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Comparative Study of Molecular Orbitals of Cobaltocene and Nickelocene Based on Molecular Mechanics

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ABSTRACT

Magnitude of contribution of AOs and contribution of electron in each occupied molecular orbital of cobaltocene and nickelocene based on eigenvalues, eigenvectors and population analysis have been studied. The 3D structure of both cobaltocene and nickelocene were drawn on workspace software associated with CAChe and their geometries were optimized with DFT method. The evaluation of eigenvalues, eigenvector and other parameters were done by using molecular mechanics with EHT option. The study has concluded that the first eight MOs in cobaltocene and 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 22.346 in cobaltocene 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 cobaltocene and nickelocene.

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

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 orbital parameters such as eigenvectors, eigenvalues and overlap matrix are well calculated with this method. In this paper I present the calculations of eigenvectors, eigenvalues and population analysis of cobaltocene 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 cobalt 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 cobaltocene and nickelocene. The 3D structure of both cobaltocene and nickelocene (Figure 1 and 2) were drawn on workspace software associated with CAChe and their geometries were optimized with DFT method. The evaluation of eigenvalues, eigenvector 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 χ_r , which are used to express the MOs ϕ_i as $\phi_i = \sum_i c_{ri} \chi_r$ (c = coefficient of χ , 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 ϕ_i is expressed as $\phi_i = \sum_i c_{ri} \chi_r$, where, the χ_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 χ_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.



Figure 1: Structure of Cobaltocene



Figure 2: Structure of Nickelocene.

RESULTS AND DISCUSSION

The MOs of cobaltocene and nickelocene are formed by linear combination of fifty AOs of two $C_5H_5^-$ units and nine orbital of cobalt or nickel. The fifty-nine AOs (χ_1 to χ_{59}) on LCAO approximation for fifty-nine MOs (ϕ_1 to ϕ_{59}). These AOs are χ_1 to χ_{40} for 2s, $2p_x$, $2p_y$, $2p_z$ of 1C to 10C; χ_{41} to χ_{49} for 4s, $4p_x$, $4p_y$, $4p_z$, $3dx^2-y^2$, $3dz^2$, 3dxy, 3dxz, 3dyz of 11M; and χ_{50} to χ_{59} for 1s for 12H to 21H, respectively. Where, M = Co and Ni for cobaltocene and nickelocene, respectively. The 2s and $2p_x$, $2p_y$ orbitals of each carbon atom of $C_5H_5^-$ units are involved in the formation of σ bond between C-C and C-H. The orbitals involved in σ bond are not of our interest, hence shall remain out of discussion. The $2p_z$ orbitals of ten carbons [32] and nine orbitals of cobalt or nickel i.e. in total nineteen orbitals are relevant to our discussion in respect of bonding between cobalt or nickel orbital and $2p_z$ orbital of $C_5H_5^-$. These atomic orbitals are χ_4 , χ_8 , χ_{12} , χ_{16} , χ_{20} , χ_{24} , χ_{28} , χ_{32} , χ_{36} and χ_{40} of carbon and χ_{41-49} of cobalt or nickel. The coefficients [23, 33] of these orbitals are the eigenvector values of χ . They express the forms of molecular orbital i.e. the extent of involvement of χ in the formation of ϕ .

We know that there are fifty-nine MOs, ϕ_1 to ϕ_{59} for both cobaltocene (Scheme-1) and nickelocene (Scheme-2). The eigenvalues of MOs of cobaltocene are -1.1027, -1.0916, -0.9068, -0.9022, -0.8721, -0.8670, -0.6877, -0.6820, -0.6797, -0.6779, -0.6064, -0.6014, -0.5610, -0.5479, -0.5443, -0.5355, -0.5234, -0.5171, -0.5110, -0.5093, -0.5079, -0.5073, -0.4935, -0.4798, -0.4753, -0.4716, -0.4627, -0.4495, -0.4374, -0.3906, -0.3583, -0.2812, -0.2718, -0.2345, -0.2311, -0.0875, -0.0530, 0.0158, 0.0917, 0.0954, 0.1197, 0.2197, 0.2847, 0.2875, 0.2982, 0.3228, 0.3621, 0.4308, 0.4363, 0.4550, 0.5015, 0.7381, 0.7600, 1.0022, 1.0718, 2.0412, 2.0771, 2.2583 and 2.2719, respectively. Where as the eigenvalues of MOs 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.









In cobaltocene and nickelocene the first eight MOs i.e., ϕ_{23-28} ; ϕ_{30} ; ϕ_{31} and ϕ_{23-27} ; ϕ_{30-31} ; ϕ_{35} , have contributions from 3d orbitals and the remaining twelve molecular orbitals i.e., ϕ_{36-38} ; ϕ_{41-42} ; ϕ_{46-1} 47; \$\phi_{50-51}; \$\phi_{54-55}; \$\phi_{56}\$ and \$\phi_{36-40}; \$\phi_{42-43}; \$\phi_{50}; \$\phi_{52-54}; \$\phi_{59}\$ have contributions from vacant 4s, 4p orbitals of the of the cobalt 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 $3dx^2-y^2$, 3dz², 3dxy, 3dxz, 3dyz, 4s, 4p_x, 4p_y, and 4p_z of cobaltocene are 1.4437, 1.5086, 1.9817, 1.6596, 1.8055, 4.4247, 2.5598, 2.9101 and 4.0523, 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 $C_5H_5^-$ of both cobaltocene and nickelocene and their summation values are 1.4493, 0.9282, 0.7761, 2.4908, 1.0034, 1.0322, 0.7443, 0.4953, 1.0411, 1.0274 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, 4p orbital of cobalt and nickel, and the involvement of $2p_z$ of ten carbon atoms of both the units of $C_5H_5^-$ in cobaltocene 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 4s and $4p_v$ orbital of cobaltocene and nickelocene, respectively has the maximum involvement out of 4s and 4p orbitals, while 3dxy and 3dyz orbital has the maximum involvement out of 3d orbitals. The sequences of these two series are 4s 4s and $3dyz > 3dxz > 3dz^2 > 3dx^2 - y^2 > 3dxy$, for nickelocene. Figure 4 clearly indicates that $2p_z$ orbitals of 4C of both cobaltocene and nickelocene have maximum involvement out of 2p_z orbitals of ten carbon atoms. The sequences of these carbon atoms are 4C > 1C > 9C > 6C > 10C> 5C > 2C > 3C > 7C > 8C for cobaltocene, and 4C > 5C > 10C > 8C > 1C > 9C > 2C > 7C > 10C > 8C > 10C > 10C > 8C > 10C > 10C > 8C > 10C > 10C3C > 6C for nickelocene.



Figure 3: Trend of summation values of eigenvectors of metal orbitals.



Figure 4: Trend of summation values of eigenvectors of 2pz orbitals carbon atoms.

The above study clearly indicates that in cobaltocene 3dxy and in nickelocene the 3dyz orbital has the highest involvement. The total involvement of d orbitals of cobaltocene is 8.3991 and of nickelocene are 7.0476. Since, the total involvement of these orbitals in cobaltocene is more as compared to nickelocene, hence cobaltocene is more stable than nickelocene. The involvement of 4s and 4p orbitals also differ in the two cases. In case of cobaltocene 4s orbital has the maximum involvement but in nickelocene 4p_y has the maximum involvement. The total involvement of these orbitals (4s, 4p_x, 4p_y, 4p_z) in cobaltocene is 13.9469 and in nickelocene is 16.5240. Thus, the total involvement of these orbitals in nickelocene is more as compared to cobaltocene. The total involvement of coefficients of $2p_z$ orbitals of ten carbon atoms of both the $C_5H_5^-$ units in twenty MOs of cobaltocene and nickelocene are 10.9881 and 8.9905 respectively. The comparison of the involvement of coefficients of $2p_z$ orbitals clearly indicates that the total involvement of cobaltocene is more than the involvement of carbon atom of nickelocene is more than nickelocene.

The eigenvalues of fifty-nine MOs of cobaltocene and nickelocene are described as above, out of which I shall discuss only twenty MOs of each. The first eight MOs of both the molecule are formed by various 3d orbitals of metal and $2p_z$ orbitals of $C_5H_5^-$. These orbitals are the most stable orbitals between metal and $2p_z$ orbitals of $C_5H_5^-$. The contributions of 3d orbitals of metal and $2p_z$ orbitals of carbon in the formation of these MOs are described as below:

Cobaltocene

 $\phi_{23} = 0.2610\chi_{16} + 0.2507\chi_{45} + 0.4737\chi_{46} + 0.473\chi_{46} + 0.47\chi_{46} + 0.4\chi_{46} + 0.$ $\phi_{23} = -0.4179\chi_{45}$ $0.2664\chi_{47} - 0.2327\chi_{48}$ $\varphi_{24}=0.5537\chi_{45}-0.4186\chi_{47}+0.2781\chi_{49}$ $\varphi_{24} = -\ 0.3849 \chi_{47} + 0.4986 \chi_{48}$ $\varphi_{25}=0.5218\chi_{46}+0.3033\chi_{48}+0.5717\chi_{49}$ $\phi_{25} = -0.5232\chi_{45} + 0.3369\chi_{46} +$ $0.2396\chi_{48} - 0.2782\chi_{49}$ $\varphi_{26} = -\ 0.2652 \chi_{45} - 0.5281 \chi_{47} + 0.3717 \chi_{48}$ $\phi_{26} = 0.7408\chi_{46} + 0.4949\chi_{49}$ $-0.3035\chi_{49}$ $\varphi_{27}=-\ 0.3281\chi_8-0.2463\chi_{12}+0.2716\chi_{16}$ $\phi_{27} = 0.6697\chi_{47} + 0.2358\chi_{49}$ $+ 0.2369\chi_{24} + 0.2931\chi_{47}$ $\phi_{30} = 0.3293\chi_4 - 0.3232\chi_{12} + 0.3096\chi_{24} - 0.3232\chi_{12} + 0.3096\chi_{24} - 0.309\chi_{24} - 0.300\chi_{24} -$ $\phi_{28} = -0.2825\chi_4 + 0.2548\chi_{12} + 0.2836\chi_{24}$ $+ 0.2755 \chi_{28} - 0.2362 \chi_{36} - 0.2339 \chi_{47} +$ $0.3219\chi_{32} + 0.2300\chi_{40} + 0.2979\chi_{46} - 0.0000$ $0.4786\chi_{48} - 0.3521\chi_{49}$ $0.2297\chi_{49}$ $\phi_{31} = 0.2778\chi_4 + 0.3589\chi_8 - 0.3213\chi_{20} +$ $\phi_{30} = 0.2899 \chi_4 - 0.2750 \chi_{12} + 0.2474 \chi_{20} + 0.2474$ $0.3565\chi_{28} + 0.2941\chi_{32} - 0.3259\chi_{36} +$ $0.2537\chi_{24} - 0.2649\chi_{32} + 0.5131\chi_{46} - 0.2649\chi_{46} - 0.2644\chi_{46} - 0.264\chi_{46} - 0.26\chi_{46} - 0.26$ $0.2416\chi_{47} - 0.3996\chi_{48}$ $0.4183\chi_{48} - 0.4178\chi_{49}$ $\phi_{35} = -0.4661\chi_4 + 0.4010\chi_8 - 0.2519\chi_{16}$ $\phi_{31} = 0.2835 \chi_4 + 0.3653 \chi_8 - 0.2853 \chi_{16} - 0.2853 \chi_{16}$ $0.2495 \chi_{20} + 0.2476 \chi_{28} + 0.3741 \chi_{45} + \\$ $+ 0.3856\chi_{20} + 0.3854\chi_{28} - 0.4635\chi_{32} +$ $0.3523\chi_{48} - 0.4225\chi_{49}$ $0.4048\chi_{36} - 0.2893\chi_{40} + 0.2624\chi_{45}$

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

Cobaltocene

 $\phi_{36} = -0.2348 \chi_8 + 0.2304 \chi_{32} 0.3346\chi_{41} - 0.9288\chi_{42} + 0.4070\chi_{44}$ $\phi_{37} = -0.3009\chi_4 + 0.2413\chi_{16} +$ $0.2212\chi_{28} - 0.3259\chi_{41} + 0.8777\chi_{43} 0.5655\chi_{44}$ $\phi_{38} = 0.2835\chi_{36} - 0.6188\chi_{41} +$ $0.2691\chi_{44}$ $\phi_{41} = 0.2925 \chi_4 + 0.5471 \chi_{16} +$ $0.2847\chi_{20} + 0.3195\chi_{41} + 0.3626\chi_{43} +$ $0.4823\chi_{44}$ $\phi_{42} = -0.3148\chi_{41} - 0.3549\chi_{43} 0.3479\chi_{44}$ $\phi_{46} = -0.2580\chi_{24} + 0.2860\chi_{36} 0.2767\chi_{41} + 0.3026\chi_{42} + 0.3002\chi_{44}$ $\phi_{47} \!=\! -0.3743 \chi_{16} \!- 0.3329 \chi_{41} \! 0.2688\chi_{42} - 0.2911\chi_{44}$ $\phi_{50} = -0.2733\chi_{16} + 0.2233\chi_{40} 0.7239\chi_{41} - 0.2913\chi_{43} - 0.3794\chi_{44}$ $\phi_{51} = 0.5771 \chi_{40} - 0.5741 \chi_{41} +$ $0.5317\chi_{42} + 0.3413\chi_{43} + 0.7871\chi_{44}$ $\phi_{54} = 0.2218 \chi_{20} + 0.2354 \chi_{36} +$ $0.2270\chi_{40} - 0.2380\chi_{42} - 0.2945\chi_{43} - 0.294\xi\chi_{43} - 0.29$ $0.2227\chi_{44}$ $\phi_{55} = 0.3738\chi_{41} - 0.2889\chi_{42} + 0.0000$ $0.3878\chi_{43}$ $\phi_{56} = 0.2369 \ \chi_{16} - 0.2297 \ \chi_{41}$

Nickelocene

Nickelocene

 $\phi_{36} = 0.3003\chi_{40} + 0.5037\chi_{42} + 0.5563\chi_{43} - 0.556\chi_{43} - 0.55\chi_{43} - 0.55\chi_{43} - 0.55\chi_{43} - 0.55\chi_{43} - 0.55\chi_{43} - 0.55\chi_{43} - 0.5\chi_{43} - 0.5\chi_{$ $0.2729\chi_{44}$ $\phi_{37} = -0.2255\chi_{20} - 0.4088\chi_{41} - 0.3254\chi_{42} +$ $0.2960\chi_{43}$ $\phi_{38} = 0.6732\chi_{41} + 0.2423\chi_{42} - 0.3695\chi_{43}$ $0.3261\chi_{44}$ $\phi_{40} = -0.4239\chi_{16} - 0.2473\chi_{41} + 0.2201\chi_{42} - 0.2473\chi_{41} + 0.2473\chi_{$ $0.3706\chi_{43}$ $\phi_{42} = 0.2725 \chi_{16} - 0.3487 \chi_{42} - 0.3318 \chi_{43}$ $\varphi_{43}=0.6971\chi_{42}-0.7470\chi_{43}$ $\phi_{50} = -0.4095\chi_{16} + 0.3640\chi_{40} - 1.0725\chi_{41}$ $\phi_{52} = -0.3086\chi_{42} - 0.2441\chi_{43}$ $\phi_{53} = -0.2723\chi_{20} + 0.3020\chi_{42} - 0.2283\chi_{44}$ $\phi_{54} = -0.6421\chi_{41} + 0.4372\chi_{42} - 0.5633\chi_{43}$ $\phi_{59} = -0.4436\chi_{42} - 1.0762\chi_{43} - 3.1256\chi_{44}$

A comparison of eigenvalues of cobaltocene and nickelocene shows that most stable orbitals formed between 3d orbitals and $2p_z$ orbitals are eight in cobaltocene and in nickelocene. The energies of these orbitals are in the range of -0.4935 to -0.3583 eV and -0.5021 to -0.2296 eV for cobaltocene and nickelocene, respectively. The less stable orbitals are twelve in both the cases. The energies of these orbitals are in the range -0.0875 to 2.0412 eV in cobaltocene and 0.0713 to 4.2942 eV in nickelocene. The energy of the first MO or in other word the most stable orbital in cobaltocene is -1.1027 and in nickelocene -1.1902eV. The energy of highest occupied molecular orbital (HOMO) is -0.3906 eV in cobaltocene, and -0.3764 eV, in nickelocene. The MO is 30^{th} of both 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 χ_r . Let there be n_i electrons in the molecular orbital ϕ_i ($n_i = 0. 1, 2$) and let n_i symbolize the contribution of electrons in the MO ϕ_i to the net population in χ_r we have

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

where c_{ri} is the coefficient of atomic orbital for the ith MO (r–1 = 30) in cobaltocene and (r = 30) in nickelocene. Equation-1 has been solved for fifty-nine electrons of thirty MOs in cobaltocene and sixty electrons of thirty MOs in nickelocene. Each MO has two electrons in nickelocene whereas in case of cobaltocene the 30th MO has one electron. The coefficient of atomic orbitals [29] i.e. c_{ri} is the eigenvector value. The orbitals having eigenvector values above 0.22 have only been considered. Our interest is only in eight MOs 23-30 in cobaltocene and 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 MOs of cobaltocene and nickelocene; hence they are not of our interest. For cobaltocene and nickelocene the results of solution of equation-1 for MOs 23-30 is given below:

Cobaltocene

MO	χ	AO	c _{ri}	n _{r,i}	MO	χ	AO	c _{ri}	n _{r,i}
23	16	$4C-2p_z$	0.2610	0.13624	28	4	1C-2pz	0.2825	0.15961
	45	11Co -3 dx ² -y ²	0.2507	0.12570		12	3C-2pz	0.2548	0.12984
	46	11Co -3 dz ²	0.4737	0.44878		24	6C-2pz	0.2836	0.16085
	47	11Co-3dxy	0.2664	0.14193		28	7C–2pz	0.2755	0.15180
	48	11Co-3dxz	0.2327	0.10829		34	$9C-2p_x$	0.2290	0.10480
24	45	11Co -3 dx ² -y ²	0.5537	0.61316		36	9C-2pz	0.2362	0.11158
	47	11Co-3dxy	0.4186	0.35045		47	11Co-3dxy	0.2339	0.10941
	49	11Co-3dyz	0.2781	0.15467		49	11Co-3dyz	0.2297	0.10552
25	46	11Co -3 dz ²	0.5218	0.54455	29	34	9C-2p _x	0.2557	0.13076
	48	11Co-3dxz	0.3033	0.18398		38	10C-2px	0.3190	0.20352
	49	11Co-3dyz	0.5717	0.65368		39	$10C-2p_y$	0.3829	0.29322
26	34	9C-2p _x	0.2568	0.13189		40	$10C-2p_z$	0.3061	0.18739
	45	11Co -3 dx ² -y ²	0.2652	0.14066		48	11Co-3dxz	0.2946	0.17357
	47	11Co-3dxy	0.5281	0.55777	30	4	1C-2pz	0.2899	0.08404
	48	11Co-3dxz	0.3717	0.27632		12	3C-2pz	0.2750	0.07562
	49	11Co-3dyz	0.3035	0.18422		20	5C-2pz	0.2474	0.06120
27	8	$2C-2p_z$	0.3281	0.21529		24	6C-2pz	0.2537	0.06436
	12	3C-2pz	0.2463	0.12132		32	8C-2pz	0.2649	0.07017
	16	$4C-2p_z$	0.2716	0.14753		46	11Co -3 dz ²	0.5131	0.26327
	24	6C-2pz	0.2369	0.11224		47	11Co-3dxy	0.2416	0.05837
	47	11Co-3dxy	0.2931	0.17181		48	11Co-3dxz	0.3996	0.15968
Nicke	locene	2							
MO	χ	AO	c _{ri}	n _{r.i}	МО	X	AO	c _{ri}	n _{r.i}
23	45	11Ni -3 dx ² -y ²	0.4179	0.34928		24	6C-2pz	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 -3 dx ² $-$ y ²	0.5232	0.54747	29	8	2C-2pz	0.4179	0.34928
	46	11Ni -3 dz ²	0.3369	0.22700		16	4C-2pz	0.2561	0.13117
	48	11Ni-3dxz	0.2396	0.11481		20	5C-2pz	0.2707	0.14655
	49	11Ni–3dyz	0.2782	0.15479		28	7C–2pz	0.3600	0.25920
26	46	11Ni -3 dz ²	0.7408	1.09756		40	10C-2pz	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-2pz	0.3232	0.20891
	39	10C-2py	0.2367	0.11205		24	6C-2pz	0.3096	0.19170
	47	11Ni–3dxy	0.6697	0.89699		32	8C-2pz	0.3219	0.20723
	49	11Ni–3dyz	0.2358	0.11120		40	10C-2pz	0.2300	0.10580
28	4	$1C-2p_z$	0.2818	0.15882		46	11Ni -3 dz ²	0.2979	0.17748
	12	3C-2pz	0.3050	0.18605		48	11Ni–3dxz	0.4786	0.45811
	20	5C-2pz	0.2252	0.10143		49	11Ni–3dyz	0.3521	0.24794

The above data very clearly indicate that only $2p_z$ orbital of carbon of $C_5H_5^-$ and 3d orbitals of cobalt or nickel provide electrons to MOs of cobaltocene and nickelocene. However, it is prominently noticeable that electrons are provided from different orbitals in the cobaltocene and nickelocene, and their n_{ri} also differs.

CONCLUSION

The eigenvalues and eigenvectors of cobaltocene and nickelocene show that the first eight MOs in cobaltocene and 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 twelve MOs in ferrocene and 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. In cobaltocene the 3dxy orbital out of 3d

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orbitals and 4s orbital out of 4s, 4p orbitals of cobalt has maximum involvement which is in the order $3dxy > 3dyz > 3dz^2 > 3dz^2 - y^2$ and $4s > 4p_z > 4p_y > 4p_x$. 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 $4p_y > 4p_x > 4p_z > 4p_z > 4s$. The total involvement in respect of bonding between $C_5H_5^-$ and the metal orbitals as derived from coefficient value is 22.346 in cobaltocene and in nickelocene are 23.5716. 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 33.3314 and 32.135. The most stable MOs have their energies in the range -0.4935 to -0.3583 eV in cobaltocene and the range -0.5021 to -0.2296 eV in nickelocene. In cobaltocene the energy of most stable MO is -1.1027eV and highest occupied molecular orbital is -0.3906 eV. In nickelocene the energy of most stable MO is -1.1902 eV and highest occupied molecular orbital is -0.3764 eV. 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 cobaltocene and nickelocene.

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