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Density Functional Study of Molecular Orbitals of Ferrocene and Cobaltocene Molecules

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Abstract

The electronic structure and geometry optimization of ferrocene and cobaltocene 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 the first 13 molecular orbitals in ferrocene and 12 in cobaltocene have contribution from 2pz orbitals of carbon of $(C_5H_5)^-$ and 4s, 4p and 3d orbitals of iron and cobalt respectively. We found that the extent of involvement of metal orbitals in the two cases is different. In ferrocene the maximum involvement out of 4s and 4p orbital is in the order 4pz>4py>4s>4px and out of 3d orbitals the order of involvement is 3dyz>3dxz>$3d^2z$>$3dx^2$-y^2>3dxy. The involvement of corresponding orbital in cobaltocene with respect to the 4s and 4p orbitals is in the order of 4s>4pz>4py>4px and in 3d orbitals the order is $3dx^2$-y^2>3dxz>$3d^2z$>$3dx^2$-y^2 and 4py>4px>4s>4pz molecules. The total involvement of 3d, 4s and 4porbitals of metal and 2pz orbitals of the ten carbon atoms of both ligands of $(C_5H_5)^-$ in ferrocene and cobaltocene respectively are 42.2528 and 40.2388 hence we can conclude that ferrocene is more stable than cobaltocene. 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 cobaltocene.

Keywords: Ferrocene; Cobaltocene; Eigen vector; Population analysis; Eigen values; Atomic and molecular orbitals

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 of eigenvectors, Eigen values and population analysis of ferrocene and cobaltocene in order to study the extent of contribution of 3d, 4s and 4p orbital in the formation of MOs. Such a quantitative study will provide correct information about the involvement of 4p orbital of Iron and cobalt in bonding will help to resolve the controversy raised by other workers [16-23] (Figure 1).

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 per-formed 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. 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 cobaltocene 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.

Results and Discussion

This thesis is aimed to study the electronic structure and optimized geometry of ferrocene and cobaltocene 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 cobaltocene 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 Figures 1A and 1B respectively for ferrocene and cobaltocene. The significant computed

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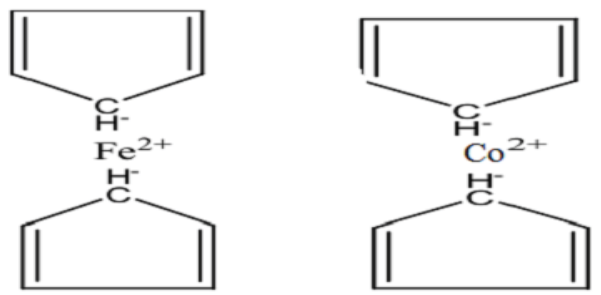

Figure 1: Structure of Ferrocene, and Cobaltocene molecules.

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, and cobaltocene 1.36-1.96°A at DFT/ B3LYP, levels through 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 and cobaltocene and according to its bond length are in the order of C = C<C- C. From Tables 1 and 2 we observe a slight difference in the bond lengths, bond angles and dihedral angles throughout the molecules of ferrocene and cobaltocene. This indicates that the aromatic iron atom in ferrocene and cobalt atom in cobaltocene are relatively stable metabolically.

As shown in Figure 2A and Table 1, due to the effect of the partial charge distribution of iron atom in ferrocene molecule, the bond connectivity of Fe-Cp of the two ligands are asymmetrical. The iron atom in ferrocene is bonded withC12 atom with bond length of 1.954 (°A) in one side of the ligand and C4 with bond length of 1.856(°A) and with C2 atom 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 ofC2-C4 which possess more energy to attract iron atom to-wards itself than the single bond on the other side, hence Fe-C2 and Fe-C4 bonds measure shorter distance than the bond inFe-C12. In the ferrocene molecule the iron atom is located between the two ligands but inclined by -67.604° from the plane of the cyclopentadiene 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.

As shown in Figure 2B and Table 2 the bond connectivity of Co-Cp of the two ligands are asymmetrical. The optimized bond length of cobalt atom with the two carbon atoms has fewer variations. The cobalt atom in cobaltocene is bonded with C_2 atom of bond length 1.969 (°A) in one side of the ligand and with C_{12} of bond length 1.994(°A) on the opposite side. In the cobaltocene molecule the cobalt atom is located between the two ligands but inclined by -80.623˚ measured from the plane of the cyclopentadiene and the two ligands are parallel but with a slide of one from the other by a center of mass separation 1.33°A. Generally comparing the bond length and bond angles between metal atom and carbon in ferrocene and cobaltocene 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 cobaltocene is more reactive and less stable than the others. In the calculations of Mulliken charge distributions of ferrocene and cobaltocene 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) (Figure 3). Energies of molecular

Entry	Bond length (˚A)	Entry	Bond angle (˚A)	Entry	Dihedral angle (˚)
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				

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

Entry	Bond length (˚A)	Entry	Bond angle (˚)	Entry	Dihedral angle (˚)
C1-C2	1.509	C6-C1-C2	109.511	C6-C1-C2-C4	0.027
C1-C6	1.509	C8-C6-C1	109.511	C8-C6-C1-C4	-0.028
C8-C6	1.359	C10-C11-C1	109.511	C10-C11-C14-C16	-78.168
C10-C11	1.509	C10-C12-C1	109.560	C16-C12-C10-C11	84.623
C10-C12	1.509	Co-C2-C1	79.123	Co-C2-C1-C6	-80.623
C11-C14	1.909				
C12-C16	1.559				
C2-C4	1.359				
C4-C8	1.47				

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

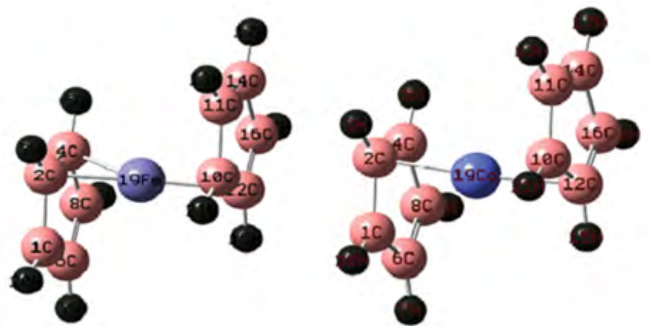

Figure 2: The optimized structures of (A) ferrocene and (B) cobaltocene molecules.

orbitals are called Eigen values. The main focus has been on the molecular structure and the properties that will be evaluated can be used to determine the molecular reactivity as well as the molecular stability. The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are very important aspects to consider for these types of observations. This is because the HOMO and LUMO are the most likely locations where reaction will occur. The reaction is likely to occur there because the electrons in the HOMO have the highest energy and therefore the electrons are most

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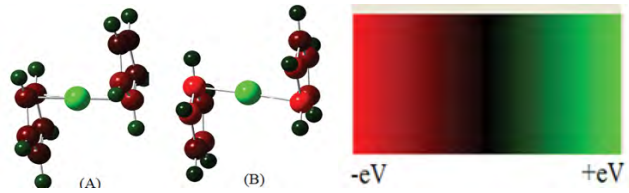

Figure 3: The Milliken charge distributions of (A) ferrocene, (B) cobaltocene Molecules.

willing to react. The LUMO is likely the location for a bond to occur as well because any invading electrons for another molecules will fill in to the LUMO, that is why 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. At the DFT/B3LYP level the HOMO energy of ferrocene is -0.6491 eV which is slightly more negative than the cobaltocene -0.6427 eV and nickelocene of -0.6427 eV and the LUMO energy of ferrocene is -0.5628 eV, and cobaltocene -0.5626 eV. The HOMO-LUMO gap of ferrocene and cobaltocene are 0.0863 and 0.0826 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 cobaltocene molecule. The most stable MO energy of ferrocene and cobaltocene are respectively -254.0054, and -277.5151 -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 the molecules. Hard molecules have large HOMO-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 and cobaltocene molecule, ferrocene is harder than cobaltocene. In Table 3 the HOMO-LUMO gap, as a characteristic of reactivity, shows ferrocene has lower chemical reactivity comparing to cobaltocene molecule. 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 the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap. So for more energetically stable and less reactive ferrocene molecule, the HOMO-LUMO energy gap and hardness, η is larger comparing to cobaltocene molecules. The dipole moments and Mulliken charge ranges as displayed in Table 3, cobaltocene would have more charge than the ferrocene molecule. This is due to higher dipole moment and lower HOMO-LUMO energy gap indicated that the molecule is better reactive. This indicates that cobaltocene is 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 to accept 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 Cobaltocene (Figure 4). Figure 3 shows the visualized structures of ferrocene and cobaltocene show the population of electrons on their orbitals. The HOMO orbitals

Molecular properties	Ferrocene	Cobaltocene
RB-HF-LYP (eV)	-1896.275	-1769.5679
εHOMO(eV)	-0.6491	-0.6452
εLUMO(eV)	-0.5628	-0.5626
εLUMO-εHOMOenergy gap (eV)	0.0863	0.0826
Ionization potential (I in eV)	0.6491	0.6452
Electron affinity (A in eV)	0.5628	0.5626
Global hardness (ηin eV)	0.0431	0.04129
Global softness (Sin eV)	23.1803	24.216
Electro negativity (χin eV)	0.60591	0.6039
Chemical potential (μin eV)	-0.6059	-0.6039
Dipole moment (μin Debye)	1.464	1.695
Mulliken charge distributions (M.C.D in e)	± 1.093	± 1.13

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

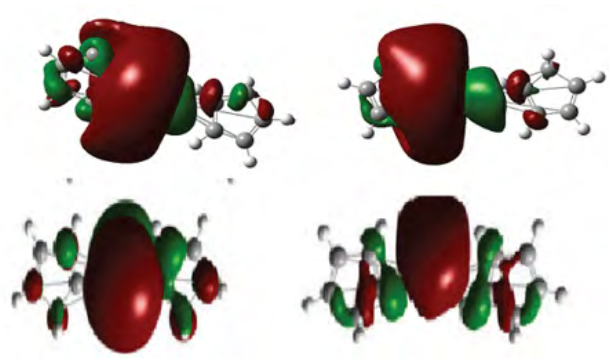

Figure 4: The left side of HOMO and the right side of LUMO surfaces of ferrocene and cobaltocene compounds, down of the column respectively.

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, cobaltocene molecule are concentrated throughout the compound except at the right and left terminals where some 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 cobaltocene are formed by linear combination of fifty AOs of two $(C_5H_5)^-$and nine orbital of iron and cobalt. These fifty-nine AOs χ1 to χ59 on LCAO approximation form same number of MOs, Φ1 to Φ59. The AOs χ1 to χ40 for 2s, 2px, 2py, 2pz of 1C to 10C, χ41 to χ49 for 4s, 4px, 4py, 4pz,$3dx^2$-y2, $3d^2$z, 3dxy, 3dxz, 3dyz of 11M and χ50 to χ59 for 1s of 12H to 21H respectively, where M = Fe and Co, for ferrocene and cobaltocene, respectively. The 2s, 2px and 2py orbitals of each carbon atom of $(C_5H_5)^-$are involved in the formation of σ bond between C-C and C-H. The orbitals involved in σ bond hence shall remain out of discussion. The 2pz orbitals of ten carbons and nine orbitals of iron or cobalt i.e., in total nineteen orbitals are relevant to our discussion in respect of bonding between iron or cobalt orbitals and 2pz orbital of $(C_5H_5)^-$. These atomic orbitals are χ4, χ8, χ12, χ16, χ20, χ24, χ28, χ32, χ36 and χ40 of carbon and χ41 to χ49 of iron and cobalt. The coefficients of these orbitals are the eigenvector values of χ. They express the forms of MOs i.e., the extent of involvement of χ in 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 Table 4 to 1.11 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 of χ in the formation of Φ. The calculated Eigen vector values of atomic orbitals of Fe and Co in the formation of molecular orbitals in ferrocene and cobaltocene in Tables 4, 5, 8 and 9 respectively and the calculated Eigen vector values of 2pz orbital of carbon are given in Tables 6, 7, 10 and 11. Tables 5 and 7 are summation of Eigen vector values of ferrocene and cobaltocene. Negative, Zero and near zero coefficient values are negligible contributions of electrons and have been excluded from the Tables. Out of the 59 molecular orbitals of ferrocene molecule only 22 molecular orbitals shall be 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 Φ35 are formed by only two atomic orbitals, 3d orbital of iron and 2pz orbital $(C_5H_5)^-$. These orbitals are the most stable molecular orbital and have their energies in the range -2.03849 to -0.54008 eV. The next nine

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	-	-	-	-	-	-
S	2.9498	2.1483	3.101	3.8741	2.375	2.1071	1.3597	2.0227	2.601

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.

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

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

molecular orbital Φ36-Φ37, Φ40-Φ41, Φ43, Φ50-Φ51, Φ54-Φ55 have formed from contribution of vacant 4s, 4px, 4py and 4pz orbital of the iron and 2pz orbital 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 4p orbital in the formation of molecular orbitals the values of coefficient of each orbital have been added as shown in Table 5. 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 4porbitals, and 3dyz orbital has the maximum involvement out of the 3d orbital. The exact order of availability of atomic orbital 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>$3d^2$z>3dxz>3dxy

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>$3d^2$z>$3dx^2$-y^2>3dyz

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

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

Out of 59 molecular orbital Eigen values of cobaltocene we shall discuss only 24 of them described in Table 8. For cobalt orbitals and Table 10 for carbon orbitals. The first 12MOs are Φ20-Φ31formed by various 3d orbital of cobalt and 2pz orbital of $(C_5H_5)^-$. These orbital with energies in the range of -0.86738 to -0.56256 eV are the most stable molecular orbitals. The next 12 molecular orbitals are Φ36-Φ38, Φ41-Φ42, Φ46-Φ47, Φ50-Φ51; Φ54-Φ55 and Φ56 have contributions from vacant 4s, 4px, 4py and 4pz orbital of cobalt and 2pz orbital of carbon. These MOs with energies between -0.37685 to -0.03634 eV are comparatively less stable. To examine the extent of involvement of 3d, 4s, and, 4p orbital in the formation of molecular orbital the values of coefficient of each orbital have been added to see the total involvement in all the 24 molecular orbital shown in Table 9. The summation values given in Table 9 and plotted in Figure 7 show the total contributions from each atomic orbital. It is clearly indicated that 4s 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:

4s>4pz>4py>4px and 3dyz>3dxy>3dxz>3d2z>$3dx^2$-y^2

Sum of contributions of atomic orbitals of cobalt in the formation

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MOs	1C	2C	4C	6C	8C	10C	11C	12C	14C	16C
	$\chi 4$	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	-	-	-
S	2.2594	2.3582	1.6466	1.8916	1.8301	1.2089	2.3373	2.3034	1.2575	2.776

Table 6: Contributions of 2pz orbitals 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.

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

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

MOs	4s	4px	4py	4pz	$3dx^2$-y^2	$3dz^2$	3dxy	3dxz	3dyz
	$\chi 41$	$\chi 42$	$\chi 43$	$\chi 44$	$\chi 45$	$\chi 46$	$\chi 47$	$\chi 48$	$\chi 49$
Φ20	-	-	-	-	-	-	-	-	0.2124
Φ21	-	-	-	-	-	-	-	0.2335	0.3224
Φ22	-	-	-	-	-	-	0.2113	-	-
Φ23	-	-	-	-	0.2507	0.4737	0.2664	0.2327	0.1436
Φ24	-	-	-	-	0.5537	0.1378	0.4186	0.1448	0.2731
Φ25	0.1198	-	-	-	-	0.5281	-	0.3033	0.5717
Φ26	-	-	-	-	0.2652	0.1081	0.5281	0.3717	0.3035
Φ27	-	-	-	-	0.1445	-	0.2931	0.2063	-
Φ28	-	-	-	-	0.1103	0.1402	0.2339	-	0.2297
Φ29	-	-	-	-	-	0.2052	0.2116	0.1243	-
Φ30	-	-	-	-	-	0.5131	0.2416	0.3996	0.1363
Φ31	-	-	-	-	0.3741	-	-	0.3523	0.4225
Φ36	0.3346	0.9288	-	0.4070	-	-	-	-	-
Φ37	0.3259	-	0.8777	0.5650	-	-	-	-	-
Φ38	0.6188	-	-	0.2691	-	-	-	-	-
Φ41	0.3195	-	0.3626	0.4823	-	-	- -	-	-

Φ42	0.3148	-	0.3549	0.3479	-	-	-	-	-
Φ46	0.2767	0.3026	-	0.3002	-	-	-	-	-
Φ47	0.3329	-	0.2698	0.2911	-	-	-	-	-
Φ50	0.7259	-	0.2913	0.3794	-	-	-	-	-
Φ51	0.5741	0.5317	0.3413	0.7871	-	-	-	-	-
Φ54	-	0.2380	0.2945	0.2227	-	-	-	-	-
Φ55	0.3738	0.2889	0.3878	-	-	-	-	-	-
Φ56	0.2297	-	-	-	-	-	-	2.3685	-
S	4.4267	2.29	3.1799	4.0518	1.6985	2.1062	2.4046	-	2.6152

Table 8: Contributions of orbitals of cobalt and their summation values in the formation of molecular orbitals of cobaltocene. SS of 4s and 4p orbital=13.9484. And 3d orbitals=11.193. N.B; Orbitals having coefficient values above 0.10 have only been considered.

Atomic orbital's of Co	Sum of contributions of orbital's of Co	Sum of reactivity
4s	4.5465	0.2199
$4p_x$	2.29	0.4367
$4p_y$	3.1799	0.3145
$4p_z$	4.0518	0.2468
$3dx^2$-y^2	1.6985	0.58875
$3d^2_z$	2.1062	0.4748
$3d_{xy}$	2.4046	0.4159
$3d_{xz}$	2.3685	0.4222
$3d_{yz}$	2.6152	0.3824

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

MOs	1C	2C	4C	6C	8C	10C	11C	12C	14C	16C
	X^4	X^8	X^{12}	X^{16}	X^{20}	X^{24}	X^{28}	X^{32}	X^{36}	X^{40}
Φ20	0.3731	-	-	-	-	-	-	-	-	-
Φ21	-	-	-	-	-	0.3214	-	-	-	-
Φ22	-	-	-	-	-	-	-	0.3794	-	-
Φ23	0.1117	-	-	0.2610	-	0.1332	-	0.1701	0.1118	-
Φ24	-	-	0.1153	-	-	0.1220	-	0.1060	-	-
Φ25	-	-	-	0.1338	-	0.1464	-	-	-	-
Φ26	-	0.1818	-	0.1756	-	-	-	-	-	0.1472
Φ27	-	0.3281	0.2463	0.2716	0.2181	0.2369	0.2113	-	-	0.1374
Φ28	0.2825	-	0.2548	0.1501	0.1591	0.2836	0.2755	-	0.2362	-
Φ29	-	0.2024	0.1605	-	0.1336	0.1537	0.1515	-	-	0.3061
Φ30	0.2899	-	0.2750	0.1276	0.2474	0.2537	-	0.2649	0.1558	0.2073
Φ31	0.2835	0.3653	-	0.2853	0.2495	-	0.2476	-	-	-
Φ36	-	0.2348	-	-	-	-	-	0.2304	-	-
Φ37	-	-	-	0.2413	-	-	0.2212	-	-	-
Φ38	-	-	-	0.5191	-	0.1146	-	0.1874	0.2835	-
Φ41	0.2925	-	-	0.5471	0.2847	-	-	-	-	-
Φ42	-	-	-	-	-	-	-	-	-	-
Φ46	-	-	-	-	-	0.2580	-	-	0.260	-
Φ47	-	-	-	0.3743	-	-	-	-	-	-
Φ50	-	-	-	0.2733	-	-	-	-	-	0.2233
Φ51	-	-	-	-	-	-	-	-	-	0.5771
Φ54	-	-	-	-	0.2218	-	-	-	-	-
Φ55	-	-	-	-	-	-	-	-	-	-
Φ56	-	-	-	-	-	-	-	-	-	-
S	1.6332	1.3124	1.0519	3.3601	1.5142	2.0235	1.1071	1.3382	1.0473	1.5984

Table 10: Contributions of 2pz orbitals of carbon atoms in $(C_5H_5)^-$ and their summation values in the formation of molecular orbitals of cobaltocene. SS of, 2pz orbitals=15.9863. N.B; orbital having coefficient value above, 0.10 have only been considered.

of molecular orbitals of cobaltocene is shown in Table 9 and Figure 7 that the sum of contributions of $3dx^2$-y^2 orbital in the formation of molecular orbitals is least out of the 3d orbitals and 4px orbital is least out of 4s and 4p orbitals. Hence $3dx^2$-y^2 and 4px are comparatively free for complex formations. The exact order of availability of atomic orbitals of Co in cobaltocene for complex formation is given below;

4px>4py>4pz>4s and $3dx^2$-y^2>$3dz^2$>3dxz>3dxy>3dyz

The summation values shown in Table 11 and Figure 8 clearly indicates that contribution of 2pz orbital of 6C has the maximum

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Atomic orbital's of carbon	Sum of contribution of carbon orbital's	Sum of reactivity
1C	1.6332	0.6123
2C	1.3124	0.7619
4C	1.0519	0.9507
6C	3.3601	0.2976
8C	1.5142	0.6604
10C	2.0235	0.4942
11C	1.1071	0.9033
12C	1.3382	0.7473
14C	1.0473	0.9549

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

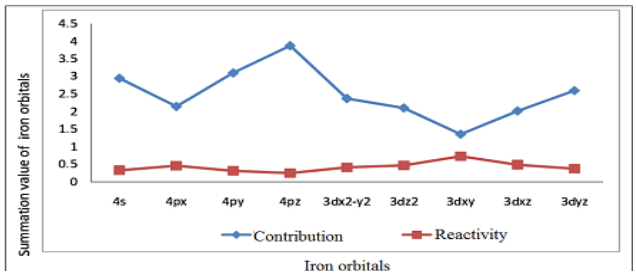

Figure 5: Sum of contributions and reactivity of atomic orbitals of, iron in the formation of molecular orbitals of ferrocene

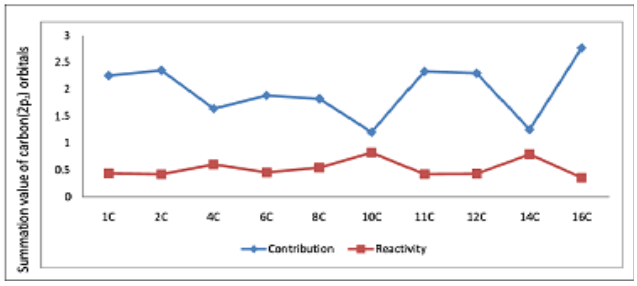

Figure 6: Sum of contributions and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of ferrocene.

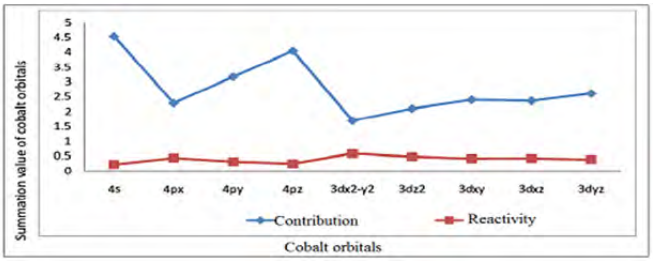

Figure 7: Sum of contributions and reactivity of atomic orbital's of cobalt in the formation of molecular orbitals of cobaltocene.

involvement out of the ten carbon atoms in $(C_5H_5)^-$. The sequence from the three series are given below:

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

Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of cobaltocene is shown in Table 11 and

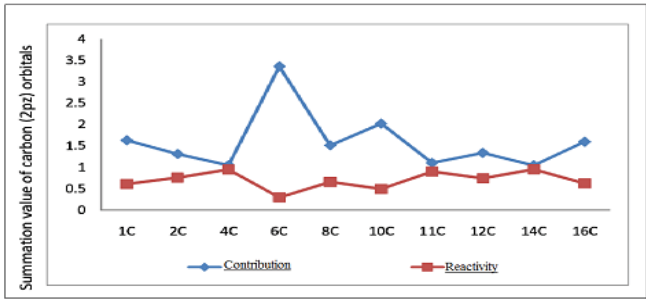

Figure 8: Sum of contributions and reactivity of atomic orbital's of Co in the formation of molecular orbitals of cobaltocene.

Figure 8 where the sum of contribution of 14C of 2pz orbital's in the formation of molecular orbitals are least out of the ten carbon atoms. Hence 14C are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:

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

The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene, and 24.2528 in cobaltocene hence cobaltocene 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 15.986 in ferrocene and cobaltocene respectively, hence ferrocene is more stable than cobaltocene. 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 cobaltocene respectively are 42.2528, and 40.2388 hence we can conclude that ferrocene is more stable than cobaltocene and nickelocene.

Population analysis

The contribution of electrons in each occupied MO is calculated by using the population analysis method introduced by Mulliken. This method apportions the electrons of n-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 in the MO Φ_i to the net population in χ_r we have:

$$n_{ri}=n_i c^2_{ri}$$

Where, c_{ri} is the coefficient of atomic orbital for the i^{th}MO r=1-29 in ferrocene and r=1-30 in cobaltocene. Equation 4.1 has been solved for, 58 electrons of 29 molecular orbitals in ferrocene and 59 electrons of 30 molecular orbitals in cobaltocene. Each MOs has two electrons in ferrocene and cobaltocene but (the 30th MOs of cobaltocene has only

one electron). The coefficient of atomic orbital c_{ri} is treated as Eigen vector value. 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 Table 12 of cobaltocene. It is indicated that in MOs 1-17 of ferrocene, in MOs 1-19 of cobaltocene, only 2s, 2py and 2px electrons of carbon have contributions in the formation of molecular orbital of ferrocene and cobaltocene 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 orbitals of metal provide electrons to MOs of ferrocene, and cobaltocene. Figure 8. clearly indicates that occupied molecular orbitals of ferrocene are more electrons population contribution for the formation of molecular orbitals than cobaltocene molecule.

Conclusion

We studied the electronic structure and geometry optimization of ferrocene and cobaltocene 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 -0.86738 to -0.56256 eV in cobaltocene) 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 -0.37685 to -0.03634 eV in cobaltocene. Eigenvectors of ferrocene and cobaltocene show that the first 13 MOs in ferrocene 12 MOs cobaltocene 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 12 MOs of cobaltocene 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 cobaltocene 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 4s orbital out of 4s and 4p orbital of cobalt show maximum involvement, in the order of 4pz>4py>4s>4px and $3dyz>3dx^2-y^2>3dz^2>3dxz$ in ferrocene, and 4s>4pz>4py>4px and $3dyz>3dxy>3xz>3dz^2>3dx^2-y^2$ in cobaltocene. The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene and 24.2528 in cobaltocene hence cobaltocene 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 15.986 in ferrocene and cobaltocene respectively, hence ferrocene is more stable than cobaltocene. 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 cobaltocene respectively are 42.2528 and 40.2388 hence we can conclude that ferrocene is more stable than cobaltocene. 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 cobaltocene.

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 offerrocene is 10.3302

Table 12: The Sum of contribution of electrons 3d orbitals of iron and 2pz orbitals of carbon 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})
Φ20	2	0.5855	4	0.3344
Φ21	3	0.8773	6	0.5154
Φ22	2	0.5907	4	0.3470
Φ23	10	2.1549	20	1.2661
Φ24	8	1.8713	16	1.0994
Φ25	6	1.8031	12	1.0593
Φ26	8	2.6812	16	1.3475
Φ27	10	2.2936	20	1.1527
Φ28	11	2.3559	22	1.1829
Φ29	9	1.6489	18	0.8279
Φ30	12	2.9759	12	0.9391

Sum of Summation value of population analysis, (n_{ri}) of occupied molecular orbital of cobaltocene is 10.0715

Table 13: The Sum of contribution of electrons, 3d orbitals of iron and, 2pz orbitals of carbon in the formation of molecular orbitals of cobaltocene.

Recommendation

We recommend higher capacity computing facilities 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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