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Eigen Vector Based Study Of Molecular Structure Of Cyclopentadienyl Anion

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ABSTRACT

The MO of $C_5H_5^-$ are formed by linear combination of atomic orbitals of five carbon (2s, 2px, 2py, 2pz) and five hydrogen atom(1s). The energy levels of molecular orbitals have been quantitatively evaluated and energy level diagram have been drawn. The most stable molecular orbital has eigen value -1.0886 e.V and highest occupied molecular orbital (HOMO) has eigen value of -0.4407. The eigen vector analysis shows that HOMO has contribution of only 2pz orbitals of carbon. The population analysis also indicates that only 2pz orbitals are present in molecular orbitals 13 that is HOMO. The contribution of electrons in the formation of molecular orbitals is described on the basis of coefficient of eigen vector.

KEYWORDS

$C_5H_5^-$;
Energy level;
Eigen vector;
Population analysis.

INTRODUCTION

In our recent communication[1-3], we have made new studies on molecular structure of ferrocene and its derivatives. The study was based on calculation of energy levels, eigen vector values, and population analysis. Since the calculation of the relative energy levels and involvement of various atomic orbitals in the formation of molecular orbital in metallocenes and cyclopentadienyl anion is still a subject of uncertainty[4], we present a study on cobaltocene[5] which has a sandwich structure similar to ferrocene and also of $C_5H_5^-$. The application of molecular mechanics to organometallic and transition metal chemistry is growing[6]. With the help of this technique we present a study on the molecular structure of cobaltocene, and the cyclopentadienyl anion ($C_5H_5^-$). In this paper we present a study on molecular structure of $C_5H_5^-$ only.

MATERIAL AND METHOD

The study material of this paper is cyclopenta dienyl anion ($C_5H_5^-$). The 3D modeling and geometry optimization of($C_5H_5^-$) have been done by CAChe software using molecular mechanics method with EHT option[5]. 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 studied.

Theory

The theory has been described in our earlier work[1], and is also presented here. 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)[7-9]. An STO centered on atom a has the form$(Nr_a^{n-1} e^{-\zeta ra} Y_l^m(\theta_a, \phi_a)$. Each MO$\phi_i$ is expressed as $\phi_i=\Sigma_i c_{ri} \chi_r$, where, the χ_r's are the STO basis functions. Here we use the STO-6G basis set(which is contracted Gaussian)[10-13] for the SCF calculation.

The coefficients in linear combination for each MO being found by solution of the Roothaan equation[14]. The most efficient way to solve the Roothaan equation is to use matrix-algebra methods. In matrix–algebra methods, the matrix elements are computed[15], and the secular equation is solved to give the set of orbital energies(i.e. eigenvalues). These orbital energies[16] are used to solve Roothaan equations for the set of coefficients(i.e. eigenvectors) giving a set of MOs. The calculations are done using a computer.

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

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken[17-18]. He proposed a method that apportions the electrons of an n-electron molecule into net population's 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, $_{2...}$ 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 MOϕ_i 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 MOϕ_i(n_i=0, 1, 2) and let $n_{r,i}$ and $n_{r-s,i}$ 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 $n_{r,i} = n_i c_{ri}^2$, $n_{r-s,i}=n_i(2c_{ri}c_{si}S_{rs})$

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

RESULT AND DISCUSSION

The molecular orbitals of $C_5H_5^-$ are formed by linear combination of five carbon atoms and five hydrogen atoms. Each carbon provides four atomic orbitals(2s, $2p_x$, $2p_y$ and $2p_z$) and each hydrogen atom provides only one atomic orbital(1s). As such 25 atomic orbitals of carbon and hydrogen are involved in the formation of molecular orbitals of $C_5H_5^-$ The LCAO approximations of these orbitals will form 25 molecular orbitals, the eigen values of these orbitals are shown in TABLE 1.

The involvement of various atomic orbitals in the formation of MOs is indicated by coefficients of eigen vector.

The basis functions commonly known as atomic orbitals are represented by χ and molecular orbitals by Φ. The details of χ representing various atomic orbital are as below :

TABLE 1: Eigen values

M.Os. -Φ	Eigen values(eV)	M.Os.-Φ	Eigen values (eV)
1	-1.0886	13	-0.4407
2	-0.8865	14	-0.236
3	-0.8865	15	-0.236
4	-0.6808	16	0.1629
5	-0.6808	17	0.1629
6	-0.6051	18	0.289
7	-0.5352	19	0.4018
8	-0.5224	20	0.4359
9	-0.5224	21	0.4359
10	-0.5077	22	0.9223
11	-0.5077	23	0.9223
12	-0.4407	24	2.1715

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Atomic orbital

C_1	=>	2s	=	χ_1	2py	=	χ_{11}		
2px	=	χ_2			2pz	=	χ_{12}		
2py	=	χ_3			C_4	=>	2s	=	χ_{13}
2pz	=	χ_4			2px	=	χ_{14}		
C_2	=>	2s	=	χ_5	2py	=	χ_{15}		
2px	=	χ_6			2pz	=	χ_{16}		
2py	=	χ_7			C_5	=>	2s	=	χ_{17}
2pz	=	χ_8			2px	=	χ_{18}		
C_3	=>	2s	=	χ_9	2py	=	χ_{19}		
2px	=	χ_{10}			2pz	=	χ_{20}		

The contribution of , in the formation of molecular orbitals is indicated by coefficient of eigen vector. A higher value of coefficient indicates major combination of atomic orbital, the lower value shows weak contribution. The weak contributions have been omitted, and major contributions are illustrated below:-

LCAO–presentation

Equation -1

Molecular orbitals		Coefficients eigen vector of χ(Major contribution)	Atomic orbitals
Φ_1	=	χ_1(-0.3110), χ_5(-0.3110), χ_9(-0.3110), χ_{13}(-0.3110), χ_{17}(-0.3110)	2s, 2s, 2s, 2s, 2s
Φ_2	=	χ_1(-0.2634), χ_5(-0.4362), χ_{10}(0.0880), χ_{13}(0.4324), χ_{17}(0.2734)	2s, 2s, 2px, 2s, 2s
Φ_3	=	χ_1(-0.3731), χ_5(0.1352), χ_9(0.4567), χ_{13}(0.1470), χ_{17}(-0.3658)	2s, 2s, 2s, 2s, 2s
Φ_4	=	χ_1(0.1932), χ_5(-0.2867), χ_9(0.2706), χ_{15}(-0.1655), χ_{18}(-0.1622)	2s, 2s, 2s, 2py, 2px
Φ_5	=	χ_1(0.2218), χ_7(0.1257), χ_{11}(0.1520), χ_{13}(0.2523), χ_{17}(-0.2930)	2s, 2py, 2py, 2s, 2s
Φ_6	=	χ_2(-0.2270), χ_7(-0.1953), χ_{11}(-0.1873), χ_{14}(0.2228), χ_{19}(0.2365)	2px, 2py, 2py, 2py, 2px,
Φ_7	=	χ_4(0.3549), χ_8(0.3549), χ_{12}(0.3549), χ_{16}(0.3549), χ_{20}(0.3549)	2pz, 2pz, 2pz, 2pz, 2pz
Φ_8	=	χ_3(0.2395), χ_7(-0.3391), χ_{10}(0.1789), χ_{14}(-0.3653), χ_{19}(-0.2170)	2py, 2py, 2px, 2px, 2py
Φ_9	=	χ_2(0.3327), χ_6(-0.2459), χ_{11}(-0.3011), χ_{15}(0.2431), χ_{19}(-0.3133)	2px, 2px, 2py, 2py, 2py
Φ_{10}	=	χ_3(-0.3398), χ_6(-0.4017), χ_{10}(0.3844), χ_{15}(-0.2719), χ_{19}(0.1715)	2py, 2px, 2px, 2py, 2py
Φ_{11}	=	χ_3(-0.3043), χ_7(0.1933), χ_{11}(-0.2415), χ_{15}(0.3572), χ_{18}(0.4704)	2py, 2py, 2py, 2py, 2px
Φ_{12}	=	χ_4(-0.3452), χ_8(-0.5832), χ_{12}(- 0.0165), χ_{16}(0.5750), χ_{20}(0.3718)	2pz, 2pz, 2pz, 2pz, 2pz
Φ_{13}	=	χ_4(-0.5031), χ_8(0.1728), χ_{12}(0.6100), χ_{16}(0.2041), χ_{20}(-0.4838)	2pz, 2pz, 2pz, 2pz, 2pz
Φ_{14}	=	χ_4(0.5143), χ_8(-0.7728), χ_{12}(0.7362), χ_{16}(0.4183), χ_{20}(-0.0593)	2pz, 2pz, 2pz, 2pz, 2pz
Φ_{15}	=	χ_4(-0.6069), χ_8(0.1887), χ_{12}(0.3016), χ_{16}(-0.6767), χ_{20}(0.7933)	2pz, 2pz, 2pz, 2pz, 2pz
Φ_{16}	=	χ_2(-0.4634), χ_7(-0.5169), χ_{11}(-0.3187), χ_{14}(-0.5630), χ_{19}(-0.4763)	2px, 2py, 2py, 2px, 2py
Φ_{17}	=	χ_2(0.5214), χ_7(-0.3805), χ_{11}(-0.5417), χ_{14}(0.3989), χ_{19}(-0.5331)	2px, 2py, 2py, 2px, 2py
Φ_{18}	=	χ_2(-0.3498), χ_5(0.3274), χ_9(0.3274), χ_{14}(0.3435), χ_{19}(0.3645)	2px, 2s, 2s, 2px, 2py
Φ_{19}	=	χ_3(0.8155), χ_6(-0.7016), χ_{10}(-0.6731), χ_{15}(-0.8005), χ_{18}(0.8496)	2py, 2px, 2px, 2py, 2px
Φ_{20}	=	χ_2(0.6486), χ_7(-0.1888), χ_{11}(-0.2186), χ_{14}(-0.6645), χ_{19}(0.8579)	2px, 2py, 2py, 2px, 2py
Φ_{21}	=	χ_2 (-0.5079), χ_7 (0.6831), χ_{11}(-0.6440), χ_{14}(-0.6408), χ_{19}(-0.0249)	2px, 2py, 2py, 2px, 2py
Φ_{22}	=	χ_3(-0.6865), χ_5(-0.8430), χ_{10}(-0.6482), χ_{13}(0.7942), χ_{18}(-0.6143)	2py, 2s, 2px, 2s, 2px
Φ_{23}	=	χ_1(-0.7428), χ_6(-0.6686), χ_9(0.8608), χ_{15}(0.7187), χ_{17}(-0.6499)	2s, 2px, 2s, 2py, 2s
Φ_{24}	=	χ_1(0.8999),χ_5(-1.3489), χ_9(1.2827),χ_{13}(-0.7265), χ_{18}(0.3259)	2s, 2s, 2s, 2s, 2px
Φ_{25}	=	χ_1(-1.0563), χ_5(0.3256), χ_9(0.5295), χ_{13}(-1.1823), χ_{17}(1.3835)	2s, 2s, 2s, 2s, 2s

Figure 1: Energy level diagram of $C_5H_5^-$

M.Os.-Φ	Eigen value(e.V)	Energy levels	Atomic orbitals
24	2.1715	-	2s, 2s, 2s, 2s, 2px 2s, 2s, 2s, 2s, 2s
22	0.9223	-	2py, 2s, 2px, 2s, 2px 2s, 2px, 2s, 2py, 2s
19	0.4359	-	2py, 2px, 2px, 2py, 2px 2px, 2py, 2py, 2px, 2py
18	0.289	-	2px, 2py, 2py, 2px, 2py 2px, 2s, 2s, 2px, 2py
16	0.1629	-	2px, 2py, 2py, 2px, 2py 2px, 2py, 2py, 2px, 2py
14	-0.236	-	2pz, 2pz, 2pz, 2pz, 2pz 2pz, 2pz, 2pz, 2pz, 2pz
13	-0.4407	-	2pz, 2pz, 2pz, 2pz, 2pz, 2pz, 2pz, 2pz, 2pz, 2pz 2py, 2py, 2py, 2py, 2px 2py, 2px, 2px, 2py, 2py 2px, 2px, 2py, 2py, 2py 2py, 2py, 2px, 2px, 2py 2pz, 2pz, 2pz, 2pz, 2pz 2px, 2py, 2py, 2py, 2px
4	-0.6806	- -	2s, 2py, 2py, 2s, 2s 2s, 2s, 2s, 2py, 2px
2	-0.8865	- -	2s, 2s, 2px, 2s, 2s 2s, 2s, 2s, 2s, 2s 2s, 2s, 2s, 2s, 2px 2s, 2s, 2s, 2s, 2s
1	-1.0886	-	2s, 2s, 2s, 2s, 2s

Linear combination of atomic orbitals as presented in equation-1 shows that 2s orbitals are involved in sigma bonding between carbon and carbon, and between carbon and hydrogen. The p orbitals are involved mostly in pi bonding and are also further avail-

TABLE : 2

MO(Φ)	Atomic orbital	Eigen vector(c_{ri})	No.of electrons(n_i)	$n_{ri}= n_ic^2_{ri}$
1	1C-2s	-0.311	2	0.193442
	2C-2s	-0.311	2	0.193442
	3C-2s	-0.311	2	0.193442
	4C-2s	-0.311	2	0.193442
	5C-2s	-0.311	2	0.193442
	6H-1s	-0.0118	2	0.000278
	7H-1s	-0.0118	2	0.000278
	8H-1s	-0.0118	2	0.000278
	9H-1s	-0.0118	2	0.000278
	10H-1s	-0.0118	2	0.000278
2	1C-2s	-0.2634	2	0.13875912
	2C-2s	-0.4362	2	0.38054088
	4C-2s	0.4324	2	0.37393952
	5C-2s	0.2734	2	0.14949512
3	1C-2s	-0.3731	2	0.27840722
	3C-2s	0.4567	2	0.41714978
	5C-2s	-0.3658	2	0.26761928
4	1C-2s	0.1932	2	0.074652
	2C-2s	-0.2867	2	0.16439378
	3C-2s	0.2706	2	0.14644872
	7H-1s	-0.3073	2	0.18886658
	8H-1s	0.2901	2	0.16831602
5	1C-2s	0.2218	2	0.09839
	4C-2s	0.2523	2	0.12731058
	5C-2s	-0.293	2	0.171698
	6H-1s	0.2377	2	0.11300258
	9H-1s	0.2704	2	0.14623232
	10H-1s	-0.3141	2	0.19731762

TABLE : 3

MO(Φ)	Atomic orbital	Eigen vector(c_{ri})	No. of electrons(n_i)	$n_{ri} = n_ic^2_{ri}$
6	1C-2px	-0.227	2	0.103058
	2C-2py	-0.1953	2	0.076284
	3C-2py	-0.1873	2	0.070162
	4C-2px	0.2228	2	0.09928
	5C-2py	0.2365	2	0.1118645
	6H-1s	0.2219	2	0.09848
	7H-1s	0.2219	2	0.09848
	8H-1s	0.2219	2	0.09848
	9H-1s	0.2219	2	0.09848
	10H-1s	0.2219	2	0.09848
7	1C-2pz	0.3549	2	0.25190802
	2C-2pz	0.3549	2	0.25190802
	3C-2pz	0.3549	2	0.25190802
	4C-2pz	0.3549	2	0.25190802
	5C-2pz	0.3549	2	0.25190802
8	1C-2py	0.2395	2	0.1147205
	2C-2py	-0.3391	2	0.22997762
	4C-2px	-0.3653	2	0.26688818
	5C-2py	-0.217	2	0.094178
	6H-1s	0.1927	2	0.074266
	7H-1s	0.3089	2	0.19083842
	9H-1s	-0.31	2	0.1922
	10H-1s	-0.1898	2	0.072048

TABLE : 4

MO(Φ)	Atomic orbital	Eigen vector(c_{ri})	No. of electrons(n_i)	$n_{ri}=n_ic^2_{ri}$
9	1C-2px	0.3327	2	0.22137858
	2C-2px	-0.2459	2	0.12093362
	3C-2px	0.2337	2	0.221378
	3C-2py	-0.3011	2	0.18132242
	4C-2py	0.2431	2	0.11819522
	5C-2py	-0.3133	2	0.19631378
	6H-1s	-0.2622	2	0.13749768
	8H-1s	0.3253	2	0.21164018
	10H-1s	-0.2643	2	0.13970898
10	1C-2py	-0.3398	2	0.23092808
	2C-2px	-0.4017	2	0.32272578
	2C-2py	0.2319	2	0.107556
	3C-2px	0.3844	2	0.29552672
	3C-2py	0.2082	2	0.086694
	4C-2py	-0.2719	2	0.14785922
	1C-2px	-0.2089	2	0.087278
	1C-2py	-0.3043	2	0.18519698
	2C-2py	0.1933	2	0.07473
11	3C-2py	-0.2415	2	0.1166445
	4C-2px	-0.2181	2	0.095136
	4C-2py	0.3572	2	0.25518368
	5C-2px	0.4704	2	0.44255232
	7H-1s	-0.2155	2	0.09288
	8H-1s	0.2012	2	0.080962
12	1C-2pz	-0.3452	2	0.23832608
	2C-2pz	-0.5832	2	0.68024448
	4C-2pz	0.575	2	0.66125
	5C-2pz	0.3718	2	0.27647048
13	1C-2pz	-0.5031	2	0.506219
	3C-2pz	0.61	2	0.7442
	5C-2pz	-0.4838	2	0.468125

able for pi bonding with iron in ferrocene, and with cobalt in cobaltocene. In order to examin the availability of p orbitals for such a bonding we have drawn the energy level diagram of $C_5H_5^-$ shown in figure 1. The most stable energy level has eigen value of -1.088eV, this level has sigma bonds composed of 2s orbitals of carbon, followed by four more energy levels which are also formed by 2s orbitals. The involvement of p orbitals starts from molecular energy level six, and continues up to energy level 13, which is the highest occupied molecular orbital(HOMO). The eigen value of this level is -0.4407e.V. The energy level prior to this level also has eigen value of -0.4407e.V. The orbitals available for further bonding with ferrocene or cobaltocene are from these energy

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levels which are composed of 2pz orbitals of carbon.

Population analysis

The population analysis method, introduced by Mulliken, is used to calculate the contribution of electrons in each occupied MO. The method apportions the electrons of n electron molecule into net population n_r in the basic function χ_r.

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

$$n_{r,i}=n_i C^2_{ri}$$

where C_{ri}=Coefficients of atomic orbital for the i^{th} MO(r=1-13)

The above equation has been solved for 26 electrons of 13 molecular orbitals each having two electrons. The twelve molecular orbitals having no electrons are left over. The coefficient of atomic orbitals that is C_{ri} values are eigen vector values. Zero or nearly zero values have not been considered. The results are included in TABLES 2, 3, 4.

The population analysis also clearly indicates that in molecular orbital 12 and 13, the major contribution is from 2pz orbitals. Since MO 13 is the HOMO and comprises of 2pz orbital it is clear that 2pz orbital of $C_5H_5^-$ will form pi bonding in ferrocene and cobaltocene.

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