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A New Study On Molecular Structure Of Ferrocene

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ABSTRACT

The molecular orbitals of ferrocene are formed by linear combination of 50 orbitals of two $C_5H_5^-$ and 9 orbitals of iron but only 19 molecular orbitals comprising nine orbitals of iron (3d, 4s, 4p) and ten p orbitals of carbon of two C_5H_5, have been studied quantitatively. The summation of eigen vector values shows the order of involvement of various metal orbitals as 4pz (3.1559) > 4py (3.101) > 4s (2.8046) > 4px (2.1483) > 3dyz (2.1293) > 3dxz (1.7494) > $3dz^2$ (1.6924) > $3dx^2$-y^2 (1.4940) > 3dxy (1.3597). The energy level diagram has also been drawn; the eigen values indicate that energies of ten lowest molecular orbitals are in the range -0.4898 to -0.2314 ev.

KEYWORDS

Ferrocene;
Population analysis;
Eigen vector;
Eigen value;
Molecular orbital;
Atomic orbital.

INTRODUCTION

The sandwich structure of ferrocene was established by crystographic studies in 1956, and valence bond structure was suggested by Fisher as well as by Dunitz and Orgel. Qualitative molecular orbital diagram was also proposed[1,2]. The calculation of the relative energy levels and involvement of various atomic orbital in the formation of molecular orbital is still a subject of uncertainty[2]. There is a scope in respect of making a detail calculation of molecular orbital parameter of ferrocene and its congener. In recent years attempts have been made to make detail study of atomic and molecular orbitals of transition metal compounds with the help of computational chemistry and in this connection a special volume has been published by chemical review[3]. Application of molecular mechanic[4] to organomettalic and transition metal compounds is growing; hence we have used this technique in our study.

We in this paper present a study on the eigen values, eigen vector and population analysis of fer-

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rocene in order to examine the extent of involvement of 3d, 4s and 4p orbitals of iron and also to give a quantitative support to molecular orbital diagram.

Theory

The 3D modeling and geometry optimization of ferrocene have been done by CAChe software using molecular mechanics with EHT option. Eigen values and eigen vectors values have been obtained with the same software, using the same option. With the help of these values, eigen vector analysis and magnitude of contribution of atomic orbital in MO formation have been made and discussed.

The MOs are formed by the linear combination of basis functions. Most molecular quantum mechanical methods (such as-SCF, CI etc.) begin the calculation with the choice of a basis functions χ_r, which are used to express the MOs ϕ_i as $\phi_i = \Sigma_i c_{ri} \chi_r$. The use of an adequate basis set is an essential requirement for the calculation. The basis functions are usually taken as AOs. Each AO can be represented as a linear combination of one or more Slater-type orbitals (STOs)[5-7]. An STO centered on atom **a** has the form $(Nr_a^{n-1} e^{-\zeta r a} Y_l^m(\theta_a, \phi_a)$. Each MO ϕ_i is expressed as $\phi_i = \Sigma_i c_{ri} \chi_r$, where, the $\chi_{r's}$ are the STO basis functions. Here we use the STO–6G basis set (which is contracted Gaussian)[8-11] for the SCF calculation.

The coefficients in linear combination for each MO being found by solution of the Roothaan equation [12]. The most efficient way to solve the Roothaan equation is to use matrix–algebra methods. In matrix–algebra methods, the matrix elements are computed[13], and the secular equation is solved to give the set of orbital energies (i.e. eigen values). These orbital energies[14] are used to solve Roothaan equations for the set of coefficients (i.e. eigen vectors) giving a set of MOs. The calculations are done using a computer.

By the above calculation, the values of orbital energies (eigen values) and eigen vectors (coefficients) have been calculated.

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken [15-16]. He proposed a method that apportions the electrons of an n–electron molecule into net populations n_r in the basis functions χ_r and overlap populations n_{r-s} for all possible pairs of basis functions.

For the set of basis functions χ_1, $\chi_{2...}$ χ_b, each MO ϕ_i has the form $\phi_i = \Sigma_s c_{si} \chi_s = c_{1i}\chi_1 + c_{2i}\chi_2 + ... + c_{bi}\chi_b$. For simplicity, we shall assume that the c_{si}'s and χ_s's are real. The probability density associated with one electron in ϕ_i is

$$|\phi_i|^2 = c_{1i}^2\chi_1^2 + c_{2i}^2\chi_2^2 + ... + 2c_{1i}c_{2i}\chi_1\chi_2 + 2c_{1i}c_{3i}\chi_1\chi_3 + 2c_{2i}c_{3i}\chi_2\chi_3 + ...$$

Integrating this equation over three-dimensional space and using the fact that ϕ_i and the χ_s's are normalized, we get

$$1 = c_{1i}^2 + c_{2i}^2 + ... + 2c_{1i}c_{2i}S_{12} + 2c_{1i}c_{3i}S_{13} + 2c_{2i}c_{3i}S_{23} + ... \quad (A)$$

Where the S's are overlap integrals: $S_{12} = \int \chi_1\chi_2 d\nu_1 d\nu_2$, etc. Mulliken proposed that the terms in (A) be apportioned as follows. One electron in the MO ϕi contributes c_{1i}^2 to the net population in χ_1, c_{2i}^2 to the net population in χ_2, etc., and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between χ_1 and χ_2, $2c_{1i}c_{3i}S_{13}$ to the overlap population between χ_1 and χ_3, etc.

Let there be n_i electrons in the MO ϕ_i (n_i = 0, 1, 2) and let $n_{r,i}$ and $n_{r\text{-}s,i}$ symbolize the contributions of electrons in the MO ϕ_i to the net population in χ_r and to the overlap population between χ_r and χ_s, respectively. We have

$$n_{r,i} = n_i c_{ri}^2, \qquad n_{r\text{-}s,i} = n_i(2c_{ri}c_{si}S_{rs})$$

Based on the above principle, the contribution of electrons in each occupied MO has been calculated with the help of eigen vector values.

RESULT AND DISCUSSION

The ferrocene has a sandwich structure and its optimized geometry as obtained from molecular mechanics method is shown in figure 1.

The molecular orbitals of ferrocene are formed by linear combination of 50 orbitals of $C_5H_5^-$ and 9 orbital of iron, as detailed in TABLE 1. The 59 atomic orbitals give LCAO approximation to 59 molecular orbitals. The eigen values of MOs are included in TABLE 2. The atomic orbitals are represented by χ and MOs by ϕ. 1-40χ are atomic orbit-

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TABLE 1: Atomic orbitals (χ) of ferrocene

χ	Atom	AO	χ	Atom	AO	χ	Atom	AO	χ	Atom	AO
1	1C	2S	16	4C	2Pz	31	8C	2Py	46	11Fe	3Dz2
2	1C	2Px	17	5C	2S	32	8C	2Pz	47	11Fe	3Dxy
3	1C	2Py	18	5C	2Px	33	9C	2S	48	11Fe	3Dxz
4	1C	2Pz	19	5C	2Py	34	9C	2Px	49	11Fe	3Dyz
5	2C	2S	20	5C	2Pz	35	9C	2Py	50	12H	1S
6	2C	2Px	21	6C	2S	36	9C	2Pz	51	12H	1S
7	2C	2Py	22	6C	2Px	37	10C	2S	52	12H	1S
8	2C	2Pz	23	6C	2Py	38	10C	2Px	53	12H	1S
9	3C	2S	24	6C	2Pz	39	10C	2Py	54	12H	1S
10	3C	2Px	25	7C	2S	40	10C	2Pz	55	12H	1S
11	3C	2Py	26	7C	2Px	41	11Fe	2S	56	12H	1S
12	3C	2Pz	27	7C	2Py	42	11Fe	2Px	57	12H	1S
13	4C	2S	28	7C	2Pz	43	11Fe	2Py	58	12H	1S
14	4C	2Px	29	8C	2S	44	11Fe	2Pz	59	12H	1S
15	4C	2Py	30	8C	2Px	45	11Fe	3Dx2-y2			

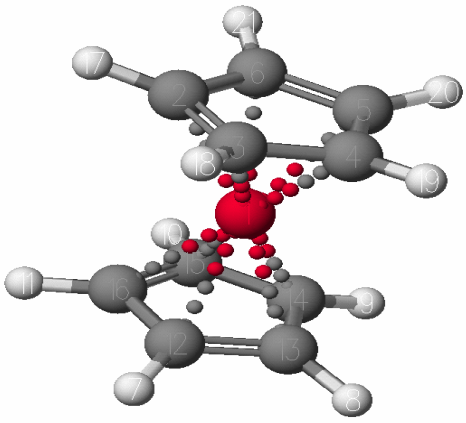

Figure 1

als of carbon, 41-49χ of iron and 50-59χ of hydrogen.

The population analysis as discussed later indicates that 2s and 2px, 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 bonding are not of interest, hence shall remain out of our discussion. The 2pz orbitals of ten carbons and nine orbital of iron, which is in total 19 orbitals, are relevant to our discussion in respect of bonding between iron orbital and 2pz orbital of $C_5H_5^-$. These atomic orbitals are $\chi_4, \chi_8, \chi_{12}, \chi_{16}, \chi_{20}, \chi_{24}, \chi_{28}, \chi_{32}, \chi_{36}, \chi_{40}$ of carbon and χ_{41}-χ_{49} of iron. The co-

TABLE 2: Eigen values of molecular orbitals (ϕ) of ferrocene

MO(ϕ)	Eigen values	MO(ϕ)	Eigen values	MO(ϕ)	Eigen values	MO(ϕ)	Eigen values
1	-1.1084	16	-0.5265	31	-0.3273	46	0.4071
2	-1.0916	17	-0.5234	32	-0.2775	47	0.4112
3	-0.9049	18	-0.5187	33	-0.2565	48	0.431
4	-0.9018	19	-0.5131	34	-0.2323	49	0.4315
5	-0.8728	20	-0.5129	35	-0.2314	50	0.4732
6	-0.8666	21	-0.5087	36	-0.0656	51	0.5249
7	-0.6916	22	-0.5074	37	-0.031	52	0.7326
8	-0.6895	23	-0.4898	38	0.0985	53	0.763
9	-0.6799	24	-0.4831	39	0.0996	54	1.048
10	-0.6792	25	-0.4608	40	0.1246	55	1.128
11	-0.6078	26	-0.4541	41	0.1454	56	2.0102
12	-0.6044	27	-0.4505	42	0.1816	57	2.0624
13	-0.5468	28	-0.4464	43	0.1873	58	2.2399
14	-0.5456	29	-0.4402	44	0.2782	59	2.2436
15	-0.5389	30	-0.3694	45	0.2796		

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TABLE 3: Eigen vector values of orbitals of iron in 19 MOs of ferrocene and their summation values

MOs	4s	4px	4py	4pz	$3dx^2-y^2$	$3dz^2$	3dxy	3dxz	3dyz
	χ_{41}	χ_{42}	χ_{43}	χ_{44}	χ_{45}	χ_{46}	χ_{47}	χ_{48}	χ_{49}
ϕ_{23}					0.4708			0.2893	0.2288
ϕ_{24}							0.2847	0.4762	0.2718
ϕ_{25}					0.6472				0.3147
ϕ_{26}						0.2269	0.8185		
ϕ_{27}						0.5776	0.2565		0.4672
ϕ_{28}					0.3760				
ϕ_{29}						0.5383			
ϕ_{30}						0.3496		0.5271	0.3891
ϕ_{31}								0.4573	0.4577
ϕ_{35}					0.2392				
ϕ_{36}		0.7335	0.6722	0.4698					
ϕ_{37}	0.5031	0.7533	0.6885						
ϕ_{40}	0.7981		0.2865						
ϕ_{41}			0.2780	0.7412					
ϕ_{43}				0.3154					
ϕ_{50}	0.9232								
ϕ_{51}			0.3489	0.9974					
ϕ_{54}		0.2810	0.3923	0.6228					
ϕ_{55}	0.5802	.03805	0.4346						
Summation Values	2.8046	2.1483	3.101	3.1559	1.4940	1.6924	1.3597	1.7499	2.1293

N.B. Orbitals having eigen vector values above 0.22 have only been considered

efficients of these orbitals are the eigen vector values of χ which have been evaluated by molecular mechanics method using Cache software. They express the forms of molecular orbital that is the extent of involvement of χ in the formation of ϕ. These values are included in TABLE 3, for metal orbitals and TABLE 4 for 2pz orbitals of carbon. The zero or near zero values have been excluded from the TABLE.

The first ten molecular orbitals, that is $\phi_{23\text{-}31}$ and ϕ_{35}, have contributions from 3d orbitals of the metal, and 2pz orbitals of different carbon atoms of two $C_5H_5^-$. The remaining nine molecular orbitals (ϕ_{36}-ϕ_{37}, ϕ_{40}-ϕ_{41}, ϕ_{43}, ϕ_{50}-ϕ_{51}, ϕ_{54}-ϕ_{55}) have contribution from vacant 4s, and 4px, 4py and 4pz orbitals of the metal, and 2pz orbitals of carbon. To examine the extent of involvement of 3d, 4s and 4p orbitals in the formation of molecular orbitals the values of coefficient of each orbital have been added to see the total involvement in all the 19 molecular orbitals. The summation values are placed at the bottom of the TABLE, and the total contribution from each atomic orbital is shown in figure 2. It is clearly indicated that 4pz orbital has the maximum involvement out of 4s and 4p orbitals, and 3dyz orbital has the maximum involvement from the 3d orbitals. The sequence from the two series is as below.

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

Eigen values

The eigen values of 59 molecular orbitals of ferrocene are listed in TABLE 2, out of which we shall discuss only 19 molecular orbitals described in TABLE 3 and 4. The first ten MOs are formed by various 3d orbitals and 2pz orbitals $C_5H_5^-$ radicals. These orbitals are the most stable molecular orbitals

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TABLE 4: Eigen vector values of 2pz orbitals of ten carbon atoms of both the $C_5H_5^-$ in 19 molecular orbitals of ferrocene and their summation values

MOs	1c	2c	3c	4c	5c	6c	7c	8c	9c	10c
	χ_4	χ_8	χ_{12}	χ_{16}	χ_{20}	χ_{24}	χ_{28}	χ_{32}	χ_{36}	χ_{40}
ϕ_{23}		0.2151		0.2796			0.2336			0.2841
ϕ_{24}	0.2133							0.2312		
ϕ_{25}	0.2062		0.2511							
ϕ_{26}			0.1668							
ϕ_{27}		0.2685					0.2273			
ϕ_{28}		0.2347		0.2169		0.3799	0.2591	0.2011	0.3185	
ϕ_{29}		0.3310			0.2399		0.2523			0.2543
ϕ_{30}	0.2886		0.3015			0.2907		0.2767		
ϕ_{31}	0.2644	0.3474			0.3104		0.3409	0.2797	0.3116	
ϕ_{35}	0.4567	0.4381			0.3623		0.4564	0.4820	0.3912	
ϕ_{36}	0.2629									0.2243
ϕ_{37}		0.2973					0.2673	0.2552		
ϕ_{40}				0.3089						0.3653
ϕ_{41}	0.2114			0.2234						0.2387
ϕ_{43}				0.2661						
ϕ_{50}				0.4338						0.3828
ϕ_{51}				0.3149						0.3416
ϕ_{54}					0.1856					
ϕ_{55}							0.3004			
Summation Values	2.1382	1.1119	0.9363	1.8267	0.7359	0.6706	1.8809	1.4492	1.0213	2.0911

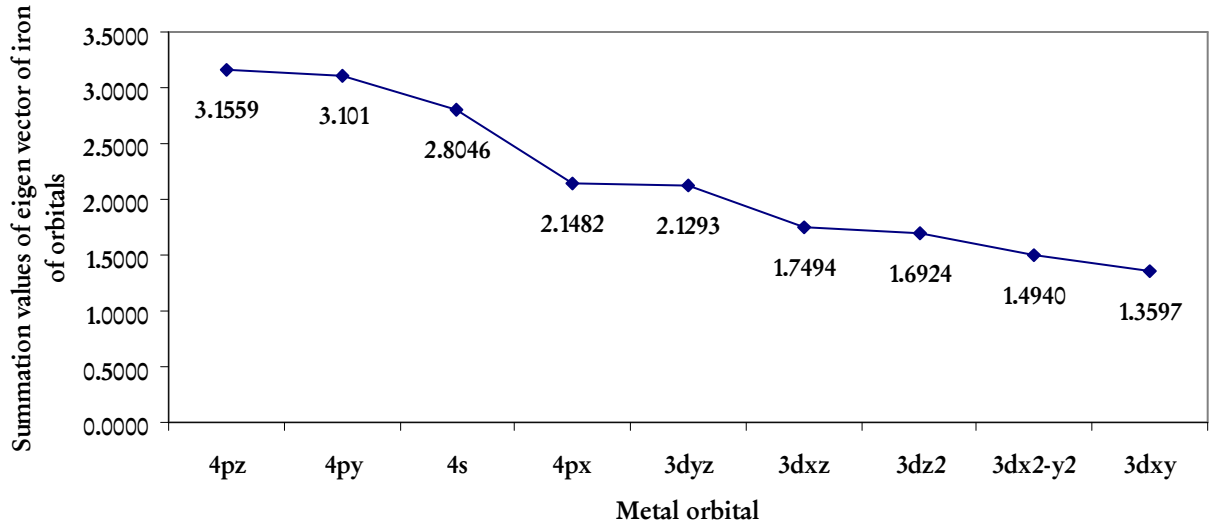

Figure 2: Graphical representation of involvement of 3d, 4s, 4p orbital of iron in ferrocene

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and have their energies in the range –0.4898 to –0.2314 ev. The contribution of 3d metal and 2pz of carbon in the formation of ten MOs is described as below.

ϕ_{23} - χ_{48},χ_{49},χ_{45},χ_{8},χ_{16},χ_{28},χ_{40}.
ϕ_{24} - χ_{48}, χ_{49}, χ_{45}, χ_{4},χ_{12},
ϕ_{25} - χ_{49},χ_{45},χ_{4}, χ_{12},
ϕ_{26} - χ_{47},χ_{46},χ_{12},
ϕ_{27} - χ_{47}, χ_{49}, χ_{8},χ_{28},
ϕ_{28} - χ_{45},χ_{4}, χ_{12}, χ_{24},χ_{28},χ_{32},χ_{36}.
ϕ_{29} - χ_{46},χ_{8}, χ_{12},χ_{28}, χ_{40},
ϕ_{30} - χ_{48},χ_{49},χ_{46},χ_{4},χ_{12}, χ_{24},χ_{32}
ϕ_{31} - χ_{48},χ_{49},χ_{4}, χ_{8}, χ_{20},χ_{28},χ_{36},
ϕ_{35} - χ_{45},χ_{4},χ_{8}, χ_{20},χ_{28},χ_{32},χ_{36}

The next nine molecular orbitals are formed by interaction of 4s, 4px, 4py, and 4pz orbitals of metal and 2pz orbitals of carbon. These MOs are comparatively less stable and have their energies between –0.0656 and 1.1280 ev. The contribution of various atomic orbitals in the formation of molecular orbitals is presented below.

ϕ_{36} - χ_{42}, χ_{43}, χ_{44}, χ_{4}, χ_{40},
ϕ_{37} - χ_{41}, χ_{42}, χ_{43}, χ_{8}, χ_{28}, χ_{32},
ϕ_{40} - χ_{41}, χ_{43}, χ_{16}, χ_{40},
ϕ_{41} - χ_{43}, χ_{44}, χ_{4}, χ_{16}, χ_{40},
ϕ_{43} - χ_{44}, χ_{16},
ϕ_{50} - χ_{41}, χ_{16}, χ_{40},
ϕ_{51} - χ_{43}, χ_{44}, χ_{16}, χ_{40},
ϕ_{54} - χ_{42}, χ_{43}, χ_{44}, χ_{20},
ϕ_{55} - χ_{41}, χ_{42}, χ_{43}, χ_{28},

Energy level diagram has been drawn for representing molecular orbital, their eigen values and involvement of atomic orbitals and is shown in figure 3.

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 into net population n_r in the basis function χ_r. Let there be n_i electrons in the MO ϕ_i (n_i = 0, 1, 2) and let $n_{r,i}$ symbolize the contribution of electrons in the MO ϕ_i to the net population in χ_r, we have

$$n_{r,i} = n_i c^2_{ri} \quad \text{.....Eq. 1}$$

Where, c_{ri} is the coefficient of atomic orbitals for the i^{th} MO (r = 1-29).

Eq.-1, has been solved for 58 electrons of 29

Molecular orbital (ϕ)	Eigen values (e.v.)	Energy Levels	Atomic orbitals (χ)
55	1.1280		Fe(4s,4px,4py) C(2pz)
54	1.0480		Fe(4p), C(2pz)
51	0.5249		Fe(4py.4pz), C(2pz)
50	0.4732		Fe(4s), C(2pz)
43	0.1873		Fe(4pz), C(2pz)
41	0.1454		Fe(4pz,4py), C(2pz)
40	0.1246		Fe(4s,4py), C(2pz)
37	-0.031		Fe(4s,4px,4py), C(2pz)
36	-0.0656		Fe(4p), C(2pz)
35	-0.2314		Fe(3dx2-y2), C(2pz)
31	-0.3273		Fe(3dxz,3dyz), C(2pz)
30	-0.3694		e(3dxz,3dyz,3dz2), C(2pz
29	-0.4402		Fe(3d), C(2pz)
↑	-0.4898		
23			

Figure 3: Energy level diagram of ferrocene

TABLE 5: Contribution of electrons in molecular orbitals-23

χ	Atomic orbital	Eigen vector	No. of electrons	$n_{ri} = n_i c^2_{ri}$
2	1C-2px	0.1823	2	0.0664666
6	2C-2px	0.1296	2	0.0335923
8	2C-2pz	0.2151	2	0.092536
15	4C-2py	0.1227	2	0.0301106
16	4C-2pz	0.2280	2	0.1039315
18	5C-2px	0.1332	2	0.0354845
28	7C-2pz	0.2336	2	0.1091379
31	8C-2py	0.1644	2	0.0540547
35	9C-2py	0.1398	2	0.0390881
40	10C-2pz	0.2841	2	0.1614256
45	11Fe-3dx²-y²	0.4708	2	0.4433053
46	11Fe-3dz²	0.1156	2	0.0267267
48	11Fe-3dxz	0.2893	2	0.167389
49	11Fe-3dyz	0.2288	2	0.1046989

TABLE 6: Contribution of electrons in molecular orbitals-24

χ	Atomic orbital	Eigen vector	No. of electrons	$n_{ri} = n_i c^2_{ri}$
3	1C-2py	0.1193	2	2.0000
4	1-2pz	0.2133	2	0.0909938
10	3C-2px	0.1260	2	0.031752
12	3C-2pz	0.1544	2	0.0476787
14	4C-2px	0.1266	2	0.0320551
15	4C-2py	0.1275	2	0.0325125
16	4C-2pz	0.1005	2	0.0202005
18	5C-2px	0.1288	2	0.0331789
20	5C-2pz	0.1385	2	0.0383645
23	6C-2py	0.1024	2	0.0209715
24	6C-2pz	0.1852	2	0.0685981
32	8C-2pz	0.2311	2	0.1068144
35	9C-2py	0.1435	2	0.0411845
36	9C-2pz	0.1199	2	0.028752
38	10C-2px	0.1215	2	0.0295245
39	10-2py	0.1483	2	0.0439858
40	10C-2pz	0.1272	2	0.0323597
45	11Fe-3dx²-y²	0.1041	2	0.0216736
46	11Fe-3dz²	0.2013	2	0.0810434
47	11Fe-3dxy	0.2847	2	0.1621082
48	11Fe-3dxz	0.4762	2	0.4535329
49	11Fe-3dyz	0.2718	2	0.1477505

molecular orbitals in ferrocene, each MO has two electrons. The coefficient of atomic orbitals that is c_{ri} is the eigen vector value. These values have been obtained from Cache software using molecular mechanic method. Zero or near zero values have not been considered. The results are included in TABLES 5-11. It is indicated that in MOs 1-22, only 2s, 2py and 2px electrons of carbon have their contribution in the formation of molecular orbitals of ferrocene. The result of solution of equation-1 for MOs of 23-29 clearly indicates that main contribution of electrons in MO-23 is from 2pz orbitals of 4c, 7c and

TABLE 7: Contribution of electrons in molecular orbitals-25

χ	Atomic orbital	Eigen vector	No. of electrons	$n_{ri} = n_i c^2_{ri}$
2	1C-2px	0.1315	2	0.0345845
4	1C-2pz	0.2062	2	0.0850369
6	2C-2px	0.1055	2	0.0222605
12	3C-2pz	0.2511	2	0.1261024
24	6C-2pz	0.1770	2	0.062658
31	8C-2py	0.1600	2	0.0512
32	8C-2pz	0.1981	2	0.0784872
40	10C-2pz	0.1486	2	0.0441639
45	11Fe-3dx²-y²	0.6472	2	0.8377357
46	11Fe-3dz²	0.2173	2	0.0944386
48	11Fe-3dxz	0.2138	2	0.0914209
49	11Fe-3dyz	0.3140	2	0.197192

TABLE 8: Contribution of electrons in molecular orbitals-26

χ	Atomic orbital	Eigen vector	No.of electrons	$n_{ri} = n_i c^2_{ri}$
10	3C-2px	0.1351	2	0.036504
11	3C-2py	0.1119	2	0.0250432
12	3C-2pz	0.1668	2	0.0556445
14	4C-2px	0.1758	2	0.0618113
19	5C-2py	0.1701	2	0.057868
24	6C-2pz	0.1761	2	0.0620224
31	8C-2py	0.1158	2	0.0268193
34	9C-2px	0.1125	2	0.0253125
39	10C-2py	0.1217	2	0.0296218
46	11Fe-3dz²	0.2269	2	0.1029672
47	11Fe-3dxy	0.8185	2	1.3398845
49	11Fe-3dyz	0.1004	2	0.0201603

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TABLE 9: Contribution of electrons in molecular orbitals-27

χ	Atomic orbital	Eigen vector	No.of electrons	$n_{ri} = n_i c^2_{ri}$
8	2C-2pz	0.2685	2	0.1441845
16	4C-2pz	0.1949	2	0.075972
18	5C-2px	0.1068	2	0.0228125
20	5C-2pz	0.1218	2	0.0296705
28	7C-2pz	0.2273	2	0.1033306
40	10C-2pz	0.1848	2	0.0683021
41	11Fe-4s	0.1004	2	0.0201603
45	11Fe-3dx²-y²	0.1063	2	0.0225994
46	11Fe-3dz²	0.5776	2	0.6672435
47	11Fe-3dyz	0.2565	2	0.1315845
49	11Fe-3dyz	0.4672	2	0.4365517

TABLE 10: Contribution of electrons in molecular orbitals-28

χ	Atomic orbital	Eigen vector	No.of electrons	$n_{ri} = n_i c^2_{ri}$
4	1C-2pz	0.2347	2	0.1101682
11	3C-2py	0.1003	2	0.0201202
12	3C-2pz	0.2169	2	0.0940912
15	4C-2py	0.1632	2	0.0532685
16	4C-2pz	0.1190	2	0.028322
19	5C-2py	0.1620	2	0.052488
20	5C-2pz	0.1844	2	0.0680067
24	6C-2pz	0.3799	2	0.288648
28	7C-2pz	0.2591	2	0.1342656
32	8C-2pz	0.2011	2	0.0808824
34	9C-2px	0.1902	2	0.0723521
35	9C-2py	0.2112	2	0.0892109
36	9C-2pz	0.3185	2	0.2028845
39	10C-2py	0.1119	2	0.0250432
45	11Fe-3dx²-y²	0.3760	2	0.282752
49	11Fe-3dyz	0.1352	2	0.0365581

10c. From Fe it is from $3dx^2-y^2$ and $3dz^2$, In MO-24 it is from 2pz of 8c, and 3dxy, 3dxz and 3dyz of iron. Briefly the other MOs can be presented as below:

MO-25 -3c-2pz, Fe-3dx²-y² and 3dyz.
MO-26 - Fe-3dz² and 3dxy.
MO-27 - 2c-2pz, 7c-2pz, Fe-3dxy, and 3dyz.
MO-28 - 6c-2pz, 7c-2pz, 9c-2pz, Fe-3d x²-y².
MO-29 - 2c-pz, 5c-2pz, 10c-2pz, Fe-3dz².

TABLE 11: Contribution of electrons in molecular orbitals-29

χ	Atomic orbital	Eigen vector	No.of electrons	$n_{ri} = n_i c^2_{ri}$
8	2C-2pz	-0.3310	2	0.219122
11	3C-2py	-0.1108	2	0.0245533
12	3C-2pz	-0.1780	2	0.063368
15	4C-2py	0.1742	2	0.0606913
16	4C-2pz	0.1828	2	0.0668317
19	5C-2py	0.1227	2	0.0301106
20	5C-2pz	0.2399	2	0.115104
28	7C-2pz	0.2523	2	0.1273106
36	9C-2pz	-0.1163	2	0.0270514
38	10C-2px	-0.1654	2	0.0547143
40	10C-2pz	-0.2543	2	0.129337
41	11Fe-4s	-0.1452	2	0.0421661
45	11Fe-3dx²-y²	-0.1367	2	0.0373738
53	15H-1s	0.1072	2	0.0229837
59	21H-1s	0.1261	2	0.0318024

The results very clearly indicate that only 2pz orbitals of carbon of $C_5H_5^-$, and 3d orbitals of iron provide electrons to molecular orbitals 23-29.

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