PHYSICAL ORGANIC CHEMISTRY

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Textbook:


References:


Grading: One midterm (45%) one final exam (45%) and 4 quizzes (10%) homeworks
Review of Concepts in Organic Chemistry

§ Quantum number and atomic orbitals
Atomic orbital wavefunctions are associated with four quantum numbers: principle q. n. \((n=1,2,3)\), azimuthal q. n. \((m=0,1,2,3\) or \(s,p,d,f,..\)), magnetic q. n. \((\text{for } p, -1, 0, 1; \text{for } d, -2, -1, 0, 1, 2)\), electron spin q. n. \(=1/2, -1/2\).

§ Molecular dimensions

Atomic radius
ionic radius, \(r_i\) : size of electron cloud around an ion.
covalent radius, \(r_c\) : half of the distance between two atoms of same element bond to each other.
van der Waal radius, \(r_{vdw}\) : the effective size of atomic cloud around a covalently bonded atoms.

![Figure 1.1: Radii values for chlorine.](image)

Cl⁻ Cl₂ CH₃Cl

<table>
<thead>
<tr>
<th>Atom</th>
<th>van der Waals Radius ((r_{vdw})^{31})</th>
<th>Ionic Radius(^{32})</th>
<th>Covalent Radii ((r_c)^{33})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.11 Å</td>
<td>H⁻ 2.08 Å</td>
<td>0.30 Å(^{34})</td>
</tr>
<tr>
<td>C</td>
<td>1.68</td>
<td>C⁴⁻ 2.60</td>
<td>0.772</td>
</tr>
<tr>
<td>N</td>
<td>1.53</td>
<td>N³⁻ 1.71</td>
<td>0.70</td>
</tr>
<tr>
<td>O</td>
<td>1.50</td>
<td>O²⁻ 1.40</td>
<td>0.66</td>
</tr>
<tr>
<td>F</td>
<td>1.51</td>
<td>F⁻ 1.36</td>
<td>0.64</td>
</tr>
<tr>
<td>Cl</td>
<td>1.84</td>
<td>Cl⁻ 1.81</td>
<td>0.99</td>
</tr>
<tr>
<td>Br</td>
<td>1.96</td>
<td>Br⁻ 1.95</td>
<td>1.14</td>
</tr>
<tr>
<td>I</td>
<td>2.13</td>
<td>I⁻ 2.16</td>
<td>1.33</td>
</tr>
<tr>
<td>P</td>
<td>1.85</td>
<td>P³⁻ 2.12</td>
<td>1.10</td>
</tr>
<tr>
<td>S</td>
<td>1.82</td>
<td>S²⁻ 1.84</td>
<td>1.04</td>
</tr>
<tr>
<td>Si</td>
<td>2.04</td>
<td>Si⁴⁻ 2.71</td>
<td>1.17</td>
</tr>
</tbody>
</table>
**Bond length** measures the distance between nucleus (or the local centers of electron density).

**Bond angle** measures the angle between lines connecting different nucleus.

### Table 1.1 Bond lengths and bond angles for methyl halides. *

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$r_{\text{C-H}}$ (Å)</th>
<th>$r_{\text{C-X}}$ (Å)</th>
<th>$&lt;\text{H-C-H}$</th>
<th>$&lt;\text{H-C-X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$F</td>
<td>1.105</td>
<td>1.385</td>
<td>109°54’</td>
<td>109°2’</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>1.096</td>
<td>1.781</td>
<td>110°52’</td>
<td>108°0’</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>1.11</td>
<td>1.939</td>
<td>111°12’</td>
<td>107°14’</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>1.096</td>
<td>2.139</td>
<td>111°50’</td>
<td>106°58’</td>
</tr>
</tbody>
</table>

*Data from reference 22.

Molecular volume and surface area can be the sum of atomic volume (or group volume) and surface area.

→ Principle of additivity (group increment)

### Table 1.3 Group contributions to van der Waals atomic volume ($V_w$) and surface area ($A_w$). *

<table>
<thead>
<tr>
<th>Group</th>
<th>$V_w$, cm$^3$/mole</th>
<th>$A_w$, cm$^2$/mole × 10$^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane, C bonded to four other carbon atoms</td>
<td>3.33</td>
<td>0</td>
</tr>
<tr>
<td>Alkane, CH bonded to three other carbon atoms</td>
<td>6.78</td>
<td>0.57</td>
</tr>
<tr>
<td>Alkane, CH$_2$ bonded to two other carbon atoms</td>
<td>10.23</td>
<td>1.35</td>
</tr>
<tr>
<td>Alkane, CH$_3$ bonded to one other carbon atom</td>
<td>13.67</td>
<td>2.12</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>17.12</td>
<td>2.90</td>
</tr>
<tr>
<td>F, bonded to a 1° carbon atom</td>
<td>5.72</td>
<td>1.10</td>
</tr>
<tr>
<td>F, bonded to a 2° or 3° carbon atom</td>
<td>6.20</td>
<td>1.18</td>
</tr>
<tr>
<td>Cl, bonded to a 1° carbon atom</td>
<td>11.62</td>
<td>1.80</td>
</tr>
<tr>
<td>Cl, bonded to a 2° or 3° carbon atom</td>
<td>12.24</td>
<td>1.82</td>
</tr>
<tr>
<td>Br, bonded to a 1° carbon atom</td>
<td>14.40</td>
<td>2.08</td>
</tr>
<tr>
<td>Br, bonded to a 2° or 3° carbon atom</td>
<td>14.60</td>
<td>2.09</td>
</tr>
<tr>
<td>I, bonded to a 1° carbon atom</td>
<td>19.18</td>
<td>2.48</td>
</tr>
<tr>
<td>I, bonded to a 2° or 3° carbon atom</td>
<td>20.35</td>
<td>2.54</td>
</tr>
</tbody>
</table>

*Data from reference 26.

Physical basis of additivity law: the forces between atoms in the same molecule or different molecules are very "short range".
Theoretical determination of molecular size: depending on the boundary condition.

**Figure 1.2**
Contour maps and van der Waals radii for methane (left) and propane (right). (Reproduced from reference 35.)

Boundary is a certain minimum value of electron density.

Molecular volume (1 au = 6.748e/Å³),

<table>
<thead>
<tr>
<th></th>
<th>0.001au</th>
<th>0.02au</th>
<th>expt'l</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>25.53</td>
<td>19.58</td>
<td>17.12</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>39.54</td>
<td>31.10</td>
<td>27.34</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>53.64</td>
<td>42.76</td>
<td>37.57</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>67.64</td>
<td>44.13</td>
<td>47.80</td>
</tr>
</tbody>
</table>
§ Heats of formation and reaction

**Heat of formation**: Difference in enthalpy between the compound and starting elements in their standard states

- obtained indirectly from other components of known $\Delta H_f^\circ$
- correct for necessary phase change (such as vaporization, sublimation)
- correct for $\Delta H$ at different $T$ by heat capacity
- experimental measurement by calorimeter

$$m \, C_{(gr)} + \frac{n}{2} \, H_2(g) \rightarrow C_mH_n \quad \Delta H_f^\circ$$

To calculate the heat of formation of

$$6 \, C_{(gr)} + 4 \, H_2(g) + O_2(g) \rightarrow 6 \, CO_2(g) + 4 \, H_2O(g) \quad \Delta H_f^\circ$$

$$\Delta H_{comb} = -735.9 \, \text{Kcal/mol}$$

$$6 \, C_{(gr)} + 6 \, O_2(g) \rightarrow 6 \, CO_2(g) \quad \Delta H_{comb} = -94.05 \, (\text{Kcal/mol C}) \times 6$$

$$4 \, H_2(g) + O_2(g) \rightarrow 4 \, H_2O(g) \quad \Delta H_{comb} = -68.32 \, (\text{Kcal/mol H}_2)$$

$$\Delta H_{subl} = 21.46 \, \text{Kcal/mol}$$

$$\Delta H_f^\circ = 6 \times (-94.05) + 4 \times (-68.32) + 735.9 + 21.46$$

$$= -80.22 \, (\text{Kcal/mol})$$
Relative difference in heat of formation

\[ \text{Relative difference in heat of formation} \]

\[ \text{The heat of hydrogenation is much smaller than the heat of combustion. Both will give the difference of the stability of the two isomers.} \]

\[ \text{§ Bond increment calculation of heat of formation} \]

\[ \text{Principle of additivity} : \text{ The property of a large molecule can be approximated by adding the contribution of its component.} \]

\[ \begin{array}{|c|c|c|}
\hline
\text{Compound} & \Delta H_f^0 \text{ (kcal/mol) obs.} & \Delta H_f^0 \text{ (kcal/mol) calc.*} \\
\hline
\text{Methane} & -17.89 & -15.32 \\
\text{Ethane} & -20.24 & -20.25 \\
\text{Propane} & -24.82 & -25.18 \\
\text{Butane} & -30.15 & -30.11 \\
\hline
\end{array} \]

*Calculations are based on bond increment values in Table 1.5.
For butane

\[ (-3.83) \times 10^3 + 3 \times (2.73) = -30.11 \text{ Kcal/mol} \]
§ Group increment calculation of heat of formation

<table>
<thead>
<tr>
<th>Group</th>
<th>$\Delta H^\circ_{f,298}$ (kcal/mol)</th>
<th>Group</th>
<th>$\Delta H^\circ_{f,298}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C $\rightarrow$ (H)$_2$(C)</td>
<td>-10.08</td>
<td>C$\rightarrow$(C)</td>
<td>8.64</td>
</tr>
<tr>
<td>C $\rightarrow$ (H)$_2$(C)$_2$</td>
<td>-4.95</td>
<td>C$\rightarrow$(C)$_2$(H)$_2$</td>
<td>-4.86</td>
</tr>
<tr>
<td>C $\rightarrow$ (H)(C)$_3$</td>
<td>-1.90</td>
<td>C$\rightarrow$(C)$_4$(H)$_2$</td>
<td>-0.98</td>
</tr>
<tr>
<td>C $\rightarrow$ (C)$_4$</td>
<td>0.50</td>
<td>C$\rightarrow$(C)</td>
<td>26.93</td>
</tr>
<tr>
<td>C$\rightarrow$(H)$_2$</td>
<td>6.26</td>
<td>C$\rightarrow$(C)$_2$</td>
<td>27.55</td>
</tr>
<tr>
<td>C$\rightarrow$(H)(C)</td>
<td>8.59</td>
<td>C$\rightarrow$(C)$_4$</td>
<td>29.20</td>
</tr>
<tr>
<td>C$\rightarrow$(C)$_4$</td>
<td>10.34</td>
<td>C$\rightarrow$(H)</td>
<td>3.30</td>
</tr>
<tr>
<td>C$\rightarrow$(C)$_2$(H)</td>
<td>6.78</td>
<td>C$\rightarrow$(C)$_2$(H)</td>
<td>5.51</td>
</tr>
<tr>
<td>C$\rightarrow$(C)$_4$(H)</td>
<td>8.88</td>
<td>C$\rightarrow$(C)$_4$(H)</td>
<td>5.68</td>
</tr>
<tr>
<td>[C$_4$$\rightarrow$(C)$_2$(H)]</td>
<td>6.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reproduced from Table XXXIII, p. 316 of reference 48.

Figure 1.4 Gauche interactions in hexane isomers.

3 x (-10.08) + 2 x (-4.95) + 1 x (-1.90) = -42.04 Kcal/mol (obs. -41.66)

4 x (-10.08) + 2 x (-1.90) = -44.12 Kcal/mol (obs. -42.49)

Further refinements correct for van der Waal strain, angle strain.

The electrostatic model for the stability of branched alkanes

Charge on H: $0.278 \times 10^{-10}$ esu
Charge on C: neutralizing charge
Branched more stable

JACS 1975, 97, 704.
**Homolytic & Heterolytic Dissociation Energies**

\[
\begin{align*}
A - B_{(g)} & \overset{\text{homolysis}}{\rightleftharpoons} A \cdot_{(g)} + B \cdot_{(g)} & \Delta H^\circ_{\text{hom}} : \text{standard homolytic bond dissociation energy} \\
& \overset{\text{heterolysis}}{\rightleftharpoons} A^+_{(g)} + B^-_{(g)} & \\
& \overset{\text{electron transfer}}{\rightleftharpoons} & \\
\end{align*}
\]

\[\Delta H^\circ_{\text{het}} : \text{standard heterolytic bond dissociation energy}\]

In gas phase: \(\Delta H^\circ_{\text{het}} > \Delta H^\circ_{\text{hom}}\)

In solution: solvation of ions can lower \(\Delta H^\circ_{\text{het}}\), so that heterolysis becomes favorable.

Use bond dissociation energy to calculate reaction \(\Delta H^\circ_r\)

e.g. \(\text{CH}_3 - H \rightarrow \text{CH}_3 \cdot + H \cdot \quad \Delta H^\circ_r = +104 \text{ Kcal/mol}\)

\(\text{Cl} - \text{Cl} \rightarrow \text{Cl} \cdot + \text{Cl} \cdot \quad \Delta H^\circ_r = +58 \text{ Kcal/mol}\)

\(\text{Cl} \cdot + \text{CH}_3 \cdot \rightarrow \text{CH}_3\text{Cl} \quad \Delta H^\circ_r = -84 \text{ Kcal/mol}\)

\(\text{Cl} \cdot + H \cdot \rightarrow H - \text{Cl} \quad \Delta H^\circ_r = -103 \text{ Kcal/mol}\)

\(\text{CH}_3 - H + \text{Cl} - \text{Cl} \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \quad \Delta H^\circ_r = -25 \text{ Kcal}\)

**Hess Law**: The difference in enthalpy between products and reactants is independent of the path of the reaction.

by heat of formation

\[
\Delta H^\circ_r = \sum \Delta H^\circ_f(\text{prd}) - \sum \Delta H^\circ_f(\text{pre})
\]

\[= -23.7 \text{ Kcal/mol at 300}^\circ\text{C}\]
§ Bond length and bond energy

Bond length is nearly a constant property between

Table 1.4

Typical Bond Lengths of Some Covalent Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single bonds</td>
<td></td>
<td>Double bonds</td>
<td></td>
</tr>
<tr>
<td>C(sp²)-C(sp²)</td>
<td>1.53-1.55</td>
<td>C(sp²)-C(sp²)</td>
<td>1.31-1.34</td>
</tr>
<tr>
<td>C(sp²)-C(sp³)</td>
<td>1.49-1.52</td>
<td>C(sp²)-C(sp³)</td>
<td>1.38-1.40</td>
</tr>
<tr>
<td>C(sp²)-C(sp³)</td>
<td>1.45-1.46</td>
<td>C(sp²)-O(sp³)</td>
<td>1.19-1.22</td>
</tr>
<tr>
<td>C(sp³)-C(sp³)</td>
<td>1.47-1.48</td>
<td>C(sp²)-O(sp³)</td>
<td>1.19-1.20</td>
</tr>
<tr>
<td>C(sp³)-O(sp³)</td>
<td>1.37-1.38</td>
<td>C(sp²)-O(sp³)</td>
<td>1.22-1.24</td>
</tr>
<tr>
<td>C(sp³)-N(sp³)</td>
<td>1.42-1.44</td>
<td>C(sp²)-N(sp³)</td>
<td>1.35</td>
</tr>
<tr>
<td>C-F</td>
<td>1.39-1.43</td>
<td>C(sp³)-C(sp³)</td>
<td>1.17-1.20</td>
</tr>
<tr>
<td>C-Cl</td>
<td>1.78-1.85</td>
<td>bond</td>
<td></td>
</tr>
<tr>
<td>C-Br</td>
<td>1.95-1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-I</td>
<td>2.15-2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(sp³)-H</td>
<td>1.09-1.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(sp³)-H</td>
<td>1.075-1.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(sp³)-H</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(sp³)-H</td>
<td>1.00-1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-H</td>
<td>0.96-0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-H</td>
<td>1.00-1.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 1.3. Bond Energies (kcal/mol)

A. Some Common Bond Energies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>103</td>
</tr>
<tr>
<td>C–C</td>
<td>81</td>
</tr>
<tr>
<td>O–O</td>
<td>34</td>
</tr>
<tr>
<td>Cl–Cl</td>
<td>57</td>
</tr>
<tr>
<td>Br–Br</td>
<td>45</td>
</tr>
<tr>
<td>I–I</td>
<td>36</td>
</tr>
<tr>
<td>C–H</td>
<td>98</td>
</tr>
<tr>
<td>N–H</td>
<td>92</td>
</tr>
<tr>
<td>O–H</td>
<td>109</td>
</tr>
<tr>
<td>Cl–H</td>
<td>102</td>
</tr>
<tr>
<td>Br–H</td>
<td>87</td>
</tr>
<tr>
<td>I–H</td>
<td>71</td>
</tr>
<tr>
<td>C≡C</td>
<td>145</td>
</tr>
<tr>
<td>C≡C</td>
<td>198</td>
</tr>
<tr>
<td>N≡N</td>
<td>225</td>
</tr>
<tr>
<td>C≡O</td>
<td>173</td>
</tr>
<tr>
<td>C–O</td>
<td>79</td>
</tr>
<tr>
<td>C–N</td>
<td>66</td>
</tr>
</tbody>
</table>

B. Some Specific Bond Dissociation Energies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃C–H</td>
<td>104</td>
</tr>
<tr>
<td>CH₃CH₂–H</td>
<td>98</td>
</tr>
<tr>
<td>H₂C≡CH–H</td>
<td>104</td>
</tr>
<tr>
<td>H₂C=CH–H</td>
<td>85</td>
</tr>
<tr>
<td>PhCH₂–H</td>
<td>85</td>
</tr>
<tr>
<td>H₂N–H</td>
<td>103</td>
</tr>
<tr>
<td>CH₃NH–H</td>
<td>92</td>
</tr>
<tr>
<td>CH₃O–H</td>
<td>102</td>
</tr>
<tr>
<td>H₃C–CH₂</td>
<td>88</td>
</tr>
<tr>
<td>PhC=CH₂</td>
<td>85</td>
</tr>
<tr>
<td>H₂C≡CH</td>
<td>163f</td>
</tr>
<tr>
<td>H₂C=CH₂</td>
<td>163f</td>
</tr>
<tr>
<td>H₂C≡CH</td>
<td>230f</td>
</tr>
</tbody>
</table>

§ Polarizability

The ability of electron cloud to distort in response to external field, defined as the magnitude of dipole induced by one unit of field gradient.

<table>
<thead>
<tr>
<th>Atomic Polarizabilities</th>
<th>He 0.205</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.6668</td>
</tr>
<tr>
<td>C</td>
<td>1.76</td>
</tr>
<tr>
<td>N</td>
<td>1.10</td>
</tr>
<tr>
<td>O</td>
<td>0.802</td>
</tr>
<tr>
<td>F</td>
<td>0.557</td>
</tr>
<tr>
<td>P</td>
<td>3.13</td>
</tr>
<tr>
<td>S</td>
<td>2.90</td>
</tr>
<tr>
<td>Cl</td>
<td>2.18</td>
</tr>
<tr>
<td>Br</td>
<td>3.05</td>
</tr>
<tr>
<td>I</td>
<td>4.7 (or 5.35)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selected molecular polarizabilities</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>2.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.91</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>3.6</td>
</tr>
<tr>
<td>Benzene</td>
<td>10.32</td>
</tr>
</tbody>
</table>


- Polarizability decreases across a row of the periodic table, (C>N>O>F, CH₄>NH₃>H₂O)
- Polarizability increases along a column,(S>O, P>M, H₂S>H₂O)
- C-I bond is more polarizable than C-Cl
- Alkanes are more polarizable than alkenes, may due to Electronegativity. sp² carbons are more electronegative than sp³ carbons.
§ Bonding Model

Valence Bond Theory (VB) G.N. Lewis 1916

Chemical bonds result from the sharing of electron pairs between two approaching atoms.

The bond is localized.  

\[ \text{H} + \text{H} \rightarrow \text{H} - \text{H} \]

means two bonding electrons in the region between two atom

The region is orbital.

\[ \text{Cl} + \text{Cl} \rightarrow \text{Cl} : \text{Cl} : \]

\[ \text{H} + \text{Cl} \rightarrow \text{H} : \text{Cl} : \]

σ bond from S and P  
σ bond by P and P

σ : cylindrical symmetry

For complex molecules, hybridization and resonance are used to describe molecules in terms of orbitals which are mainly localized between two atoms.
**Hybridization Theory:**

For carbon \(1s^22s^22p^2\)

- The 2s, 2px, 2py, 2pz hybridize to form four equivalent sp\(^3\) orbitals.
- 4 bonds can be formed on carbon.
- Highly directional sp\(^3\) orbitals provide for more efficient overlap.

#### Methane \(\text{CH}_4\)

\[ \text{C} - \equiv - \equiv - \equiv - \text{H} \]

\[ s + 3p \rightarrow 4sp^3 \]

#### Ethene \(\text{H}_2\text{C} = \text{CH}_2\)

\[ \text{C} - \equiv - \equiv - \text{H} \]

\[ s + 2p \rightarrow 3sp^2 \]

#### Acetylene \(\text{H}_2\text{C} \equiv \text{CH}\)

\[ s + p \rightarrow 2sp \]

<table>
<thead>
<tr>
<th>No. of ligand</th>
<th>Hybridization</th>
<th>Geometry</th>
<th>Formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>sp(^3)</td>
<td>Tetrahedral</td>
<td>(\text{CH}_4, \text{CCl}_4, \text{CH}_3\text{OH},)</td>
</tr>
<tr>
<td>3</td>
<td>sp(^2)</td>
<td>Trigonal</td>
<td>(\text{CH}_2=\text{CH}_2, \text{H}_2\text{C}=\text{O}, \text{C}_6\text{H}_6, \text{CO}_3^-, \text{CH}_3\cdot)</td>
</tr>
<tr>
<td>2</td>
<td>sp</td>
<td>linear</td>
<td>(\text{H} \equiv \text{C} = \text{H}, \text{CO}_2, \text{HCN}, \text{H}_2\text{C} = \text{C} = \text{CH}_2)</td>
</tr>
</tbody>
</table>
Resonance Theory:

An extension of valence bond theory for molecules that more than one Lewis structure can be written. Useful in describing electron delocalization, in conjugate system and reactive intermediates.

(a) If more than one Lewis structure can be written, which has nuclear positions constant, but differ in assignment of electrons, the molecule is described by a combination of these structure (a hybrid of all).

(b) The most favorable (lowest energy) resonance structure makes the greatest contribution to the true structure.

**Determining energy**: maximum number of covalent bond, minimum separation of unlike charge, placement of negative charge on most electronegative atom (vice versa).

(c) Those with delocalized electrons are usually more stable than single localized structure.

![Diagram of resonance structures](image-url)
§ **Dipole moment**: the vector quantity that measures the separation of charges.

\[
\begin{align*}
\text{bond dipole} &= q \times d = 0.1 \times (4.8 \times 10^{-10} \text{esu}) \times 1.5 \times 10^{-8} \text{ cm} \\
&= 0.72 \times 10^{-18} \text{esu} \cdot \text{cm} \\
&= 0.72 \text{ D} \quad (1 \text{ Debye} = 10^{-18} \text{esu} \cdot \text{Cm})
\end{align*}
\]

Molecular dipole is the vector sum of various “bond dipoles”. It provides information about molecular structure and bonding.

*e.g.* \( \text{CH}_3\text{F} \quad \mu = 1.81 \text{ D} \)

\[
\begin{align*}
\text{q} &= \frac{1.81 \times 10^{-18}}{1.385 \times 4.8 \times 10^{-10}} = 0.27 \text{ e}^{-}
\end{align*}
\]

For dichlorobenzene
\( \mu = 2.30, \quad 1.55, \quad 0 \)

From trigonometry, the calculated angles between two bond “dipole moment” are 89°, 122°, 180°.
\( \Rightarrow \) support the concept that benzene is planar.

The dipole moment results from unequal sharing of the electron. \( \Rightarrow \) due to different attraction for electron \( \Rightarrow \) electronegativity

\[
\text{Polar bond} = [\text{covalent bond}] + \lambda \ [\text{ionic bond}]
\]

\[
\lambda = \text{weighing factor}
\]

\[
\% \text{ ionic character} = \frac{\lambda^2}{(1 + \lambda^2)} \times 100 \%
\]

\( \text{HCl} \quad +0.17 \text{ electron charge on H} \cdot \)

\( -0.17 \text{ electron charge on Cl} \cdot \lambda = 0.45 \)
§ Electronegativity & Bond Polarity

**Electronegativity**: The power of an atom in a molecule to attract electrons to itself.  
*Pauline 1932*

\[ \chi_p : \text{based on the difference in bond energy of AB and } \frac{A-A + B-B}{2} \text{ other scale of electronegativity, more related to atomic properties.} \]

*Mulliken 1934*  
\[ \chi_M = \frac{I + A}{2} \]  
I : ionization potential of atom  
A : e\text{-} affinity of atom

*Allen 1989*  
\[ \chi_{\text{spec}} : \text{based on the average I.P. of all of the valence P and S electrons.} \]

*Nagle 1990*  
\[ \chi_\alpha : \text{based on atomic polarizability} \]

*Benson 1988*  
\[ V_X : \text{no. of valence electron /covalent radii} \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \chi_p )</th>
<th>( \chi_M )</th>
<th>( \chi_{\text{spec}} )</th>
<th>( \chi_\alpha )</th>
<th>( V_X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.20</td>
<td>3.059</td>
<td>2.300</td>
<td>2.27</td>
<td>2.70</td>
</tr>
<tr>
<td>Li</td>
<td>0.91</td>
<td>1.282</td>
<td>0.912</td>
<td>0.94</td>
<td>0.75</td>
</tr>
<tr>
<td>Be</td>
<td>1.57</td>
<td>1.987</td>
<td>1.576</td>
<td>1.55</td>
<td>2.08</td>
</tr>
<tr>
<td>B</td>
<td>2.04</td>
<td>1.828</td>
<td>2.051</td>
<td>2.02</td>
<td>3.66</td>
</tr>
<tr>
<td>C</td>
<td>2.55</td>
<td>2.671</td>
<td>2.544</td>
<td>2.56</td>
<td>5.19</td>
</tr>
<tr>
<td>N</td>
<td>3.04</td>
<td>3.083</td>
<td>3.066</td>
<td>3.12</td>
<td>6.67</td>
</tr>
<tr>
<td>O</td>
<td>3.44</td>
<td>3.215</td>
<td>3.610</td>
<td>3.62</td>
<td>8.11</td>
</tr>
<tr>
<td>F</td>
<td>3.98</td>
<td>4.438</td>
<td>4.193</td>
<td>4.23</td>
<td>9.915</td>
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<tr>
<td>Na</td>
<td>0.93</td>
<td>1.212</td>
<td>0.869</td>
<td>0.95</td>
<td>0.65</td>
</tr>
<tr>
<td>Mg</td>
<td>1.31</td>
<td>1.630</td>
<td>1.293</td>
<td>1.32</td>
<td>1.54</td>
</tr>
<tr>
<td>Al</td>
<td>1.61</td>
<td>1.373</td>
<td>1.613</td>
<td>1.55</td>
<td>2.40</td>
</tr>
<tr>
<td>Si</td>
<td>1.90</td>
<td>2.033</td>
<td>1.916</td>
<td>1.87</td>
<td>3.41</td>
</tr>
<tr>
<td>P</td>
<td>2.19</td>
<td>2.394</td>
<td>2.253</td>
<td>2.22</td>
<td>4.55</td>
</tr>
<tr>
<td>S</td>
<td>2.58</td>
<td>2.661</td>
<td>2.589</td>
<td>2.49</td>
<td>5.77</td>
</tr>
<tr>
<td>Cl</td>
<td>3.16</td>
<td>3.535</td>
<td>2.869</td>
<td>2.82</td>
<td>7.04</td>
</tr>
<tr>
<td>K</td>
<td>0.82</td>
<td>1.032</td>
<td>0.734</td>
<td>0.84</td>
<td>0.51</td>
</tr>
<tr>
<td>Ca</td>
<td>1.00</td>
<td>1.303</td>
<td>1.034</td>
<td>1.11</td>
<td>1.15</td>
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<tr>
<td>Br</td>
<td>2.96</td>
<td>3.236</td>
<td>2.685</td>
<td>2.56</td>
<td>6.13</td>
</tr>
<tr>
<td>I</td>
<td>2.66</td>
<td>2.880</td>
<td>2.359</td>
<td>2.27</td>
<td>5.25</td>
</tr>
</tbody>
</table>

Figure 1. Electronegativity, $x_{\text{ave}} = (m_{e_p} + m_{e_s})/(m + n)$, where $m_{e_p}$, $n_{e_p}$, $n_{e_s}$, are the number and ionization potentials (multiplet averaged) of $p$ and $s$ electrons in the valence shell of representative elements through the 5th row. $x_{e_p}$ and $x_{e_s}$ were obtained from National Bureau of Standards high-resolution atomic energy level tables (ref 1). Cross-hatched atoms are those of the metalloid band.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Empirical Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>2.3</td>
</tr>
<tr>
<td>CH$_2$Cl</td>
<td>2.75</td>
</tr>
<tr>
<td>CHCl$_2$</td>
<td>2.8</td>
</tr>
<tr>
<td>CCl$_3$</td>
<td>3.0</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>3.35</td>
</tr>
<tr>
<td>Ph</td>
<td>3.0</td>
</tr>
<tr>
<td>CH=CH$_2$</td>
<td>3.0</td>
</tr>
<tr>
<td>C≡CH</td>
<td>3.3</td>
</tr>
<tr>
<td>C≡N</td>
<td>3.3</td>
</tr>
</tbody>
</table>


In complex molecules with many polar bonds involved, electrostatic potential surfaces (from quantum mechanic calculation) are used to view the charge distribution in the whole molecule.

red ----negative potential  
blue --- positive potential  
green---neutral
Molecular Orbital Method

Electrons are distributed among a set of molecular orbitals of discrete energies. The orbitals extend over the entire molecule.

First Approximation:
the MO is a linear combination of contributing atomic orb.

\[ \Psi = c_1 \phi_1 + c_2 \phi_2 + \cdots + c_n \phi_n \]

\( \phi \)'s are basis set

c’s coefficient, reflect contribution

The no. of MO’s (bonding + non-bonding +antibonding) = total no. of a.o.’s

For H₂, 2e⁻

For HHe+, 2e⁻

For CO, 10e⁻
MO for methane

First approach

\[
\begin{align*}
\psi_{sp^3_1} &= \frac{1}{2} (C_{2s} + C_{2p_x} + C_{2p_y} + C_{2p_z}) \\
\psi_{sp^3_2} &= \frac{1}{2} (C_{2s} + C_{2p_x} - C_{2p_y} - C_{2p_z}) \\
\psi_{sp^3_3} &= \frac{1}{2} (C_{2s} - C_{2p_x} + C_{2p_y} - C_{2p_z}) \\
\psi_{sp^3_4} &= \frac{1}{2} (C_{2s} - C_{2p_x} - C_{2p_y} + C_{2p_z})
\end{align*}
\]

Each \( sp^3 \) overlap with a 1s of H to form \( CH_4 \) bond angle 109.5°

This implies identical bonds for the bonding electrons.

But ESCA data of methane shows

\[
\begin{align*}
1s & \quad 290eV \\
& \quad 23.0eV \\
& \quad 12.7eV
\end{align*}
\]

The M.O. formed above is symmetry incorrect.
The symmetry of the M.O. must conform to the symmetry of the molecule in such a way that the M.O.’s are either symmetric or antisymmetric to all the symmetry elements of the molecule.

Solution: form the delocalized methane M.O. directly form unhybridized orbitals: 1C\(_{2s}\), 3C\(_{2p}\)’s, 4H\(_{1s}\)

\[
\phi_1 = 0.545 \text{C}_{2s} + 0.272 (H_1 + H_2 + H_3 + H_4)
\]

\[
\phi_2 = 0.545 \text{C}_{2p_x} + 0.272 (H_1 + H_2 - H_3 - H_4)
\]

\[
\phi_3 = 0.545 \text{C}_{2p_y} + 0.272 (H_1 - H_2 + H_3 - H_4)
\]

\[
\phi_4 = 0.545 \text{C}_{2p_z} + 0.272 (H_1 - H_2 - H_3 + H_4)
\]

The energy of on M.O. increase with the no. of nodes in the M.O.
Group orbitals from qualitative molecular orbital theory (QMOT)

planar methyl

pyramidal methyl

Walsh diagram
Building larger molecule from group orbitals

Figure 1.12
The orbital mixing diagram for the formation of ethane from two pyramidal CH₃ groups.
The computed MOs are shown in Figure 1.13.
Valence Shell Electron Pair Repulsion Theory (VSEPR)

In predicting the shape of molecules, bonds are treated as repulsive points and the repulsive points made as far apart as possible.

- counting the number of electron groups: unshared pair is a group, each bond is a group, whether single or multiple.
- 2 groups $\xrightarrow{\text{linear}}$
- 3 groups $\xrightarrow{\text{trigonal}}$
- 4 groups $\xrightarrow{\text{tetrahedral}}$
- non-bonding electron pair $\xrightarrow{\text{more repulsive}}$
- bonding pair to electronegative groups $\xrightarrow{\text{less repulsive}}$

$\angle \text{H-C-H} = 109.5^\circ$
$\angle \text{H-C-H} = 109.3^\circ$
$\angle \text{H-N-H} = 107^\circ$
$\angle \text{H-O-H} = 104.5^\circ$

$\text{Cl} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{Cl}$

predicted $\angle \text{H-C-H} = 109.5^\circ$
$\angle \text{H-C-Cl} = 109.5^\circ$
$\angle \text{H-C-H} = 110^\circ 52'$
$\angle \text{H-C-Cl} = 108^\circ 0'$
**Effect of lone pair on bond angle**

Repulsion: lone pair occupies larger domain
lone pair: lone pair > bond pair: bond pair

\[
\begin{align*}
\text{angle PBr}_3 & = 96.9^\circ < 98.2^\circ \\
\text{angle POCl}_3 & = 100.3^\circ < 96.9^\circ \\
\text{angle PCl}_3 & = 101.0^\circ < 96.2^\circ \\
\text{angle POBr}_3 & = 101.0^\circ < 98.2^\circ \\
\end{align*}
\]

Increasing electronegativity, the bonding pair shifts further away from the central atom. The adjacent bond longer

**Effect of electronegativity on bond angle**

Increasing electronegativity, the bonding pair shifts further away from the central atom. angle decreases

**Effect of lone pair on bond length**

The closer and larger domain of lone pair prevents a bonding pair getting closer. The adjacent bond longer

**Multiple bond domain**

\[
\begin{align*}
\text{angle SO}_2 & = 122^\circ \\
\text{angle SO}_3 & = 109^\circ \\
\end{align*}
\]

Multi-center bond occupies less domain than a single bond
Trigonal bipyramidal molecules

5 points are non-equivalent

(1) the axial bond is longer than eq. bond \( r_{ax}/r_{eq} = 1\sim1.4 \)
(2) larger domain electron pair (lone pair, multiple bond) occupies equatorial position
(3) more electronegative atom occupies axial position
eg. PF₃Cl₂, PF₂Cl₃

Limitations:
- not applicable to ionic comp’d
- for localized bonding/non-bonding pair, not for delocalized
- for sufficiently large ligands, steric interaction prevails
§ Variable Hybridization and Molecular Geometry

For carbon bonded to different atom, different hybridizations are proposed.
For CH₄, CCl₄: sp³ hybridization

% S = 25
% P = 75

For spⁿ, define \( \lambda^2 = n \),

\[ \lambda: \text{hybridization parameter} \]

\[ \% S = \frac{1}{(1 + \lambda^2)} \quad \% P = \frac{\lambda^2}{(1 + \lambda^2)} \]

sum of P-fraction \( \sum \frac{\lambda_i^2}{(1 + \lambda_i^2)} = n \),

sum of S-fraction \( \sum \frac{1}{(1 + \lambda_i^2)} = 1 \)

Interorbital angle \( \theta_{ab} \),

\[ 1 + \lambda_a \lambda_b \cos \theta_{ab} = 0 \]

if \( a = b \),

\[ 1 + \lambda_a^2 \cos \theta_{aa} = 0, \cos \theta_{aa} = \frac{-1}{\lambda_a^2} \]

For CA₃B

\( \text{sp}^3 \rightarrow \theta_{aa} = 109.5^\circ \) the S character ↑, \( \lambda \) ↓

\( \text{sp}^2 \rightarrow \theta_{aa} = 120^\circ \)

\( \text{sp} \rightarrow \theta_{aa} = 180^\circ \)

\[ 3\sin^2 \theta_{ab} = 2 (1 - \cos \theta_{aa}) \]

from \( \theta_{ab} = 108^\circ \), \( \theta_{aa} = 110.5^\circ \)

from \( \theta_{aa} = 110.5^\circ \), \( \lambda_a^2 = 2.86 \)

\( \therefore \text{sp}^{2.86} \) for C−H

from 3 \( \left( \frac{1}{1 + 2.86} \right) + \frac{1}{1 + \lambda_b^2} = 1 \), \( \lambda_b^2 = 3.5 \)
For CH₂Cl₂

\[
\begin{align*}
\lambda_{\text{Cl}}^2 &= \frac{-1}{\cos 111.47°} = 2.69 \\
\therefore &\text{sp}^{2.69} \text{ for } \text{C—Cl}
\end{align*}
\]

∴ from \(2 \left( \frac{1}{1 + 2.69} \right) + 2 \left( \frac{1}{1 + \lambda_{\text{H}}^2} \right) = 1\)

\(\lambda_{\text{H}}^2 = 3.37, \quad \therefore \text{sp}^{3.37} \text{ for } \text{C—H}\)

from \(\cos \theta_{\text{HH}} = \frac{-1}{\lambda_{\text{H}}^2}, \theta_{\text{HH}} = 107° \neq 112° \text{ (expt’l)}\)

\(\lambda_{\text{HH}}^2 = 2.67, \quad \lambda_{\text{Cl}}^2 = 3.39, \quad \therefore \theta_{\text{ClCl}} = 107°\)

the inter-orbital bond angle smaller than the inter nuclear bond angle

Experimental support of variable hybridization:
NMR coupling constants \(J^{13\text{C—H}}:\)
cyclopropane 161, cyclobutane 134, cyclopentane 128,
cyclohexane 124, cycloheptane 123, cyclooctane 122
Cyclopropane

bent bond from sp³ hybridization (or variable hybridization)

Walsh orbital:
from sp² hybridization

Figure 1.21 The Walsh hybridization model for cyclopropane. Each carbon is sp³ hybridized, oriented as shown in (a). Two of the three hybrids of each carbon form σ bonds with the hydrogens; the third hybrid extends toward the center of the ring. The unhybridized p orbitals lie in the ring plane (b).

Figure 1.22 Schematic representation of the Walsh orbitals of cyclopropane. The view is from directly above the ring plane. (a) The "σ-type" orbitals made from sp³ hybrids; "σ₁" is bonding; "σ₂" and "σ₃" are degenerate and antibonding. (b) The "π-type" orbitals made from p orbitals; "π₁" and "π₂" are degenerate and bonding; "π₃" is antibonding.
Prediction of Physical Properties with diff. Bonding model

1. Alkene Geometry

C—C
bond length 1.54Å 1.34Å 1.20Å

by $\sigma$, $\pi$ formulation:

- sp$^3$ hybrid. % S = 25
- in ethene sp$^2$ hybrid. % S = 33.3  S $\uparrow$ bond legth dec. addition $\pi$ bond, shorter bond
- in ethyne sp hybrid. % S = 50, no quantitative prediction

by bent bond formulation:

- only sp$^3$ hybridization
  - $\Leftrightarrow$ C—C distance 1.32Å
  - $\Leftrightarrow$ C—C distance 1.18Å

2. Acidity

- ethane 10$^{-42}$ sp$^3$ S character increase greater e$^-$-pulling power for the orbital better stabilization of the anion
- ethene 10$^{-36.5}$ sp$^2$
- ethyne 10$^{-25}$ sp

bent bond formulation

decreased repulsion

further decrease in repulsion
conformation of propene

\[
\begin{align*}
\sigma, \pi \text{-formation predicts } II \text{ to be more stable, because more} \\
\text{repulsion between double bond and the } C—H \text{ bond in I} \\
\text{Bent bond formulation:}
\end{align*}
\]

The bent bond (Ω bond) is agreed in cyclopropane proposed or shown to more suitable than σ, π description in CF\(_2=CF_2\), CO\(_2\), CO, benzene

**Conclusion**