Atomic Charges and Molecular Orbital Analysis of Naphthalene Under External Electric Field

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KEYWORDS : Atomic charges, Metal electrodes, Density of states, Quantum chemical calculations

*** Dr. K. Selvaraju** HOD of Physics, Kandaswami Kandar's College, Velur-638182, Tamil nadu, India.
* Corresponding Author

Mrs. B. Jothi Assistant Prof. of Physics, Kandaswami Kandar's College, Velur-638182, Tamil nadu, India

ABSTRACT

The effect of Au metal electrodes on the Naphthalene molecule under external electric field and the corresponding electrostatic properties have been studied by analyzing the geometrical parameters as well as MPA and NPA atomic charges. All the quantum chemical calculations have been carried out with density functional theory (DFT) coupled with Bader's AIM theory under various applied EFs using Gaussian09 program package. As the field increases, the observed structural variations are small; however, in most cases it is found to be systematic and almost uniform. When the field increases from 0.00 to 0.15 $VÅ^{-1}$ the hybridization of molecular levels broadens the DOS and decreases the HLG from 2.45 to 1.98 eV. Overall, the terminal groups of the Naphthalene are found to be very sensitive to applied field in comparison with those molecular regions.

1.Introduction

Theoretical chemistry is the assessment of the structural and dynamic properties of molecules and molecular materials using the stuff of quantum chemistry [1]. Nowadays numerous quantum chemical calculations on structural and electrostatic properties of organic molecules have been carried out and reported [2,3]. Generally, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of conjugated molecules being smaller (~2.0 eV), which posses charge transfer ability [4]. Naphthalene is a simplest polycyclic aromatic hydrocarbon with a structure of a fused pair of benzene rings. The present study reports the effect of applied electric field on Au and thiol substituted Naphthalene (Fig.1) in which, Au atoms act as metal electrodes and thiol atoms act as linker between the molecule and electrodes. Further, this study provides the variation in atomic charges and energy levels of the molecule under the application of various levels of external electric field.

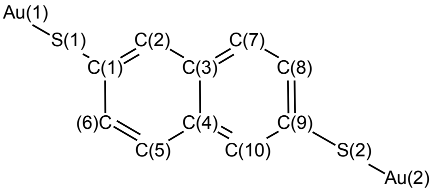


Fig. 1 Au and thiol substituted Naphthalene molecule

2. Computational details

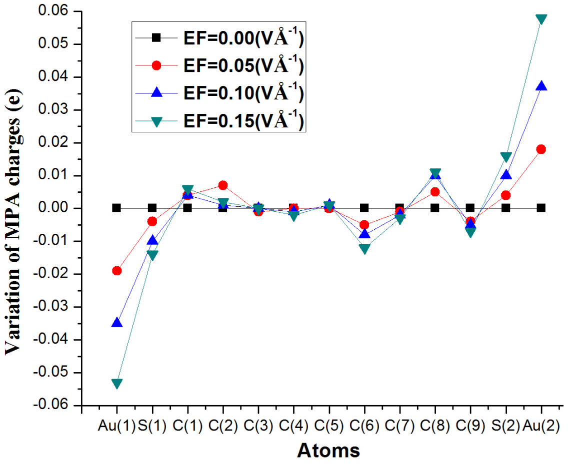
The Au and thiol substituted Naphthalene molecule has been optimized for the zero and applied field of three biasing steps (0.05, 0.10, and 0.15 $VÅ^{-1}$) by Density Functional Theory (DFT) method using Gaussian09 program package [5-7]. A combination of Becke's three parameters exchange function and Lee, Yang and Parr gradient-corrected correlation function (B3LYP hybrid function) is applied for whole DFT calculation along with LANL2DZ (Los Alamos National Laboratory of Double Zeta) basis set, which provide effective core potential and the detailed description of the effect of heavy metal atoms in the molecule [8,9]. The GaussSum program has been used to determine the density of states spectrum (DOS) at various levels of applied EFs [10]. The variation of atomic charges of the molecule has been plotted by using Origin software.

3. Results and Discussion

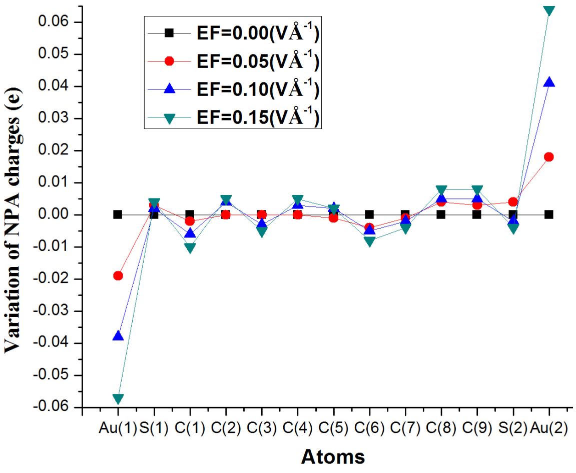
3.1 Atomic charges

Atomic charges for a given compound can be derived in multiple ways with a high level of convergence to the same values and only then, knowing the remaining uncertainty, are suited for molecular simulations. Mulliken charges arise from the Mulliken population analysis [11,121 and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry. Generally, Mulliken population analysis (MPA) and Natural population analysis (NPA) methods are used to calculate the atomic charges of atoms in molecules. The MPA charges of all C-atoms for zero fields vary from -0.394e to 0.382e. When the applied field increases, the maximum observed variation is 0.012e. The linker atoms on either ends [S(1) and S(2)] possess same MPA charge (~0.087e) for zero field, as the field increases this value increases to 0.101e for S(1), whereas the charge of S(2) decreases to 0.072e. For the zero field, the charge of Au atom at either ends are equal (~ 0.046). As the field increases, the charge of Au atom in the L-end varies to 0.007e, whereas, for the Au present at the R-end, the charge varies to -0.105e. The maximum observed variation of MPA charges of Au (1) and Au (2) atoms are 0.053 and 0.058e respectively. The MPA charges for the zero and various applied EFs of the molecule are presented in Table 1. The variations of MPA charges for various EFs with reference to zero field are plotted as in Fig. 2(a)

For the zero field, the NPA charge for all C-atoms are found negative; the charges vary with the increase of field. The NPA charges of linker S(1) atom increases from -0.149e to -0.153e whereas, the charge of S(2) atom decreases from -0.146e to -0.142e for various applied EFs. For the applied field, the charge of Au-atom at the L-end increases from 0.207 to 0.283e, while at the R-end, the charge decreases from 0.246 to 0.164e. On the whole, large variation of charges in the terminal atoms have been observed for various applied EFs. The difference of NPA charge distribution for zero and various applied EFs are listed in Table 1. The variations of NPA charges for various EFs with reference to zero field are plotted as in Fig. 2(b)



(a)



(b)

Fig. 2 Variation of (a) MPA charges and (b) NPA charges of the molecule for various applied EFs with reference to zero field.

Table 1 Selected MPA and NPA atomic charges (e) of the molecule for various applied EFs ($V\text{Å}^{-1}$).

		MPA				NPA		
Atoms		Applied electric field				Applied electric field		
	0.00	0.05	0.10	0.15	0.00	0.05	0.10	0.15
C(1)	0.226	0.222	-0.230	-0.232	0.154	0.156	-0.148	-0.144
C(2)	0.370	0.363	-0.364	-0.365	-0.183	-0.183	-0.187	-0.188
C(3)	0.380	0.381	0.380	0.380	-0.047	-0.047	-0.044	-0.042
C(4)	0.380	0.380	0.381	0.382	-0.045	-0.045	-0.048	-0.050
C(5)	-0.392	-0.392	-0.393	-0.393	-0.179	-0.178	-0.181	-0.181
C(6)	-0.190	-0.185	-0.182	-0.178	0.209	0.213	-0.204	-0.201
C(7)	-0.394	-0.393	-0.392	-0.391	0.179	0.180	-0.177	-0.175
C(8)	-0.176	-0.181	-0.186	-0.187	0.211	0.207	-0.216	-0.219
C(9)	0.223	0.227	-0.218	-0.216	0.153	0.150	-0.158	-0.161
C(10)	-0.374	-0.368	-0.371	-0.372	-0.186	-0.186	-0.181	-0.179
S(1)	-0.087	0.083	0.097	0.101	-0.149	0.146	-0.151	-0.153
S(2)	-0.088	0.088	0.078	0.072	-0.146	-0.150	-0.144	-0.142
Au(1)	0.046	0.065	-0.011	0.007	0.207	0.226	0.264	0.283
Au(2)	0.047	0.029	-0.084	-0.105	0.246	0.228	0.187	0.164

3.2 Molecular orbital analysis

The charge transport properties of a molecule mainly depends on the HOMO-LUMO gap (HLG), which is the difference of energy between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [13]. Hence, it is necessary to study the variations in molecular orbital energy levels and the corresponding HLG for the applied EFs. For the applied field (0.00 - 0.15 $V\text{Å}^{-1}$) the HLG decreases from 2.45 to 1.98 eV. Fig. 3 illustrates the energy levels of the molecule for various applied EFs.

Fig. 4 [(a)-(b)], shows the density of states (DOS) Spectrum for the zero and various applied fields, in which the green lines indicate the HOMO and the blue is LUMO; Here, the hybridization of the molecular level with that of the gold atom broadens the DOS peaks. At zero field, the DOS peaks are in minima, indicates the discrete molecular level with HLG, 2.45 eV, further increase of field to 0.15 $V\text{Å}^{-1}$, both HOMO and LUMO levels approach each other and their gap decreases to 1.98 eV. The conductivity of the molecule is irrespective of the direction of external EF, since the energy level variations of the molecule are almost symmetric for both positive as well as negative bias. The large decrease of HLG facilitates large electron conduction through the molecule, hence, the Au and thiol substituted Naphthalene molecule can act as a better electrical conductor.

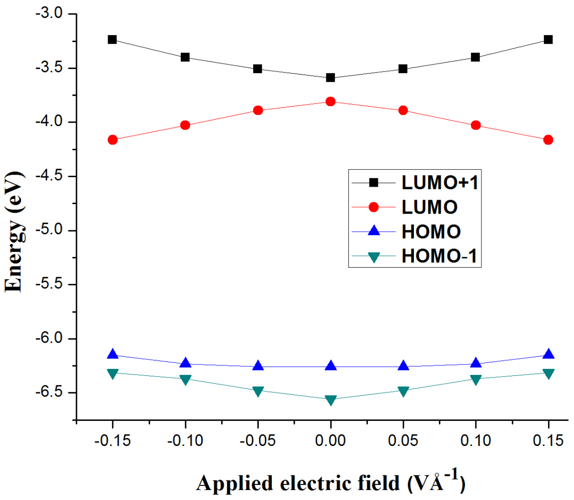
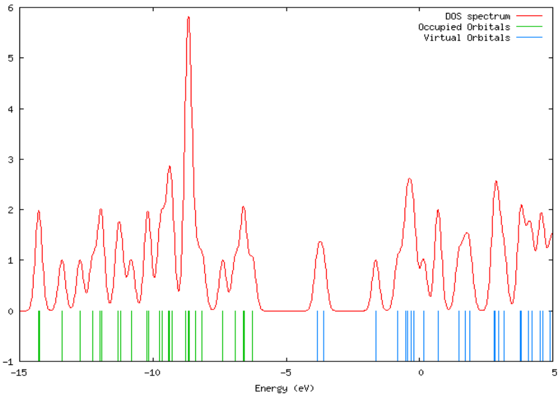
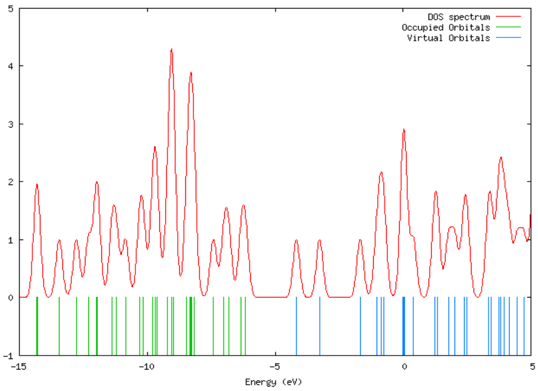


Fig. 3 Energy level diagram of Au and S substituted Naphthalene molecule for the zero and various applied EFs.



4 (a)

Fig. 4 [(a)-(b)] shows the density of states (DOS) spectrum for the zero and maximum applied EF (0.15 $V\text{Å}^{-1}$)



4(b)

4. Conclusion

The present theoretical study on Naphthalene describes the variation in electrostatic and transport properties for zero and various external applied fields. The variation in MPA and NPA charges are small due to the application of EFs; however, in most cases it is found to be systematic and almost uniform. When the field increases from 0.00 to 0.15 V$Å^{-1}$, the hybridization of molecular levels broadens the DOS and decreases the HLG from 2.45 to 1.98 eV; the decrease of band gap at the high field indicates that this molecule exhibit considerable electrical conductivity. On the whole, the linker thiol atoms and terminal Au electrodes of the Naphthalene are found to be very sensitive to applied field. This study may be useful to design new molecules with more electrical conductivity.

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