The Chemical Bond (Chapter 12)
Quantum mechanics explains why $H_2$ forms but not $He_2$, why $H_2O$ is bent but not $CO_2$.

Earlier theory of bonding: **Lewis structures**

Chemical bond involves **sharing electrons**:  

2 $H$ atoms form bond: $H: \dot{H}$ --> $H-H$.

**Octet rule**: atom (besides $H$) tends to form bonds until surrounded by 8 valence electrons.

**Problems with theory**: Many exceptions to octet rule, no information about bond lengths, strengths.

Better: 2 theories based on orbitals  
1. **Valence Bond Theory** (VB): Electrons in molecules occupy atomic orbitals.  
2. **Molecular Orbital Theory** (MO): Electrons occupy molecular orbitals formed from atomic orbitals.
The Chemical Bond (Chapter 12)

1. **Valence bond theory (VB):** Bonds form when atomic orbitals overlap. Consider $\text{H}_2$:

If one electron (1) belongs to one atom (A), other electron (2) belongs to atom B, then wave function for $\text{H}_2$:

$$\Psi = \Psi_A(1)\Psi_B(2)$$

$\Psi_A$, $\Psi_B$ = 1s orbitals for A & B
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**Improvement:**

$$\Psi = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)$$

Electron just as likely to be found near atom B as near A.

**Even better:**

$$\Psi = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1) + \lambda[\Psi_A(1)\Psi_A(2) + \Psi_B(1)\Psi_B(2)]$$

Allows for both electrons to be near A or B. Not likely, $\lambda \ll 1$, but possible, so $\lambda \neq 0$.

**VB:** Build better approximations in terms of atomic orbitals.
The Chemical Bond (Chapter 12)

1. Valence bond theory (VB): Bonds form when atomic orbitals overlap. Consider $H_2$:

\[ \Psi = \Psi_A(1)\Psi_B(2) \] (a)

\[ \Psi = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1) \] (b)

\[ \Psi = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1) + \lambda [\Psi_A(1)\Psi_A(2) + \Psi_B(1)\Psi_B(2)] \] (c)

Improved potential energy using better wave function. Wave function (a) gives binding energy of 24 kJ mol\(^{-1}\); (c) gives \(\approx\) actual binding energy of 432 kJ mol\(^{-1}\).
Hybridization of Atomic Orbitals

Atomic orbitals **that bond** not necessarily lowest energy atomic orbitals. Consider 3 examples:

(1) **Methane** (CH\(_4\)): All 4 C-H bonds have same length; ground state of C atom: 1s\(^2\)2s\(^2\)2p\(^2\).

Electrons are equivalent if **hybrid orbitals** are formed:
- Promote one 2s electron to 2p orbital.
- 2s\(^1\)2p\(^3\) forms sp\(^3\) hybrid.

\[ \begin{array}{cccc}
\uparrow \downarrow & \uparrow & \uparrow & \\
2s & 2p & & \\
\end{array} \quad \rightarrow \quad \begin{array}{cccc}
\uparrow & \uparrow & \uparrow & \uparrow \\
4 & sp^3 \text{ orbitals} & \\
\end{array} \]

Each electron in equivalent sp\(^3\) orbital
Hybridization of Atomic Orbitals

(1) Methane (CH₄):

\[ \begin{array}{c}
\uparrow \downarrow \\
2s \\
\uparrow \\
2p \\
\end{array} \rightarrow \begin{array}{c}
\uparrow \\
4 \text{ sp}^3 \text{ orbitals}
\end{array} \]

Each electron in equivalent sp³ orbital

Bond energy lowered: Hybrid orbitals form lower-energy bonds with 1s orbitals of H atom.
Hybridization of Atomic Orbitals

(2) Ethylene (\(C_2H_4\)): Planar molecule, each C bonds to 3 atoms.

This can be explained if 2s orbital of C mixes with two 2p orbitals:

\[
\begin{align*}
2s &\quad \quad \quad \quad \quad 2p \\
\downarrow &\quad \quad \quad \quad \quad \uparrow \\
\end{align*}
\]

3 hybrid \(sp^2\) orbitals form 3 \(\sigma\) bonds. 1 \(2p_z\) orbital forms remaining \(\pi\) bond.
Hybridization of Atomic Orbitals

(3) Acetylene ($C_2H_2$): Linear molecule.

Hybridization:

$$
\begin{align*}
\uparrow \downarrow & \quad \uparrow \quad \uparrow \\
2s & \quad 2p & \quad 2p_x, 2p_y \\
& \quad 2 \text{ sp orbitals}
\end{align*}
$$

2 sp orbitals form 2 $\sigma$ bonds:

$2p_x, 2p_y$ orbitals form 2 $\pi$ bonds:
The Chemical Bond (Chapter 12)

2. Molecular orbital theory (MO): Constructive and destructive interference of adding atomic orbitals leads to new set of orbitals:

\[ 2H(1s) \rightarrow H_2 \]

- **Antibonding orbital**: Low electron density between nuclei.
- **Bonding orbital**: High electron density between nuclei.

**Constructive interference**
- \( \psi (\sigma) \)
- \( \psi^2 (\sigma) \)

**Destructive interference**
- \( \psi (\sigma^*) \)
- \( \psi^2 (\sigma^*) \)
Electron configuration of molecules satisfy Pauli Principle and Hund’s Rule.

Consider $\text{H}_2$:

Lowest energy is $(\sigma_{1s})^2$
Molecular Orbital Theory (MO)

Bond Order: Number of bonds joining atoms in MO theory.

Definition:

$$\text{Bond order} = \frac{1}{2} \left[ \left( \# \text{ of electrons in bonding MO} \right) - \left( \# \text{ of electrons in antibonding MO} \right) \right]$$

$H_2$ has 2 electrons in bonding MO and none in antibonding MO.

Bond order of $H_2 = (1/2)[2 - 0] = 1$ $\rightarrow$ 1 covalent bond.

• Bond order can be fraction.

• If bond order $\leq 0$ then molecule is unstable.
Molecular Orbital Theory for Diatomic Molecules

Homonuclear diatomics: Both atoms the same.

Consider homonuclear diatomics of second period elements:

Li₂: Electron configuration of Li atom is 1s²2s

Ground state configuration of Li₂: \((σ_{1s})^2(σ^*_{1s})^2(σ_{2s})^2\)

Bond order = \(\frac{1}{2} \left[ \left( \text{# of electrons in bonding MO} \right) - \left( \text{# of electrons in antibonding MO} \right) \right] \)

Li₂ has 4 electrons in bonding MO’s and 2 in antibonding MO’s.

Bond order of Li₂ = \((1/2)[4 - 2] = 1\) --> 1 covalent bond.

All electrons paired in MO’s: diamagnetic.
$B_2, C_2, N_2$: 

$O_2, F_2$: 

Energy
Molecular Orbital Theory for Diatomic Molecules

Heteronuclear diatomics: MO’s depend on electronegativity (X) of atoms - the tendency to attract electrons.

Electronegativity difference between atoms A & B:

\[ |X_A - X_B| = \sqrt{D_{AB} - (D_{AA} D_{BB})^{1/2}} \]

D<sub>AB</sub> = bond dissociation energy of A-B.

If X<sub>A</sub> known, X<sub>B</sub> found by measuring D<sub>AA</sub>, D<sub>BB</sub>, D<sub>AB</sub>.

Reference: Let X<sub>fluorene</sub> = 4.0

Energy of MO’s depends on |X<sub>A</sub>-X<sub>B</sub>|:

Small differences for X<sub>C</sub> ( = 2.5), X<sub>N</sub> (= 3.0) and X<sub>O</sub> (=3.5).

MO’s of N<sub>2</sub> and CO, with same # of electrons, are similar in energy.
Heteronuclear diatomics:

Example: What is the electronic configuration of NO? Bond order? Magnetic properties?

Electronic configuration is:

\[(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_x)^2(\pi_y)^2(\sigma_{2p})^2(\pi^*_x)^1\]

1 unpaired electron: paramagnetic.
Bond order = \((1/2)(10-5) = 2.5\).
Resonance and Electron Delocalization:

Example: Benzene

Just as with ethylene:

2s  2p  2p

\[ \text{Each C forms 3 } \sigma \text{ bonds (sp}^2\text{ electrons) & 1 } \pi \text{ bond (2p}_z\text{)} \]

Electrons in \( \sigma \) bonds localized to bond between C-C, C-H.

p\(_z\) orbitals overlap to form delocalized \( \pi \) bonds
Resonance and Electron Delocalization:

Electrons in $\sigma$ bonds localized to bond between C-C, C-H. $p_z$ orbitals overlap to form delocalized $\pi$ bonds.

Lowest energy $\pi$ orbital is bonding:

Overlapping $2p_z$ orbitals add constructively to give 6 $\pi$ bonds: electrons delocalized in ring around benzene.
Bonding in Coordination Compounds

Coordination compounds: Metal ion + ligand

Coordination Number (CN):

- Linear: $CN = 2$
- Trigonal planar: $CN = 3$
- Octahedral: $CN = 6$

Crystal field theory: Helps to understand energetics, color, magnetic properties of coordination compounds.

Valence electrons of metal ions in d-orbitals.
5 d-orbitals, all degenerate (same energy). BUT, ligands interact with electrons in d orbitals, changing energies.
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Electron density high in direction of ligands - raises energy due to electron repulsion.

Electron density low in direction of ligands - lower energy.
Orbital energies:

\[ \Delta = \text{Crystal field splitting} \]

Crystal Field Stabilization Energy (CFSE): Net energy decrease of d-orbital in complex relative to d-orbital in spherically symmetric field.

\[
\text{CFSE} = (0.6\Delta)n(e_g) - (0.4\Delta)n(t_{2g})
\]

\( n(e_g) \) = # electrons in \( e_g \) orbitals

\( n(t_{2g}) \) = # electrons in \( t_{2g} \) orbitals
\[ \Delta = \text{Crystal field splitting} \]

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\( n(e_g) \) = \# electrons in \( e_g \) orbitals \hspace{1cm} \( n(t_{2g}) \) = \# electrons in \( t_{2g} \) orbitals

If no d electrons (\( d^0 \)): \( \text{CFSE} = 0 \) \hspace{1cm} \text{no stabilization}

If 10 d electrons (\( d^{10} \)): \( \text{CFSE} = 4(0.6\Delta) - 6(0.4\Delta) = 0 \)

If > 0 \& < 10 d electrons, \( \text{CFSE} < 0 \) and complex is stabilized.
$\Delta$ = Crystal field splitting

If no d electrons ($d^0$): CFSE = 0 no stabilization

If 10 d electrons ($d^{10}$): CFSE = $4(0.6\Delta) - 6(0.4\Delta) = 0$

If $> 0 \& < 10$ d electrons, CFSE < 0 and complex is stabilized.

Magnitude of $\Delta$ determines color of compound:

For example, Ti(H$_2$O)$_6^{3+}$ ($d^1$ electron) appears violet because it absorbs yellow/green light around 500 nm.

$\Delta$ = energy of 500 nm photon = $h\nu = hc/\lambda$

$\Delta$ = (6.626 x 10$^{-34}$ J s)(3.00 x 10$^8$ m/s)/(500 x 10$^{-9}$ m)

$\Delta$ = 3.98 x 10$^{-19}$ J. For 1 mole ions: $\Delta$ = 240 kJ mol$^{-1}$
Weak field ligands

\[ I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < O_2, CO \]

\[ \Delta \ increases \]

Strong field ligands

How are orbitals of metal ion filled? Consider \( d^5 \) electrons:

**Weak field ligand**

- Orbitals filled using Hund’s rule

**Strong field ligand**

- Orbitals filled using Hund’s rule

\[ \Delta = 112.7 \, \text{kJ/mol} \]

\[ \Delta = 1464.8 \, \text{kJ/mol} \]
How are orbitals of metal ion filled? Consider $d^5$ electrons:

Weak field ligand

Strong field ligand

$\Delta = 112.7 \text{ kJ/mol}$

$\Delta = 1464.8 \text{ kJ/mol}$

FeF$_6^{3-}$ much more magnetic than Fe(CN)$_6^{3-}$: ligand affects magnetic properties as well as color.
Coordination Compounds in Myoglobin, Hemoglobin:

Metal ion is $\text{Fe}^{2+}$; lies in porphyrin ring. $\text{Fe}^{2+}$ bonds to 4 N’s in ring & bonds with N of proximal histidine.

1 ligand can still bind to form octahedral complex, either $\text{O}_2$ or $\text{H}_2\text{O}$ (if $\text{O}_2$ absent):

$\text{O}_2$ tilted due to obstruction in heme pocket, which also obstructs binding of toxic ligands (CO).
Coordination Compounds in Myoglobin, Hemoglobin:

When $O_2$ binds, $Fe^{2+}$ shrinks, changing shape of porphyrin, triggering cooperative binding.

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Why does $Fe^{2+}$ “shrink” when $O_2$ binds?
Coordination Compounds in Myoglobin, Hemoglobin:
When \( \text{O}_2 \) binds, \( \text{Fe}^{2+} \) shrinks, changing shape of porphyrin, triggering cooperative binding.

Why does \( \text{Fe}^{2+} \) “shrink” when \( \text{O}_2 \) binds?

Deoxyhemoglobin: \( \text{H}_2\text{O} \)
weak field ligand (\( \Delta \) small)

Oxyhemoglobin: \( \text{O}_2 \)
strong field ligand (\( \Delta \) large)

Oxyhemoglobin: \( \text{Fe}^{2+} \) electrons avoid orbitals that repel electrons of ligands. \( \text{Fe-O}_2 \) complex is smaller than \( \text{Fe-H}_2\text{O} \) in deoxyhemoglobin.

Deoxyhemoglobin is “high spin”, paramagnetic.
Oxyhemoglobin is “low spin”, diamagnetic.