Theories describing bonding
- Octet (extended octet) rules, Lewis structure: valence electron pairs, dot structures, resonance structures
- Valence Bond Theory: product of valence atomic, hybridization, shared electron pairs, overlap
- VSEPR Theory: Coulombic repulsion between valence electron pairs, gross and fine structure

Molecular Orbital Theory:
- All electrons are considered and the linear combinations of atomic orbitals (LCAO) form molecular orbitals (MO) and apply Pauli exclusion principle and Hund’s rules (maximize M_s) to occupy them
- LCAO (Ψ = Σ c_i φ_i) is limited by symmetry (s, ⊥ p) and relative energy (ionization potential/electron affinity)

\[ \begin{align*}
\text{H}_2 & \text{ molecule (two component system)} \\
& \text{atomic orbitals: } \phi_{1s}(A) \text{ and } \phi_{1s}(B); \text{ secular equation } c_A (H - E) \phi_1 + c_B (H - E) \phi_2 = 0; \text{ and } \int \int \int \phi_1 \phi_2 dx dy dz = 1
\end{align*} \]

- then for orbital A: \[ c_A (H - E) \phi_1 + c_B (H - E) \phi_2 = 0, \text{ since } E \text{ is constant} \]
- \( c_A (H_{AA} - E) + c_B (H_{AB} - E S_{AB}) = 0 \) \( \text{H}_2 \text{ energy of } \phi_A \); \( H_{AB} \) interaction energy of \( \phi_A, \phi_B \); \( S_{AB} \) overlap of \( \phi_A, \phi_B \)

- similarly for orbital B: \( c_A (H_{BA} - E S_{BA}) + c_B (H_{BB} - E) = 0 \) ⇒ with orbital A gives

the determinat form of the secular equation

\[ \begin{bmatrix}
H_{AA} - E & H_{AB} - ES_{AB} \\
H_{BA} - ES_{BA} & H_{BB} - E
\end{bmatrix} = 0 \]

(for larger molecules secular determinat can be block-diagonalized - get atomic orbitals, define irred.reps, each block-diagonal element must be zero)

- linear combination: bonding at \( E_1 \): \( \phi_{1s}(A) + \phi_{1s}(B) \text{ rot.symm. } C_{\infty v} \Rightarrow \sigma \Rightarrow \text{inversion} \Rightarrow \sigma_u^* \)
  - antibonding at \( E_2 \): \( \phi_{1s}(A) - \phi_{1s}(B) \text{ rot.symm. } C_{\infty v} \Rightarrow \sigma^* \Rightarrow \text{inversion} \Rightarrow \sigma_u^* \)
  - (nonbonding: \( \phi_{1s}(A), \phi_{1s}(B) \) both occupied with 2 electrons, lonepairs in VB)

- molecular orbital energy level diagram
- bond order change in \( H_2^+, H_2, H_2^-, H_2^{2-} \)

- types of orbital interactions (remember these to recognize/draw MOs):
  - \( \sigma \) bonding: largest overlap, electron density continuous between atoms (no nodal plane)
  - \( \pi \) bonding: electron density continuous above and below atom-atom vectors (single nodal plane)
  - \( \delta \) bonding: smallest overlap, two perpendicular nodal planes (transition metal multiple bonds)
  - antibonding combination (\( \sigma^*, \pi^*, \delta^* \)) introduces an additional nodal plane \( \perp \) to atom-atom vectors

Molecular orbitals of main group homodimers with 2p valence electrons

a) \( B_2 \): paramagnetic defines the order of MOs ⇒ \( \sigma \) (better overlap) vs. \( \pi \) (degenerate set)

possibilities: \( \phi_p^0 \pi_1^0 \pi_2^0 \) or \( \phi_p^1 \pi_1^1 \pi_2^0 \) or \( \phi_p^0 \pi_1^0 \pi_2^1 \) ⇒ HOMO (SOMO) degenerate due to mixing of MOs with same symmetry (configuration interaction)

b) \( C_2, N_2 \): diamagnetic ⇒ MO theory configuration interaction = VB theory hybridization (2s and 2p orbitals close in energy and has same irred.reps ⇒ can mix/hybridize)

\[ \Psi(h_1) = \frac{1}{\sqrt{1^2 + c^2}} [\phi_s + c \phi_p] \quad \Psi(h_2) = \frac{1}{\sqrt{c^2 + 1^2}} [c \phi_s - \phi_p] \]

( \( c \): mixing coefficient, dependent on the energy difference of s and p atomic orbitals )
c) $\text{O}_2$: paramagnetic $\Rightarrow$ 2s and 2p orbitals separated in energy due to greater $Z_{\text{eff}}$ (issues with VB theory)

possibilities: $(\sigma_p^*)^2 (\pi_1^*)^0 (\pi_2^*)^0$ or $(\sigma_p^*)^1 (\pi_1^*)^1 (\pi_2^*)^0$ or $(\sigma_p^*)^0 (\pi_1^*)^1 (\pi_2^*)^1$

lone pairs: $(2\sigma_g^g)^2 (2\sigma_u^g)^2$

$\sigma$ bond: $(3\sigma_g^g)^2 (3\sigma_u^g)^0$

$\pi$ bond: $(1\pi_u^g)^2 (1\pi_u^u)^2 (1\pi_g^g)^1 (1\pi_g'^g)^1$

changes in bond order/length/strength: $\text{O}_2^{2+}$, $\text{O}_2^+$, $\text{O}_2^-$, $\text{O}_2^{-2}$

(note that CI mixing/hybridization is present, but to smaller extent)

molecular ground and excited states - use microstates as did for atomic electron configuration

- ignore double occupied MOs $\Rightarrow$ give $^1S$ or $^1A_1g$ or $^1\Sigma^+_g$
- $(\pi_g^g)^1(\pi_g'^g)^1$ $\Rightarrow$ angular momentum for $\pi$ orbital $l=1$ $\Rightarrow m_l = \pm 1$ (no 0!), spin $\Rightarrow m_s = \pm 1/2$
- number of microstates = $4\cdot3 / 2 = 6$

\[
\begin{array}{c|ccc}
M_1/M_S & +2 & 1 & 0 \\
M_L = \Sigma m_l & 0 & 2 & 1 \\
-2 & 1 & 0 & -1 \\
\end{array}
\]

$M_S = \Sigma m_s$

- $L = 2$ $S = 0$ covers 3 states (vertical) and gives $^1\Delta_g$ (or $^1D$) note: $g \times g = g$ and $g \times u = u$
- $L = 0$ $S = 1,0$ cover 3 states (horizontal) and give $^3\Sigma_g$ (ground state, max $S$) and $^1\Sigma_g$

Molecular orbitals of heterodimers:

a) HF: example for low IP(H) and high EA(F) $\Rightarrow$ result in limited covalent interaction between s and $p_z$

b) CO (important in organometallic chemistry):

- key difference in the $Z_{\text{eff}}$ $\Rightarrow$ O orbitals are more stabilized than C, larger 2s/2p splitting in $\text{O}_2$
  (compare the MO levels in homodimeric structures)
- another problematic molecule for VB theory
- Molecular orbital levels:
  - 1s orbitals: asymmetric orbital picture $\Rightarrow \Psi = \alpha \phi_C + \sqrt{1-\alpha^2} \phi_O$; $\Psi^* = \sqrt{1-\alpha^2} \phi_C - \alpha \phi_O$
  - 2s, 2p orbitals: asymmetry remains $\Rightarrow$ O based orbitals are lower in energy than C based $\Rightarrow$ allow for mixing of 2s and 2p orbitals along the C-O bond
  - orbital energy order: $(1\sigma_0)^2 (1\sigma_0^*)^2 (2\sigma_{\text{nb},O})^2 (3\sigma_{\text{O},C})^2 (1\pi_{O,C})^4 (4\sigma_C)^2 (1\pi_{C,O}^*)^0 (2\sigma_{C,O}^*)^0$
  - shape of the orbitals: bonding more on the O, antibonding more on the C
Molecular orbitals of trinuclear molecules:

a) Linear molecules: Example is CO$_2$ - focus only on valence orbitals

- use character table ($D_{sh}$) to organize the atomic orbitals and aid their combination to form LCAOs:

C 2s is $a_{1g}$ (totally symmetric)
2p$_z$ is $a_{1u}$ (antisymmetric to inversion)
2p$_x$, 2p$_y$ are $e_{1u}$ (degenerate)

O + O
2s+2s is $a_{1g}$
2s-2s is $a_{1u}$
2p$_z$+2p$_z$ is $a_{1u}$
2p$_z$-2p$_z$ is $a_{1g}$
(2p$_x$,2p$_y$)+(2p$_x$,2p$_y$) are $e_{1u}$
(2p$_x$,2p$_y$)-(2p$_x$,2p$_y$) are $e_{1g}$

- Orbitals within the same irred.rep. can be combined! Order is based on the extent of overlap ($\sigma > \pi$):

1$a_{1g}$ (O s(p$_z$) + O s(p$_z$)) 1$a_{1u}$ (O s(p$_z$) - O s(p$_z$)): non-bonding electron pairs (lone pairs)
2$a_{1g}$ (C s + O p$_z$ - O p$_z$) 2$a_{1u}$ (C p$_z$ - O p$_z$ - O p$_z$): $\sigma$ bonds
1$e_{1u}$ (C p$_x$/p$_y$ + O p$_x$/p$_y$ + O p$_x$/p$_y$):
1$e_{1u}$* (C 2p$_x$/p$_y$ - O p$_x$/p$_y$ - O p$_x$/p$_y$): $\pi^*$ orbitals
2$a_{1g}$* (C 2s - O p$_z$ + O p$_z$) 3$a_{1u}$* (C p$_z$ + O p$_z$ + O p$_z$): $\sigma^*$ orbitals

b) Angular molecules: Example is H$_2$O

- symmetry is $C_{2v}$, character table gives A$_1$, A$_2$, B$_1$, B$_2$ irred.reps. (molecule is in the yz plane)

O 2s is $a_1$ (totally symmetric)
2p$_z$ is $a_1$ (totally symmetric)
2p$_x$ is $b_1$ (C$_2$ inverts sign, in $\sigma_v$)
2p$_y$ is $b_2$ (C$_2$ and $\sigma_v$ invert sign)

H + H 1s+1s is $a_{1g}$
1s-1s is $b_2$

- Orbitals within the same irred.rep. can be combined! Order is based on the extent of overlap ($\sigma > \pi$):

2$a_1$ (O s(p$_z$)): non-bonding (lone pair)
1$b_2$ (O p$_y$ + H s - H s) 3$a_1$ (O p$_z$(s) + H s + H s): $\sigma$ bonding
1$b_1$ (O p$_x$): non-bonding
3$a_1$* (O p$_z$(s) - H s + H s) 1$b_2$* (O p$_y$ + H s + H s): $\sigma^*$ orbitals

- Start opening up the bond angle from 104.5° to 180° (going back to linear trinuclear system):

2$a_1$: slightly increases in energy (less good overlap s/p $\rightarrow$ s/s) $\Rightarrow$ 2$a_{1g}$
1$b_2$: slightly decreases in energy (better overlap s/p $\rightarrow$ s/p) $\Rightarrow$ 1$a_{1u}$
3$a_1$: sharply increases in energy (complete loss of overlap s/p $\rightarrow$ s$\perp$p) $\Rightarrow$ 1$e_{1u}$
b$_1$: remain constant (remains non-bonding p $\rightarrow$ p) $\Rightarrow$ 1$e_{1u}$

The correlation of orbital energies upon geometry change give the Walsh diagrams