# 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 $H_2$ 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.

➢ Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. ***It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed***. In contrast, molecular orbital theory predicts wavefunctions that cover the entire molecule.

➢ The simplest case to consider is the hydrogen molecule, $H_2$. When we say that the two hydrogen nuclei share their electrons to form a covalent bond, what we mean in VB theory terms is that the two spherical 1s orbitals (each with the electron configuration H: $(1s)^1$; the grey spheres in Figure 5.2.1) overlap and contain two spin-paired electrons.

Figure 5.2.1: These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.
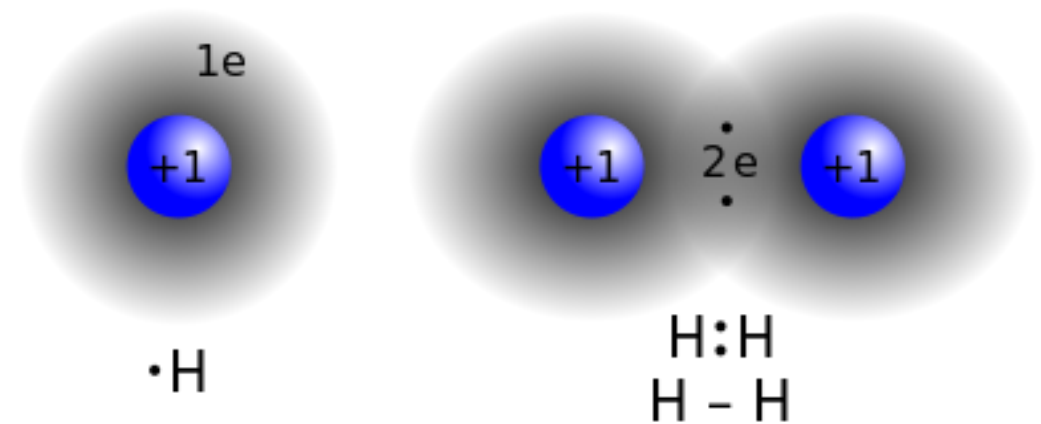
➤ How far apart are the two nuclei? If they are too far apart, their respective 1s orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, attractive positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second (Figure 9.1). However, something else is happening at the same time: as the atoms get closer, the repulsive positive-positive interaction between the two nuclei also begins to increase.

➤ At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have an unstable, high-energy situation. ***There is a defined optimal distance between the nuclei in which the potential energy is at a minimum***, meaning that the ***combined attractive and repulsive forces add up to the greatest overall attractive force***. This optimal internuclear distance is the **bond length**; the distance is 74 pm for $H_2$. Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the ***bond dissociation energy***, or, more simply, ***bond strength***; the $H_2$ bond strength is 435 kJ/mol.
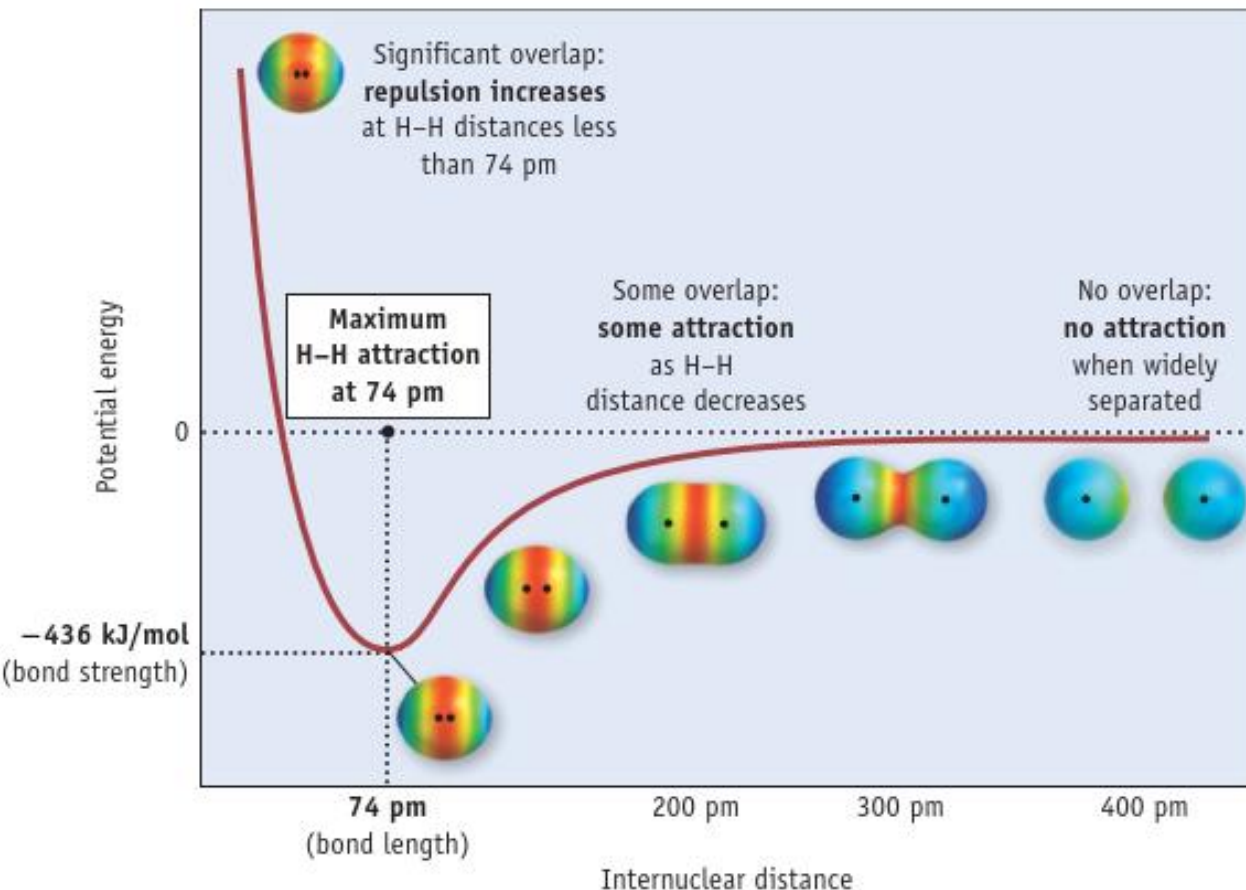
**FIGURE 9.1 Potential energy change during H–H bond formation from isolated hydrogen atoms.**
The red color in the orbital pictures reflects the increase in electron density between the H atoms as the distance decreases.

➤ 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.

# Overlap

➢ Valence bond theory describes a covalent bond as the ***overlap of half-filled atomic orbitals*** (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms.

➢ We say that ***orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space***.

➢ According to valence bond theory, a covalent bond results when two conditions are met:

▪ an orbital on one atom overlaps an orbital on a second atom and

▪ the single electrons in each orbital combine to form an electron pair.

➢ The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond.

➢ The ***strength of a covalent bond depends on the extent of overlap of the orbitals involved.***

➢ ***Orbitals that overlap extensively form bonds that are stronger*** than those that have less overlap.

➢ In addition to the ***distance between two orbitals***, the ***orientation of orbitals*** also affects their overlap (other than for two s orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 5.2.3 illustrates this for two p orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

Figure 5.2.3: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

(a)

(b)
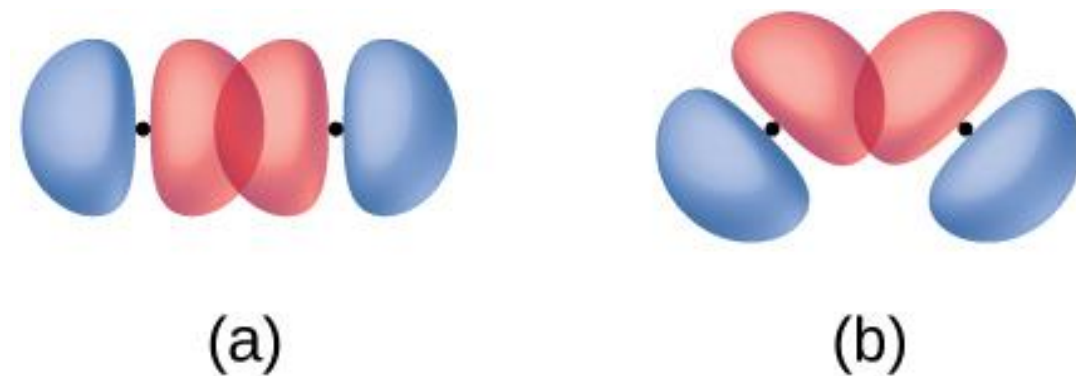
➢ The overlap of two s orbitals (as in H2), the overlap of an s orbital and a p orbital (as in HCl), and the end-to-end overlap of two p orbitals (as in Cl2) all produce sigma bonds (σ bonds), as illustrated in Figure 5.2.4. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

Three diagrams are shown and labeled "a," "b," and "c." Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

**Figure 5.2.4: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.**

➢ A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two p orbitals, as illustrated in Figure 5.2.5. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.
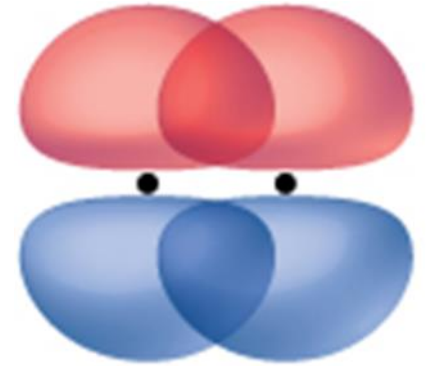


Figure 5.2.5: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

➢ While *all single bonds are σ bonds*, multiple bonds consist of both σ and π bonds.

➢ **Two-Atom Bonds**: ***The central gist of VB theory*** is that a covalent bond is formed between the **two** atoms by the ***overlap*** of half-filled valence **atomic orbitals** of each atom containing one unpaired electron.

# ❑ The Valence Bond Wavefunction

## ❖ Single Bonds

➤ In the hydrogen molecule, VB theory uses two electrons (electron 1 and electron 2) in two 1s atomic orbitals ($\psi_A$ and $\psi_B$) on the hydrogen atoms (atom A and atom B). The simplest description of a $H_2$ molecule with two electrons and two nuclei is:

➤ $\Psi = \psi_A(1)\psi_B(2)$

**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 $r_{12}$.
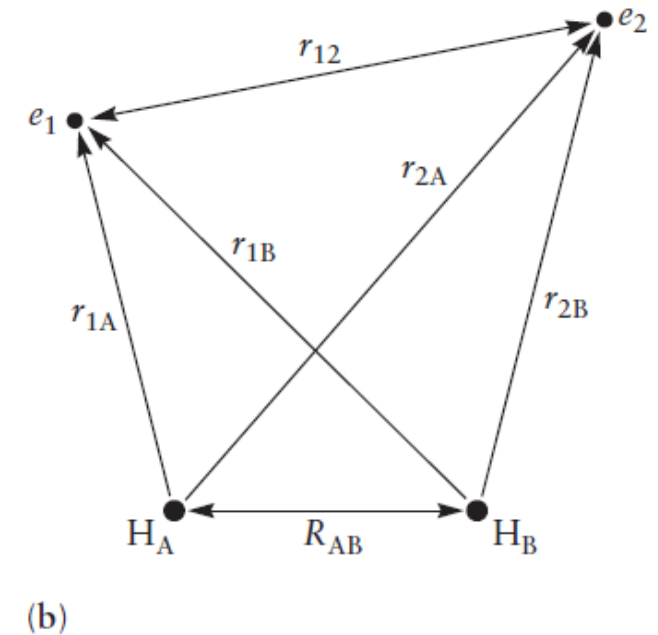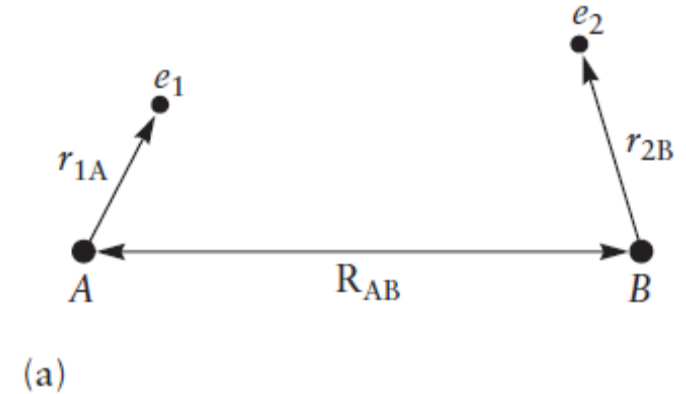
➢ The protons are separated by the distance $R_{AB}$. **At very large separations**, each electron is bound to its own proton, and is located by coordinate $r_{1A}$ or $r_{2B}$. At very large distances, the atoms are independent of each other, and the wave function describing the pair of them is:

➢ $\psi_A(1)\psi_B(2)$

➢ 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

$$\psi_{\text{simple}} = \psi^{el}(r_{1A}, r_{2B}; R_{AB}) = c(\boldsymbol{R_{AB}})\psi_A(1)\psi_B(2) \qquad \text{........Eq. (5.2.1)}$$

in which the **coefficient $c(R_{AB})$ compensates** for the fact that the *product form is strictly valid only at very large values of $R_{AB}$*.

➢ Equation 5.2.1 means electron 1 is in $\psi_A$ of atom A and electron 2 is in $\psi_B$ on the atom B. Where $\psi_A$ and $\psi_B$ may be the 1s orbitals as the simplest wavefunction ($n=1, l=0, m_l$).

➢ Taking $\psi_{simple}$ as the **total wavefunction** as shown in Equation (5.2.1), one predicts an **energy** only 25 kJ/mol *that is about 6% of the experimental value at a bond length of 0.90 pm, which is considerably longer than the experimental value of 0.74 pm (Table 5.2.1).*

➢ It shows that *amendments to the VB wavefunction is essential* for the hydrogen molecule. 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. Equation 5.2.1 does not address the indistinguishability of the problem, i.e, we cannot distinguish each electron from the other.

➢ **To account for the indistinguishable nature of the two electrons** in the system, **a covalent wavefunction** that is better than Equation 5.2.1 can be constructed (ignoring spin effect):

➢ $\Psi_{covalent} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$ .......Eq. (5.2.2)

➢ Equation 5.2.2 means electron 1 is sometimes in $\psi_A$ on atom A and electron 2 is on the atom B (left term of right-hand side of Equation) and sometime electron 1 is sometimes in $\psi_B$ on atom B and electron 2 is in $\psi_A$ on the atom a (right term of right-hand side of Equation).

➢ Notice that in contrast to Equation 5.2.1, if the two electron labels are switched, the wavefunction in Equation 5.2.2 does not change.

➢ The potential energy curve for the $\psi_{covalent}$ wavefunction predicts a bond energy that is about 72% at a bond length of 0.87 pm (Table 5.2.2), so the **$\psi_{covalent}$ wavefunction is more accurate than $\psi_{simple}$.**

➢ *To be more accurate* within VB theory, *the possibility that both electrons may be on atom* **A** ($\psi_A(1)\psi_A(2)$) **or** *on atom* **B** ($\psi_B(1)\psi_B(2)$) *should also be taken into account*.

➢ This introduces an ionic contribution:

➢ $\psi_{ionic} = \psi_A(1)\psi_A(2) + \psi_B(2)\psi_B(1)$ .........Eq. (5.2.3)

➢ Notice that Equation 5.2.3 addresses indistinguishability since the wavefunction is unchanged if the two electron labels are switched.

➢ *The more complete VB wavefunction* is a linear combination of both $\psi_{covalent}$ and $\psi_{ionic}$:

➢ $\psi_{AB} = \Psi_{covalent} + \lambda\psi_{ionic}$ .....Eq. (5.2.4)

➢ where ***λ quantifies the amount of ionic character*** to the bond, e.g., if λ=0, then the bond is purely covalent.

➤ The potential energy curve for the $\psi_{AB}$ **wavefunction** predicts a bond energy that is ~80% of the experimental value and a reasonably accurate bond length of 0.77 pm (Table 5.2.1).

➤ Additional tinkering with the wavefunction leads to even better results but is beyond the scope of this discussion. It should be noted that the wavefunctions in Equations 5.2.2, 5.2.3, and 5.2.4 are unnormalized.

Table 5.2.2: Valence Bond Theory Results for $H_2$

| Wavefunction | Bond Energy (kJ mol$^{-1}$) | Bond Length (pm) |
|---|---|---|
| Experiment | 435 | 0.74 |
| $\psi_{simple}$ | 25 | 0.90 |
| $\psi_{covalent}$ | 301 | 0.87 |
| $\psi_{AB}$ | 335 | 0.77 |

➤ 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.



**FIGURE 10.1**
Artist's rendering of the theoretical potential energy curves (*a*)–(*c*) constructed using the data given by Equations (5.2.1, 5.2.2, & 5.2.4), along with the ***experimentally observed attractive potential (d)*** for the $H_2$ molecule. Curve (*e*) is the experimental repulsive term.
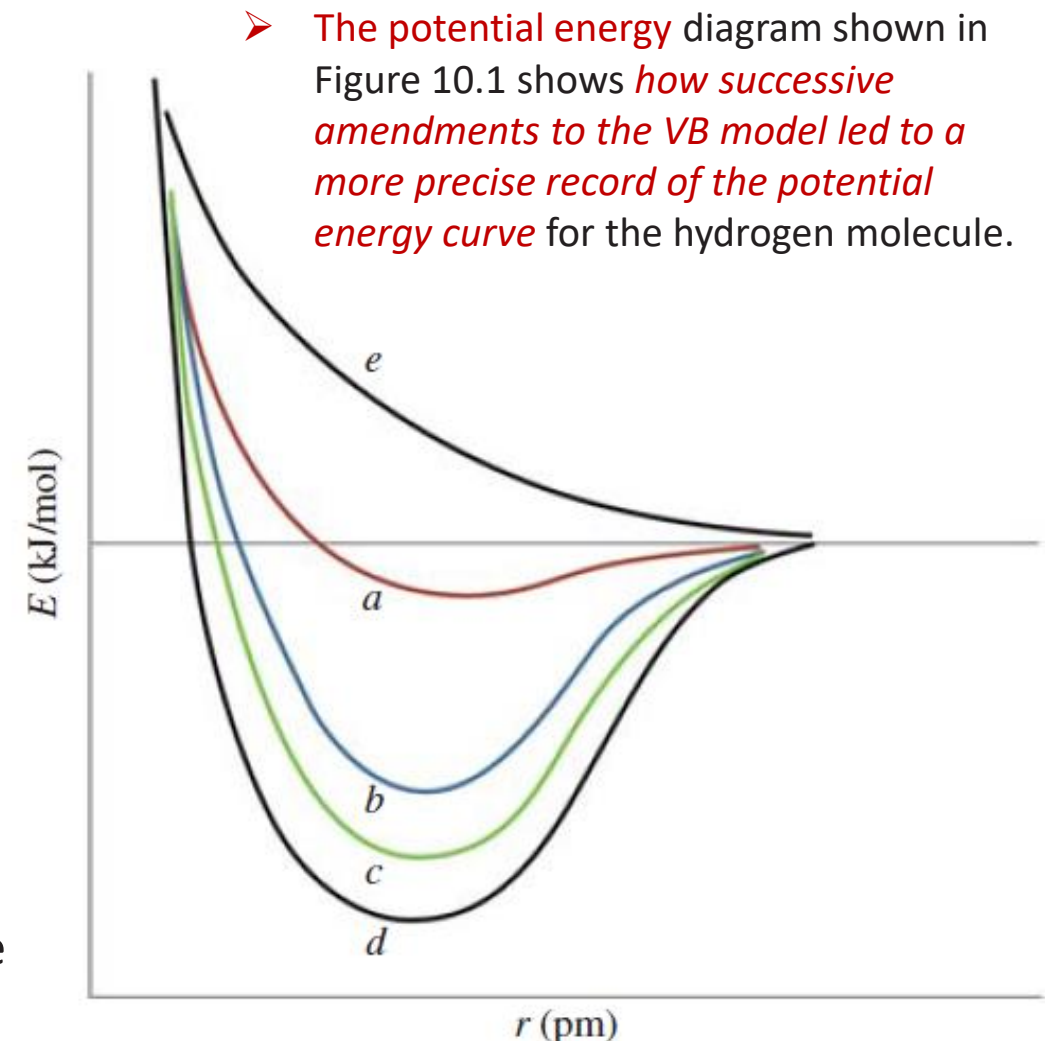
- Let us ***discuss little more in details about the wavefunction improvements***.

- The ***covalent wavefunction*** is ***a sum of two of the product forms*** just discussed above.

- The result can be written as:

$$\psi^{el}(r_{1A}, r_{2B}; R_{AB}) = c_{1(R_{AB})}\varphi^A(r_{1A})\varphi^B(r_{2B}) + c_2(R_{AB})\varphi^A(r_{2A})\varphi^B(r_{1B})$$

- 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.

$$\psi_g^{el} = c_{1(R_{AB})}[\varphi^A(r_{1A})\varphi^B(r_{2B}) + \varphi^A(r_{2A})\varphi^B(r_{1B})]$$

$$\psi_u^{el} = c_{1(R_{AB})}[\varphi^A(r_{1A})\varphi^B(r_{2B}) - \varphi^A(r_{2A})\varphi^B(r_{1B})]$$

$\psi_A(1)\psi_B(2)$

$\psi_A(2)\psi_B(1)$

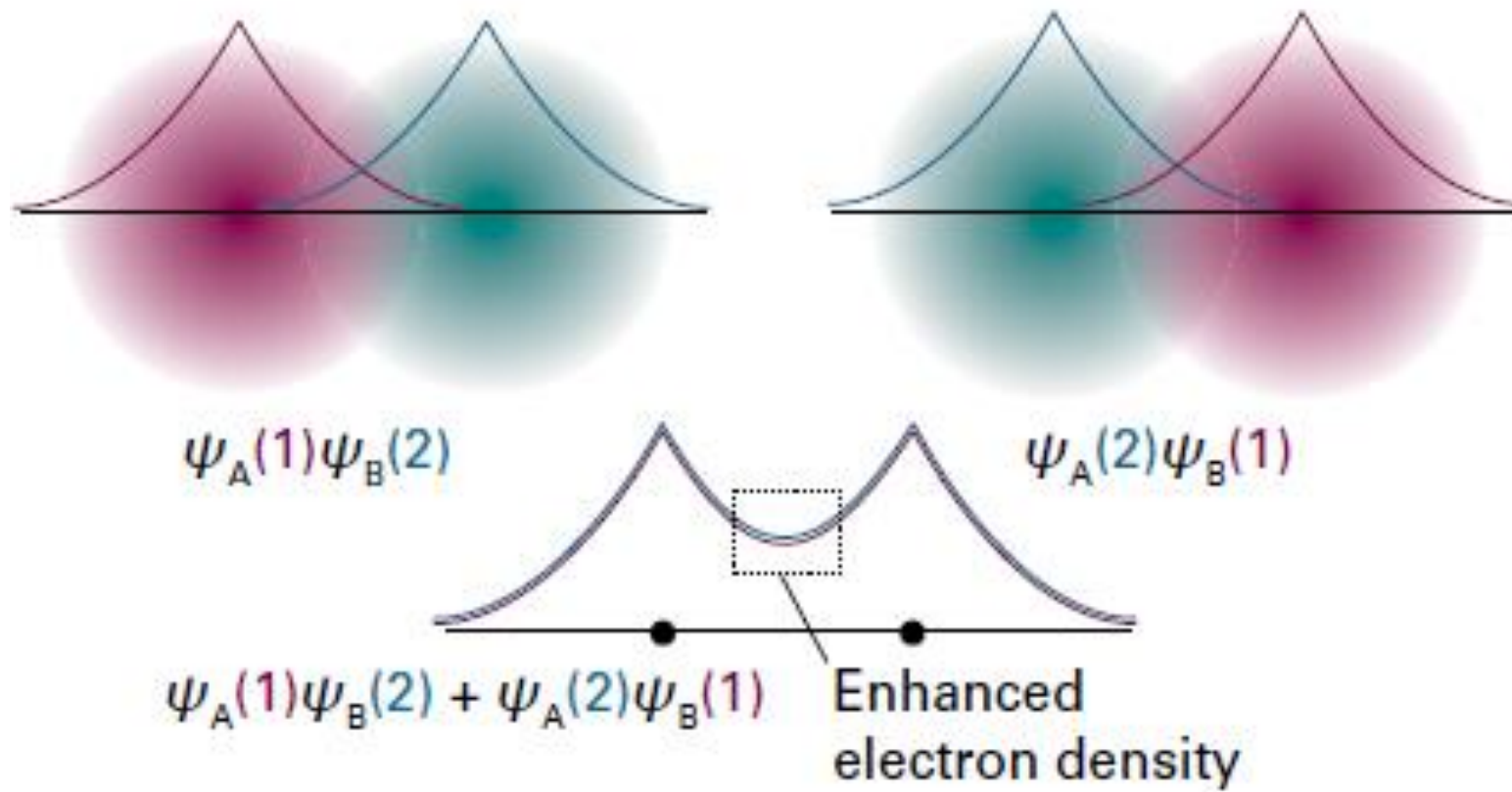$\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$ Enhanced electron density

**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 $\psi_g^{el}$ and $\psi_u^{el}$. 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 $\psi_g^{el}$ and $\psi_u^{el}$ are shown in Figure 6.26a.

- The wave function $\psi_g^{el}$ shows increased electron density between the nuclei, whereas $\psi_u^{el}$ 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.
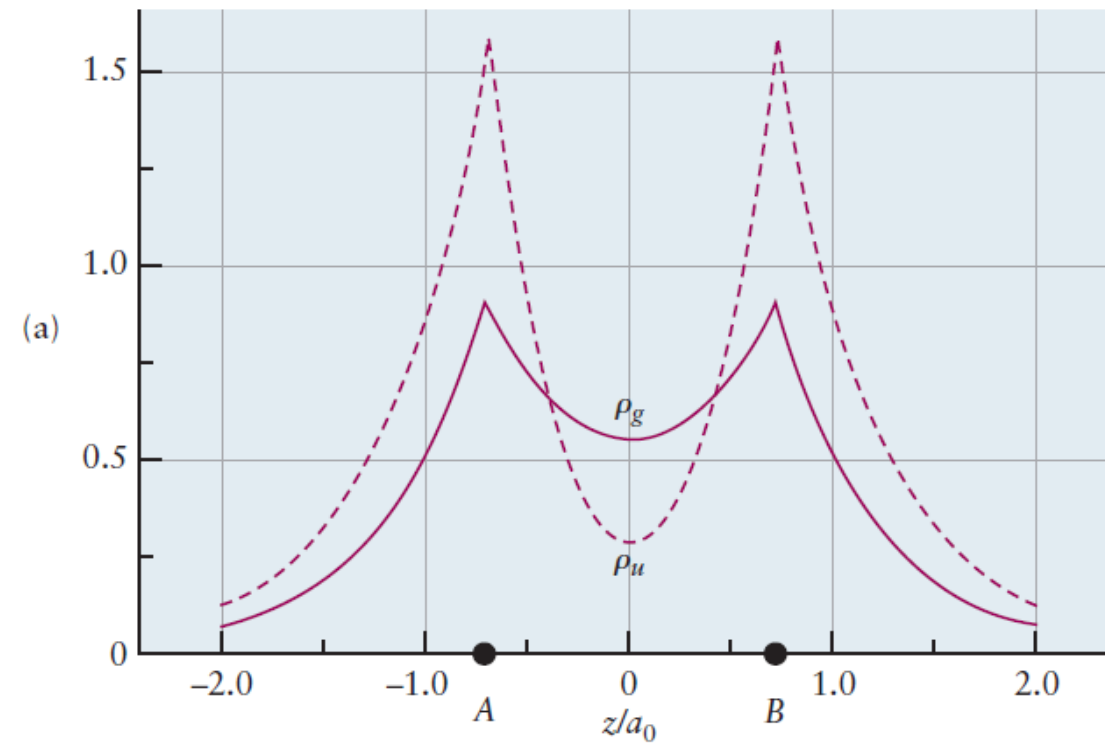- Figure 6.26b shows a three-dimensional isosurface of the electron density for $H_2$ calculated from $\psi_g^{el}$.

**FIGURE 6.26** The electron density for the $\psi_g^{el}$ and $\psi_u^{el}$ wave functions in the simple valence bond model for $H_2$.
(a) The electron density $\rho_g$ for $\psi_g^{el}$ and $\rho_u$ for $\psi_u^{el}$ calculated analytically as described in the text.
(b) Three-dimensional isosurface of the electron density for the $\psi_g^{el}$ 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 $H_2$ 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 $\psi_g^{el}$ and $\psi_u^{el}$.

➢ 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 $\psi_g^{el}$ describes a state with lower energy than that of the separated atoms, whereas $\psi_u^{el}$ 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 $\psi_u^{el}$), symmetric state ($E+$ for $\psi_g^{el}$) and the experimental curve ($E_{exp}$).
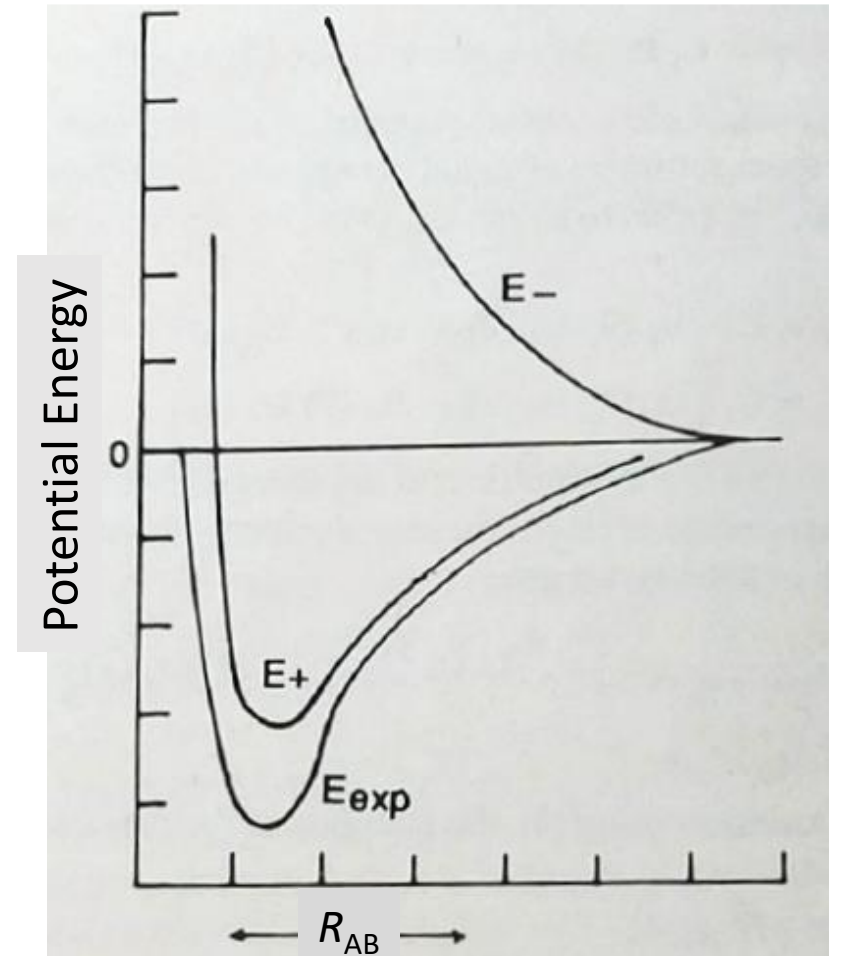


➤ *There is discrepancy* between the calculated ($E_+$) and experimental ($E_{exp}$) potential energy curves for the hydrogen molecule.

➤ The ***valence bond wave function can be further 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

➤ $\psi(H_2) = 1s^A(1)1s^A(2) + 1s^B(1)1s^B(2)$         (10.2)

➤ The complete molecular wave function then becomes

$$\psi_{VB}^{el} = c_1 1s^A(1)1s^B(2) + c_2 1s^A(2)1s^B(1) + c_3 1s^A(1)1s^A(2) + c_4 1s^B(1)1s^B(2)$$

➤ 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 $\lambda$ 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.

➤ $\psi(H_2) = \psi^A(1)\psi^B(2) + \psi^A(2)\psi^B(1) + \lambda\psi^A(1)\psi^A(2) + \lambda\psi^B(1)\psi^B(2)$      (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.]
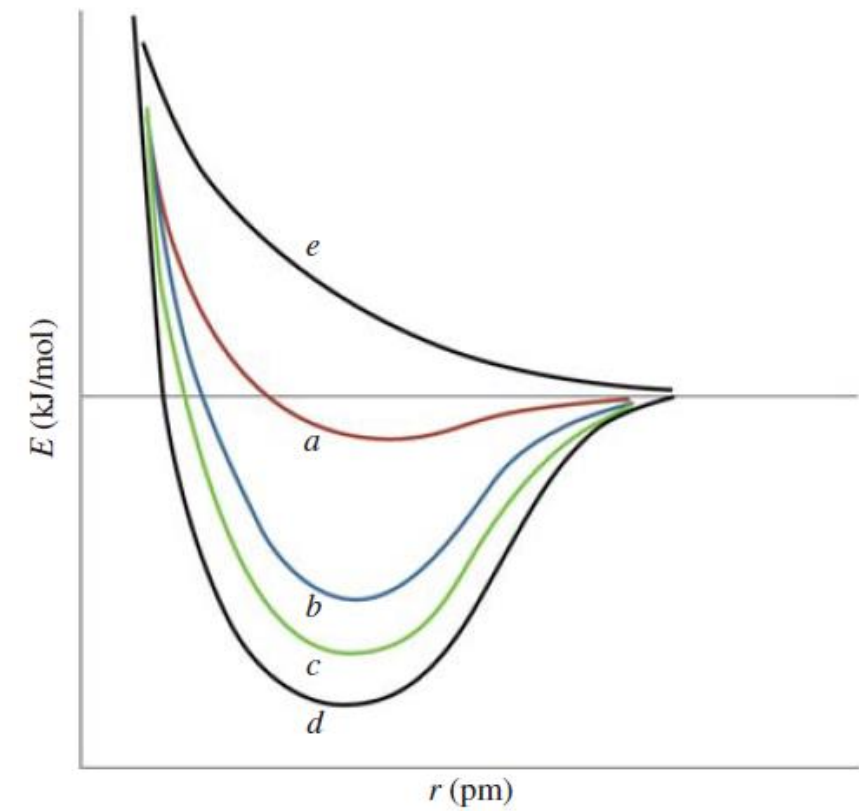
❑ Now let's consider the **formation of F$_2$**, represented by its Lewis diagram, from two F atoms each with electron configuration F: $(1s)^2(2s)^2(2p_x)^2(2p_y)^2(2p_z)^1$.

➢ 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

$$\psi_g^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

➢ 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).
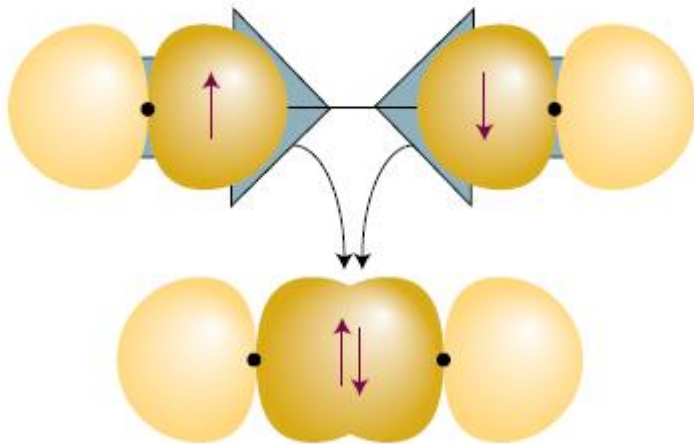
**Figure 9A.2** The orbital overlap and spin pairing between electrons in two collinear *p* orbitals that results in the formation of a σ bond.
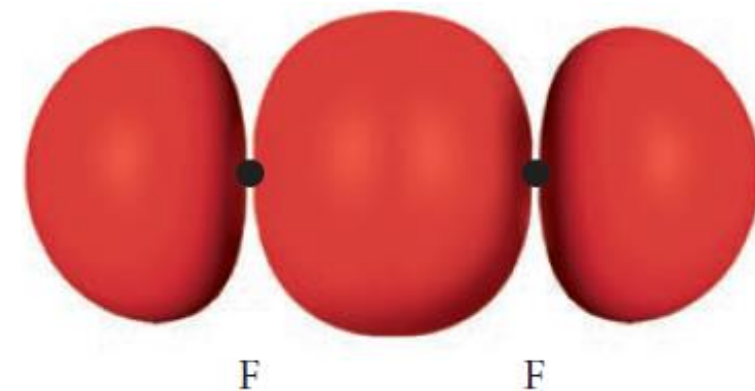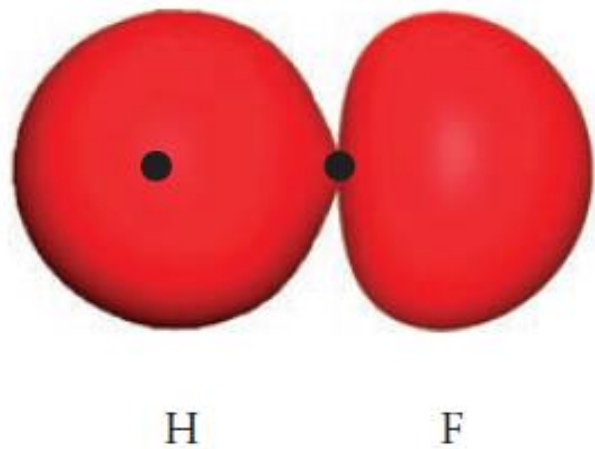


**FIGURE 6.27** Isosurface representation of the electron density in the $F_2$ σ bond formed from a pair of electrons initially localized in a $2p_z$ orbital on each F atom.
(Courtesy of Mr. Hatem Helal and Professor William A. Goddard III, California Institute of Technology, and Dr. Kelly P. Gaither, 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

$$\psi^{bond} = C_1[2p_z^F(1)1s^H(2)] + C_2[2p_z^F(2)1s^H(1)]$$

➢ However, $C_1$ and $C_2$ 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.)

H          F

- 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 <span style="color:red">not</span> be called <span style="color:red">MOs</span>, 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.

$$\Psi(1,2) = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1) \qquad \text{A valence-bond wavefunction} \qquad (9A.2)$$

❖ 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** $\sigma(2,1) = -\sigma(1,2)$.

➢ 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.

➤ If we attempt to construct a two-electron wavefunction as a product of individual electron orbitals, $\phi_a$ and $\phi_b$, then neither $\phi_a(1)\phi_b(2)$ nor $\phi_a(2)\phi_b(1)$ alone are satisfactory since we require that the **electrons be indistinguishable**. The combinations $\phi_a(1)\phi_b(2) \pm \phi_a(2)\phi_b(1)$ do meet the requirement of indistinguishability, but these functions just describe the **spatial distribution of the electrons**; we must also consider their spin.

➤ If the two electrons have **different spin eigenfunctions**, **indistinguishability means** that neither $\alpha_1\beta_2$ nor $\alpha_2\beta_1$ is satisfactory, but $\alpha_1\beta_2 \pm \beta_1\alpha_2$ are acceptable – as are $\alpha_1\alpha_2$ and $\beta_1\beta_2$, of course. As we've noted, the overall wavefunction for two electrons must be antisymmetric with respect to interchange of the electrons' labels. This admits four possibilities, as long as both $\phi_a$ and $\phi_b$ are singly occupied (normalization constants included):

$$^1\Psi = \overbrace{\tfrac{1}{\sqrt{2}}\left(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\right)}^{\text{Symmetric}} \times \overbrace{\tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}^{\text{Antisymmetric}} \qquad \begin{matrix} M_S \\ 0 \end{matrix}$$

$$^3\Psi = \overbrace{\tfrac{1}{\sqrt{2}}\left(\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right)}^{\text{Antisymmetric}} \times \overbrace{\left\{ \begin{matrix} \alpha_1\alpha_2 \\ \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{matrix} \right.}^{\text{Symmetric}} \quad \begin{matrix} 1 \\ 0 \\ -1 \end{matrix}$$

## ❖ Multiple Bonds

➤ To see how the VB method describes multiple bonds, let's examine $N_2$. 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

$$\psi_\sigma^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

➤ 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



+ 
+ 
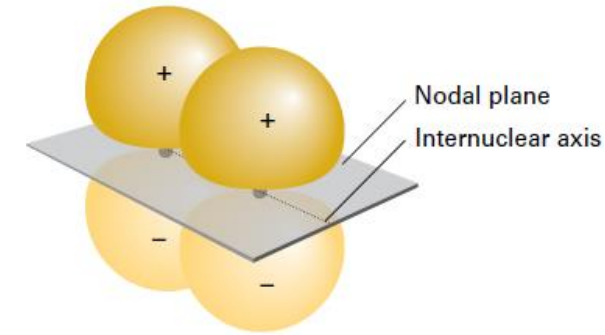Nodal plane
Internuclear axis
−
−

**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.

$$\psi_{\pi_x}^{bond}(1,2) = C_1[2p_x^A(1)2p_x^B(2)] + C_1[2p_x^A(2)2p_x^B(1)] \qquad \psi_{\pi_y}^{bond}(1,2) = C_1[2p_y^A(1)2p_y^B(2) + 2p_y^A(2)2p_y^B(1)]$$

➤ 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.
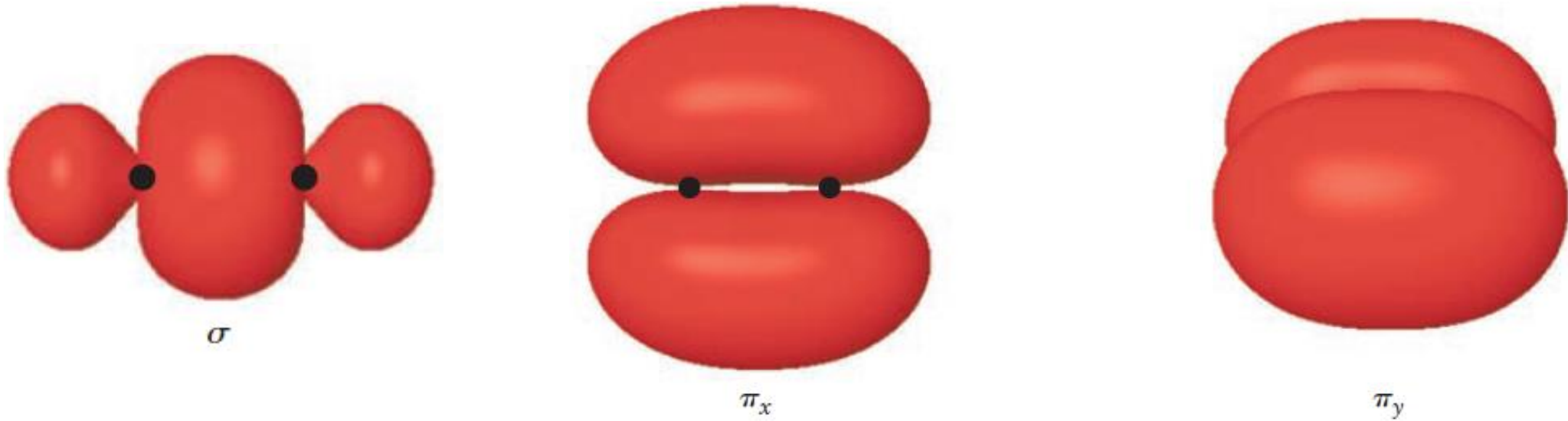


$\sigma$   $\pi_x$   $\pi_y$

**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.

H : Be : H

**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*.
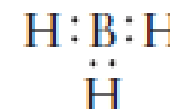
H : B : H

H

**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.

Amplitude

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.
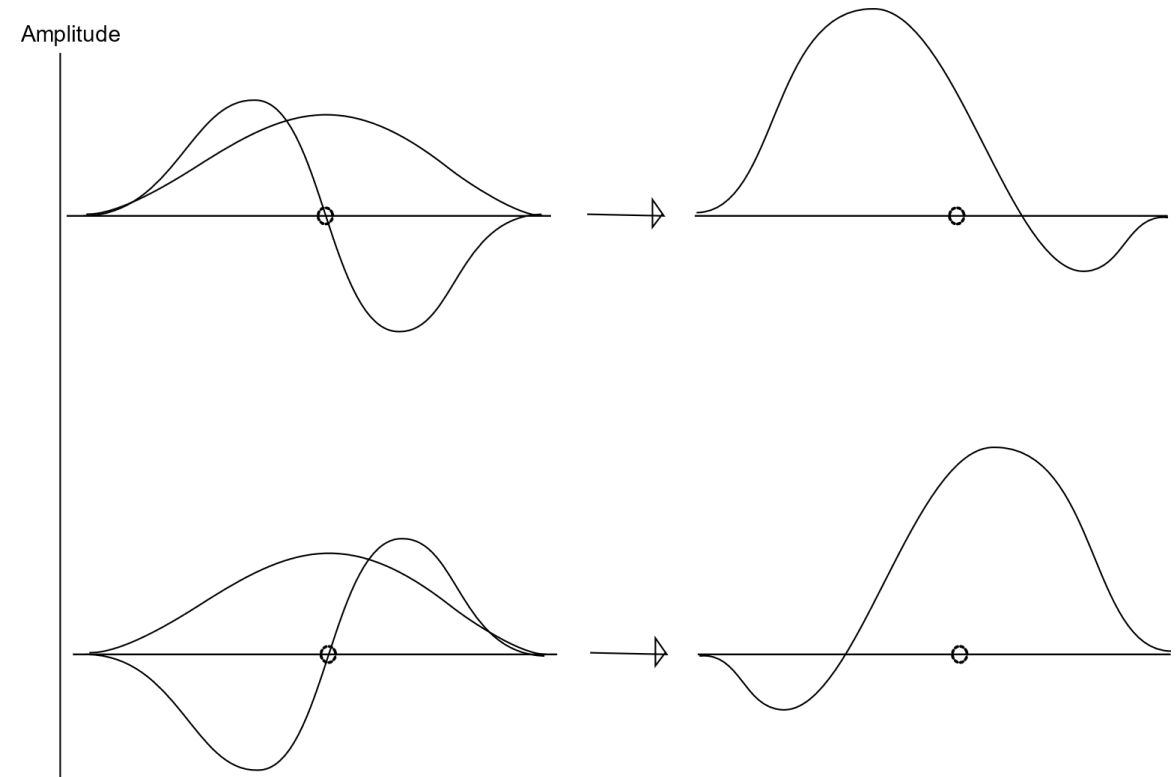
❑ **Rules for orbital hybridization:**

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 coefficents 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" $\chi$ 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 2*s* 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.
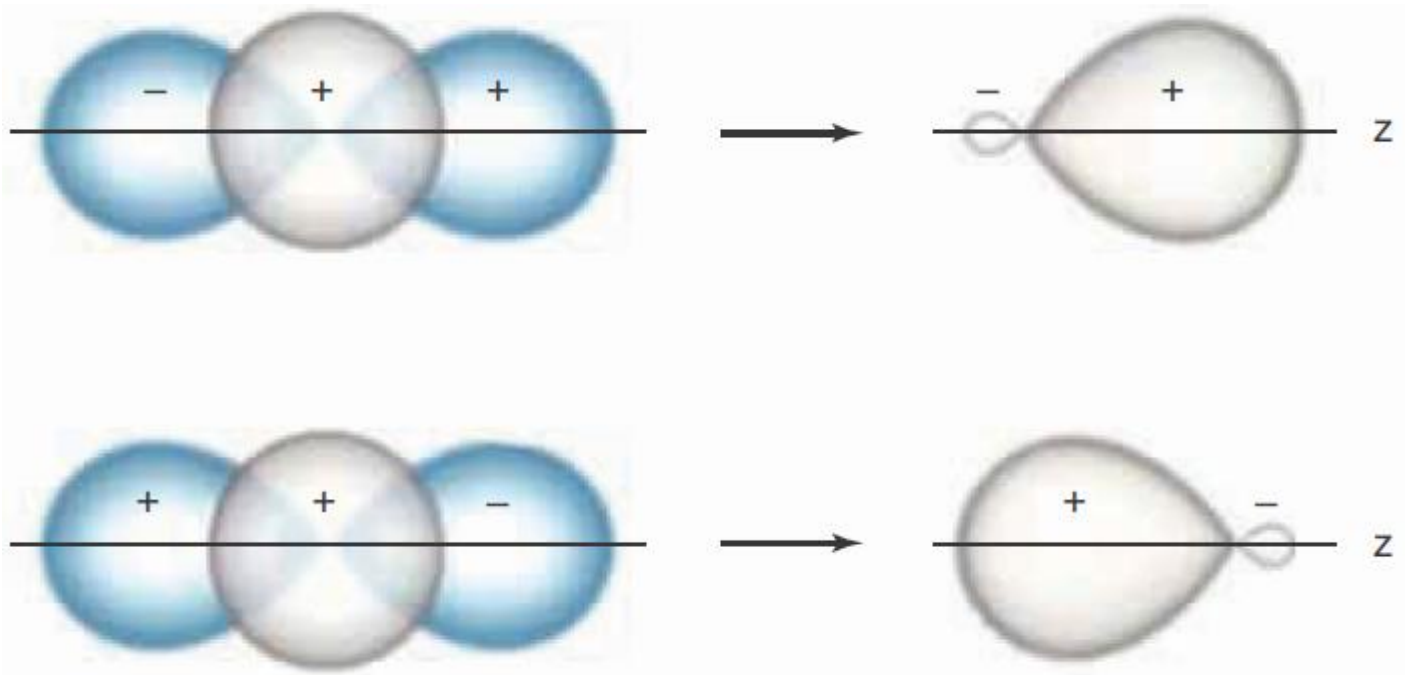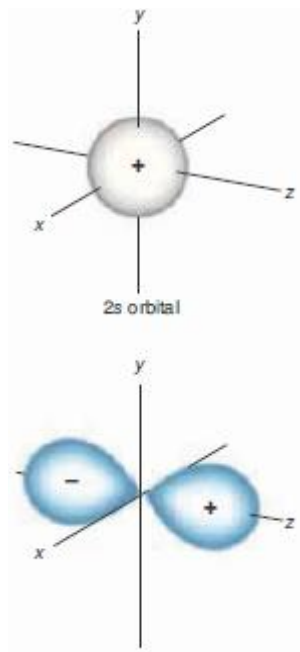
Figure 9.16 The formation of two *sp* hybrid orbitals from a 2*s* and a 2*p* atomic orbital oriented along the bonding axis. The two resulting *sp* orbitals are 180° apart.

Addition and subtraction of the 2*s* and 2*p* atomic orbitals may be illustrated by reversing the signs on the 2*p* orbital, as shown here. The 2*s* and 2*p* 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.

-2s

$2p_z$

Atomic orbitals

(a)

sp hybrid orbitals
from Equation 6.20

(b)

Hybrid orbital overlap
with each H atom 1s orbital

(c)

Electron density
of resulting MO

(d)
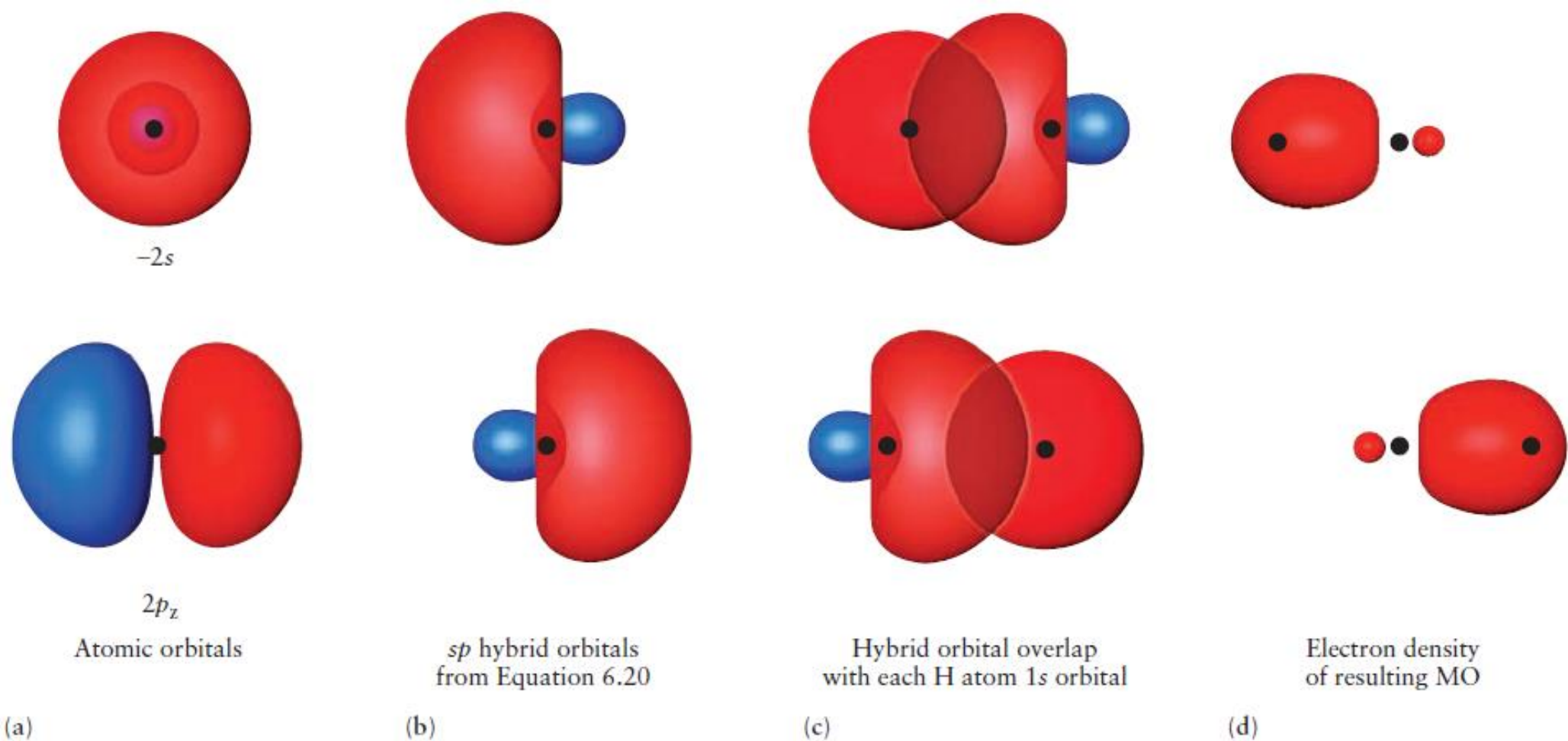
FIGURE 6.37 Formation, shapes, and bonding of the sp hybrid orbitals in the $BeH_2$ molecule.
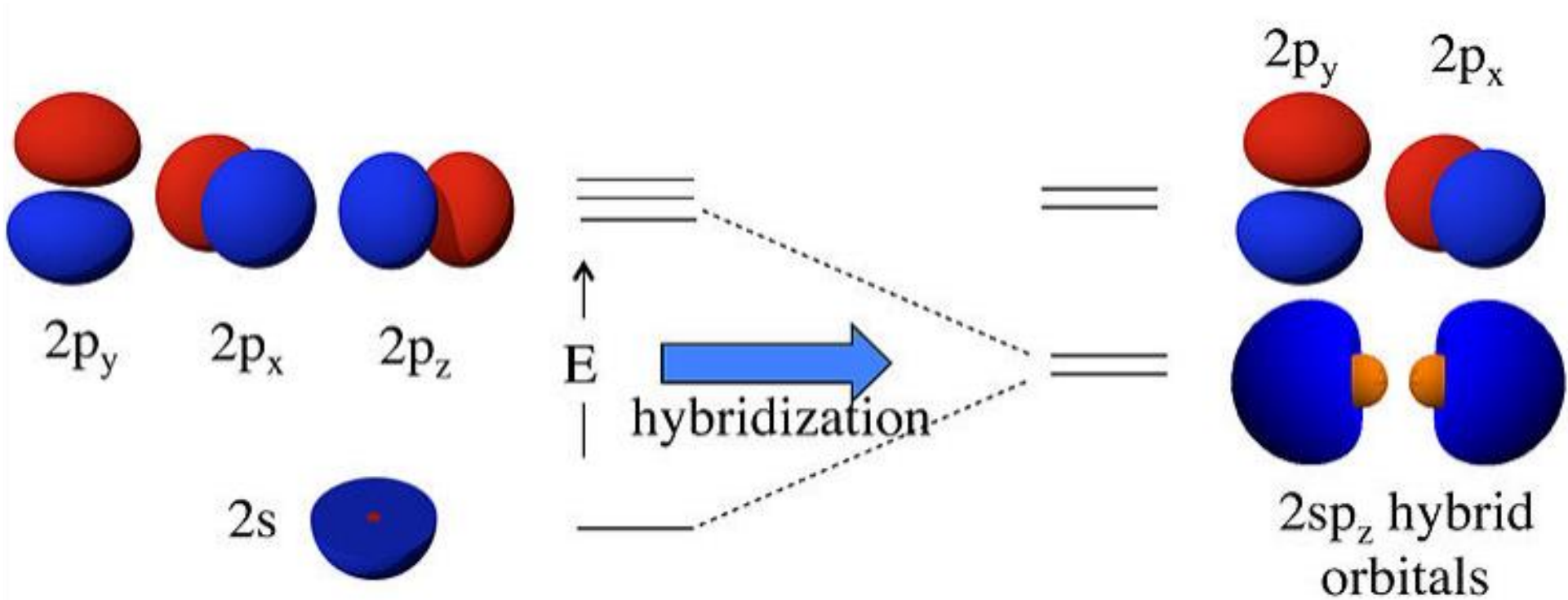
(a) The -2s and $2p_z$ orbitals of the Be atom.

(b) The two sp hybrid orbitals formed from the 2s and $2p_z$ orbitals on the beryllium atom.

(c) 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.

(d) 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 2*s* orbital and one 2*p* 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**.
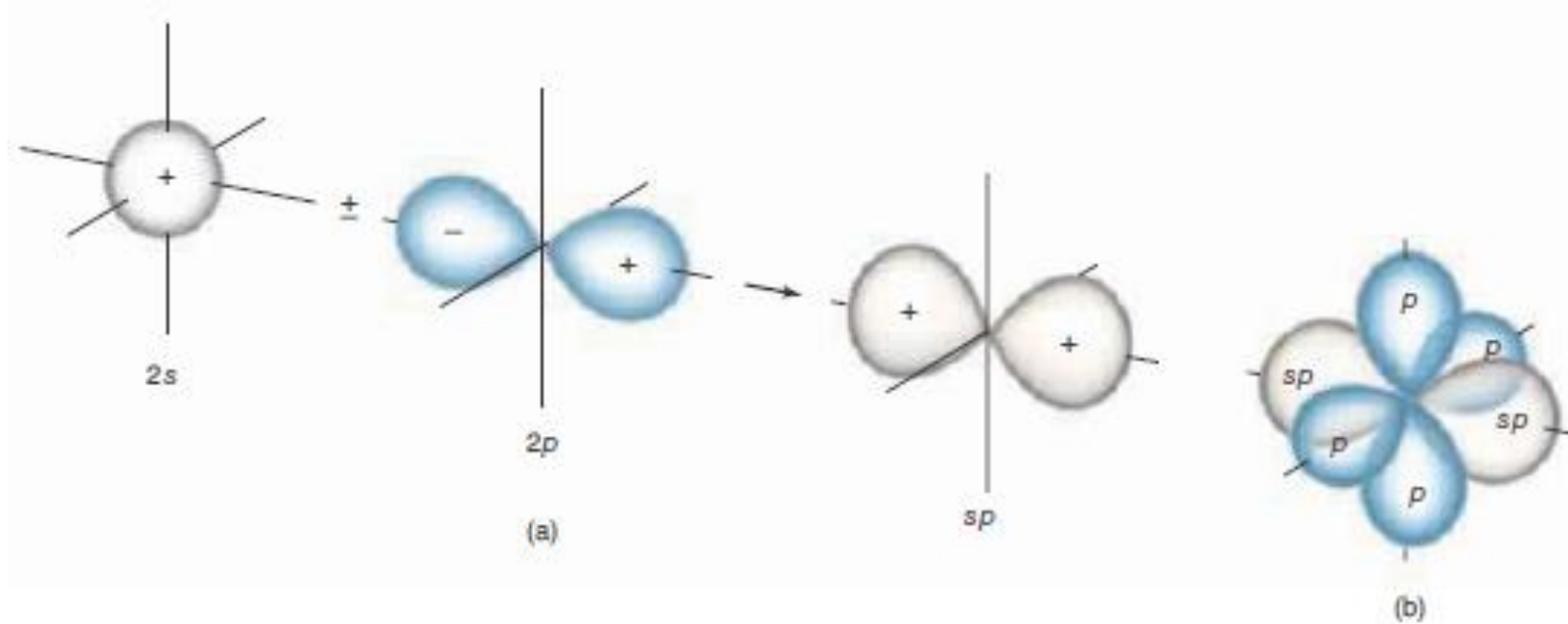
Figure 9.17 The formation of *sp* hybrid orbitals results from combining the 2*s* orbital and one 2*p* orbital on a single atom.

The two *sp* orbitals are equivalent and are 180° apart.

In (a), for simplicity, only the 2*p* orbital that is combined with the 2*s* orbital is shown.

In (b), all the orbitals are shown.

The two 2*p* orbitals that are not combined with the 2*s* 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.
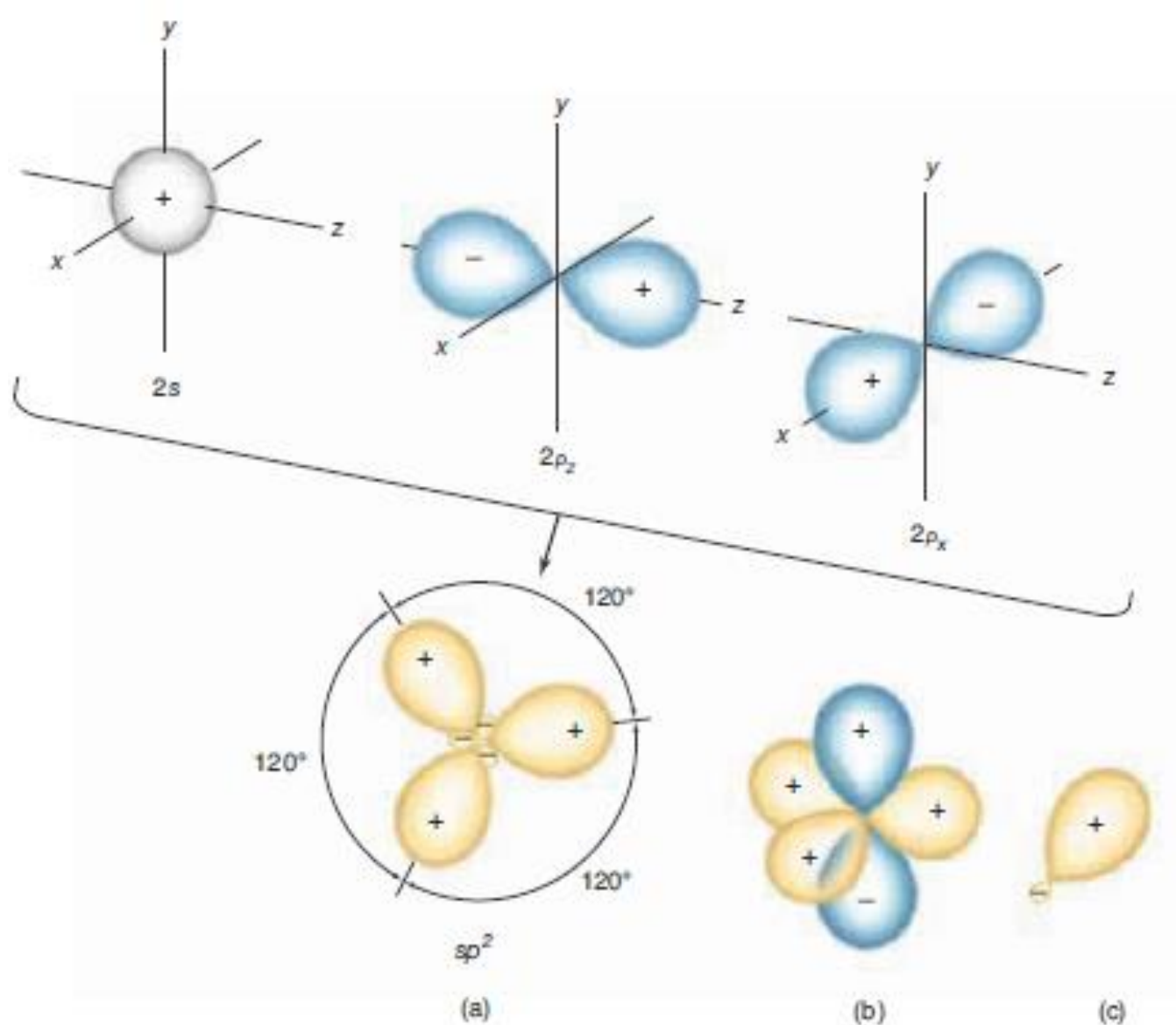
Figure 9.20 The **formation of $sp^2$ hybrid orbitals** by combining the 2s orbital and two 2p orbitals on a single atom.
(a) The three $sp^2$ orbitals formed are equivalent, lie in a plane, and are 120° apart. For simplicity, only the two 2p orbitals that are combined with the 2s orbital are shown.
(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 **sp² hybrid orbital**.

## ❑ *sp³* hybrid orbitals

The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$h_1 = s + p_x + p_y + p_z$$
$$h_2 = s - p_x - p_y + p_z$$
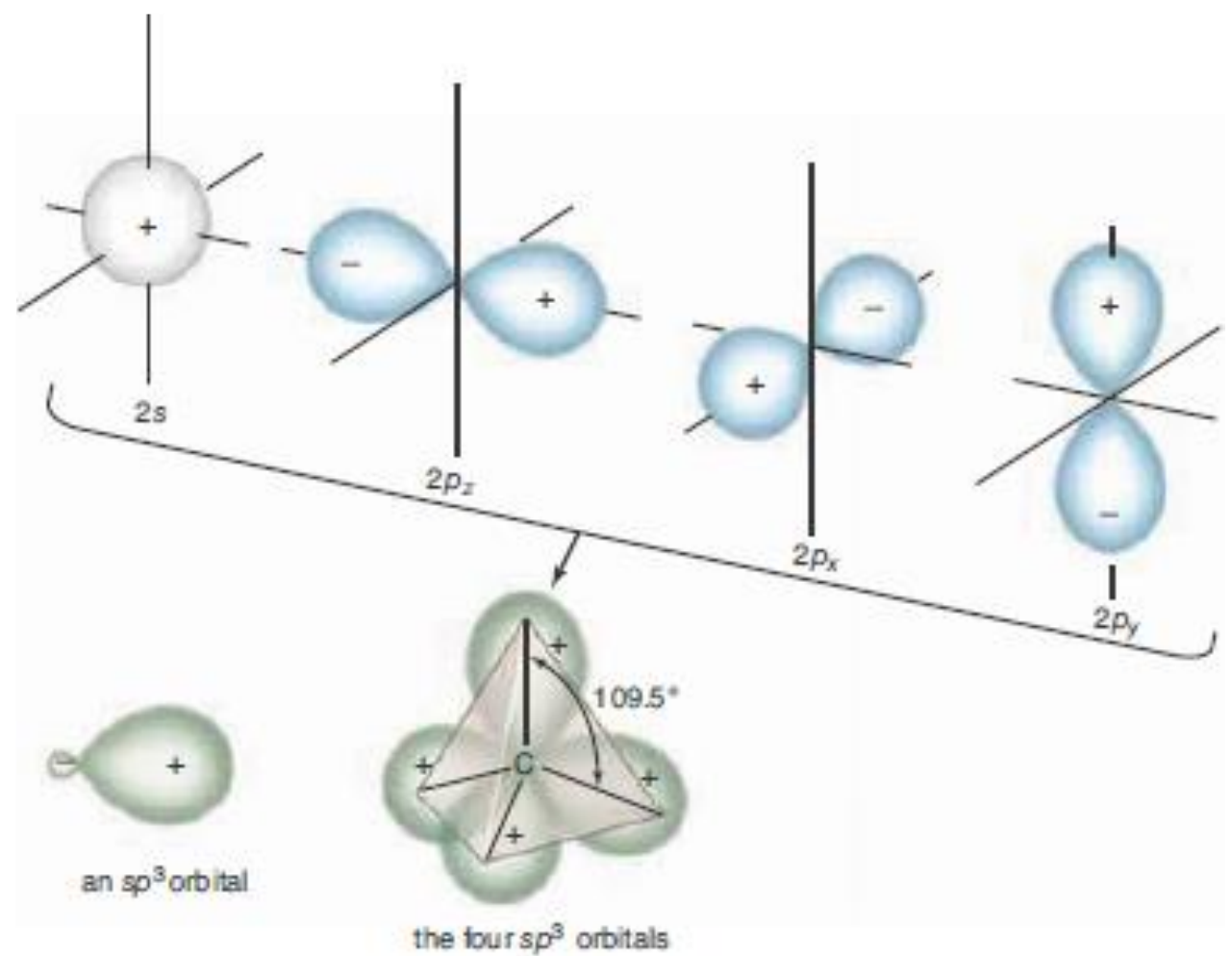$$h_3 = s - p_x + p_y - p_z$$
$$h_4 = s + p_x - p_y - p_z$$



Figure 9.22 The 2*s* and three 2*p* orbitals on an atom can be combined to form four *sp³* hybrid orbitals that are all equivalent and point toward the vertices of a tetrahedron. The angle between *sp³* orbitals is the tetrahedral bond angle, 109.5°. The small negative value regions of the *sp³* orbitals are omitted from the tetrahedral figure to simplify the figure. A single *sp³* orbital is shown to the left of the set of four *sp³* orbitals.

# $sp^3$ hybrid orbitals and $CH_4$
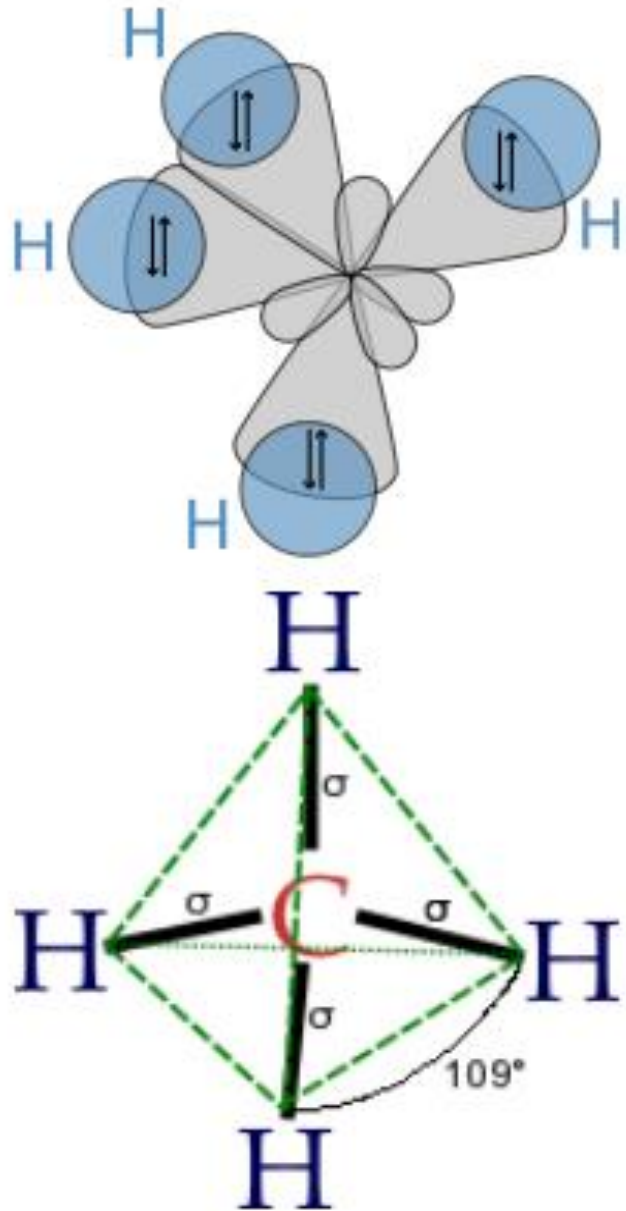


> ➤ As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the appropriate direction.
> ➤ A **hybrid orbital has enhanced amplitude in the internuclear region**, which arises from the constructive interference between the s orbital and 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 **$sp^n$-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 $sp^n$ 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 $sp^n$ hybrid.

✓ Thus, $sp$ orbitals have greater overlap with the ligand orbitals than do $sp^2$ or $sp^3$ orbitals.

# ❑ Nonequivalent hybrids

➤ In the above cases, a given number of simple atomic orbitals were combined to give the same number of hybrid orbitals which were all equivalent to each other. These modes of hybridization correspond to the basic shapes discussed above. It is quite possible, however, to form **nonequivalent hybrids**. For example, an **unsymmetrical beryllium compound, BeXY**, would almost certainly have a more favorable bonding structure if nonequivalent 's+p' hybrids were used with, say, the Be-X bond formed by a hybrid with rather more $s$ character and the Be-Y bond from one with more $p$ character.

➤ In the same way, trigonal or tetrahedral hybrids may be nonequivalent. For example, in chloromethane, $CH_3Cl$, the C-Cl bond will be formed by an 's+$p^3$' hybrid which has a different amount of $s$ character from the other three 's+$p^3$' hybrids which form the C-H bonds.

➤ The optimum amount of $s$ character in such hybrids will vary from molecule to molecule, although the shape and basic hybrid structure are still tetrahedral.

➤ **Such nonequivalent hybrids become even more necessary when molecules containing lone pairs** are under discussion. To get the bond *angles of 107° in ammonia, the p character of the N-H bonds has to be significantly increased over the 3/4 p of the equivalent $sp^3$ hybrid, and the* **orbital holding the lone pair has proportionately more s character**. Similar remarks apply to the case of water with a bond angle of 105°.

➤ There is indeed a complete range of possible hybrids from the four equivalent $sp^3$ hybrids at 109.5° in methane, through the ***nonequivalent 's+p³' hybrids in $CH_3Cl$, $NH_3$ and $H_2O$, down to the hybrids in $PH_3$ and $H_2S$ which correspond to bond angles of just over 90° and are mainly p orbitals with a little s character for the bonds*** and *s plus a little p for the lone pair*.

➤ Moving the other way, towards larger angles, there is the same continuous variation from equivalent $sp^3$ hybrids at 109.5°, through nonequivalent arrangements, to the case of equivalent $sp^2$ hybrids at 120° plus an unused atomic p orbital. There is thus a complete continuity of bond angle versus percentage p character in $sp^n$ hybrids, as indicated in the following Fig.
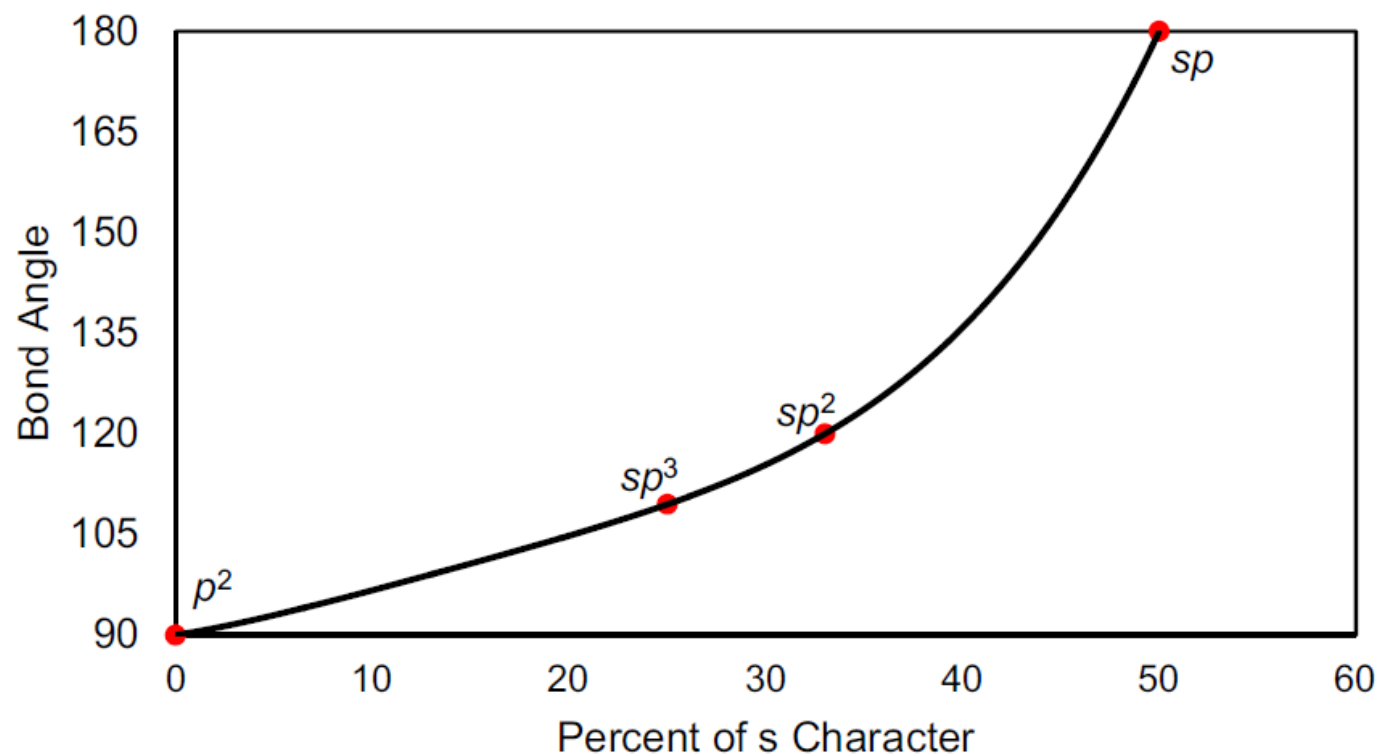
FIGURE 4.4 Variation in calculated bond angle in hybrid orbitals with percent *s* character in $sp^n$ (n = 1-3).

# 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 ($\theta$)** and the *decimal* percent **s-character (S)** is given by Equation (10.8).

$$\cos \theta = \frac{S}{S-1} \qquad\qquad (10.8)$$

➤ The angle between the axes of the **sp³** hybrid orbitals is the tetrahedral angle, arccos(−1/3) = 109.47°.

❑ **Calculate** the **bond angle ($\theta$)** 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 θ = (1/3)/[(1/3) - 1] = -0.5 for which θ = 120º.

➢ The **composition of hybrids** can be discussed quantitatively. The outcome is that, if two equivalent hybrids composed of an s-orbital and two p-orbitals make an angle θ to each other, then the ***hybrids can be regarded as sp$^λ$***, with

➢ ***λ = -cosθ/cos²(θ/2).***

➢ What is the hybridization of the O orbitals that form the two O—H bonds in $H_2O$?

➢ 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 180º, 120º, and 109º28', 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 90º, 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 that $NH_3$.

## ❖ 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.
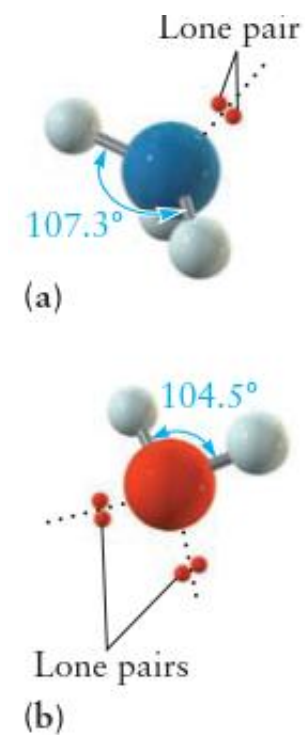


FIGURE 6.41 (a) Ammonia ($NH_3$) has a pyramidal structure (b) Water ($H_2O$) has a bent structure (both has bond angles less than 109.5°).

- ✓ 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 $\quad\quad\quad\quad \psi = c_1 2s + c_2 2p_y + c_3 2p_z \quad\quad\quad\quad$ (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 NH₃ 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 3x(23.3%)=69%, the ***lone pair*** in ammonia has approximately ***31% s-character***.

✓ As a result, the lone pair in NH₃ will have ***slightly* greater** *s*-character than will the lone pair in H₂O (H₂O lone pair has 30% *s*-character).

✓ The ***greater basicity*** *of NH₃ relative to H₂O* 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 sp³ hybridization with a lone pair in one of the hybrid AOs explains the trigonal pyramid structure for AX₃ 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, sp³ 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 91.0º and 91.8º, 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 ($H_2Te$, 90º; $SbH_3$, 91.3º).
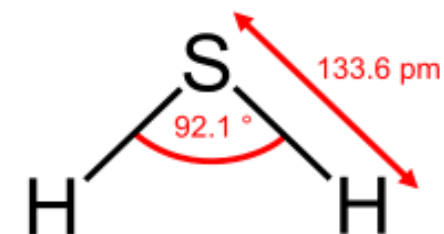
➢ It should be clear from the above discussion that the idea of hybridization is very valuable in providing a description of the electron density in a molecule but that it does not provide any explanation of the electron arrangements or of the shapes of molecules. It is common to see statements such as 'methane is tetrahedral because it is $sp^3$ hybridized' but this description is incorrect.

➢ As with other wave-mechanical calculations, hybridization presents a potential method of predicting molecular shapes. It is possible, in principle, to find the optimum hybridization scheme for a molecule such as water which will give the most favourable energy of formation and hence the bond lengths and angles.

➢ However, just as in the cases discussed earlier, the necessity of introducing approximate methods to solve the wave equations adds so much uncertainty to the values which result that the predictions are rather crude in the present state of the art.

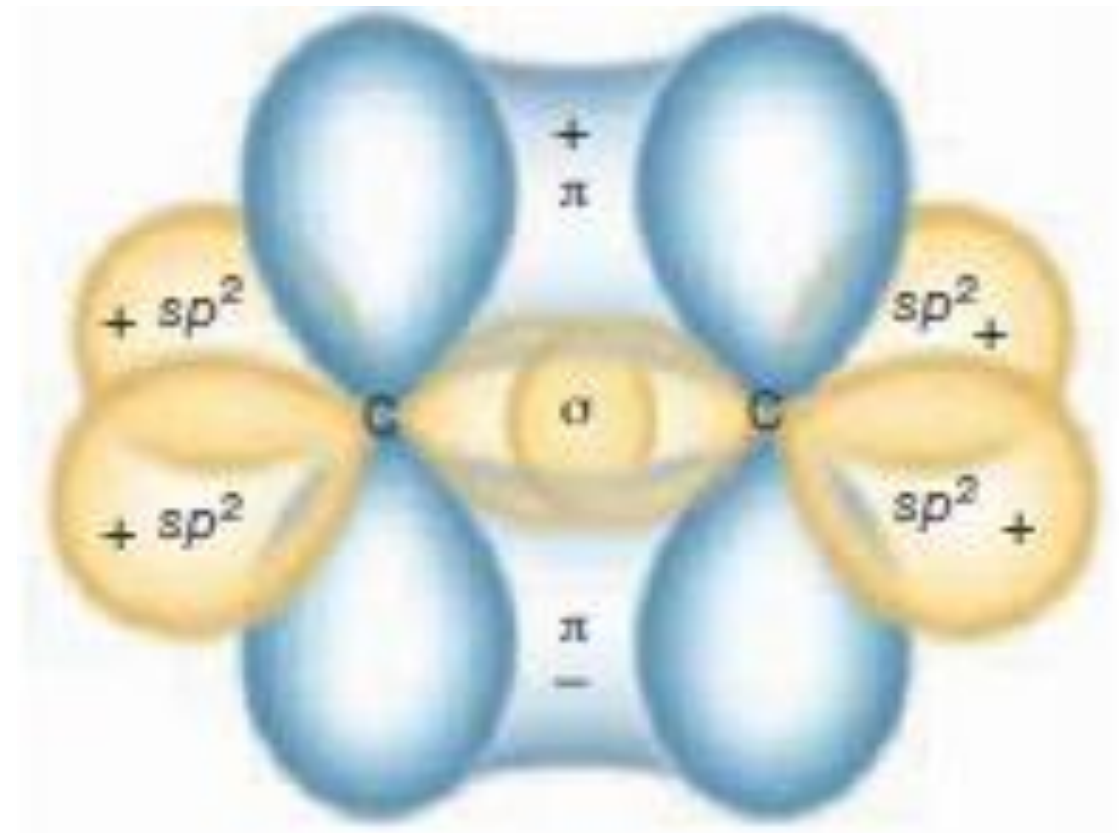❑ π bond formation: Multiple bonding in a molecule



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 *sp²* orbitals, one from each carbon atom.
The π bond results from the combination (lateral overlap) of two 2*p* orbitals, one from each carbon atom.
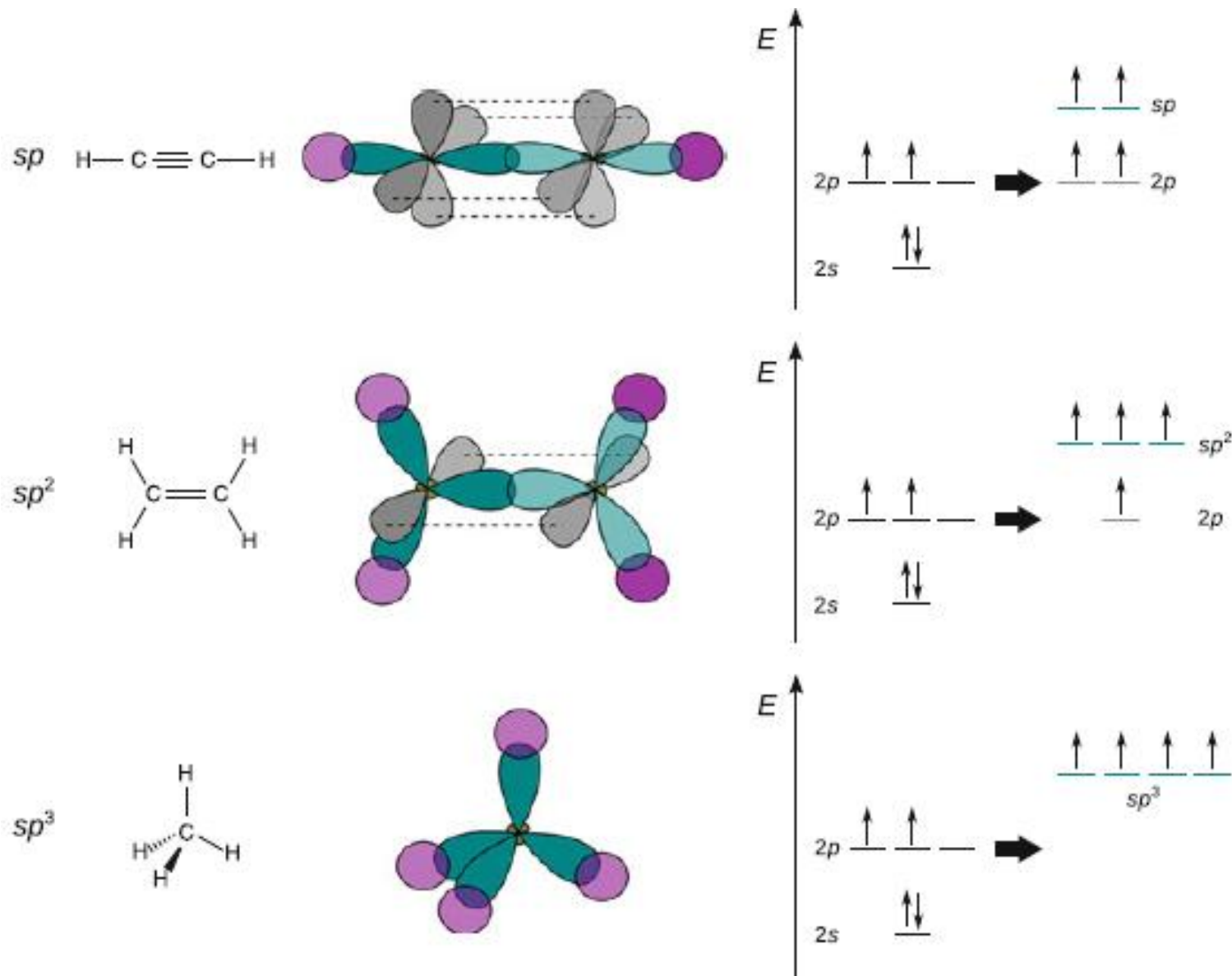The π orbital maintains the σ-bond framework in a planar shape and prevents rotation about the double bond.

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 **sp³ 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 <span style="color:red">includes hybridization schemes that include d orbitals, thus accounting for</span> <span style="color:darkred">**hypervalence**</span>.

*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.

**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 |

# 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.
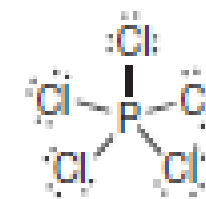


**15** $PCl_5$
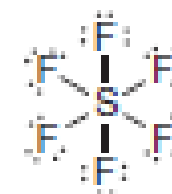


**16** $SF_6$

# 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 $\Psi_{H-Cl} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$, with $\psi_A$ now a H1s orbital and $\psi_B$ 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 ($\Psi_{H^+Cl^-} = \psi_B(1)\psi_B(2)$, representing the ionic form $H^+Cl^-$) or both are on the H atom ($\Psi_{H^+Cl^-} = \psi_A(1)\psi_A(2)$, 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) $\Psi_{HCl} = \Psi_{H-Cl} + \lambda\,\Psi_{H^+Cl^-}$ with $\lambda$ (lambda) some numerical coefficient.

➢ In general,  $\Psi = \Psi_{covalent} + \lambda\Psi_{ionic}$          (9A.3)
where $\Psi_{covalent}$ is the two-electron wavefunction for the purely covalent form of the bond and $\Psi_{ionic}$ 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 $\lambda^2$.

- If $\lambda^2 << 1$, the covalent description is dominant.

- If $\lambda^2 >> 1$, 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 $\lambda$ 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 $\lambda$*, then *the best value of $\lambda$ is the one that results in the lowest energy*. The ionic contribution to the resonance is then proportional to $\lambda^2$.

➢ 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 $\Psi = \Psi_{covalent} + 0.1\Psi_{ionic}$.

✓ 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:

$$\Psi = \Psi(\text{⬡}) + \Psi(\text{⬡}) \tag{9A.4}$$

➢ 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.



**1**
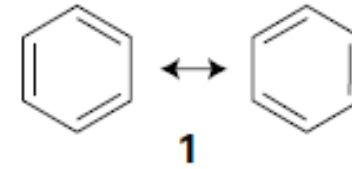
➤ *The wavefunction is improved by allowing resonance because it allows the electrons to adjust into a distribution of lower energy*. This lowering is called the **resonance stabilization** of the molecule and, in the context of VB theory, is largely responsible for the unusual stability of aromatic 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**).



**2**
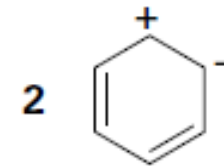
# Resonance Structures and Electron Delocalization

➤ 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 x 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 entire 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



Resonance structures

Aromatic structure
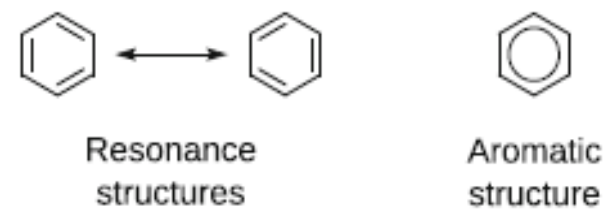
➢ In benzene, the C atoms and their attached H atoms all lie in the same plane, with the C atoms forming a hexagonal ring.

➢ To describe the bonding in the Kekule structures of benzene in terms of VB theory, we need hybrid orbitals that match the 120º 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 -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).
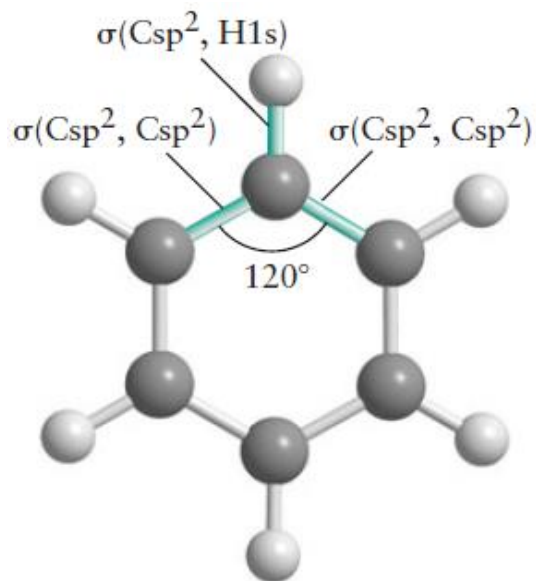
**FIGURE 3.20** The framework of σ-bonds in benzene: each carbon atom is sp² hybridized, and the array of hybrid orbitals matches the bond angles (of 120°) in the hexagonal molecule. The bonds around only one carbon atom are labeled; all the others are the same.
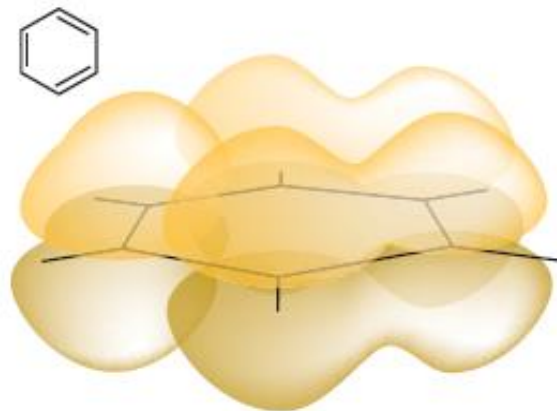


**FIGURE 3.21** Unhybridized carbon 2p-orbitals can form a π-bond with either of their immediate neighbors. Two arrangements are possible, each one corresponding to a different Kekulé structure. One Kekulé structure and the corresponding π-bonds are shown here.
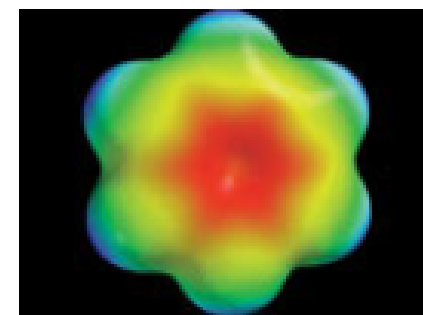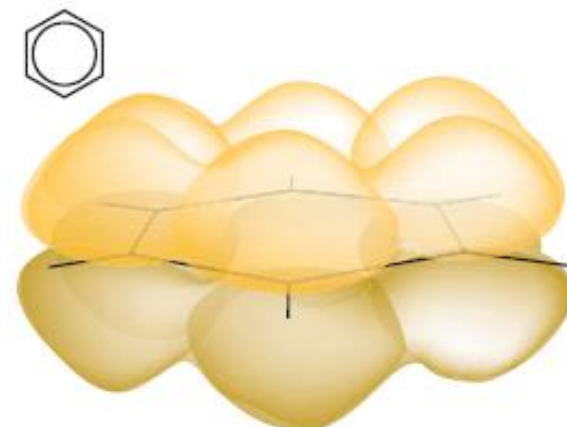


**FIGURE 3.22** As a result of resonance between two structures like the one shown in Fig. 3.21 (corresponding to resonance of the two Kekulé structures), the π-electrons form a double doughnut-shaped cloud above and below the plane of the ring.

➢ *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
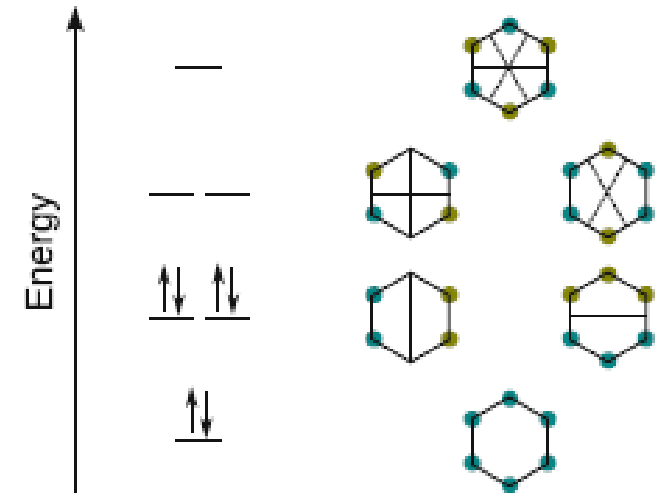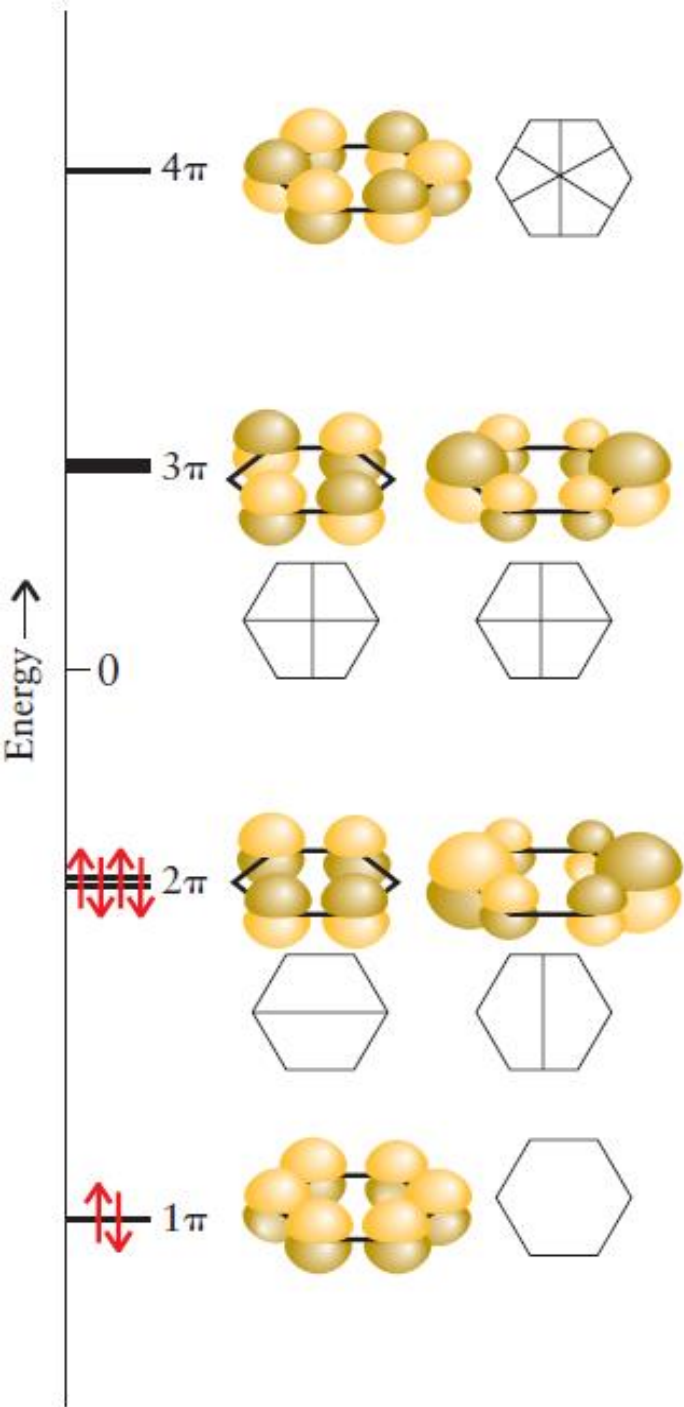
**FIGURE 3.37** The six π-orbitals of benzene; locations of nodes are shown with line drawings. Note that the orbitals range from fully bonding (no internuclear nodes) to fully antibonding (six internuclear nodes). The zero of energy corresponds to the total energy of the separated atoms. The three orbitals with negative energies have net bonding character.
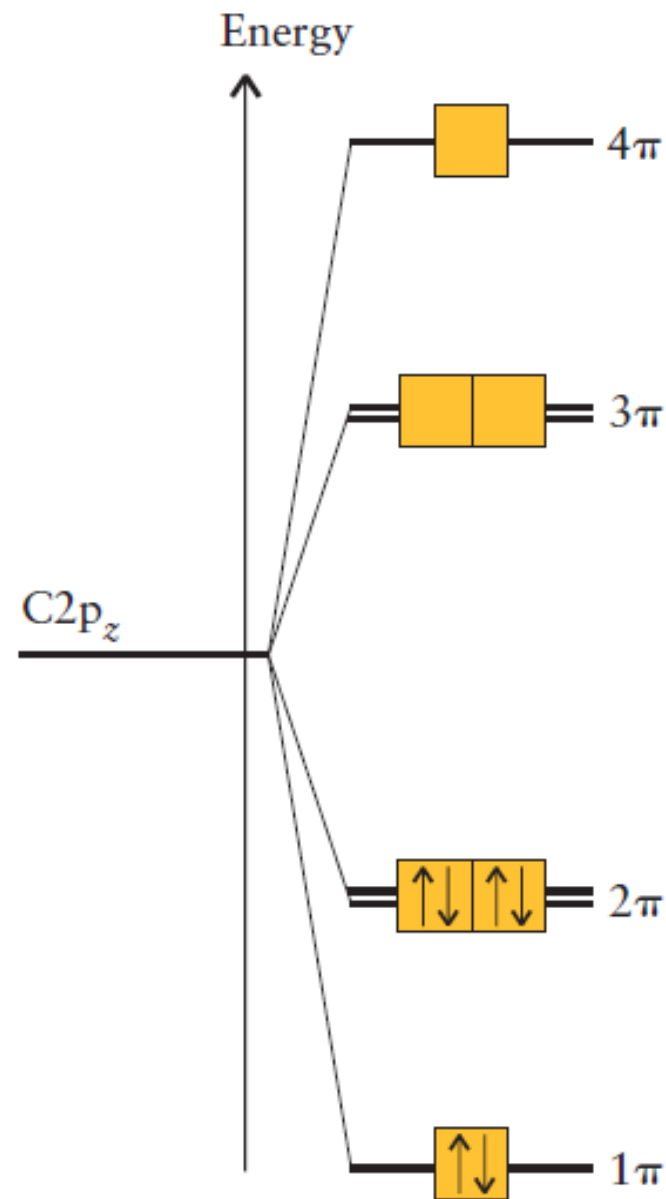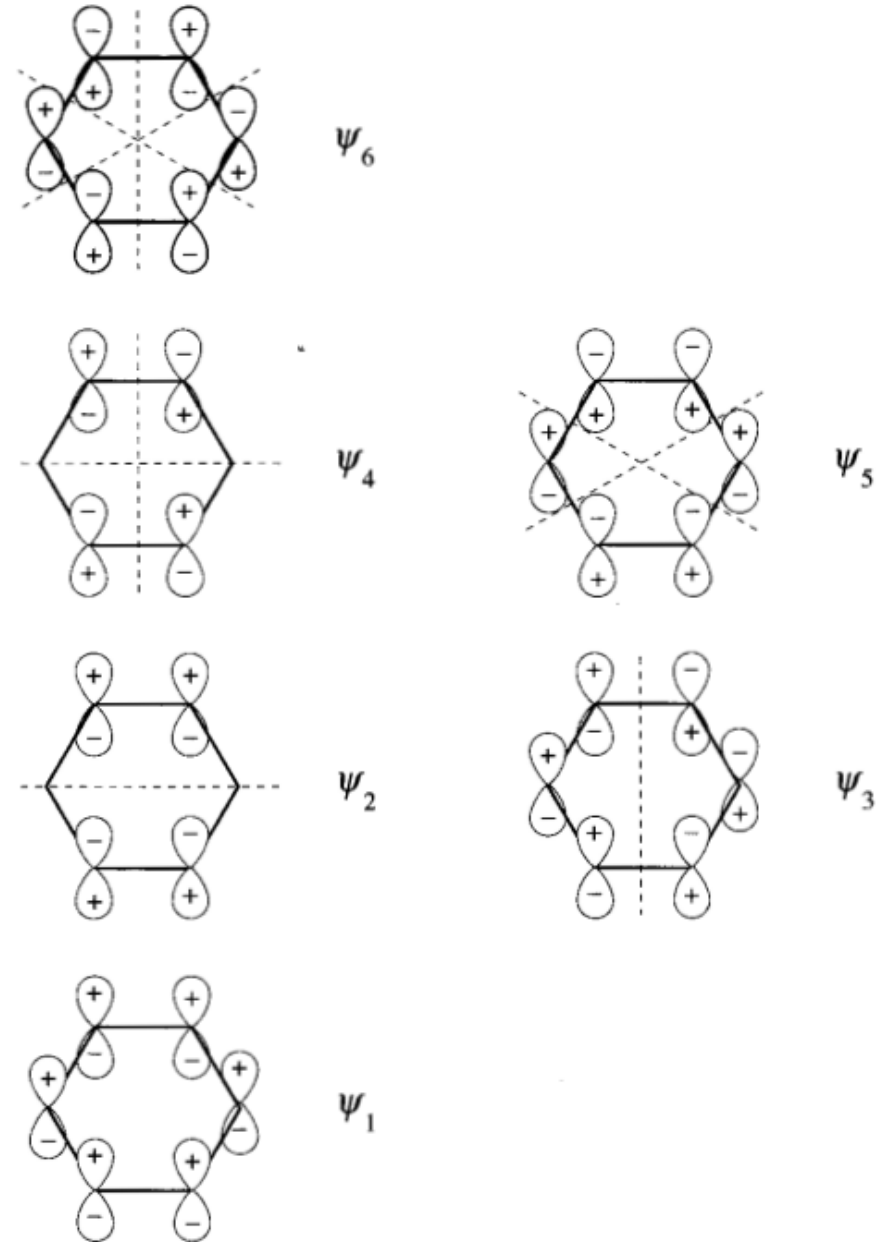


**FIGURE 3.38** The molecular orbital energy-level diagram for the π-orbitals of benzene. In the ground state of the molecule, only the net bonding orbitals are occupied.

➢ The π molecular orbitals for benzene and the nodal planes.



$\psi_6$

$\psi_4$
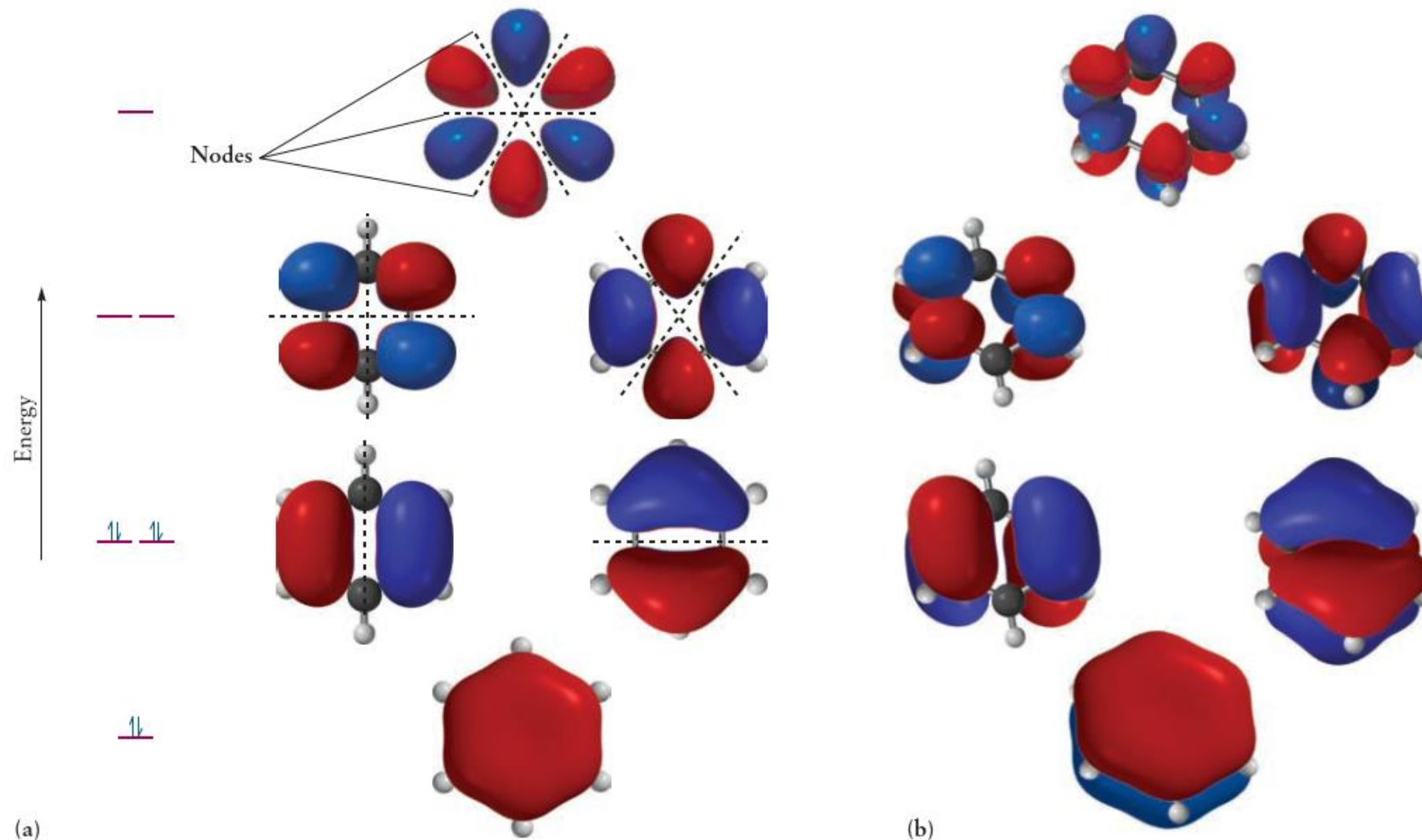
$\psi_5$

$\psi_2$

$\psi_3$

$\psi_1$

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.