).
- Here we shall first consider octahedral complexes, initially taking into account only the ***metal–ligand σ bonding***.
- We then consider the ***effect of π bonding*** and see that it is *essential for understanding* Δ_o (which is one reason why crystal-field theory cannot explain the spectrochemical series).

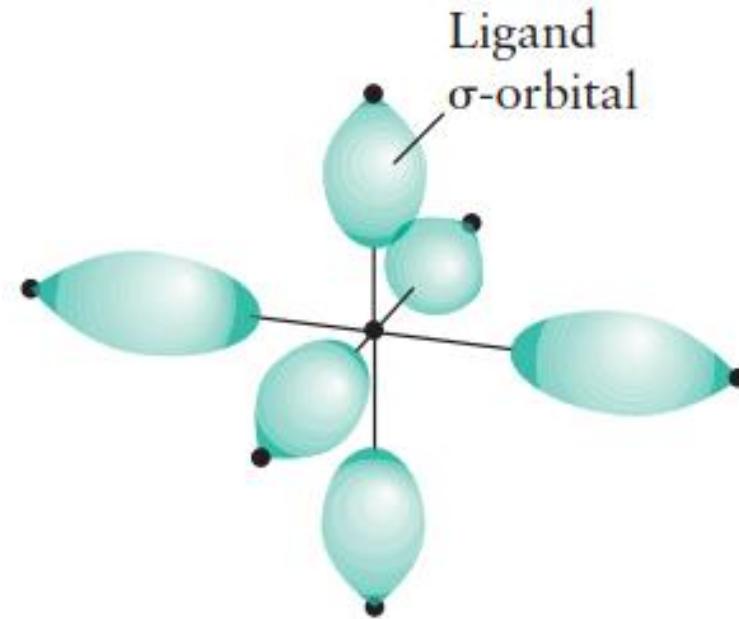
❖ σ Bonding

- We begin by considering an octahedral complex in which each ligand (L) has a single valence orbital directed towards the central metal atom (M); each of these orbitals has local σ symmetry with respect to the M–L axis. Examples of such ligands include the NH_3 molecule and the F^- ion.
- In an octahedral (O_h) environment, the orbitals of the central metal atom divide by symmetry into four sets:

Metal orbital	Symmetry label	Degeneracy
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
$d_{x^2-y^2}, d_{z^2}$	e_g	2
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3

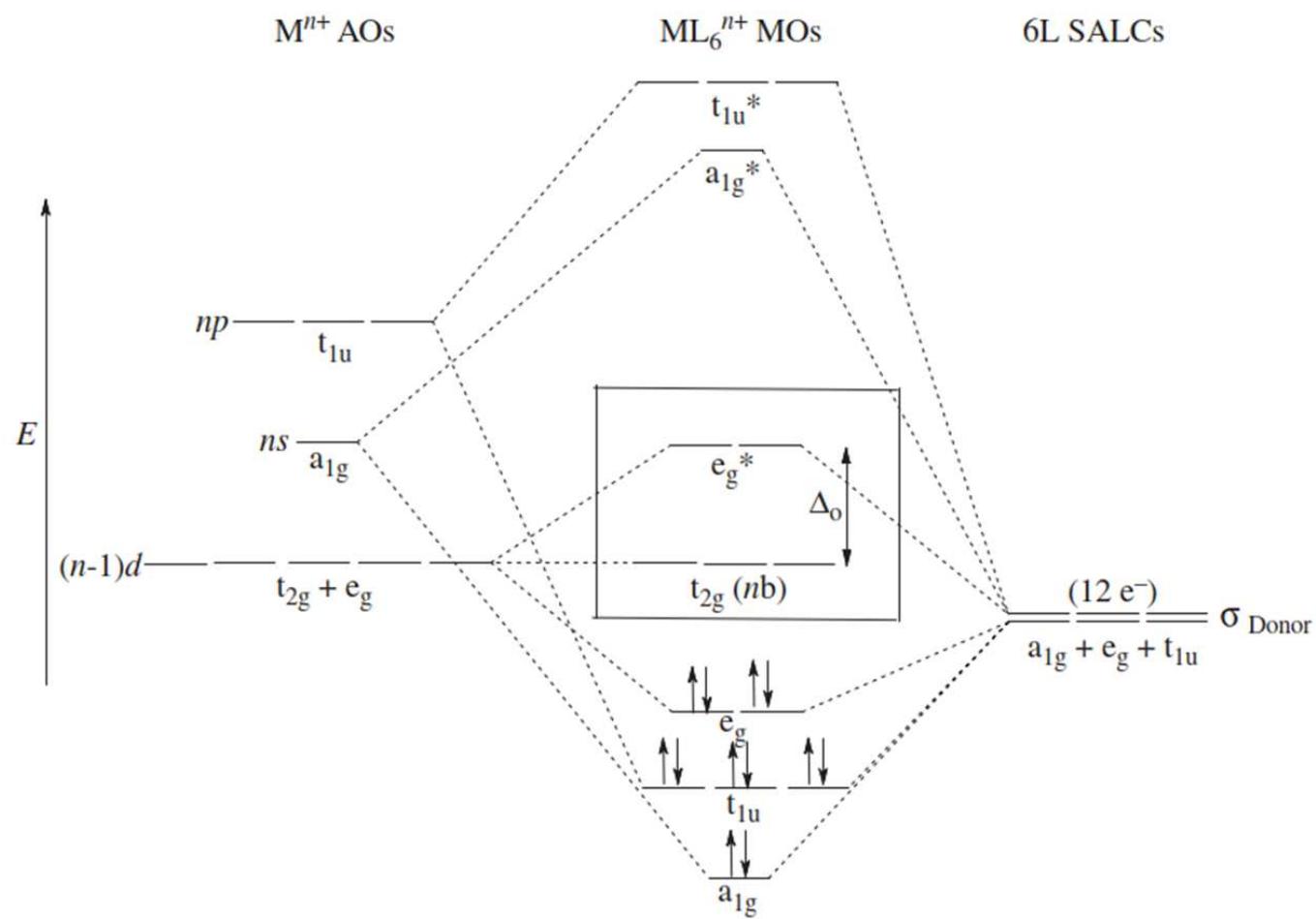
- Consider an octahedral complex of a d-metal in Period 4, such as iron, cobalt, or copper.
- We need to *consider the nine 4s-, 4p-, and 3d-orbitals of the central metal ion, because all these orbitals have similar energies*.
- To simplify the discussion, we *use only one atomic orbital on each of the ligands*. For instance, for a Cl⁻ ligand, we use the Cl 3p-orbital directed toward the metal atom; for an NH₃ ligand, we use the *sp*³ lone-pair orbital of the nitrogen atom.
- ✓ The *six orbitals provided by the six ligands in an octahedral complex* are represented by the tear-shaped lobes in Fig. 16.36. Each of these orbitals has cylindrical symmetry around the metal–ligand axis, so each can form a σ-orbital.

FIGURE 16.36 The tear-shaped objects are representations of the six ligand atomic orbitals that are used to build the molecular orbitals of an octahedral complex in ligand field theory. They might represent s- or p-orbitals on the ligands or hybrids of the two.



- Molecular orbitals are formed by combining SALCs and metal-atom orbitals of the same symmetry. For example, the (unnormalized) form of an a_{1g} molecular orbital is $c_M \psi_{Ms} + c_L \psi La_{1g}$, where ψ_{Ms} is the s orbital on the metal atom M and ψLa_{1g} is the ligand SALC of symmetry a_{1g} .
- ✓ The metal s orbital and ligand a_{1g} SALC overlap to give two molecular orbitals, one bonding and one antibonding.
- ✓ Similarly, the doubly degenerate metal e_g orbitals and the ligand e_g SALCs overlap to give four molecular orbitals (two degenerate bonding, two degenerate antibonding),
- ✓ and the triply degenerate metal t_{1u} orbitals and the three t_{1u} SALCs overlap to give six molecular orbitals (three degenerate bonding, three degenerate antibonding).
- ✓ ***There are therefore six bonding combinations in all and six antibonding combinations.***
- ✓ The *three triply degenerate metal t_{2g} orbitals remain nonbonding and fully localized on the metal atom.*
- ✓ Calculations of the resulting energies (adjusted to agree with a variety of spectroscopic data) result in the molecular orbital energy-level diagram shown in Fig. 16.19.

- There are *nine valence orbitals on the metal atom* (one *s* + three *p* + five *d* orbitals) and *six on the ligands* (one each from six ligands), giving 15 in all.
- We can therefore expect to find 15 molecular orbitals: it turns out, as we have explained above, that *six are bonding, six are antibonding, and three are nonbonding*.
- The energies of all 15 are displayed in Fig..., together with the labels that they are commonly given.



➤ Employing the usual group theoretical approach, the symmetries of the metal ion valence orbitals are listed on the left-hand side of the diagram and their Mulliken symbol designations are determined from the way in which each of the AOs transforms in the O_h point group. Thus, the lower lying d-orbitals transform as $e_g + t_{2g}$, the s-orbital as the spherically symmetric a_{1g} , and the higher lying p-orbitals as the triply degenerate t_{1u} set.

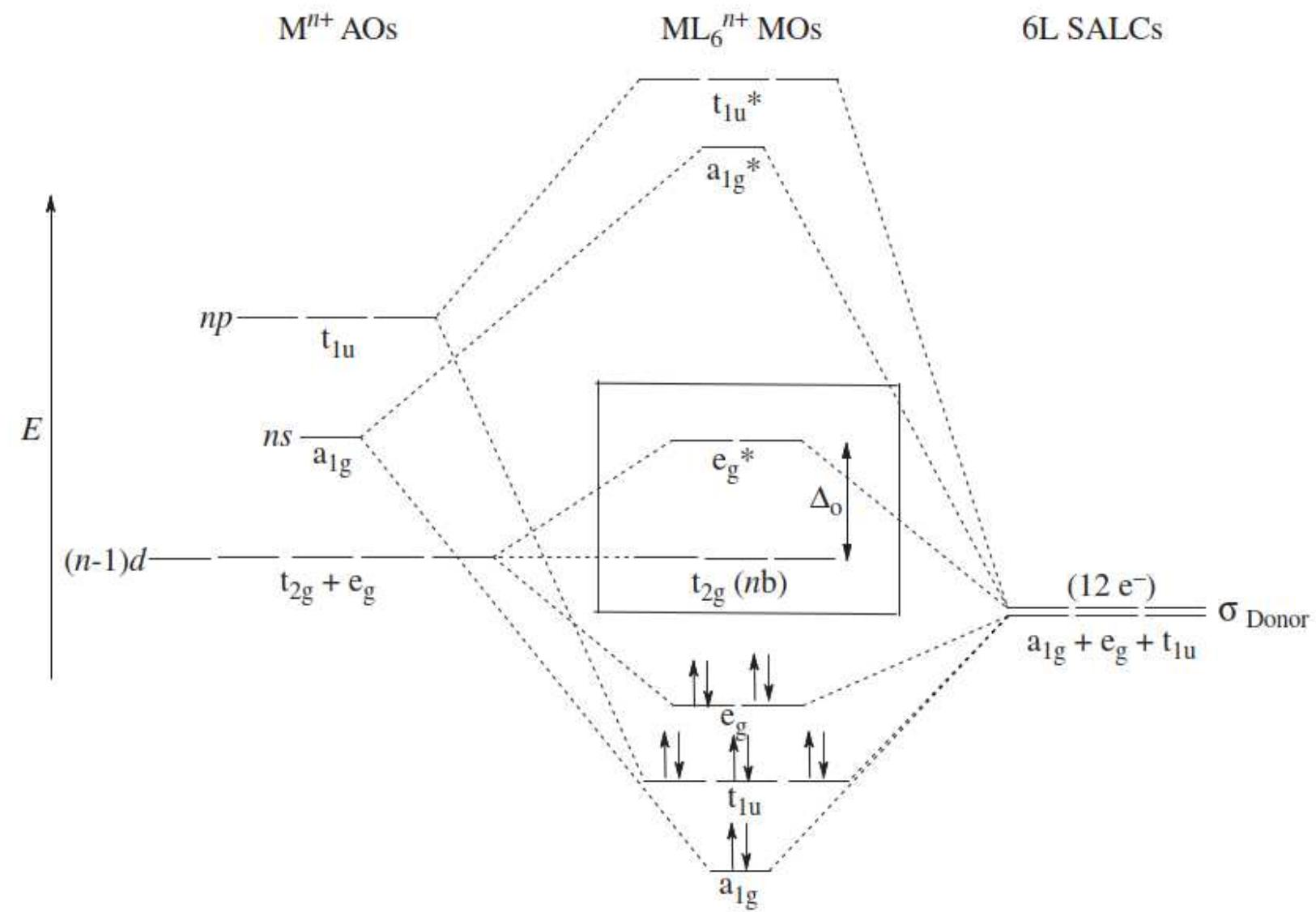
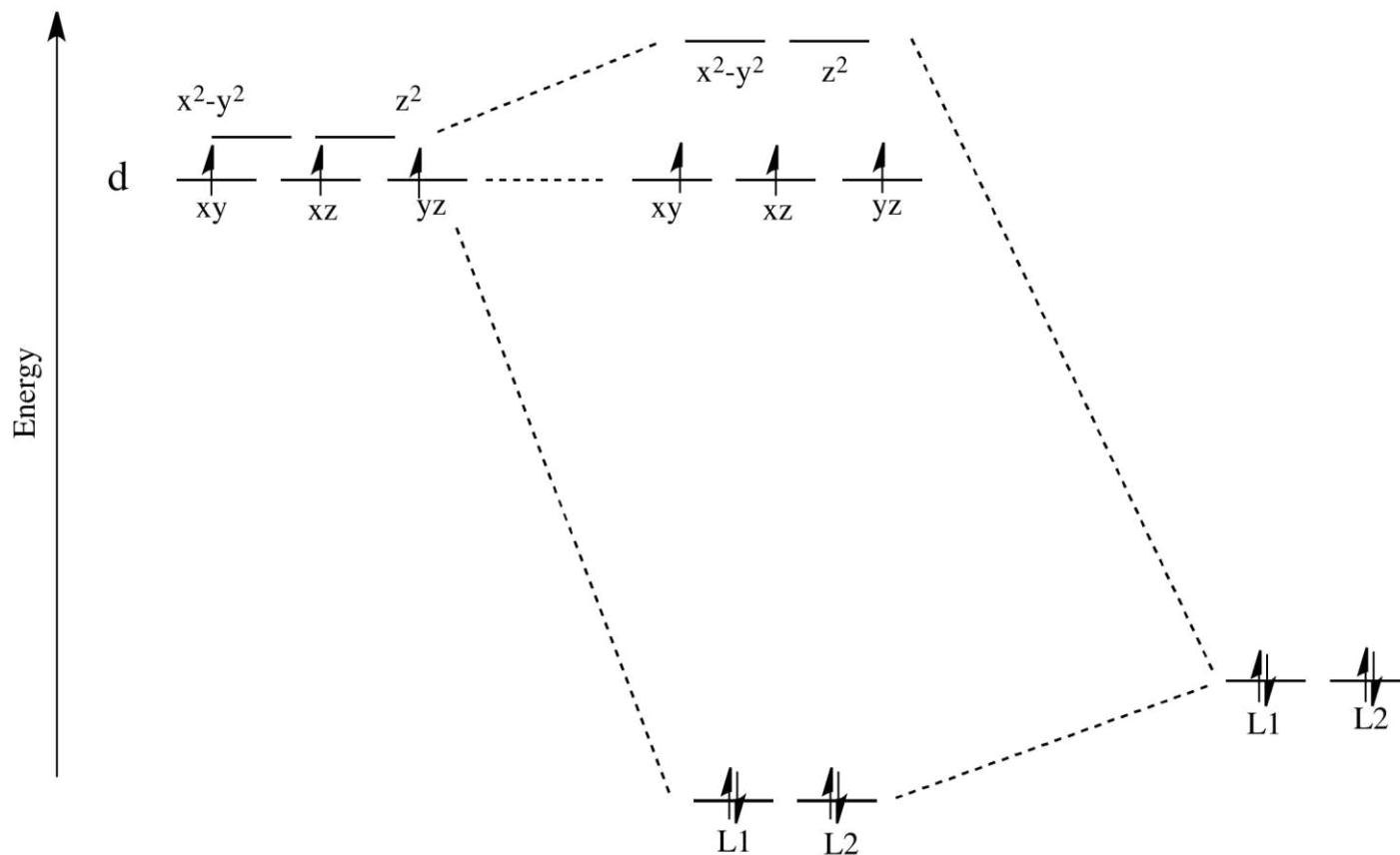


FIGURE 16.19 MO diagram for the formation of $[ML_6]^{n+}$, where the metal–ligand bonding involves only σ -interactions.

- The greatest contribution to the molecular orbital of lowest energy is from atomic orbitals of lowest energy.
- ✓ For NH_3 , F^- , and most other ligands, *the ligand σ orbitals are derived from atomic orbitals with energies that lie well below those of the metal d orbitals.*
- ✓ As a result, *the six bonding molecular orbitals of the complex are mainly ligand-orbital in character* (that is, $c_L^2 > c_M^2$).
- ✓ These six bonding orbitals can accommodate the 12 electrons provided by the six ligand lone pairs.
- ✓ The electrons that we can regard as provided by the ligands are, therefore, largely confined to the ligands in the complex, just as the crystal-field theory presumes.
- ✓ However, because the coefficients c_M 's are nonzero, the bonding molecular orbitals do have some d-orbital character, and the 'ligand electrons' are partly delocalized onto the central metal atom.

- Remember that metals usually have d electrons that are much higher in energy than those on typical donor atoms (like oxygen, sulfur, nitrogen or phosphorus).
 - That means the antibonding combinations will be much closer in energy to the original d orbitals, because both are relatively high in energy.
 - The bonding combination will be much closer in energy to the original ligand orbitals, because these ones are all relatively low in energy.
 - That energetic similarity generally translates into a similarity in shape and location as well.
- ✓ In other words, *the antibonding combination between a d orbital and a ligand orbital is much like the original d orbital.*
- ✓ *The bonding combination is more like the original ligand orbital than the original d orbital.*
- ✓ Because of those similarities, inorganic chemists often refer to those antibonding orbitals as if they were still the original d orbitals.

➤ The drawing below is simplified. The ligands will also interact with s and p orbitals, but because those level have no electrons in them, we're not going to worry about them. We also won't worry about interactions from the other four ligands with the d orbitals (possible by symmetry considerations, but also a more complicated picture).



- The total number of electrons to accommodate, in addition to those supplied by the ligands, now depends on the number of d electrons, n, supplied by the metal atom. These additional electrons enter the orbitals next in line for occupation, which are the nonbonding d orbitals (the t_{2g} orbitals) and the antibonding combination (the upper e_g orbitals) of the d orbitals and ligand orbitals.
- The t_{2g} orbitals are wholly confined (in the present approximation) to the metal atom, and the antibonding e_g orbitals are largely metal-atom in character too, so the n electrons supplied by the central atom remain largely on that atom. The frontier orbitals of the complex are, therefore, the nonbonding entirely metal t_{2g} orbitals and the antibonding, mainly metal e_g orbitals.
- Thus, we have arrived at an arrangement that is qualitatively the same as in crystal-field theory. In the ligand-field approach the octahedral ligand-field splitting parameter, Δ_O , is the separation between the molecular orbitals largely, but not completely, confined to the metal atom (Fig. 16.37).

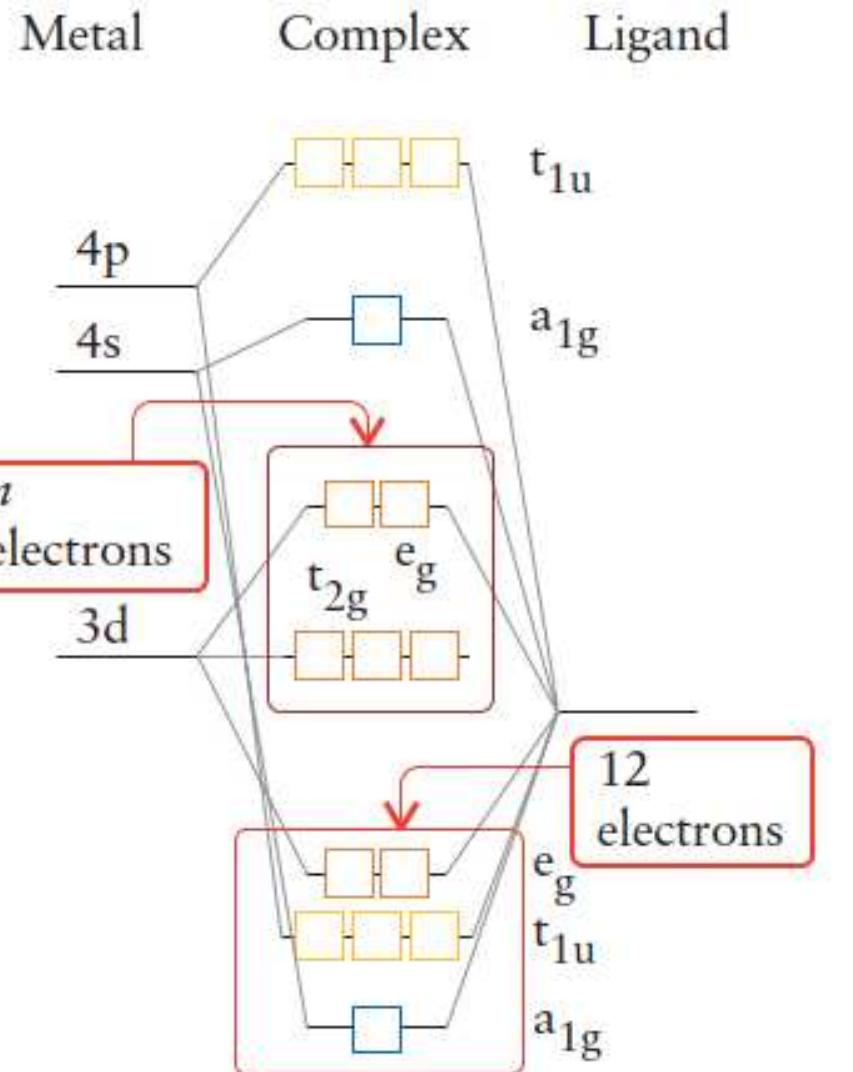


FIGURE 16.37 The molecular orbital energy-level diagram for an octahedral complex. The 12 electrons provided by the six ligands fill the lowest six orbitals, which are all bonding orbitals. The n d-electrons provided by the central metal atom or ion are accommodated in the orbitals inside the upper box. The ligand field splitting is the energy separation of the nonbonding (t_{2g}) and antibonding (e_g) orbitals in the box.

- With the molecular orbital energy-level diagram established, we use the building-up principle to construct the ground-state electron configuration of the complex. For a six-coordinate d^n complex, there are $12 + n$ electrons to accommodate.
- The six bonding molecular orbitals accommodate the 12 electrons supplied by the ligands. The remaining n electrons are accommodated in the nonbonding t_{2g} orbitals and the antibonding e_g orbitals.
- Now the story is essentially the same as for crystal-field theory, the types of complexes that are obtained (high-spin or low-spin, for instance) depending on the relative values of Δ_0 and the pairing energy P .
- The **principal difference from the crystal-field** discussion is that ligand-field theory gives **deeper insight into the origin of the ligand-field splitting**, and we can begin to understand why some ligands are strong, and others are weak.
- For instance, a good σ -donor ligand should result in **strong metal–ligand overlap, hence a more strongly antibonding e_g set** and consequently **a larger value of Δ_0** .
- However, before drawing further conclusions, we must consider what **crystal-field theory ignores completely: the role of π bonding**.

This concept is illustrated for $[\text{FeCl}_6]^{3-}$ in Fig. 11.12. The Fe^{3+} ion possesses five electrons in the 3d orbitals and has empty 4s and 4p orbitals. Energetically, the 3d, 4s and 4p orbitals are at a level that allows molecular orbital formation with the atomic orbitals provided by the six chloride ligands. In this scheme, a total of 17 electrons need to be filled, twelve of which occupy the bonding orbitals. The three non-bonding d orbitals (colored violet in Fig. 11.12) and the two anti-bonding orbitals (upper pair of yellow-colored orbitals in Fig. 11.12) arising from the linear combination of two 3d orbitals with the two ligand orbitals results in an energetic scheme we have already seen in the discussion of the crystal field theory. Therefore, the crystal field splitting Δ is also observed in the ligand field theory. These relative energies can be verified and positioned more precisely by comparison with experimental data (particularly UV-visible absorption and photoelectron spectroscopy).

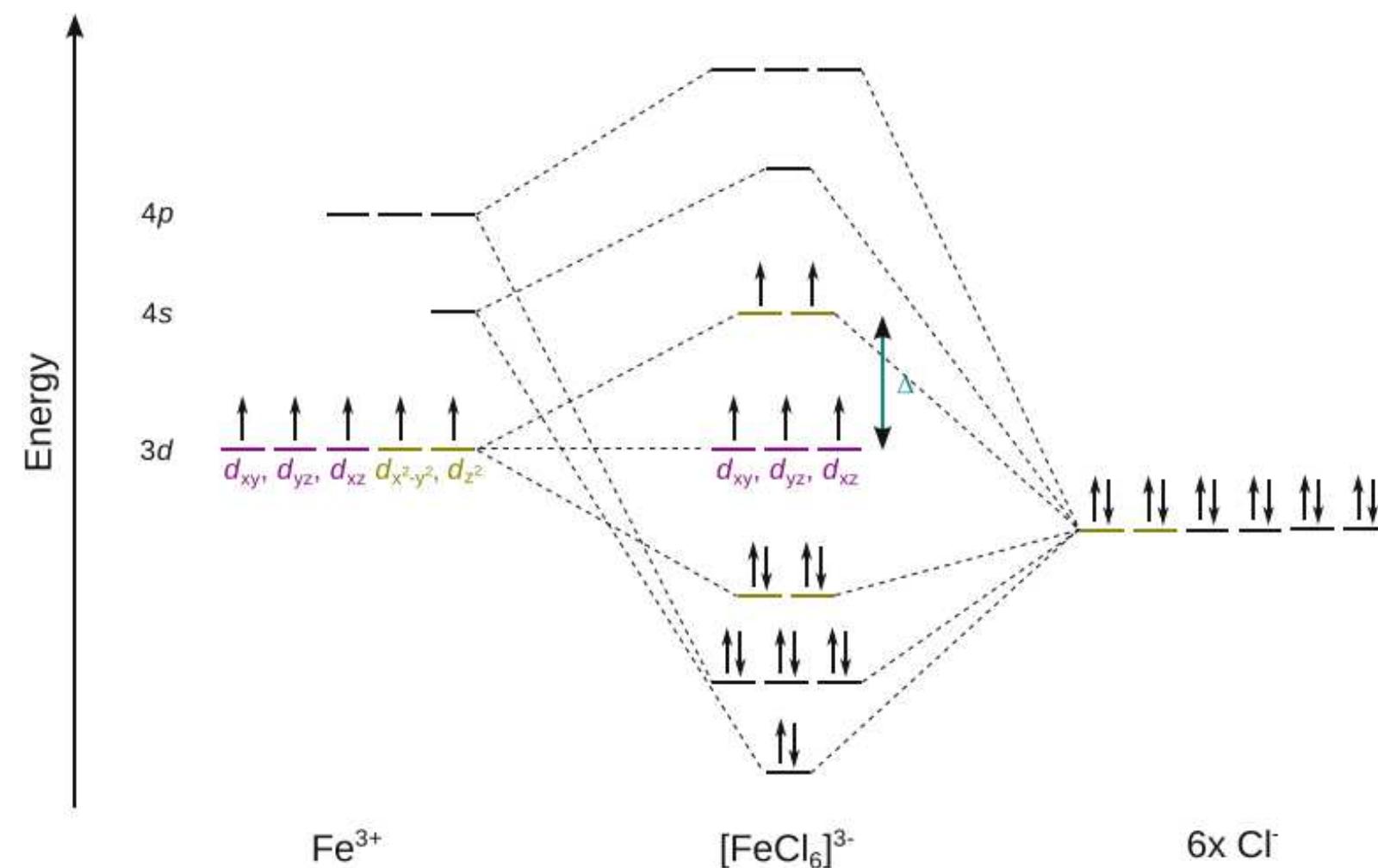


Fig. 11.12 Molecular orbitals for $[\text{FeCl}_6]^{3-}$

- MO theory identifies the t_{2g} orbitals as the nonbonding MOs and the e_g^* orbitals as the antibonding orbitals; **the crystal field splitting Δ_o is the energy difference between them.**
- The energies of the nb orbitals are unaffected by bonding, but the energies of the antibonding orbitals that lie above them are determined by the strength of the metal-ligand bonds.
- Recall that the energy of bonding MOs decreases with increasing bond strength while the energy of the corresponding antibonding MOs increases with increasing bond strength.
- The increase in crystal field splitting observed through the middle of the spectrochemical series correlates well with the strength of the metal-ligand σ bonds, but MO theory cannot account for the order observed throughout the rest of the series without considering π bonding.
- Let's consider the effects of π bonding by first examining the nature of the bonds formed between a metal atom or ion and a single ligand.
- We then extend the treatment to examine the effects of π bonding on the energy level structure and properties of octahedral complexes.

After placing the 12 electrons from the ligand lone pairs in the six bonding orbitals, the nonbonding t_{2g} set of 3d orbitals and the antibonding e_g^* pair are the next five orbitals available to accommodate the d electrons on the metal. *Thus, the descriptions in the electrostatic and molecular orbital theories are very similar.* Both theories produce five orbitals in a lower set of three and an upper set of two, separated by ΔE (Δ_0), to accommodate the d electrons. In the electrostatic theory these sets are, respectively, the atomic d_{xy} , d_{yz} and d_{zx} orbitals and the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals, while, in the molecular orbital theory, the lower set are the same atomic orbitals and the upper set are antibonding molecular orbitals composed of the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals with ligand orbital contributions.

Thus, in their essential description of the varying magnetic properties and d-d transitions, these two theories are identical. The molecular orbital theory has the advantage that it is easily extended to include π -bonding and it gives a prediction of the alteration of energy levels in such a case. It is also more useful for the interpretation of spectra as it provides information, not only about the d levels, but also about the higher energy antibonding orbitals to which excitations occur when higher energy quanta are absorbed. On the other hand, the molecular orbital theory suffers from the disadvantage of all wave mechanics, that it is impossible to calculate bond energies, heats of formation and the like directly.

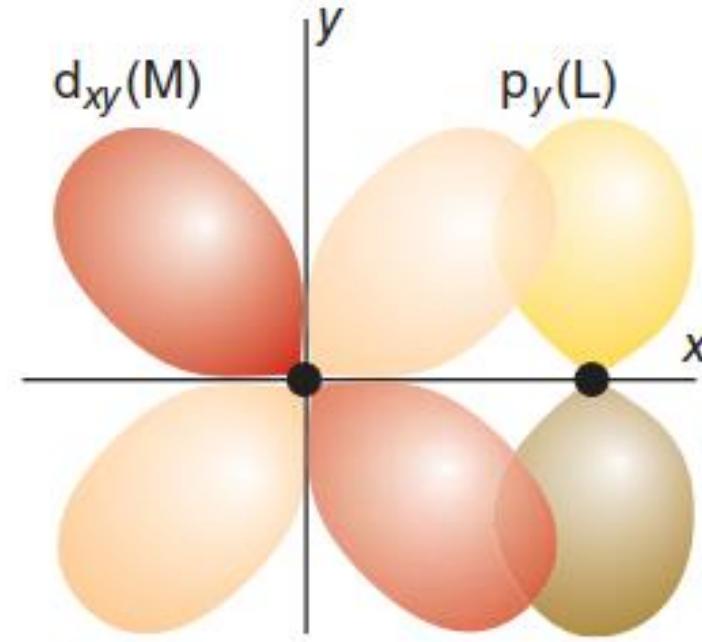
In practice, these two theories may be used interchangeably, as most convenient. Both rely on experimental data to fix the energy levels; for example, ΔE is usually determined spectroscopically.

π Bonding:

- Now we shall answer why CO is a strong-field ligand whereas Cl^- is a weak-field ligand despite its negative charge.
- ❖ Key points: π -Donor ligands decrease Δ_o whereas π -acceptor ligands increase Δ_o ; *the spectrochemical series is largely a consequence of the effects of π bonding when such bonding is feasible.*
- While it is satisfying that the LF (MO) approach yields much the same result as CFT, we have yet to explain why ligands such as CO, CN^- , PR_3 , R^- , NO_2^- , phen, and bpy (particularly those that are neutral) lie so high in the spectrochemical series.
- The answer involves the fact that in addition to acting as σ -donor ligands, this subset of ligands can also undergo what is known as pi back-bonding.

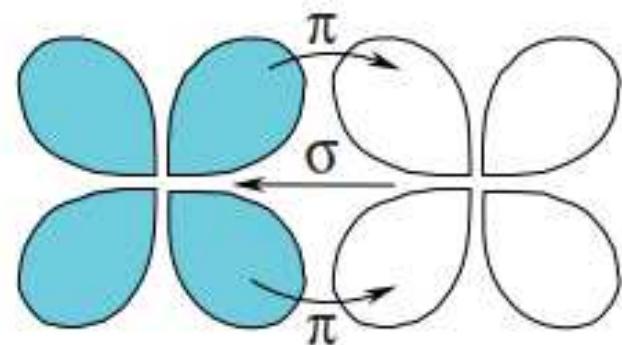
- Following Figures illustrate different types of pi-bonding between metal ions and ligands.
- Pi backbonding can occur from a filled t_{2g} orbital on the metal to
 - ✓ (i) an empty, low-lying d-orbital on the ligands, such as that which occurs for PR_3 , AsR_3 , or SR_2 ;
 - ✓ (ii) an empty π^* MO on a ligand containing multiple bonds, such as that which occurs in CO , CN^- , NO_2^- , bpy, or phen; or
 - ✓ (iii) an empty σ^* MO on the ligands such as that which occurs when H–H or C–H single bonds coordinate to the metal.

Figure 20.19 The π overlap that may occur between a ligand p orbital perpendicular to the M–L axis and a metal d_{xy} orbital.



Metal

Ligand



Filled d

Empty d

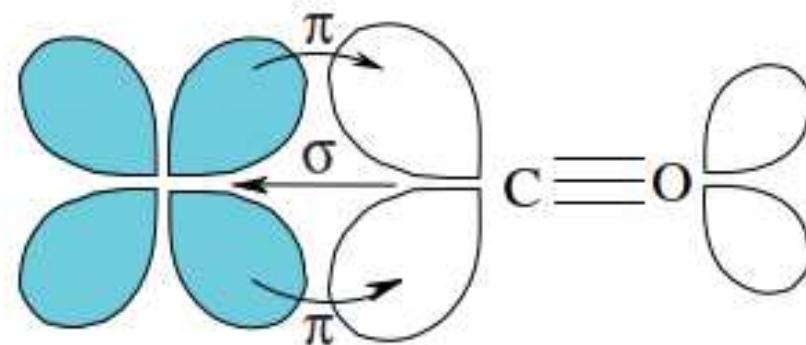
$$d_{\pi} - d_{\pi}$$

$L = PR_3, AsR_3, SR_2$

(a)

Metal

Ligand



Filled d

Empty π^*

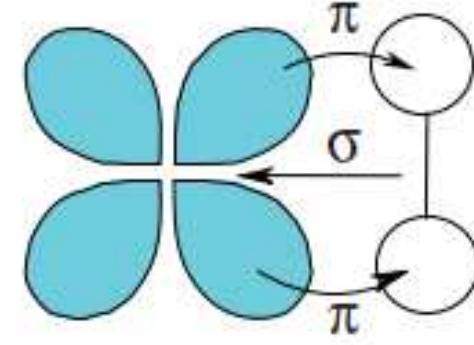
$$d_{\pi} - L_{\pi^*}$$

$L = CO, CN^-, NO^{2-}, bpy, phen$

(b)

Metal

Ligand



Filled d

Empty σ^*

$$d_p - L_{\sigma^*}$$

$L = H_2, \text{alkanes}$

(c)

FIGURE 16.21 (a–c) Three different types of pi backbonding interactions.

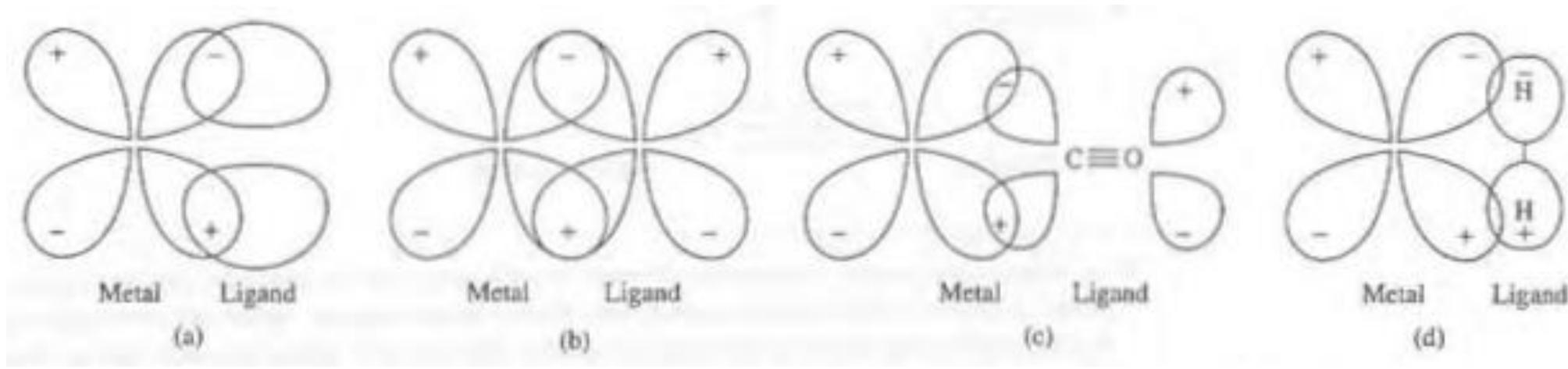


Fig.11.23 Pi overlap of a metal d orbital with various types of *ligand orbitals*: (a) p, (b) d, (c) π^* , and (d) σ^* .

Four potential metal–ligand π interactions: (1) $d_{\pi} - p_{\pi}$, (2) $d_{\pi} - d_{\pi}$, (3) $d_{\pi} - \pi^*$, and (4) $d_{\pi} - \sigma^*$.

- When pi back-bonding does occur, it helps to stabilize the coordination compound by shuttling some of the built-up electron density on the metal from σ -donation back onto the ligands.
- ✓ Because electron density is transferred from the metal to the ligands, pi back-bonding is especially favored by electropositive metals (typically metals from the left-hand side of the periodic table) having low oxidation numbers and strong σ -donor ligands in the other coordination sites.
- We need to develop the model by considering the effects of other ligand orbitals. When we constructed the molecular orbitals above, we considered only ligand orbitals that pointed directly at the central metal atom.
- Ligands also have orbitals perpendicular to the metal–ligand (M–L) axis with local π symmetry, which we expect to form bonding and antibonding π orbitals with the metal orbitals.
- For an octahedral complex, the combinations that can be formed from the ligand π orbitals include SALCs of t_{2g} symmetry. These ligand combinations have net overlap with the metal t_{2g} orbitals, which are therefore no longer purely nonbonding on the metal atom.

- Depending on the relative energies of the ligand and metal orbitals, the energies of the now molecular t_{2g} orbitals lie above or below the energies they had as nonbonding atomic orbitals, so Δ_0 is decreased or increased, respectively.
- To explore the ***role of π bonding*** in more detail, we need two of the general principles described earlier in MO theory. First, we shall make use of the idea that, **when atomic orbitals overlap effectively, they mix strongly: the resulting bonding molecular orbitals are significantly lower in energy and the *antibonding molecular orbitals are significantly higher in energy than the atomic orbitals*.** Second, we note that atomic orbitals with similar energies interact strongly, whereas those of very different energies mix only slightly, even if their overlap is large.
- There are no disputes over which ligand orbitals have the correct symmetry to participate in π bonding, but the extent to which this actually occurs for some ligands is vigorously debated. Even when ligand and metal orbitals have the proper symmetry for π bond formation, ***an energy or size mismatch may lead to insignificant interaction.***

- In the metal carbonyl complexes, the direct bearing of the π -back donation is observed on the M–C bond distance that becomes shorter as compared to that of a normal M–C single bond distance.
- ✓ For example, the $\text{CpMo}(\text{CO})_3\text{CH}_3$ complex, exhibits two kind of M–C bond distances that comprise of a longer Mo– CH_3 distance (2.38 Å) and a much shorter Mo–CO distance (1.99 Å) arising out of a metal to ligand π -back donation.
- It becomes thus apparent that the metal–CO interaction can be easily characterized using X-ray crystallography.
- The infrared spectroscopy can also be equally successfully employed in studying the metal–CO interaction. Since the *metal to CO π -back bonding involves a π -donation from the metal d_{π} orbital to a π^* orbital of a C–O bond, a **significant shift of the $\nu(\text{CO})$ stretching frequency towards the lower energy** is observed in metal carbonyl complexes with respect to that of free CO (2143 cm^{-1}).*
- The energies of the ν_{CO} band for the metal carbonyls correlate with the strength of the carbon-oxygen bond and inversely correlated with the strength of the π -back-bonding between the metal and the carbon.

Backbonding and IR Absorption

- CO ligands are carbon monoxide ligands that participate readily in transition metal complexes via coordinate bonds with a transition metal center.
- CO ligands are neutral 2 electron donors and first form a sigma bond with a metal center.
- As discussed above, the d orbitals of the transition metal are symmetric about the π^* orbitals of the CO compound and back-bonding occurs between the metal and the CO. This process is illustrated in Figure 1.20.1. Pi back-donation is supported by IR (infrared spectroscopy) data of various metal-carbonyl complexes. Using group theory, one can consider the consequences of back-bonding and the effects this would have on the IR absorption of a carbonyl-containing compound.

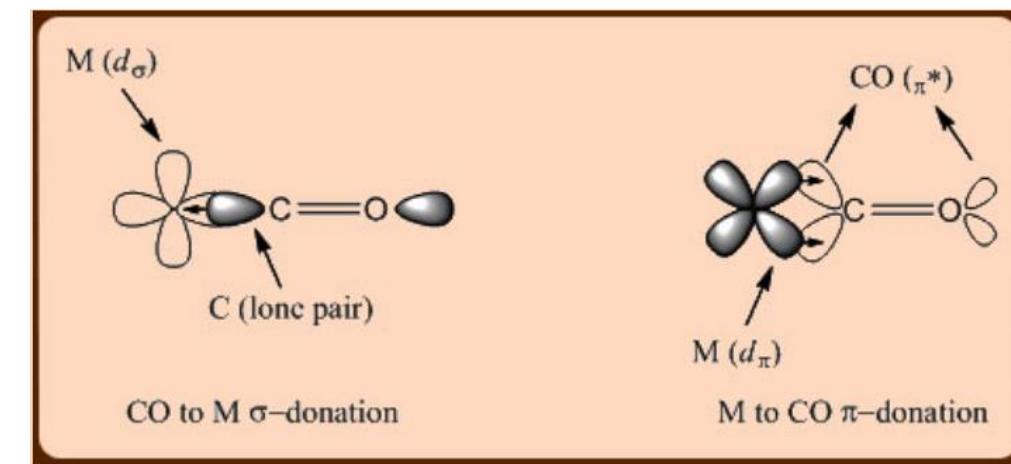
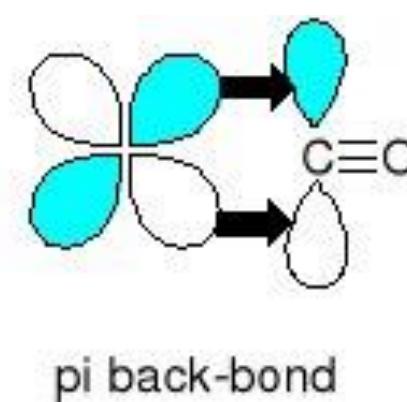
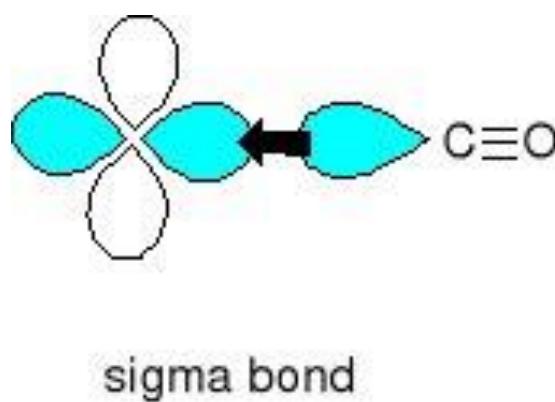


Figure 1.20.1: Sigma Donation and Pi Backbonding

- Pi back-bonding donates electrons from the transition metal center to the pi* antibonding orbital of CO, the LUMO of this ligand (Lowest Unoccupied Molecular Orbital).
- ✓ This, in turn, lowers the bond order between carbon and oxygen, weakening their interaction.
- ✓ This would cause one to suspect that metal carbonyl complexes would absorb light of a lower frequency upon excitation by infrared radiation.
- ✓ This is consistent with experimental data, with few exceptions, for several metal carbonyl complexes when compared to the IR absorption of free carbonyls. This is depicted in Table 1.20.1.

Table 1.20.1. IR Absorption Frequencies for Metal Carbonyls

Compound	ν_{CO} (cm⁻¹)
CO	2143
V(CO) ₆ ¹⁻	1859
Cr(CO) ₆	2000
Mn(CO) ₆ ⁺	2100
Fe(CO) ₆ ²⁺	2204
Fe(CO) ₅	2022, 2000
Ru(CO) ₅	2038, 2022

- Some convincing arguments for covalency and the most convincing evidence in support of pi backbonding comes from the IR spectra of the metal carbonyls, $M(CO)_6$.
- For the isoelectronic series of compounds listed in Table 16.6, the **$\nu(CO)$ stretching frequency decreases as the electron density on the metal accumulates.**
- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at $\sim 2140\text{ cm}^{-1}$.
- For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively.
- Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is *consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals* of the CO group.

TABLE 16.6 IR frequencies for the $\nu(\text{CO})$ stretch in a series of isoelectronic metal carbonyls.

Compound	M^{n+}	$\nu(\text{CO}), \text{cm}^{-1}$
$\text{Mn}(\text{CO})_6^+$	Mn^+	2090
$\text{Cr}(\text{CO})_6$	Cr^0	2000
$\text{V}(\text{CO})_6^-$	V^-	1860
$\text{Ti}(\text{CO})_6^{2-}$	Ti^{2-}	1748

- Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

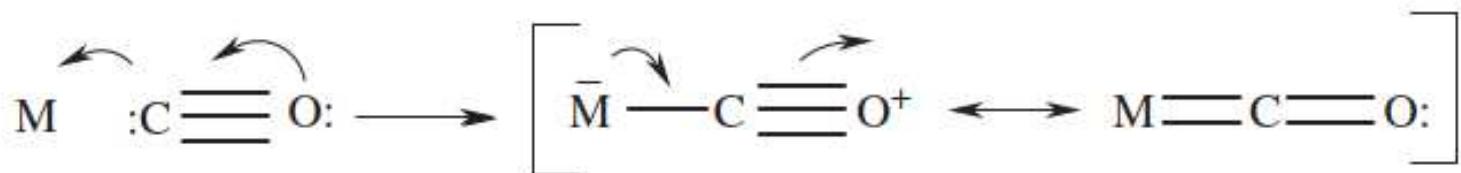


FIGURE 16.22 Two canonical forms for metal-carbonyl bonding, showing the pi character in the resonance hybrid.

➤ SOME FACTS Typical stretching frequencies:

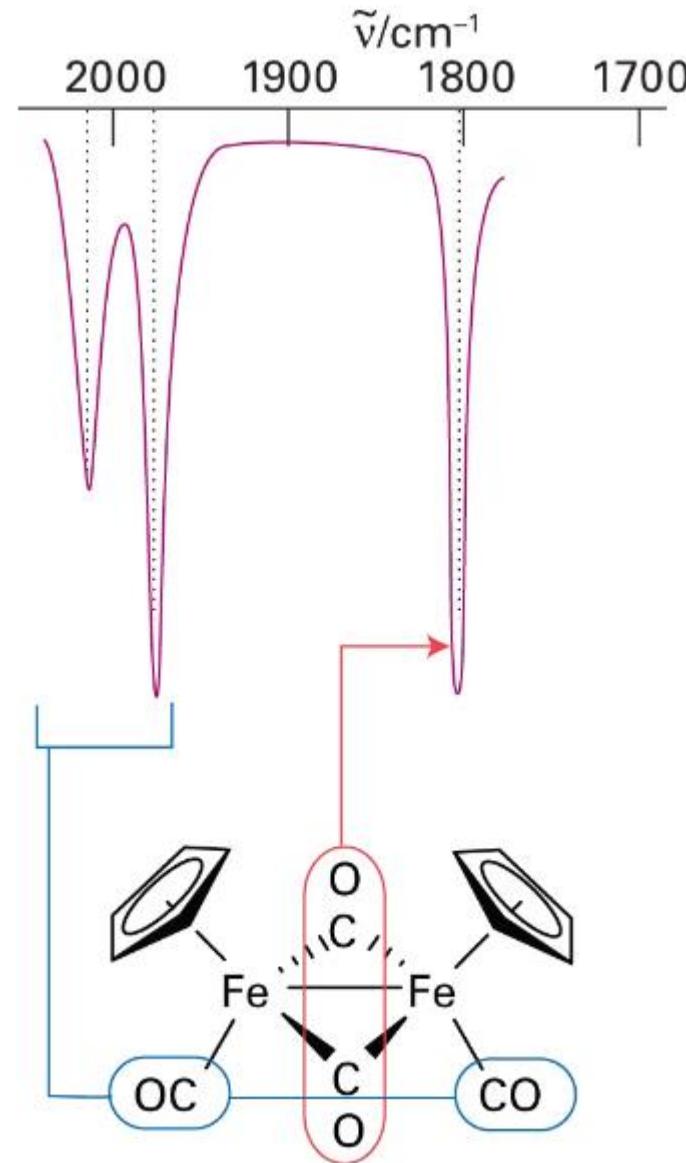
- Uncoordinated or "free" CO: 2143 cm⁻¹
- Terminal M-CO: 2125 to 1850 cm⁻¹
- Doubly bridging (μ -2): 1850 to 1750 cm⁻¹
- Triply bridging (μ -3): 1675 to 1600 cm⁻¹
- Semi-bridging: somewhere between terminal and μ -2.

➤ Trends observed in the IR spectra of carbonyl complexes that are consistent with the concept of π -back-bonding:

1. With each charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm⁻¹.
2. The better the sigma-donating capability (or worse the pi-acceptor ability) of the other ligands on the metal, the lower the CO stretching frequency.
3. For simple carbonyl complexes, counting the number of IR and Raman CO stretching frequencies will often permit one to make a structural assignment.

The number of CO stretches expected for possible geometries/isomers can be predicted using group theory and the calculated results compared to the experimental data.

Infrared spectra report on types of CO groups in the organometallic.



❖ The effect of π -bonding on ligand field splitting

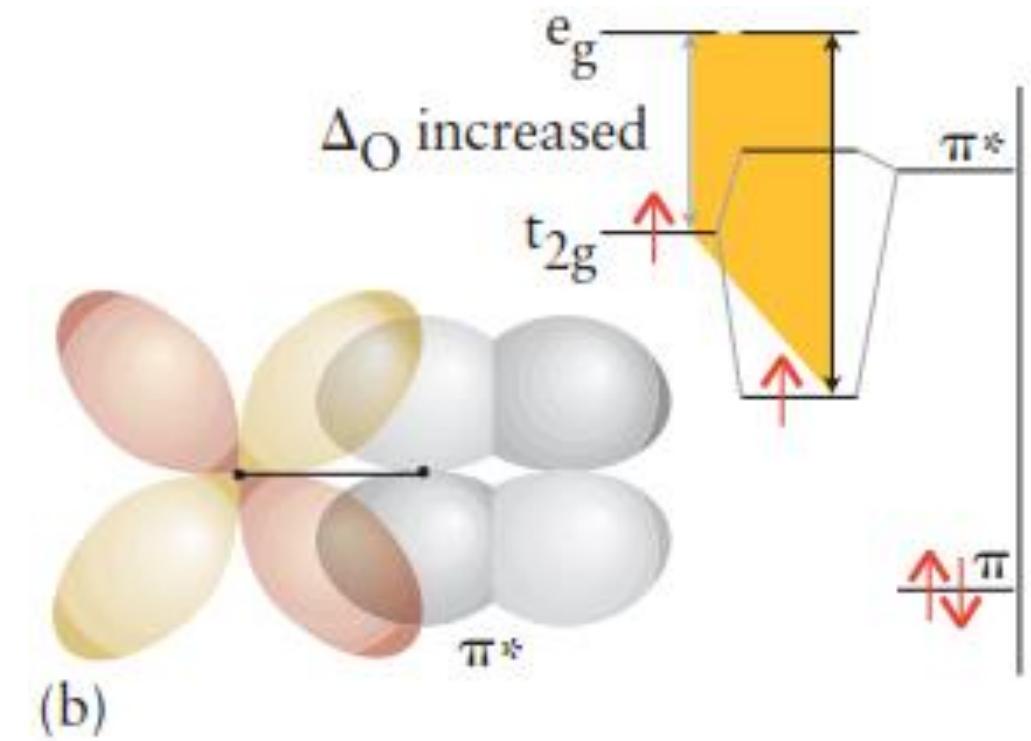
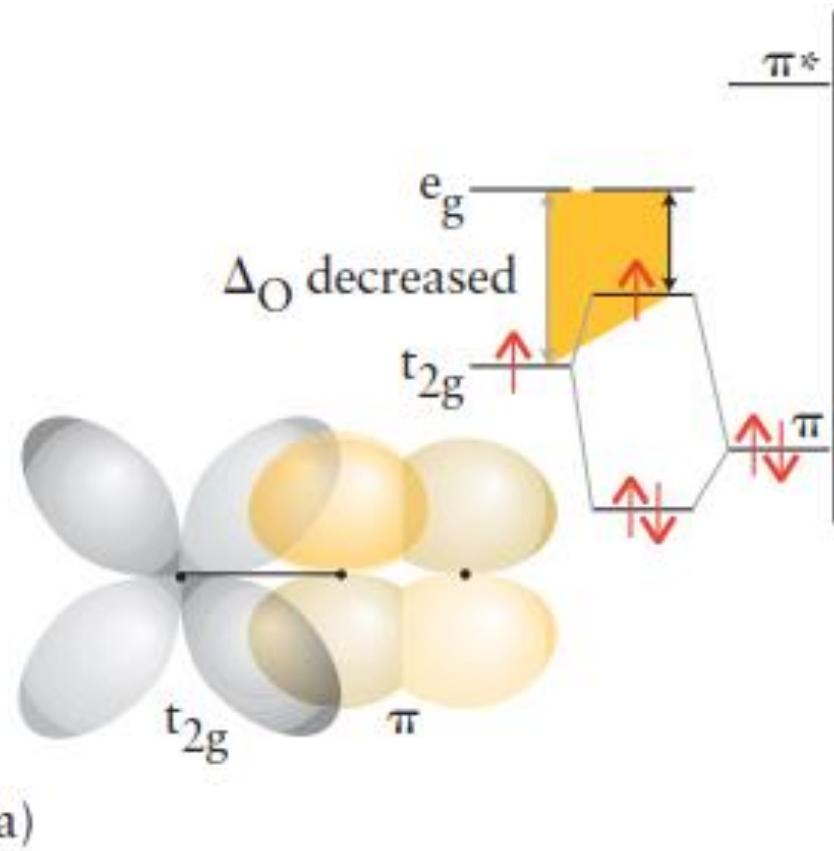


FIGURE 16.38 The effect of π -bonding on ligand field splitting. (a) In this case, the occupied π -orbital of the ligand is close in energy to the t_{2g} orbitals, and they overlap to form bonding and antibonding combinations. *The ligand-field splitting is reduced.*

(b) In this case, the unoccupied antibonding π^* -orbital of the ligand is close in energy to the t_{2g} orbitals, and they overlap to form bonding and antibonding combinations. In this case, the *ligand-field splitting is increased.*

❖ The effect of π -bonding on ligand field splitting

- As Figs. 8.31 (a and b) show that a p-orbital on the ligand perpendicular to the axis of the metal–ligand bond can overlap with one of the t_{2g} -orbitals to produce two new molecular orbitals, one bonding and one antibonding. The resulting bonding orbital lies below the energy of the original t_{2g} -orbitals; the antibonding orbital lies above them.

Fig. 8.31 (a): In this case *when the occupied π -orbital of the ligand is full*, the π -orbital is close in energy to the t_{2g} orbitals and they overlap to form bonding and antibonding combinations. In this case, **the ligand-field splitting is reduced**.

Fig. 8.31 (b): In this case, the unoccupied antibonding π^* -orbital of the ligand is close in energy to the t_{2g} orbitals and they overlap to form bonding and antibonding combinations. In this case, **the ligand-field splitting is increased**.

Left: LGOs of t_{2g} symmetry;
Right: MOs for the σ system of the complex;
Center: MOs after π interaction.

- Note that Δ_0 is diminished by the π interaction.
- When the occupied π -orbital of the **ligand is full**, the π -orbital is close in energy to the ligand t_{2g} orbitals and they overlap to form bonding and antibonding combinations, **the ligand-field splitting (Δ_0) is reduced**.

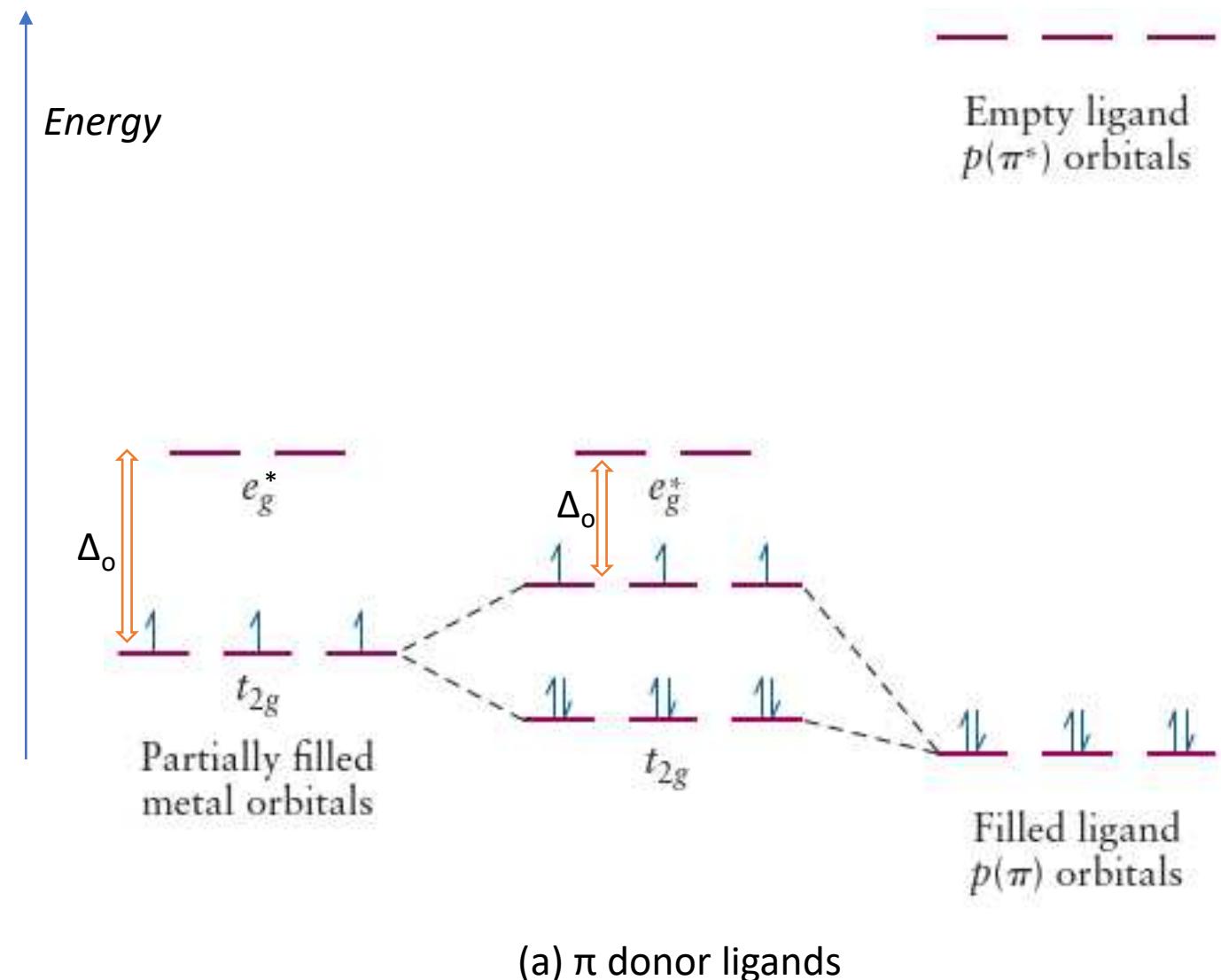
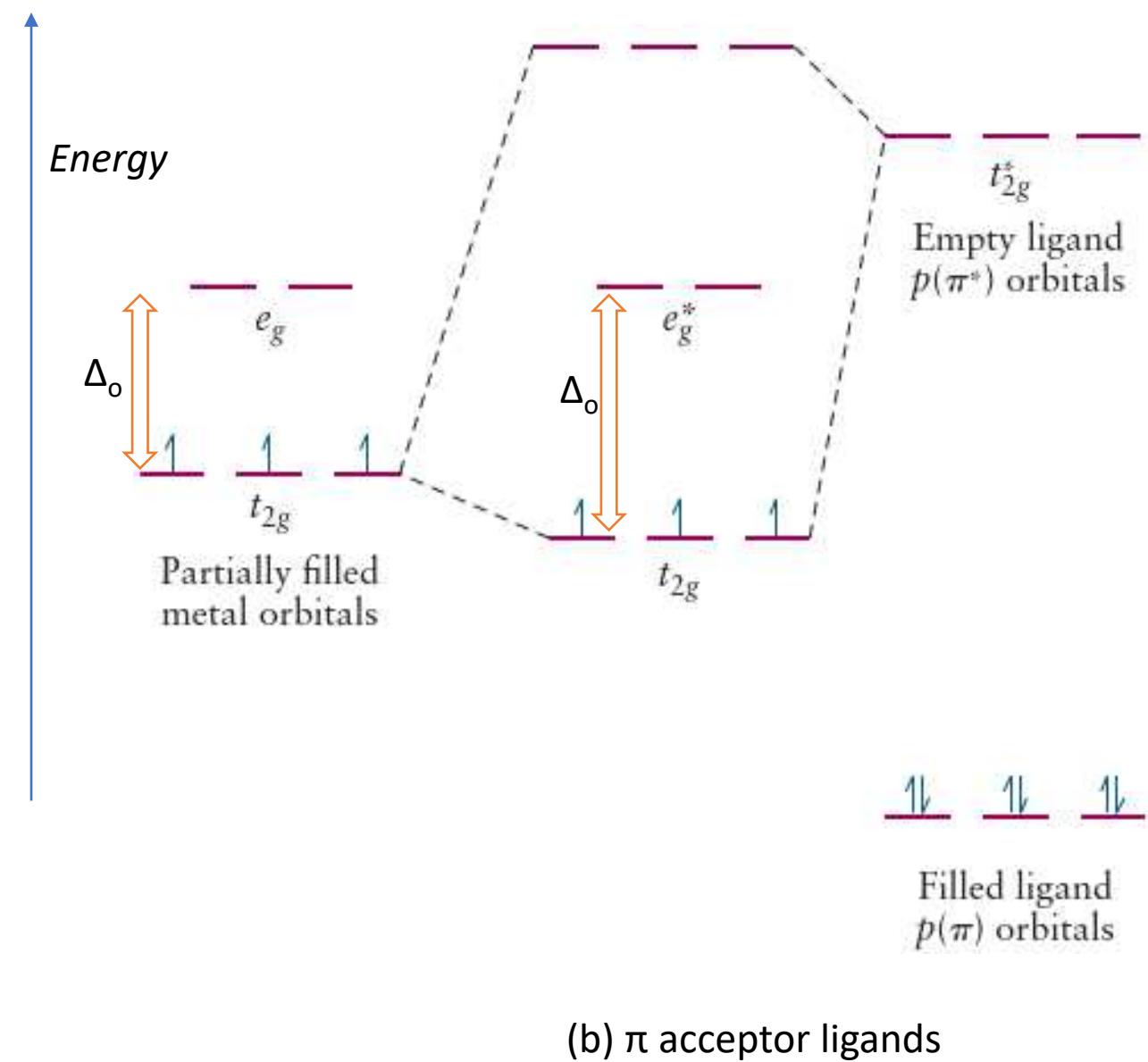


FIGURE 8.31 (a) Ligand-to-metal π donation showing the formation of bonding and antibonding MOs and a reduction in Δ_0 compared with that from s bonding alone.

MO diagram for the π system of an octahedral complex with acceptor ligands such as CO, PR₃, or SR₂.

- Note that the π interaction in this case increases Δ_0 .
- When the unoccupied antibonding π^* -orbital of the ligand is close in energy to the ligand t_{2g} orbitals and they overlap to form bonding and antibonding combinations, **the ligand-field splitting is increased.**



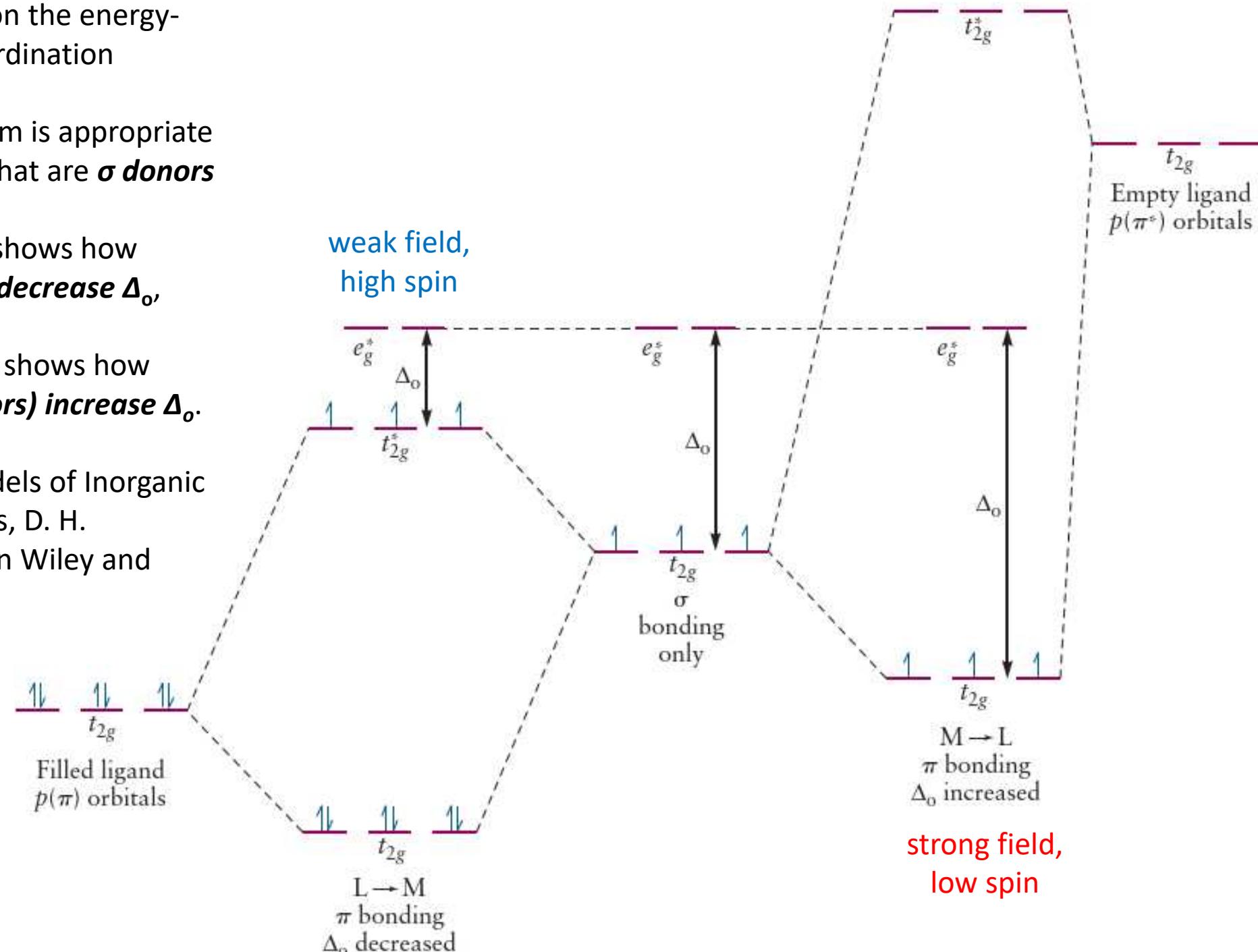
(b) π acceptor ligands

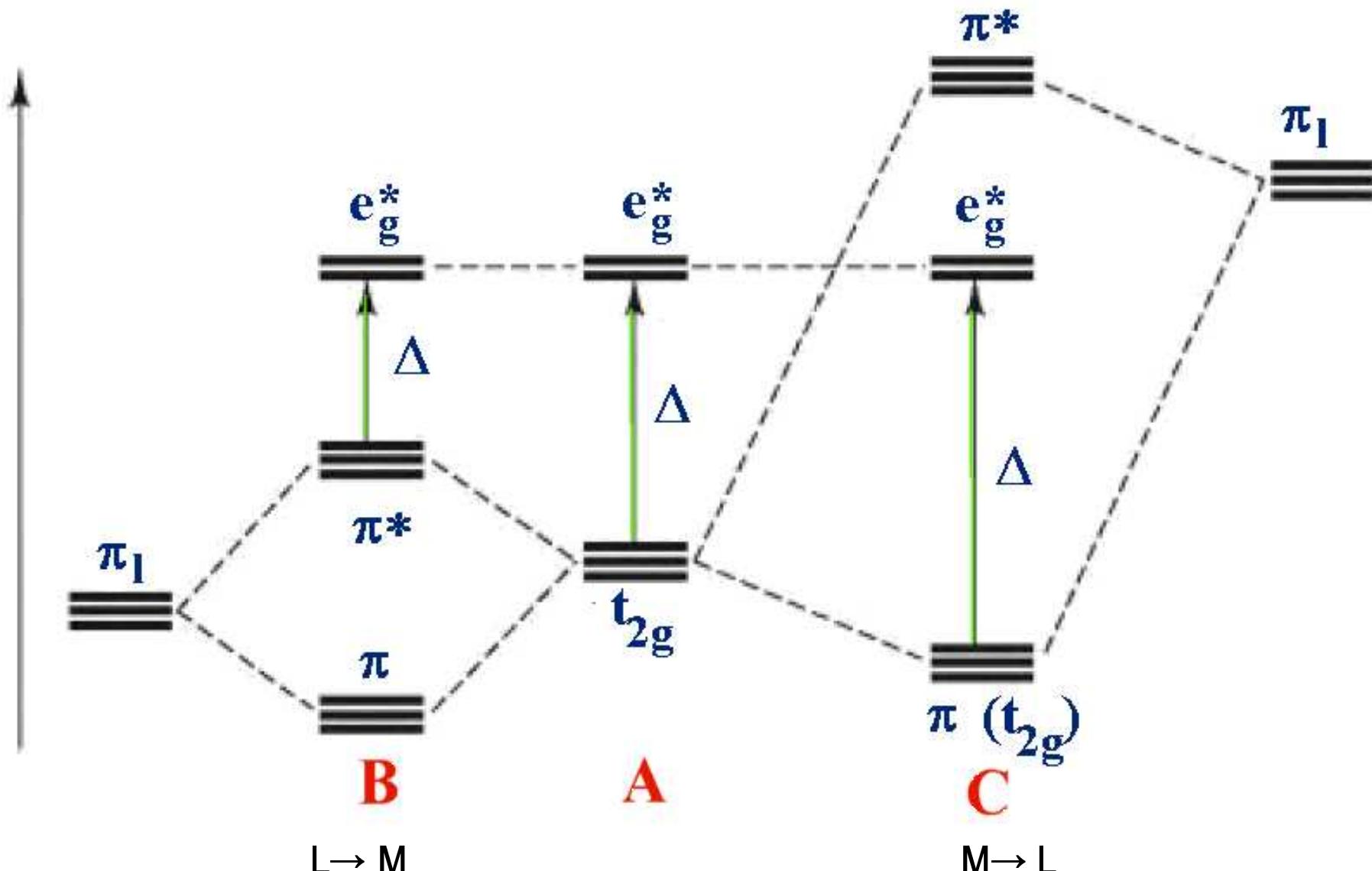
FIGURE 8.31(b) Metal-to-ligand π donation showing the formation of bonding and antibonding MOs and an increase in Δ_0 compared with that from s bonding alone.

FIGURE 8.32 Effect of π bonding on the energy-level structure for octahedral coordination complexes.

- ✓ The **center** energy-level diagram is appropriate for intermediate field ligands that are **σ donors only**.
- ✓ The **left** energy-level diagram shows how **weak field ligands (π donors) decrease Δ_o** , and
- ✓ the **right** energy-level diagram shows how **strong field ligands (π acceptors) increase Δ_o** .

(Adapted from Concepts and Models of Inorganic Chemistry, 2nd edition, B. Douglas, D. H. McDaniel, and J. J. Alexander, John Wiley and Sons, New York, 1983, p. 293.)





For example:



- Now we count the number of electrons to accommodate. If the ligand is Cl^- , the $\text{Cl}3\text{p}$ -orbital that we have used to build the metal–ligand π -orbital is full. It provides two electrons, which occupy a new molecular orbital, the bonding metal–ligand combination. The n d-electrons provided by the metal must therefore occupy the antibonding metal–ligand orbital. Because this molecular orbital is higher in energy than the original t_{2g} -orbitals, the ligand field splitting is decreased by π -bonding. Therefore, we see how Cl^- can be a weak-field ligand despite its negative charge.
- Now suppose the ligand is CO. The orbital that overlaps with the metal t_{2g} -orbitals in this case is either the full bonding π -orbital or the empty antibonding π^* -orbital of the CO molecule. It turns out that the latter orbital is closer in energy to the metal orbitals, and so it plays the dominant role in bond formation to the metal. There are no electrons from the ligand to accommodate because its π^* -orbital is empty. The n d-electrons therefore enter the bonding metal–ligand orbital. Because this new molecular orbital is lower in energy than the original t_{2g} -orbitals, the ligand field splitting is increased by π -bonding and CO is a strong-field ligand despite being electrically neutral.

NOTE: The increase in Δ_O caused by π bonding is substantial enough in many cases that the absorption maximum for the t_{2g} -to- e_g^* electronic transition is blue-shifted out of the visible region into the ultraviolet portion of the electromagnetic spectrum, with the result that the complexes are **colorless**. This is the case for the metal carbonyls, for example.

A **π -donor ligand** is a ligand that, before any bonding is considered, has **filled orbitals of π symmetry** around the M–L axis. Such ligands include Cl^- , Br^- , OH^- , O^{2-} , and even H_2O . In Lewis acid–base terminology, a π -donor ligand is a **π base**. *The energies of the full π orbitals on the ligands will not normally be higher than their σ -donor orbitals (HOMO) and must therefore also be lower in energy than the metal d orbitals.* Because the full π orbitals of π -donor ligands lie lower in energy than the partially filled d orbitals of the metal, when they form molecular orbitals with the metal t_{2g} orbitals, the bonding combination lies lower than the ligand orbitals and the antibonding combination lies above the energy of the d orbitals of the free metal atom (Fig. 20.20). The electrons supplied by the ligand π orbitals occupy and fill the bonding combinations, leaving the electrons originally in the d orbitals of the central metal atom to occupy the antibonding t_{2g} orbitals. *The net effect is that the previously nonbonding metal t_{2g} orbitals become antibonding and hence are raised closer in energy to the antibonding e_g orbitals.* It follows that π -donor ligands decrease Δ_0 .

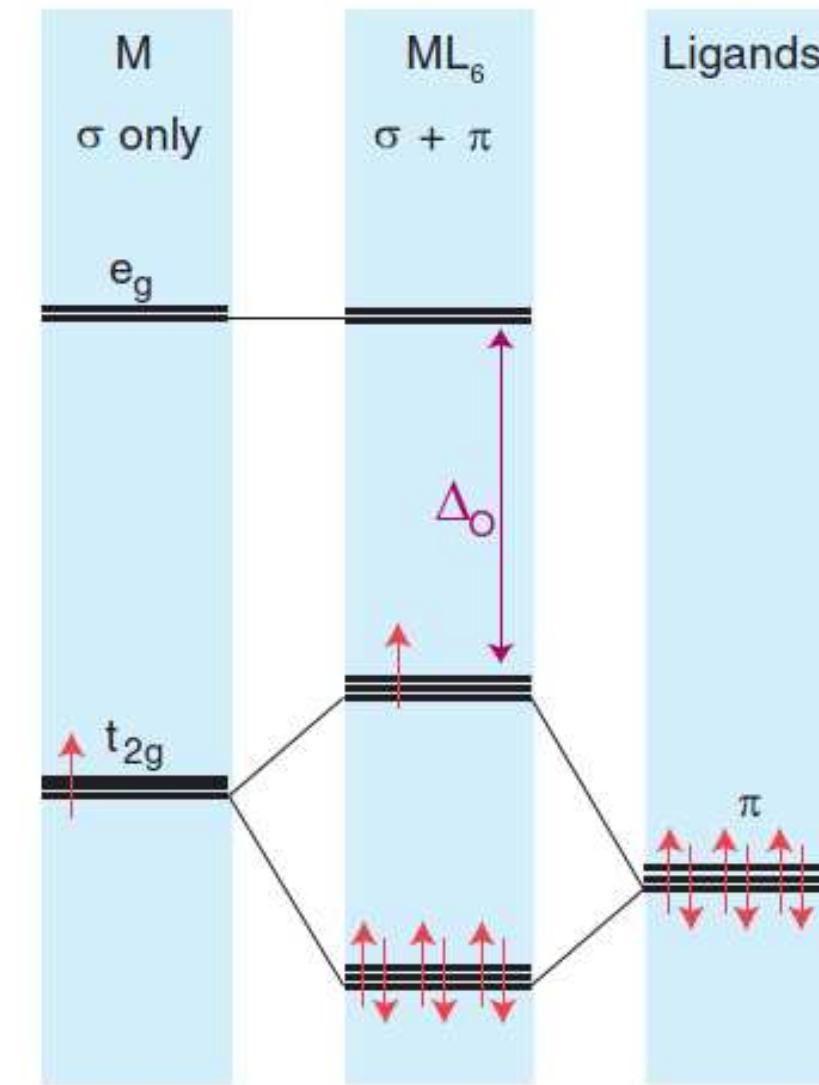


Figure 20.20 The effect of π bonding on the ligand-field splitting parameter. Ligands that act as π donors decrease Δ_0 . Only the π orbitals of the ligands are shown.

A **π -acceptor ligand** is a ligand that **has empty π orbitals** that are available for occupation. In Lewis acid–base terminology, a π -acceptor ligand is a π acid. *Typically, the π -acceptor orbitals are vacant antibonding orbitals on the ligand (usually the LUMO), as in CO and N₂, which are higher in energy than the metal d orbitals.* The two π^* orbitals of CO, for instance, have their largest amplitude on the C atom and have the correct symmetry for overlap with the metal t_{2g} orbitals, so **CO can act as a π -acceptor ligand**. **Phosphines (PR₃)** are also able to **accept π -electron density** and also act as π acceptors.

Because the π -acceptor orbitals on most ligands are higher in energy than the metal d orbitals, they form molecular orbitals in which the bonding t_{2g} combinations are largely of metal d-orbital character (Fig. 20.21). These bonding combinations lie lower in energy than the d orbitals themselves. The net result is that π -acceptor ligands increase Δ_0 .

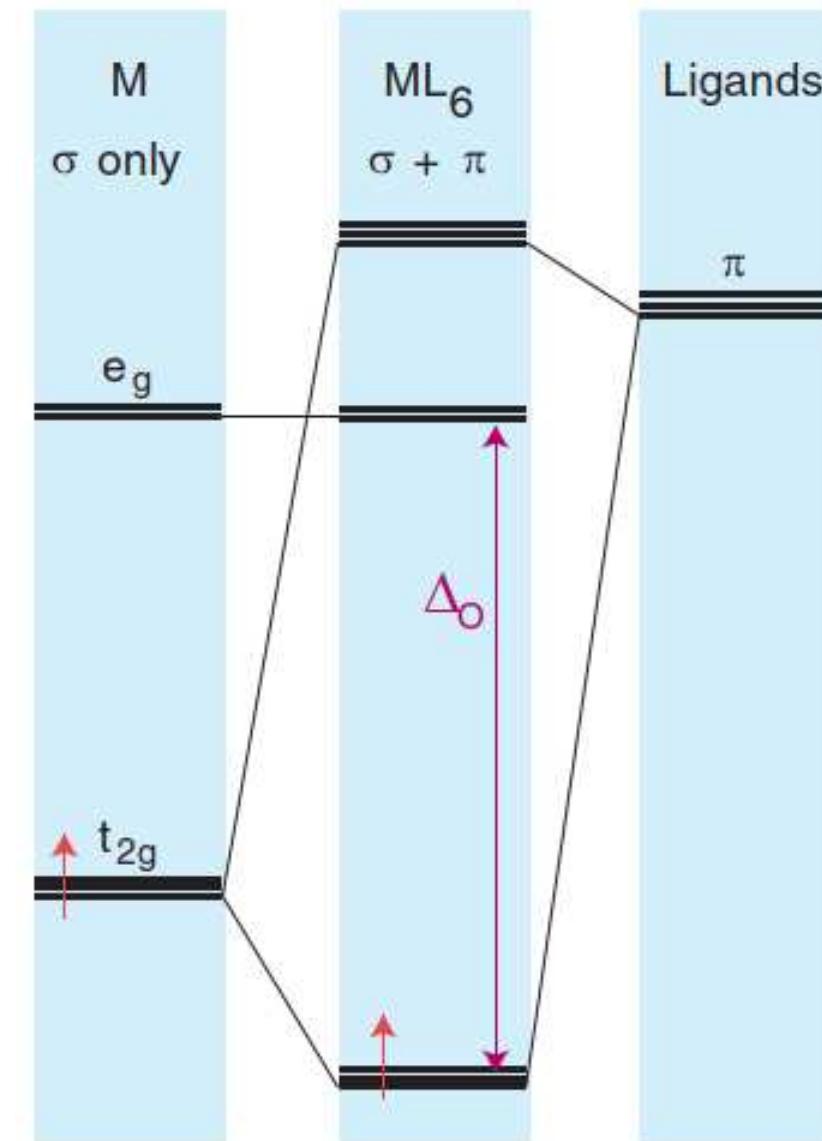


Figure 20.21 The effect of π bonding on the ligand-field splitting parameter. Ligands that act as π acceptors increase Δ_0 . Only the π orbitals of the ligands are shown.

We can now put the role of π bonding in perspective. The order of ligands in the spectrochemical series is partly that of the strengths with which they can participate in M–L σ -bonding. For example, both CH_3^- and H^- are *high in the spectrochemical series* (similar to NCS^-) because they are *very strong σ donors*. However, *when π bonding is significant*, it has a strong influence on Δ_o : **π -donor ligands decrease Δ_o and π -acceptor ligands increase Δ_o** . This effect is responsible for CO (a strong π acceptor) being high on the spectrochemical series and for OH^- (a strong π donor) being low in the series. The overall order of the spectrochemical series may be interpreted in broad terms as dominated by π effects (with a few important exceptions), and in general the series can be interpreted as follows:

—increasing $\Delta_o \rightarrow$
 π donor, weak π donor, no π effects, π acceptor

Representative ligands that match these classes are

π donor	π acceptor	π donor	π acceptor
I^- , Br^- , Cl^- , F^-	H_2O	NH_3	PR_3 , CO

Notable examples of where the effect of σ bonding dominates include amines (NR_3), CH_3^- , and H^- , none of which has orbitals of π symmetry of an appropriate energy and thus are neither π -donor nor π -acceptor ligands. It is important to *note* that ***the classification of a ligand as strong-field or weak-field does not give any guide as to the strength of the M–L bond.***

❖ Strong field ligands

- Strong field ligands are ones that produce large splittings between the d orbitals and form low spin complexes. Examples of strong field ligands include CO, CN⁻, and NO₂.
- From a ligand field theory perspective all three of these ligands have strong π bonds (either double or triple bonds) and have empty π^* molecular orbitals available for back-bonding. Strong field ligands are both sigma donors (all ligands are sigma donors) and π acceptors. π back-bonding between a metal and a ligand stabilizes the metal based t_{2g} molecular orbital and increases Δ_o .

❖ Weak field ligands

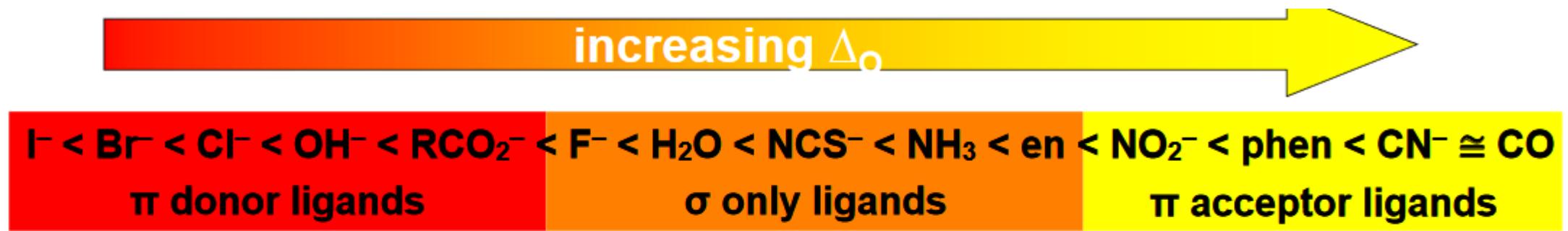
- Weak field ligands are ones that produce small splittings between the d orbitals and form high spin complexes. Examples of weak field ligands include the halogens, OH⁻ and H₂O.
- From a ligand field perspective these ions or molecules all have filled orbitals which can π bond with the metal d orbitals. In the case of the halogens these are filled p orbitals and *in the case of OH and H₂O these are lone pairs which are perpendicular to the metal-ligand bond*. Weak field ligands are both sigma donors and π donors. The π donation from the ligand to the metal destabilizes the metal based t_{2g} molecular orbital and decreases Δ_o .

❖ Intermediate field ligands

- Intermediate field ligands produce intermediate splittings between the d orbitals and could form high or low spin complexes.
- Examples of intermediate field ligands include NH₃ or ethylenediamine (en).
- From a ligand field perspective ***these ligands only have a single lone pair available for sigma bonding.***
- *Intermediate ligands are those which are only sigma donors and are not π donors or π acceptors.*
- In this case the t_{2g} symmetry d orbitals are nonbonding and the Δ_o is determined by the strength of the metal-ligand sigma interaction (and amount of destabilization of the e_g* molecular orbital).

❖ Spectrochemical Series

➤ The trend in Δ_o that arises from π -donor, σ -only, and π -acceptor ligands is the basis for the Spectrochemical Series. For $[ML_6]^{n+}$ complexes:



- weak-field ligands
- high-spin complexes for $3d$ metals*

- strong-field ligands
- low-spin complexes for $3d$ metals*

The value of Δ_o also depends systematically on the metal:

1. Δ_o increases with increasing oxidation number.

2. Δ_o increases down a group.

→ both trends are due to stronger metal-ligand bonding.

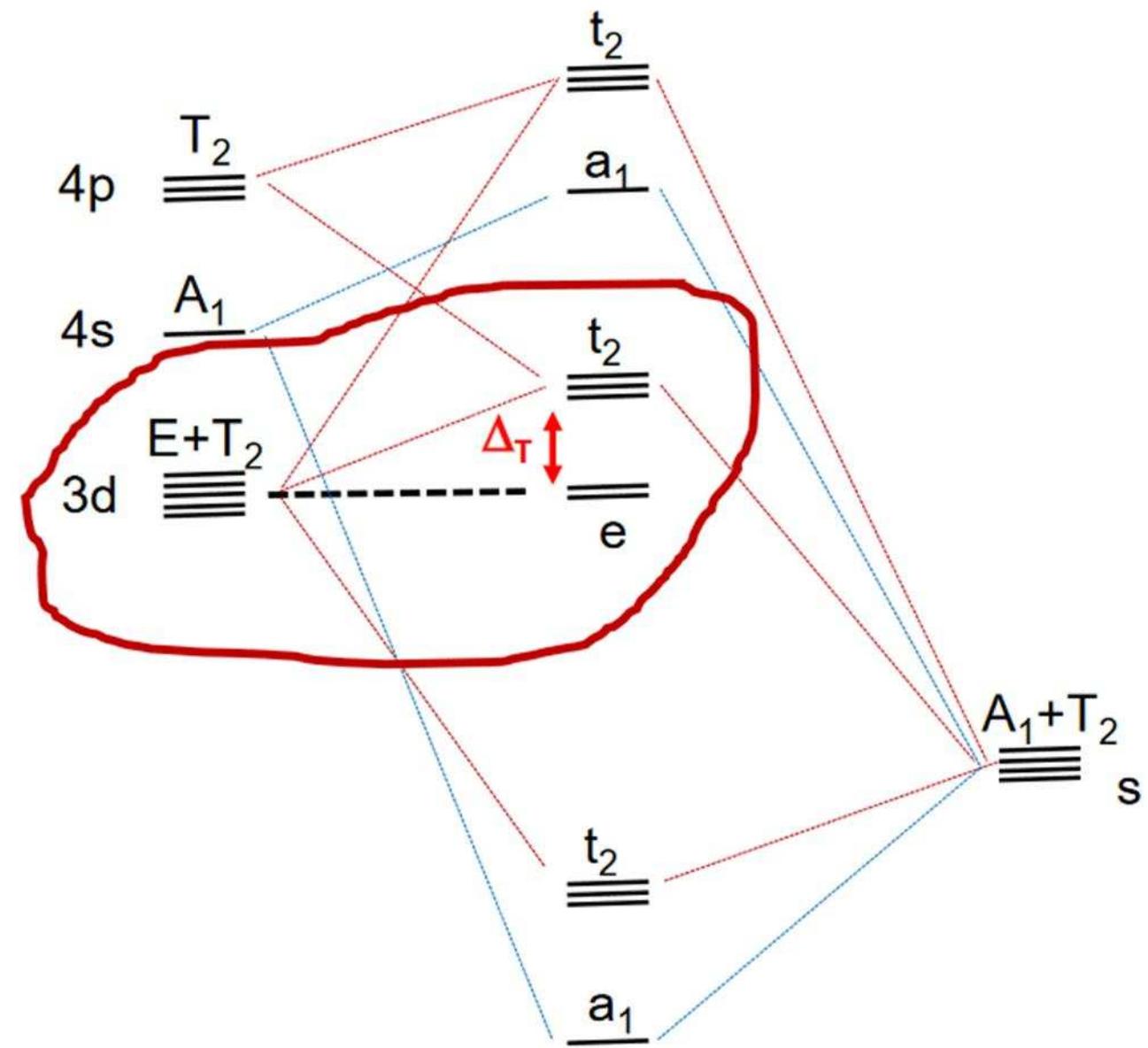
* Due to effect #2, octahedral $3d$ metal complexes can be low spin or high spin, but $4d$ and $5d$ metal complexes are always low spin.

Tetrahedral ML_4

Metal

ML_4

4 Ligands



The effect of π bonding on geometries other than octahedral is qualitatively similar, though we should note that in the *tetrahedral geometry it is the e orbitals that form the π interactions*. In the case of square-planar complexes the order of some of the notionally metal d orbitals changes compared with the pure crystal-field picture. Figure 20.22 shows the arrangement of metal d orbitals with π interactions considered; if we compare this picture with that in Fig. 20.10, where only electrostatic interactions with a crystal field were considered, we see that in both cases it is the $d_{x^2 - y^2}$ orbital that is highest in energy, and therefore unoccupied in complex with a d⁸-metal ion.

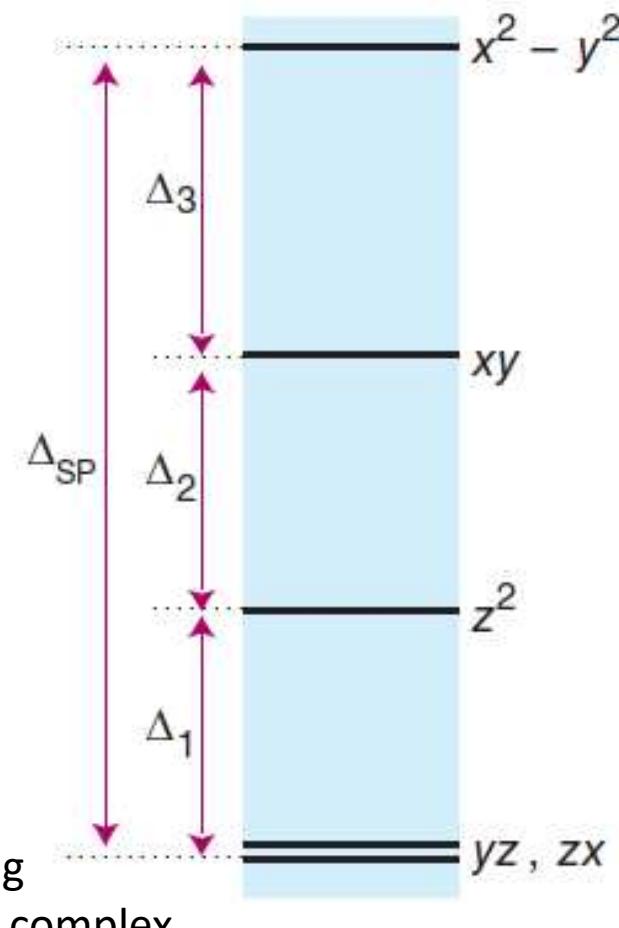


Figure 20.10 The orbital splitting parameters for a square-planar complex.

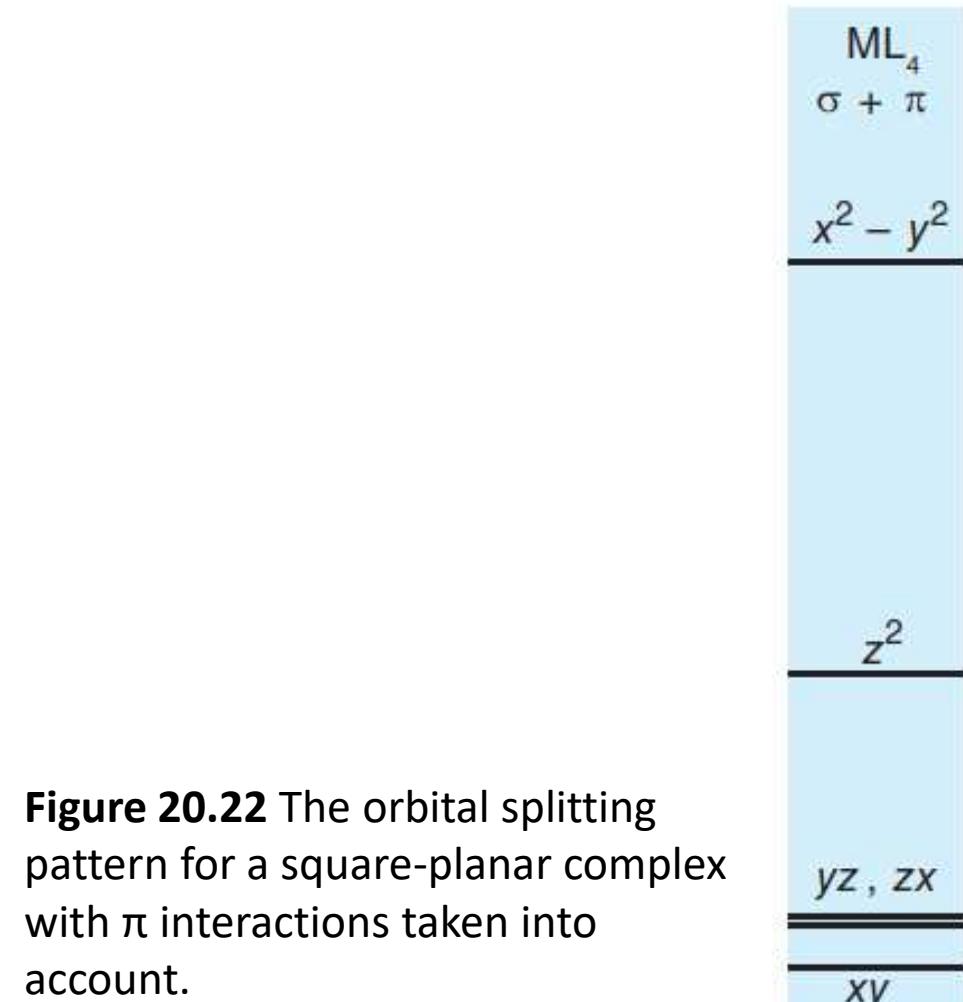


Figure 20.22 The orbital splitting pattern for a square-planar complex with π interactions taken into account.

Cisplatin: A Cancer-Fighting Drug

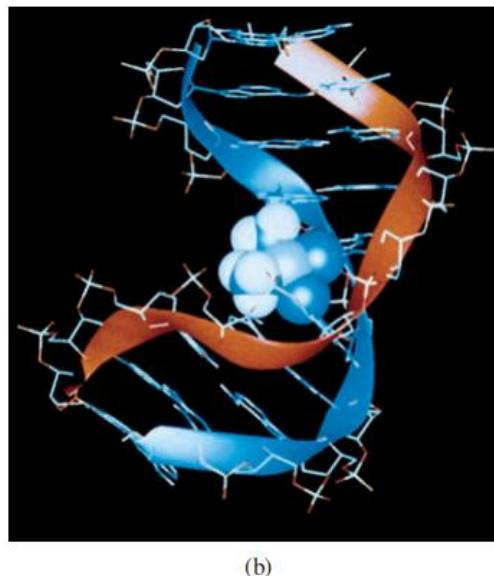
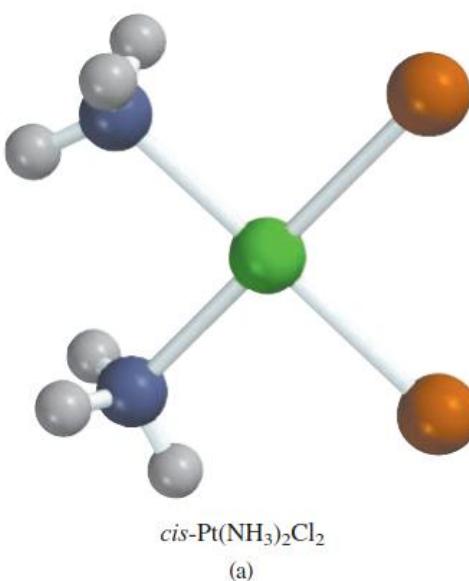
Chemotherapy is a treatment used for some types of cancer. The treatment employs anticancer drugs to destroy cancer cells. An important cancer-fighting drug is *cisplatin*, which is commonly used to treat testicular, bladder, lung, esophagus, stomach, and ovarian cancers. In the mid-1960s, scientists discovered that *cis*-diamminedichloroplatinum(II), $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, also called *cisplatin*, is an effective drug for certain types of cancers.

The **mechanism for the action** of cisplatin is the chelation of DNA (deoxyribonucleic acid). *Cisplatin binds* to DNA by forming cross-links in which *the two chloride ions on cisplatin are replaced by nitrogen donor atoms* on the DNA molecule (Figure 20.21). *This action leads to a mistake (mutation) in the DNA's replication and the eventual destruction of the cancerous cell.* Interestingly, the geometric isomer, *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, has no anticancer effect because it lacks the ability to bind to DNA.

Worldwide annual sales of platinum-based anticancer drugs are currently in excess of \$2 billion.

Figure 20.21

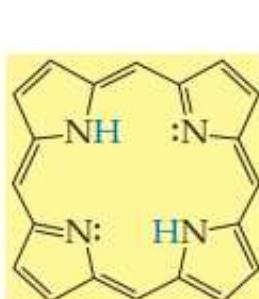
- (a) $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
- (b) Cisplatin disrupts DNA replication and transcription by binding to the double helix. The structure of this major DNA adduct, depicted here, was elucidated by Professor Stephen Lippard's group at MIT.



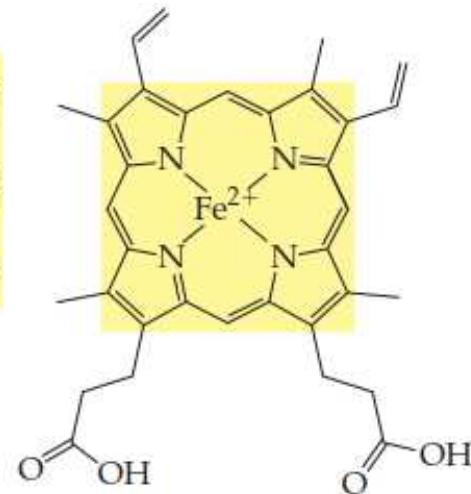
Transition Metal Complexes in Biological Systems

In addition to four building-block elements (C, O, H, and N) and seven elements known as macronutrients (Na, Mg, P, S, Cl, K, and Ca), organisms contain a large number of trace elements, most of which are transition metals. With the exception of Sc, Ti, and Ni (in most species), the Period 4 transition elements are essential to many organisms (Table 22.10), and plants require Mo (from Period 5) as well. The principles of bonding and d-orbital splitting are the same in complex biomolecules containing transition metals as in simple inorganic systems. We focus here on an iron-containing complex.

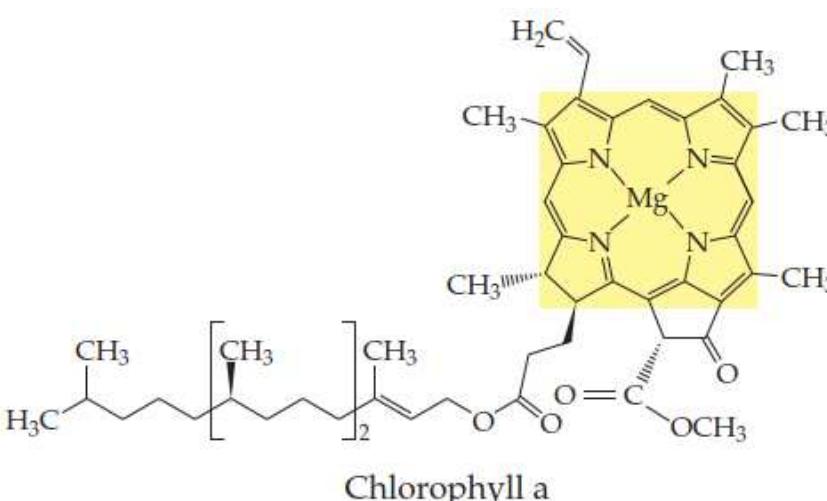
The d-block metals catalyze redox reactions, form components of membrane, muscle, skin, and bone, catalyze acid–base reactions, control the flow of energy and oxygen, and carry out nitrogen fixation.



Porphine



Heme b



Chlorophyll a

Table 22.10 Essential Transition Metals in Humans

Element	Function
Vanadium	Fat metabolism
Chromium	Glucose utilization
Manganese	Cell respiration
Iron	Oxygen transport; ATP formation
Cobalt	Component of vitamin B ₁₂ ; development of red blood cells
Copper	Hemoglobin synthesis; ATP formation
Zinc	Elimination of CO ₂ ; protein digestion

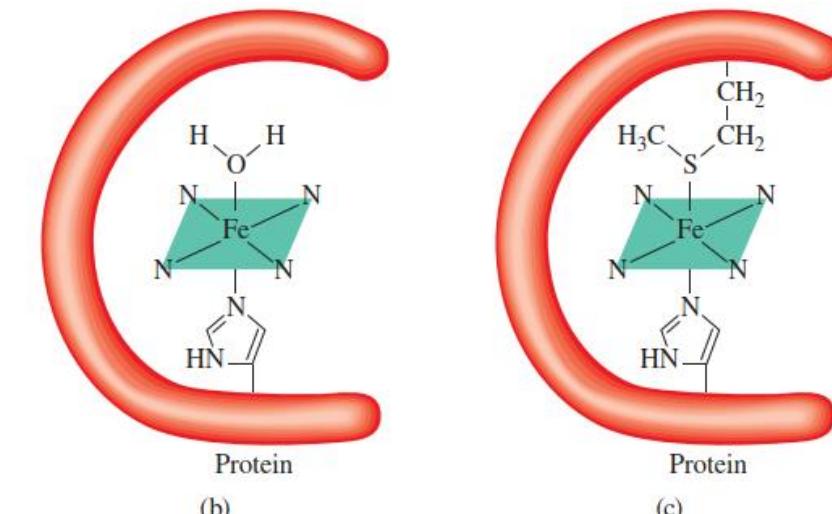
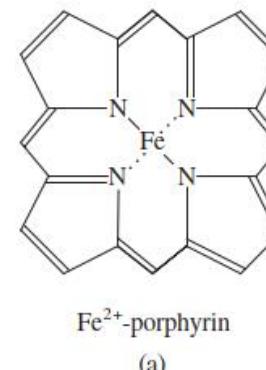
Coordination compounds play many roles in animals and plants. They are essential in the storage and transport of oxygen, as electron transfer agents, as catalysts, and in photosynthesis. Here we will briefly discuss the coordination compounds containing the porphyrin group and cisplatin as an anticancer drug.

Hemoglobin and Related Compounds

Hemoglobin functions as an oxygen carrier for metabolic processes. The molecule contains four folded long chains called subunits. Hemoglobin carries oxygen in the blood from the lungs to the tissues, where it delivers the oxygen molecules to myoglobin. Myoglobin, which is made up of only one subunit, stores oxygen for metabolic processes in muscle.

The heme group in each subunit is a complex ion formed between a Fe^{2+} ion and a porphyrin group [Figure 20.20(a)]. The Fe^{2+} ion is coordinated to the four nitrogen atoms in the porphyrin group and also to a nitrogen donor atom in a ligand that is part of the protein molecule. ***The sixth ligand is a water molecule***, which binds to the ion on the other side of the planar ring to complete the octahedral geometry [Figure 20.20(b)]. In this state, the molecule is called ***deoxyhemoglobin and imparts a bluish tinge to venous blood***. The ***water ligand can be replaced readily by molecular oxygen to form the red oxyhemoglobin found in arterial blood***.

Figure 20.20 (a) Structure of Fe^{2+} -porphyrin. (b) The heme group in hemoglobin. The Fe^{2+} ion is coordinated with the nitrogen atoms of the heme group. The ligand below the porphyrin is the histidine group, which is part of the protein. The sixth ligand is a water molecule, which can be replaced by oxygen. (c) The heme group in cytochromes. The ligands above and below the porphyrin are the methionine group and histidine group of the protein molecule.

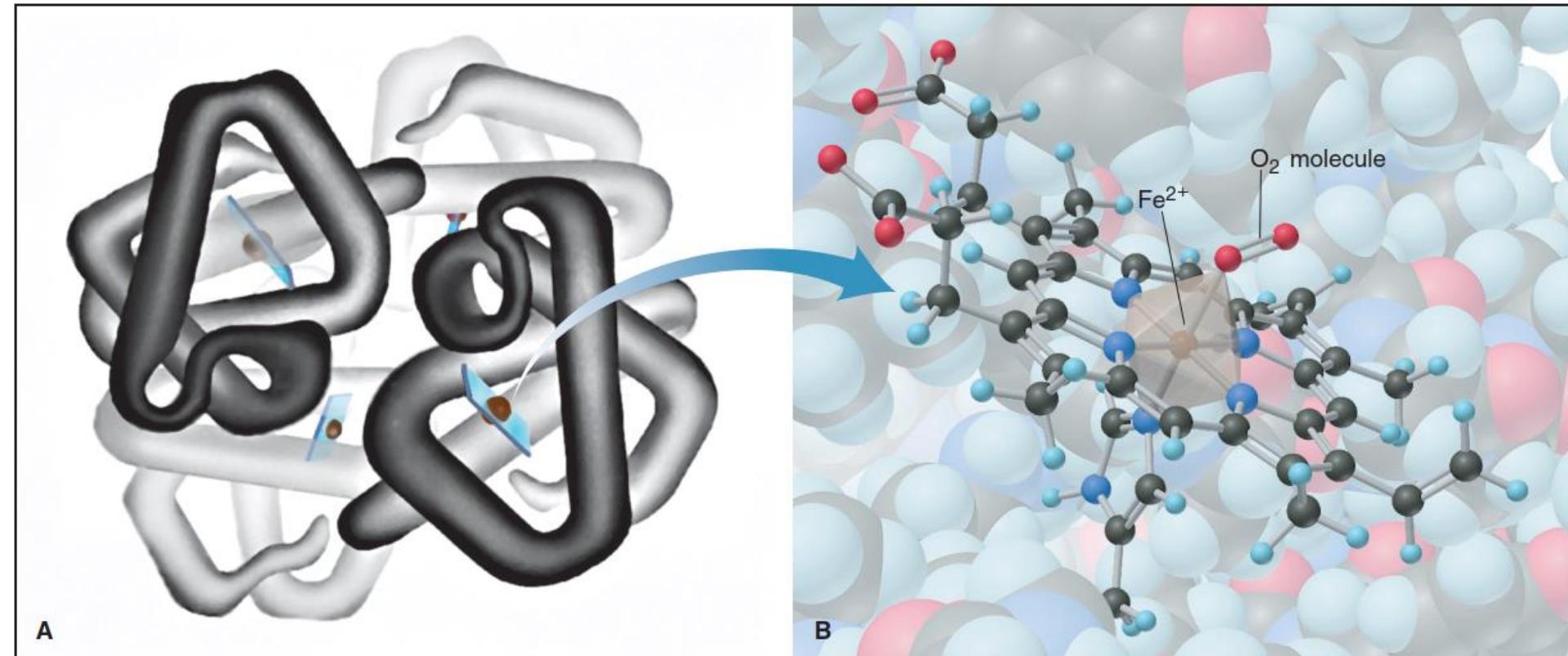


Iron plays a crucial role in oxygen transport in all vertebrates. The O₂-transporting protein hemoglobin (Figure 22.25A) consists of four folded chains, each cradling the Fe-containing complex heme. Heme consists of iron(II) bonded to four N lone pairs of a tetradentate ring ligand known as a **porphin** to give a square planar *complex (porphyrins)*. (Porphins are common biological ligands that are also found in chlorophyll, with Mg²⁺ at the center, and in vitamin B₁₂, with Co³⁺ at the center.)

In *hemoglobin* (Figure 22.25B), the *complex is octahedral*, with the fifth ligand of iron(II) being an N atom from a nearby amino acid (histidine), and the sixth an O atom from either an O₂ (shown) or an H₂O molecule.

Figure 22.25 Hemoglobin and the octahedral complex in heme.

A: Hemoglobin consists of four protein chains, each with a bound heme.
(Illustration by Irving Geis. Rights owned by Howard Hughes Medical Institute. Not to be used without permission.) B: In oxyhemoglobin, the octahedral complex in heme has an O₂ molecule as the sixth ligand for iron(II).



- In the arteries and lungs, the Fe^{2+} ion in heme binds to O_2 ; in the veins and tissues, O_2 is replaced by H_2O . Because H_2O is a weak-field ligand, the $d^6 \text{Fe}^{2+}$ ion is part of a high-spin complex, and the *relatively small d-orbital splitting makes venous blood absorb light at the red (low-energy) end of the spectrum and look purplish blue.*
- ..On the other hand, O_2 is a strong-field ligand, so it increases the splitting energy and gives a low-spin complex. Thus, *arterial blood absorbs at the blue* (high-energy) end of the spectrum, which *accounts for its bright red color.*
- In hemoglobin, the heme is linked to a protein (globin) through an additional Fe–N bond. In addition, the Fe(II) can bond to an O_2 molecule to give the six-coordinate, octahedral complex present in oxyhemoglobin. The three-dimensional shape of the protein part of the molecule makes possible the reversible binding of O_2 .

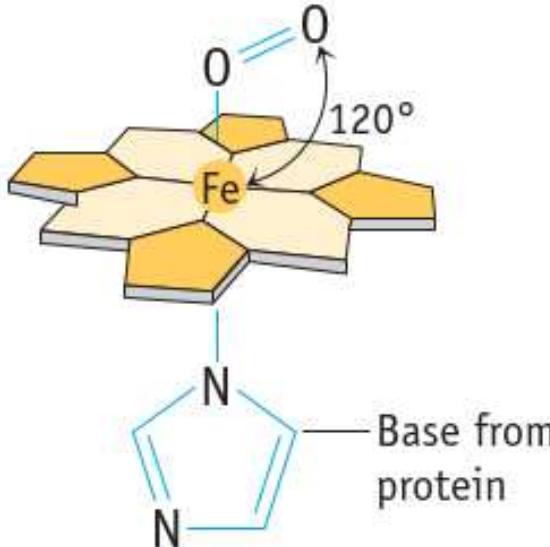


Figure. Oxygen binding. Oxygen binds to the iron of the heme group in *oxyhemoglobin* (and in myoglobin). Interestingly, the $\text{Fe}-\text{O}-\text{O}$ angle is bent.

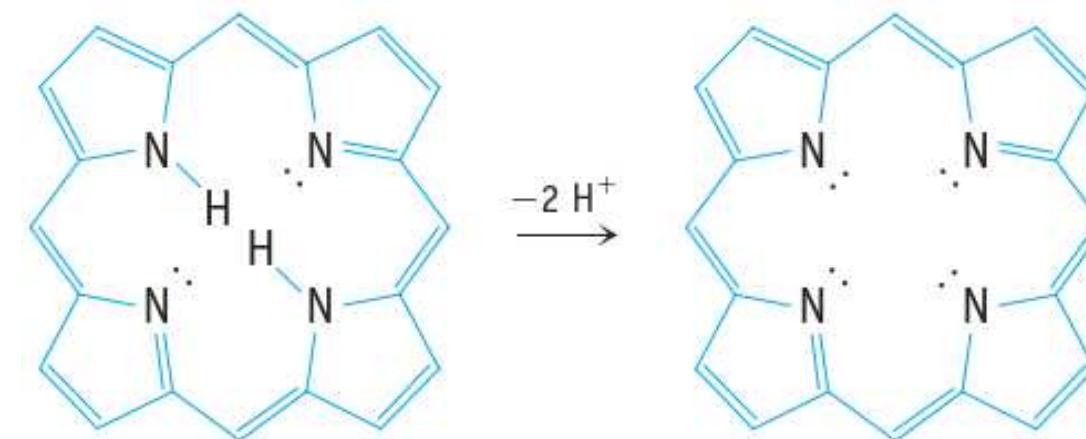
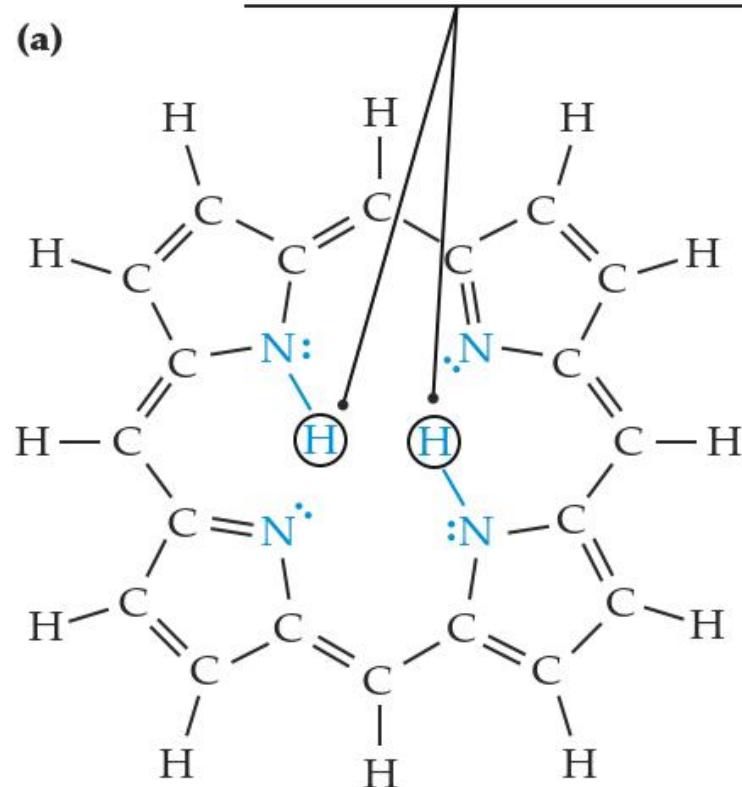


Figure. Porphyrin ring of the heme group. The tetradentate ligand surrounding the iron(II) ion in hemoglobin is a dianion of a molecule called a porphyrin. Because of the double bonds in this structure, all of the carbon and nitrogen atoms in the dianion of the porphyrin lie in a plane. The nitrogen lone pairs are directed toward the center of the ion, and *the molecular dimensions are such that a metal ion may fit nicely into the cavity.*

Loss of the two NH protons gives a planar, tetradentate 2⁻ ligand that can bond to a metal cation.

(a)



The Fe(II) ion has a six-coordinate, octahedral environment, and the O₂ acts as a monodentate ligand.

(b)

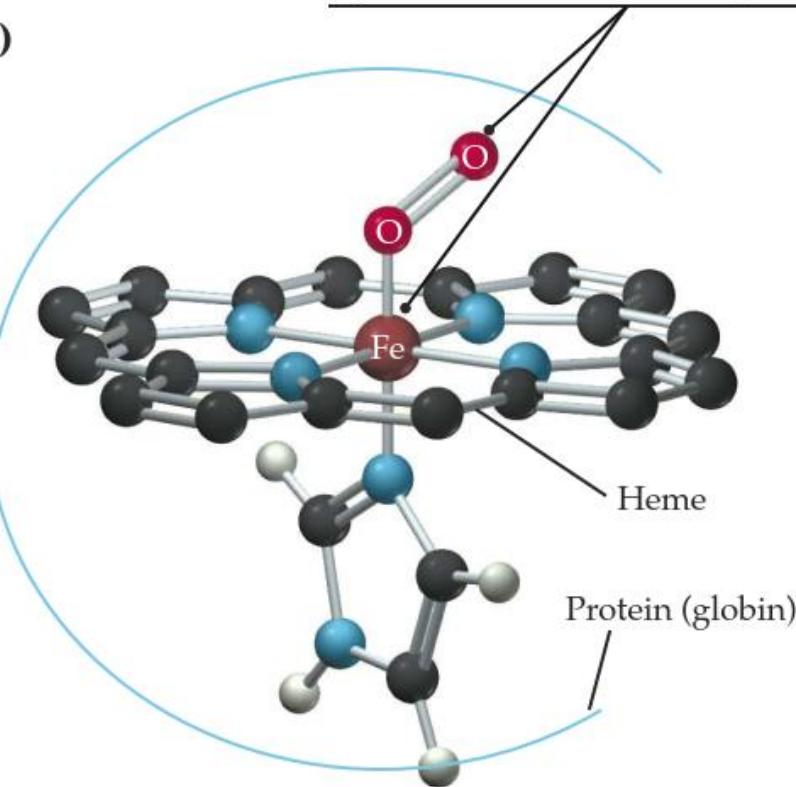


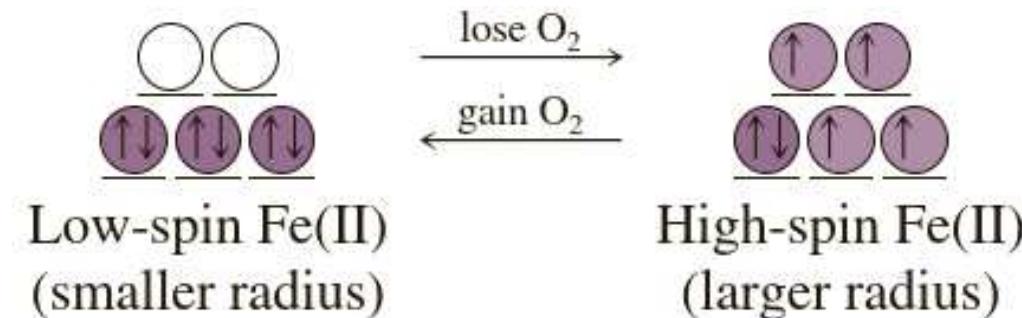
FIGURE 20.15 Chelating ligands in biomolecules. (a) The structure of the *porphin* molecule. The *porphyrins* are *derivatives of porphin* in which some of *the peripheral H atoms are replaced by various substituent groups*. (b) Schematic of the planar heme group, the attached protein chain, and the bound O₂ molecule in oxyhemoglobin. The *porphin* is a tetradentate ligand for the central metal, and the *metal–porphin complex is called a porphyrin*. Specific porphyrins differ in their central metals and in the substituent groups on the porphin rings.

Although hemoglobin is a tetramer of myoglobin, it does not function simply as four independent units of myoglobin. For it to function efficiently as a transporter of O₂ from the lungs and then be able to release that O₂ easily to myoglobin, hemoglobin *must be less strongly attached to O₂* in the vicinity of a muscle cell than is myoglobin.

In hemoglobin, the release of O₂ from one heme group triggers the release of O₂ from another heme group of the same molecule. In other words, there is a ***cooperative release of O₂*** from hemoglobin that makes it possible for it to give up its O₂ to myoglobin.

The ***mechanism postulated for this cooperative release of O₂ depends on a change of iron(II) from a low-spin to a high-spin form***, with a ***corresponding change in the radius of the iron atom***. In oxyhemoglobin, iron(II) exists in the low-spin form. When O₂ leaves, the iron atom goes to a high-spin form with two electrons in the higher-energy d orbital. ***These higher-energy orbitals are somewhat larger than the lower-energy d orbitals.***

- When an O₂ molecule leaves a heme group, the radius of the iron atom increases, and the atom pops out of the heme plane by about 70 pm. In hemoglobin, this change triggers the cooperative release of another O₂ molecule.
- As the iron atom moves, the attached globin group moves with it. This motion of one globin group causes an adjacent globin group in the tetramer to alter its shape, which in turn makes possible the easy release of an O₂ molecule from its heme unit.



- There is another interesting event that happens when oxygen binds to the iron in hemoglobin. After binding O₂, the iron actually transfers a single electron to the oxygen, becoming a Fe³⁺ cation. Although deoxyhaemoglobin, the Fe²⁺ or Fe(II) species, is purple, many Fe³⁺ or Fe(III) compounds are red. Thus, oxyhaemoglobin is red.
- It is also interesting to note that we are used to seeing iron-containing materials turn a sort of red-brown color when they have been exposed to oxygen for a long time, especially in the presence of water and salts. Our cars, trains and bridges eventually rust as the iron in their steel turns to reddish iron oxide. William Tolman, a researcher in bioinorganic chemistry at the University of Minnesota, likes to raise the following question: we rely on iron complexes to carry oxygen through our salt-water bloodstream, so ***why don't we get rusty?***
- The ***answer*** is that, in a sense, ***we do***.
- It has been estimated that after several passes through our bloodstream, a hemoglobin molecule meets its end when the oxygen fails to detach and the iron complex decomposes to an iron oxide. That's one reason why you need to eat a diet that contains iron, to replenish your iron stores in order to make new hemoglobin on a regular basis.

➤ ***Carbon monoxide is toxic*** because it binds to Fe^{2+} ion in heme about 200 times more strongly than O_2 , which prevents the heme group from functioning:



Like O_2 , CO is a strong-field ligand, which results in a bright red color of the blood. Because the binding is an equilibrium process, breathing extremely high concentrations of O_2 displaces CO from the heme and reverses CO poisoning:



The iron-heme complex is present in another class of proteins called the *cytochromes*. Here too, the iron forms an octahedral complex, but both the fifth and sixth ligands are part of the protein structure [Figure 20.20(c)]. Because the ligands are firmly bound to the metal ion, they cannot be displaced by oxygen or other ligands. Instead, the ***cytochromes act as electron carriers***, which are essential to metabolic processes. In cytochromes, iron undergoes rapid reversible redox processes:



which are coupled to the oxidation of organic molecules such as the carbohydrates.

- The chlorophyll molecule, which is necessary for plant photosynthesis, also contains the porphyrin ring, but in this case the metal ion is Mg^{2+} rather than Fe^{2+} .
- Green is the complementary color of magenta—a purplish red—so we should expect **chlorophyll** to absorb light in the red region of the spectrum (about 670–680 nm). This suggests that ***green plants should grow more readily in red light*** than in light of other colors, and *some experimental evidence indicates that this is the case*. For example, the maximum rate of formation of $O_2(g)$ during photosynthesis occurs with red light.

Experimental Technique: UV-VISIBLE ABSORPTION SPECTROSCOPY

Ultraviolet (UV)-visible absorption spectroscopy is a spectroscopic method that measures the light absorption by the molecular species in a solution in the UV (200–380 nm) to visible (380–750 nm) wavelength range. The ultraviolet region below 200 is called the vacuum UV because oxygen in the air absorbs strongly in this region. Measurements of sample absorption below 200 nm require specialized instrumentation that can purge oxygen from the light path to remove the interference.

UV-visible spectroscopy is commonly used for organic molecules but can also be used for light absorbing transition metal complexes and nanomaterials.

The selective absorption and transmittance of visible light and ultraviolet radiation are the basis of a spectroscopic technique for identifying compounds and for determining their concentrations in samples.

The Technique

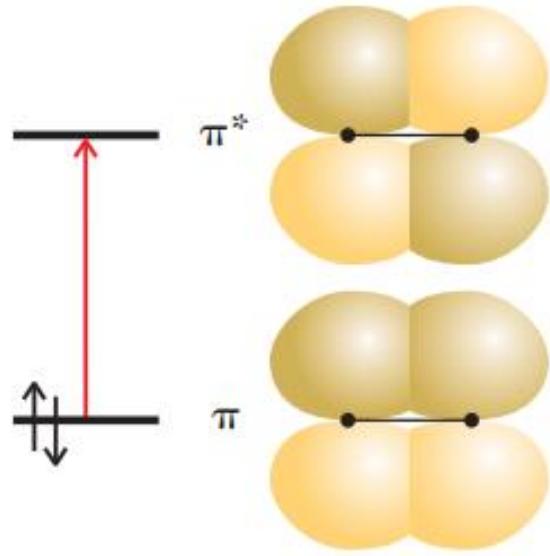
When electromagnetic radiation falls on a molecule, the electrons in the molecule can be excited to a higher energy state. Radiation of frequency ν (nu) can raise the energy of the molecule by an amount ΔE ,

$$\Delta E = h\nu \quad (1)$$

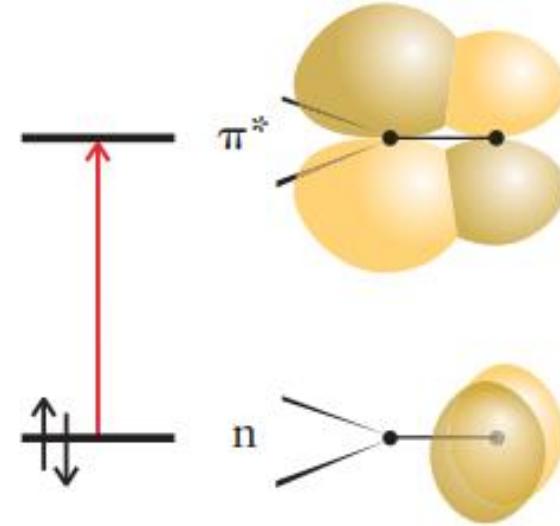
where h is Planck's constant. This equation is the Bohr frequency condition. Provided that an empty orbital exists at the right energy, the incoming radiation can excite an electron into it and hence be absorbed. For typical ultraviolet wavelengths (of 300 nm and less, corresponding to a frequency of about 10^{15} Hz), each photon brings enough energy to excite the electrons in a molecule into a different distribution. Therefore, the study of visible and ultraviolet absorption gives us information about the electronic energy levels of molecules.

Chromophores

Chromophores are the light absorbing moieties within a molecule. The presence of certain absorption bands in visible and ultraviolet spectra can often be traced to the presence of characteristic groups of atoms in the molecules. These groups of atoms are called chromophores, from the Greek words for “color bringer.” An important chromophore is a carbon–carbon double bond ($\text{C}=\text{C}$). Another important chromophore is the carbonyl group, $\text{C}=\text{O}$.



A π -to- π^* transition (e.g., in $\text{C}=\text{C}$): an electron in a bonding π orbital is excited into an empty antibonding π^* -orbital.



In an n -to- π^* transition ((e.g., in $\text{C}=\text{O}$, a carbonyl group), an electron in a nonbonding orbital (one localized wholly on the oxygen atom) is excited into an antibonding π^* -orbital spread over both atoms.

A d-metal ion may also be responsible for color, as is apparent from the varied colors of many d-metal complexes. Two types of transitions may be involved. In one, which is called a *d-to-d transition*, an electron is excited from a d-orbital of one energy to a d-orbital of higher energy. Because the energy differences between d-orbitals are quite small, visible light brings enough energy to cause this excitation, and so colors are absorbed from white light and the sample takes on colors complementary to those absorbed. In a second type of transition involving d-orbitals, called a charge-transfer transition, electrons migrate from the atoms attached to the central metal atom into the latter's d-orbitals or vice versa. This transfer of charge can result in very intense absorption; it is responsible, for instance, for the deep purple of permanganate ions, MnO_4^- .

Visible and ultraviolet absorption spectra are measured in an absorption spectrometer (Fig.1). The source gives out intense visible light or ultraviolet radiation. The wavelengths can be selected with a glass prism for visible light and with a quartz prism or a diffraction grating for ultraviolet radiation (which is absorbed by glass). The absorbed/transmitted as well as the incident light beams are sent to a photodetector, which measures the ratio of the **intensity of the reference beam (I_0)** to the **intensity of the sample beam (I)**. This is converted to the sample **absorbance ($A = \log (I_0/I)$)** for each wavelength by a data system and a plot of **absorbance versus wavelength**, called the *spectrum*, is recorded and displayed.

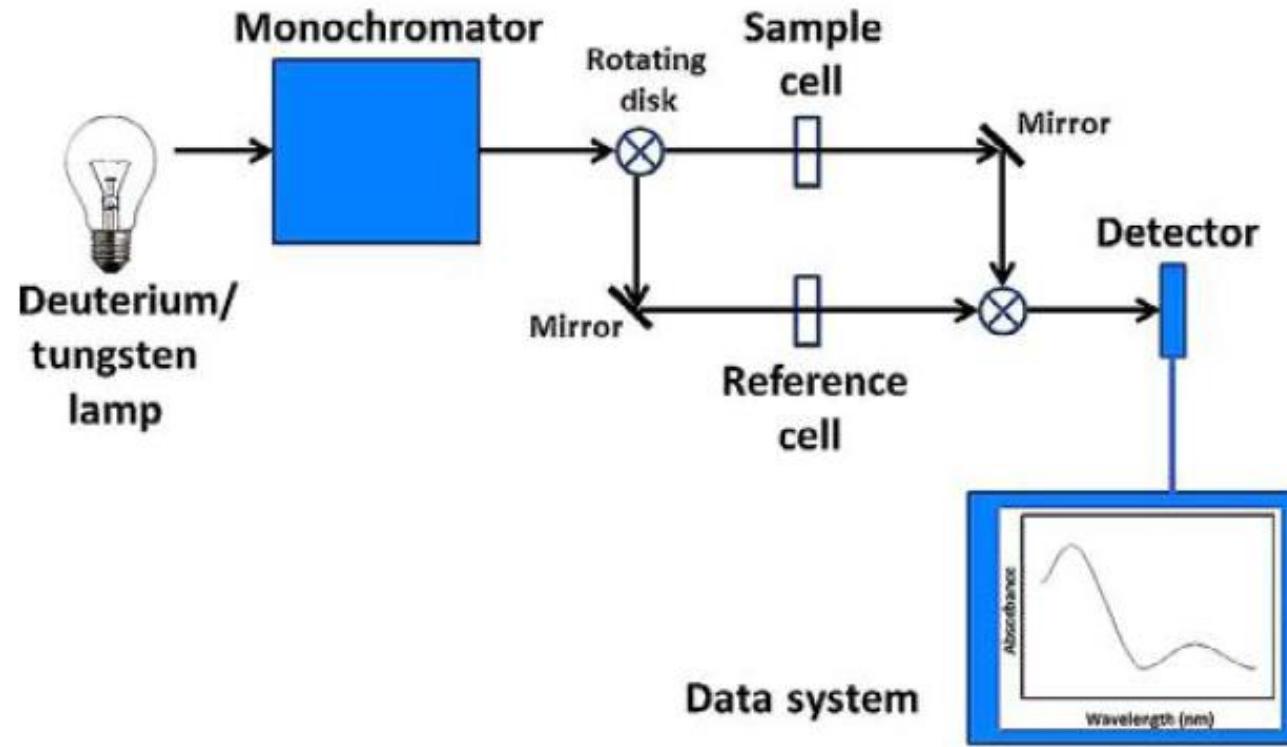


FIG 1. Schematic diagram of a double beam UV-visible absorption spectrometer.

A typical absorption spectrum, that of chlorophyll, is shown in Fig. 2. Note that chlorophyll absorbs red and blue light, leaving the green light present in white light to be reflected. That is why most vegetation looks green. The spectrum can help us to assess the absorption quantitatively and to make a precise analysis of the energy-capturing power of the molecule.

Unlike the atomic line spectra, molecular absorption spectra give broad bands with a measurable band width, as shown in Fig. 2. This is because, unlike atoms, molecules have vibrational energy levels that contribute to the ΔE between the electronic energy levels. A number of these molecular vibrational energy levels are available at each electronic energy level and transitions can occur between each of these vibrational levels. This results in a broadening of the absorption peak that occurs from the electronic transition. The more atoms there are in the molecule, the larger the number of molecular vibrational levels and the broader the absorption bands.

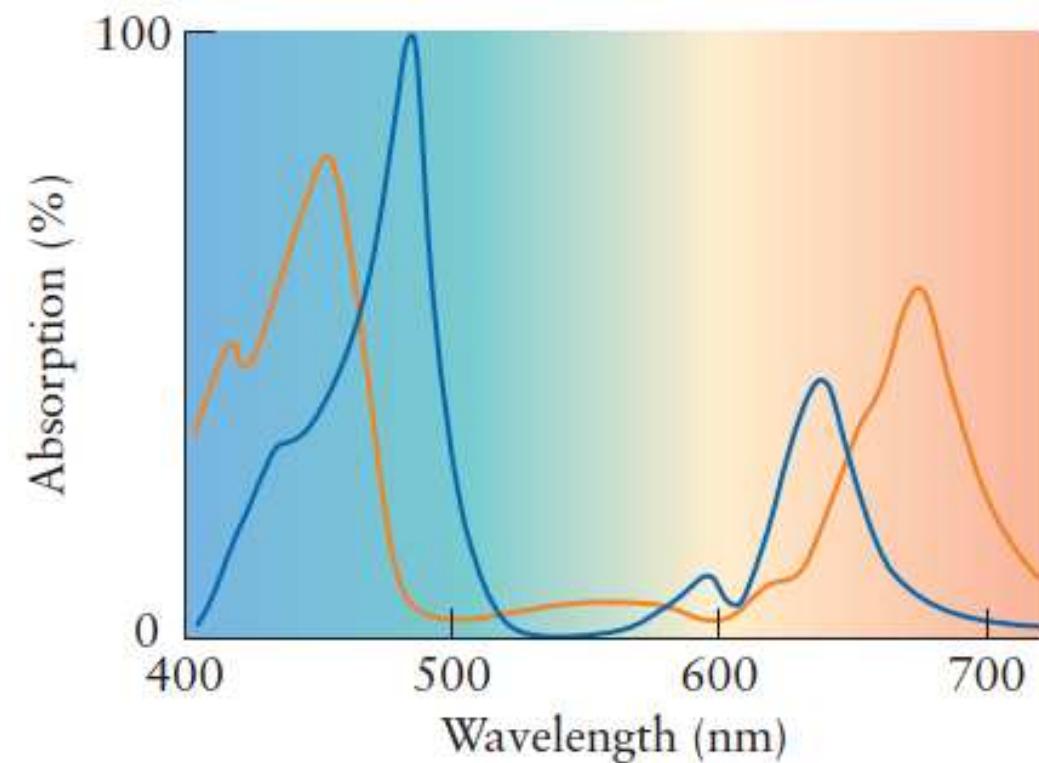


FIGURE 2 The optical absorption spectrum of chlorophyll as a plot of percentage absorption against wavelength. Chlorophyll a is shown in orange, and chlorophyll b in blue.

- The absorbance (A) is directly proportional to the concentration of the absorbing species and can be used to determine the amount of the species from the relationship known as Beer's Law, named for August Beer who discovered the relationship in 1852.
- Beer's Law for UV-visible absorption is written as;

$$A = \log (I_0/I) = \varepsilon c l$$

where ε is the molar absorptivity in units of $M^{-1} cm^{-1}$, c is the molar concentration (M), and l is the path length (cm).

- ε , the molar absorptivity, is the function of the wavelength.
- Although Beer's Law is followed at all wavelengths of an absorption band, it gives the best results at the wavelength of maximum absorption (λ_{max}).
- The molar absorptivity varies with the absorption across the band with ($\varepsilon = A/c/l$) and is also at a maximum value at λ_{max} , so the values for ε are always given at this wavelength.

SOLIDS AND MODERN MATERIALS

□ LEARNING OBJECTIVES

- ❖ Conducting Polymers
- ❖ Liquid Crystals
- ❖ Bonding in metals and semiconductors
- ❖ Crystal structures and Miller Indices
- ❖ How properties such as piezoelectricity arise from the crystal symmetry
- ❖ Nanomaterials

SOLIDS AND MODERN MATERIALS

Introduction

Key points: The goal of this topic is to be familiar with the **structure and properties of solids**, especially some of the solid materials used in modern technology.

- We are familiar with the 3 (THREE) states of aggregation of a Matter: ***Solid, Liquid & Gas***
- **Liquids** form when we strengthen the intermolecular interactions enough to bring all the molecules together while still preserving some of the fluidity—the freedom of motion—that characterizes the gas phase. The molecular environment in a liquid is crowded and boisterous.
- A **solid** is what we get when we turn the intermolecular attractions up enough to *stifle* the freedom of motion.
 - Like the liquid, the solid is a condensed phase, but it is not fluid.
 - Both the *volume and shape of a solid substance are essentially independent of weak forces, such as gravity*.

SOLIDS AND MODERN MATERIALS

Introduction

- ❑ *Look around and see:* Most of the materials such as the cell phone, computer, wrist-watch, dress materials, etc. are solids.
 - ❑ Solids are the materials used in many technologies: **alloys** for magnets and airplane turbines, **semiconductors** for solar cells and light-emitting diodes, and polymers for packaging and biomedical applications, and so on.
 - ❑ Do you know that the *Integrated electronic circuit (intel®)* which is at the heart of many electronic devices is built from semiconductors like silicon, metals like copper, and insulators like hafnium oxide
- In this section, we are going to explore:

➤ In this section, we are going to explore:

□ Bonding in Solids

□ Structures of Solids .. & the *Major Techniques of Structure Determination*

□ Classification of Solids .. Classification of solids according to the *types of bonding interactions* that hold the atoms together. *This classification helps us make general predictions* about the **properties** of solids.

- Ionic Solids: *solids formed by the mutual attractions between cations and anions*
- Metallic Solids & *Metallic Bonding*: *close packing of atoms with mobile electrons*
- Molecular Solids: *molecules are held together by weak intermolecular forces*
- Covalent-Network Solids: *atoms are held together by extended networks of covalent bonds*
- Polymers: *covalently bonded chain-like molecules and various nonbonding interactions*
- Nanomaterials: *lower-dimensional forms of materials....sizes in the range of 1–100 nm*

➤ *We will examine the structures and properties of these solids below.*

TABLE 10.9 Types of Crystalline *Solids* and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
<i>Ionic</i>	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, MgCl ₂
<i>Metallic</i>	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe
<i>Molecular</i>	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H ₂ O, Br ₂ , CO ₂ , CH ₄
<i>Covalent network</i>	Covalent bonds	Hard, high-melting	SiO ₂ , C (diamond)

Amorphous Solids, Polymers, and Crystals

- The *molecular structures* of solids range between *two extremes*: ***nearly random*** like the liquid, and ***highly ordered***.
- We begin our exploration of *solids* by *dividing them into these two classes*, and also briefly describing *a class that tends to lie between these two extremes*.

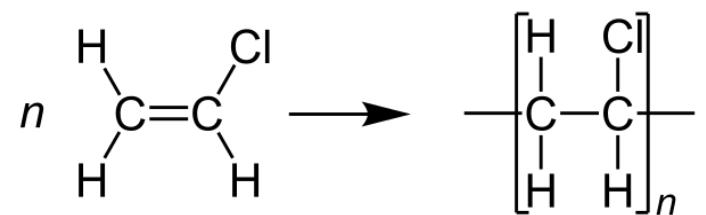
□ Amorphous Solids

- Amorphous solids are solids that do not have long-range order.
- They include all forms of glass, which is the solid formed when a liquid cools to rigidity without adopting any ordered arrangement.
- *The amorphous liquid structure is preserved in a glass, but too little kinetic energy remains for the molecules to flow freely, even over long periods.*
- The short-range order of an amorphous solid may be characterized by determining the pair correlation function $G(R)$ (the probability of finding the center of a particle a given distance from the center of another particle). At values of R equal to two or three molecular diameters, $G(R)$ will converge rapidly to one, just as it does for the liquid. The only difference between a glass and a liquid is that the liquid will keep shifting in time.

- Not all amorphous solids are glasses.
- For example, liquid silicon dioxide is structurally identical to window glass: the bonding mechanisms, short-range order, electrical properties, density, and so forth, are the same.
- ***Pure elemental silicon, on the other hand, has a liquid state that is very different from the amorphous solid state. The liquid is a metal, and correspondingly dense***, whereas the amorphous solid has a much less dense, tetrahedrally bound structure akin to that of diamond and is not metallic.
- ✓ If silicon could be made to form a glass, it would be a dense metal, like the liquid.

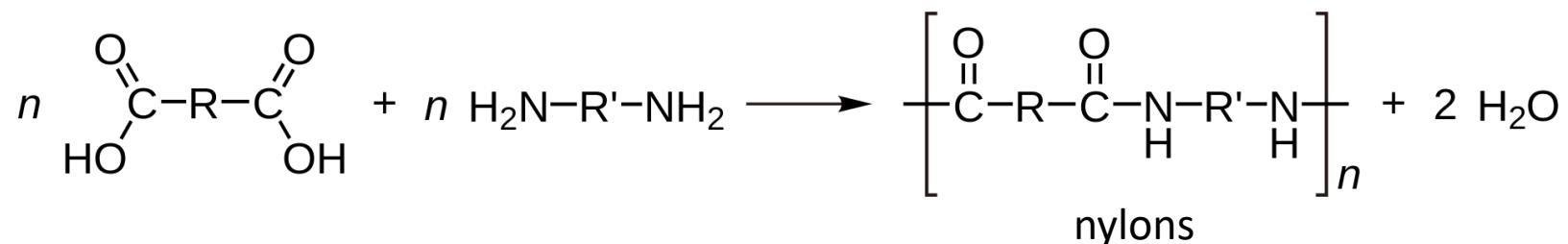
❖ Polymers

- **Polymers** are generally any molecule made up of several identical subunits, but not necessarily possessing the long-range symmetry of crystals.
- The term has come to be closely associated with the particular case of a long-chain hydrocarbon composed chiefly of a repeating link.
- ✓ Among the best known are the polyvinyl plastics, in which the repeating sequence is of the form $\text{—CR}'\text{R}''\text{—CR}'\text{R}''\text{—}$.
- ✓ Although “vinyl” actually refers to the functional group $\text{H}_2\text{C=CH}$, the polyvinyl plastics are single-bond carbon chains, so named because they are derived from vinyl precursors.
- Similarly, polyesters, polyamides (the nylons), and polyisoprenes (rubbers) are made from ester, amine, and butadiene (isoprene) precursors.

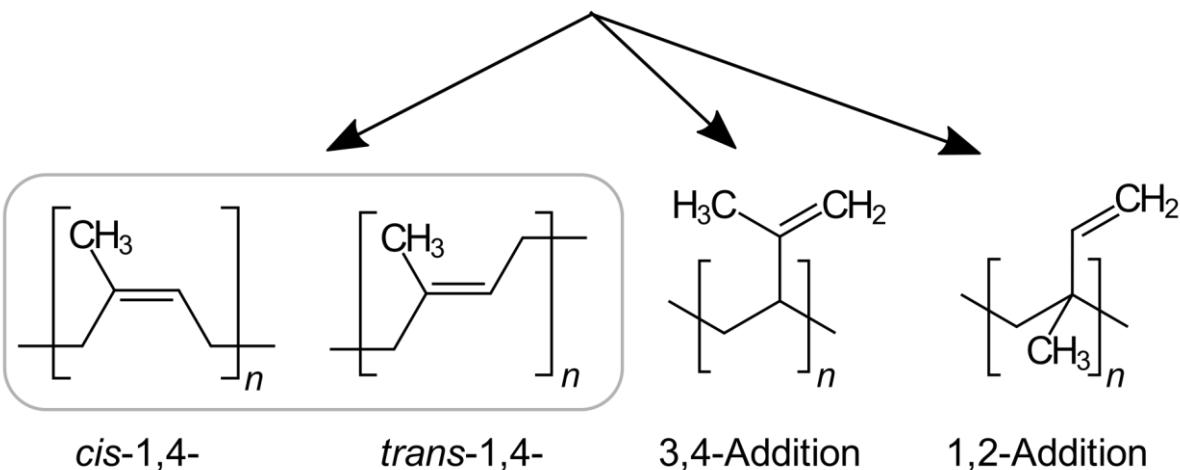
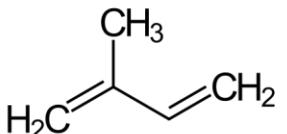


Vinyl chloride (VC)

Polyvinyl chloride (PVC)



Isoprene, or 2-methyl-1,3-butadiene



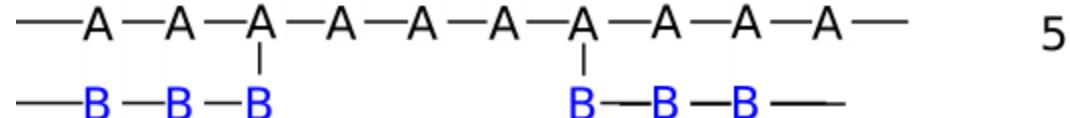
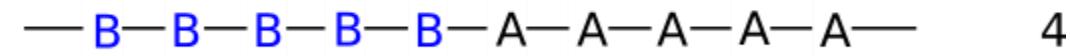
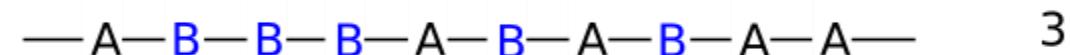
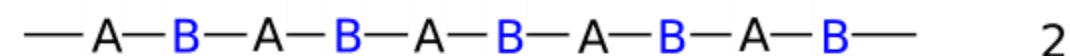
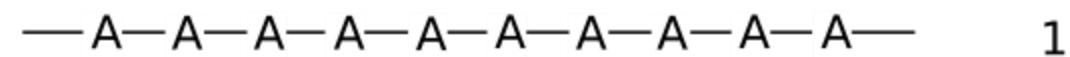
□ **Copolymers**, polymers made from more than one different monomeric subunit, are also possible.

➤ These may appear in any of a variety of forms, each with different macroscopic properties and different synthetic procedures.

- **Alternating copolymers** are formed with each monomer bonded to a different monomer.
- **Random copolymers** have no order to the appearance of one type of monomeric unit over another.
- **Block copolymers** have large isolated groups of each monomer, and the groups are then bound together.

Different types of polymers:

- 1) homopolymer
- 2) alternating copolymer
- 3) random copolymer
- 4) block copolymer
- 5) graft copolymer.



Polymers encompass a wide range of physical properties, including:

- **plastics**: Compounds that distort under stress, such as polyethylene.
- **elastomers**: Compounds that distort under stress but return to their original structure when the stress is removed, such as rubber.
- **fibers**: Essentially one-dimensional polymers, forming long, thin strands, such as nylon.

Bulk polymers may be either ***crystalline*** or ***amorphous***, or ***a mixture of both***.

- The *crystalline regions* within the bulk are called *crystallites*.
- ✓ The fraction of the bulk that exists in crystallites depends on the *regularity of the polymer chain* but can also be controlled in some cases by *the rate of solidification*.
- ✓ *Stressing a polymer tends to increase the size and number of crystalline regions*, because external forces tend to push or pull the polymer units into line with one another.
- *The amorphous regions allow the polymer to yield to stress, giving the substance **plasticity***.
- *Crystallites, on the other hand, will resist any stress that opposes alignment of the molecules, and may fracture if the stress force exceeds the bonding force.*

Conducting Polymers (CPs)

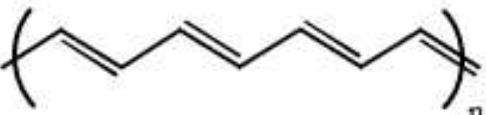
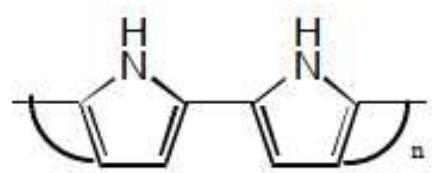
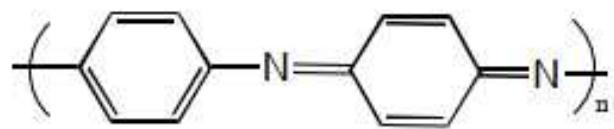
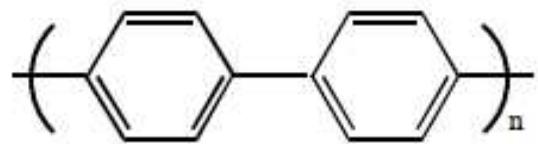
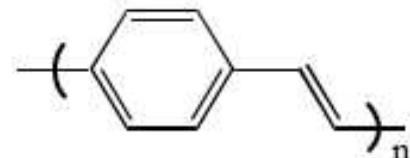
- Polymers are typically utilized in electrical and electronic applications as **insulators** where advantage is taken of their **very high resistivities**.
 - Typical properties of polymeric materials: Strength, flexibility, elasticity, stability, mouldability, ease of handling, etc.
- There are polymers which are good conductors of electricity. They are called (*intrinsically conducting (conductive) polymers or organic metals (synthetic metals)*).
- ✓ The chemistry Nobel prize in 2000 was awarded to Alan J. Heeger, Alan G MacDiarmid, and Hideki Shirakawa for the discovery and study of conducting polymers.
- ✓ We are going to discuss **those conducting polymers whose backbones are responsible for the generation and propagation of charge carriers**.
- Here we are **not** considering the “conductive polymer *composites*” which are polymers **filled with the conductive materials** such as carbon black, metal flakes or fibers, and so on.
- ✓ In these materials, the major practical function of the *polymer matrix* is to serve as a “glue” to hold the conductive elements together in a solid entity. The interest in such material derives from the *low cost, lightweight, mechanical durability, and ease of processability of the polymer component, in concert with reasonably good bulk conductivity*.

Conducting Polymers

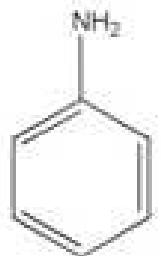
- Potential ***advantages include variable conductivity by controlling the extent of oxidation or reduction, the ability to dictate the nature of the majority carriers, and facile cycling between conductive and insulating states.***
- Can be used as hole injecting electrodes for OLEDs (organic light-emitting diodes)
- Usage in electroluminescent displays (mobile telephones)
- In use as emissive layer in full-color video matrix displays
- Some are promising for field-effect transistors (Usage in supermarket checkouts)
- Can be used as antistatic coating material to prevent electrical discharge exposure on photographic emulsions
- Can provide electromagnetic shielding of electronic circuits
- Some absorb microwaves: stealth technique

Examples of Conducting Polymers

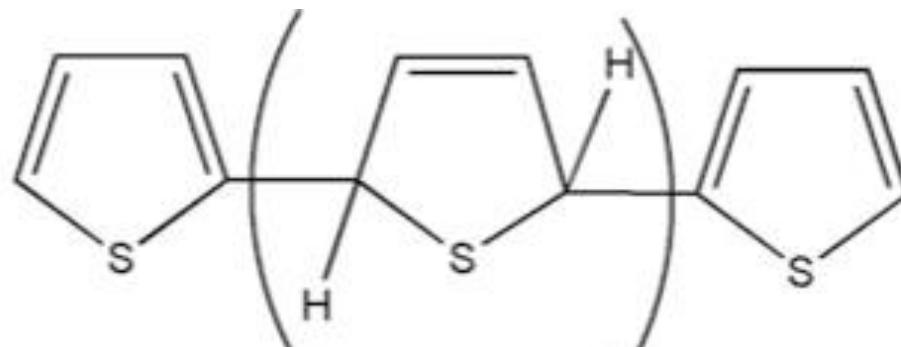
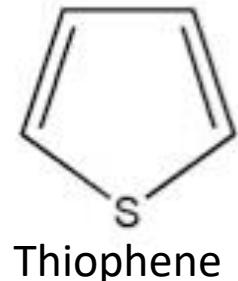
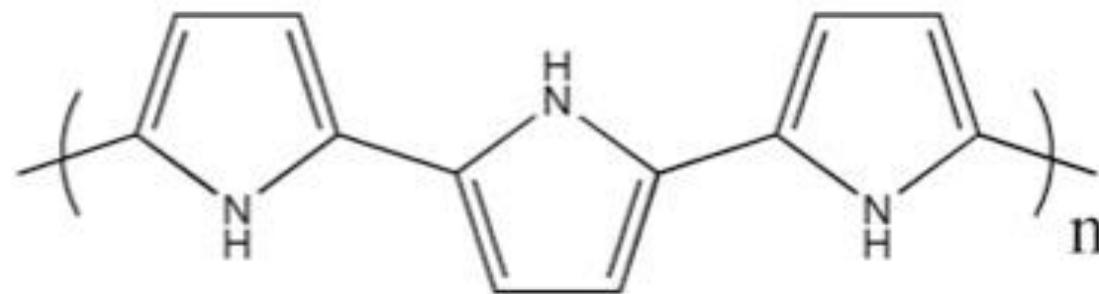
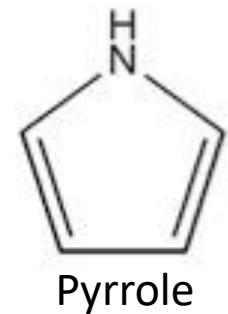
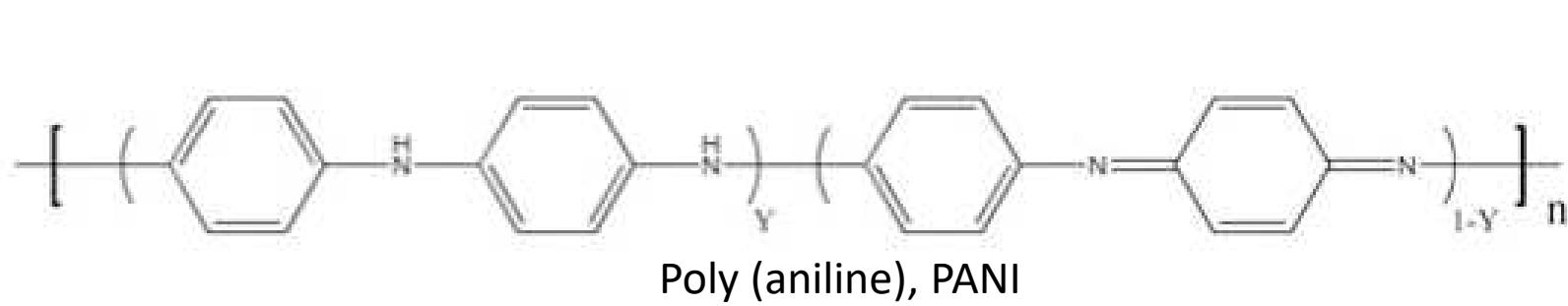
- **Polyacetylene**, in view of possessing the simplest molecular framework, has attracted the most attention, especially of physicists, with an emphasis on understanding the mechanism of conduction. However, its *insolubility, infusibility* and *poor environmental stability* has rendered it rather *unattractive* for technological applications.
- The technologically relevant front runners belong to essentially four families: **polyaniline** (PAni), **polypyrroles** (PPy), **polythiophenes** (PT) and **polyphenylene vinylenes** (PPV).
- *Polyaniline is rather unique as it is the only polymer that can be doped by a protic acid and can exist in different forms depending upon the pH of the medium.*
- While polyaniline is soluble in the neutral emeraldine form in highly polar aprotic solvents like, N-methyl pyrrolidone (NMP), all other polymers are insoluble.
- *However, laterally substituted derivatives of the remaining three classes are soluble in pristine form and are solution processable.*

	Structure	Maximum conductivity S/cm	Stability	Processability
Polyacetylene		1.5×10^5	Reacts with air	Film not soluble or fusible
Polypyrrole		2000	Reasonably stable	Insoluble and infusible
Polythiophene		100	Stable	Insoluble and infusible
Polyaniline		10	Stable	Soluble in neutral form
Polyphenylene		1000	Stable	Insoluble and infusible
Polyphenylene-vinylene		1000	Stable undoped form	Soluble precursor route available

Precursor Monomer



Polymer

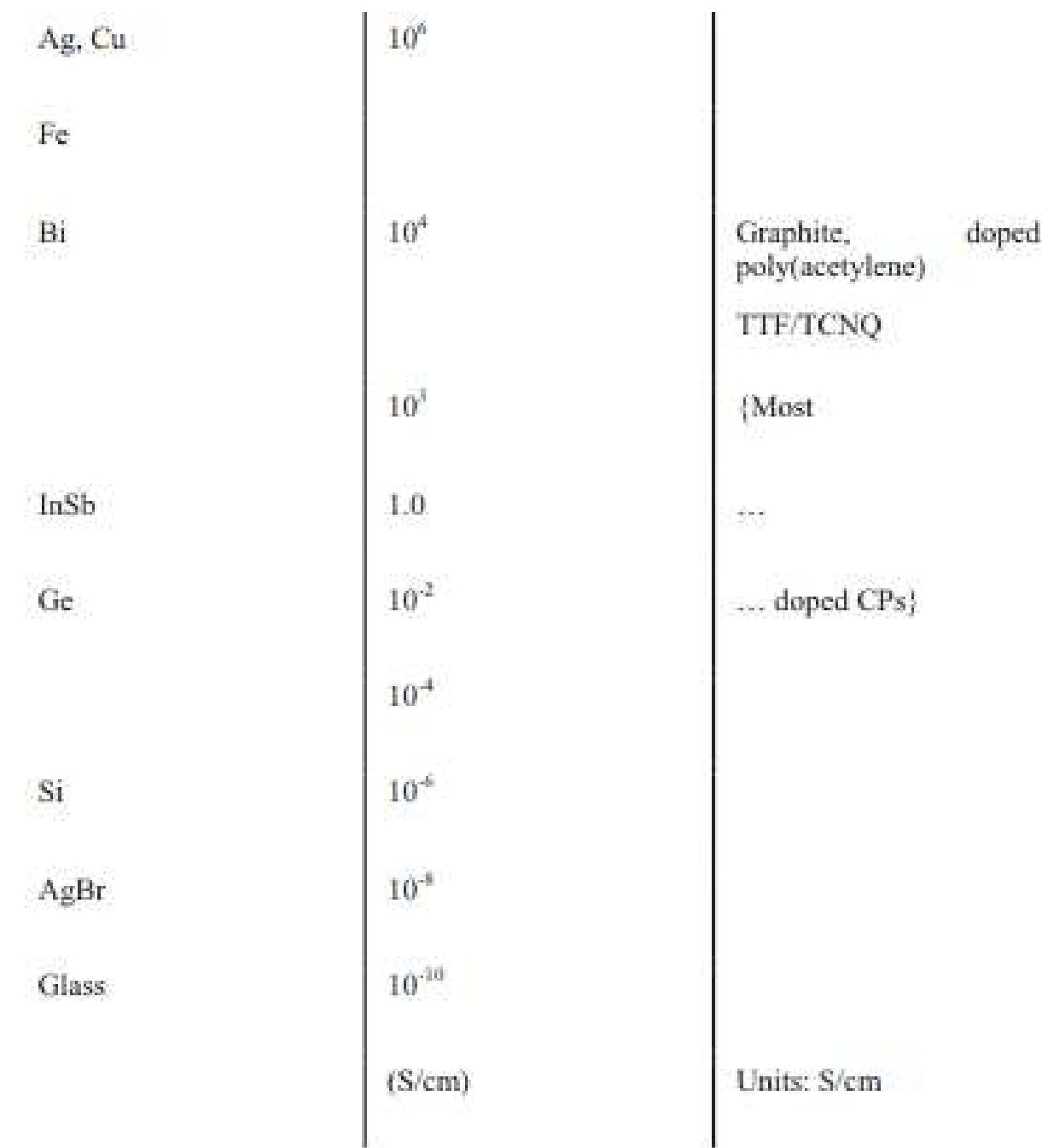


- Researchers have shown that certain classes of polymers, which are conjugated (those that possess an extended π -conjugation along the polymer backbone), *exhibit semiconducting behavior.*
- The discovery of **doping** led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S/cm (compare Copper $\sigma_{\text{room temp}}=10^6$ S/cm).
- *Doping is a process by which the polymer is either oxidized or reduced to create charge carriers.*
- The chemical origins of such a remarkable difference in the material properties between various types of polymers can be readily rationalized.
- Traditional polymers, such as polyethylene or polypropylene, are made up of essentially σ -bonds and hence *a charge once created on any given atom on the polymer chain is not mobile.*
- *The presence of an extended π -conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting.*

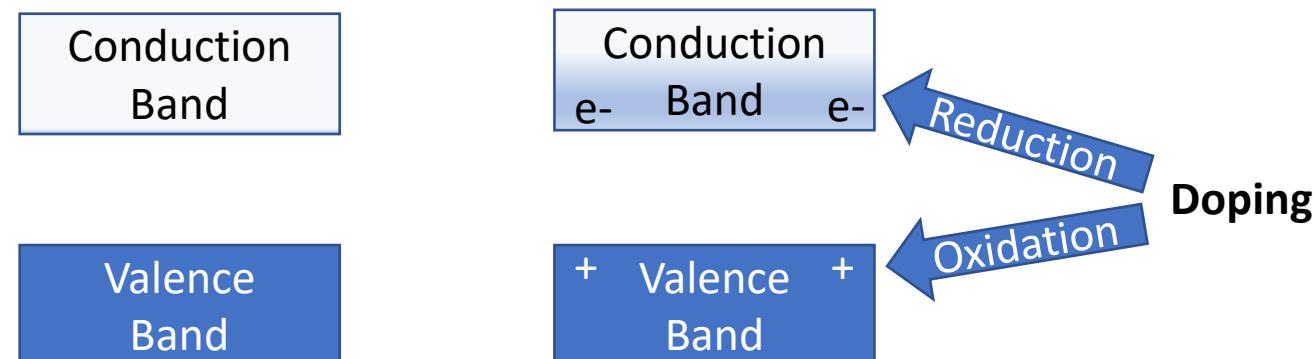
- This conductivity of CPs is achieved through simple **chemical or electrochemical oxidation**, or in some cases **reduction**, by a number of simple anionic or cationic species, **called dopants**.

- That is to say, the polymeric backbone of these materials needs to be *oxidized or reduced* to *introduce charge centers* before conductivity is observed, and the oxidation or reduction is performed by anions or cations somewhat misnamed dopants, a term borrowed from condensed matter physics.

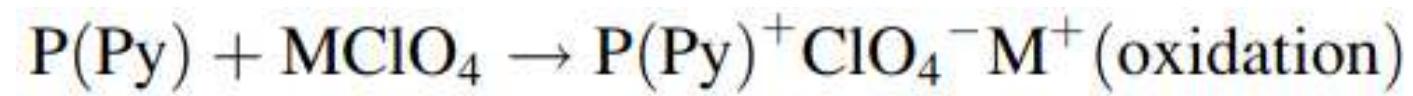
A better idea of the place of CPs among the three broad conductivity classifications of materials, i.e., **insulators, semiconductors, and metals**, can be garnered from a comparison of conductivities, as shown in Fig.



- The semiconductor band structure of CPs permits electronic excitation or electron removal/addition, e.g., from the valence to the conduction band, leading to most of the properties that are of interest in CPs.
- Excitation of electrons from the valence band to the conduction band, e.g., by photons, yields typical excited state properties such as photoluminescence and nonlinear optical properties (e.g., third-harmonic generation).
- On the other hand, **a chemical or other oxidation of the CP, i.e., essentially a removal of electrons from the valence band, leads to the presence of charges on the CP. These charges are in general strongly delocalized**, over several monomer units in the polymer. These charges also cause a relaxation of the geometry of the (now charged) polymer to a more energetically favored conformation.
- A charge may also be donated to the conduction band of the CP, causing reduction of the CP.



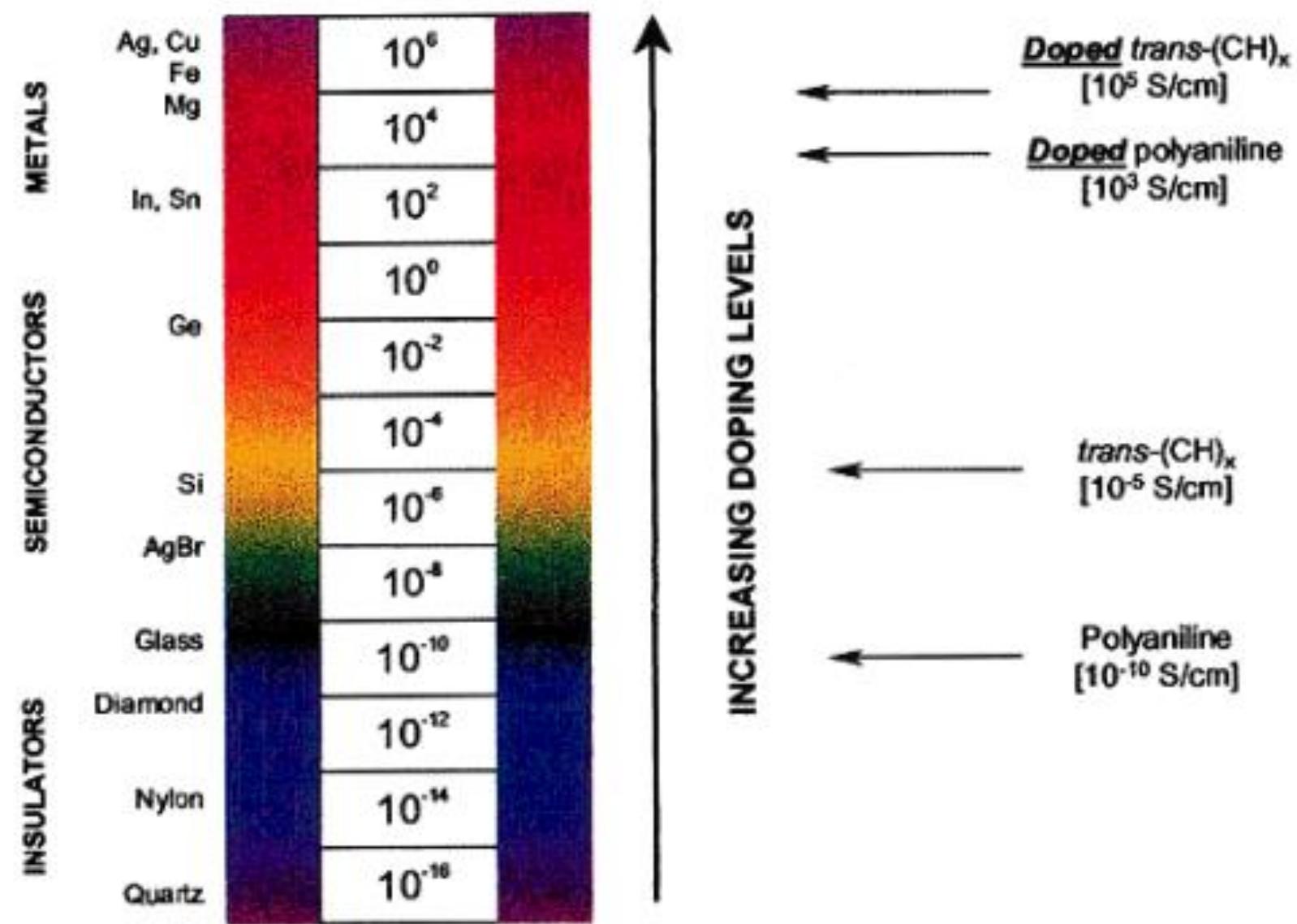
- Oxidation caused by a chemical species generates a positively charged CP and an associated anion.
 - Reduction similarly generates a negatively charged CP and an associated cation.
- ✓ Examples of these processes, also designated “doping/de-doping,” are, respectively, in very rough schematic, where M and A are any cation and anion, respectively:

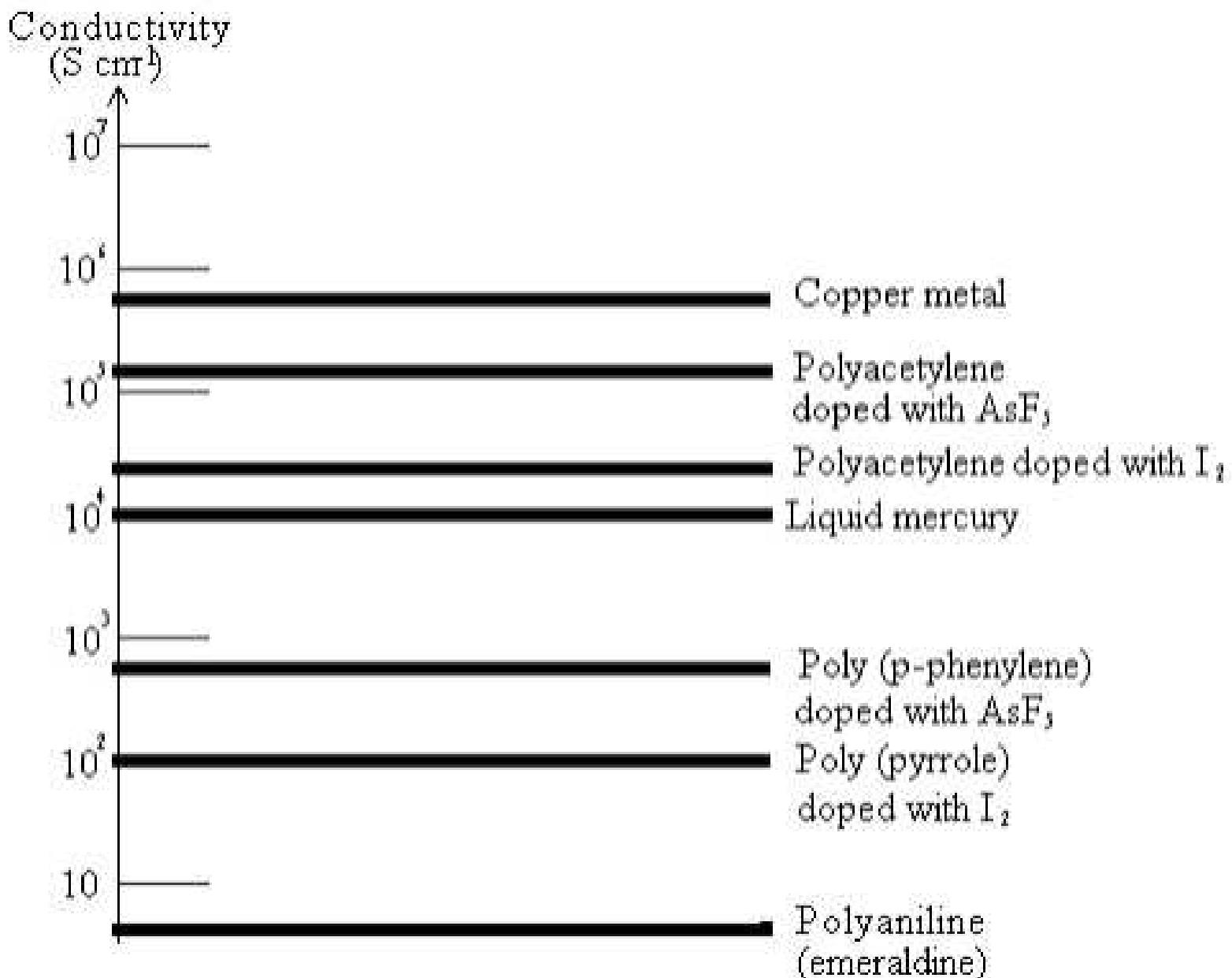


- ***Both the above processes, oxidation and reduction, impart conductive properties to the CP.***
- Because of the analogy with impurities which cause the removal or addition of charges from the valence or conduction band and thence impart higher conductivity in inorganic semiconductors such as silicon or CdSe, the chemical oxidation of the CP by anions, or its reduction by cations, was originally called ***doping***. The ***associated anions/cations, i.e., the counterions, were called dopants.***

- A CP that is in its **undoped**, i.e., neutral, state is generally termed ***pristine*** (sometimes, *virgin*).
- During the doping process, ***an organic polymer, either an insulator or semiconductor*** having a small conductivity, typically in the range 10^{-10} to 10^1 S/cm, is converted to a polymer which is in the '***metallic***' conducting regime (1 to 10^4 S/cm).
- The ***extent of oxidation/reduction***, i.e., doping, is called the ***doping level*** and *is generally measured as the proportion of dopant ions or molecules incorporated per monomer unit*. This is then generally expressed either as a fraction or as a molar percentage. For instance, a CP with *one dopant anion per four monomer units* would have a doping level of 0.25 or 25%.
- *The controlled addition of known, usually small (≤ 10 per cent) nonstoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer.*
- ***Doping is reversible*** to produce the original polymer with little or no degradation of the polymer backbone.

Figure 2. Effect on conductivity of polyacetylene and polyaniline after doping (figure taken from Nobel Lecture, 2000 by Alan G. MacDiarmid)





Logarithmic conductivity ladder locating some metals and conducting polymers

➤ This ***unique intrinsic conductivity of these organic materials***, which generally are comprised simply of C, H, and simple heteroatoms such as N and S, and the myriad of properties emanating from it **arise uniquely from π -conjugation**. That is to say, a sometimes fairly extended and delocalized conjugation originating in overlap of π -electrons. Such conjugation is illustrated somewhat simplistically in Fig. 27.1 for poly(acetylene), a prototypical CP.

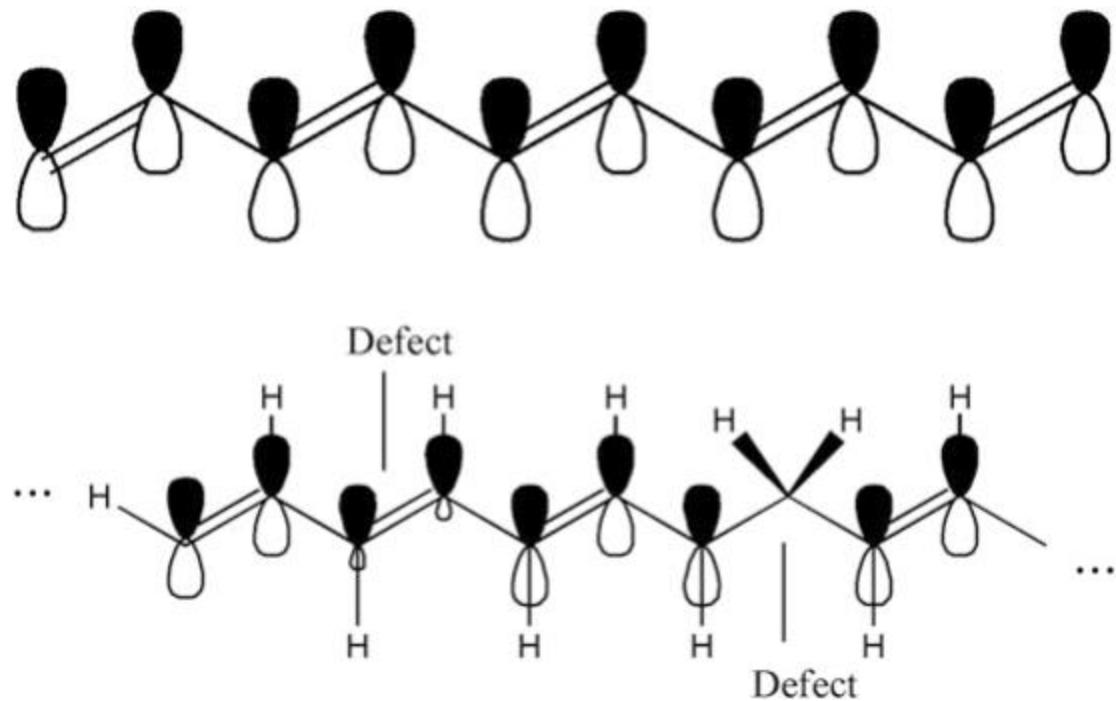
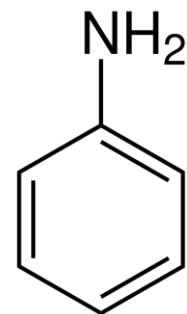


Fig. 27.1 Schematic representation of π -conjugation in the conducting polymer (CP) poly(acetylene).

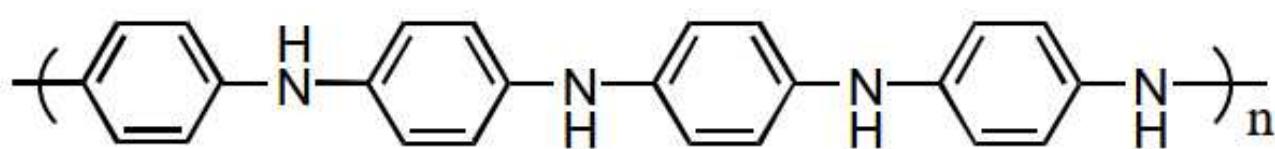
Top: Basic schematic. Bottom: Three-dimensional, including defects

The Case of Polyaniline

- Polyaniline has a rather unique structure, containing an alternating arrangement of benzene rings and nitrogen atoms.
- The nitrogen atoms can exist either as an **imine** (in an sp^2 hybridized state) or an **amine** (sp^3 hybridized).



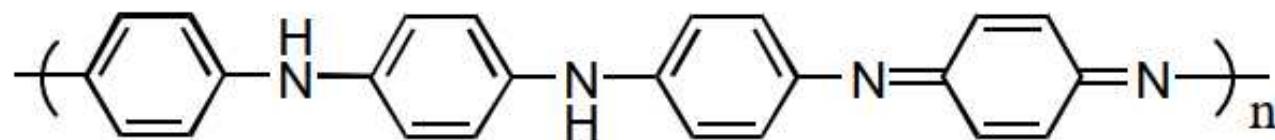
- Depending on the relative composition of these two states of nitrogen, and further on whether they are in their quarternized state or not, various forms of polyaniline can result.
- The structures of these forms can be best represented by choosing a minimum of four repeat units, as shown below.



Leucoemeraldine

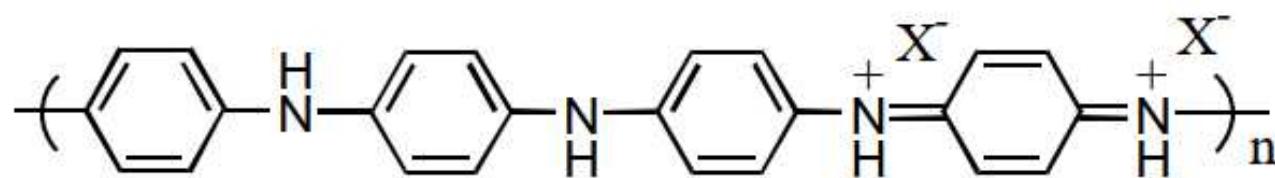
Attributes

Pale brown, insulating



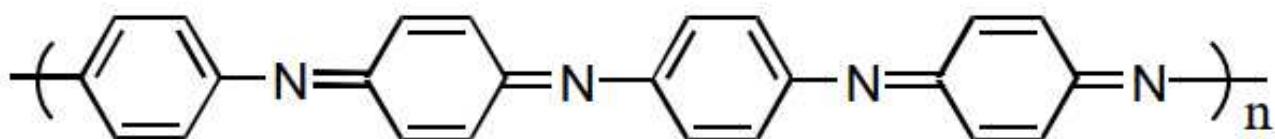
Emeraldine

Blue, insulating



Protonated Emeraldine

Green, partially oxidized
conducting form



Pernigraniline

Black, insulating

- The only form that is *conducting*, among the four, is the green protonated emeraldine form, which has both the *oxidized iminium and reduced amine nitrogens*, in equal amounts (i.e., it is half oxidized).
- Thus, the blue insulating emeraldine form can be transformed into the conducting form by lowering the pH of the medium and vice-versa.
- Another interesting feature of polyaniline is that, by use of an organic counterion (X^-), for instance, by using camphor sulfonic acid as the dopant acid, polyaniline can be retained in solution even in the doped conducting form, further enhancing its versatility.
- The transport of charge in these systems can be understood in a simple fashion, by causing *the imine and amine nitrogens to exchange places along the polymer backbone* (in protonated emeraldine).
➤ Try and push arrows to cause this change and observe that this process effectively causes the charges to move along the polymer backbone!

- One problem is that, *due to the presence of this extended conjugation along the polymer backbone, the chains are rigid and possess strong interchain interactions resulting in insoluble and infusible materials.* These **conjugated polymers**, hence, lacked one of the most important and useful properties of polymers, namely their **ease of processability**.
- More recently, however, it was demonstrated that when *lateral substituents were introduced*, even **conjugated polymers can be made soluble** (hence, processable) without significant loss in their conductivity.
- One other *problem* that plagued this field from its inception, is the *inherent instability of these polymers (especially, in the doped form) to ambient conditions*. Today, conducting polymers that are stable even in the doped form have been prepared.
- We shall highlight some specific examples of their potential applications.

Applications

Although several conducting polymers have been prepared, it was soon realized that they cannot compete with metals in traditional electrical applications, like wiring, transmission cables etc. Researchers have, therefore, focused on other applications that exploit the existence of extended conjugation in these polymers. A few interesting possibilities are mentioned below.

❖ **Polymeric Batteries**

- One of the first applications of conducting polymers, that was the focus of attention worldwide, was that of **light-weight batteries**.
- While a lot of the conjugated polymers were tried most of them failed to exhibit the desired properties, specifically with respect to stability. However, **batteries made using either polypyrrole or polyaniline as the positive electrode (cathode) and lithium–aluminium alloy as the negative electrode (anode)** exhibited much more respectable properties.
- ✓ The *electrolyte in these cases* were either LiClO_4 or LiBF_4 in propylene carbonate (a highly polar aprotic solvent, which is also fairly resistant to oxidation).
- ***During the battery discharge***, electrons move from the lithium alloy (which gets oxidized) to the polyaniline cathode (which gets reduced), as Li^+ from the anode and the anion, say, BF_4^- from the cathode enter the electrolyte.

- One major drawback of this battery is that the *energy density or energy storage capacity is low* and *its recyclability* (charging–discharging cycles) is relatively poor.
- More recently, however, some composites of an ***alkali metal alloy and polyphenylene*** have been very effectively used ***as anode materials*** in batteries that exhibit much higher energy densities, of around 65mWH/g (compare with standard nickel–cadmium batteries which have about 39mWH/g).
- In these cases, the conducting polymer serves as a binder for the alkali metal alloy, forming a multiply connected electronically and ionically conductive network within which the alloy particles are held. The mixed ionic and electronic conductivity of the conducting polymer binder allows the alloy particles to continue the electronic and ionic processes associated with the charge-discharge cycles, consequently extending the battery cycle life. Thus, the prospect of a polymeric battery is still promising and is awaiting further technological refinement.

❖ *Electrochromic Displays*

- Electrochromic display is another interesting application that utilizes the ***electrochemical doping and undoping*** of conducting polymers.
- The basic idea, in such devices, is to effect a ***significant change in the color (both the wavelength of absorption and its intensity) upon application of an electric potential.***
- ***Depending on the conducting polymer chosen, either the doped or undoped state can be essentially colorless or intensely colored.***
- In general, ***the absorption of the doped state is dramatically red-shifted (moves to longer wavelength) from that of the undoped state.***
- Because of their ***very high absorption coefficients (ca. 10^5 cm^{-2}) in the visible range of the electromagnetic spectrum, only very thin films are required to provide display devices with high contrast and a very broad viewing angle.***
- Polyaniline, polypyrrole, polythiophene, and their derivatives have been successfully used to prepare such display devices.

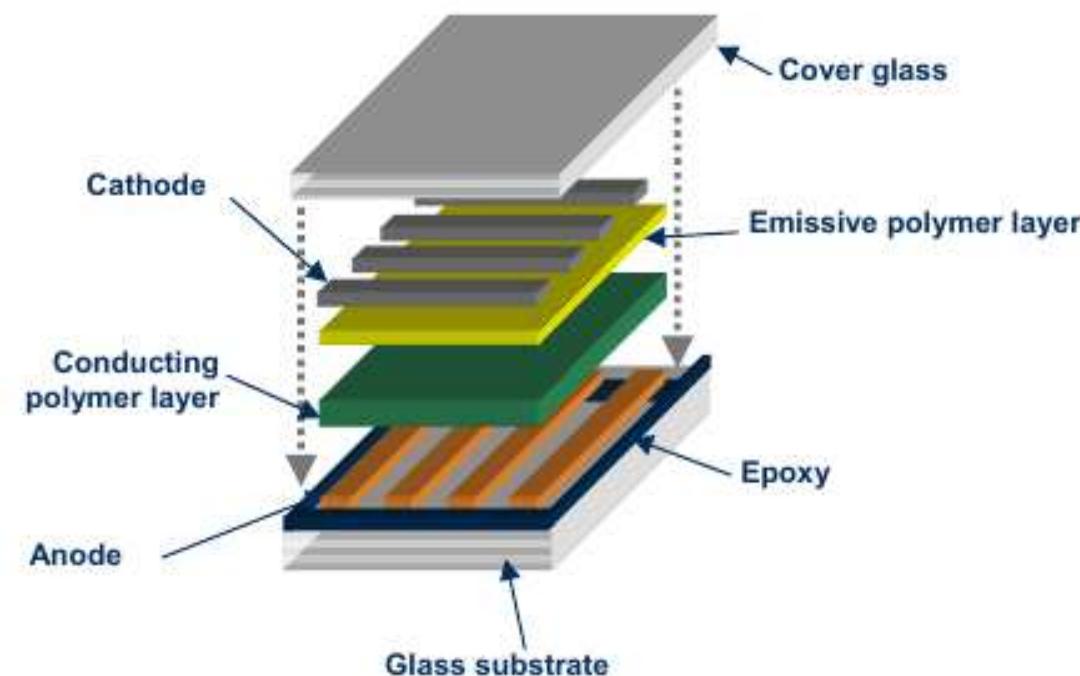
- However, for successful commercial utilization of these materials in display devices, one important aspect is again the cycle life, which should be $> 10^7$. A maximum of about 10^6 cycles has been achieved using 50 nm thick polyaniline films, wherein the switching occurs between transparent yellow and green in less than 100ms.
- Thus, while these materials are yet to achieve the set target (in terms of their life cycle) for use as electrochromic displays, *other interesting and innovative applications, such as electrochromic windows and other applications in the automotive industry are being actively pursued.*
- *Electro-chromic windows*, for instance, are windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential.

- Most polymers contain sp^3 -hybridized carbon atoms lacking delocalized p electrons, so they are usually electrical insulators and are colorless (which implies a large band gap). However, if the backbone of the polymer has resonance, the electrons can become delocalized over long distances, which can lead to semiconducting behavior in the polymer. Such “plastic electronics” are of great current interest for lightweight and flexible organic solar cells, organic transistors, organic light-emitting diodes, and other devices that are based on carbon rather than inorganic semiconductors like silicon.
- When a light source is viewed through graphene it absorbs 2.3 per cent of the light, which makes a single film visible to the naked eye. However, the high overall light transmission, in conjunction with the high electrical conductivity, leads to potential applications in displays, particularly flexible electronic displays and ‘**smart windows**’. In a smart window of this type, a layer of polar liquid-crystal molecules is sandwiched between two flexible electrodes comprised of graphene and a transparent polymer.
- ✓ With no voltage applied to the device the random alignment of liquid crystals scatters light and the smart window is opaque. Application of a voltage across the graphene layers will align the polar molecules, allowing some light to pass through the device, and the smart window turns transparent.

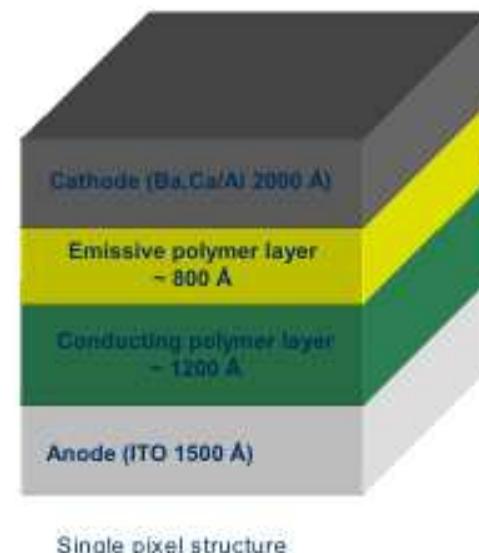
❖ ***Light Emitting Diodes***

- Other exciting phenomena that have caught the imagination of both scientists and technologists alike are the phenomena of ***photoluminescence and electroluminescence*** in conjugated polymers.
- Emission of light upon irradiation is termed as ***photoluminescence***, while the emission on application of a voltage is termed ***electroluminescence***.
- *Light emitting diode* is an example of *utilization of the electroluminescence*.
- It was recently demonstrated that PPV (**Poly(*p*-phenylene vinylene)**) films can be used as the emissive layer in electroluminescent devices.
- Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e., after thermal elimination of the precursor).
- Electrode materials are chosen with a low work function for use as negative, electron-injecting contact, and with a high work function as the positive hole-injecting contact.
- At least one of these layers must be semi-transparent for light emission normal to the plane of the device. Both indium-tin oxide and thin aluminium films (7–15 nm) have been used as the transparent electrode.

Display

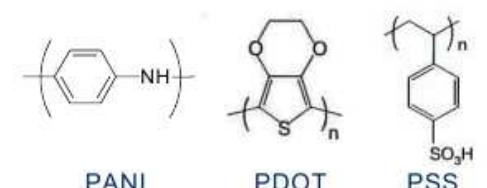


Pixel



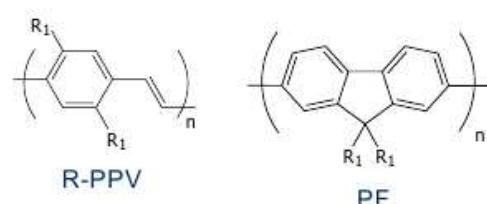
Conducting polymers

- Polyaniline (PANI:PSS)
- Polyethylenedioxythiophene (PDOT:PSS)



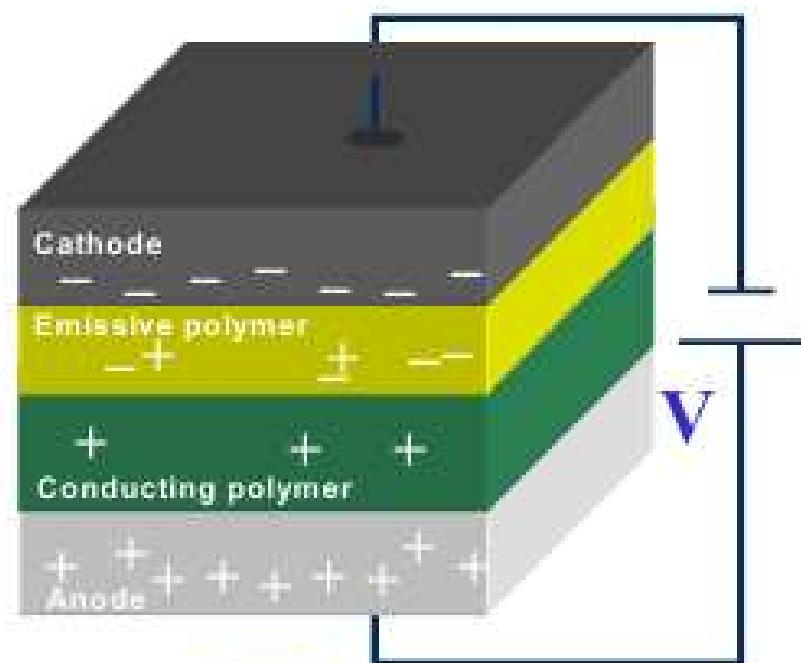
Emissive polymers

- Polyphenylenevinylene (R-PPV)
- Polyfluorene (PF)



Processed by :

Spin casting, Printing, Roll-to-roll web coating



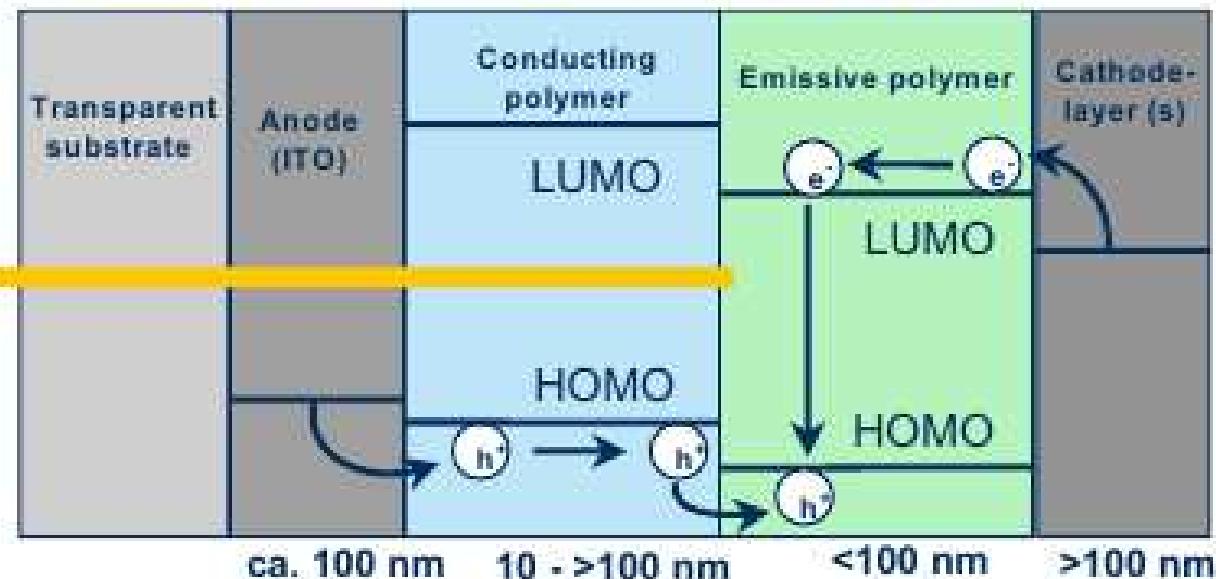
light

Light

OLEDs rely on organic materials (polymers or small molecules) that give off light when tweaked with an electrical current

- Electrons injected from cathode
- Holes injected from anode
- Transport and radiative recombination of electron hole pairs at the emissive polymer

OLED device operation (energy diagram)



- These devices are believed to operate by double charge injection of electrons and holes from the negative and positive electrodes, respectively.
- These singly charged excitations combine to form excitons which can then decay by photoemission.
- Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap.
- For polymer films, of about 100 nm, the forward voltages were as low as 10 V. Further improvements, using soluble PPV derivatives such as 2,5-dialkoxy PPV's and lower work function metals, particularly calcium, as the electron-injecting contact layer, have resulted in a further drop in forward voltage to about 5 V, and an increase in the efficiency to about 1% (photons per electron injected).
- Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to lead to improved devices of greater technological relevance.

- Polymer light-emitting diodes (PLEDs) have been become the topic of intense academic and industrial research. PLEDs based on PPVs are now coming out as commercial products.
- When compared to inorganic or organic materials for LEDs, the main advantages of the polymer electroluminescence (EL) devices are their fast response times, processability, the possibility of uniformly covering large areas, low operating voltages, and the many methods were applied to fine-tune their optical and electrical properties by varying the structure.

❖ ***Field Effect Transistors (FET)***

- Conducting polymers' advantages over conventional materials, such as silicon and germanium, include low cost and ease of processing.
- Organic or polymer-based semiconductors have been applied to fabricate field-effect transistors (FETs) since 1983. There have been many ongoing efforts to form organic or polymer-based FETs.
- Organic or polymer-based transistors have already found their application, such as in smart pixels and sensors.

❖ ***Conducting Fabric***

- When a fabric that is impregnated with an aqueous catalyst solution is brought into contact with pyrrole vapor, a thin coating of polypyrrole is formed in the surface of the fibre – leading to the formation of a conducting fabric.
- The chemical oxidation of pyrrole is often carried out by using ferric chloride, FeCl_3 . It has been shown that the growth of the polymer can be made to occur even at a liquid-liquid interface, such as one of water and an organic solvent. Thus, in an unstirred system, when aqueous FeCl_3 and chloroform solution of pyrrole are brought into contact, it leads to the formation of a polypyrrole film at the interface.
- The ***unique electromagnetic shielding and microwave absorbing properties*** of such a fabric are expected to find many interesting applications.
- Similarly, other materials such as paper, microporous membranes etc., have also been coated with a conducting polymer using this chemical oxidation route.
- It should be noted here that the oxidation potential of the monomer would be less than that of the dimer, which would in turn be less than that of the polymer. Hence, the polymer generated by this oxidative polymerization approach will be in the oxidized (doped) conducting form, which is also generally true in the case of all oxidative polymerization approaches (both chemical and electrochemical) for the preparation of conjugated polymers.

Polyelectrolytes

Polyelectrolytes are polymers with ionizable groups along their chains. One example of their use in nanotechnology is for the preparation of thin films by layer-by-layer (LbL) deposition. Some examples of the polyelectrolytes are (Fig. 13.11):

- (i) Polyacids such as poly (acrylic acid), poly(methacrylic acid), poly sodium styrene sulfonate.
- (ii) Polybases such as poly(vinylamine), poly(4-vinyl pyridine), nucleic acids and proteins.

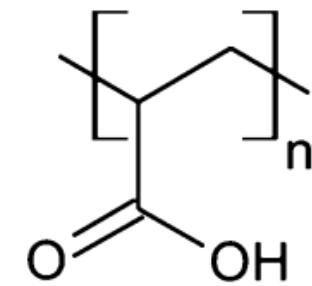
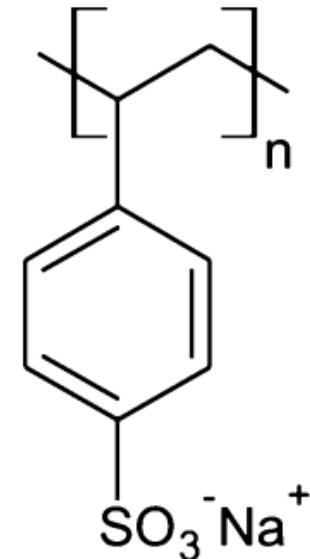
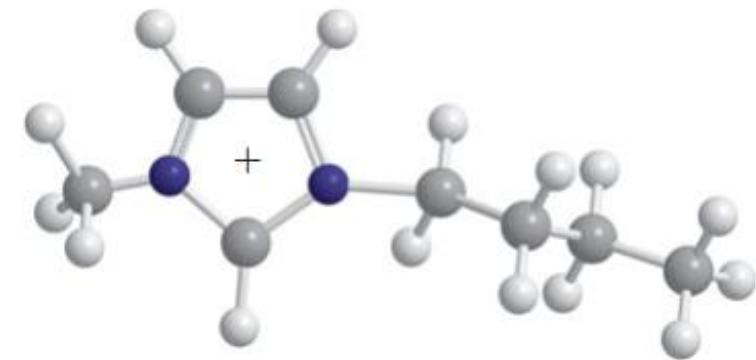


Fig. 13.11. Chemical structures of two synthetic polyelectrolytes. To the left is poly(sodium styrene sulfonate) (PSS), and to the right is poly(acrylic acid) (PAA). Both are negatively charged polyelectrolytes when dissociated. PSS is a 'strong' polyelectrolyte (fully charged in solution), whereas PAA is 'weak' (partially charged).

- The polyelectrolytes get ionized in aqueous solutions.
- The *repulsion between the similar charges on a chain causes the chain to expand much more than the normal polymers do in good solvents.*
- Furthermore, *the degree of ionization depends on the concentration of the polymer as well as that of any added salts.*
- Due to these factors, *the properties of polyelectrolytes such as viscosity and the intensity of light scattering behave quite differently as compared to the normal polymers.*
- The polyelectrolytes behave as a normal polymer in nonionizing solvent as well as in ionizing solvents containing large amount of salt so that the double layer around the polyelectrolyte chain is completely screened.

Ionic Liquids

- We have seen that molecular substances tend to have low melting points, whereas network, ionic, and metallic substances tend to have high melting points. Therefore, with a few exceptions, such as mercury, a substance that is liquid at room temperature is likely to be a molecular substance. Liquid solvents are heavily used in industry to extract substances from natural products and to promote the synthesis of desired compounds. Because *many of these solvents have high vapor pressures and so give off hazardous fumes, liquids that have low vapor pressures but dissolve organic compounds have been sought.*
- A new class of solvents called **ionic liquids** has been developed to meet this need.
- A typical ionic liquid has a relatively small anion, such as BF_4^- , and a relatively large, organic cation, such as 1-butyl-3-methylimidazolium (Fig.).
- Because *the cation has a large nonpolar region and is often asymmetrical, the compound does not crystallize easily and so is a liquid at room temperature.* It can also dissolve nonpolar organic compounds. However, *the attractions between the ions reduce the vapor pressure to about the same as that of an ionic solid, thereby reducing air pollution.*



1-Butyl-3-methylimidazolium ion

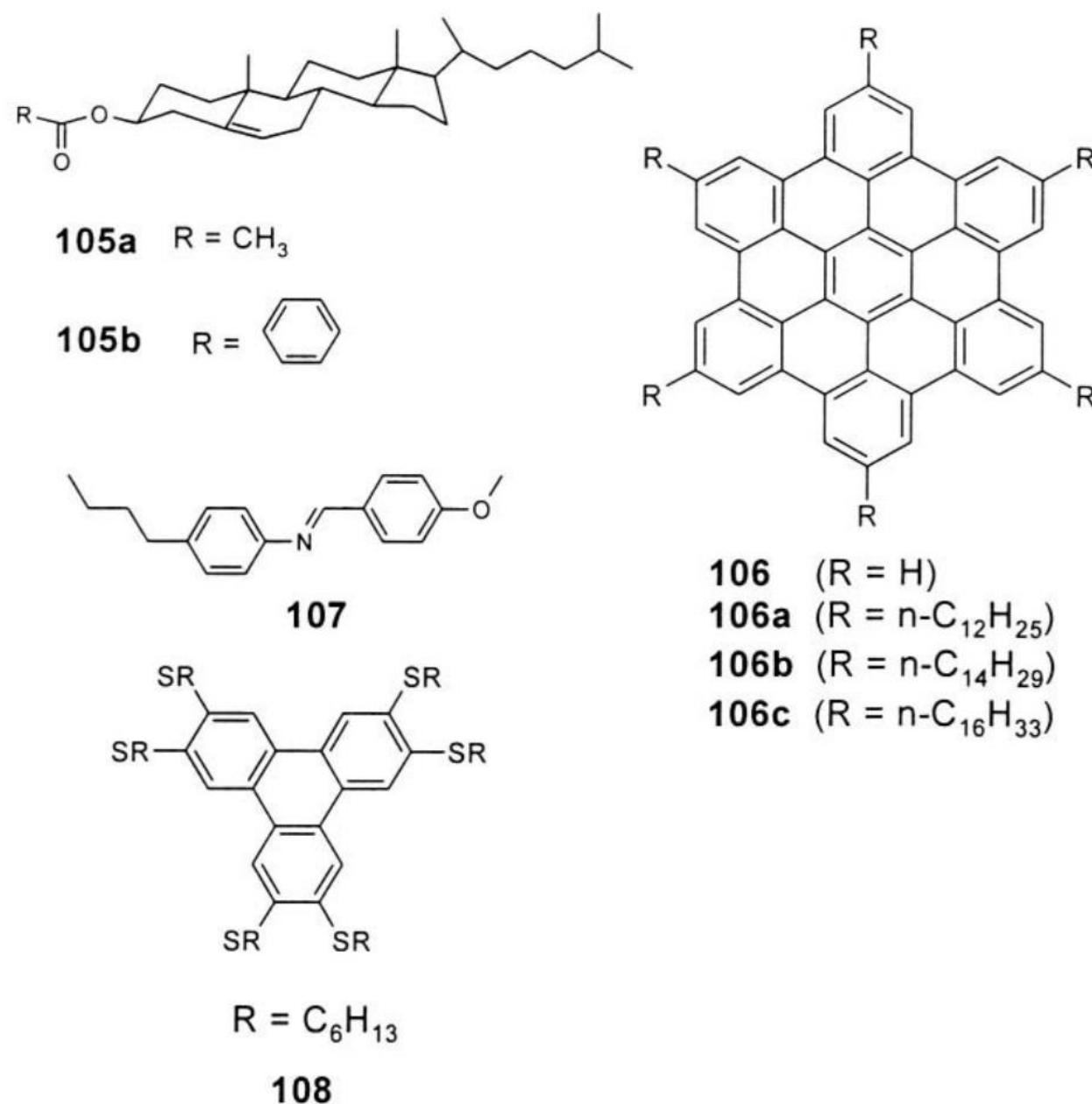
- *Ionic liquids are compounds in which one of the ions is a large, organic ion that prevents the liquid from crystallizing at ordinary temperatures. The low vapor pressures of ionic liquids make them desirable solvents that reduce pollution.*
- Because different cations and anions can be used, solvents can be designed for specific applications.
- For example, one formulation can dissolve the rubber in old tires so that it can be recycled.
- Other solvents can be used to extract radioactive waste from groundwater.

Liquid Crystals

Key point: Organic molecules and inorganic metal complexes with disc- or rod-like geometries can show liquid crystalline properties.

- Melting point describing the temperature at which the solid to liquid transition takes place is one of the main characteristics of chemical substances. When heat is supplied to a crystalline species its temperature usually rises until it starts to melt. This temperature corresponding to the melting point is maintained until all the substance is liquefied.
- During this process, the long-range order of the crystalline solid is destroyed. **Simultaneously anisotropy of the crystal, that is, a dependence of its optical and some other properties on the direction of, for instance, incident light, subsides during the melting process, which leads to an isotropic liquid.**
- Ordinary ***fluids are isotropic*** in nature: *they appear optically, magnetically, electrically, etc. to be the same from any direction in space.*
- Although the molecules which comprise the fluid are generally anisometric in shape, this anisometry generally plays little role in macroscopic behavior.

- However, **this is not always the case.** There is a large class of highly anisometric molecules which gives rise to unusual, fascinating, and potentially technologically relevant behavior.
- To the great surprise of the Austrian botanist Reinitzer, two cholesteryl esters **105a** and **105b** did not give a clear, transparent liquid on melting. The ‘liquid’, later called a **thermotropic liquid crystal**, was *anisotropic until the clearance temperature was reached*.
- Thermotropic liquid crystals are built from **form-anisotropic** molecules bearing the name ***mesogens***.



Some liquid crystal forming molecules

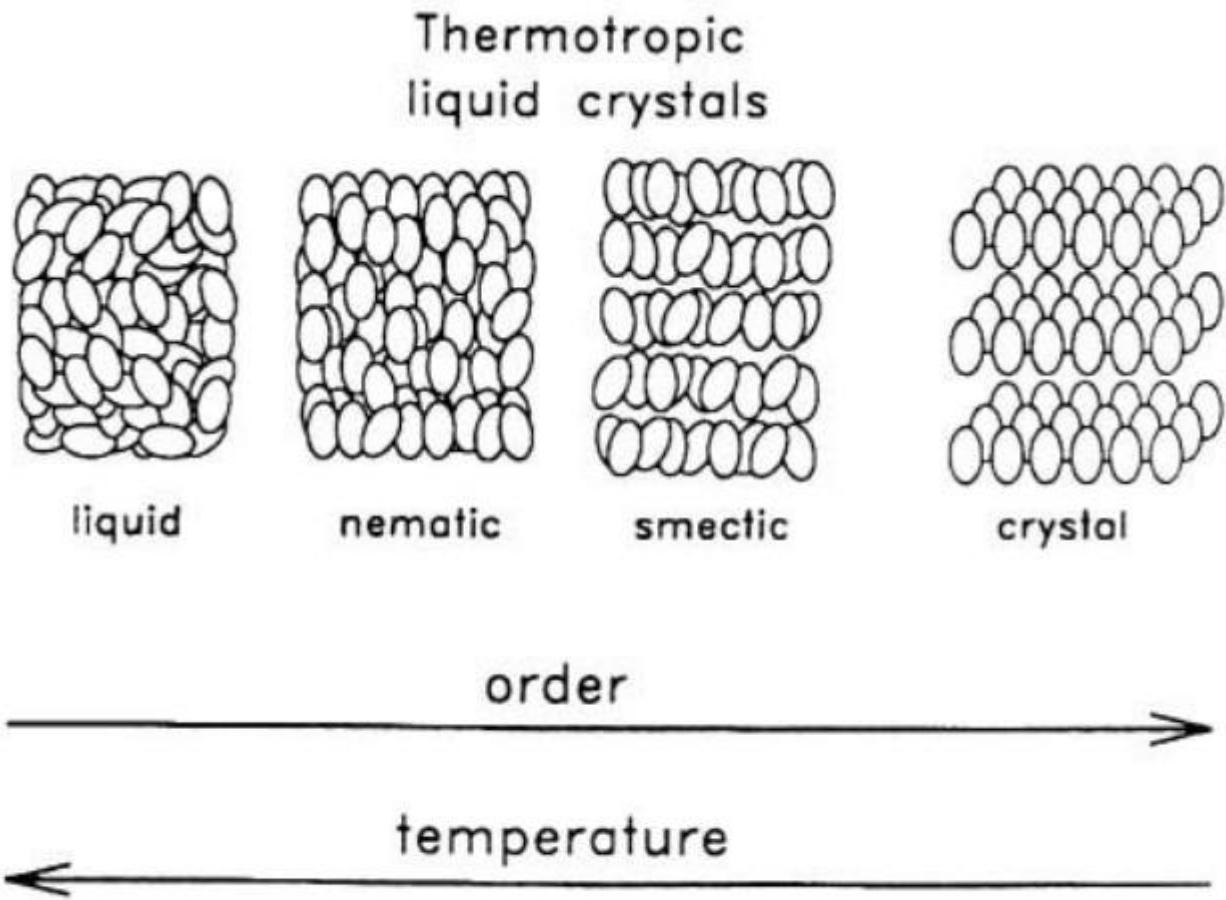
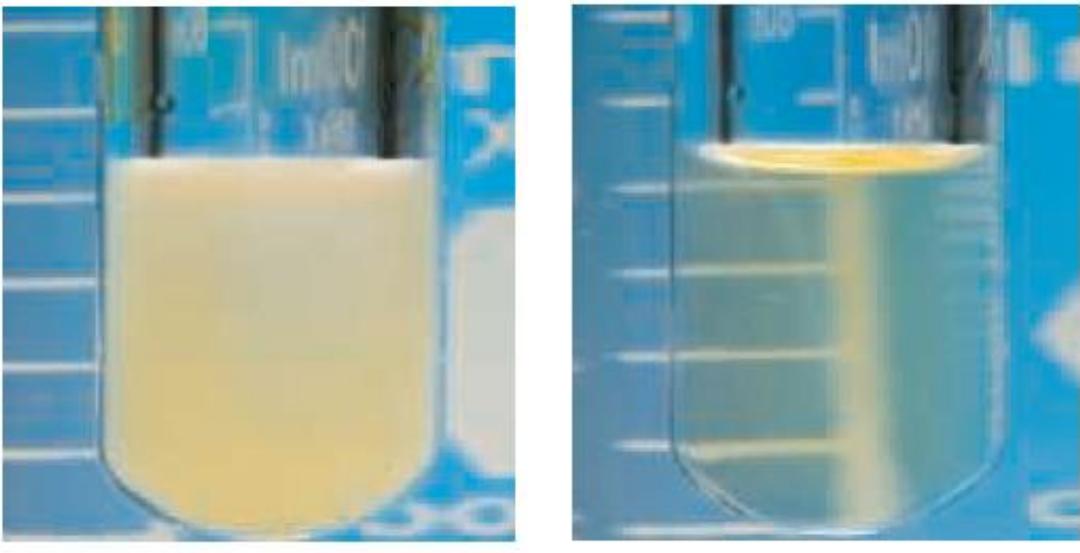


Figure 4.14. Schematic presentation of ordering in liquid, liquid crystal, and crystal.



$145 \text{ }^\circ\text{C} < T < 179 \text{ }^\circ\text{C}$
Liquid crystalline phase

$T > 179 \text{ }^\circ\text{C}$
Liquid phase

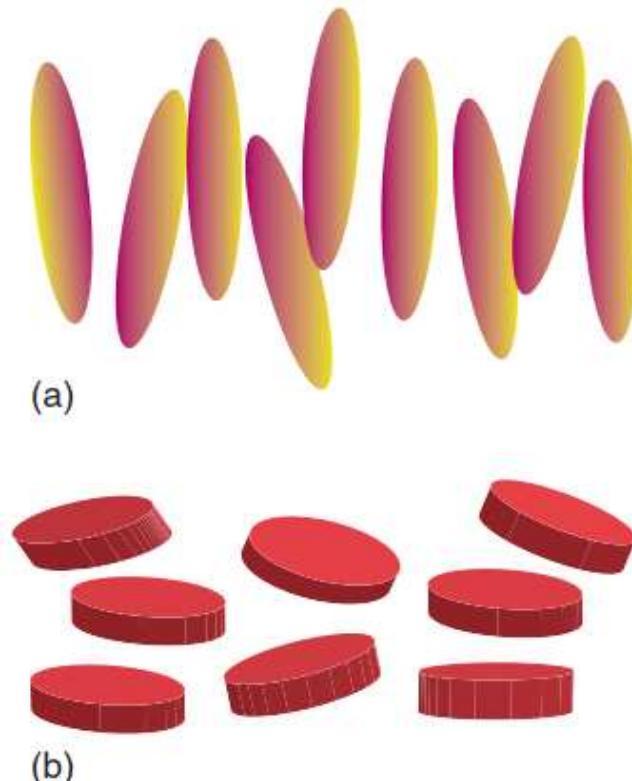
Figure 11.31 Cholesteryl benzoate in its liquid and liquid crystalline states.

- By varying the temperature between those corresponding to the *crystalline and liquid phases one can generate a **nematic phase with a preferred orientation of the longitudinal molecular axis** and one of the **smectic phases characterized by a layered arrangement of mesogens orientated perpendicularly or at an angle to the layers**.*

Liquid Crystals

- *Liquid crystalline, or mesogenic, compounds possess properties that lie between those of solids and liquids and include both.*
- For instance, *they are fluid, but with positional order in at least one dimension.*
- Such materials have become widely used in displays.
- *The molecules that form liquid crystalline materials are generally calamitic (rod-like) or discotic (disc-like), and these shapes lead to the ordered liquid-type structures in which the molecules align in a particular direction (Fig. 24.74).*
- Although most liquid crystalline materials are totally organic, there is a growing number of inorganic liquid crystals based on the *coordination compounds of metals and on organometallic compounds*. These metal-containing liquid crystals show similar properties to the purely organic systems but *offer additional properties associated with a d-metal centre, such as redox and magnetic effects.*

Figure 24.74 Schematic diagram of liquid crystalline materials based on (a) calamitic (rod-like) and (b) discotic (disc-like) molecules.



- At high temperatures, the molecules will be oriented arbitrarily, as shown in the figure below, forming ***an isotropic liquid***.
- Because of their elongated shape, under appropriate conditions, the molecules exhibit ***orientational order*** such that all the axes line up and form a so-called ***nematic*** liquid crystal.
- ✓ The molecules are still able to move around in the fluid, but their orientation remains the same.
- Not only *orientational order* can appear, but also a ***positional order*** is possible. Liquid crystals exhibiting some ***positional order*** are called **smectic** liquid crystals.
- ✓ In smectics, the molecular centers of mass are arranged in layers and the movement is mainly limited inside the layers.
- ✓ If the molecules are on average oriented ***perpendicular to the layers*** one speaks of a ***Smectic A*** phase, if they are ***oriented at an angle to the layer normal*** one speaks of ***Smectic C***.

Diagrammatic representation of forms of ***thermotropic*** liquid crystals.

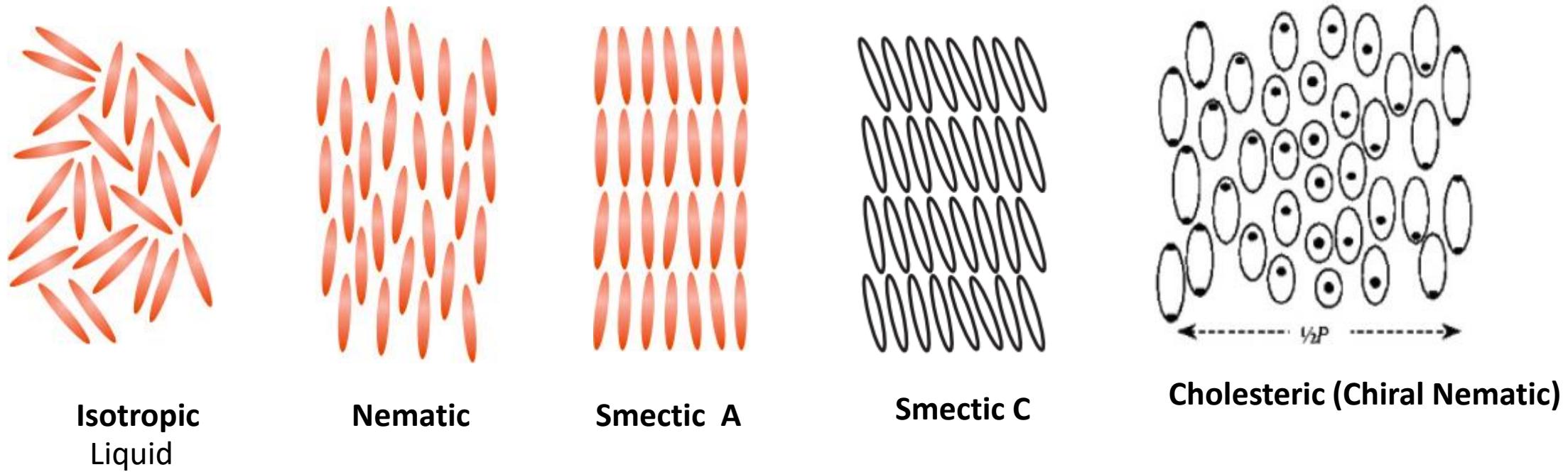


Figure 2.1: Different phases of a ***thermotropic*** liquid crystals.

- The ***nematic phase (orientational order)***: The molecules tend to have the same alignment but their positions are not correlated.
- **Smectic** liquid crystals: *exhibit some positional order*. In smectics, the molecular centers of mass are arranged in layers.
- The ***cholesteric phase***: The molecules tend to have the same alignment which varies regularly through the medium with a periodicity distance $p/2$. The positions of the molecules are not correlated.

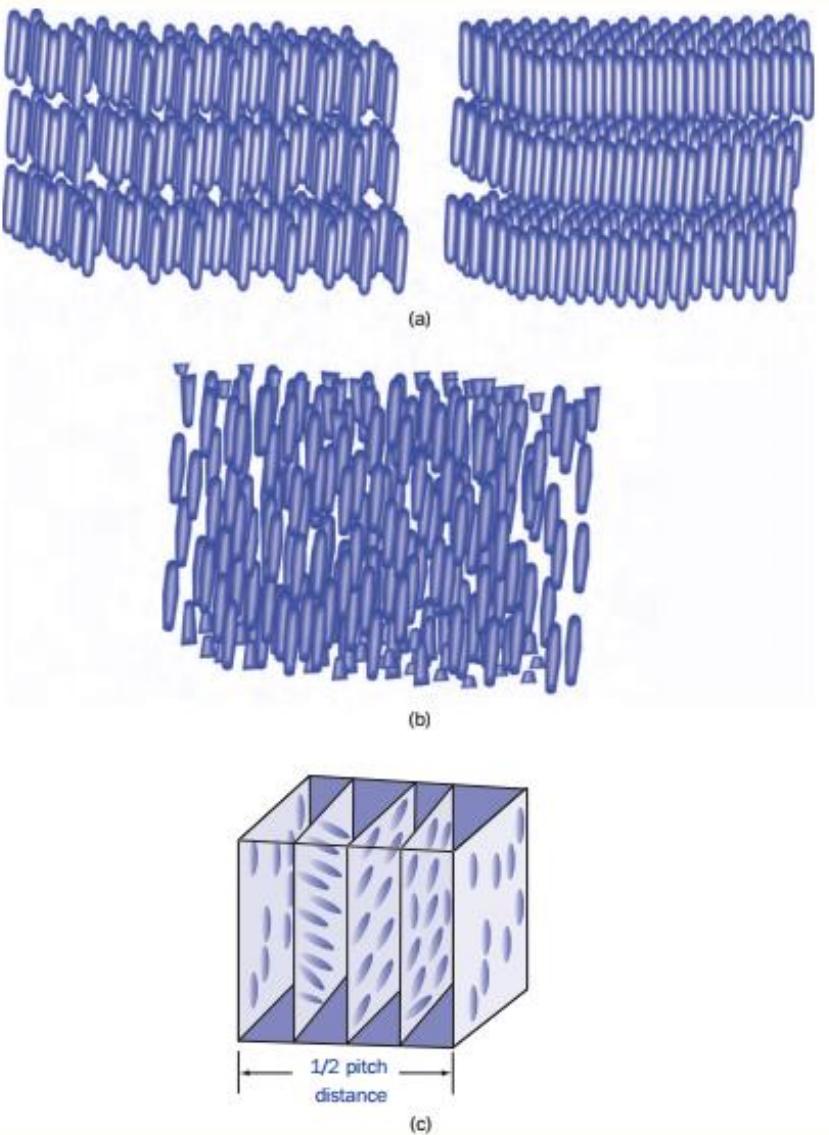


Figure 4.11 Diagrammatic representation of forms of ***thermotropic*** liquid crystals.
(a) smectic,
(b) nematic and
(c) cholesteric liquid crystals.

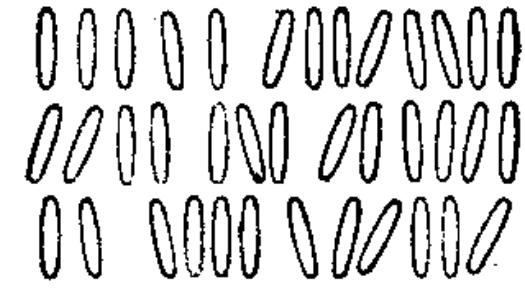
In the ***nematic*** phase all molecules are aligned approximately parallel to each other. In each point a unit vector can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighborhood.

Classification of Smectic Liquid Crystals

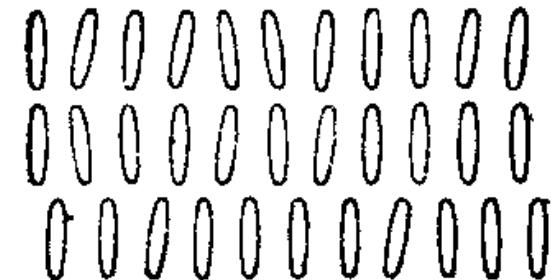
A type: molecular alignment perpendicular to the surface of the layer, but lack of order within the layer.

B type: molecular alignment perpendicular to the surface of the layer, ***having order within the layer.***

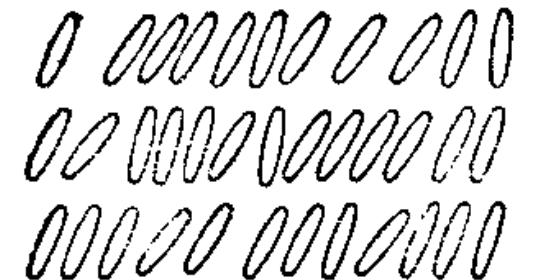
C type: having a tilted angle between molecular alignment and the surface of the layer.



Smectic A



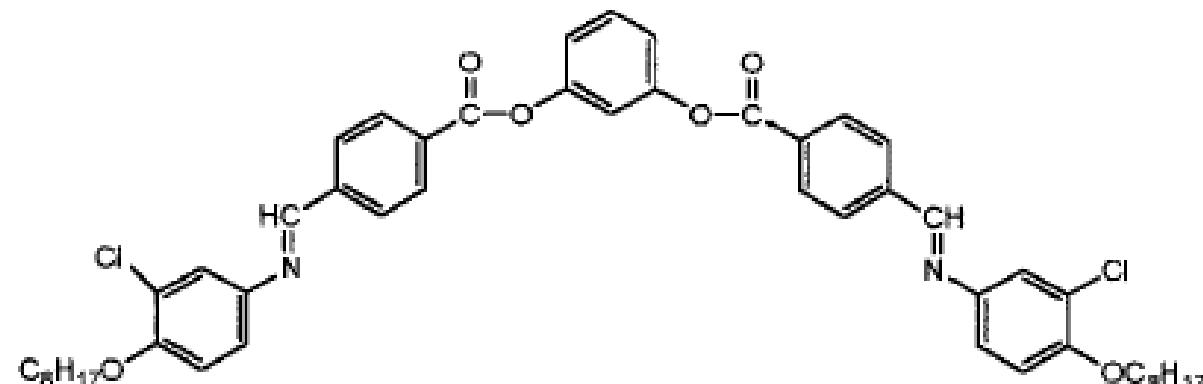
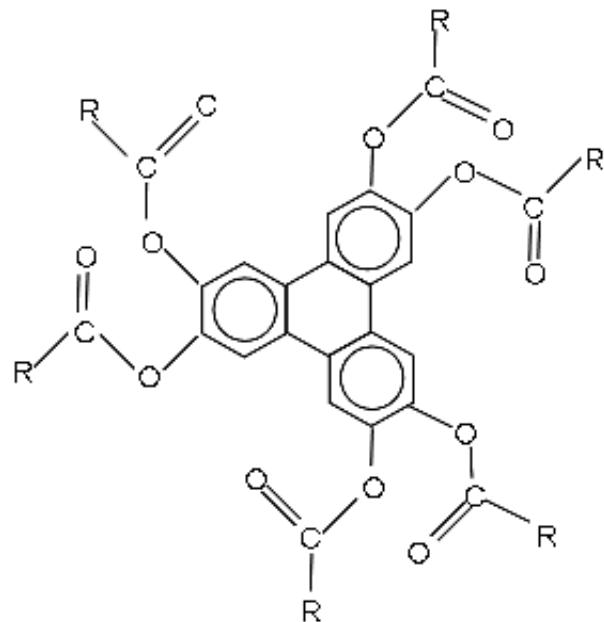
Smectic B



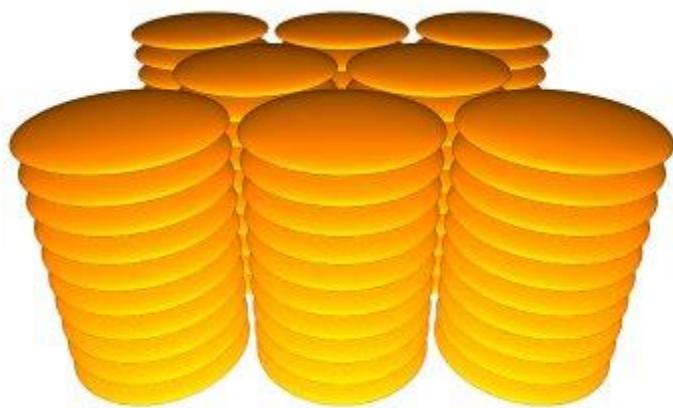
Smectic C

➤ Beside these simple examples, ***more complicated ways of stacking are possible, giving rise to many other types of liquid crystals.*** ***Chiral molecules***, molecules without mirror symmetry, can give rise to helices comprising cholesteric liquid crystal phases. In *ferroelectric* or *antiferroelectric* liquid crystals, the *smectic layers possess a permanent polarization* which is constant or alternating between successive layers respectively. Apart from the rod-like molecules, more advanced-shaped liquid crystals are possible such as disk-like or banana-shaped liquid crystals which can give rise to other types of ordering. Discotic liquid crystals can be stacked a columnar phase, the bottom picture illustrates a possibility for stacking banana shaped liquid crystals. Examples of molecules which give rise to discotic and banana shaped liquid crystal phases are shown below.

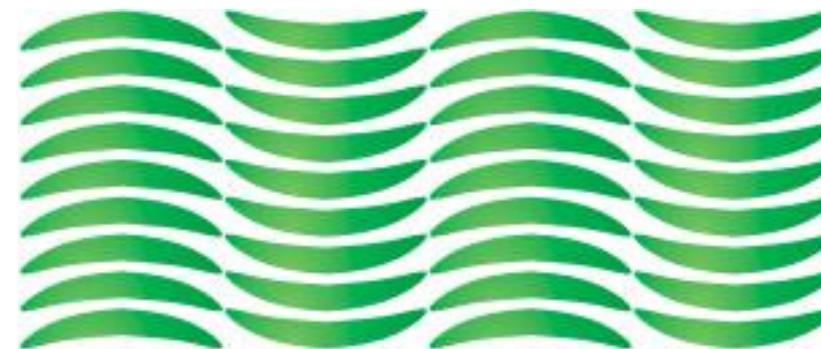
Discotic shaped liquid crystal molecule



Banana shaped liquid crystal molecule



Discotic shaped liquid crystals



Banana shaped liquid crystals

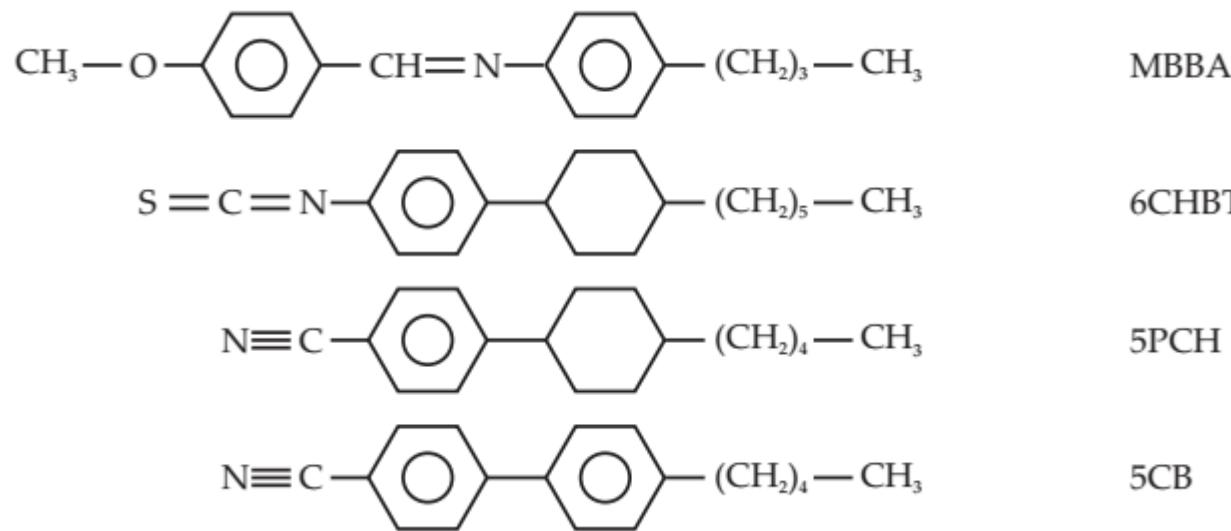
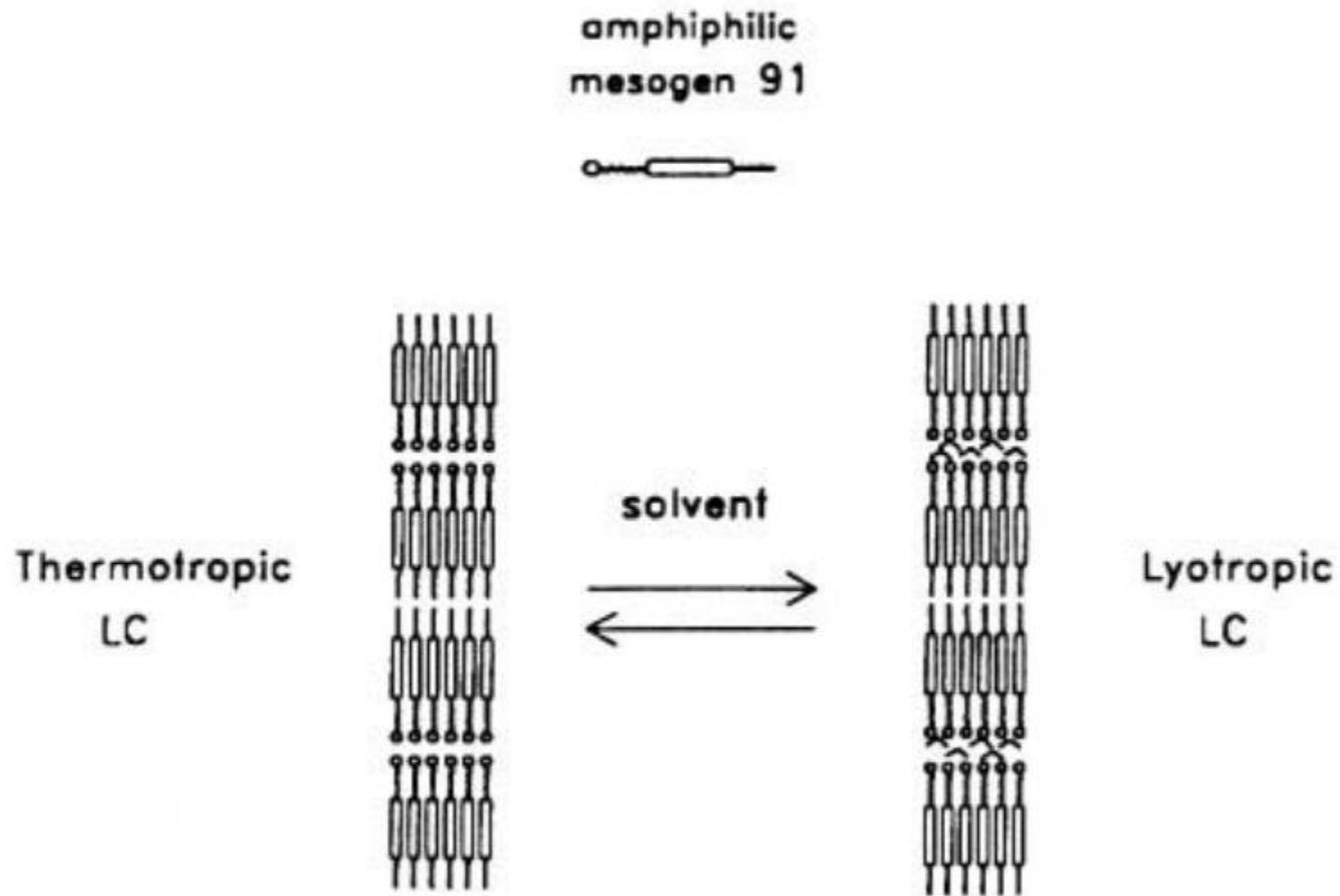


Figure 2.4: The molecular structure of four liquid crystal materials:
MBBA (4' - methoxybenzylidene - 4 - butylaniline), 6CHBT (4 - trans
- n - hexyl - cyclohexyl - isothiocyanatobenzene), 5PCH (4 - (trans
- 4' - pentyl - cyclohexyl) - benzonitril) and 5CB (4 - pentyl - 4' -cyanobiphenyl).

- ***One type of liquid crystal molecule can exhibit many different liquid crystal phases.*** The phase in which a pure liquid crystal (with only one type of molecule) exists depends on the temperature. *Pure liquid crystals, or mixtures of them, in which the phase is controlled by temperature are called **thermotropic** liquid crystals.* The Brownian motion of the molecules increases with the temperature, reducing the order in the material. At high temperature, orientational order is lost and the material changes to the isotropic phase.
- When ***decreasing the temperature, the material changes to the nematic phase.*** The temperature at which the phase transition occurs, is specific for each material and is called ***the nematic-isotropic transition temperature or clearing point.***
- *By further lowering the temperature, the phase can change to the smectic A phase, the smectic C and finally to the solid state.*
- Each of the phase transitions occurs at a specific temperature, but depending on the material additional phases can appear or some can be missing.
- *Beside the thermotropic liquid crystals, a different class of liquid crystals is called **lyotropic**. These are mixtures of rod-like molecules ***in an isotropic solvent and the concentration of the solution is primarily responsible*** for the occurring phase.* Lyotropic liquid crystals are mainly of interest in biological applications and exhibit a considerable number of different phases.

- The kind of liquid crystal requiring a solvent for formation bears the name **lyotropic liquid crystals**.



Criteria for a molecule being liquid crystalline

- The molecule must be elongated in shape; length should be significantly greater than its width
- Molecule must have some rigidity in its central region
- The ends of the molecule are somewhat flexible

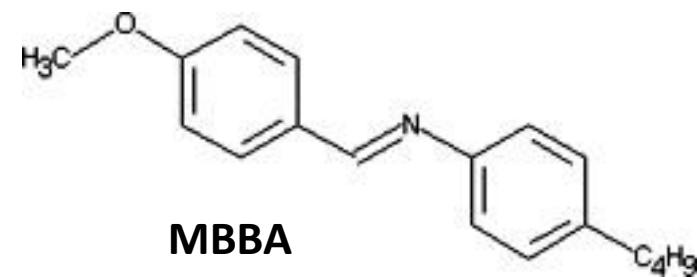
❖ Typical representation of a LC molecule

The figure below shows the molecular structure of a **typical rod-like liquid crystal molecule**. It consists of two or more ring systems connected by a central linkage group.

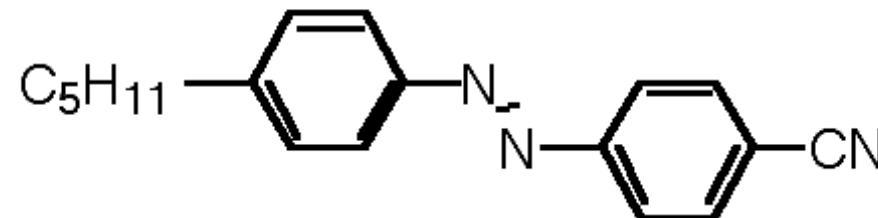
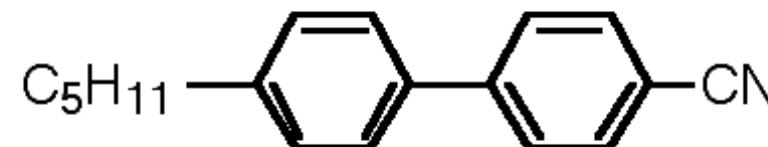
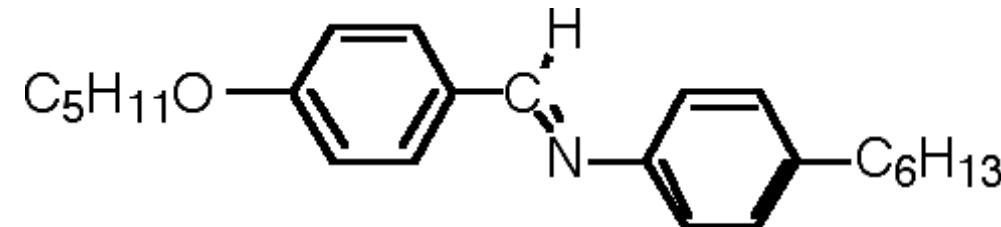


Typical shape of a liquid crystal molecule

The **presence of the rings provides the short-range molecular forces needed to form the nematic phase**, but **also affects the electrical and elastic properties**. The chemical stability of liquid crystals, their resistance to, e.g., moisture or ultraviolet radiation, depends strongly on the central linkage group. Compounds with a single bond in the center are among the most stable ones. At one side of the rings, there is a **long side chain** which strongly **influences the elastic constants and the transition temperature** of the liquid crystal phases. At the other end, **a terminal group is connected, which determines the dielectric constant and its anisotropy**. A few examples of molecules that exhibit a liquid crystal phase are shown below.



Some Typical examples of LC molecules



Mesogens

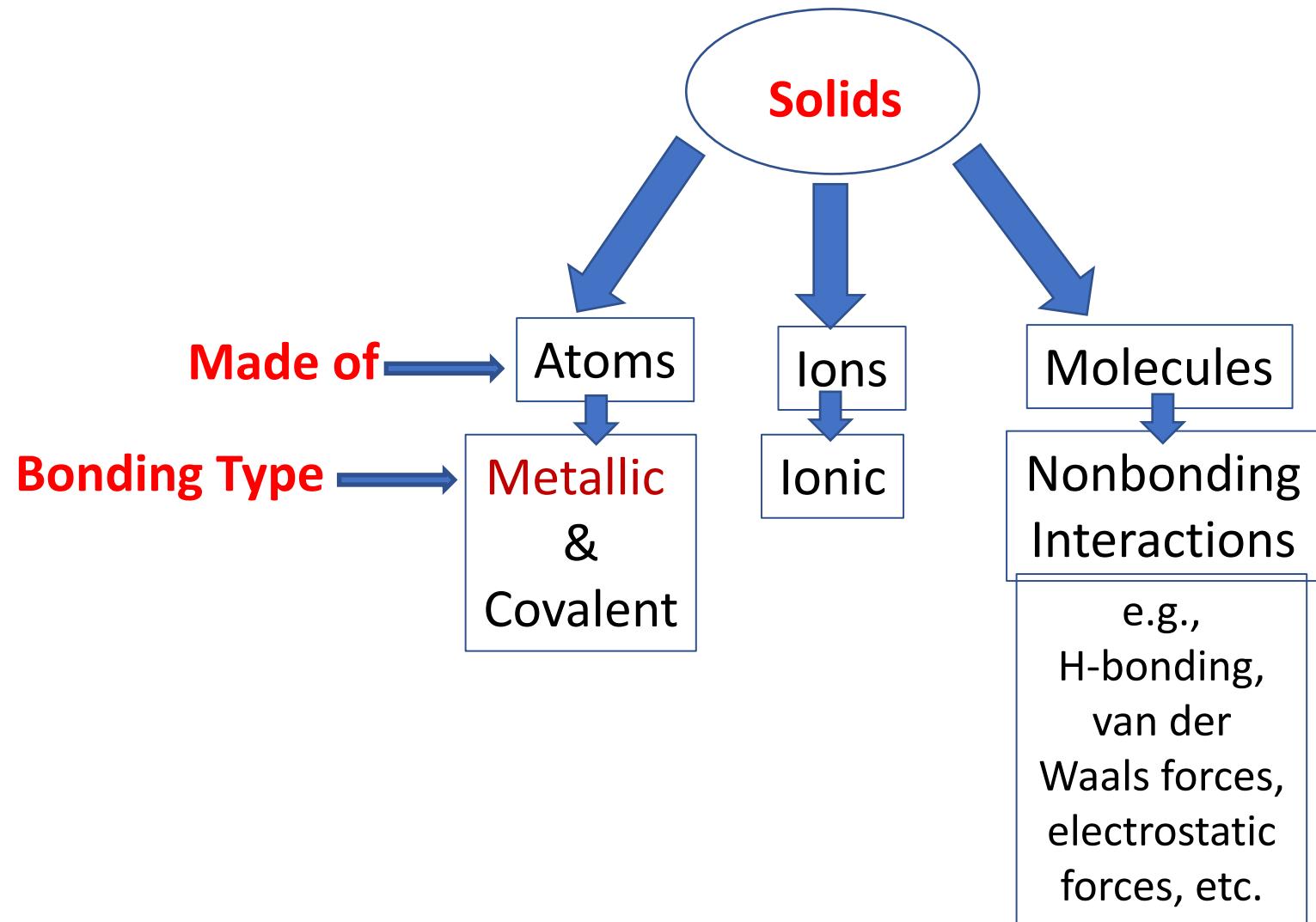
Note: these molecules possess very strong dipole moments

Why Liquid Crystals Form?

- **Uneven distribution of electrons in the molecule**
- **Intermolecular forces strong enough to cause the molecule line up in the same overall direction but not strong enough to hold them firmly in one place (over a certain range of temperatures)**

- For almost 80 years studies of these and other substances exhibiting similar behaviour were thought to be a mere curiosity of no practical significance.
- The situation has changed rapidly with the development of the first compound **exhibiting liquid crystal behaviour at room temperatures** 4-methoxybenzylidene-4'-n-butylaniline (**107**).
- The ***nematic liquid crystal phase is by far the most important phase for applications***. At present there are huge industrial application of liquid crystals ***in wrist watches and high contrast computer displays***.
- Many other applications of ferroelectric liquid crystals as sophisticated optical computing systems, flat panels for high definition computer and video displays, and materials exhibiting nonlinear optical properties are foreseen in the near future.
- Notably, some high strength polymeric materials, such as the famous Kevlar, are spun out of lyotropic liquid crystal.

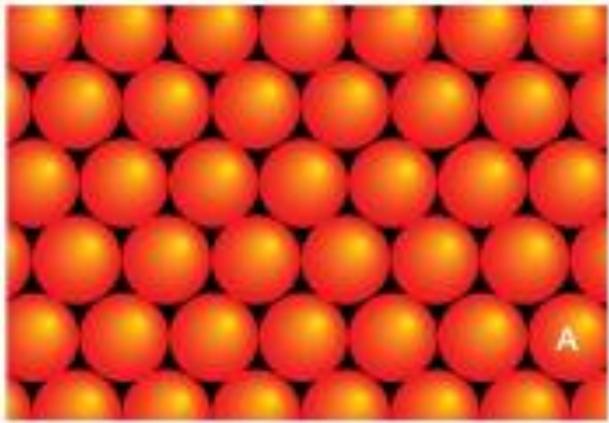
BONDING in SOLIDS



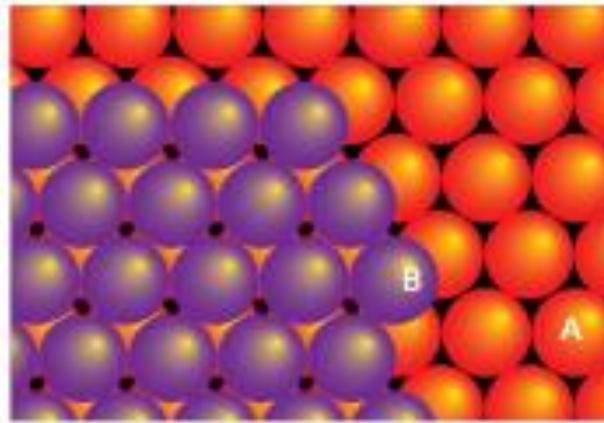
- ✓ We have discussed Ionic and Covalent Bondings earlier in details.
- Next, the Metallic Bonding.....

Metallic solids

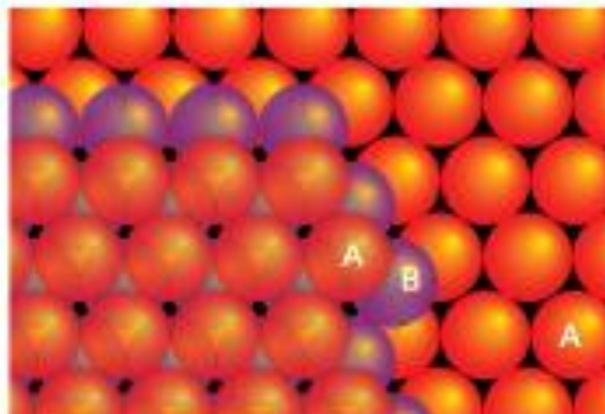
- Most metallic elements crystallize in one of three simple forms, *two of which* can be explained *in terms of stacking rigid spheres as close together as possible*.
- In such close-packed structures the spheres representing the atoms are packed together with least waste of space and each sphere has the greatest possible number of nearest neighbors.
- A single close-packed layer, one with maximum utilization of space, of identical spheres can be formed as shown in Fig. given below.
- A second close-packed layer can then be formed by placing spheres in the depressions of the first layer (note there are two types of depressions: *downward triangles* and *upward triangles*).
- The third layer may be added in either of two ways, both of which result in the same degree of close packing.
- In one, the spheres are placed so that they reproduce the first layer, to give an ***ABAB*** pattern of layers.
- Alternatively, the spheres may be placed over the gaps in the first layer (where the 2nd layer spheres were not placed), so giving an ***ABC ABC*** pattern.



2nd Layer

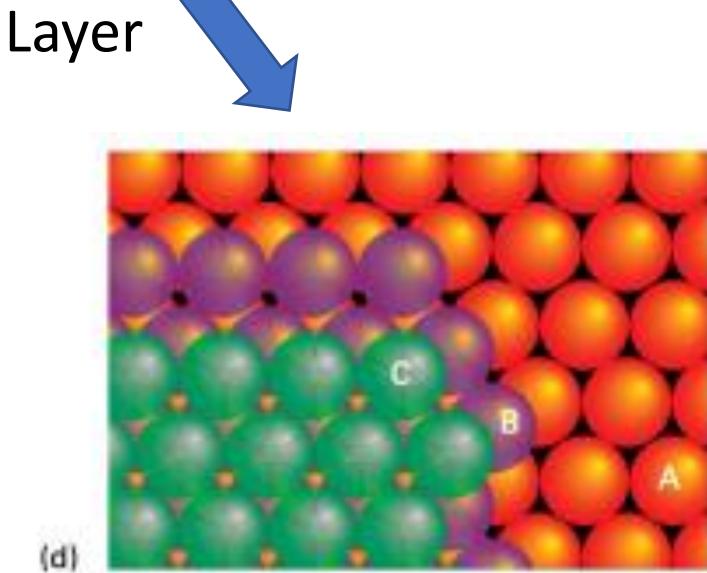


3rd Layer



The spheres are placed so that they reproduce the first layer.
AB AB AB

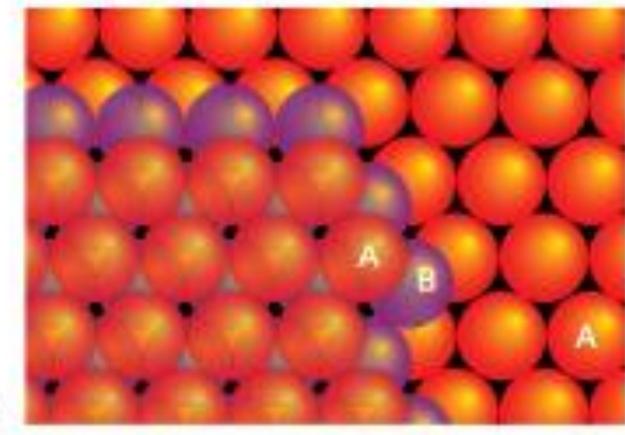
Hexagonal close packing (hcp)



Cubic close packing (ccp)

The spheres are placed over the gaps in the first layer.
ABC ABC ABC

The spheres are placed so that they reproduce the first layer.
AB AB AB



Hexagonal close packing (hcp)

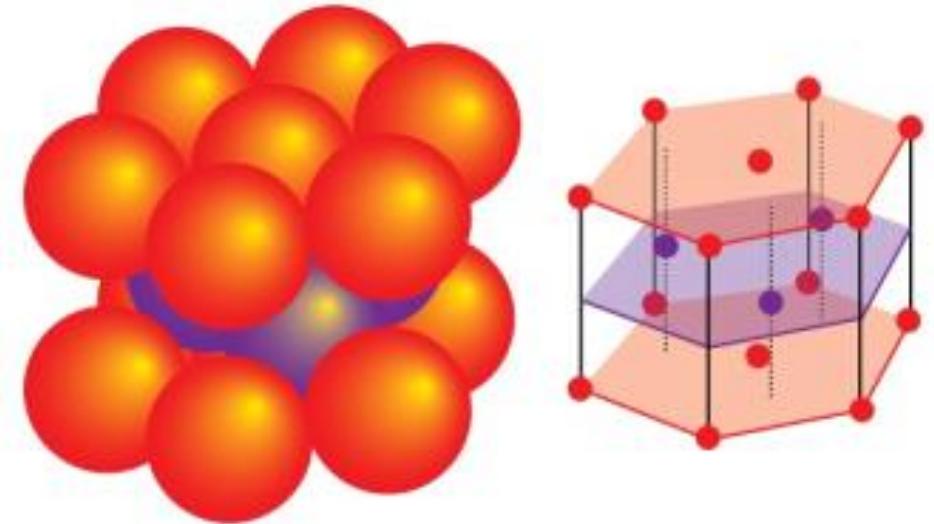
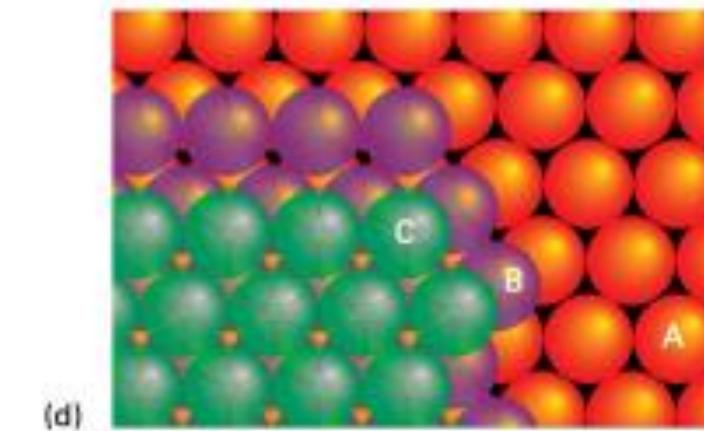


Fig. 2 A hexagonal close-packed structure.



Cubic close packing (ccp)

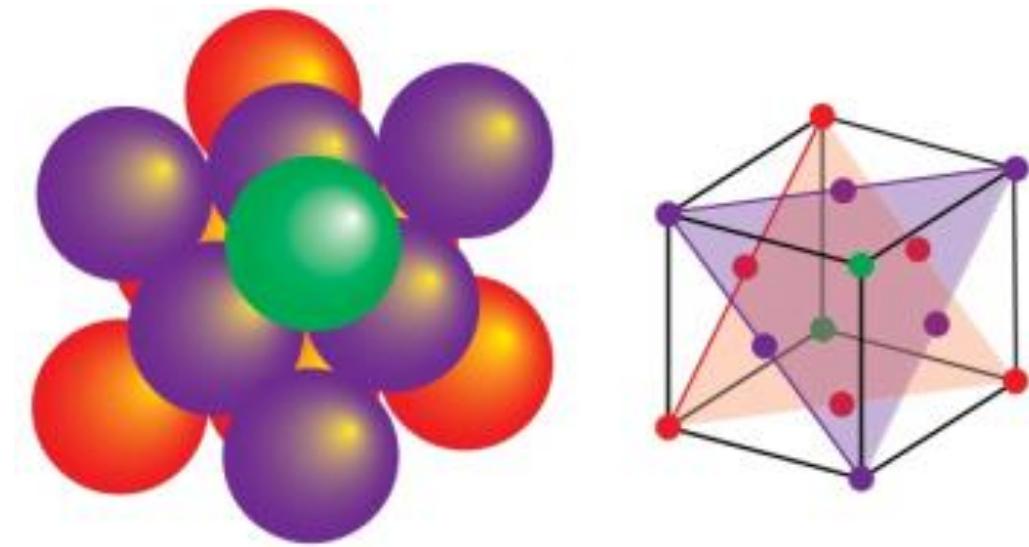
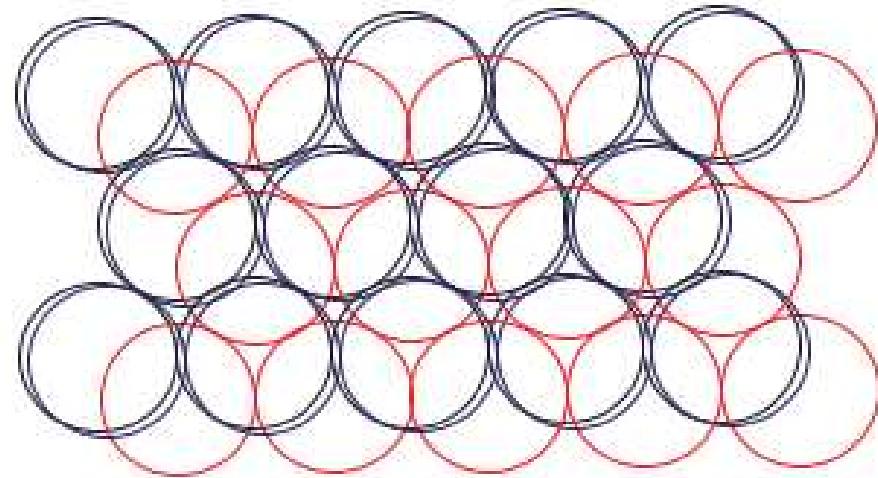
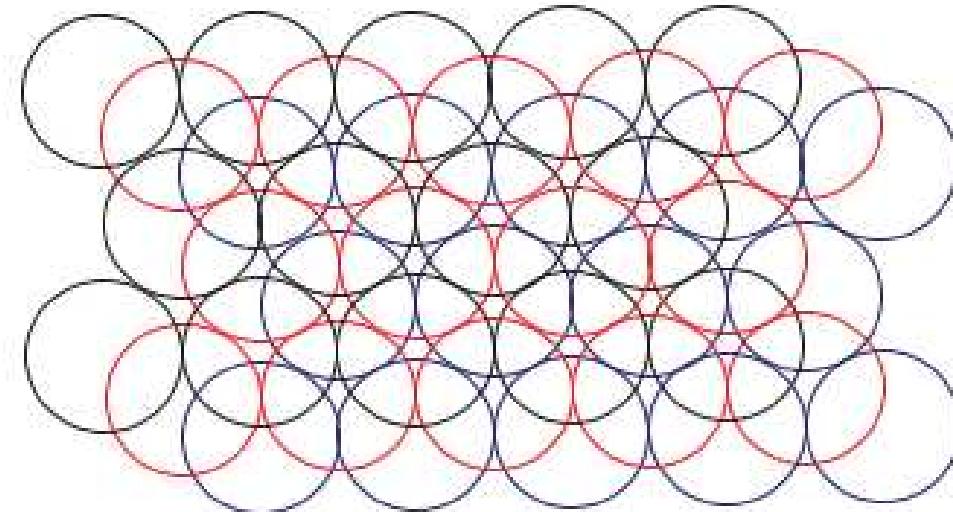


Fig. 3 A cubic close-packed structure.

The spheres are placed over the gaps in the first layer.
ABC ABC ABC



(a)



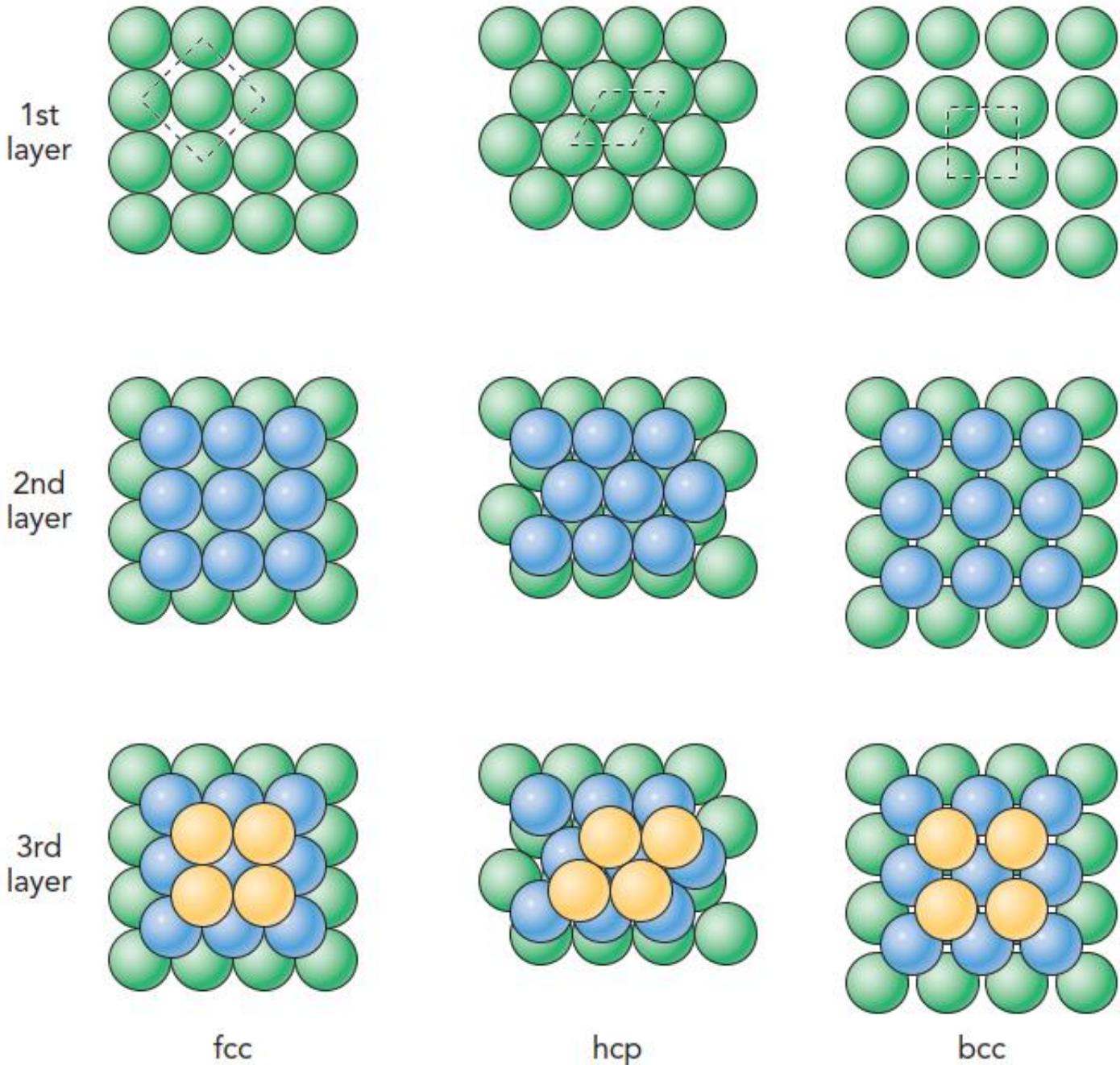
(b)

Addition of a third layer to the closest-packing of spheres in the first two layers. (a) If the third (blue) layer occupies the downward-pointing indentations of the second (red) layer, then the first (black) and third layers will become coincident, forming an ABABAB repeat pattern. (b) If the third layer occupies the upward-facing indentations, then an ABCABC repeating lattice will result.

- The spheres are hexagonally close-packed (hcp) if the ABA pattern is repeated to give the sequence of layers ABABAB... .
- The name reflects the symmetry of the unit cell (Fig.2).
- *Metals with hcp structures include beryllium, cadmium, cobalt, manganese, titanium, and zinc.* Solid helium (which forms only under pressure) also adopts this arrangement of atoms.
- Alternatively, the spheres are cubic close-packed (ccp) if the ABC pattern is repeated to give the sequence of layers ABCABC
- Here too, the name reflects the symmetry of the unit cell (Fig. 3).
- *Metals with this structure include aluminium, silver, gold, calcium, copper, nickel, lead, and platinum.* The noble gases other than helium also adopt a ccp structure in the solid state.
- The **compactness** of the ccp and hcp structures is indicated by their **coordination number**, the number of atoms immediately surrounding any selected atom, which is **12** in both cases. Another **measure of their compactness is the packing fraction**, the fraction of space occupied by the spheres, which is 0.740, as you have learnt earlier.
- That is, in a close-packed solid of identical hard spheres, 74.0 per cent of the available space is occupied and only 26.0 per cent of the total volume is empty space.

- Not all metals can take advantage of these arrangements, however, because a high density of metal cations **needs** to be **stabilized** by a high density of valence electrons.
- Metals such as the **alkali metals**, having a low number of valence electrons, often tend instead to adopt the **body-centered cubic** (bcc) lattice shown in Fig. 13.8c.
- In this pattern, the first plane of atoms consists of identical rows of atoms with a spacing of $2/\sqrt{3}$ diameters between the centers of the nearest neighbor atoms. **The second plane is identical to the first but placed with the centers of its atoms over the gaps in the first plane.** The third plane is identical to the first, and each subsequent plane is identical to the plane two levels below it. **The coordination number is 8, and the packing efficiency is 68%.**

Figure 13.8 The structure of the face-centered cubic, hexagonal closest packing, and body-centered cubic lattices. To form each lattice, start with the first layer (green atoms), add the second layer as shown (blue atoms), and then the third layer (yellow atoms). The cycle repeats, with every other layer being identical in each lattice. One face of one unit cell is outlined on the first layer of each lattice. ***This representation illustrates the (100) surface of each lattice.***



A ccp metal is more malleable than hcp metal

- The fact that many metals are close-packed accounts for one of their common characteristics, their high density. However, ***there is a difference between ccp and hcp metals.***
- In cubic close packing, the faces of the cubes extend throughout the solid, and give rise to a **slip plane**. Careful analysis of the ccp structure shows that there are *eight slip planes* in various orientations whereas an *hcp structure has only one set of slip planes* (parallel to the planes of atoms). ***When the metal is under stress, the layers of atoms may slip past one another along a slip plane.***
- Because a ccp metal has more slip planes than an hcp metal, ***a ccp metal is more malleable*** than an hcp metal. Thus, copper, which is ccp, is highly malleable, but zinc, which is hcp, is more brittle.
- *It must be born in mind*, however, that metals in real use are not single crystals: they are polycrystalline, with numerous grain-like regions and defects that permeate the structure. Much of metallurgy is associated with the control of the density of grains and grain boundaries.

- Ultimately, many factors determine ***whether a particular metal adopts*** the fcc, hcp, bcc lattice, or some other configuration.
- ***One of the conclusions is that the bcc lattice is better suited to metals with few valence electrons.***
- A more subtle argument allows us to distinguish between the hcp and fcc lattices. The crystallographic point group for the ***fcc lattice is O_h , significantly higher in symmetry than*** the D_{3h} point group of the hcp lattice.
- ***The greater symmetry results in a higher degeneracy of electronic energy levels in the fcc lattice*** than in the hcp.
- This means that ***metals with a high density of electrons are more likely to adopt the fcc*** than the hcp lattice because **highly degenerate levels can support more electrons without having to occupy high-energy states.** This tendency is shown schematically in Fig. 13.9.

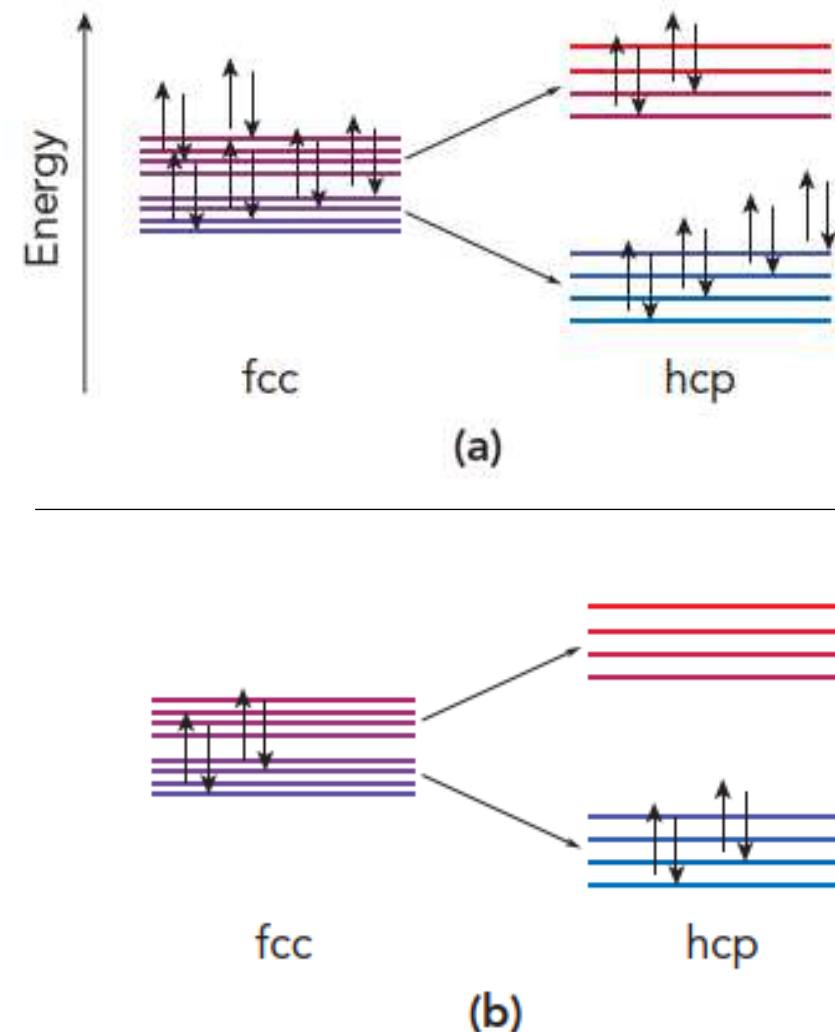


Figure 13.9 Schematic energy level diagrams of electronic states in the fcc and hcp lattices. The diagrams illustrate how **the higher degeneracy of the fcc lattice better accommodates electron-rich metals** (a), whereas electron-poor metals will tend to prefer the lower symmetry hcp lattice (b).

- As a general rule, therefore, we expect that ***metals in the lower group numbers of the periodic table should tend to adopt either bcc or hcp lattices***, and the fcc lattice will be more stable for metals with high group numbers.
- But ***there are several exceptions***, including lattice structures we haven't even discussed.
- The *exceptions* arise from less obvious contributions of the electronic wavefunctions to the stability of the solid, as well as other effects.
- ✓ For example, as we heat or cool a particular metal, we often observe that the most stable crystal structure changes. *Iron, heated above 912 K, changes from its bcc structure (called α -Fe) to fcc (γ -Fe).*
- ✓ *Tin, when cooled below 286 K, is more stable in a lattice with the structure of diamond, rather than the tetragonal crystal.*
- ***These different crystal structures of the same material are called allotropes.***
- ***One rule applies fairly well to both pure and alloyed metal crystals:*** the bond energy tends to increase with the number of unpaired electrons available for bonding. *This accounts for the peak in melting points of the transition metals in Group 6 of the periodic table, because these atoms may have as many as six unpaired electrons.*

Three types of packing present in the metals are represented in a classification: there are

- 40 of cubic I (**dark blue**),
 - 33 elements of **hexagonal close-packed type** (**medium blue**), and
 - 28 of cubic F (**light blue**) that refer to metals and rare gases (see Figure 2.14).
 - Non-metals (except for rare gases) yield diversified types that have not been mentioned here.
 - Only the diamond packing is evidenced for column 14 (except for lead).
 - Some metals may have various types of packing depending on temperature; for example, lithium, iron and thallium present all three types.

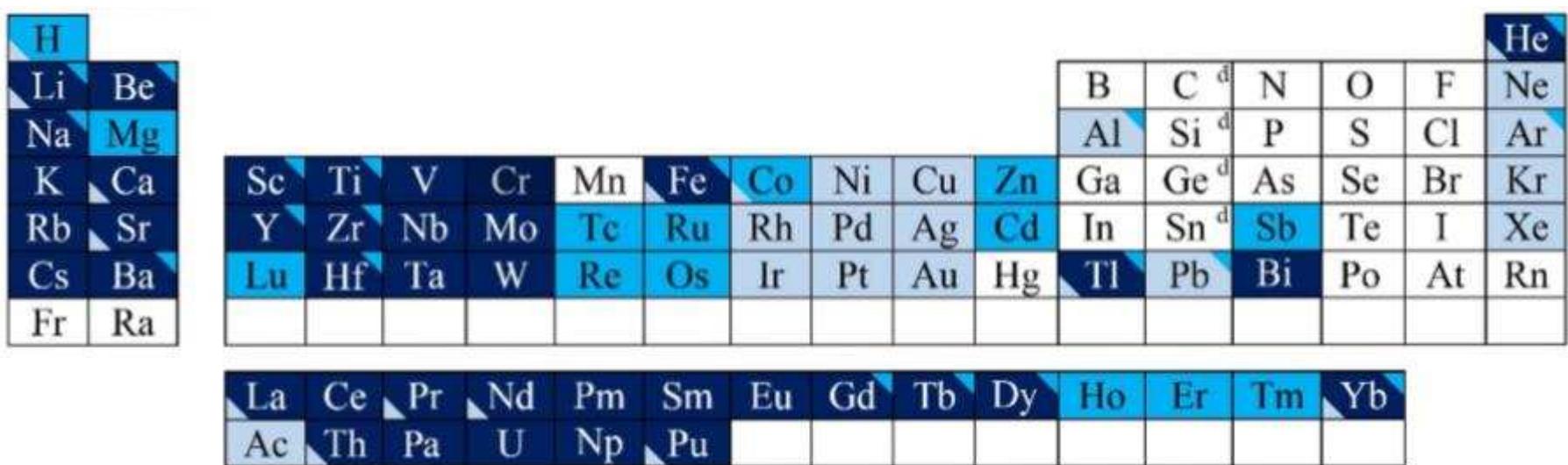


Figure 2.14. Main types of packing in metals.

High period packings

- Some structures are formed of dense and periodical planes of type AB/AB/... or ABC/ABC/..., but more complex structures of type ABAC/... for La, Pr, Nd and Am or of type ABACACBCB/... for Sm can sometimes be observed, and they all have the same packing density as they are close packings of planes that are in their turn close-packed. This is referred to as ***polytypism*** characterized by a sequence of high period packings.
- Random packings of close-packed planes are also observed but they correspond to amorphous materials and not to crystalline materials.

BONDING in SOLIDS: Metallic Bonding

Background: Consider the elements of the third period of the periodic table (Na–Ar) and their bondings (see Fig.).

Each of these elements forms $(8 - N)$ bonds, where N is the number of valence electrons. This behavior can easily be understood through the application of the octet rule.

- Argon with eight valence electrons has a complete octet; as a result it does not form any bonds.
- Chlorine ($N=7$): each Cl atom forms one bond as in Cl_2 molecule, $(8 - 7 = 1)$;
- Sulfur ($N=6$): each S atom forms 2 bonds as in S_8 molecule $(8 - 6 = 2)$;
- Phosphorus ($N=5$): each P atom forms 3 bonds as in P_4 molecule $(8 - 5 = 3)$;
- Silicon ($N=4$): each Si atom forms 4 bonds which favors an extended network solid in which each atom is bonded to four equidistant neighbors.

If the $8 - N$ trend continued, we would expect aluminum (three valence electrons) to form five bonds. However, aluminum adopts a close-packed structure with 12 nearest neighbors. Magnesium and sodium also adopt metallic structures. What is responsible for this abrupt change in the preferred bonding mechanism? The answer is that metals do not have enough valence-shell electrons to satisfy their bonding requirements by forming localized electron-pair bonds. WAY OUT?? In response to this deficiency, the valence electrons are collectively shared. A structure in which the atoms are close-packed facilitates this delocalized sharing of electrons.

Octet rule: Elements form $(8 - N)$ bonds (via electron sharing), where N is the number of valence electrons.

Figure: Bonding in period 3 elements.

$$N =$$

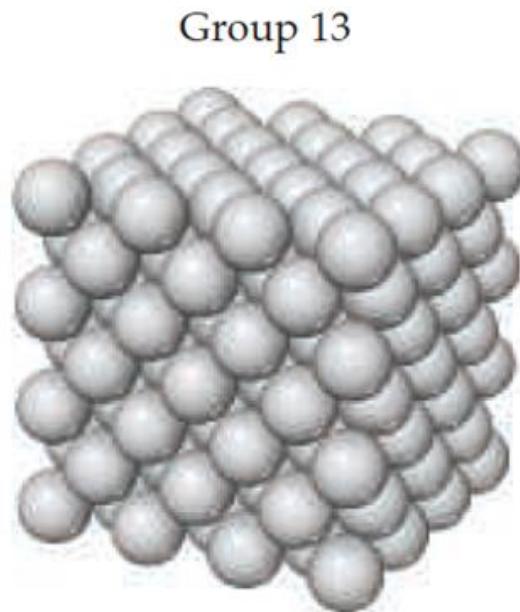
3

4

5

6

7

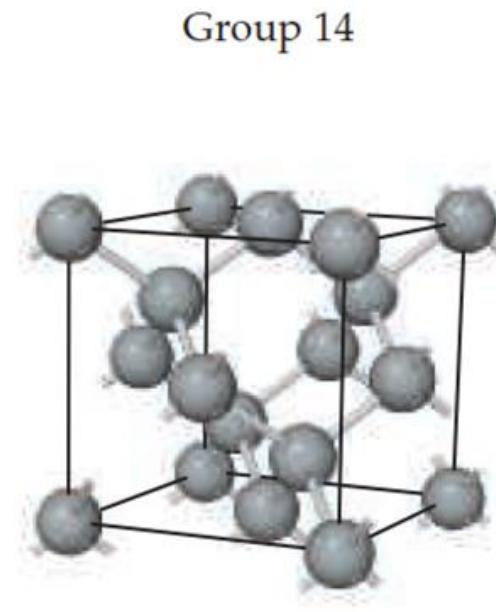


Al
12 nearest neighbors

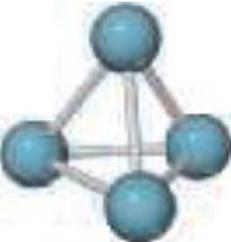
$$8 - 3 = 5.. ?? \times$$

e- sharing

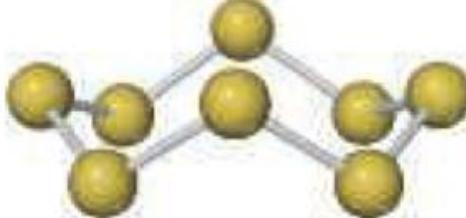
Metallic bonding



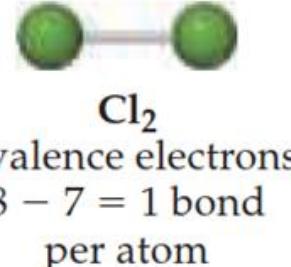
Si
4 valence electrons
 $8 - 4 = 4$ bonds per atom



P₄
5 valence electrons
 $8 - 5 = 3$ bonds per atom



S₈
6 valence electrons
 $8 - 6 = 2$ bonds per atom



7 valence electrons
 $8 - 7 = 1$ bond per atom

Covalent bonding

BONDING in SOLIDS: Metallic Bonding

- The majority of solids comprises ordered arrays of atoms, ions, or molecules.
- Some of the simplest solids are the metals, the structures of which can be described in terms of regular, space-filling arrangements of the metal atoms.
- These metal centers interact through metallic bonding, a type of bonding that can be described in two ways.

-One view is that bonding occurs in metals when each atom loses one or more electrons to a **common ‘sea’** ("electron-sea model"). The strength of the bonding results from the combined attractions between all these freely moving electrons and the resulting cations.

-An alternative view is that metals are effectively enormous molecules with a multitude of atomic orbitals that overlap to produce **molecular orbitals** extending throughout the sample.

- *Metallic bonding is characteristic of elements with low ionization energies*, such as those on the left of the periodic table, through the d block, and into part of the p block close to the d block.
- *Metallic bonding also occurs in many other solids, especially compounds of the d-metals such as their oxides and sulfides*. Compounds such as the lustrous-red rhenium oxide ReO_3 and ‘fool’s gold’ (iron pyrites, FeS_2), illustrate the occurrence of metallic bonding in compounds.

BONDING in SOLIDS: Metallic Bonding

- The familiar properties of a metal stem from the characteristics of its bonding and in particular *the delocalization of electrons throughout the solid*.
- Thus, metals are *malleable (easily deformed by the application of pressure)* and *ductile (able to be drawn into a wire)* because the **electrons can adjust rapidly to relocation of the metal atom nuclei** and there is **no directionality** in the bonding.
- They are lustrous because the electrons can respond almost freely to an incident wave of electromagnetic radiation and *reflect* it.
- The above properties can be explained by the "*electron-sea model*" of metallic bonding. Why do we need a different model for metallic bonding than the electron-sea model?
 - ✓ Although it explains some general properties of metals, like malleability and conductivity, it *doesn't explain* the relative properties of metals, like their *hardness* and *melting points*.
 - ✓ These properties depend on how strong the bonding in the metals is.
 - ✓ By the electron-sea model, we might think that more electrons make the bonds stronger, so hardness and melting point would increase across the periodic table.

The electronic structure of Metallic and Ionic Solids: MO Theory

- *Metallic and ionic solids* can both be treated by molecular orbital theory.
- The advantage of that approach is that both types of solid can be regarded as two extremes of a single kind.
- In each case, the electrons responsible for the bonding are delocalized throughout the solid (like in a benzene molecule, but on a much bigger scale).
- *In an elemental metal, the electrons can be found on all the atoms with equal probability*, which matches the primitive picture of metal as consisting of cations embedded in a nearly uniform electron 'sea'.
- In an ionic solid, the wavefunctions occupied by the delocalized electrons are almost entirely concentrated on the anions, so the Cl atoms in NaCl, for instance, are present as Cl^- ions, and the Na atoms, which have *low valence electron density*, are present as Na^+ ions.

- To set up the molecular orbital theory of solids consider initially a single, infinitely long line of identical atoms, each one having an s orbital available for forming molecular orbitals (as in sodium). One atom of the solid contributes an s orbital with a certain energy (Fig. 10).
- When a second atom is brought up it forms a bonding and antibonding orbital. For a homonuclear diatomic, such as Li_2 , there are two MOs: one bonding and one antibonding, as shown in Figures 10 & 12.12. In a homogeneous metallic solid, the valence AOs can combine with one another to form MOs.
- For a metallic solid containing only three metal atoms, three MOs will result: one bonding MO (*with no nodes*), one nonbonding MO (*having one node*), and one antibonding MO (*having two nodes*).
- For n metal atoms, n MOs will form, each pair of which has a slightly different energy from its neighboring pair on the MO diagram.
- The relative energies of each MO can be determined on the basis of the number of nodal planes that exist. The lowest energy MO will have zero nodes and the highest will have $(n-1)$ nodes.
- For an infinite number of metal atoms, the MOs become so closely spaced that they blur together into a “**band**” of MOs, as shown at the right in Figure 10.

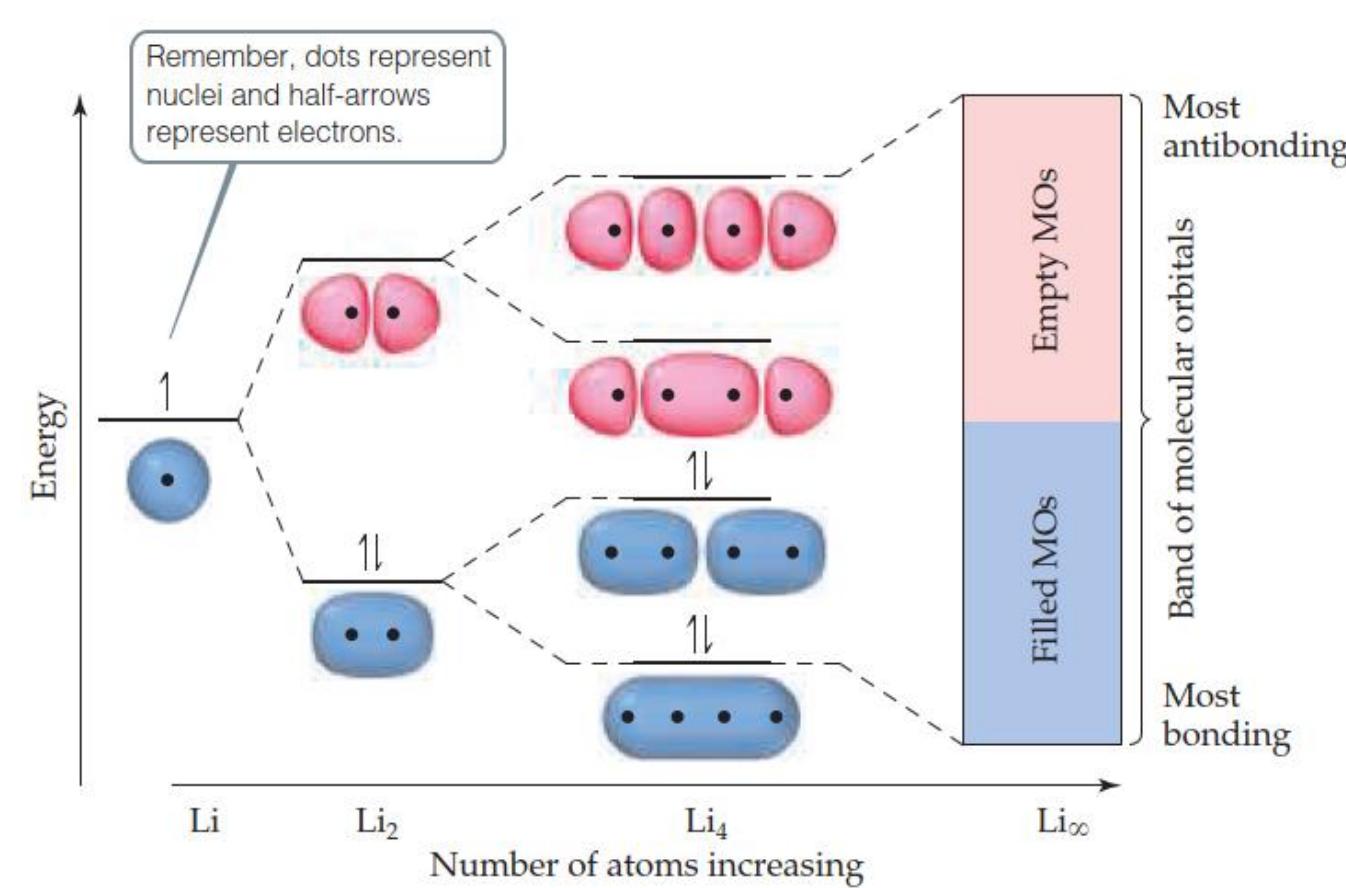


Figure 12.22 Discrete energy levels in individual molecules become continuous energy bands in a solid. Occupied orbitals are shaded blue, and empty orbitals pink.

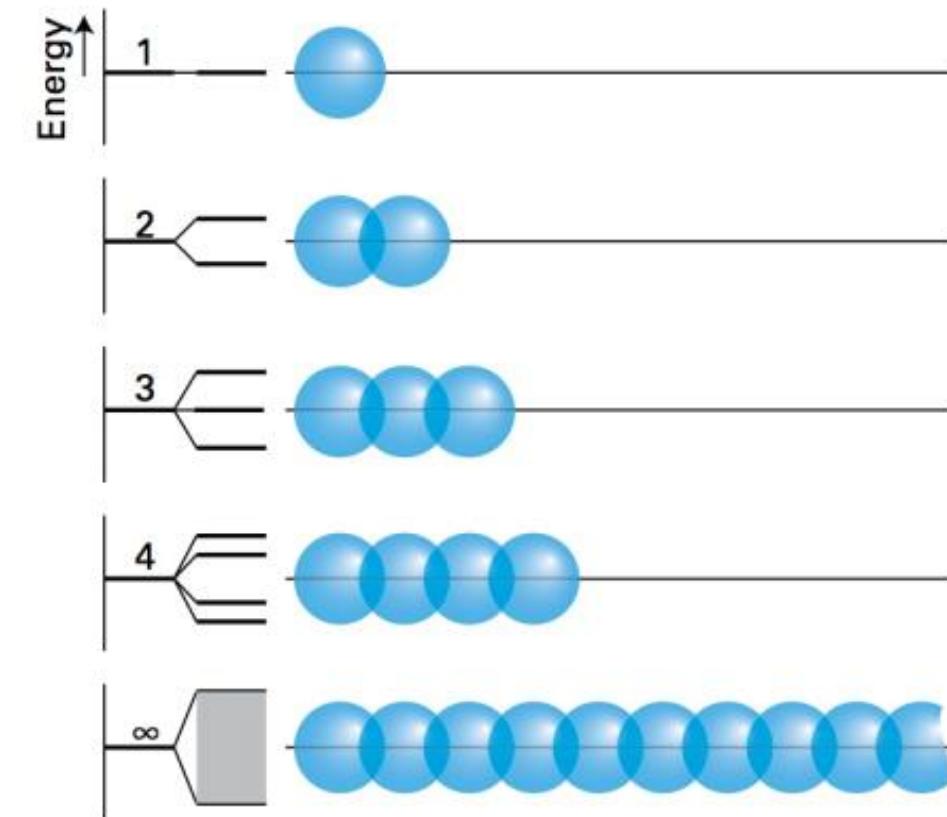


Fig. 10 The formation of a band of N molecular orbitals by successive addition of N atoms to a line. Note that the band remains of finite width, and although it looks continuous when N is large, it consists of N different orbitals.

- When we have a really big number of MOs, some interesting things happen.
- One mole of Fe is about 7 mL or 7 cc (a pretty small amount).
- In each atom of Fe, we have **one** 4s orbital, **five** 3d orbitals, and **three** 4p orbitals that can be *involved in bonding*.
- In a mole of Fe, we have **9** times Avogadro's number of AOs that can be involved in bonding. That's about 10^{24} AOs, which means the same number of MOs.
- There just isn't space to have much difference in energy between all those MOs.
- The MOs have to have energies not too different from the AOs (they are definitely higher and lower, but not by too much), so they are limited to a relatively narrow range of energies. This means that the energies form **bands** rather than separate energy levels.

- When N atoms have been added to the line, there are N molecular orbitals covering a band of finite width. The lowest-energy orbital of this band is fully bonding and the highest-energy orbital is fully antibonding between adjacent atoms (Fig. 11).
- A band formed from overlap of s orbitals is called an ***s band***. If the atoms have p orbitals available, then the same procedure leads to a ***p band*** (with different values of α and β).
- If the atomic p orbitals lie higher in energy than the s orbitals, then the p band lies higher than the s band, and there *may be* a ***band gap***, a range of energies for which no molecular orbitals exist. If the separation of the atomic orbitals is not large, the two types of bands might overlap.

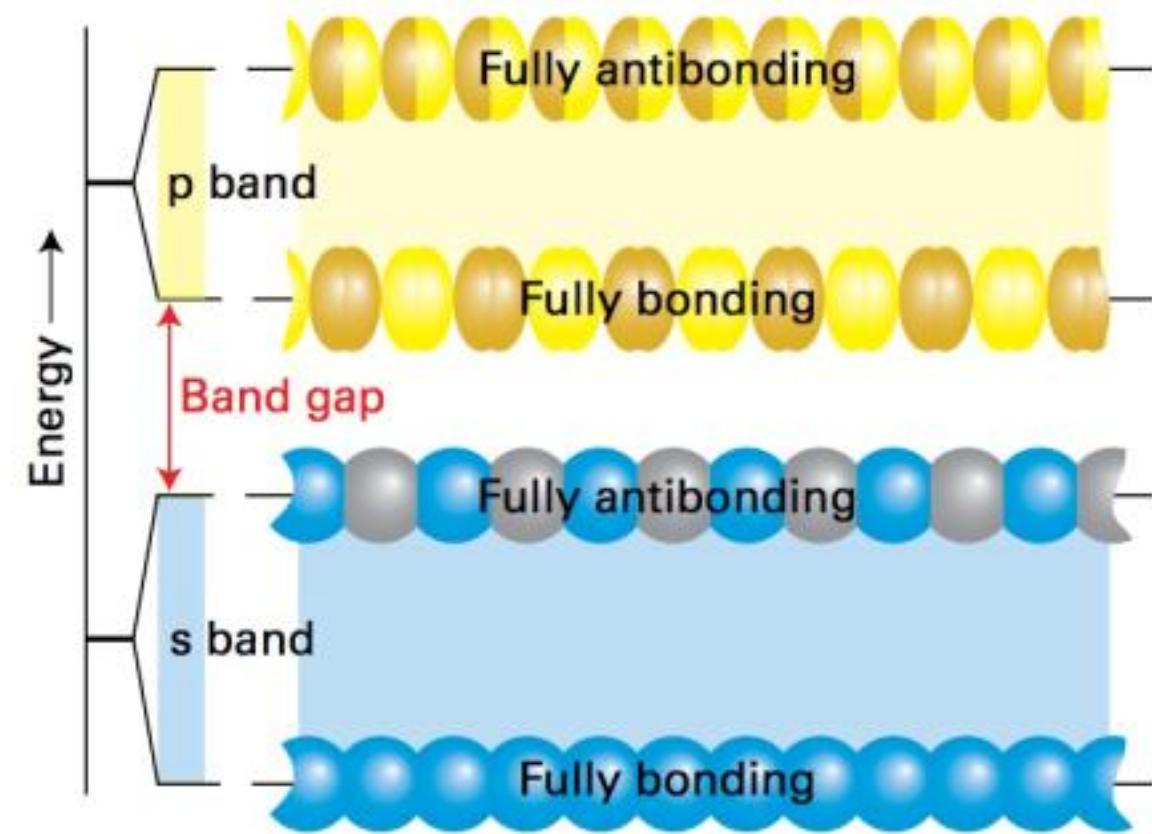


Fig. 11 The overlap of s orbitals gives rise to an s band, and the overlap of p orbitals gives rise to a p band. In this case the s and p orbitals of the atoms are so widely spaced that there is a ***band gap***. In many cases the separation is less, and the bands overlap.

In the Hückel approximation, it turns out that the energies of the orbitals are given by

$$E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right) \quad k = 1, 2, \dots, N$$

where α is approximately equal to $-\frac{1}{2}(I + E_{ea})$, where I is the ionization energy of the atom and E_{ea} its electron affinity, and β is a negative quantity that represents the *lowering of energy due to interaction between neighboring atoms*.

When N is infinitely large, the separation between neighboring levels, $E_{k+1} - E_k$ is infinitely small,

but the band still has finite width overall (as drawn in Fig. 10):

$$E_N - E_1 \rightarrow -4\beta \text{ as } N \rightarrow \infty$$

Note that because $\beta < 0$, $-4\beta > 0$ and the band width is a positive quantity.

As $N \rightarrow \infty$,

(1)Show that : $E_1 = \alpha + 2\beta$
(the term $\pi/(N + 1)$ tends to zero so
the cosine tends to 1; therefore, in
this limit, $E_1 = \alpha + 2\beta$)

(2)Show that : $E_N = \alpha - 2\beta$.

(3)Show that : $E_{k+1} - E_k \rightarrow 0$

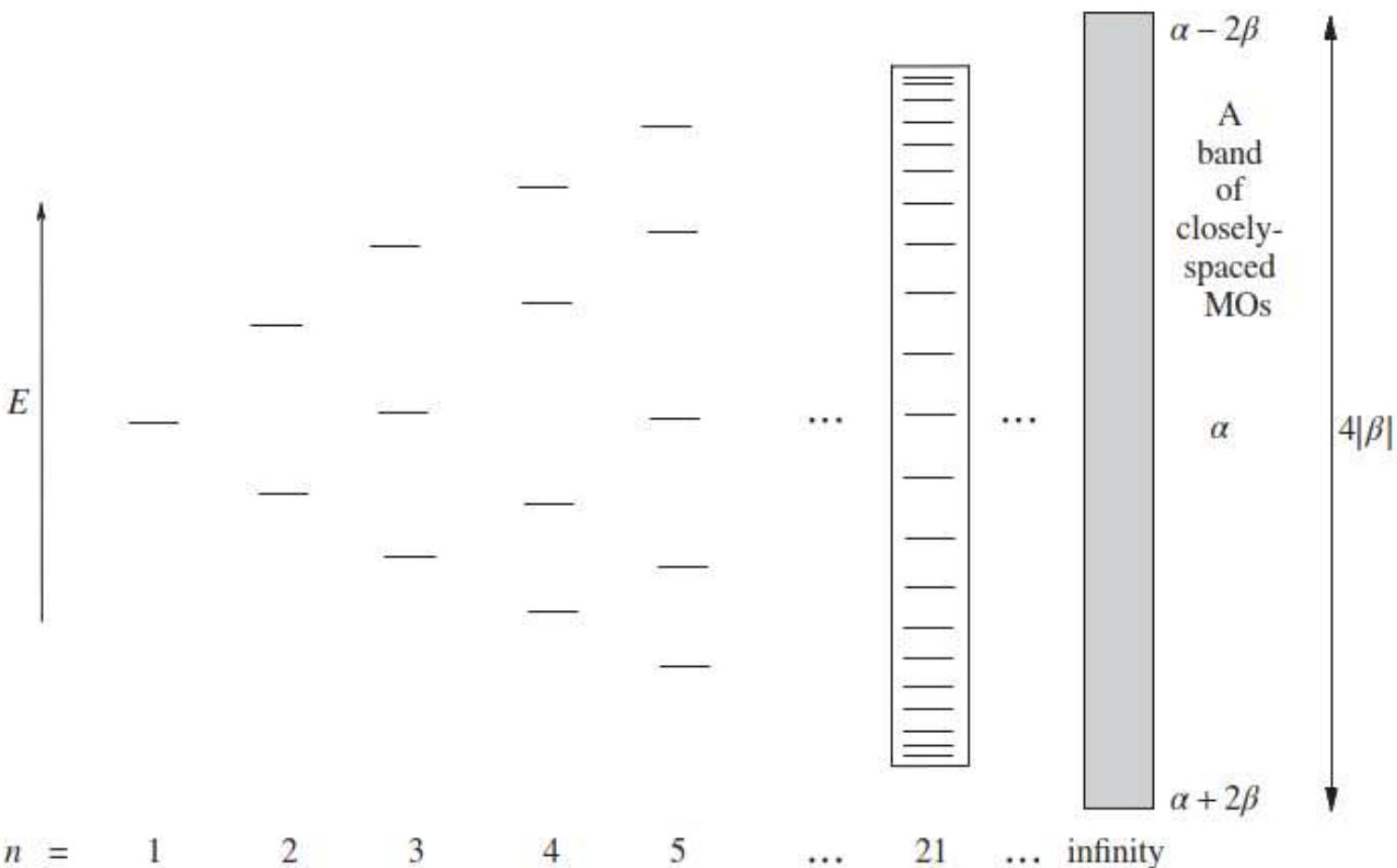


FIGURE 11.22
Molecular orbital diagram for a
linear chain of n metal atoms,
showing how the closely-spaced
MOs blur into a band as n
approaches infinity.

$\cos(n\pi) = +1$ whenever n is even
and
 $\cos(n\pi) = -1$ whenever n is odd.

The energy of the level with $k=1$ is

$$E_1 = \alpha + 2\beta \cos \frac{\pi}{N+1}$$

As $N \rightarrow \infty$, the cosine term approaches $\cos 0 = 1$. Therefore, in this limit

$$E_1 = \alpha + 2\beta$$

When k has its maximum value of N ,

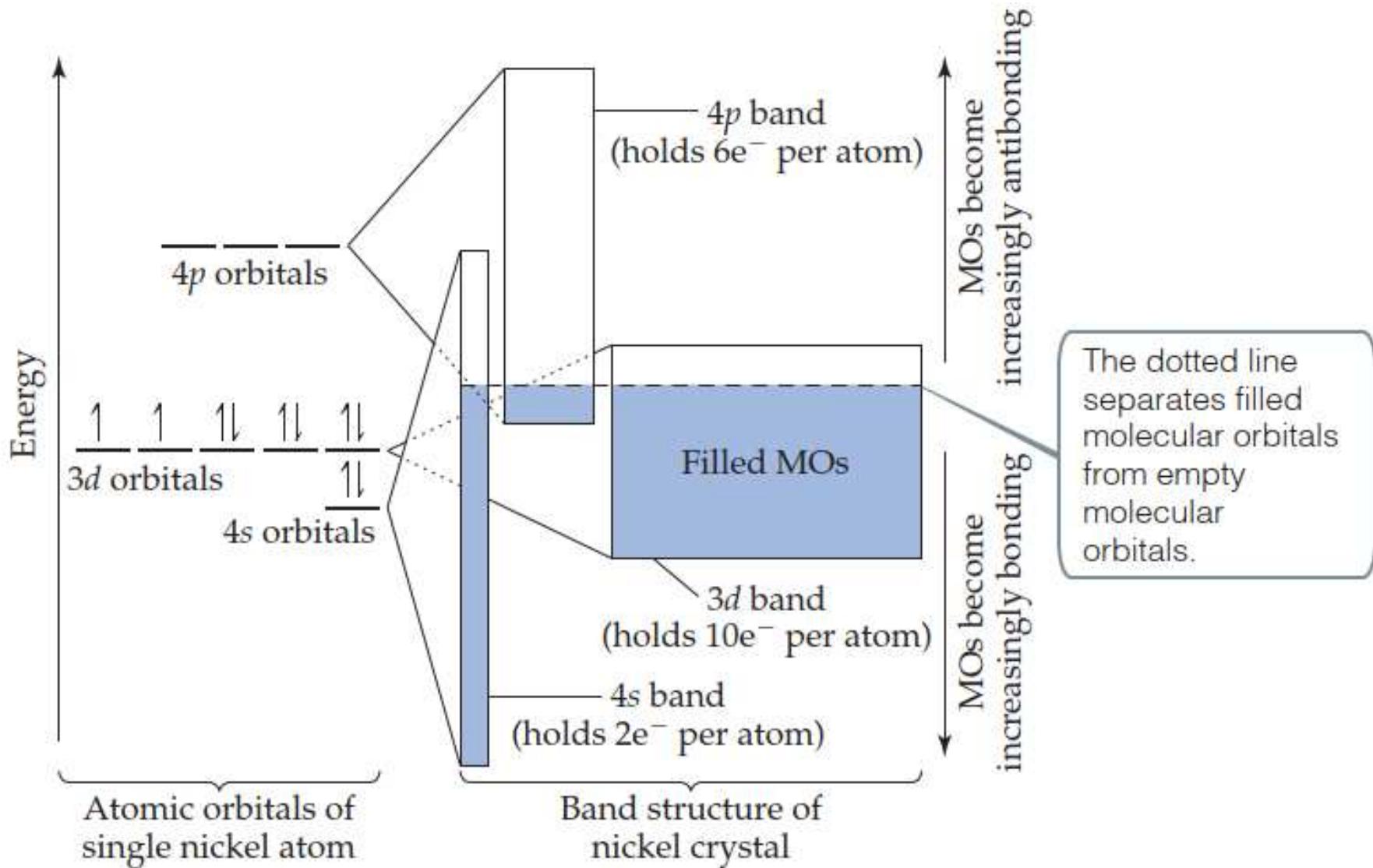
$$E_N = \alpha + 2\beta \cos \frac{N\pi}{N+1}$$

As $N \rightarrow \infty$, it is possible to ignore the 1 in the denominator, and the cosine term becomes $\cos \pi = -1$. Therefore, in this limit $E_N = \alpha - 2\beta$, and $E_N - E_1 \rightarrow -4\beta$, as in eqn 2b.

- Show the derivation of the expression for the energy difference between two neighboring levels.

- It is the energies and shapes of these bands that will determine the physical and chemical properties of metals.
- *This improvement over the Drude–Sommerfield model of metallic bonding is known as **band theory**.*
- In practice, this approach is directly analogous to the way we made molecular orbitals in covalently bonded compounds by taking linear combinations of atomic orbitals having similar energies and the appropriate symmetry to yield a net nonzero overlap. Thus, if there are N atomic orbitals in the lattice, there will be N molecular orbitals (known as the **Bloch orbitals**) in the crystalline solid.
- The electronic structures of most metals are more complicated than those shown in Figure 12.22 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of *a series of bands*. The electronic structure of a bulk solid is referred to as a **band structure**.

Figure 12.23 The electronic band structure of nickel.



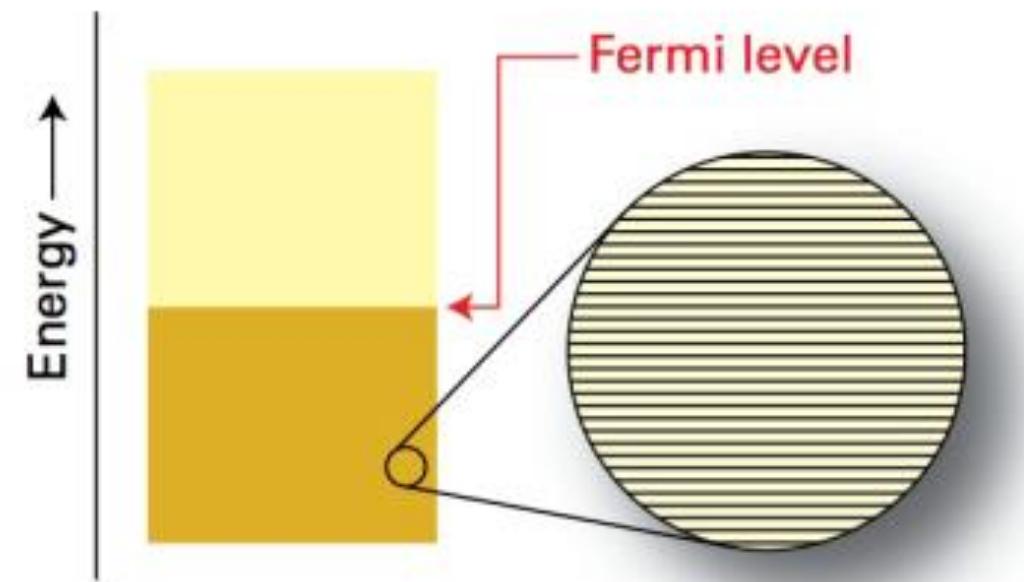
- The band structure of a typical metal is shown schematically in Figure 12.23.
- The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is $[Ar]4s^23d^8$, as shown on the left side of the figure.
- The energy bands that form from each of these orbitals are shown on the right side.
- The 4s, 4p, and 3d orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, *these overlapping bands are not completely independent of each other*, but for our purposes this simplification is reasonable.
- The 4s, 4p, and 3d *bands differ from one another in the energy range they span* (represented by the *heights of the rectangles* on the right side of Figure 12.23) and in *the number of electrons they can hold* (represented by the *area of the rectangles*).
- The 4s, 4p, and 3d bands can hold 2, 6, and 10 electrons per atom, respectively, corresponding to two per orbital, as dictated by the Pauli exclusion principle.
- The *energy range* spanned by the 3d band is smaller than the range spanned by the 4s and 4p bands because the *3d orbitals are smaller* and, *therefore, overlap with orbitals on neighboring atoms less effectively*.

- We can **explain melting point, hardness, and other properties using MO theory.**
- In this case, we imagine combining many atomic orbitals (1 or more for each atom) to make an equal number of MOs that extend over the whole solid.
- Some MOs will have fewer nodes and be lower energy, while others will have more nodes and be higher energy.
- Each MO can hold no more than 2 electrons.
- While the conductivity of metals can be qualitatively understood using either the *electron-sea model* or the *molecular orbital model*, many physical properties of transition metals, such as the melting points plotted in Figure 12.21, can be explained only with the latter model.
- *The molecular orbital model predicts that bonding first becomes stronger as the number of valence electrons increases, and the bonding orbitals are increasingly populated.*
- *Upon moving past the middle elements of the transition metal series, the bonds grow weaker as electrons populate antibonding orbitals.*
- **Strong bonds between atoms lead to metals with higher melting and boiling points, higher heat of fusion, higher hardness, and so forth.**

- Filling the lower energy MOs (bonding MOs) makes the bonds stronger.
- Alkali metals have low melting points and are soft for not many bonding MOs filled.
- Filling the higher energy MOs (**antibonding** MOs) makes the bonds weaker, which is why Cu, Ag, Au and Zn are soft and melt at low temperatures (Hg is a liquid at RT!).

- Consider the electronic structure of a solid formed from atoms each of which is able to contribute one valence orbital and one electron (for example, the alkali metals).
- There are N atomic orbitals and therefore N molecular orbitals squashed into a band of finite width. There are N electrons to accommodate; they form pairs that occupy the lowest $\frac{1}{2}N$ molecular orbitals (Fig. 12).
- *The highest occupied molecular orbital is called the **Fermi level**.*
- However, unlike in the discrete molecules, there are empty orbitals just above and very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons.
- Some of the electrons are therefore very mobile and give rise to electrical conductivity.

Fig. 12 When N electrons occupy a band of N orbitals. it is **only half full** and the electrons near the Fermi level (the top of the filled levels) are mobile.



- Without the overlap of energy bands, the periodic properties of metals could not be explained.
- In the absence of the d- and p-bands, we would expect the s-band to be half-filled for the alkali metals (group 1) and *completely filled* for the alkaline-earth metals (group 2). If that were true, *metals like magnesium, calcium, and strontium would not be good electrical and thermal conductors*, in disagreement with experimental observations.

- To describe **an ionic solid**, consider a line of atoms with different electronegativities, such as a one-dimensional array of sodium and chlorine atoms rather than the identical atoms treated so far.
- Each sodium atom contributes an *s* orbital and one electron. Each chlorine atom contributes an electron from a *p* orbital.
- The *s* and *p* orbitals are used to build molecular orbitals that spread throughout the solid. Now, ***though, there is a crucial difference.***
- The ***orbitals on the two types of atom have markedly different energies***, so (just as in the construction of molecular orbitals for hetero-diatomc molecules) they *can be considered separately.*

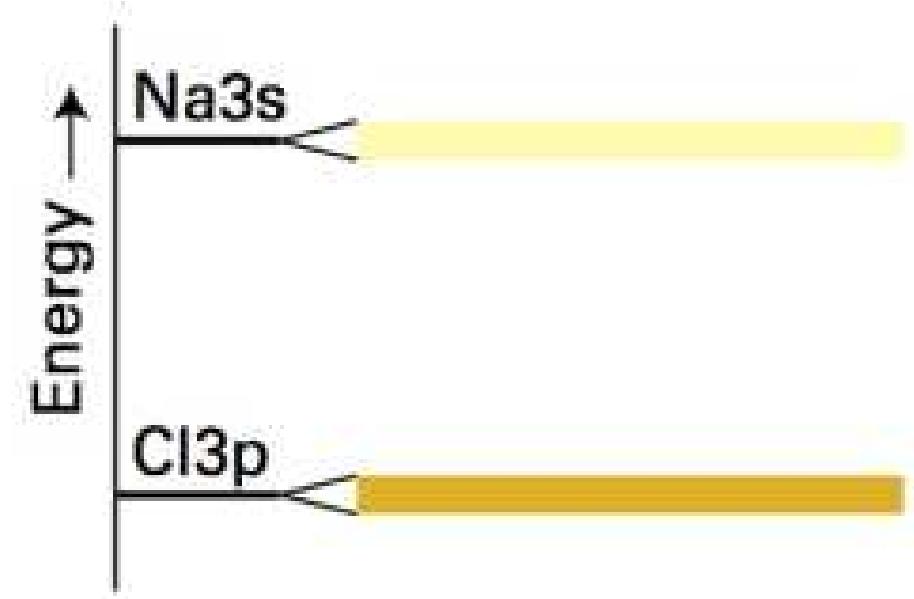


Fig. 13 The bands formed from two elements of *widely different electronegativity* (such as sodium and chlorine): they are widely separated and narrow. *If each atom provides one electron, the lower band is full and the substance is an insulator.*

- The Cl3p orbitals interact to form one band and the higher energy Na3s orbitals interact to form another band. However, because the *sodium atoms have very little overlap with one another (they are separated by a chlorine atom)*, the Na3s band is very narrow; so is the Cl3p band, for a similar reason.
 - As a result, *there is a big gap between the two narrow bands* (Fig. 13).
-
- If there are N sodium atoms and N chlorine atoms, there will be $2N$ electrons to accommodate (one from each Na atom and one from each Cl atom).
 - ***These electrons occupy and fill the lower Cl3p band.***
 - As a result, *the electron density is almost entirely on the chlorine atoms.*
 - In other words, *the solid can be thought of as composed of Na^+ cations and Cl^- anions*, just as in an elementary picture of ionic bonding.

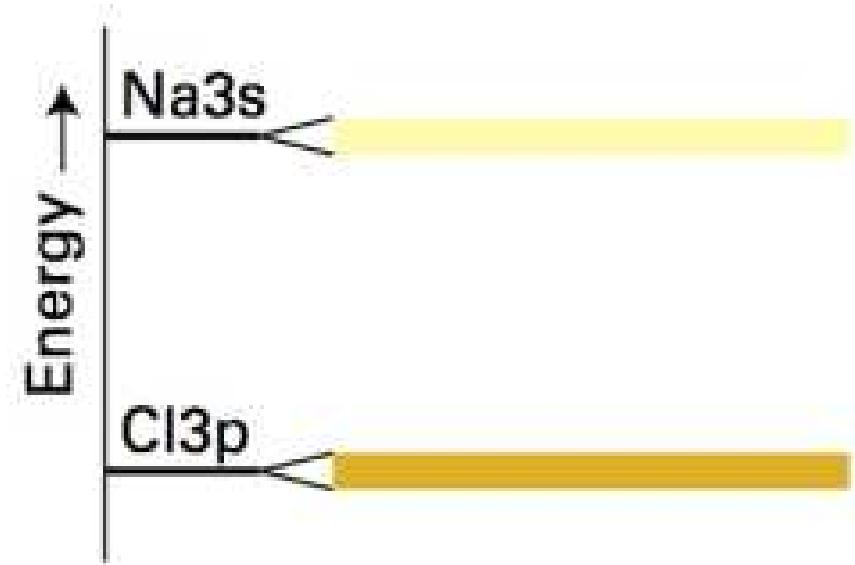


Fig. 13 The bands formed from two elements of widely different electronegativity (such as sodium and chlorine): they are widely separated and narrow. *If each atom provides one electron, the lower band is full and the substance is an insulator.*

CONDUCTIVITY IN SOLIDS

- Band theory is a quantum-mechanical treatment of the bonding in metals.
- When the number of atoms N in a crystal is very large, the spacing between the energy levels in the band is infinitesimally small so that promotion to the next highest energy level within the band can occur quite readily.
- Whenever a band is fully occupied with valence electrons, it is known as the VB.
- If a band is unoccupied or empty, it is known as the CB.
- In a metal such as Li, as shown in Figure 11.36, the band constructed from a linear combination of the valence 2s AOs is exactly half-filled, so that the VB and the CB derive from the same set of orbitals and are only distinguished from each other by the presence or absence of electrons.
- The energy of the highest filled MO at 0K is known as the ***Fermi level***. Because the Fermi level lies inside a band in Li, *this metal is a conductor*.
- For a metal such as Mg, the band formed by the 2s AO basis set (in other words, the VB) is completely filled. *The only reason that Mg is a conductor is because 2s band overlaps with the empty band formed by the 2p basis set* (or the CB), as shown in Figure 11.47 (at left).

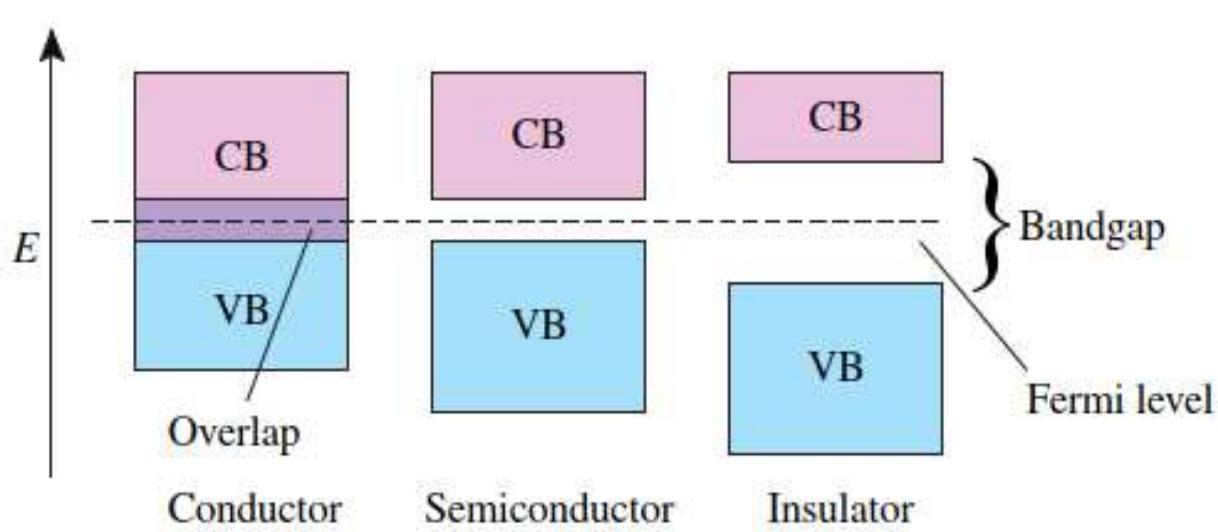


FIGURE 11.47 Simplified band diagram showing the differences between a conductor, a semiconductor, and an insulator. The main difference has to do with the band gap energy, or separation between the top of the valence band (VB) and the bottom of the conduction band (CB). The Fermi level is indicated by a dashed line on the diagram.

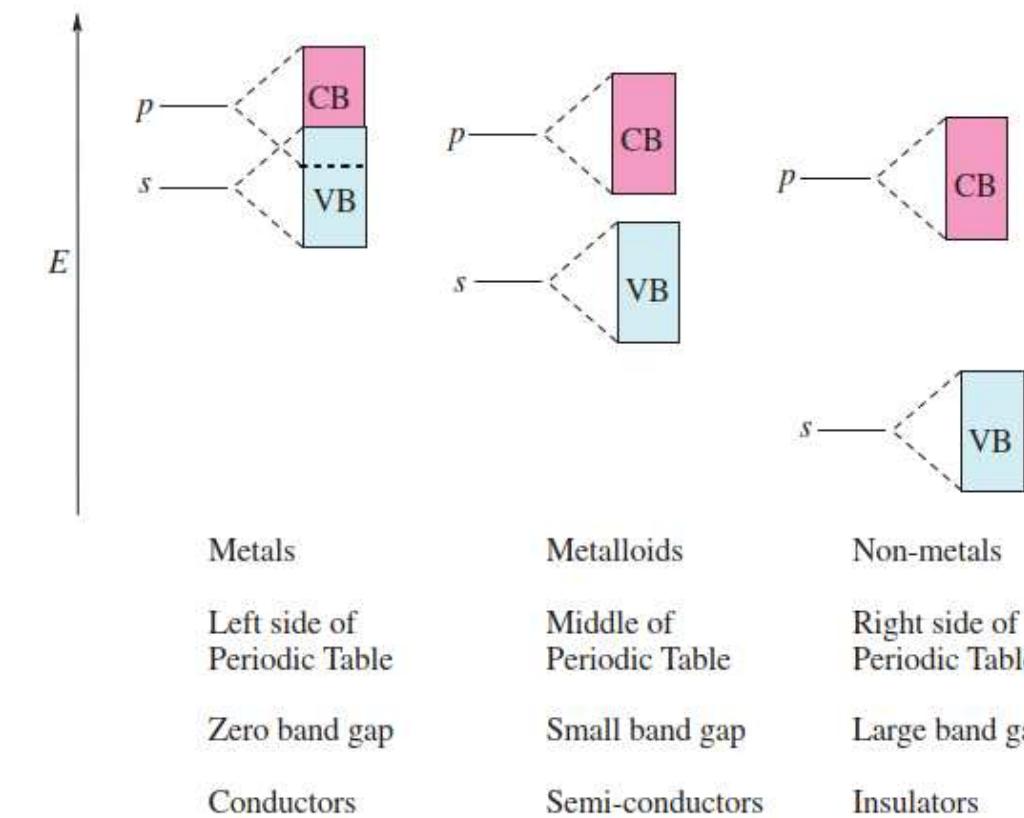


FIGURE 11.48 A simplistic rationalization for the electrical conductivity of the elements in the periodic table based on their band structures.

- In the ground electronic state of the solid, the occupied molecular orbitals make up the **valence band** of the solid. The **unoccupied orbitals**, if they extend over large distances in the solid, comprise **the conduction band**.
- If the valence band ends just where the conduction band begins, the slightest electronic energy pushes the electrons into orbitals where they have more mobility.

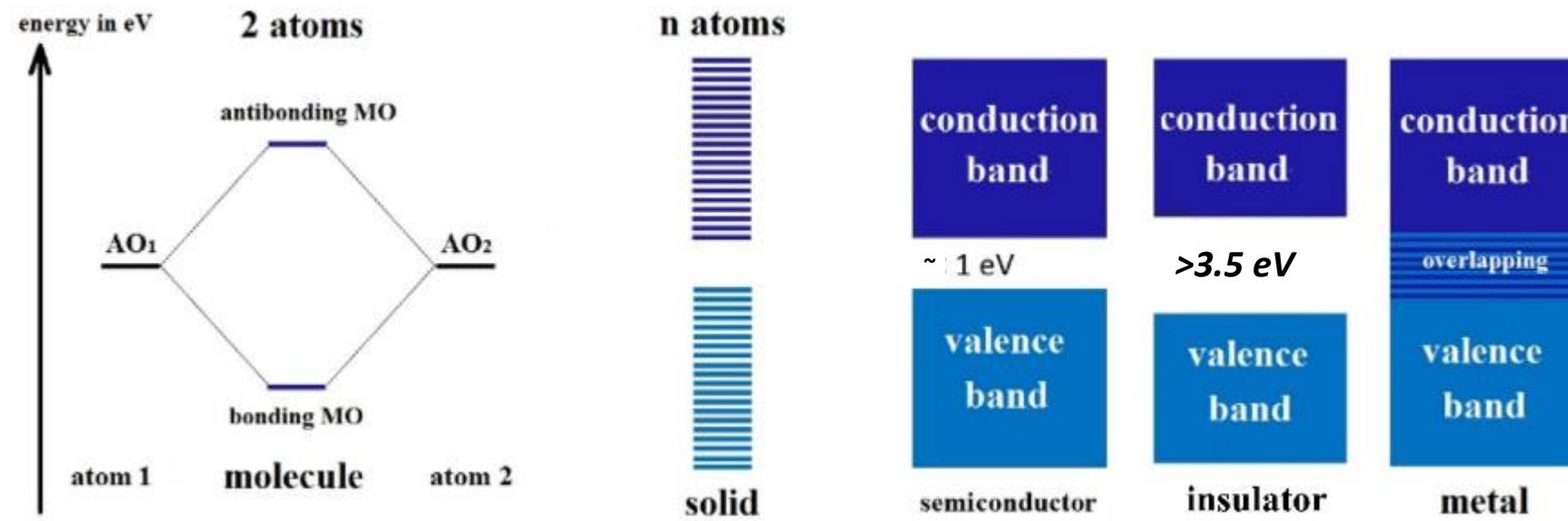


Figure 2.1. Simplified diagram of the energy-band model.

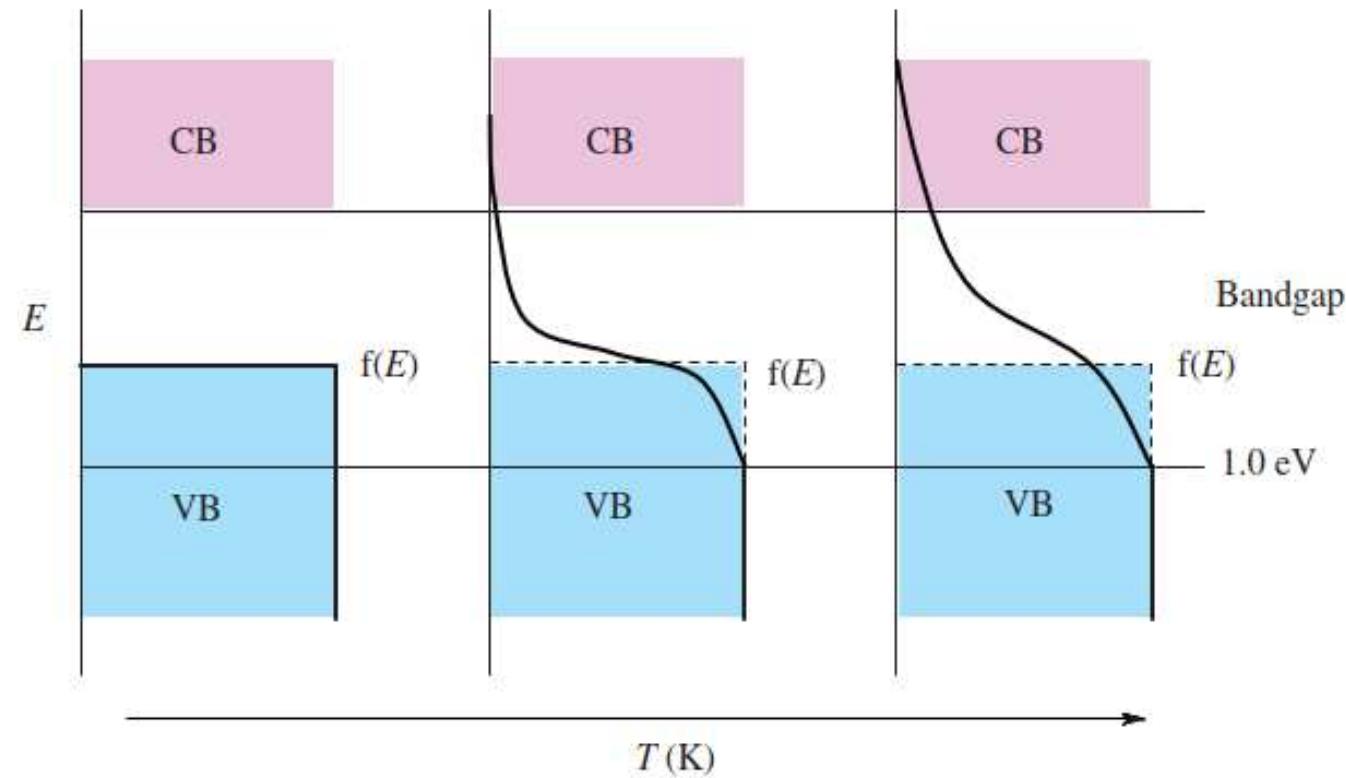
- A simplified version of band theory can therefore be used to make a rather sweeping generalization about the electrical properties of the elements, as shown in Figure 11.48.
- ***One primary difference between the metals and nonmetals is related to the energies of their valence s and p AOs. This energy difference increases across a row of the periodic table because of increased shielding of the p-electrons by the more penetrating s-electrons.***
- The metals, which lie to the left in the periodic table, are excellent electrical conductors because their valence and CBs overlap and there is essentially no energy gap at all between the bands.
- On the other end of the spectrum, the nonmetals, which lie to the right in the periodic table, are typically electrical insulators because of the sizable band gap that exists between their VBs and CBs.
- In the *middle of the periodic table*, there is a gray area that is intermediate in its electrical properties between those of a metal and those of a nonmetal. These are the ***metalloids***, which are usually delineated by a bold diagonal “staircase” on the periodic table. The metalloids tend to be semiconductors because they have only a small band gap.

- Often **metal** is defined as a material that has an electrical conductivity *greater than 10^2 S/m* (where S is the SI unit Siemens, which has the value $1\text{S}=1\Omega^{-1}$).
- The *conductivities of metals typically decrease with increasing temperature* because there are *more disruptive lattice vibrations* at higher temperatures.
- An **insulator** is defined as a material that has an electrical conductivity of less than 10^{-5} S/m .
- Lastly, **semiconductors are defined as having conductivities between 10^{-5} and 10^2 S/m .**
- The **band gap** (E_g , the energy gap between the VB and CB) in a semiconductor is fairly small (typically less than 2 eV); but unlike the metals, the bands do not overlap with one another.
- At low temperatures, a semiconductor will act as an insulator; but as the temperature is raised and an external potential is applied, a portion of the electrons in the VB can “jump” across the band gap into the CB.
- This is because of the temperature dependence of the Fermi–Dirac distribution, which spreads out at higher temperatures over a greater range of energy levels, as shown in Figure 11.50.
- *Unlike the metals, whose conductivities generally decrease with increasing temperature, the conductivity of a semiconductor increases as the temperature* is raised because a greater fraction of the electrons possess enough thermal energy to jump across the barrier. The electrons can also cross the band gap in a semiconductor by the absorption of visible light.

FIGURE 11.50

The Fermi–Dirac distribution as a function of temperature in a semiconductor.

The Fermi–Dirac distribution is really nothing more than a modified Boltzmann distribution that takes into account the fact that each energy level can hold no more than two electrons. The shape of the Fermi–Dirac distribution decays exponentially according to Equation(11.26), where μ is the field potential.



At absolute zero
(0 K), there is
no band bending

At moderate temps,
some e^- have E above
the Fermi level

At high temps,
there is more
band bending

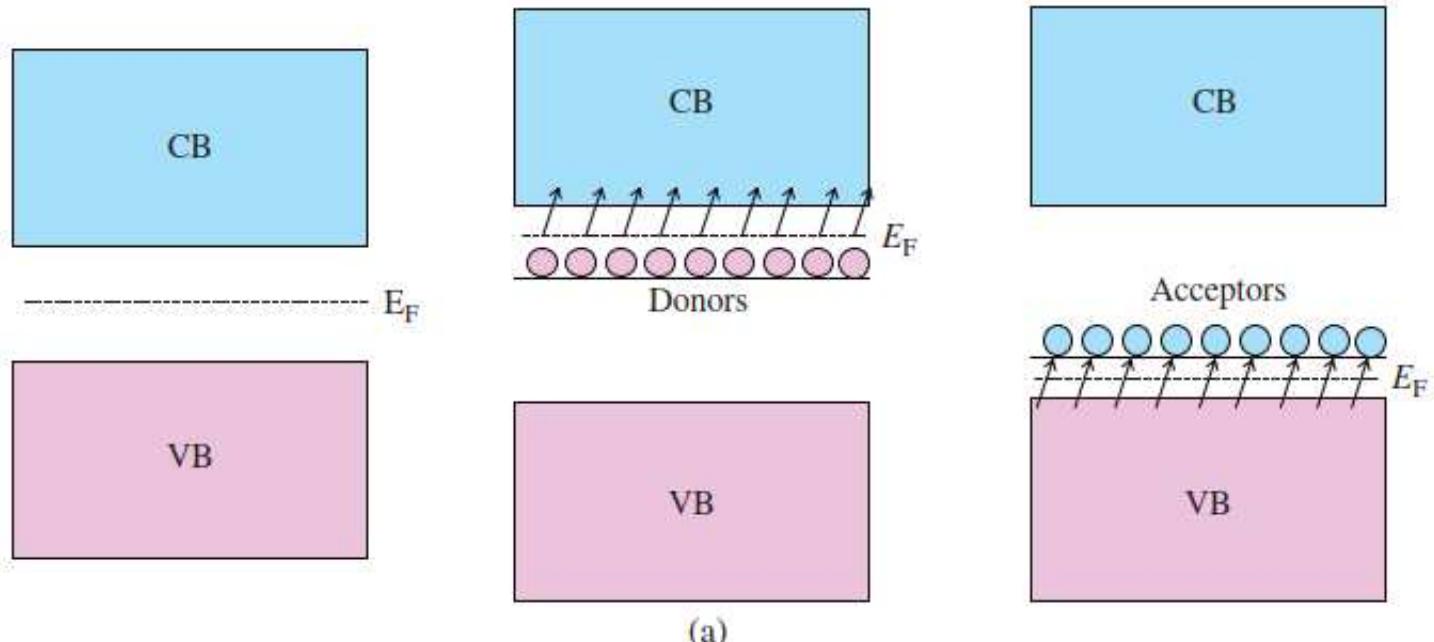
$$f(E) = \frac{1}{e^{(E-\mu)/kT} + 1}$$

- Some of the metalloids, such as Si (band gap= 1.1 eV) and Ge (band gap= 0.74 eV), are ***intrinsic semiconductors***, which means that the pure substance can exhibit semiconducting properties.
 - ✓ This is one of the reasons that the entire modern electronics era is based on Si microchips.
- ***Band gaps greater than ~3.5 eV*** are so large that the material is not a semiconductor; it is ***an insulator*** and does not conduct electricity.
- The conductivity of Si can be enhanced, however, with the addition of small amounts of ***dopants*** that increase the number of charge carriers. For every so many Si atoms, for example, if we were to replace one of these Si atoms with an As atom, the conductivity would increase because the lattice acquires an extra electron (As has five valence electrons, while Si only has four).
- There is no room for the extra electrons from the As atoms to occupy MOs in the VB of Si, so they occupy a very narrow set of orbitals of their own (narrow because they are few and far between so that their valence orbitals have very little overlap).
- The As ***orbital energies are intermediate between those of the VB and CB*** of Si, as shown in Figure 11.51(a).

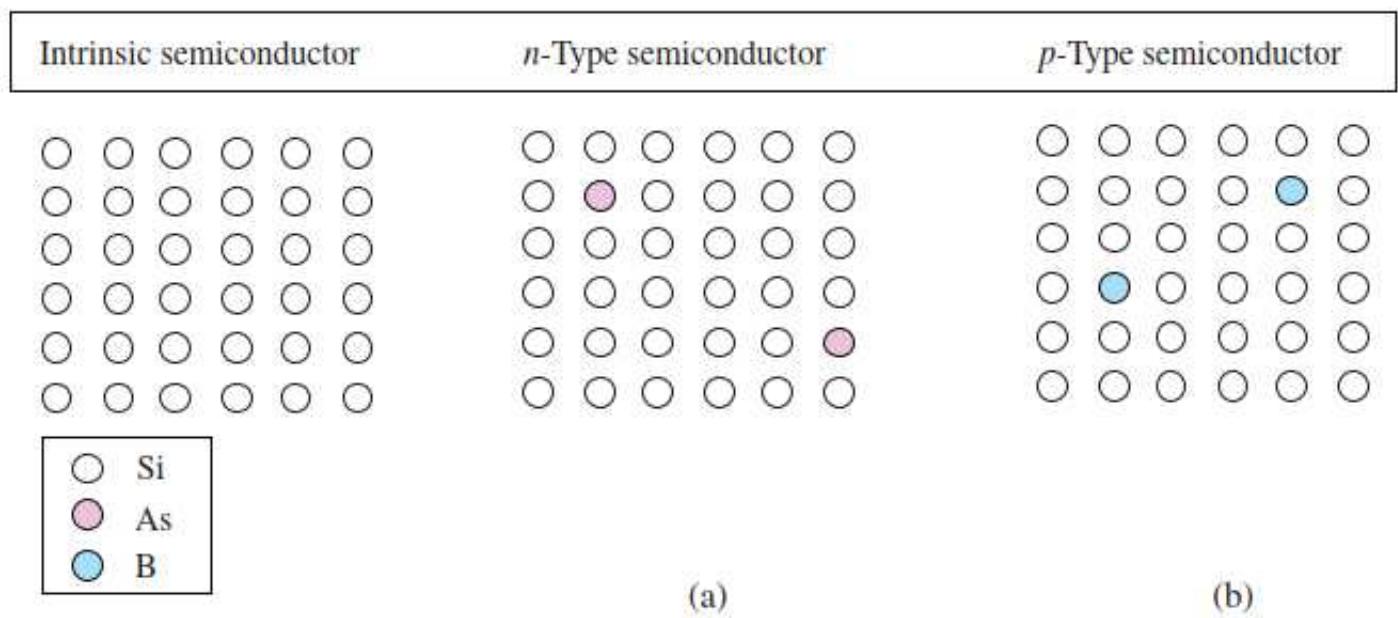
- Whenever the dopant adds electrons to the lattice, the material is called an ***n-type semiconductor*** because the dopant adds negative charge carriers. The conductivity of an n-type semiconductor is enhanced because the electrons in the As orbitals lie higher in energy than those in the VB of Si.
- The energy difference (band gap) between the highest occupied MOs and the lowest unoccupied MOs is now significantly smaller. This makes it easier for electrons to jump across the barrier into the CB.

FIGURE 11.51

(a, b) The difference between an intrinsic semiconductor, an n-type semiconductor, and a p-type semiconductor.



(a)



- An *alternative way to improve the conductive properties of a semiconductor* (or to convert an insulator into an extrinsic semiconductor) is to *dope* it with an element that contains less electrons.
- One example is to dope a Si wafer such that dopant atoms occupy some of the lattice sites of the material. Because *dopant atom* has only *three valence electrons*, the dopant provides a set of *low-lying empty MOs*, as shown in Figure 11.51(b).
- The band gap between the top of the VB for Si and these empty MOs is very small, so that some of the electrons in the VB can be thermally excited into the empty dopant MOs.
- When this occurs, the electron deficiency creates holes in the VB, which act as *positive charge carriers*. Because the dopant increases the number of positive charge carriers, the material is called a *p-type semiconductor*.
- Almost every modern electronic device (from laptops to cell phones to mp3 players) contains a p–n junction as part of its integrated circuitry.

Superconductors

- As mentioned previously, *the conductivity of a semiconductor will increase* (resistance decreases) as *the temperature is raised* because there are more charge carriers at the higher temperature.
- *By contrast, the conductivity of a metal decreases as the temperature is raised* because there will be a greater number of lattice distortions, causing an electronic instability.
- ✓ The **resistance** to flow of electrical current of a normal metallic conductor **decreases** smoothly with **decreasing temperature but never vanishes**.
- However, a **superconductor** conducts electricity without resistance once the temperature is below the critical temperature, T_c .
- In **a superconductor**, there is zero resistance to the flow of electricity at temperatures lower than a certain critical temperature, T_c , which is characteristic of the material.
- *Even in the absence of an applied potential, a small current can still flow* with zero resistance through the superconductor.
- In 1911, Heike Kamerlingh Onnes discovered that Hg becomes superconducting at temperatures lower than 4.2K , the normal boiling point of liquid helium.
- Metals, such as tungsten, mercury, and lead, have T_c values below about 10 K.

- In 1986, Bednorz and Müller discovered that if La_2CuO_4 is doped with Ba and partially oxidized, it will become superconducting at $T_c = 35\text{K}$. By changing the cations to Y, the familiar 1–2–3 superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$, was discovered to have $T_c > 90\text{K}$, a temperature higher than the boiling point of liquid nitrogen (77K), and the modern field of **high-temperature superconductors (HTSCs)** was born.
- Several *ceramics*, inorganic powders that have been fused and hardened by heating to a high temperature, containing oxocuprate motifs, Cu_mO_n , are now known with T_c values well above 77 K, the boiling point of the inexpensive refrigerant liquid nitrogen. For example, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ has $T_c = 153\text{ K}$.
- In 1933, Meissner Ochsenfeld noticed that *superconductors exclude an internal magnetic field*, a phenomenon now known as the **Meissner effect**. Thus, **a superconducting solid cooled below its T_c will appear to float above a bar magnet**.
- As a result of the *Meissner effect*, superconducting materials have found practical application in the magnets of nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), and particle accelerators.

- Because HTSC materials can be cooled relatively inexpensively using liquid nitrogen, high-temperature superconductors have been envisioned in a variety of practical applications, including high-performance transformers, electric motors, and **magnetically levitated high-speed trains**.
- They are already commercially employed in superconducting quantum interference devices (SQUIDs), which are the most sensitive magnetometers on the market.
- The **mechanism of superconduction** is well-understood for *low-temperature materials*. The principal *model of superconductivity* is the **BCS theory**, which was proposed by Bardeen, Cooper, and Schrieffer in 1957, for which they won the 1972 Nobel Prize.
- According to the BCS theory, the conducting electrons in a superconducting solid **cause a transitory deformation** in the lattice, which **creates a region of positive charge density**.
- Thus, if one electron is in a particular region of a solid, the nuclei there move towards it to give a distorted local structure (Fig. 15E.9).

- Because that ***local distortion is rich in positive charge***, it is *favorable* for a second electron to join the first. Hence, a second electron having ***opposite spin*** is then attracted to the positive charge and they move together as a pair (known as a ***Cooper pair***) as there is a virtual attraction or a certain binding energy between the two electrons.
- A ***Cooper pair*** is a pair of electrons that exists on account of the ***indirect*** electron–electron interactions mediated by the nuclei of the atoms in the lattice.
- The ***local distortion is disrupted*** by thermal motion of the ions in the solid, so ***the virtual attraction occurs only at very low temperatures***.

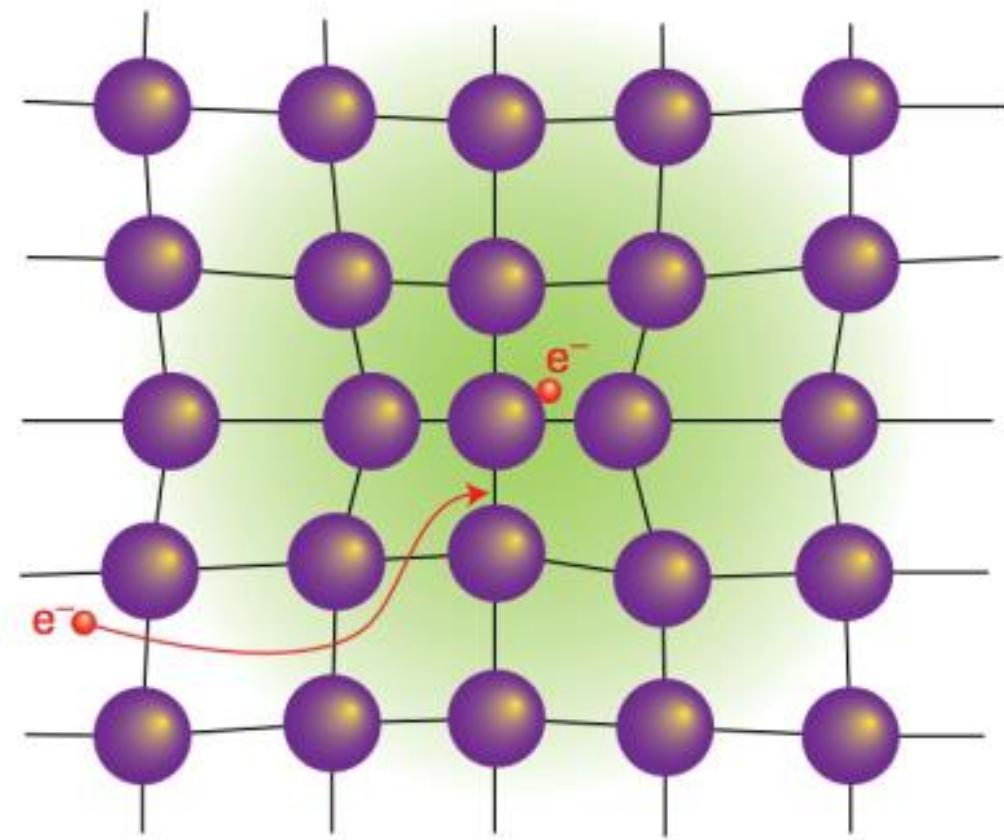


Figure 15E.9 The formation of a ***Cooper pair***. One electron distorts the crystal lattice and the second electron has a lower energy if it goes to that region. These electron–lattice interactions effectively bind the two electrons into a pair.

In one analogy, the Cooper pair moves through the lattice similar to *fans in a stadium doing the wave*.

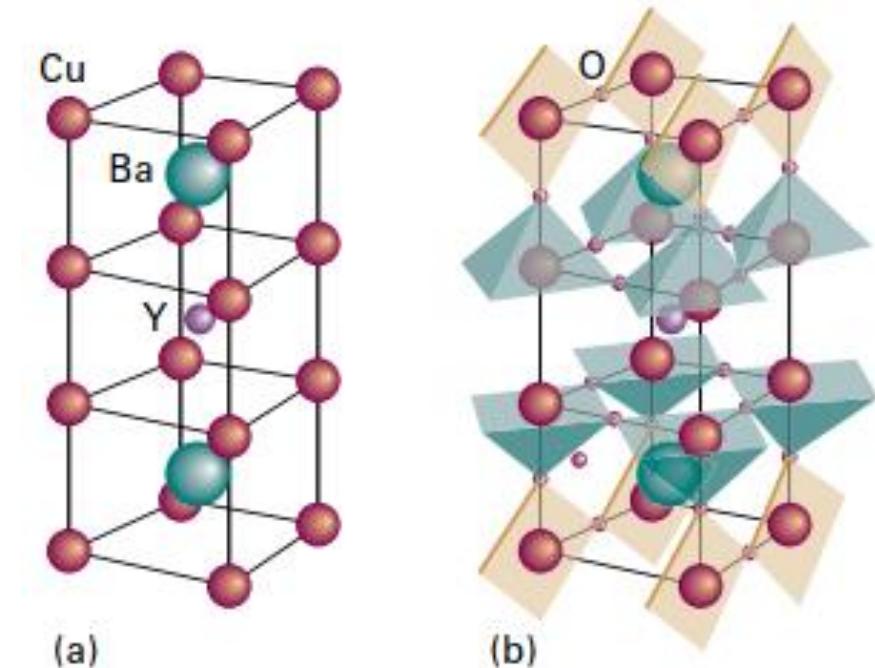
- The local distortion is disrupted by thermal motion of the ions in the solid, so the virtual attraction occurs only at very low temperatures.
- As long as the binding energy of the Cooper pair is greater than the energy of the lattice vibrations that tend to disrupt the pair, the two electrons will travel together throughout the lattice having zero resistance.
- This will be true at lower temperatures, where the disrupting forces from the oscillating atoms in the lattice have insufficient energy to overcome the binding energy of the Cooper pair.
- A Cooper pair undergoes less scattering than an individual electron as it travels through the solid because the distortion caused by one electron can attract back the other electron should it be scattered out of its path in a collision.
- Because the Cooper pair is stable against scattering, it can carry charge freely through the solid, and hence give rise to superconductivity.

- The Cooper pairs responsible for low-temperature superconductivity are likely to be important in HTSCs, but *the mechanism for pairing is hotly debated*.
- The superconducting properties of the high-temperature copper oxides, such as $\text{YBa}_2\text{Cu}_3\text{O}_7$, are *believed to result from systematic vacancies in the oxide layers of the tetragonal perovskite-type structure*.
- One of the most widely studied oxocuprate superconductors $\text{YBa}_2\text{Cu}_3\text{O}_7$ (informally known as ‘123’ on account of the proportions of the metal atoms in the compound) has the structure shown in Fig. 15E.8.
- The square-pyramidal CuO_5 units arranged as two-dimensional layers and the square planar CuO_4 units arranged in sheets are common structural features of oxocuprate HTSCs.
- There is evidence implicating the arrangement of CuO_5 layers and CuO_4 sheets in the mechanism.
- It is believed that *movement of electrons along the linked CuO_4 units accounts for superconductivity*, whereas the linked CuO_5 units act as ‘charge reservoirs’ that maintain an appropriate number of electrons in the superconducting layers.

Figure 15E.8 Structure of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor.

(a) Metal atom positions.

(b) The polyhedra show the positions of oxygen atoms and indicate that the Cu ions are either in square-planar or square-pyramidal coordination environments.



- Superconductors have unique **magnetic properties**.
- Some superconductors, classed as **Type I superconductors**, show ***abrupt loss of superconductivity when an applied magnetic field exceeds*** a critical value H_c characteristic of the material.
- Type I superconductors are also completely diamagnetic – the lines of force are completely excluded – below H_c . This exclusion of a magnetic field in a material is known as the **Meissner effect**, which can be demonstrated by the [levitation of a superconductor above a magnet](#).
- It is also the basis for a number of potential applications of superconductors that include magnetic levitation, as in '**maglev**' trains.
- **Type II superconductors**, which include the HTSCs, *show a gradual loss of superconductivity* and diamagnetism with increasing magnetic field.

Optical properties of solids

- The electrical properties of semiconductors can be put to good use in optical devices. As shown in Fig. 7 there is a frequency $\nu_{min} = E/h$ below which light absorption cannot occur. Above this frequency threshold, a wide range of frequencies can be absorbed by the material.

Brief illustration: The optical properties of a semiconductor

The energy of the band gap in the semiconductor cadmium sulfide (CdS) is 2.4 eV (equivalent to 0.38 aJ). It follows that the minimum electronic absorption frequency is

$$\nu_{min} = \frac{3.8 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 5.8 \times 10^{14} \text{ s}^{-1}$$

This frequency, of 580 THz, corresponds to a wavelength of 520 nm (green light). Lower frequencies, corresponding to **yellow, orange, and red, are not absorbed and consequently CdS appears yellow-orange.**

$$➤ E (\text{eV}) = 1239.8 / \lambda (\text{nm})$$

Self-test:

Show that the colors of the following materials, given their band-gap energies (in parentheses): GaAs (1.43 eV), HgS (2.1 eV), and ZnS (3.6 eV) are **black, red, and colorless**, respectively.

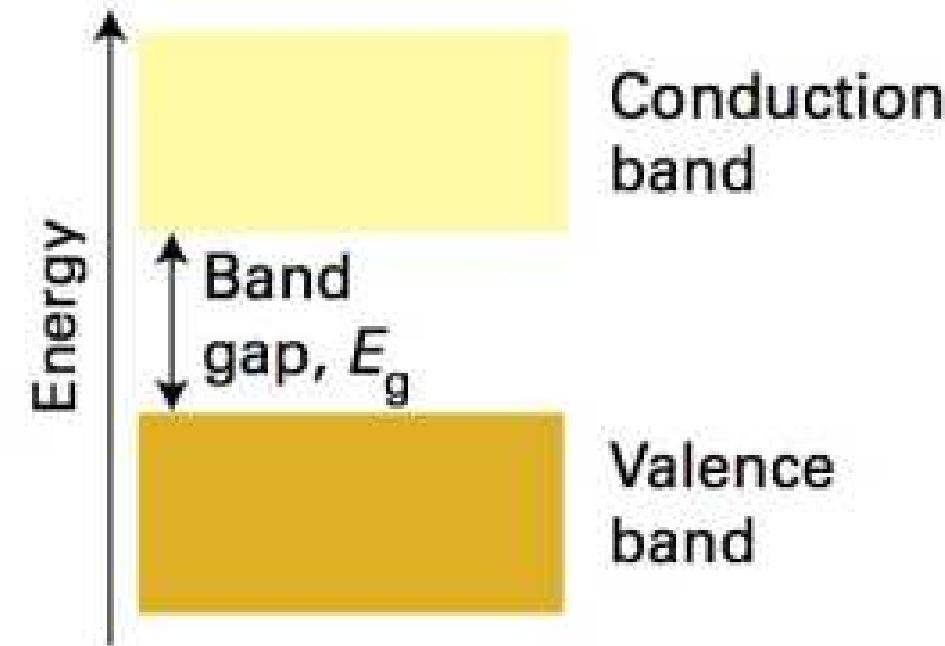


Fig . 7 In some materials. the band gap E_g is very large and electron promotion can occur only by excitation with electromagnetic radiation.

p-n Junction and Light-emitting diodes (LEDs)

- We know that major savings in energy would be realized if incandescent lights could be replaced by ***light-emitting diodes (LEDs)***.
- A *light-emitting diode (LED)* is a p–n junction semiconductor diode that emits light when current is passed.
- Let us take a closer look at the operation of an LED.
- The heart of an LED is a p–n diode, which is formed by bringing an n-type semiconductor into contact with a p-type semiconductor. A p–n junction can be constructed from two pieces of silicon, one of which is n-type and the other p-type.
- The Fermi levels in the differently doped materials are different but when they are placed in contact *electrons will flow from the n-type (high potential) to the p-type (low potential) region across the junction so as to reach an equilibrium distribution in which the Fermi levels are equal.*

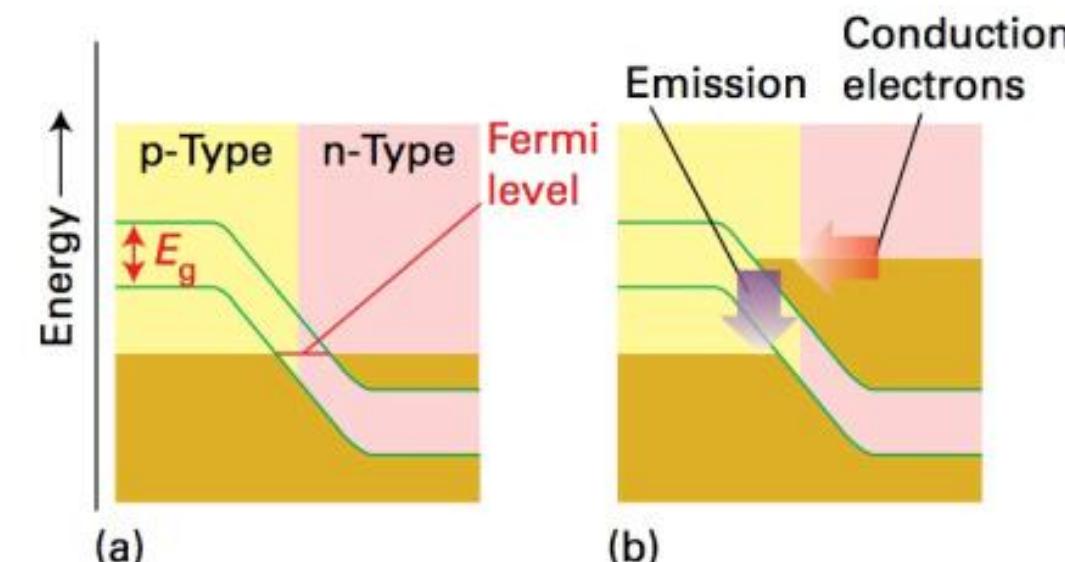


Figure. The band structure of a p–n junction (a) without bias, (b) with bias (that is, with a potential difference applied).

- The surplus of electrons in the n-type semiconductor is attracted to the surplus of holes in the p-type semiconductor. When the electrons and holes meet in the center, they annihilate each other in a process known as **recombination** and a nonconductive **depletion zone** (or barrier) is formed.
- In the absence of an applied potential, there is no net flow of charge carriers in the p–n junction.
- When the p–n junction is connected to an external power source, such as a battery, with the positive electrode attached to the p-type semiconductor and the negative electrode attached to the n-type semiconductor, the material operates under a *forward bias* (Figure 11.53(a)).
- The holes in the p-type semiconductor are repelled away from the positive terminal and toward the depletion zone, while the electrons in the n-type semiconductor are repelled away from the negative terminal toward the depletion zone. As a result of this bias, the **barrier at the p–n junction gets thinner** and, ultimately, **electrons are able to tunnel across the barrier** so that current flows through the material from right to left in the diagram.

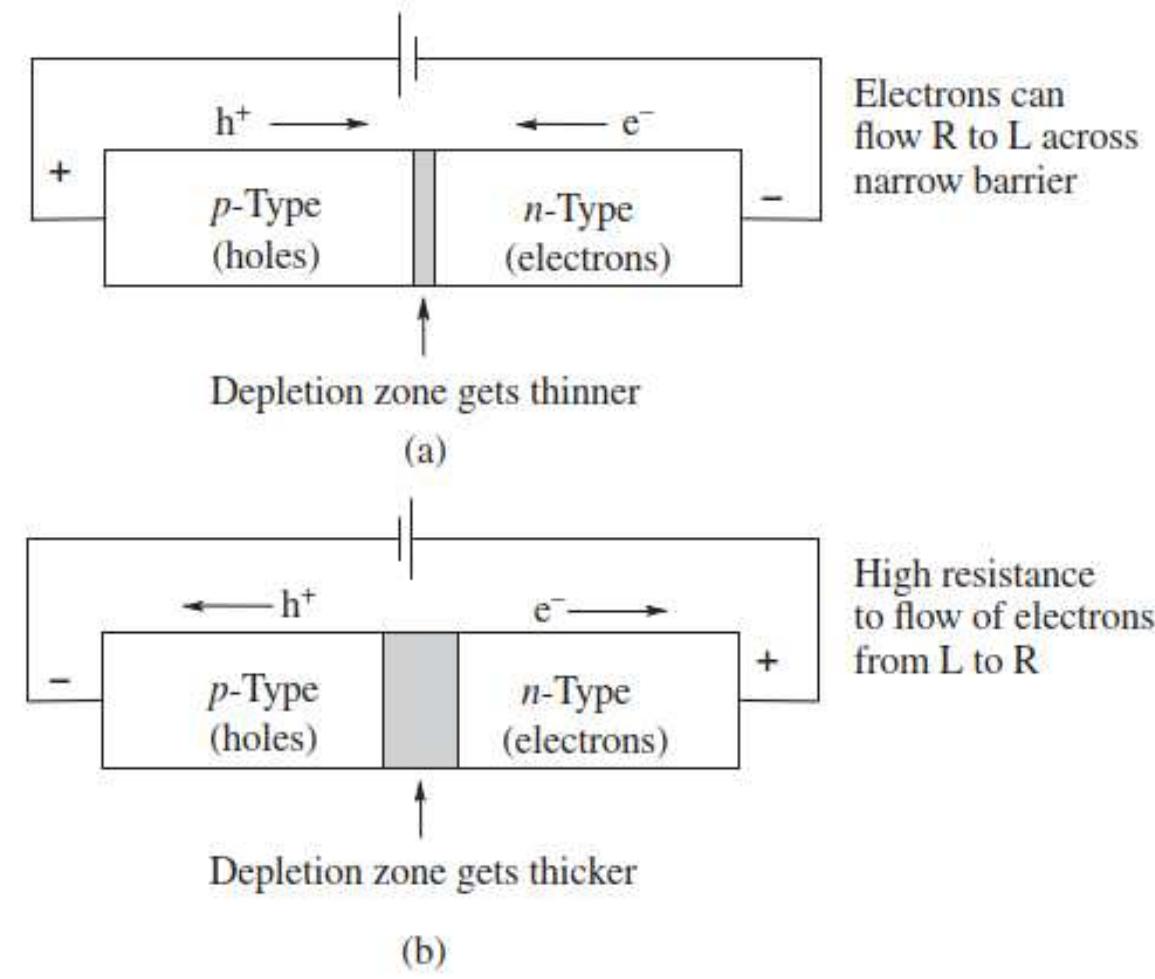


FIGURE 11.53 A p–n junction under:

(a) forward bias allows the flow of electrons from right to left and

(b) reverse bias prevents the flow of electrons from left to right.

- On the other hand, if the p-type semiconductor is connected to the negative terminal of a power source and the n-type semiconductor connected to the positive terminal, the material acts under a *reverse bias*, as shown in Figure 11.53(b). The holes in the p-type semiconductor are attracted to the negative terminal and the electrons in the n-type semiconductor are attracted to the positive terminal. The net result is that the ***depletion zone at the p–n junction gets larger*** and there is a *high resistance to electron flow across the circuit*. Thus, the p–n junction acts as a **diode**, an electrical switch that allows current to flow in only one direction (from right to left in Figure 11.53) and not in the opposite direction.
- Diodes lie at the heart of all sorts of electronic devices, from photovoltaic cells (where light energy is used to produce the charge carriers) to transistors (which consist of two p–n junctions in series, such as the common n–p–n bipolar junction transistor, or BJT).
- The unique electrical properties of p–n junctions between semiconductors can be put to good use in ***optical devices, light-emitting diodes (LEDs)***.
- ✓ In some materials, the ***energy from electron–hole recombination is released not as heat but is carried away by photons*** as electrons move across the junction driven ***by the appropriate potential difference***.
- ✓ Practical ***light-emitting diodes*** of this kind are widely used in electronic displays.

- When an appropriate voltage is applied, electrons are driven from the conduction band of the n-doped side into the junction, where they meet holes that have been driven from the valence band of the p-doped side. *The electrons fall into the empty holes, and their energy is converted into light whose photons have energy equal to the band gap* (Figure 12.32).
- As the electrons fall from the upper band into the lower, they release energy. This way electrical energy is converted into thermal or optical energy.

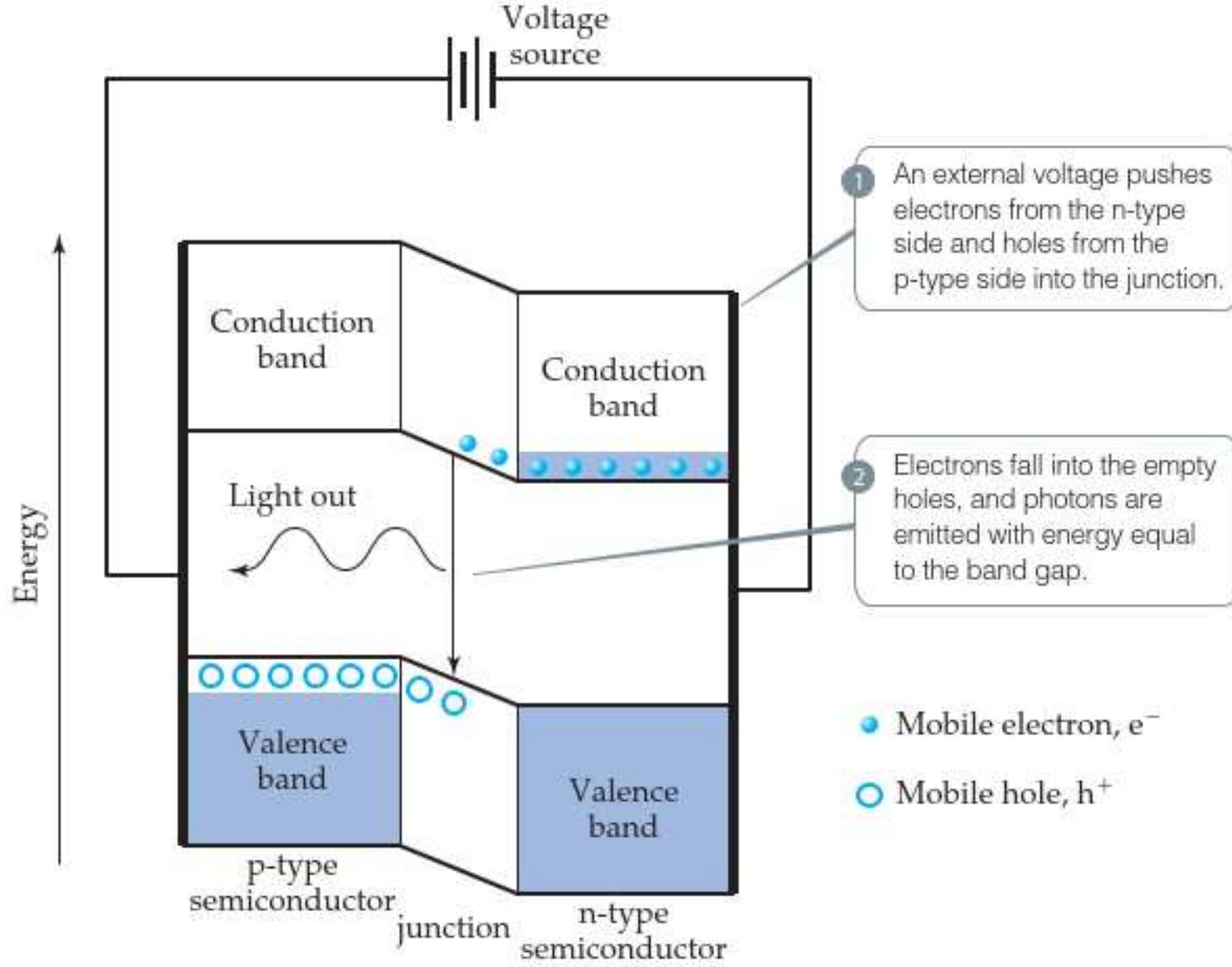


Figure 12.32 Light-emitting diodes. An applied voltage drives electrons and holes together at the light-emitting diode is a p–n junction where they combine and give off light.

- In some solids the wavelengths of the wavefunctions in the upper and lower states are different, which means that *the linear momenta* (through the de Broglie relation, $p = h/\lambda$) of *the electron in the initial and final states are different*. As a result, **the transition can occur only if the electron transfers linear momentum to the lattice**: the *device becomes warm* as the atoms are stimulated to vibrate.
- ✓ This is the case for silicon semiconductors and is one reason why computers need efficient cooling systems.
- In some materials, most notably gallium arsenide, GaAs, *the wavefunctions of the initial and final states of the electron have the same wavelengths and therefore correspond to the same linear momentum*. As a result, transitions can occur without the lattice needing to participate by mopping up the difference in linear momenta. **The energy difference is therefore emitted as light**.
- Practical light-emitting diodes of this kind are widely used in electronic displays.

- Because the wavelength of light that is emitted depends on the band gap of the semiconductor, the color of light produced by the LED can be controlled by appropriate choice of semiconductor.
- Most red LEDs are made of a mixture of GaP and GaAs. The band gap of GaP is 2.26 eV ($3.62 * 10^{-19} \text{ J}$), which corresponds to a *green photon* with a wavelength of 549 nm, while GaAs has a band gap of 1.43 eV ($2.29 * 10^{-19} \text{ J}$), which corresponds to an *infrared photon* with a wavelength of 867 nm.
- Gallium arsenide itself emits infrared light, but the width of the **band gap is increased by incorporating phosphorus**. By forming solid solutions of these two compounds, with stoichiometries of $\text{GaP}_{1-x}\text{As}_x$, the band gap can be adjusted to any intermediate value. Thus, **$\text{GaP}_{1-x}\text{As}_x$ is the solid solution of choice for red, orange, and yellow LEDs**. Green LEDs are made from mixtures of GaP and AlP ($E_g = 2.43 \text{ eV}$, $\lambda = 510 \text{ nm}$).
- For example, a material of composition approximately $\text{GaAs}_{0.6}\text{P}_{0.4}$ emits red light, and diodes emitting orange and amber light can also be made with different proportions of Ga, As, and P.
- The spectral region ranging from yellow to blue can be covered by using gallium phosphide (yellow or green light) and gallium nitride (green or blue light).
- White LEDs are commonly formed from yellow and blue LEDs mixed in various proportions.

- Red LEDs have been in the market for decades, but to make white light, an efficient blue LED was needed.
- The first prototype bright blue LED was demonstrated in a Japanese laboratory in 1993. In 2010, less than 20 years later, over \$10 billion worth of blue LEDs were sold worldwide.
- The blue LEDs are based on combinations of GaN ($E_g = 3.4$ eV, $\lambda = 365$ nm) and InN ($E_g = 2.4$ eV, $\lambda = 517$ nm).
- Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights.
- Because the light emission results from semiconductor structures that can be made extremely small and because they emit little heat, LEDs are replacing standard incandescent and fluorescence light bulbs in many applications.

- LEDs are ***highly monochromatic***, emitting a pure color in a narrow frequency range.
- ***The color is controlled by the band gap***, with small band gaps producing radiation in the infrared and red regions of the electromagnetic spectrum and larger band gaps resulting in emission in the blue and ultraviolet regions (see table).
- It is possible to produce white light with a single LED by using a phosphor layer (yttrium aluminium garnet, YAG) on the surface of a blue, gallium nitride, LED. These white light LEDs are highly efficient at converting electricity into light, much more so than incandescent lamps and even 'low-energy' fluorescent lights.

LED colours

LED colour	Chip material	
	Low brightness	High brightness
Red	GaAsP/GaP	AllnGaP
Orange	GaAsP/GaP	AllnGaP
Amber	GaAsP/GaP	AllnGaP
Yellow	GaP	—
Green	GaP	GaN
Turquoise	—	GaN
Blue	—	GaN

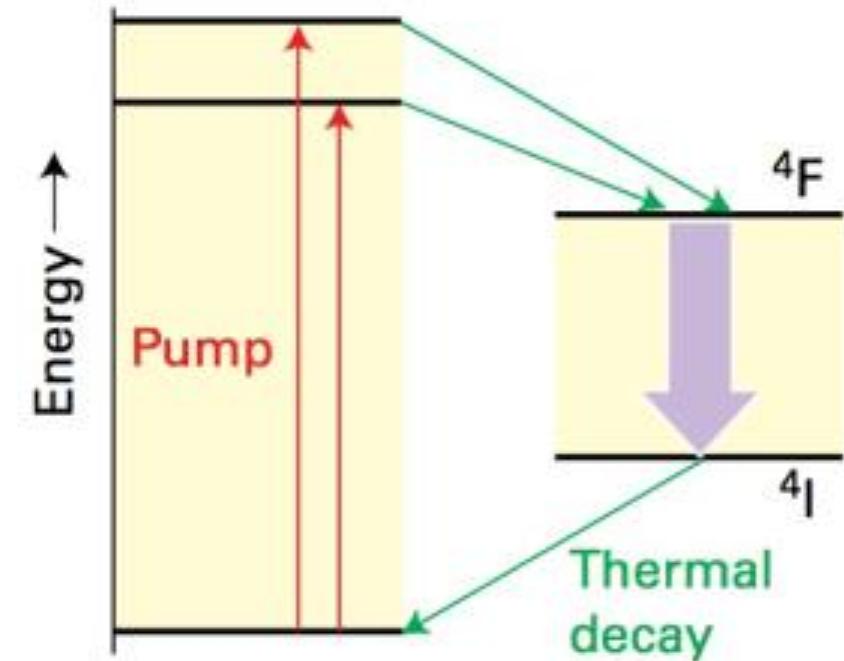
Diode lasers

- Another advantage of being able to produce blue LEDs is that they can be used as lasers in high-capacity optoelectronic storage devices.
- In **diode lasers** are used in **CD players** and **bar-code readers**.
- A *light-emitting diode is not a laser because stimulated emission is not involved*.
- In diode lasers, light emission due to electron–hole recombination is employed as the basis of laser action, and ***the population inversion can be sustained by sweeping away the electrons that fall into the holes of the p-type semiconductor***. This process is arranged to occur in a cavity formed by making use of the abrupt difference in refractive index between the different components of the junction, and the radiation trapped in the cavity enhances the production of more radiation.
- One widely used material is GaAs doped with aluminium ($\text{Ga}_{1-x}\text{Al}_x\text{As}$), which produces 780 nm red laser radiation and is widely used in CD players.
- The newer generation of DVD players that use blue rather than red laser radiation, so allowing a greater density of information on the surface of the disc, use GaN as the active material.

High-power diode lasers are also used to pump other lasers. One example is the pumping of Nd:YAG lasers by $\text{Ga}_{0.91}\text{Al}_{0.09}\text{As}/\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ diode lasers.

Fig. 10 The transitions involved in a neodymium laser.

The neodymium laser is an example of a four-level solid-state laser. In one form it consists of Nd^{3+} ions at low concentration in yttrium aluminium garnet (YAG, specifically $\text{Y}_3\text{Al}_5\text{O}_{12}$) and is then known as a Nd:YAG laser. A neodymium laser operates at a number of wavelengths in the infrared. The most common wavelength of operation is 1064 nm, which corresponds to the electronic transition from the ^4F to the ^4I state of the Nd^{3+} ion.



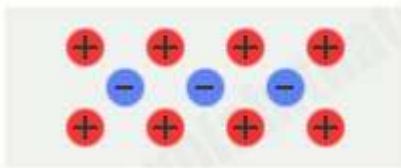
Other Electrical and Optical Properties of Crystals

❖ Electrical Properties of Crystals

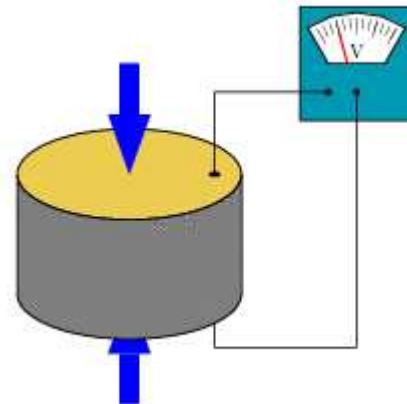
- The symmetry elements of a molecule tell us much about its properties, and the symmetry elements of a unit cell tell us much about the properties of the crystal.
- For example, the unit cell of a crystal has no dipole moment if it meets either or both of these criteria:
 - 1. All the bond dipoles lie perpendicular to either a C_n proper rotation axis or to a σ mirror plane.
 - 2. The molecule has a S_{2n} symmetry element (including inversion, because $I = S_2$).
- As a result, only certain crystallographic point groups yield polar unit cells.
- **If the unit cell is polar, the charge density at one end of the unit cell is greater than at the other end, and this pattern is repeated throughout the crystal.**
- *Polar crystals, whatever the bonding mechanism, may exhibit some useful electrical characteristics that arise from the high degree of order not found in amorphous solids.*
- A **ferroelectric crystal** has a **net charge separation from one end to the other** due to a large number of co-aligned dipole moments. Such a crystal, if left to move freely, will align itself under the influence of an electric field.

- The aligned dipole moments in the ferroelectric crystal correspond to a net charge separation throughout the crystal and therefore correspond to an electrostatic potential energy—what we call voltage—from one end of the crystal to the other.
- This voltage is sensitive to the *spacing between the molecular dipoles*, so when the crystal is compressed, the voltage changes.
- Looking at it from the other perspective, applying a voltage to such a crystal can compress it or expand it.
- Crystals that deform under the influence of applied voltages are called **piezoelectric crystals**.
- Piezoelectricity is possible in crystals belonging to any of the crystallographic point groups except O (orthogonal group) and those with *centers of inversion* (called centrosymmetric crystals).
- Of the 20 remaining crystallographic point groups, some are polar and will compress or expand along one axis when a voltage is applied. Some others are not normally polar (and therefore not ferroelectric) but may become polar when twisted.
- The piezoelectric crystal is a common component in **applications that require very fast and precise distance adjustments**. The crystal dimensions are usually changed by a factor of only 10^{-6} or less using the piezoelectric effect, but for small distance measurements, such as those in atomic force microscopy, this is ideal.

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- A related effect is **pyroelectricity**, which is the **generation of voltage** by the **heating or cooling of a crystal**.
- Because substances tend to expand when heated and contract when cooled, *changes in temperature of polar crystals tend to change the overall dipole moment and voltage of the crystal.*
- Many polar crystals also have valuable **optical properties** resulting from the interaction of the electrons with the electric field of the radiation. For example, **the frequency of a beam of electromagnetic radiation may be doubled** by sending the beam through a non-centrosymmetric crystal.
- The incident radiation carries an oscillating electric field through the crystal, a field that deforms the electronic wavefunction, and therefore the electric field, of the crystal. The extent to which the electric field of the crystal is changed increases with the polarizability of the electrons and with the intensity of the radiation.
- In any of the non-centrosymmetric crystals, the electron distribution is more easily pushed in one direction than in the opposite direction by the radiation's electric field. This is equivalent to multiplying a fraction of the incident radiation by a damping factor that varies at the frequency of the radiation's electric field.

Other Electrical and Optical Properties of Crystals

❖ Nonlinear optical phenomena

- *Nonlinear optical phenomena arise* from changes in the optical properties of a material *in the presence of intense electromagnetic radiation.*
- In frequency doubling (or '*second harmonic generation*'), an intense laser beam is converted to radiation with twice (and in general a multiple) of its initial frequency as it passes through a suitable material.
- It follows that frequency doubling and tripling of an Nd:YAG laser, which emits radiation at 1064 nm, produce green light at 532 nm and ultraviolet radiation at 355 nm, respectively.
- Common materials that can be used for frequency doubling in laser systems include crystals of potassium dihydrogenphosphate (KH_2PO_4), lithium niobate (LiNbO_3), and β -barium borate ($\beta\text{-BaB}_2\text{O}_4$).

❖ Nonlinear optical phenomena

- Frequency doubling can be explained by examining how a substance responds nonlinearly to incident radiation of frequency $\omega = 2\pi\nu$.
- Radiation of a particular frequency arises from oscillations of an electric dipole at that frequency and the *incident electric field E of the radiation induces an electric dipole moment of magnitude μ* , in the substance.
- At low light intensity, most materials respond linearly, in the sense that $\mu = \alpha E$, where **α is the polarizability**.
- At high light intensity, the **hyperpolarizability β** of the material becomes important and the induced dipole becomes $\mu = \alpha E + \frac{1}{2}\beta E^2 + \dots$.
- The *nonlinear term βE^2* can be expanded as follows if it is supposed that *the incident electric field is $E_0 \cos \omega t$* :

$$\beta E^2 = \beta(E_0 \cos \omega t)^2 = \beta E_0^2 \cos^2 \omega t = \frac{1}{2} \beta E_0^2 (1 + \cos 2\omega t). \text{ (using: } \cos^2 \theta = \frac{1}{2} (1 + \cos 2\theta) \text{)}$$

- Hence, *the nonlinear term contributes an induced electric dipole that includes a component that oscillates at the frequency 2ω and that can act as a source of radiation of that frequency*.