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Ab-initio-RHF Methods Calculation to Study the Fundamental Vibrational Frequency of Benzophenone (C_6H_5-CO-C_6H_5)

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Abstract: The electronic distribution and energy level as well as modes of vibration of Benzophenone molecule are studied theortically using ab-initio methods .The geometry optimization of the benzophenone was obtained depending on the Hartree - Fock equation for the restricted system by using STO - 3G basis sets.The modes of vibrationes were calculated under the steady state geometry condition and presented in graphically with frequency,intensity and symmetry for each mode.The molecular orbital calculation and energy level diagram appears that paired electron . The Ionization potential is equal to = 7.4939 eV , while the low electron affinity is equal to = 5.64372 eV.The total energy of benzophenone is equal to = (-15397.47644 eV) where calculated by Ab-initio method compared with different semi-empirical methods, indicate that Ab-initio method is very high accurate method to give the geometry more stable .

Keywords: Ab-initio rhf methods for benzophenone modes .

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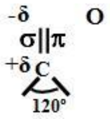
1. Introduction

Theoretical computation in physics and chemistry using various methods depandant on ab-initio and semi empirical methods are widely used. These methods are very important to the studies of matter and its physical properties. The advancement in computer systems enabled the improvement in the increased accuracy and speed of evaluating theoretical results.

Many searchers used ab-initio and semi empirical methods for example , (Laref,2000) studied the band structure of Germanium crystal using semi empirical methods (Benzair and Aourag , 2003) studied the electronic properties and total energy of Zinc-blende compounds using ab-initio and density functional methods.

In this work,the distribution,energy levels and normal modes of vibration of benzophenone molecule which consist a Carbonal group are studied using ab-initio methods .



The main goal is to classify the benzophenone as an example of non-linear molecule theoretically according to group theory using the linear combination of benzophenone orbitals (LCAO) .

2. Methods

In Hartree Fock HF theory , the wave function is represented by a single N-dimentional slater determinant $\phi(x_1,x_2,\ldots\ldots x_N)$ made up of N orthonormal spin orbital {Xi(x)}, where x represents both the position r and the spin ω of an electron . Each spin orbital can be have both a spin up α and spin down β part; ψi(r) and ψi(r) respectively (parr and yang 1989).

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 $\overset{\alpha}{C}_{\mu i}$, $\overset{\beta}{C}_{\mu i}$

For a given nuclear configuration Ri that includes a system of M nuclei and a given set of orthonormal spin orbitals , the electronic energy E_e ({$\overset{\alpha}{C}_{\mu i}$, $\overset{\beta}{C}_{\mu i}$ },{ R_i}) is (Sherrill,2000) :

$$E_e = \sum_{i=1}^{N} \langle X_i \left| -\frac{1}{2}\nabla_I + \sum_{I=1}^{N} V_I(r_i,R_I) \right| X_i \rangle + \sum_{i=1}^{N} \sum_{j\langle i} \Big[\langle X_i X_j | X_i X_j \rangle - \langle X_i X_j \,|\, X_i X_j \rangle \tag{1}$$

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 (Sherrill,2000;klienert,1999) approximation separates the electron and nuclear motions because the nuclear mass is so much larger than that of the electrons , and the nuclei move on a potential energy surface given by :

$$E(\{\overset{\alpha}{C}_{\mu i}, \overset{\beta}{C}_{\mu i}\},\{R_i\}) = E_{ele}\; E(\{\overset{\alpha}{C}_{\mu i}, \overset{\beta}{C}_{\mu i}\},\{R_i\}) + \sum_{I,J\langle 1}^{M} \frac{Z_I Z_J}{|R_I R_J|} \tag{2}$$

Where Z_I , Z_J are the atomic number for I and J atoms respectively .

Π - Ab-initio Methods.

In ab-initio ,the calculations of electronic structure are based on the HF wave functions. The approximation ab-initio treatments are based on the variation principle which requires an evalution of (szabo,and ostlund 1982) .

$$E[\Psi] = <\Psi|H|\Psi> / <\Psi|\Psi> \tag{3}$$

$$H = \sum_{i} h(i) + \sum_{i\langle j} \frac{1}{r_{ij}} \tag{4}$$

Where h(i) represents the single ith electron term which includes the kinetic energy of the electron as well as its energy associated with its interaction with the nucleus . The two electron term r_{ij} denotes the distance between electron i and j .

An application of the variation principle implies that all, integrals for Ψ should factorize into low dimensional cases .

This condition is achieved by building Ψ from the one electron function ϕi that are called molecular orbitals (Mo) , and this leads to the general properties :

$$\psi = \sum_{I} C_I \phi_I \tag{5}$$

$$\phi_I = [\phi_{iI} .... \phi_{in}] \tag{6}$$

$$\langle \phi_i | \phi_j \rangle = s_{ij} \tag{7}$$

3. Results and Discussion

Before starting the calculation , it is necessary to select a geometry that enables the optimization of the compound studied in order to minimize its energy .

In this geometry , the force on the atoms can be calculated by evaluating the gradient of the energy with respect to atomic coordinates analytically .

In quantum mechanics computer programs, such as Mopac 7.21 and hyperchem 6.01, the form of geometry in put called z-matrix . This matrix specifies the positions of an 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) .
3- The dihedral angle φ between the two planes defined by i-j-k and j-k-ℓ meeting at the line j-k , φ (i,j,k,ℓ) .

The structure of the benzophenone was optimized at the restricted Hartree-Fock level of theory using the slater-type orbital (STO-3G) basis sets .

Table (1) shows the geometry of Benzophenone molecule as follow .

Table 1: Geometry parameters of C_6H_5-CO-C_6H_5.

Bond	Bond length(A^O)	Bond angle(degree)
C-O	1.21	———
C-C	1.52	———
O-C-C	———	122.9

Using the coordinate system shown in fig (1) , one can describe the molecular orbitals of the studied compound in terms of basis orbital derived from ;

(i) The 2s,2p orbitals of the oxigyen ion .
(ii) The carbon ion 2s,2p orbitals .
(iii) The hydrogen ion is orbitals .

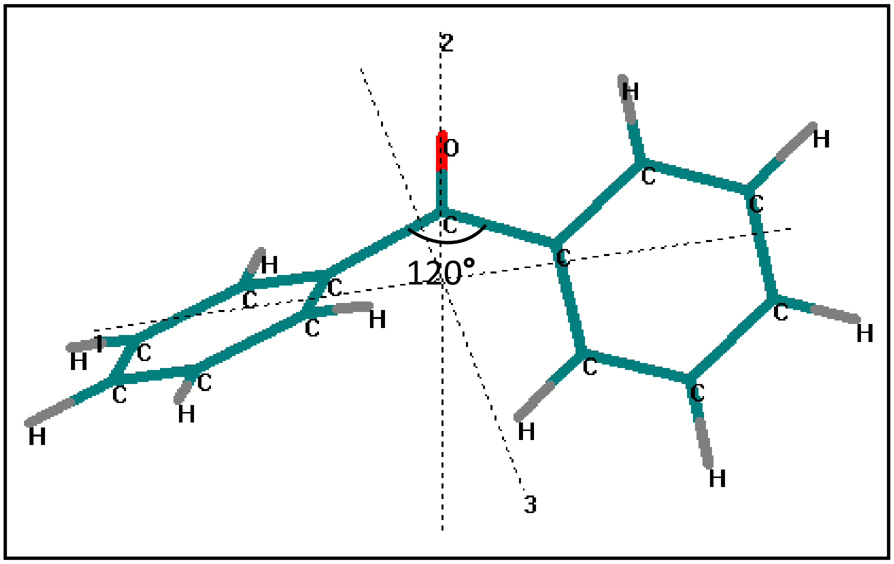


Figure 1: Coordinates system diagram of the Benzophenone C_6H_5-CO-C_6H_5. molecule .

Table (2) shows the net charges and coordinates of the geometry more stable of benzophenone molecule.

Ab-initio calculation of the benzophenone total energy is the sum of the electronic energy plus core-core repulsion and ionization potential as well as dipole moment compare with different semi-empirical methods as presented in table (3) .

Table 2: Net charge and coordinates of benzophenone molecule.

Atom	Z	Charge (Mulliken)	Coordinates(Angstrom)			Mass
			X	Y	Z	
O	8	-0.220974	-0.4130539	1.74338527	-2.03575726	15.99900
C	6	0.190394	-0.31069007	0.99759468	-1.06898388	12.01100
C	6	-0.021513	-1.51587369	0.20257209	-0.57271982	12.01100
C	6	-0.021447	1.02391535	0.85043947	-0.34199995	12.01100
C	6	-0.056145	1.88096714	1.94656367	-0.28997973	12.01100
C	6	-0.063444	3.11571284	1.84607265	0.32946562	12.01100
C	6	-0.061943	-1.71874376	-0.06749160	0.77728233	12.01100
C	6	-0.063725	-2.85025254	-0.75178160	1.19149221	12.01100
C	6	-0.057848	-3.78728338	-1.17581619	0.26122335	12.01100
C	6	-0.056099	-2.46976107	-0.21242885	-1.49817130	12.01100
C	6	-0.063413	-3.59626825	-0.90461315	-1.08558521	12.01100
C	6	-0.062001	1.43286833	-0.35673594	0.21685045	12.01100
C	6	-0.057866	3.51224371	0.64124404	0.89061083	12.01100
C	6	-0.063669	2.67201299	-0.46044761	0.82834478	12.01100
H	1	0.067972	-0.99561071	0.26708158	1.50998550	1.00800
H	1	0.065506	-3.00209652	-0.95327560	2.24404930	1.00800
H	1	0.066330	-4.66892835	-1.71372966	0.58645359	1.00800
H	1	0.066485	-4.32754862	-1.23063650	-1.81421558	1.00800
H	1	0.073612	-2.31954722	0.01294299	-2.54708331	1.00800
H	1	0.073550	1.56952409	2.88116766	-0.74026394	1.00800
H	1	0.066514	3.77067450	2.70682869	0.37256567	1.00800
H	1	0.066303	4.47841804	0.55905716	1.37247091	1.00800
H	1	0.065489	2.98383756	-1.40459954	1.25641735	1.00800
H	1	0.067934	0.78559006	-1.22263168	0.16526170	1.00800

Table 3: Some physical properties calculated by Ab-initio method of benzophenone molecule,compare with different semi-empirical methods.

Quantity	Ab-initio (present work)	Semi-empirical methods			
		MNDO-PM3	MNDO-AM$_1$	MINDO/3	MNDO
Total Energy (eV)	-15397.47644	-1986.821	-2121.205	-2105.6	-2124.24
Electronic Energy (eV)	-36473.24409	-11324.4	-11574.23	-11143.27	-11474.5
Core-Core Repulsion (eV)	21075.76765	9337.526	9453.0225	9037.6446	9350.294
Ionization Potential (eV)	7.493904	9.92867	9.79087	8.95864	9.56394
Dipole Moment (Deby)	1.9074	2.78	2.97	3.43	2.8
No. of Filled Levels	48	34	34	34	34
Molecular Weight(amu)	182.22	182.22	182.22	182.22	182.22
Zero Point Energy(eV)	5.9954	5.1587	5.3509	5.2426	5.1593

The normal modes of vibration of benzophenone nonlinear molecule are calculated which indicate 66 modes of vibration , 23 of these modes are stretching and the rest 43 is bending , are presented with frequency, intensity and symmetry for each modes as shown in table (4) .

Table 4: Represents the normal modes of vibration with frequency,intensity,symmetry and types of modes.

No	Intensity	$\bar{v}$	(λ)/µm	Types	symmetry	No	Intensity	$\bar{v}$	(λ)/µm	Types	symmetry
1	0.472	32.60	306.748	bending	1A	3	0.2845	1205.58	8.2953	bending	34A
2	0.040	55.43	180.407	bending	2A	3	0.1737	1206.97	8.2852	bending	35A
3	0.088	94.60	105.708	bending	3A	3	0.0296	1208.12	8.2773	bending	36A
4	0.849	151.82	65.8674	bending	4A	3	4.1976	1211.25	8.2559	bending	37A
5	2.014	233.05	42.9092	bending	5A	3	1.0979	1270.11	7.8733	bending	38A
6	0.030	238.99	41.8427	bending	6A	3	0.4117	1271.03	7.8676	bending	39A
7	0.041	315.94	31.6515	bending	7A	4	0.1867	1352.1	7.3959	bending	40A
8	4.182	396.94	25.1927	bending	8A	4	4.3062	1368.7	7.3062	bending	41A
9	0.077	476.52	20.9854	bending	9A	4	0.2602	1371.5	7.2912	bending	42A
10	0.015	483.06	20.7013	bending	10A	4	0.9649	1375.35	7.2708	bending	43A
11	0.331	503.86	19.8467	bending	11A	4	0.1371	1378.64	7.2535	Stretchin	44A
12	0.085	514.23	19.4465	bending	12A	4	129.52	1500.64	6.6638	Stretchin	45A
13	0.199	642.12	15.5734	bending	13A	4	1.6277	1546.79	6.465	Stretchin	46A
14	0.501	709.73	14.0898	bending	14A	4	21.978	1547.77	6.4609	Stretchin	47A
15	0.008	713.13	14.0226	bending	15A	4	21.415	1720.5	5.8122	Stretchin	48A
16	32.745	728.68	13.7234	bending	16A	4	22.857	1721.79	5.8079	Stretchin	49A

17	**9.766**	**776.17**	**12.8837**	**bending**	**17A**	**5**	**5.1986**	**1784.29**	**5.6044**	**Stretchin**	**50A**
18	**0.354**	**828.36**	**12.0720**	**bending**	**18A**	**5**	**1.6074**	**1791.59**	**5.5816**	**Stretchin**	**51A**
19	**18.756**	**835.35**	**11.9710**	**bending**	**19A**	**5**	**1.6952**	**1912.88**	**5.2277**	**Stretchin**	**52A**
20	**3.780**	**838.69**	**11.9233**	**bending**	**20A**	**5**	**2.1541**	**1913.1**	**5.2271**	**Stretchin**	**53A**
21	**5.255**	**908.93**	**11.0019**	**bending**	**21A**	**5**	**0.7330**	**1938.08**	**5.1597**	**Stretchin**	**54A**
22	**4.725**	**940.49**	**10.6327**	**bending**	**22A**	**5**	**3.8022**	**1939.9**	**5.1549**	**Stretchin**	**55A**
23	**0. 469**	**1035.1**	**9.66095**	**bending**	**23A**	**5**	**30.365**	**2050.06**	**4.8779**	**Stretchin**	**56A**
24	**0.090**	**1037.3**	**9.64041**	**bending**	**24A**	**5**	**0.0805**	**3708.7**	**2.6963**	**Stretchin**	**57A**
25	**65.899**	**1063.6**	**9.40132**	**bending**	**25A**	**5**	**0.1437**	**3708.8**	**2.6963**	**Stretchin**	**58A**
26	**0.282**	**1123.9**	**8.89743**	**bending**	**26A**	**5**	**0.4219**	**3721.4**	**2.6872**	**Stretchin**	**59A**
27	**3.686**	**1128.1**	**8.86446**	**bending**	**27A**	**6**	**0.5859**	**3723.48**	**2.6856**	**Stretchin**	**60A**
28	**1.114**	**1158.0**	**8.63498**	**bending**	**28A**	**6**	**8.9624**	**3728.78**	**2.6818**	**Stretchin**	**61A**
29	**0.027**	**1160.3**	**8.61779**	**bending**	**29A**	**6**	**3.5492**	**3729.39**	**2.6814**	**Stretchin**	**62A**
30	**1.597**	**1168.2**	**8.55988**	**bending**	**30A**	**6**	**12.561**	**3735.78**	**2.6768**	**Stretchin**	**63A**
31	**0.983**	**1170.8**	**8.54087**	**bending**	**31A**	**6**	**13.568**	**3736.9**	**2.6760**	**Stretchin**	**64A**
32	**0.402**	**1190.9**	**8.39637**	**bending**	**32A**	**6**	**4.7428**	**3744.18**	**2.6708**	**Stretchin**	**65A**
33	**0.011**	**1193.3**	**8.37956**	**bending**	**33A**	**6**	**0.9841**	**3745.3**	**2.6700**	**Stretchin**	**66A**

The vibrational frequencies and its corresponding intensities compare with IR absorption spectrum as shown in fig (2) [8] .

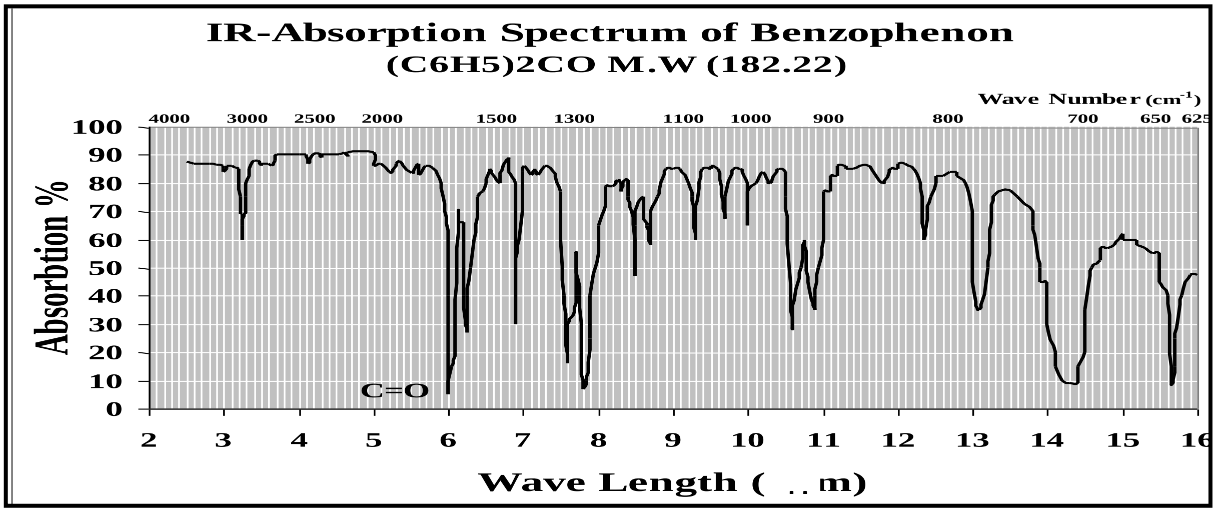


Figure 2: IR absorption spectrum of benzophenone $C_6H_5COC_6H_5$ **[8]**

The total charge density distribution and electrostatic potential of benzophenone molecule in two and three dimension as shown in fig (3) and fig (4) respectively .

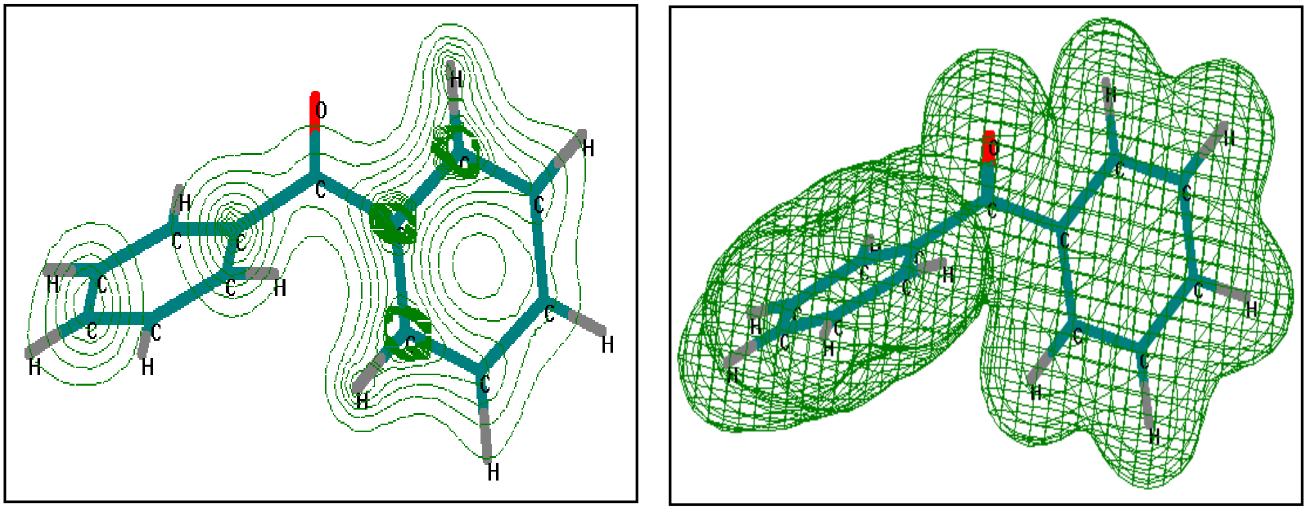


Figure 3: Illustrated total charge distribution for benzophenone molecule in 2D and 3D.

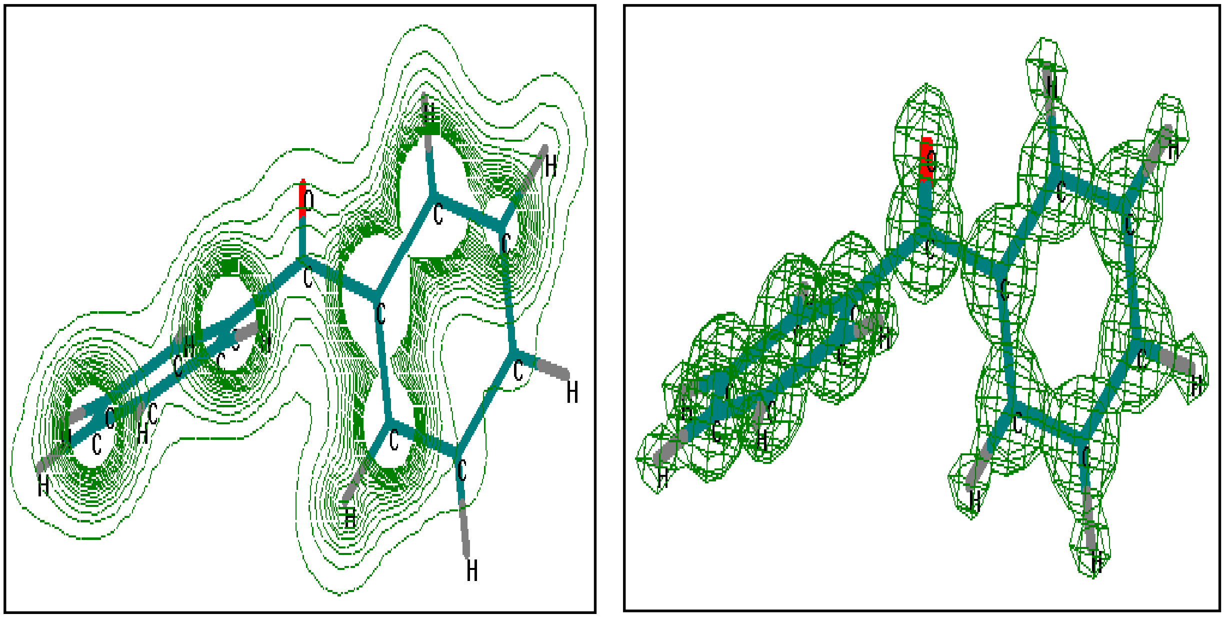
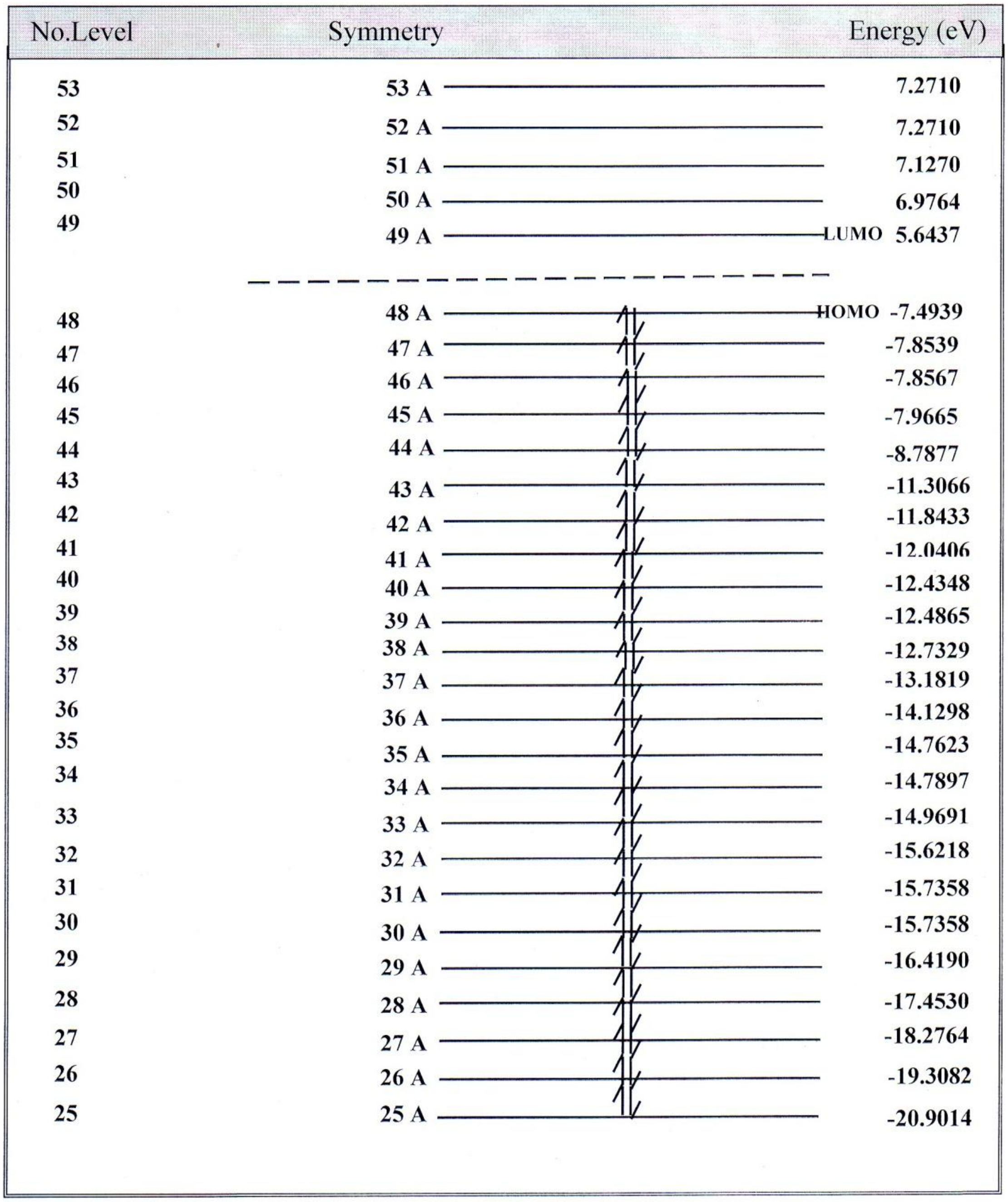


Figure 4: Illustrated electrostatic potential for benzophenone molecule in 2D and 3D.

Fig (5) shows an act final level HOMO and energy value $E_{\mathbf{HOMO}}$ = -7.4939 eV while symmetry of this level was 48A ,and the first LUMO with energy value $E_{\mathbf{LUMO}}$ = 5.64372 eV with symmetry 49B. The absolute value of the final level HOMO gives the Ionization potential which is equal to (7.4939) eV, while the first level LUMO represent electron affinity which is equal to (5.64372 eV) .They determined the Fermi level as the center of the HOMO and LUMO energies and calculated the gap between them to be (13.1376) eV according to Fischer and Herriksson[9] is defined as $\Delta E = E_{LUMO} - E_{HOMO}$.



No.Level	Symmetry		Energy (eV)
53	53 A		7.2710
52	52 A		7.2710
51	51 A		7.1270
50	50 A		6.9764
49	49 A	LUMO	5.6437
48	48 A	HOMO	-7.4939
47	47 A		-7.8539
46	46 A		-7.8567
45	45 A		-7.9665
44	44 A		-8.7877
43	43 A		-11.3066
42	42 A		-11.8433
41	41 A		-12.0406
40	40 A		-12.4348
39	39 A		-12.4865
38	38 A		-12.7329
37	37 A		-13.1819
36	36 A		-14.1298
35	35 A		-14.7623
34	34 A		-14.7897
33	33 A		-14.9691
32	32 A		-15.6218
31	31 A		-15.7358
30	30 A		-15.7358
29	29 A		-16.4190
28	28 A		-17.4530
27	27 A		-18.2764
26	26 A		-19.3082
25	25 A		-20.9014

Figure 5: Schematic diagram for energy levels values for benzophenone shows EHOMO , ELUMO and symmetry .

4. Conclusion

Benzophenone is non-linear molecule has 3N-6 mode of vibration .66 modes are the total number of fundamental modes, 23 of these modes are stretching according to rule (N-1) is the number of stretching , and 43 is the number of bending according to the rule (2N-5) is the number of bending . The Ab-initio calculation of total energy compare with different semi-empirical methods is given too low values, indicate the geometry more stable . Ab-initio method given a data more accuracy, but it taken long time because it take all electrons .The screw (Chair-form) shape of benzophenone molecule is more stable than a boat (Butter-fly) shape.

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