Lecture 35 — Homonuclear Diatomic Molecules & MO Diagrams

Reading: Engel 4th ed., Chapter 12 (Sections 12.4–12.6)

Learning Objectives

- Construct MO diagrams for homonuclear diatomics from Li_2 to Ne_2
- Define and calculate bond order
- Predict magnetic properties from MO configurations
- Explain the s-p mixing effect and its impact on orbital ordering
- Correlate MO theory with experimental data (bond lengths, dissociation energies, magnetism)

1. Building MO Diagrams: From AOs to MOs

Symmetry Requirement

Only AOs of the **same symmetry** (same irreducible representation under $D_{\infty h}$) can combine to form MOs.

AO pair	MO type	MO symmetry
$s + s$	σ	σ_g, σ_u^*
$p_z + p_z$	σ	σ_g, σ_u^*
$p_x + p_x$	π	π_u, π_g^*
$p_y + p_y$	π	π_u, π_g^*

Note: p_x cannot combine with s or p_z (different symmetry).

> [!NOTE] **Concept Check 35.1** Why is it that only atomic orbitals of the same symmetry can combine to form molecular orbitals? What would happen to the
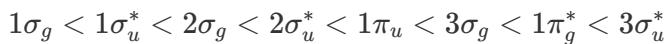
Bonding and Antibonding

Type	Node between nuclei?	Energy	Label
σ bonding	No	Lower	σ
σ antibonding	Yes (on axis)	Higher	σ^*
π bonding	No (one nodal plane containing axis)	Lower	π
π antibonding	Yes (additional node)	Higher	π^*
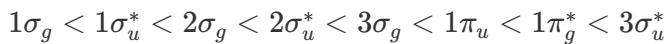
2. MO Ordering

Standard Ordering (O₂, F₂, Ne₂)

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* < 1\pi_u < 3\sigma_g < 1\pi_g^* < 3\sigma_u^*$$
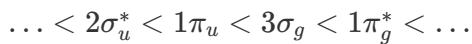
Modified Ordering (Li₂ through N₂) — with s-p Mixing

For lighter atoms, the $2s$ and $2p_z$ orbitals are close in energy. Their MOs mix (s-p **hybridization** at the MO level), pushing $3\sigma_g$ above $1\pi_u$:

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* < 3\sigma_g < 1\pi_u < 1\pi_g^* < 3\sigma_u^*$$

Wait — flipped: the $1\pi_u$ drops below $3\sigma_g$:

$$\ldots < 2\sigma_u^* < 1\pi_u < 3\sigma_g < 1\pi_g^* < \ldots$$

The crossover occurs between N₂ and O₂.

> [!NOTE] **Concept Check 35.2** s-p mixing occurs when s and p_z orbitals are close in energy. How does this mixing affect the relative energy levels of the $3\sigma_g$ and $1\pi_u$ orbitals in nitrogen (N_2)?

3. Bond Order

$$\text{Bond Order} = \frac{1}{2}\left(n_{\text{bonding}} - n_{\text{antibonding}}\right)$$

Molecule	Bonding e^-	Antibonding e^-	Bond Order
H_2	2	0	1
He_2	2	2	0 (doesn't exist)
Li_2	2	0	1 (counting valence only)
N_2	10	4	3
O_2	10	6	2
F_2	10	8	1
Ne_2	10	10	0

4. Electronic Configurations of Second-Row Diatomics

Molecule	e^-	Configuration (valence)	Bond Order	D_e (eV)	R_e (pm)	Magnetic
Li_2	6	$(2\sigma_g)^2$	1	1.07	267	Diamagnetic
Be_2	8	$(2\sigma_g)^2(2\sigma_u^*)^2$	0	~0.1	245	—
B_2	10	$(1\pi_u)^2$	1	3.0	159	**Paramagnetic**
C_2	12	$(1\pi_u)^4$	2	6.3	124	Diamagnetic
N_2	14	$(1\pi_u)^4(3\sigma_g)^2$	3	9.8	110	Diamagnetic
O_2	16	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2$	2	5.2	121	**Paramagnetic**
F_2	18	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4$	1	1.6	142	Diamagnetic

Key Observations

1. **O_2 is paramagnetic** — MO theory correctly predicts two unpaired electrons in π_g^* (Hund's rule). Lewis structures and VB theory fail here!

2. **B₂ is paramagnetic** — explained by the modified ordering with $1\pi_u$ below $3\sigma_g$

3. Higher bond order → shorter bond → stronger bond (general trend)

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5. Photoelectron Spectroscopy (PES)

PES confirms the MO ordering by measuring orbital ionization energies:

$$h\nu = IE + KE_{\text{electron}}$$

The **photoelectron spectrum** shows peaks corresponding to electrons ejected from each occupied MO, with energies matching Koopman's theorem ($IE \approx -\epsilon_i$).

N₂ PES Evidence

The PES of N₂ shows that the $3\sigma_g$ orbital is less tightly bound than $1\pi_u$, confirming the modified ordering with s-p mixing.

Key Equations Summary

Equation	Expression
Bond order	$\frac{1}{2}(n_b - n_{ab})$
LCAO-MO	$\psi = c_A\phi_A + c_B\phi_B$
Symmetry rule	Only AOs of same Γ combine
PES	$h\nu = IE + KE$

Recent Literature Spotlight

"Singlet Oxygen: Applications in Biosciences and Nanosciences" *P. R. Ogilby*, Chemical Reviews, **2010**, 110, 3790–3837. DOI

Molecular oxygen's ground state is a triplet ($^3\Sigma_g^-$), making it one of the few common molecules with unpaired electrons. This review explains how the excited singlet states ($^1\Delta_g$ and $^1\Sigma_g^+$) of O₂ are generated, detected, and harnessed in photodynamic therapy and materials science. The singlet-triplet distinction, rooted in the same electronic term symbols taught in this lecture, determines O₂'s unique reactivity.

Practice Problems

1. **MO diagram.** Draw the complete MO diagram for O_2. Show all electrons, label each MO with its symmetry label, and calculate the bond order. Explain why O_2 is paramagnetic.

2. **Ions.** Predict the bond order, number of unpaired electrons, and magnetic behavior of (a) O_2^+, (b) O_2^-, (c) O_2^{2-}. Which has the strongest bond?

3. *s-p* **mixing.** Explain why the MO ordering changes between N_2 and O_2. What experimental evidence (PES) supports the modified ordering for N_2?

Next lecture: Heteronuclear Diatomics & Valence Bond Theory