THEORETICAL STUDY FOR THE ELECTRONIC DISTRIBUTION OF MNO_2CL_2

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Abstract

In this work, the electronic distribution of MnO_2Cl_2 is studied theoretically using ab-initio and semiempirical methods.

The molecular orbital calculations and energy level diagram appears that the unpaired electron lies in the metal 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. From the calculations carried out the spread of unpaired electron population on ligand atomic orbitals besides the metal $d_{x^2-y^2}$ and d_{z^2} orbitals makes from this metal complex is very useful as a catalyst.

Introduction

Theoretical computations in physics and chemistry using various methods were widely used in last years. These methods are very important introduce to the matter and its physical properties, also, the hyper successful of the programming and computer systems of highly accuracy and speed leads to improvement in the theoretical results.

Many searchers were used ab-initio and semiempirical methods. For example, in (2000), A. Laref, et al (1), studied the band structure of Germanium crystal using semiempirical methods. A. Benzair and H. Aourag in (2003) (2), studied the electronic properties and total energy of zinc-blende compounds using the density functional ab-initio methods.

In (2004), Jingzhi Pu, et al (3), studied the electronic structure of some chemical compounds using the combining ab-initio Hartree-Fock wave functions with molecular mechanics.

In (2004), H. I. Aboud (4), studied the electronic structure of some metal complexes using ab- initio and semiempirical methods.

Methods

I.**Hartree-Fock Theory**

In Hartree-Fock HF theory, the wave function is represented by a single N-dimensional Slater determinant $\Phi(x_1, x_2, ..., x_N)$ made up of N orthonormal spin orbitals $\{\chi_i(x)\}$, where x represents both the position r and the spin w of an electron. Each spin orbital can have both a spin up α and a spin down β part, $\psi_i^\alpha(r)$ and $\psi_i^\beta(r)$ respectively (5,6).

$$\chi_i(x) = \psi_i^\alpha(r)\alpha(w) + \psi_i^\beta(r)\beta(w) \qquad (1)$$

In restricted Hartree-Fock RHF and unrestricted Hartree-Fock UHF methods, each spin orbital is either pure α or pure β. In UHF theory, the two sets of molecular orbitals are defined by two sets of coefficients:

$$\psi_i^\alpha = \sum_{i=1}^{N} C_{\mu i}^\alpha \phi_\mu \quad ; \quad \psi_i^\beta = \sum_{i=1}^{N} C_{\mu i}^\beta \phi_\mu \qquad (2)$$

For a given nuclear configuration R_I for a system of M nuclei and a given set of orthonormal spin orbitals, the electronic energy $E_{elec}\left(\{C^{\alpha}_{\mu i}, C^{\beta}_{\mu i}\}, \{R_I\}\right)$ is $^{(7)}$:

$$E_{elec} = \sum_{i=1}^{N} \langle \chi_i | -\frac{1}{2}\nabla_i^2 + \sum_{I=1}^{M} V_I(r_i, R_I) | \chi_i \rangle + \sum_{i=1}^{N}\sum_{j<i} \left[\langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_i \chi_j \rangle \right] \quad (3)$$

where

$$V_I(r_i, R_I) = \frac{Z_I}{|r_i - R_I|}$$ for the electronic r_i and nuclear R_I .

The Born-Oppenheimer $^{(7,8)}$ BO approximation separates the electron and nuclear motions because the nuclear mass is so much larger than electron mass, and the nuclei move on a potential energy surface given by:

$$E\left(\{C^{\alpha}_{\mu i}, C^{\beta}_{\mu i}\}, \{R_I\}\right) = E_{elec}\, E\left(\{C^{\alpha}_{\mu i}, C^{\beta}_{\mu i}\}, \{R_I\}\right) + \sum_{I,J<I}^{M} \frac{Z_I Z_J}{|R_I - R_J|} \quad (4)$$

II. Ab-Initio Methods $^{(9)}$

In ab-initio, the calculations of electronic structure are based on the HF wave functions. The approximate ab-initio treatments are based on the variation principle which requires an evaluation of

$$E[\psi] = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle \quad (5)$$

$$H = \sum_{i} h(i) + \sum_{i<j} \frac{1}{r_{ij}} \quad (6)$$

where h(i), the one electron terms include the kinetic energy of electrons and their interaction with the nuclei.

In the two-electron terms r_{ij} denotes the distance between electrons i and j.

An application of the variation principle requires that all integrals for ψ should factorize into low dimensional cases. This is achieved by building ψ from the one-electron functions ϕ_i called molecular orbitals MO, and this lead to the general configuration interaction:

$$\psi = \sum_{I} C_I \Phi_I \quad (7)$$

$$\Phi_I = [\phi_{i1} \ldots\ldots\ldots \phi_{in}] \quad (8)$$

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (9)$$

III. Semiempirical Methods

Semiempirical Methods are based on the molecular orbital theory. These methods are neglect many smaller integrals to speed up the calculations. Compared with ab-initio methods, semiempirical calculations are much faster, typically by several orders of magnitude $^{(10)}$.

In zero-differential overlap ZDO semiempirical approximation, all repulsion or exchange integrals between any two different atomic orbitals are neglected $^{(11)}$.

Ab-initio self-consistent field SCF methods solve the Roothaan-Hall eigenvalue problem:

$$F\,C = S\,C\,E \quad (10)$$

where F, C and S denoted the Fock, eigenvector and overlap matrix, respectively, and E is the diagonal matrix of orbital energies, orthogonalization of the basis leads to a standard eigenvalue problem:

$$^{\lambda}F\,^{\lambda}C = ^{\lambda}C\,E \quad (11)$$

where λ denotes a quantity expressed in an orthogonalized basis. The semiempirical methods solve a secular equation,

$$^{NDDO}F\ ^{NDDO}C = \ ^{NDDO}C\ E$$

where NDDO is a neglect of diatomic differential overlap approximation.

The semiempirical Fock matrix implicitly refers to an orthogonal basis:

$$^{NDDO}F \approx \ ^{\lambda}F \qquad (12)$$

The NDDO Fock matrix elements $F_{\mu\upsilon}$ are given as:

$$F_{\mu^A\upsilon^B} = H_{\mu^A\upsilon^B} - \frac{1}{2}\sum_{\lambda^A}\sum_{\sigma^B}\rho_{\lambda^A\sigma^B}\left(\mu^A\lambda^A, \upsilon^B\sigma^B\right) \qquad (13)$$

where the subscripts A, B refers to an atom A or B with index μ, υ, λ, σ. $H_{\mu\upsilon}$, $\rho_{\lambda\sigma}$ are elements of the one electron core Hamiltonian and density matrix, respectively.

They are written as:

$$H_{\mu\upsilon} = \int \psi_{\mu}\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi_{\upsilon}\, dv \qquad (14)$$

$$\rho_{\lambda\sigma} = 2\sum_{i=1}^{occ} C_{\lambda i}\, C_{\sigma i} \qquad (15)$$

The two-electron integral written as:

$$(\mu\upsilon\,|\,\lambda\sigma) = \iint \psi_{\mu}(1)\,\psi_{\upsilon}(1)\frac{1}{r_{12}}\psi_{\lambda}(2)\,\psi_{\sigma}(2)\, dv_1\, dv_2 \qquad (16)$$

The neglect of all three-center and four-center two electron integrals in NDDO approximation is consistent with this interpretation because these integrals are vanishing small (12).

These basic ideas have implemented in two steps. First, the exchange repulsions have been introduced as valence-shell orthogonalization corrections only in the one-center part of the core Hamiltonian. In the second step, they have also been incorporated in the resonance integrals (12, 13).

Results and Discussion

It is necessary before the calculations, to find the geometry optimization of the compound to give a lower energy. This geometry calculates the forces on the atoms by evaluating the gradient of the energy with respect to atomic coordinates analytically.

In the quantum mechanics programs, such as, Gaussian, the form of geometry input called Z-matrix. This matrix specifies the positions of atom (n) by three geometric parameters: (1) the bond length r between two atoms r(i,j), (2) the bond angle θ at atom j between lines j-i and j-k, θ(i,j,k) and (3) the dihedral angle ϕ between the two planes defined by i-j-k and j-k-l meeting at the line j-k, $\phi(i, j, k, l)$.

The structure of the compound was optimized at the unrestricted Hartree-Fock level of theory using the Slater-type orbitals (STO-3G) basis set. The geometry optimization of the compound MnO_2Cl_2 is shown in figure (1). The geometry parameters are listed in Table (1).

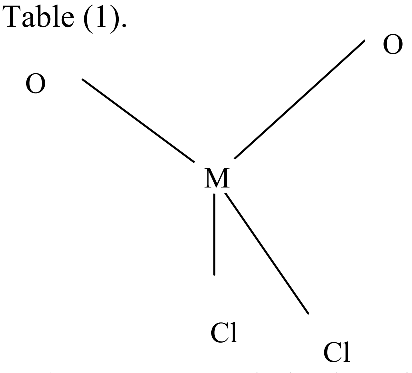

Fig. (1) Geometry Optimization of MnO_2Cl_2

Table (1) Geometry parameters of MnO_2Cl_2.

	Bond length ($\mathring{A}$)	Bond angle (degree)
Mn-O	1.61	
Mn-Cl	2.17	
O-Mn-O		108
O-Mn-Cl		112
Cl-Mn-Cl		116

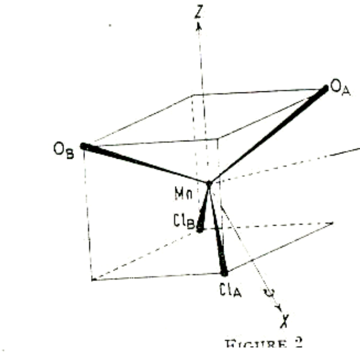

Fig. (2) Coordinate system of MnO_2Cl_2

Table (2) Basis orbitals for the molecular orbitals of MnO_2Cl_2.

class	A_1	A_2
Manganese ion orbitals	4s, $4p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$	$3d_{xy}$
Chloride ion orbitals	$3p_x(A_1)=\frac{1}{\sqrt{2}}(3p_{x_A}-3p_{x_B})$	$3p_y(A_2)=\frac{1}{\sqrt{2}}(3p_{y_A}-3p_{y_B})$
	$3p_z(A_1)=\frac{1}{\sqrt{2}}(3p_{z_A}+3p_{z_B})$	
	$3s(A_1)=\frac{1}{\sqrt{2}}(3s_A+3s_B)$	
Oxide ion orbitals	$2p_x(A_1)=\frac{1}{\sqrt{2}}(2p_{x_A}-2p_{x_B})$	$2p_y(A_2)=\frac{1}{\sqrt{2}}(2p_{y_A}-2p_{y_B})$
	$2p_z(A_1)=\frac{1}{\sqrt{2}}(2p_{z_A}+2p_{z_B})$	
	$2s(A_1)=\frac{1}{\sqrt{2}}(2s_A+2s_B)$	
class	B_1	B_2
Manganese ion orbitals	$3d_{xz}$, $4p_x$	$3d_{yz}$, $4p_y$
Chloride ion orbitals	$3p_x(B_1)=\frac{1}{\sqrt{2}}(3p_{x_A}+3p_{x_B})$	$3p_y(B_2)=\frac{1}{\sqrt{2}}(3p_{y_A}+3p_{y_B})$

	$3p_z(B_1)=\frac{1}{\sqrt{2}}\left(3p_{z_A}-3p_{z_B}\right)$	
	$3s(B_1)=\frac{1}{\sqrt{2}}\left(3s_A-3s_B\right)$	
Oxide ion orbitals	$2p_x(B_1)=\frac{1}{\sqrt{2}}\left(2p_{x_A}+2p_{x_B}\right)$	$2p_y(B_2)=\frac{1}{\sqrt{2}}\left(2p_{y_A}-2p_{y_B}\right)$
	$2p_z(B_1)=\frac{1}{\sqrt{2}}\left(2p_{z_A}-2p_{z_B}\right)$	
	$2s(B_1)=\frac{1}{\sqrt{2}}\left(2s_A-2s_B\right)$	

Using the coordinate system in Figure (2), one can describe the molecular orbitals in this compound in terms of basis orbitals derived from: (i) the 3d, 4s and 4p orbitals of the manganese ion, (ii) 3s and 3p orbitals of the chlorine atoms, and (iii) 2s and 2p orbitals of the oxide ion.

According to C_{2v} group symmetry classes, these orbitals can be grouped as shown in Table (2).

The results of electronic distribution in the molecular orbitals of MnO_2Cl_2 using ab-initio molecular orbital calculations method are listed in Table (3). These results represent the energy levels and atomic orbital coefficients in the linear combination atomic orbitals LCAO molecular orbital. The unpaired electron is in the starred $\overset{*}{A_1}$ orbital. The energy level diagram of the compound from the molecular orbital calculations using ab-initio methods is shown in Figure (3). In this figure the unpaired electron is located in the antibonding $\overset{*}{A_1}$ orbital, numbered 17.

The electronic distribution calculations for MnO_2Cl_2 using semiempirical methods are presented in Table (4). The resultant energy diagram obtained from these calculations is also presented in Figure (4). The unpaired electron is located in $\overset{*}{A_1}$ molecular orbital.

Table (3) Energy Levels and Atomic orbital coefficients of MnO_2Cl_2 using ab-initio method.

A_1 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients									
		4s	$4p_z$	$3d_{z^2}$	$3d_{x^2-y^2}$	3s	$3p_z$	$3p_x$	2s	$2p_z$	$2p_x$
1	-45.2	-0.070	0.002	0.056	-0.011	0.020	-0.003	0.009	-0.865	-0.008	0.001
3	-37.6	-0.095	-0.040	0.088	0.010	0.655	0.015	-0.016	0.070	-0.000	0.002
5	-27.5	-0.100	-0.102	-0.196	0.320	0.105	-0.052	0.098	-0.101	0.410	0.000
9	-26.9	0.085	-0.110	0.095	0.220	0.095	0.075	0.432	-0.210	0.005	-0.025
10	-25.7	0.420	-0.250	-0.371	-0.072	0.126	0.028	-0.011	-0.230	-0.120	0.000
15	-24.9	-0.060	-0.130	-0.261	0.280	-0.301	0.176	-0.104	-0.750	-0.104	0.000
17*	-23.8	0.110	0.020	-0.450	0.506	0.040	0.550	0.220	0.092	0.285	-0.001
21	-22.7	0.050	0.750	-0.227	-0.050	-0.278	0.128	0.410	0.020	-0.000	0.055
23	14.2	-0.105	-0.380	0.720	0.030	0.507	-0.305	0.026	0.870	0.025	0.000
25	40.1	0.790	0.156	-0.205	-0.110	0.030	-0.110	-0.401	0.125	0.905	0.000

A_2 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients		
		$3d_{xy}$	$3p_y$	$3p_y$
8	-27.1	-0.355	-0.742	-0.420
16	-25.3	0.075	0.722	-0.301
18	-23.6	-0.630	-0.207	-0.365

B_1 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients							
		$4p_x$	$3d_{xz}$	3s	$3p_z$	$3p_x$	2s	$2p_z$	$2p_x$
2	-44.8	-0.012	-0.201	-0.120	0.205	-0.104	0.675	0.016	0.000
4	-38.0	-0.000	0.106	-0.305	0.160	0.098	0.106	0.000	0.025
7	-26.9	-0.105	0.200	-0.001	0.008	0.107	0.320	1.002	0.000
11	-24.9	0.210	0.000	-0.201	-0.405	0.320	0.006	0.000	0.000
13	-24.7	-0.205	0.198	0.220	-0.310	-0.480	-0.010	0.000	0.000
14	-24.5	0.010	-0.110	0.102	-0.014	-0.090	-0.025	-0.101	0.470
20	-22.1	0.110	0.375	-0.075	0.351	0.353	-0.001	0.061	0.905
24	+15.8	0.550	0.405	-0.330	0.130	0.095	0.000	0.887	0.000

B_2 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients			
		$4p_y$	$3d_{yz}$	$3p_y$	$2p_y$
6	-27.5	0.905	-0.310	-0.330	0.005
12	-25.4	-0.725	0.810	-0.034	0.000
19	-23.2	-0.310	-0.076	0.000	0.985
22	-15.1	0.580	-0.550	0.092	0.110

Table (4) Energy Levels and Atomic orbital coefficients of MnO_2Cl_2 using semiempirical methods.

A_1 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients									
		4s	$4p_z$	$3d_{z^2}$	$3d_{x^2-y^2}$	3s	$3p_z$	$3p_x$	2s	$2p_z$	$2p_x$
1	-26.2	0.101	-0.002	0.098	-0.001	0.025	-0.010	0.006	-0.995	-0.052	0.000
3	-19.1	0.302	-0.040	0.101	-0.020	0.862	0.011	-0.145	-0.075	0.000	0.007
5	-8.5	0.080	0.095	0.220	0.370	-0.105	0.076	-0.178	0.101	0.000	0.825
9	-8.1	0.087	0.105	0.360	0.620	-0.220	0.475	-0.098	0.065	0.007	0.000
10	-6.8	0.370	-0.098	0.100	0.087	0.106	0.105	0.580	0.102	0.550	0.000
15	-6.2	0.009	0.065	0.101	0.002	0.005	0.401	0.010	0.007	0.980	0.000
17*	-5.8	-0.055	0.022	-0.465	-0.705	0.010	0.501	0.198	-0.098	-0.265	0.000
21	-2.2	0.100	0.095	0.595	-0.305	-0.087	-0.185	0.405	0.095	-0.580	0.000
23	0.8	0.009	0.901	-0.165	0.019	0.220	-0.310	-0.110	-0.201	0.000	-0.120
25	20.8	0.795	-0.098	-0.102	0.090	-0.505	-0.225	0.102	-0.355	0.000	0.330

A_2 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients		
		$3d_{xy}$	$3p_y$	$3p_y$
8	-7.9	0.910	0.355	0.000
16	-5.8	0.022	0.001	0.990
18	-4.6	0.590	0.801	0.000

B_1 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients							
		$4p_x$	$3d_{xz}$	3s	$3p_z$	$3p_x$	2s	$2p_z$	$2p_x$
2	-25.9	-0.002	0.001	0.004	0.000	0.001	0.980	0.018	0.003
4	-18.8	0.050	0.100	0.965	0.000	-0.008	-0.005	0.000	0.000
7	-8.1	-0.101	-0.650	-0.095	-0.210	0.370	-0.505	0.000	0.000
11	-6.2	-0.085	0.010	-0.895	0.060	0.096	0.077	0.000	0.000
13	-5.9	0.070	0.065	0.011	-0.750	0.072	0.000	0.735	0.000
14	-5.6	0.005	0.000	0.001	0.000	0.011	0.000	0.980	0.000
20	-2.9	0.000	0.001	0.001	0.010	0.000	0.990	0.000	0.010
24	1.3	0.905	0.098	0.480	-0.230	-0.020	-0.095	0.000	0.000

B_2 Symmetry

Orbital no.	Energy (eV)	Atomic orbital coefficients			
		$4p_y$	$3d_{yz}$	$3p_y$	$2p_y$
6	-8.7	0.009	0.825	0.198	0.540
12	-6.0	0.401	-0.092	0.885	0.107
19	-3.7	0.187	0.810	0.101	0.495
22	-1.2	0.905	-0.180	-0.275	0.370

From the molecular orbital calculations, the general formula of the bonding and antibonding molecular orbitals for MnO_2Cl_2 using semiempirical methods can be written as:

$$\overset{*}{\psi}(A_1)=\overset{*}{\alpha}_1(a\,d_{x^2-y^2}+b\,d_{z^2})+\overset{*(I)}{\alpha_1}\,3p_z(A_1)+\overset{*(II)}{\alpha_1}\,2p_z(A_1)$$

$$\psi(A_2)=\alpha_2\,d_{xy}+\alpha_2^{(I)}\,3p_y(A_2)+\alpha_2^{(II)}\,2p_y(A_2)$$

$$\psi(B_1)=\beta_1\,d_{xz}+\beta_1^{(I)}\,4p_x+\beta_1^{(II)}\,3p_z(B_1)+\beta_1^{(III)}\,3p_x(B_1)+\beta_1^{(IV)}\,2p_z(B_1)$$

$$\psi(B_2)=\beta_2\,d_{yz}+\beta_2^{(I)}\,4p_y+\beta_2^{(II)}\,3p_y(B_2)+\beta_2^{(III)}\,2p_y(B_2)$$

The molecular orbital calculations show that in this compound only contributions from the metal ion $d_{x^2-y^2}$ and d_{z^2} orbitals and from the chloride ion $3p_z$ and the oxide ion $2p_z$ orbitals are important.

According to the results which discussed in this section it may be include that the unpaired electron is located in antibonding $\overset{*}{A}_1$ molecular orbitals. There are two kinds of excited state are produced either by promoting the unpaired electron into the empty antibonding orbitals of A_2, B_1 or B_2 symmetry which lie immediately above $\overset{*}{\psi}(A_1)$ in Figures (3) and (4), or by promoting an electron into $\overset{*}{\psi}(A_1)$ orbital from the filled bonding orbitals of A_2, B_1 or B_2 symmetry immediately below $\overset{*}{\psi}(A_1)$.

In this compound, the most populated atomic orbitals are $d_{x^2-y^2}$ and d_{z^2} orbitals. From the molecular orbital calculations it may be appeared that the semiempirical calculation is the most convenient methods to calculate the molecular orbitals of this compound since the ab-initio calculation is a complex method because it enclosed even small integral and nuclear-nuclear interactions is the calculation of molecular orbitals. While semiempirical method treatments employed a minimal basis set for the valence electrons. From the results the spread of unpaired electron population on ligand atomic orbitals besides the metal $d_{x^2-y^2}$ and d_{z^2} orbitals makes from this compound is useful as a catalyst.

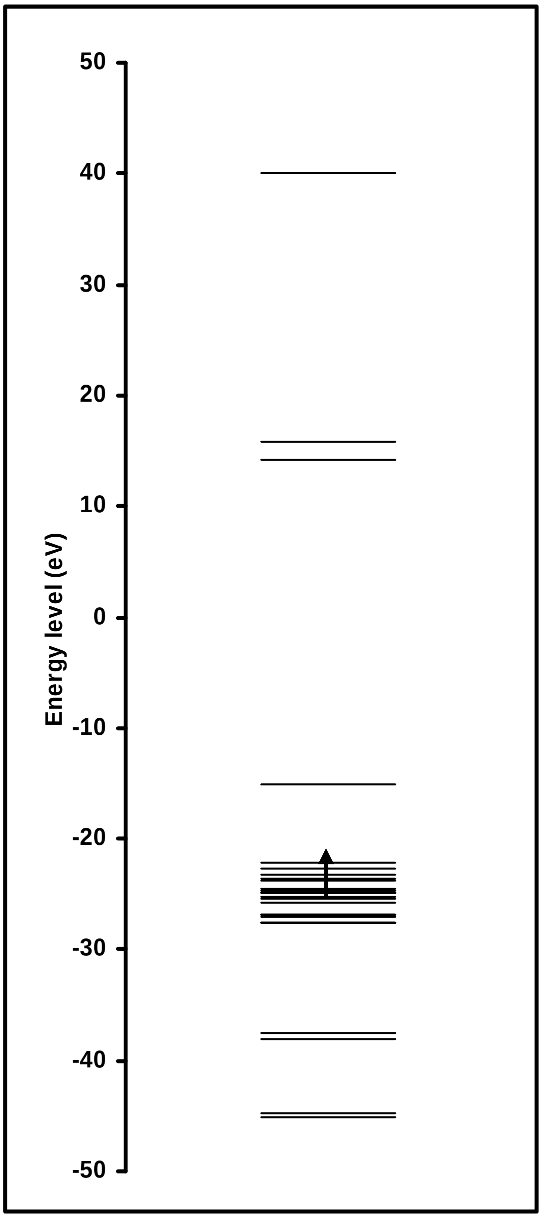

Figure (3) Energy levels orbital from ab-initio method

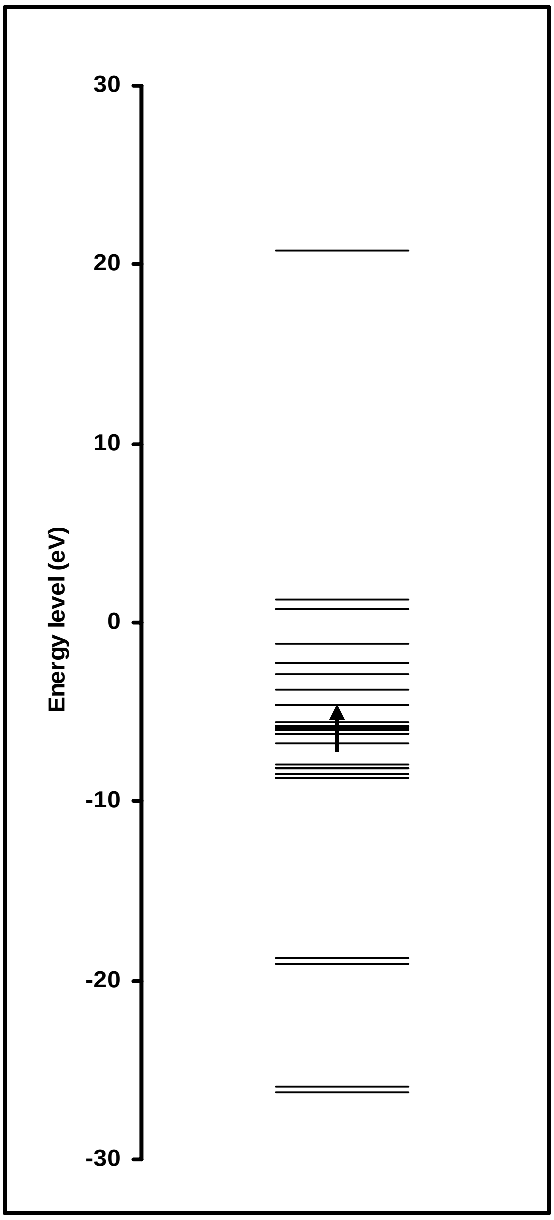

Figure (4) Energy levels orbital from semiempirical method

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الخلاصة

تم في هذا البحث دراسة نظرية للتوزيع الالكتروني للمركب MnO_2Cl_2 باستخدام الطرائق التامة Ab-initio methods والطرائق شبه التجريبية Semiempirical methods.

الامثلية الهندسية للمركب تم الحصول عليها باعتماد طريقة هارتري-فوك للأنظمة غير المقيدة باستخدام الدوال الأساسية من نوع STO-3G.

أظهرت حسابات الاوربتال الجزيئي لهذا المركب أن الالكترون المنفرد يقع في الاوربتال $3d_{x^2-y^2}$ لايون المعدن Mn. وتبين من خلال النتائج لمخطط مستويات الطاقة للمركب أن الفاصلة في التوزيع الالكتروني على الاوربتالات الذرية لايونات O و Cl مع اوربتالات ايون المعدن $d_{x^2-y^2}$ و d_{z^2} يجعل من مركبات هذا المعدن أن تلعب دوراً كبيراً كعوامل مساعدة في تسريع التفاعلات الكيميائية.