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**Archives of Physics Research, 2011, 2 (3):125-137**
(http://scholarsresearchlibrary.com/archive.html)

**ISSN : 0976-0970**
**CODEN (USA): APRRC7**

# Molecular Mechanics and Quantum Chemistry Study of Ferrocene and Nickelocene

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## ABSTRACT

*Magnitude of contribution of AOs and contribution of electron in each occupied molecular orbital of ferrocene and nickelocene based on eigenvalues, eigenvectors and population analysis have been studied. The 3D structure of both ferrocene and nickelocene were drawn on workspace software associated with CAChe and their geometries were optimized with DFT method. The evaluation of eigenvalues, eigenvectors and other parameters were done by using molecular mechanics with EHT option. The study has concluded that the first ten MOs in ferrocene and eight MOs in nickelocene have contribution from* $2p_z$ *orbitals of carbon of* $C_5H_5^-$ *and 3d orbitals of metal. The total involvement in respect of bonding between* $C_5H_5^-$ *and the metal orbitals as derived from coefficient value is 20.3087 in ferrocene and 23.5716 in nickelocene. The population analysis shows that only* $2p_z$ *orbitals of carbon of* $C_5H_5^-$ *and 3d orbitals of metal provide electrons to MOs of ferrocene or nickelocene.*

**Keywords:** Ferrocene, Nickelocene, atomic orbital, molecular orbital, eigenvector, eigenvalue, and population analysis.

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## 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 molecular mechanics to organometallic [13, 14] and transition metal compounds is growing [15]. Molecular orbital parameters such as eigenvectors, eigenvalues and overlap matrix are well calculated with this method. In this paper we present the calculations of eigenvectors, eigenvalues and population analysis of ferrocene and nickelocene, 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 nickel in bonding will help to resolve the controversy raised by other workers [16-20].

## MATERIALS AND METHODS

The study materials of this paper are ferrocene and nickelocene. The 3D structure of both ferrocene and nickelocene (Figure 1 and 2) were drawn on workspace software associated with CAChe [21, 22] and their geometries were optimized with DFT method. The evaluation of eigenvalues, eigenvectors and other parameters were done by using molecular mechanics with EHT option. The method adopted for various calculations is based on following principles.

The molecular orbitals 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 $\chi_r$, which are used to express the MOs $\phi_i$ as $\phi_i = \Sigma_i c_{ri} \chi_r$ (c = coefficient of $\chi$, r is the number of atomic orbital, i = molecular orbital number). 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) [15, 23, 24]. Each molecular orbital $\phi_i$ 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) [25-28] for the SCF calculation.

The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan equation [29]. By the above calculation, the values of orbital energies (eigenvalues) and eigenvectors (coefficients) have been calculated.

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken [30, 31]. He proposed a method that apportions the electrons of an n-electron molecule into net population $n_r$ in the basis functions $\chi_r$ and overlap populations $n_{r-s}$ for all possible pairs of basis functions. With the help of these values, magnitude of contribution of atomic orbital (AO) and population analysis i.e., contribution of electron have been made.

## RESULTS AND DISCUSSION

The MOs of ferrocene and nickelocene are formed by linear combination of fifty AOs of two $C_5H_5^-$ and nine orbital of iron or nickel. These fifty-nine AOs ($\chi_1$ to $\chi_{59}$) on LCAO approximation form same number of MOs ($\phi_1$ to $\phi_{59}$). The AOs are $\chi_1$ to $\chi_{40}$ for 2s, $2p_x$, $2p_y$, $2p_z$ of 1C to 10C; $\chi_{41}$ to $\chi_{49}$ for 4s, $4p_x$, $4p_y$, $4p_z$, $3dx^2$-$y^2$, $3dz^2$, 3dxy, 3dxz, 3dyz of 11M; and $\chi_{50}$ to $\chi_{59}$ for 1s of 12H to 21H, respectively. Where, M = Fe and Ni for ferrocene and nickelocene, respectively. The 2s and $2p_x$, $2p_y$ orbitals of each carbon atom of $C_5H_5^-$ are involved in the formation of $\sigma$ bond between C-C and C-H. The orbitals involved in $\sigma$ bond are not of our interest, hence shall remain out of discussion. The $2p_z$ orbitals of ten carbons [32] 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 orbital and $2p_z$ orbital of $C_5H_5^-$. These atomic orbitals are $\chi_4$, $\chi_8$, $\chi_{12}$, $\chi_{16}$, $\chi_{20}$, $\chi_{24}$, $\chi_{28}$, $\chi_{32}$, $\chi_{36}$ and $\chi_{40}$ of carbon and $\chi_{41\text{-}49}$ of iron or nickel. The coefficients [23, 33] of these orbitals are the eigenvector values of $\chi$. They express the forms of MO i.e. the extent of involvement of $\chi$ in the formation of $\phi$.

In ferrocene the first ten MOs ($\phi_{23-31}$; $\phi_{35}$) and in nickelocene the first eight MOs ($\phi_{23-27}$; $\phi_{30-31}$; $\phi_{35}$) have contributions from 3d orbitals, respectively and the remaining ten MOs ($\phi_{36-37}$; $\phi_{40-41}$; $\phi_{43}$; $\phi_{50}$; $\phi_{51}$; $\phi_{54-55}$; $\phi_{57}$) and twelve MOs ($\phi_{36-40}$; $\phi_{42-43}$; $\phi_{50}$; $\phi_{52-54}$; $\phi_{59}$) have contribution from vacant 4s, 4p orbitals of the iron and nickel atoms, respectively. To examine the extent of involvement of AOs of constituent atoms in the formation of MOs, the values of coefficient of each orbital have been added to see the total involvement in all the twenty MOs. The summation values of $3dx^2$-$y^2$, $3dz^2$, 3dxy, 3dxz, 3dyz, 4s, $4p_x$, $4p_y$, and $4p_z$ of ferrocene are 1.7332, 1.6924, 1.3597, 1.7499, 2.1293, 2.8046, 2.1483, 3.1010 and 3.5903, respectively and that of nickelocene are 1.2035, 1.3756, 1.0546, 1.6351, 1.7788, 3.0439, 4.5856, 4.9416 and 3.9529, respectively. While, the total involvement of $2p_z$ orbitals of ten carbon atoms of both the units of $C_5H_5^-$ in both ferrocene and nickelocene and their summation values are 1.5073, 1.6823, 0.5526, 1.8267, 0.9126, 0.6706, 2.0369, 1.5247, 1.0215, 2.0911 and 1.0732, 0.7599, 0.3232, 1.3578, 1.2047, 0.3096, 0.7419, 1.0795, 0.9571, 1.1836 for 1C to 10C, respectively. The graphical representation of involvement of 3d, 4s and 4p orbitals of iron and nickel, and the involvement of $2p_z$ of ten carbon atoms of both the units of $C_5H_5^-$ in ferrocene and nickelocene are shown in the Figure 3 and Figure 4 respectively. Note that the orbitals having eigenvector values above 0.22 have only been considered. Figure 3 clearly indicates that $4p_z$ and $4p_y$ orbital of ferrocene and nickelocene, respectively has the maximum involvement out of 4s and 4p orbitals, while 3dyz orbital has the maximum involvement out of 3d orbitals in both. The sequences of these two series are $4p_z > 4p_y$ > 4s > 4px and 3dyz > 3dxz> $3dx^2$-$y^2$ > $3dz^2$ > 3dxy for ferrocene, and $4p_y > 4p_x > 4p_z$ > 4s and 3dyz > 3dxz > $3dz^2$ > $3dx^2$-$y^2$ > 3dxy for nickelocene. Figure 4 clearly indicates that $2p_z$ orbitals of 10C and 4C of ferrocene and nickelocene, respectively has maximum involvement out of $2p_z$ orbitals of ten carbon atoms. The sequences of these carbon atoms are 10C > 7C > 4C > 2C > 8C > 1C > 9C > 5C > 6C > 3C for ferrocene, and 4C > 5C > 10C > 8C > 1C > 9C > 2C > 7C > 3C > 6C for nickelocene.

The above study clearly indicates that in ferrocene and nickelocene 3dyz orbital has the highest involvement. The total involvement of d orbitals in ferrocene is 8.6645 and nickelocene is 7.0476. Since, the total involvement of these orbitals in ferrocene is more as compared to nickelocene, hence ferrocene is more stable than nickelocene. The involvement of 4s and 4p orbitals also differ in the two cases. In case of ferrocene $4p_z$ orbital has the maximum involvement whereas in nickelocene $4p_y$ has the maximum involvement. The total involvement of 4s, $4p_x$, $4p_y$ and $4p_z$ in ferrocene is 11.6442 and nickelocene is 16.5240. Thus the total involvement of these orbitals in nickelocene is more as compared to ferrocene. The total involvement of coefficients of $2p_z$ orbitals of ten carbon atoms of both the $C_5H_5^-$ units in the twenty MOs of ferrocene are 13.8263 and nickelocene are 8.9905. The comparison of the involvement of coefficients of $2p_z$ orbitals clearly indicates that the total involvement of carbon atom of ferrocene is more than the involvement of carbon atom of nickelocene. So ferrocene is more stable than nickelocene.

The eigenvalues of fifty-nine MOs ($\phi_1$ to $\phi_{59}$) of ferrocene are -1.1084, -1.0916, -0.9049, -0.9018, -0.8728, -0.8666, -0.6916, -0.6895, -0.6799, -0.6792, -0.6078, -0.6044, -0.5468, -0.5456, -0.5389, -0.5265, -0.5234, -0.5187, -0.5131, -0.5129, -0.5087, -0.5074, -0.4898, -0.4831, -0.4608, -0.4541, -0.4505, -0.4464, -0.4402, -0.3649, -0.3273, -0.2775, -0.2565, -0.2323, -0.2314, -0.0656, -0.0310, 0.0985, 0.0996, 0.1246, 0.1454, 0.1816, 0.1873, 0.2782, 0.2796, 0.4071, 0.4112, 0.4310, 0.4315, 0.4732, 0.5249, 0.7326, 0.7630, 1.0480, 1.1280, 2.0102, 2.0624, 2.2399 and 2.2436 respectively (Scheme-1) and of nickelocene are -1.1902, -1.0928, -0.9118, -0.9043, -0.8786, -0.8681, -0.6920, -0.6901, -0.6799, -0.6792, -0.6101, -0.6043, -0.5547, 0.5477, -0.5462, -0.5287, -0.5260, 0.5212, -0.5163, -0.5139, -0.5124, -0.5095, -0.5021, -0.5005, -0.4801, -0.4753, -0.4718, -0.4471, -0.4405, -0.3764, -0.3307, -0.2742, -0.2460, -0.2322, -0.2296, 0.0713, 0.0922, 0.1114, 0.1387, 0.1596, 0.1715, 0.1913, 0.2601, 0.2791, 0.2802, 0.4072, 0.4080, 0.4305, 0.4311, 0.5372, 0.7424, 0.8078, 0.9106, 1.1110, 1.9357, 2.0230, 2.2459, 2.2539 and 4.2942 respectively (Scheme-2). Out of fifty-nine MOs we shall discuss only twenty MOs of each. The first ten MOs of ferrocene and eight MOs of nickelocene are formed by various 3d orbitals of metal and $2p_z$ orbitals of carbon of $C_5H_5^-$. These orbitals are the most stable MOs between metal and $2p_z$ orbitals of carbon of $C_5H_5^-$. The contribution of 3d orbitals of metal and $2p_z$ of carbon in the formation of these MOs is described as below:

**Ferrocene**

$\phi_{23} = -0.2796\chi_{16} + 0.2336\chi_{27} - 0.2841\chi_{40} - 0.4708\chi_{45} - 0.2893\chi_{48} - 0.2288\chi_{49}$.
$\phi_{24} = 0.2311\chi_{32} + 0.2847\chi_{47} - 0.4762\chi_{48} - 0.2718\chi_{49}$.
$\phi_{25} = 0.2511\chi_{12} - 0.6472\chi_{45} - 0.3147\chi_{49}$.

$\phi_{26} = 0.2269\chi_{46} - 0.8185\chi_{47}$.
$\phi_{27} = 0.2685\chi_{8} - 0.2273\chi_{28} + 0.5776\chi_{46} + 0.2565\chi_{47} + 0.4672\chi_{49}$.
$\phi_{28} = -0.2347\chi_{4} + 0.3799\chi_{24} + 0.2591\chi_{28} - 0.3185\chi_{36} + 0.3760\chi_{45}$.

$\phi_{29} = -0.3310\chi_{8} + 0.2399\chi_{20} + 0.2523\chi_{28} - 0.2543\chi_{40} + 0.5383\chi_{46}$.

$\phi_{30} = 0.2886\chi_{4} - 0.3015\chi_{12} + 0.2907\chi_{24} - 0.2767\chi_{32} + 0.3496\chi_{46} - 0.5271\chi_{48} - 0.3891\chi_{49}$.

$\phi_{31} = -0.2644\chi_{4} - 0.3474\chi_{8} + 0.3104\chi_{20} - 0.3409\chi_{28} - 0.2797\chi_{32} + 0.3136\chi_{36} - 0.4573\chi_{48} + 0.4577\chi_{49}$.
$\phi_{35} = 0.4567\chi_{4} - 0.4381\chi_{8} - 0.3623\chi_{20} - 0.4564\chi_{28} + 0.4820\chi_{32} + 0.3914\chi_{36} - 0.2392\chi_{45}$.

**Nickelocene**

$\phi_{23} = -0.4179\chi_{45}$.

$\phi_{24} = -0.3849\chi_{47} + 0.4986\chi_{48}$.
$\phi_{25} = -0.5232\chi_{45} + 0.3369\chi_{46} + 0.2396\chi_{48} - 0.2782\chi_{49}$.
$\phi_{26} = 0.7408\chi_{46} + 0.4949\chi_{49}$.
$\phi_{27} = 0.6697\chi_{47} + 0.2358\chi_{49}$.

$\phi_{30} = 0.3293\chi_{4} - 0.3232\chi_{12} + 0.3096\chi_{24} - 0.3219\chi_{32} + 0.2300\chi_{40} + 0.2979\chi_{46} - 0.4786\chi_{48} - 0.3521\chi_{49}$.
$\phi_{31} = 0.2778\chi_{4} + 0.3589\chi_{8} - 0.3213\chi_{20} + 0.3565\chi_{28} + 0.2941\chi_{32} - 0.3259\chi_{36} + 0.4183\chi_{48} - 0.4178\chi_{49}$.
$\phi_{35} = -0.4661\chi_{4} + 0.4010\chi_{8} - 0.2519\chi_{16} + 0.3856\chi_{20} + 0.3854\chi_{28} - 0.4635\chi_{32} + 0.4048\chi_{36} - 0.2893\chi_{40} + 0.2624\chi_{45}$.

The next ten MOs of ferrocene and twelve MOs of nickelocene are formed by interaction of 4s, $4p_x$, $4p_y$ and $4p_z$ orbitals of metal and $2p_z$ orbitals of carbon of $C_5H_5^-$. These MOs are comparatively less stable and the contribution of various AOs in the formation of these MOs is presented below:

**Ferrocene**

$\phi_{36} = 0.2629\chi_{8} - 0.2243\chi_{40} - 0.7335\chi_{42} - 0.6722\chi_{43} + 0.4698\chi_{44}$.
$\phi_{37} = -0.2973\chi_{8} + 0.2673\chi_{28} + 0.2552\chi_{32} - 0.5031\chi_{41} - 0.7533\chi_{42} + 0.6885\chi_{43}$.
$\phi_{40} = 0.3089\chi_{16} - 0.3653\chi_{40} + 0.7981\chi_{41} + 0.2865\chi_{43}$.
$\phi_{41} = 0.2234\chi_{16} + 0.2387\chi_{40} + 0.2780\chi_{43} + 0.7412\chi_{44}$.

$\phi_{43} = 0.2661\chi_{4} - 0.3154\chi_{44}$.

$\phi_{50} = 0.4338\chi_{16} - 0.3828\chi_{40} + 0.9232\chi_{41}$.
$\phi_{51} = 0.3149\chi_{16} - 0.3416\chi_{40} - 0.3489\chi_{43} - 0.9974\chi_{44}$.

**Nickelocene**

$\phi_{36} = 0.3003\chi_{40} + 0.5037\chi_{42} + 0.5563\chi_{43} - 0.2729\chi_{44}$.
$\phi_{37} = -0.2255\chi_{20} - 0.4088\chi_{41} - 0.3254\chi_{42} + 0.2960\chi_{43}$.
$\phi_{38} = 0.6732\chi_{41} + 0.2423\chi_{42} - 0.3695\chi_{43}$.
$\phi_{39} = 0.2264\chi_{36} + 0.7569\chi_{42} + 0.3868\chi_{43} - 0.3261\chi_{44}$.
$\phi_{40} = -0.4239\chi_{16} - 0.2473\chi_{41} + 0.2201\chi_{42} - 0.3706\chi_{43}$.
$\phi_{42} = 0.2725\chi_{16} - 0.3487\chi_{42} - 0.3318\chi_{43}$.
$\phi_{43} = 0.6971\chi_{42} - 0.7470\chi_{43}$.

$\phi_{54} = -\,0.2810\chi_{42} - 0.3923\chi_{43} - 0.6228\chi_{44}.$
$\phi_{55} = 0.5802\chi_{41} - 0.3805\chi_{42} + 0.4346\chi_{43}.$
$\phi_{57} = 0.4437\,\chi_{44}.$

$\phi_{50} = -\,0.4095\chi_{16} + 0.3640\chi_{40} - 1.0725\chi_{41}.$
$\phi_{52} = -\,0.3086\chi_{42} - 0.2441\chi_{43}.$
$\phi_{53} = -\,0.2723\chi_{20} + 0.3020\chi_{42} - 0.2283\chi_{44}.$
$\phi_{54} = -\,0.6421\chi_{41} + 0.4372\chi_{42} - 0.5633\chi_{43}.$
$\phi_{59} = -\,0.4436\chi_{42} - 1.0762\chi_{43} - 3.1256\chi_{44}.$

A comparison of eigenvalues of ferrocene and nickelocene shows that most stable orbitals formed between 3d orbitals and $2p_z$ orbitals are ten in ferrocene and eight in nickelocene. The energies of these orbitals are in the range -0.4898 to -0.2314 eV in ferrocene and -0.5021 to -0.2296 eV in nickelocene. The less stable orbitals are ten in ferrocene and twelve in nickelocene. The energies of these orbitals are in the range -0.0656 to 2.0624 eV in ferrocene and 0.0713 to 4.2942 eV in nickelocene. The energy of the first molecular orbital or in other word the most stable orbital in ferrocene is -1.1084 eV and in nickelocene -1.1902 eV. The energy of highest occupied molecular orbital (HOMO) is –0.4402 eV in ferrocene, and –0.3764 eV, in nickelocene. The MO is twenty-nine and thirty respectively.

## Population analysis:

The contribution of electrons in each occupied MO is calculated by using the population analysis method introduced by Mulliken [30, 31]. This method apportions the electrons of n-electron molecule into net population $n_r$ in the basis function $\chi_r$. Let there be $n_i$ electrons in the molecular orbital $\phi_i$ ($n_i$ = 0. 1, 2) and let $n_i$ symbolize the contribution of electrons in the MO $\phi_i$ to the net population in $\chi_r$ we have

$$n_{r,i} = n_i\, c_{ri}^2 \qquad [1]$$

where $c_{ri}$ is the coefficient of AO for the i$^{th}$ MO (r = 29) in ferrocene and (r = 30) nickelocene.

Equation-1 has been solved for fifty-eight electrons of twenty-nine MOs in ferrocene and sixty electrons of thirty MOs in nickelocene. Each MO has two electrons in ferrocene and in nickelocene. The coefficient of AOs [29] i.e. $c_{ri}$ is the eigenvector value. The orbitals having eigenvector values above 0.22 have only considered. Our interest is only seven MOs 23-29 in ferrocene and eight MOs 23-30 in nickelocene; we have solved equation-1 for these orbitals only. But in MOs 1-22, only 2s, $2p_x$ and $2p_y$ electrons of carbon have their contribution in the formation of molecular orbitals of ferrocene and nickelocene; hence they are not of our interest. For ferrocene and nickelocene the results of solution of equation–1 for MOs 23–29 and 23–30 is given below:

**Ferrocene**

| MO | $\chi$ | AO | $c_{ri}$ | $n_{r,i}$ |
|---|---|---|---|---|
| 23 | 16 | 4C–$2p_z$ | 0.2280 | 0.10393 |
| | 28 | 7C–$2p_z$ | 0.2336 | 0.10913 |
| | 40 | 10C –$2p_z$ | 0.2841 | 0.16142 |
| | 45 | 11Fe–3d$x^2$-$y^2$ | 0.4708 | 0.44330 |
| | 48 | 11Fe–3dxz | 0.2893 | 0.16738 |
| | 49 | 11Fe–3dyz | 0.2288 | 0.10469 |
| 24 | 32 | 8C–$2p_z$ | 0.2311 | 0.10681 |
| | 47 | 11Fe–3dxy | 0.2847 | 0.16210 |
| | 48 | 11Fe–3dxz | 0.4762 | 0.45353 |
| | 49 | 11Fe–3dyz | 0.2718 | 0.14775 |
| 25 | 12 | 3C–$2p_z$ | 0.2511 | 0.12610 |
| | 45 | 11Fe–3d$x^2$-$y^2$ | 0.6472 | 0.83773 |
| | 49 | 11Fe–3dyz | 0.3140 | 0.19719 |
| 27 | 8 | 2C–$2p_z$ | 0.2685 | 0.14418 |
| | 28 | 7C–$2p_z$ | 0.2273 | 0.10333 |
| | 46 | 11Fe–3d$z^2$ | 0.5776 | 0.66724 |
| | 47 | 11Fe–3dxy | 0.2565 | 0.13158 |
| | 49 | 11Fe–3dyz | 0.4672 | 0.43655 |
| 28 | 4 | 1C–$2p_z$ | 0.2347 | 0.11016 |
| | 24 | 6C–$2p_z$ | 0.3799 | 0.28864 |
| | 28 | 7C–$2p_z$ | 0.2591 | 0.13426 |
| | 36 | 8C–$2p_z$ | 0.3185 | 0.20288 |
| | 45 | 11Fe–3d$x^2$-$y^2$ | 0.3760 | 0.28275 |
| 29 | 8 | 2C – $2p_z$ | 0.3310 | 0.21912 |
| | 20 | 5C – $2p_z$ | 0.2399 | 0.11510 |
| | 28 | 7C – $2p_z$ | 0.2523 | 0.12731 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 26 | 46 | 11Fe–3dz$^2$ | 0.2269 | 0.10296 | | 40 | 10C – 2p$_z$ | 0.2543 | 0.12933 |
| | 47 | 11Fe–3dxy | 0.8185 | 1.33988 | | | | | |

**Nickelocene**

| MO | χ | AO | $c_{ri}$ | $n_{r,i}$ | MO | χ | AO | $c_{ri}$ | $n_{r,i}$ |
|---|---|---|---|---|---|---|---|---|---|
| 23 | 45 | 11Ni–3dx$^2$-y$^2$ | 0.4179 | 0.34928 | | 24 | 6C–2p$_z$ | 0.4088 | 0.33423 |
| 24 | 47 | 11Ni–3dxy | 0.3849 | 0.29629 | | 28 | 7C–2p$_z$ | 0.2304 | 0.10616 |
| | 48 | 11Ni–3dxz | 0.4986 | 0.49720 | | 36 | 9C–2p$_z$ | 0.3089 | 0.19083 |
| 25 | 45 | 11Ni–3dx$^2$-y$^2$ | 0.5232 | 0.54747 | 29 | 8 | 2C–2p$_z$ | 0.4179 | 0.34928 |
| | 46 | 11Ni–3dz$^2$ | 0.3369 | 0.22700 | | 16 | 4C–2p$_z$ | 0.2561 | 0.13117 |
| | 48 | 11Ni–3dxz | 0.2396 | 0.11481 | | 20 | 5C–2p$_z$ | 0.2707 | 0.14655 |
| | 49 | 11Ni–3dyz | 0.2782 | 0.15479 | | 28 | 7C–2p$_z$ | 0.3600 | 0.25920 |
| 26 | 46 | 11Ni–3dz$^2$ | 0.7408 | 1.09756 | | 40 | 10C–2p$_z$ | 0.3209 | 0.20595 |
| | 49 | 11Ni–3dyz | 0.4949 | 0.48985 | 30 | 4 | 1C–2p$_z$ | 0.3293 | 0.21687 |
| 27 | 14 | 4C–2p$_x$ | 0.2444 | 0.11946 | | 12 | 3C–2p$_z$ | 0.3232 | 0.20891 |
| | 39 | 10C–2p$_y$ | 0.2367 | 0.11205 | | 24 | 6C–2p$_z$ | 0.3096 | 0.19170 |
| | 47 | 11Ni–3dxy | 0.6697 | 0.89699 | | 32 | 8C–2p$_z$ | 0.3219 | 0.20723 |
| | 49 | 11Ni–3dyz | 0.2358 | 0.11120 | | 40 | 10C–2p$_z$ | 0.2300 | 0.10580 |
| 28 | 4 | 1C–2p$_z$ | 0.2818 | 0.15882 | | 46 | 11Ni–3dz$^2$ | 0.2979 | 0.17748 |
| | 12 | 3C–2p$_z$ | 0.3050 | 0.18605 | | 48 | 11Ni–3dxz | 0.4786 | 0.45811 |
| | 20 | 5C–2p$_z$ | 0.2252 | 0.10143 | | 49 | 11Ni–3dyz | 0.3521 | 0.24794 |

The above results very clearly indicate that only 2p$_z$ orbital of carbon of $C_5H_5^-$ and 3d orbitals of iron or nickel provide electrons to molecular orbitals of ferrocene and nickelocene. However, it is prominently noticeable that electrons are provided from different orbitals in the ferrocene and nickelocene, and their $n_{r,i}$ also differs.

The study of eigenvalues, eigenvector and population analysis as presented above has provided valuable information, which in the form of summary is presented below:

1. The eigenvalues and eigenvector of ferrocene and nickelocene shows that the first ten MOs of ferrocene and eight MOs of nickelocene are formed by various 3d orbitals of metal and 2p$_z$ orbitals of carbon of $C_5H_5^-$, these orbitals are the most stable MOs. The next ten MOs of ferrocene and twelve MOs of nickelocene are formed by interaction of 4s, 4p orbitals of metal and 2p$_z$ orbitals of carbon of $C_5H_5^-$, these MOs are comparatively less stable.
2. In ferrocene the 3dyz orbital out of 3d orbitals and 4p$_z$ orbital out of 4s, 4p orbitals of iron has maximum involvement which is in the order 3dyz > 3dxz > 3dx$^2$-y$^2$ > 3dz$^2$ > 3dxy and 4p$_z$ > 4p$_y$ > 4s > 4p$_x$. Whereas in nickelocene the 3dyz orbital out of 3d orbitals and 4p$_y$ orbital out of 4s, 4p orbitals of nickel has maximum involvement which is in the order 3dyz > 3dxz > 3dz$^2$ > 3dx$^2$-y$^2$ > 3dxy and 4p$_y$ > 4p$_x$ > 4p$_z$ > 4s.
3. The total involvement in respect of bonding between $C_5H_5^-$ and the metal orbitals as derived from coefficient value is 20.3087 in ferrocene and 23.5716 in nickelocene.
4. The total involvement of 3d, 4s, 4p orbitals of metal and 2p$_z$ orbitals of ten carbon atoms of both the units of $C_5H_5^-$ in ferrocene and nickelocene, respectively are 34.135 and 32.135.
5. The most stable molecular orbitals have their energies in the range -0.4898 to -0.2314 eV and -0.5021 to -0.2296 eV for ferrocene and nickelocene, respectively.
6. In ferrocene the energy of most stable MO is -1.1084 eV and highest occupied molecular orbital is –0.4402 eV. In nickelocene the energy of most stable MO is -1.1902 eV and highest occupied molecular orbital is –0.3764 eV.
7. The population analysis shows that only 2p$_z$ orbitals of carbon of $C_5H_5^-$ and 3d orbitals of metal provide electrons to MOs of ferrocene or nickelocene.

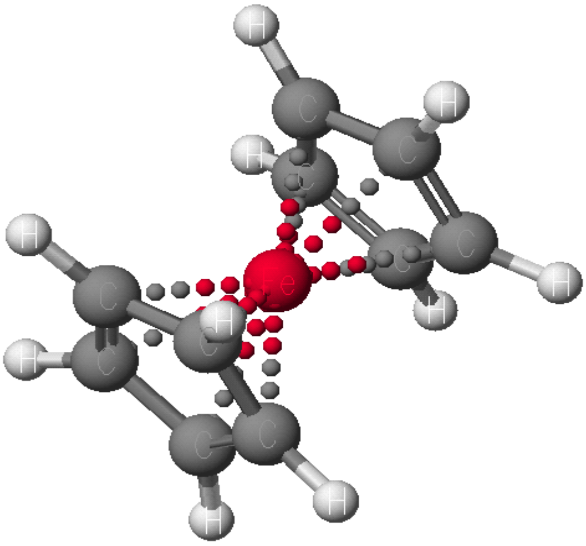


**Figure 1. Structure of Ferrocene.**

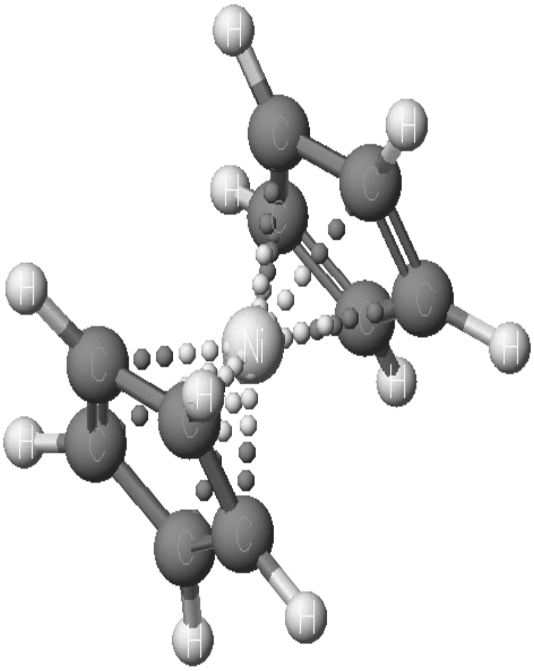
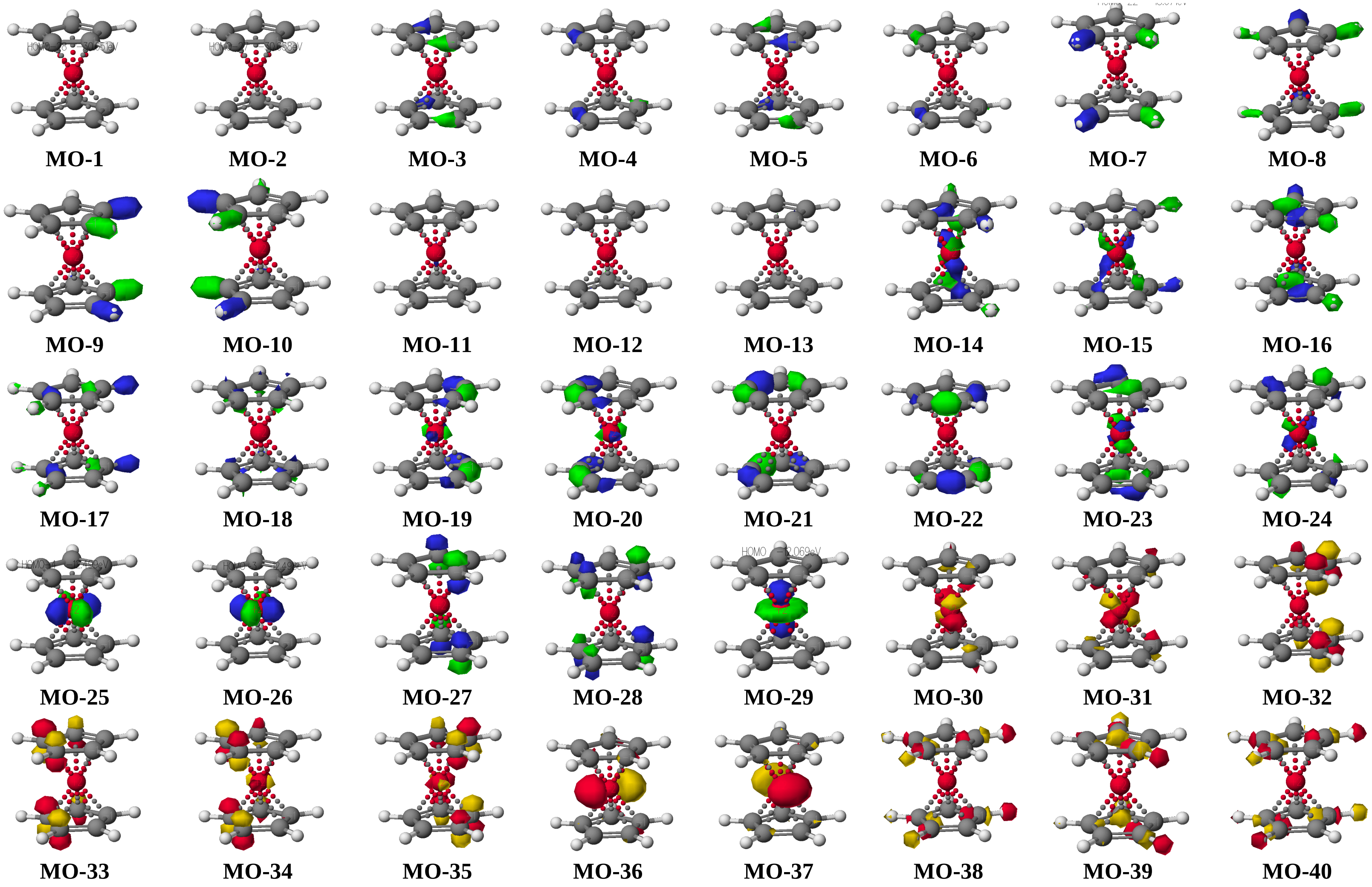


**Figure 2. Structure of Nickelocene.**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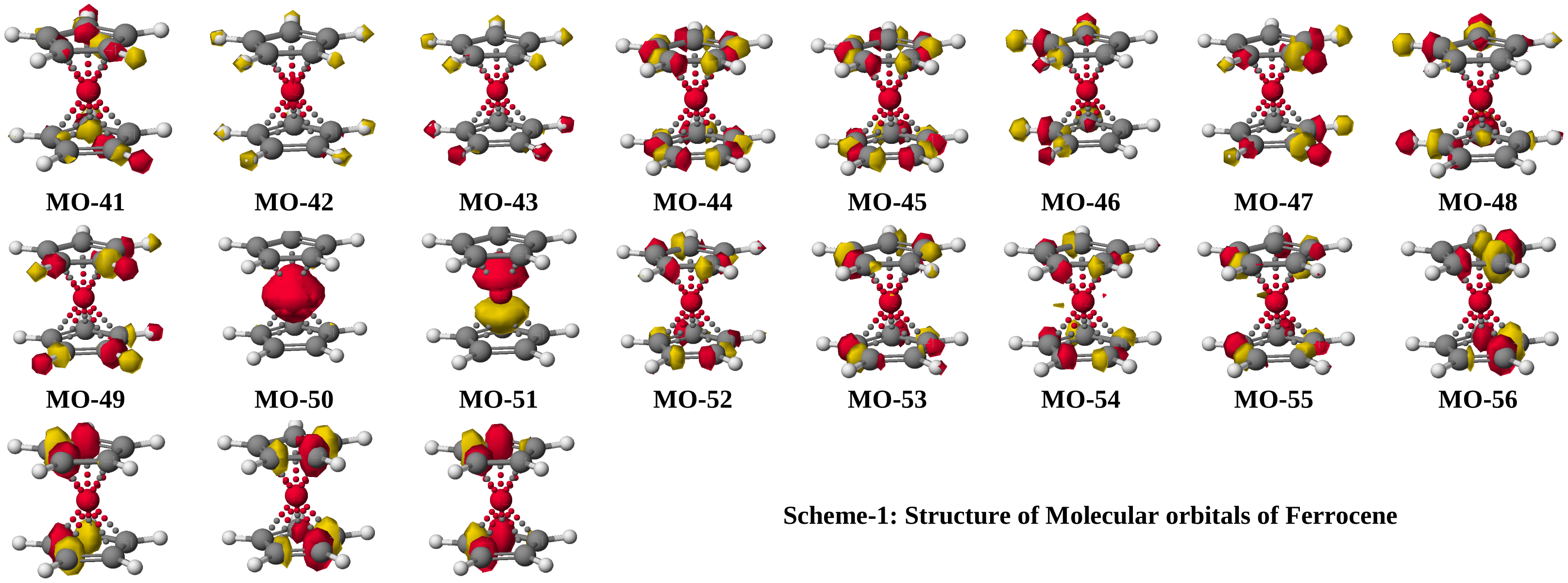

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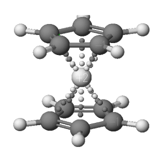
MO-57 MO-58 MO-59

**Scheme-1: Structure of Molecular orbitals of Ferrocene**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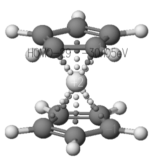
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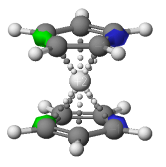
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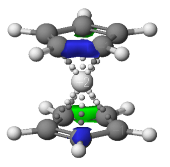
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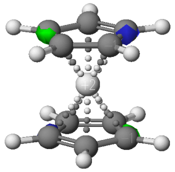
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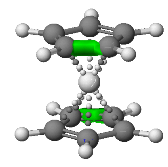
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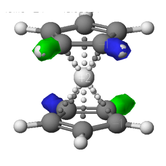
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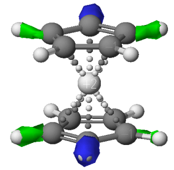
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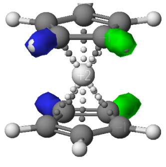
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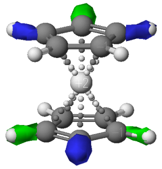
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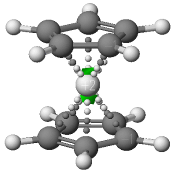
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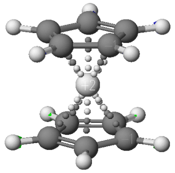
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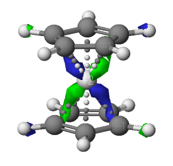
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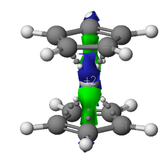
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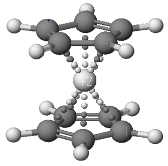
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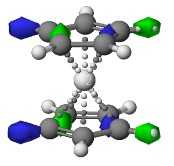
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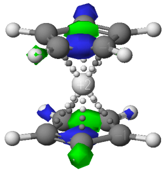
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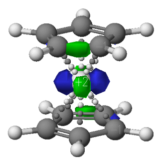
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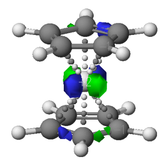
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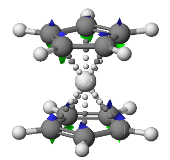
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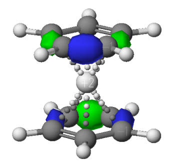
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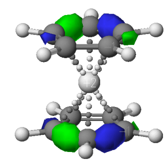
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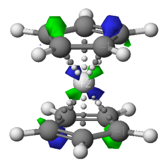
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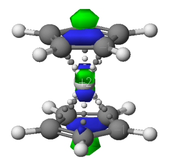
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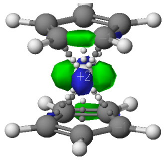
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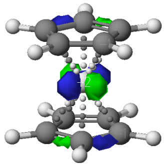
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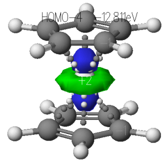
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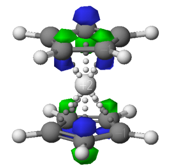
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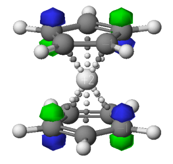
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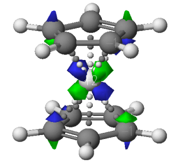
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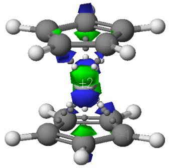
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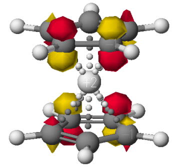
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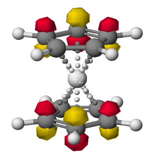
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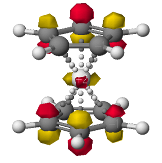
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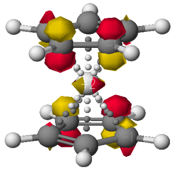
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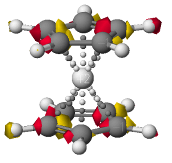
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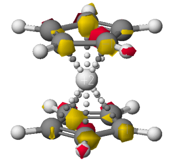
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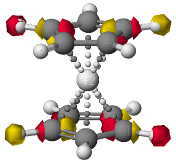
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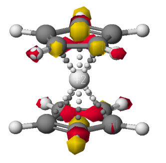
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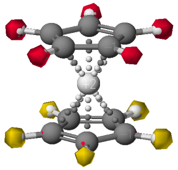
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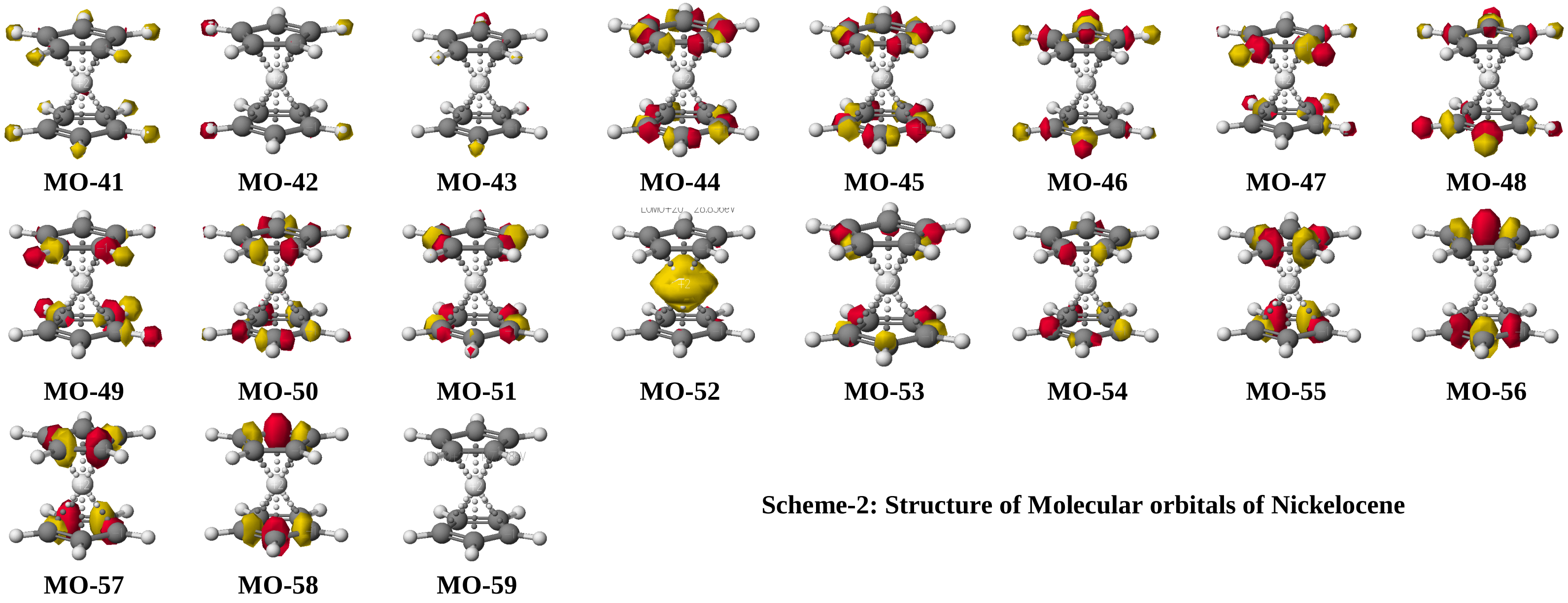
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**Scheme-2: Structure of Molecular orbitals of Nickelocene**

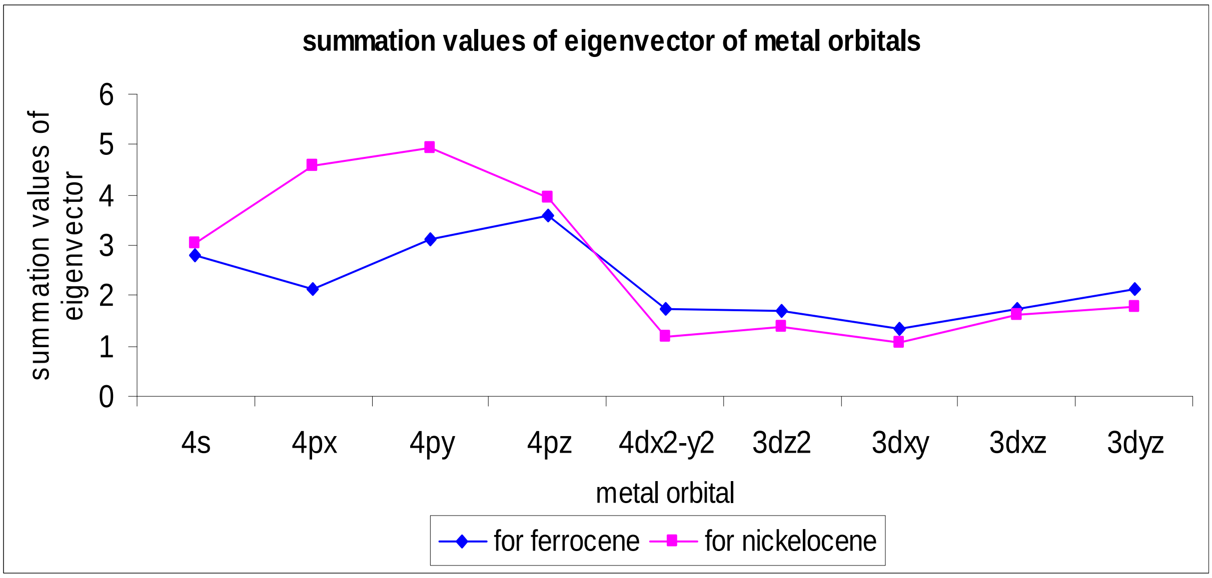

**Figure 3: Trend of summation values of eigenvector of metal orbitals.**

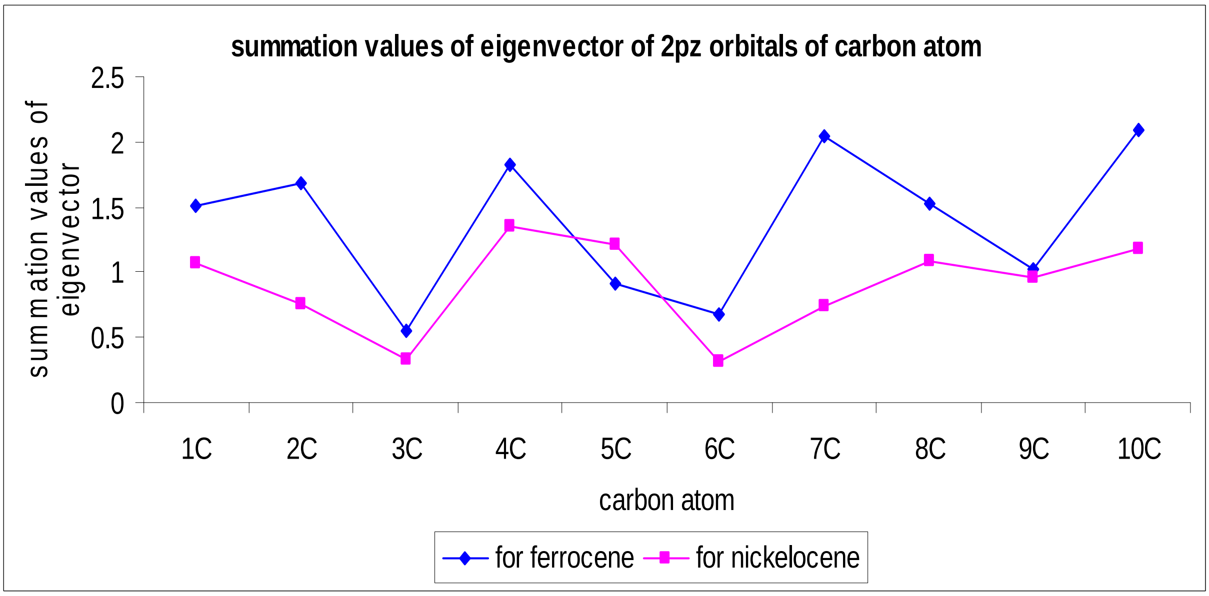

**Figure 4: Trend of summation values of eigenvector $2p_z$ orbitals of carbon atoms.**

**Acknowledgement:** The paper is dedicated to the Parents of the corresponding author. We are thankful to Dr. Mohd Arshad, Principal Maulana Azad Degree College Domariyaganj, Siddharth Nagar, for valuable help.

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