Chapter 9

Covalent Bonding: Orbitals

The Localized Electron Model

- Draw the Lewis structure(s)
- Determine the arrangement of electron pairs (VSEPR model).
- Specify the necessary hybrid orbitals.

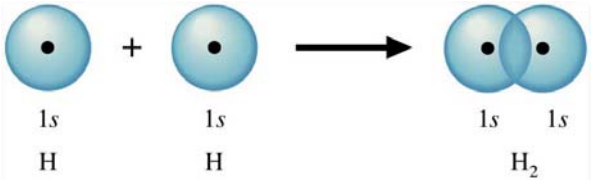
Valence Bond Theory

- **Valence bond theory or hybrid orbital theory** is an approximate theory to explain the covalent bond from a quantum mechanical view.
  - According to this theory, a bond forms between two atoms when the following conditions are met. (see Figures 10.21 and 10.22)
    1. Two atomic orbitals "overlap"
    2. The total number of electrons in both orbitals is no more than two.

Hybridization

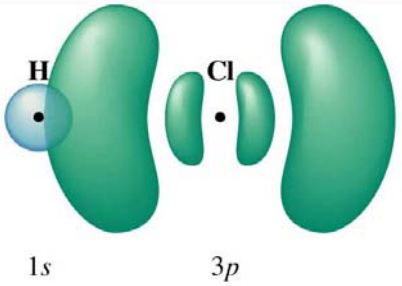
- The mixing of atomic orbitals to form special orbitals for bonding.
- The atoms are responding as needed to give the minimum energy for the molecule.

Figure 10.20: Formation of H_2.



Bond formed between two s orbitals

Figure 10.21: Bonding in HCl.



Bond formed between an s and p orbital

Hybrid Orbitals

- One might expect the number of bonds formed by an atom would equal its unpaired electrons.
  - Chlorine, for example, generally forms one bond and has one unpaired electron.
  - Oxygen, with two unpaired electrons, usually forms two bonds.
  - However, carbon, with only two unpaired electrons, generally forms four bonds. For example, methane, CH_4, is well known.

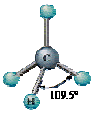
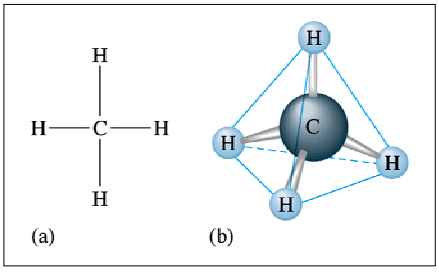
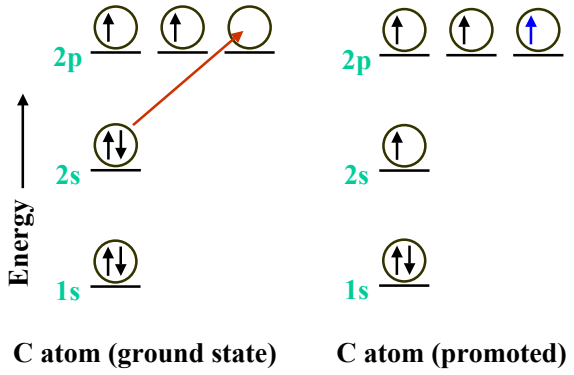


Figure 9.1: (a) The Lewis structure of the methane molecule. (b) The tetrahedral molecular geometry of the methane molecule.



Hybrid Orbitals

- The bonding in carbon might be explained as follows:
  - Four unpaired electrons are formed as an electron from the 2s orbital is **promoted** (excited) to the vacant 2p orbital.
  - The following slide illustrates this excitation. (Recall that in the excited state for an element, a ground state electron is promoted to a higher orbital)
  - More than enough energy is supplied for this promotion from the formation of two additional covalent bonds.



Hybrid Orbitals

- One bond on carbon would form using the 2s orbital while the other three bonds would use the 2p orbitals.
  - This does not explain the fact that the four bonds in CH_4 appear to be identical.
  - Valence bond theory assumes that the four available atomic orbitals in carbon combine to make **four equivalent "hybrid" orbitals**.

Hybrid Orbitals

- **Hybrid orbitals** are orbitals used to describe bonding that are obtained by taking combinations of atomic orbitals of an isolated atom.
  - In this case, a set of hybrids are constructed from one "s" orbital and three "p" orbitals, so they are called **sp^3 hybrid orbitals**.
  - The four sp^3 hybrid orbitals take the shape of a **tetrahedron** (see Figure 10.23).

Figure 9.2: The valence orbitals on a free carbon atom: 2*s*, 2*px*, 2*py*, and 2*pz*.

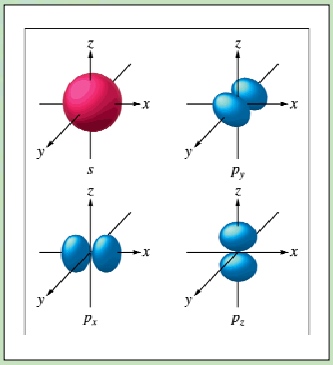


Figure 9.3: The "native" 2*s* and three 2*p* atomic orbitals characteristic of a free carbon atom are combined to form a new set of four sp^3 orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

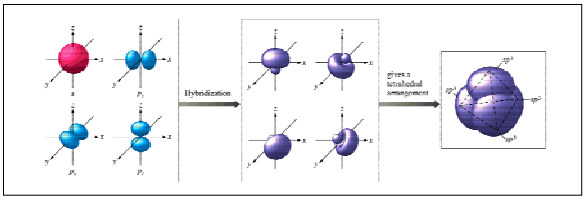


Figure 9.4: Cross section of an sp^3 orbital.

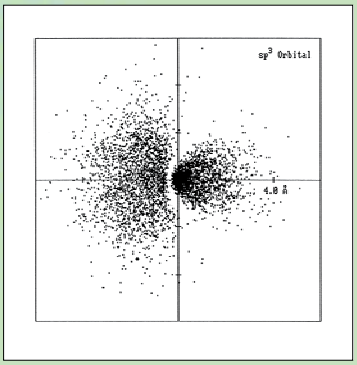


Figure 9.6: The tetrahedral set of four sp^3 orbitals of the carbon atom are used to share electron pairs with the four 1*s* orbitals of the hydrogen atoms to form the four equivalent C—H bonds. This accounts for the known tetrahedral structure of the CH4 molecule.

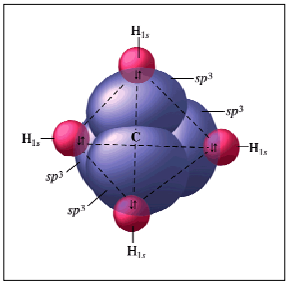


Figure 9.7: The nitrogen atom in ammonia is sp^3 hybridized.

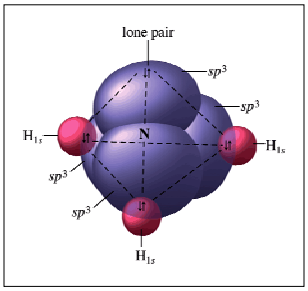
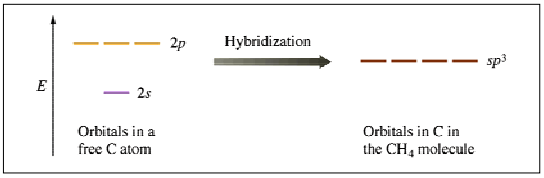
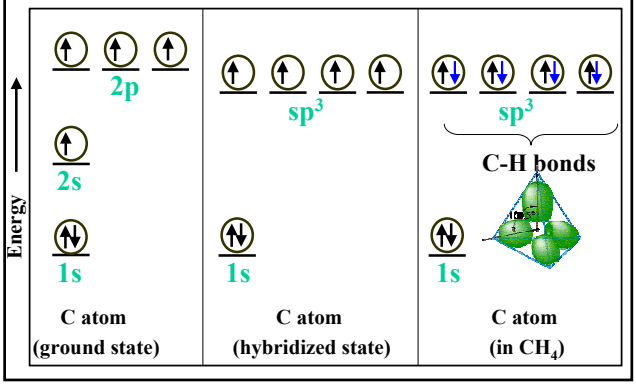


Figure 9.5: An energy-level diagram showing the formation of four sp^3 orbitals.



You can represent the hybridization of carbon in CH_4 as follows.

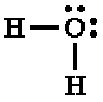


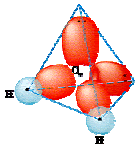
A Problem to Consider

- Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.
  - From the **Lewis formula** for a molecule, determine its geometry about the central atom using the VSEPR model.

A Problem to Consider

- Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.
  - The Lewis formula for H_2O is





A Problem to Consider

- Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.
  - From this geometry, **determine the hybrid orbitals on this atom**, assigning its valence electrons to these orbitals one at a time.

A Problem to Consider

- Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.
  - Note that there are four pairs of electrons about the oxygen atom.
  - According to the VSEPR model, these are directed **tetrahedrally**, and from the previous table you see that you should use **sp^3 hybrid orbitals.**

A Problem to Consider

- Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.
  - Each **O-H** bond is formed by the overlap of a **1s orbital** of a hydrogen atom with one of the singly occupied **sp^3 hybrid orbitals** of the oxygen atom.

You can represent the bonding to the oxygen atom in H_2O as follows:

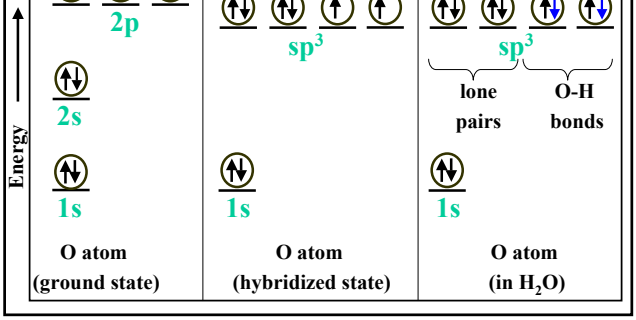


Figure 10.24: Bonding in H_2O.

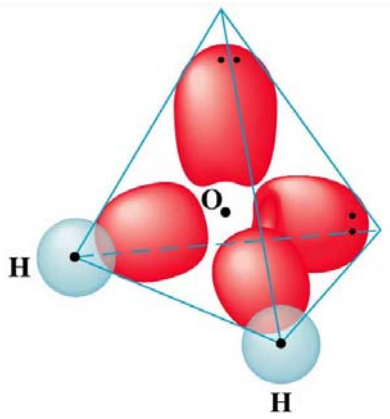


Figure 9.9: An orbital energy-level diagram for sp^2 hybridization. Note that one *p* orbital remains unchanged.

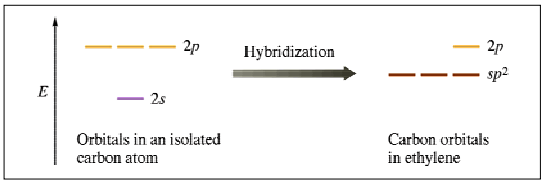


Figure 9.8: The hybridization of the *s*, *px*, and *py* atomic orbitals results in the formation of three sp^2 orbitals centered in the *xy* plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

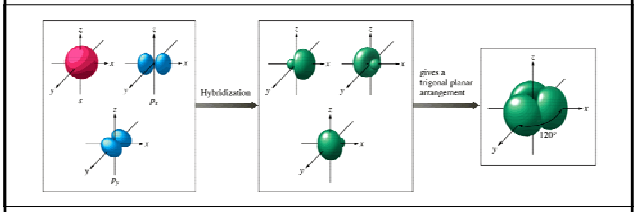


Figure 9.14: When one *s* orbital and one *p* orbital are hybridized, a set of two *sp* orbitals oriented at 180 degrees results.

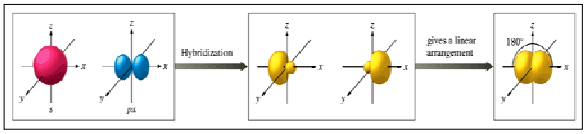


Figure 9.21: A set of dsp^3 hybrid orbitals on a phosphorus atom. Note that the set of five dsp^3 orbitals has a trigonal bipyramidal arrangement. (Each dsp^3 orbital also has a small lobe that is not shown in this diagram.)

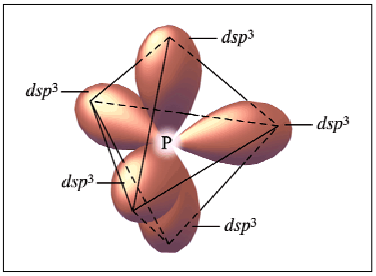


Figure 9.22: (a) The structure of the PCI5 molecule. (b) The orbitals used to form the bonds in PCI5. The phosphorus uses a set of five dsp3 orbitals to share electron pairs with sp3 orbitals on the five chlorine atoms. The other sp3 orbitals on each chlorine atom hold lone pairs.

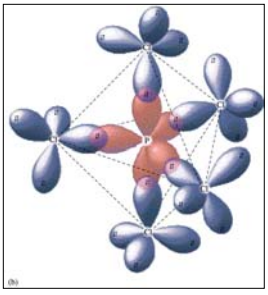
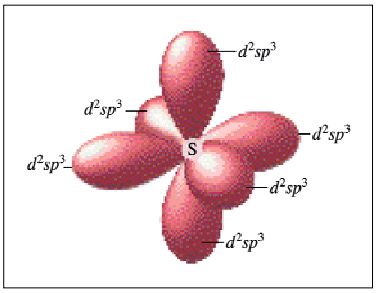


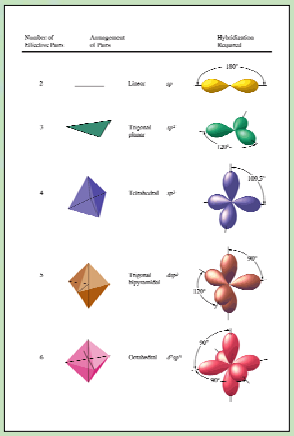
Figure 9.23: An octahedral set of d^2sp^3 orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.



Hybrid Orbitals

- Note that there is a relationship between the **type of hybrid orbitals** and the **geometric arrangement** of those orbitals.
  - Thus, **if you know the geometric arrangement, you know what hybrid orbitals to use** in the bonding description.
  - Figure 9.24 summarizes the types of hybridization and their spatial arrangements.

Figure 9.24: The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.



Hybrid Orbitals

Hybrid Orbitals	Geometric Arrangements	Number of Orbitals	Example
sp	**Linear**	2	Be in BeF_2
sp^2	**Trigonal planar**	3	B in BF_3
sp^3	**Tetrahedral**	4	C in CH_4
dsp^3	**Trigonal bipyramidal**	5	P in PCl_5
d^2sp^3	**Octahedral**	6	S in SF_6

Hybrid Orbitals

- To obtain the bonding description of any atom in a molecule, you proceed as follows:
  1. Write the **Lewis electron-dot formula** for the molecule.
  2. From the Lewis formula, use the VSEPR theory to **determine the arrangement of electron pairs** around the atom.

Hybrid Orbitals

- To obtain the bonding description of any atom in a molecule, you proceed as follows:

3. From the geometric arrangement of the electron pairs, **obtain the hybridization type.**

4. Assign **valence electrons** to the hybrid orbitals of this atom one at a time, pairing only when necessary.

Hybrid Orbitals

- To obtain the bonding description of any atom in a molecule, you proceed as follows:

5. Form bonds to this atom by overlapping singly occupied orbitals of other atoms with the singly occupied hybrid orbitals of this atom.

A Problem to Consider

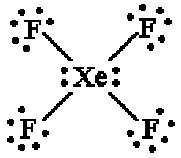
- Describe the bonding in XeF_4 using hybrid orbitals.
  - From this geometry, **determine the hybrid orbitals** on this atom, assigning its valence electrons to these orbitals one at a time.

A Problem to Consider

- Describe the bonding in XeF_4 using hybrid orbitals.
  - From the Lewis formula for a molecule, determine its geometry about the central atom using the VSEPR model.

A Problem to Consider

- Describe the bonding in XeF_4 using hybrid orbitals.
  - The Lewis formula of XeF_4 is

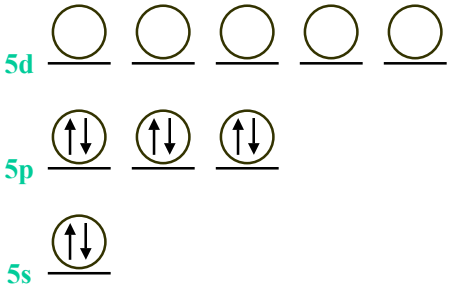


A Problem to Consider

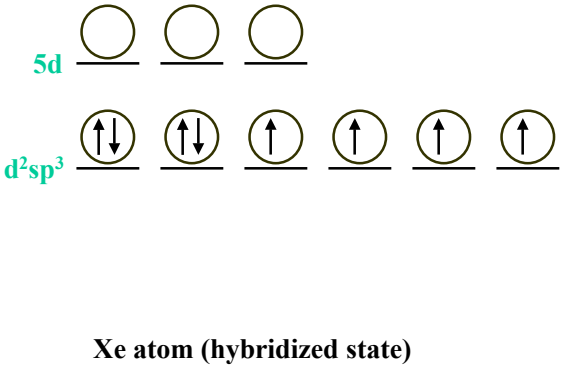
- Describe the bonding in XeF_4 using hybrid orbitals.
  - The xenon atom has four single bonds and two lone pairs. It will require **six orbitals** to describe the bonding.
  - This suggests that you use **d^2sp^3 hybrid orbitals** on xenon.

A Problem to Consider

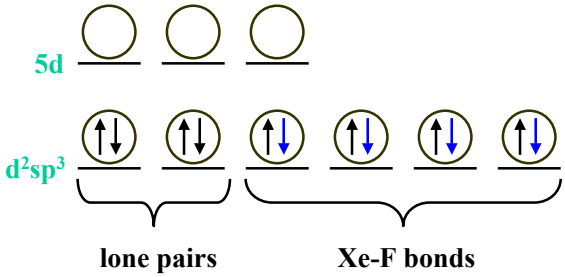
- Describe the bonding in XeF_4 using hybrid orbitals.
  - Each Xe-F bond is formed by the overlap of a xenon d^2sp^3 hybrid orbital with a singly occupied fluorine 2p orbital.
  - You can summarize this as follows:



Xe atom (ground state)



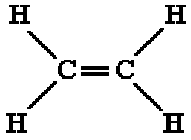
Xe atom (hybridized state)



Xe atom (in XeF_4)

Multiple Bonding

- According to valence bond theory, **one hybrid orbital** is needed **for each bond** (whether a single or multiple) and **for each lone pair**.
  - For example, consider the molecule ethene.



Multiple Bonding

- To describe the multiple bonding in ethene, we must first distinguish between two kinds of bonds.
  - A **σ (sigma) bond** is a "head-to-head" overlap of orbitals with a cylindrical shape about the bond axis. This occurs when two "s" orbitals overlap or "p" orbitals overlap along their axis.
  - A **π (pi) bond** is a "side-to-side" overlap of parallel "p" orbitals, creating an electron distribution above and below the bond axis.

Multiple Bonding

- Each carbon atom is bonded to three other atoms and no lone pairs, which indicates the need for three hybrid orbitals.
  - This implies **sp^2 hybridization**.
  - The third 2p orbital is left **unhybridized** and lies perpendicular to the plane of the trigonal sp^2 hybrids.
  - The following slide represents the sp^2 hybridization of the carbon atoms.

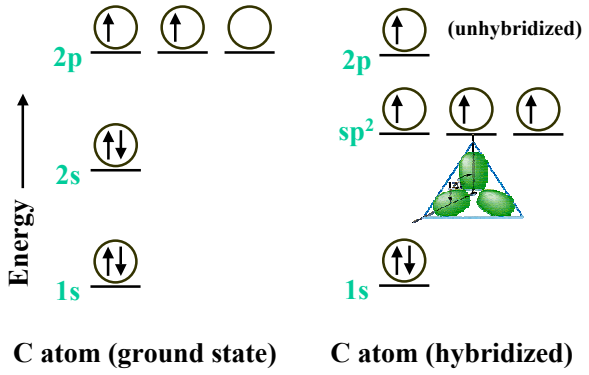
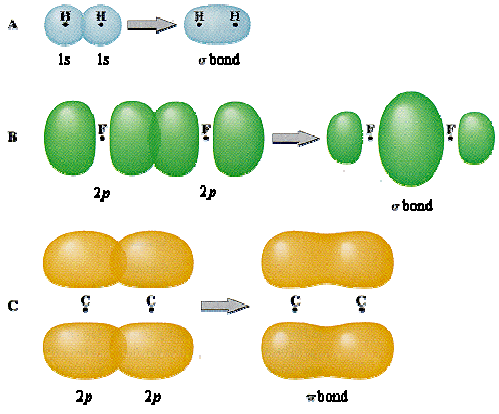
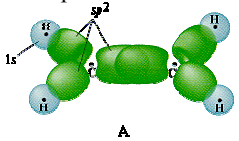


Figure 10.26

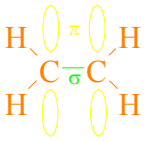


Multiple Bonding

- Now imagine that the atoms of ethene move into position.
  - Two of the **sp^2 hybrid orbitals** of each carbon overlap with the **1s orbitals** of the hydrogens.
  - The remaining sp^2 hybrid orbital on each carbon overlap to form a **σ bond**.



- A sigma (σ) bond centers along the internuclear axis.
- A pi (π) bond occupies the space above and below the internuclear axis.



Multiple Bonding

- The remaining "unhybridized" 2p orbitals on each of the carbon atoms overlap side-to-side forming a **π bond**.

- You therefore describe the carbon-carbon double bond as **one σ bond** and **one π bond**.

Figure 9.10: When an *s* and two *p* orbitals are mixed to form a set of three sp^2 orbitals, one *p* orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with narrowed lobes to show their orientations more clearly.

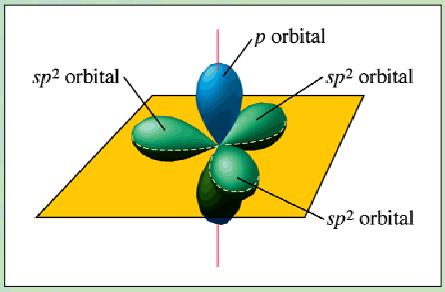


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Figure 9.11: The *s* bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

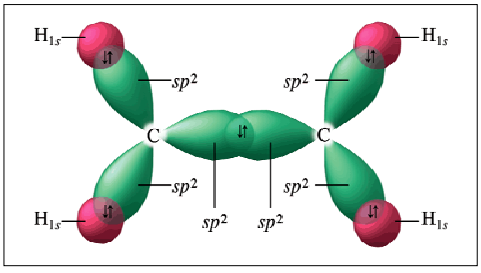


Figure 9.12: A carbon-carbon double bond consists of a *s* bond and a *p* bond. In the *s* bond the shared electrons occupy the space directly between the atoms. The *p* bond is formed from the unhybridized *p* orbitals on the two carbon atoms. In a *p* bond the shared electron pair occupies the space above and below a line joining the atoms.

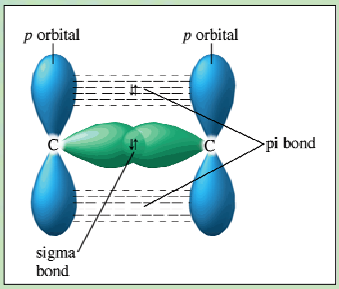


Figure 9.13: (a) The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene.

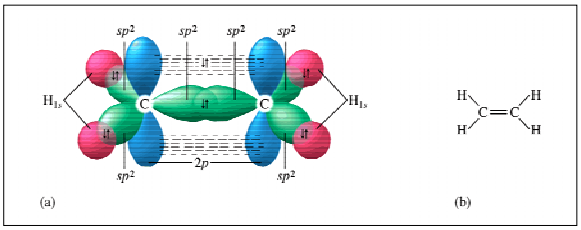


Figure 9.15: The hybrid orbitals in the CO_2 molecule.

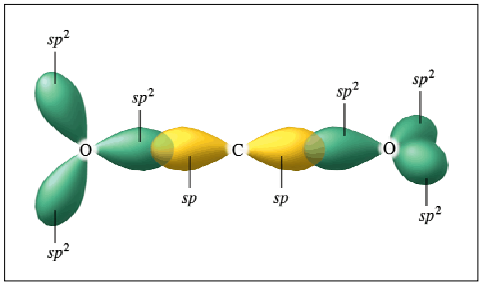


Figure 9.16: The orbital energy-level diagram for the formation of *sp* hybrid orbitals on carbon.

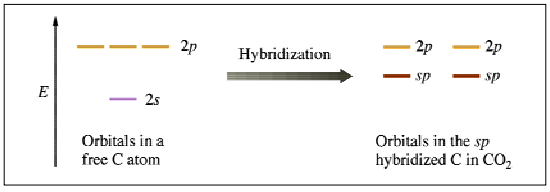


Figure 9.17: The orbitals of an *sp* hybridized carbon atom.

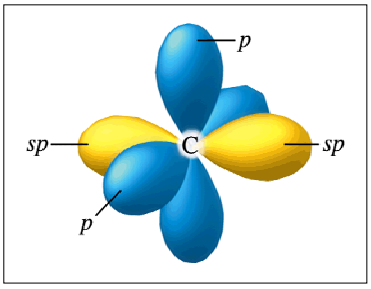


Figure 9.18: The orbital arrangement for an sp^2 hybridized oxygen atom.

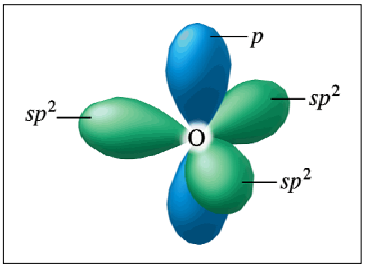


Figure 9.19: (a) The orbitals used to form the bonds in carbon dioxide. Note that the carbon-oxygen double bonds each consist of one *s* bond and one *p* bond. (b) The Lewis structure for carbon dioxide.

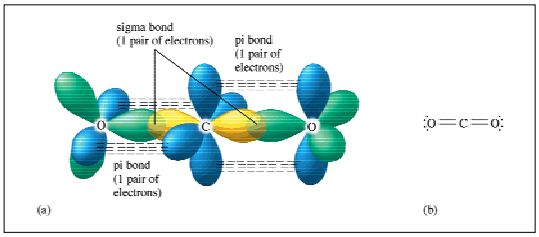
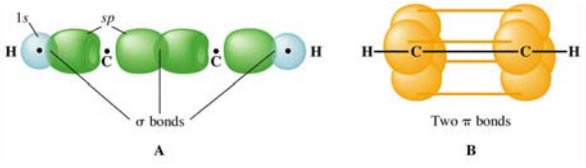


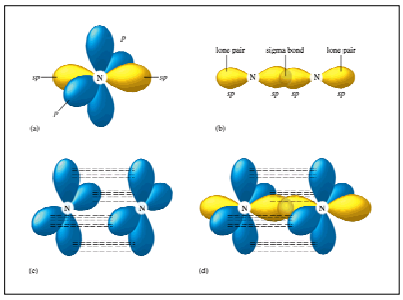
Figure 10.28: Bonding in acetylene.



H-C≡C-H

Figure 9.20: (a) An *sp* hybridized nitrogen atom. (b) The *s* bond in the N_2 molecule. (c) The two *p* bonds in N_2 are formed when electron pairs are shared between two sets of parallel *p* orbitals. (d) The total bonding picture for N_2.

:N≡N:



Molecular Orbitals (MO)

- Analagous to atomic orbitals for atoms, MOs are the quantum mechanical solutions to the organization of valence electrons in molecules.

Molecular Orbital Theory

- **Molecular orbital theory** is a theory of the electronic structure of molecules in terms of **molecular orbitals**, which may spread over several atoms or the entire molecule.
  - As atoms approach each other and their atomic orbitals overlap, molecular orbitals are formed.
  - In the quantum mechanical view, both a **bonding** and an **antibonding** molecular orbital are formed.

Figure 10.31: Formation of bonding and anti-bonding orbitals from 1 s orbitals of hydrogen atoms.