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Electrostatic properties and molecular orbital analysis of 1,2-di(cyclopenta-1,3-dienyl)ethyne molecular nanowire by computational study

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ABSTRACT

The electrical characteristics and molecular orbital analysis of 1,2-di(cyclopenta-1,3-dienyl)ethyne molecule has been studied by using quantum chemical calculations coupled with density functional theory (DFT) using Gaussian09 program package. The molecule has been substituted with thiol, Au and Pt atoms at both ends of the molecule one by one and the corresponding variations in structural, electrostatic and transport properties have been analyzed. In this study, thiol atom acts as linker whereas Au and Pt atoms act as electrodes. Comparing with thiol substituted molecule the Au and Pt substituted molecules exhibit more variations in their structural properties. Atomic charges of the free molecule as well as all the substituted molecules have been compared with MPA and NPA charges. The HOMO-LUMO gap (HLG) of the molecule decreases gradually for S, Au and Pt substituted molecules respectively. The existence of small HLG of Au substituted molecule enhances the conductivity. Using Au as electrodes with thiol as linker, 1,2-di(cyclopenta-1,3-dienyl)ethyne can acts as an efficient molecular wire.

Introduction

Computational chemistry may be defined as the application of mathematical and theoretical principles to the solution of the chemical problems. Molecular modeling, a subset of computational chemistry, mainly focuses on predicting the behavior of individual molecules within a chemical system [1, 2]. Molecular electronics, a branch of nanotechnology mainly deals with the fabrication and the utilization of molecular electronic devices [3,4]. The key components of molecular electronic devices are molecular nanowires, which are composed of repeating molecular units either organic or inorganic. They typically have non-linear current-voltage characteristics, and do not behave as simple ohmic conductors [5,6]. 1,2-di(cyclopenta-1,3-dienyl)ethyne molecule is a conjugated one, which may be acts as molecular nanowire. The molecule is attached with Au or Pt atoms at both ends, which can be act as electrodes for applying external electric field. The thiol atom forms good link between the conjugated 1,2-di(cyclopenta-1,3-dienyl)ethyne and the Au or Pt atoms. The present study reports the effect of substitution of Au and Pt atoms in the 1,2-di(cyclopenta-1,3-dienyl)ethyne molecular nanowire and the corresponding variations in the structural and electrostatic properties by using Density Functional Theory (DFT).

Computational details

1,2-di(cyclopenta-1,3-dienyl)ethyne molecule known as free molecule (molecule-I) has been optimized by DFT method using Gaussian09 program package [7-10]. A combination of Becke's three parameters exchange function and Lee, Yang and Parr gradient–corrected correlation function (B3LYP hybrid function) is applied for whole DFT calculation.

The thiol, Au and Pt and substituted 1,2-di(cyclopenta-1,3-dienyl)ethyne (molecule-II, molecule-III and molecule-IV) (Fig.1) have been optimized in a similar way as that of free molecule along with LANL2DZ basis set, which provide effective core potential and the detailed description of the effect of heavy metal atoms in the molecule [11,12]. The quantum chemical calculations have been carried out using GaussView program to determine the HOMO-LUMO energy values of all the molecules. The GaussSum program has been used to determine the density of states (DOS) of all the molecules [13].

Results and discussion

Structural aspects

The 1,2-di(cyclopenta-1,3-dienyl)ethyne molecular wire has two cyclopentadiene rings in which Au or Pt atoms are attached at both ends of the molecule through thiol atoms. The Optimized geometry of the molecules is shown in Fig.2. The variations in geometrical parameters such as variation in bond length of a molecule give an outline of the conducting properties [14,15]. The average of the difference in the length between adjacent carbon-carbon bonds is known as bond-length alternation, which closely relates with the band gap of the organic conjugated molecules. Further, several researchers reported that reduction of the HOMO–LUMO gap results from a relaxation of bond length alternation.[14-16]. The single bond C−C distances of 1,2-di(cyclopenta-1,3-dienyl)ethyne (free molecule) are ~1.5 Å. This value gradually increases for thiol, Au and Pt substituted molecules. The double bond C−C distance of the free molecule is ~1.35 Å this value gradually increases for molecule-II, molecule-III and molecule-IV. Similar trend is observed in the C−C triple bond in which, the bond distance for free molecule is 1.216 Å and this value gradually increases for thiol, Au and Pt substituted molecules to 1.217, 1.236 and 1.257 Å respectively. However, the C−H bond distances of all the molecules (free as well as substituted molecules) are almost same (~1.08 Å). The S−C bond distances of the molecule with S, Au and Pt are 1.763, 1.795 and 1.737 Å respectively. The distances of Au−S bonds are found equal (2.422 and 2.422 Å) on both ends of the Au substituted molecule. Similarly, the distances of Pt−S bonds are found equal (~ 2.260 Å) on both ends of the Pt substituted molecule. The bond lengths values of S-C and Au-S bonds determined from this study are almost matched with the reported experimental and theoretical results [17,18].

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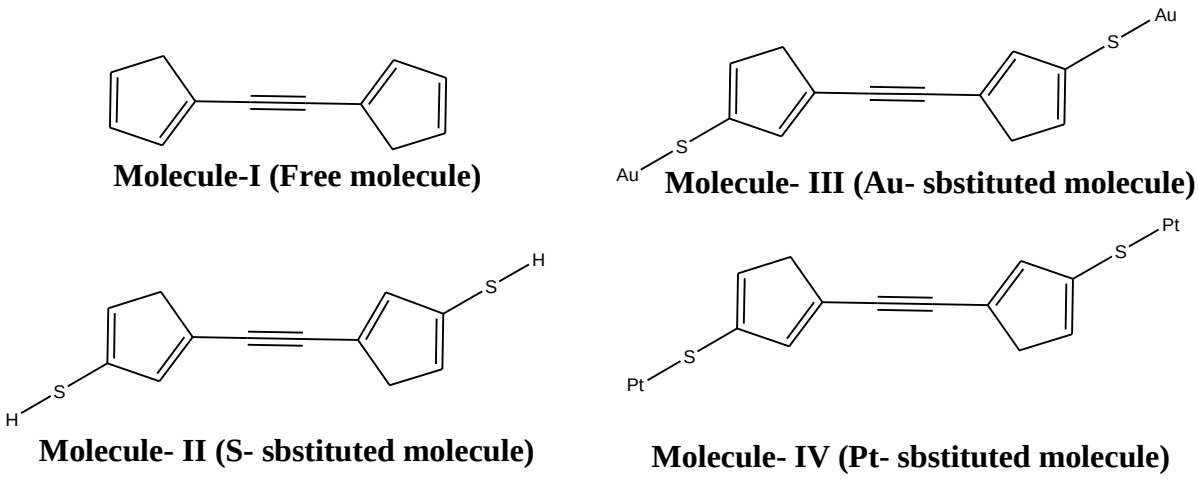


Fig.1 The thiol, Au and Pt and substituted 1,2-di(cyclopenta-1,3-dienyl)ethyne molecules

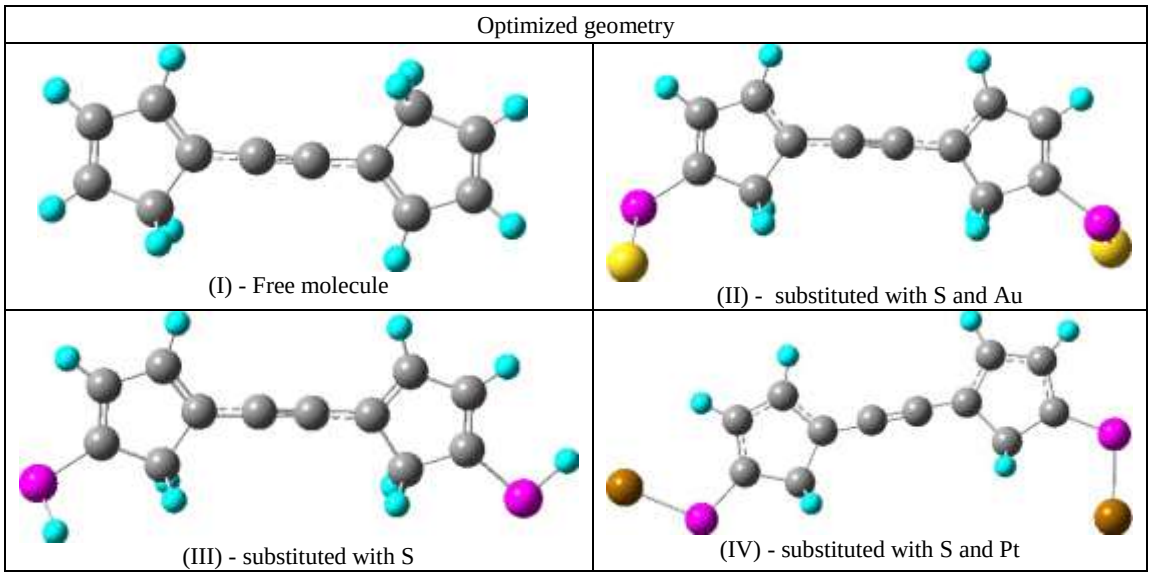


Fig 2. Optimized geometry of 1,2-di(cyclopenta-1,3-dienyl)ethyne [molecule-I(free molecule), molecule-II(substituted with S), molecule-III (substituted with S and Au) and (molecule-IV (substituted with S and Pt)

Table 1. Selected bond lengths (Å) of the 1,2-di(cyclopenta-1,3-dienyl)ethyne molecules [(I–free molecule), (II– substituted with S), (III– substituted with S and Au) and (IV– substituted with S and Pt)]

Bonds	I	II	III	IV	Bonds	I	II	III	IV
Carbon Bonds					Carbon Bonds				
C(1)−C(2)	1.349	1.354	1.381	1.423	C(11)−C(12)	1.456	1.508	1.516	1.524
C(2)−C(3)	1.456	1.452	1.451	1.402	Hydrogen Bonds				
C(3)−C(4)	1.364	1.365	1.389	1.432	C(2)−H(2)	1.082	1.082	1.084	1.083
C(4)−C(5)	1.518	1.520	1.527	1.529	C(3)−H(3)	1.082	1.082	1.084	1.084
C(4)−C(6)	1.403	1.401	1.405	1.364	C(10)−H(10)	1.081	1.082	1.084	1.083
C(5)−C(1)	1.502	1.508	1.516	1.515	Terminal bonds				
C(6)−C(7)	1.216	1.217	1.236	1.257	S(1)−C(1)	—	1.768	1.795	1.737
C(7)−C(8)	1.403	1.400	1.405	1.364	S(2)−C(11)	—	1.763	1.795	1.737
C(8)−C(9)	1.518	1.364	1.389	1.432	Au(1)−S(1)	—	—	2.422	—
C(8)−C(12)	1.364	1.520	1.527	1.530	Au(2)−S(2)	—	—	2.422	—
C(9)−C(10)	1.502	1.451	1.451	1.401	Pt(1)−S(1)	—	—	—	2.259
C(10)−C(11)	1.349	1.355	1.381	1.421	Pt(2)−S(2)	—	—	—	2.260

Table 2. MPA atomic charges (e) of the molecules

Atoms	I	II	III	IV	Atoms	I	II	III	IV
C(1)	-0.139	-0.283	-0.152	-0.131	C(10)	-0.139	-0.040	-0.200	-0.112
C(2)	-0.065	-0.029	-0.195	-0.202	C(11)	-0.065	-0.250	-0.150	-0.145
C(3)	-0.028	-0.008	-0.403	-0.372	C(12)	-0.028	-0.100	-0.510	-0.522
C(4)	-0.314	-0.336	0.346	0.342	S(1)	—	0.038	0.083	0.148
C(5)	-0.125	-0.073	-0.513	-0.477	S(2)	—	0.057	0.083	0.135
C(6)	0.108	0.118	-0.105	-0.107	Au(1)	—	—	-0.090	—
C(7)	0.108	0.117	-0.105	-0.115	Au(2)	—	—	-0.090	—
C(8)	-0.314	-0.350	0.346	0.333	Pt(1)	—	—	—	-0.277
C(9)	-0.125	0.003	-0.403	-0.385	Pt(2)	—	—	—	-0.261

Table 3. NPA Atomic charges (e) of the molecules

Atoms	**I**	**II**	**III**	**IV**	**Atoms**	**I**	**II**	**III**	**IV**
C(1)	-0.164	-0.137	-0.145	-0.139	C(10)	-0.164	-0.267	-0.203	-0.211
C(2)	-0.224	-0.236	-0.203	-0.222	C(11)	-0.224	-0.123	-0.145	-0.147
C(3)	-0.174	-0.168	-0.174	-0.143	C(12)	-0.174	-0.427	-0.469	-0.468
C(4)	-0.088	-0.086	-0.055	-0.052	S(1)	—	0.035	-0.117	0.152
C(5)	-0.428	-0.430	-0.469	-0.475	S(2)	—	0.062	-0.117	0.145
C(6)	-0.007	-0.01	-0.005	0.012	Au(1)	—	—	0.170	—
C(7)	-0.007	-0.004	-0.005	0.006	Au(2)	—	—	0.170	—
C(8)	-0.088	-0.098	-0.055	-0.050	Pt(1)	—	—	—	-0.169
C(9)	-0.428	-0.155	-0.174	-0.141	Pt(2)	—	—	—	-0.158

From the analysis of bond length, it is found that Au electrodes lengthen the S-C bonds and hence it is weakened, whereas Pt electrodes shorten the S-C bonds and hence it is strengthened. Fig. 3 shows the variation of bond lengths of the molecules substituted with S, Au and Pt with reference to the free molecule. Table 1 shows bond lengths (Å) of the free molecule and the molecules substituted with S, Au and Pt.

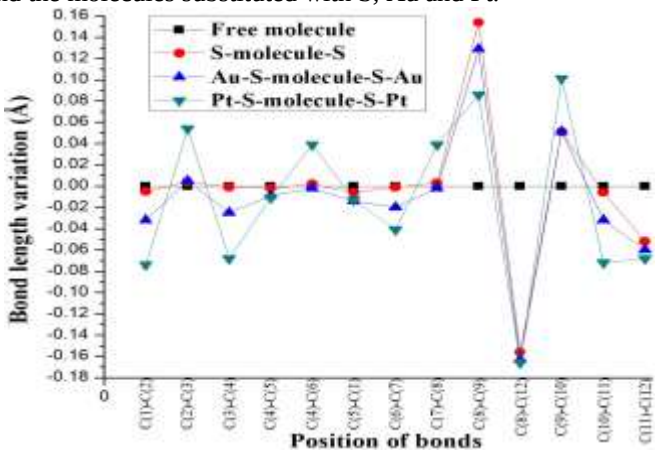


Fig. 3 Variation of bond lengths of the molecules substituted with S, Au and Pt with reference to the free molecule.

Atomic charges

Atomic charges and charge transfer are often used concept in chemical reasoning about molecular behavior and reactivity. As a result, atomic charges continue to play significant role in quantum chemistry. Hence, much research continues to being done to enhance the concept of an atomic charge. The description of atomic populations was initiated by Mullikan [19], many alternative definitions of atomic charges and populations have been presented to refine the preceding statements [20]. Recently, several researchers reported the atomic charges by Mullikan population analysis (MPA) and natural population analysis (NPA) methods [17,18]. In the present work, the atomic charges the free molecule, S, Au and Pt substituted molecules have been estimated from MPA as well as NPA methods.

Further, both MPA and NPA models predict almost negative charge for all C-atoms in all the molecules (I, II, III and IV). The MPA charges of all C-atoms for all the four kinds of molecules vary from -0.008 to 0.346e. The MPA charges of linker atoms on either ends [S(1) and S(2)] are unequal for molecule-II (0.038 & 0.057e) and molecule-IV (0.148 to 0.135 e), whereas, the same for molecule-III (0.083e). The charges of Au atom at both ends of the molecule-III are equal (-0.093e), whereas the charges of Pt atom at both ends of the molecule- IV are unequal (-0.277 & -0.261 e). The MPA charges for all the four kinds of molecules are presented in Table 2. The variations of MPA for the molecules-II, III and IV with reference to molecule-I are plotted as in Fig. 4.

The NPA charges of all C-atoms for all the four kinds of molecules vary from -0.005 to -0.475e. The linker atoms [S(1) and S(2)] on either ends possess slightly different NPA charges for molecule-II (0.035 and 0.062 e) and molecule-IV (0.152 and 0.145 e). However, the atoms [S(1) and S(2)] of molecule–III posses same (-0.117 e) NPA charges. The NPA charges of Au atom at both ends of the molecule-III are equal (0.170 e), whereas, the charges of Pt atom at both ends of the molecule-IV are unequal (-0.169 and -0.158 e).

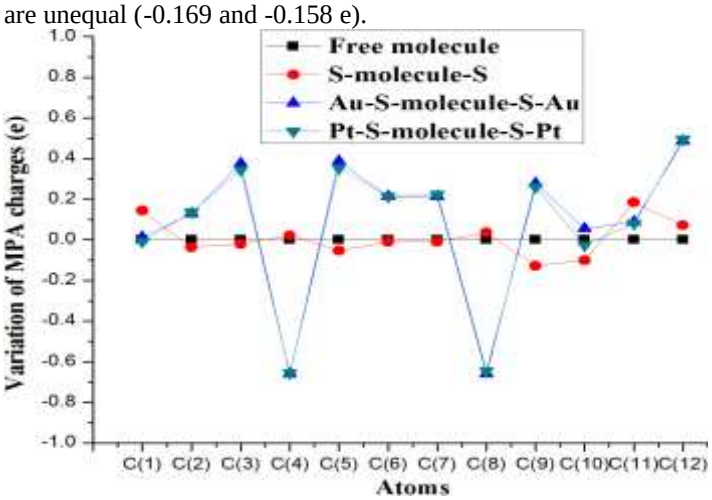


Fig. 4 Variation of MPA charges of the molecules- II, III and IVth with reference to molecule -I

The difference of NPA charge distribution for all the molecules are listed in Table 3. The variations of NPA charges for the molecules-II, III and IV with reference to molecule-I are

plotted as in Fig. 5. From the overall analysis of MPA and NPA charges, it is found that, linker thiol atoms and Au atoms at both end of the molecule-III posses same charges.

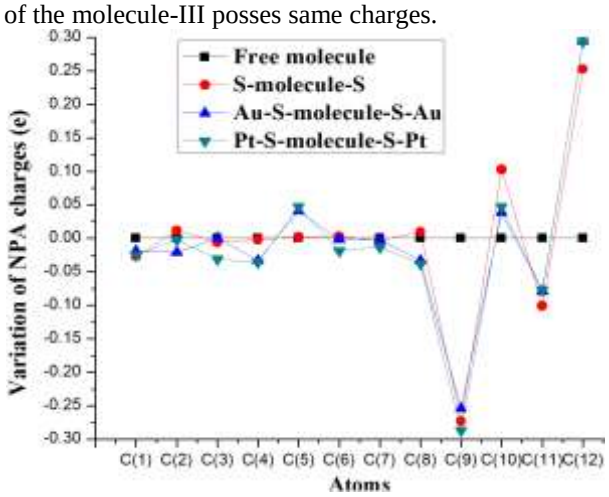


Fig. 5 Variation of NPA charges of the molecules-II, III and IV with reference to Molecule-I.

Molecular orbital analysis

Atomic orbitals are the quantum states of the individual electrons forming the electron cloud and moving around an atom. The combination of atomic orbitals or wave interaction of atomic orbitals forms molecular orbitals. The interaction between two atomic or molecular orbitals will form two new orbitals. One new orbital is antibonding orbital which has the higher energy than the original molecule orbital. The other new orbital is the bonding orbital which is lower in energy than the initial one [21]. The stabilization of the bonding molecular orbital and destabilization of the anti-bonding can increase when the overlap of two orbitals increases. In the molecular interaction, there are the two important orbitals that interact with each other. One is the highest energy occupied molecular orbital known as HOMO and the other one is the lowest energy unoccupied molecular orbital known as LUMO [21, 22]. The electrical conductivity of a molecule depends on the difference in energy between HOMO and LUMO known as HOMO-LUMO Gap (HLG). Hence, the variations in HLG of the free molecule and all the substituted molecules have been determined from quantum chemical calculations. The HLG of the free molecule is 3.51 eV; however, it gradually decreases for S substituted molecule (3.16 eV), Au substituted molecule 1.71 eV and Pt substituted molecule (1.22 eV). Fig. 6 illustrates the energy levels of the molecule for free molecule and various substituted molecules.

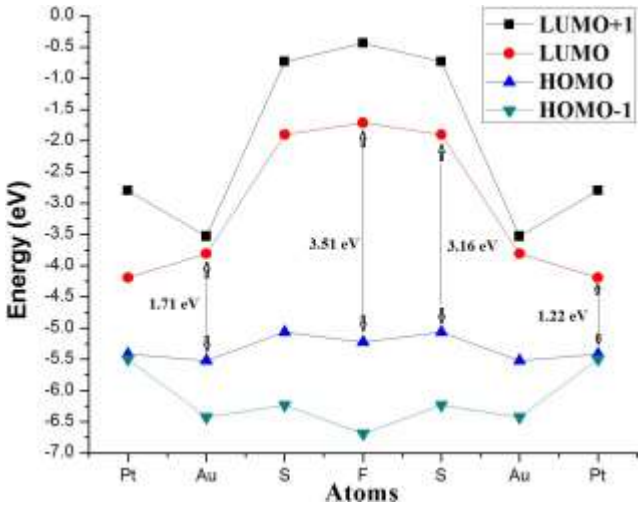
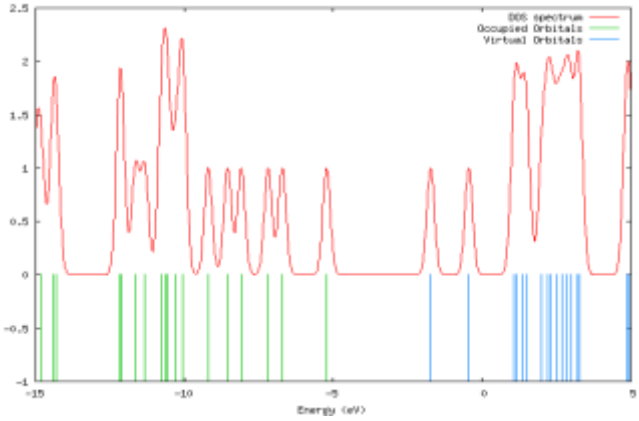
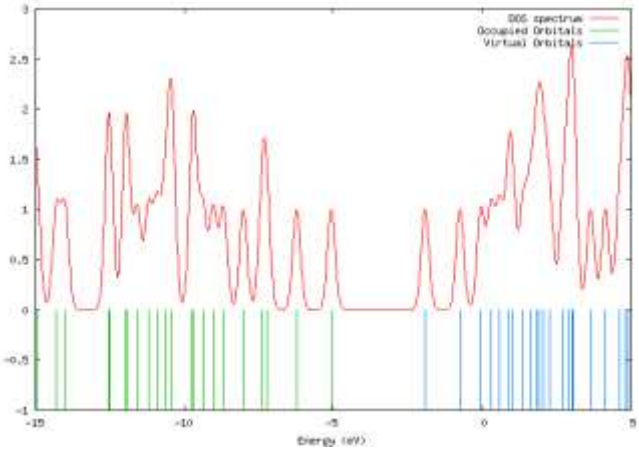


Fig. 6 Energy level diagram of Au and S and Pt substituted 1,2-di(cyclopenta-1,3- dienyl)ethyne molecules.

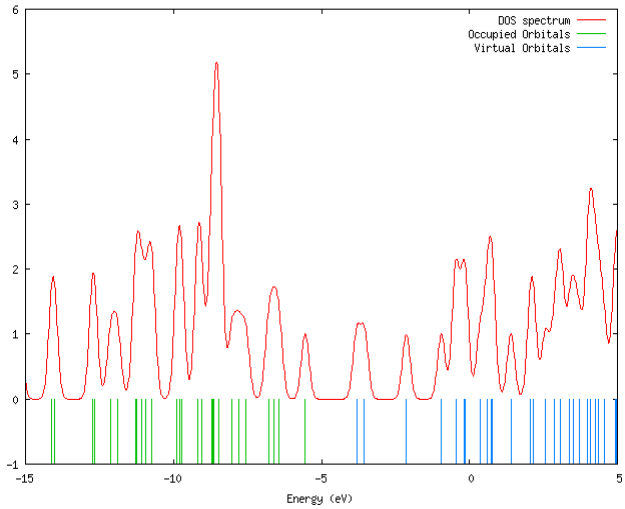
The density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level [23]. Fig. 7 shows the density of states DOS spectrum for the molecules-I, II, III and IV, in which the green lines indicate the HOMO and the blue is LUMO. From the DOS spectrum, it is found that the HLG gradually decreases for the molecules substituted with S, Au and Pt. The large decrease of HLG of the Au as well as Pt substituted molecule facilitates large electron conduction through the molecule 1,2-di(cyclopenta-1,3-dienyl)ethyne molecule.



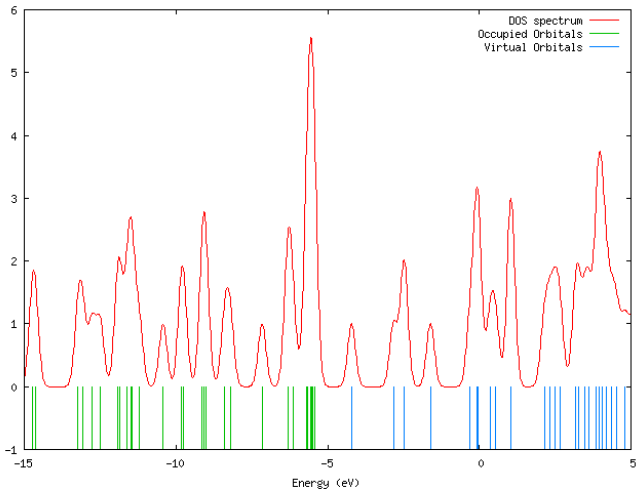
molecule-I



molecule-II



molecule-III



molecule-IV

Fig. 7 Shows the density of states (DOS) for the molecules- I, II, III and IV.

Conclusion

The present computational study describes the geometrical and electrostatic properties, and molecular orbital analysis of 1,2-di(cyclopenta-1,3-dienyl)ethyne molecular nanowire. The effect of Au and Pt metal electrodes using thiol as linker in the molecule and the corresponding transport properties have been studied and the bond lengths of S-C, Au-S and Pt-S bonds determined from this study are almost matched with the reported experimental and theoretical results. The structural confirmation, analysis of MPA and NPA atomic charges and the electrostatic properties of the molecule allow to understand the molecule at electronic level. The small HLG for the molecule-III (Au electrodes) facilitates large electron conduction through the molecule. The molecule-IV (Pt electrodes) has very small HLG, it can also acts as good conductor. But, Au metal electrodes are user friendly on comparing with Pt electrodes. Hence, the Au substituted 1,2-di(cyclopenta-1,3-dienyl)ethyne molecule using thiol as linker can act as an efficient molecular nanowire.

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