ChemE 2200 – Applied Quantum Chemistry Lecture 3

Today:

The Quantum Chemistry of Chemical Bonds
The Born-Oppenheimer Approximation
Molecular Orbitals (MOs) from the Linear Combinations of Atomic Orbitals (LCAOs)
Bonding and Anti-bonding Molecular Orbitals

Defining Questions:

Why is He_2 unstable?
Why does bond strength decrease from N_2 to O_2 to F_2?

Reading for Today's Lecture:

McQuarrie & Simon – The Chemical Bond – Diatomic Molecules: 9.1-9.3, 9.5-9.13.

Reading for Quantum Lecture 4:

McQuarrie & Simon - 13.1, 13.2, 13.11, and 13.12.

Weekly Quizzes

Conducted first 10-15 minutes of Calculation Session.

Based on homework assigned previous Wednesday.

Will strive for a mean of 9-10 out of 10
if you learned from working the homework.

You may use your handwritten reference sheet
you are preparing for prelims.

Quizzes	5%
1st Preliminary Examination	30%
2nd Preliminary Examination	30%
3rd Preliminary Examination	30%
Professional Participation	5%

No make-up quizzes. Two lowest scores will be dropped.

TA Office Hours

Sunday and Tuesday (not Wednesday) evenings.
7:00-9:00 p.m., 128 Olin Hall

Recall – Homework solutions are posted
when the homework is assigned.

Chemical Bonds

Why do two H atoms form a stable diatomic molecule, H_2?

Why do two He atoms *not* form a stable diatomic molecule?

Our plan: H atom + proton $\rightarrow$ H_2^+

H_2^+ + electron $\rightarrow$ H_2

He atom + He atom $\rightarrow$ He_2

multi-electron atom + multi-electron atom $\rightarrow$ diatomic molecule

H_2^+: start with the hydrogen Hamiltonian $$\hat{H} = \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}\right)$$

and add terms. kinetic energy of proton 2: $$\frac{\hbar^2}{2m_p}\nabla_{p_2}^2$$

proton 2 – electron electrostatic attraction: $$-\frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_2}\right)$$

proton 1 – proton 2 electrostatic repulsion: $$+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}\right)$$

H_2^+ is another ‘three-body problem.’ *Insoluble analytically.* What to do?

The Born-Oppenheimer Approximation

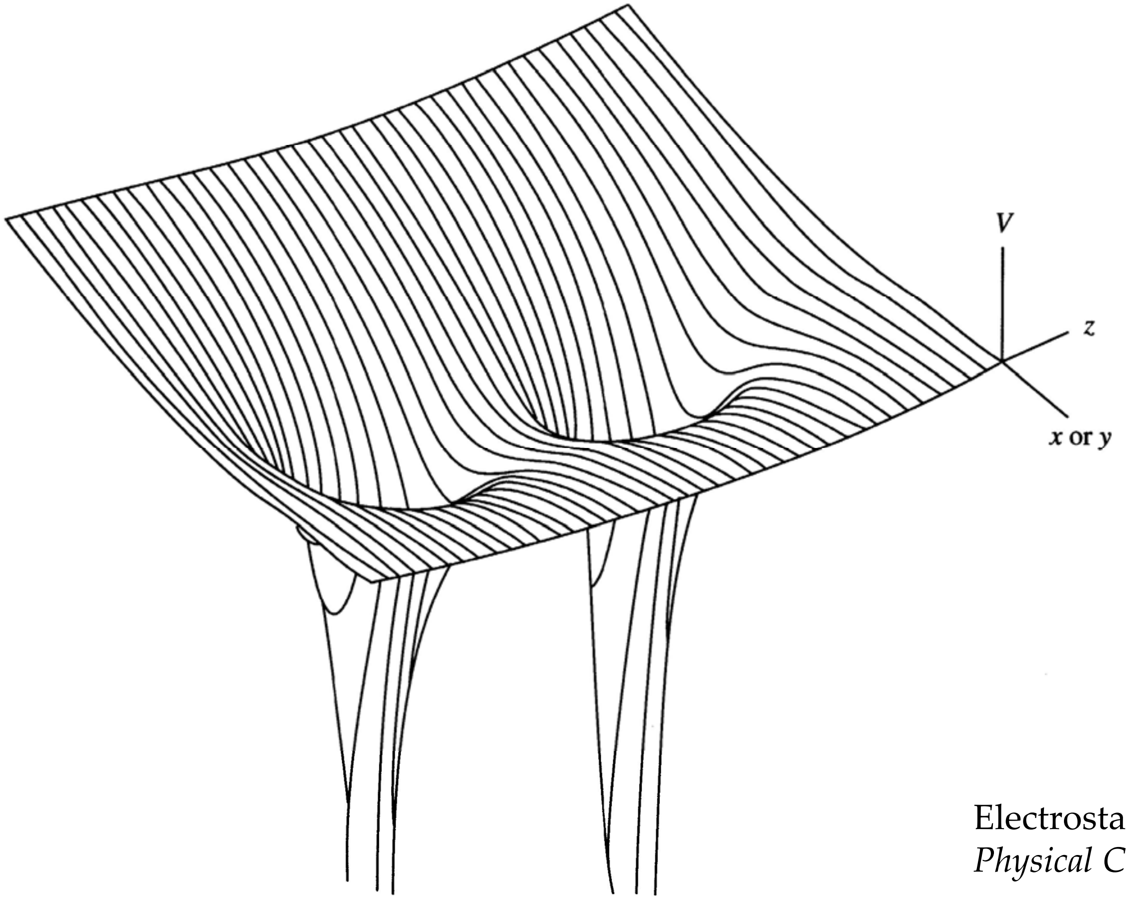
The proton mass is 1836 times the electron mass.

Assume the electron responds immediately to the positions of the protons (nuclei).

Set the internuclear distance (bond length) and calculate the electron state function.

The Born Oppenheimer Approximation reduces H_2^+ to a one-particle problem.

The electron moves in the electrostatic potential of two fixed protons.



Electrostatic potential from J. H. Noggle,
Physical Chemistry, 3rd ed. (1996), p. 764.

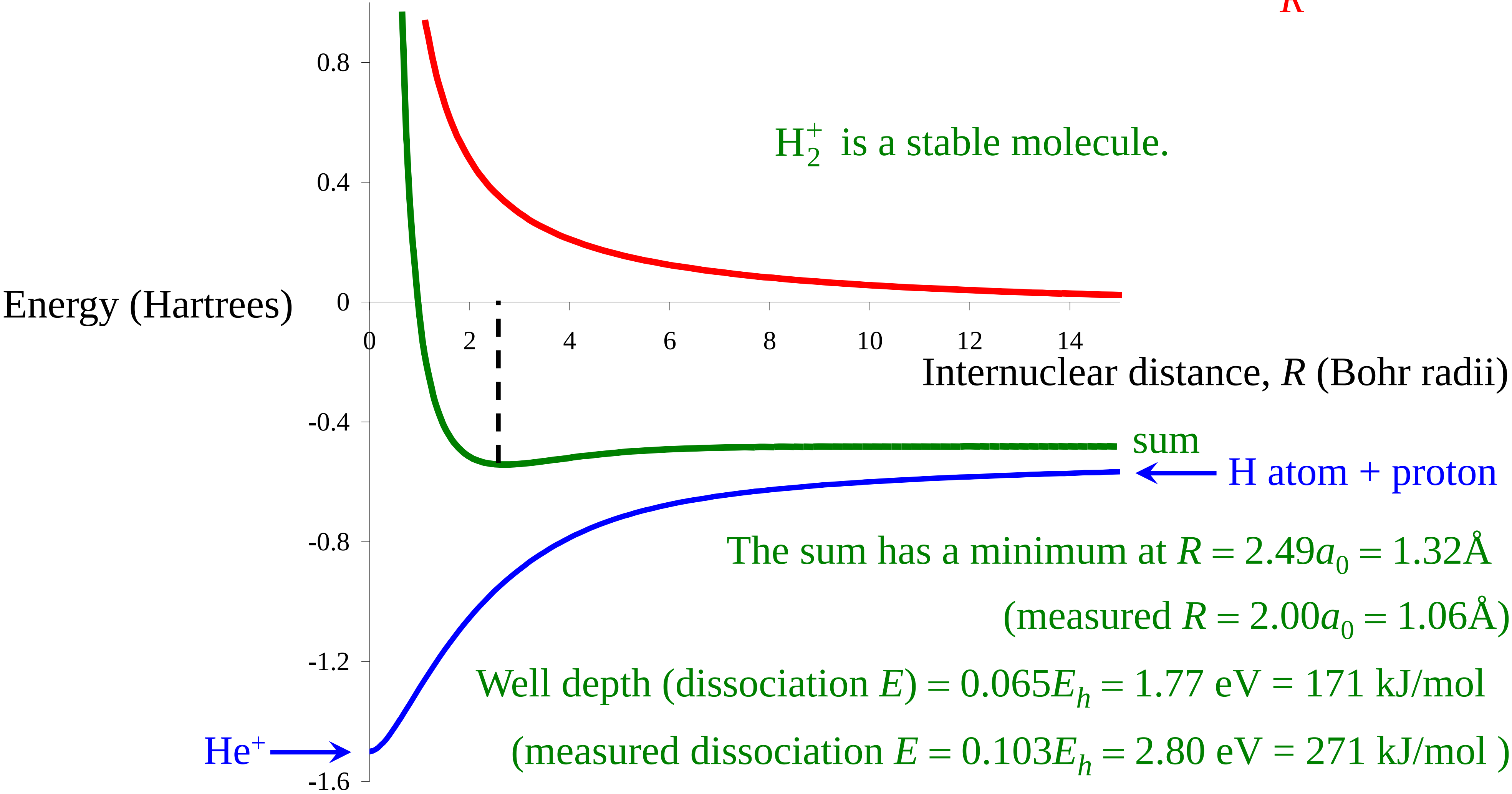
H_2^+

Solve $\hat{H}\Psi = E\Psi$ for a fixed internuclear distance R.

$$E(R) = -\frac{1}{2} + \frac{(R+1)e^{-2R} - R(R+1)e^{-R} - 1}{R\left[\left(1+R+\frac{1}{3}R^2\right)e^{-R} + 1\right]}$$

in units of Hartrees: $E_h = \dfrac{e^2}{4\pi\varepsilon_0 a_0} = 27.21\,\text{eV}$

Add the repulsive energy between the two protons: $E(R) = +\dfrac{1}{R}$



H_2^+ is a stable molecule.

The sum has a minimum at $R = 2.49a_0 = 1.32\text{Å}$

(measured $R = 2.00a_0 = 1.06\text{Å}$)

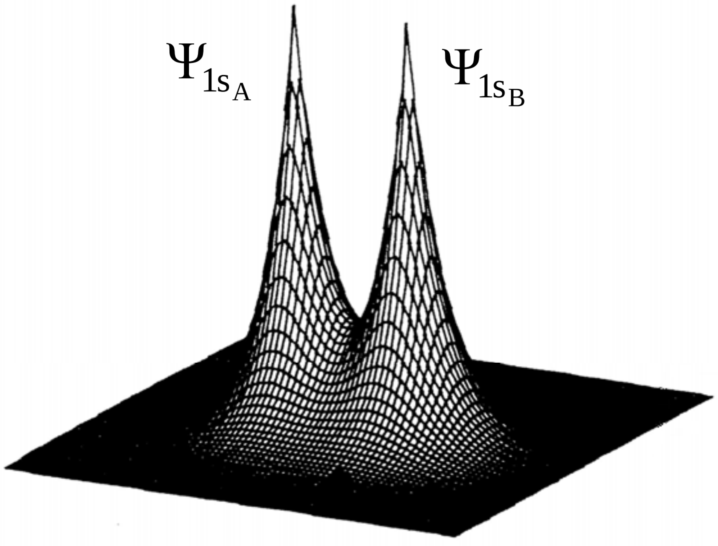
Well depth (dissociation E) = $0.065E_h$ = 1.77 eV = 171 kJ/mol

(measured dissociation $E = 0.103E_h$ = 2.80 eV = 271 kJ/mol)

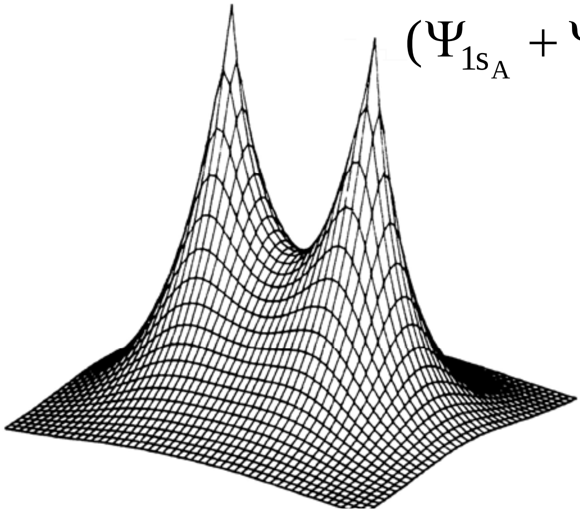
Molecular Orbitals from Atomic Orbitals

Analytical solutions (like $E(R)$ on the previous slide) offer little insight.

Instead, let’s approximate Molecular Orbitals as Linear Combinations of Atomic Orbitals

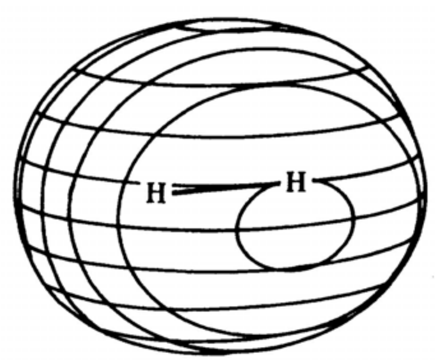


Ψ_{1s_A} Ψ_{1s_B}

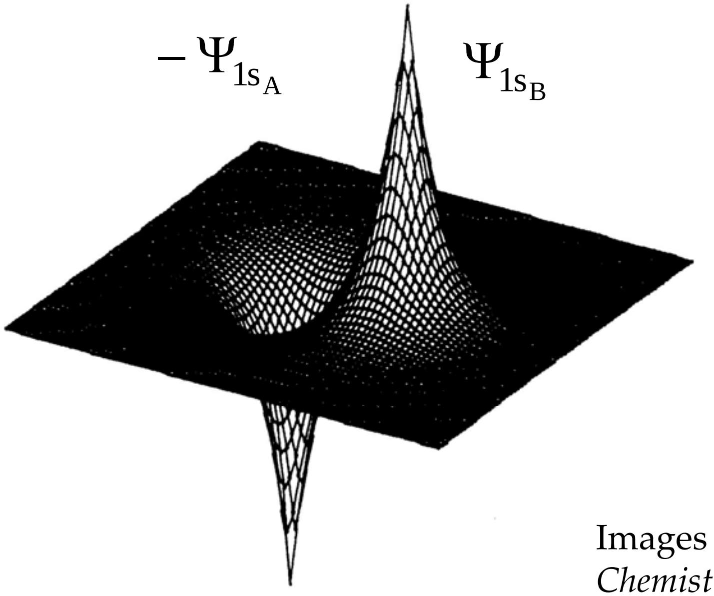


$(\Psi_{1s_A} + \Psi_{1s_B})^2$

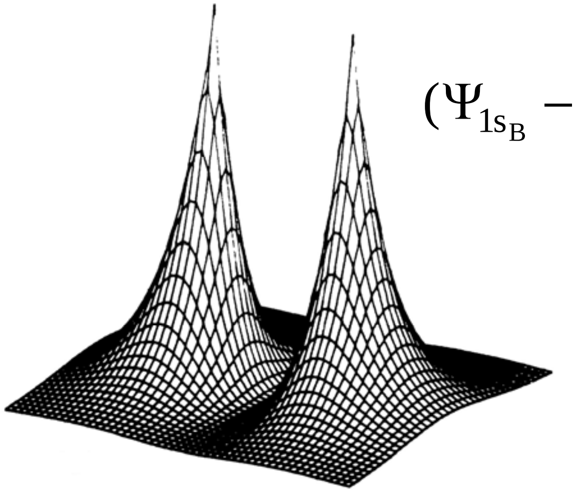
$1s\sigma$



a bonding orbital

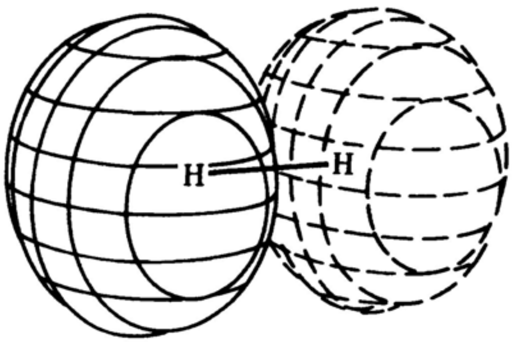


$-\Psi_{1s_A}$ Ψ_{1s_B}



$(\Psi_{1s_B} - \Psi_{1s_A})^2$

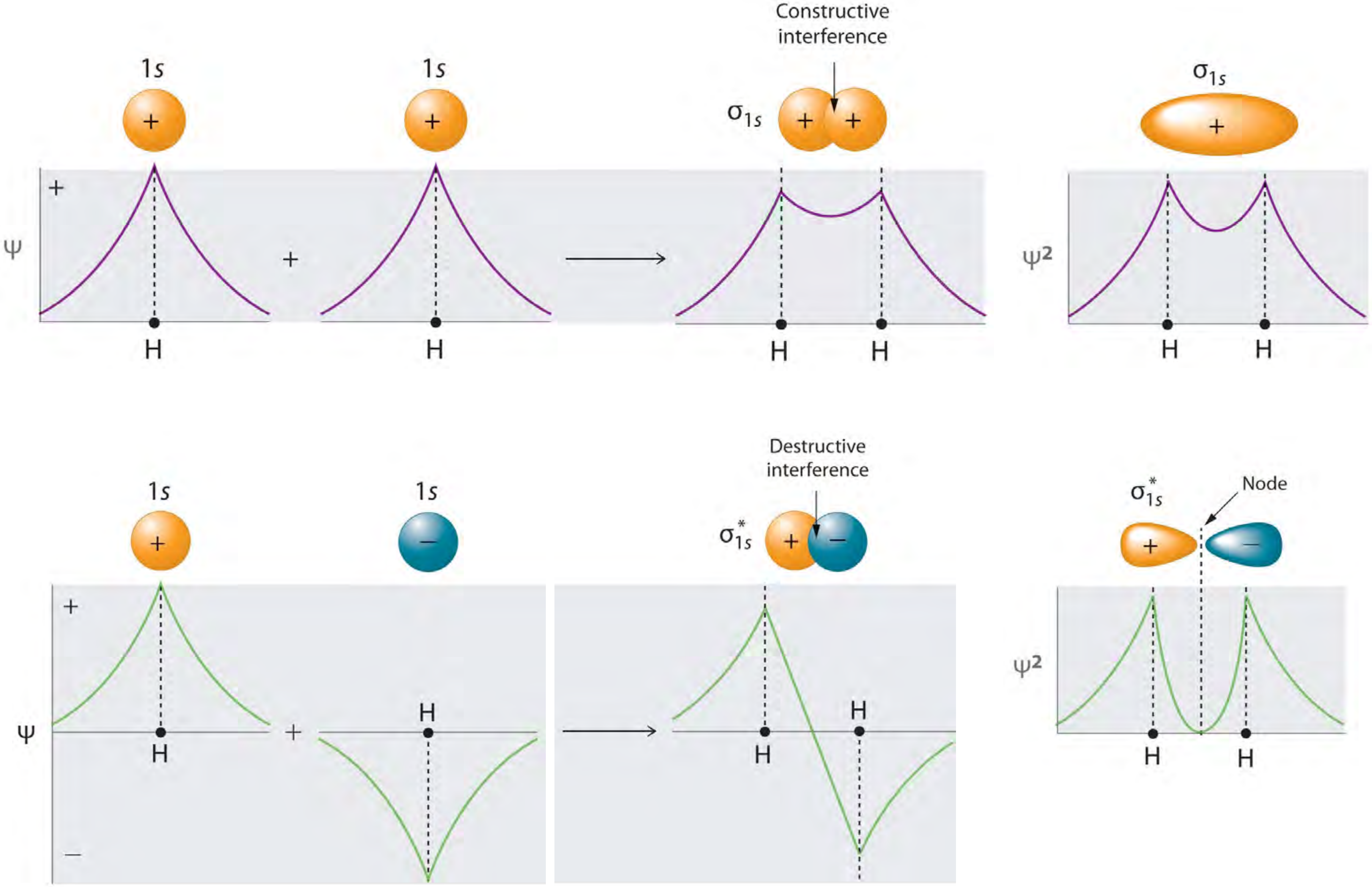
$1s\sigma^*$



an anti-bonding orbital

Images from F. L. Pillar, *Elementary Quantum Chemistry*, 2nd ed. (1990), pp. 347, 348, 362.

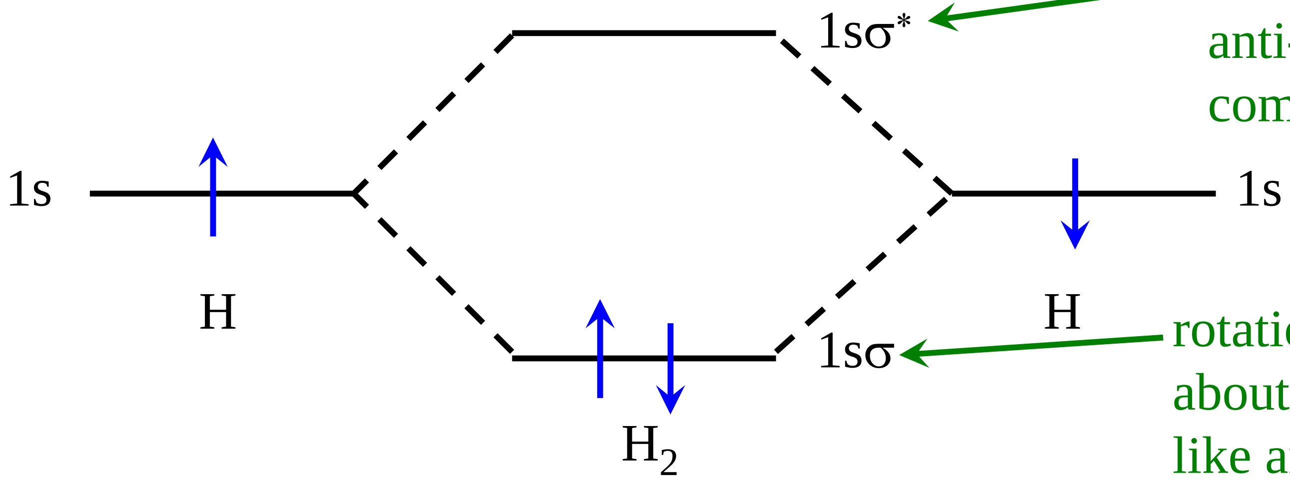
Molecular Orbitals from Atomic Orbitals



Images from chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbooks/
Quantum_States_of_Atoms_and_Molecules_(Zelinski_et_al)

The Molecular-Orbital Energy-Level Diagram

atomic orbital molecular orbital atomic orbital

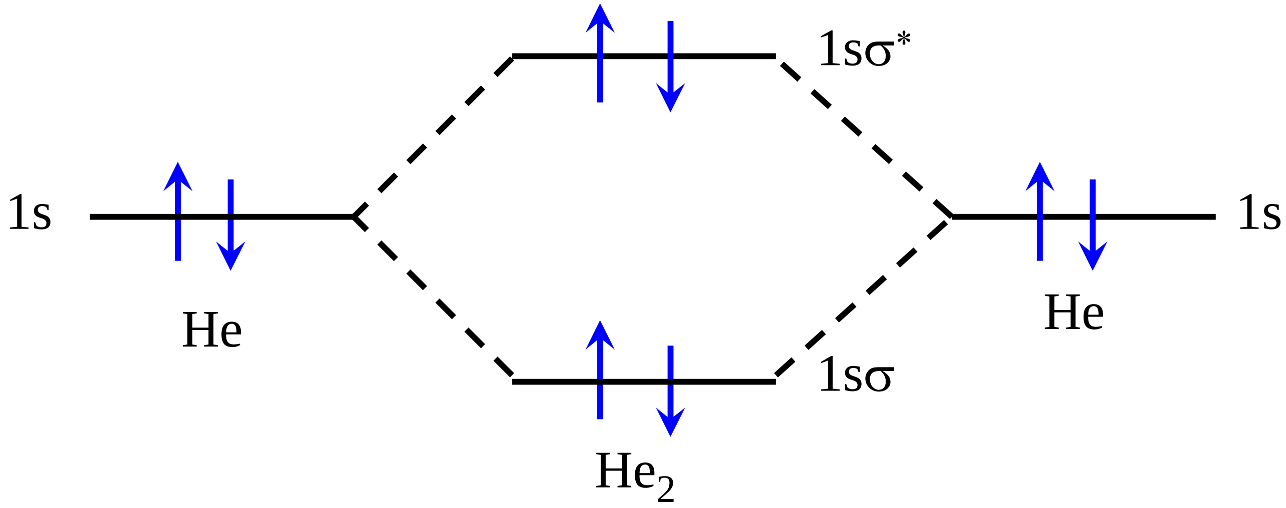


asterisk indicates anti-bonding, not complex conjugate.

rotational symmetry about the bond axis, like an s orbital.

bond order = ½(number of bonding electrons – number of anti-bonding electrons)

H_2: bond order = ½(2 – 0) = 1 a single bond



He_2: bond order = ½(2 – 2) = 0 no bond

Linear Combinations of Atomic Orbitals

Two overlapping atomic orbitals can be combined to form two molecular orbitals.

One molecular orbital has lower energy.

One molecular orbital has higher energy.

The energy shifts are proportional to the overlap.

Combine 1s and $2p_z$ atomic orbitals on the same atom?

$$\int \psi^*_{1s}\psi_{2p_z}\,d\tau \;=\; 0$$

Atomic orbitals are mutually orthogonal.

No overlap.

Combine $1s\sigma$ and $1s\sigma^*$ molecular orbitals to yield even better molecular orbitals?

$$\int \psi^*_{1s\sigma}\psi_{1s\sigma^*}\,d\tau \;=\; \int (\psi_{1s_A}+\psi_{1s_B})(\psi_{1s_A}-\psi_{1s_B})\,d\tau$$

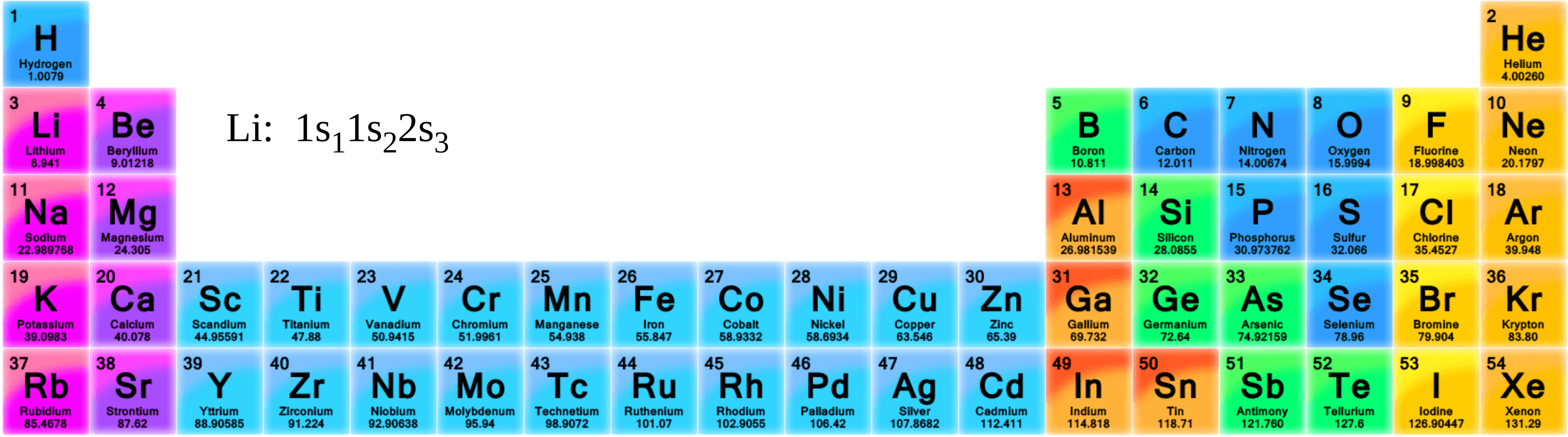
cancels

$$=\; \int \psi_{1s_A}\psi_{1s_A}\,d\tau \;-\; \cancel{\int \psi_{1s_A}\psi_{1s_B}\,d\tau} \;+\; \cancel{\int \psi_{1s_B}\psi_{1s_A}\,d\tau} - \int \psi_{1s_B}\psi_{1s_B}\,d\tau$$

$$=\; 1 \;-\; 1 \;=\; 0$$

The $1s\sigma$ and $1s\sigma^*$ molecular orbitals are orthogonal. No overlap.

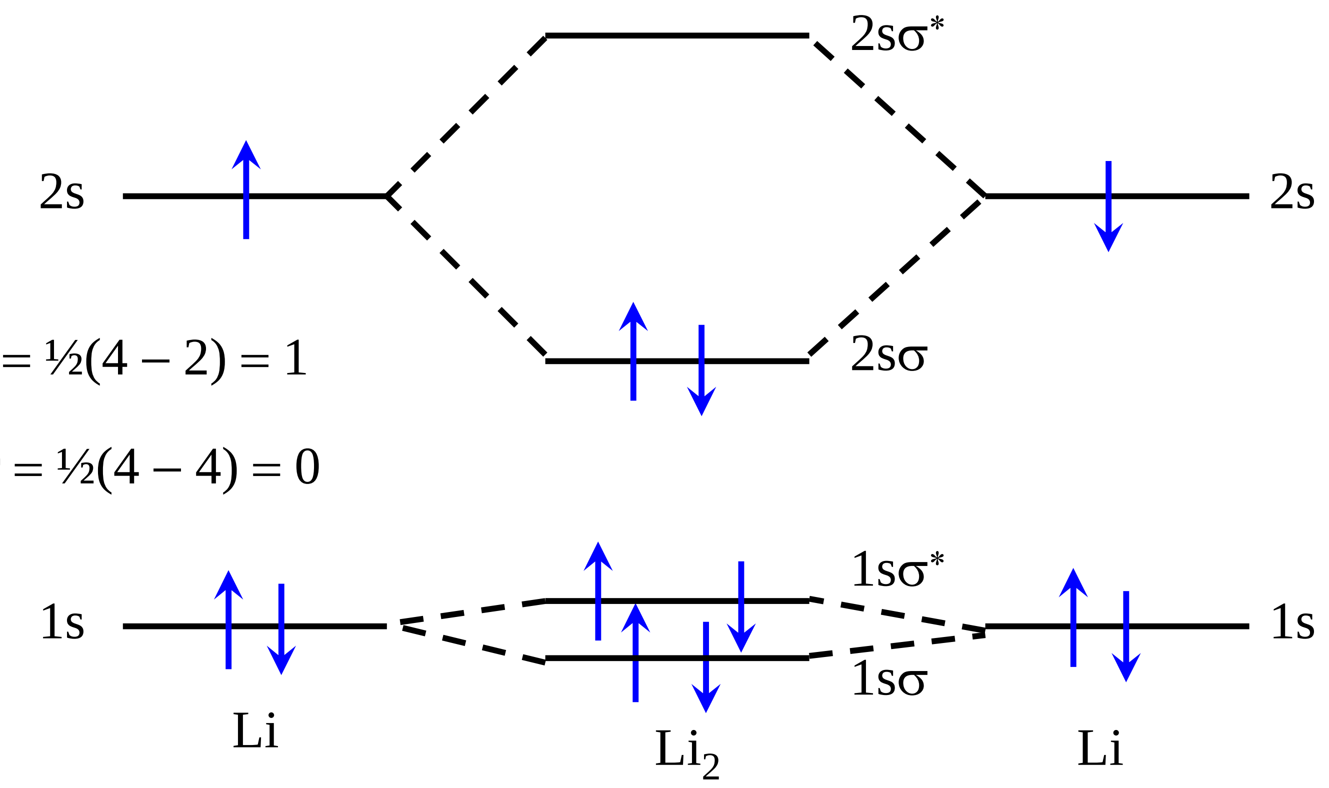
Diatomic Molecules of Second Period Elements



1 H Hydrogen 1.0079																	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29

Li: $1s_1 1s_2 2s_3$

Like the 1s atomic orbitals, the 2s atomic orbitals combine to form molecular orbitals.

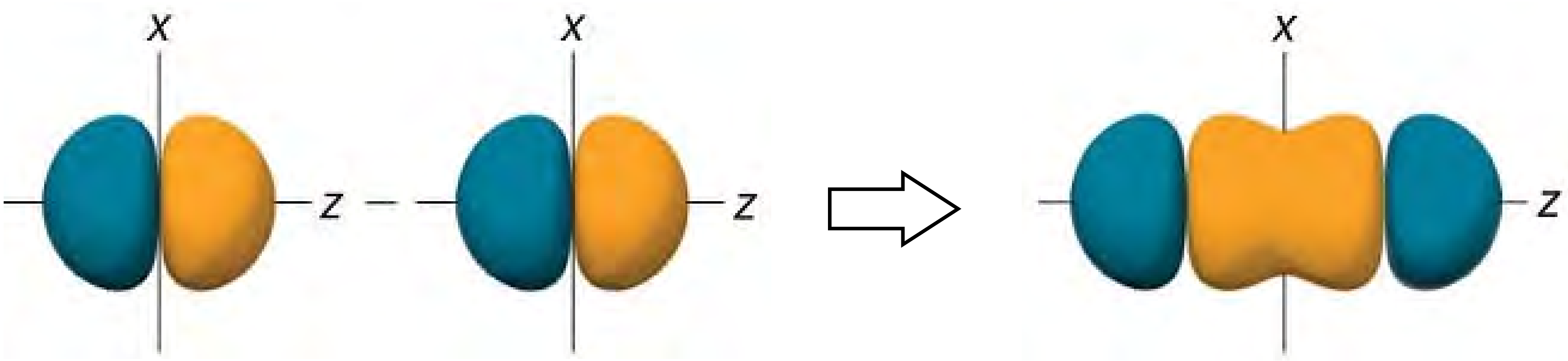


Li_2 : bond order = ½(4 – 2) = 1

Be_2 : bond order = ½(4 – 4) = 0

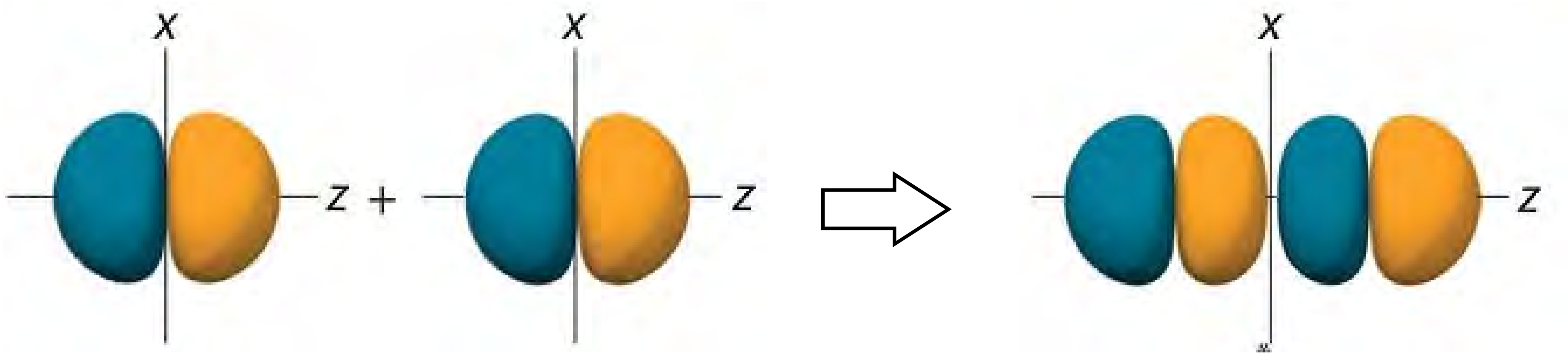
less overlap of
tightly held
1s electrons

Linear Combinations of the 2p Atomic Orbitals



$2p_{zA}$ $2p_{zB}$ $2p_{zA} – 2p_{zB} = 2p_z\sigma$

a bonding orbital

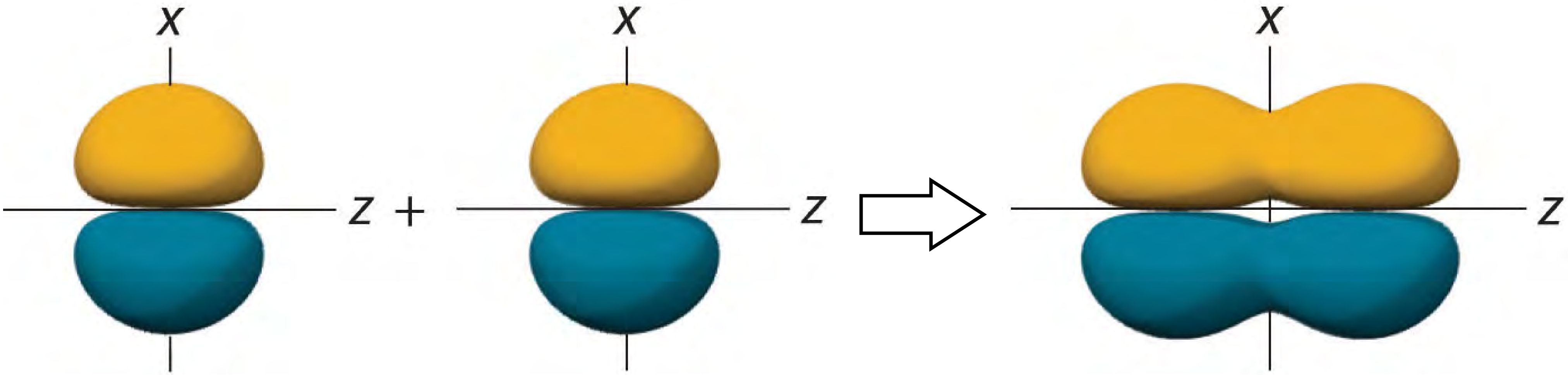


$2p_{zA}$ $2p_{zB}$ $2p_{zA} + 2p_{zB} = 2p_z\sigma^*$

an anti-bonding orbital

Images from chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbooks/Quantum_States_of_Atoms_and_Molecules_(Zelinski_et_al)

Linear Combinations of the 2p Atomic Orbitals

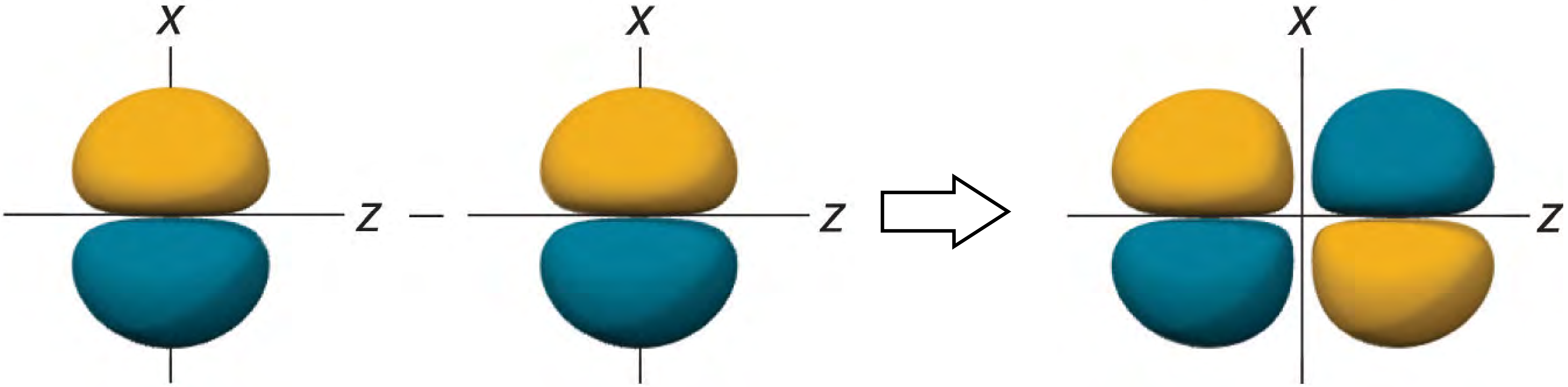


$2p_{xA}$

$2p_{xB}$

$2p_{xA}+2p_{xB} \;=\; 2p_x\pi$

a bonding orbital



$2p_{xA}$

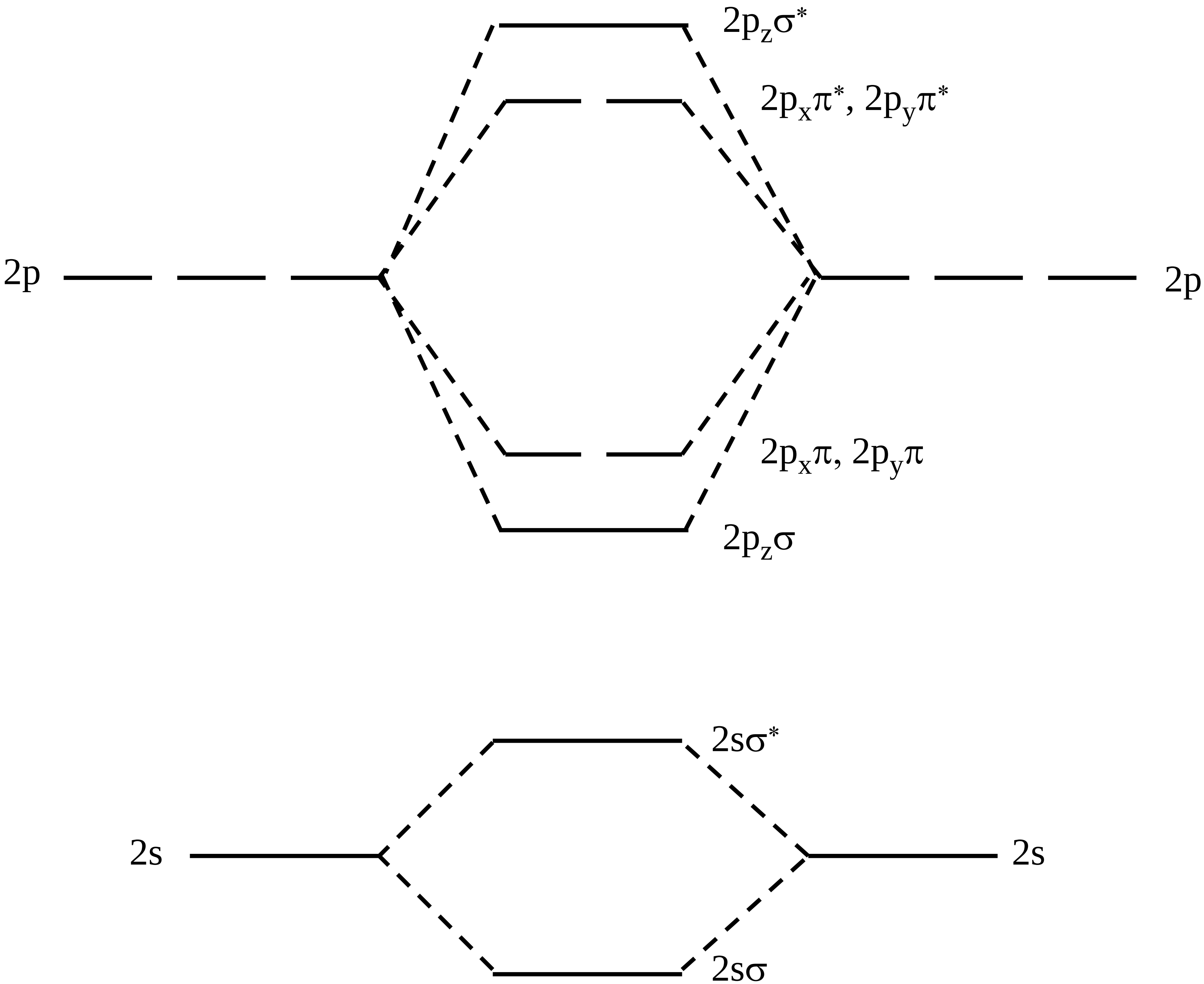
$2p_{xB}$

$2p_{xA}-2p_{xB} \;=\; 2p_x\pi^*$

an anti-bonding orbital

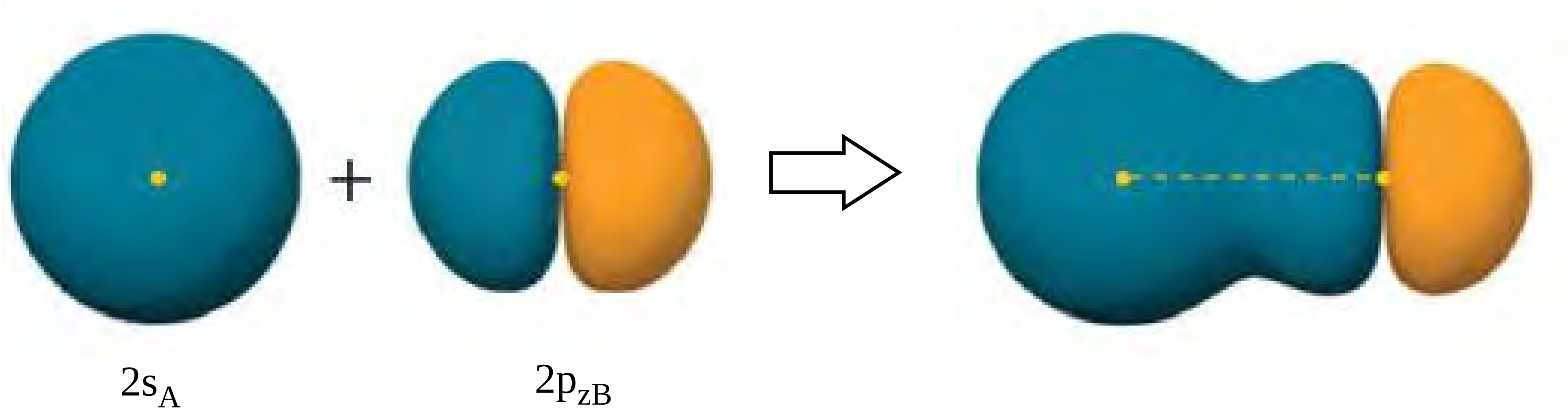
Images from chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbooks/Quantum_States_of_Atoms_and_Molecules_(Zelinski_et_al)

The Molecular-Orbital Energy-Level Diagram



Linear Combinations of the 2p Atomic Orbitals, cont'd

The 2s and 2pz atomic orbitals overlap.



The overlap shifts the energy of the $2s\sigma$ down

and shifts the energy of the $2p_z\sigma$ up.

Images from chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbooks/
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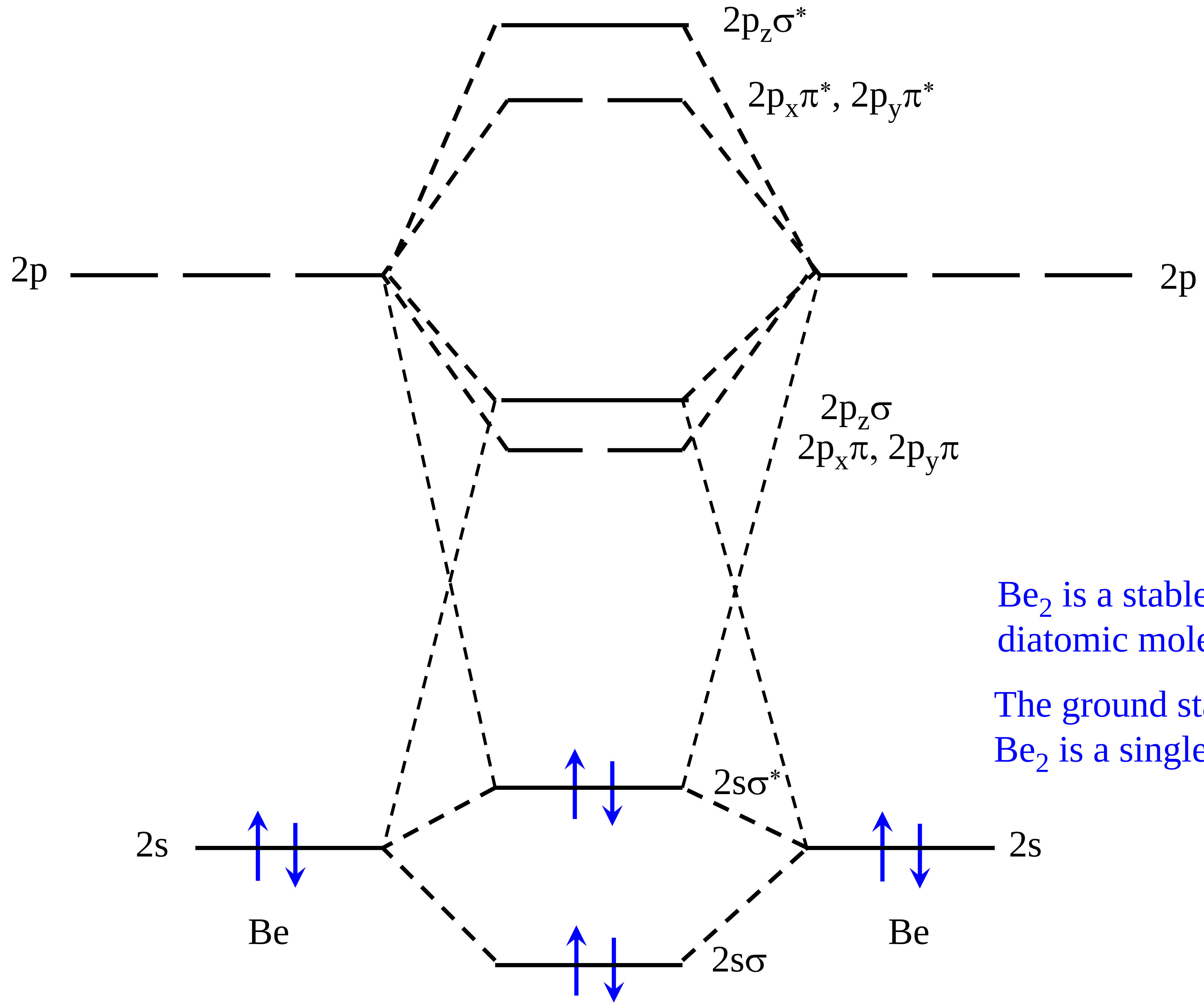
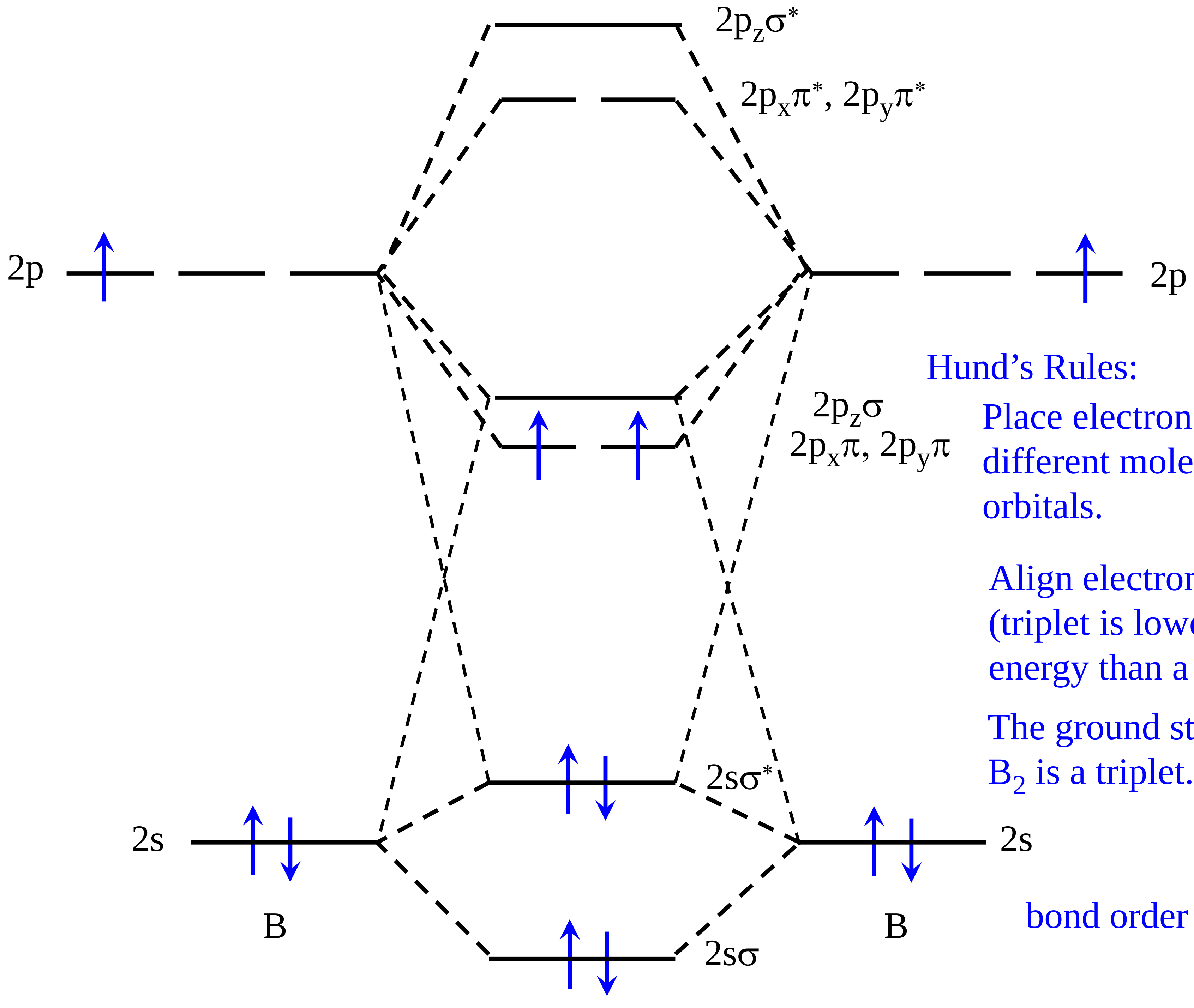
The Molecular-Orbital Energy-Level Diagram



Be_2 is a stable diatomic molecule.

The ground state of Be_2 is a singlet.

B_2



Hund's Rules:

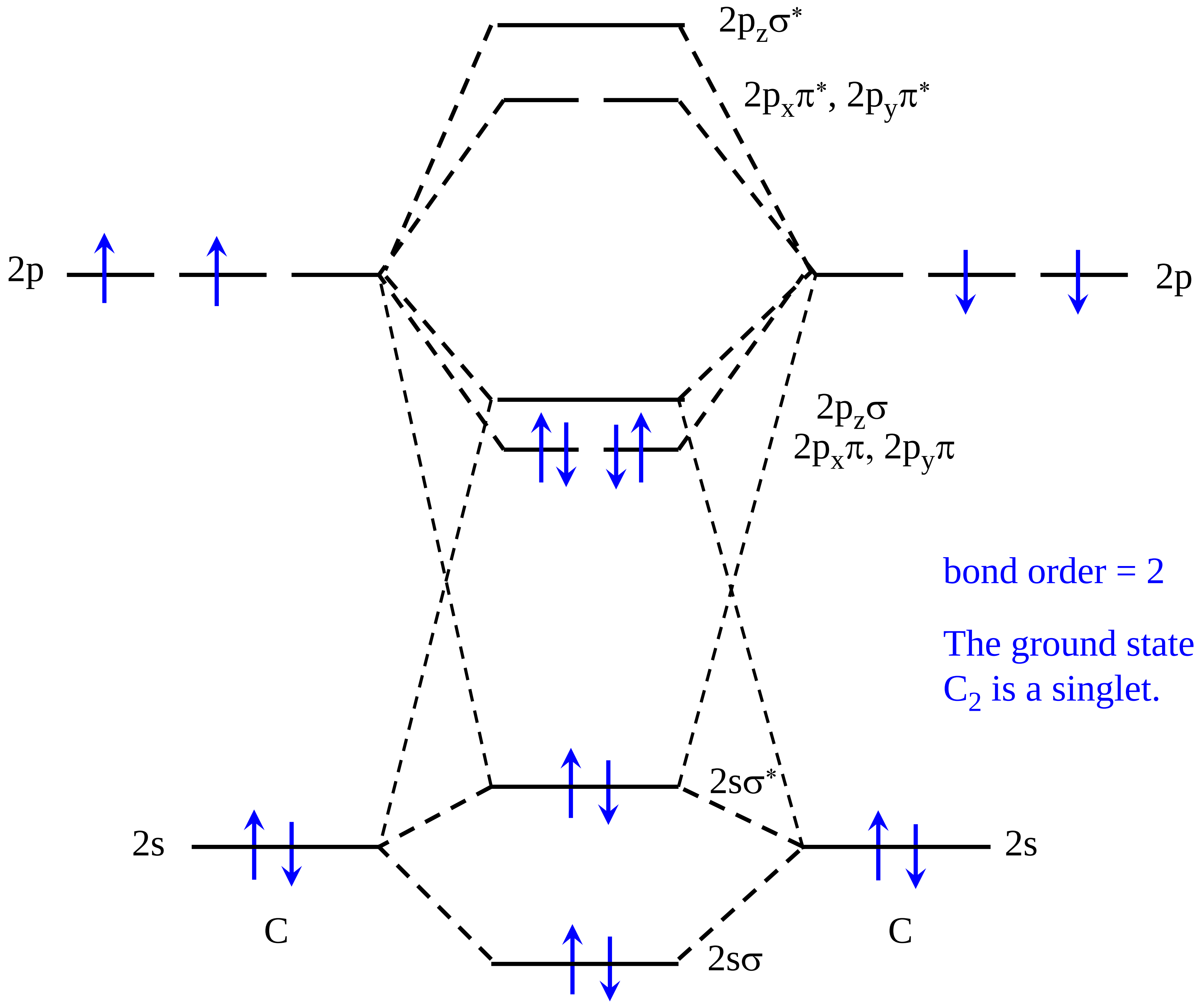
Place electrons in different molecular orbitals.

Align electron spins. (triplet is lower energy than a singlet)

The ground state of B_2 is a triplet.

bond order = 1

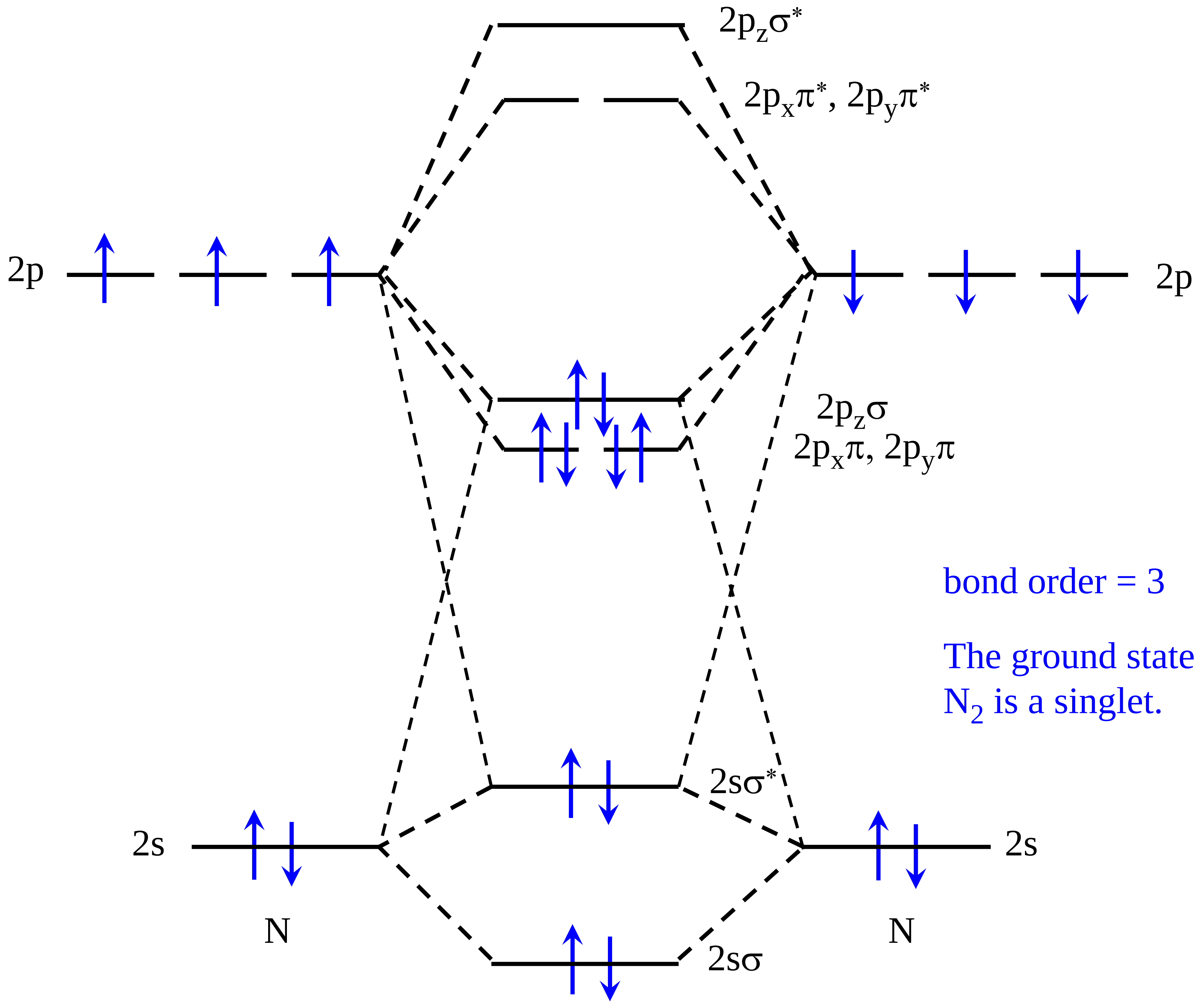
C_2



bond order = 2

The ground state of C_2 is a singlet.

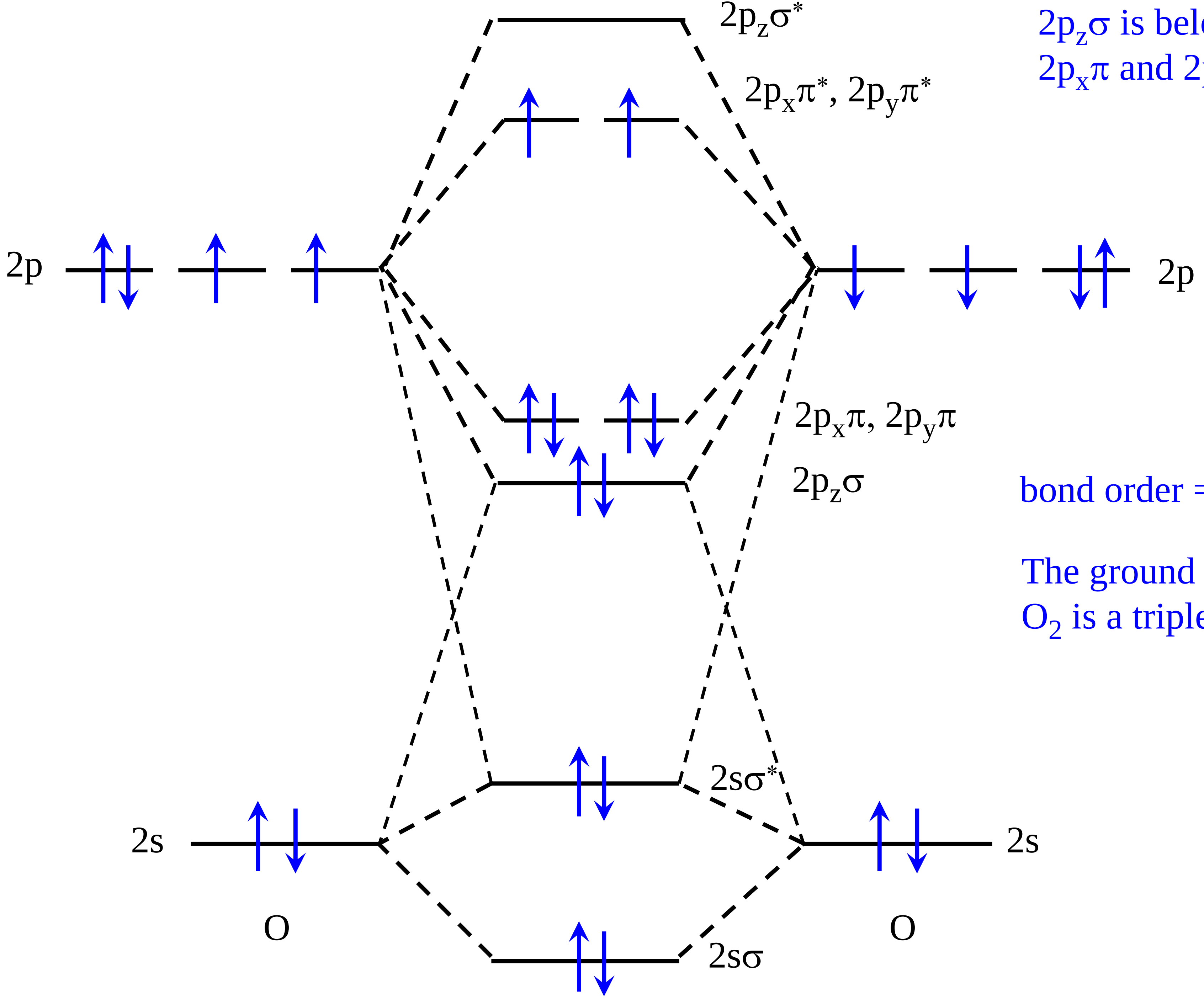
N_2



bond order = 3

The ground state of N_2 is a singlet.

O_2

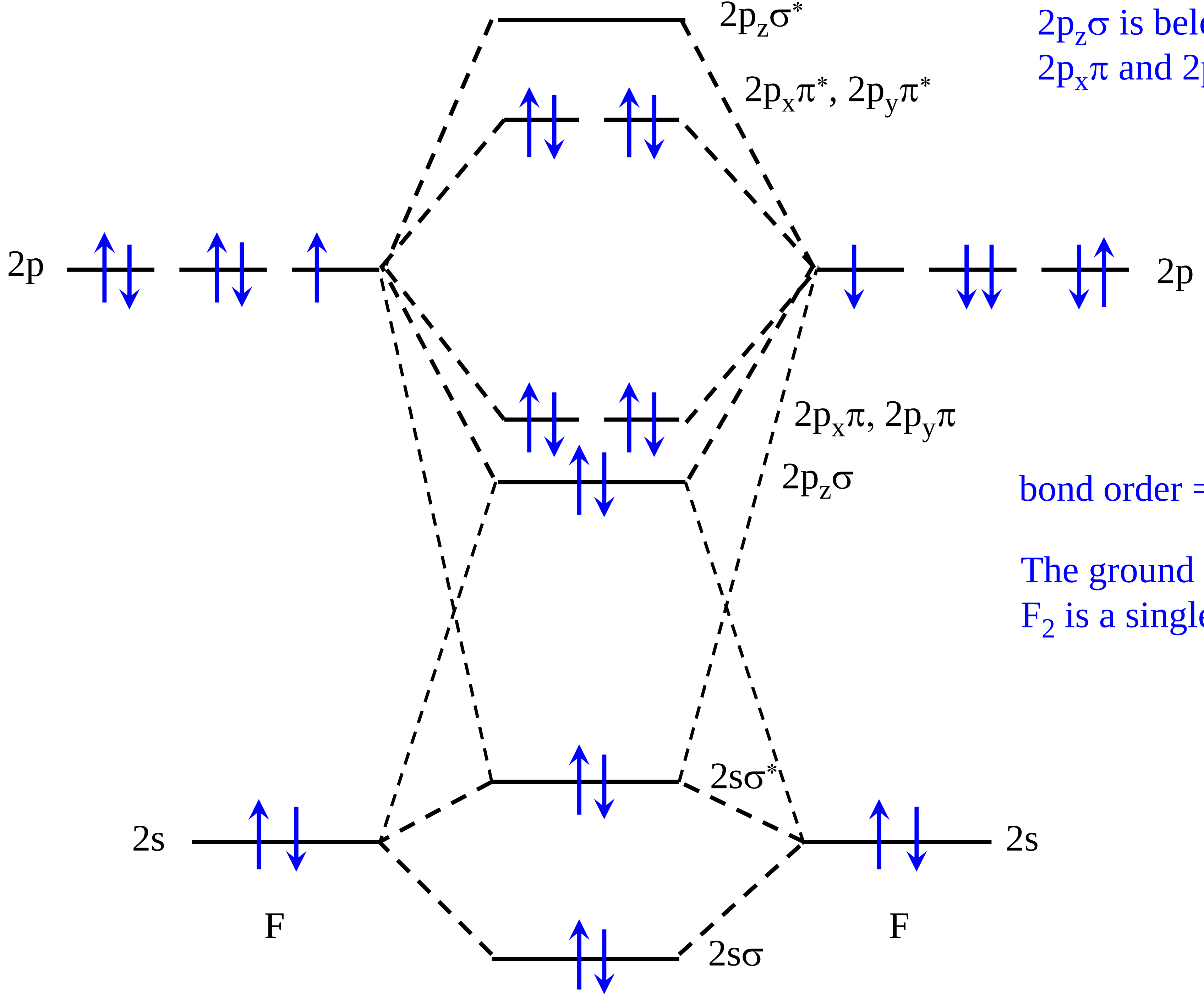


For O_2 and F_2,
$2p_z\sigma$ is below
$2p_x\pi$ and $2p_y\pi$

bond order = 2

The ground state of
O_2 is a triplet.

F_2

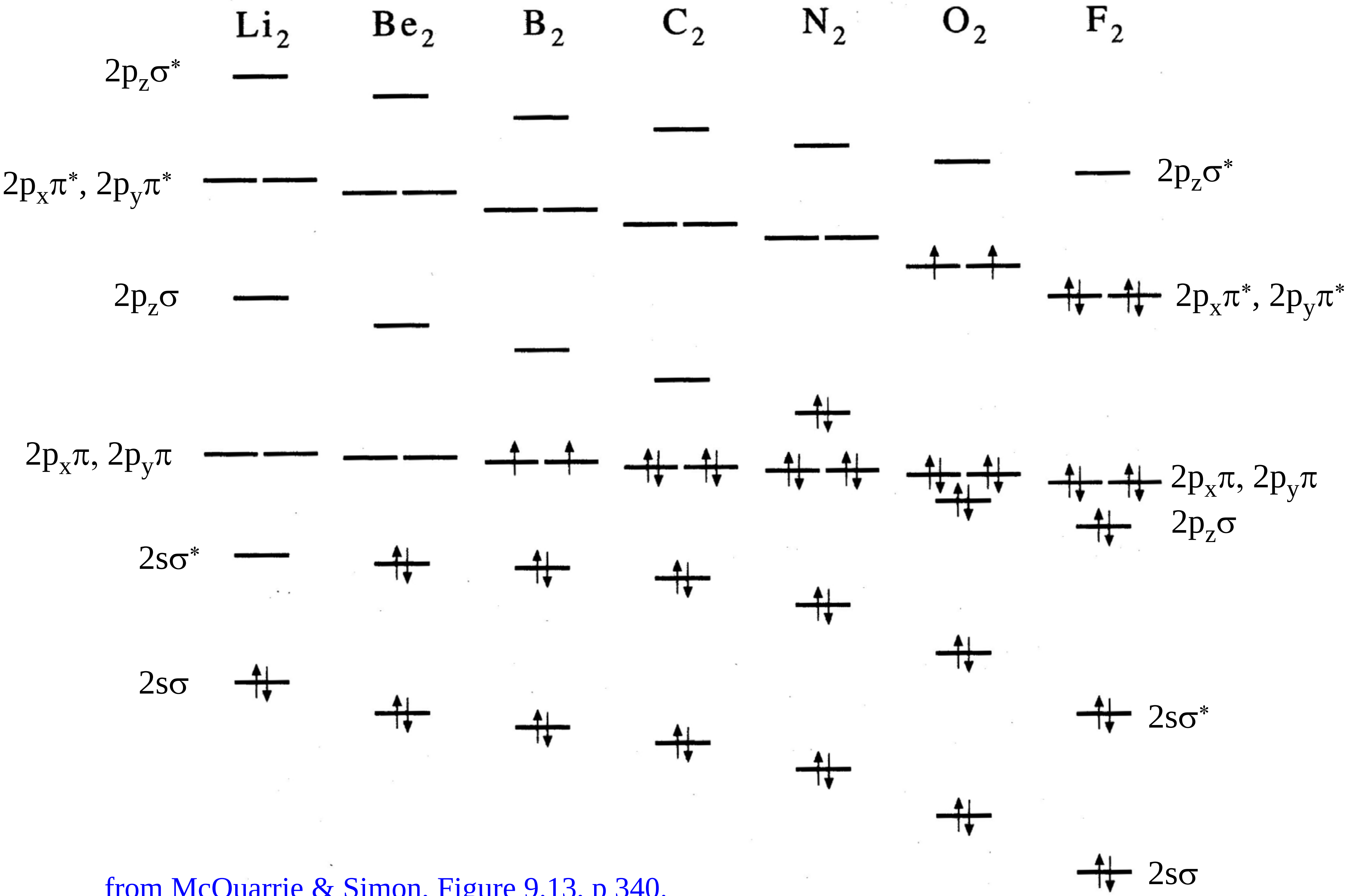


For O_2 and F_2,
$2p_z\sigma$ is below
$2p_x\pi$ and $2p_y\pi$

bond order = 1

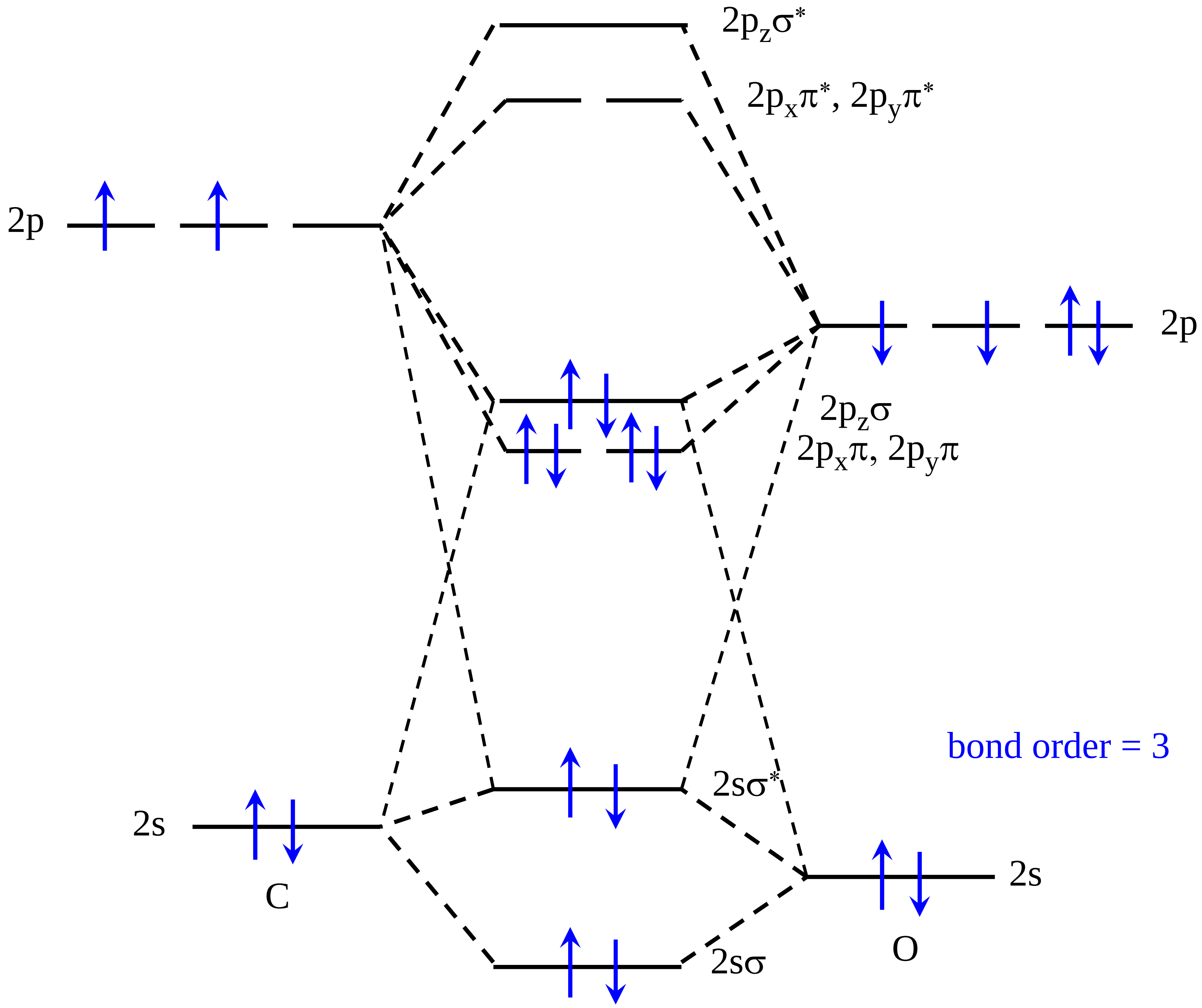
The ground state of F_2 is a singlet.

Relative Energy Levels for 2nd Period Diatomic Molecules

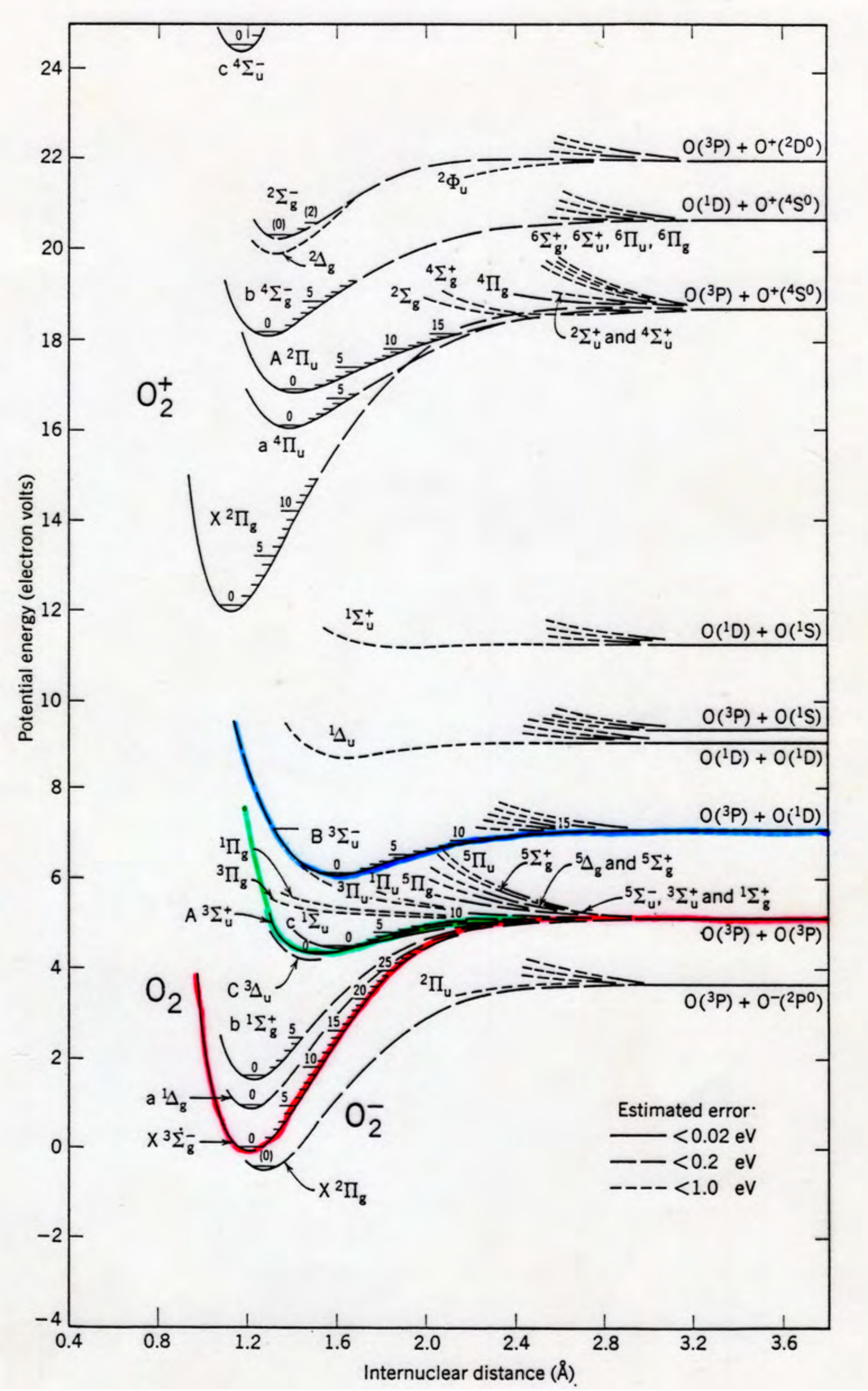


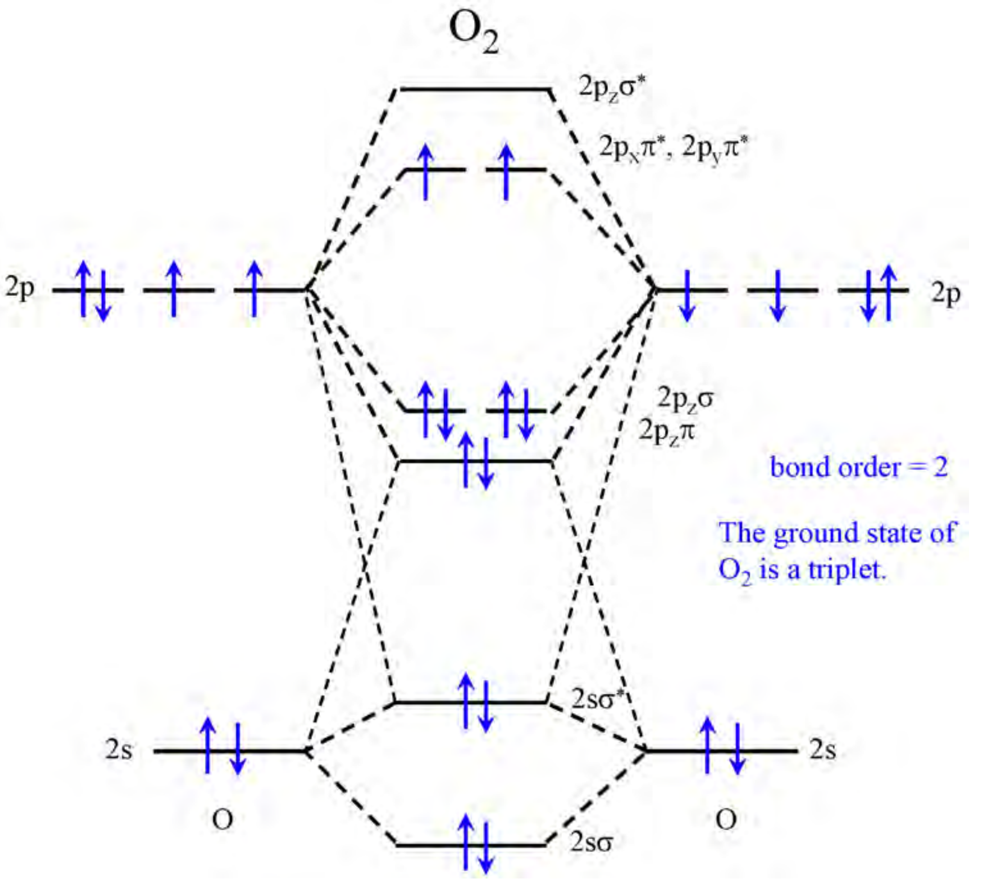
from McQuarrie & Simon, Figure 9.13, p 340.

CO and BF (isoelectric with N_2)



bond order = 3





bond order = 2

The ground state of O_2 is a triplet.

Why is the O_2 bond stronger than the O_2^- bond?

Why is the O_2 bond weaker than the O_2^+ bond?

What is the electronic excitation from the red line to the green line?

to the blue line?

from F. R. Gilmore, RAND Corporation
Memorandum R-4034-PR (June 1964).