Lecture B7
Molecular Orbital Theory, Part 2

Different is interesting.

Covalent Bond Theories

1. VSEPR (valence shell electron pair repulsion model).
   A set of *empirical* rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

2. Valence Bond theory.
   A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals.
   Works especially well for organic molecules.

3. Molecular Orbital theory.
   The most modern and powerful theory of bonding. Based upon QM.

Molecular Orbital Theory - LCAO-MO

Robert S. Mulliken realized that a Linear Combination of Atomic Orbitals (LCAO) could be used to make a set of new Molecular Orbitals (MO). The energies of these new molecular orbitals could be calculated and then filled with valence electrons.

Robert S. Mulliken
1896-1986

Mulliken received the 1966 Nobel Prize for his work.

MO energies come from Quantum Mechanics, of course!

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

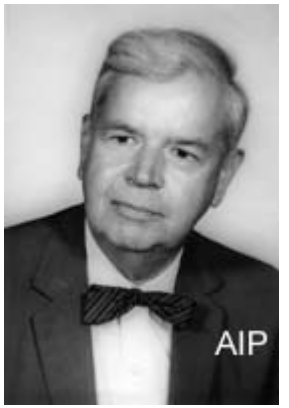
WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstates.
2. a set of eigenstate energies.

If you are interested, please look up the "Hartree-Fock Method" and "Slater Determinants."

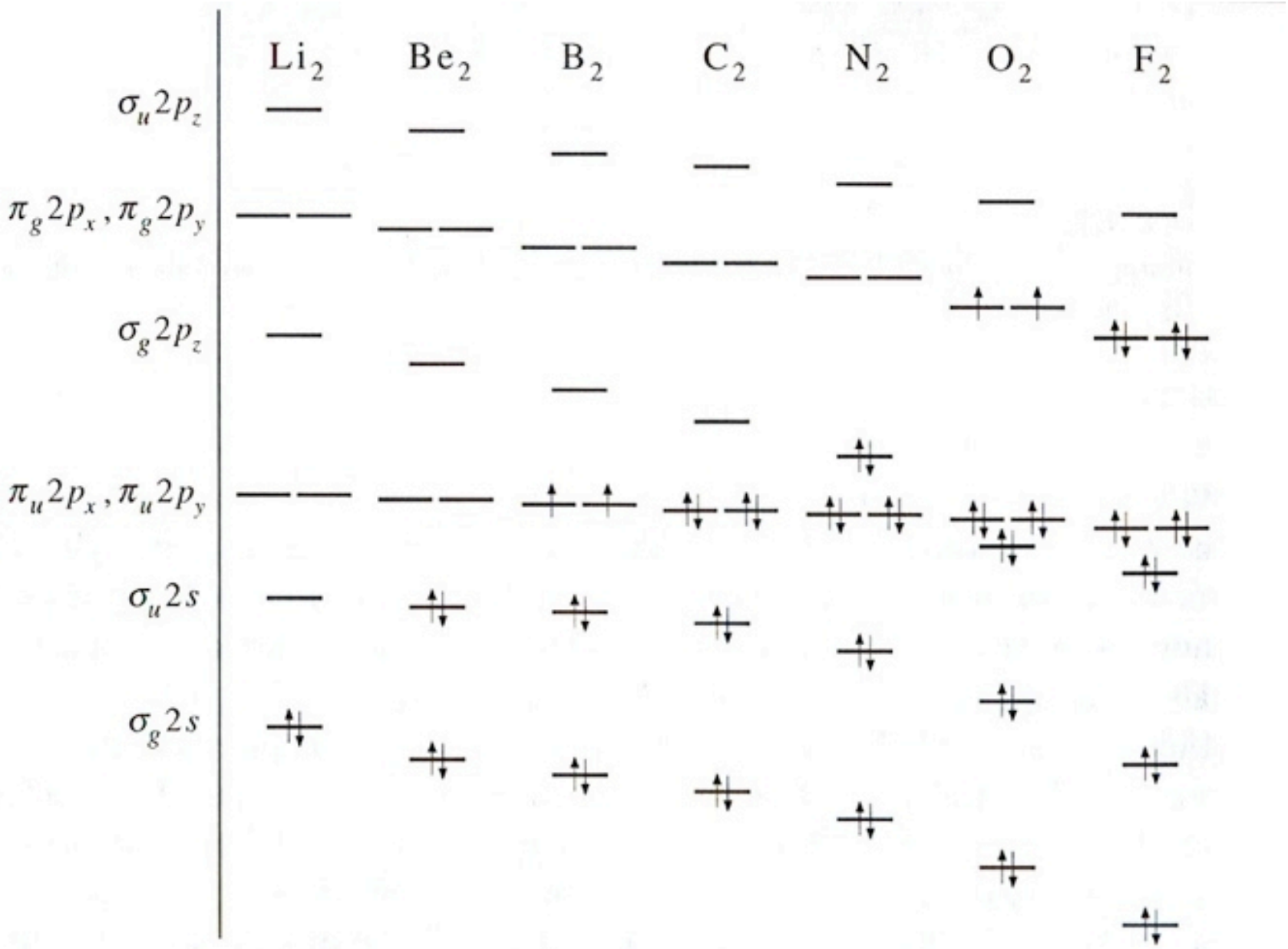
D. R. Hartree
1897-1958

V. A. Fock
1898-1974



J. C. Slater
1900-1976

Hartree-Fock QM energy calculations for first row homonuclear diatomics from Li_2 to F_2:



Molecular Orbital theory introduces the concept of *Bond Order*.

The bond order is given by:

$$B.O. = \frac{1}{2}[\#\ bonding\ electrons - antibonding\ electrons]$$

The bond order does not need to be an integer number.

We are also able to predict the *paramagnetic properties* of a molecule from MO theory, based on whether it possesses unpaired electrons:

For a molecule, there are two possibilities:

Diamagnetic: All electrons are paired.

Paramagnetic: Unpaired electrons are present.

$\mu = \chi B$

$\chi < 0$: Diamagnetic

$\chi > 0$: Paramagnetic

B is the applied magnetic field. μ is the induced magnetic dipole. χ is the magnetic susceptibility. Paramagnetic molecules are attracted by a magnetic field.

For homonuclear diatomic molecules, you should be able to predict:

I. Electron Configuration

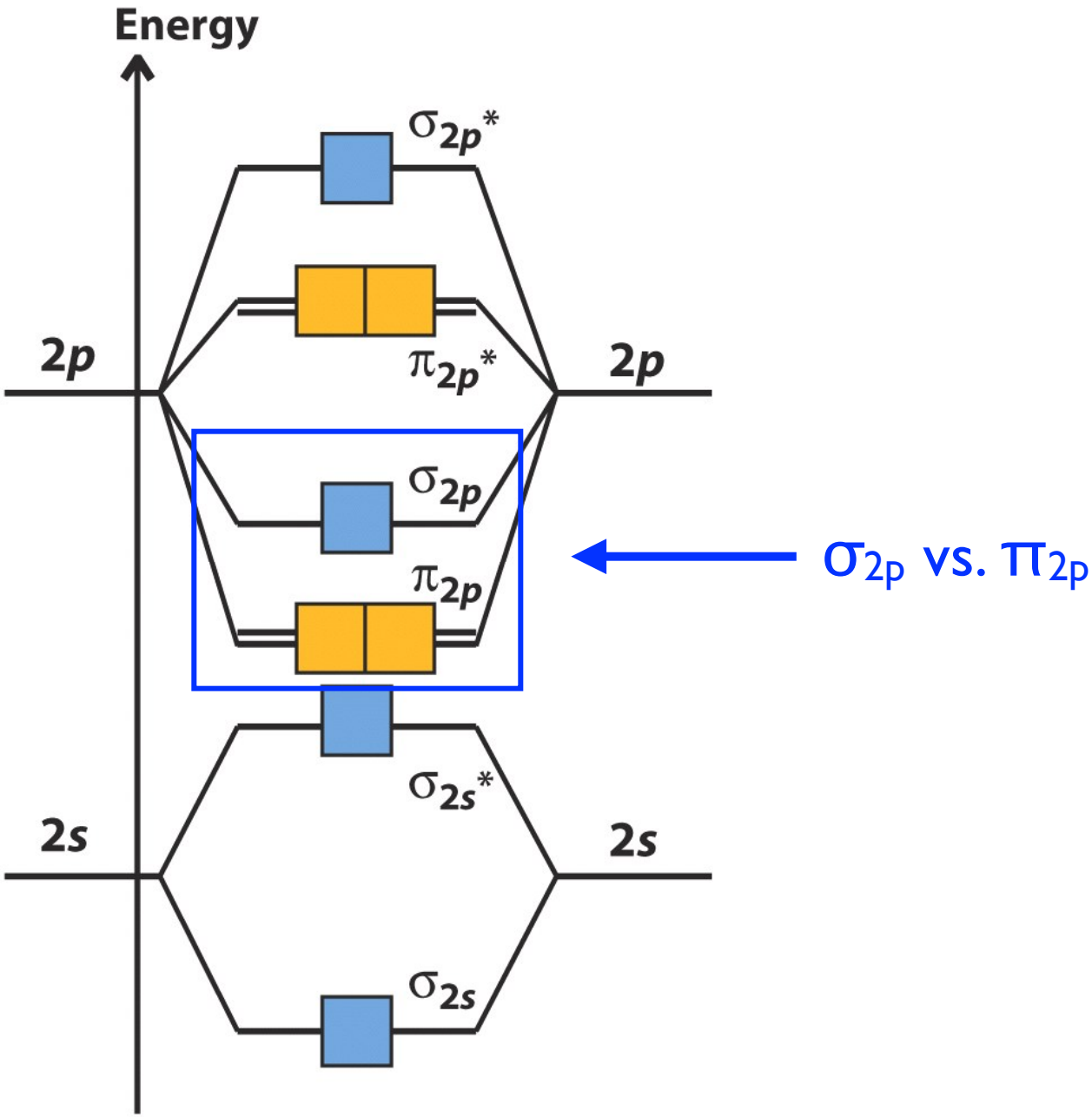
II. Bond Order

III. Paramagnetic or Diamagnetic

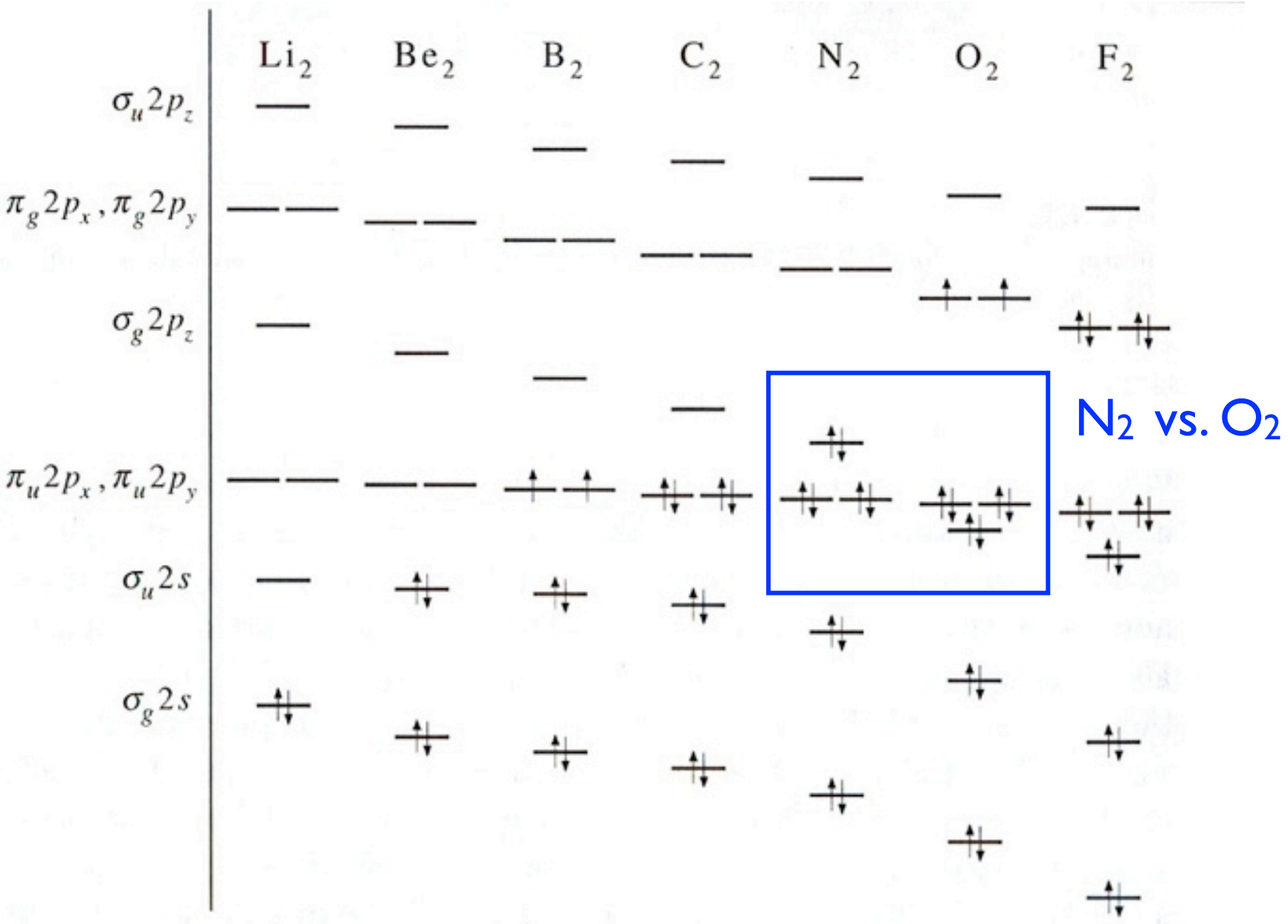
IV. Number of electrons in the HOMO

V. Estimate (set limits on) the IP of the molecule

Another example: $\mathbf{N_2}$ (007). Note that the E levels flip from O_2.

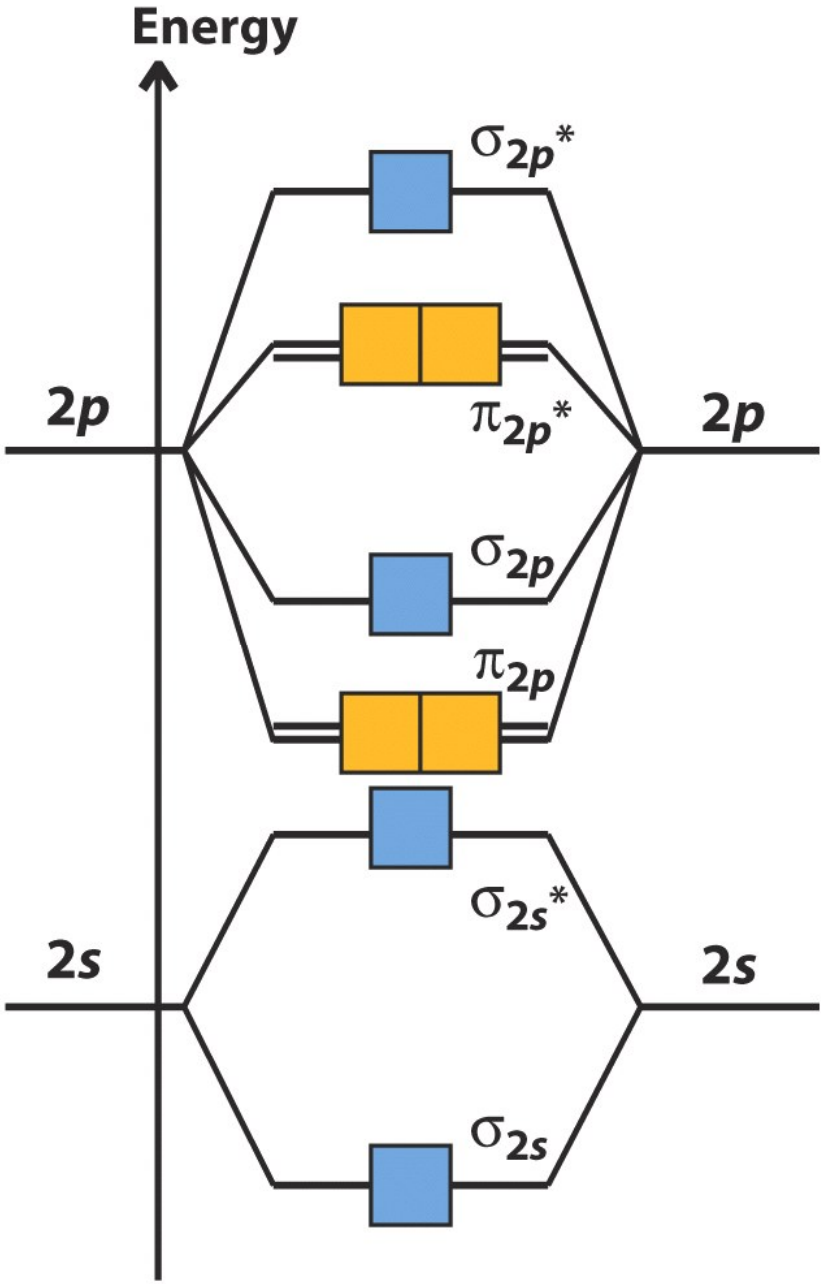


QM energy calculations for the first row elements show that O and F are "normal", and everything else is "abnormal" --



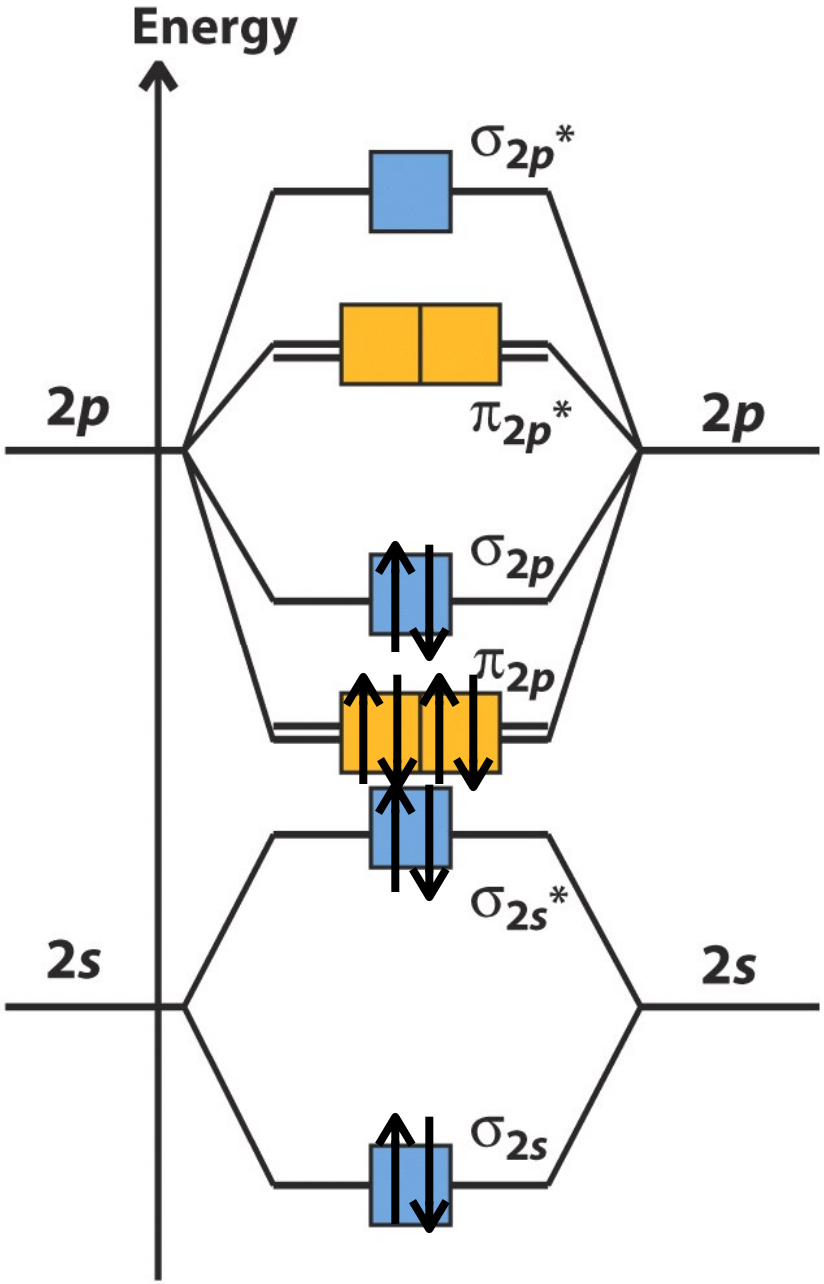
Another example: $\mathbf{N_2}$ (007).

How many valence electrons?



Another example: $\mathbf{N_2}$ (007).

10
valence electrons!



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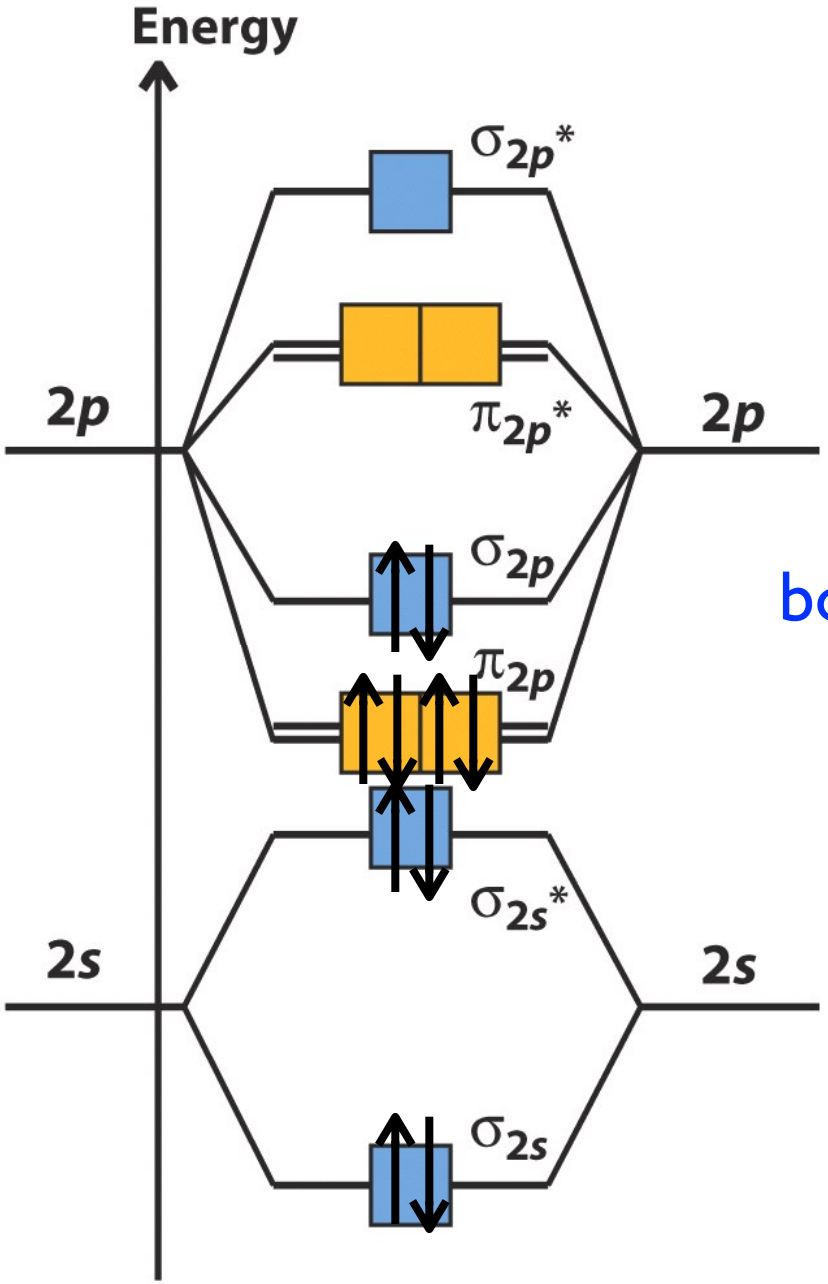

bond order = ?

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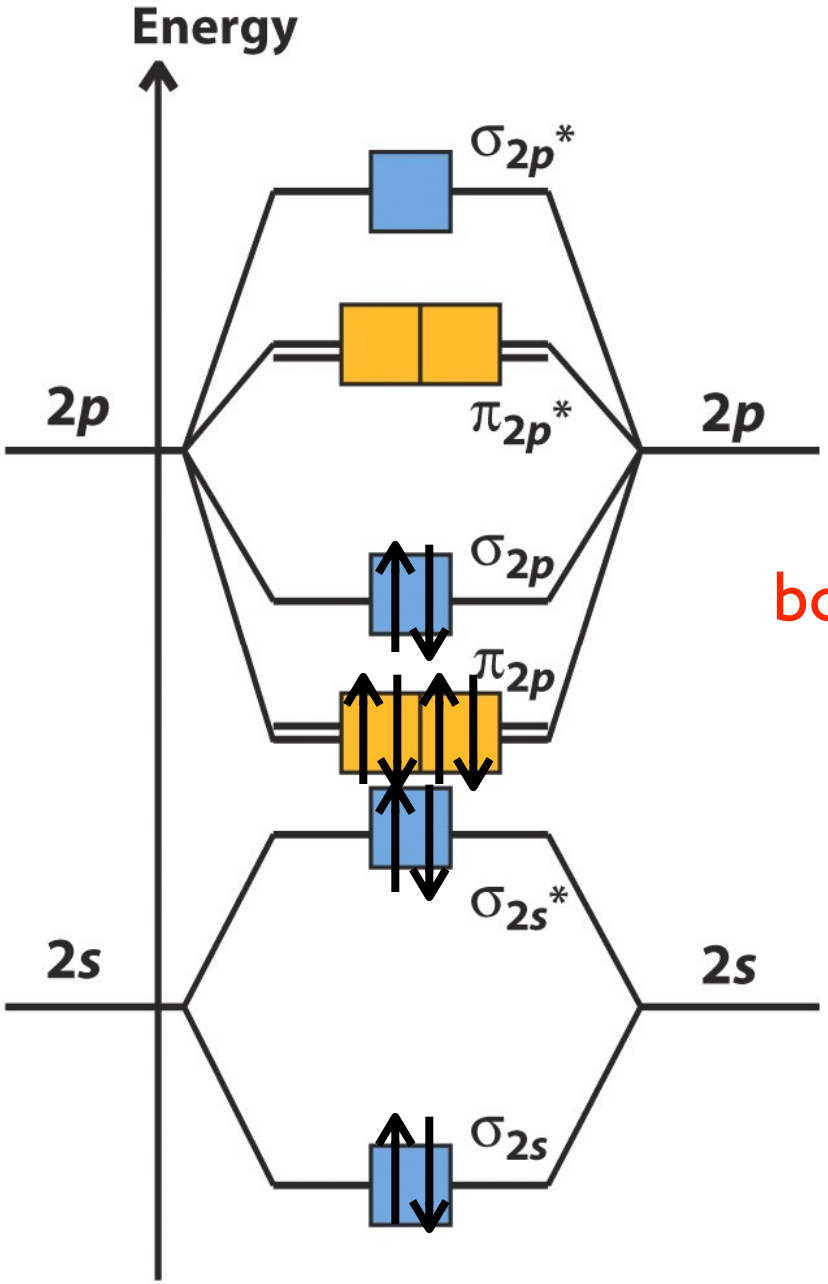
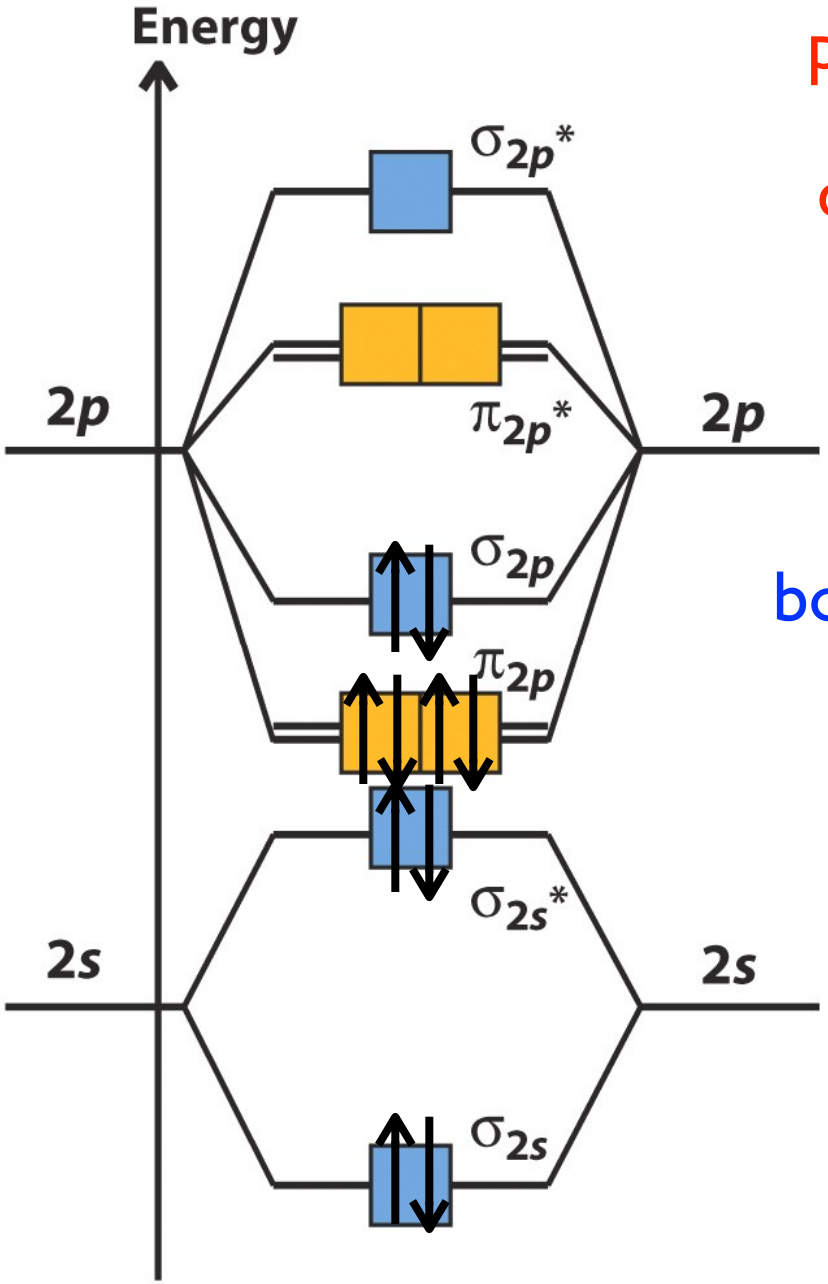


bond order = 3

Another example: $\mathbf{N_2}$ (007).

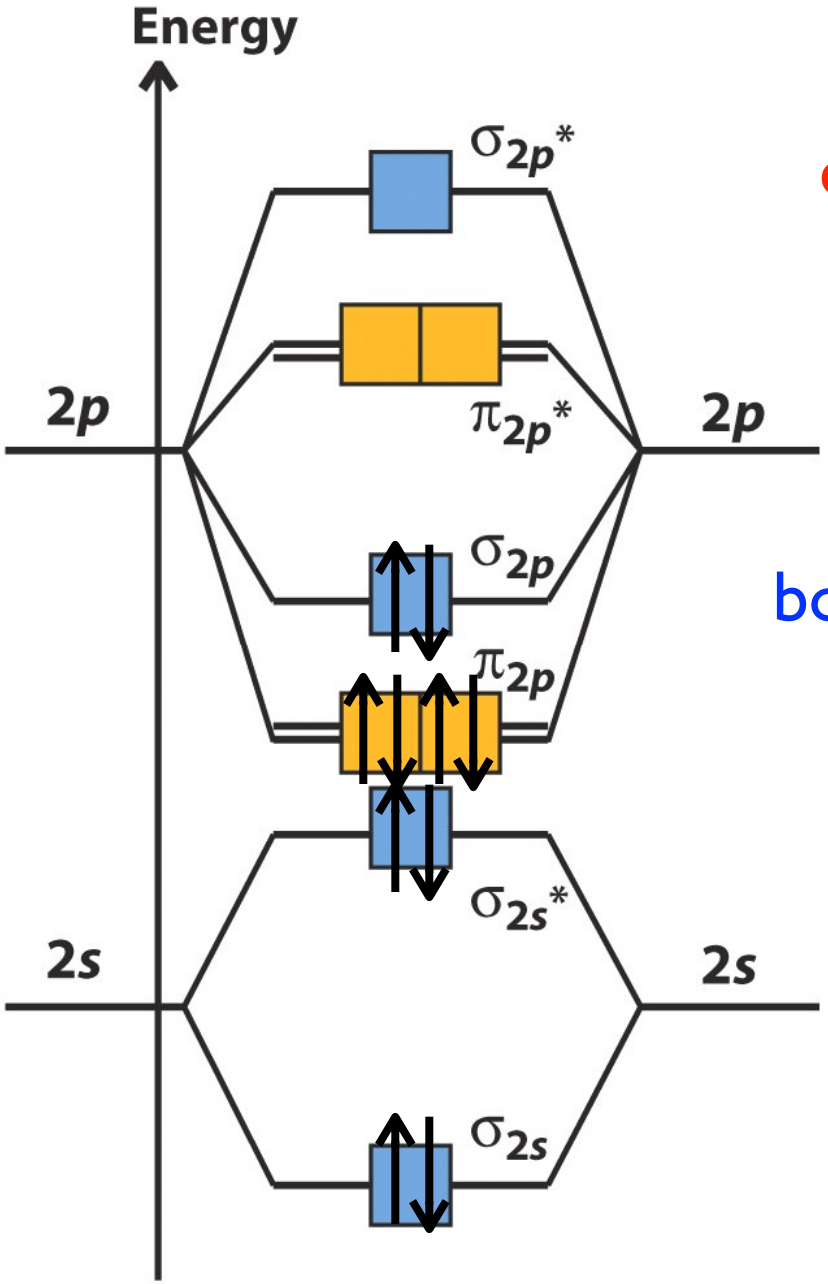


paramagnetic
or
diamagnetic?

10
valence electrons!

bond order = 3

Another example: $\mathbf{N_2}$ (007).



10
valence electrons!

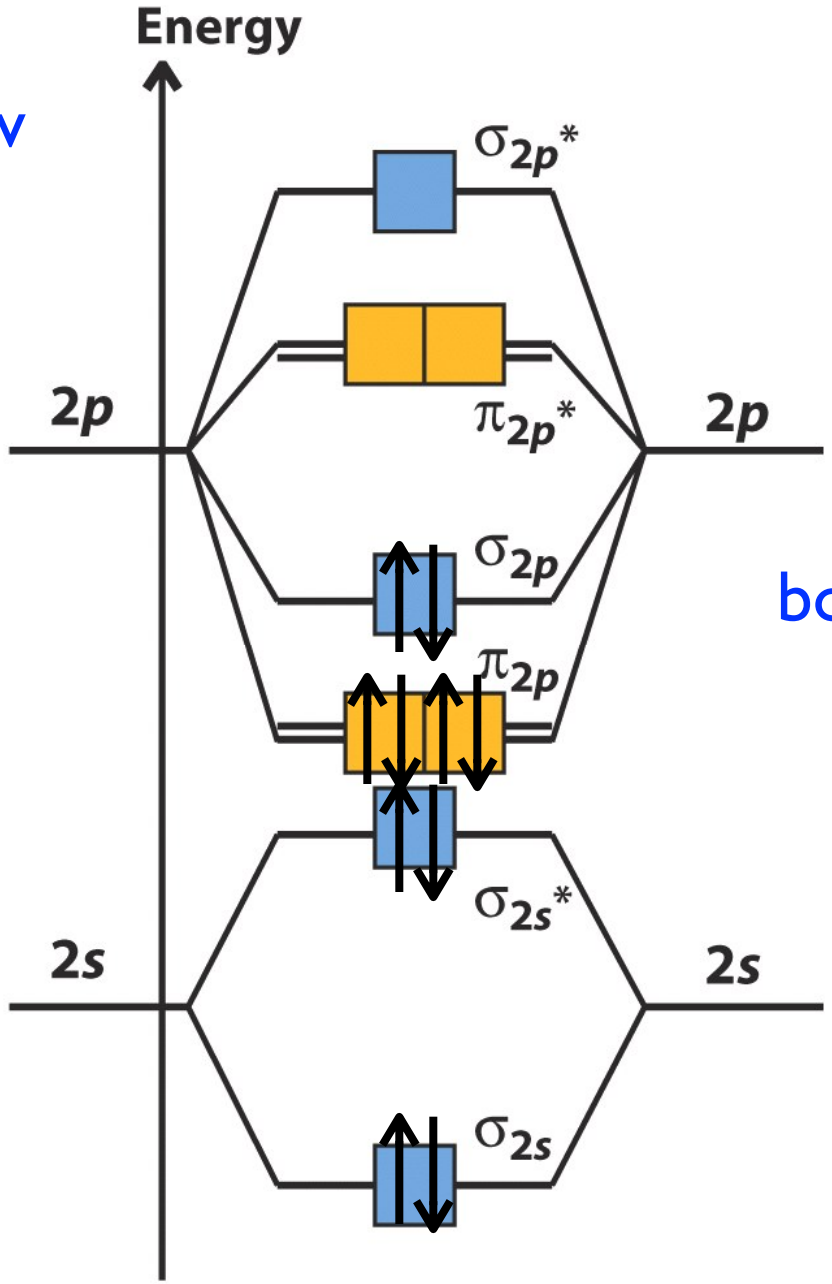
diamagnetic!

bond order = 3

Another example: $\mathbf{N_2}$ (007).

IP of N = 14.53 ev
The IP of N_2 is
greater or less
than 14.53 eV?

10
valence electrons!



diamagnetic

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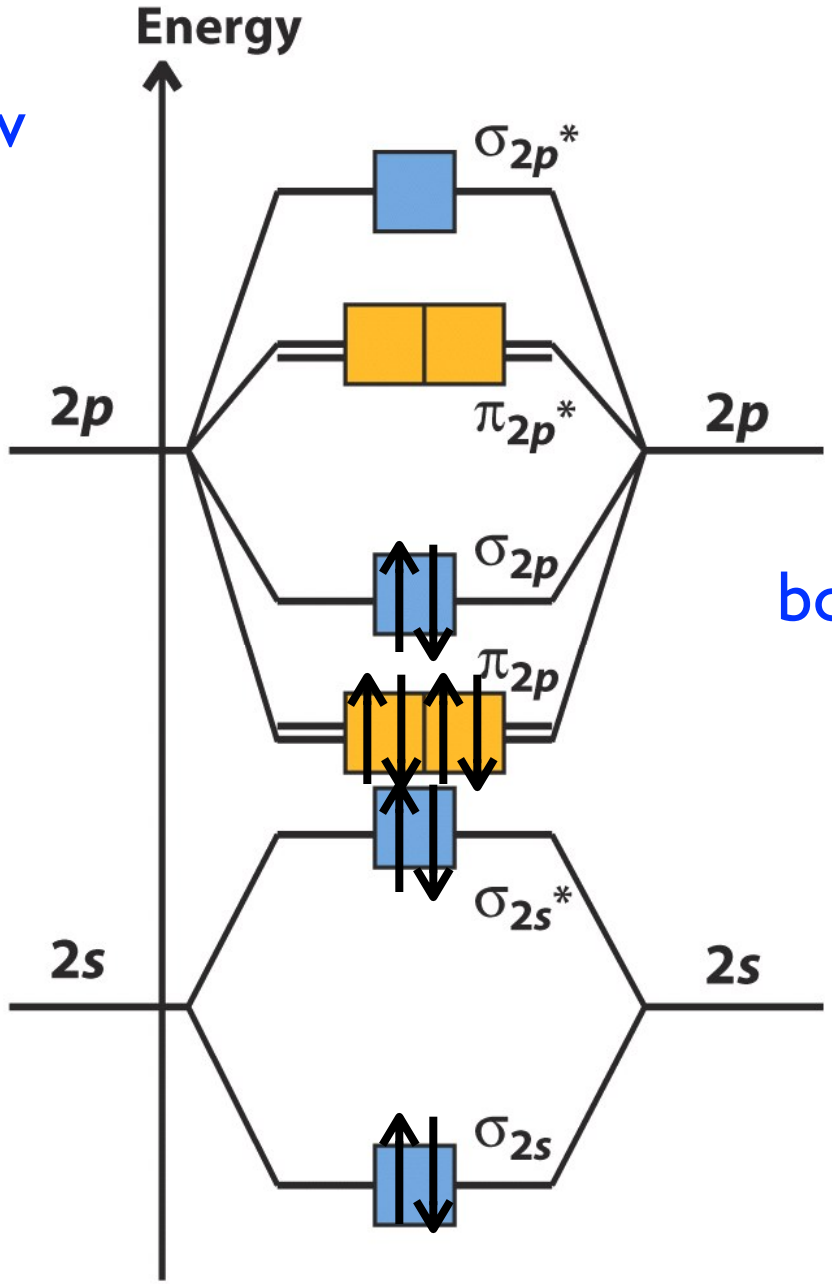


diamagnetic

bond order = 3

Another example: **N_2** (007).

We therefore predict for N_2:

bond order = **3.0**

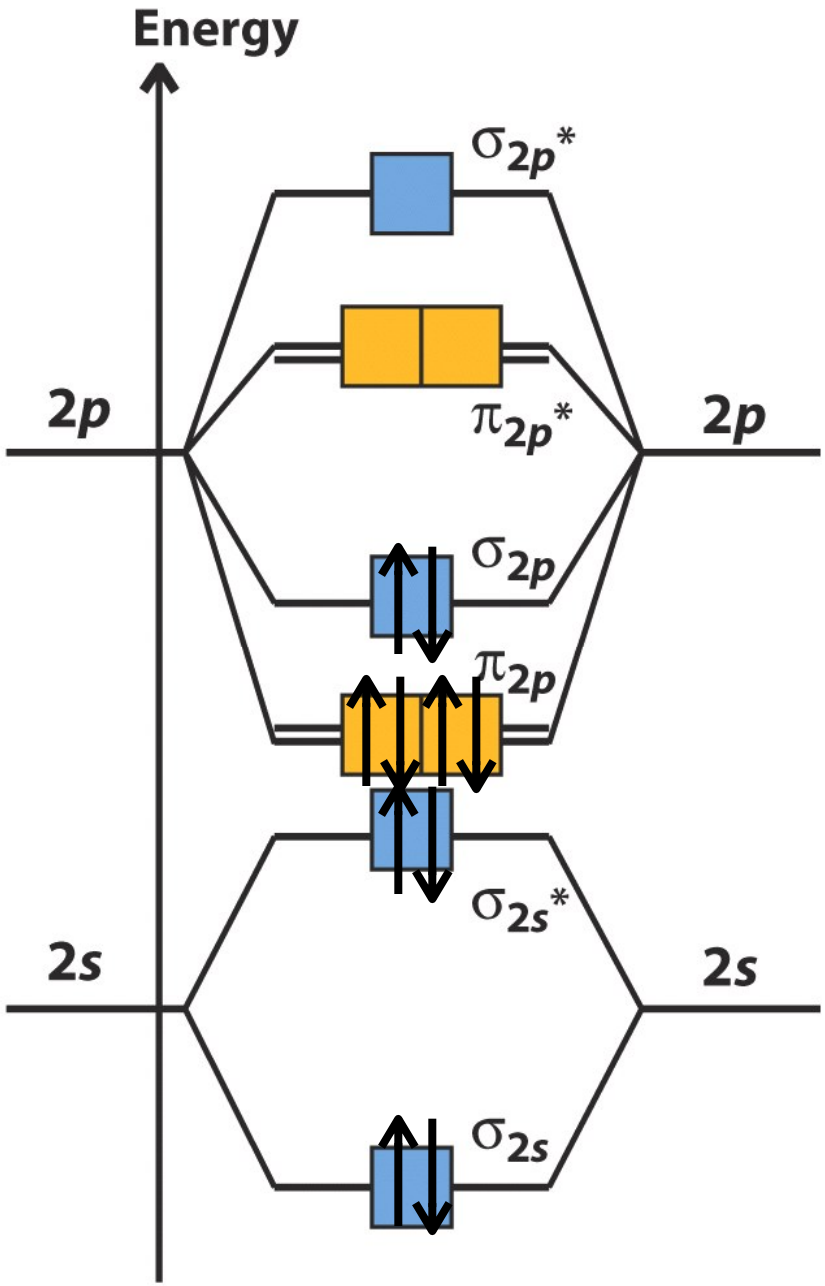
N_2 is **diamagnetic**

IP is greater than 14.53 eV

Electron configuration is:

$\sigma_{2s}^2 \sigma^*_{2s}^2 \pi_{2p}^4 \sigma_{2p}^2$

Two electrons in the HOMO



For homonuclear diatomic molecules, you should be able to predict:

I. Electron Configuration

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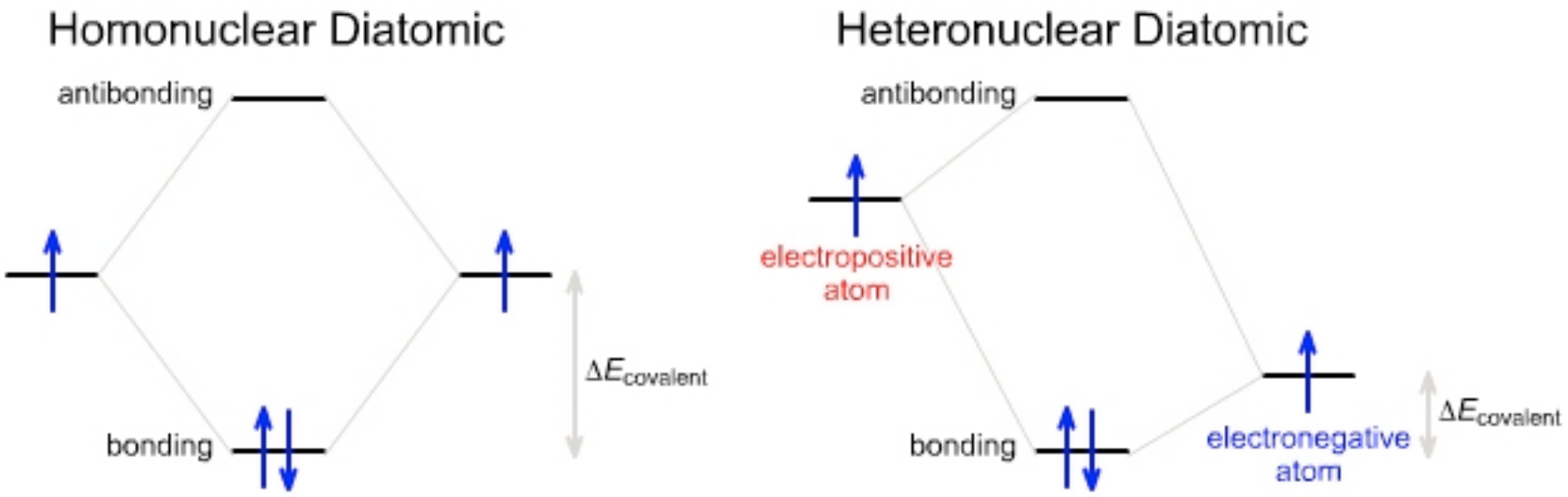
Heteronuclear Diatomic Molecules

When the component atomic levels are not at the same energy...



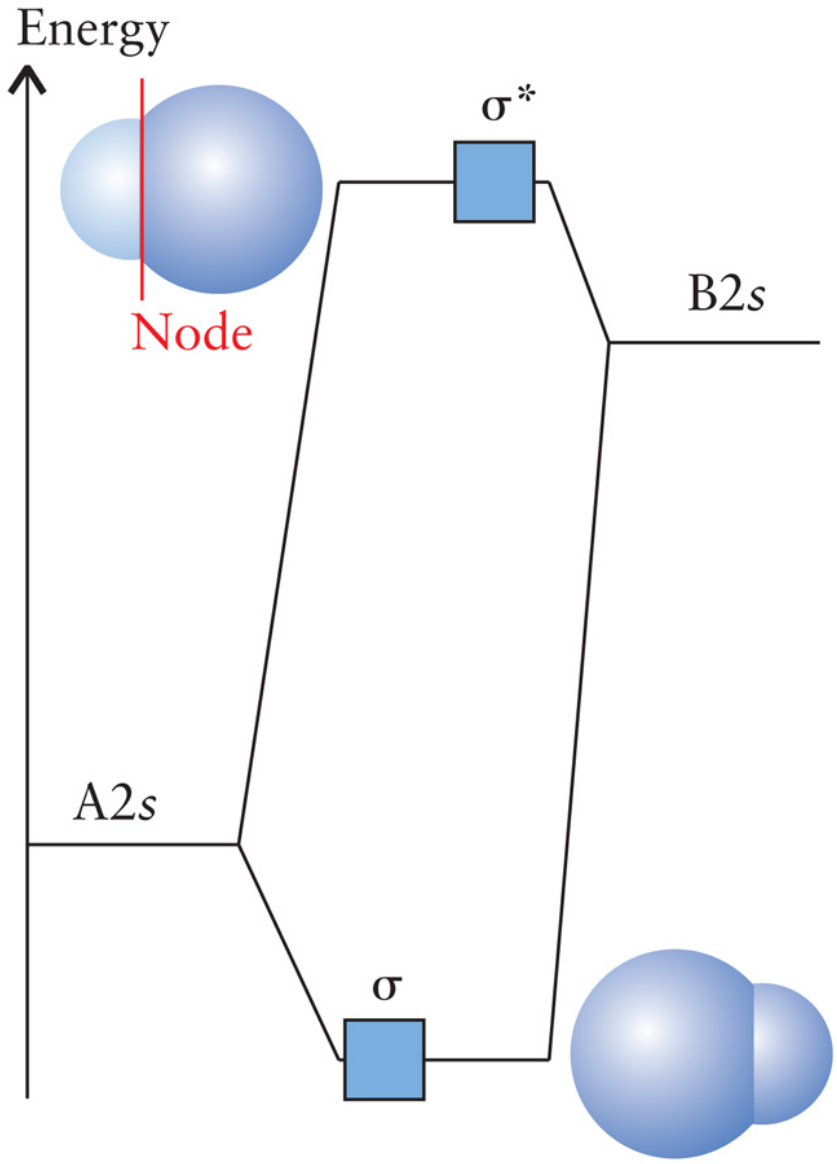
The wavefunctions are no longer symmetric:

For example:

$$\sigma_{2s} = c_1\psi_{2s_A} + c_2\psi_{2s_B}$$

$$\sigma^*_{2s} = c_1\psi_{2s_A} - c_2\psi_{2s_B}$$

The wavefunctions are no longer symmetric:



The AOs can be placed relative to the vacuum level by IPs

No.	Atomic Weight	Name	Sym.	M.P. (°C)	B.P. (°C)	Density* (g/cm^3)	Earth crust (%)*	Discovery (Year)	Group*	Electron configuration	Ionization energy (eV)
1	1.0079	Hydrogen	H	-259	-253	0.09	0.14	1776	1	$1s^1$	13.5984
2	4.0026	Helium	He	-272	-269	0.18		1895	18	$1s^2$	24.5874
3	6.941	Lithium	Li	180	1347	0.53		1817	1	[He] $2s^1$	5.3917
4	9.0122	Beryllium	Be	1278	2970	1.85		1797	2	[He] $2s^2$	9.3227
5	10.811	Boron	B	2300	2550	2.34		1808	13	[He] $2s^2$ $2p^1$	8.298
6	12.0107	Carbon	C	3500	4827	2.26	0.094	ancient	14	[He] $2s^2$ $2p^2$	11.2603
7	14.0067	Nitrogen	N	-210	-196	1.25		1772	15	[He] $2s^2$ $2p^3$	14.5341
8	15.9994	Oxygen	O	-218	-183	1.43	46.71	1774	16	[He] $2s^2$ $2p^4$	13.6181
9	18.9984	Fluorine	F	-220	-188	1.7	0.029	1886	17	[He] $2s^2$ $2p^5$	17.4228
10	20.1797	Neon	Ne	-249	-246	0.9		1898	18	[He] $2s^2$ $2p^6$	21.5645

Link is on the H2A website: http://www.science.co.il/PTelements.asp

The procedure for constructing energy correlation diagrams:

0. Draw the vacuum level.

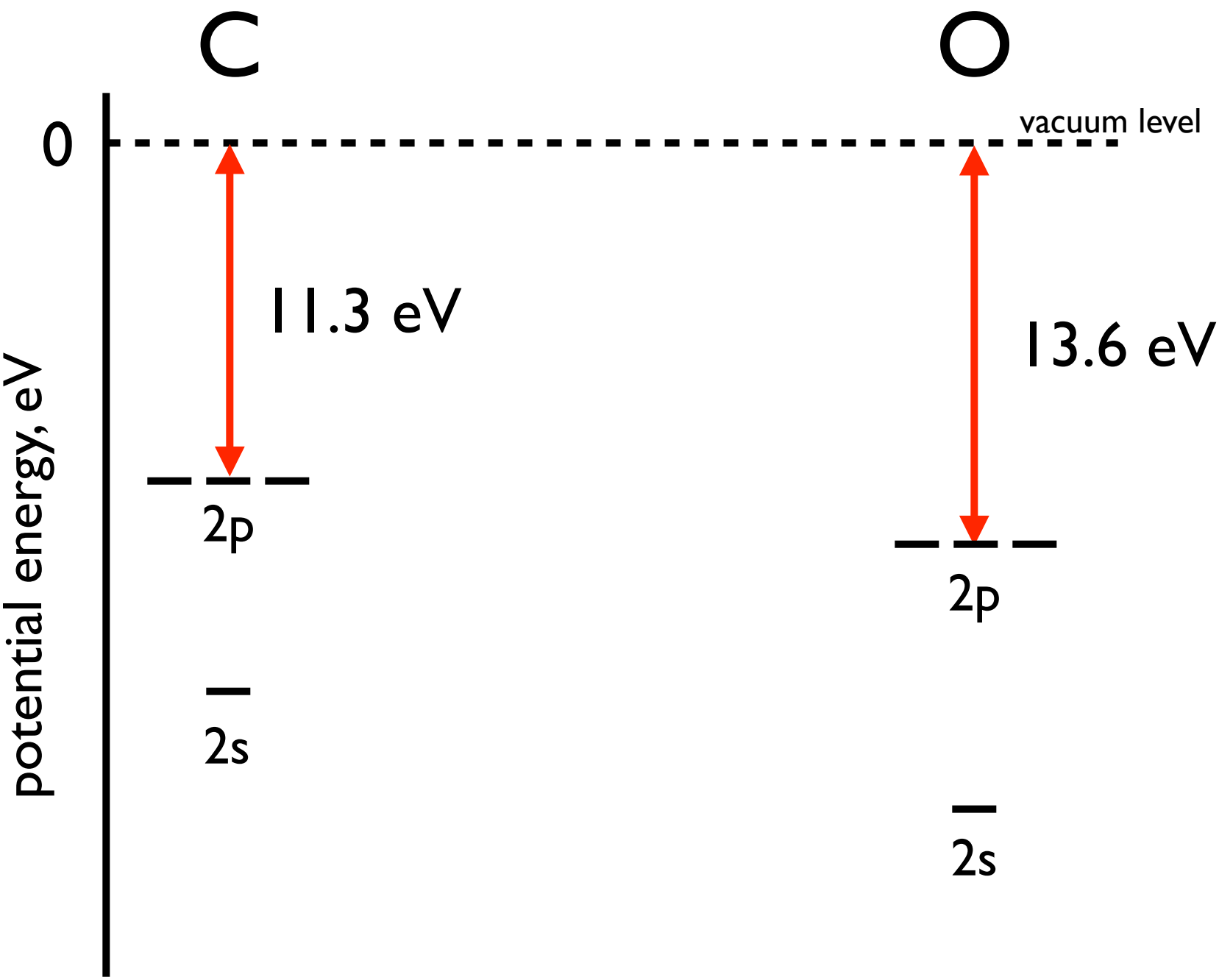
1. Put the atomic orbitals for each bonding partner in your diagram. *Position the HOAO based upon the IP of the atom.*

2. Draw in the energy levels for your MOs. *You'll need one for each atomic state.*

3. Fill them with electrons. *Make sure to follow Aufbau and Hund's rules.*

NOTE: bonding MOs are lower in energy than either "parent" atomic state, and antibonding MOs are higher.

An example: Carbon Monoxide (CO)



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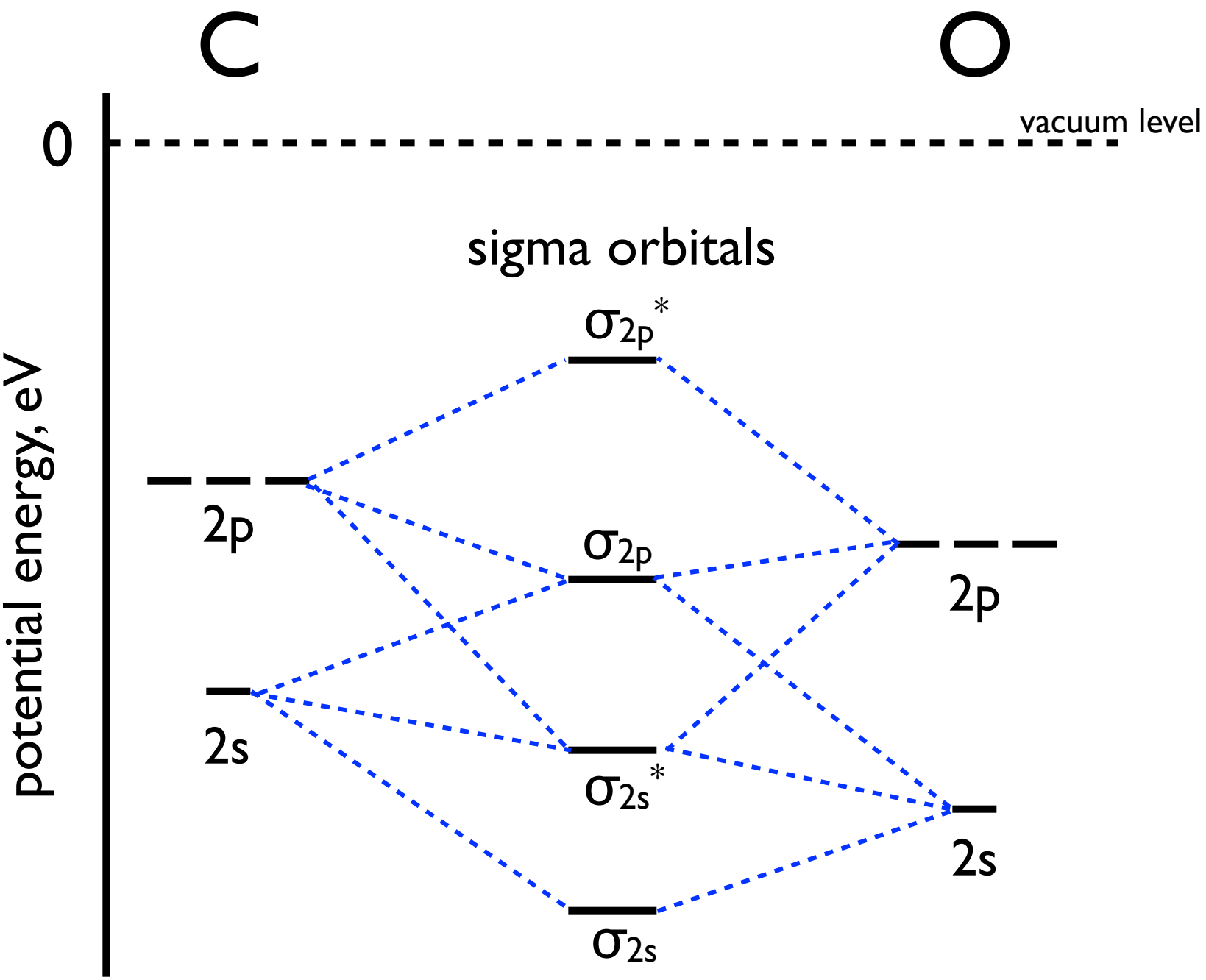

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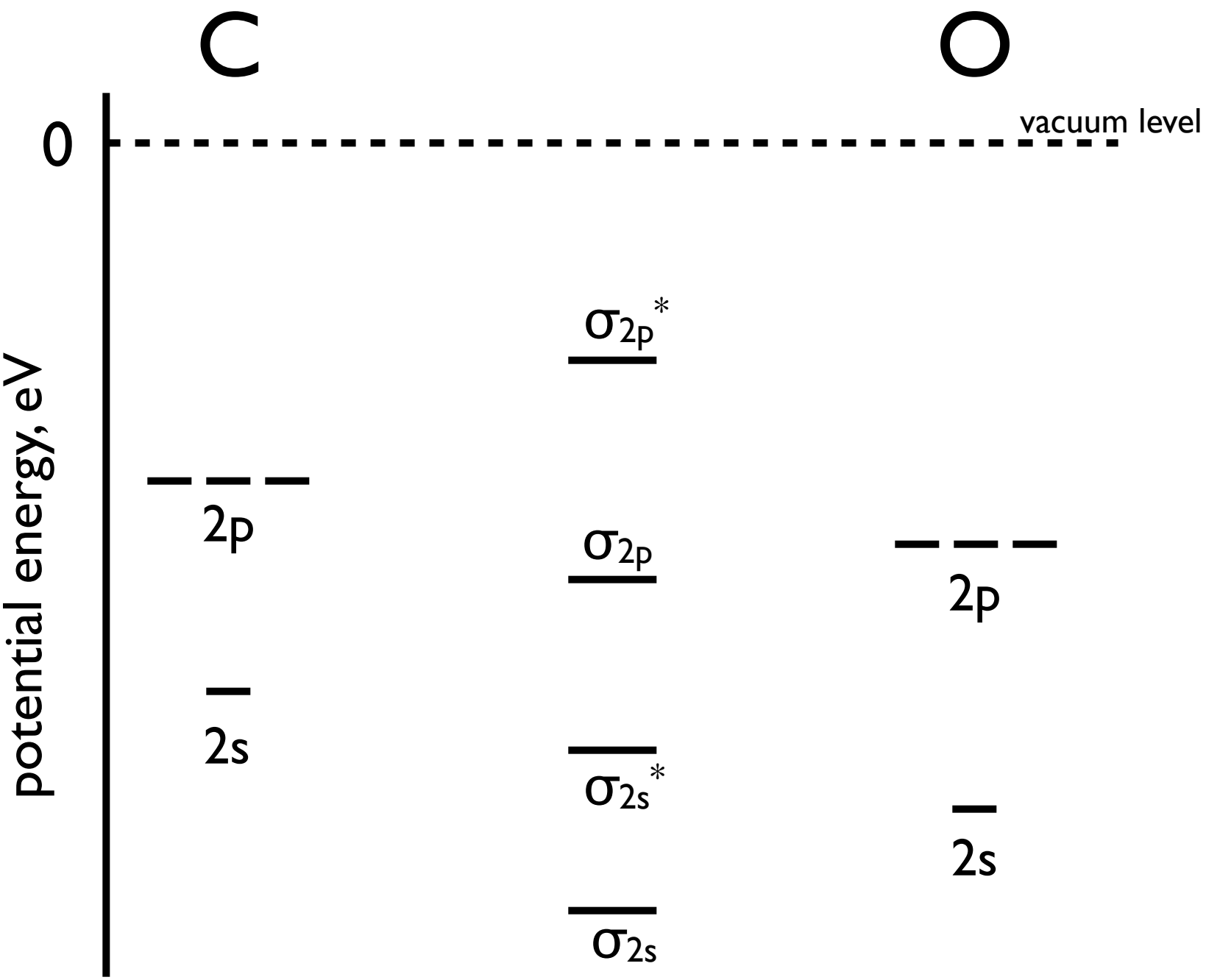

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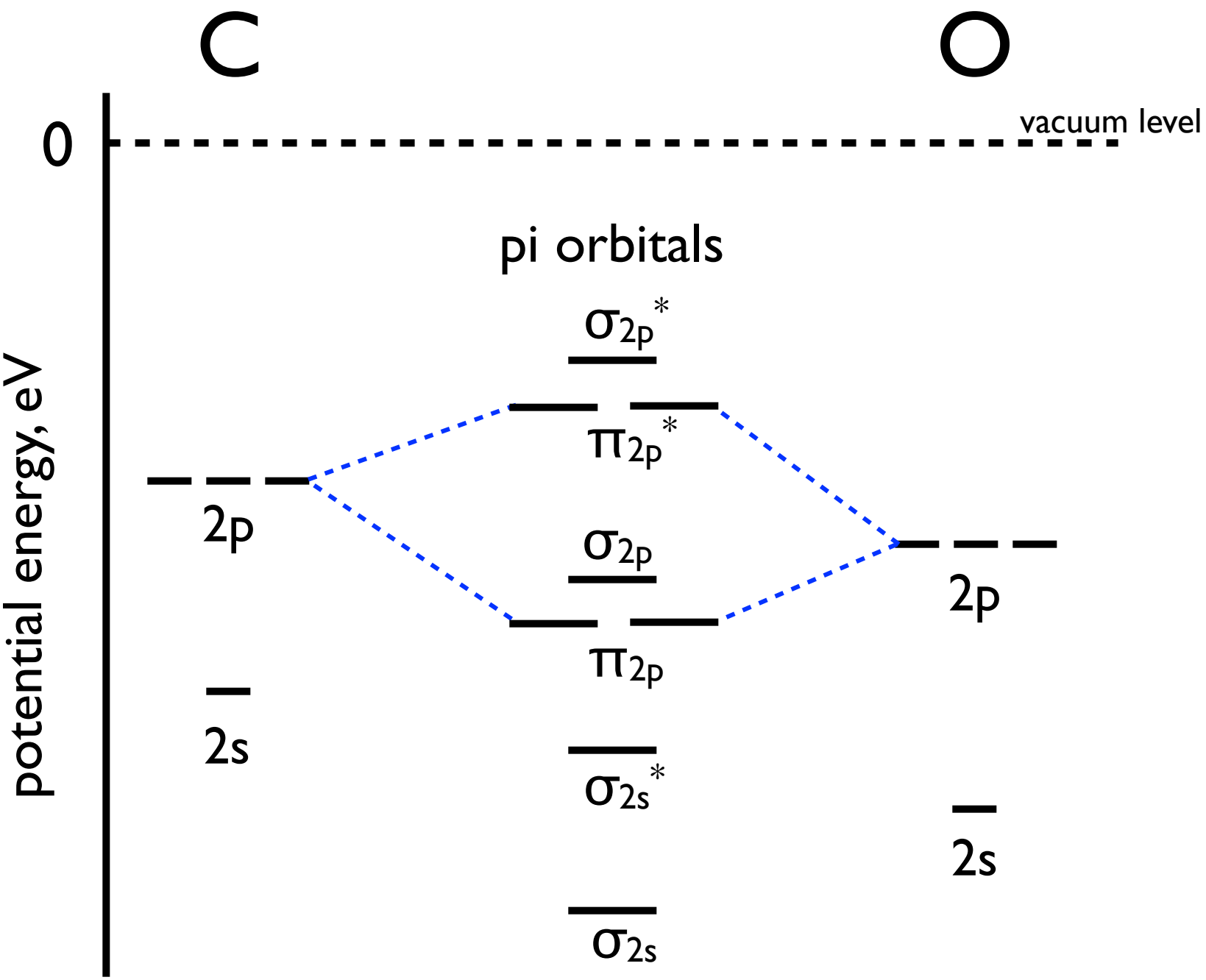
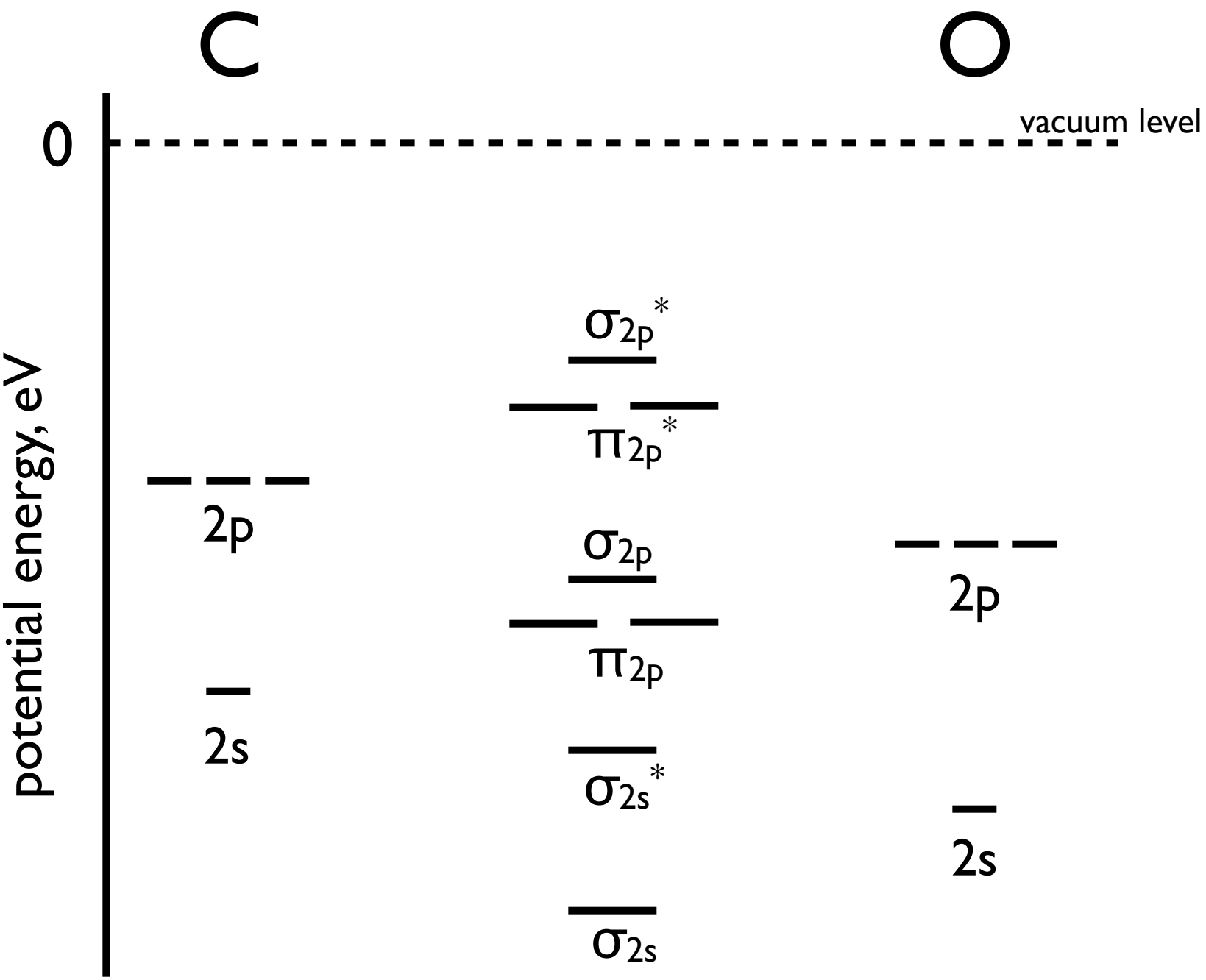


An example: Carbon Monoxide (CO) - 10 valence electrons



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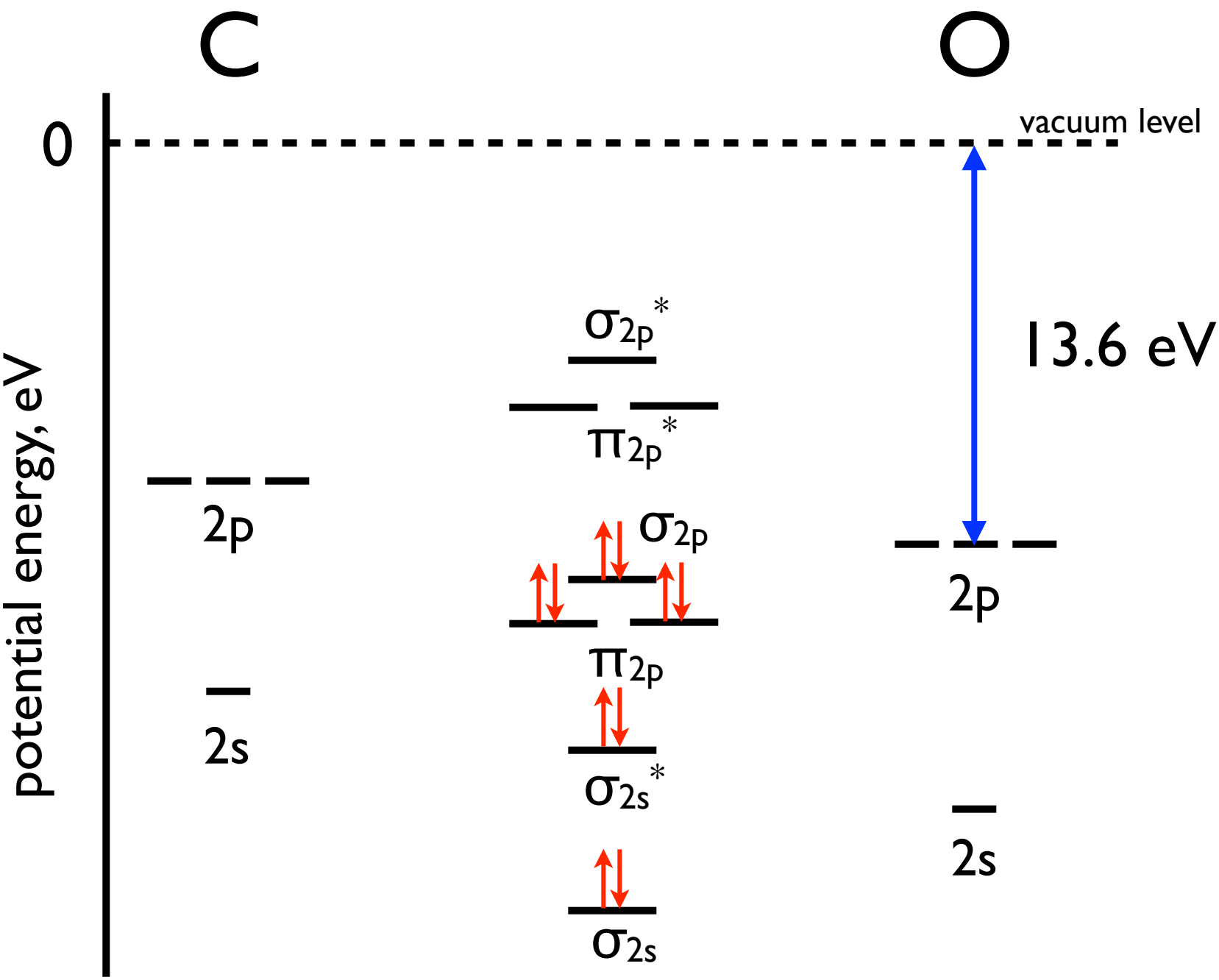


So heteronuclear diatomic molecules are a bit more complicated, but still we can make predictions:

For CO:

bond order = **3.0**

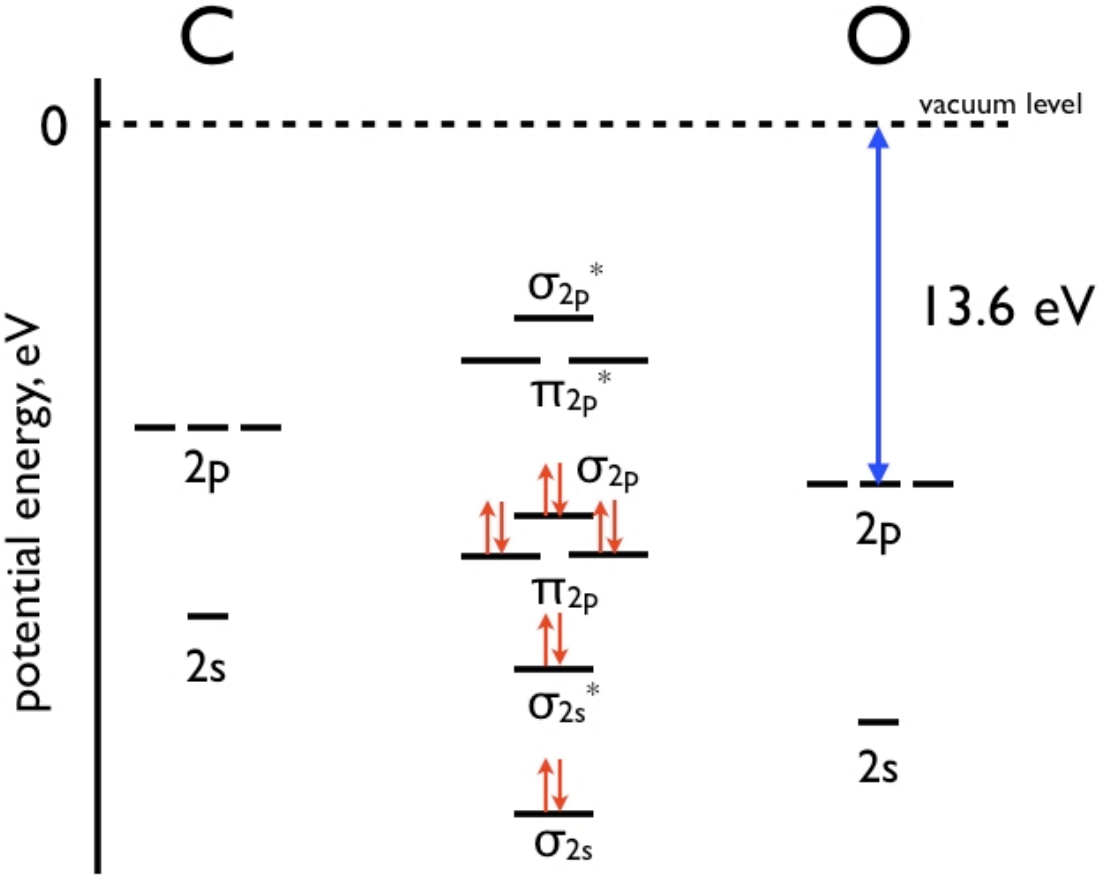
CO is **diamagnetic**

IP is greater than 13.6 eV
(Actual is 14.0 eV)

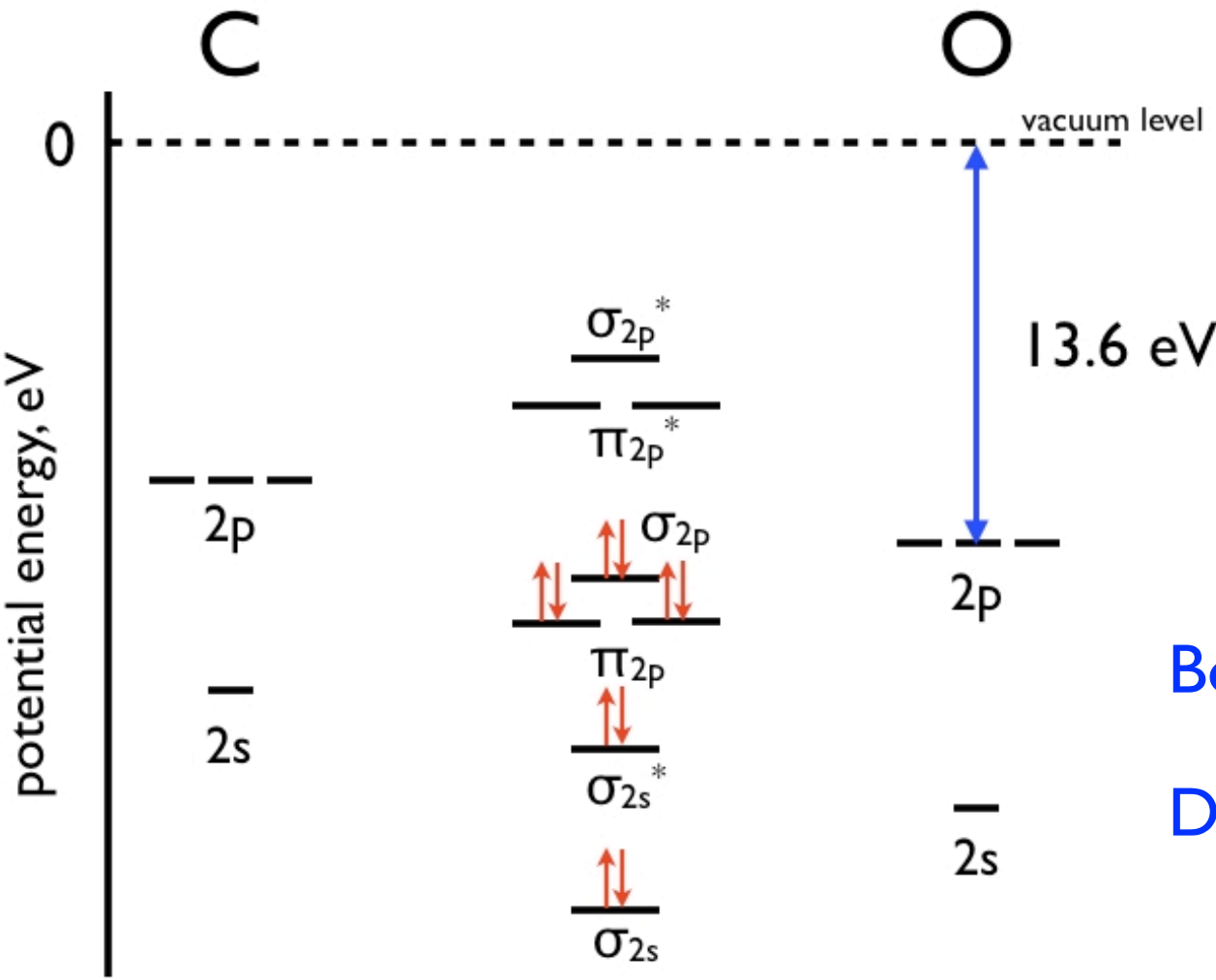
Electron configuration is:

$\sigma_{2s}^2\, \sigma^*_{2s}{}^2\, \pi_{2p}^4 \sigma_{2p}^2$

Two electrons in the HOMO



Some additional facts about CO:



Bond Length: 112.8 pm

Dipole Moment: 0.112D