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Study of The Electronic Distribution for Di-Chloride Di-Oxide Manganese : B3LYP Density Functional Calculation

دراسة التوزيع الالكتروني لثنائي كلوريد ثنائي اوكسيد المنغنيز بطريقة دالة الكثافة B3LYP

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Abstract

The electronic distribution of di-chloride di-oxide manganese MnO_2Cl_2 was calculated by employing B3LYP/6-31G** density functional theory.

The linear combination of atomic orbitals-molecular orbital calculation and the energy level diagram showed that the unpaired electron lies in the manganese ion $3d_{x^2-y^2}$ orbital mixed with a small amount of the d_{z^2} orbital and it is strongly delocalized on the ligands.

The results showed that the spread of unpaired electron population on ligand atomic orbitals besides the metal $3d_{x^2-y^2}$ and d_{z^2} orbitals makes from this metal complex studied in this work is very useful as a catalyst . All calculations are carried out by employing Gaussian 09 package of program

الخلاصة :

تم حساب التوزيع الالكتروني للمركب داي – كلورو – داي اوكسيد المنغنيز بتطبيق طريقة دالة الكثافة بالمستوى B3LYP/6-31G** . حسابات الاتحاد الخطي للمدارات الذرية حسب نظرية المدار الجزيئي ومخطط مستويات الطاقة التي تم الحصول عليها تبين ان الالكترون المنفرد يقع في مدارات d_{z^2} $3d_{x^2-y^2}$, لمعدن المنغنيز. كما تبين النتائج ان الفاصلة في تعدادية الالكترون بين مدارات ايونات كل من الكلور و الاوكسجين وبين مدارات المعدن d_{z^2} $d_{x^2-y^2}$, يحصل من هذا المعقد المعدني ويلعب دور كبير ومهم كعامل مساعد في تسريع التفاعلات الكيميائية. ان جميع الحسابات اجريت بتطبيق برنامج Gaussian 09.

Introduction

Theoretical computations in physics and chemistry using various methods were widely used in last years. One of the important method is the density functional theory used to study the physical properties of atomic and molecular systems. The hyper successful of the programming and computer systems of highly accuracy and speed enabled the improvements in the increased accuracy and speed of evaluating theoretical results.

Many studies of electronic properties depend on computational methods[1]. Benzair and Aurag [2] in 2003 studied the electronic properties of crystals using density functional theory in 2004, Aboud[3] studied the electronic distribution of some metal complexes using ab-initio method. Electronic properties for different molecular systems using density functional theory are studied [4].

The present work aims to classify MnO_2Cl_2 compound theoretically according to group theory using linear combination atomic orbitals–molecular orbital (LCAO-MO) and study of the electronic details.

In this work, density functional theory has been used to calculate the electronic distribution of di-chloride di-oxide manganese at B3LYP functional with 6-31G** basis sets [5]. The geometry optimization and energies have been done using Gaussian 09 program [6].

Theory

The total energy E_T according to the density functional theory can be written in the form [7]:

$$E_T = T(\rho_o) + \int V_{en}(r)\rho_o(r)dr + J(\rho_o) + E_{NC}(\rho_o) \; \ldots\ldots\ldots\ldots..(1)$$

The particle density $p_{(r)}$ for a normalized wave function is given by ;

$$\rho(r) = \sum_{i}^{ni} [\psi_i(r)]^2 \qquad \ldots\ldots..(2)$$

Where ni is the number of electrons in orbital (i) , and the summation is over the occupied molecular orbitals . the kinetic energy of the system is [8]:

$$T[\rho] = T_s[\rho] + J[\rho] + V_{en}[\rho] + E_{xc}[\rho] \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

$T_s[\rho]$, $J[\rho]$, $V_{en}[\rho]$ and $E_{xc}[\rho]$ are the kinetic energy of non interacting electron system, classical coulomb energy, and exchange correlation energy, respectively [9].

$$T_S[\rho] = -\frac{1}{2}\sum_i \left\langle \phi_i \middle| \nabla^2 \middle| \phi_i \right\rangle$$

$$J_1[\rho] = \frac{1}{2}\iint \frac{\rho(r_2)\rho(r_1)}{|r_1 - r_2|} dr_1 dr_2$$

$$V_{en}[\rho] = \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + E_{NC}[\rho]$$

According to B3LYP functional, the exchange correlation energy E_{XC}^{B3LYP} is given by[10].

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + a_o(E_X^{HF} - E_X^{LDA}) + a_x(E_X^{GGA} - E_X^{LDA}) + a_c(E_C^{GGA} - E_C^{LDA})$$

Where the three parameters $a_o = 0.20$, $a_x = 0.72$ and $a_c = 0.81$.

Results and discussion

Figure 1 show the optimized structure for the studied metal complex , this structure was optimized at the three parameters Lee-Yang-Parr (B3LYP) functional using 6-31G** basis sets. the bond length Mn-Cl is 2.15 A, the bond length Mn-O is 1.58 A. The angles in degree between the atoms results from the geometry optimization: O-Mn-O, O-Mn-Cl and Cl-Mn-Cl are 106, 114 and 117, respectively.

The calculations of optimization illustrate that this compound can be classified according to C_{2v} group symmetry classes, in which the molecular orbitals can be grouped and derived from the 2s and 2p orbitals of the oxide ions, 3s and 3p orbitals of the chlorine atoms, and 3d, 4s and 4p orbitals of the manganese ion.

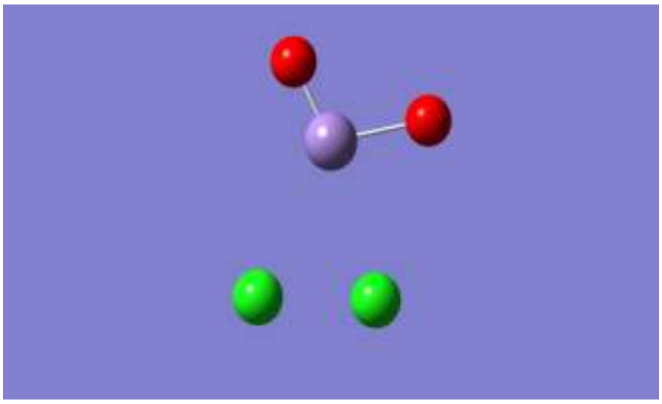

Figure 1: The optimized structure for MnO_2Cl_2 from B3LYP/DFT

Table 1 shows the standard orientation of the compound represents the coordinates of atoms in three dimension obtained from the optimization at B3LYP density functional theory.

Table 1: The standard orientation of atoms

Atom	**Atomic Number**	**Coordinates (Angstroms)**		
		X	Y	Z
MN	25	0.000000	0.917739	0.000000
O	8	1.667199	1.233551	0.000000
O	8	-0.704323	2.454359	0.000000
Cl	17	0.839799	-1.594607	0.000000
Cl	17	-1.292917	-1.490496	0.000000

Table 2 shows the electronic distribution results analyzed from the calculations of B3LYP density functional theory. these results include the eigen values (energy levels) in electron volt and the atomic orbital coefficients in terms of liner combination atomic orbitals –molecular orbitals (LCAO-MO). The eigen values in table 2 are classified according to C_{2v} group symmetry, therefore they distributed in four groups A_1, A_2, B_1 and B_2 . As we see in this table, the unpaired electron is in the starred orbital (orbital number 17 in A_1 symmetry).

Table 2: Eigen value and atomic orbital coefficients of MnO_2Cl_2 from B3LYP/ DFT

A_1 symmetry

Molecular orbital no.	**Energy eV**	**Atomic orbital coefficients**		
		$4p_y$	**$3d_{yz}$**	**$3p_y$**	**$2p_y$**
6	-9.8	-0.010	0.901	0.202	0.385
12	-7.2	0.398	-0.102	0.855	0.097
19	-4.9	0.202	0.795	-0.098	0.515
22	-2.5	0.892	-0.210	0.295	0.295

Mol-ecular Orbit-al no.	**Ener-gy eV**	**Atomic orbital coefficients**									
		4s	**$4p_z$**	**$3d_{z^2}$**	**$d_{x^2-y^2}$**	**3s**	**$3p_z$**	**$3p_x$**	**2s**	**$2p_z$**	**$2p_x$**
1	-27.4	0.098	0.001	0.102	-0.001	-0.031	-0.007	-0.000	-0.985	0.048	-0.000
3	-20.2	0.295	-0.035	-0.098	0.018	0.795	0.020	-0.162	-0.101	-0.000	0.001
5	-9.4	-0.101	0.101	0.305	0.405	0.201	0.092	-0.192	0.020	0.000	0.795
9	-9.1	-0.097	0.096	0.338	0.598	0.198	-0.505	0.101	0.072	0.002	-0.000
10	-8.2	0.392	0.105	-0.098	0.095	-0.115	-0.130	0.605	0.130	0.602	0.000
15	-7.7	0.020	-0.070	0.095	0.000	-0.000	0.398	0.004	-0.001	0.895	0.000
17*	-6.9	-0.075	-0.035	-0.522	-0.695	0.000	0.488	0.205	0.076	-0.301	0.000
21	-3.5	-0.098	0.101	0.605	0.292	-0.101	-0.204	0.395	-0.195	0.605	0.000
23	2.1	-0.010	0.895	-0.172	0.025	0.240	-0.330	0.201	-0.198	0.000	-0.101
25	10	0.805	-0.101	-0.098	-0101	-0.495	-0.245	-0.110	-0401	0.000	0.295

A_2 symmetry

B_1 symmetry

Molecular orbital no.	**Energy eV**	**Atomic orbital coefficients**		
		$3d_{xy}$	**$3p_y$**	**$2p_y$**
8	-8.8	0.895	0.402	0.000
16	-7.1	0.035	-0.000	0.987
18	-5.8	0.605	0.785	-0.000

B_2 symmetry

Molecu-lar Orbital no.	**Energy eV**	**Atomic orbital coefficients**							
		$4p_x$	**$3d_{xz}$**	**3s**	**$3p_z$**	**$3p_x$**	**2s**	**$2p_2$**	**$2p_x$**
2	-27.1	0.000	0.000	0.001	0.001	0.000	0.975	0.020	0.000
4	-19.9	0.075	0.087	0.895	0.000	-0.010	-0.001	-0.000	0.000
7	-0.9	-0.095	-0.705	0.101	-0.305	0.402	-0.495	0.000	0.001
11	-7.4	-0.101	-0.005	-0.905	0.082	0.102	0.085	0.000	0.000
13	-7.1	0.088	0.072	-0.030	-0.802	0.085	-0.001	0.802	0.000
14	-6.9	-0.001	-0.000	0.000	-0.001	0.009	0.000	0.990	0.000
20	-4.1	0.002	-0.002	-0.002	0.021	-0.000	0.985	-0.001	-0.002
24	2.6	0.895	0.105	0.510	-0.302	-0.035	0.088	0.000	0.000

The results of Mulliken atomic spin densities are distributed as below:

Atom	Spin density
Mn	2.862385
O	-0.969311
O	-1.055087
Cl	0.083365
Cl	0.078647

And the dipole moment as a field-independent basis in Debye are taken the values:

X= -5.5577 Y= -8.0348 Z= 0.0000 Tot= 9.7696 Debye

If the dipole coupling is taken into account, the results of spin dipole couplings can be represented in table 3, in which the total energy from SCF (E= - 60355.93016902801 e V) with -V/T = 2.0002.

Table 3: The spin dipole couplings of the compound

Atom	**XX**	**YY**	**ZZ**	**X Y**	**XZ**	**YZ**
MN	0.066945	2.169741	-2.236686	1.923229	0.000000	0.000000
O	-2.519758	1.523090	0.996667	0.776249	0.000000	0.000000
O	-3.195791	1.777736	1.418055	-0.221087	0.000000	0.000000
Cl	0.182659	-0.006009	-0.176650	0.300393	0.000000	0.000000
Cl	-0.428245	0.412629	0.015616	-0.336295	0.0000 00	0.0000 0

Using the linear combination atomic orbitals-molecular orbitals calculations, the A_1 antibonding molecular orbital can be takes the form

$$\Psi^*(A_1) = \alpha_1^*(ad_{X^2-Y^2} + bd_{z^2}) + \alpha_1^{*(I)} 3\rho_z(A_1) + \alpha_1^{*(II)} 2\rho_Z(A_1)$$

The bonding molecular orbitals for di- oxide manganese complex using the results of DFT method can be written in the forms :

$$\Psi(A_2) = \alpha_2 d_{xy} + \alpha_2^{(I)} 3P_y(A_2) + \alpha_2^{(II)} 2\rho_y(A_2)$$

$$\Psi(B_1) = \beta_1 d_{xz} + \beta_1^{(I)} 4\rho_X + \beta_1^{(II)} 3\rho_z(B_1) + B_1^{(III)} 3\rho_X(B_1) + \beta_1^{(IV)} 2\rho_z(B_1)$$

$$\Psi(B_2) = \beta_2 d_{yz} + \beta_2^{(I)} 4\rho_2 + \beta_2^{(II)} 3\rho_2(B_2) + \beta_2^{(III)} 2\rho_2(B_2)$$

The important orbitals from the molecular orbital calculations are contributions only from the $d_{x^2-y^2}$ and d_{z^2} for the manganese ion and from $3d_z$ for chlorine atoms and $2p_z$ for oxide ion. Other orbitals contributed by very small amount of their atomic orbital coefficients, as we see in table2.

The unpaired electron is located in antibonding A_1^* molecular orbital, numbered 17. The excited states for this metal complex can be discussed as: These states are produced either by promoting an electron into A_1 molecular orbital from the filled bonding orbitals of A_2,B_1 and B_2 symmetry immediately below A_1 or by promoting the unpaired electron into the empty anti bonding orbitals of A_2, B_1 or B_2 symmetry that lie immediately above A_1.

From the results, we suggest that the spread of unpaired the manganese $d_{x^2-y^2}$ and d_{z^2} orbitals makes from this metals complex is very useful as a catalyst in polymerization.

Conclusions

From the results obtained in present study, we conclude that the level of theory used with large basis sets is a suitable to determine the optimized parameters for metal complexes. The linear combination of atomic orbitals-molecular orbital calculations show that a large spread of unpaired electron population on ligand atomic orbitals besides the d- orbitals of the metal according to C_{2v} group symmetry and this makes from the metal complex is very useful as a catalyst.

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