6.1 Quantum Picture of the Chemical Bond
6.2 Exact Molecular Orbital for the Simplest Molecule: \( \text{H}_2^+ \)
6.3 Molecular Orbital Theory and the Linear Combination of Atomic Orbitals Approximation for \( \text{H}_2^+ \)
6.4 Homonuclear Diatomic Molecules: First-Period Atoms
6.5 Homonuclear Diatomic Molecules: Second-Period Atoms
6.6 Heteronuclear Diatomic Molecules
6.7 Summary Comments for the LCAO Method and Diatomic Molecules
Potential energy diagram for the decomposition of the methyl methoxy radical

\[
\text{CH}_3\text{OCH}_2 + \rightarrow \text{\textbullet CH}_3 + \text{H}_2\text{CO}
\]
Key question: how can we describe chemical bond in terms of quantum mechanics?
Born-Oppenheimer Approximation: Slow Nuclei, Fast Electrons

- Nuclei are much more massive than the electrons, the nuclei in the molecules will move much more slowly than the electrons.

→ decoupling of the motions of the nuclei and the electrons

(A) Consider the nuclei to be fixed at a specific set of positions. Then solve Schrödinger’s equation for the electrons moving around and obtain the energy levels and wave functions. Next, move the nuclei a bit, and repeat the calculation. Continue this procedure in steps.

Getting each electronic energy $E_{\alpha}^{(el)}$ to the nuclear coordinates $R_{AB}$

$\alpha$: the proper set of quantum numbers
- Visualizing a group of electrons moving rapidly around the sluggish nuclei, to establish a dynamic distribution of electron density.

(a) General Chemistry I

(b) General Chemistry I
Nature of the Chemical Bond in $\text{H}_2^+$

The diagram illustrates the energy levels of molecular orbitals (MOs) for the $\text{H}_2^+$ molecule. It shows two orbitals:

- $1\sigma_g$: This is the bonding MO, which has a lower energy and is responsible for the bonding between the two hydrogen atoms.
- $1\sigma_u^*$: This is the antibonding MO, which has a higher energy and stabilizes the overall system.

The energy is plotted against the internuclear distance $R_{AB}/a_0$, where $a_0$ is the Bohr radius.
6.2 EXACT MOLECULAR ORBITALS FOR THE SIMPLEST MOLECULE: H$_2^+$

- **H$_2^+$ ion**: a single electron bound to two protons
  bond length 1.06 Å; bond dissociation energy 2.79 eV = 269 kJ mol$^{-1}$

\[
V = -\frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_B} \right) + \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{R_{AB}} \right) = V_{en} + V_{nn}
\]

- For a fixed value of $R_{AB}$, the position of the electron:
  \((x, y, z) \rightarrow (r_A, r_B, \phi)\)

- The potential energy has cylindrical (ellipsoidal) symmetry around the $R_{AB}$ axis.
Electronic Wave Functions for H$_2^+$

- isosurface comprising the wave function with 0.1 of its maximum value.
- red: + amplitude; blue: - amplitude

- **molecular orbital**: each of exact one-electron wave functions
- Four labels summarize the energy and the shape of each wave function.

1) **integer**: an index tracking the relative energy of the wave functions of each symmetry type.

   i.e.) $1\sigma_g$: the first (the lowest energy) of the $\sigma_g$ wave functions

2) **Greek letter**: how the amplitude of the wave function is distributed around the internuclear axis.

   - $\sigma$: the amplitude with cylindrical symmetry around the axis
   - $\pi$: the amplitude with a nodal plane that contains the internuclear axis
3) **g or u**: how the wave function changes as we invert our point of observation through the center of the molecule

- the wave function at \((x, y, z)\) and \((-x, -y, -z)\)

- **g**: symmetric, the same at these points
  - **gerade**
- **u**: antisymmetric, the opposite at these points
  - **ungerade**

4) **\***: how the wave function changes when the point of observation is reflected through a plane perpendicular to the internuclear axis

- **no symbol**: no changing sign upon reflection
  - **\***: changing sign upon reflection
Nature of the Chemical Bond in $\text{H}_2^+$

Energy (eV)

$R_{AB}/a_0$

$\sigma_g$  
$\sigma_u^*$  
$\sigma_u$  
$1\sigma_g$  
$1\sigma_u$  
$1\sigma_u^*$

bonding MO  
antibonding MO
Summary of the Quantum Picture of Chemical Bonding

1. **The Born-Oppenheimer approximation**: fixing the nuclei position

2. **Molecular orbital**: one-electron wave function, its square describes the distribution of electron density

3. **Bonding MO**: increased e density between the nuclei decreased effective potential energy

4. **Antibonding MO**: a node on the internuclear axis high effective potential energy

5. **σ orbital**: cylindrical symmetry; cross-sections perpendicular to the internuclear axis are discs.

6. **π orbital**: a nodal plane containing the internuclear axis
6.3 MOLECULAR ORBITAL THEORY AND THE LINEAR COMBINATION OF ATOMIC ORBITALS APPROXIMATION FOR $H_2^+$

- **LCAO method**: selecting sums and differences (linear combinations) of atomic orbitals to generate the best approximation to each type of molecular orbital

- The general form for $H_2^+$

$$\psi_{MO} = C_A(R_{AB})\varphi_A^{1s} \pm C_B(R_{AB})\varphi_B^{1s}$$

$\psi$: generic wave function

$\varphi$: wave function of atomic orbitals

The two nuclei are identical, then $C_A = \pm C_B$
MOs of the $\sigma$ bonding

$$1\sigma_g \approx \sigma_{g1s} = C_g[\phi_{1s}^A + \phi_{1s}^B]$$

$$1\sigma_u^* \approx \sigma_{u1s}^* = C_u[\phi_{1s}^A - \phi_{1s}^B]$$

The distribution of electron probability density

$$[\sigma_{g1s}]^2 = C_g^2 \left( (\phi_{1s}^A)^2 + (\phi_{1s}^B)^2 + 2\phi_{1s}^A \phi_{1s}^B \right)$$

$$[\sigma_{u1s}^*]^2 = C_u^2 \left( (\phi_{1s}^A)^2 + (\phi_{1s}^B)^2 - 2\phi_{1s}^A \phi_{1s}^B \right)$$
Antibonding

\[ \sigma_{n1s}^* = C_n [\varphi_{1s}^A - \varphi_{1s}^B] \]

[\sigma_{n1s}^*]^2

Bonding

\[ \sigma_{g1s} = C_g [\varphi_{1s}^A + \varphi_{1s}^B] \]

[\sigma_{g1s}]^2

Noninteracting

\[ \psi^2_{\text{n.i.}} = C_3^2 [ (\varphi_{1s}^A)^2 + (\varphi_{1s}^B)^2 ] \]

Wave functions

Electron densities
<table>
<thead>
<tr>
<th>Exact MO Notation</th>
<th>LCAO MO Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\sigma_g$</td>
<td>$\sigma_{g1s}$</td>
</tr>
<tr>
<td>$1\sigma_u^*$</td>
<td>$\sigma_{u1s}^*$</td>
</tr>
<tr>
<td>$2\sigma_g$</td>
<td>$\sigma_{g2s}$</td>
</tr>
<tr>
<td>$2\sigma_u^*$</td>
<td>$\sigma_{u2s}^*$</td>
</tr>
<tr>
<td>$1\pi_u$</td>
<td>$\pi_{u2p_x}$, $\pi_{u2p_y}$</td>
</tr>
<tr>
<td>$3\sigma_g$</td>
<td>$\sigma_{g2p_z}$</td>
</tr>
<tr>
<td>$1\pi_g^*$</td>
<td>$\pi_{g2p_x}^<em>$, $\pi_{g2p_y}^</em>$</td>
</tr>
<tr>
<td>$3\sigma_u^*$</td>
<td>$\sigma_{u2p_z}^*$</td>
</tr>
</tbody>
</table>
Energy of H$_2^+$ in the LCAO Approximation

$\sigma_{g1s}, \ R_{AB} = 1.32 \ \text{Å}, \ D = 1.76 \ \text{eV}$

$1\sigma_g, \ R_{AB} = 1.06 \ \text{Å}, \ D_0 = 2.79 \ \text{eV}$
Correlation diagram: the energy-level diagram within the LCAO
6.4 HOMONUCLEAR DIATOMIC MOLECULES: FIRST-PERIOD ATOMS

For He$_2^+$ and He$_2$,

$$\sigma_{g1s} = C_g \left[ \psi_{He ls}^A + \psi_{He ls}^B \right] = C_g \left[ 1s^A + 1s^B \right]$$

$$\sigma_{u1s}^* = C_u \left[ \psi_{He ls}^A - \psi_{He ls}^B \right] = C_g \left[ 1s^A - 1s^B \right]$$

Fig. 6.11. Correlation diagram for H$_2$.

Fig. 6.12. Correlation diagram for He$_2^+$. 
- **H₂**: Stabilization of bonding MO by \(2\times(-\Delta E)\) for \(\text{H}_2\) compared to the noninteracting system.

- **\(\text{He}_2^+\)**: Stabilization of bonding MO by \(2\times(-\Delta E)\) compensated by destabilization of antibonding MO by \(+\Delta E\).
  
  Net stabilization energy = \(-\Delta E\)
**Bond order**

Bond order = \((1/2) \times (\text{number of electrons in bonding MOs} \quad \text{– number of electrons in antibonding MOs})\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Electron Configuration</th>
<th>Bond Order</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2^+)</td>
<td>((\sigma_{g1s})^1)</td>
<td>(\frac{1}{2})</td>
<td>255</td>
<td>1.06</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>((\sigma_{g1s})^2)</td>
<td>1</td>
<td>431</td>
<td>0.74</td>
</tr>
<tr>
<td>(\text{He}_2^+)</td>
<td>((\sigma_{g1s})^2(\sigma_{u1s})^1)</td>
<td>(\frac{1}{2})</td>
<td>251</td>
<td>1.08</td>
</tr>
<tr>
<td>(\text{He}_2)</td>
<td>((\sigma_{g1s})^2(\sigma_{u1s})^2)</td>
<td>0</td>
<td>(~0)</td>
<td>Large</td>
</tr>
</tbody>
</table>
6.5 HOMONUCLEAR DIATOMIC MOLECULES: SECOND-PERIOD ATOMS

- LCAO-MO approximation
  
  - Combination of 2s AOs to form $\sigma_{g2s}$ and $\sigma_{u2s}^*$ MOs
    
    \[
    \sigma_{g2s} = C_g [2s^A + 2s^B] \\
    \sigma_{u2s}^* = C_u [2s^A - 2s^B]
    \]

  - Combination of 2$p_z$ AOs to form $\sigma_{g2p_z}$ and $\sigma_{u2p_z}^*$ MOs
    
    \[
    \sigma_{g2p_z} = C_g [2p_z^A - 2p_z^B] \\
    \sigma_{u2p_z}^* = C_u [2p_z^A + 2p_z^B]
    \]
Fig. 6.14. Formation of (a) $\sigma_{2p_z}$ bonding and (b) $\sigma_{u2p_z}^*$ antibonding MOs from $2p_z$ orbitals on atoms A and B.
Doubly degenerate $\pi_{2p_x}$ & $\pi_{u2p_y}$ MO’s

\[
\begin{align*}
\pi_{u2p_x} &= C_u [2p_x^A + 2p_x^B] \\
\pi_{u2p_y}^* &= C_g [2p_y^A - 2p_y^B] \\
\pi_{g2p_x} &= C_g [2p_x^A + 2p_y^B] \\
\pi_{g2p_y}^* &= C_g [2p_y^A - 2p_y^B]
\end{align*}
\]
- **Construction of MOs**
  1. Two AOs contribute significantly to bond formation only if their atomic energy levels are very close to one another
  2. Two AOs on different atoms contribute significantly to bond formation only if they overlap significantly

- **Determination of energy ordering**
  1. Average energy of bonding-antibonding pair of MOs similar to that of original AO’s
  2. Energy difference between a bonding-antibonding pair becomes large as the overlap of AO’s increases
**Fig. 6.16.** Energy levels for the homonuclear diatomics $\text{Li}_2$ through $\text{F}_2$. 

General Chemistry I
Fig. 6.17. Correlation diagrams for second-period diatomic molecules, \( \text{N}_2 \) & \( \text{F}_2 \).
General Chemistry I

$Z \geq 8$

$\sigma_{u2p_z}^*$

$\pi_{g2p_x}^*$, $\pi_{g2p_y}^*$

$\pi_{u2p_x}$, $\pi_{u2p_y}$

$\sigma_{g2p_z}$

$\sigma_{g2p_z}$

$\sigma_{u2s}$

$\sigma_{u2s}$

$\sigma_{g2s}$

$\sigma_{g2s}$

$\sigma_{u2s}$

$\sigma_{u2s}$

$\sigma_{g2s}$

$\sigma_{g2s}$

$\sigma_{u2p_z}$

$\pi_{g2p_x}^*$, $\pi_{g2p_y}^*$

$\pi_{u2p_x}$, $\pi_{u2p_y}$

$\sigma_{g2p_z}$

$\sigma_{g2p_z}$

$\sigma_{u2s}$

$\sigma_{u2s}$

$\sigma_{g2s}$

$\sigma_{g2s}$

$\sigma_{u2p_z}$
Cross-over in the correlation diagrams of Li$_2$~N$_2$ and O$_2$~Ne$_2$

- Reversed ordering of energy for Li$_2$ ~ N$_2$
  \[ \sigma_{g2p_z} > \pi_{u2p_x} \text{ (or } \pi_{u2p_y} \text{)} \]
  ~ Due to large electron-electron spatial repulsions between electrons in $\sigma_{g2p_z}$ and $\sigma_{2u2s}^*$ MO’s.

- Normal ordering of energy for O$_2$, F$_2$, Ne$_2$
  \[ \sigma_{g2p_z} < \pi_{u2p_x} \text{ (or } \pi_{u2p_y} \text{)} \]
  ~ As Z increases, the repulsion decreases since electrons in $\sigma_{g2s}$ and $\sigma_{2u2s}^*$ MO’s are drawn more strongly toward the nucleus.
**Fig. 6.18.** (a) Paramagnetic liquid oxygen, $\text{O}_2$, and (b) diamagnetic liquid nitrogen, $\text{N}_2$, pours straight between the poles of a magnet.

**TABLE 6.3**

Molecular Orbitals of Homonuclear Diatomic Molecules

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of Valence Electrons</th>
<th>Valence Electron Configuration</th>
<th>Bond Order</th>
<th>Bond Length (Å)</th>
<th>Bond Energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>2</td>
<td>$(\sigma_{g1s})^2$</td>
<td>1</td>
<td>0.74</td>
<td>431</td>
</tr>
<tr>
<td>$\text{He}_2$</td>
<td>4</td>
<td>$(\sigma_{g1s})^2(\sigma^*_{u1s})^2$</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Li}_2$</td>
<td>2</td>
<td>$(\sigma_{g2s})^2$</td>
<td>1</td>
<td>2.67</td>
<td>105</td>
</tr>
<tr>
<td>$\text{Be}_2$</td>
<td>4</td>
<td>$(\sigma_{g2s})^2(\sigma^*_{u2s})^2$</td>
<td>0</td>
<td>2.45</td>
<td>9</td>
</tr>
<tr>
<td>$\text{B}_2$</td>
<td>6</td>
<td>$(\sigma_{g2s})^2(\sigma^*<em>{u2s})^2(\pi</em>{u2p})^2$</td>
<td>1</td>
<td>1.59</td>
<td>289</td>
</tr>
<tr>
<td>$\text{C}_2$</td>
<td>8</td>
<td>$(\sigma_{g2s})^2(\sigma^*<em>{u2s})^2(\pi</em>{u2p})^4$</td>
<td>2</td>
<td>1.24</td>
<td>599</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>10</td>
<td>$(\sigma_{g2s})^2(\sigma^*<em>{u2s})^2(\pi</em>{u2p})^4(\pi_{g2p})^2$</td>
<td>3</td>
<td>1.10</td>
<td>942</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>12</td>
<td>$(\sigma_{g2s})^2(\sigma^*<em>{u2s})^2(\sigma</em>{g2p_u})^2(\pi_{u2p})^4(\pi_{g2p})^2$</td>
<td>2</td>
<td>1.21</td>
<td>494</td>
</tr>
<tr>
<td>$\text{F}_2$</td>
<td>14</td>
<td>$(\sigma_{g2s})^2(\sigma^*<em>{u2s})^2(\sigma</em>{g2p_u})^2(\pi_{u2p})^4(\pi_{g2p})^4$</td>
<td>1</td>
<td>1.41</td>
<td>154</td>
</tr>
<tr>
<td>$\text{Ne}_2$</td>
<td>16</td>
<td>$(\sigma_{g2s})^2(\sigma^<em><em>{u2s})^2(\sigma</em>{g2p_u})^2(\pi_{u2p})^4(\pi_{g2p})^4(\sigma^</em>_{u2p})^2$</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\pi_{u2p}$ refers to the $\pi$ orbitals constructed from the $2p_x$ and/or the $2p_y$ orbitals.
Fig. 6.19. Trends in several properties with the number of valence electrons in the second-row diatomic molecules.
6.8 Valence Bond Theory and the Electron Pair Bond
6.9 Orbital Hybridization for Polyatomic Molecules
6.10 Predicting Molecular Structures and Shapes
6.11 Using the LCAO and Valence Bond Methods Together
6.12 Summary and Comparison of the LCAO and Valence Bond Methods
6.8 VALENCE BOND THEORY AND THE ELECTRON PAIR BOND

- Explains the Lewis electron pair model
- VB wave function for the bond is a product of two one-electron AOs
- Easily describes structure and geometry of bonds in polyatomic molecules

Nobel Prizes
Chemistry (‘54) “The Nature of Chemical Bonding”
Peace (‘62)

Walther Heitler (DE, 1904-1981)
Fritz London (DE, 1900-1954)
John C. Slater (US, 1900-1976)
Linus Pauling (US, 1901-1994)
➢ Single Bonds

- At very large values of $R_{AB}$,

$$\psi^{el}(r_1A, r_2B; R_{AB}) = c(R_{AB})\phi^A(r_1A)\phi^B(r_2B)$$

independent atoms

- As the atoms begin to interact strongly,

$$\psi^{el}(r_1A, r_2B; R_{AB}) = c_1(R_{AB})\phi^A(r_1A)\phi^B(r_2B)$$

$$+ c_2(R_{AB})\phi^A(r_2A)\phi^B(r_1B)$$

indistinguishable

$$c_1 = \pm c_2$$

cf) LCAO-MO approximation

$$\sigma_{g2s} = C_g[2s^A + 2s^B]$$

$$\sigma_{u2s}^* = C_u[2s^A - 2s^B]$$
**VB wave function for the single bond in a H₂ molecule**

\[
\psi_g^{\text{el}} = C_1 \left[ 1s^A (1) 1s^B (2) + 1s^A (2) 1s^B (1) \right]
\]

\[
\psi_u^{\text{el}} = C_1 \left[ 1s^A (1) 1s^B (2) - 1s^A (2) 1s^B (1) \right]
\]

**Fig. 6.24.** (a) The electron density \( \rho_g \) for \( \psi_g^{\text{el}} \) and \( \rho_u \) for \( \psi_u^{\text{el}} \) in the simple VB model for H₂. (b) Three-dimensional isosurface of the electron density for the \( \psi_g^{\text{el}} \) wave function in the H₂ \( \sigma \) bond.
For $\text{F}_2 \sigma$ bond,

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

Lewis diagram for $\text{F}_2$.

For $\text{HF} \sigma$ bond,

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

Lewis diagram for $\text{HF}$. 
Multiple Bonds

N: \((1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1\)

\[ \psi_{\sigma}^{bond} = C_1[2p^A_x(1)2p^B_x(2) + 2p^A_x(2)2p^B_x(1)] \]

\[ \psi_{\pi_x}^{bond}(1,2) = C_1[2p^A_x(1)2p^B_x(2)] + C_1[2p^A_x(2)2p^B_x(1)] \]

\[ \psi_{\pi_y}^{bond}(1,2) = C_1[2p^A_y(1)2p^B_y(2)] + C_1[2p^A_y(2)2p^B_y(1)] \]

Lewis diagram for \(N_2\).
Polyatomic Molecules

Electron promotion: electron relocated to a higher-energy orbital

Promotion

Hybridization

all C-H bonds equivalent

C\text{2s} \quad \text{C2p}

35 \quad \text{Carbon, [He]}2s^22p_x^12p_y^1

1 \quad \text{Methane, CH}_4

36 \quad \text{Carbon, [He]}2s^12p_x^12p_y^12p_z^1

38 \quad \text{sp}^3 \text{ hybridized carbon}
6.9 ORBITAL HYBRIDIZATION FOR POLYATOMIC MOLECULES

- **sp-hybridization**  \[ \text{BeH}_2 \]

Promotion:  \[ \text{Be}: (1s)^2(2s)^2 \rightarrow \text{Be}: (1s)^2(2s)^1(2p_z)^1 \]

Two equivalent \textit{sp} hybrid orbitals:

\[
\chi_1(r) = \frac{1}{\sqrt{2}}[2s + 2p_z] \quad \text{and} \quad \chi_2(r) = \frac{1}{\sqrt{2}}[2s - 2p_z]
\]

New electronic configuration, \( \text{Be}: (1s)^2(\chi_1)^1(\chi_2)^1 \)

Wave functions for the two bonding pairs of electrons:

\[
\psi_{\sigma_1}^{\text{bond}}(1, 2) = c_+ \left[ \chi_1(1)1s^H(2) + \chi_1(2)1s^H(1) \right]
\]

\[
\psi_{\sigma_2}^{\text{bond}}(3, 4) = c_- \left[ \chi_2(3)1s^H(4) + \chi_2(4)1s^H(3) \right]
\]

A pair of \( \sigma \) bonds at an angle 180° apart \( \rightarrow \) linear molecule
Fig. 6.28. Formation, shapes, and bonding of the $sp$ hybrid orbitals in the BeH$_2$ molecule. (a) The 2s and 2$p_z$ orbitals of the Be atom. (b) The two $sp$ hybrid orbitals formed from the 2s and 2$p_z$ orbitals on the Be atom. (c) The two $\sigma$ bonds that form from the overlap of the $sp$ hybrid orbitals with the H1s orbitals, making two single bonds in the BeH$_2$ molecule. (d) Electron density in the two $\sigma$ bonds.
sp\textsuperscript{2}-hybridization \quad BH\textsubscript{3}

Promotion: \quad B: (1s)^2(2s)^2(2p_x)^1 \rightarrow B: (1s)^2(2s)^1(2p_x)^1(2p_y)^1

Three equivalent sp\textsuperscript{2} hybrid orbitals:

\begin{align*}
\chi_1(r) &= 2s + 2^{1/2}2p_y \\
\chi_2(r) &= 2s + (3/2)^{1/2}2p_x - (1/2)^{1/2}2p_y \\
\chi_3(r) &= 2s - (3/2)^{1/2}2p_x - (1/2)^{1/2}2p_y
\end{align*}

New electronic configuration, B: (1s)^2(\chi_1)^1(\chi_2)^1(\chi_3)^1

Three bonds at an angle 120° in a plane \rightarrow trigonal planar
Gene (a) Atomic orbitals  (b) $sp^2$ hybrid orbitals  (c) Hybrid orbital overlap  (d) Electron density
**sp³-hybridization**  \( \text{CH}_4 \)

Promotion: \( \text{C}: (1s)^2(2s)^2(2p_x)^1(2p_y)^1 \rightarrow \text{C}: (1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1 \)

Four equivalent \( sp^3 \) hybrid orbitals:

\[
\begin{align*}
\chi_1(r) & = \frac{1}{2} \left[ 2s + 2p_x + 2p_y + 2p_z \right] \\
\chi_2(r) & = \frac{1}{2} \left[ 2s - 2p_x - 2p_y + 2p_z \right] \\
\chi_3(r) & = \frac{1}{2} \left[ 2s + 2p_x - 2p_y - 2p_z \right] \\
\chi_4(r) & = \frac{1}{2} \left[ 2s - 2p_x + 2p_y - 2p_z \right]
\end{align*}
\]

New electronic configuration, \( \text{C}: (1s)^2(\chi_1)^1(\chi_2)^1(\chi_3)^1(\chi_4)^1 \)

Four bonds at an angle 109.5° generating tetrahedral geometry
Fig. 6.30. Shapes and relative orientations of the four $sp^3$ hybrid orbitals in CH$_4$ pointing at the corners of a tetrahedron with the C atom at its center.
### Summary of Hybridization Results

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Hybrid orbitals on central atom</th>
<th>Molecular geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX$_2$</td>
<td>$sp$</td>
<td>Linear</td>
<td>BeH$_2$</td>
</tr>
<tr>
<td>AX$_3$</td>
<td>$sp^2$</td>
<td>Trigonal planar</td>
<td>BH$_3$</td>
</tr>
<tr>
<td>AX$_4$</td>
<td>$sp^3$</td>
<td>Tetrahedral</td>
<td>CH$_4$</td>
</tr>
</tbody>
</table>
Hybridization and Lone Pairs

- **NH$_3$:** $sp^3$ hybrid orbitals
  - trigonal pyramid with three equivalent bonds

- **H$_2$O:** $sp^3$ hybrid orbitals
  - two lone pairs → the bent or angular structure
Multiple Bonds in Organic Compounds

Ethylene, C₂H₄

Promotion, C: (1s)^2(2s)^2(2pₓ)^1(2pᵧ)^1 → C: (1s)^2(2s)^1(2pₓ)^1(2pᵧ)^1(2p₂)^1

Formation of three sp² hybrid orbitals from the 2s and two 2p orbitals

New electronic configuration, C: (1s)^2(χ₁)^1(χ₂)^1(χ₃)^1(2p₂)^1

Five σ bonds: C₁χ₁-H₁s, C₁χ₂-H₁s, C₂χ₁-H₁s, C₂χ₂-H₁s, C₁χ₃ - C₂χ₃

One π bond: C₁2p₂-C₂2p₂

One double bond (C=C): σ(C₁χ₃ - C₂χ₃) + π(C₁2p₂-C₂2p₂)
**Fig. 6.33.** Formation of σ bonds in ethylene.

**Fig. 6.34.** Formation of a π bond in ethylene.
Acetylene, $\text{C}_2\text{H}_2$ \[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]

Linear, triple bond, H-C-C bond angles of 180°

Promotion, C: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1 \rightarrow \text{C: (1s)}^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$

Formation of two sp hybrid orbitals from the 2s and the 2p\text{z} orbitals

New electronic configuration, C: $(1s)^2(\chi_1)^1(\chi_2)^1(2p_x)^1(2p_y)^1$

Three $\sigma$ bonds: $C_1\chi_1$-H1s, $C_2\chi_1$-H1s, $C_1\chi_2$- $C_2\chi_2$

Two $\pi$ bonds: $C_12p_x$-$C_22p_x$, $C_12p_y$-$C_22p_y$

One triple bond: $\sigma (C_1\chi_2$- $C_2\chi_2) + \pi (C_12p_x$-$C_22p_x$, $C_12p_y$-$C_22p_y)$
**Fig. 6.35.** Formation of $\sigma$ bonds in acetylene.

**Fig. 6.36.** Formation of two $\pi$ bonds in acetylene.
6.10 PREDICTING MOLECULAR STRUCTURES AND SHAPE

- Description of the structure and shape of a molecule

(1) Determine the empirical formula.
(2) Determine the molecular formula.
(3) Determine the structural formula from a Lewis diagram.
(4) Determine the molecular shape from experiments.
(5) Identify the hybridization scheme that best explains the shape predicted by VSEPR.
EXAMPLE 6.4

Hydrazine: Elemental analysis shows its mass per cent composition to be 87.419% nitrogen and 12.581% hydrogen. The density of hydrazine at 1 atm and 25 °C is 1.31 gL⁻¹. Determine the molecular formula for hydrazine. Predict the structure of hydrazine. What is the hybridization of the N atoms?

1. Elemental analysis: N(87.419%), H (12.581%)
2. Empirical formula: \( \text{NH}_2 \rightarrow (\text{Molar mass})_{\text{emp}} \)
3. Molar mass calculate from the ideal gas law (with known \( \rho \))
4. Molar mass / (Molar mass)\(_{\text{emp}}\) = 2, Molecular formula: \( \text{N}_2\text{H}_4 \)
5. Lewis diagram, steric number (4) \( \rightarrow \text{sp}^3 \) hybrid orbitals
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Steric Number</th>
<th>Number of Lone Pairs</th>
<th>Orbital Hybridization</th>
<th>Predicted Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX₂</td>
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<td>sp</td>
<td>Linear</td>
<td>BeH₂, CO₂</td>
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<td>0</td>
<td>sp²</td>
<td>Trigonal planar</td>
<td>BF₃, SO₃</td>
</tr>
<tr>
<td>AX₂</td>
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<td>1</td>
<td>sp²</td>
<td>Bent</td>
<td>SO₂</td>
</tr>
<tr>
<td>AX₄</td>
<td>4</td>
<td>0</td>
<td>sp³</td>
<td>Tetrahedral</td>
<td>CF₄, SO₄²⁻</td>
</tr>
<tr>
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<td>4</td>
<td>1</td>
<td>sp³</td>
<td>Trigonal pyramidal</td>
<td>NH₃, PF₃, AsCl₃</td>
</tr>
<tr>
<td>AX₂</td>
<td>4</td>
<td>2</td>
<td>sp³</td>
<td>Bent</td>
<td>H₂O, H₂S, SF₂</td>
</tr>
</tbody>
</table>

Table 6.5: Molecular Shapes Predicted by the Valence Shell Electron-Pair Repulsion Theory and Rationalized by Orbital Hybridization.
Key question: how can we describe chemical bond in terms of quantum mechanics?
Problem Sets

For Chapter 6,

2, 18, 48, 52, 66, 72