

Approach of Density Functional Theory to Molecules Using Gaussian

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Abstract

Conceptual studies play key role in understanding the inherent studies of molecules. These studies gained importance are implemented with Molecule Editors and navigated with software tools like Gaussian, GAMESS, GABEDIT etc that opens a new microscopic world of science. Molecules are represented in ball and stick model using Molecular Editor Avagadro. Proper selection of basis set with electron density method i.e. Density Functional Theory (DFT) provides an approach in interpretation of molecules for various spectroscopic properties like HOMO-LUMO, ESP contours, generation of theoretical FTIR spectra and Mulliken charge distribution. Interpretation of these properties in terms of electron correlation and exchange interaction of electron density provides basis for determination of physical, chemical and biological properties. An illustrative procedure in implementation of this approach is presented with necessary steps and illustrations for typical molecule.

Keywords: DFT, Avagadro, Gaussian, wavenumbers, electron density

1. INTRODUCTION

Computational chemistry is the way of dealing physical and chemical problems of molecular systems by computer stimulations [1-3] that cannot be solved analytically complement the information provided with experiment. It provides approximate solutions for systems interaction with each other wherein affects interaction energies and exchanges of energies dominate. Researchers and Scientists need to study the

nature of molecules in terms of their structures rather than examining them experimentally for each property. Wave function provides complete microscopic information of system with large numbers of particles under consideration. These systems are specified with Hamiltonian with nuclei at rest and electrons are in orbital motion relative to nuclei. Certain set of approximations necessitates to introduce new field of science covering majors aspects like condensed matter physics, quantum chemistry, atomic physics and molecular physics. Approaches to fields of science are investigated with methods like (i) Mean field theory (ii) Hartree-Fock method (iii) Density functional method. Wave function completely determines system attributed with Schrödinger equation and its solution this equation provides information about Eigen values (Energies) and Eigen functions of systems. Generally for large numbers of systems under consideration solution of Schrödinger equation is tedious and an attempt to provide solution to these molecular systems that has its roots with basic method (i) Ab-initio, based on quantum mechanics and their physical constants (ii) Semi empirical methods utilise additional empirical parameters. These methods involve Born–Oppenheimer approximation providing solution to Schrödinger equation with assumption that total wave function is expressed as product of individual wave function of electron and nuclei. This approximation results due to change in masses of nuclei and electron further with difference in electronic energies arises due to repulsive interaction between electrons, nuclei and attraction of electron and nucleus. These methods attempt to determine solution of Schrödinger equation with position of nuclei, electron densities and energies of system.

Density functional theory aims in determining properties of systems as function of spatial dependence of electron density particularly in ground state. Many electron systems gained importance wherein electron correlation and exchange interactions prevail that are expressed as function of functional. DFT aims in predicting the behavior of materials with construct of potential as sum of external potential arise due to structure and composition of material and effective potential due to inter electronic interactions.

Computational techniques with various methods enable to understand and design new molecular systems in relation structure with accuracy. The investigated parameters dependent on structure and geometry [4-9] are bond lengths, bond angles, dipole moment, molecular energies, reaction rate, vibration studies, transition probabilities and chemical reactivity.

These properties are primarily influenced by the concentration of electrons to form nucleophilic sites and electrophilic sites enable to understand the properties responsible for physical and chemical phenomena. Physical properties lie on accurate description of electronic structure computed using electron correlation energy and dominant relativistic effects. These effects include dipole moment, rotational energies, strength, energy gaps, entropy, enthalpy, wave length etc. Chemical properties like

electrostatic separation, electron donor acceptors ,bonding interactions, surfaces and interfaces of materials, substitution of atoms at respective locations responsible for hardness, electrophilicity index, vibration frequencies, bonding mechanism, atomic charge distribution etc are determined. Biological significant properties enable to study drug analysis, drug design, physiochemical process, hydrophobicity, hydrophilicity, and insilico studies etc. These physical, chemical and biological interpretations of molecules were determined from the spectra using computational method that provide new dimension for experimental studies [10-12].

Computational chemistry is a peak stage of chemistry that confirms behavior of organic and inorganic molecules with real entities providing comprehensive explanation with physical and mathematical affirmation [13] with specified method.. These methods are based on quantum mechanical calculation and interpretation is the basis of computational chemistry. The approach to computational chemistry is with LCAO[14] and determining potential energy surfaces[15] to understand reaction dynamics of molecules. These methods are computational chemical models of molecules in every aspect that correlates experimental values with great accuracy

Geometry optimization is a method of taking rough approximations to perform computational calculations on a molecule [16] wherein geometry of molecules provides a vital role in performing computations with a series of iterations performed on a molecule until it reaches its minimum value. Initial geometry of a molecule is determined along with a specific basis set [17]. Density functional theory originates from electron density concept and put in forth by Thomas-Fermi model. Later on by Hohenberg-Kohn theorems[18], the DFT concept was developed and is implemented through Kohn-Sham method.

2. METHODOLOGY

Molecular mechanism of molecules is very important to envisage their behavior. Calculations of any sized molecular system are done anticipated with the help of computers. Methodology is implemented with Molecular editor Avogadro an important scientific tools that visualizes and edits molecules in concise form with optimized geometry [19]. This tool provides input to packages like Gaussian, GAMESS and MOPAC etc with flexibility in building molecules essential in quantum chemical calculations [20].

With a click on Avogadro icon, formative procedure for building molecular structure and providing input data is detailed as follows.

Step 1:

From the tool Settings menu select Draw settings. The periodic table of elements with specific color to each one will appear.

Step 2:

Specific structure of typical molecule is drawn by using Ball and Stick model and optimized as illustrated in figure1.

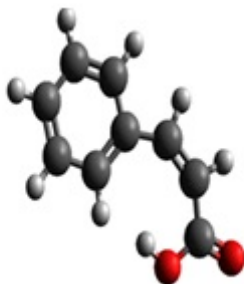


Fig.1.Ball and Stick Optimized Molecular Structure

These completed molecular structures are optimized by navigating Extension. In the View dialogue box the properties like molecular weight, expected dipole moment, number of atoms, number of bonds, bond properties (bond length) and bond angle.

Step 3:

With the **Gaussian package** the optimized molecular structure is processed as an input file termed as **Gaussian input**.

Step 4:

The construct of Gaussian input is specified with (i)Frequencies calculation (ii) Theory (B3LYP/MP2) (iii) basis set (iv) Charge and multiplicity depending on molecular structure (v) Output standard (vi) Format Z matrix (compact) generates an input file that needs to be saved with extension **.com**.

Step 5:

In **Gaussian 03W**, the File menu is displayed with click on file the New, job entry dialogue box is opened. The input file is Load at navigation bar. This provides properties which are similar to the properties obtained in Step 2. The Load input file is subjected to **Exit & Run**.

Step 6:

An output file with extension **.Out** is generated for the optimized molecular structure.

Step 7:

Many properties are obtained from the generated output file corresponding to Theory (B3LYP). Spectroscopic properties essential in determination of electrooptical activity are considered. Properties like Mulliken atomic charges, Dipole moment (Debye) , IR wave numbers, IR intensities, Eigen values of occupied and virtual states, Quadrupole moment (Debye-Ang) and Octopole moment(Debye-Ang*2).

Step 8:

These energy values are in agreement with Eigen values of the corresponding alpha occupied Eigen values (last value) and Alpha unoccupied Eigen values (first value).

The spectroscopic properties (computed) corresponding to wave numbers is in agreement with FTIR spectra are analysed for bonding between the systems. These spectral observations are Raman inactive confirmed with reduced intensities in spectra.

Step 9**Confirmation of HOMO-LUMO i.e., step 8 with Gauss View.**

Gauss view provides the pictorial representation of the occupied states (HOMO) and virtual unoccupied states (LUMO). The following are the steps for visualization: With right click on structure opens navigation bar.

Builder
File
Edit
View
Calculate
Results

With **Builder** option allows to draw molecular structure with associated bonds using

Element Fragment-----Ring Fragment----- Modify Bond

Optimized structure saved as *.gif *.com in **File** option.

Selection of **MOs** opens a new window with **Edit**

New MOs----- Method----- Model-----Basis set

Visualize-----HOMO-----LUMO-----HOMO-LUMO-----

With **New MOs**

Generate New Chk file provides Alpha MOs highlighting HOMO and LUMO

With **Visualize**

Add type-----HOMO-LUMO-----Update opens a new window containing FMOs were illustrated in figure 2 for a typical molecule. The Highest Occupied Molecular Orbital (HOMO) is represented in green which are electron donating and positively charged areas of contour. Lowest Unoccupied Molecular Orbital (LUMO) is represented in red which are electrons accepting and contours are negatively charged.

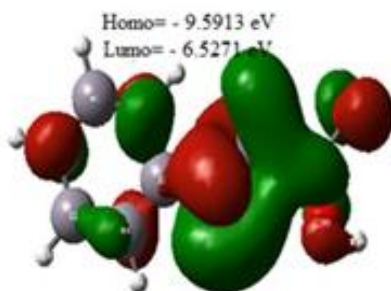


Fig. 2. HOMO-LUMO Contours

Results—opens new window **Surfaces and Contours**

With option of **Cube actions----- Surface Action** visualizes **HOMO and LUMO**.

Bonding phenomena arises due to sharing of electrons corresponding to given nuclei in terms of either single /double/triple in specified region i.e special distribution of electron is atomic orbital. Extending to molecules, bonding and anti bonding molecular orbital [20-21] suffer change in electron density with coulomb integral and resonance integral changes in energies leads to energy spectrum.

Bonding molecular orbital results due to paired electron originates due to interaction of filled MO and vacant MO with favorable energy. As these interactions are large, virtual levels plays role due to difference in energy between the filled and vacant MO termed as HOMO and LUMO and difference in these energy levels is HOMO-LUMO energy gap.

Knowledge of Molecular orbital theory helps in understanding frontier molecular orbital's, particularly in bonding and anti bonding of metal organics elucidating the structure and reactivity of molecules. Insight of metallic complexes primarily concerns with redistribution of electrons in particular d orbital's in relevance of occupation of electrons described with electron donating(HOMO) and electron accepting (LUMO) often termed as nucleophilic and the later as electrophilic.

Effects of electron correlation are reduced with computational methods with linear combination of energies in analyzing chemical properties [22] the susceptibility χ , chemical hardness η , chemical potential μ of the representative organic and in organic molecules with Koopmann's theorem [23].

Contour Maps of ESP are obtained by

Contour Actions----New Contour----generate values for planar grid----Type menu (Select ESP) ----Density matrix (SCF)

The results of Step 9 are in agreement with step 8. Contour Maps of ESP were shown in figure 3.

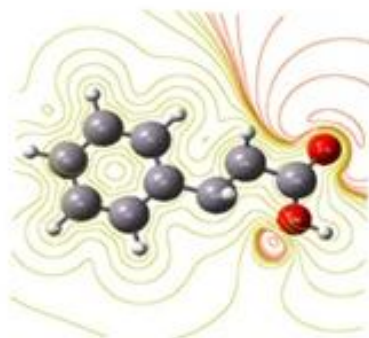


Fig.3 ESP Contour

ESP is a space around a molecule representing the electrostatic effect at that point by a total charge distribution. ESP contours illustrate a gradient of colors that signify the electron distribution. The high probability of electron density is shaded in red (low potential) and yellow for low probability (high potential). Studies of these contours explain the properties responsible for energy gap, dipole moment, chemical potential, and electrophilicity index[24].

2.1. Generation of Spectra from Wave numbers

Frequency Plot Software is used in generation of spectra with wave numbers and intensities obtained from Gaussian.

The following are the necessary steps, In the setup menu-----home

Step1 Execute grip.exe

Step2 Select specific file name from Gaussian file (*.out)

Step 3 Columns of Frequency/cm and Intensity AU

Step 4 Click on Recalculate (lines with intensity zero are removed. Frequencies are rounded and intensities are normalised)

Step 5 Show plot

The plot so obtained is Abs vs. wavelength for specified system of molecules is in agreement with wave numbers of experimental spectra. The spectrum generated using

this software for typical molecule is illustrated in figure 4.

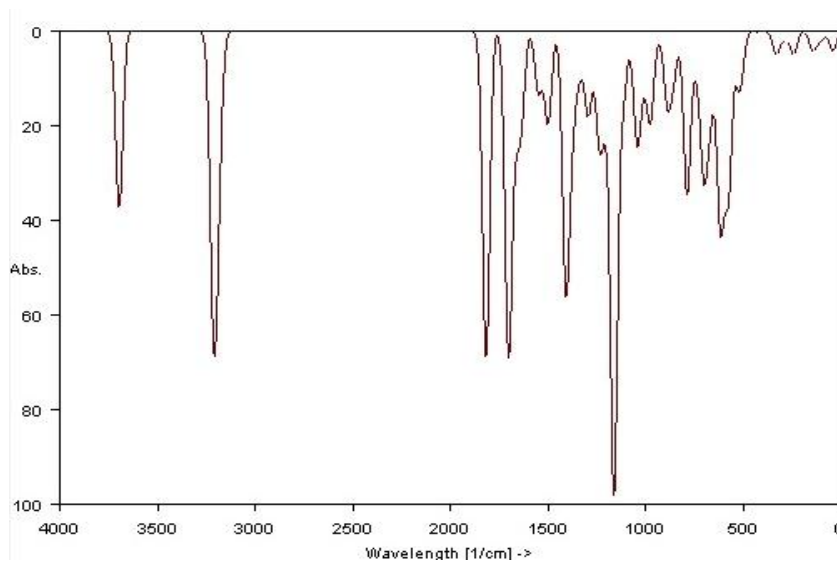


Fig.4. FTIR Spectra

As the these spectroscopic properties depend on the total charge distribution, a plot of Mulliken atomic charge distributions with number of atoms were illustrated using Orign 6.1 for the typical molecule in figure 5.

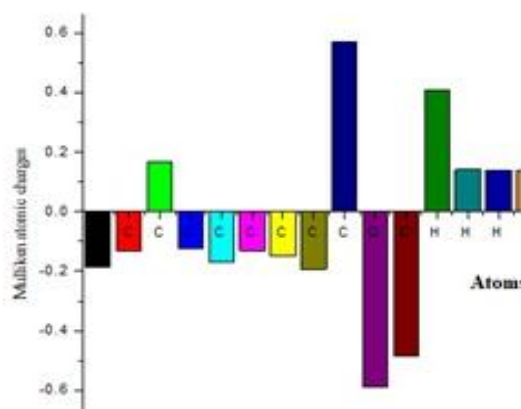
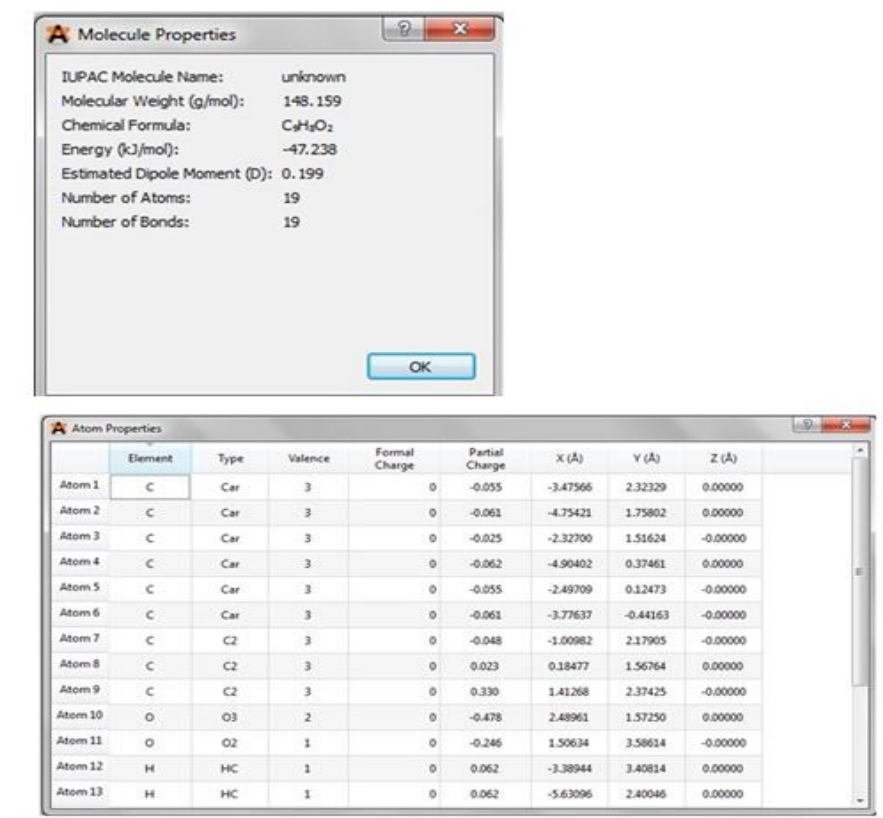


Fig.5. Mulliken Charge Distribution

A feature of illustration is the variation in colors of atoms with their respective charge distributions at their atomic positions.

The procedures involved in performing computational studies as specified in above steps are depicted in pictorial form for a typical molecule in figures 6-9.



The figure shows two windows from the Gaussian 09 software. The top window, 'Molecule Properties', displays calculated molecular data. The bottom window, 'Atom Properties', provides a detailed table of atomic parameters for each of the 13 atoms in the molecule.

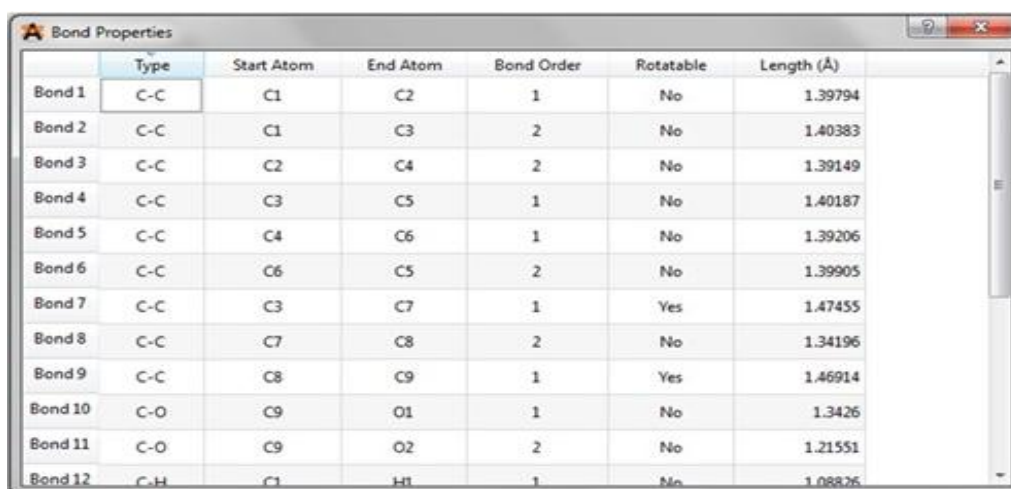
Molecule Properties

IUPAC Molecule Name:	unknown
Molecular Weight (g/mol):	148.159
Chemical Formula:	C ₉ H ₆ O ₂
Energy (kJ/mol):	-47.238
Estimated Dipole Moment (D):	0.199
Number of Atoms:	19
Number of Bonds:	19

Atom Properties

	Element	Type	Valence	Formal Charge	Partial Charge	X (Å)	Y (Å)	Z (Å)
Atom 1	C	Car	3	0	-0.055	-3.47566	2.32329	0.00000
Atom 2	C	Car	3	0	-0.061	-4.75421	1.75802	0.00000
Atom 3	C	Car	3	0	-0.025	-2.32700	1.51624	-0.00000
Atom 4	C	Car	3	0	-0.062	-4.90402	0.37461	0.00000
Atom 5	C	Car	3	0	-0.055	-2.49709	0.12473	-0.00000
Atom 6	C	Car	3	0	-0.061	-3.77637	-0.44163	-0.00000
Atom 7	C	C2	3	0	-0.048	-1.00982	2.17905	-0.00000
Atom 8	C	C2	3	0	0.023	0.18477	1.56764	0.00000
Atom 9	C	C2	3	0	0.330	1.41268	2.37425	-0.00000
Atom 10	O	O3	2	0	-0.478	2.48961	1.57250	0.00000
Atom 11	O	O2	1	0	-0.246	1.50634	3.58614	-0.00000
Atom 12	H	HC	1	0	0.062	-3.38944	3.40814	0.00000
Atom 13	H	HC	1	0	0.062	-5.63096	2.40046	0.00000

Fig.6

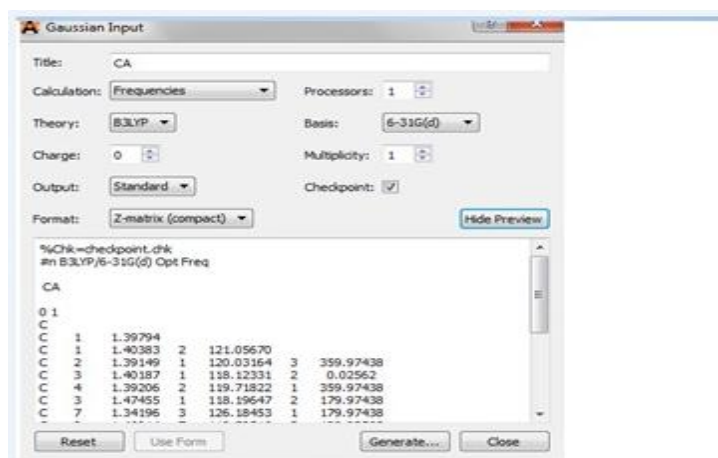


The figure shows the 'Bond Properties' window, which lists the 12 bonds in the molecule with their respective types, atom indices, bond orders, rotatability, and lengths.

Bond Properties

	Type	Start Atom	End Atom	Bond Order	Rotatable	Length (Å)
Bond 1	C-C	C1	C2	1	No	1.39794
Bond 2	C-C	C1	C3	2	No	1.40383
Bond 3	C-C	C2	C4	2	No	1.39149
Bond 4	C-C	C3	C5	1	No	1.40187
Bond 5	C-C	C4	C6	1	No	1.39206
Bond 6	C-C	C6	C5	2	No	1.39905
Bond 7	C-C	C3	C7	1	Yes	1.47455
Bond 8	C-C	C7	C8	2	No	1.34196
Bond 9	C-C	C8	C9	1	Yes	1.46914
Bond 10	C-O	C9	O1	1	No	1.3426
Bond 11	C-O	C9	O2	2	No	1.21551
Bond 12	C-H	C1	H1	1	No	1.08826

Fig.7



Gaussian output:

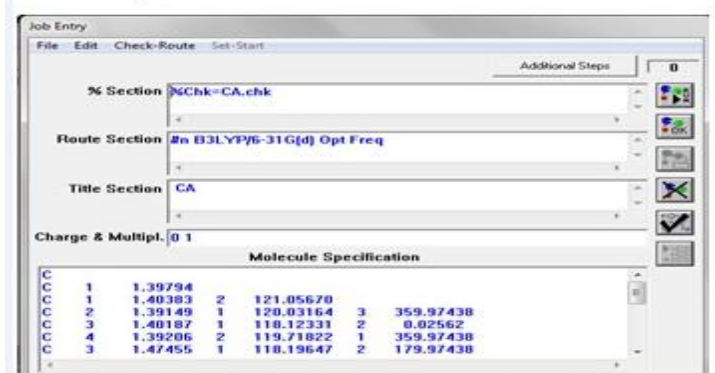


Fig.8

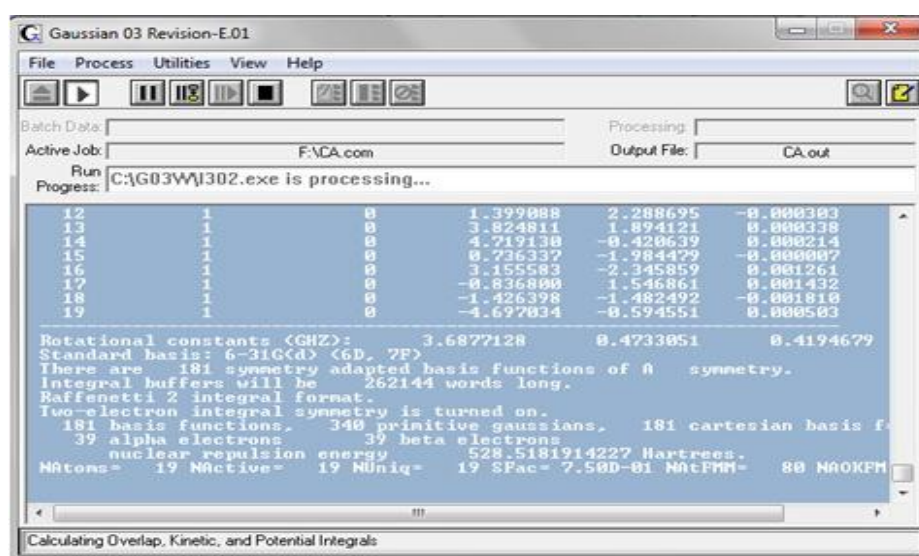


Fig.9

CONCLUSIONS

A brief of computational methods with various theories and importance of density functional theory is attributed. An insight of molecular study with molecular editor enables to obtain various parameters and interpret for physical and chemical properties. Generation of theoretical spectra can be approximated to experimental FTIR spectra. Atomic charges with its dependence of atoms specify participation in formation of complexes. Illustrative procedure with Molecular Editor and navigating with Gaussian with various steps involved helps for interpretation of physical and chemical properties.

Acknowledgements

The author acknowledges support extended by Department of Electronics & Physics, Department of Chemistry under DST- FIST program in providing computational facilities.

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