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Iron and Nickel -ligand bonding in metallocene: Differentiation between bond Stability and reactivity

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Abstract**—** *The electronic structure and geometry optimization of ferrocene and nickelocene molecules are calculated using DFT/B3LYP with the basis set of 6-31G (d).The Eigen values, Eigen vector and population analysis of the molecules show that thefirst 13 molecular orbitals in ferrocene and 14 in nickelocene have contribution from 2pzorbitals of carbon of* $(C_5H_5)^-$ *and 4s, 4pand 3dorbitals of iron andnickel respectively. We found that the extent of involvement of metal orbitals in thetwo cases is different. In ferrocene the maximum involvement out of 4sand 4porbital is in the order 4pz > 4py > 4s > 4pxand out of 3d orbitals the order of involvement is 3dyz >3dxz >*$3d^2z$*>* $3dx^2-y^2$ *> 3dxy. The involvement of corresponding orbital innickelocene with respect to the 4sand 4porbitals is in the order of 4py> 4px> 4s> 4pz and in 3d orbitals the order is 3dyz >*$3dx^2-y^2$ *>3dxy >3dxz >*$3dz^2$*molecules. The total involvement of 3d, 4s and 4porbitals of metal and 2pz orbitals of the ten carbon atomsof both ligands of* $(C_5H_5)^-$*in ferrocene and nickelocene respectively are 42.2528 and 38.3776 hence we can conclude that ferrocene is more stable than nickelocene. Similar results are found from calculation of parameters like dipole moment, HOMO-LUMO gap and Mullikan charge distribution. The population analysis shows that only 2pz orbitals of carbon of* $(C_5H_5)^-$ *and 3d orbitals of metal provide electrons to MOs of ferrocene and nickelocene.*

Keywords**— *Ferrocene, Nickelocene, Eigen vector, population analysis, Eigen values, atomic and molecular orbitals.***

I. INTRODUCTION

In the last decade, there has been a phenomenal advancement in theoretical inorganic chemistry [1, 2], much faster computers are available and commercial programs incorporating the latest methods have become widely available and are capable of providing more information about molecular orbitals (MOs), with a sample input of chemical formula. The focus of attention has been on computational transition-metal chemistry [3, 4]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecules, particularly of the heavier atoms [5-8] and in the use of small-core relativistic effective core potential [9-11] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy [8, 12]. Application of density functional calculation to organometallic [13,14] and transition metal compounds is growing [15]. density functional parameters such as eigenvectors, eigenvalues and population analysis are well calculated with this method. In this paper present the calculations ofeigenvectors, Eigen values and population analysis offerrocene and nickelocene in order tostudy the extent of contribution of *3d*, *4s*and *4p* orbital in the formation of MOs. The significant of Ferrocene and nickelocene are contribute of atomic orbitals in the formation of molecular orbital, chemical stability, mediator, asymmetric catalysis and more reactive material such as Ferrocene and

Nickelocene as the commercially important for production of various metallocene, polymers and co-polymers. Such a quantitative study will provide correct information about the involvement of *3d*, *4s* and *4p* orbital of Iron and nickel in bonding will help to resolve the controversy raised by other workers [16-20].

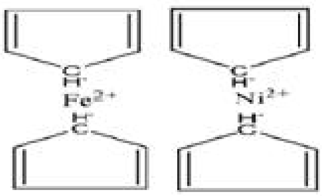


Fig.1: Stricture of Ferrocene, and nickelocene molecules

II. MATERIALS AND METHODS

In computational chemistry tools the DFT offers the fundamentals for interpreting multiple chemical concepts used in different branches of chemistry. In modern computational chemistry, quantum chemical calculations are typically performed with in a finite set of basic functions. When molecular calculations are performed, it is common to use a basis sets composed of a finite number of atomic orbitals, centered at each atomic nucleus with in the molecule, for example linear combination of atomic orbitals. The methods most commonly used for this research are DFT/B3LYP a combination of Beck's three-parameter exchange functional and Lee-Yang-Parr correlation functional with 6-31G (d) basis set.

These methods are found in Gaussian 03W program. B3LYP is a DFT method with hybrid functional that provides qualitative results at a lower cost than abinitio methods with a comparable accuracy [21]. By using these methods we have optimized the energy, eigenvalues, eigenvector , population analysis, HOMO-LUMO energy gap, hardness, softness, electronegativity, visualize the HOMO and LUMO orbitals' of ferrocene and nickelocene molecules. The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan-equation. A widely used method to analyze SCF wave function is population analysis, introduced by Mullikan population methods [22]

III. RESULT AND DISCUSSION

This research is aimed to study the electronic structure and optimized geometry of ferrocene and nickelocene molecules. Geometry optimization is used to find minima on the potential energy surface representing equilibrium structure and used to obtain structure for a single-point quantum mechanical calculation, which provides a large set of structural and electronic properties. The electronic structure and geometry of ferrocene and nickelocene molecules are found through DFT/B3LYP with a basis set of 6-31G (d) calculations. The optimized structures of these two compounds are shown in Fig 1, A and B respectively for ferrocene and nickelocene. The significant computed parameters are available in Tables 1 and 2 including the bond lengths, bond angles and dihedral angles of these two compounds. The optimized bond length of C-C double and single bonds in ferrocene rings fall in the range 1.36-1.83˚A, andnickelocene1.392-1.98 ˚A at DFT/ B3LYP, levelsthrough 6-31G (d) basis set.

There are two types of C-C bonds involved in these species. These are C-C single bonds and C-C double bonds of ferrocene andnickeloceneand according to its bond length are in the order of C=C <C-C. From Tables 1and 2 we observe a slight difference in the bond lengths, bond angles and dihedral angles throughout the molecules of ferrocene and nickelocene. This indicates that the aromatic iron atom in ferrocene and nickel atom in nickelocene are relatively stable metabolically.

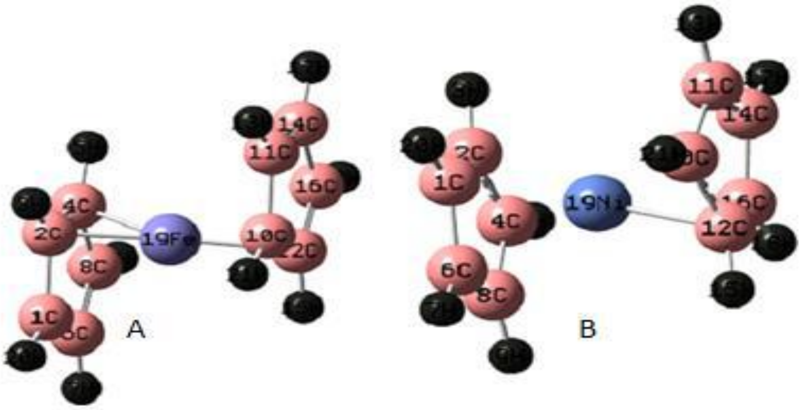


Fig.2: The optimized structures of (A) ferrocene, (B) nickelocene molecules

Table.1: The selected bond lengths in˚A, some bond angles and Dihedral angles of theoptimized structure of ferrocene using DFT levels with B3LYP / 6-31G (d) basis set.

Entry	Bond length(˚A)	Entry	Bond angle (ºA)	Entry	Dihedral angle (o)
C1−C2	1.509	C6−C1−C2	109.511	C6−C1−C2−C4	0.027
C1−C6	1.509	C8−C6−C1	109.560	C8−C6−C1−C4	-0.027
C8−C6	3.359	C12−C10−C11	92.513	C10−C11−C14−C16	-85.951
C10−C11	1.509	C14−C10−C12	92.513	C16−C12−C10−C11	91.533
C10−C12	1.509	C10−C11−C14	85.520	Fe−C2−C1−C6	-67.604
C11−C14	1.359	C10−C12−C16	109.510		
C12−C16	1.359	Fe−C2−C1	88.83		
C2−C4	1.359				
C4−C8	1.47				
Fe−C2	1.825				

As shown in Fig 2. (A) and Table 1.due to the effect of the partial charge distribution of iron atom in ferrocene molecule, the bond connectivity of Fe-$(C_5H_5)_2$ of the two ligands are asymmetrical. The iron atom in ferrocene is bonded withC_{12} atom with bond lengthof 1.954 (˚A) in one side of the ligand and $C_4$with bond length of 1.856(˚A) and with C_2atom of bond length 1.856 (˚A) on the opposite side. The Fe-C bond length on the two sides of the ligand have small variations due to the double bond ofC_2−C_4 which possess more energy to attract iron atom to-wards itself than the single bond on the other side,henceFe−C_2 and Fe−C_4 bonds measure shorter distance than the bond inFe−C_{12}.In the ferrocene molecule the iron atom is located between the two ligands but inclined by -67.604ºfrom the plane of the cyclopentadienyl and the two ligands are almost parallel but with a slide of one from the other by a center of mass separation of 1.67˚A.

Table.2: The selected bond length˚A, bond angles and Dihedral angles of the optimized Structure of nickelocene using DFT levels with B3LYP / 6-31G (d) basis set.

Entry	Bond length(˚A)	Entry	Bond angle (o)	Entry	Dihedral angle (o)
C1−C2	1.424	C1−C2−C4	106.850	C6−C1−C2−C4	-174.834
C2−C4	1.419	C2−C1−C6	108.850	C2−C1−C6−C8	-8.963
C1−C6	1.448	C1−C6−C8	107.560	C1−C2−C4−C8	6.050
C6−C8	1.391	C10−C11−C14	93.450	C10−C11−C14−C16	-85.112
C10−C11	1.471	C12−C10−C11	97.468	C12−C10−C11−C14	87.862
C10−C12	1.427	C10−C12−C16	105.110	C10−C11−C14−C16	82.950
C11−C14	1.366	Ni−C12−C10	72.433	C14−C16−C12−Ni	-67.377
C12−C16	1.427				
Ni−C2	1.976				

As shown in Figure 2, B and Table 2. The bond connectivity of Ni-$(C_5H_5)_2$of the two ligands are asymmetrical. The nickel atom in nickelocene is bonded withC_{12} atom of bondlength 1.976 (˚A) only from one side of the ligand. This is due to the weak ligand fields of nickelocene having high spin arrangement with two delectrons and low spin arrangement with six delectrons of nickel atom which resulted in more reactivity of nickelocene molecule with respect to the other two molecules. In the nickelocene molecule the nickel atom is located between the two ligands but inclined by -67.377ºas measured from the plane of the cyclopentadienyl and the two ligands are almost parallel but with a slide of one fromthe other by a center of mass separation of only 0.22˚A.

Generally comparing the bond length and bond angles between metal atom and carbon in ferrocene and nickelocene molecules the former molecule possesses higher bond angles and the later molecule possesses larger bond length. The large the bond length the less stability but more reactivity, hence nickelocene is more reactive and less stable than the ferrocene. In the calculations of Mullikan charge distributions of ferrocene and nickelocene molecules, given in Figure 2, the red color indicates for excess of negative charges (-Ve) while the green color indicates for excess of positive charges (+Ve) among the bonded atoms, where electrons can flow from positions of excess of negative charges (-Ve) to the positions of excess of positive charges (+Ve).

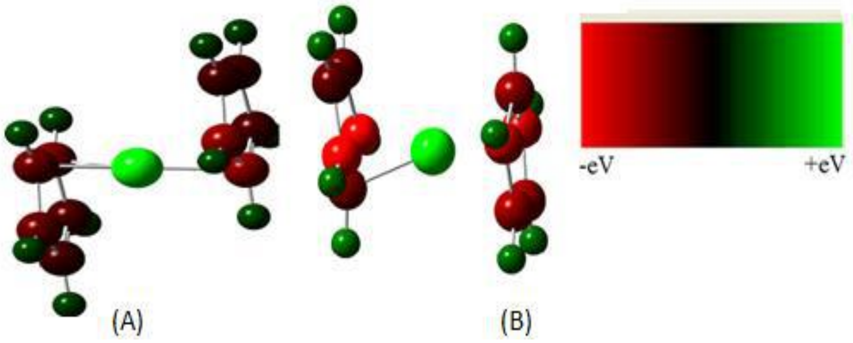


Fig.3: The Milliken charge distributions of (A) ferrocene, (B) nickelocene Molecules.

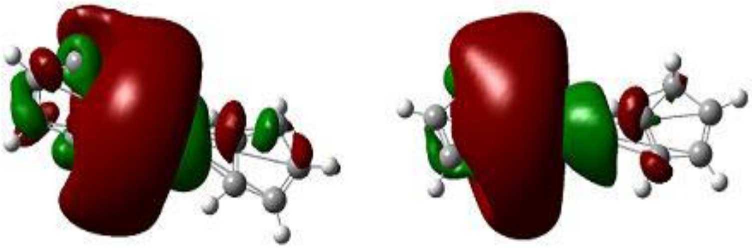
Energies of molecular orbitals are called Eigen values. The main focus has been on themolecular structure and the properties that will be evaluated can be used to determinethe molecular reactivity as well as the molecular stability. The HOMO (Highest OccupiedMolecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are very importantaspects to consider for these types of observations. This is because the HOMO and LUMOare the most likely locations where reaction will occur. The reaction is likely to occur therebecause the electrons in the HOMO have the highest energy and therefore the electronsare most willing to react. The LUMO is likely the location for a bond to occur as wellbecause any invading electrons for another molecules will fill in to the LUMO, that iswhy comparing the energies of these orbitals create an idea of how reactive a molecule is important parametric properties of the molecules at the DFT/B3LYP levels in 6-31G (d) basis set has been calculated and are given in Table 3

Table.3: Important parametric properties of the molecules calculated at the DFT/B3LYPLevels in 6-31G (d) basis set.

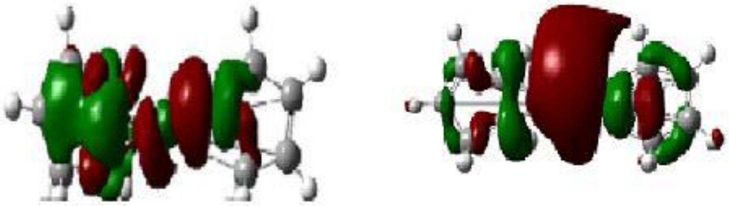
Molecular properties	ferrocene	nickelocene
RB-HF-LYP (eV)	-1896.275	-1650.740
εHOMO(eV)	-0.6491	-0.6427
εLUMO(eV)	-0.5628	-0.5614
εLUMO−εHOMOenergy gap (eV)	0.0863	0.0813
Ionization potential(I in eV)	0.6491	0.6427
Electron affinity(A in eV)	0.5628	0.5614
Global hardness (ηin eV)	0.0431	0.04065
Global softness (Sin eV)	23.1803	24.6030
Electro negativity (χin eV)	0.60591	0.6021
Chemical potential (μin eV)	-0.6059	-0.6021
Dipole moment (μin Debye)	1.464	1.931
Mullikan charge distributions (M.C.D in e)	±1.093	±1.692

At the DFT/B3LYP level the HOMO energy of ferrocene is -0.6491 eV which is slightly more negative than the and nickelocene of -0.6427 eV and the LUMO energy of ferrocene is -0.5628 eV, andnickelocene -0.56142eV. The HOMO-LUMO gap of ferrocene and nickelocene are 0.0863 and0.0813 eV respectively. These proves that the positions of HOMO, LUMO and the HOMO-LUMO gap can predict the stability and reactivity of the molecules, and the ferrocene molecule shows relatively high energy gap value and the data here suggested that ferrocene is relatively less reactive and more stable than nickelocene molecule. The most stable MO energy of ferrocene and nickelocene are respectively -254.0054, and -295.6703 -eV. In general the HOMO and LUMO energy gap reveals the chemical activity of the molecules. LUMO as an electron acceptor represents the ability to obtain an electron (i.e. the electron affinity) and HOMO as an electron donor represents the ability to donate an electron from its orbital (i.e. the Ionization Potential). The less values in the HOMO-LUMO energy gap explains eventually charge transfer interaction taking place within themolecules. Hard molecules have largeHOMO-LUMO energy gaps and soft molecule have small HOMO-LUMO energy gaps. So soft molecules (molecules with small energy gap) are favorable for easy reactions. This description also supports for ferrocene andnickelocene molecule, ferrocene is harder than nickelocene. In Table 3, the HOMO-LUMO gap, as a characteristic of reactivity, shows ferrocene has lower chemical reactivity comparing to nickelocenemolecule. Absolute hardness and softness are important properties to measure the molecular stability and reactivity. Itis apparent that the chemical hardness fundamentally signifies the resistance towards thedeformation or polarization of the electron cloud of the atoms, ions or molecules undersmall perturbation of chemical reaction. A hard molecule has a large energy gap and asoft molecule has a small energy gap. So for more energetically stable and less reactiveferrocene molecule, the HOMO-LUMO energy gap and hardness, ηis larger comparing tonickelocene molecules.

The dipole moments and Mullikan charge ranges as displayed in Table 3, Nickelocene would have more charge than the ferrocenemolecule. This is due to higher dipole moment and lower HOMO-LUMO energy gap indicated that the molecule is better reactive. This indicates that nickeloceneis more polar so that it will react with polar solvents like water.Since the separation between mass centers of the two ligands is small. The higher the dipole moment, the more polar a molecule is. This could mean that the receptor is more likely toaccept polar molecules into its active site. The receptor’s active sites may serve as home to atoms that have very high electron affinities that attract the negatively charged end of a polar molecule



Ferrocene



Nickelocene

Fig.4: The left side of HOMO and the right side of LUMO surfaces of ferrocene and nickelocene compounds, down of the column respectively.

The above Figure shows the visualized structures of ferrocene and nickelocene show the population of electrons on their orbitals. The HOMO orbitals represented by green color, whereas for LUMO is represented by red color. The red color represents the negatively charged areas of surface (i.e. those areas where accepting the electrophiles is most favorable) while the green color represents the positively charged areas of surface (i.e. those areas where accepting the nucleophiles is more favorable). The electron density of HOMO and LUMO of ferrocene and nickelocene molecule are concentrated throughout the compound except at the right and left terminals wheresome of the π∗orbitals may be empty.

Eigen vector values of atomic orbitals have been evaluated for the study of linear combination of atomic orbitals (LCAO). The MOs of ferrocene and nickelocene are formed by linear combination of fifty AOs of two $(C_5H_5)^{-}$and nine orbital of iron and nickel. These fifty-nine AOsχ1to χ59on LCAO approximation form same number of MOs, Φ1 to Φ59. The AOs χ1toχ40for 2s, 2px, 2py, 2pzof 1C to 10C, χ41toχ49for4s, 4px, 4py, 4pz, $3dx^2-y^2$, $3d^2z$, 3dxy, 3dxz, 3dyzof 11M andχ50to χ59for 1s of 12H to21H respectively, where M = Fe and Ni, for ferrocene and nickelocene, respectively. The 2s, 2pxand 2pyorbitals of each carbon atom of $(C_5H_5)^-$are involved in the formation of σbond between C-C and C-H. The orbitals involved in σ bond hence shall remain out of discussion. The 2pzorbitals of ten carbons and nine orbitals of iron or nickel i.e. in total nineteen orbitals are relevant to our discussion in respect of bonding between iron or nickel orbitals and 2pzorbital of $(C_5H_5)^-$. These atomic orbitalsareχ4, χ8, χ12, χ16, χ20, χ24, χ28, χ32, χ36andχ40of carbon and χ41to χ49of iron and nickel. The coefficients of these orbitals are the eigenvector values of χ[21].They express the forms of MOs i.e. the extent of involvement of χin the formation of Φ.In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals. The Eigen vector analysis has been made and studied and data are given tables 1 to 11 respectively. The coefficients of these orbital are the Eigen vector values of, χ which have been evaluated by density functional method using Gaussian-03 software.They express the form of molecular orbital that is the extent of involvement ofχin theformation of Φ. The calculated Eigen vector values of atomic orbitals of Feand Ni inthe formation of molecular orbitals in ferroceneandnickelocene in Table 4, 5, 8, and 9 respectively and the calculated Eigen vector values of 2pzorbital of carbon are given in Table 6, 7, 10 and 11. Table 5, 7, 9 and 11 are summation of Eigen vector values of ferrocene and nickelocene. Negative, Zero and near zerocoefficient values are negligible contributions[21, 23] of electrons and have been excludedfrom the Tables.

Out of the 59 molecular orbitals of ferrocene molecule only 22 molecular orbitals shallbe discussed as described in Table 4 for Iron orbital and Table 6 for Carbon orbital. In ferrocene the first 13 molecular orbitals Φ18,Φ20,Φ22,Φ23−Φ31 and Φ35are formed byonly two atomic orbitals, 3d orbital of iron and2pzorbital $(C_5H_5)^-$. These orbitals are the most stable molecular orbital and have their energies in the range -2.03849 to -0.54008eV. The next nine molecular orbital Φ36−Φ37, Φ40−Φ41, Φ43, Φ50−Φ51, Φ54−Φ55haveformed from contribution of vacant 4s, 4px, 4pyand 4pzorbital of the iron and 2pzorbital of carbon. These MOs are comparatively less stable and have their energies between -0.53616and -0.107076 eV. To examine the extent of involvement of 3d, 4s and 4porbital in thef ormation of molecular orbitals the values of coefficient of each orbital have been added as shown in Table 5.

Table.4: Contributions of orbitals of iron and their summation values in the formation of molecular orbitals of ferrocene. .S = summation SS = sum of summation, SS of 3d orbitals = 10.4655 and SS of 4s and 4p orbitals = 12.0732.N.B; orbitals having coefficient values above 0.1 have only been considered.

MOs	4s	4p x	4py	4pz	$3dx^2$-y^2	$3dz^2$	3dxy	3dxz	3dyz
	χ41	χ42	χ43	χ44	χ45	χ46	χ47	χ48	χ49
Φ18	-	-	-	-	0.2947	0.2991	-	-	-
Φ20	-	-	-	-	-	-	-	-	0.2361
Φ22	-	-	-	-	-	-	-	0.2728	-
Φ23	-	-	-	-	0.4708	0.1156	-	0.2893	0.2288
Φ24	-	-	-	-	0.1041	-	0.2847	0.4762	0.2718
Φ25	-	-	-	-	0.6472	-	-	-	0.3147
Φ26	-	-	-	-	-	0.2269	0.8185	-	0.1004
Φ27	-	-	-	-	0.1063	0.5776	0.2565	-	0.4672
Φ28	-	-	-	-	0.3760	-	-	-	0.1352
Φ29	0.1452	-	-	-	0.1367	0.5383	-	-	-
Φ30	-	-	-	-	-	0.3496	-	0.5271	0.3891
Φ31	-	-	-	-	-	-	-	0.4573	0.4577
Φ35	-	-	-	-	0.2392	-	-	-	-
Φ36	-	0.7335	0.6722	0.4698	-	-	-	-	-
Φ37	0.5031	0.7533	0.6888	-	-	-	-	-	-
Φ40	0.7981	-	0.2865	-	-	-	-	-	-
Φ41	-	-	0.2780	0.7412	-	-	-	-	-
Φ43	-	-	-	0.3154	-	-	-	-	-

Φ50	0.9232	-	-	0.7275	-	-	-	-	-	-
Φ51	-	-	0.3489	0.9974	-	-	-	-	-	-
Φ54	-	0.2810	0.3923	0.6228	-	-	-	-	-	-
Φ55	0.5802	0.3805	0.4346	-	-	-	-	-	-	-

Table.5: Sum of contributions and reactivity of atomic orbital's of iron in the formation of molecular orbitals of ferrocene

Atomic orbital's of Fe	Sum of contributions of orbital's of Fe	Sum of reactivity
4s	2.9498	0.3390
$4p_x$	2.1483	0.4655
$4p_y$	3.101	0.3225
$4p_z$	3.8741	0.2581
$3dx^2{-}y^2$	2.375	0.4215
$3d^2_z$	2.1071	0.4746
$3d_{xy}$	1.3597	0.7356
$3d_{xz}$	2.0227	0.4944
$3d_{yz}$	2.601	0.3845

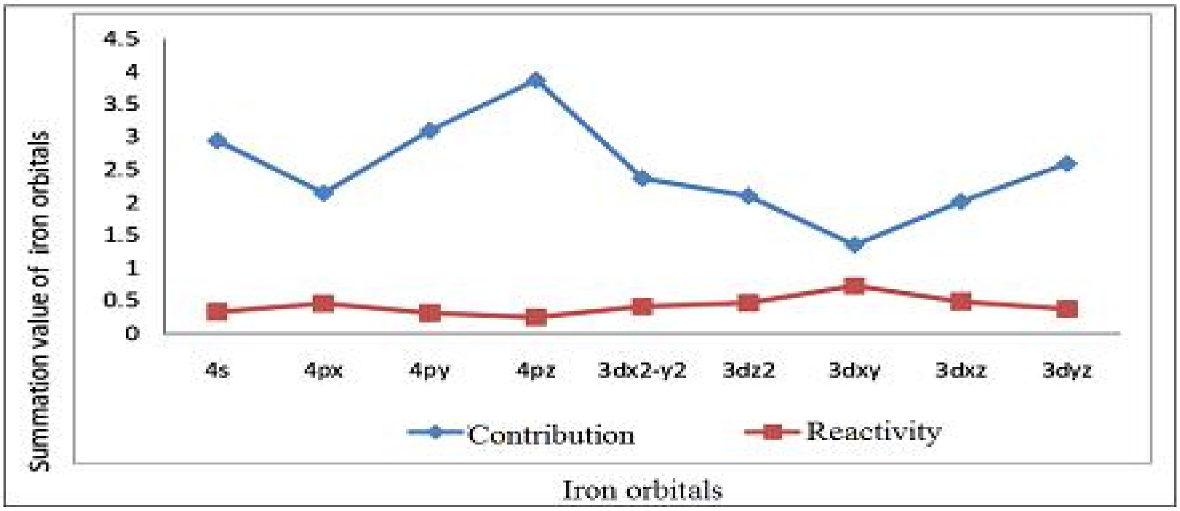


Fig.5: Sum of contributions and reactivity of atomic orbitals of, iron in the formation of molecular orbitals of ferrocene.

The summation of contributions of iron orbitals are placed in Table 5 and the total contribution from each atomic orbital is shown in Figure 5. It is clearly indicated that *4pz*orbital has the maximum involvement out of *4s*and *4p*orbitals, and *3dyz* orbital has the maximum involvement out of the *3d*orbital. The exact order of availability of atomicorbital of Fe in ferrocene for contributions of atomic orbitals for the formation of molecular orbital is given below;

$4pz > 4py > 4s > 4px$ *And*
$3dyz > 3dx^2{-}y^2 > 3d^2z > 3dxz > 3dxy$ Eq (1)

Sum of contributions of atomic orbitals of iron in the formation of molecular orbitals of ferrocene is shown in Table 5, in here the sum of contributions of *3dxy*orbital in the formation of molecular orbitals is least out of the *3d*orbitals and *4px*orbital in the formation of molecular orbitals is least out of *4s* and *4p* orbitals. Hence *3dxy*and *4px*are comparatively free for complex formations. The exact order of availability of atomic orbital of Fe in ferrocene for complex formation is given below;

$4px > 4s > 4py > 4pzx$ *and* $3dxy > 3dxz > 3d^2z > 3dx^2{-}y^2 > 3dyz$
Eq (2)

Table.6: Contributions of2pzorbitals of carbon atoms in $(C_5H_5)^-$*and their summation values in the formation of molecular orbitals of ferrocene.SS of 2pz orbitals are 19.869.N.B; orbitals having coefficient values above 0.1 have only been considered*

MOs	***1C***	***2C***	***4C***	***6C***	***8C***	***10C***	***11C***	***12C***	***14C***	***16C***
	$\chi4$	χ^{8}	χ^{12}	χ^{16}	χ^{20}	χ^{24}	χ^{28}	χ^{32}	χ^{36}	χ^{40}
Φ18	-	-	-	-	0.2872	-	-	-	-	-
Φ20	0.3559	-	-	-	-	-	-	-	-	0.2361
Φ22	-	0.2261	-	-	-	-	-	0.3794	-	-
Φ23	-	0.2151	-	0.2796	-	-	0.2336	-	-	0.2841
Φ24	0.2133	-	-	0.1005	0.1385	0.1852	-	0.2312	0.1199	0.1272
Φ25	0.2062	-	0.2511	-	-	0.1770	-	0.1981	-	0.1486
Φ26	-	-	0.1668	0.1949	0.1218	0.1761	-	-	-	0.1848
Φ27	-	0.2685	-	-	-	-	0.2273	-	-	-
Φ28	-	0.2347	0.2169	0.1190	0.1844	0.3799	0.2591	0.2011	0.3185	-
Φ29	-	0.3310	0.1780	0.1828	0.2399	-	0.2523	-	0.1163	0.2543
Φ30	0.2886	-	0.3015	-	-	0.2907	-	0.2767	-	-
Φ31	0.2644	0.3474	-	-	0.3104	-	0.3409	0.2797	0.3116	-
Φ35	0.4567	0.4381	-	-	0.3623	-	0.4564	0.4820	0.3912	0.2243
Φ36	0.2629	-	-	-	-	-	-	-	-	0.2243
Φ37	-	0.2973	-	-	-	-	0.2673	0.2552	-	-
Φ40	-	-	0.3089	-	-	-	-	-	-	0.3653
Φ41	0.2114	-	0.2234	-	-	-	-	-	-	0.2387
Φ43	-	-	-	0.2661	-	-	-	-	-	-
Φ50	-	-	-	0.4338	-	-	-	-	-	0.3828
Φ51	-	-	-	0.3149	-	-	-	-	-	0.3416
Φ54	-	-	-	-	0.1856	-	-	-	-	-
Φ55	-	-	-	-	-	-	0.3004	-	-	-

Table.7: Sum of contribution values and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of ferrocene

Atomic orbital's of carbon	**Sum of contribution of carbon orbital's**	**Sum of reactivity**
1C	2.2594	0.4426
2C	2.3582	0.4241
4C	1.6466	0.6073
6C	1.8916	0.0.4589
8C	1.8301	0.5465
10C	1.2089	0.8274
11C	2.3373	0.4278
12C	2.3034	0.4341
14C	1.2575	0.7955

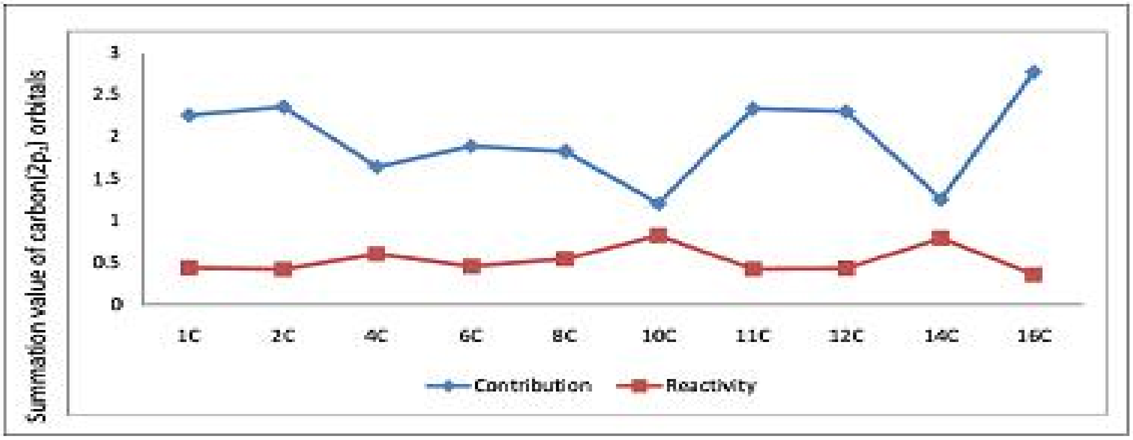


Fig.6: Sum of contributions and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of ferrocene.

Table 7 and Figure 6 show the summation values where the total contributions from each atomic orbital of carbon clearly indicates that eigenvector value of *2pz* orbital of *16C*has the maximum involvement out of the ten carbon atoms in both $(C_5H_5)^-$ ligands. The sequences from the series are as below:

16C >2C >11C >12C >1C >6C >8C >4C >14C >10C. Eq (3)

Sum of contributions of atomic orbitals of carbon (*2pz*) in the formation of molecular orbitals of ferrocene is shown in Table 7 and Figure 6 where the 10C contributions in the formation of molecular orbitals are least out of the ten carbon atoms. Hence 10C is comparatively free for complex formation. The sequence from the series is shown below*:*

10C >14C >4C >8C >6C > 1C >12C >11C >2C >16C. Eq (4)

Out of 59 molecular orbital Eigen values of nickelocene we shall discuss only 25 of them described in Table 8, for nickel orbitals and Table 10 for carbon orbitals. The first 14 MOsare Φ15−Φ16, Φ18−Φ20, Φ21 and Φ23−Φ30, areformed by various *3d* and *2pz* orbitals of (C_5H_5) −. These orbitals with energies in the range of -9.9338 to -0.64271eV are the most stable molecular orbital between nickel and*2pz*orbital of (C_5H_5) −. The next eleven MOs i.e.Φ36−Φ40, Φ42−Φ43, Φ50, Φ53, Φ54andΦ59are formed by interaction of *4s*, *4px*, *4py*and *4pz* orbital of metal and *2pz* orbital of carbon of (C_5H_5)−. These MOs with energies in the range -0.56142 to -0.10622 eV are comparatively less stable. To examine the extent of involvement of *3d*, *4s*, *4p*and *2pz* orbitals in the formation of molecular orbitals the values of coefficient of each orbital are tabulated in Table 9.

Table.8: Contributions of orbitals of nickel and their summation values in the formation of molecular orbitals of nickelocene. SS of 4s and 4p orbitals = 13.0598. And3d orbitals = 9.3888.

N.B; Orbitals having coefficient values above 0.10 have only been considered.

MOs	*4s*	*4p x*	*4py*	*4pz*	*$3dx^2$-y^2*	*$3dz^2$*	*3dxy*	*3dxz*	*3dyz*
	χ41	χ42	χ43	χ44	χ45	χ46	χ47	χ48	χ49
Φ15	-	-	-	-	-	-	-	0.3209	0.3365
Φ16	-	-	-	-	-	-	-	0.2294	0.1991
Φ18	-	-	-	-	-	-	0.3605	-	-
Φ19	-	-	-	-	-	-	0.3125	-	-
Φ20	-	-	-	-	0.5297	-	-	-	-
Φ21	-	-	-	-	0.3029	-	-	-	-
Φ23	-	-	-	-	0.3279	-	-	-	0.1838
Φ24	-	-	-	-	-	-	0.3849	0.4986	0.2011
Φ25	-	-	-	-	0.5232	0.3369	-	0.2396	0.2782
Φ26	-	-	-	-	-	0.7408	-	-	0.4949
Φ27	-	-	-	-	-	-	0.6697	-	0.2358
Φ28	-	-	-	-	0.1702	-	-	-	-

Φ29	-	-	-	-	-	0.2012	-	-	-
Φ30	-	-	-	-	-	0.2979	0.1819	0.4786	0.3521
Φ36	-	0.5037	0.5563	0.2729	-	-	-	-	-
Φ37	0.4088	0.3254	0.2960	-	-	-	-	-	-
Φ38	0.6732	0.2423	0.3695	-	-	-	-	-	-
Φ39	-	0.7569	0.3868	0.3261	-	-	-	-	-
Φ40	-	0.2201	0.3706	-	-	-	-	-	-
Φ42	-	0.3487	0.3318	-	-	-	-	-	-
Φ43	-	0.6971	0.7470	-	-	-	-	-	-
Φ50	0.7225	-	-	-	-	-	-	-	-
Φ53	-	0.3020	-	0.2283	-	-	-	-	-
Φ54	0.6421	0.4372	0.5633	-	-	-	-	-	-
Φ59	-	0.4436	0.7620	1.1256	-	-	-	-	-

Table.9: Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

Atomic orbital's of Ni	Sum of contributions of orbital's of Ni	Sum of reactivity
$4s$	2.4466	0.4087
$4p_x$	4.277	0.2338
$4p_y$	4.3833	0.2281
$4p_z$	1.9529	0.5121
$3dx^2-y^2$	1.9439	0.5144
$3d^2_z$	1.5768	0.6342
$3d_{xy}$	1.9095	0.5237
$3d_{xz}$	1.7671	0.5657
$3d_{yz}$	2.2815	0.4383

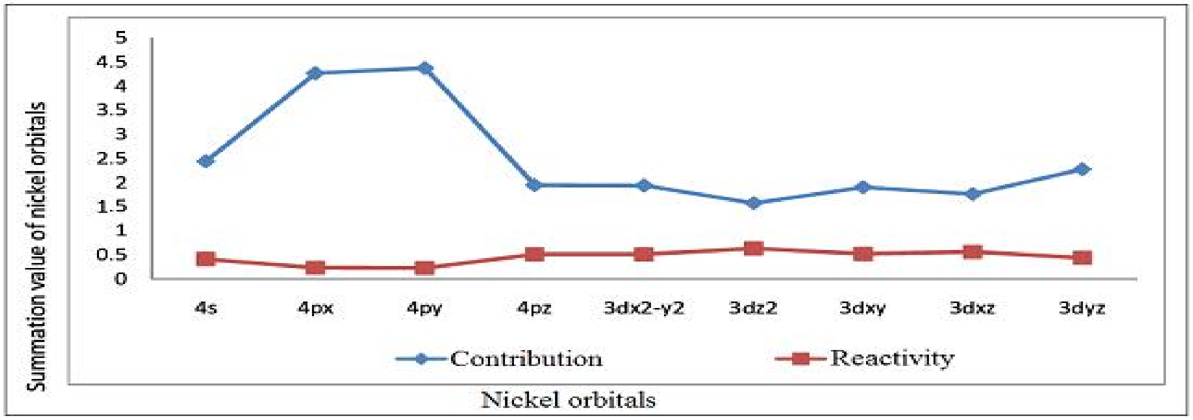


Fig.7: Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

The summation values given in Table 9 and plotted in Fig. 7 show the total contributions from each atomic orbital. It is clearly indicated that *4py*orbital has the maximum involvement out of *4s*and *4p*orbital and *3dyz*orbital has the maximum involvement out of *3d*orbitals. The sequence from the two series is given below:

$$4py > 4px > 4s > 4pz \text{ and } 3dyz > 3dx^2-y^2 > 3dxy > 3dxz > 3d^2z. \qquad \text{Eq (5)}$$

Sum of contributions of atomic orbitals of nickel in the formation of molecular orbitals of nickelocene is shown in Table 9 and Figure 7 that the sum of contributions of $3d^2z$orbital in the formation of molecular orbitals is least out of the 3dorbitals and *4pz*orbital is least out of 4sand 4porbitals. Hence $3d^2z$and *4pz* are comparatively free for complex formations. The exact order of availability of atomic orbitals of Ni in nickelocene for complex formation is given below;

$$4pz > 4s > 4px > 4py \text{ and } 3dyz > 3dxz > 3dxy > 3dx^2-y^2 > 3dyz \qquad \text{Eq (6)}$$

Table.10: Contributions of2pz orbitals of carbon atoms in $(C_5H_5)^-$and their summation values in the formation of molecular orbitals of nickelocene. SS of, 2pz orbitals are, 11.8502. N.B; orbital having coefficient value above, 0.10 have onlybeen considered

MOs	***1C***	***2C***	***4C***	***6C***	***8C***	***10C***	***11C***	***12C***	***14C***	***16C***
	$\chi4$	χ^{8}	χ^{12}	χ^{16}	χ^{20}	χ^{24}	χ^{28}	χ^{32}	χ^{36}	χ^{40}
Φ15	-	-	-	-	-	-	-	-	0.1678	-
Φ16	-	-	-	-	-	-	-	-	-	-
Φ18	-	-	-	-	-	-	-	-	-	-
Φ19	-	-	-	-	-	-	-	-	-	-
Φ20	-	-	-	-	-	-	-	-	-	-
Φ21	-	-	-	0.2019	-	-	-	-	-	0.1986
Φ23	-	-	-	0.2182	-	-	0.1815	-	-	-
Φ24	-	-	-	-	0.1692	-	-	0.1544	-	0.1707
Φ25	-	-	-	-	-	-	-	-	-	0.2018
Φ26	-	-	-	-	-	-	-	-	-	-
Φ27	-	-	0.2142	-	-	0.1666	-	-	-	-
Φ28	0.2818	-	0.3050	-	0.2252	0.4088	0.2304	-	0.3089	-
Φ29	-	0.4189	0.2037	0.2561	0.2707	-	0.3600	-	0.2006	0.3209
Φ30	0.3293	-	0.3232	0.1812	0.1505	0.3096	-	0.3219	0.1864	0.2300
Φ36	-	-	0.2106	-	-	0.2172	-	-	0.3003	-
Φ37	0.2124	0.2023	-	-	-	0.2123	-	-	-	-
Φ38	-	-	-	-	-	-	-	-	-	-
Φ39	-	-	-	-	-	-	0.2029	0.2264	-	-
Φ40	-	-	-	-	0.4239	-	-	-	-	-
Φ42	-	-	-	-	0.2725	-	-	-	-	-
Φ43	-	-	-	-	-	-	-	-	-	-
Φ50	-	-	-	-	0.4095	-	-	-	-	0.3640
Φ53	-	-	-	0.2129	-	-	-	-	-	-
Φ54	-	-	-	-	-	0.2723	-	-	-	-
Φ59	-	-	-	-	0.2227	-	-	-	-	-

Table.11: Sum of contributions and reactivityof atomic orbitals of carbon (2pz) in the formation of molecular orbitals in nickelocene.

Atomic orbital's of carbon	**Sum of contribution of carbon orbital's**	**Sum of reactivity**
1C	0.8235	1.2143
2C	0.6212	1.6098
4C	1.2567	0.7957
6C	1.0703	0.9344
8C	2.1442	0.4667
10C	1.5868	0.6302
11C	0.9748	1.0259
12C	0.7027	1.4231
14C	1.164	0.8591
16C	1.486	0.6729

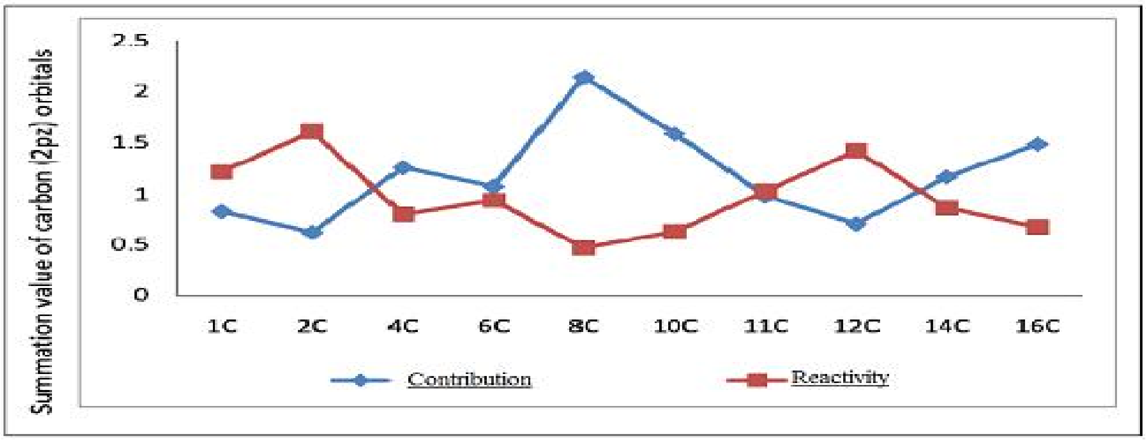


Fig.8: Sum of contributions and reactivity of atomic orbital's of, Ni in the formation of molecular orbitals of nickelocene.

The summation values shown in Table 11 and Figure 8 clearly indicates that contribution of *2pz* orbital of *8C* has the maximum involvement out of the ten carbon atoms in $(C_5H_5)^-$The sequence from the series are given below:

8C >10C >16C >4C >14C >6C >11C >1C >12C >2C.

Eq (7)

Sum of contributions of atomic orbitals of carbon (*2pz*) in the formation of molecular orbitals of nickelocene is shown in Table 11 and Figure 8 where the sum of contribution of *2C* of *2pz*orbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence *2C* are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:

2C >12C >1C >11C >6C >14C >4C >16C >10C >8C.

Eq (8)

The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene, and 22.8486 in nickelocene hence nickeloceneis more stable than ferrocene. The total involvement in relation to the bonding between *2pz* orbital of the ten carbon atoms of both ligands of $(C_5H_5)^-$ 19.889 and 15.529 in ferrocene and nickelocene respectively, hence ferrocene is more stable than nickelocene. The total involvement of *3d*, *4s* and *4p* orbitals of metal and *2pz*orbitals of the ten carbon atoms of both ligands of $(C_5H_5)^-$ in ferrocene and nickelocene respectively are 42.2528, and 38.3776 hence we can conclude that ferrocene is more stable than nickelocene.

Population analysis

The contribution of electrons in each occupied MO is calculated by using the population analysis method introduced by Mullikan [24, 25, and 26]. This method apportions the electrons ofn-electron molecule in to net population $n_r$in the basis function $\chi(r)$. Let there be n_i electrons in the MO Φ_i (n_i= 0, 1, 2) and let n_{ri} symbolize the contribution of electrons inthe MO $\Phi_i$to the net population in$\chi_r$we have:

$$n_{ri} = n_i c^2_{ri} \qquad \text{Eq (9)}$$

Where, $c_{ri}$is the coefficient of atomic orbital for the ithMO r =1-29 in ferrocene andr=1-30 in nickelocene. Eq(9) has been solved for, 58 electrons of 29 molecular orbitals in ferrocene and 60 electrons of 30molecular orbitals in nickelocene. Each MOs has two electrons inferrocene and nickelocene but (the 30thMOs of nickelocene has only oneelectron). The coefficient of atomic orbital$c_{ri}$is treated as Eigen vector value [24, 25, and 26].Values less than 0.1 have negligible contributions and are omitted in the calculations. Only *3d*orbitals of metal and *2pz*orbitals of carbon are considered in the calculation.

The summation value of population analysis of these orbitals is shown in Table 12 of ferrocene, and 13 of nickelocene. It is indicated that in MOs 1-17 of ferrocene, in MOs 1-14 of nickelocene only *2s*, *2py*and *2px* electrons of carbon have contributions in the formation of molecular orbital of ferrocene andnickelocene hence are out of discussion.

The summation value of population analysis of these orbitals to contribute electrons in the formation of molecular orbital is shown Tables 12 and 13 the result of the population analysis shows that only *2pz*orbitals of carbon of $(C_5H_5)^-$and *3d*orbitalsof metal provide electrons to MOs of ferrocene, and nickelocene.

Table.12: The Sum of contribution of electrons 3d orbitals of iron and2pzorbitals ofcarbon in the formation of molecular orbitals of ferrocene.

MOs	No. of atomic orbitals	Eigenvector (c_{ri})	No. of electrons (n_i)	Net population (n_{ri})
Φ18	3	0.8811	6	0.5176
Φ20	3	0.8256	6	0.4850
Φ22	3	0.8783	6	0.5161
Φ23	8	2.1169	16	1.2437
Φ24	11	2.2446	22	1.3187
Φ25	7	1.9429	14	1.1414
Φ26	8	1.9902	16	1.1692
Φ27	6	1.9034	12	1.1182
Φ28	10	2.4248	20	1.4246
Φ29	10	2.3758	20	1.3958

Sum of summation value of population analysis, (n_{ri}) of occupied molecular orbital of ferrocene is, 10.3302.

Table.13: The Sum of contribution of electrons,3d orbitals of nickel and, 2pzorbitals ofcarbon in the formation of molecular orbitals of nickelocene.

MOs	No. of atomic orbitals	Eigenvector (c_{ri})	No. of electrons (n_i)	Net population (n_{ri})
Φ15	3	0.8252	6	0.4884
Φ16	2	0.4285	4	0.2537
Φ18	1	0.3605	2	0.2134
Φ19	1	0.4718	2	0.2793
Φ20	1	0.5297	2	0.4163
Φ21	3	0.7034	6	0.5529
Φ23	4	1.1606	8	0.9122
Φ24	6	1.5789	12	1.2410
Φ25	5	1.7438	10	1.0979
Φ26	2	1.2357	4	0.7780
Φ27	4	0.9055	8	0.5701
Φ28	7	1.9303	14	1.1425
Φ29	8	2.2311	16	1.3206
Φ30	12	1.3426	24	0.7947

Sum of Summation value of population analysis, (n_{ri}) of occupied molecular orbital of nickelocene is, 10.0609

IV. CONCLUSION

We studied the electronic structure and geometry optimization of ferrocene and nickelocene molecules using DFT/B3LYP with the basis set of 6-31G (d) calculations. We found that orbitals corresponding to the Eigen values (energy ranges -2.03849 to -0.54008eV in ferrocene and -9.90743 to -0.64271 eV in nickelocene) formed between *3d* orbitals and *2pz* orbitals are the most stable molecular orbitals. The less stable orbitals are in the energy ranges of -0.53616 to -0.10707 eV in ferrocene and in -0.56142 to -0.10622 eV nickelocene. Eigenvectors of ferrocene and nickelocene show that the first 13 MOs in ferrocene 14 MOs nickelocene are formed by various *3d* orbitals of metal and *2pz* orbital of carbon of $(C_5H_5)^-$and the most stable MOs. The next 9 MOs in ferrocene and 11 MOs of nickelocene are formed by the interaction of 4s and 4p orbitals of metal and*2pz* orbital of carbon of $(C_5H_5)^-$and these MOs are comparatively less stable orbitals. Out of the 3d orbitals of ferrocene and nickelocene molecules the *3dyz* orbitals have maximum involvement in the formation of molecular orbitals, whereas the*4pz* orbital out of *4s* and *4p* orbital of iron and 4pyorbital out of *4s* and *4p* orbital of nickel show maximum involvement, in the order of *4pz >4py >4s >4px* and *3dyz* $>3dx^2-y^2>3dz^2$ *>3dxz* in ferrocene, and *4py >4px >4s >4pz and3dyz* $>3dx^2-y^2>3dxy>3dxz>3dz^2$ in nickelocene.. The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene and 22.8486 in nickelocene hence nickelocene is more stable than ferrocene. The total involvement in relation to the bonding between *2pz*orbital of the ten carbon atoms of both ligands of $(C_5H_5)^-$19.889, and 15.529 in ferrocene and nickelocene respectively, hence ferrocene is more stable than nickelocene. As a summary, the total involvement of *3d,4s* and *4p* orbitals of metal and *2pz* orbitals of the ten carbon atoms of both ligands of $(C_5H_5)^-$in ferrocene and nickelocene respectively are 42.2528 and 38.3776 hence we can conclude that ferrocene is more stable than nickelocene. This is in support of the results shown in terms of the parameters like dipole moment, HOMO-LUMO gap, Ionization potential etc discussed in the above. The population analysis shows that only *2pz* orbitals of carbon of $(C_5H_5)^-$and *3d* orbitals of metal provide electrons to MOs of ferrocene and nickelocene.We recommend to simulate bigger molecules using higher basis sets and to study more properties of the molecules. Larger basis sets provide approximations more accurately by imposing fewer restrictions on the interaction of electrons in space.

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