Molecular Orbital Theory

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The Valence Bond Theory fails to answer certain questions like

O_2 is paramagnetic. why ?
He_2 and Ne_2 does not exist. Why ?

Therefore in 1932 F. Hund and R.S. Mulliken came up with Molecular Orbital Theory to explain questions like the ones above.

We know that electrons behaves as particle as well as wave. Therefore, an atomic orbital is represented by a wave function Ψ., derived from the Schrodinger wave equation.

We can obtain the wave function of a molecular orbital by Linear combination of atomic orbitals (LCAO)

Postulates of Molecular Orbital Theory

1. Atomic orbitals of comparable energy and proper symmetry combine together to form molecular orbitals.

2. The number of molecular orbitals formed is equal to the number of combining atomic orbitals.

3. When two atomic orbitals (AO's) combine together, two molecular orbitals (MO's) are formed.

   a. **Bonding Molecular Orbital (BMO):** possess lower energy than that of corresponding atomic orbitals and

   b. **Anti bonding molecular orbital (ABMO):** has higher energy than that of corresponding atomic orbitals

4. Filling of electrons follows
   Pauli's exclusion principle, Aufbau principle and Hund's rule

Linear Combination of Atomic Orbitals (LCAO)

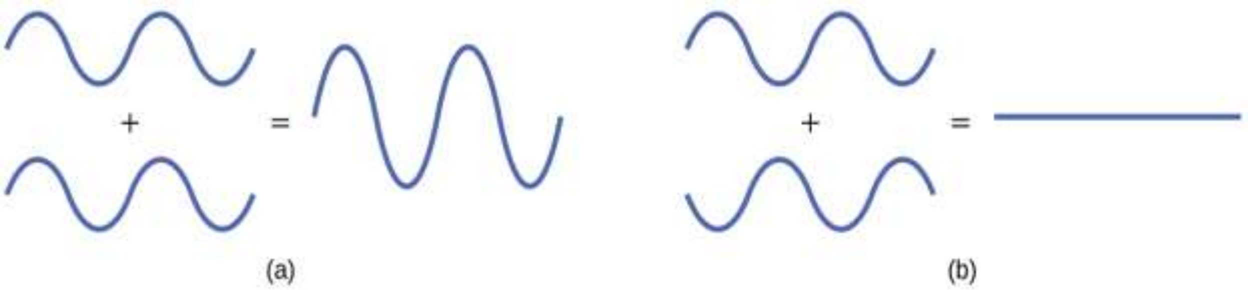
If two atomic orbitals are A & B and there wave functions Ψ_A & $\Psi_{B,}$ Then

Bonding Molecular Orbitals: formed by addition of wave function When the electronic waves overlap in same direction.

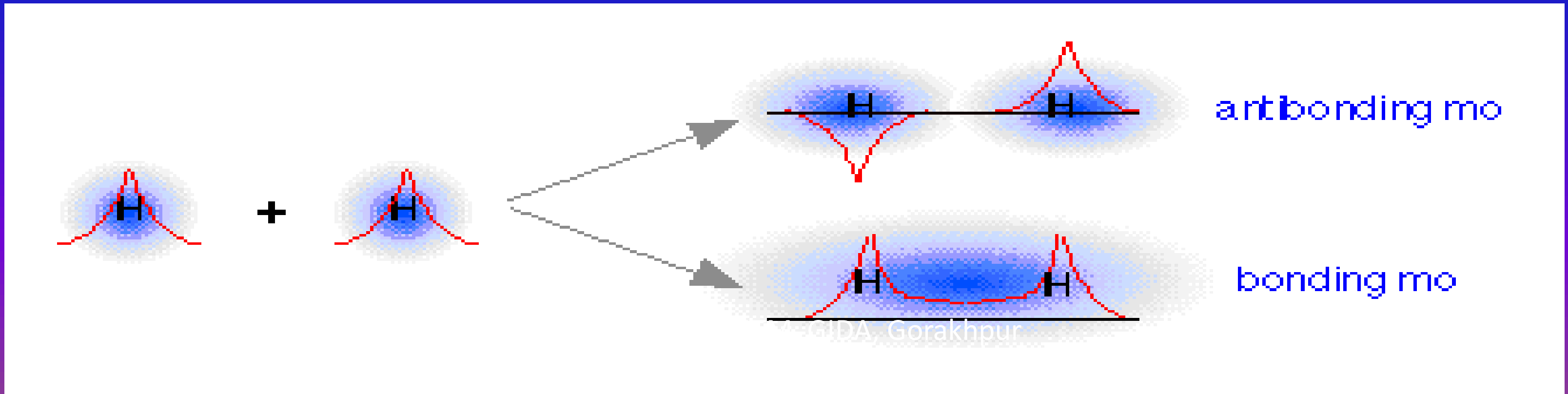
$\Psi_{AB} = \Psi_A + \Psi_{B.}$ (Lower energy than atomic orbitals involved)

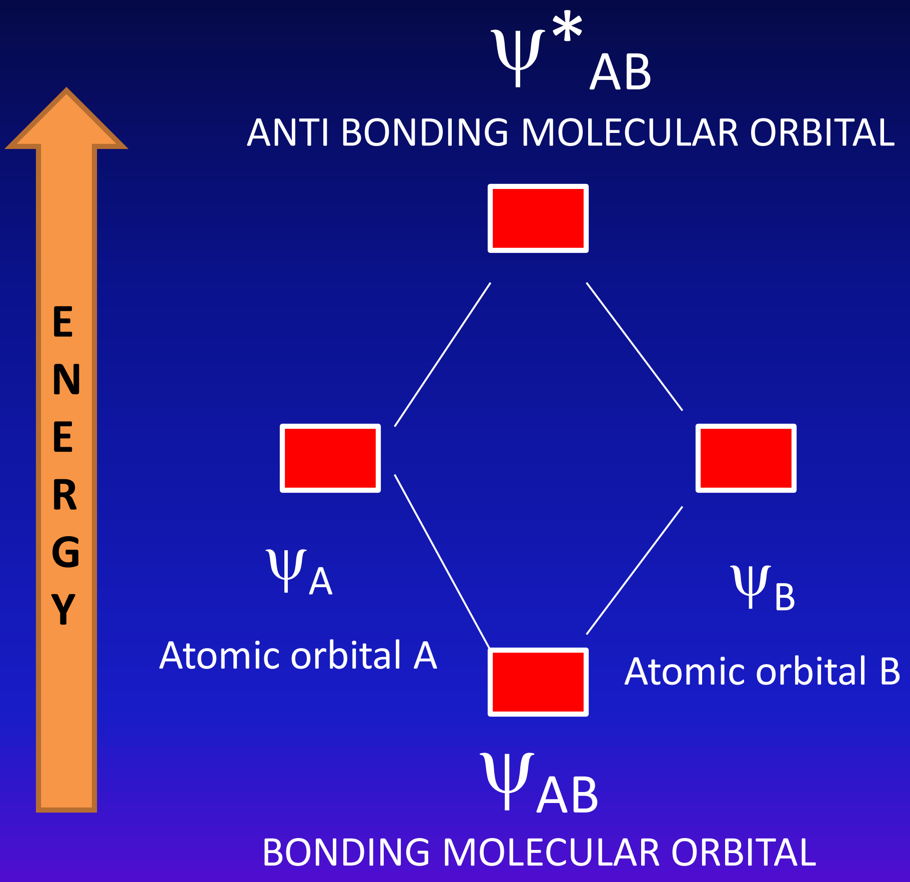
Anti-Bonding Molecular Orbitals: formed by subtraction of wave function When the electronic waves overlap in opposite direction.

$\Psi^*_{AB} = \Psi_A - \Psi_{B.}$ (Higher energy than atomic orbitals)



Constructive interference **Destructive interference**





ψ^*_{AB}

ANTI BONDING MOLECULAR ORBITAL

ENERGY

ψ_A

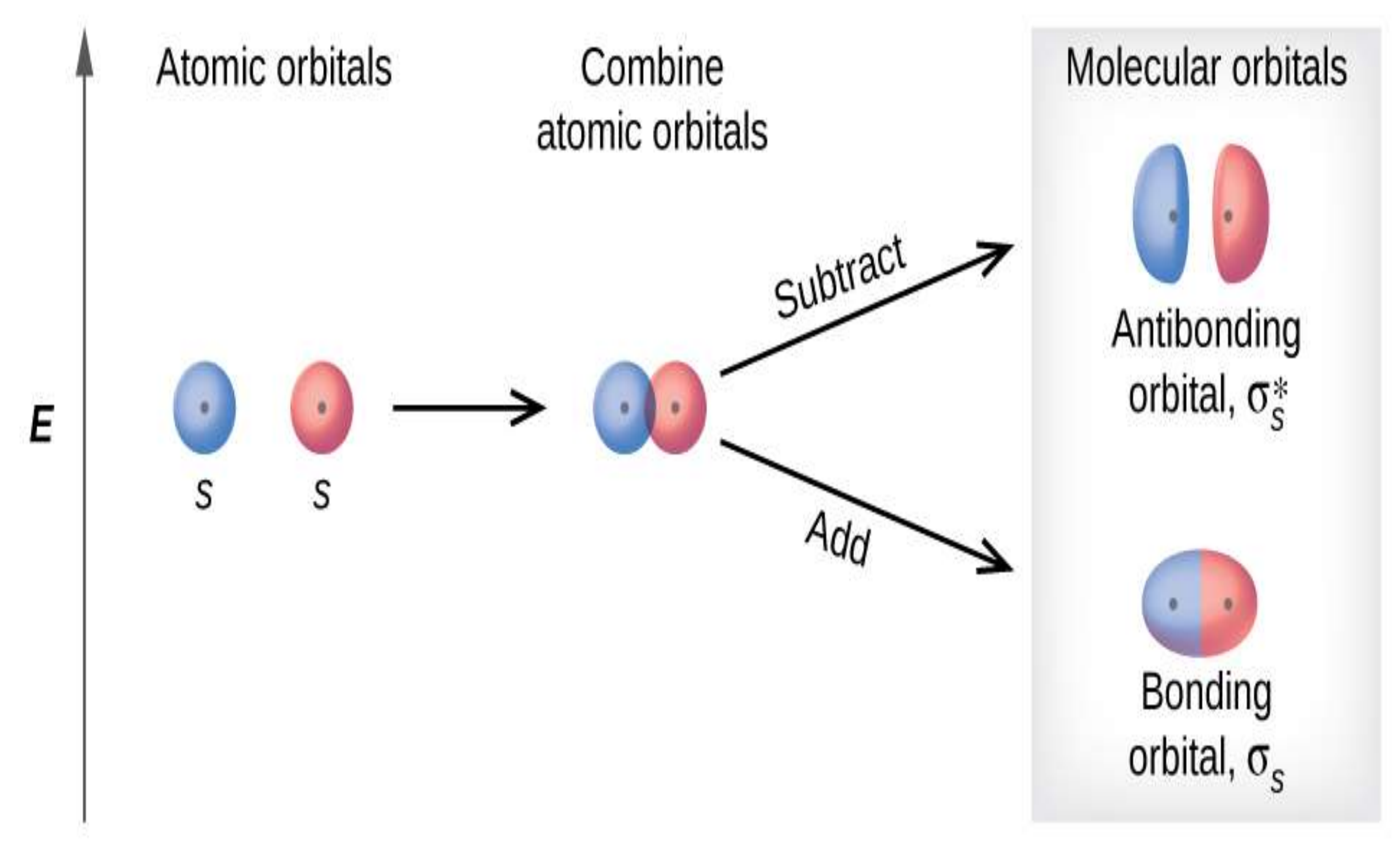
Atomic orbital A

ψ_B

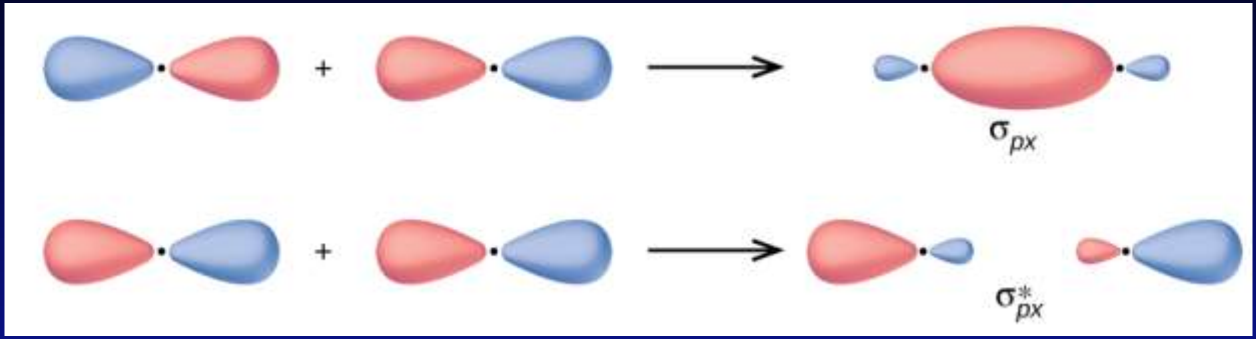
Atomic orbital B

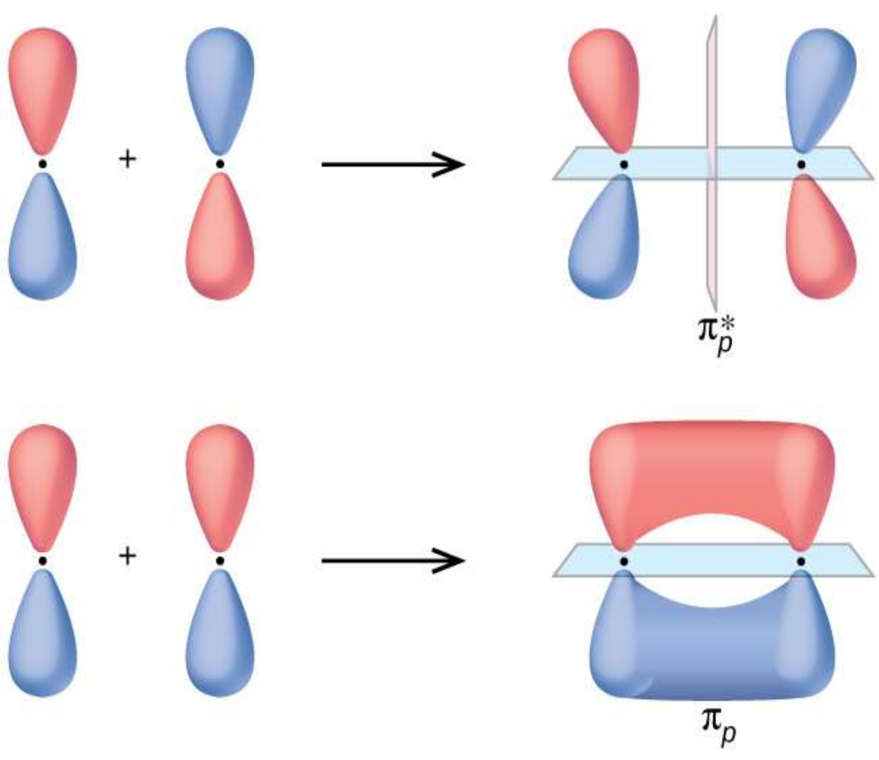
ψ_{AB}

BONDING MOLECULAR ORBITAL

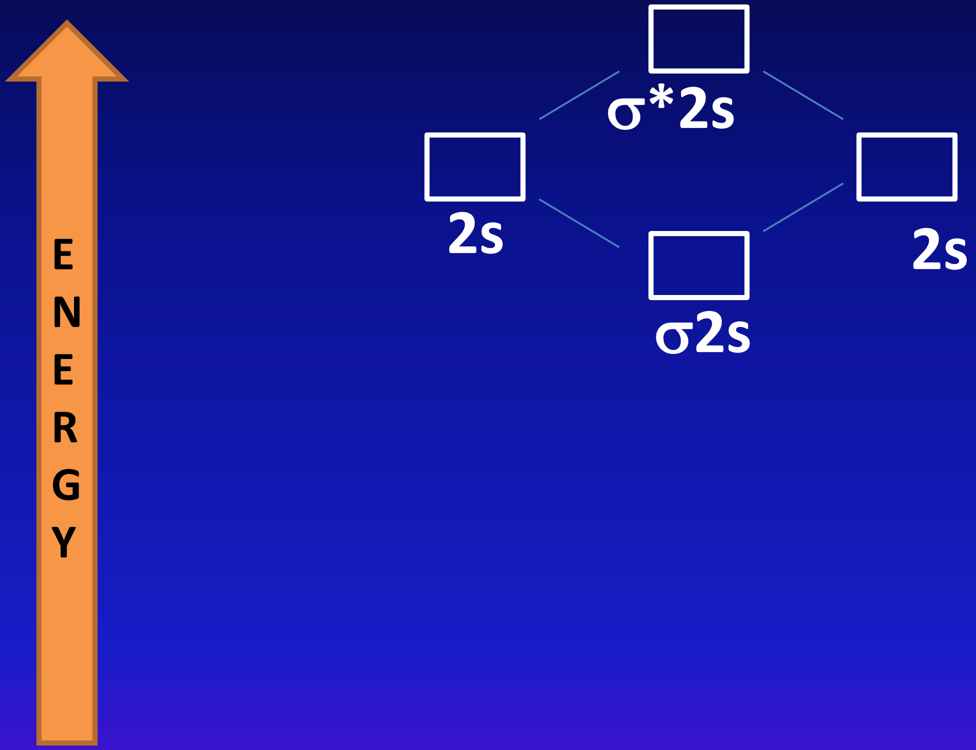

E
Atomic orbitals
s
s
Combine
atomic orbitals
Subtract
Add
Molecular orbitals
Antibonding
orbital, σ_s^*
Bonding
orbital, σ_s

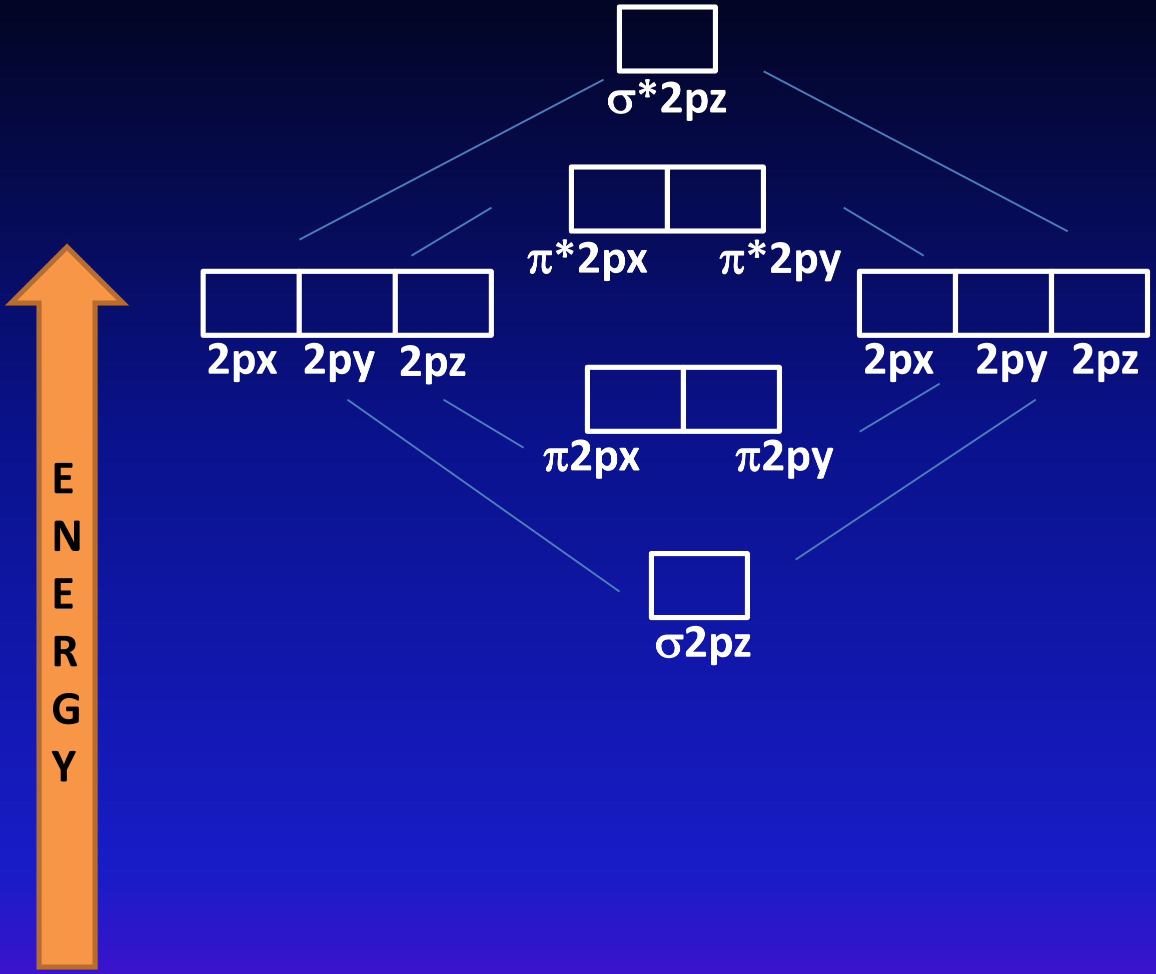
Overlapping of p-orbitals: formation of σ_p & σ^*_p and π_p & π^*_p






E
N
E
R
G
Y
σ*1s
1s
1s
σ1s


E N E R G Y
σ*2s
2s
2s
σ2s



σ*2pz

π*2px π*2py

2px 2py 2pz

2px 2py 2pz

π2px π2py

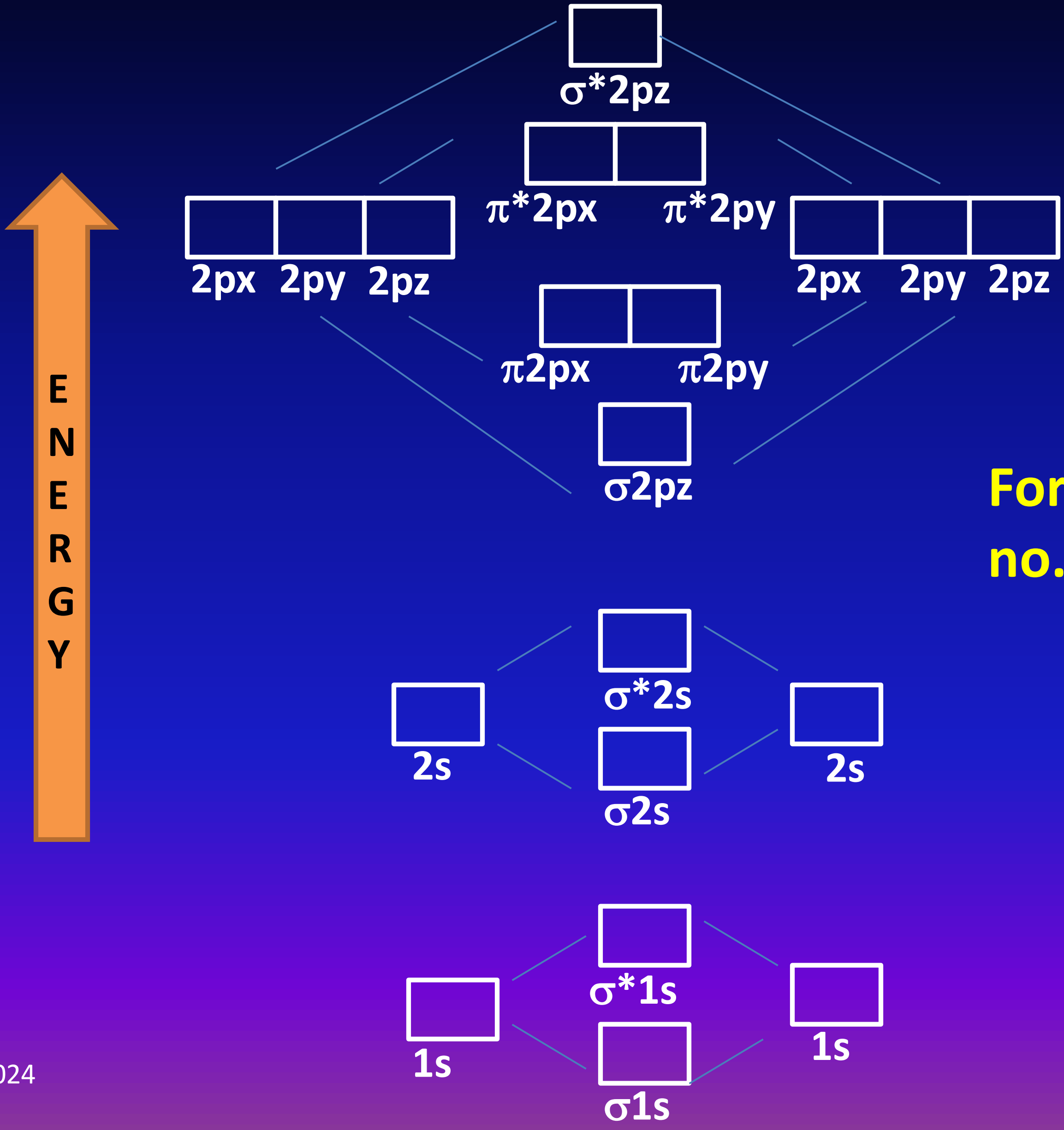
σ2pz

ENERGY

$\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2p_z$, $\pi 2p_x = \pi 2p_y$, $\pi^* 2p_x = \pi^* 2p_y$, $\sigma^* 2p_z$

Energy →

M O Diagram

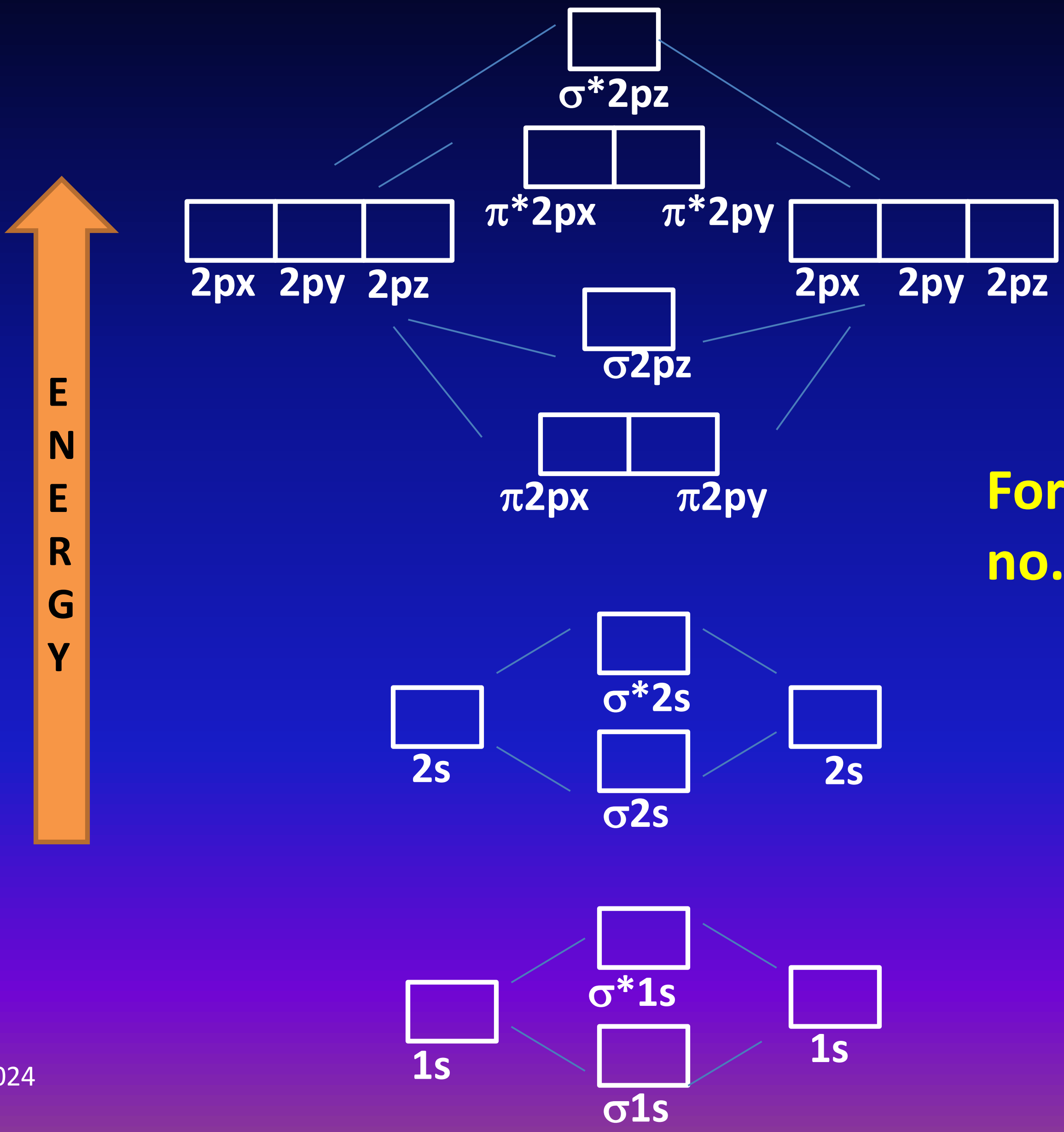


For molecules having no. of electrons ≥ 15

$\sigma 1s$, $\sigma^{*}1s$, $\sigma 2s$, $\sigma^{*}2s$, $\pi 2p_x = \pi 2p_y$, $\sigma 2p_z$, $\pi^{*}2p_x = \pi^{*}2p_y$, $\sigma^{*}2p_z$

Energy →

M O Diagram



For molecules having no. of electrons ≤ 14

Bond Order =[(No. of Bonding e^- (N_b) – No. of Antibonding e^- (N_a)] /2

Properties

1. Bond order $\propto$ Stability of molecule
   stability increases with increasing bond order.

2. Bond order $\propto$ 1/ Reactivity
   Reactivity decreases with increasing bond order.

3. Bond order $\propto$ 1/Bond length (Size)
   Molecular size (bond length) decreases with increasing bond order

4. If, bond order = 0
   Molecule does not exist .

Magnetic Behaviour

1. Diamagnetic: No unpaired electrons (Magnetic moment = 0)
   Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM, n is no. of unpaired e^-

2. Paramagnetic: Unpaired electrons present

Filling Of Electrons In Atomic & Molecular Orbitals

Aufbau Principle

The orbitals which have the lowest energy are filled first then higher energy orbitals in increasing order.

Pauli’s Exclusion Principle

“No two elctrons in atom can have all the four quantum numbers equal.”

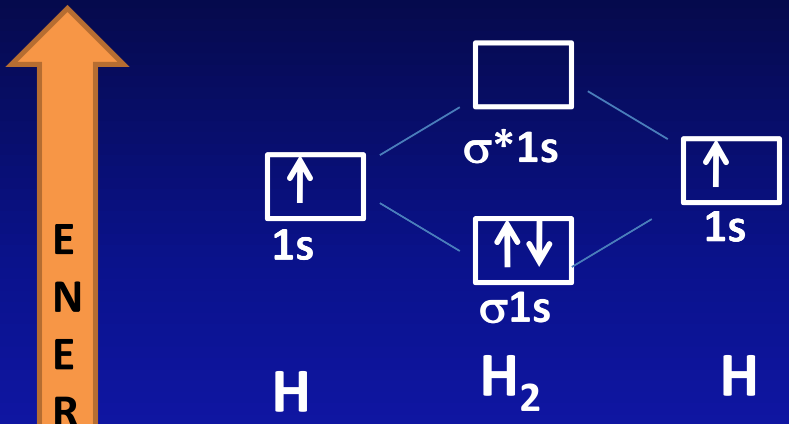
According to this principle, each orbital can accommodate a maximum of two electrons having opposite spins.

Hund’s Rule

The orbitals with equal energies are not paired up until they are singly occupied.

M O diagram of H_2

$\sigma 1s^2$



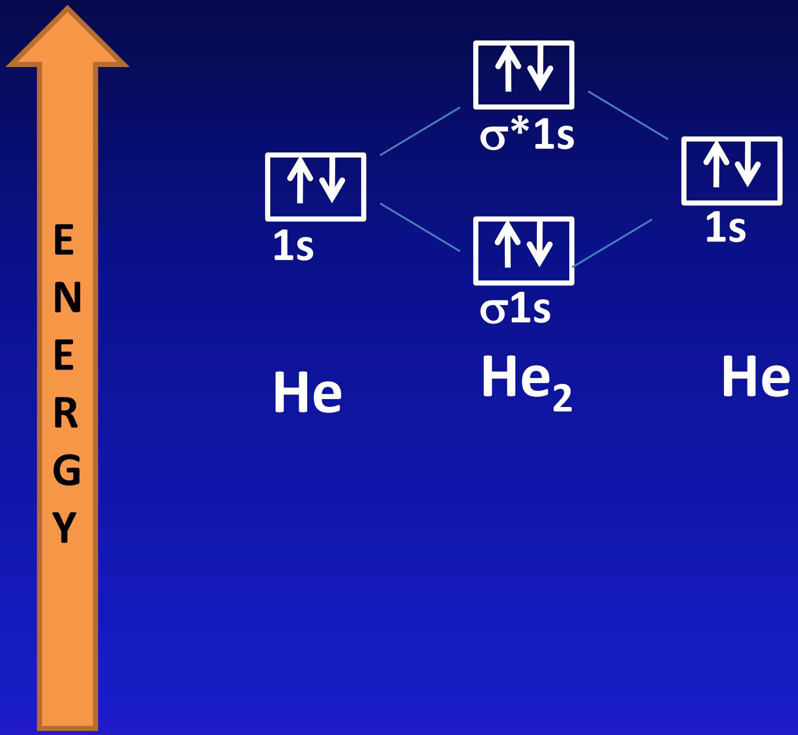
Bond Order = $\frac{1}{2}(N_b - N_a)$
= $\frac{1}{2}(2 - 0)$
= 1

Diamagnetic

H(1) $1s^1$
H_2 = 2 e^-

M O diagram of He_2

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

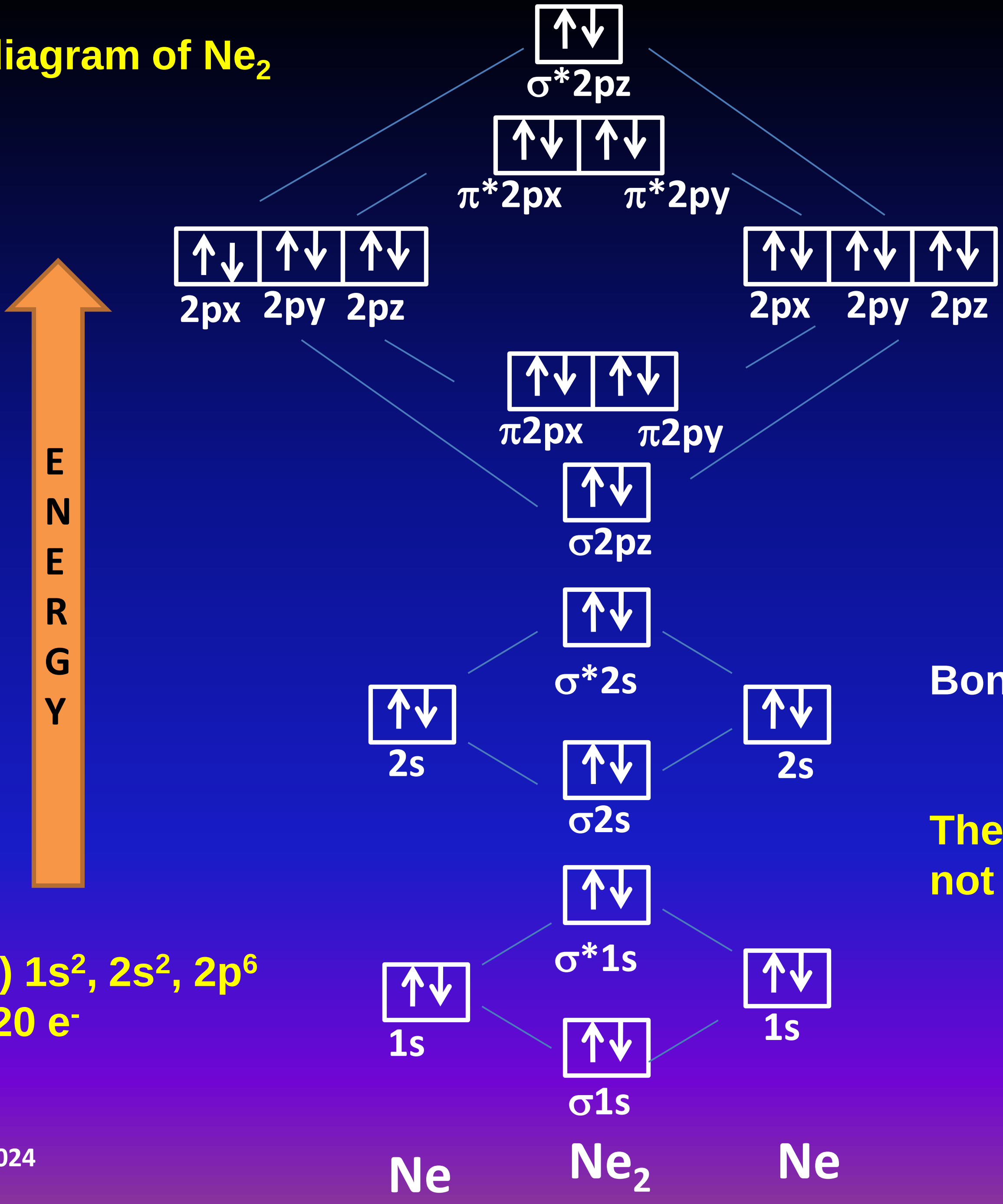


Bond Order = $\frac{1}{2}(N_b - N_a)$
= $\frac{1}{2}(2 - 2)$
= 0

Does not exist

$He(2)\ 1s^2$
$He_2 = 4e^-$

M O diagram of Ne_2

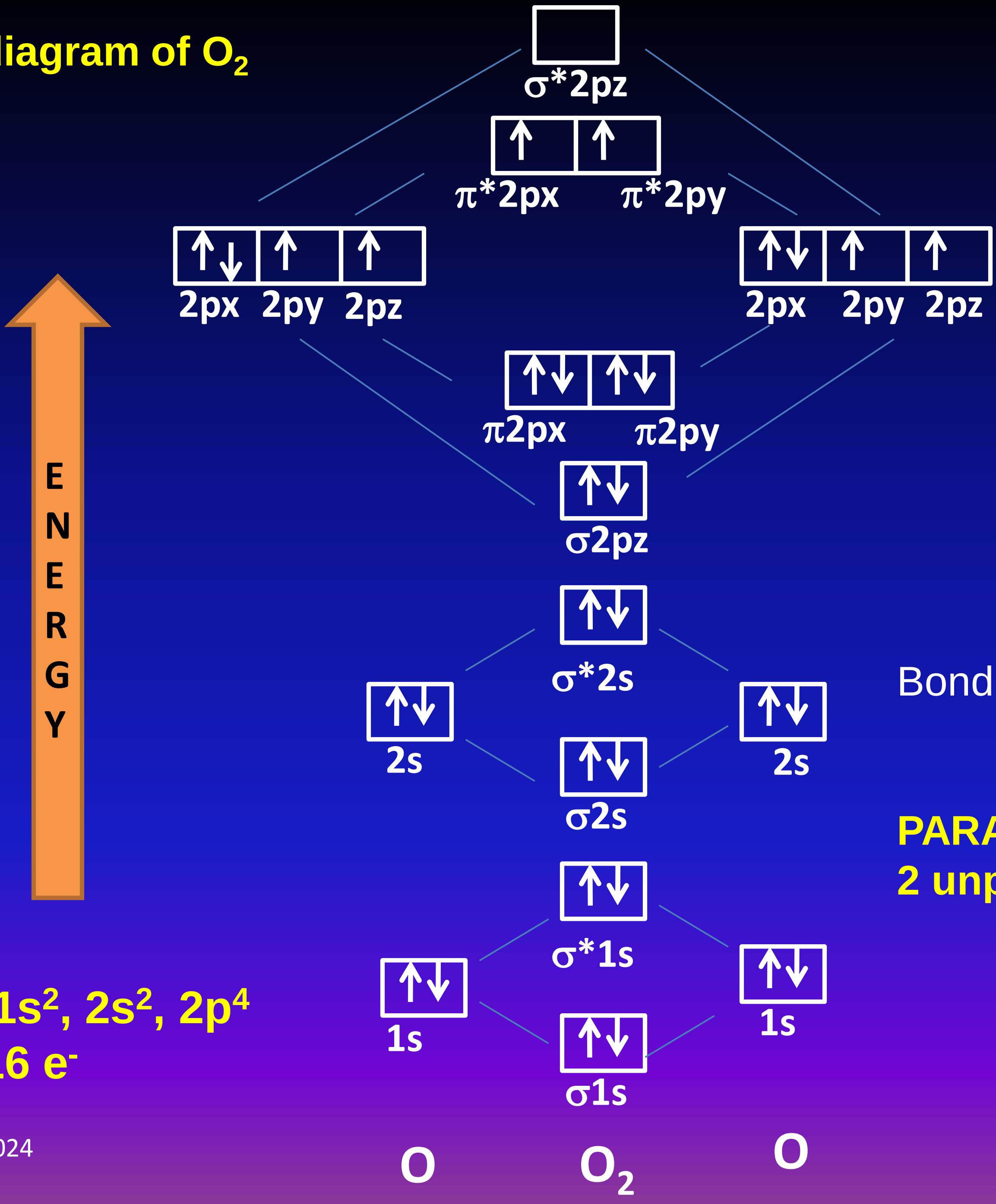


Bond Order = ½(N_b – N_a)
= ½(10 – 10)
= 0

Therefore molecule does not exist.

Ne (10) $1s^2$, $2s^2$, $2p^6$
Ne_2 = 20 e^-

M O diagram of O_2



Bond Order = ½(N_b – N_a)

= ½(10 – 6)

= 2

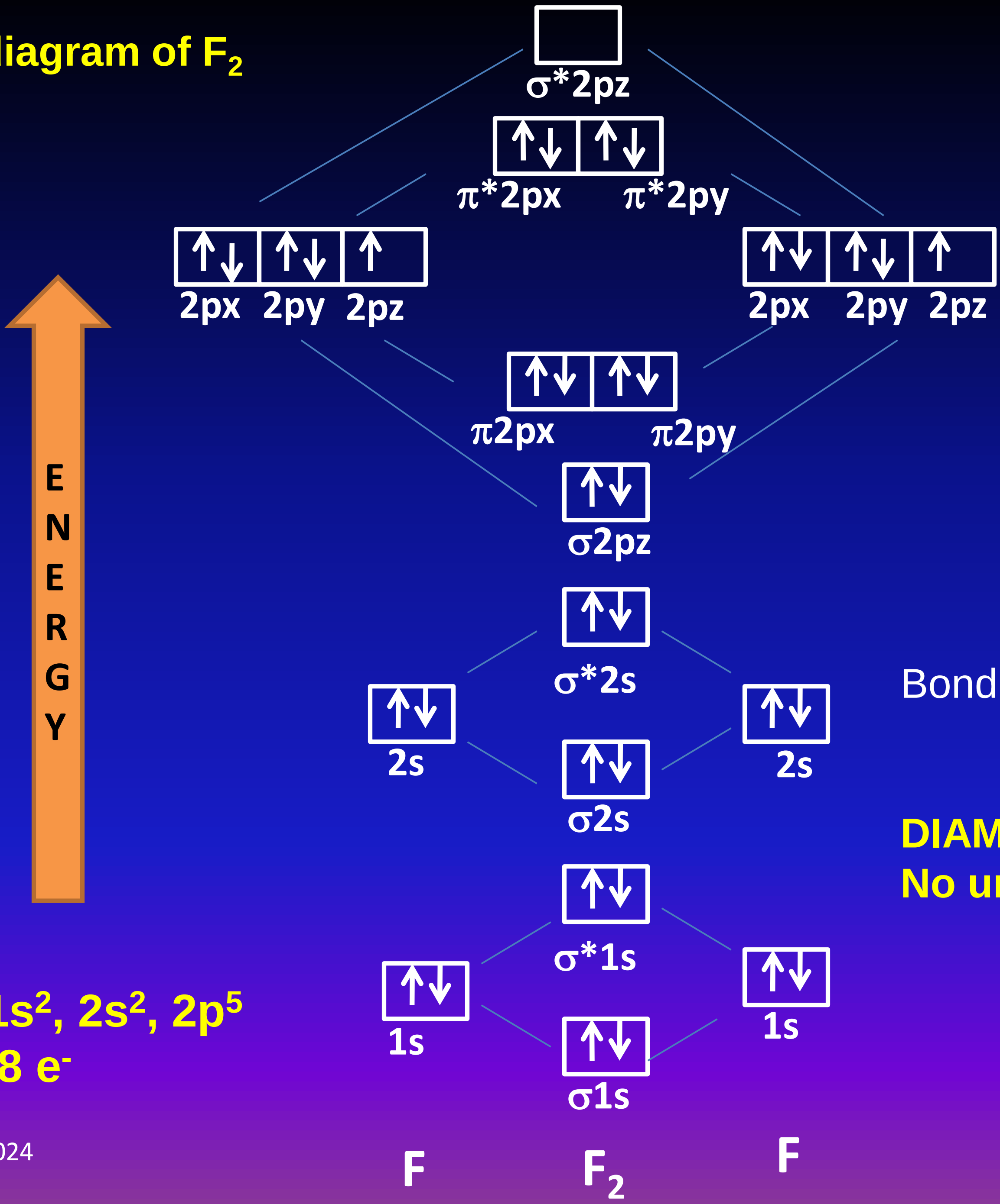
PARAMAGNETIC

2 unpaired electrons

O (8) $1s^2$, $2s^2$, $2p^4$

O_2 = 16 e^-

M O diagram of F_2



σ*2pz

↑↓ ↑↓

π*2px π*2py

↑↓ ↑↓ ↑

2px 2py 2pz

↑↓ ↑↓ ↑

2px 2py 2pz

↑↓ ↑↓

π2px π2py

↑↓

σ2pz

↑↓

σ*2s

↑↓

2s

↑↓

2s

↑↓

σ2s

↑↓

σ*1s

↑↓

1s

↑↓

1s

↑↓

σ1s

F

F_2

F

ENERGY

Bond Order = ½(N_b – N_a)
= ½(10 – 8)
= 1

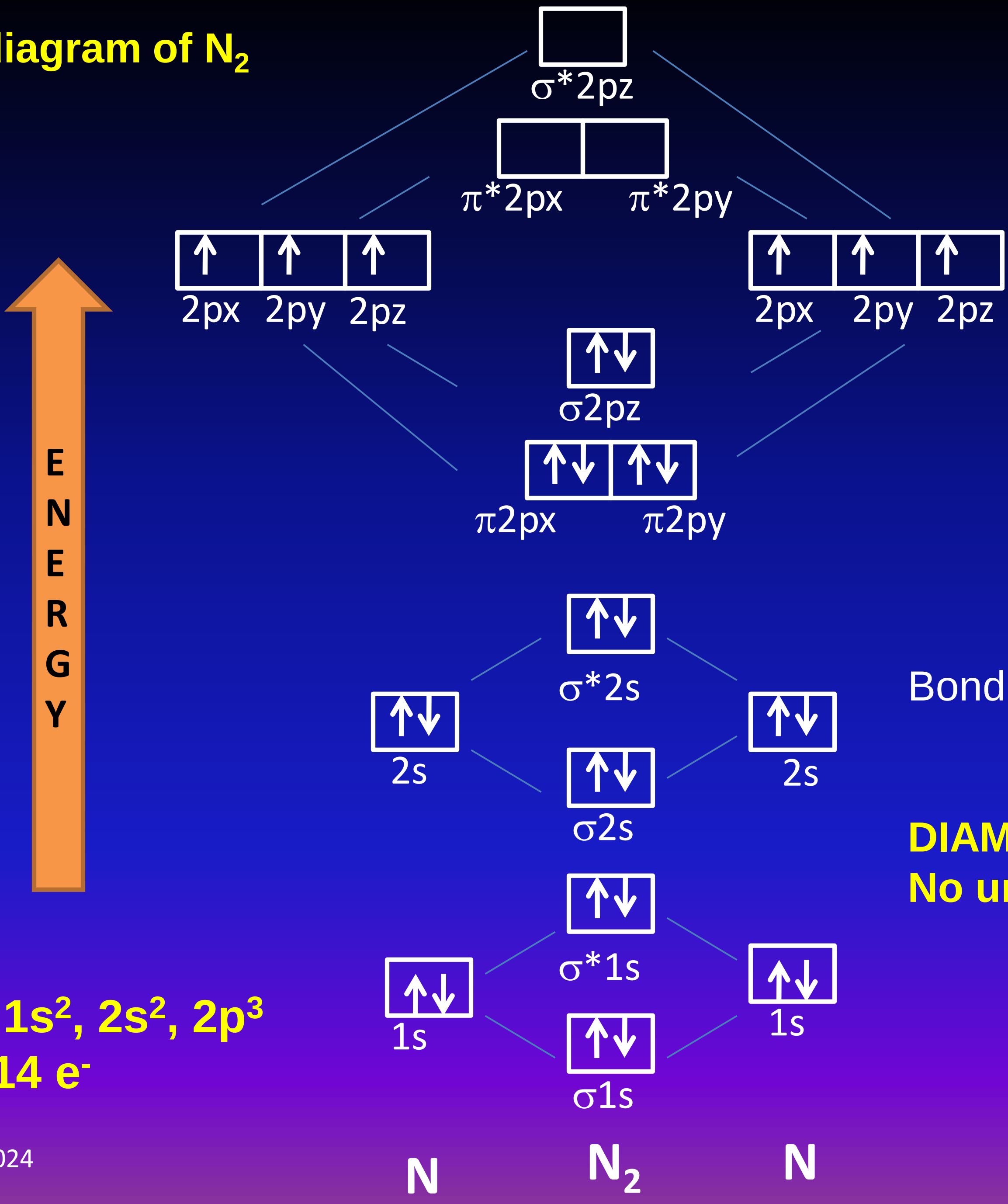
DIAMAGNETIC

No unpaired electron

F (9) $1s^2$, $2s^2$, $2p^5$

F_2 = 18 e^-

M O diagram of N_2

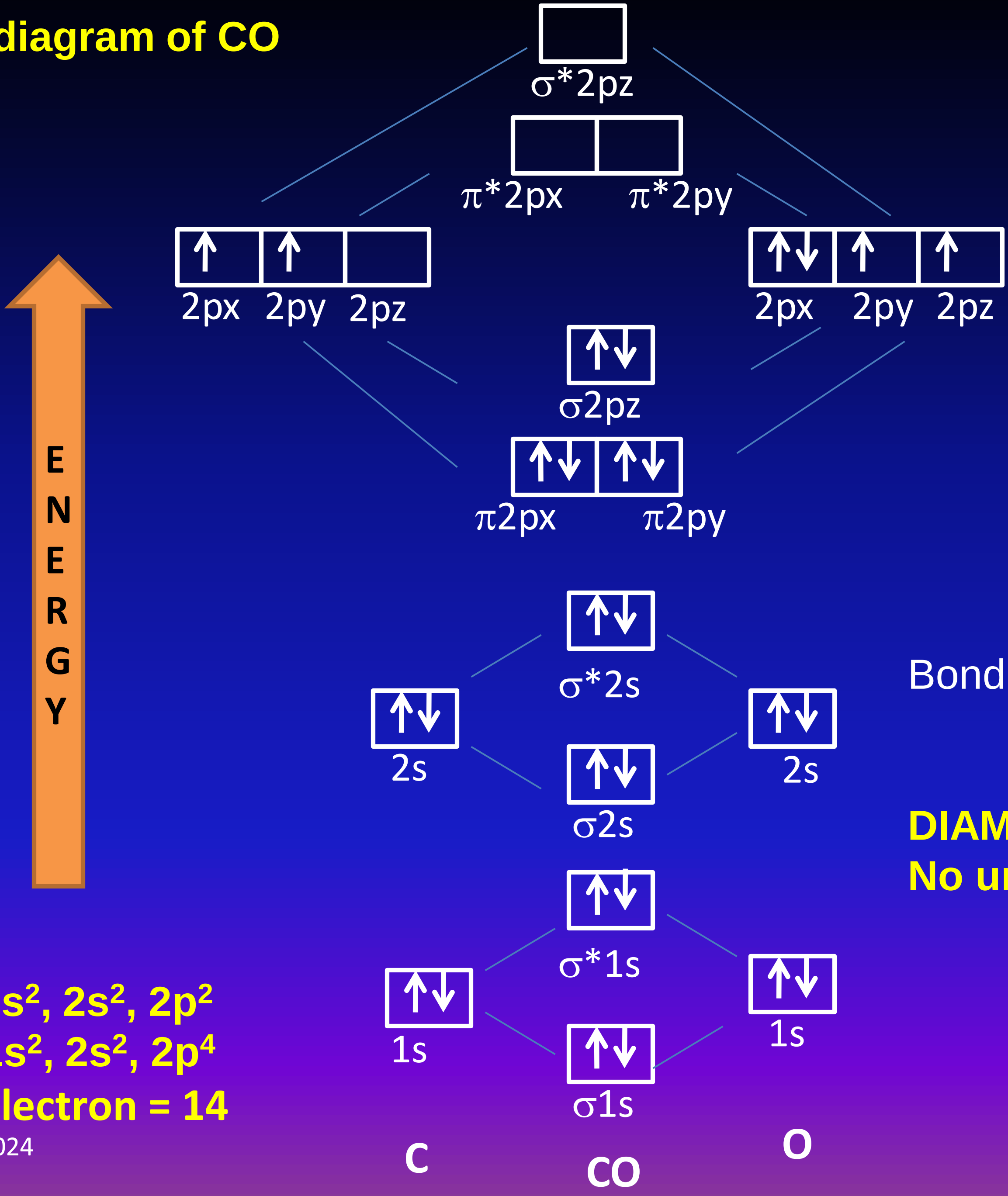


Bond Order = ½(N_b – N_a)
= ½(10 – 4)
= 3

DIAMAGNETIC
No unpaired electron

N (7) $1s^2, 2s^2, 2p^3$
$N_2 = 14\ e^-$

M O diagram of CO



σ^*2pz

π^*2px π^*2py

2px 2py 2pz

2px 2py 2pz

$\sigma 2pz$

$\pi 2px$ $\pi 2py$

σ^*2s

2s

2s

$\sigma 2s$

σ^*1s

1s

1s

$\sigma 1s$

C

CO

O

ENERGY

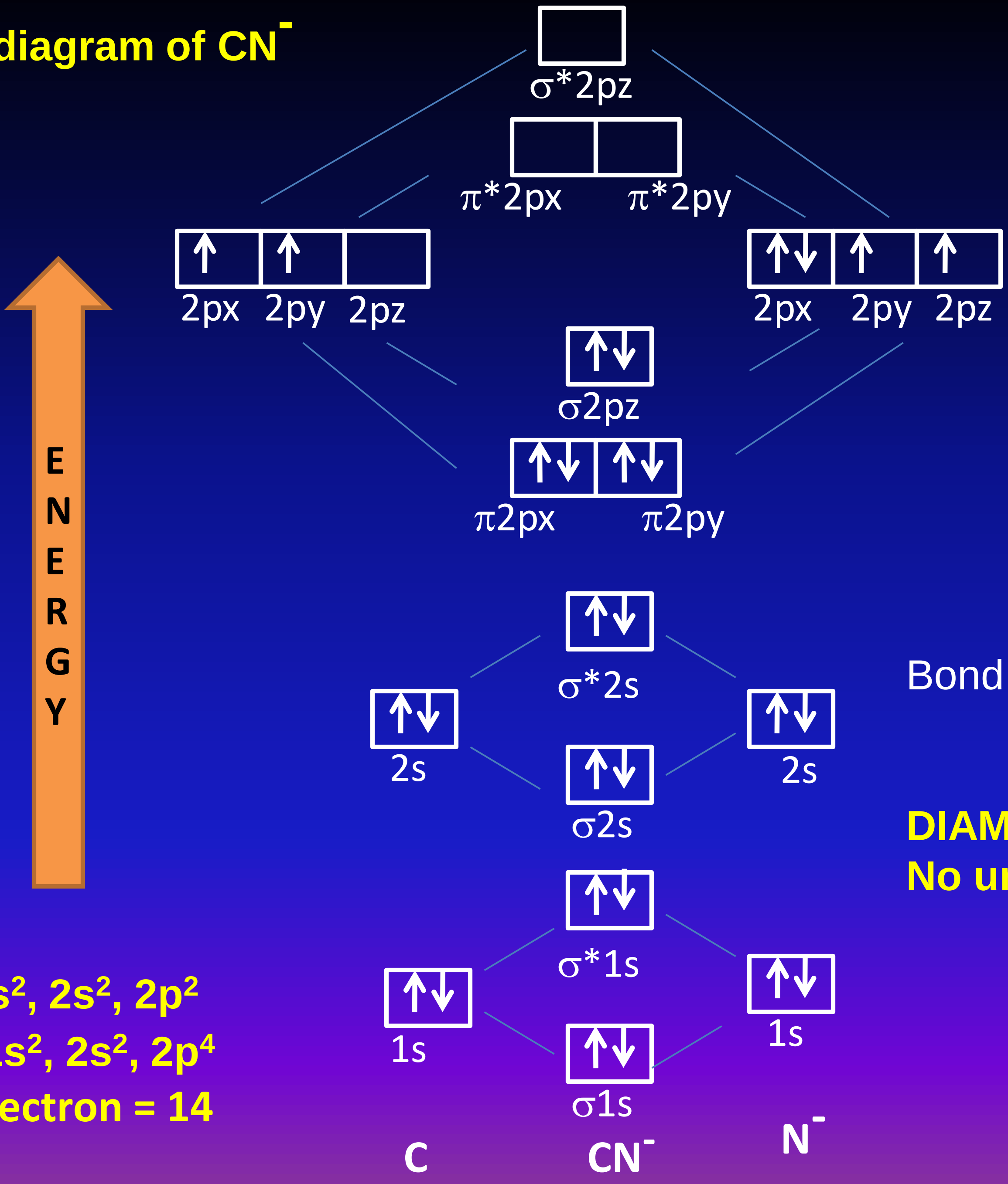
Bond Order = ½(N_b – N_a)
= ½(10 – 4)
= 3

DIAMAGNETIC

No unpaired elctron

C (6) $1s^2$, $2s^2$, $2p^2$
O (8) $1s^2$, $2s^2$, $2p^4$
Total electron = 14

M O diagram of CN^-



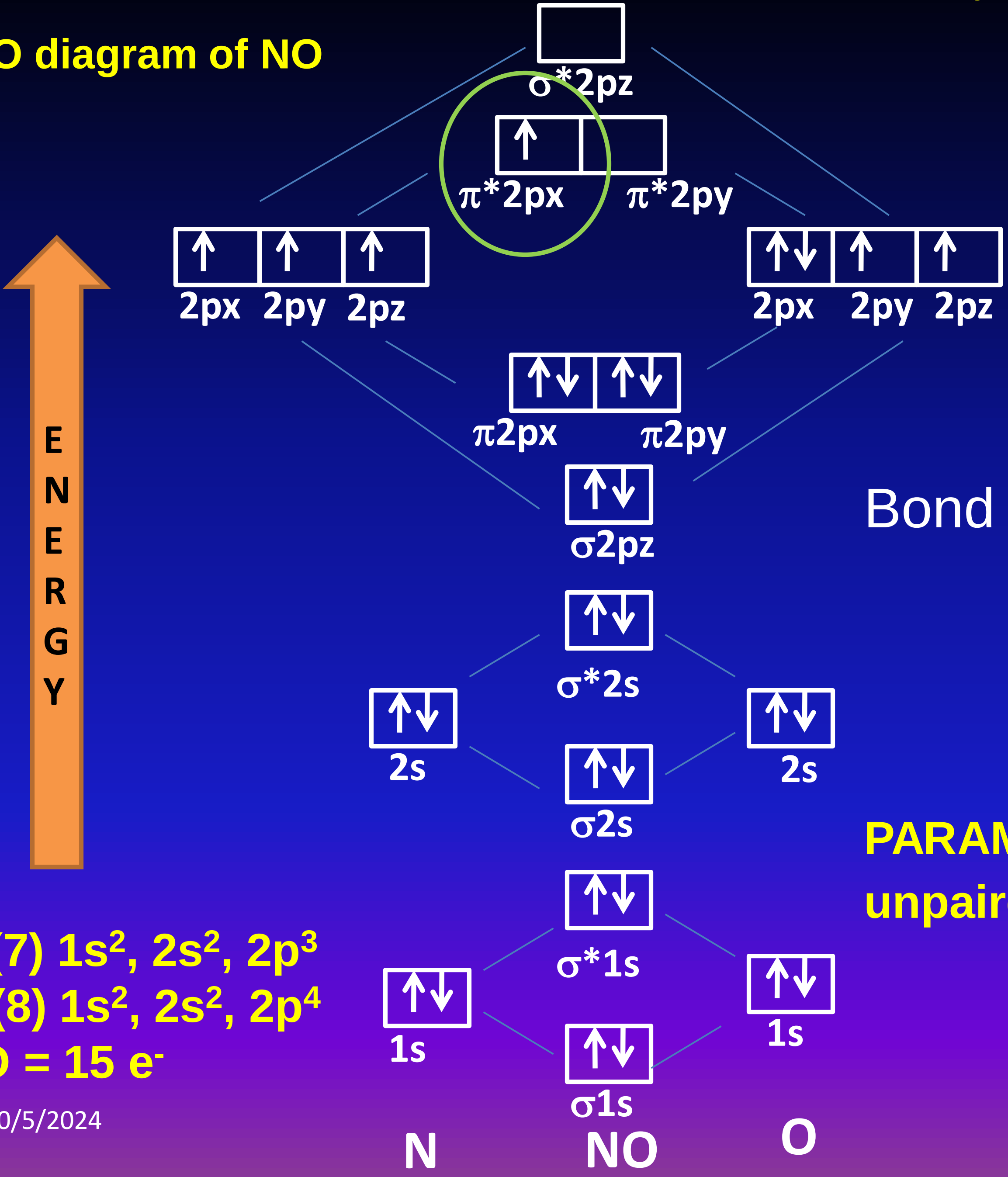
Bond Order = $\frac{1}{2}(N_b - N_a)$
= $\frac{1}{2}(10 - 4)$
= 3

DIAMAGNETIC
No unpaired electron

C (6) $1s^2, 2s^2, 2p^2$
N^- (8) $1s^2, 2s^2, 2p^4$
Total electron = 14

$\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi 2p_y^2$, $\pi^* 2p_x^1 = \pi^* 2p_y$, $\sigma^* 2p_z$

MO diagram of NO

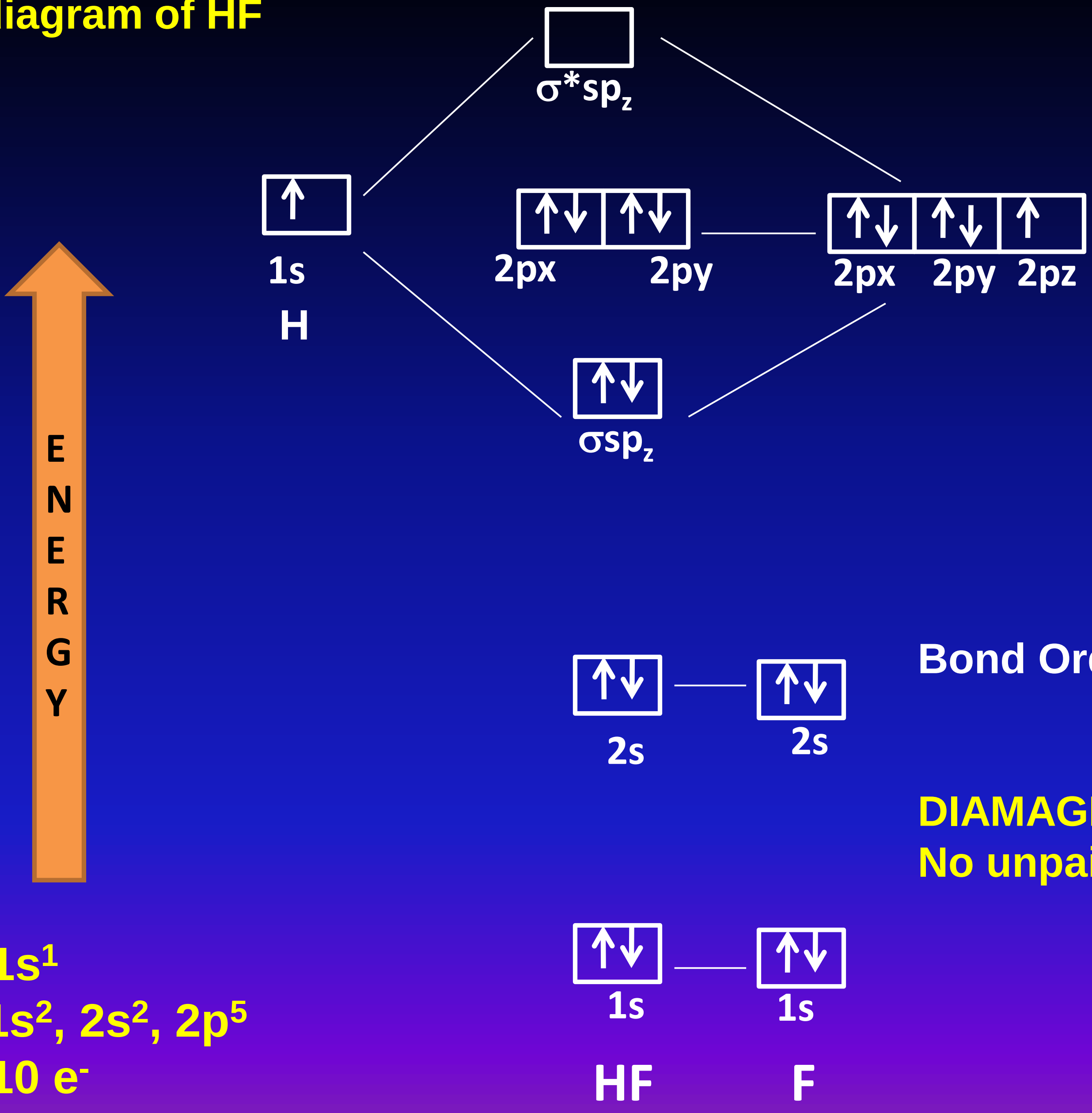


Bond Order $= \frac{1}{2}(N_b - N_a)$
$= \frac{1}{2}(10 - 5)$
$= 2.5$

PARAMAGNETIC due to 1 unpaired e present in π*2px

N (7) $1s^2$, $2s^2$, $2p^3$
O (8) $1s^2$, $2s^2$, $2p^4$
NO = 15 e^-

M O diagram of HF



Bond Order = $\frac{1}{2}(N_b - N_a)$

$= \frac{1}{2}(2 - 0)$

$= 1$

DIAMAGNETIC

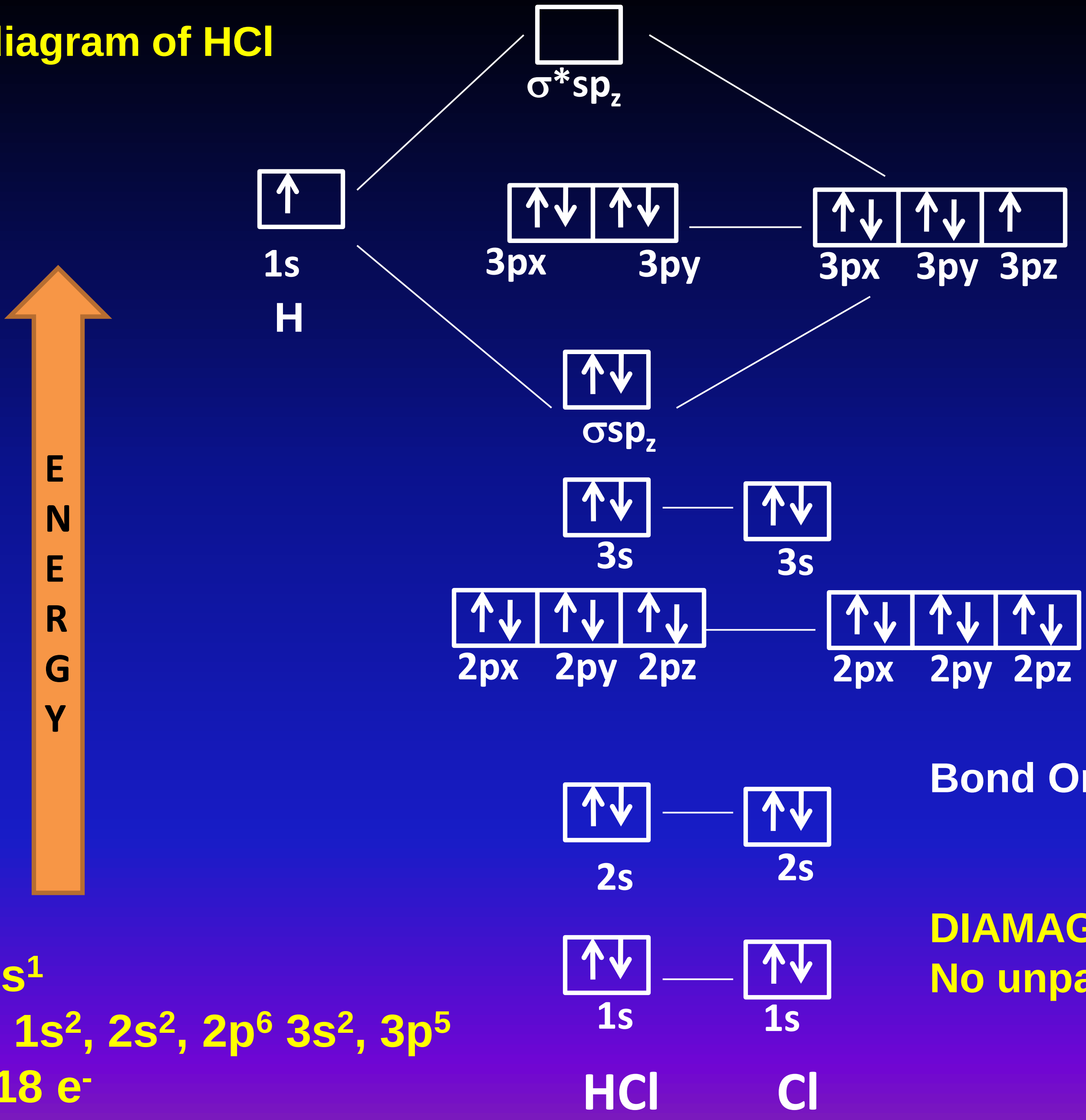
No unpaired electrons

H (1) $1s^1$

F (9) $1s^2$, $2s^2$, $2p^5$

HF = 10 e^-

M O diagram of HCl



Bond Order = ½(N_b – N_a)
= ½(2 – 0)
= 1

DIAMAGNETIC
No unpaired electrons

H (1) $1s^1$
Cl (17) $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^5$
HCl = 18 e^-

Thank you