

Research Article

Theoretical Investigation of Design Methodology, Optimized Molecular Geometries, and Electronic Properties of Benzene-Based Single Molecular Switch with Metal Nanoelectrodes

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Understanding the electronic properties at the single molecular level is the first step in designing functional electronic devices using individual molecules. This paper proposes a simulation methodology for the design of a single molecular switch. A single molecular switch has two stable states that possess different chemical configurations. The methodology is implemented for 1,4-benzene dithiol (BDT) molecule with gold, silver, platinum, and palladium metal nanoelectrodes. The electronic properties of the designed metal-molecule-metal sandwich structure have been investigated using density functional theory (DFT) and Hartree-Fock (HF) method. It has been perceived that the DFT and HF values are slightly different as HF calculation does not include an electron-electron interaction term. Computation of the switching ratio gives the insight that BDT with gold has a high switching ratio of 0.88 compared with other three metal nanoelectrodes. Further, calculations of quantum chemical descriptors, analysis of the density of states (DOS) spectrum, and frontier molecular orbitals for both the stable states (i.e., ON and OFF state geometries) have been carried out. Exploring the band gap, ionization potential, and potential energy of two stable states reveals that the ON state molecule shows slightly higher conductivity and better stability than the OFF state molecule for every chosen electrode in this work. The proposed methodology for the single molecular switch design suggests an eclectic promise for the application of these new materials in novel single molecular nanodevices.

1. Introduction

Future computational devices will feasibly consist of logic gates that are ultradense, ultrafast, and molecular-sized. Existing computational architectures trade off between computational speed and power [1–3]. To overcome the physical size scalability and fabrication cost of conventional semiconductor devices, molecular electronics has a predominant role. Molecular electronics utilizes electronics application at the molecular level [4]. Potential benefits include dramatically increased computational speed, miniaturization down to the size of atoms and molecules, and lower fabrication costs. Molecular scale electronics has made substantial progress in

recent years and a variety of important theoretical and experimental insights have been investigated, which could have implications for the development of molecular devices instead of traditional complementary metal-oxide-semiconductor (CMOS) devices in the very near future [5–8]. Single-molecule electronics entails the integrated struggle of chemists, physicists, material scientists, and electronics engineers in both theoretical and experimental ways. Molecular electronics or moletronics is the combination of molecules and electronics [9]. It is a multidisciplinary area that spans physics, chemistry, material science, and electronics engineering [10]. This is a revolutionary concept even today when considering the increasing device variability of CMOS technology

and the struggle to control the position and distance of smaller and smaller numbers of atoms in the active regions of devices made using top-down methods. In contrast to silicon where experiments were expedited by the availability of large crystals, the size of an individual molecule cannot be easily scaled up, which means that atomic-sized nanoelectrodes are needed to contact an individual molecule [11–13].

Among the functional devices in molecular electronics on which significant progress has been made in recent years is the molecular switch [14]. Recently, Kim et al. reviewed comprehensive delineations of material-based approaches of the sundry conducting/semiconducting nanocomposites, together with their electrical/mechanical properties and paradigms of device applications [15]. Usually, a molecular switch consists of three major building blocks, namely, left electrode, switching molecule, and right electrode [16–18]. The central molecule or switching molecule can shift between two stable states with two different electrical conductivities. The trigger used to switch between two states can be an electrical current, temperature difference, chemical environment, contact geometry between electrode and molecule, or even a light. These two stable states/geometries are considered as ON/OFF states of the switch [19]. Generally, the state change is reversible. Depending on the type of trigger/stimuli, molecular switches are broadly classified into three: electronic, photochromic, and mechanically interlocked switches. BDT is an excellent example of an electronic molecular switch [17, 20].

Two researchers named Huang and Li more recently reported an intensive analysis of assorted photochromic molecules for their photoswitching molecular junctions with a minimum of two interconvertible molecular states with different absorption spectra on exposure to light [21]. Moreover, the significant promise for building logical devices and memories at the molecular level impends to the successful transformation of various conformational or electronic states of photochromic molecules into electrical switching signals. In 2020, Audi et al. introduced benzo-bis (imidazole)-based molecular switch addressed by chemical stimuli [22]. By virtue of theoretical calculations which ascribe the various behaviors to the position of the HOMO resonances corresponding to the Fermi energy of the electrodes, a multiscale characterization of the electron transport across the molecular junction upon protonation demonstrated that their conductance switching relies on the lateral functional groups in such molecular switches. More recently, Han et al. reported molecular diode and variable resistor supported the choice of molecular backbone within the device geometry, leading to a molecular-scale 1D–1R RRAM with a current rectification ratio, resistive on/off ratio, and a low drive voltage of 2.5×10^4 , 6.7×10^3 , and 0.89 V, respectively [23]. The switching depends on the dimerization of redox units, following in hybridization of molecular orbitals ushered by directional ion migration. A group of molecular devices where multiple electronic functions are preprogrammed inside one molecular crystal layer with a thickness of only 2 nm authorizes this electric-field-driven molecular switches operating in the tunneling mechanism.

The preferred materials for electrodes are metal and non-metal electrodes. Once the core of a switching molecular

structure is geometrically optimized, then it is possible to attach geometrically optimized nanoelectrodes at both ends and the geometrically optimized stable combined molecular structure will make a functional molecular switch. Recently, Karimi-Maleh et al. synthesized nanohybrid composites using platinum nanoparticle nanosheets as a high conductive mediator [24]. Also, in another recent article, Karimi-Maleh et al. synthesized and described the detailed DFT investigation of the magnetite/graphene oxide nanocomposite. It was used for the removal of phenazopyridine residues from water samples as a high-efficiency adsorbent [25]. Similarly, Orooji et al. have fabricated silver iodide/graphitic carbon nitride (AgI/g-C₃N₄) nanocomposites in their recent research article. The as-prepared AgI/g-C₃N₄ nanocomposites possessed higher photocatalytic activity than the pure AgI and g-C₃N₄. The band gap of the nanocomposite was determined, and it was noticed that it can vary with increasing the quantity of silver iodide in the nanocomposites. Also, the photocatalytic activity of AgI/C₃N₄ has been studied due to their suitable band gap [26]. More recently, Orooji et al. synthesized and reported the photocatalytic study of GZMO NCs. Magnetic, optical, and photocatalytic behaviors of nanocomposites were investigated experimentally [27]. Recently Rad et al. reported the effectiveness of 2D nanostructure in an aquatic phase. Two trimetal layered double hydroxides (LDHs) are evaluated and compared for the sonophotocatalytic degradation of AB113 in an aquatic phase [28]. Although among other molecular devices molecular switch is a simple device, a suitable selection of a molecular switch could be the basis for complicated molecular machines [29]. For the development of molecular electronic applications, the control over the metal-molecule junction is very vital [30–32].

Once the agreement between the computational calculations and experimental results is strikingly good, then that metal-molecule-metal sandwich structure is suitable for functional molecular switch device. The interest in molecular electronics can be discovered back in 1971, but molecular electronics is a vibrant and dynamic area of science and technology, and numerous challenges and opportunities lie ahead [33]. Inexpensive, functional, and atomically explicit molecules could be the basis of future electronic computing devices; but integrating them into circuits will require the development of new ways to control the interface between molecules and nanoelectrodes [34].

Motivated by these ideas, this paper proposes a simulation methodology for the design of a single molecular switch. This molecular structure possessed two stable states, i.e., ON and OFF state geometries for the electric current conduction (bistable molecular electronic switch). This research work is aimed at accomplishing the design and analysis of benzene dithiol- (BDT-) based molecular switch with gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) nanoelectrodes separately using the proposed comparative computational approach. Both the geometrically optimized stable states of molecular structures have been investigated using density functional theory (DFT) and Hartree-Fock (HF) method with the same basis set. Also, frontier molecular orbitals and density of states (DOS) spectrums were analyzed.

Evaluation of switching ratio, quantum chemical descriptors, and potential energy extends great insight into the switching characteristics of the BDT molecule with the right choice of electrode and anchoring group in the design procedure.

2. Materials and Methods

In this paper, the first principle study of metal-molecule-metal sandwich structure for both ON/OFF states of benzene dithiol molecule is investigated using Gaussian 09 software [35] with BPV86 (Becke Perdew 1983 functional modified by Vosko) type exchange-correlation functional and the popular SDD (Stuttgart/Dresden) basis set. The frontier molecular orbital analysis of benzene dithiol (BDT) molecule with four different metal nanoelectrodes (Au, Ag, Pt, and Pd) has been done using density functional theory (DFT) and Hartree-Fock (HF) study. GaussSum [36], a Gaussian user interface (GUI) software, is used to draw the density of states (DOS) spectrum of designed molecular switches.

Polyphenylene-based organic molecules are the significant molecular backbones in moletronics, since it has conjugated π -type (i.e., “ π ”-type) molecular orbitals that enable conductivity in a polyphenylene-based wire. The molecular wires, diodes, switches, transistors, rectifiers, and sensors can be designed using polyphenylene-based chains of organic aromatic benzene rings [37]. Recent research papers have been showing experimentally the conductivity of polyphenylene-based single molecules [38]. Benzene dithiol (BDT) is one of the smallest principal molecules in single-molecule electronics since it forms the fundamental building block for aromatic and conjugated systems. There are experimental papers to prove this star compound will conduct current [39, 40]. BDT may come in different connectivity sites of the thiol group with a benzene ring and a variety of lengths [41]. It has very well-defined chemistry and great synthetic flexibility. BDT is an aromatic, conjugated organosulfur compound consists of a single benzene ring attached to two thiol (-SH) groups at both sites by losing a hydrogen atom on both. Its formula is $C_6H_6S_2$. Electrode material connects the switching molecule to the outside world. It is an essential component in the metal-molecule-metal sandwich structure. Tunneling of electrons happens across the left and right nanoelectrodes of the switching molecule via the anchoring group [42]. The possible options for the design of an efficient single molecular switch lie in the selection of electrode material. Electrodes are broadly classified into two, metal and nonmetal. Nonmetal is again classified into carbon and non-carbon based [43, 44].

3. Results and Discussion

3.1. Design Methodology of Single Molecular Switch. A flowchart depicting the general simulation methodology for designing and analyzing the selected molecule and electrode combination as a single molecular switch is shown in Figure 1. Using the above simulation methodology, it is easy to identify whether the selected molecule and electrode combination works as a single molecular switch and it can be functionally suitable for the replacement of semiconductor

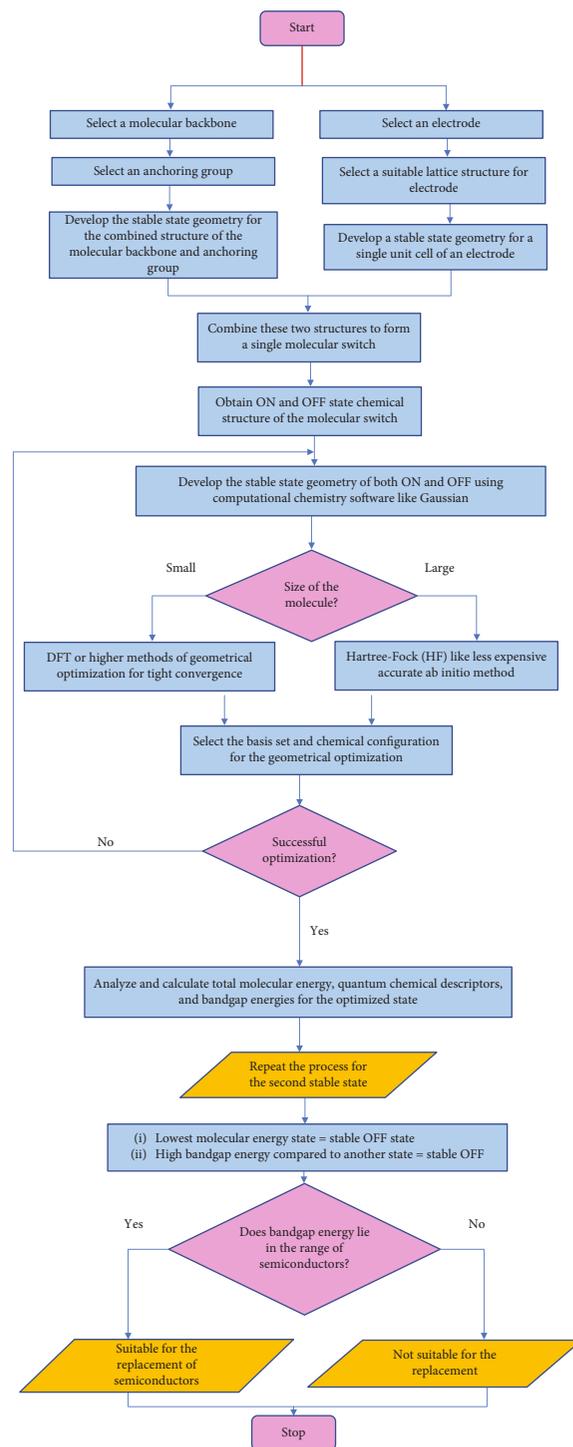


FIGURE 1: Flowchart of the design of a single molecular switch.

switches. Design and modeling of a molecular switch using gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) electrodes attached to a benzene ring as the central molecular part and thiol (-SH) as the clip alligator or anchoring group have been investigated in this work. The simulation methodology used here explores the chemical configuration of both ON and OFF states of a single molecular switch with nanoelectrodes. The elementary steps in a simulation are

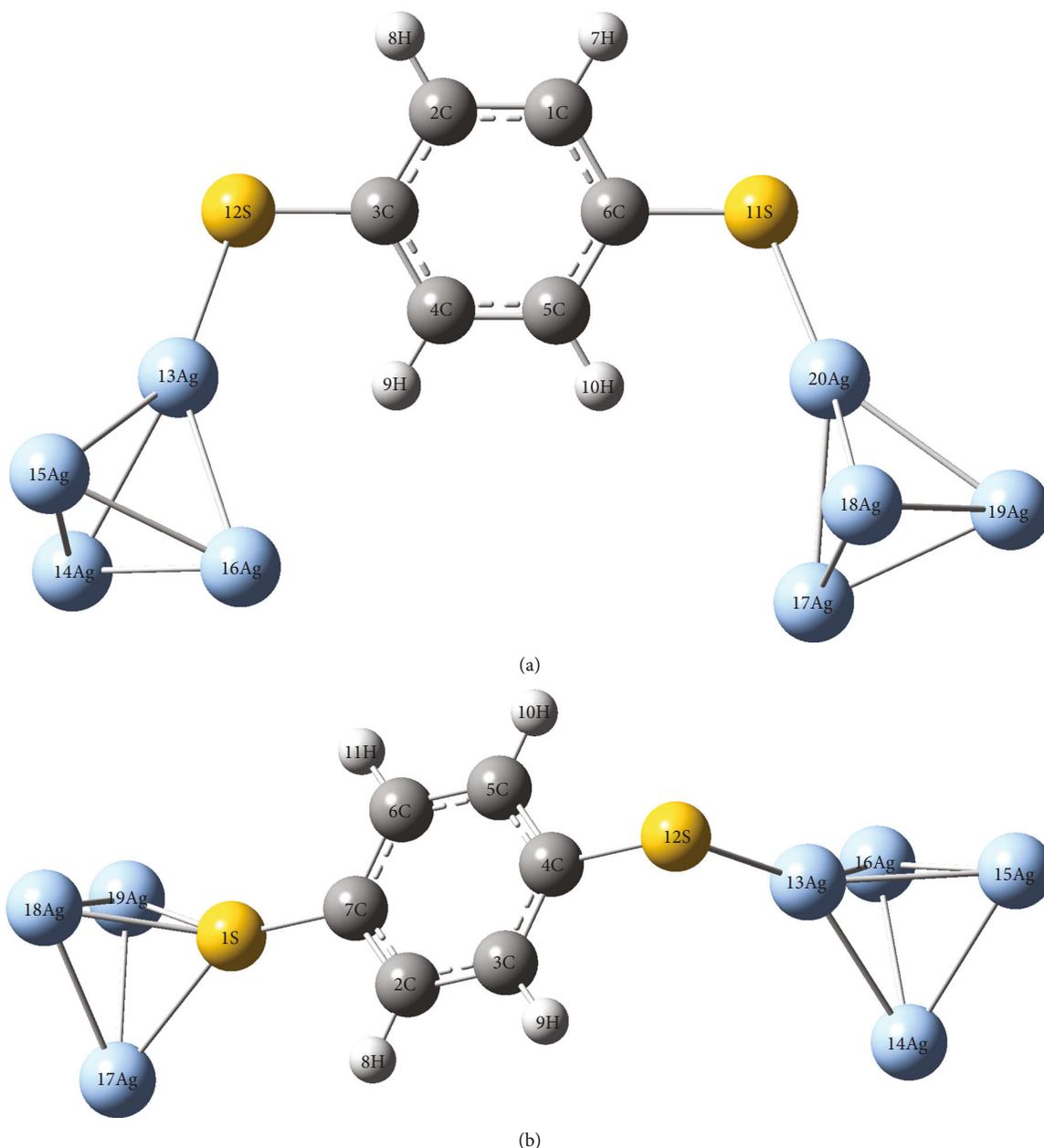


FIGURE 2: Optimized electronic structure of (a) Ag-BDT-Ag OFF state and (b) Ag-BDT-Ag ON state molecules using the DFT method.

the selection of molecular backbone, anchoring group, and electrode. The selection of a lattice structure for the nanoelectrode is very crucial in the design of a nanoelectrode-molecule-nanoelectrode sandwich structure. Because the nature of the electrode has a great dependence on the conductivity of that specific molecular device formed by the metal-molecule-metal sandwich structure [45], then develop a nanoelectrode of a single unit cell. In this work, $\langle 111 \rangle$ lattice structure is selected and a tetrahedral unit cell of Au, Ag, Pt, and Pd is developed. The next step in the simulation is combining the molecular central part with the unit cells of nanoelectrode. This step develops a single molecular switch. Identify two stable states (ON and OFF states) of the chemical configuration of the developed single molecular switch. Computational chemistry software like Gaussian 09 is used

for the geometrical optimization of both the states of the chosen molecular switch. Based on the type of molecular switch, the number of atoms and chemical configuration heterogeneous parameters for molecular structure optimization will be decided. In this work, two methods are used for the investigation: DFT and Hartree-Fock (HF). For larger molecular systems like rotaxane, the HF method is the least expensive accurate ab initio method, while for smaller molecular systems like benzene dithiol with metal nanoelectrodes, DFT or higher method can be used for analysis as it will give more accurate and better result [46]. The basis set for the geometrical optimization has to be chosen in accordance with the method, type, and the number of atoms in the structure. Here, when the optimization for state 1 is successfully completed, the optimized stable geometry is further analyzed

TABLE 1: Optimized geometrical parameters of Ag-BDT-Ag for the OFF state using the DFT and HF methods.

Parameters	Ag-BDT-Ag OFF state		Parameters	DFT	HF
	DFT	HF			
Bond length (Å)			Bond angle (°)		
C1-C2	1.401	1.398	C1-C2-C3	119.99	120.62
C2-C3	1.402	1.391	C2-C3-C4	120.00	119.72
C3-C4	1.401	1.399	C3-C4-C5	119.99	120.99
C4-C5	1.404	1.399	C4-C5-C6	120.05	121.00
C5-C6	1.401	1.402	C5-C6-C1	119.89	120.83
C6-C1	1.403	1.401	C6-C1-C2	120.50	119.54
C3-S12	1.780	1.692	C3-S12-Ag13	109.44	110.81
S12-Ag13	2.350	2.352	S12-Ag13-Ag16	145.62	144.81
Ag13-Ag14	2.725	2.723	Ag13-Ag14-Ag15	60.73	60.32
Ag13-Ag15	2.725	2.719	Ag13-Ag15-Ag16	60.72	60.71
Ag13-Ag16	2.725	2.721	Ag13-Ag16-Ag14	60.73	60.05
Ag14-Ag15	2.665	2.662	C6-S11-Ag20	109.49	106.32
Ag14-Ag16	2.664	2.670	S11-Ag20-Ag18	145.63	146.67
Ag15-Ag16	2.664	2.669	Ag20-Ag17-Ag18	60.74	60.54
C6-S11	1.780	1.666	Ag20-Ag18-Ag19	60.70	60.20
S11-Ag20	2.350	2.351	Ag20-Ag19-Ag17	60.75	60.12
Ag20-Ag17	2.725	2.691	Torsion angle (°)		
Ag20-Ag18	2.714	2.714	C3-S12-Ag13-Ag16	9.90	9.91
Ag20-Ag19	2.725	2.734	C3-S12-Ag13-Ag15	129.9	129.7
Ag17-Ag18	2.666	2.666	C3-S12-Ag13-Ag14	-110.08	-110.0
Ag17-Ag19	2.664	2.667	C6-S11-20Ag-Ag17	50.09	50.10
Ag18-Ag19	2.665	2.691	C6-S11-20Ag-Ag18	-69.90	-70.00
			C6-S11-20Ag-Ag19	170.09	170.09

for the molecular energies, quantum chemical descriptors, band gap energy, and potential energy. These are the critical parameters to check whether state 1 is ON or OFF in a molecular switch compare to other states in view of conductance, stability, etc.

The whole process is then repeated as the next step for state 2, and the different parameters are calculated. The OFF state is considered as the lowest total molecular energy with a comparatively high band gap of a bistable molecule. The stability and conductivity of both states can be calculated separately by investigating potential energy and ionization energy, respectively. After the successful design completion, the fabrication of the molecular switch is the next stage. Although it is in the infancy stage, now more papers are there to explain the experimental setup for the molecular switch devices [47].

3.2. Optimized Geometric Structure. Optimization of a metal-molecule-metal sandwich structure identifies the feasibility of using any switching molecule as a molecular electronic switch. Metal-BDT-metal possesses two stable states with two different contact geometries known as top-top and top-hollow geometries [48]. In this paper, geometrical optimization of BDT molecule with Au, Ag, Pt, and Pd has been done for both ON and OFF states successfully. The effect of the

TABLE 2: Optimized geometrical parameters of Ag-BDT-Ag for the ON state using the DFT and HF methods.

Parameters	Ag-BDT-Ag ON state		Parameters	DFT	HF
	DFT	HF			
Bond length in (Å)			Bond angle (°)		
C2-C3	1.401	1.399	C2-C3-C4	120.09	120.12
C3-C4	1.402	1.397	C3-C4-C5	119.00	119.99
C4-C5	1.402	1.395	C4-C5-C6	120.00	120.99
C5-C6	1.401	1.399	C5-C6-C7	120.01	121.30
C6-C7	1.401	1.404	C6-C7-C2	119.99	120.13
C7-C2	1.402	1.402	C7-C2-C3	119.99	119.24
C7-S1	1.780	1.781	C7-S1-Ag17	142.99	140.81
S1-Ag17	2.451	2.442	S1-Ag17-Ag18	57.40	58.81
S1-Ag18	2.456	2.459	S1-Ag18-Ag19	57.40	58.32
S1-Ag19	2.456	2.449	S1-Ag19-Ag17	57.26	58.71
Ag17-Ag18	2.649	2.691	C4-S12-Ag13	109.47	110.05
Ag17-Ag19	2.649	2.662	S12-Ag13-Ag14	145.63	146.32
Ag18-Ag19	2.646	2.670	Ag13-Ag14-Ag15	60.73	59.97
C4-S12	1.780	1.786	Ag14-Ag15-Ag16	60.00	60.10
S12-Ag13	2.350	2.356	Ag15-Ag16-Ag14	59.99	60.62
Ag13-Ag14	2.725	2.791			
Ag13-Ag15	2.724	2.734			
Ag13-Ag16	2.756	2.734			
Ag14-Ag15	2.644	2.666			
Ag14-Ag16	2.668	2.669			
Ag15-Ag16	2.666	2.698			

binding site on the conductance of BDT molecules with these metal electrodes is investigated, and it was found that top-molecule-top (top-top) geometry (where both S atoms of the molecule occupy the top site of the nanoelectrode surface) is the OFF state geometry and the top-molecule-hollow (top-hollow) geometry (with one S atom being connected to the threefold hollow site) is the ON state. In this paper, it is observed that BDT as a molecular switch shows different electronic properties for different metal nanoelectrodes. To get an optimized structure, bond lengths and bond angles were very crucial. The electrode orientation used in the simulation is (111) lattice structure. In the present article, the calculation of molecular structures has been discussed using DFT incorporated with the basis set BPV86/SDD. And the Hartree-Fock (HF) theory with the same basis set also has been studied. Figure 2 shows the optimized electronic structure of Ag (111)-BDT-Ag (111) for both ON and OFF states. Optimized bond lengths, bond angles, and dihedral angles at the DFT/BPV86/SDD level and the HF/BPV86/SDD level of molecules have been given in Tables 1 and 2 for the OFF state and the ON state, respectively.

It is noticed that the bond lengths and bond angles obtained for both OFF and ON states of 1,4-benzene dithiol are slightly different for DFT and HF calculations. It is because HF calculations do not include the electron-electron interaction term. Furthermore, geometrical optimization is highly dependent on the basis set selection and

TABLE 3: HOMO, LUMO, and band gap energies of ortho- and meta-BDT molecule with gold, silver, platinum, and palladium electrode.

	Ortho				Meta			
	Au	Ag	Pt	Pd	Au	Ag	Pt	Pd
HOMO	0.0384	-0.1466	0.0372	-0.0363	0.0376	-0.1472	0.0318	-0.0363
LUMO	0.0414	-0.1145	0.1771	-0.0066	0.1366	-0.0682	0.3379	0.1491
Band gap	0.003	0.0321	0.1399	0.0297	0.099	0.079	0.3061	0.1854

geometrical parameters are sensitive to the hydrogen bonding as well. These incongruities are due to the intramolecular hydrogen bonding. Nevertheless, this study provides a deep understanding of the microscopic and macroscopic behavior of molecules.

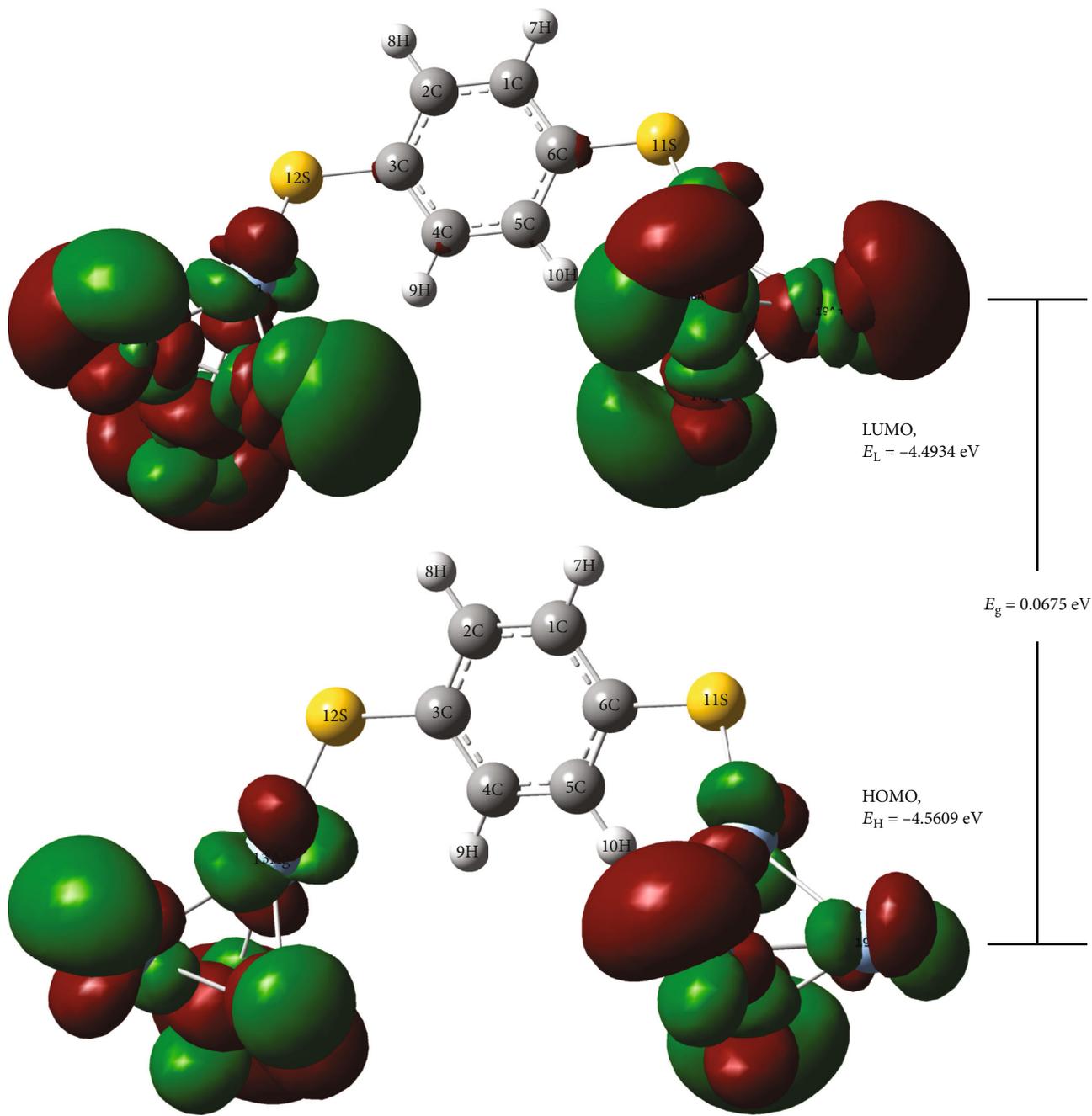
3.3. Frontier Molecular Orbital Analysis. In molecular electronics, the smallest molecular electronic switch can be formed by 1,4-benzene dithiol (BDT) molecule bridging between two gold (Au) leads [38]. Investigation of molecular orbitals and electronic properties of BDT molecule with different metal nanoelectrodes explores the different metal-molecule-metal designs. It can be helpful for the suitable choice of a molecular switch for the design of complicated molecular systems like molecular switch arrays, molecular memory, and nano-FPGA. BDT can be ortho, para, and meta according to the connectivity site of the anchoring group thiol (-SH) on the benzene ring [30]. Ortho-BDT (1,2-benzene dithiol), para-BDT (1,4-benzene dithiol), and meta-BDT (1,3-benzene dithiol) with Au, Ag, Pt, and Pd electrodes were simulated independently for the comprehensive understanding of semiconductor behavior with the various electrodes in terms of HOMO-LUMO gap. For the design of a molecular switch, the quantum interference (QI) effect in the charge transport through single-molecule junctions has been theoretically investigated [42]. It is noticed that in the development of an efficient molecular switch with an exceptional ON/OFF switching ratio, the constructive and destructive interference in the charge transport mechanism has a prominent role. Here, in this paper, para-BDT has been scrutinized for a single molecular switch with the various metal nanoelectrodes for both ON and OFF states. In line with the simulated band gap value, the electrical conductance of BDTs in its OFF state is in the order ortho-BDT>para-BDT>meta-BDT. The simulation result is eminently consonant with recent experimental results by Yang et al. [41]. The calculated band gap of ortho-BDT is 0.003 eV, very less compared to all the combinations of electrodes and BDTs in the OFF state geometry given in the table. Experimental results reveal ortho-BDT with a gold electrode manifests high conductivity of $10^{-1}G_0$. Among ortho-, para-, and meta-BDT, it is examined that the ortho-BDT is the best suitable molecule and Au (111) is the corresponding electrode for the good junction conduction in terms of HOMO-LUMO gap. From Table 3, it is realized that for the design of a molecular switch, the meta-BDT is the worst option for all the metal nanoelectrodes (Au, Ag, Pt, and Pd) considered here. Consequently, the priority in the selection of BDTs in the design of a molecular switch concerning the junction conductance is in the order ortho>para>meta. Regarding the band gap energy of

ortho-BDT-based molecular switch, the order for electrode selection is Au>Pd>Ag>Pt. Similarly, for para-BDT and meta-BDT, the order for electrode selection is Au>Ag>Pt>Pd and Ag>Au>Pd>Pt, respectively, for the high junction conductance of the OFF state molecular geometry.

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in the tunneling of an electron from the left to the right electrode via switching molecule [49]. The HOMO energy (E_H) and LUMO energy (E_L) represent the ability to donate and accept an electron, respectively [50]. The energy gap between HOMO and LUMO of metal-molecule-metal structure characterizes the molecular chemical stability and electron conductivity of a molecular switch [51]. HOMO and LUMO energies are well-known quantum chemical parameters. A higher value of E_H stipulates the ease of donating an electron to the unoccupied orbital of the receptor molecule. When the value of E_L is small, then the molecule has a small resistance to accept electrons [52]. The electronic absorption corresponds to the transition of an electron from the HOMO energy level to the LUMO energy level. That is the transition of an electron from the ground state to an excited state. The HOMO and LUMO energies and energy gap (E_g) of the BDT molecule with Au, Ag, Pt, and Pd nanoelectrodes have been studied in detail. The features of these molecular orbitals can be seen in Figure 3. Calculated HOMO (E_H), LUMO (E_L), and band gap energies (E_g) of the BDT molecule with Au, Ag, Pt, and Pd electrodes for OFF and ON state optimized molecular geometries separately are shown in Tables 4 and 5, respectively.

Tsutsui et al. [40] show experimental results on the conductance states of single BDT molecules bridging over Mechanically Controllable Break Junction (MCBJ) electrodes. The two definite states had conductance in the region of $0.01 G_0$ and $0.1 G_0$ for OFF and ON state geometries, respectively ($G_0 = 2e^2/h = 77.5 \mu S$). The research team concluded that the lower conductance was noticed for the top-top geometry and the higher conductance was noticed for the top-hollow geometry. Therefore, the simulations in this work are broadly consistent with the earlier experimental results.

3.4. Switching Ratio. Another crucial factor in determining the ON/OFF state of a molecular switch is the location of the Fermi energy of metallic contact relative to the molecular energy levels [53]. The switching ratio is the ratio between electrical conductance of a molecular switch in its ON and OFF states. Furthermore, it is a critical parameter of molecular devices, for the selection of the best suitable electrode in the design procedure [20]. The high ON/OFF switching ratio



(a)

FIGURE 3: Continued.

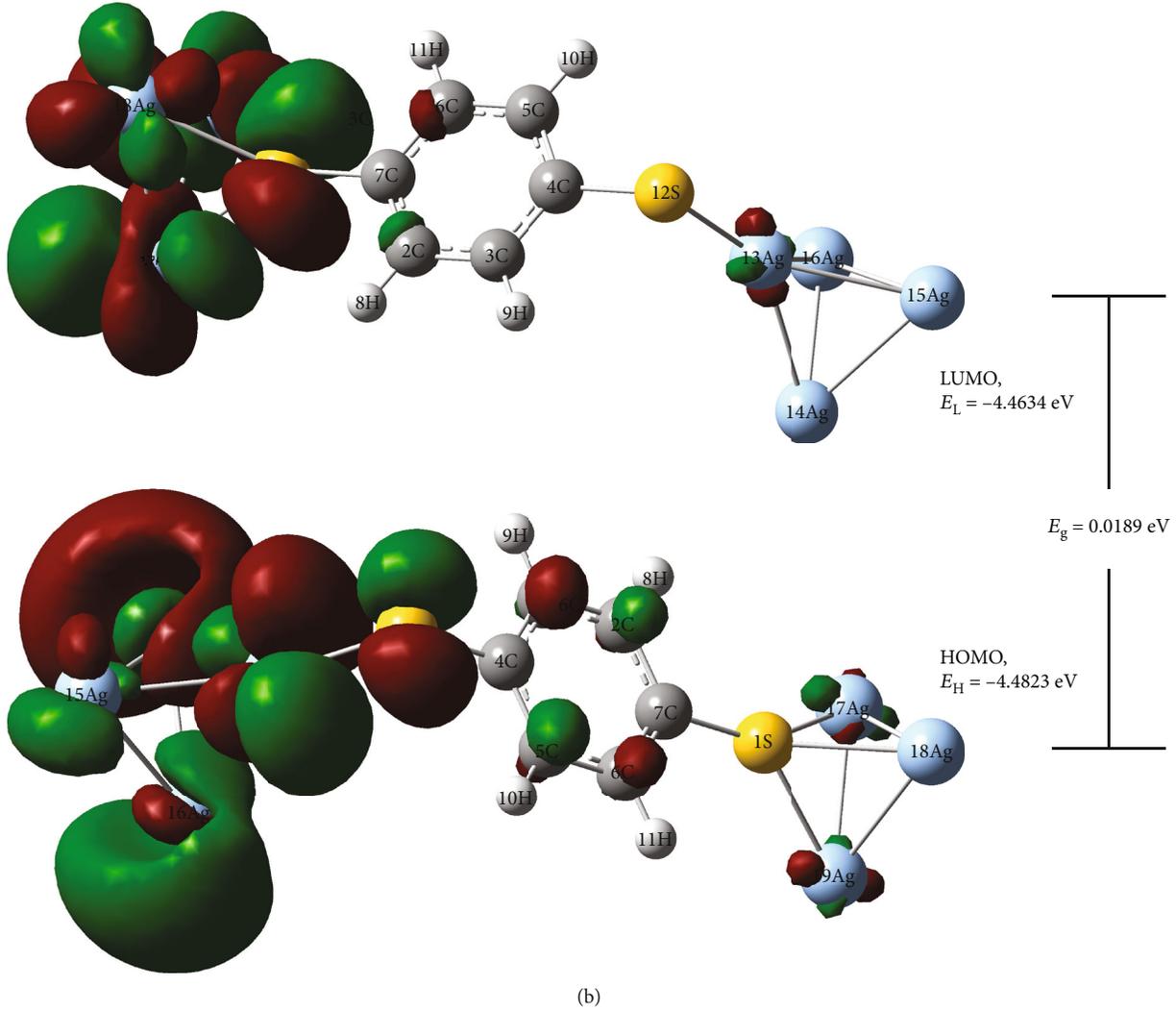


FIGURE 3: (a) HOMO and LUMO patterns of Ag-BDT-Ag OFF state molecule. (b) HOMO and LUMO patterns of Ag-BDT-Ag ON state molecule.

TABLE 4: HOMO (E_H), LUMO (E_L), and band gap energies (E_g) of the BDT molecule with Au, Ag, Pt, and Pd electrodes, for the OFF state optimized molecular geometry.

OFF state/geometry	Gold (Au)	Silver (Ag)	Platinum (Pt)	Palladium (Pd)
HOMO (E_H)	1.05 eV	-4.5609 eV	1.0484 eV	-0.8708 eV
LUMO (E_L)	1.113 eV	-4.4934 eV	1.1883 eV	-0.6854 eV
Band gap (E_g)	0.063 eV	0.0675 eV	0.1578 eV	0.0327 eV
$[E_g = E_L - E_H]$				

is explained in terms of configuration-related changes in the electrode-molecule interface energetics (changes in the energy position of the molecular orbitals with respect to the Fermi energy of electrodes for gold, silver, platinum, and palladium). First-principles density functional calculations demonstrate a better delocalization of the frontier orbitals as well as a stronger electronic coupling between BDT and the metal nanoelectrodes for top-hollow geometry over the

TABLE 5: HOMO (E_H), LUMO (E_L), and band gap energies (E_g) of the BDT molecule with Au, Ag, Pt, and Pd electrodes, for the ON state optimized molecular geometry.

ON state/geometry	Gold (Au)	Silver (Ag)	Platinum (Pt)	Palladium (Pd)
HOMO (E_H)	0.9883 eV	-4.4823 eV	0.7834 eV	0.8574 eV
LUMO (E_L)	1.044 eV	-4.4634 eV	0.8604 eV	0.8709 eV
Band gap (E_g)	0.0557 eV	0.0189 eV	0.0770 eV	0.0135 eV
$[E_g = E_L - E_H]$				

top-top geometry. In this paper, the switching ratio of the BDT molecule with Au, Ag, Pt, and Pd nanoelectrode in view of the HOMO-LUMO gap has been calculated.

An ideal electronic molecular switch must have well-defined ON and OFF states between top-hollow and top-top with fast and large changes in electronic conductance. The high top-hollow/top-top ratio (ON/OFF) measured here is an intrinsic phenomenon due to constitutionally

TABLE 6: Switching ratio for different metal-BDT-metal combinations in view of the HOMO-LUMO gap.

Parameter	Gold (Au)	Silver (Ag)	Platinum (Pt)	Palladium (Pd)
ON/OFF ratio	0.88	0.21	0.55	0.61

influenced changes in the electronic structure of the metal-molecule-metal junction. Moreover, this can be consistently explained by a combination of factors like changes in the electronic structure of the metal-molecules-metal junction or changes in the molecule-electrode coupling. The energy offset between the metal Fermi energy and HOMO energy slightly increases when switching from top-top to top-hollow geometry. In Table 6, the switching ratio of the BDT molecule has been calculated for different metals. It has been investigated that for 1,4-benzene dithiol (BDT) switching molecule, gold shows a high switching ratio of 0.88 and silver shows the least value 0.21. The order is as follows: Au>Pd>Pt>Ag.

3.5. Quantum Chemical Descriptors. Quantum chemical descriptors such as ionization potential (I), electron affinity (A), electronegativity (χ), electrophilicity index (ω), chemical potential (μ), hardness (η), and softness (S) of BDT-based molecular switches with Au, Ag, Pt, and Pd metal electrodes are calculated at the BPV86/SDD level of theory. Using Koopmans' theorem, ionization potential (I) and electron affinity (A) values can be expressed in terms of energies of the highest occupied (E_H) and the lowest unoccupied frontier molecular orbitals (E_L) as [54]

$$I = -E_{\text{HOMO}}, \quad (1)$$

$$A = -E_{\text{LUMO}}. \quad (2)$$

Ionization potential and ionization energy (I) refer to the same meaning that is the amount of energy required to remove an electron from a molecule. By Koopmans' approximation, the negated value of the HOMO energy gives the ionization potential. The conductivity of a molecule increases when the ionization potential decreases. Here, in Table 7, these potentials are tabulated for metal-BDT-metal sandwich structure for Au, Ag, Pt, and Pd nanoelectrodes. It is investigated that every electrode in this paper has been showing less value of ionization potential (I) for the ON state comparing to the OFF state. Therefore, calculations are greatly consistent with the definition of ionization potential. The amount of energy released when an electron is added to a neutral molecule is electron affinity (A) [52].

$$\text{Electronegativity of a molecule, } \chi = \frac{(I + A)}{2}, \quad (3)$$

$$\text{Electrophilicity index of a molecule, } \omega = \mu^2 S. \quad (4)$$

Electronegativity (χ) refers to the ability to attract electrons. The higher the correlated electronegativity value, the more an atom or a substituent group of atoms attract

TABLE 7: Calculated values of absolute ionization energy (I), electron affinity (A), electronegativity (χ), chemical hardness (η), electronic chemical potential (μ), electrophilicity index (ω), and softness (S).

Molecule	I (eV)	A (eV)	χ (eV)	η (eV)	μ (eV)	S (eV ⁻¹)	ω (eV)
Au-BDT-Au							
OFF	1.05	-1.11	-1.08	0.03	1.08	16.65	19.42
ON	0.99	-1.04	-1.02	0.02	1.02	25	26.01
Ag-BDT-Ag							
OFF	4.56	4.49	4.53	0.04	-4.53	14.29	292.60
ON	4.48	4.46	4.47	0.01	-4.47	50	999.05
Pt-BDT-Pt							
OFF	1.05	-1.19	-1.12	0.07	1.19	7.14	8.93
ON	0.78	-0.86	-0.82	0.04	0.82	12.99	8.77
Pd-BDT-Pd							
OFF	0.83	0.69	0.79	0.07	-0.79	6.88	3.95
ON	0.86	-0.97	-0.91	0.06	0.91	8.81	7.36

electrons towards itself. The measure of the ability to donate electrons describes electropositivity and is the converse of electronegativity. The stabilization energy when the system gets saturated by electrons from an external environment defines the electrophilicity index (ω). It can be calculated using the chemical potential and softness of a molecule [50].

$$\text{Chemical potential of a molecule, } \mu = -\frac{(I + A)}{2}, \quad (5)$$

$$\text{Softness of a molecule, } S = \frac{1}{2\eta}, \quad (6)$$

$$\text{Hardness of a molecule, } \eta = \frac{(I - A)}{2}. \quad (7)$$

The chemical potential is a type of potential energy that can be absorbed or released during any chemical reaction or phase transition. It is also considered as molar free energy. In thermodynamics, the molar chemical potential is referred to the partial molar free energy. Using the above relations, the electromolecular characteristics for 1,4-benzene dithiol (BDT) molecule with Au, Ag, Pt, and Pd electrodes have been investigated here.

3.6. Density of States (DOS) Spectrum. The density of states (DOS) of a single molecular switch delivers the interpretation of the density of charge for various energy intervals along with a molecular switch device [55]. It gets modified concerning the number and types of benzene rings present in the molecular backbone. In this work, BDT as a switching molecule constitutes a single benzene ring with para (the first and fourth position of the carbon attached with sulfur in the anchoring group) connection. However, the density of charge varies in a molecular switch between ON and OFF states. When the coupling strength with the electrode is good enough, then the DOS of that particular molecule-electrode combination gets modified by the broadening and shifting

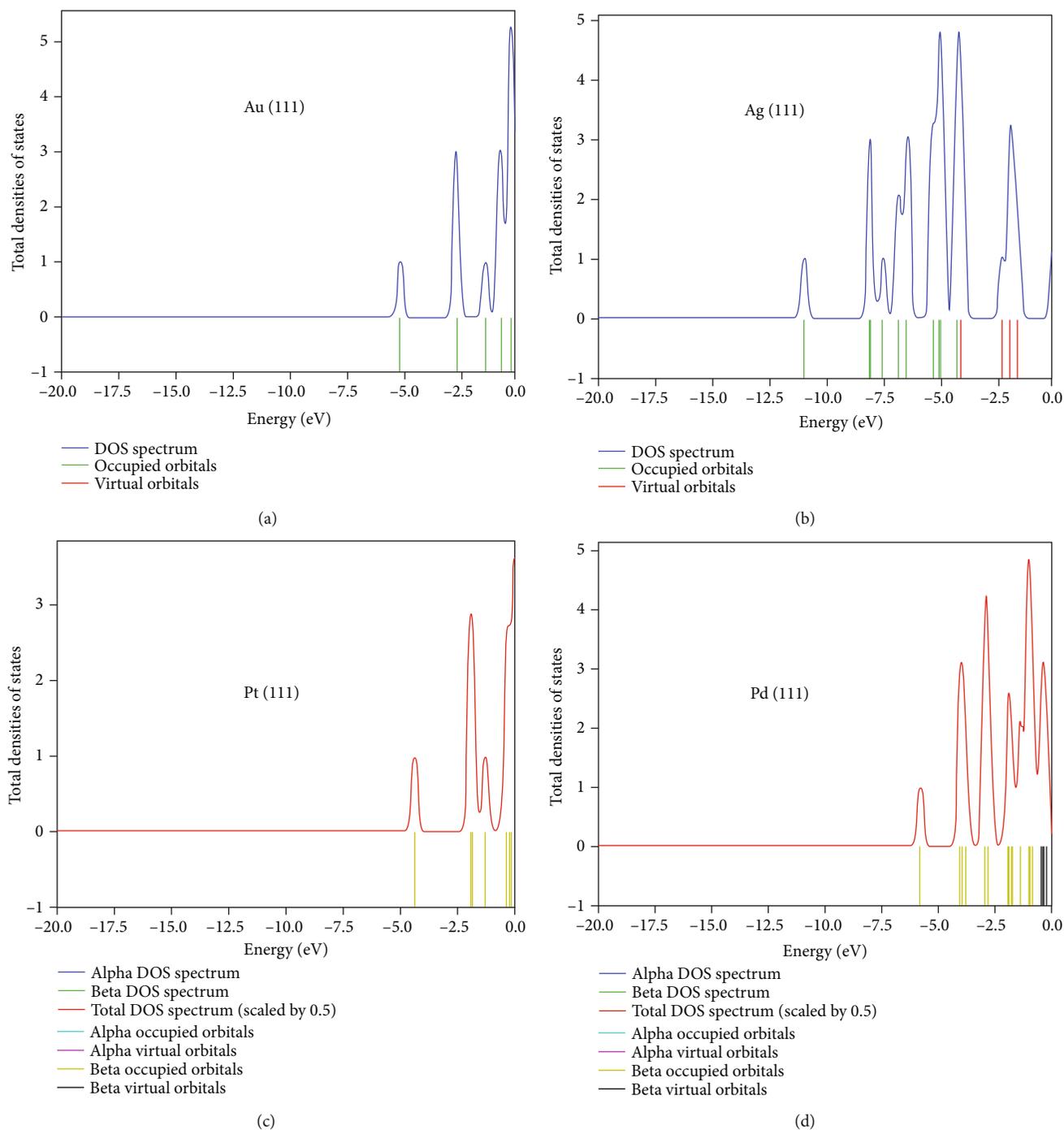


FIGURE 4: DOS spectrums of metal nanoelectrodes (a) Au (111), (b) Ag (111), (c) Pt (111), and (d) Pd (111).

of the discrete energy levels of a molecule. In Figure 4, DOS spectrums of metal electrodes chosen in this work have been shown. The expounded study of DOS spectrums of metal nanoelectrodes will undeniably lead to the increment in junction conductance and better switching ratio.

Hence, broadening can be determined by the coupling interaction between the molecular backbone and its two metal nanoelectrodes on either side. Whenever the electron orbitals are converging, the DOS becomes wider and higher and that directs to more conduction. The density of energy is observed to be more along the electrode regions due to

its metallic nature (the swirls in the DOS spectrum show higher electron density) [56]. In Figure 5, DOS spectrums of all the designed molecular switches in the OFF state have been given. Further, in the benzene ring molecular backbone, the density of electrons is found to be low. Since the molecule-anchoring group combination is bonded with Au, Ag, Pt, and Pd electrodes through different atoms, the density of charge varies in different regions. Figure 6 represents the DOS spectrums of designed ON state molecular switches. In the ON state geometry, Pd and Ag show more broadening of the states compared to other electrodes.

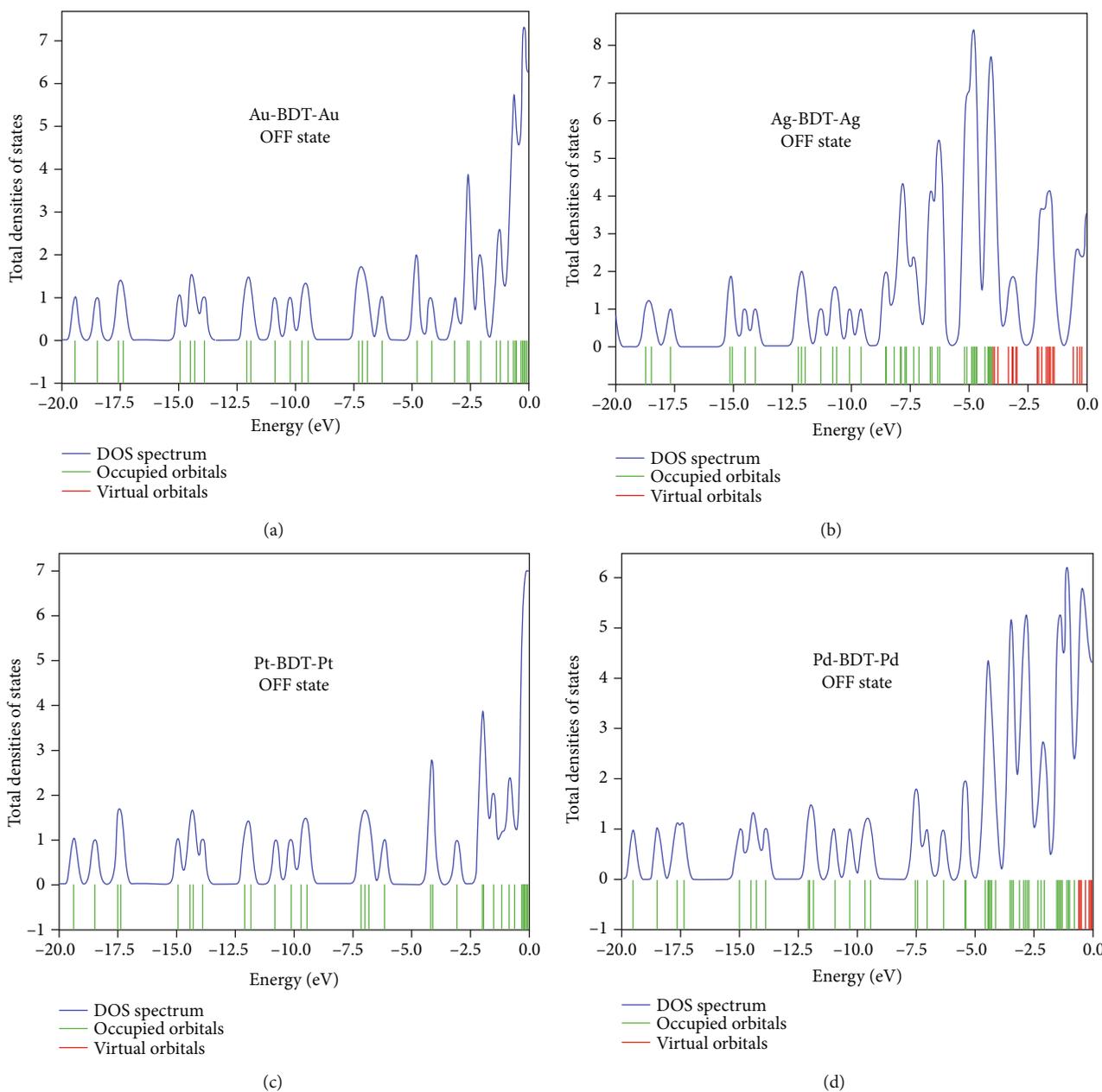


FIGURE 5: DOS spectrums of designed BDT-based molecular switches in the OFF state with (a) Au, (b) Ag, (c) Pt, and (d) Pd electrodes.

Moreover, gold, silver, platinum, and palladium metal nanoelectrodes have a high atomic number; therefore, the density of states is found to be more there, rather than the molecular backbone, which comprises hydrocarbons in the middle portion of a molecular switch.

3.7. Potential Energy of BDT-Based Molecular Switches with Au, Ag, Pt, and Pd. Theoretically, whenever the potential energy of a molecule increases, the stability of that molecule decreases [17]. It is explored that the ON state geometry (or top-hollow) is more stable than the OFF state geometry (or top-top) for every combination of metal electrodes selected in this work. BDT molecule in the ON state with Pt electrode shows top stability compared to Au, Ag, and Pd nanoelectrodes. From the DFT method study, it has been distinctly

examined that BDT is a good option for designing the molecular switch with metal electrodes since it is more stable to exist in nature compared to other aromatic switching molecules. Also, simulation results indicate slightly higher conductivity and better stability for the ON state of a molecular switch than the OFF state. Table 8 shows the calculated potential energies of designed molecular switches in this article. The calculated potential energy of BDT molecule without any nanoelectrode has the value 0.196×10^{-14} joules.

4. Conclusions

This paper proposes a simulation methodology for designing a switching molecule as an electronic molecular switch. The

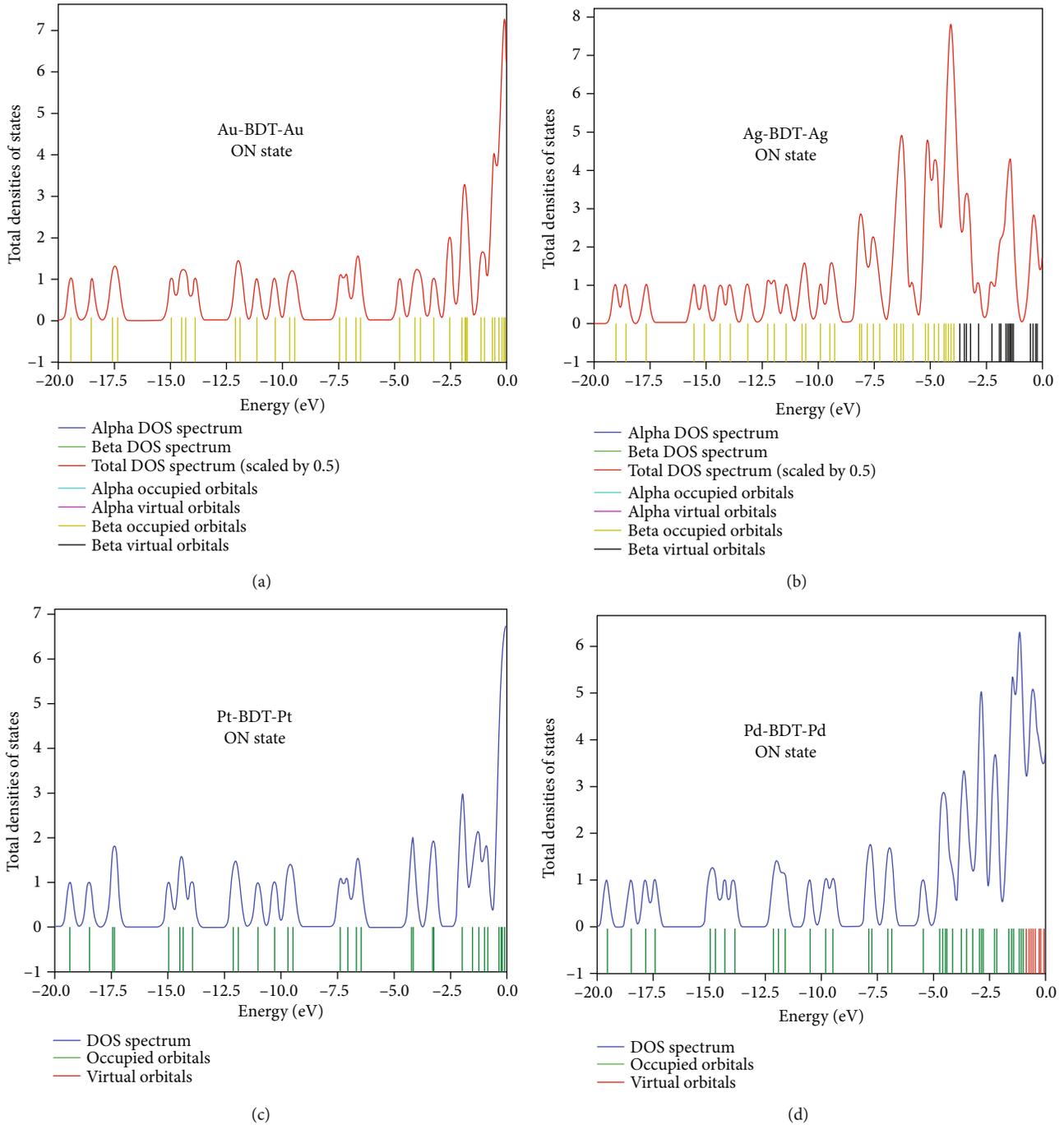


FIGURE 6: DOS spectrums of designed BDT-based molecular switches in the ON state with (a) Au, (b) Ag, (c) Pt, and (d) Pd electrodes.

TABLE 8: Calculated values of the potential energy of BDT molecular switch with Au, Ag, Pt, and Pd electrodes for OFF and ON states.

Molecule	State	Au (111)	Ag (111)	Pt (111)	Pd (111)
BDT	OFF	1.156×10^{-14}	1.16×10^{-14}	1.08×10^{-14}	1.14×10^{-14}
BDT	ON	0.996×10^{-14}	0.996×10^{-14}	0.943×10^{-14}	0.975×10^{-14}

methodology is implemented for 1,4-benzene dithiol (BDT) molecule with gold, silver, platinum, and palladium metal nanoelectrodes. The electronic properties of the designed

metal-molecule-metal sandwich structure have been investigated using density functional theory (DFT) and Hartree-Fock (HF) method. It has been perceived that the DFT and

HF values are slightly different as HF calculation does not include an electron-electron interaction term. The high ON/OFF switching ratio is explained in terms of configuration-related changes in the electrode-molecule interface energy levels. For the BDT molecule, the gold nanoelectrode has been observed with a high switching ratio of 0.88 among other nanoelectrodes chosen here. The order is Au>Pd>Pt>Ag. In line with the simulated band gap value, the electrical conductance of BDTs in its OFF state is in the order ortho-BDT>para-BDT>meta-BDT. The calculated band gap of ortho-BDT is 0.003 eV, very less compared to all the combinations of electrodes and BDTs in OFF state geometries. It is noticed that for the design of a molecular switch, the ortho-BDT is the best and meta-BDT is the worst option for all the metal nanoelectrodes (Au, Ag, Pt, and Pd) considered here. Computation of the quantum chemical descriptors has been reported using the same basis set. It is to be inspected whether the small band gap, small potential energy, and small quantum chemical descriptor characteristic difference between the two stable states can be exploited to empower the use of BDT molecule for a switching function as in a traditional transistor. But it is to be inscribed that this BDT molecule has a low conductance and therefore, a high resistance which suggests high power loss from a conventional IC design interpretation. These simulations are broadly consistent with the previous experimental/simulation results. Further, analysis of the density of states (DOS) spectrum and frontier molecular orbitals for both the stable states (ON and OFF state geometries) has been carried out. Exploring the band gap, ionization potential, and potential energy of two stable states reveals that the ON state molecule shows slightly higher conductivity and better stability than the OFF state molecule for every chosen electrode in this work. It is observed that the ionization energy for both ON and OFF states of the BDT has negative values for gold and platinum electrodes implicating instability. This stability can be further developed by using a variation of BDT with more alkane chains or a selection of anchoring groups in the structure. Additionally, a much more complex electrode structure than the simple four-gold atom tetrahedral structure of Au (111) might also enhance the stability of both ON and OFF states. A more complex electrode model will feasibly extend better band gap to distinguish the ON and OFF states. Similar models will be evaluated in the upcoming research. In the future, the proposed design methodology will be applied to the design of new molecular switches with carbon and noncarbon electrodes as well. The proposed methodology is seen to be encouraging based on primary findings but demands supplemental validation by a larger dataset: it must be applied to other switching molecules, anchoring groups, and electrodes of varying sizes, geometries, and physical properties.

Data Availability

The simulation data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

This work has been done as a part of Rafsa's doctoral research at Birla Institute of Technology and Science (BITS) Pilani, Dubai Campus.

Conflicts of Interest

The authors declare no conflict of interest.

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