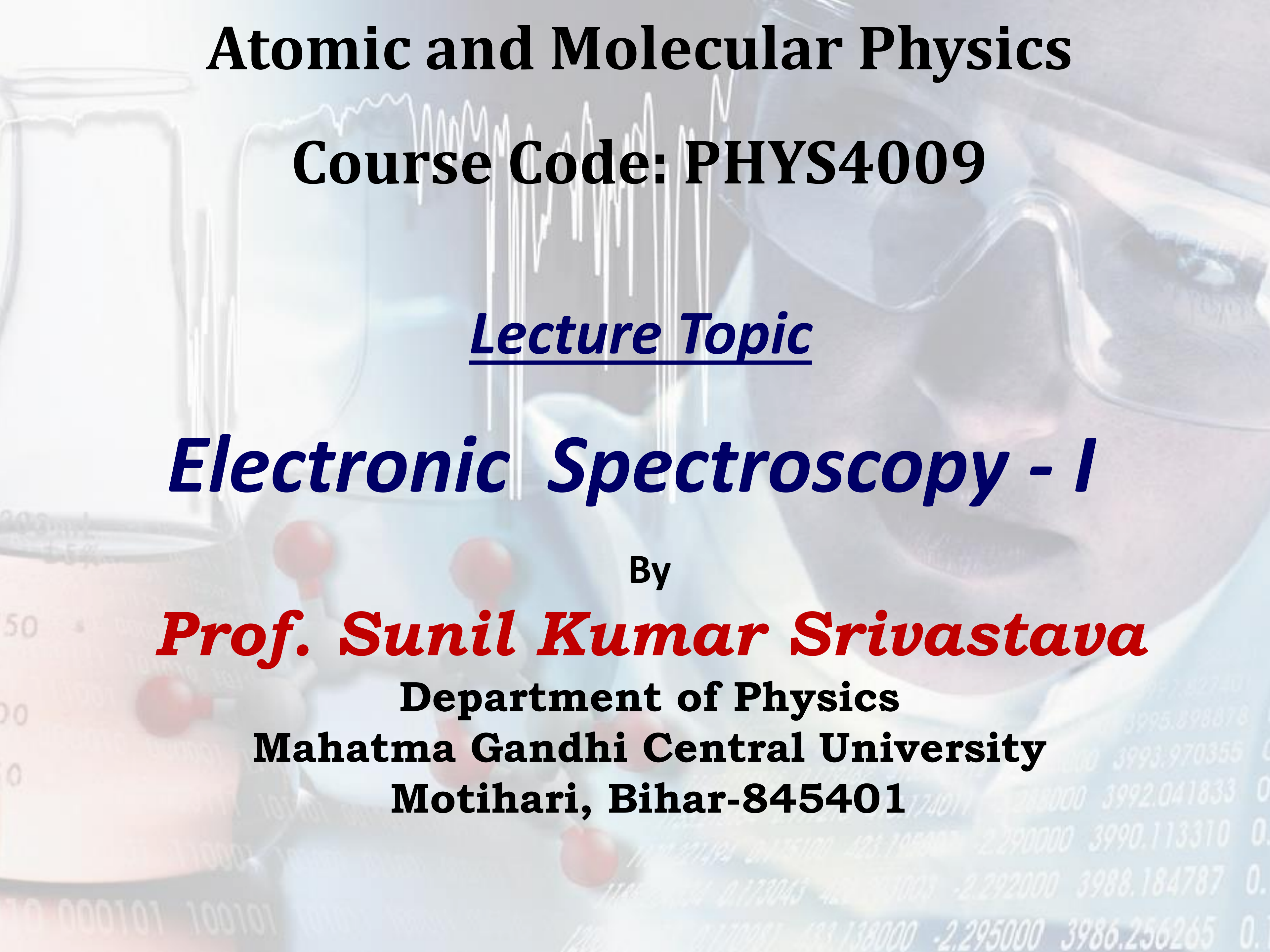

Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Electronic Spectroscopy - I

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Outline

- *What are Molecular Orbitals?*
- *Types of Molecular Orbitals*
- *Electronic Configuration of the Molecule*
- *Molecular Electronic States*
- *Electronic Transitions*

Part - I

- *Rotational Fine Structure*
- *Franck Condon Principle*
- *Fortrat Diagram*
- *Application of Electronic Absorption Spectroscopy*

Part - II

Molecular Orbitals

There are two approximate theoretical approaches which describes the formation of molecule from atoms.

1. **Molecular Orbital Theory**
2. **Valance Bond Theory**

Out the two the molecuar orbital theory is mostly used to describe the formation of molecules and other phenomenon.

According to molecular orbital theory, the Molecular Orbitals (MOs) are fromed from the Atomic orbitals (AOs) by the method of linear combination of molecular orbitals (LCAO)

In general, for any diatomic molecule, the **LCAO** method gives **MO** wavefunction, $\boldsymbol{\psi}$, of the form:

$$\psi = c_1\psi_1 + c_2\psi_2$$

Where, $\boldsymbol{\psi_1}$ and $\boldsymbol{\psi_2}$ are the AO wavefunction for the atoms 1 and 2, and $\boldsymbol{c_1}$ and $\boldsymbol{c_2}$ are constants reflecting the proportion of $\boldsymbol{\psi_1}$ and $\boldsymbol{\psi_2}$ which froms the MO.

In case of homonuclear diatomic molecule, $\boldsymbol{\psi_1}$ = $\boldsymbol{\psi_2}$ and $\boldsymbol{c_1}$ = $\pm\,\boldsymbol{c_2}$,

$$\psi = N(\psi_1 \pm \psi_2)$$

where, N is normalization constant.

The necessity of normalization constant in all wavefunctions ψ is to ensure that normalization condition :

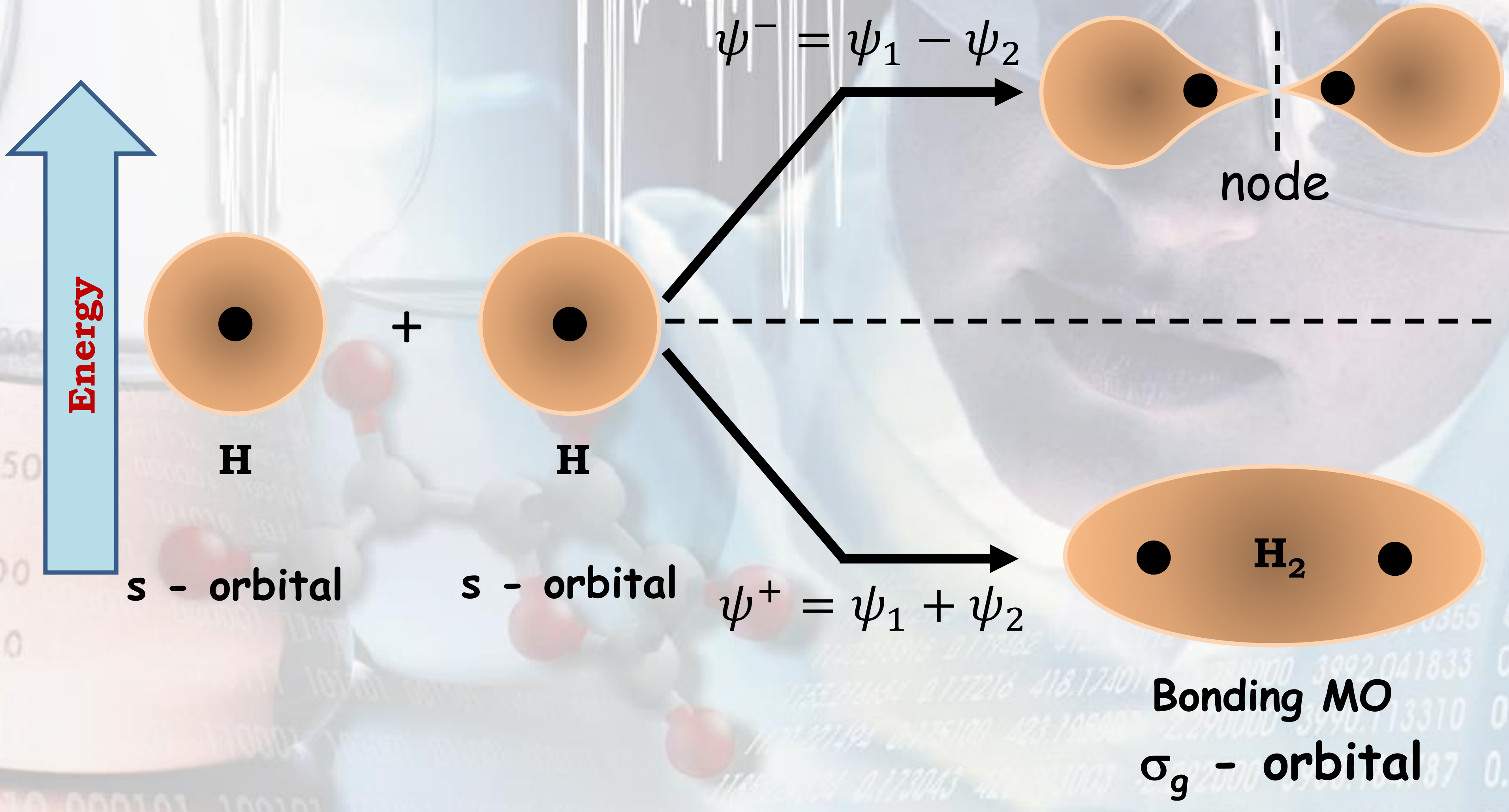
$$\int \psi^2 d\tau = 1$$

is satisfied, where $d\tau$ indicates that the integration is over all space. The quantity ψ^2 is the probability of finding the electron at a particular point in space.

According to LCAO method for a diatomic molecule, we could imagine the formation of two different molecular orbitals whose wave functions would be:

$$\psi^+ = \psi_1 + \psi_2 \quad \text{or} \quad \psi^- = \psi_1 - \psi_2$$

Formation of Molecular Orbitals



Energy

H + **H**

s - orbital

s - orbital

σ_u* - orbital

Antibonding MO

$\psi^- = \psi_1 - \psi_2$

node

$\psi^+ = \psi_1 + \psi_2$

H_2

Bonding MO

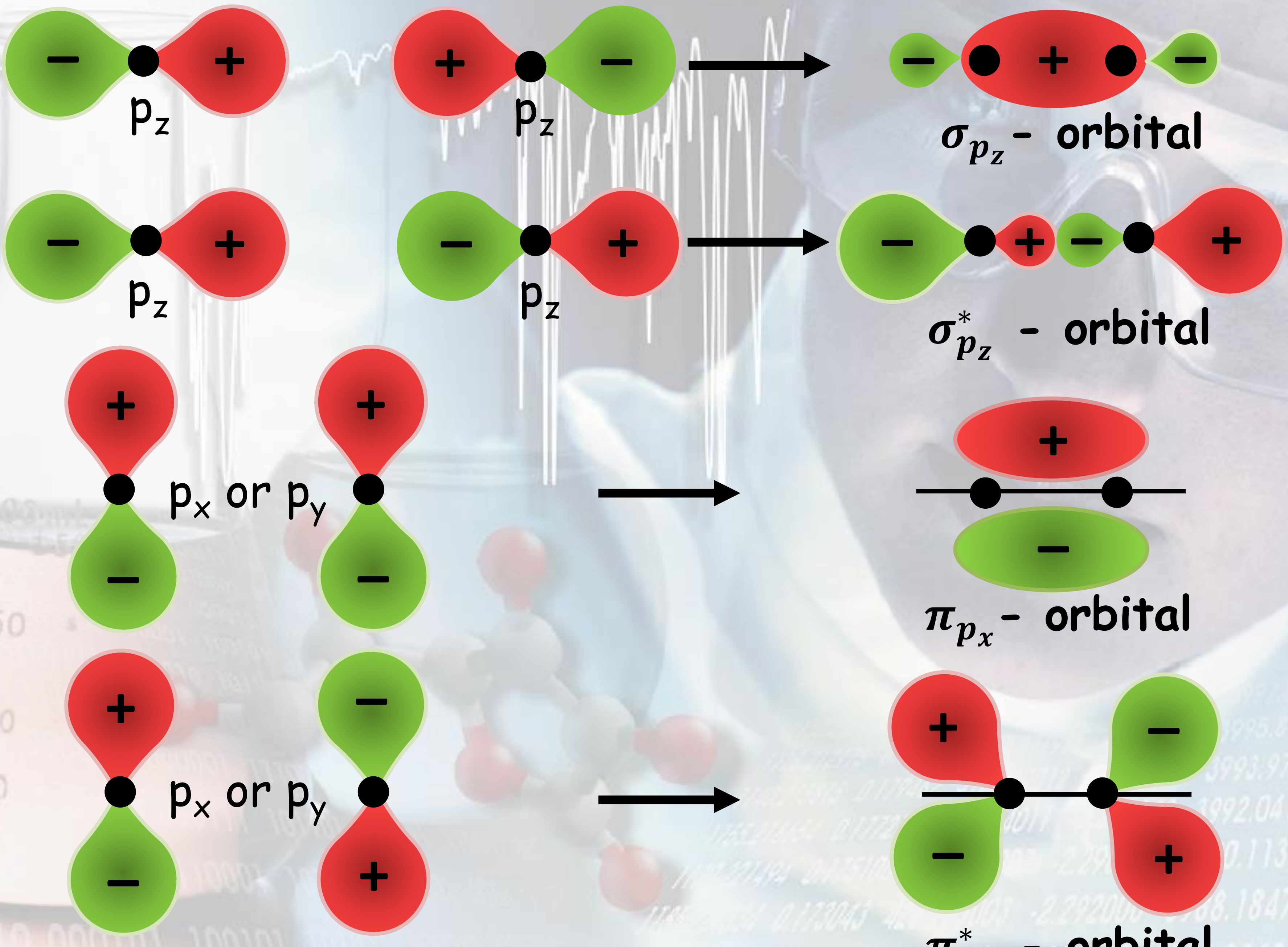
σ_g - orbital

If atom come close to each other, and when the wave function of the atomic orbitals overlap **in-phase**, the concentration of electronic charge between the nuclei increase which causes nuclei to keeping together and thus this orbital represents the formation of a bond between the atoms. It is called a **bonding orbital**.

In another case, when the wave function of the atomic orbitals overlap **out-of-phase**, the concentration of electronic charge between the nuclei decreases, and is greatest outside them; which causes nuclei to repel each other and the orbital is describes as **antibonding orbital**. It leads to a state of higher energy than the individual atom.

Atomic Orbitals

Molecular Orbitals



p_z p_z → σ_{p_z} - orbital

p_z p_z → $\sigma^*_{p_z}$ - orbital

p_x or p_y → π_{p_x} - orbital

p_x or p_y → $\pi^*_{p_x}$ - orbital

Atomic **orbitals** have phase **signs**, like waves; A **positive sign** means a **positive** displacement of the wave ("up") and a **negative sign** means a **negative** displacement ("down").

In homonuclear molecule (i.e. made of two identical atoms), the molecule has centre of symmetry and a point of inversion. The molecular properties, such as electron density, force fields, etc., are quite unchanged by inversion. However, we note that $\boldsymbol{\psi}$ (as opposed to ψ^2) may or may not be changed in sign by inversion. The orbital, in which ψ, is completely symmetrical, is described as even and usually given the symbol **g, (German: gerade = even)** as a suffix. On the other hand, the orbital which reverses the sign of ψ on inversion, is antisymmetrical. This orbital is thus odd and given the subscript **u, (German: ungerade = odd)**.

If the molecule is heteronuclear (for example CO, HCl, etc.) then there is no centre of symmetry and the odd-even classification of orbitals does not arise.

In simple diatomic molecules, there exist σ and π orbitals only, due to interaction of s and p atomic orbitals. More complex orbitals exist - δ, ϕ, etc., formed by interaction between *d*, *f*, etc., atomic orbitals - but they need not concern of us.

A molecular orbital can hold maximum two electrons with opposite spin, the upward and downward arrows indicate spin of the electrons. The electrons are filled in the molecular orbitals with increasing energy as:

$$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2(\pi_g 2p)^2(\sigma_u 2p)^2 \ldots \ldots \ldots$$

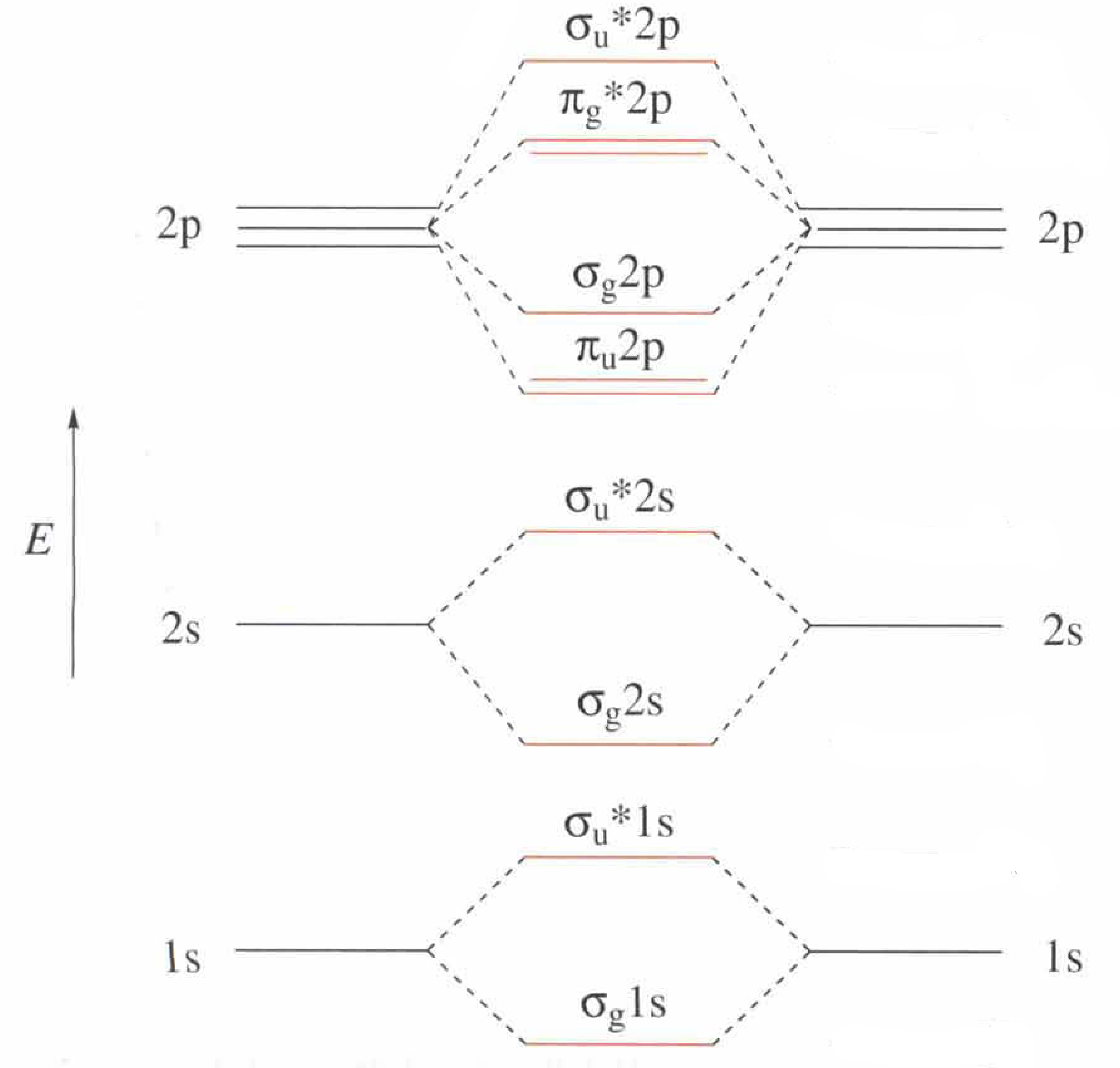
For example, in N, there are 14 electrons, and the ground electronic configuration is:

$$\boldsymbol{N_2} \qquad (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2(\pi_g 2p)^2$$

The O atom has 16 electrons, the ground electronic configuration is:

$$\boldsymbol{O_2} \qquad (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2(\pi_g 2p)^2(\sigma_u 2p)^2$$

Molecular Orbital Energy Diagram



Bond Order

In molecular orbital theory, bond order is often defined as; the difference between the number of bonding and antibonding electrons divided by two. Bond order represent the bond strength. For stable molecule the bond order has to have positive value.

$$Bond\ Order = \frac{no.of\ bonding\ electrons\ -\ no.of\ antibonding\ electrons}{2}$$

Molecule	Bond order
H_2	1
H_2^+	$\frac{1}{2}$
He_2^+	$\frac{1}{2}$
N_2	3
O_2	2

Molecular Electronic States

The electrons in the molecule are associated with an orbital angular momentum quantum number. There is a correspondence between the value of orbital angular momentum "l" and the label used for the **MO**:

$l = 0$	1	2	…….
σ	π	δ	…….

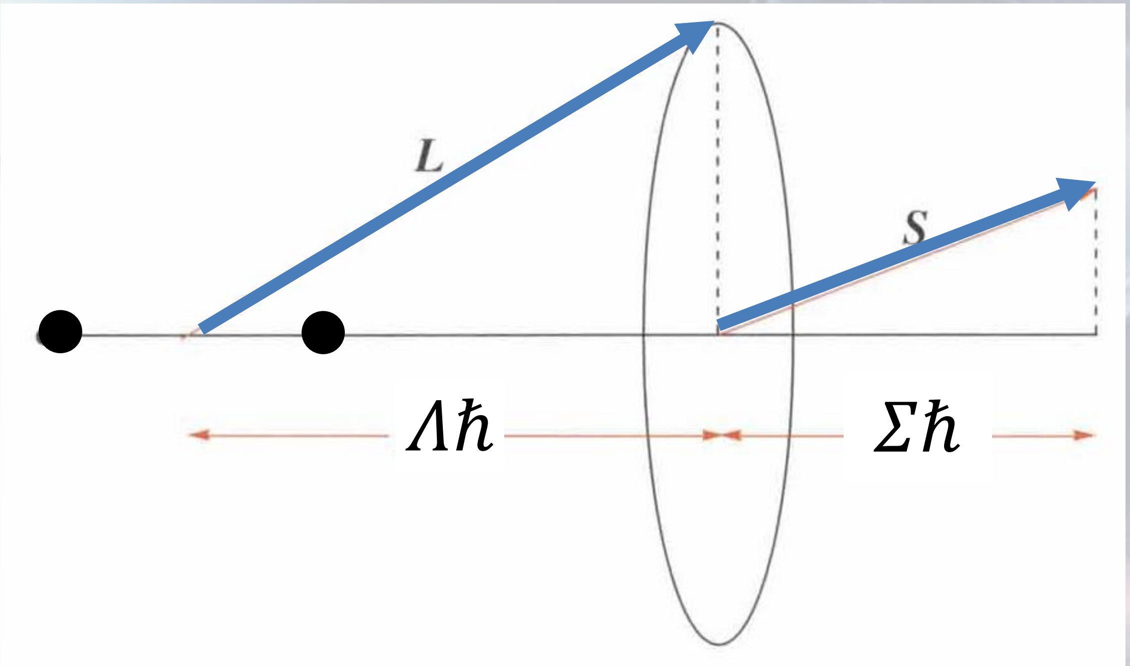
The symbols **σ, π, δ,** ….. (sigma, pi, delta, …) are used for molecular orbital, equivalent to the s, p, d … used for atoms. As in atoms, the orbital angular momenta are strongly coupled to give the total orbital angular momentum quantum number ***L***, and the electron spin angular momenta are coupled to give the total spin angular momentum quantum number ***S***.

In the process of molecule formation, the two positively charged nuclei introduces an electrostatic field. If the nuclear charge is not high enough, coupling between the total orbital and total spin angular momenta, spin-orbit coupling, can be neglected. Under this approximation, the total orbital and total spin momenta couples, independently, to the internuclear axis.

As compared to the situation in an atom, the introduction of a second nucleus, introduces two new quantum numbers, $\boldsymbol{\Lambda}$ and Σ. The component of the angular momentums along the intemuclear axis may take only the values $\Lambda\hbar$ and $\Sigma\hbar$, *respectively*, where Λ and Σ can take the values:

$\Lambda =$	0	1	2	3	4	....
	Σ	Π	Δ	Φ	Γ	....

$\Sigma = S, S - 1, \ldots, -S$



The symbolism used for electronic states is of the form ${}^{2S+1}\boldsymbol{\Lambda}_{g/u}$.

for example ${}^1\Sigma_g$, ${}^3\Pi_u$ and ${}^2\Delta_g$.

Let's calculate the ground state of H_2 molecule. H_2 molecule have 2 electrons. The ground state electronic configuration of H_2 molecule is $(\sigma_g 1s)^2$. The spin up and spin down electron in a given orbital give S = 0. Since electron in σ_g orbital gives $\Lambda = 0 \rightarrow \Sigma_g$ – state.

To complete the symbolism, we need to know whether the MO wave function is symmetric or antisymmetric (changes sign) on reflection through any plane containing the internuclear axis. If it **is** symmetric, we add a post-superscript "+"; if it is antisymmetric, we add "-". Since $\sigma_g 1s$ MO is cylindrically symmetrical, The H_2^+ molecule

The ground state of H_2 molecule is $^1\Sigma_g^+$

Similarly, the ground state of H_2^+ molecule can be determined. The H_2^+ molecule has only one electron. Therefore, S = ½, here also the electron is in $\sigma_g 1s$ MO which is cylindrically symmetrical gives the ground state of H_2^+ molecule $^2\Sigma_g^+$.

For other other examples of electronic ground states please refer to suggested books.

Selection Rules for Electronic Transition

The transition between the electronic states occur according to selection rule:

$$\Delta\Lambda = 0, \pm 1$$

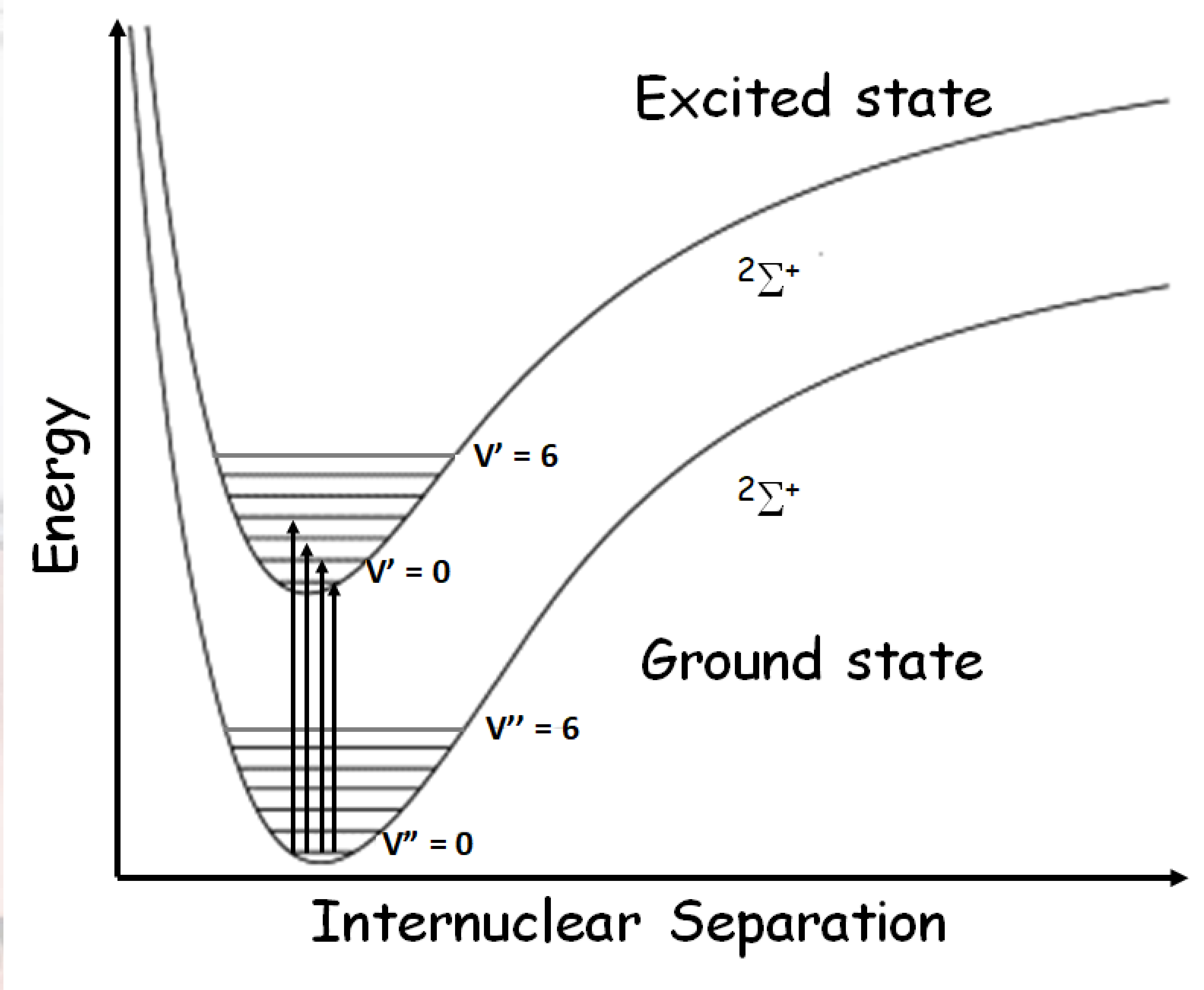
Thus, transition $\Sigma \leftrightarrow \Sigma$, $\Sigma \leftrightarrow \Pi$, $\Pi \leftrightarrow \Pi$, etc., are allowed, but $\Sigma \leftrightarrow \Delta$, is not allowed.

There are also restrictions on symmetry changes. Σ^+ states can undergo transitions only into other Σ^+ states (or into Π states) while Σ^- go only into Σ^- (or Π). That means;

$$\Sigma^+ \leftrightarrow \Sigma^+ \qquad \Sigma^- \leftrightarrow \Sigma^- \qquad \Sigma^+ \nleftrightarrow \Sigma^-$$

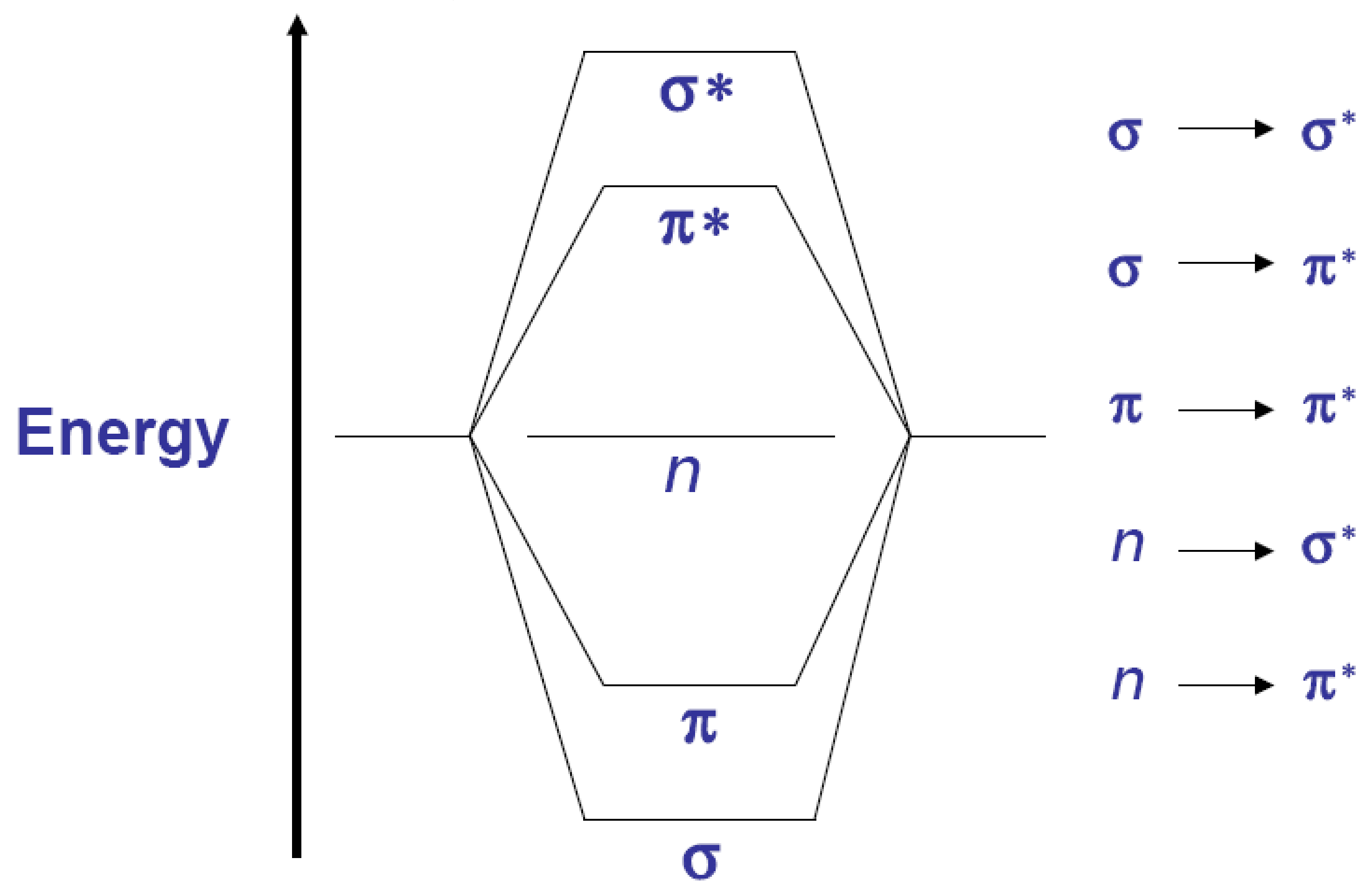
$$g \leftrightarrow u \qquad g \nleftrightarrow g \qquad u \nleftrightarrow u$$

Example of Electronic Transition



Electronic Transitions in Polyatomic Molecules

From the molecular orbital diagram, there are different possible electronic transitions that can occur in a molecule, each of a different relative energy:



$\sigma \rightarrow \sigma^*$

$\sigma \rightarrow \pi^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$

Books for Further Reading

1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)

2. Basic Atomic & Molecular Spectroscopy by J. M. Hollas (Royal Society of Chemistry)

References:

http://hyperphysics.phy-astr.gsu.edu/hbase/index.html

Thank you