BONDING IN MOLECULES PART 1: MO THEORY

General Chemistry I, Lecture Series 9

Pengxin Liu

Reading:

OGB8 §6, YY §§3.2–3.5

Outline

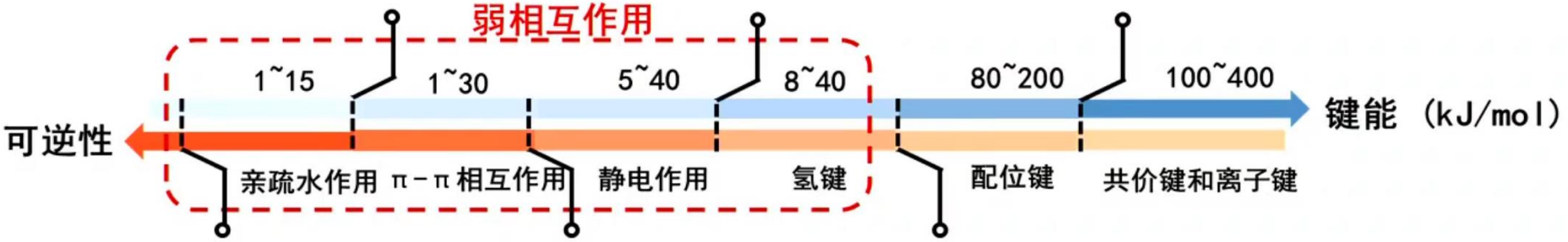
- **Overview**

- Molecular Orbital Theory (1927)
  - LCAO (1929)
  - Orbital correlation diagram

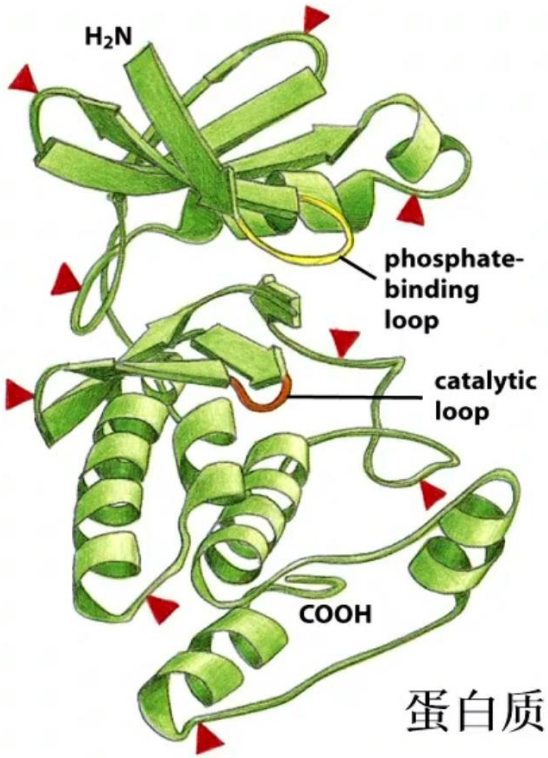
- Types of bonding
  - σ, π bonds
  - Bonding, antibonding, nonbonding
  - Bond notation

- Diatomic molecules

Chemical bonds

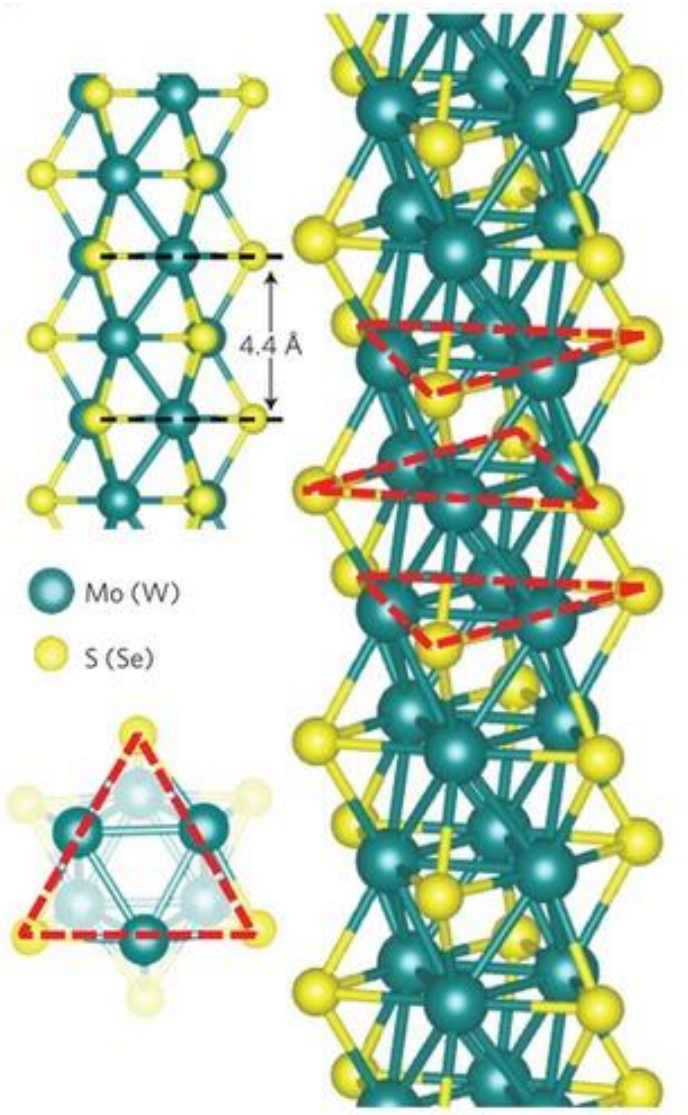


DNA



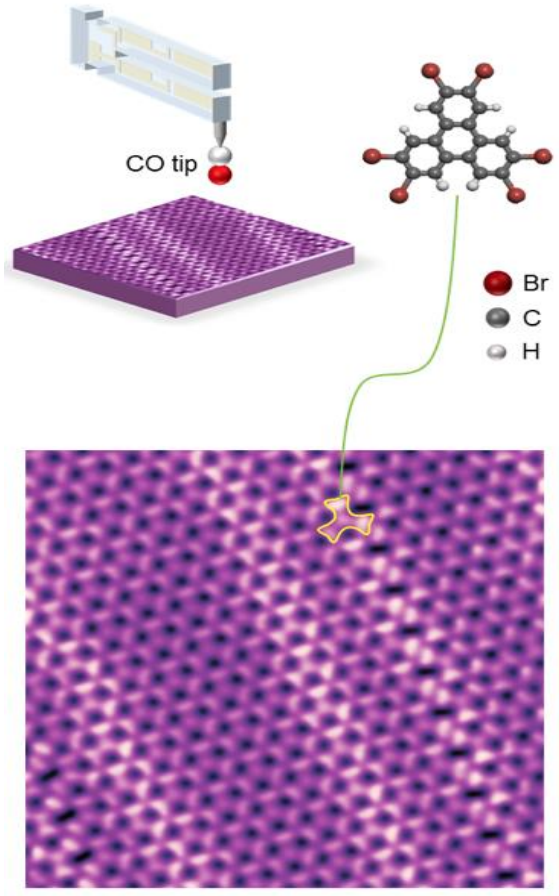
蛋白质折叠

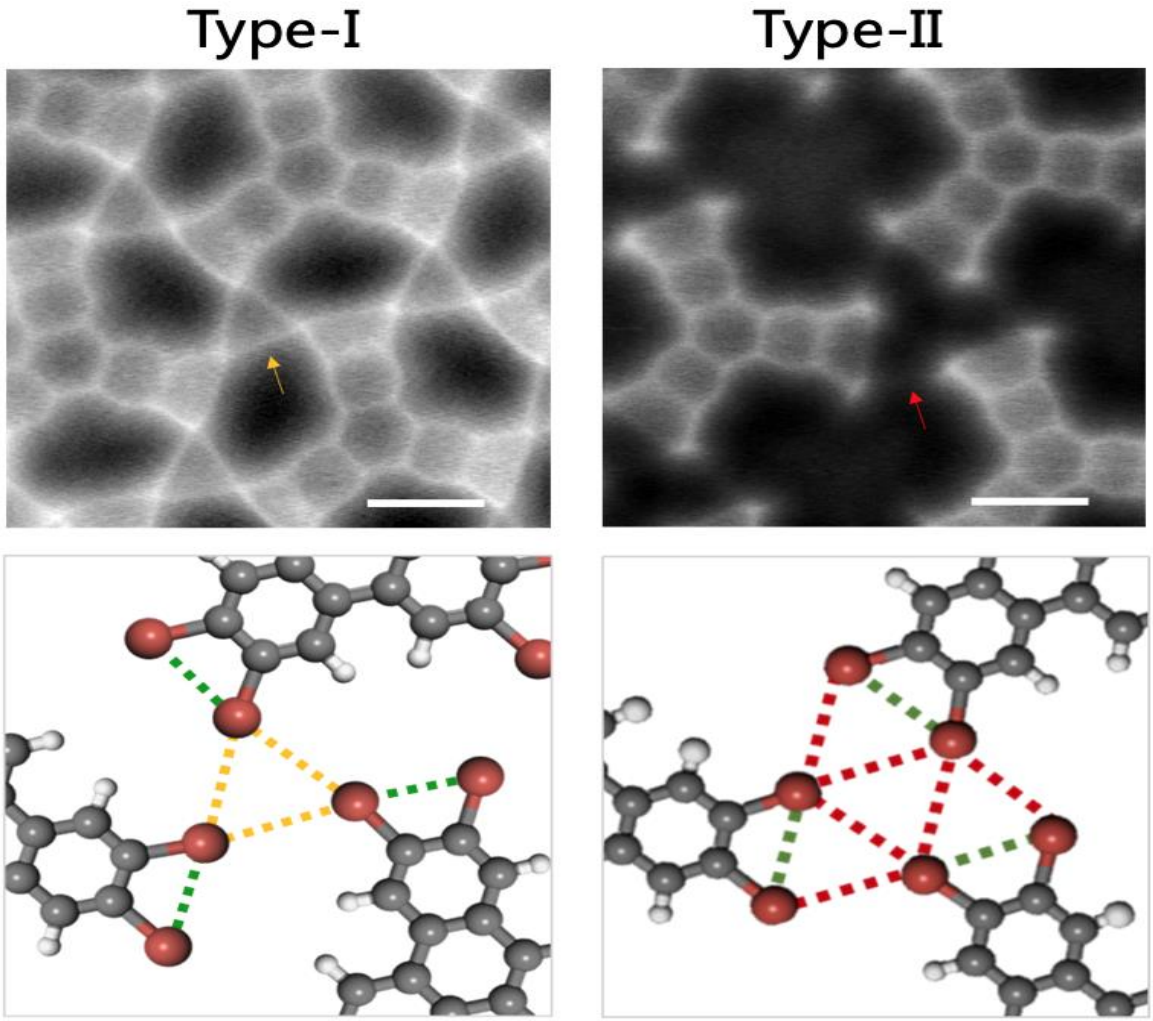
Chemical bonds – Polar covalent bonds



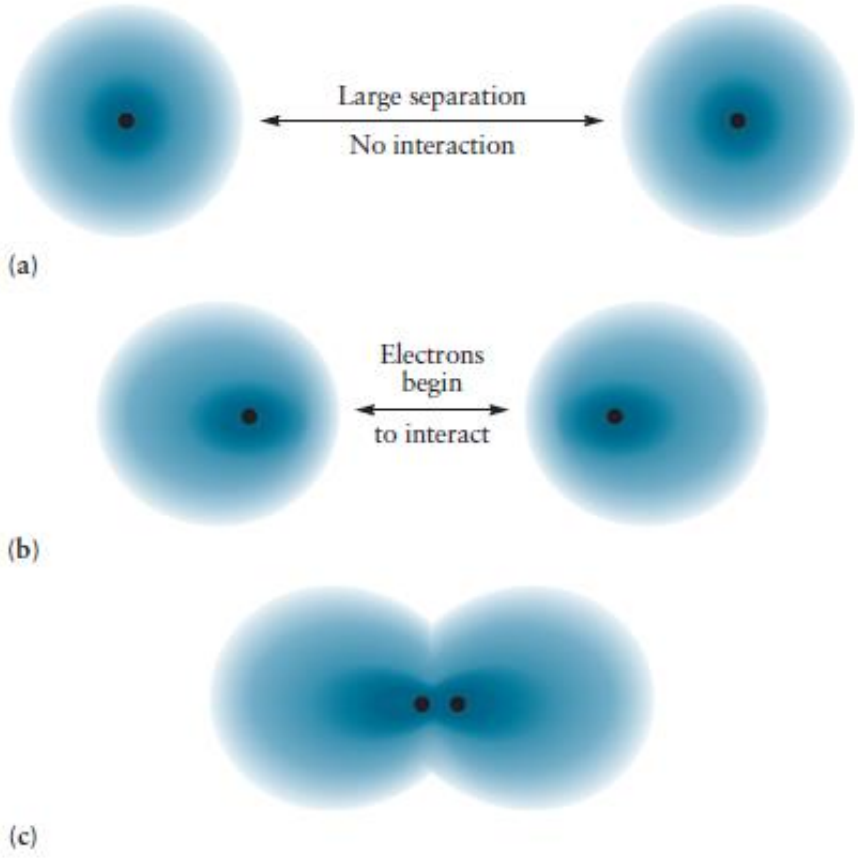
Chemical bonds – Intermolecular forces

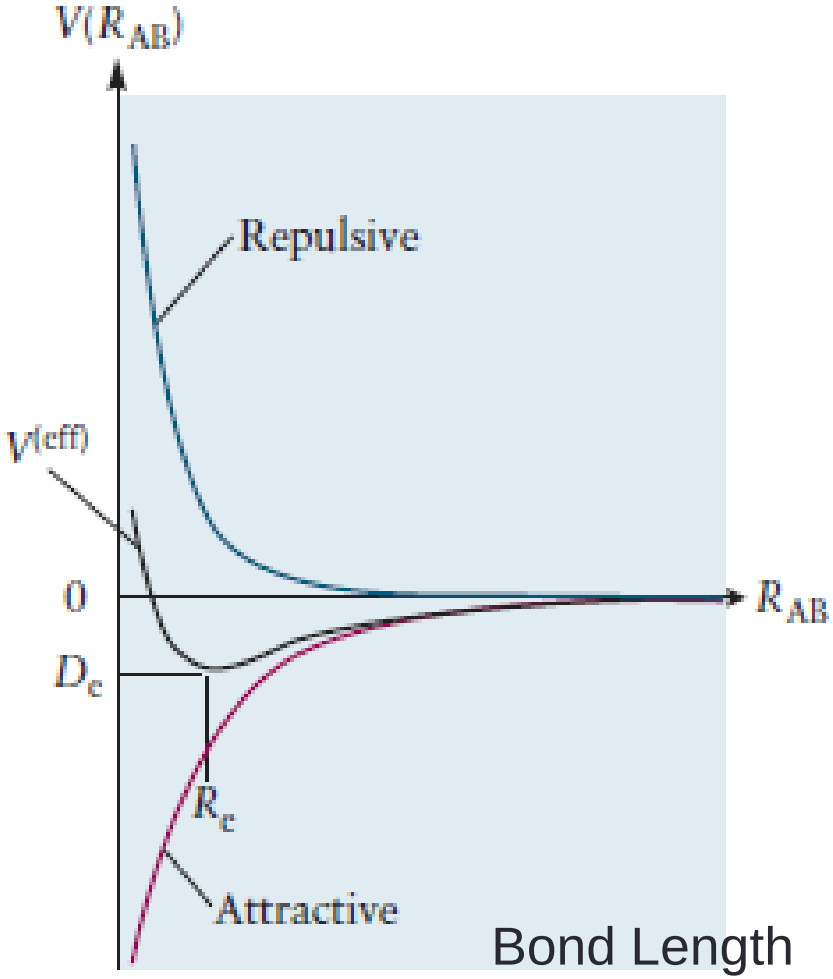
物质学院赵爱迪课题组





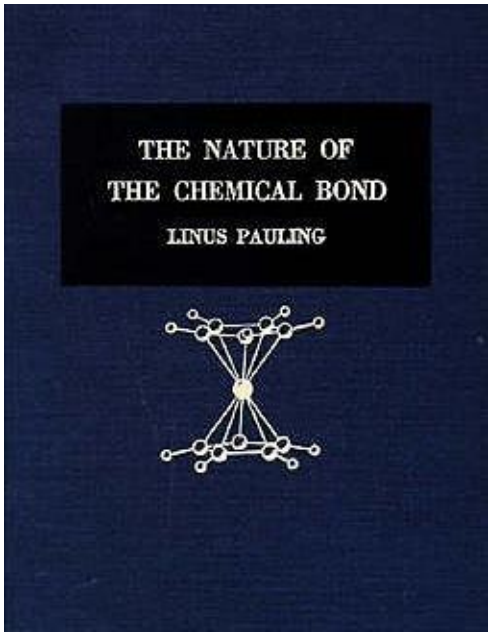
Quantum interpretation



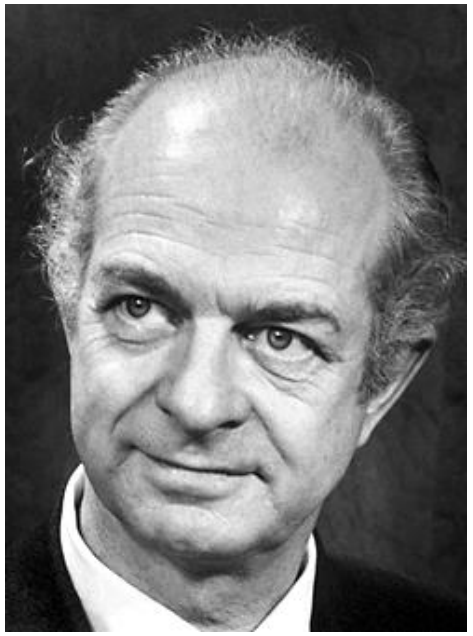


Bond Length
Bond Energy

The Nature of the Chemical Bond



The Nature of the Chemical Bond (1939)



Linus Pauling (Caltech,1901–1994)

The Nature of the Chemical Bond

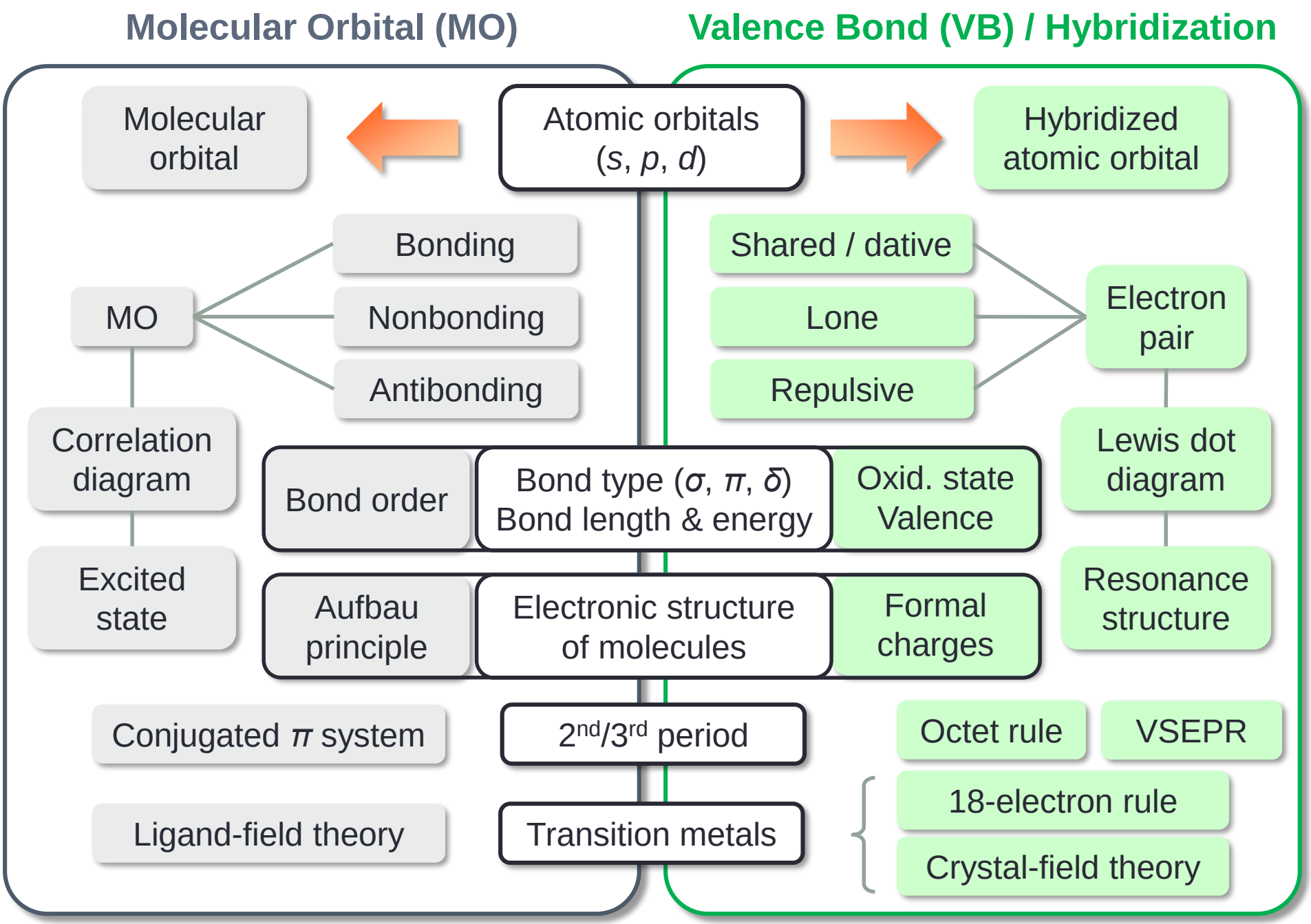
自然科学 化学

鲍林的巨著《化学键的本质》对于化学科学的发展有什么重大意义？主要体现在什么地方？

此书被公认为 20 世纪最伟大的 12 部学术专著之一，其如此卓越，主要体现是什么？

关注问题 写回答 邀请回答

第一章 共振和化学键
第二章 原子的电子结构和形成共价键的形式规则
第三章 共价键的部分离子性和原子的相对电负性
第四章 定向的共价键；键的强度和键角
第五章 络合键轨道；键型的磁性判据
第六章 分子在几个价键结构间的共振
第七章 原子间距离及其与分子和晶体结构的关系
第八章 分子中共振的类型
第九章 含有部分双键性的化学键的分子和络离子的结构
第十章 单电子键和三电子键；缺电子物质
第十一章 金属键
第十二章 氢键
第十三章 离子的大小与离子晶体的结构
第十四章 关于共振及其在化学上的意义的总结


Molecular Orbital (MO)
Valence Bond (VB) / Hybridization
Molecular orbital
Atomic orbitals (s, p, d)
Hybridized atomic orbital
Bonding
MO
Nonbonding
Antibonding
Shared / dative
Lone
Repulsive
Electron pair
Correlation diagram
Excited state
Bond order
Bond type (σ, π, δ)
Bond length & energy
Oxid. state
Valence
Lewis dot diagram
Resonance structure
Aufbau principle
Electronic structure of molecules
Formal charges
Conjugated π system
2nd/3rd period
Octet rule
VSEPR
Ligand-field theory
Transition metals
18-electron rule
Crystal-field theory

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- Overview

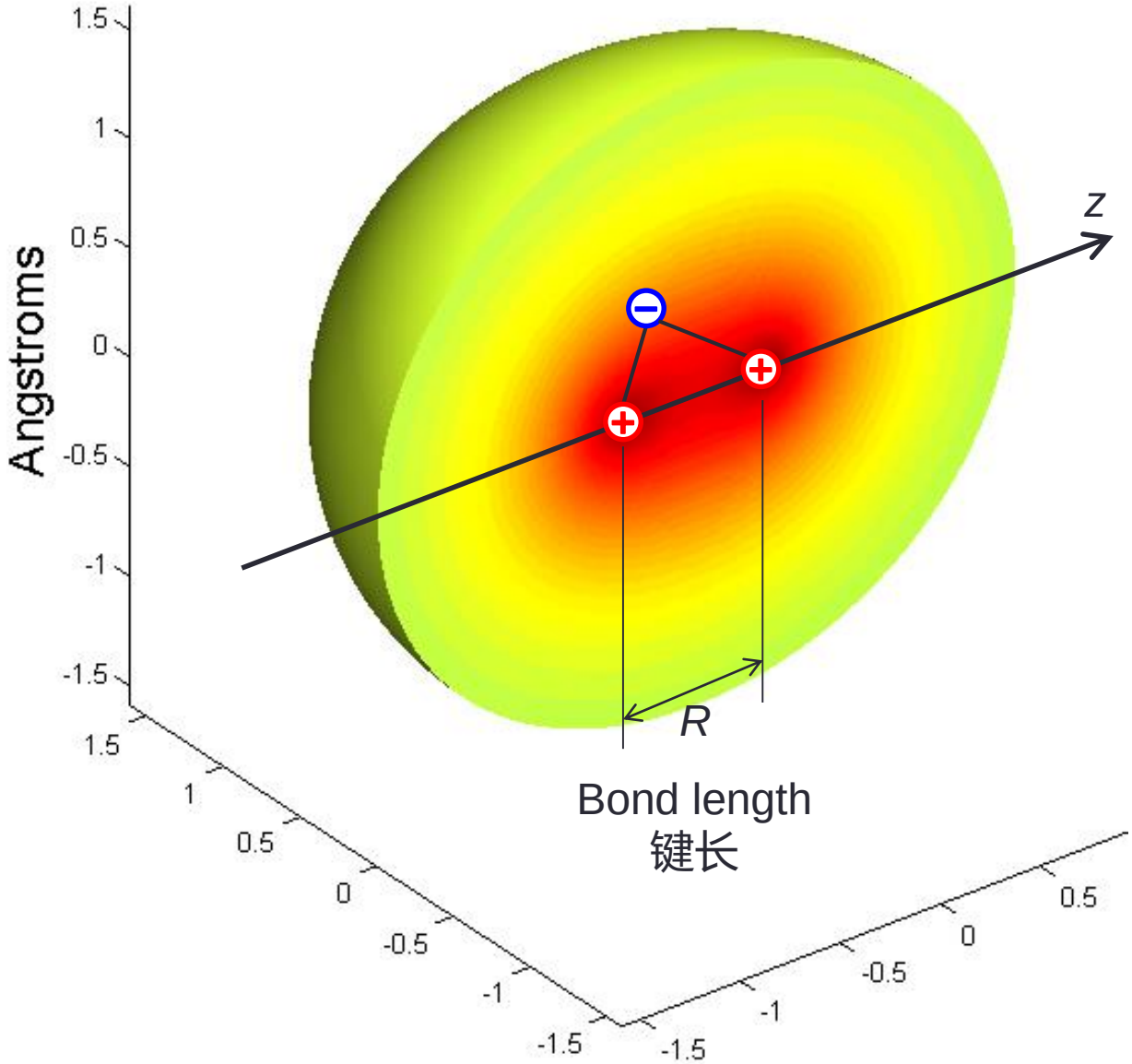
- **Molecular Orbital Theory** (1927)
  - LCAO (1929)
  - Orbital correlation diagram

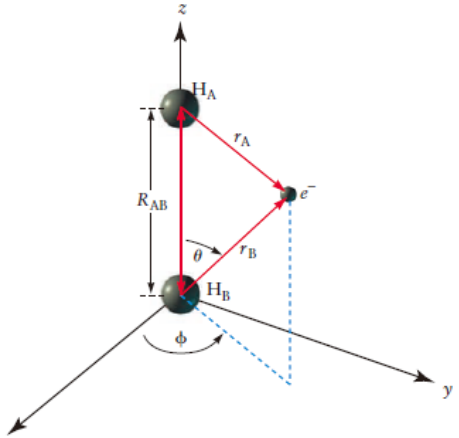
- Types of bonding
  - σ, π bonds
  - Bonding, antibonding, nonbonding
  - Bond notation

- Diatomic molecules

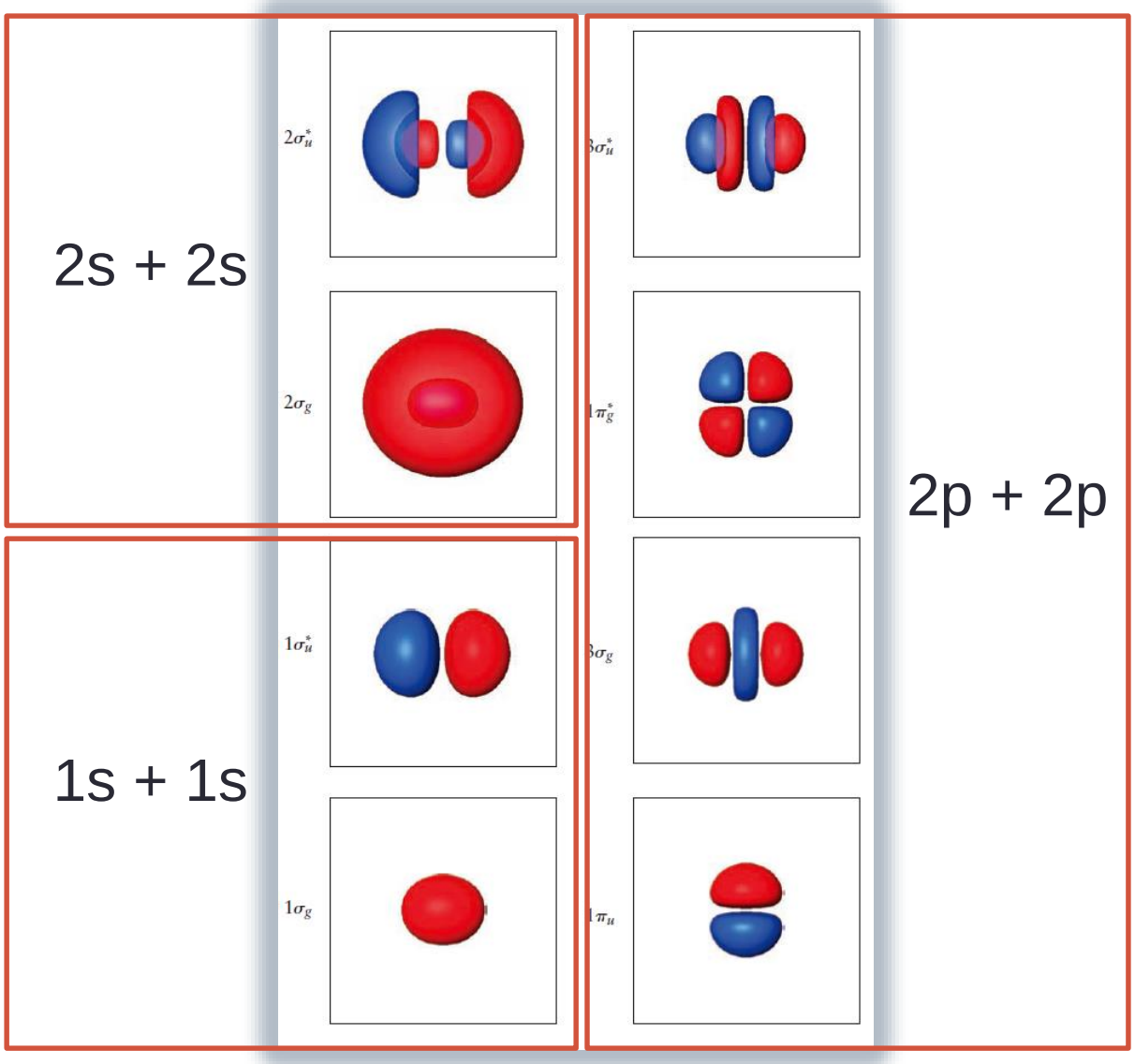
H_2^+: the Simplest Molecule

Exact Molecular Orbitals Available

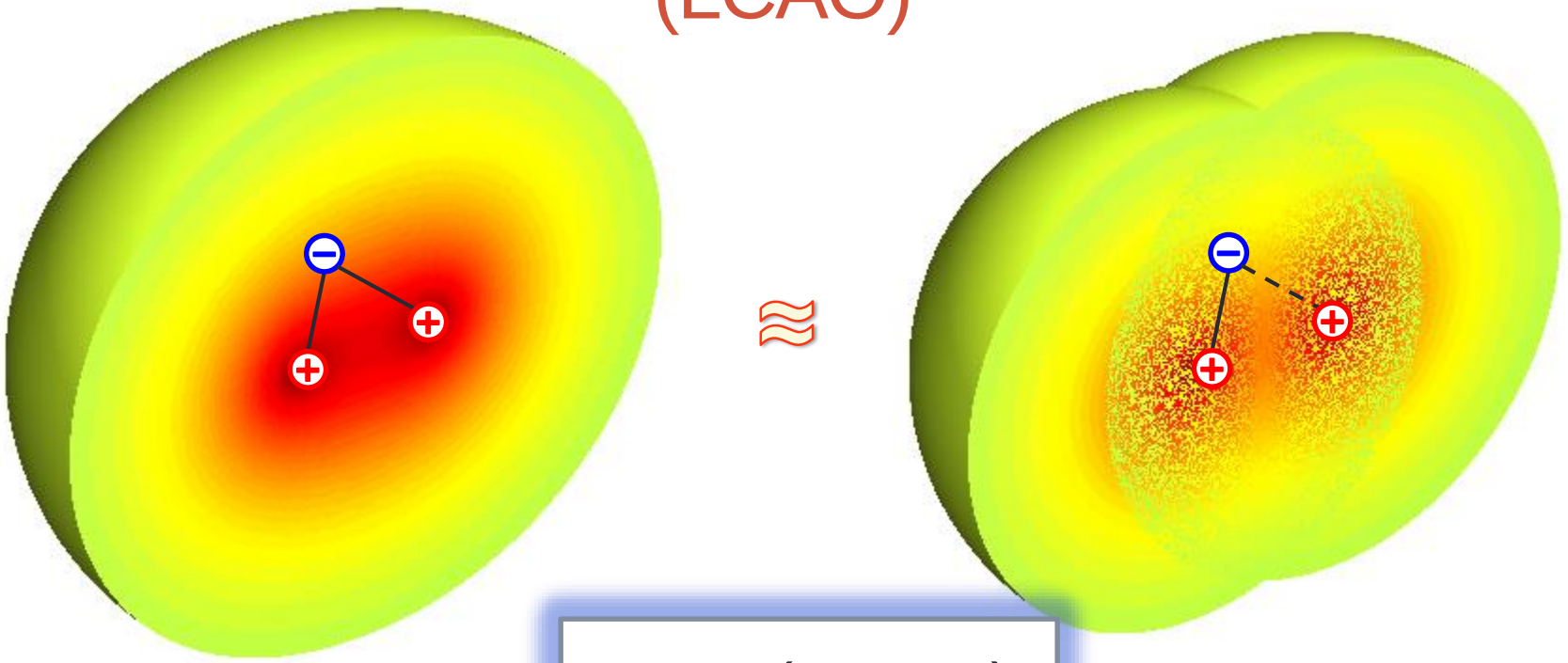




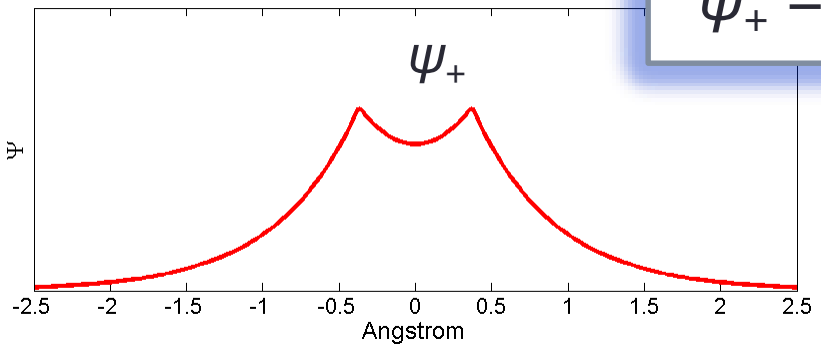
H_2^+: the Simplest Molecule

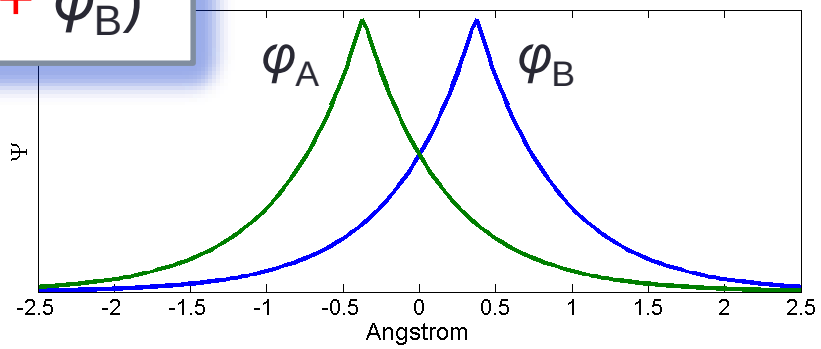


Linear Combination of Atomic Orbitals (LCAO)



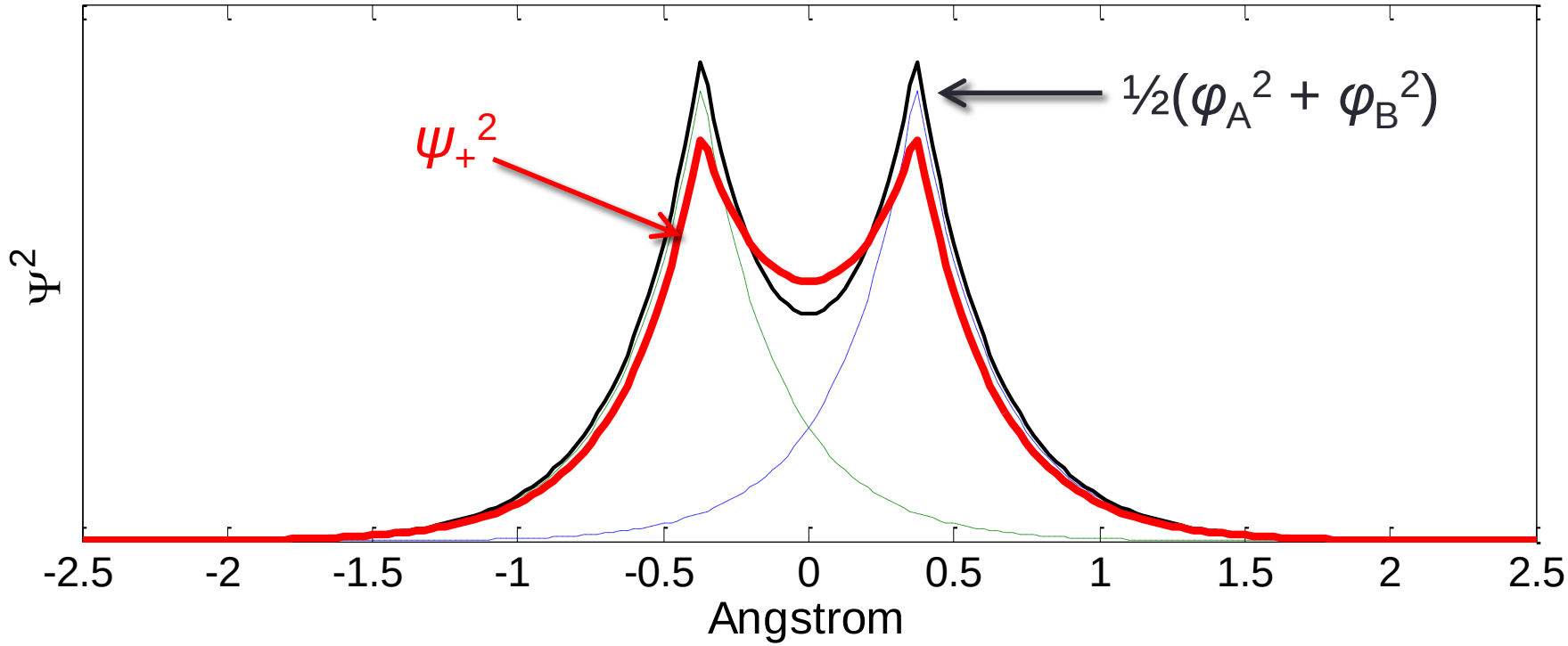
$$\psi_+ = c(\varphi_A + \varphi_B)$$



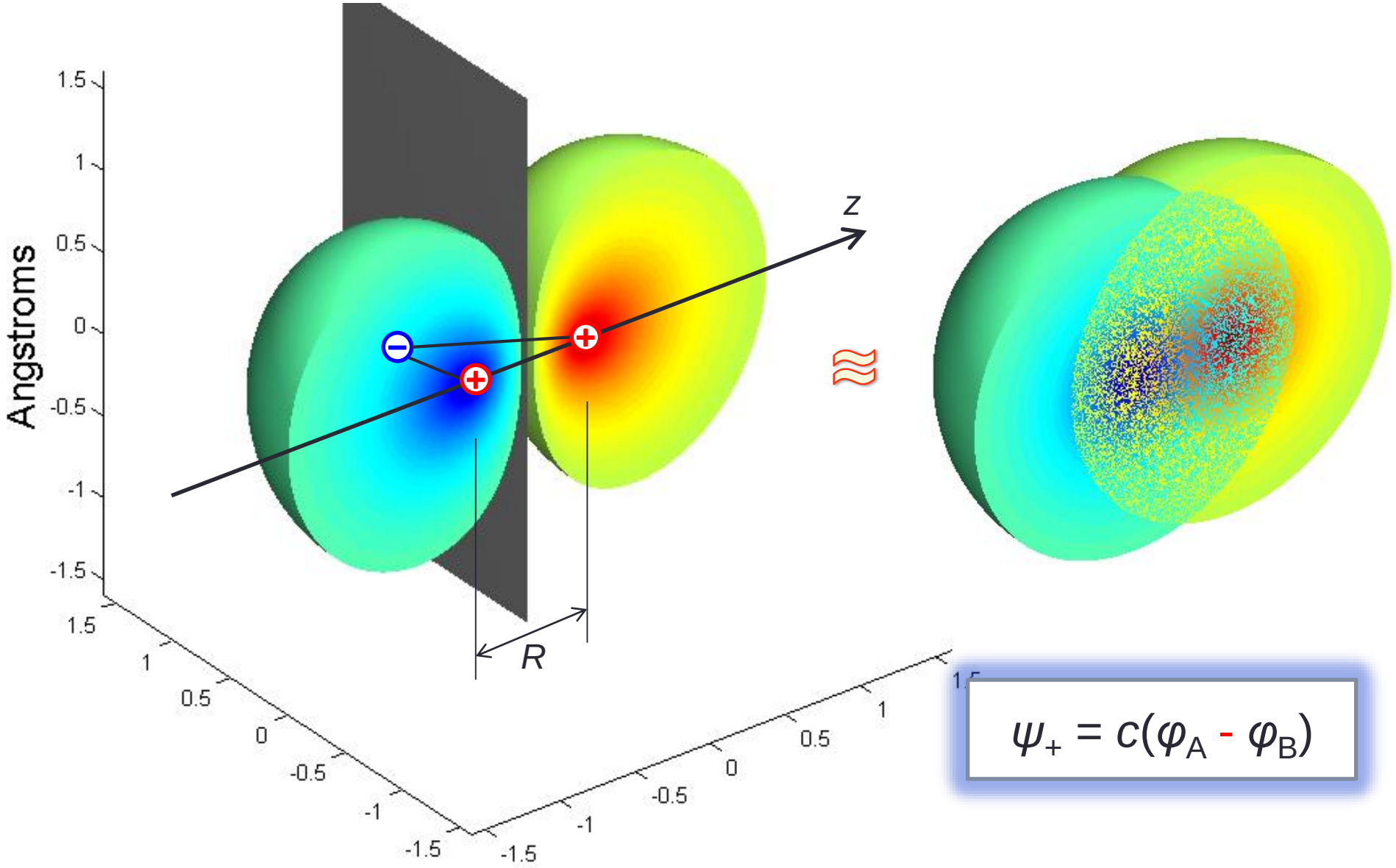


Bonding from Constructive Interference

$$\psi_+^2 = c^2(\varphi_A + \varphi_B)^2 = c^2(\varphi_A^2 + \varphi_B^2 + 2\varphi_A\varphi_B)$$



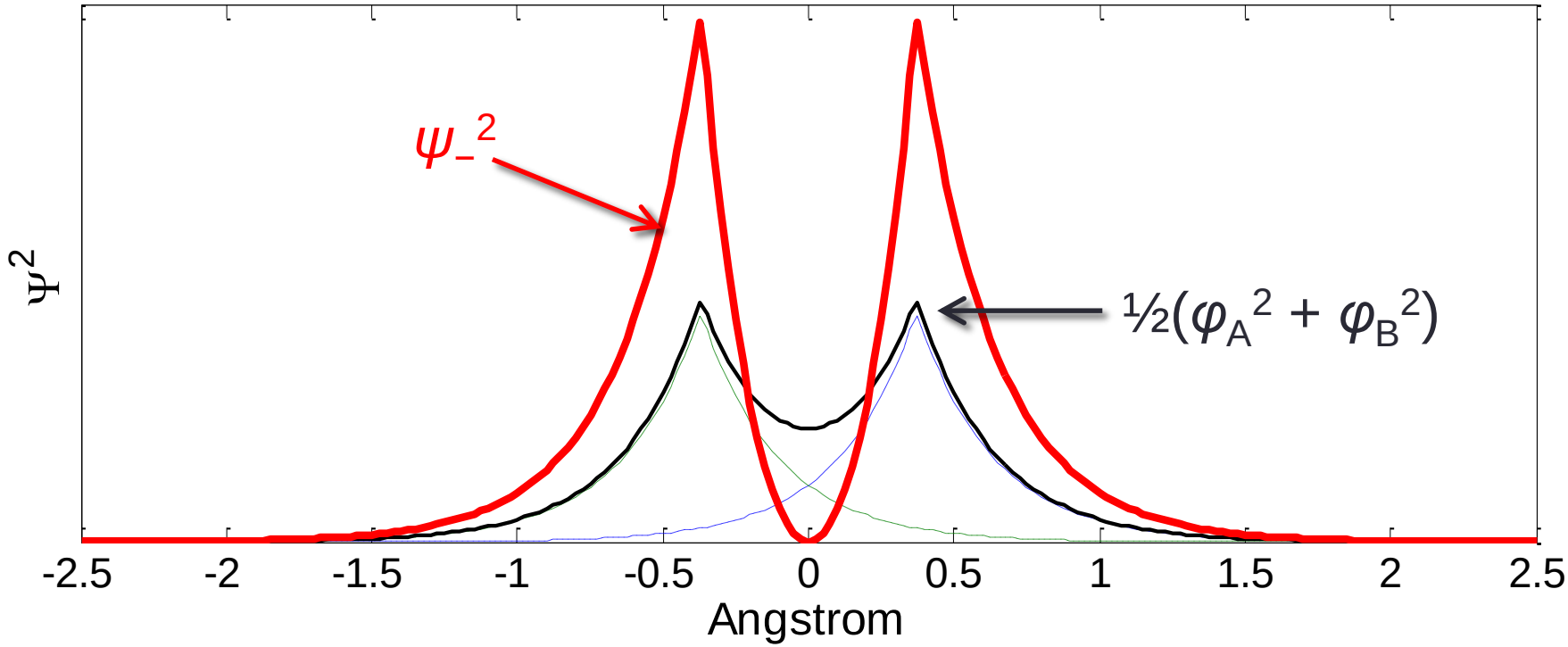
Antibonding Orbital of H_2^+



$$\psi_+ = c(\varphi_A - \varphi_B)$$

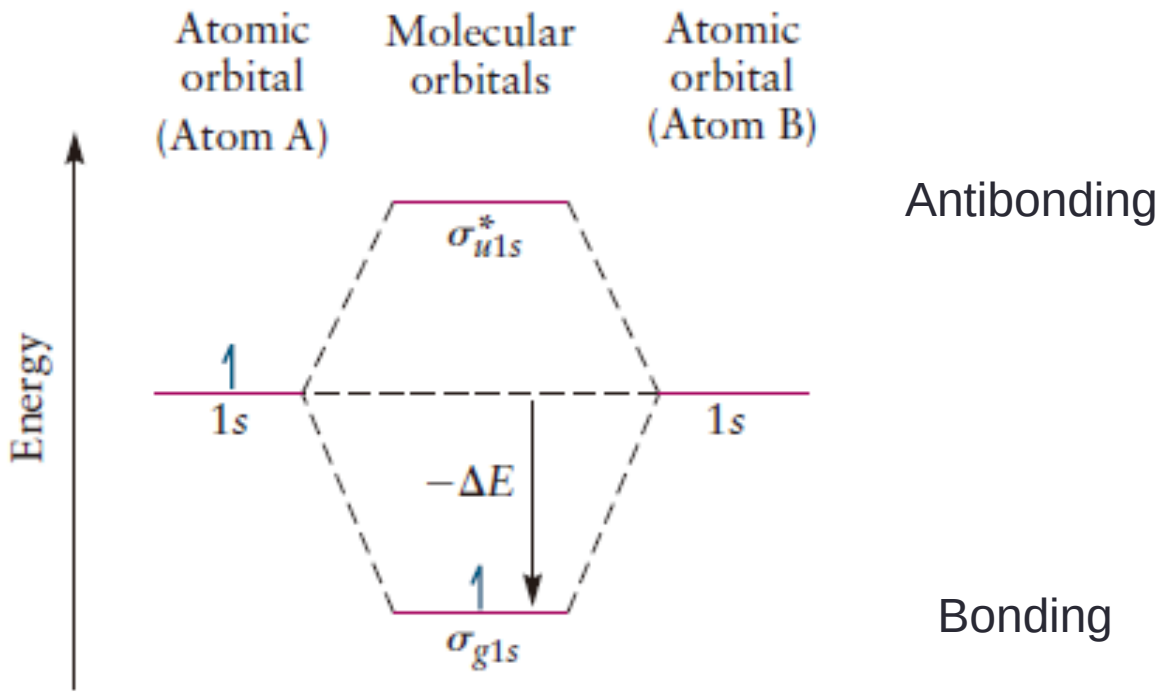
Antibonding from Destructive Interference
反键

$$\psi_-^2 = c^2(\varphi_A - \varphi_B)^2 = c^2(\varphi_A^2 + \varphi_B^2 - 2\varphi_A\varphi_B)$$



Molecular Orbital Theory using LCAO

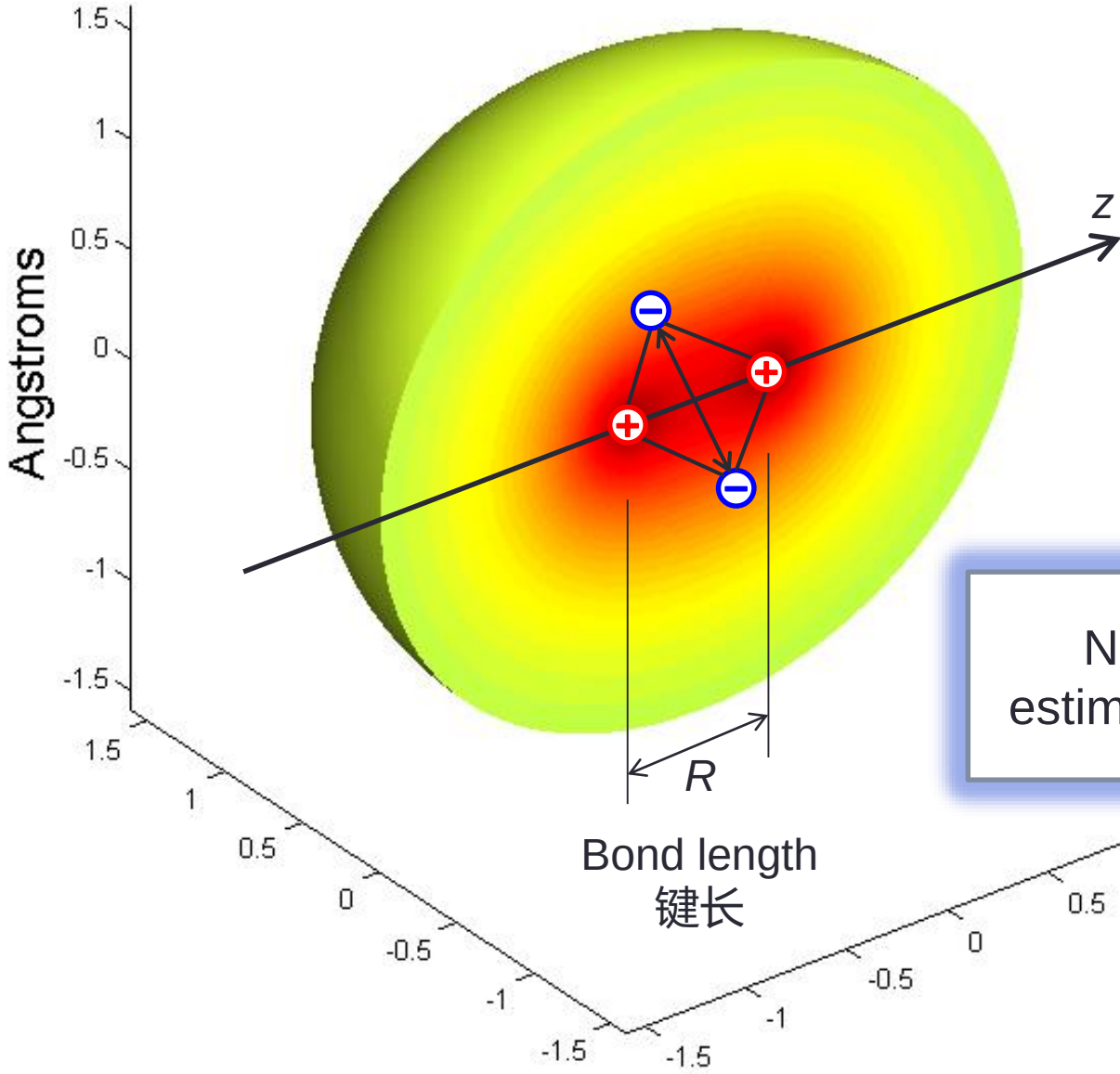
Correlation diagram of H_2^+



By Mulliken and Hund, based on the molecule spectroscopy.

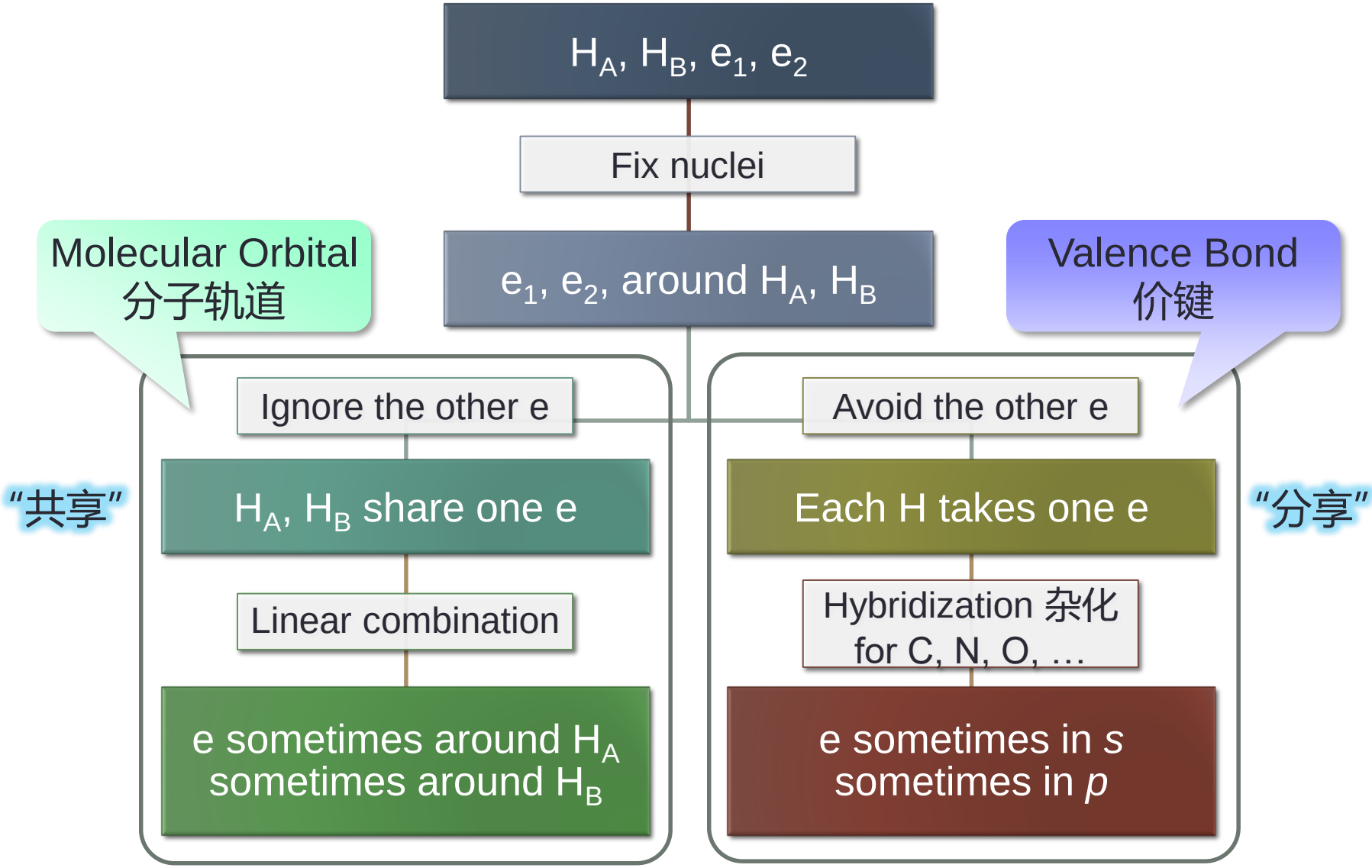
1. In a molecule, electrons belong to all the nucleus, not to any single one.
2. Arrangement of electrons on orbitals obey the Aufbau principle.
3. Molecular orbital is approximately the linear combination of all the atomic orbitals

Molecular Orbital of H_2



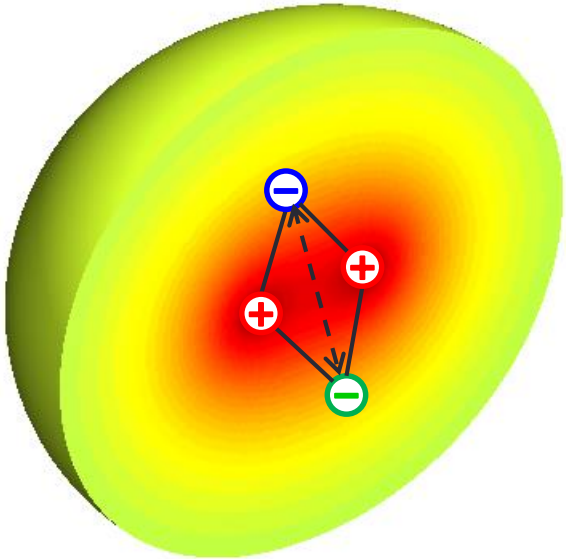
No easy way to estimate e-e repulsion

H_2: Levels of Approximation



Molecular Orbital Theory

Each (valence) electron moves around all nuclei.



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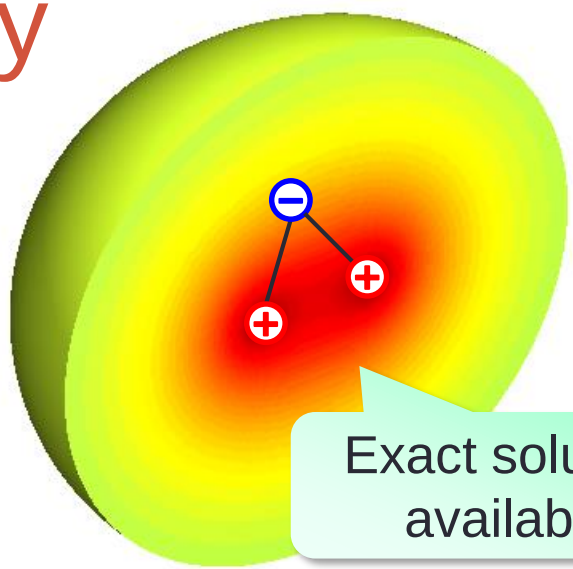
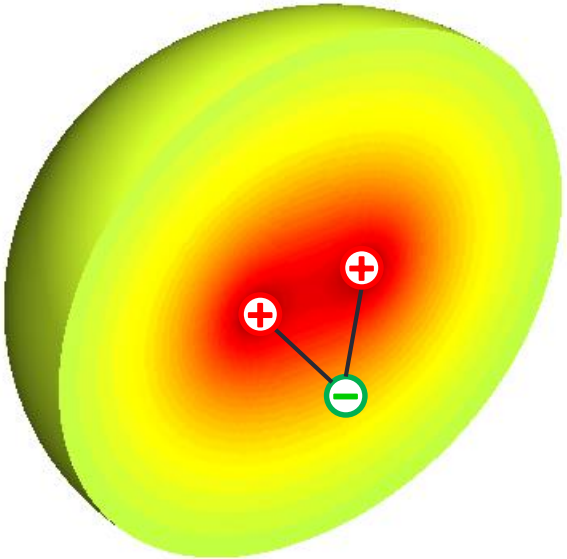


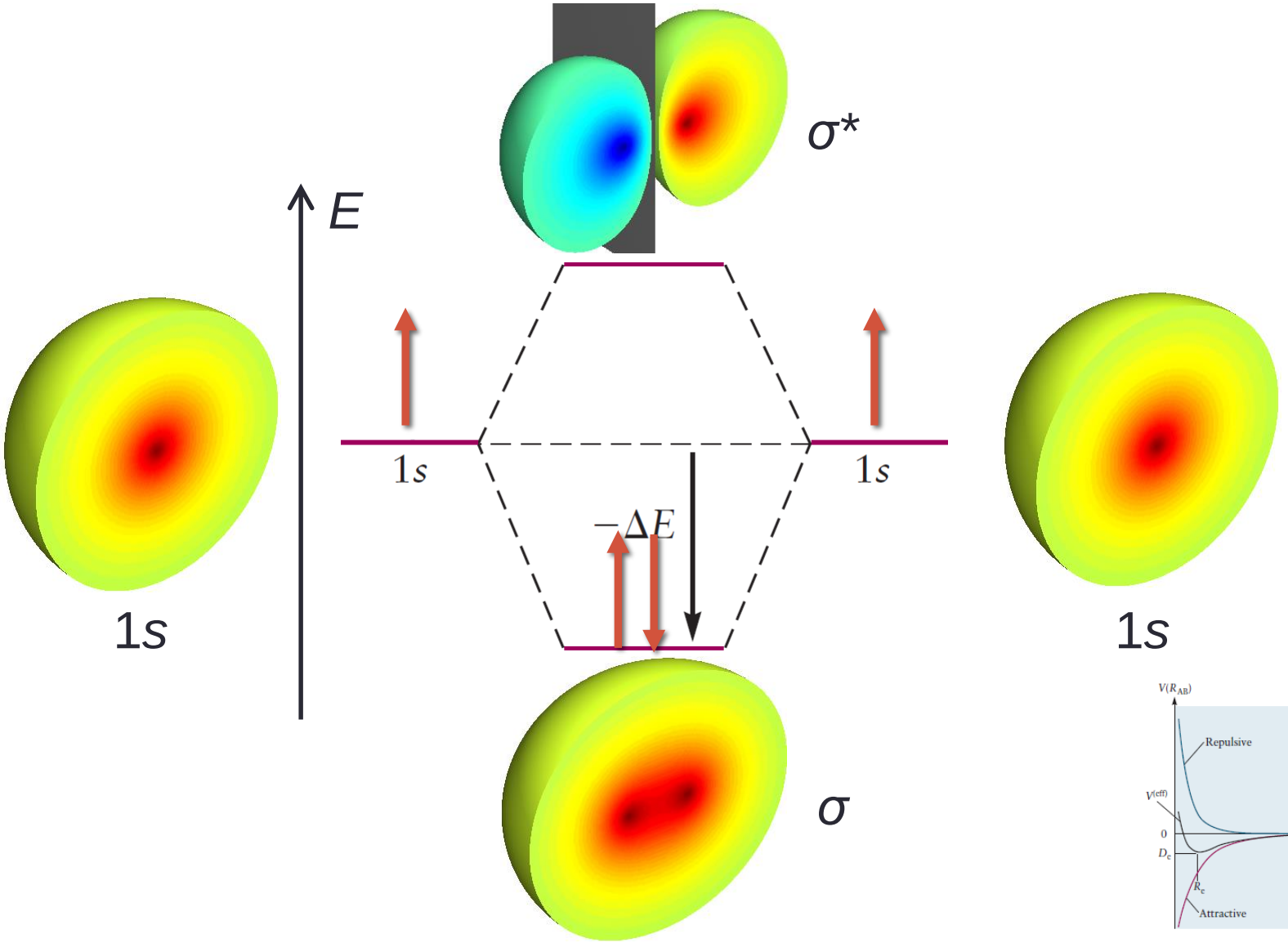
Exact solution available

×



相互独立事件

Orbital Correlation Diagram 轨道相关图



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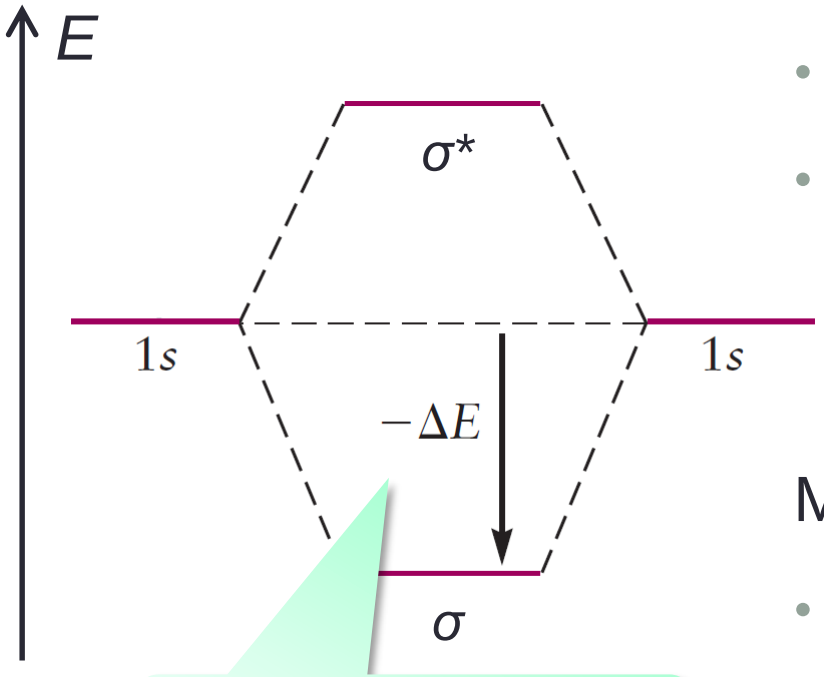
Features in the Correlation Diagram



How to estimate ΔE?

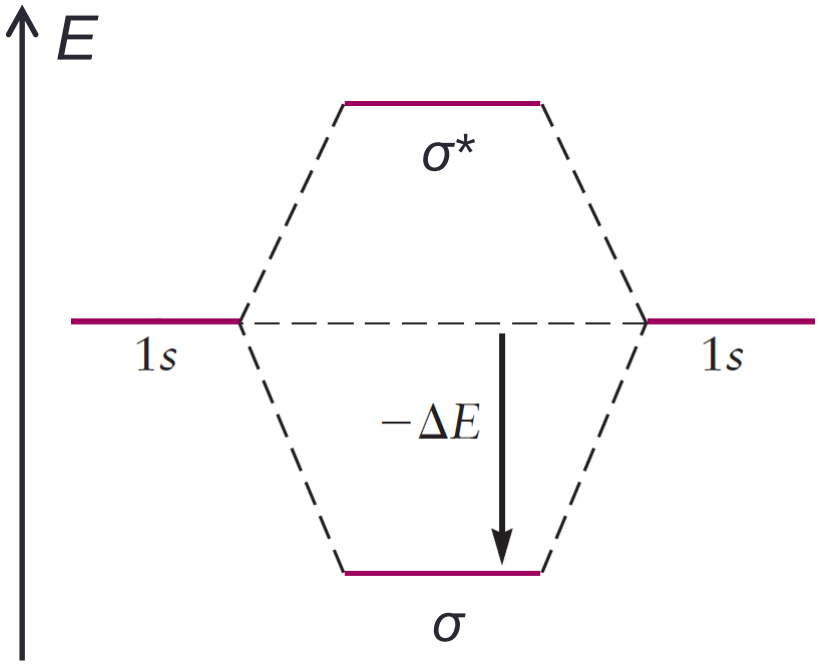
Molecular orbitals *do not* change:

- Total number of orbitals
- Total energy of all orbitals
- Total number of electrons

Molecular orbitals *allow*

- Splitting of the orbital energies
- ≥ Half of the electrons to be more stable than the rest

First-Period Diatomic Molecules



$H^{\bullet} + {}^{\bullet}H \longrightarrow H_2$ $\Delta E =$

$1s^1$ $1s^1$ σ^2 −4.47 eV

$He: + :He \nrightarrow He_2$ $\Delta E \geq 0$

$1s^2$ $1s^2$ $\sigma^2\sigma^{*2}$

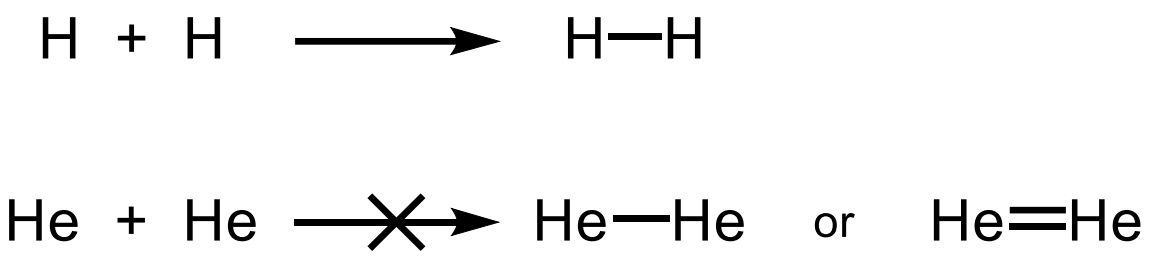
$H^{\bullet} + H^{+} \longrightarrow H_2^{+}$ $\Delta E =$

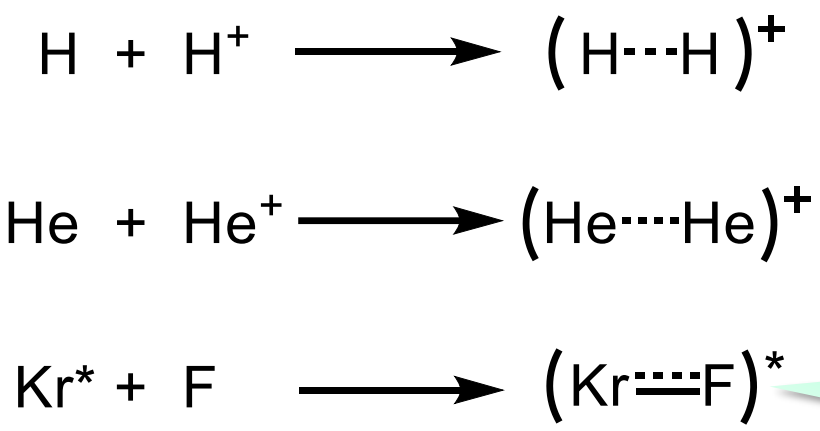
$1s^1$ $1s^0$ σ^1 −2.64 eV

$He: + {}^{\bullet}He^{+} \longrightarrow He_2^{+}$ $\Delta E =$

$1s^2$ $1s^1$ $\sigma^2\sigma^{*1}$ −2.60 eV

The Nature of the Chemical Bond





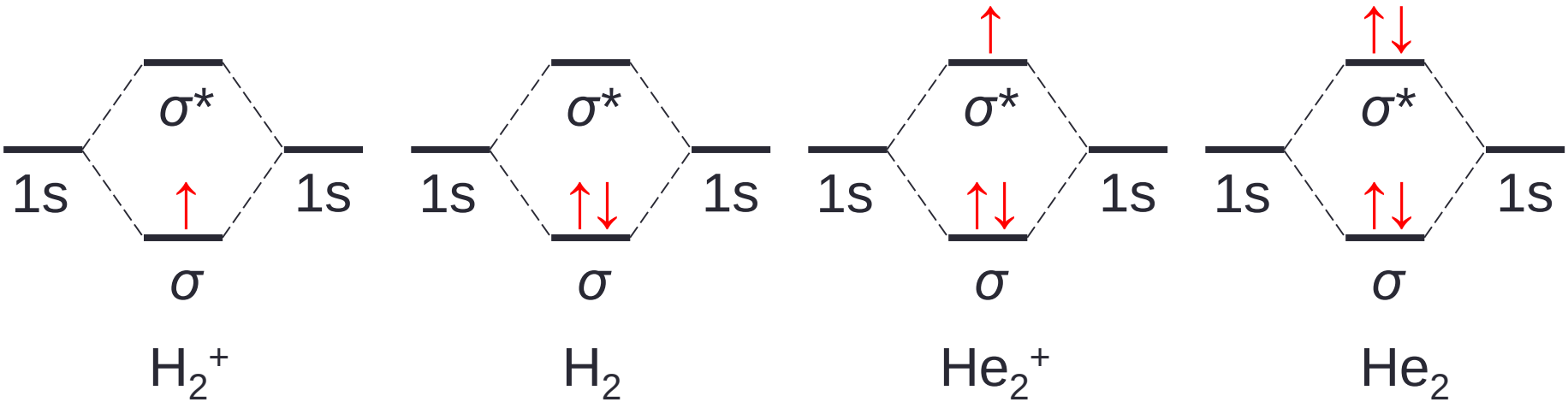
Excimer
受激准分子

Bond Order 键级

Number of bonds		Bond order
Single	单键	1
Double	双键	2
Triple	叁键	3

Bond order = (No. of bonding electrons − No. of antibonding electrons) ÷ 2

Bond Order (2)



Species	Electron Configuration	Bond Order	Bond Energy (kJ mol^{-1})	Bond Length (Å)
H_2^+	$(\sigma_{g1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{g1s})^2$	1	431	0.74
He_2^+	$(\sigma_{g1s})^2(\sigma^*_{u1s})^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{g1s})^2(\sigma^*_{u1s})^2$	0	~0	Large

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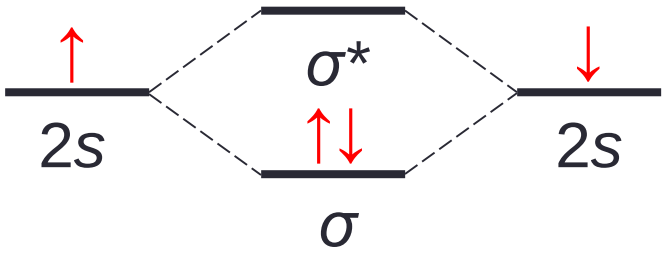
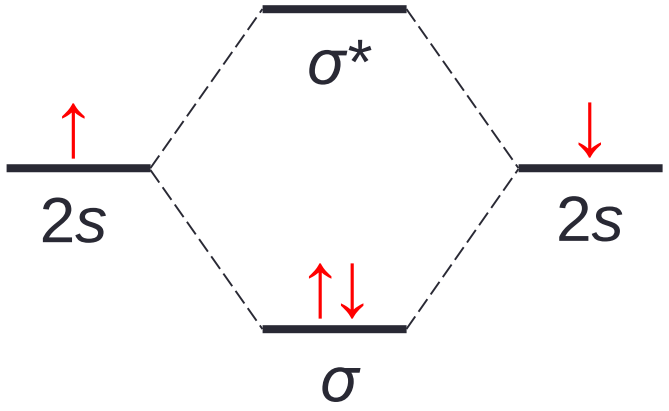
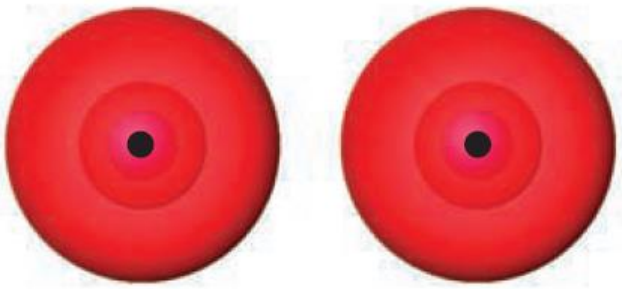
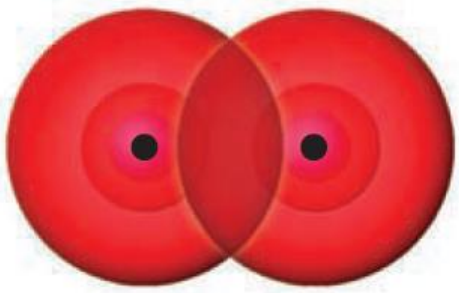
Factors for Effective Bonding

① Maximum orbital overlap



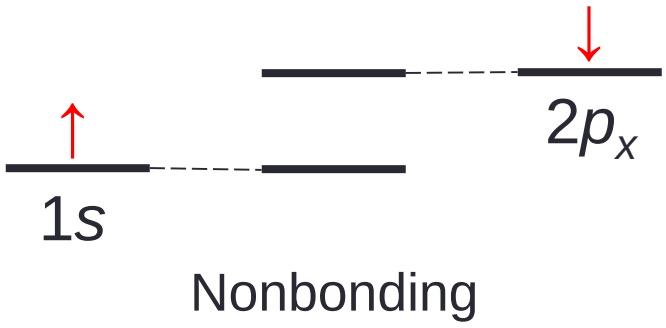


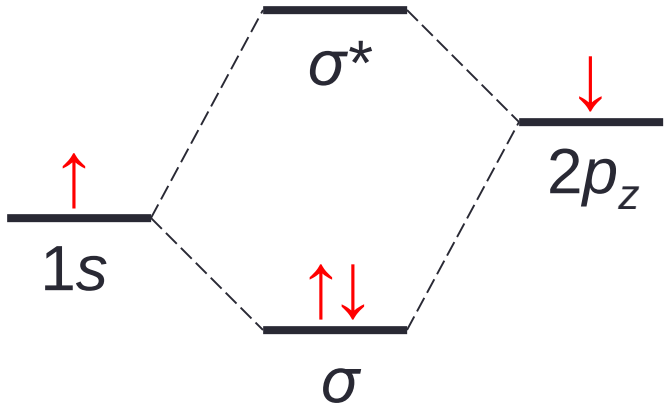


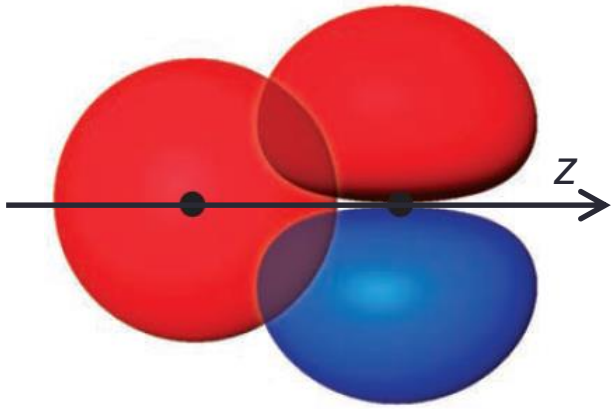


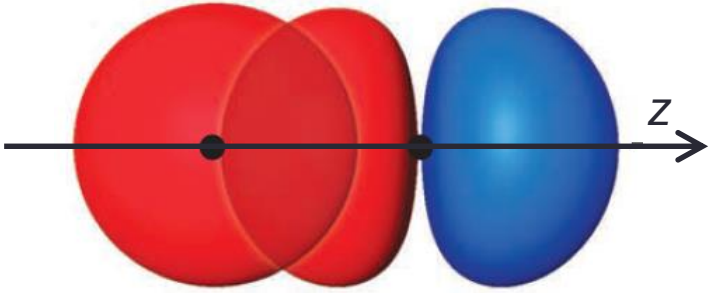
Factors for Effective Bonding

② Compatible orbital symmetries



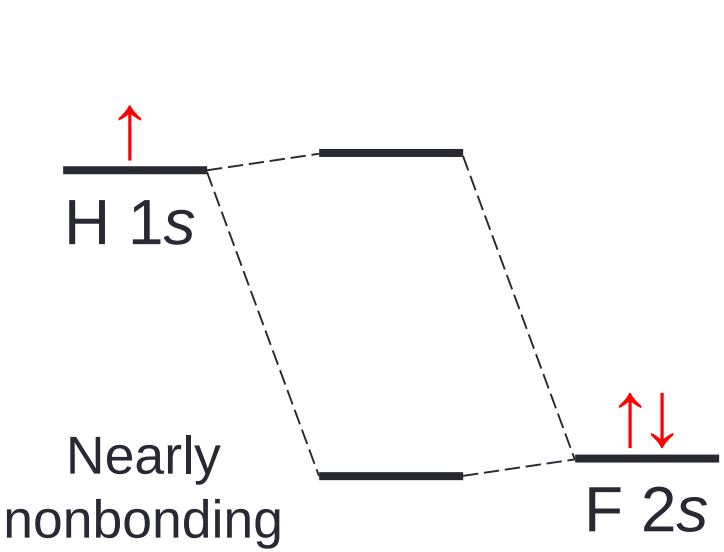


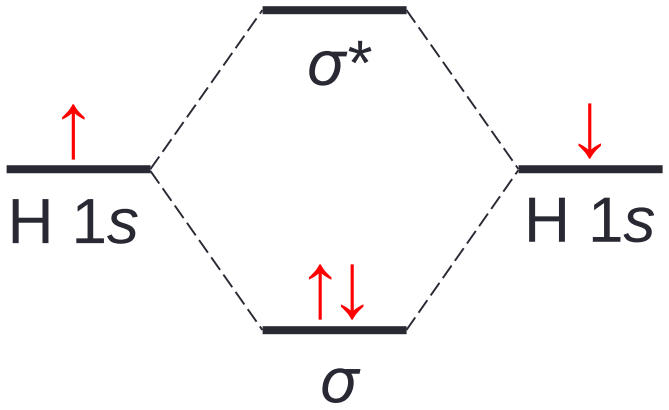


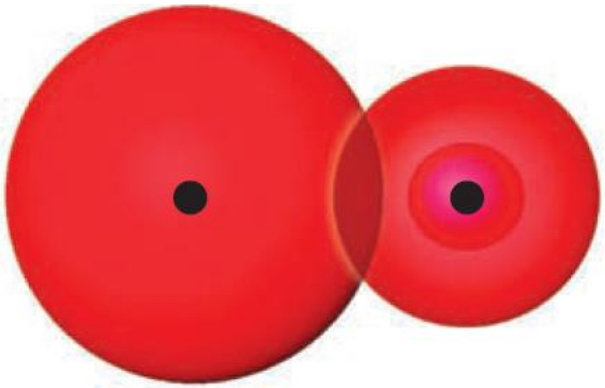


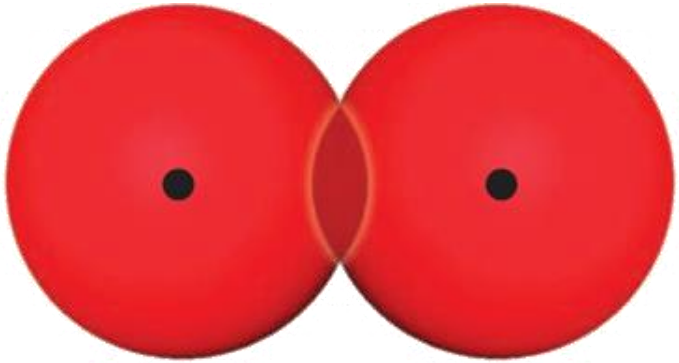
Factors for Effective Bonding

3. Approximate atomic orbital energies



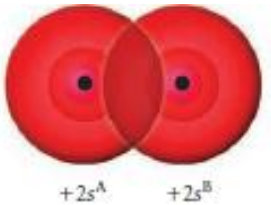


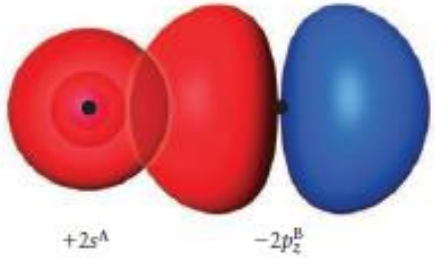


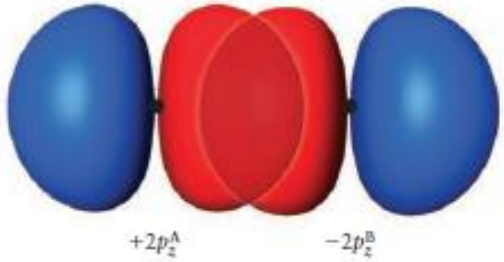


The σ Bond: $L_z = 0$

- Compatible orbital symmetries
- s + s
- p + p
- s + p
- d + p

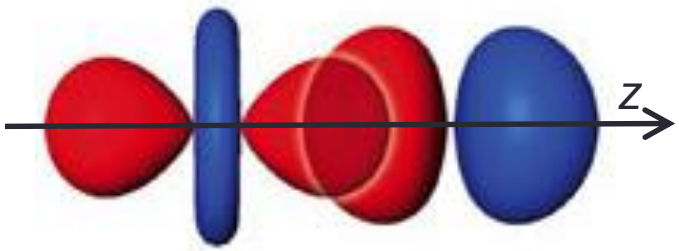




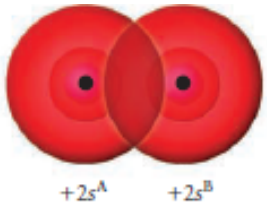


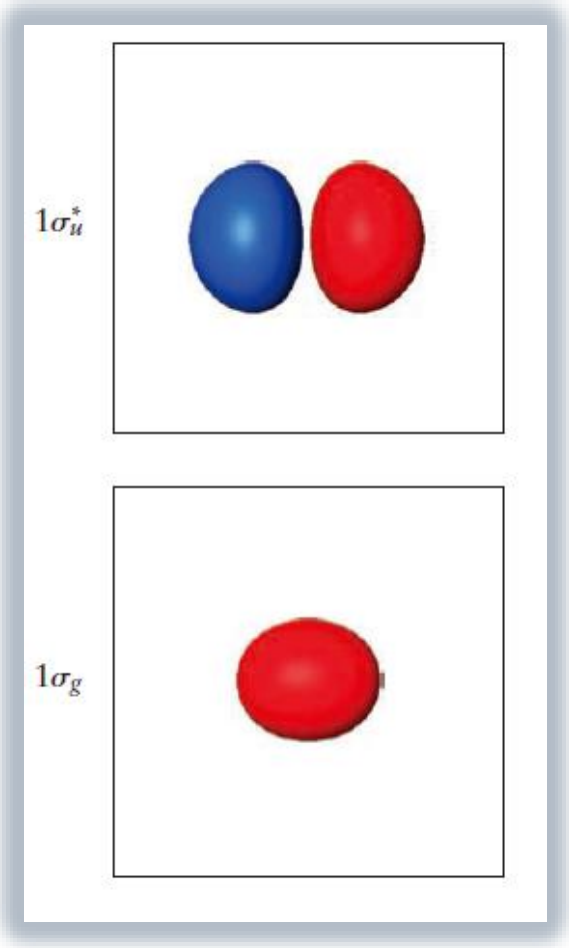
- Approximate atomic orbital energies
- heteronuclear diatomic molecule

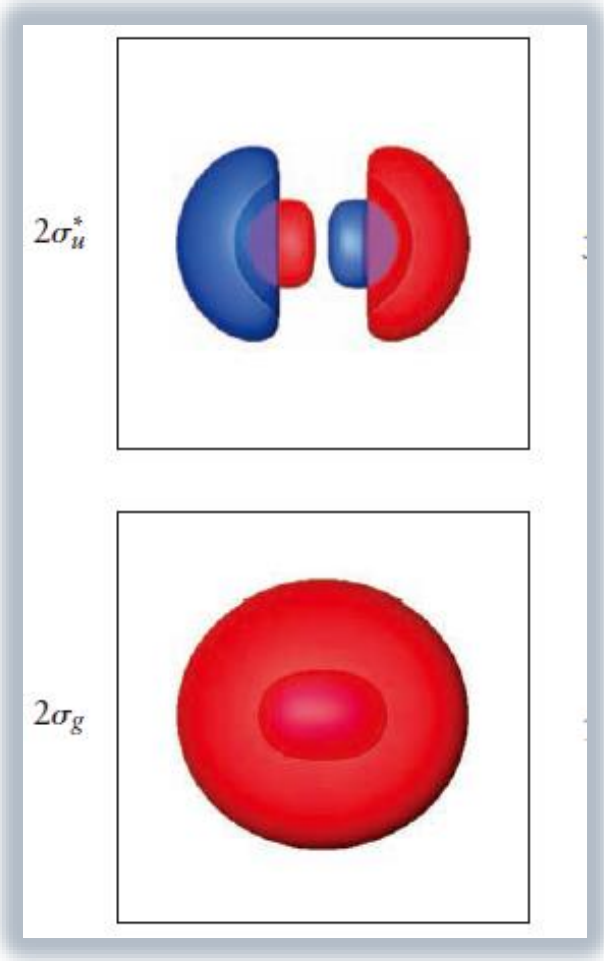
No nodal plane that contains the bond axis.



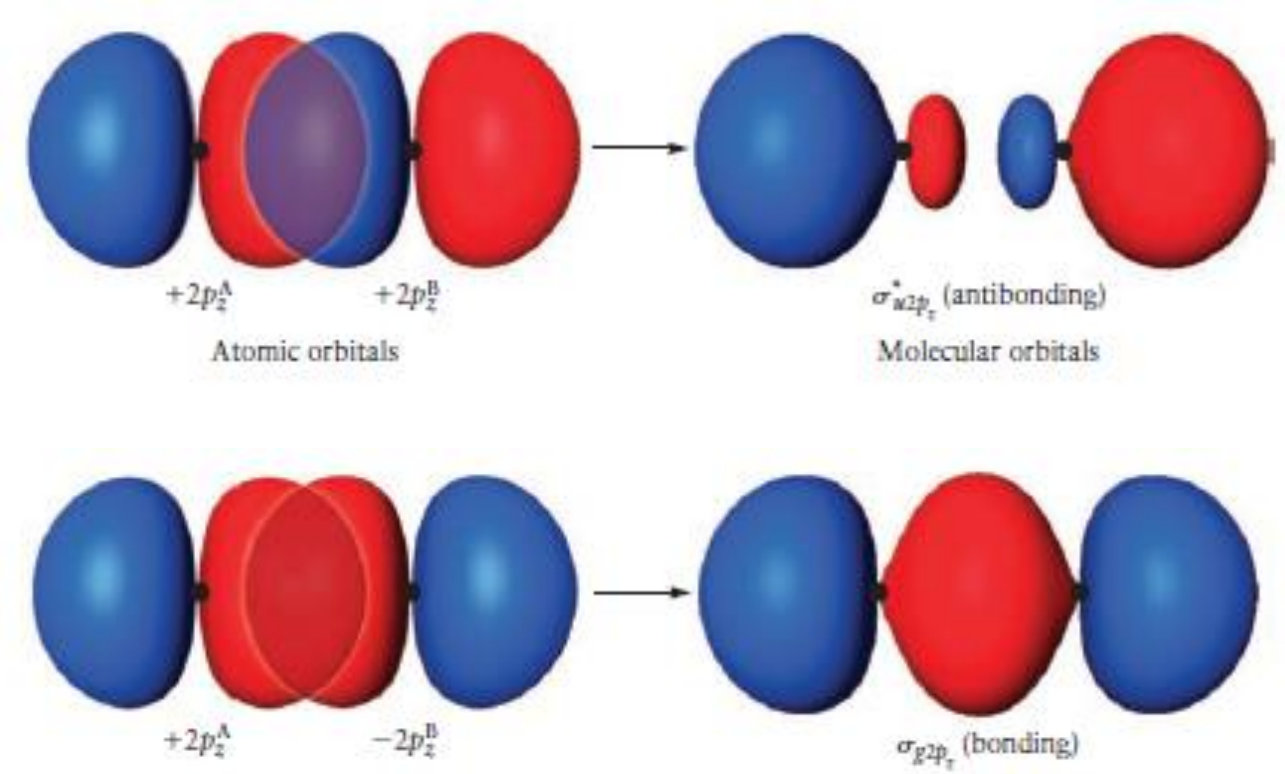
The σ Bond



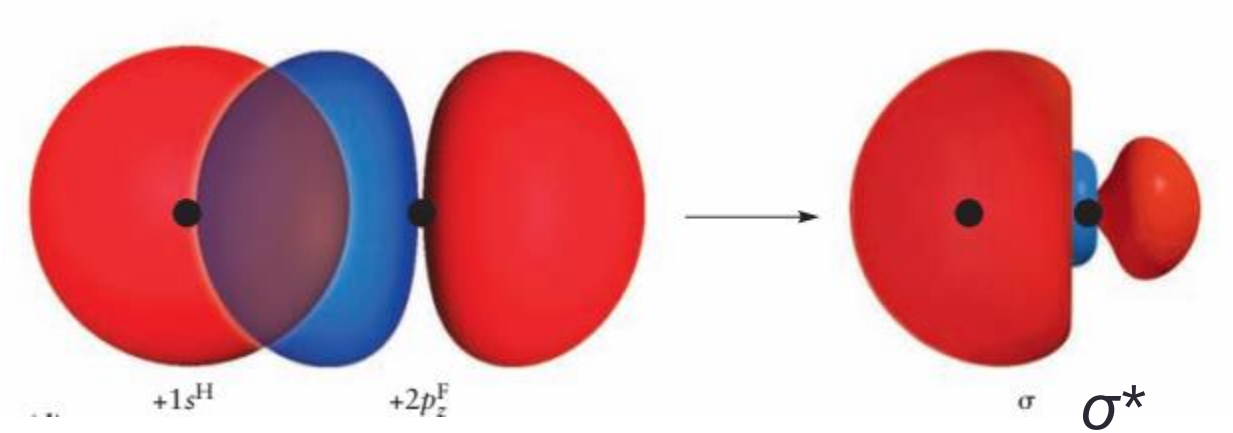


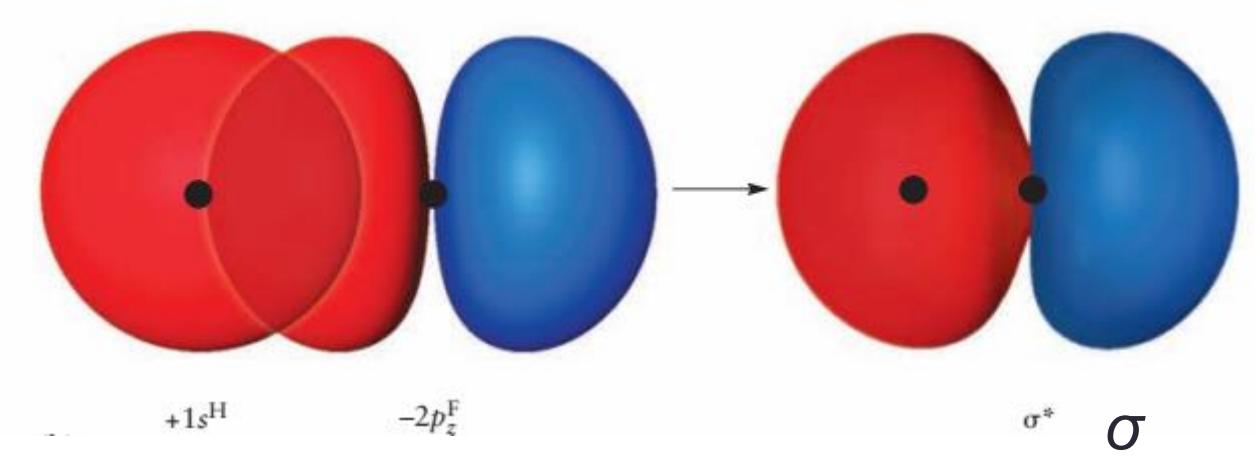


The σ Bond

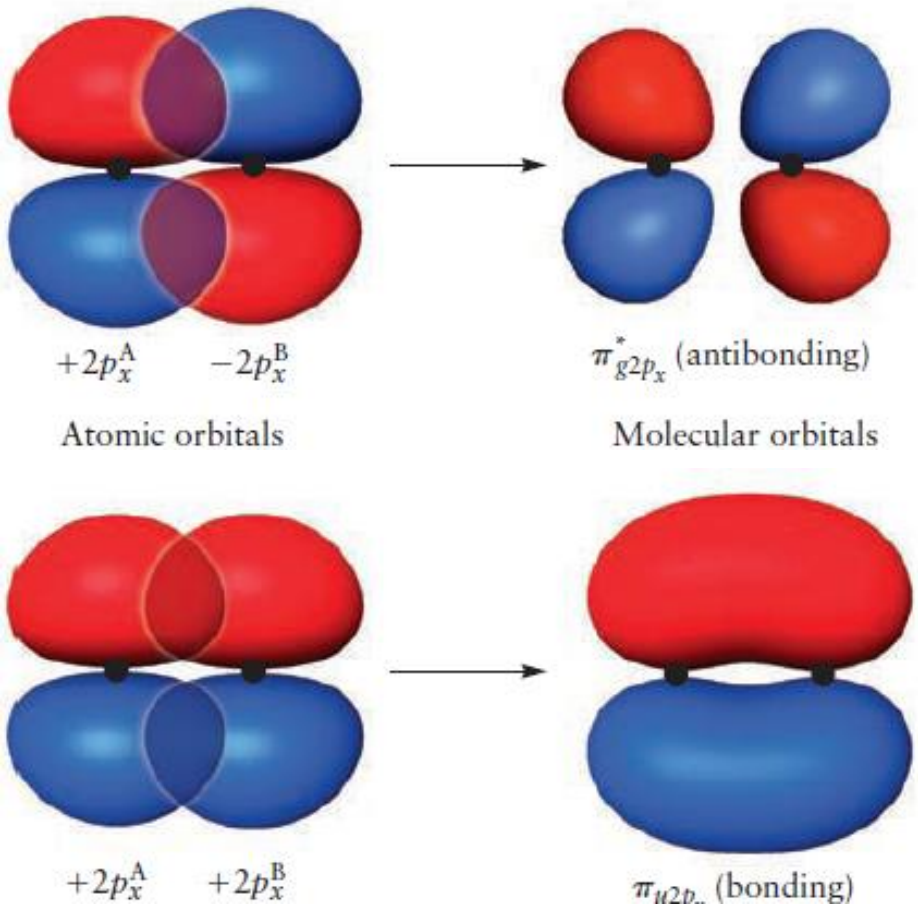

$+2p_z^A$
$+2p_z^B$
Atomic orbitals
$\sigma^*_{u2p_z}$ (antibonding)
Molecular orbitals
$+2p_z^A$
$-2p_z^B$
σ_{g2p_z} (bonding)

The σ Bond





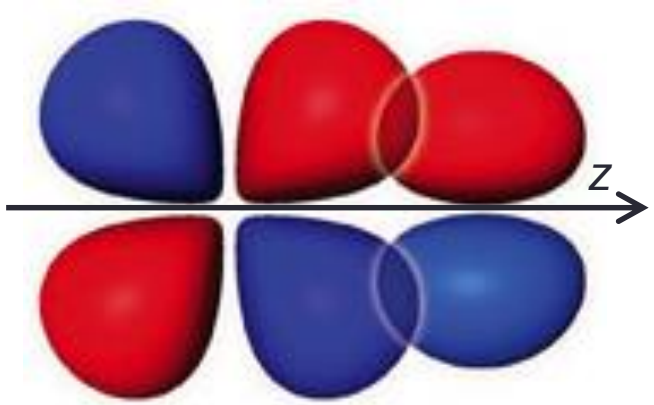
The π Bond



- 2p + 2p = 1 σ Bond and 2 π Bonds

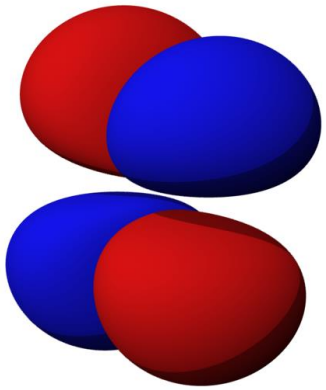
The π Bond: $L_z = \pm\hbar$

1 nodal plane that contains the bond axis.

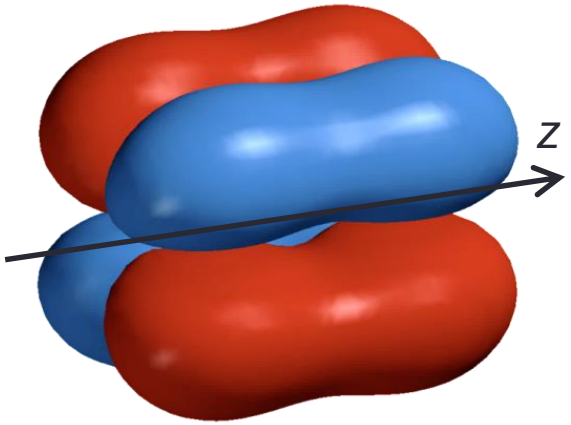


And more…

Nodal planes	Atomic orbital	L_z	Molecular orbital	L_z
0	*s*	0	σ	0
1	*p*	$-\hbar$, 0, $\hbar$	π	$\pm\hbar$
2	*d*	$-2\hbar$, $-\hbar$, 0, $\hbar$, $2\hbar$	δ	$\pm2\hbar$



d orbital



δ orbital

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- Molecular Orbital Theory (1927)
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  - Bonding, antibonding, nonbonding
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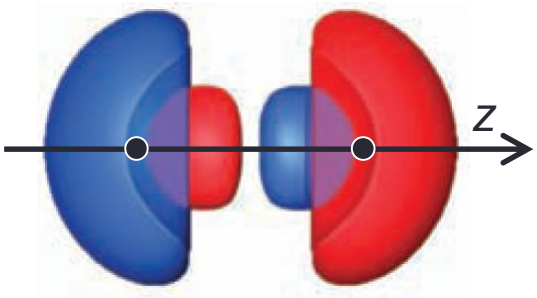
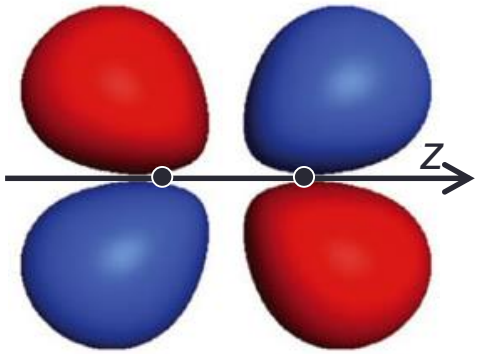
- Diatomic molecules

Node(s) in the Antibonding Orbital

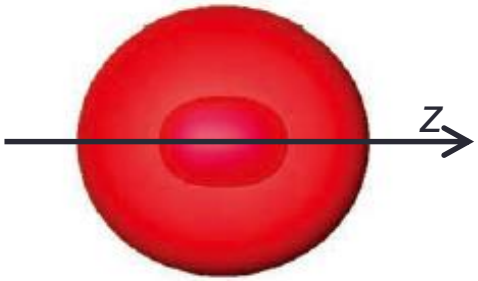
1 nodal plane in the middle of the bond.



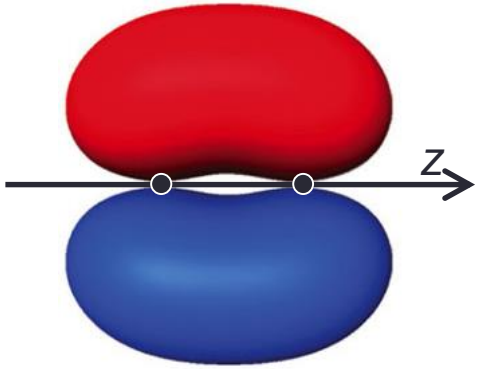
σ^*



π^*



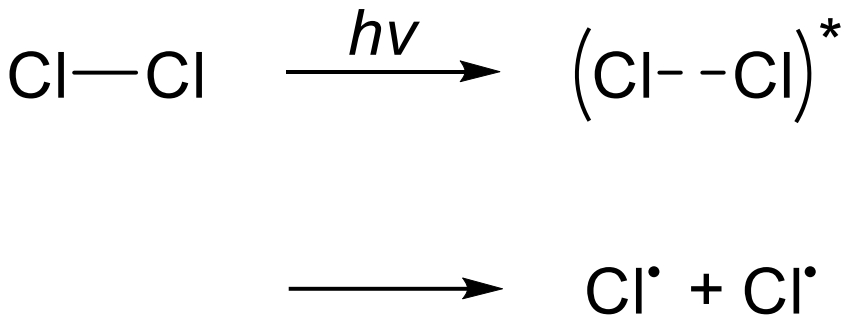
σ

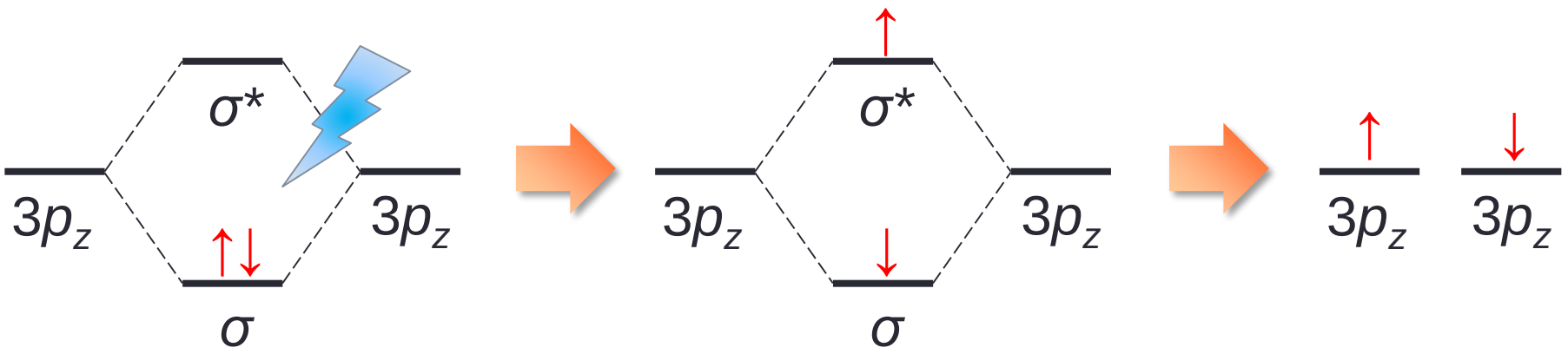


π

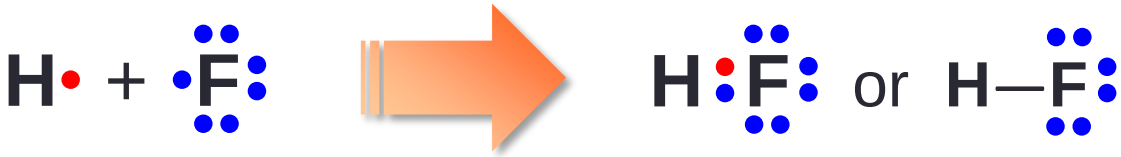
Meaning of the Antibonding Orbital

$H_2 + Cl_2 \longrightarrow 2\ HCl$



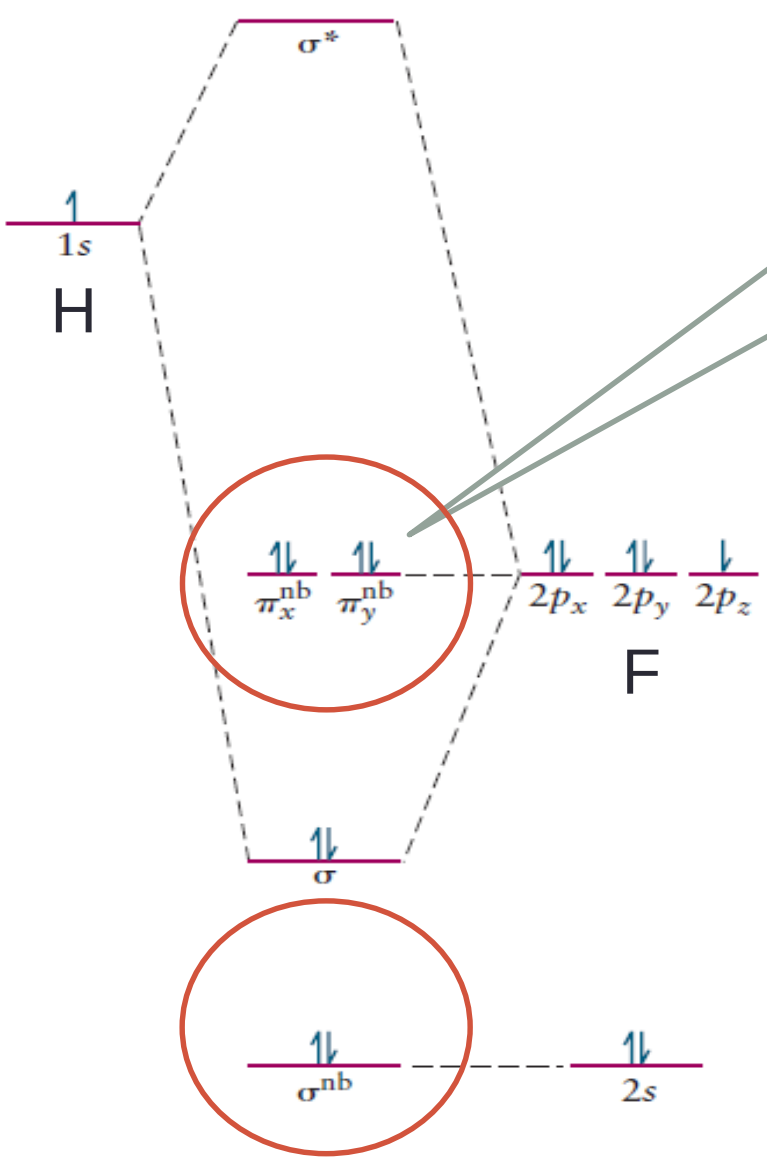


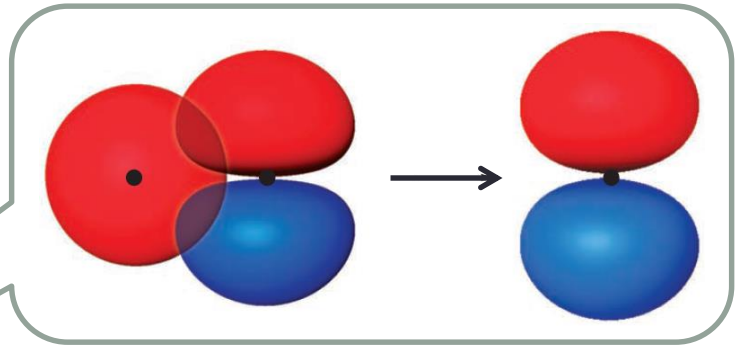
Nonbonding



Lewis: Lone electron pair
MO: e pair in nonbonding orbital

Nonbonding





MO: Nonbonding orbital

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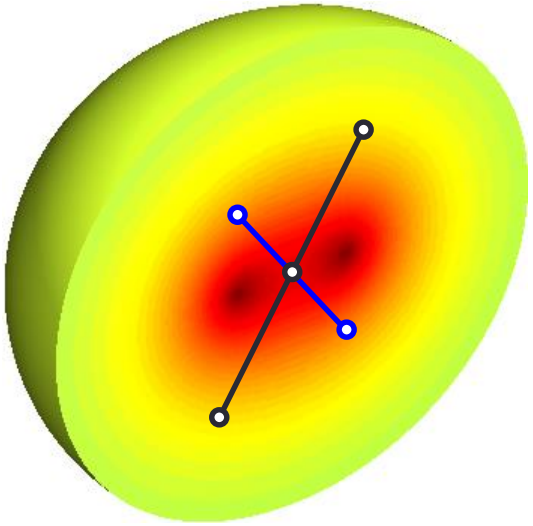
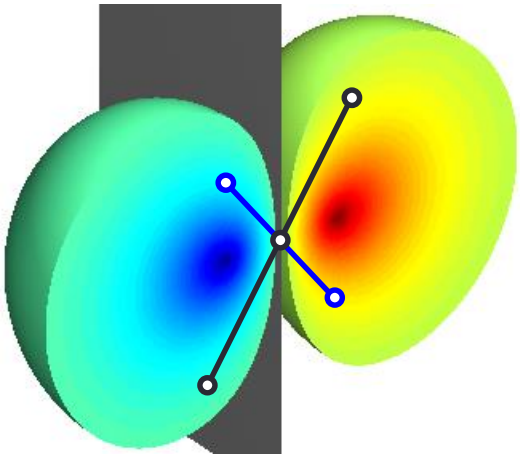
Bond Symmetry

CN	EN	DE	Label
中心对称	Centrosymmetric	gerade	*g*
(中心) 反对称	Antisymmetric	ungerade	*u*

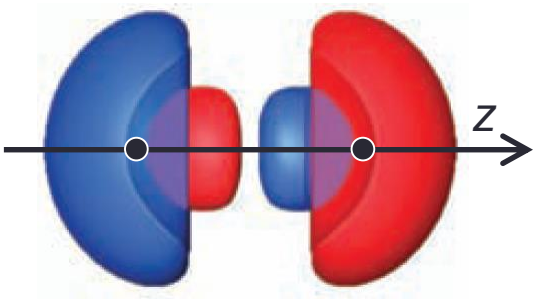


Centrosymmetric (*g*)

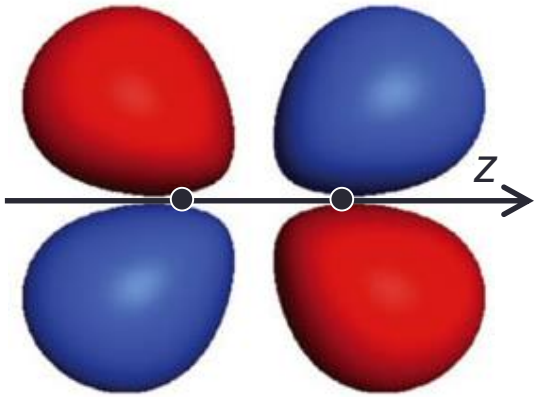


Antisymmetric (*u*)

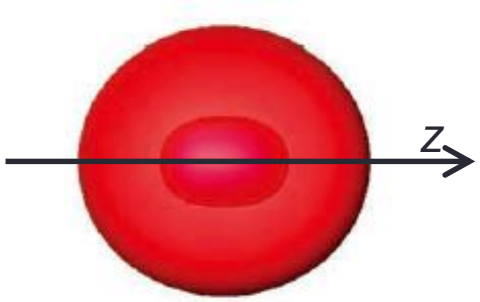
Combining Energy, Type & Symmetry



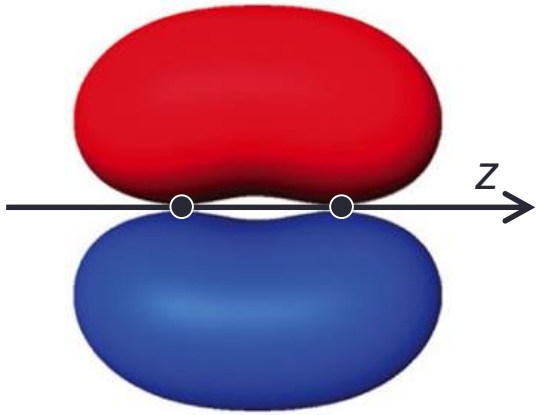
σ_u^*



π_g^*



σ_g

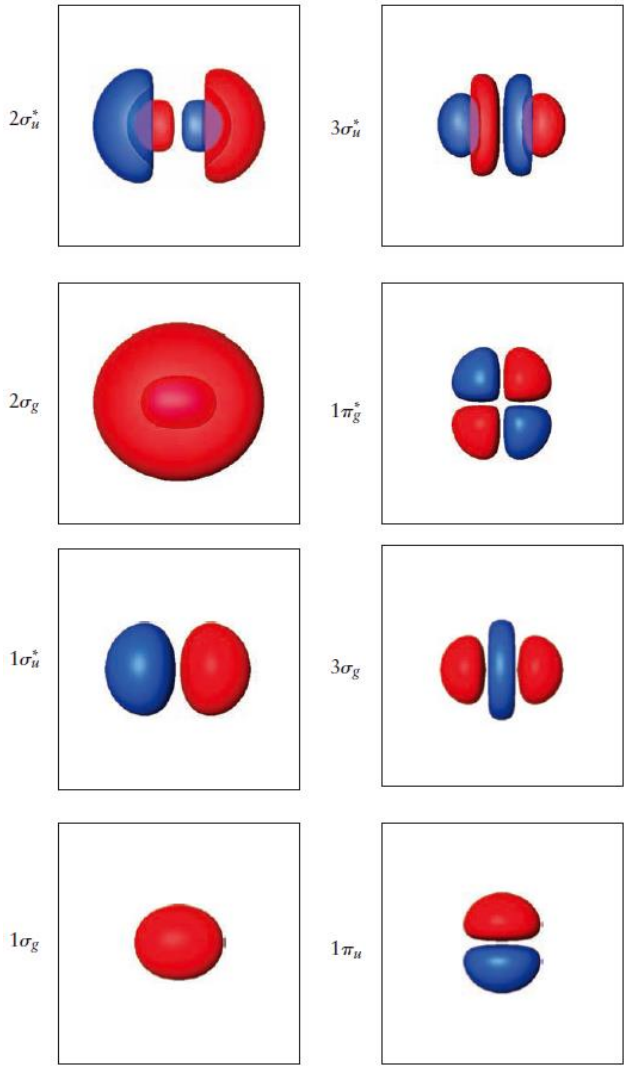


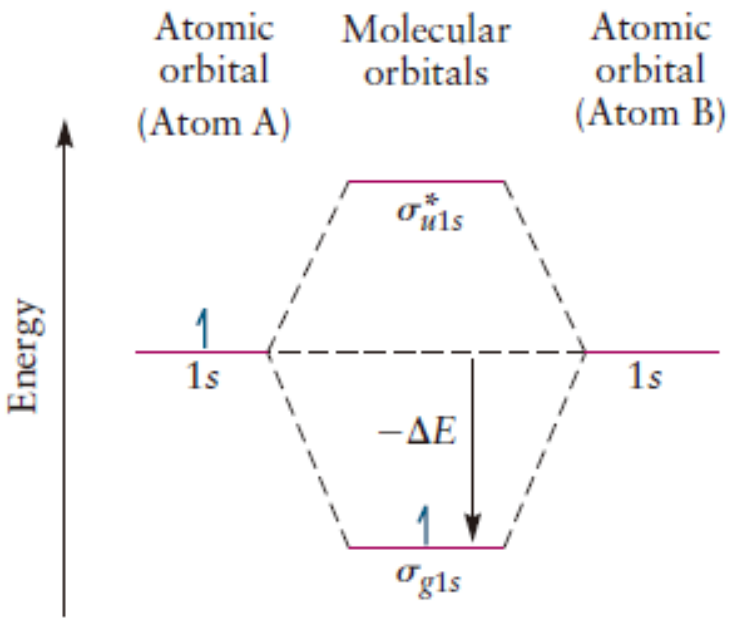
π_u

Notion of Molecular Orbitals

Exact MO Notation	LCAO MO Notation
$1\sigma_g$	σ_{g1s}
$1\sigma_u^*$	σ_{u1s}^*
$2\sigma_g$	σ_{g2s}
$2\sigma_u^*$	σ_{u2s}^*
$1\pi_u$	π_{u2p_x}, π_{u2p_y}
$3\sigma_g$	σ_{g2p_z}
$1\pi_g^*$	$\pi_{g2p_x}^*$, $\pi_{g2p_y}^*$
$3\sigma_u^*$	$\sigma_{u2p_z}^*$

H_2^+: the Simplest Molecule





Correlation diagram

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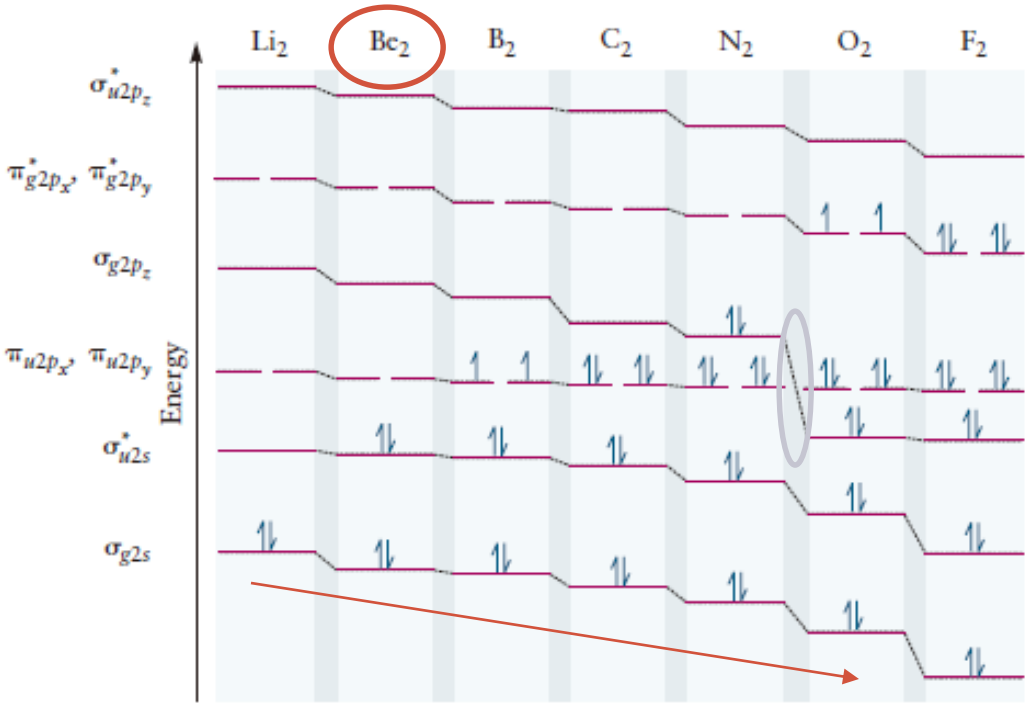
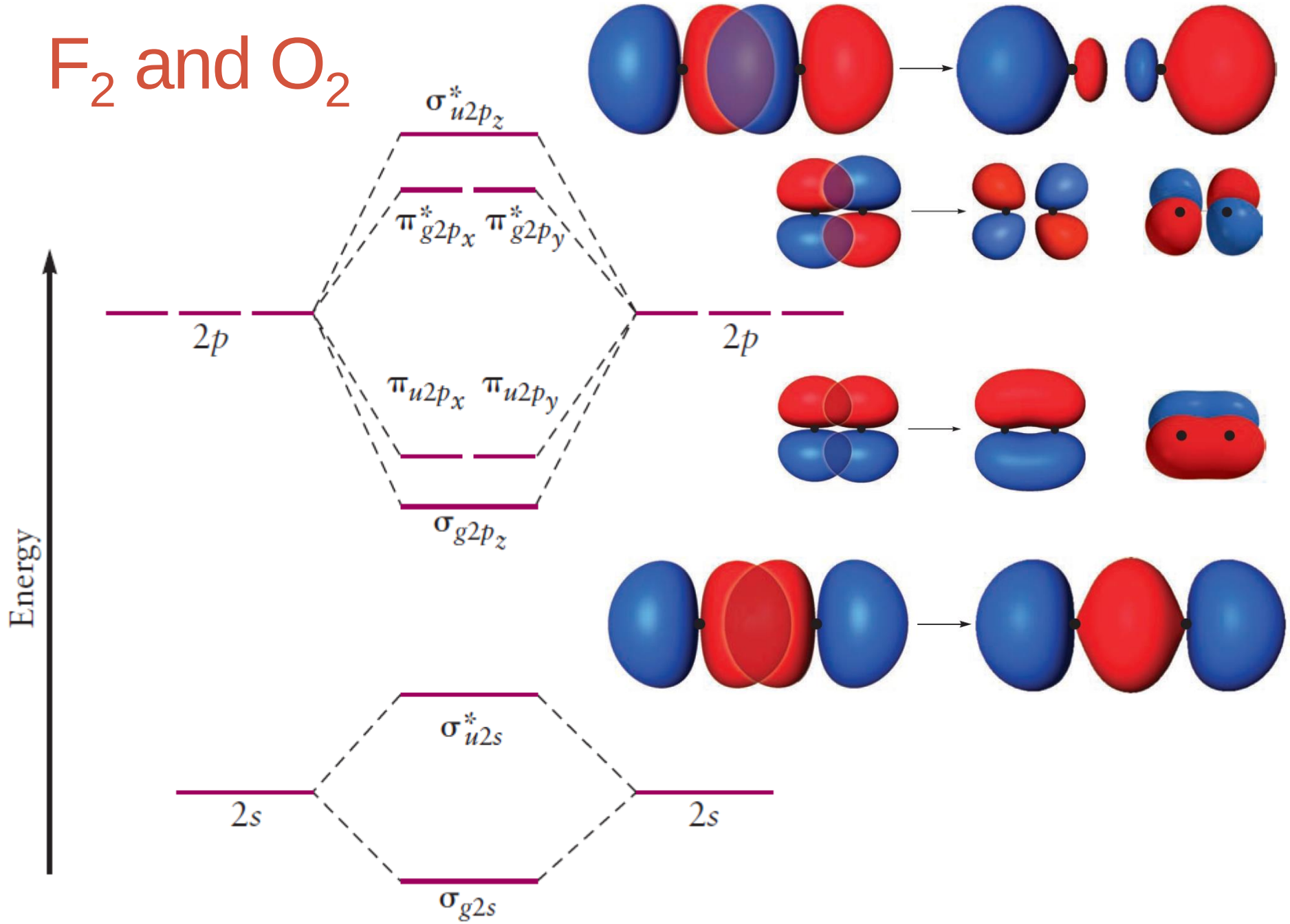
Homonuclear Diatomic Molecules

- For second period, σ_{g1s} bonding and σ^*_{u1s} antibonding orbitals are both doubly occupied, they have little net effect on bonding properties and need not be considered.

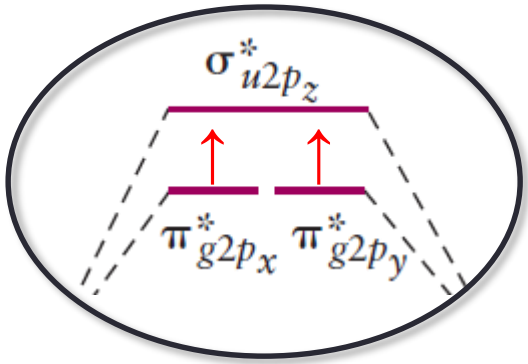


F_2 and O_2


$\sigma^*_{u2p_z}$
$\pi^*_{g2p_x}$ $\pi^*_{g2p_y}$
2p
2p
π_{u2p_x} π_{u2p_y}
σ_{g2p_z}
Energy
σ^*_{u2s}
2s
2s
σ_{g2s}

O_2: Unusual Properties (1)

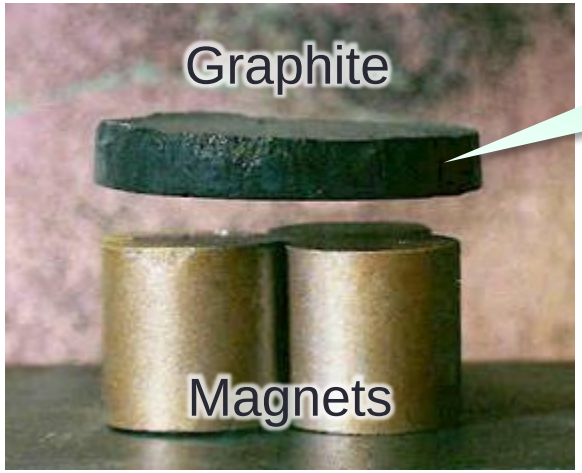
O_2 is paramagnetic due to its two unpaired electron spins.



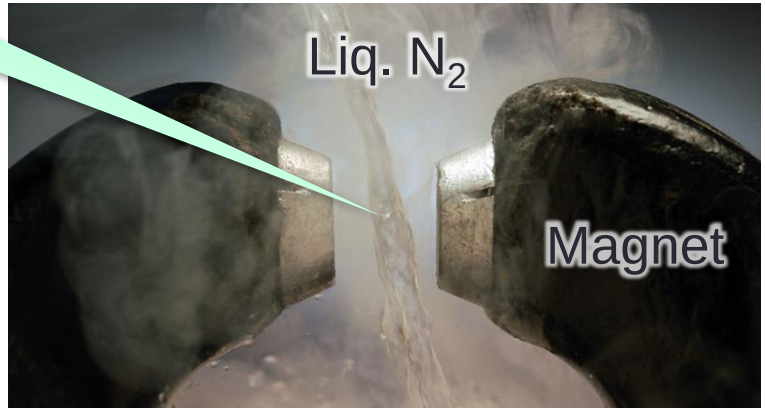
Spinning electrons

Paramagnetic 顺磁性

Orbiting electrons



Diamagnetic 反（抗、逆）磁性



Weakly diamagnetic

Lewis, G. N. *J. Am. Chem. Soc.* **1924**, *46*, 2027–2032.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MAGNETISM OF OXYGEN AND THE MOLECULE O_4

BY GILBERT N. LEWIS

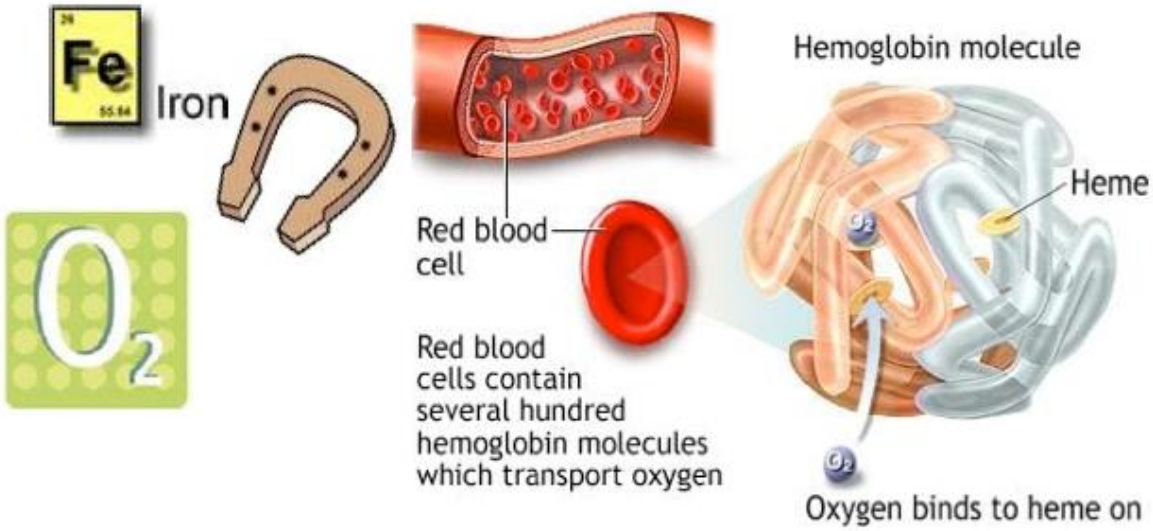
RECEIVED JUNE 25, 1924 PUBLISHED SEPTEMBER 5, 1924

One of the most characteristic properties of oxygen is its pronounced paramagnetism. This distinguishes molecular oxygen so sharply from other compounds in which oxygen is assumed to be tied by a double bond that I have recently concluded[1] that there is no double bond in the O_2 molecule. Rather I have assumed that the two electrons which have been supposed to constitute the second bond are actually separate so that each atom has an odd electron, according to the formula $:\dot{\ddot{O}}:\dot{\ddot{O}}:$. Indeed, oxygen has the chemical properties of a molecule with odd electrons, for it has an appreciable color, and a much higher reactivity than has commonly been ascribed to it.

O_2: Unusual Properties (2)

- Liquid O_2 is pale blue.

- O_2 reacts readily with transition metals, but slowly with common organics at r.t.



$$H_2C{=}CH_2 + Br_2 \xrightarrow[\text{r.t.}]{\text{Fast}} CH_2BrCH_2Br$$

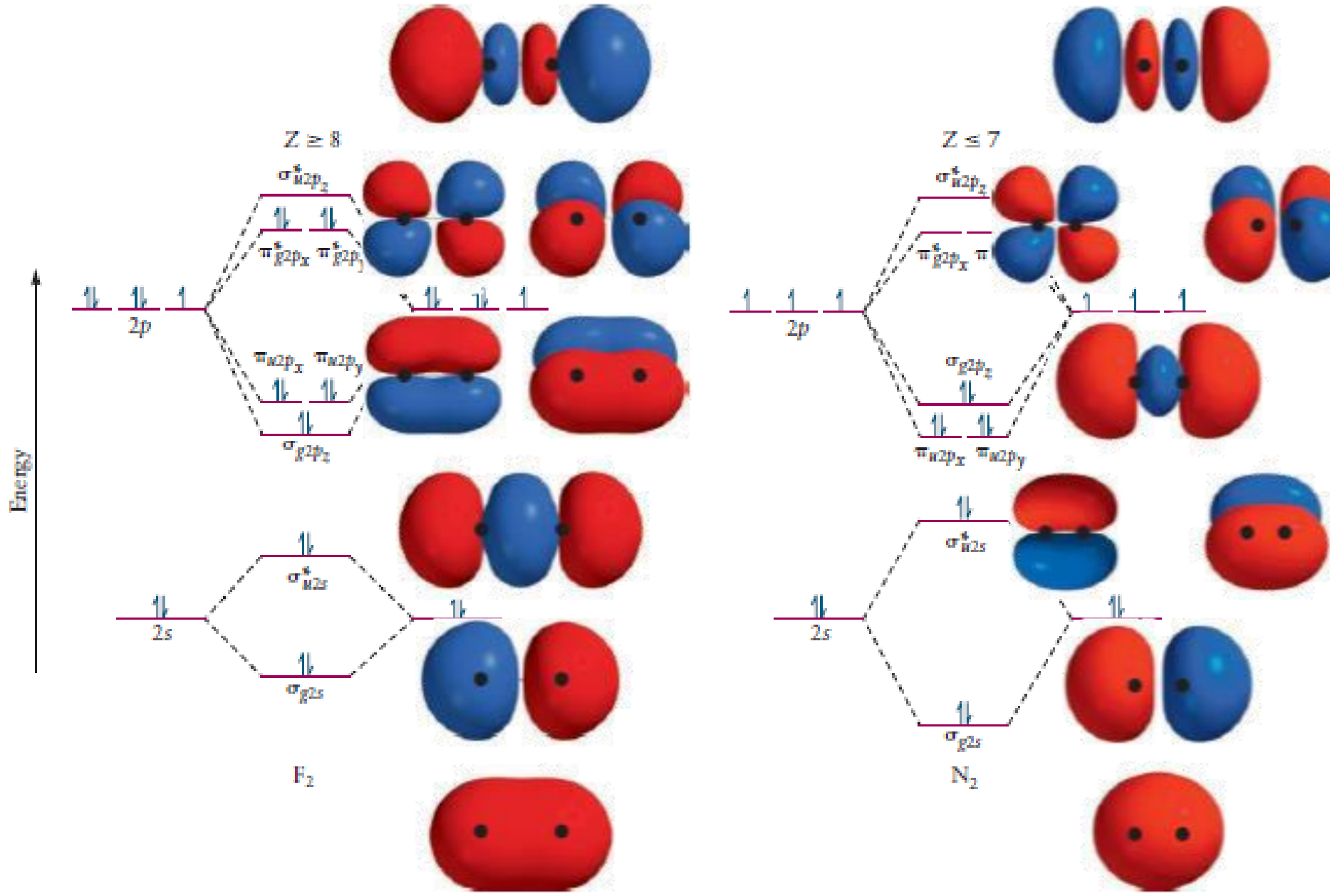
$$H_2C{=}CH_2 + O_2 \xrightarrow[\text{r.t.}]{} \not\rightarrow$$

Other Species Related to O_2

	F_2	O_2^{2-}	O_2^-	O_2	O_2^+
Electronic configuration	$\sigma^2\pi^4\pi^{*4}$	$\sigma^2\pi^4\pi^{*4}$	$\sigma^2\pi^4\pi^{*3}$	$\sigma^2\pi^4\pi^{*2}$	$\sigma^2\pi^4\pi^{*1}$
Bond order	1	1	1.5	2	2.5
Bond length (Å)	1.41	1.49	1.33	1.21	1.12
Bond energy (kJ/mol)	154	142	~370	494	625

Isoelectronic

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^- \quad (1962)$$


Energy
Z ≥ 8
$\sigma^*_{u2p_z}$
$\pi^*_{g2p_x}$ $\pi^*_{g2p_y}$
2p
π_{u2p_x} π_{u2p_y}
σ_{g2p_z}
σ^*_{u2s}
2s
σ_{g2s}
F_2
Z ≤ 7
$\sigma^*_{u2p_z}$
$\pi^*_{g2p_x}$ π
2p
σ_{g2p_z}
π_{u2p_x} π_{u2p_y}
σ^*_{u2s}
2s
σ_{g2s}
N_2

Second-Period Elements

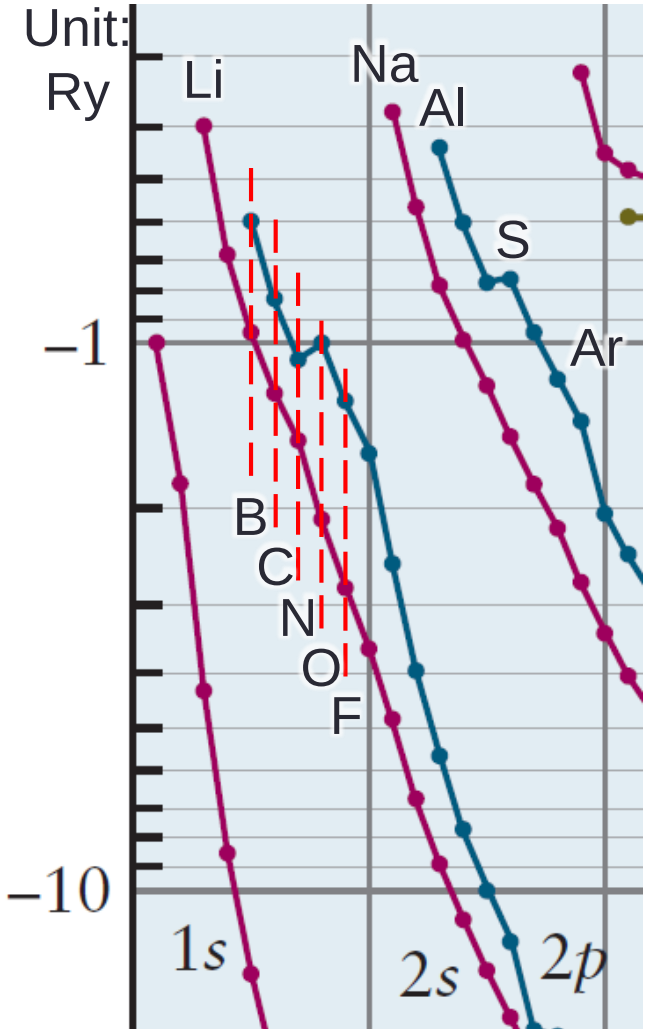
Orbital configuration and energy (in eV)

	B	C	N	O	F
2*s*	↑↓	↑↓	↑↓	↑↓	↑↓
	−14.1	−17.8	−25.4	−32.3	−40.2
2*p*	↑	↑ ↑	↑ ↑ ↑	↑↓ ↑ ↑	↑↓ ↑↓ ↑
	−8.3	−11.3	−14.5	−13.6	−17.4
2*p* − 2*s*	5.8	6.5	10.9	18.8	22.8

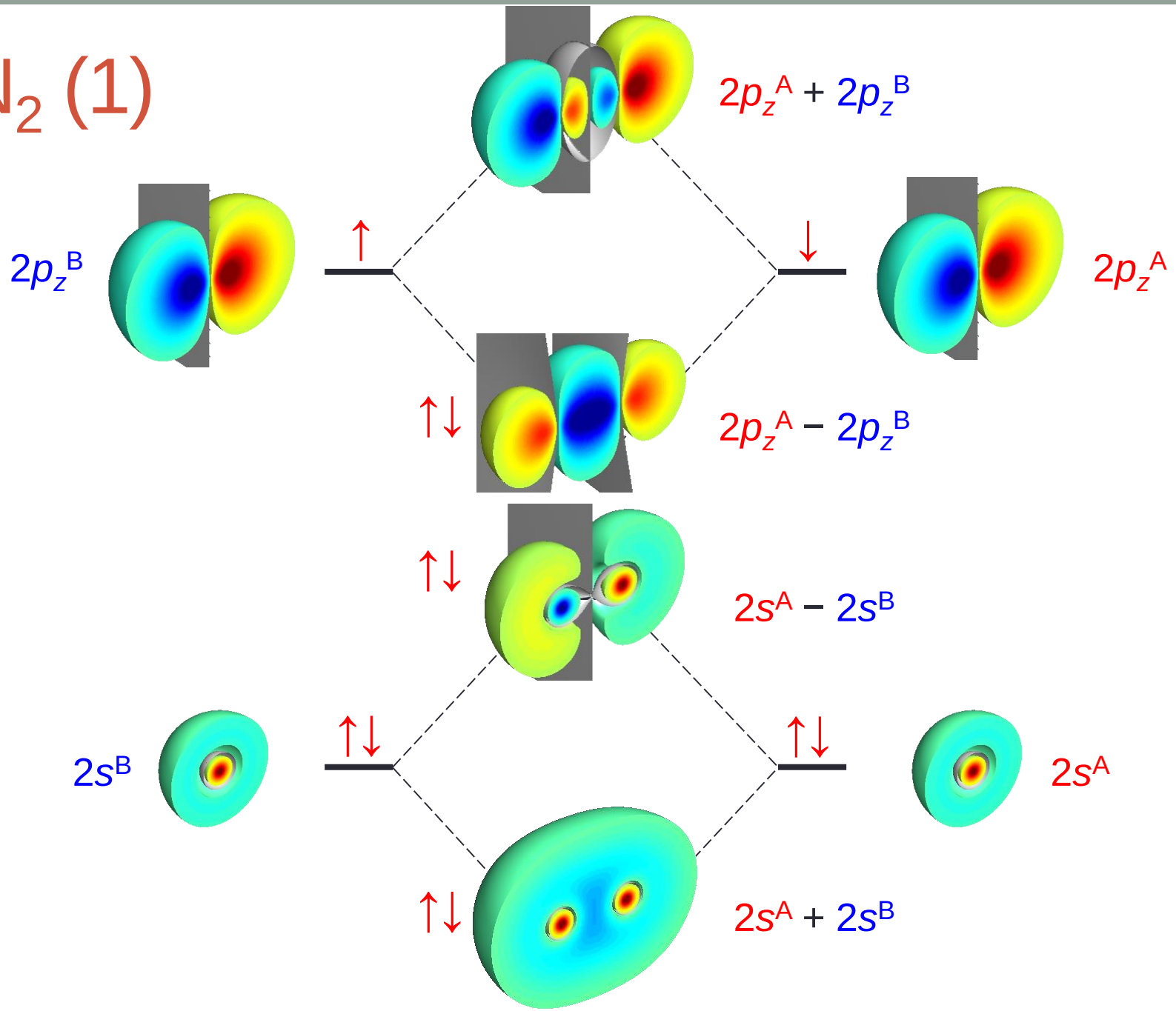
Small difference Large difference

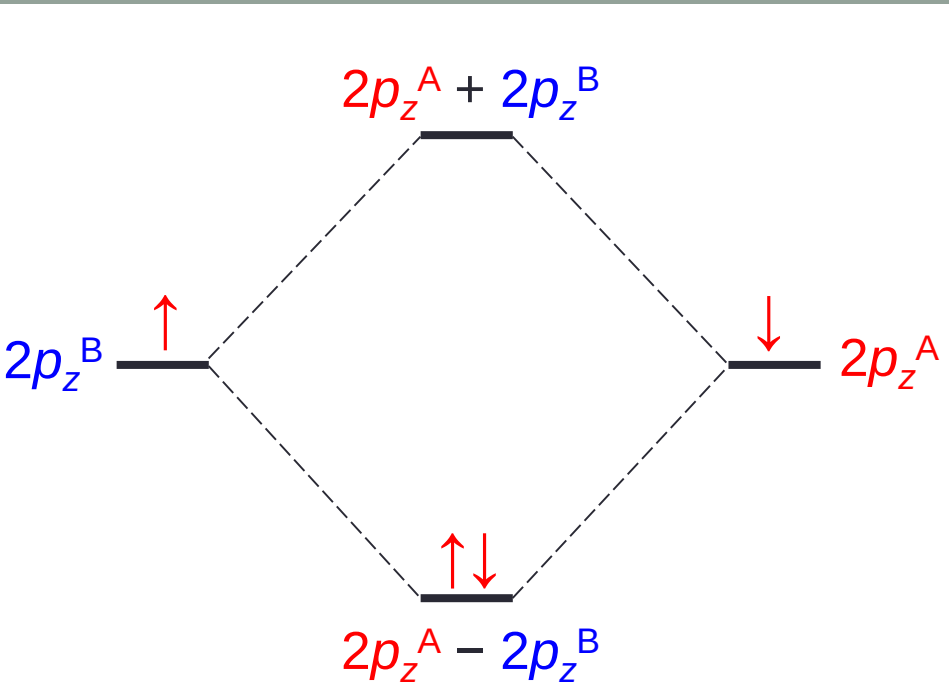
The 2*s* and 2*p* orbitals of B, C, N tend to combine / hybridize 杂化 with each other.

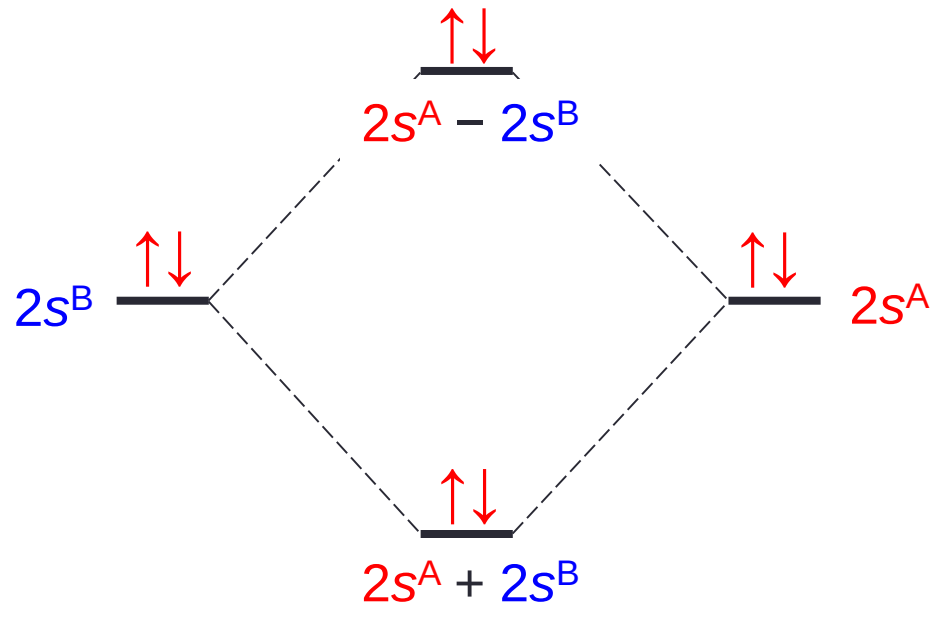
Fig. 5.26, OGB8 p.210

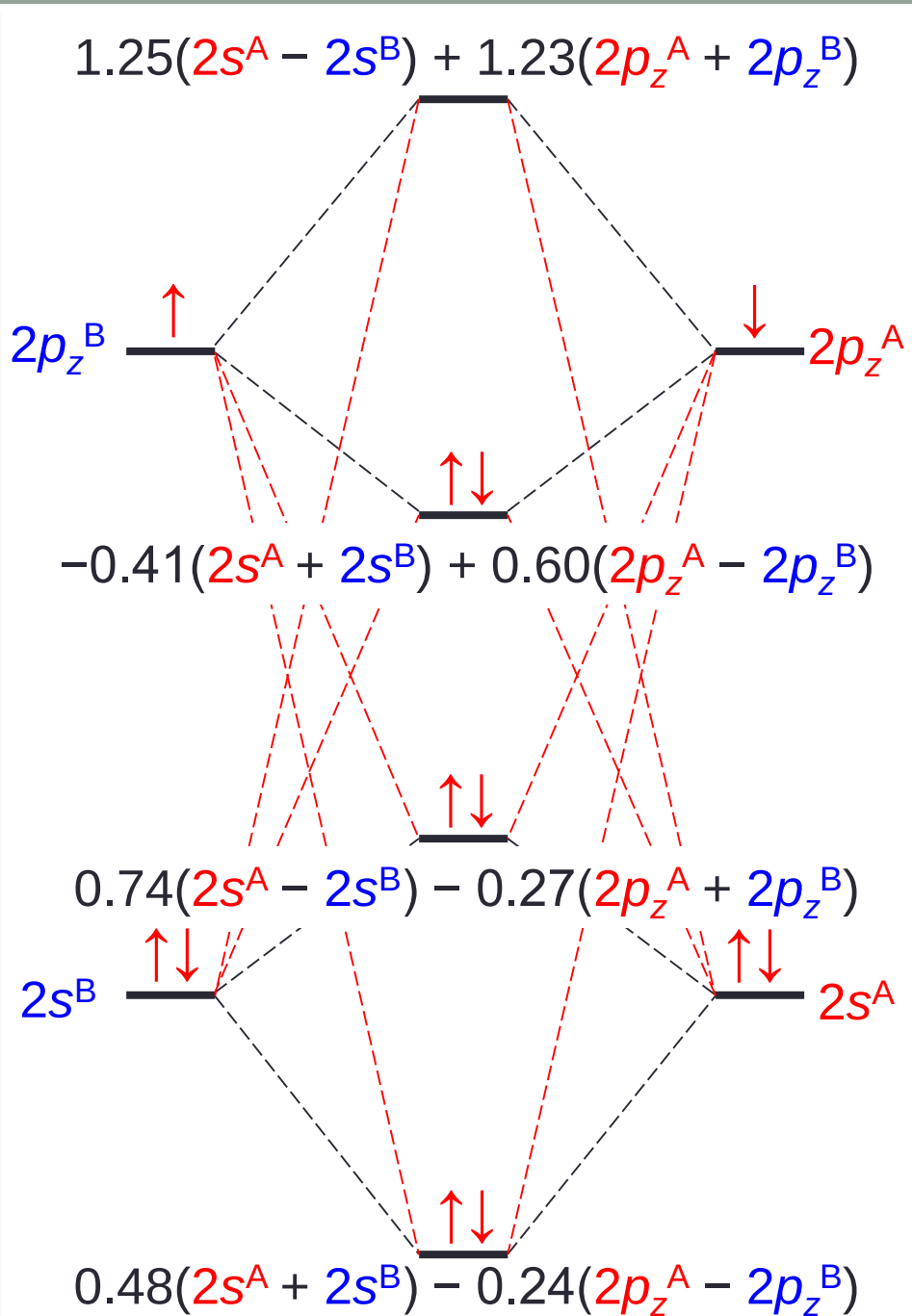


N_2 (1)

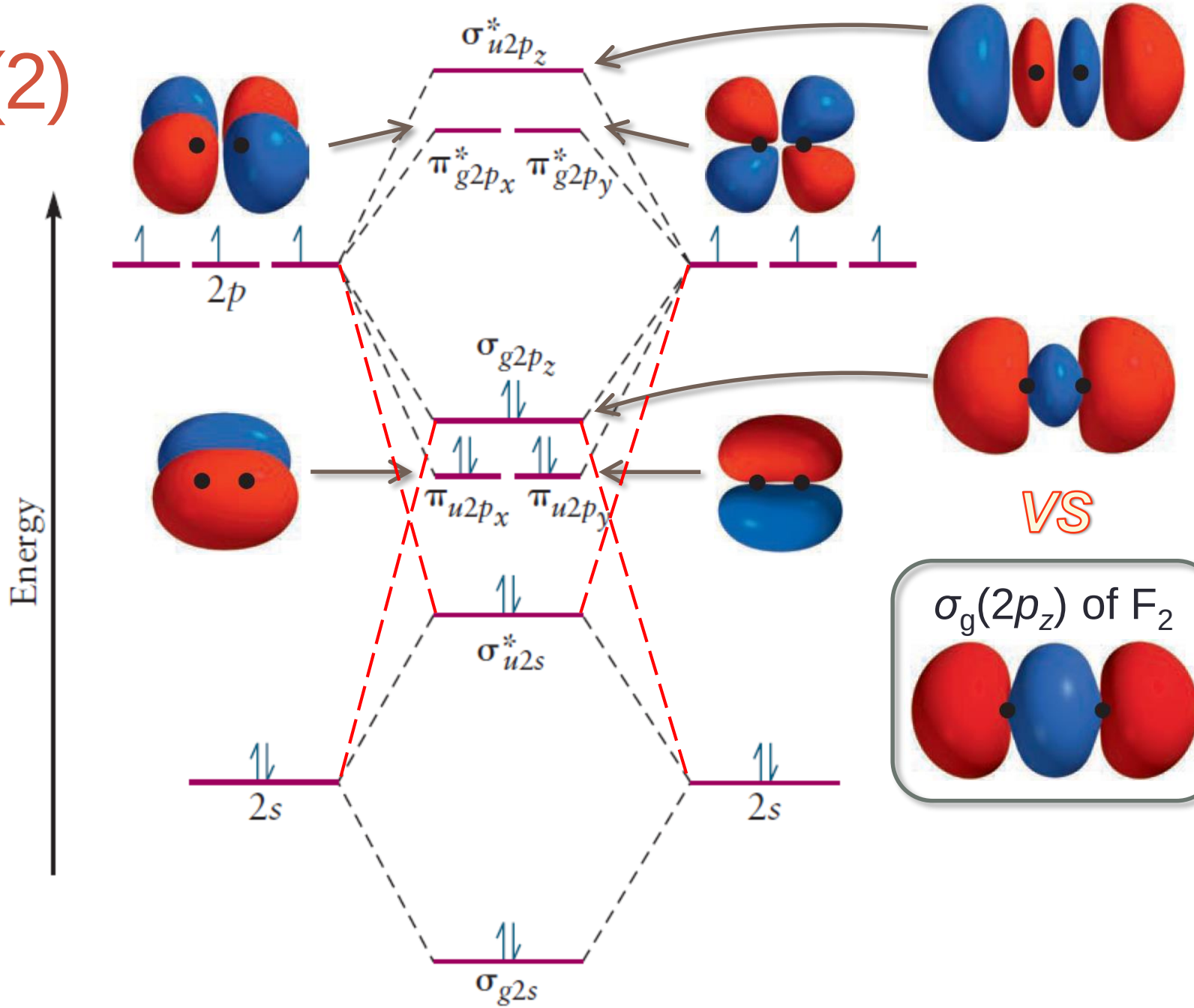



$2p_z^A + 2p_z^B$
$2p_z^B$
$2p_z^A$
$2p_z^A - 2p_z^B$

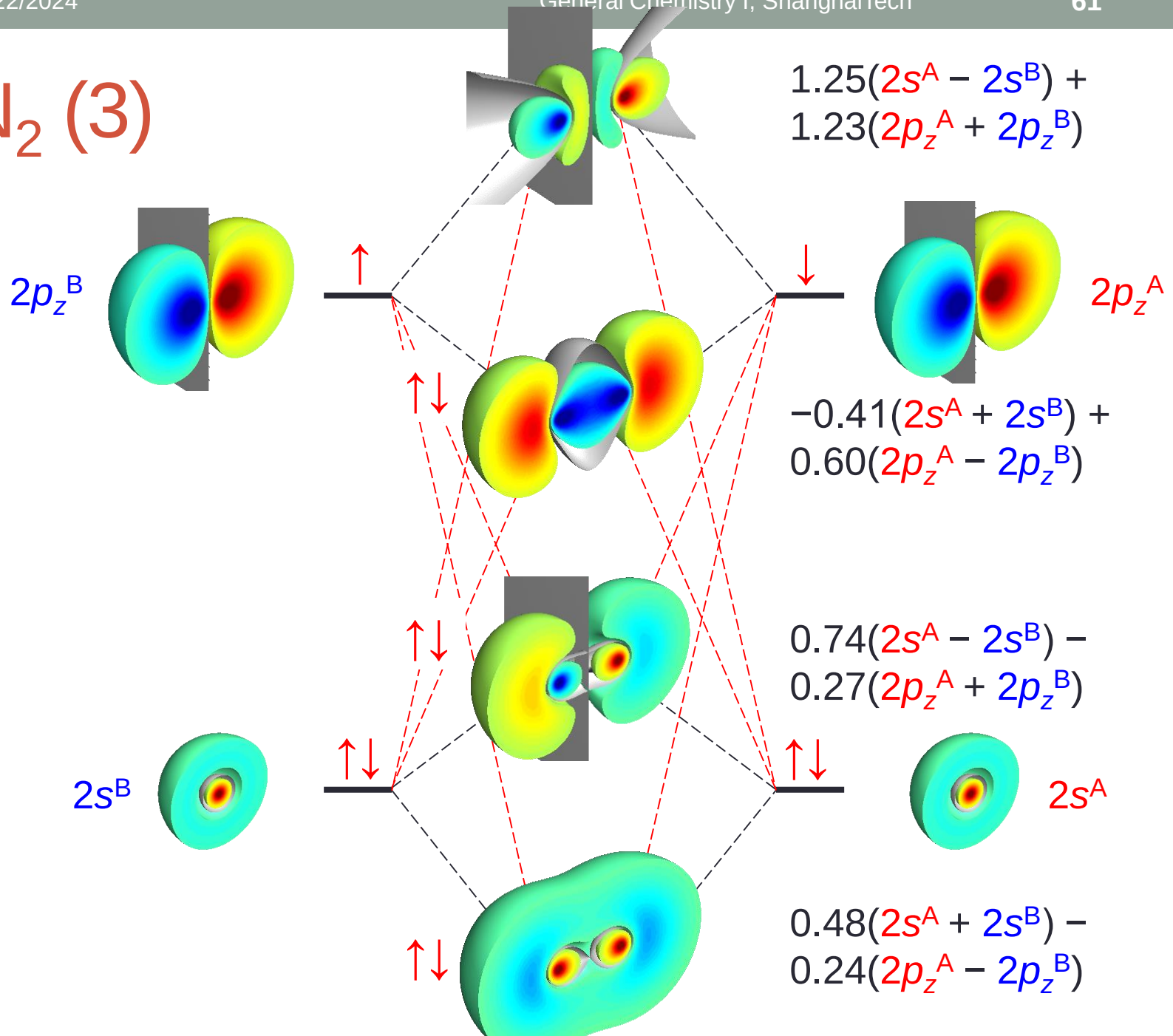

$2s^A - 2s^B$
$2s^B$
$2s^A$
$2s^A + 2s^B$


$1.25(2s^A - 2s^B) + 1.23(2p_z^A + 2p_z^B)$
$2p_z^B$
$2p_z^A$
$-0.41(2s^A + 2s^B) + 0.60(2p_z^A - 2p_z^B)$
$0.74(2s^A - 2s^B) - 0.27(2p_z^A + 2p_z^B)$
$2s^B$
$2s^A$
$0.48(2s^A + 2s^B) - 0.24(2p_z^A - 2p_z^B)$

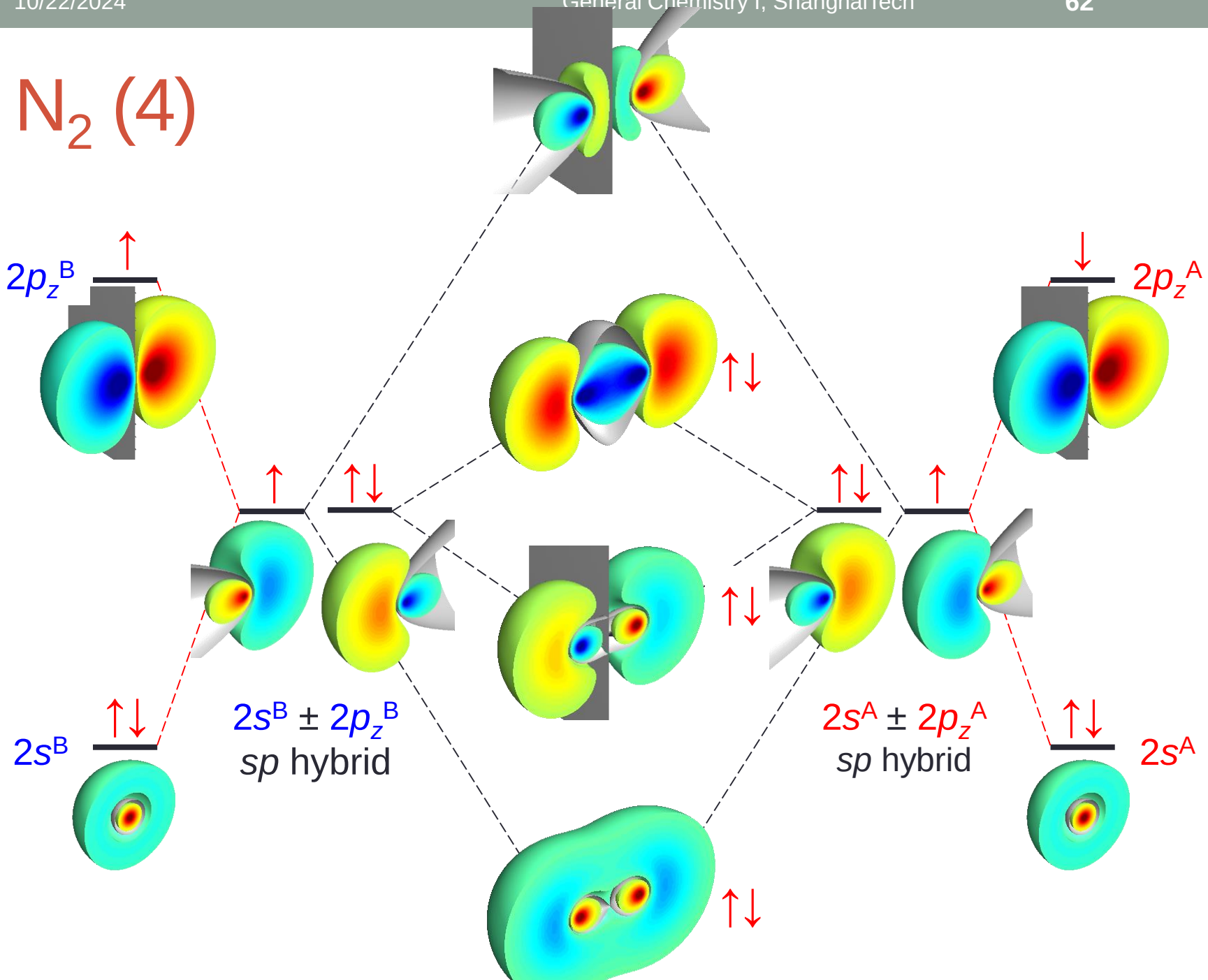
N_2 (2)


$\sigma^*_{u2p_z}$
$\pi^*_{g2p_x}$ $\pi^*_{g2p_y}$
2p
σ_{g2p_z}
π_{u2p_x} π_{u2p_y}
σ^*_{u2s}
2s
2s
σ_{g2s}
Energy
VS
$\sigma_g(2p_z)$ of F_2

N_2 (3)


1.25(2s^A − 2s^B) +
1.23(2p_z^A + 2p_z^B)
2p_z^B
2p_z^A
−0.41(2s^A + 2s^B) +
0.60(2p_z^A − 2p_z^B)
0.74(2s^A − 2s^B) −
0.27(2p_z^A + 2p_z^B)
2s^B
2s^A
0.48(2s^A + 2s^B) −
0.24(2p_z^A − 2p_z^B)

N_2 (4)

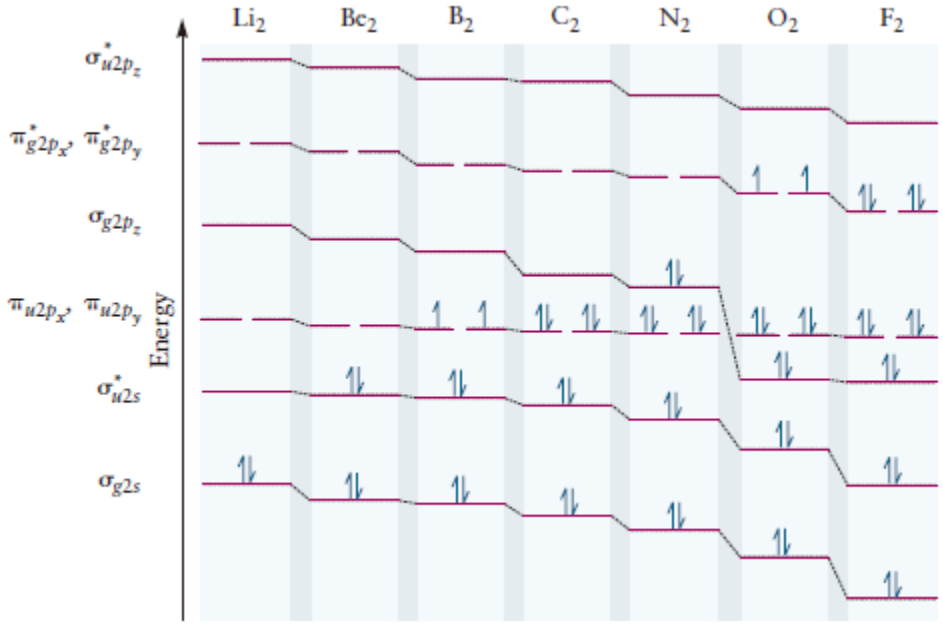


Other Species Related to N_2

	O_2	O_2^+	NO	NO^+	N_2	CO	CN^-	C_2^{2-}
Electronic configuration	$\sigma^2\pi^4\pi^{*2}$	$\sigma^2\pi^4\pi^{*1}$	$\sigma^2\pi^4\pi^{*1}$	$\pi^4\sigma^2$	$\pi^4\sigma^2$	$\pi^4\sigma^2$	$\pi^4\sigma^2$	$\pi^4\sigma^2$
Bond order	2	2.5	2.5	3	3	3	3	3
Bond length (Å)	1.21	1.12	1.15	1.06	1.10	1.13	1.15	1.20
Bond energy (kJ/mol)	494	625	607	?	942	1070	891	839

Isoelectronic

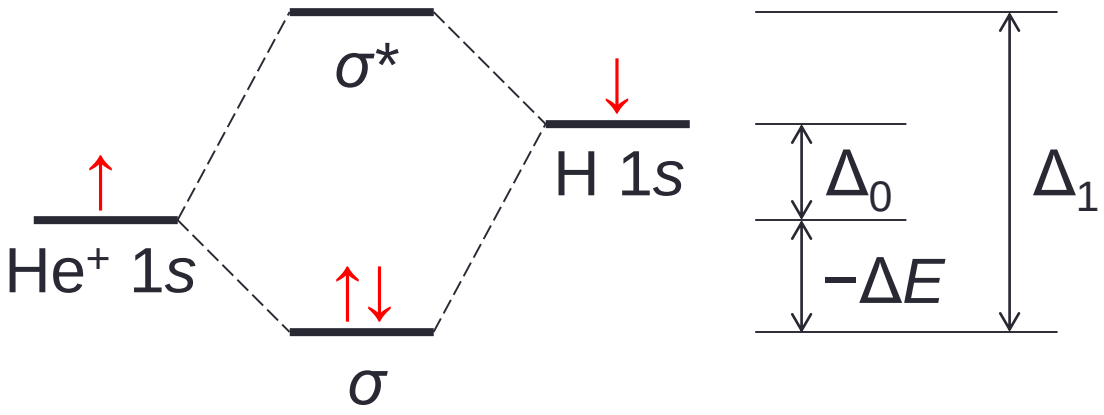
Isoelectronic



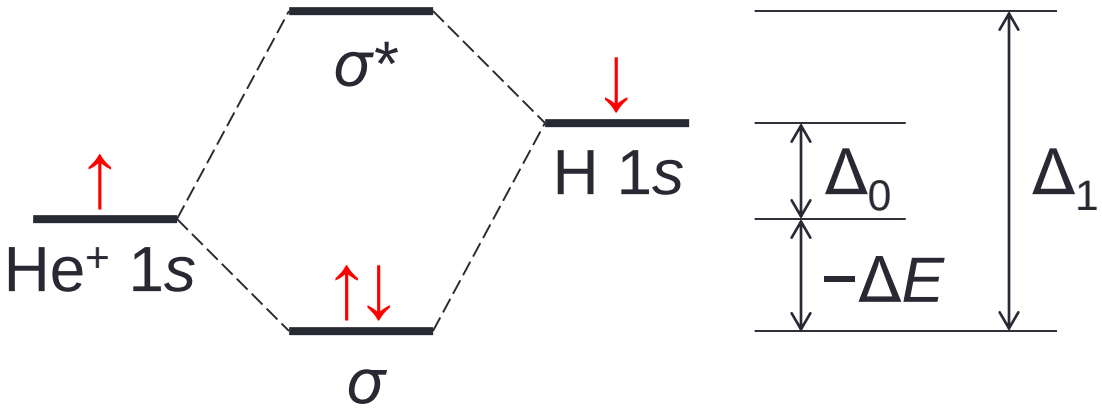
Species	Number of Valence Electrons	Valence Electron Configuration	Bond Order	Bond Length (Å)	Bond Energy (kJ mol^{-1})
H_2	2	$(\sigma_{g1s})^2$	1	0.74	431
He_2	4	$(\sigma_{g1s})^2(\sigma^*_{u1s})^2$	0		
Li_2	2	$(\sigma_{g2s})^2$	1	2.67	105
Be_2	4	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2$	0	2.45	9
B_2	6	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^2$	1	1.59	289
C_2	8	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4$	2	1.24	599
N_2	10	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4(\sigma_{g2p_z})^2$	3	1.10	942
O_2	12	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^2$	2	1.21	494
F_2	14	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^4$	1	1.41	154
Ne_2	16	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^4(\sigma^*_{u2p_z})^2$	0		

Heteronuclear diatomic molecule

- Atomic orbitals should have similar energy to form molecular orbitals.
- For a molecule AB, if the electronegativity follows B > A.
  - In bonding orbitals, electrons tend to B
  - In antibonding orbitals, electrons tend to A



A More General Correlation Diagram



$\Delta_1 = \sqrt{\Delta_0^2 + H^2}$

$H \propto$ orbital overlap is the coupling energy

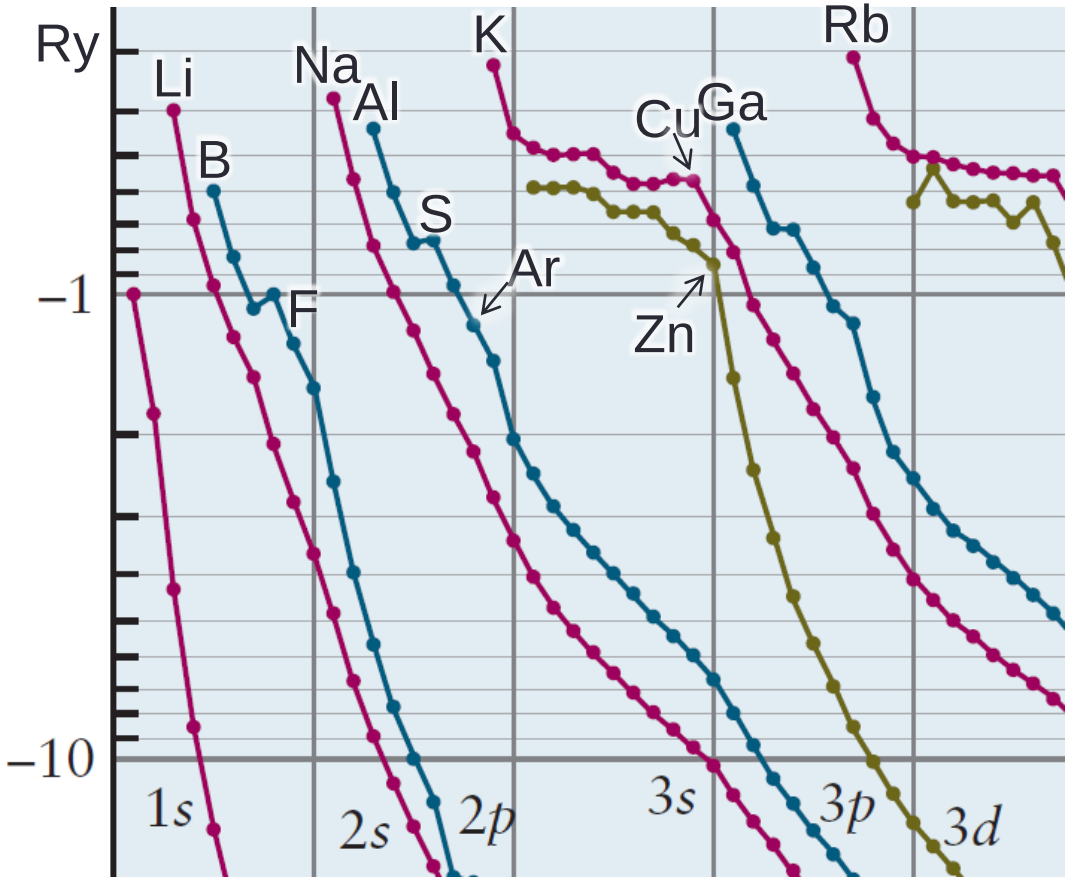
$$-\Delta E = \tfrac{1}{2}(\Delta_1 - \Delta_0) = \tfrac{1}{2}(\sqrt{\Delta_0^2 + H^2} - \Delta_0)$$

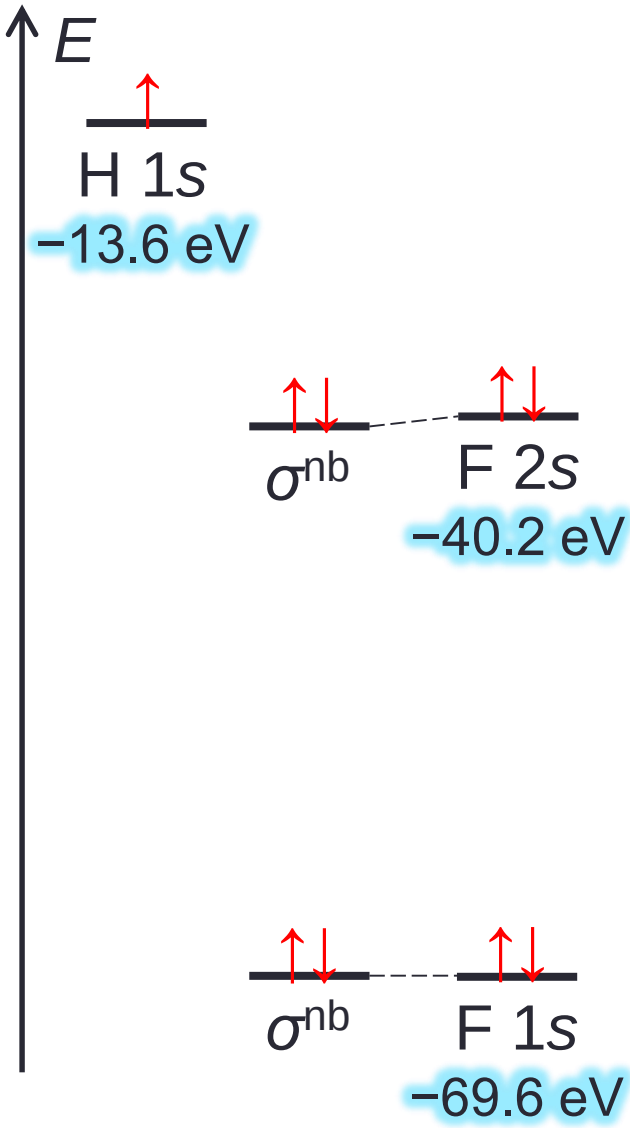
Minimize

Maximize

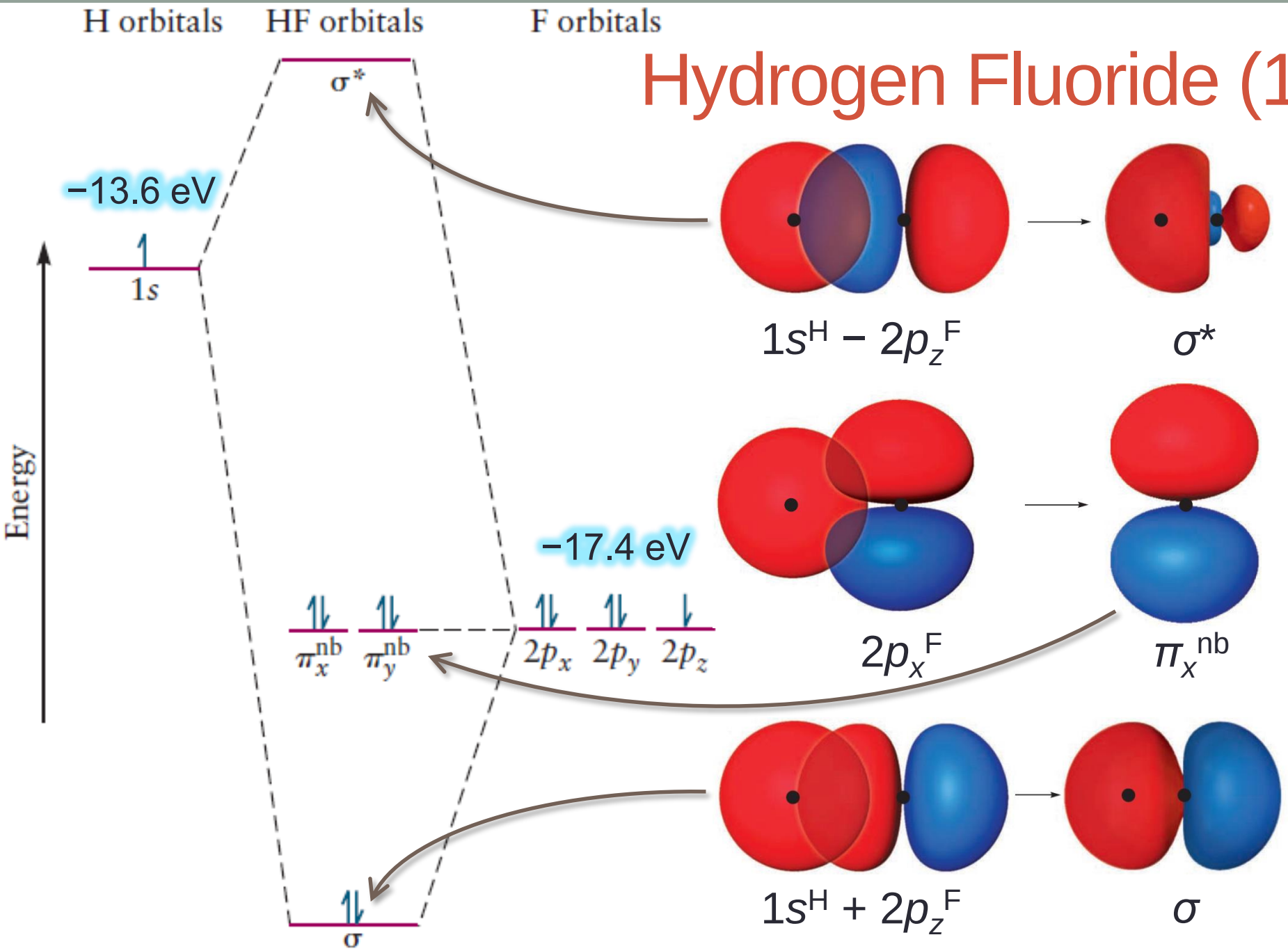
Hydrogen Fluoride (1)

Fig. 5.26, OGB8 p.210





Hydrogen Fluoride (1)



CO and NO

- CO and NO similar to N_2

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x}, \pi_{2p_y})^4(\sigma_{2p_z})^2$$

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x}, \pi_{2p_y})^4(\sigma_{2p_z})^2(\pi^*_{2p_x}, \pi_{2p_y})^1$$

- Formation of BN, CN, CN^-, NO^+

LCAO-MO: Summary

福井谦一

(Kyoto, 1918–1998)

Atomic orbitals and molecular orbitals

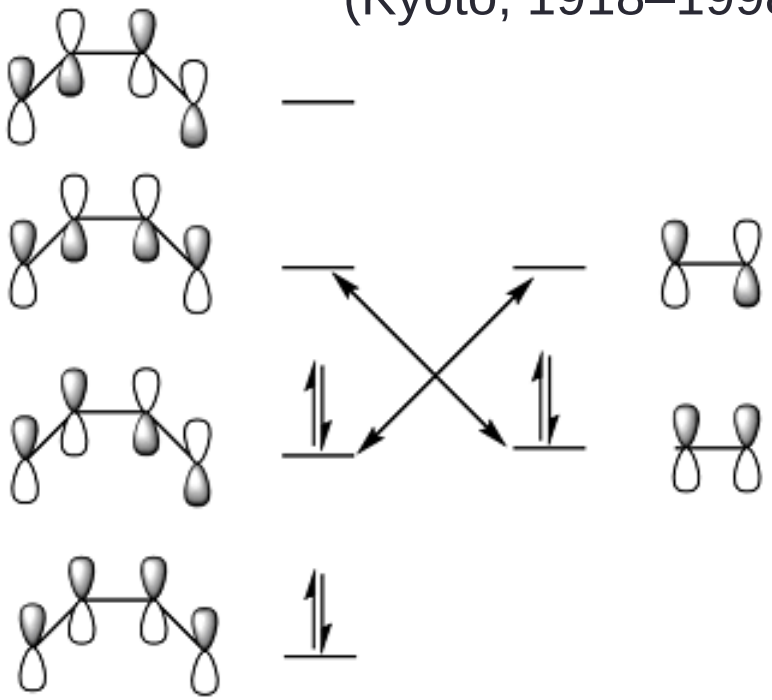
- Can be linearly combined
- Obey the Aufbau Principle

Rules of bonding

- Maximum orbital overlap
- Compatible orbital symmetries
- Approximate atomic orbital energies

Frontier orbitals (1952)

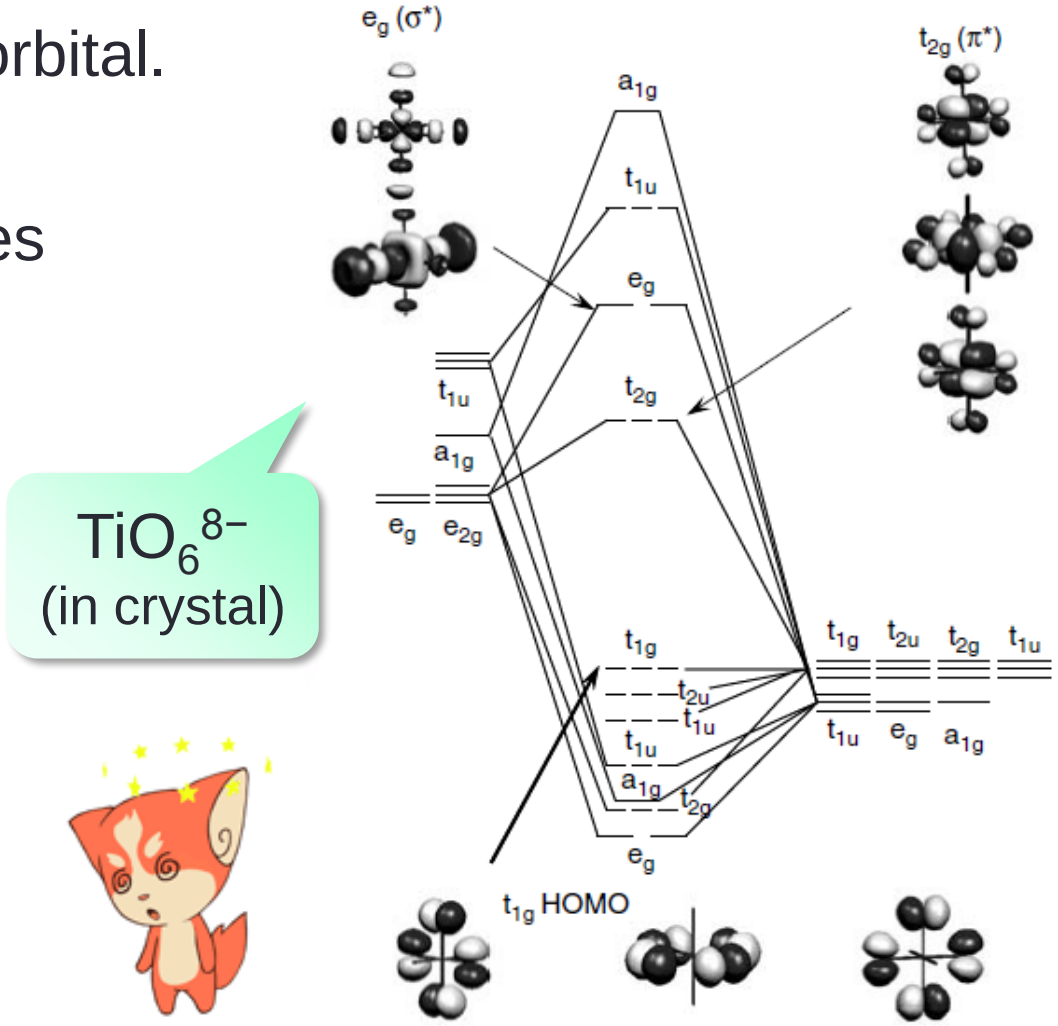
前线/前沿轨道



Weaknesses of LCAO-MO (1)

Many atomic orbitals combine to make one molecular orbital.

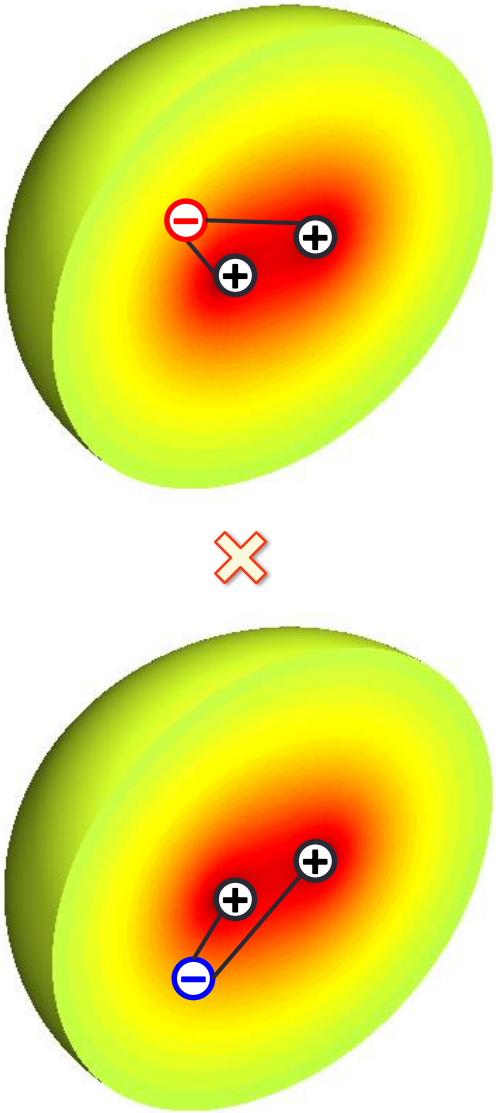
- Non-intuitive
- Require computer codes

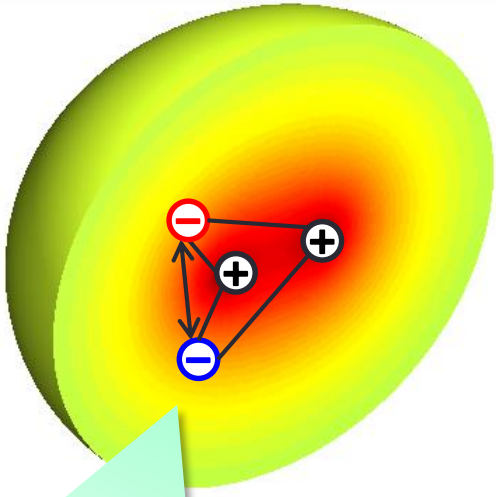


Weaknesses of LCAO-MO (2)

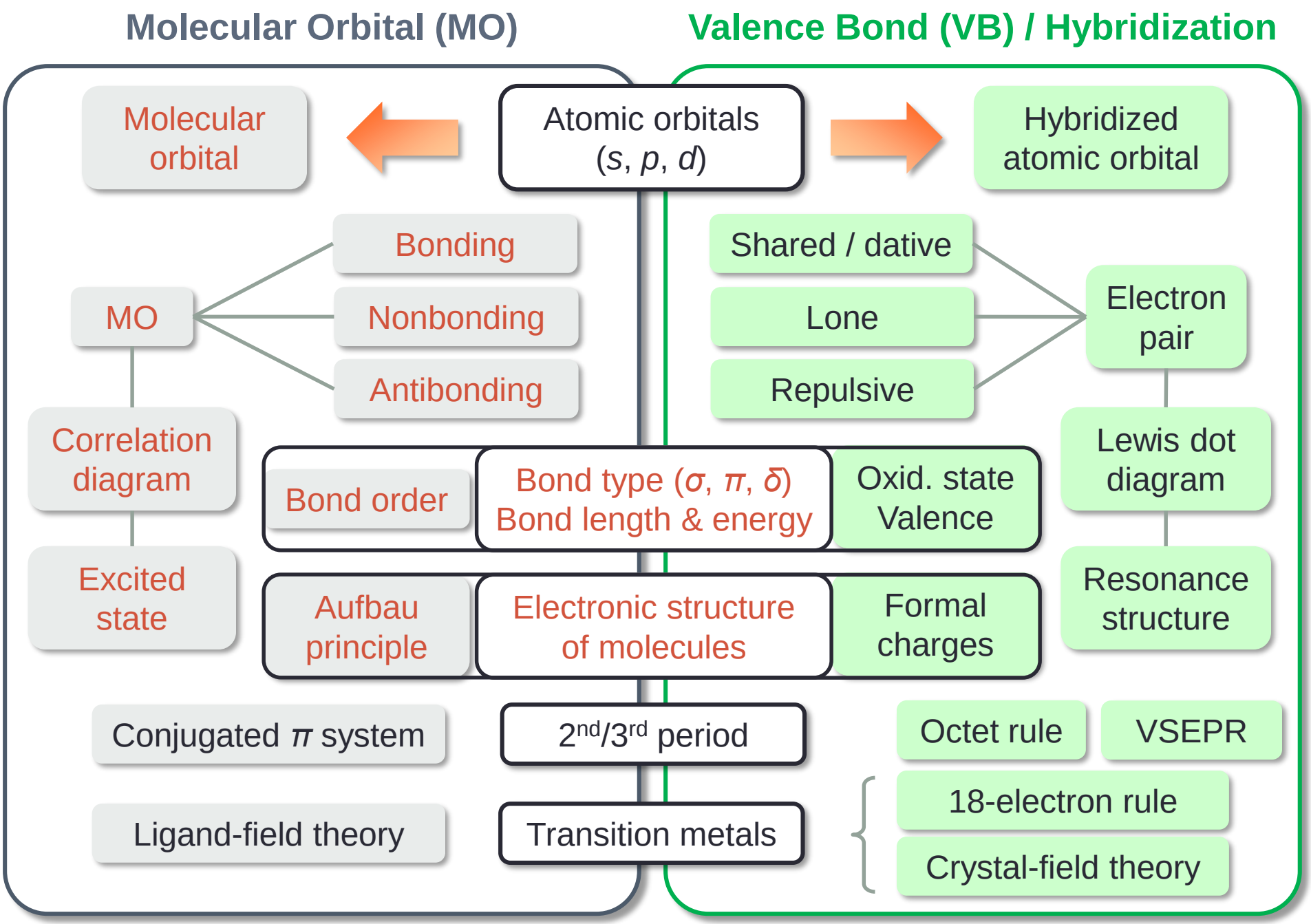
$$\psi(x_1,y_1,z_1,x_2,y_2,z_2) \approx \varphi(x_1,y_1,z_1) \cdot \varphi(x_2,y_2,z_2)$$

$$\Longrightarrow \psi(1,2) \approx \varphi(1) \cdot \varphi(2)$$





H^- H^+ is very unlikely for H_2!


Molecular Orbital (MO)
Valence Bond (VB) / Hybridization
Molecular orbital
Atomic orbitals (s, p, d)
Hybridized atomic orbital
Bonding
MO
Nonbonding
Antibonding
Shared / dative
Lone
Repulsive
Electron pair
Correlation diagram
Excited state
Bond order
Bond type (σ, π, δ)
Bond length & energy
Oxid. state
Valence
Lewis dot diagram
Resonance structure
Aufbau principle
Electronic structure of molecules
Formal charges
Conjugated π system
2nd/3rd period
Octet rule
VSEPR
Ligand-field theory
Transition metals
18-electron rule
Crystal-field theory

Next Lecture Series: Bonding in Molecules PART 2

Reading: OGB8 §3.10, §3.11