

# Theoretical Study of Geometry Optimization and Energies For Aminobenzene-Thiophene-Nitrobenzene as a Donor-bridge-Acceptor Molecular System:B3LYP/DFT Calculations

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## Abstract

This research deals with the B3LYP/6-31G (d, p) density functional theory calculations to calculate the geometry optimization and energies of donor-bridge-acceptor D-B-A molecular system. Depending on Koopman's theorem under the orbital-vertical theory, the electronic states ( HOMO and LUMO ) of such system has been calculated. The results showed that the hybrid functional used in the description of the studied molecular system has proved its validity in calculating the HOMO and LUMO energies and the other electronic properties, and it is suitable for studying the geometry optimization for the organic molecular system. The energy level diagram shows that there are localized orbitals in different parts of the D-B-A molecular system in which that satisfies important property for the D-B-A system as a molecular electronics.

**Keywords:** B3LYP , DFT, total energy , energy gap, HOMO and LUMO

## الخلاصة

هذا البحث يتناول نظرية دالة الكثافة B3LYP / 6-31G (d, p) لحساب الأمثلية الهندسية وطاقات النظام الجزيئي واهب-جسر- قابل. اعتمادا على نظرية كوبمان حسب نظرية المدار المتعامد، وقد تم حساب الحالات الإلكترونية المتمثلة بطاقات المستوي الجزيئي العلوي المشغول والمستوى الجزيئي السفلي الغير مشغول لهذا النظام. وأظهرت النتائج أن الدالة الهجينة المستخدمة في وصف النظام الجزيئي المدروس قد أثبتت صلاحيتها في حساب طاقات HOMO و LUMO والخصائص الإلكترونية الأخرى، وأنها مناسبة لدراسة الأمثلية الهندسية للنظام الجزيئي العضوي. ويظهر مخطط مستوى الطاقة ان للنظام واهب-جسر-قابل مدارات تتموضع في مناطق مختلفة منه وهذا ما يحقق خاصية مهمة للنظام الجزيئي واهب-جسر- قابل كنظام إلكتروني جزيئي. الكلمات المفتاحية: نظرية دالية الكثافة ، الطاقة الكلية، فجوة الطاقة ، المستوى الجزيئي العلوي المشغول والمستوي الجزيئي السفلي غير المشغول.

## Introduction

The electron transfer is the main process in many fields of chemistry, physics, and biology monographs[Marcus, 1985; Barbara, *et al*,1996]. The Present work stands on the design of donor-bridge-accepter molecular system to compute its electronic properties and determine the quantity of electron transfer ET [Bixon, 1999; Berlin, *et al*, 2004; Matyushov, *et al*, 2002 ; Adams, *et al*, 2003]. A convenient model system often used to probe the mechanism of ET in molecular objects with nanoscale dimensions comprises a donor (D) and an acceptor (A) of electrons or holes connected by molecular bridge (B)[Weiss, *et.al*,2005; Kuznetsov, 995:1999]. The number and variety of such donor-bridge- acceptor D-B-A systems have grown explosively in recent years[Balzani, *et al*, 2001; Wasielewski, 1992]. Molecular bridges linking between an electron donor and an electron acceptor are known to control charge transport in molecular systems [Schuddeboom, *et al*, 1991]. Extensive studies emphasized the role of different factors controlling the charge transport mechanism of donor-bridge- acceptor systems including inter-site electronic coupling, electronic energies and electronic - nuclear coupling.The present work focuses on calculating the optimization of the studied structures and energies of donor-bridge-

acceptor molecular system and compute the amount of charge transport as a measure of the maximum electronic charge that saturates the system, it is a measure of the electronic transfer that a system may accept [Ratner, 1997; Lindsay, *et al*, 2007]. The study includes a D-B-A molecular system which was designed depending on Aviram-Ratner model. The organic semiconductor materials, such as, conjugated organic molecules have been widely used as active materials for optoelectronic devices such as light emitting diodes, field effect transistor, and photovoltaic and solar cells [Jordan, *et.al*, 1992, Warman, *et.al*, 1999]. In this work, we use the original aromatic molecule (benzene) to design the donor and the acceptor connected by the thiophene as a spacer between them depending on Aviram-Ratner model [Aviram *et al*, 1974; Denniston *et al*, 2007].

### Computational Details

Berny optimization algorithm was used to calculate the full geometry optimizations of aminobenzene as a donor, nitrobenzene as an acceptor, thiophene as a bridge and the donor-bridge-acceptor to compute the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates. The gradient corrected density functional methodology was employed: Becke's exchange functional (B) and Becke's three-parameter adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee–Yang–Parr correlation functional B3LYP [Schlegel,1982; Brabec, 2001]. While the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP one contains an admixture of HF exchange (i.e. is of hybrid form). The B3 functional, in fact, contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange [Becke, 1993; Becke, 1988]. The standard 6-31G(d, p) basis set of DZP quality was used for orbital expansion to solve the Kohn–Sham equations in all cases. The number of imaginary frequencies served as a test whether the stationary points correspond to real minima, or to first-order saddle points [Katz., *et.al*, 2000; Horowitz, 1998: 1999]. The computed stationary points for which the structures and force fields are presented correspond to real minima on the molecular potential energy hyper surfaces. The DFT (LUMO-HOMO) energy for the donor-bridge-acceptor molecular system studied here was calculated at the same level of theory. All calculations were performed with the GAUSSIAN09 suite of programs.

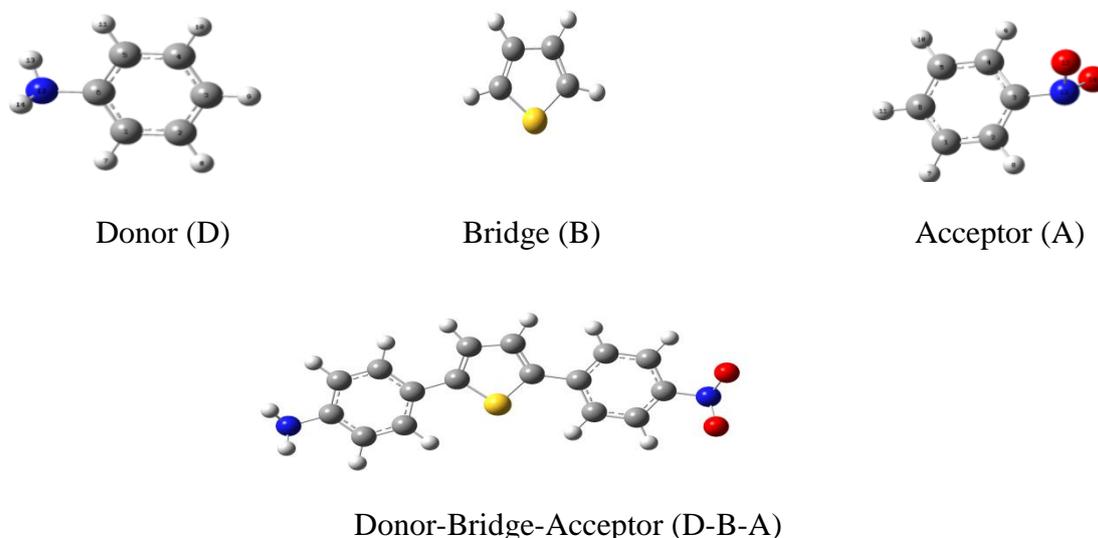


Figure 1: The optimized structures under study at B3LYP/6-31G (d, p).

Table 1: The optimized geometric parameters (lengths in angstrom, angles in degree and dihedral angles in degree) of aminobenzene (D) using B3LYP/6-31G(d, p).

Bond Length ( $\text{\AA}$ )		Bond Angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C-C)	1.392	A(C - C = C)	120.765	D(C = C - C = C)	-0.069
R(C-H)	1.084	A(C - C -H)	119.232	D(H- C - C = C)	179.911
R(C = C)	1.403	A(C = C -H)	120.002	D(H- C - C -H)	-0.366
R(N-H)	1.009	A(C = C - C)	118.694	D(C - C = C - C)	0.142
R(C -N)	1.425	A(C = C -N)	120.617	D(C - C = C -N)	177.1
		A(C-N-H)	114.584	D(H-C=C-N)	-2.622
		A(H-N-H)	111.19	D(N-C-C=C)	-177.099
				D(N-C-C-H)	2.611
				D(C=C-N-H)	156.683

Table 2: The optimized geometric parameters (lengths in angstrom, angles in degree and dihedral angles in degree) of nitrobenzene (A) using B3LYP/6-31G (d, p).

Bond Length ( $\text{\AA}$ )		Bond Angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C - C)	1.392	A(C = C - C)	118.443	D(C - C = C - C)	0.01
R(C -H)	1.08	A(C = C -H)	121.917	D(C - C = C -H)	180.005
R(C -N)	1.476	A(C - C -H)	119.64	D(H- C = C - C)	180.01
R(N-O)	1.227	A(C = C - C)	120.206	D(H- C = C -H)	0.004
R(C = C)	1.412	A(C - C = C)	122.365	D(C - C - C - C)	-0.0091
		A(C - C -N)	118.819	D(C = C - C = C)	-0.001
		A(C -N-O)	117.746	D(C = C - C -N)	-180.009
		A(O-N-O)	124.5	D(H- C - C - C)	179.989

Table 3: B3LYP/6-31G (d, p) optimized parameters of thiophene (B)

(Bond or Angle) Label	Value	Experimental Value [Aviram, 1974]
R(C = C)	1.396	1.39
R(C -S)	1.803	1.812
R(C -H)	1.086	1.1
A(C -S- C)	89.449	90.015
A(C = C - C)	120	120
A(C - C - H)	120	120

It is clear from Table 1 that the geometrical parameters calculations in present study are in a good agreement with experimental data [Aviram *et al.*, 1974], where the calculated R(C=C) is in the range (1.403-1.412) Å<sup>0</sup> and R(c-c) equals (1.392Å<sup>0</sup>).

The optimized bond lengths of the bridge backbone linking between donor and acceptor in table 3 are having double bond less than 1.44 Å<sup>0</sup>, and it can be seen that a minor deviation in the bridge bond angle and dihedral angle between the two planes containing the end substituent's. This deviation can be expected due to strict interaction coming from the presence of phenyl groups at the terminal positions of the D-B-A molecular system. It is clear from the above Tables that the geometrical parameters calculations by B3LYP method are in good agreement with experimental data [Aviram *et al.*, 1974] for amino-benzene (donor) molecule. Also, the bonds calculated in this study for thiophene (bridge) are in good agreement with experimental results, as we see in Table 3. The difference of atomic numbers for the conjugated atoms effect on the bond length between these atoms, the convergence between the bonds C-C and C-N comes from the convergence between their atomic numbers, and this reason explains the difference of C-H bond. Table 4 shows the optimized parameters of the D-B-A molecular system.

Table 4: B3LYP/6-31G (d, p) optimized parameters of (D-B-A) system

Bond Length (Å <sup>0</sup> )		Dihedral angle (deg)		Dihedral angle (deg)	
Bond	Value	Bond	Value	Bond	Value
R(C= C)	1.433	D(C = C - C -H)	-179.89	D(C - C - C = C)	0.158
R(C -H)	1.084	D(H- C - C -H)	0.322	D(C - C = C -H)	0.018
R(C -N)	1.391	D(C - C = C - C)	-0.082	D(C - C = C - C)	0.035
R(N-H)	1.009	D(C - C = C -N)	-177.26	D(N- C = C -H)	-0.057
R(C - C)	1.411	D(H- C = C -N)	2.53	D(C - C -N-O)	-0.065
R(N-O)	1.23	D(H- C = C - C)	-0.049	D(C = C - C - C)	0.062
<b>Bond Angle (deg)</b>		D(C = C - C = C)	-178.1		
Bond	Value	D(H- C = C -H)	-0.534		
A(C - C -H)	119.936	D(C = C - C -N)	177.268		
A(C - C = C)	122.027	D(H- C - C -N)	-2.567		
A(C = C - C)	116.925	D(C = C -N-H)	-23.5		
A(C - C - C)	123.969	D(C - C -N-H)	24.217		
A(C -S- C)	89.449				
A(C -N-H)	115.917	D(C - C = C -H)	0.53		
A(H-N-H)	112.505	D(C = C - C - C)	2.279		
A(C - C = C)	127.559	D(H- C - C = C)	1.841		
A(O-N-O)	124.162	D(C - C - C -H)	0.315		

Table 5 declares the results of the relaxation of the structures under study. These results of geometry optimization included the total energy  $E_T$ , virial ratio ( $-V/T$ ), symmetry and number of imaginary frequency for the donor (D), acceptor (A), bridge (B) and the D-B-A molecular system. As seen in Table 4, the total energy for D-B-A system is less than the total energy of the mentioned molecules in this work, the total energy of D-B-A system is approximately the summation of total energy for all donor, bridge and acceptor molecules, it can be found that an equation associates the total energy  $E_T$  for the donor- bridge –acceptor molecular system with its components:

$$E_T (\text{D-B-A system}) \approx E_T (\text{donor}) + E_T (\text{bridge}) + E_T (\text{acceptor})$$

The results showed that the 6-31G (d, p) functional is a suitable level of theory used for optimization geometry of these structures, in which all the studied structures have no imaginary frequency. Table 5 shows also the symmetry of the studied molecules, amino-benzene (donor) is a planar and has a low symmetry, nitrobenzene (acceptor) has high symmetry, thiophene (bridge) is a  $C_{2V}$  high symmetry and the donor- bridge-acceptor molecular system has  $C_1$  point group symmetry and this means that only a rotation of  $360^\circ$  leaves it apparently unchanged.

**Table 5: Results of the relaxation for studied molecules**

Species	$E_T(a,u)$	$-V/T$	Symmetry	NO. Of imaginary frequency
<b>Donor (D)</b>	<b>-287.647</b>	<b>2.008</b>	$C_S$	<b>0</b>
<b>Bridge (B)</b>	<b>-552.931</b>	<b>2.004</b>	$C_{2v}$	<b>0</b>
<b>Acceptor (A)</b>	<b>-436.803</b>	<b>2.007</b>	$C_{2v}$	<b>0</b>
<b>Molecular System (D-B-A)</b>	<b>-1274.712</b>	<b>2.004</b>	$C_1$	<b>0</b>

The high occupied molecular orbital energy  $E_{HOMO}$ , lower unoccupied molecular orbital energy  $E_{LUMO}$  and energy gap  $E_g$  for donor, acceptor and donor-bridge –acceptor structures are shown in Table 6. It has been found that the thiophene (bridge) used to connect the amino-benzene as a donor with nitrobenzene as an acceptor gave a new structure (donor- bridge–acceptor) system has a small energy gap compared with its components, the energy gap for D-B-A system is 2.578 eV. These results are main features in constructing new molecular electronics [Ramla *et al.*, 2014; Jaafar Tuma. *et al.*, 2014; Huda Bukheet, 2014].

The interaction between amino-benzene (D) and nitrobenzene (A) through the bridge affected HOMO and LUMO of these molecules, the main change occurs at LUMO of the donor and HOMO of the acceptor and this change depends on the type of bridge used in linking the donor and the acceptor. Figure 2 shows the energy level diagram for the three highest occupied and three lowest unoccupied molecular orbitals for the donor, bridge, acceptor and D-B-A system. From this diagram, one can see that the HOMO and LUMO for the acceptor are more stable in comparison with those of the donor. The HOMO and LUMO for donor are situated (-5.768, -0.353) eV, higher than the HOMO and LUMO for acceptor, but (LUMO-HOMO) for both donor and acceptor is approximately the same (5.415 eV for donor and 5.006 eV for acceptor). The electron injection of an electron to the LUMO of the acceptor will be a

lower energy process compared to the donor because the LUMO of the acceptor is more stable in comparison with donor. On the other hand, removal of one electron from the HOMO of the donor will be a less energetic process compared to the acceptor because the HOMO of the donor is less stable compared to HOMO of the acceptor.

The energy level diagram shows that the HOMO of the bridge is more stable like the HOMO of the acceptor and the LUMO is unstable like the LUMO of the donor, and this bridge has very high energy gap in which this indicates that the bridge can act as a suitable barrier. The (LUMO-HOMO) of the D-B-A is small (2.578 eV) compared to donor, bridge and acceptor.

Figure 3 shows the shapes of HOMO and LUMO for these structures, drawn by Gaussian View 5.0.8 using DFT-B3LYP/6-31G (d, p) level of theory.

In the system under study, the donor part and acceptor part are coupled through the bridge to produce the molecular system. As we know that the structural construction principle of organic molecular electronic is based on acceptor part and donor part connected through an insulating bridge, these three (donor, acceptor and bridge) can be considered as components in bringing out the molecular electronic.

**Table 6:  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and energy gap  $E_g$  for studied molecules**

Species	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_g$ (eV)
Donor (D)	-5.768	-0.353	5.415
Acceptor (A)	-7.863	-2.857	5.006
Molecular System (D-B-A)	-5.299	-2.721	2.578

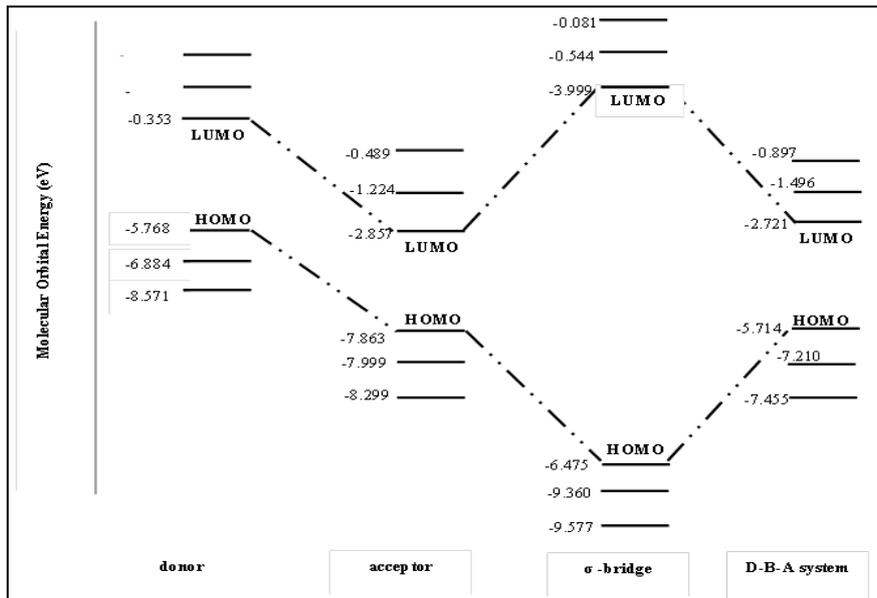


Figure 2: Energy level diagram for donor, bridge, acceptor and D-B-A.

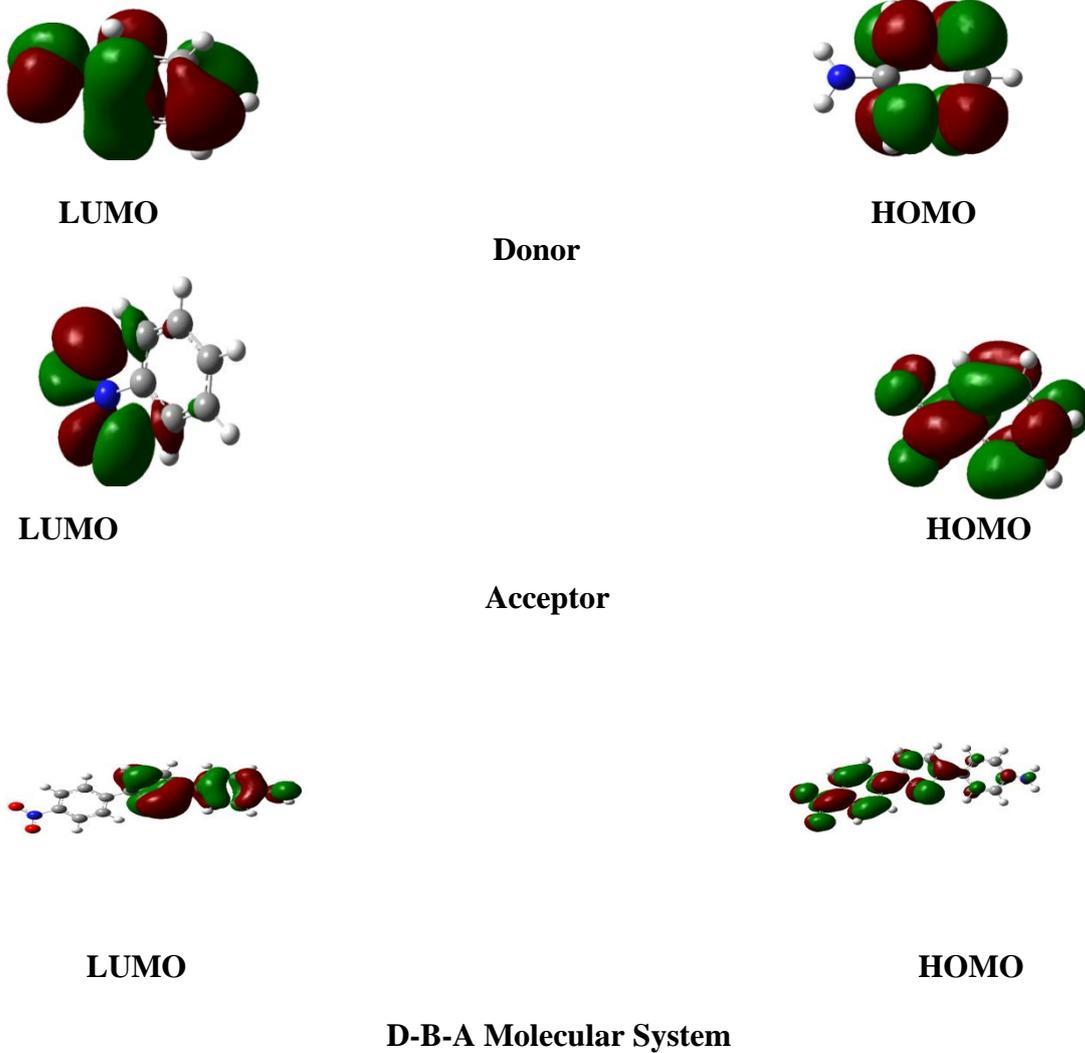


Figure 3: The shapes of HOMO and LUMO for studied structures

## Conclusions

- The hybrid functional B3LYP/6-31 G(d, p) density functional theory has proved its validity in studying the geometry optimization and calculating the geometrical parameters.
- Density functional theory presented good results in calculation of total energy for the D-B-A molecular system which comes from the summation of total energies for all donor, bridge and acceptor parts.
- The large 6-31 G(d, p) basis set used to describe the studied structures with B3LYP functional level is a significant theory for calculating the electronic states (HOMO and LUMO) and studying the spectra analysis for the studied molecular electronics, but it requires a large time compared with other small basis sets.
- The added substituents in the terminal ends of phenyl rings to construct the donor and the acceptor did not have an effect on the aromaticity of these organic molecules. So, the aromaticity of phenylenes keeps under the connection donor part and acceptor part through the bridge.
- Phenyl ring with amino group was truly predicted to be a better semiconducting material because of its lower oxidation potential, it is good electron donating group. The small value of (LUMO-HOMO) for the D-B-A molecular system compared with their individual components results from this molecular system as an molecular electronics. For device application with these structures connected to two electrodes, a decrease in (LUMO-HOMO) value plays an important role in electron injection.
- There are localized orbitals in different parts of the D-B-A molecular system as a result of the molecular orbital distribution in which that satisfies important property for the D-B-A system as a molecular electronics.

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