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## THEORETICAL STUDY OF THE ELECTRONIC CONDUCTION THROUGH ORGANIC NANOWIRES

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A substantial amount of researches have been carried out on the electron transport properties of gold surfaces. In order to study the role of linkage in the conductive properties of a molecular wire, different linkers such as sulfur, nitrogen, oxygen, CS, SH, NS, and CN are considered in our study. It is found that nitrogen or sulfur linkages can bond Au covalently to *cis*- and *trans*-butadiene, whereas on the other hand, oxygen linkage with the same shows a weak interaction and a non-covalent character. Further, this research is also an attempt to study the dependence of the molecular electronic structure of gold-molecule complexes on the external electric field. In addition, electronic conduction has been investigated from the perspective of alteration in shape of molecular orbitals and the development of the HOMO-LUMO gap of molecule-gold complexes under the effect of an electric field.

**Keywords:** *cis*- and *trans*-butadiene, molecular wire, HOMO-LUMO gap, electric field, gold cluster.

## INTRODUCTION

More than thirty years back, Aviram and Ratner theorized that molecular wires could have the potential to rectify an electronic current [ 1 ]. A comprehension of the chemical interaction between electrode metals and molecular wires is yet rather fundamental though important to the basic design of single-electron devices. A molecular wire which is in fact an organic molecule forms a conducting bridge between electronic contacts. A single organic molecule is probably the smallest entity to possess an ability to conduct electricity, so molecular wires not only offer various fascinating challenges to fundamental science but also have enormous potential for practical technological application, e.g. to name but a couple, in organic switching devices [ 2—5 ] and nanoscale memories [ 6, 7 ]. One of the most important targets in the engineering of electronic devices is miniaturization. The technology of micro-structuring semiconductor material is expected to reach its height in the next decade.

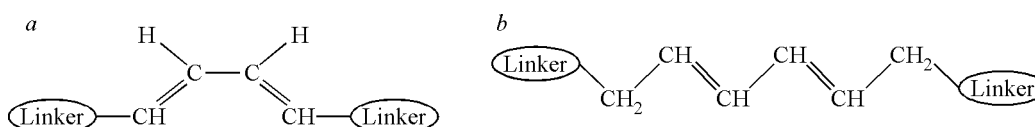
In order to construct a molecular wire, an elongated molecule consisting of conjugated molecular units, which contain alternating single and double (or triple) bonds through which electrons can flow without restriction from one end to other, are needed. In the recent past, metal/molecule/metal heterostructures have been the basis of many experimental [ 8—10 ] and theoretical studies [ 11—15 ] aimed at further understanding of the transport properties. There is a particular challenge stemming from this comprehension that the properties of molecular wires are strongly affected by (i) the molecule characteristics and (ii) the nature of the linkage and consequently, the metal—molecule interaction [ 16 ]. On the molecular level, quantum effects play an important role. To get a clearer picture of the of the structure — property relationship and ultimately the synthetic strategy and molecular engineering techniques, a theoretical analysis of the frontier molecular orbitals of these molecules and the

energy difference between HOMO and LUMO known as the HOMO-LUMO gap (HLG) can be utilized to reach reality [ 17—19 ]. Here, the HOMO denotes the highest occupied molecular orbital while the LUMO shows the lowest unoccupied molecular orbital [ 20, 21 ]. The energy gap has been estimated from two aspects, namely, HLGs and the lowest excited energies [ 22 ]. Further, as the electronic devices need to work under a large external electric field, the understanding how the molecular structure and HLG react to the external electric field [ 23, 24 ] becomes more and more essential. *Cis*- and *trans*-butadiene, which are one of the smallest conjugated oligomers, can play the role of a good theoretical model in the exploration of the structural and electronic properties controlling the electron transport [ 25—28 ]. *Cis*- and *trans*-butadiene oligomers possess both ideal conductivity [ 26 ] and rigidity [ 27 ]. Thus these materials have a great potential for a wide variety of applications in molecular electronic devices.

In this research, a theoretical investigation has been executed in detail on the electron transport properties of *cis*- and *trans*-butadiene molecules sandwiched between two gold clusters. In the system of investigation utilized, different linkers have substituted the *para*-hydrogen atoms of two phenyl rings. These linkers can be categorized as atomic linkers such as sulfur, nitrogen or oxygen and group linkers — where the said atoms are joined to the ring via carbon or nitrogen connectors — e.g. CS, SH, NS, and CN. Here, we have studied the electronic structures and geometry of linker-terminated *cis*- and *trans*-butadiene interacting with gold(III) clusters. By taking into account the shape of the electronic channels and the binding energies in the *cis*- and *trans*-butadiene based molecules, we were able to gain a deeper understanding regarding the contribution of molecular orbitals. Thus, in conclusion, we can emphasize the importance of paying sufficient attention to tuning parameters, such as a suitable electric field and the type of the linkage in making molecular wires be used in electronic devices.

#### COMPUTATIONAL DETAILS

Since it is necessary to include a metal contact in any study on molecular devices, in the present work, we have chosen a three-atom gold nanocluster: Au (III). Calculations were carried out at the density functional theory level with the B3LYP functional. The basis set included the Los Alamos National Laboratory effective core potentials with a double-zeta valence (LANL2DZ) for the gold atoms and split 6-31G\* for C, H, N, O, S atoms [ 29 ]. All calculations were performed in three steps. The first step consisted of the execution of a geometry optimization of *cis*- and *trans*-butadiene and *trans*-butadiene joined to six different linkers (Scheme 1[*cis* (*a*), *trans* (*b*)]). After which, the interaction between molecules and two gold(III) clusters was analyzed (after the removal of the terminal H atoms of SH, OH, and NH<sub>2</sub>). In this configuration, each gold cluster consists of three atoms placed as an equilateral triangle having a side of 2.88 Å to simulate the gold(III) surface [ 30 ]. In each triangle, the relative positions of the gold atoms were fixed. Relevant geometrical parameters for all the metal—molecule complexes were studied in this work. The position of the linker (or any terminal atom of the linker) in the molecular interfacial region, and the two terminal gold clusters were fixed in the space and the others were optimized. To optimize the (Au<sub>3</sub>—*cis*-butadiene—Au<sub>3</sub> and Au<sub>3</sub>—*trans*-butadiene—Au<sub>3</sub>) complexes, the range distance between the linker atom and the gold plane was adjusted between 2.13 Å and 3.93 Å. Then in Step 3, the two terminal gold clusters were fixed in space to simulate the connection to the electrodes. All other geometric parameters were, subsequently, optimized at the same level of theory in an external EF. The EF ranging from zero to 0.103 V/Å was defined uniformly and aligned along the metal/molecules/metal inter-atomic vector, and applied to each complex that could reasonably represent the working condition of the molecular wire [ 31—33 ]. All calculations were performed with the help of the GAUSSIAN 03 program [ 34 ].



Scheme 1[*a*, *b*]. Molecular junctions constructed with different linkers (linker = O, N, S, CO, CS)

## RESULTS AND DISCUSSION

**The electronic structure of free molecules.** For a molecule to act as a molecular wire it should principally possess a fully delocalized low lying vacant molecular orbital that should be spread all over the molecule. This can serve as a channel of conduction in the electron transfer process, that is to say, if the delocalization is higher, the electron transfer is faster [ 35, 36 ]. A comparison of energy levels in the HOMO and the LUMO and HLG for nine free molecules is given in Table 1 (*cis* (a), *trans* (b)). Whereas Table 2 (*cis* (a), *trans* (b)) illustrates the corresponding molecular orbital pictures for all molecules achieved from their optimized geometry.

Table 2, a shows a comparison of energy levels in HOMO and LUMO. In all the linkers under study except the NS linker, both HOMO and LUMO are completely delocalized all along the molecular backbone, thus gaining the ability to function as a conduction channel in the electron transfer process.

**Interaction with a gold cluster.** The electrical performance of a molecule sandwiched between two metal electrodes is predominated by many factors, such as the nature of the molecule itself [ 37 ], the interface between the molecule and the electrode [ 38 ], the electrode material [ 39 ], and the electrode shape [ 40 ]. The Gold-molecule interface has been selected in order to focus on the importance of the transport properties of molecular wires. Studies on the nature of the interaction between molecules and gold clusters have proven to be crucial for the replication in the field of electronic conductivity [ 41, 42 ]. The ease at which an electron makes a transfer within the structure of a molecule is the yardstick for differentiating whether the complex will act well as a metallic conductor, semiconductor, or insulator. This, undoubtedly, is of great importance in practice when selecting the most suitable material for molecular electronic applications.

The orientation and the structure of the complexes were obtained by giving the positions of the terminal atoms in the hollow section of the gold clusters. We firstly sought for the energetically optimal distance between the gold cluster and the terminal atom in each complex. It was observed that in all complexes *cis*- and *trans*-butadiene remained planar and perpendicular to the gold surfaces. Then only the bond distance between Au and the terminal atom was compared since the geometry of other atoms in butadiene were hardly influenced. Table 3 illustrates the parameters of the energetic and typical geometry for the optimal distance between the gold surfaces and the terminal atoms (or the bolded atoms). The distances between the gold cluster and the terminal atom in all complexes are within 2.13—3.44 Å. Further, the binding energy can be defined as:

$$\text{binding energy} = E(\text{Au}(111)/\textit{cis}\text{- and } \textit{trans}\text{-butadiene}/\text{Au}(111)) - [E(\textit{cis}\text{- and } \textit{trans}\text{-butadiene}) + 2E(\text{Au}(111))], \quad (1)$$

where  $E(\textit{cis}\text{- and } \textit{trans}\text{-butadiene})$  is the total energy of *cis*- and *trans*-butadiene when both ends of the molecules are substituted by CO, CN, CS, O, N, S, or NS groups. Further,  $E(\text{Au}(111))$  and  $E(\text{Au}(111)/\textit{cis}\text{- and } \textit{trans}\text{-butadiene}/\text{Au}(111))$  are the total energies of the gold cluster and the molecular complex on the gold cluster respectively.

The connection of sulfur, nitrogen, and oxygen as a linkage between the metal and molecule interfaces were then compared and three different sets of linkers were scrutinized. In the first set (SH,

T a b l e 1

*HOMO, LUMO and HLG levels (eV) in free molecules*

No	Linker	HOMO	LUMO	HLG	No	Linker	HOMO	LUMO	HLG
<i>cis</i> -Butadiene					<i>trans</i> -Butadiene				
1	SH	-7.51592	-4.5498	2.9660	1	SH	-5.31568	-0.965633	4.349434
2	OH	-7.841	-4.0801	3.7612	2	NH <sub>2</sub>	-4.364956	-0.648657	5.013614
3	NH <sub>2</sub>	-5.5179	-5.50078	0.017155	3	CS	-5.266323	-2.432056	2.834267
4	CS	-6.0767	-4.55993	1.51680	4	CN	-7.434777	-3.276508	4.158268
					5	NS	-5.270408	-4.668317	0.602091

T a b l e 2

*Shape of HOMO and LUMO in free molecules*

Linker	HOMO	LUMO
<i>cis-Butadiene</i>		
SH		
NH <sub>2</sub>		
CS		
CN		
NS		
<i>trans-Butadiene</i>		
SH		
OH		
NH <sub>2</sub>		
CS		

NH<sub>2</sub>, OH), the said links were seen to be directly connected to both gold cluster and *cis*- and *trans*-butadiene. It was observed that in this case lone pairs on N, S, and O were involved in the resonance leading to an electron delocalization that occurred all over the molecular backbone. Among the three linkers in this set, electron delocalization was least probable in the linker (OH) in *trans*-butadiene because oxygen is more electronegative than sulfur and nitrogen. Therefore, the positive charge of oxygen caused by resonance makes the molecule unstable. In the second set i.e., CN, CS complexes, the linking atoms are directly connected to the gold cluster. Their connections to *cis*- and *trans*-butadiene are through a carbon atom. So, in this case, the linkers are CS, CN. Here, the C—C bond between *cis*- and *trans*-butadiene and the linking atoms localizes the electrons even more making them difficult to move from one side of the molecule to the other. So, in reality no CN, CS complex is observed to be stable. The NS complex in the third set is similar to the CN, CS complexes only in that its connection to *cis*- and *trans*-butadiene is through a nitrogen atom.

Table 3

Distances calculated between Au and the linker (Å), binding energy, HOMO, LUMO, and HLG (Ev) for all nine complexes

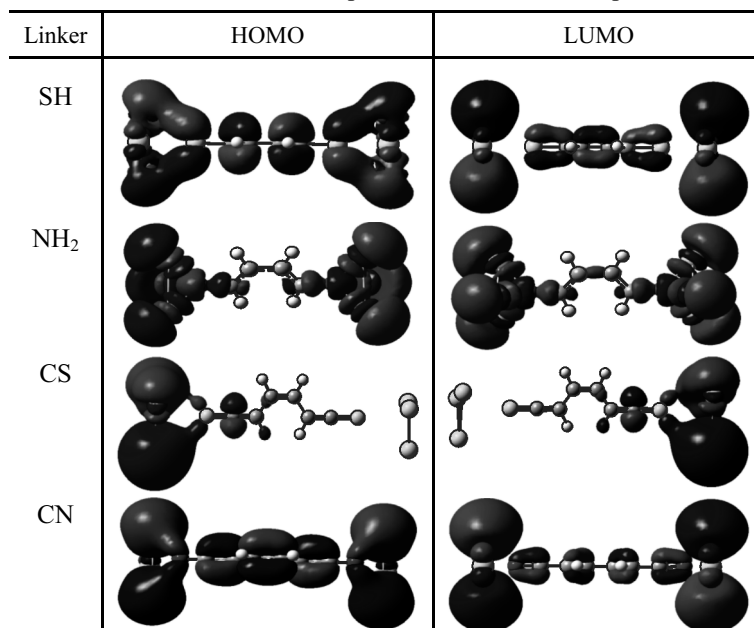
No	Complex	$D_{\text{Au-L}}$	Binding energy	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	HLG
<i>cis</i> -Butadiene						
1	SH	3.008	-1.1435	-5.337	-4.075	1.262
2	NH <sub>2</sub>	2.17	-1.8962	-4.898	-4.564	0.333
3	CS	3.43	0.6523	-4.400	-4.284	0.115
4	CN	3.042	-0.1332	-4.816	-4.046	0.769
5	NS	2.80	-2.7210	-6.132	-3.959	2.173
<i>trans</i> -Butadiene						
1	SH	3.409	-0.817	-4.957	-4.284	0.672
2	OH	2.043	0.054	-5.495	-3.832	1.663
3	NH <sub>2</sub>	2.139	-2.152	-4.865	-4.515	0.349
4	CS	3.446	0.599	-4.624	-4.386	0.237

In summary, four of the nine complexes (*cis* and *trans*) under study in this work, i.e., SH, NH<sub>2</sub>, CN, NS are stabilized because of their interaction with the gold surface. A significant point worth noting was that an analysis of the calculated binding energy showed that the nature of the interaction of the gold cluster with *cis*- and *trans*-butadiene through the oxygen interface was different compared to Au—N or Au—S bonds.

Lastly, describing changes taking place at the molecular level after the interaction with gold clusters is fascinating. The shift of the HOMO and the LUMO causes the molecule bond with the gold clusters to come into existence, in turn making a variation in the electron density. The orbital energies reported in Tables 1 and 3 exhibit that the complexes of *cis*- and *trans*-butadiene with gold clusters possess a lower HLG than isolated *cis*- and *trans*-butadiene. Table 4 illustrates the frontier molecular

Table 4

HOMO and LUMO Shapes in *cis*-butadiene complexes



orbitals of *cis*- and *trans*-butadiene molecules after the interaction with two gold(III) clusters. For the SH, CN and NS complexes, the HOMO and LUMO remain completely delocalized along the whole complex. In complexes such as these, in which the coupling to gold clusters takes place via nitrogen, sulfur, and hydrogen contact, the conduction of the HOMO and LUMO was found to be delocalized and stayed the same as in their free molecules. By introducing CS as an interfacial contact, the HOMO can be localized on one of the terminal Au—S—C groups, whereas on the other hand there is a smaller effect on the LUMO. The calculations we made show that the HOMOs of the NS linker shift downward as they are attached to the gold clusters. In the NH<sub>2</sub> complex, the HOMO and LUMO were partially localized so that the electron charge had gathered around the complex structure. However, the delocalized nature of the frontier molecular orbitals that can be looked upon as a conduction channel shows that such complexes can most likely perform well as potential molecular wire.

**Effect of the external field.** It should be noted that any component in the electronic device must be subjected to a considerable external electric field. Under this particular condition, the molecular geometry as well as the electronic structure, which plays a crucial role in determining the conductance of a molecular wire, is not considered to be the same as in the zero-electric field [43]. The application of the external electric field is feasible in theoretical simulations. The purpose of this paper is to focus on a more *in situ* theoretical approach to the design of molecular electronic devices and to reveal the dependence on the electric field by molecular geometry, electronic structure, dipole moment, and the spatial distribution of frontier orbitals of a molecular wire, which as a matter of fact was hardly the focus of attention in the previous works [44]. In this research, we have studied the effect of an electric field having a magnitude up to 0.103 V/Å and aligned the interatomic vectors related to the SH and NH<sub>2</sub> molecules. All parameters were optimized in the external field. The gold clusters and the terminal atoms were also fixed at their optimal distance. In the role of a demonstrative example, the bond length variation for complex 1 under various EF is shown in Fig. 1 (*cis* (a), *trans* (b)). It is a known fact that the bond length alternation (which is defined as the average difference between the adjacent

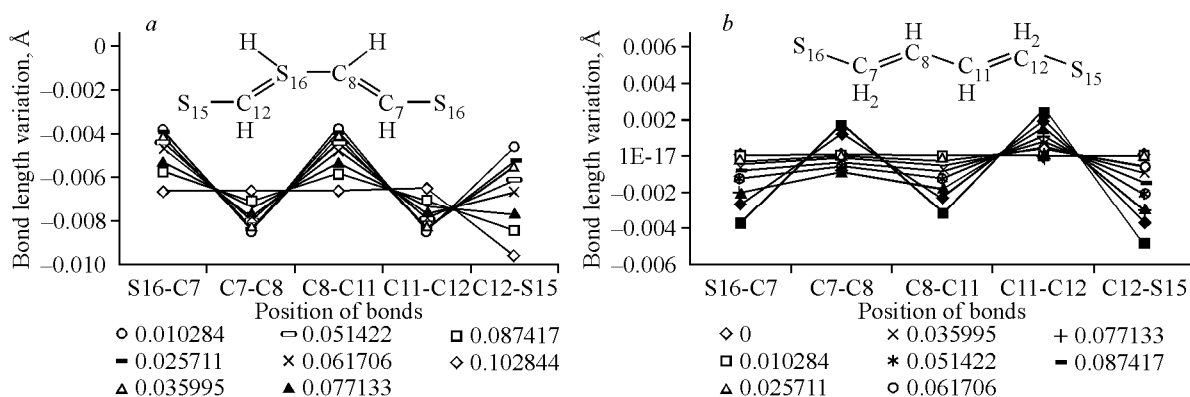


Fig. 1. Bond length evolution for complex 1 under various EFs with respect to the zero EF case

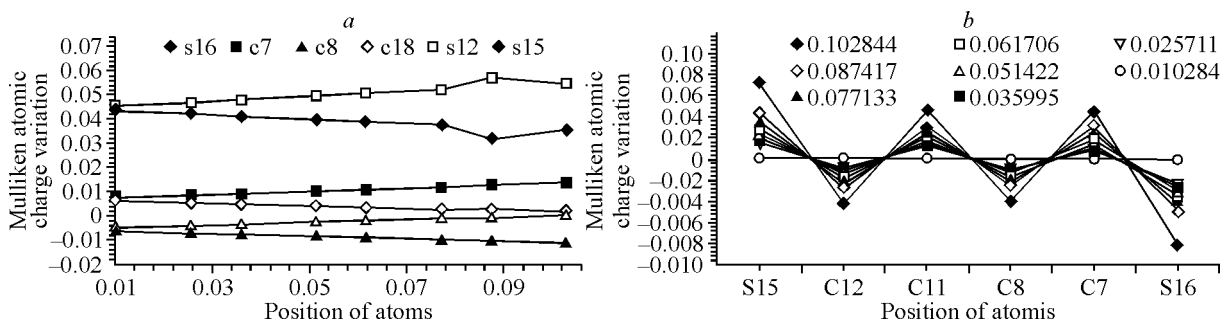
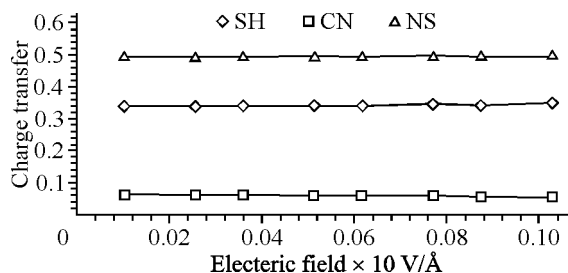


Fig. 2. Mulliken atomic charge variation for complex 1 on each atom under various EFs considering zero EF

Fig. 3. EF effect on the charge transfer for SH, CN, and NS linkers



single and double bonds) found on the length of the backbone of a conjugated system is a crucial parameter, especially, in the regulation of transportation behavior [45, 46]. *Cis*- and *trans*-butadiene have longer single bonds and shorter double bonds at zero fields. When EF rises, the carbon—carbon single bonds are shortened and the double bonds tend to lengthen resulting in a lower bond length alternation. It is worth noting that this variation in the bond length corresponds to the balance of the conjugation within the molecule as a whole while interacting with EF. Further, the charges on each atom in the molecule redistribute after EF application.

Fig. 2 (*cis* (a), *trans* (b)) shows the Mulliken charge variation on each atom for complex **1**, under the EF effect. The figure clearly demonstrates the charge transfer from one end of the molecule to another. It can be seen that with an increase in EF, the charge on S (15) increases whereas the charge on the sulfur atom of the opposite end of S (16) decreases. An investigation of charge transfer across the metal-molecule interfaces were also executed at various strengths of EFs. Fig. 3 (*cis*-butadiene) illustrates the variance of charge that was transferred from the gold cluster to the molecular region against the EF used for the linkers SH, CN, and NS. Induced charges have been fixed at low or almost zero EF. Generally, the MOs of molecules are expected to vary when an electric field is applied. So, it is important to understand how the HOMO, LUMO, and HLG would react to the external field. The evolution of the energy levels of HOMO and LUMO and HLG for the linkers (SH, NH<sub>2</sub>, NS, CN) under the external field can be seen in Fig. 4 [(a: HOMO and LUMO *cis*-butadiene), (linkage: SH, NS, CN)], Fig. 4 (b: HOMO and LUMO) *trans*-butadiene (linkage: SH, NH<sub>2</sub>); c: HLG *cis* (linkage: SH, NS, CN); d: HLG *trans* (linkage: SH, NH<sub>2</sub>)]. As can be seen HOMO and LUMO tend to shift towards each other as an increase in EF leads to a decrease in HLG. Both magnitude of the applied field and interfacial properties affect the shift of the energy levels. Between the two linkers, the HLG of *trans* (SH, NH<sub>2</sub>) linkers shows a more distinct electric field dependence. An increase in the electric field causes a decrease in the HLG of *trans* (SH, NH<sub>2</sub>) linkers. Whereas the HOMO and LUMO in the *cis* (CN, SH) linkers seem insensitive with regard to a variation in the electric field. The HOMO energy in

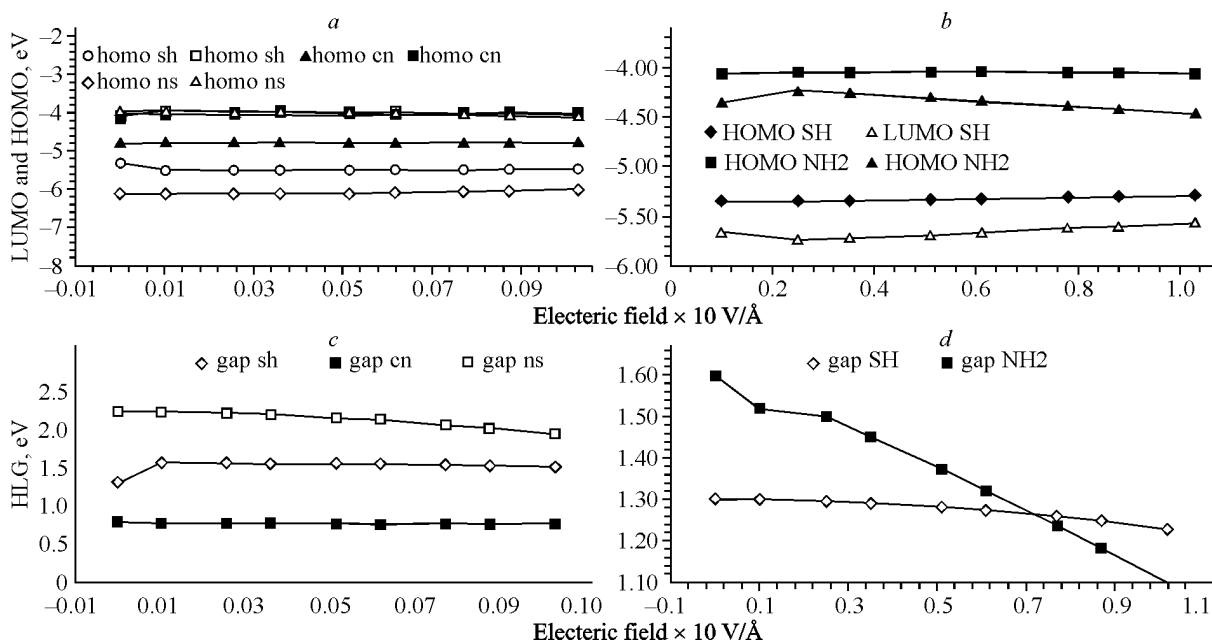


Fig. 4. EF dependence of (a) frontier orbitals, (b) HLG in SH, CN, NS, and NH linkers

*cis*, *ns* and *trans* NH<sub>2</sub> increases with the EF appliance. A dummy atom (X) was considered at the midpoint of the C—C bond in order to portray the bending angle and O—X—O is labeled as the bending angle. Then again, butadiene tends towards the bended structure because of the loose contact at the AU—O interface. As can be seen, the aforementioned observations present us with an approach on how to tune molecular structures by utilizing suitable linkage and thus achieving the properties desired.

### CONCLUSIONS AND DISCUSSION

Several studies have been executed at the density functional theory level to investigate the role that linkage plays in the interaction between *cis*- and *trans*-butadiene on one hand and gold clusters on the other. In the present research we have focused on the geometrical and electronic structures of *cis*-butadiene and *trans*-butadiene based molecular wire, nonetheless electron transport properties can also be explored through studies founded on the non-equilibrium Green's function formalism [47—50]. Among the nine different linkers studied in this paper, *cis*- and *trans*-butadiene makes the most stable complexes with sulfur, nitrogen, and NS. An analysis of the charge transfer confirms that gold can couple strongly with *cis*- and *trans*-butadiene through the nitrogen linkage. However, gold has a weak interaction with *cis*- and *trans*-butadiene through the sulfur linkage and is in fact non-covalent in nature. From our analysis on the geometrical and electronic structures of different EFs, it can be concluded that an increase in EF results in shorter bonds but longer double bonds which indicate an enhancement in the conjugation of the molecular wire. We can further conclude that the nature of the interfacial contact is the decisive factor on which the HOMO and LUMO, and HLG depend under the effect of EF. The results of this research can certainly offer more comprehension of the way in which tunable parameters such as the EF and the nature of the interfacial contact in the operation of the molecular wire can be modulated.

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