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Density functional analysis of (E)Penta-1,3-diene under external electric field using gold electrodes

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***Abstract:** A conducting molecular wire, thiol substituted (E)Penta-1,3-diene has been studied under applied electric fields (EFs) ranging from zero to 0.26 VÅ^{-1} using gold electrodes with density functional theory (DFT). Variation in atomic charges of the molecule for various EFs has been compared with MPA and NPA methods. The HOMO-LUMO gap (HLG) of the molecule calculated from quantum chemical calculations have been compared with density of states (DOS) spectrum, which shows that HLG decreases from 2.39 eV to 1.5 eV as the field increases. The increase of applied field increases the dipole moment of the molecule from 0.02 debye to 10.96 debye.*

***Key words:** Atomic charges, HOMO-LUMO, Molecular orbital analysis, Density of states, Electric dipole moment.*

I. INTRODUCTION

The capability to exploit single molecules that function as self-contained electronic devices has encouraged researchers to minimize electronic circuit elements in semiconductor industry [1-3]. Based on computation and modeling, one can propose numerous different mechanisms that take place when electrons transfer through nanoscale molecules which can be act as molecular wires [3]. Generally, a molecular wire refers to a linear chain of π-type molecular structure used to connect two electronic components in molecular electronic devices [3,4]. For electronic transport through molecules, one should familiar with the following key factors: the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), similar to the valence band and the conduction band in solid state materials, respectively, but with discrete energy levels caused by quantization effects in constricted dimension of a molecule. The difference in HOMO and LUMO is known as HOMO-LUMO gap (HLG). The molecules exhibits smaller HLG (~ 2 eV) have more charge transfer ability [5]. Normally, conjugated molecules have smaller HLG with more electrical conductance, hence, act as efficient molecular wires [5,6]. In the present study, the electrical characteristics of (E)Penta-1,3-diene (Fig. 1), a conjugated molecule with HLG 2.39 eV, has been studied under various external electric field with thiol as linker using gold electrodes.

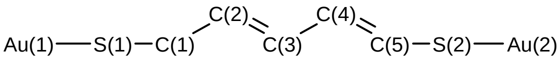


Fig. 1 Au and S substituted (E)penta-1,3-diene molecular nanowire.

II. COMPUTATIONAL DETAILS

The Au and thiol substituted (E)penta-1,3-diene molecule has been optimized for the zero field and applied field of five biasing steps (0.05, 0.10, 0.15, 0.21 and 0.26 $VÅ^{-1}$) by Density Functional Theory (DFT) method using Gaussian09 program package [7-9]. 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 [10]. The GaussSum program has been used to determine the density of states (DOS) at various levels of applied EFs [11]. The variation in bond lengths, variation of atomic charges and variation in energy levels of the molecule for various levels of applied EFs have been plotted by using Origin and *GAUSSVIEW [9]* software.

III. RESULTS AND DISCUSSION

A. Atomic charges

The bonding capability of a molecule depends on the electronic charge on the chelating atoms. Most electronic modeling programs calculate the charges by the Mullikan population analysis (MPA) method [12,13], because it is simple to do so. The natural population analysis (NPA) relies upon the wave function. It is a widely used method to determine the atomic charge distribution and this scheme corresponds to the occupancy of the so-called natural orbitals, which is based on a weighted symmetry orthogonalization procedure [13-15]. Specifically, this method treat the charges located at the atomic sites only and provides better charge distribution. Hence, in the present study, we have calculated the atomic charges by both MPA and NPA methods. Further, both models predict almost negative charge for all C-atoms in the molecule. The MPA charges of all C-atoms for zero field vary from -0.643 to -0.013e. When the applied field increases, The charges of all C-atoms vary with increase of field and the maximum variation observed is 0.103e. However, the charge of H-atoms remains the same (~0.241e) for various fields. The linker atoms on either ends S(1) and S(2) possess slightly different MPA charges for zero field; as the field increases, the charge of S(1) vary between 0.025 and 0.035e whereas, the charge of S(2) increases from 0.061e to 0.072e. For the zero field, the charge of Au atom at either ends are slightly different (-0.052 to - 0.044e). As the field increases, the charge of Au atom in the L-end increases to -0.233e, whereas, the charge of the same Au atom present at the R-end increases to -0.114e. The MPA charges for the zero and various applied EFs of the molecule are presented in Table 1.

For the zero field, the NPA charge for all C-atoms are found negative; further, the charges vary with the increase of field, whereas the charge of H-atoms remains same (~0.223e). The NPA charges of linker S(1) and S(2) atoms vary for various applied EFs, the maximum observed variation of S(1) and S(2) are 0.021e and 0.037e respectively. For the applied field, the charge of Au-atom at the L-end decreases gradually from 0.221 to 0.024e, while at the R-end, the charge increases from 0.220 to 0.396e. On the whole, the linker thiol atoms and terminal Au atoms at both ends show large variation of MPA as well as NPA charges for the various applied EFs (Fig.2 & Fig.3). Hence, it is concluded that thiol and gold atoms are more sensitive than carbon and hydrogen atoms for the applied EFs. The difference of NPA charge distribution for zero and various applied EFs is listed in Table 2.

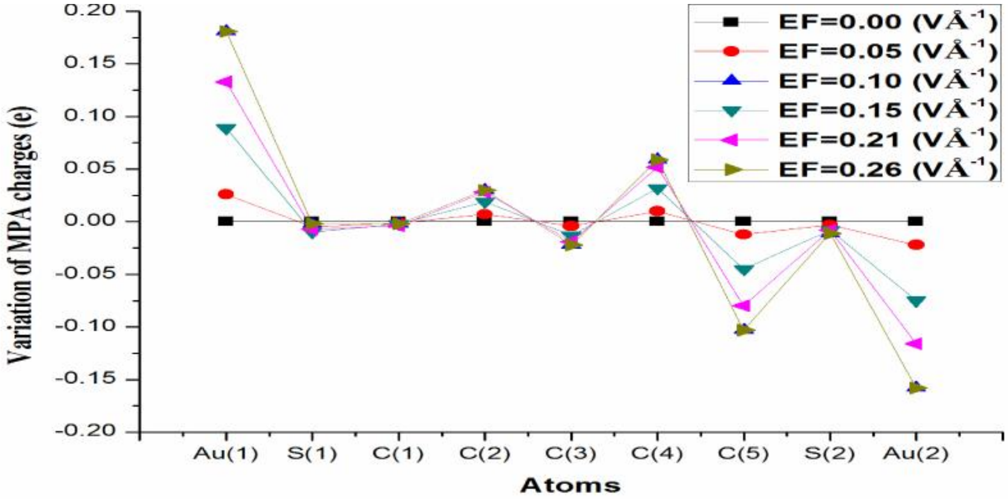


Fig. 2 Variation of MPA charges of the molecule for the zero and various applied EFs.

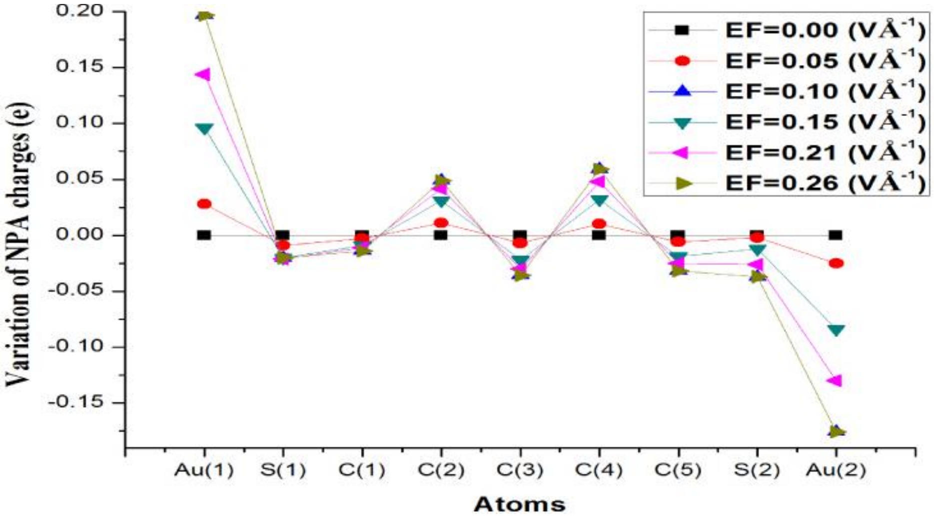


Fig. 3 Variation of NPA charges of the molecule for the zero and various applied EFs.

Table 1 MPA atomic charges (e) of the molecule for various applied EFs (VÅ^{-1}).

	Applied electric field					
Atoms	0.00	0.05	0.10	0.15	0.21	0.26
C(1)	-0.643	-0.642	-0.641	-0.641	-0.639	-0.641
C(2)	-0.123	-0.130	-0.153	-0.142	-0.151	-0.153
C(3)	-0.165	-0.161	-0.143	-0.152	-0.146	-0.143
C(4)	-0.013	-0.023	-0.072	-0.045	-0.065	-0.072
C(5)	-0.506	-0.494	-0.403	-0.461	-0.426	-0.403
H(5)	0.241	0.241	0.242	0.241	0.241	0.242
S(1)	0.025	0.030	0.027	0.035	0.032	0.027
S(2)	0.061	0.064	0.072	0.069	0.069	0.072
Au(1)	-0.052	-0.078	-0.233	-0.141	-0.185	-0.233
Au(2)	-0.044	-0.022	0.114	0.031	0.072	0.114

Table 2 NPA Atomic charges (e) of the molecule for various applied EFs (VÅ^{-1}).

Atoms	Applied electric field					
	0.00	0.05	0.10	0.15	0.21	0.26
C(1)	-0.500	-0.497	-0.486	-0.491	-0.489	-0.486
C(2)	-0.181	-0.192	-0.230	-0.212	-0.223	-0.230
C(3)	-0.210	-0.203	-0.174	-0.188	-0.180	-0.174
C(4)	-0.204	-0.214	-0.263	-0.236	-0.252	-0.263
C(5)	-0.324	-0.318	-0.292	-0.305	-0.299	-0.292
H(5)	0.223	0.223	0.223	0.224	0.223	0.224
S(1)	-0.229	-0.220	-0.209	-0.209	-0.208	-0.209
S(2)	-0.151	-0.149	-0.114	-0.139	-0.125	-0.114
Au(1)	0.221	0.193	0.024	0.125	0.077	0.024
Au(2)	0.220	0.245	0.396	0.304	0.350	0.396

B. Molecular orbital analysis

Atomic orbitals of different atoms combine to create molecular orbitals. Electrons in these molecular orbitals belong to the molecule as whole. When two atomic orbitals are added together, a set of lower energy bonding orbitals as well as a set of higher energy anti-bonding orbitals are created [16,17]. The molecular orbital that is highest in energy that contains electrons is called the highest occupied molecular orbital (HOMO). The molecular orbital that is lowest in energy that does not contain electrons is called the lowest unoccupied molecular orbital (LUMO) [18,19]. The applied EF partially localizes the frontier orbitals (HOMO and LUMO) of the molecules, which are opposite to each other. For the applied field (0.00 - 0.26 VÅ^{-1}), HOMO-LUMO Gap (HLG) decreases from 2.39 to 1.50 eV. Fig. 4 illustrates the various energy levels, HOMO-1, HOMO, LUMO and LUMO+1 of the molecule for various applied EFs, which show the decrease of HLG with the increase of field.

The electronic density of states (DOS) is a key property to analyse the solid state as well as nano scale electronics [20]. To the study of nanoscale structures, the number and density of electronic states is given for arbitrary dimensions [21]. Here, the HLG is determined by plotting DOS spectrum using GaussSum program [11]. Fig. 5 [(a)-(f)], shows the density of states (DOS) of the Au and S substituted (E)penta-1,3-diene for the zero and various applied EFs. Here, the hybridization of the molecular level with that of the electrode broadens the DOS peaks. At zero field, the DOS peaks are in minima, indicates the discrete molecular level with HLG, 2.39 eV, further increase of field to 0.26 VÅ^{-1}, both HOMO (green line) and LUMO (blue line) levels approach each other and their gap decreases to 1.50 eV. The molecule exhibit almost symmetric variations in energy levels for applying reverse EF. Hence, the electrical conductance of the molecule does not depend on the direction of external EFs. The large decrease of HLG at higher applied EF sustain more electron conduction through the molecule, hence, the Au substituted (E)penta-1,3-diene molecule can act as an efficient molecular nanowire.

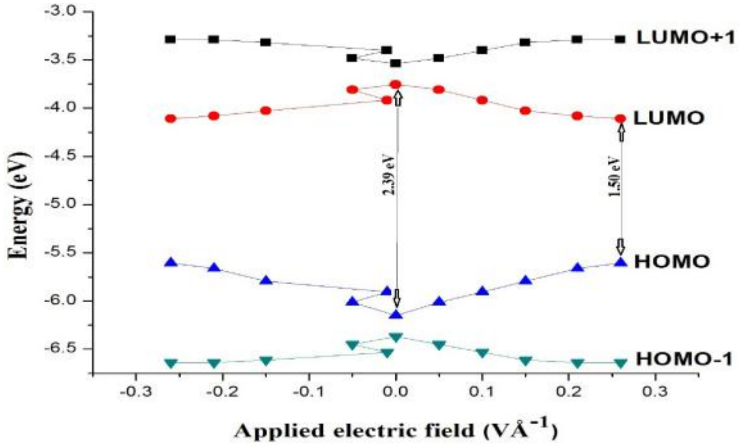


Fig 4. Energy level diagram of Au and S substituted (E)penta-1,3-diene molecule for the zero and various applied EFs.

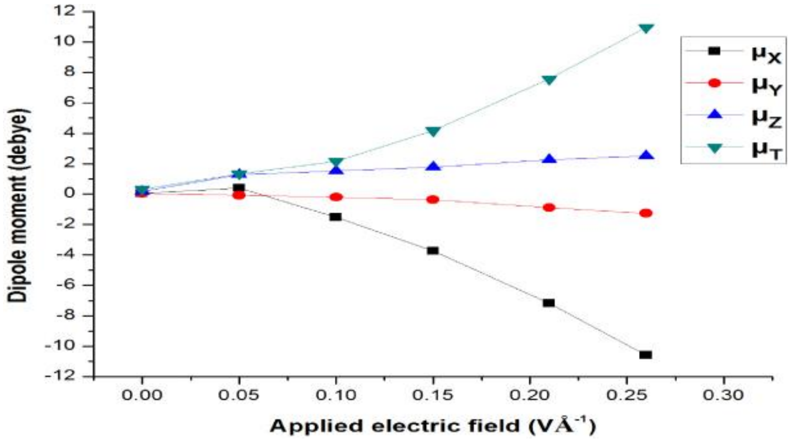
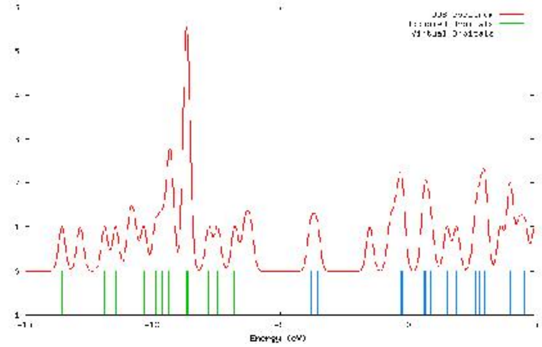
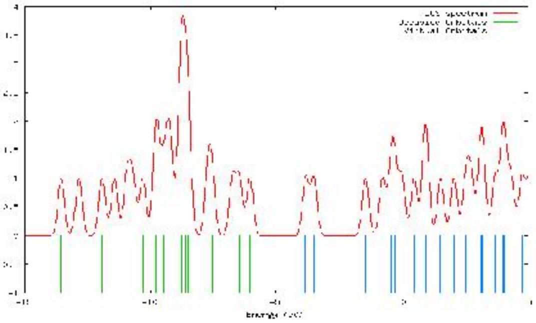


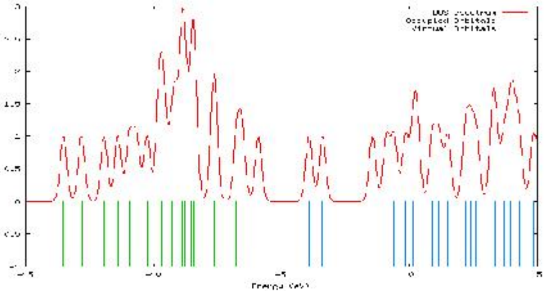
Fig. 6 Molecular dipole moment of Au and S substituted PD molecule for the zero and various applied EFs.



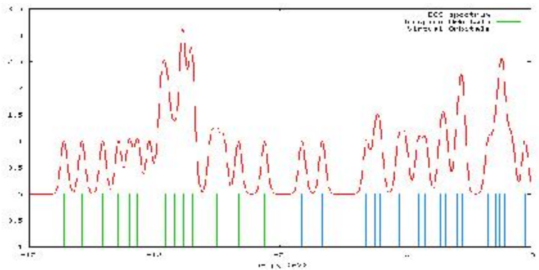
(a) EF=0.00 VÅ^{-1}



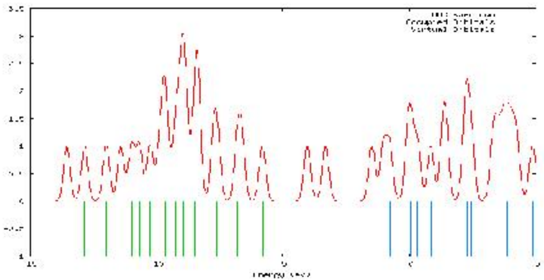
(b) EF=0.05 VÅ^{-1}



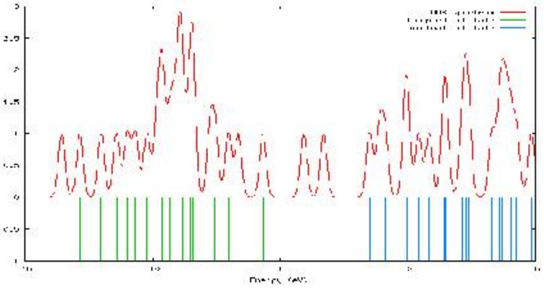
(c) EF=0.10 VÅ^{-1}



(d) EF=0.15 VÅ^{-1}



(e) EF=0.21 VÅ^{-1}



(f) EF=0.26 VÅ^{-1}

Fig. 5 [(a)-(f)] shows the density of states (DOS) of Au and S substituted (E)penta-1,3-diene for the zero and various applied EFs.

C. Molecular dipole moment

Even though the total charge on a molecule is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules. Such molecules are said to be polar because they possess a permanent dipole moment [22,23]. Even if there is no permanent dipole moment, it is possible to induce a dipole moment by the application of an external electric field. When the molecule subjected to external EF, the field polarizes the molecule, which leads to change the dipole moment of the molecule [24,25]. Nowadays, numerous theoretical quantum chemical calculations of dipole moment of the molecules have been reported, which shows that the dipole moment of the molecule increases with the increase of field [25,26]. Here, the dipole moment of the molecule has been calculated for zero as well as various applied EFs. Fig. 6 shows the variation of molecular dipole moment for various applied EFs. The molecular dipole moment for zero bias is 0.02 debye, which increases almost linearly with the increase of field. The molecule becomes highly polarized for the higher field (0.26 VÅ^{-1}); the polarization induces to have high molecular dipole moment 10.96 debye for the increase of field, which are in good agreement with the reported values.

IV. CONCLUSION

The present theoretical study on thiol substituted (E)Penta-1,3-diene molecular wire describes the electrical characteristics for zero and various external applied fields. As the field increases, the variations of atomic charges calculated from MPA and NPA methods are found to be systematic and almost uniform. When the field increases from 0.00 to 0.26 VÅ^{-1}, the hybridization of molecular levels broadens the DOS and decreases the HLG from 2.39 to 1.50 eV. The decrease of band gap at the high field indicates that this molecule exhibit more electrical conductivity. The applied EF polarizes the molecule, in consequence of that the dipole moment of the molecule increases from 0.02 to 10.96 debye. The analysis of MPA and NPA atomic charges and molecular orbital analysis of the molecule allow to understand the molecule at electronic level for zero and various applied EFs.

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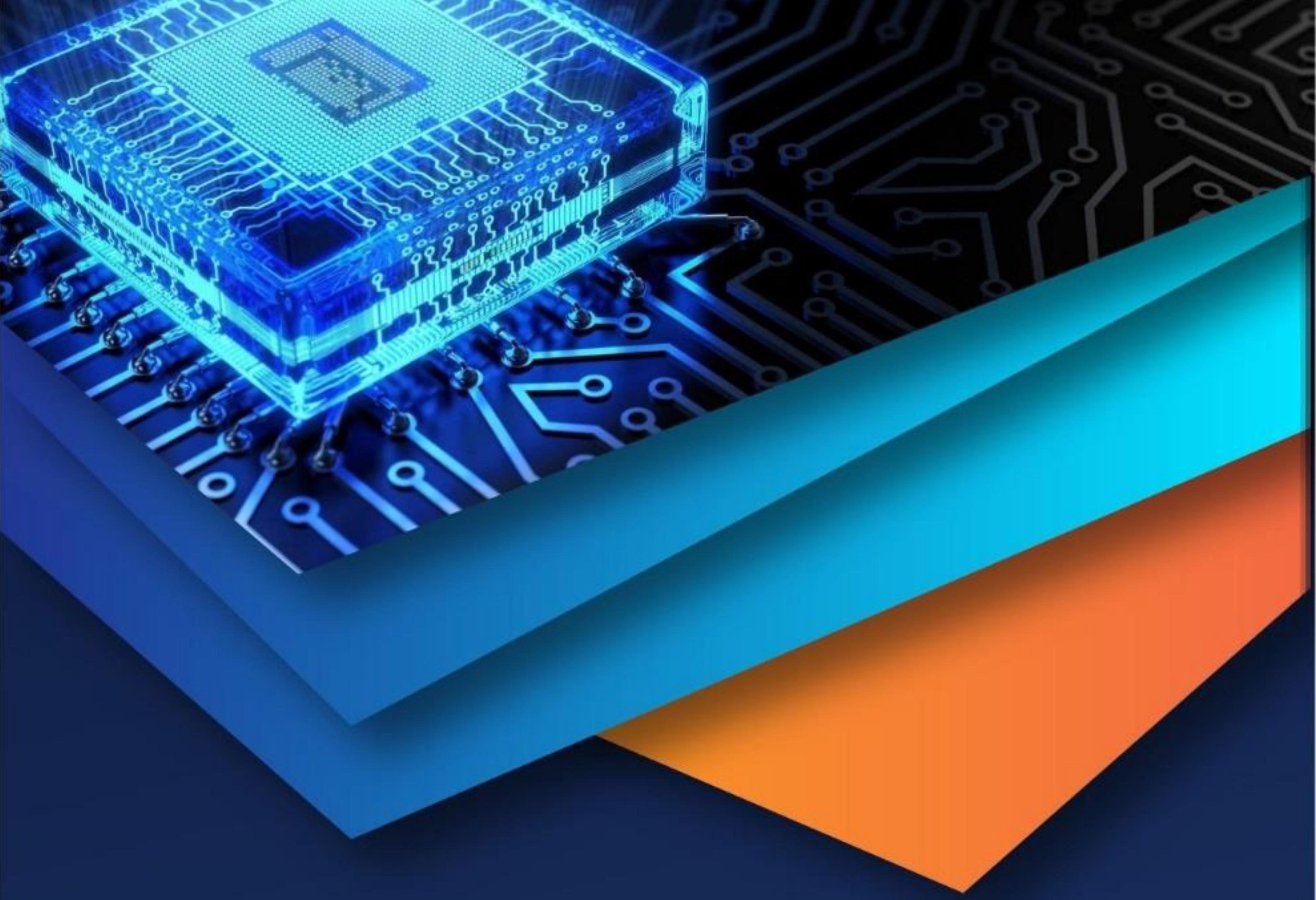

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