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Systematic Approach for the Bonding in Ferrocene.

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Research Article

ABSTRACT

Through the systematic LCAO combinations of each of same symmetric 5 group MO's on upper and lower C_5H_5 rings, LGO's are formed. Then considering the symmetries of the lobes below the upper ring and that of the lobes above the lower ring, when both the rings are either partitioned by the nodal planes in possible geographical regions or not, and simultaneously taking the co-ordinate system, it is clear that which orbital on Fe(II) will be suitable for which LGO one for chemical combination.
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INTRODUCTION

In my B.Sc. (Honours) class room, during the teaching of bonding in ferrocene, very often I receive the question from the desk of the students that they find difficulties to find out the suitable orbital(s) on Fe(II) metal ion towards chemical combination with a particular ligand group orbital (LGO). The difficulties lead me to clarify the matter from the students' corner where, along with the consideration of co-ordinate system, I have invoked the simple LCAO concept which is well known to the student.

DISCUSSION

The Fe atom in ferrocene is normally assigned to the +2 oxidation state as can be shown on the basis of Mossbauer spectroscopy. Each C_5H_5 (Cp) ring is then allocated a single –ve charge, bringing the numbers of π electrons on each ring to six and thus making them aromatic.
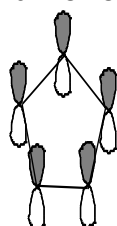
Conceptual understanding of theory of non-classical chemical bonding in ferrocene consists of three steps:

Step-1: Formation of 5 group MOs in each C5 H5 part of the molecule. (" " ′ refers corresponding to the other C5H5 part.)
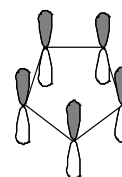
Upper C_5H_5 part   *Lower C_5H_5 part*
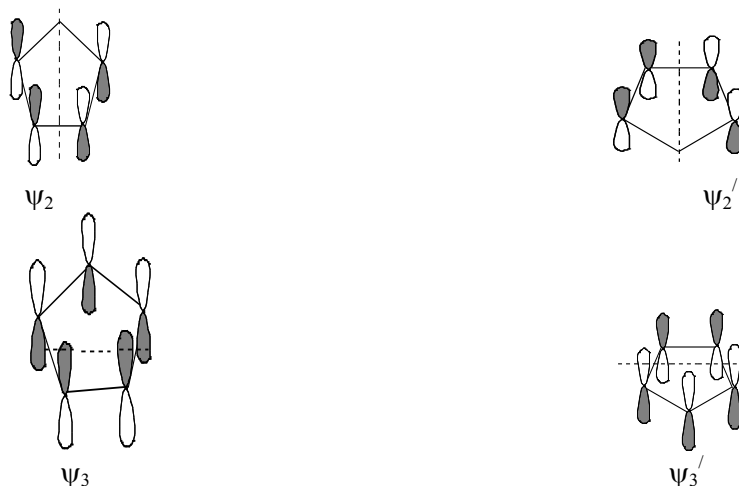
MOs with no nodal plane having symmetry A

ψ_1 $\psi_1{}'$

MOs with one nodal plane having symmetry E$_1$

ψ_2

$\psi_2^{/}$

ψ_3

$\psi_3^{/}$

MOs with two nodal planes having symmetry E$_2$

ψ_4

$\psi_4^{/}$

ψ_5

$\psi_5^{/}$

Step-2: Linear combination of those 5 group MOs of one C$_5$H$_5$ part with a similar set from the other C$_5$H$_5$ part before combining with metal orbitals leading to the formation of 10 ligand group orbitals (LGO's).

(For creation of –ve of any wave function, say, $-\psi_1^{/}$, it must be multiplied by –ve leading to the creation of reverse phase)
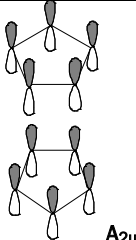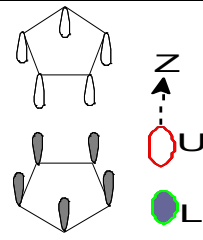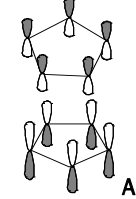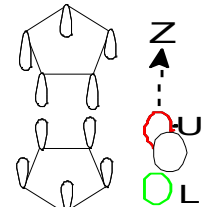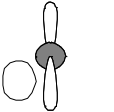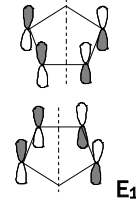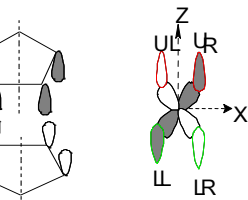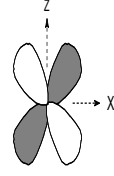
A. $\psi_1 + \psi_1^{/}$ **B.** $\psi_1 - \psi_1^{/}$
C. $\psi_2 + \psi_2^{/}$ **D.** $\psi_2 - \psi_2^{/}$
E. $\psi_3 + \psi_3^{/}$ **F.** $\psi_3 - \psi_3^{/}$
G. $\psi_4 + \psi_4^{/}$ **H.** $\psi_4 - \psi_4^{/}$
I. $\psi_5 + \psi_5^{/}$ **J.** $\psi_5 - \psi_5^{/}$
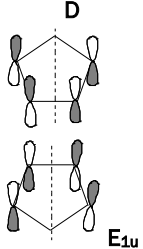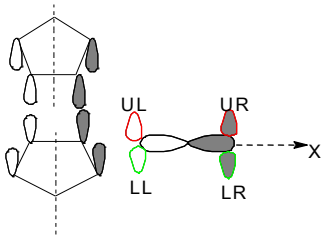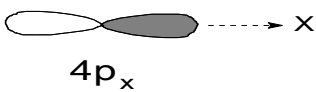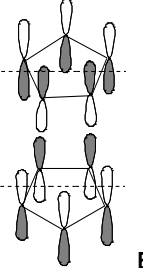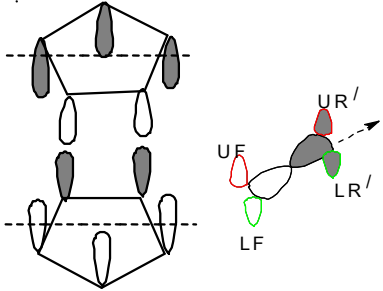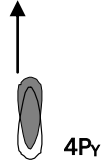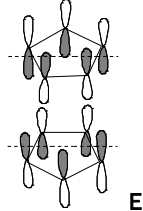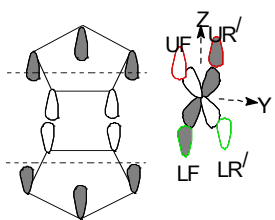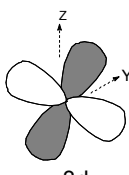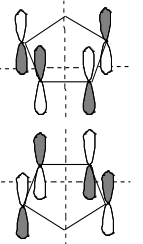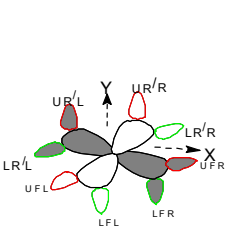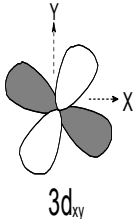
Step–3: Combination of those LGO's with symmetry matched atomic orbitals on the metal ion to form the MO's.
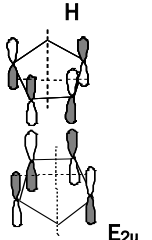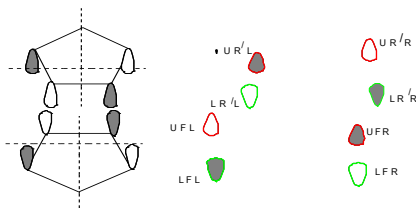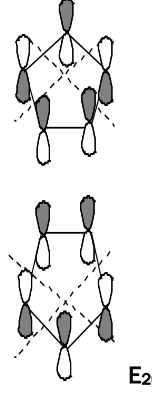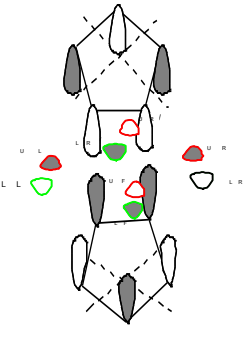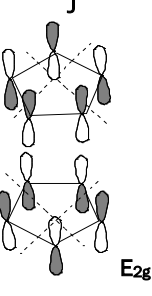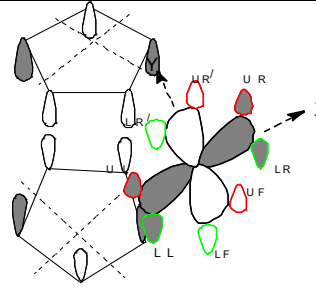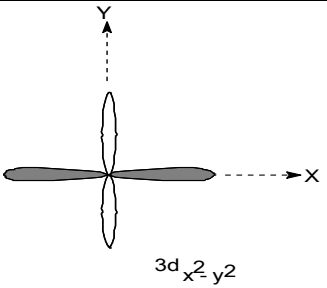
The main problem of the students arises from the portion that deals with the interaction between the symmetry matched orbitals on the metal ion and the LGO's regarding which LGO will interact with which metal orbital and how one can find it out. The present topic mainly goes to the clarification for that portion. In this regard students should keep into their minds the following points:

1. When any nodal plane is absent, then the symmetry of the p-orbital lobes below the upper ring and that of the lobes above the lower ring are to be considered.
2. In the presence of nodal plane(s), the partitioning of two Cp rings in both the upper and lower halves altogether into geographical regions will be done according to the nature of occurrence of the nodal plane(s).
3. After   that,   the   symmetry   of   the   p-orbital   lobes   below   the

4. upper ring and that of the lobes above the lower ring are to be considered for those partitioned regions only.
5. They must note that for partitioned regions, only concerned matter is the upper and lower same symmetric zones created by the suitable lobes of the orbitals but it is to be erased from their minds that how many orbitals are there in those regions.
6. Now, taking care of the co-ordinate system and from the symmetry of the concerned lobes it will be clear that which metal orbital will be suitable for a particular LGO. Thus, the ways of obtaining the suitable metal orbital(s) for each LGO are shown as follows:

LGO (Designation, orbital picture and symmetry)	Lower lobe of the upper part & Upper lobe of the lower part & Nature of combination	Consideration of co-ordinate system & Symmetry matched orbital(s) on sandwiched metal	Remarks
A A_{2u}	Z, U, L	$4p_z$	Fe(II) is sandwiched in between two C_5H_5 rings. So the two lobed valence orbital, on Fe(II), along the Z-axis having ungerade symmetry is definitely $4p_z$ orbital. There is no nodal plane. U- upper ring lobe pointing downward and L –lower ring lobe pointing upward. The shaded lobes bear one type of phase (say, +) and un-shaded ones bear another type of phase (say, –) of the wave function.
B A_{1g}	Z, U, L	$3d_{z^2}$ 4S	1. The two lobed valence orbital, on Fe(II), along the Z-axis having gerade symmetry is definitely $3d_{z^2}$. 2. The spherical valence orbital, on Fe(II), having gerade symmetry is definitely 4S. There is no nodal plane. U and L are same as before.
C E_{1g}	Z, UL, UR, X, LL, LR	$3d_{XZ}$	The four lobed valence orbital, on Fe(II), having gerade symmetry in the XZ-plane is definitely $3d_{XZ}$ orbital. Here one nodal plane makes the partitions into right and left fashion. UR-upper right, UL-upper left; LR- lower right and LL-lower left.

D E_{1u}	UL, UR, LL, LR	$4p_x$	The two lobed valence orbital, on Fe(II), having ungerade symmetry along the X-axis is definitely $4p_x$. Here partitioning fashion and abbreviations are like LGO C.
E E_{1u}	UF, UR′, LR′, LF	$4P_Y$	The two lobed valence orbital, on Fe(II), having ungerade symmetry along the Y-axis is definitely $4p_y$. Here one nodal plane makes the partitions into front and rear fashion.UR′-upper rear, LR′-lower rear; UF- upper front and LF-lower front.
F E_{1g}	UF, UR′, LF, LR′	$3d_{yz}$	The four lobed valence orbital, on Fe(II), having gerade symmetry in the YZ-plane is definitely $3d_{YZ}$ orbital. Here partitioning fashion and abbreviations are like LGO E.
G E_{2g}	UR′L, UR′R, LR′R, LR′L, UFL, UFR, LFL, LFR	$3d_{xy}$	The four lobed valence orbital, on Fe(II), having gerade symmetry in the XY-plane is definitely $3d_{XY}$ orbital. Here two nodal planes make the partitioning into rear –front and right-left fashion leading to the four geographical symmetry zones on each of upper and lower ring simultaneously. UR/R refers to lobes at upper rear right position, LR/R to lobes at lower rear right position, similarly, UR/L – upper rear left orbitals, LR/L-lower rear left, UFL-upper front left, LFL-lower front left, UFR- upper front right and LFR –lower front right.

H E₂ᵤ		No suitable metal orbital(s)	The orbitals which are just above and below each other from the upper and lower ring are mismatching in symmetry.
I E₂ᵤ		No suitable metal orbital(s)	Same as in LGO H
J E₂ₘ		$3d_{x^2-y^2}$	The four lobed valence orbital, on Fe(II), having gerade symmetry along the X and Y-axes is definitely $3d_{x^2-y^2}$ orbital. The two nodal planes make the partitioning in right-left and front-rear fashion leading to the four geographical symmetry zones on each of upper and lower ring simultaneously. UR/ refers to the lobes at upper rear position, LR/ to lobes at lower rear position, similarly, UR upper right , LR-lower right , UL-upper left, LL-lower left, UF - upper front and LF –lower front orbitals.

Finally, it is an important notification to the students that FOR EASY VISUALIZATION TOWARDS THE FINDING OF MATCHING ORBITAL(S) ON Fe(II), THEY MUST CONSIDER THE UPPER-LOWER COUPLE, i.e., UX–LX PAIR WHERE "X" STANDS FOR R,L,R′,F,R′R,R′L,FR AND FL DEPENDING ON THE SYMMETRY ZONES CREATED BY NODAL PLANE(S). R ,R′,L,F ARE DEFINED EARLIER.

Though the MO diagram will be found in any of the standard text books, [1-3] still it is shown here for the at a glance study of the present topic.

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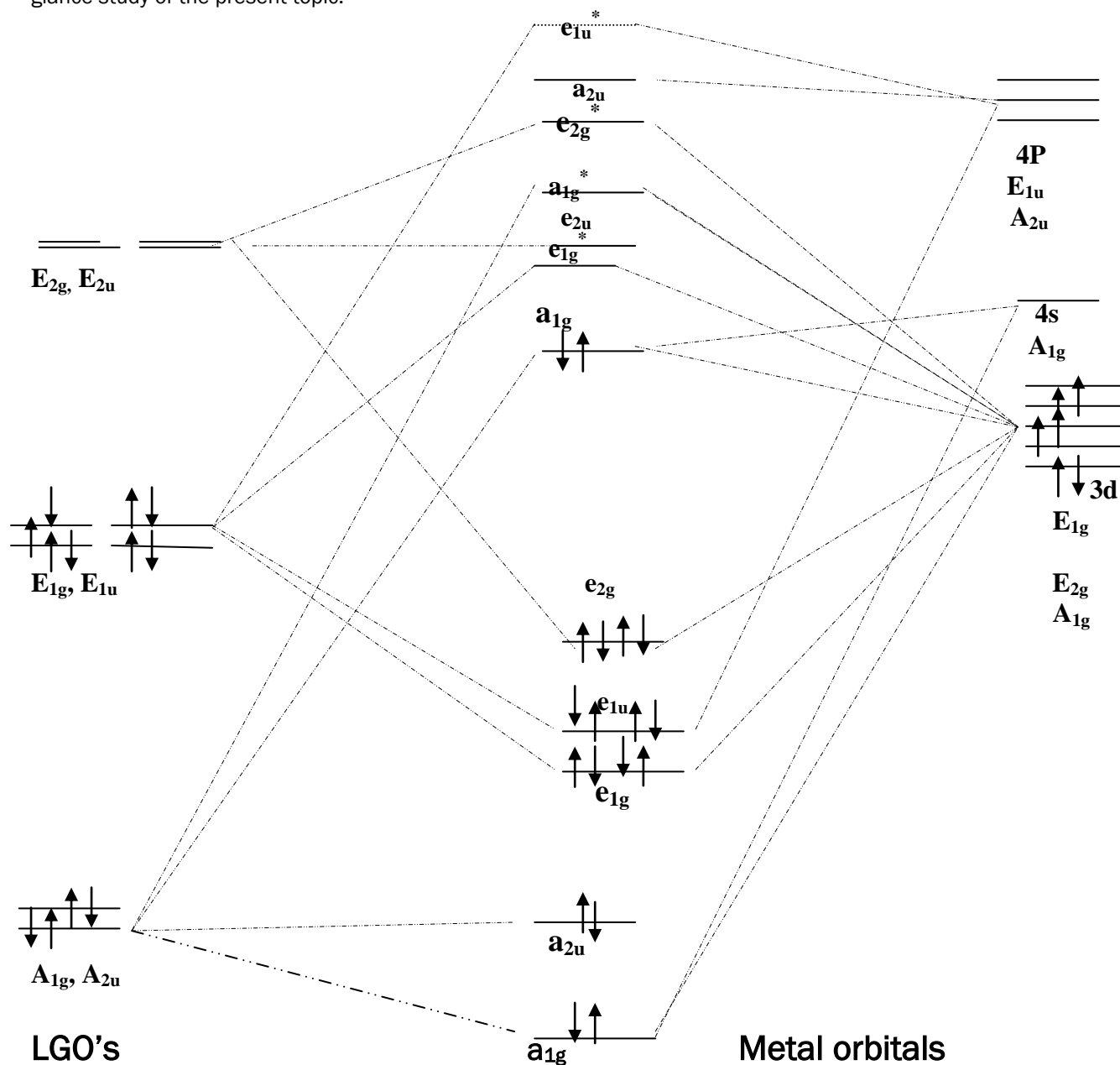
From the MO diagram it is found that there is insignificant interaction between the $A_{1g}(\sigma)$ orbitals of C_p and metal orbitals of same symmetry due to the large energy gap. Thus the ligand is a poor σ-donor. Similarly, due to the large energy gap between the orbitals on both the Cp and M having symmetry E_{1u}, their interaction is not of much importance. Further, very large energy gap between the orbitals having symmetry A_{2u} on both the Cp and M does not permit to interact. Again, $E_{2g}(\pi)$ orbitals of C_p are reluctant to interact with the orbitals of same symmetry on metal as the energy gap does not favour this. So the ligand is not a good π-acceptor. E_{2u} orbitals on C_p remains non-bonding due to the lack of same symmetric orbitals on metal.

The only energetically well matched orbitals on Cp and metal are E_{1g}'s. Thus the Cp – Mπ interaction through the drifting of electron density from Cp to M leads to the most of the stabilization to form the stable ferrocene molecule.

CONCLUSION

Systematic LCAO combinations from each of 5 group MO's having same symmetry on both the upper and lower C_5H_5 rings lead to the formation of LGO's. Then consideration of the symmetries of the lobes below the upper ring and that of the lobes above the lower ring where, both the rings are either partitioned by the nodal planes in possible geographical regions or not, and along with the taking up the co-ordinate system into careful consideration make it clear that which Fe (II) metal ion orbital will be suitable for a particular LGO for chemical combination.

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