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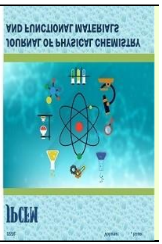

Determination the Band Gap Energy of Poly benzimidazobenzophenanthroline and Comparison between HF and DFT for Three Different Basis Sets

[a,b,*] *Dyari Mustafa MAMAND*, [b] *Niyazi BULUT*

[a] *University of Raparin, College of Science, Department of Physics, Sulaimanyah, Iraq*

[b] *Department of Physics, Faculty of Science, Firat University, 23169 Elazig Turkey*

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ABSTRACT

Nowadays the most important method and stimulation approximation is Density functional theory and Hartree-Fock approximation in quantum mechanical theory used in chemistry and physics. For explore the electronic construction of many-body frameworks, specific molecules, particles, atoms and the dense stages with this hypothesis. Quantum computational theory depended on electron density. the possessions of a many-electron framework can be controlled by utilizing functionals, for example, functions of another function. Hypothetical examinations were performed utilizing the Hartree-Fock hypothesis and Density Functional Theory at B3LYP dimension of hypothesis at 3-21G, 6-31G* and 6-311G in the Gaussian program. The assimilation and photoconduction properties of the conjugated polymer benzimidazobenzophenanthroline (BBL) are considered. The enduring state photoconductivity was estimated as a component of photon energy, electric field, temperature. The photocurrent reaction as a component of energy goes before the ingestion and demonstrates an expansive tail around the bandgap as opposed to the sharp absorption edge close 1.9 eV.

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LUMO

1. Introduction

Poly benzimidazobenzophenanthroline is shortened BBL, Is the fully conjugated polymer. the late 60's in the US was used the navy military [1]. The pristine of BBL is insulator, can be structural material. heterocyclic polymers, such as BBL [2], Figure **1.** BBL structure C20H6N4O2shows the BBL chemical structure. A great coplanar conjugated structure along the polymer backbone is dependable to some extent for the high electrical conductivity for most directing polymers such as polyacetylene (PA), poly-phenylene) (PPP) is a member of a class of polymers known as ladder polymers and heterocyclic polymers, Therefore, heteroaromatic ladder polymers appeared as attractive candidates for forming conducting complexes and also for a new class of nonlinear optical materials [3].

The logical enthusiasm for BBL was recharged at mid-80's as the conjugated structure recommended that it could be dopable into a semiconductor [2]. The thinks about on the semiconducting properties of BBL demonstrated that the conductivity can be expanded by a few requests of size from the initial insulating region of 10^{-12} S/cm of the unblemished polymer to semiconducting region of 10^{-2}-10^{2} S/cm by doping either synthetically or electrochemically. The DC conductivity of BBL start from 10^{-10} to 10^{-12} S/cm [4], dependent upon the processing situations and the form of the examples [5].

BBL is thermally truly steady and when heated in air it begins to oxidize gradually at temperatures over 500 C^0 however under nitrogen climate heat corruption begins over 700 C^0. BBL is very steady and high thermal stability at generally high temperatures and shows high elasticity

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* Corresponding author:
E-mail (diyarimustafa47@gmail.com)

[6]. These polymers, as other conjugated polymers, are fit of supporting bond shift deformities, for example, polarons and bipolarons show intriguing non-linear optical properties because of the delocalized π-electrons [7].

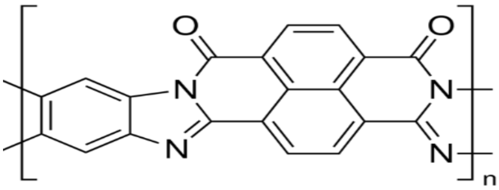

Figure 1. BBL structure $C_{20}H_6N_4O_2$.

Our examinations revealed here were spurred by the need to investigate spatially limited conductivity improvements in conjugated polymer scanty conductivity, their believable gadget applications. High-temperature conjugate polymers come from investigations of the electronic, electrochemical, what're more, physic-chemical possessions of this class of polymers [8]. Points of interest of conjugated polymers for particle establishment studies. High electron affinity of BBL has been used in double mixes of BBL and p-type directing polymers as charge move between the polymers could be actuated either by radioactivity with light [9]. BBL has additionally been demonstrated to be photoconductive [10], thermally [11], or electrochemically [12]. In this way, BBL can be drawn into fibers having rigid characteristics as high as 115 MPa, and can be spun viably into films as slight as 80 nm [13].

incorporate (1) their high-temperature steadiness could withstand inescapable example heating during particle bombardment. (2) since the fundamental consequence of ion-beam damage incited basic changes in particle embedded polymers is carbonization, this should prompt exceedingly melded graphite-like sheet structures in ion-implanted conjugated polymers. (3) the odds of holding their immaculate structure and mechanical properties are a lot higher in ion-implanted stepping stool polymers than non-stepping stool ones. The ladder conjugate polymer we have examined is the BBL.

In this paper, we describe and explain the comparison on the bandgap energy of poly benzimidazobenzophenanthroline type (BBL), according to the HOMU high occupation molecule orbital and LUMO lowest inoccupation molecule orbital by using a software ab initio case Gaussian program. Considering the different basis set 3-21G, 6-31G* and 6-311G for each one of HF and DFT at B3LYP dimension of hypothesis.

2. Theoretical methodology

For determine the exact value the band gap energy of BBL, must be try to examination for different basis sets, because each basis set consist of some special characteristics that differ from another. Table 1 illustrate the value of bandgap.

Each of the results has some shortcoming, the HF approximation is not suitable to run the BBL molecular. The large difference between of the bandgaps value is impossible. The error ratio for each basis set 3-21G, 6-31G* and 6-311G is (6.32661091, 6.4948995, 6.19109714). according to density functional theory can accept the result. actually, it is not exactly real value but is better than HF approximation. The various determinant counts require exceptionally huge premise sets due to the poor assembly of the relationship energy when the between electronic separation turns out to be exceptionally little. Be that as it may, DFT can produce exact outcomes with DFT has turned into the most prevalent and flexible strategy in computational science, representing roughly 90% of all estimations today. The purpose behind this inclination is that DFT scales with a similar request as HF theory [14]. relatively little premise sets. The error ratio of bandgap energy for DFT to 3-21G, 6-31G and 6-311G basis set is (0.98761517, 0.95688289, 1,00184502).

Both hypotheses are they have the same purpose in quantum computational theory, explain the many-electron system of the quantum state, e.g. atoms, molecules and crystals. The basic of HF and DFT is to obey the Born Oppenheimer approximation [15]. The Hartree-Fock strategy expects that the many-electron wavefunction appears as a determinant of single-electron wavefunctions, called a Slater determinant [16]. The issue with this supposition that will be that a general many-electron wavefunction can't be communicated as a solitary determinant. Accordingly, Hartree-Fock techniques don't completely fuse electronic correlation and the subsequent energies will, in general, be excessively high. Fortunately, in the event that you locate a total premise of single-electron wavefunctions. In density functional hypothesis (DFT), the many-electron wavefunction is conditions that are computationally increasingly strong [17].

Totally avoided for the electron density. On account of the Hohenberg-Kohn Theorems, the ground state energy of the framework depends extraordinarily on the electron density, for example, the absolute energy is a utilitarian of the electron density [18]. Hartree-Fock hypothesis totally overlooks electron correlation of a framework and it expects the electrons can transfer independently in a mean-field potential [19]. DFT incorporate some electron correlation of a framework and there is no mean-field estimate in it [20]. The basic DFT-based methodology is typically less difficult, don't require many computational assets, and it is exceptionally effective for the ground state calculations. Nonetheless, HF strategy, being all the more computationally demanding, can imitate energized states, which are not open within ordinary DFT techniques. HF gives in an estimated way a data about orbitals which can be utilized as a contribution for progressively exact strategies, for the most parts called post-HF techniques, for example, the configuration interaction method strategy. The disregard of electron correlation (all the more definitely Coulomb interaction) in the HF portrayal is at the foundation of the insufficiency of HF wavefunction in depicting the genuine particles and atoms [21]. In any case, DFT corrects it using density functional) and utilizes

3. Result

Theoretical investigations were achieved by means of the Hartree-Fock and Density Functional Theory at the B3LYP level of system at 3-21G, 6-31G and 6-311G using Gaussian09 program. A detailed comparison has been done about the HOMO and LUMO for BBL is a ladder-type of the conjugated polymer with the experimental measurements. Table 1 was explained the value of bandgap associated with basis sets. Figure 2, Figure 3, Figure 4 corresponds to 3-21G, for 6-31G, 6-311G basis sets respect, the bandgap energy is larger than experimental value for HF approximation, according to density functional theory Figure 5, Figure 6 and Figure 7 corresponds to 3-21G, for 6-31G, 6-311G basis sets the value is very close to the real value of BBL bandgap. The real or experimental value of bandgap is 1.9 (ev) according to density functional theory the error ratio is smaller than HF approximation, due to some disadvantage of HF method for a molecular that consist a large number of atoms. Most of the reasons and special properties of each method were explained in theoretical methodology. Because the BBL molecule has 175 electrons, but HF approximation quite ignored the exchange-correlation, it is the disadvantage of HF for the shortcoming in the output result.

Figure.2-7.show HUMO and LUMO of BBL molecule for HF approximation and DFT (3-21G, 6-31G, 6-311G) basis set at B3LYP method of quantum computational theory.

Basis sets

basis set is a lot of functions used to make the sub-atomic orbitals, which are extended as a combination with coefficients to be determined [22]. Generally, these functions are focused on particles, yet functions placed in bonds or solitary pairs have been utilized. Also, basis sets made out of sets of plane waves are regularly utilized, particularly in computations including frameworks with periodic limit conditions. At the beginning of quantum science called Slater type orbitals (STOs) were utilized as basis function because of their similitude with the eigenfunctions of the hydrogen particle. Their overall description is

$$S^{\zeta}_{nlm}(r, \upsilon\,, \varphi) = N r^{n-1} e^{-\zeta r} Y^{m}_{l}(\vartheta, \varphi) \qquad (1)$$

Y^{m}_{l} represent the spherical harmonics and normalized factor denoted by N [23]. STOs have a preferred position in that they have direct physical translation and in this way are normally the great reason for molecule orbitals. From a computational perspective, the STOs have the extreme inadequacy that the vast majority of the required integrals required over the distance of the SCF method must be determined numerically which definitely diminishes the speed of a calculation. As of late, new numerical strategies have been built up that permit very productive SCF calculation utilizing STOs [24].

The negligible basis sets are not adaptable enough for the exact portrayal of orbitals, use different functions to express to each orbital for instance, the twofold zeta basis set enables us to treat each orbital independently when we lead the Hartree-Fock estimation.

$$\Phi_{2s}(r) = \Phi^{STO}_{2s}(r, \xi_1) + d\Phi^{STO}_{2s}(r, \xi_2) \qquad (2)$$

2s atomic orbital communicated as a total of two STOs. The two conditions are the equivalent with the exception of the estimation of ξ which records for how large the orbital is. d is constant decides how much each STO will check towards the last orbital. The triple and quadruple zeta basis sets work a similar way, with the exception of utilization three also, four Slater conditions rather than two. The characteristic trade-off applies here as indeed, improved accuracy...more period/work. There are a few unique sorts of expanded basis sets split-valence, polarized sets, diffuse sets, correlation consistent sets [25].the Insignificant premise sets there are two types. Minimal basis sets that explain only most basic characteristic of the orbital, Extended basis sets that explain more than minimal basis set. The double zeta basis set is imperative to us since it enables us to treat each orbital independently when we lead the Hartree-Fock conduct. This gives us an increasingly precise portrayal of each orbital. So as to do this, each atomic orbital is communicated as the entirety of two Slater-type orbitals (STOs). Regularly it requires a lot of exertion to compute a double zeta for each orbital. Rather, many researchers streamline matters by ascertaining a double zeta just for the valence orbital. Since the inner shell electrons aren't as crucial to the calculation, they are depicted with a solitary Slater Orbital. This technique is known as a split-valence premise set. A couple of instances of regular split-valence premise sets are 3-21G and 6-31G.

Table 1. Band gap energy of BBL for different three basis set

Method		HOMO (a. u)	LUMO (a. u)	$E_g(a.u)$	$E_g(eV)$
HF	3-21G	0.32894	0.02662	0.30232	8.22661091
	6-31G	0.32787	0.03242	0.29545	8.3948995
	6-311G	0.33274	0.03540	0.29734	8.09109714
DFT	3-21G	0.24541	0.21188	0.03353	0.91238483
	6-31G	0.25023	0.14524	0.10499	2.85688289
	6-311G	0.25899	0.15235	0.10664	2.90184502
Experimental		0.2168193	0.14699613	0.06982317	1.9

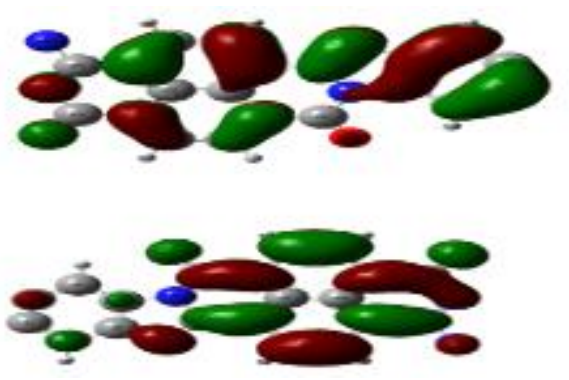

Figure 2. HF approximation 3-21G basis set.

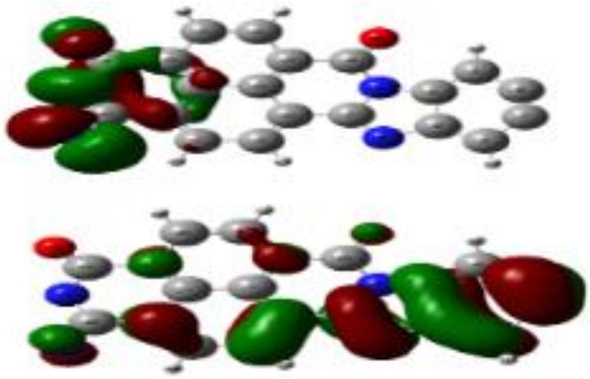

Figure 3.DFT 3-21G basis set.

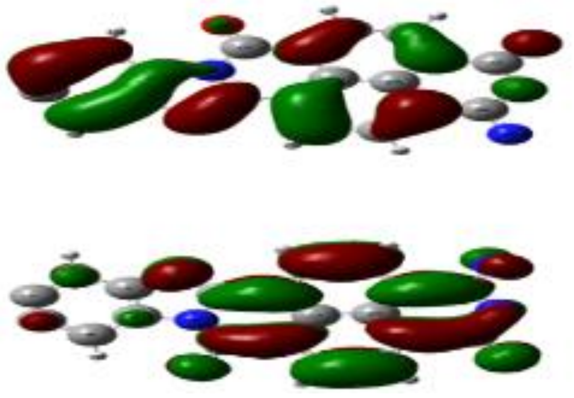

Figure 4.HF approximation 6-31G basis set.

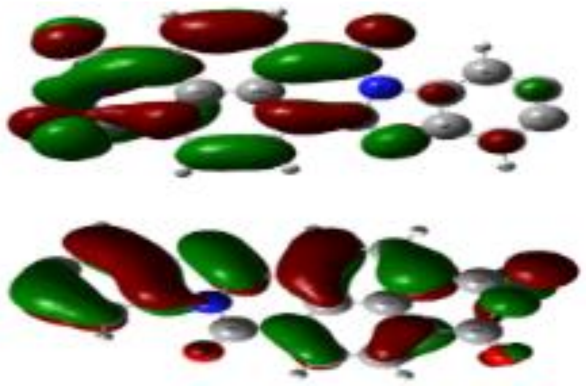

Figure 5. DFT 6-31G basis set.

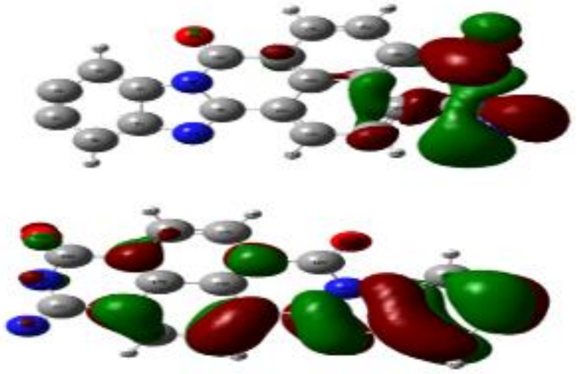

Figure 6.HF approximation 6-311G basis set

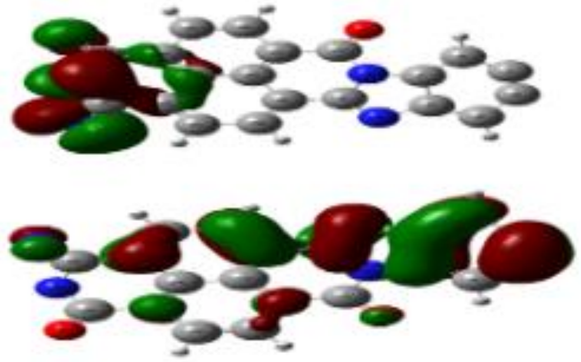

Figure 7. DFT 6-311G basis set.

4. Conclusion

All the first three basis sets were performed to determine the bandgap energy of BBL.in this communication found the bandgap energy and. Proposed the suitable basis set for this molecule, the 6-31G is the best basis set to BBL because has few shortcomings compare with another basis set. $C_{20}H_6N_4O_2$ That existence more C=C and C=O and C=N bond can meaningfully narrow down the bandgap energy or HOMO-LUMO, while the C-H directly or slightly raise up the gap. The number of bonds and atoms directly have a relation with the type of basis. For complex molecule, the simple basis set is not suitable because the basis of basis sets is different from each other

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