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## STUDY OF THE THERMOELECTRIC AND OPTICAL PROPERTIES OF MOLECULAR NANOFUNCTIONS

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### Abstract

In this study, Quantum interference (QI) is one of the most fundamentals science, which can be a powerful strategy to control and enhance the electric, thermoelectric and spectral properties of single molecules. Here, the density-functional-theory-based quantum transport calculations have been used to figure out the electrical conductance ( $G/G_0$ ), which supplies unique understanding into the thermopower ( $S$ ) and emission oscillator strength ( $f_{em}$ ) of from a series of oligophenylene-ethynylene (OPE) derivatives with thiol end-groups, and para or meta transport connections, which underpins their spectral and heat transport properties. The molecules with meta connection (OPE-4,5,6) demonstrated the signature of a destructive quantum interference, which resulted to a low conductance ( $0.65 \times 10^{-4}$ ,  $0.5 \times 10^{-6}$ , and  $0.17 \times 10^{-6}$ ) respectively produce a high thermopower (165, 182, and 266  $\mu\text{VK}^{-1}$ ). These structures yield very low emission oscillator strength (0.96, 0.75, and 0.66) respectively. In contrast, the para linking in molecules OPE-1,2,3 led to a constructive quantum interference, which was the reason for the high conductance ( $0.52 \times 10^{-3}$ ,  $0.88 \times 10^{-3}$ , and  $0.22 \times 10^{-2}$ ) respectively. These molecule exhibited a low thermopower (22, 21, and 13), and a high emission oscillator strength (2.15, 2.15, and 2.03) respectively. Finally, the properties of all molecules studied here are dominated by the highest occupied molecular orbital (HOMO) level.

**Keywords:** Quantum, Nano-electronic, Gaussian, GOLLUM, SIESTA.

### 1. Introduction

In all those of the myriad of wire like molecules that have been prepared and studied in thin film and single-molecule junctions, the oligo(phenylenevinylene) and oligo(phenyleneethynylene) (OPE) occupy a particularly prominent position. The ease of synthesis, stability under ambient conditions, ready functionalization with a wide range of electronically and sterically interesting groups, and suitability to form modular structures of regularly increasing length have made these systems idea workhorses for the explorations of electronic phenomena in molecular systems[1,2]. There are many reviews and discussion papers that address the chemistry and junction characteristics of these species; a comprehensive description of this molecular class alone would occupy at least an entire volume. The OPE backbone is thought to offer a wider range of conformations, given the essentially barrierless rotation of the phenylene moieties around the ethynyl axis, the great advantage of this fragment is the (relative) simplicity of synthetic approach based on sequential and convergent crosscoupling methods[3,4]. In fact, Oligo(phenylene-ethynylene) (OPE) compounds represent a particular unique family of molecular wires. They are fully  $\pi$ -conjugated rigid rod-like molecules with a HOMO–LUMO gap of  $\sim 3$  eV[5].

Received: June, 13, 2022 / Revised: July, 21, 2022 / Accepted: 19, July, 2022 / Published: 31, July, 2022

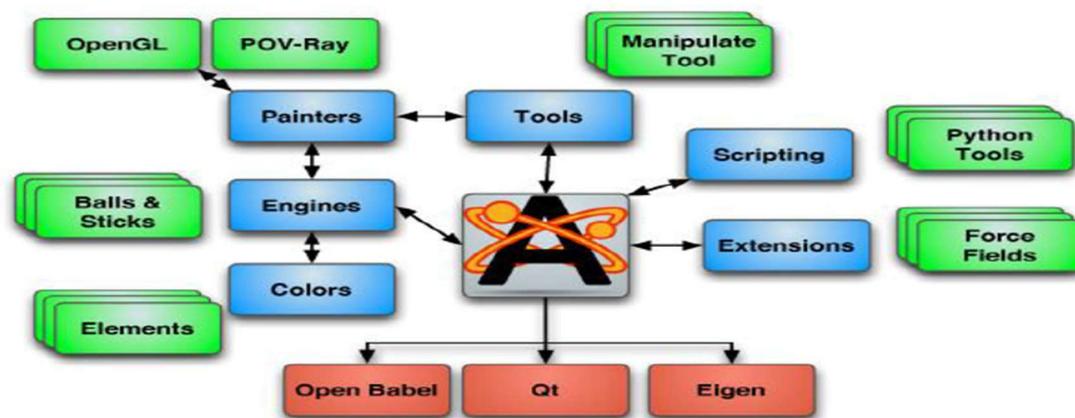
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Although the idea of using quantum interference (QI) effects [6] in single molecules has been talked about for a long time [7–14], experimental evidence of room-temperature QI in single molecules has only lately [15–22] been found. We believe the next major development will be the active and continuous regulation of QI-based activity in single-molecular junctions by external triggers, such as electrostatic. Indeed, it has been shown both experimentally and theoretically that the chemical composition [23], tuning the position of intra-molecular energy levels relative to the work function of metallic electrodes [24, 25], systematically lengthening single molecules, changing the binding groups within a family of molecules [26–30,31], and controlling the transport of molecules at the molecular scale can all be used to manipulate the optical, electronic, and thermoelectric properties[32].

## 2. System Description

To get the structure of all systems in theory, have been utilized Avogadro programming. Avogadro is a propelled particle manager and visualizer intended for cross-stage use in computational science, molecular modeling, bioinformatics, materials science, and related areas (see figures 1). It offers flexible high quality rendering and a powerful plugin architecture [33]. Avogadro offers a semantic compound developer and stage for perception and investigation. For clients, it offers a simple to-utilize manufacturer, incorporated help for downloading from basic databases, for example, PubChem and the Protein Data Bank, separating synthetic information from a wide assortment of arrangements, including computational science yield [34].



**Figure 1:** The abilities and tools of atomic building using Avogadro

## 3. Theoretical Considerations

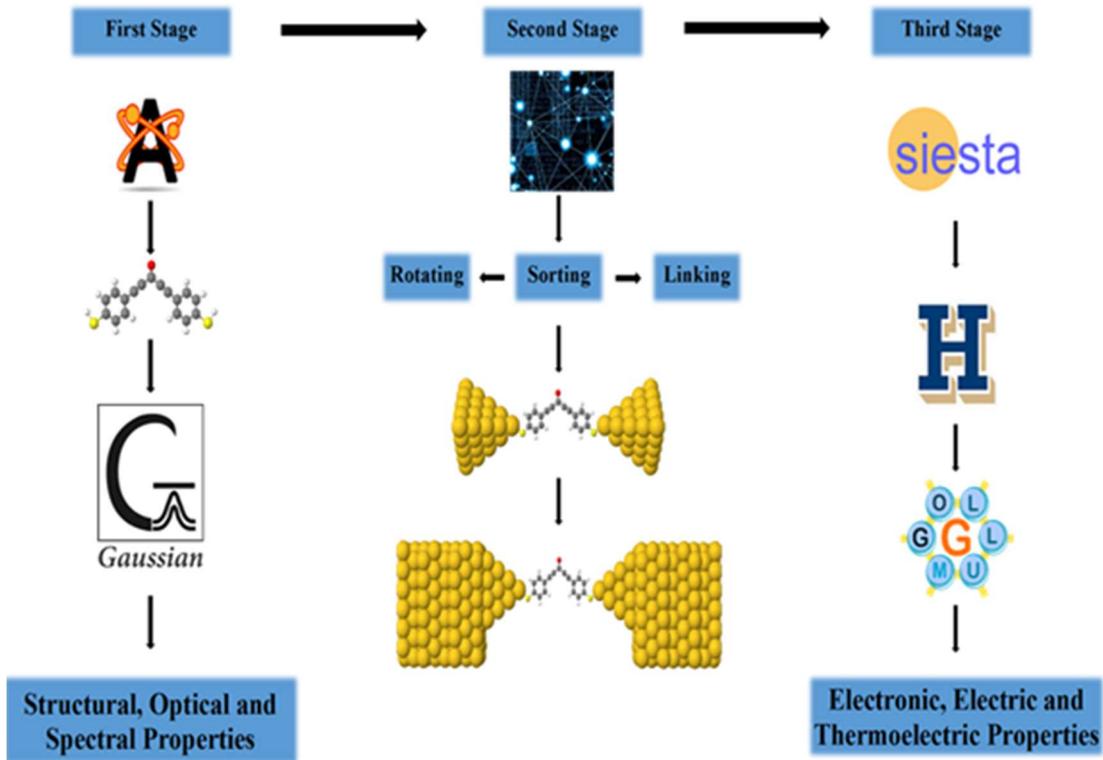
A set of equations, the Thomas-Fermi screening wavenumber whereas  $r_s$  is the local Seitz radius. The second expression is the correlation energy  $E_x^{GG}[n(r^{\rightarrow})]$  and given by:

$$E_x^{GGA}[n(r^{\rightarrow})] = \int (E_c^{homo}[n(r^{\rightarrow})] + \chi[n(r^{\rightarrow})]) dr^{\rightarrow}, \dots (1)$$

$$\chi [n(\vec{r})] = \frac{e^2}{a_0} \gamma \ln \left( 1 + \frac{\beta}{\gamma} t^2 \frac{1+At^2}{1+At^2+A^2t^4} \right),$$

$$A = \frac{\beta}{\gamma} \left[ e^{\left( \frac{E_c^{homo}[n(\vec{r})]}{\gamma} \right)^{-1}} \right]^{-1}$$

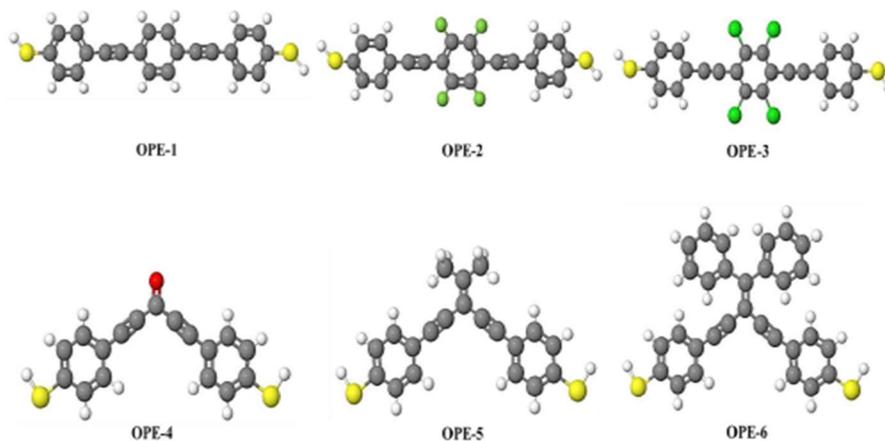
where  $\gamma = (1 - \ln(2)/\pi^2)$ ,  $t = |\nabla n(\vec{r})/2kT - Fn(\vec{r})|$  is another dimensionless density gradient,  $\beta = 0.066725$ , and  $a_0 = \hbar/me^2$ .



**Figure 2:** Steps of transport calculations.

#### 4. Results and Discussions

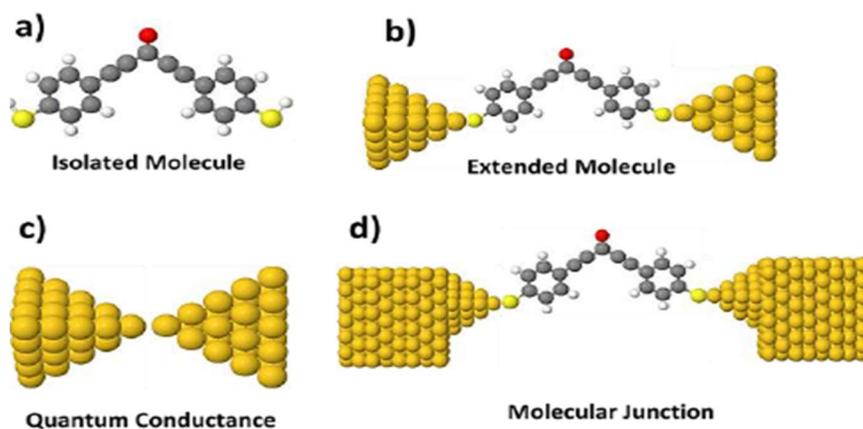
A family of modified sulfur-functionalized Oligo(phenylene-ethynylene)(OPE) Molecules, as shown in figures 3 has been created to investigate their electronic, thermoelectric, spectral and some of optical properties.



**Figure 3:** The optimized single molecules

Au...Au atoms. X is the bond length (Au...S).

Figure 3.1 show there is an obvious difference in molecule length. Since, L of molecules with para connection is almost equals 2 nm, while molecules with meta have almost 1.45 nm molecule length. In addition, these results introduce a hint that these structures are  $\pi$ - conjugated molecules and they have an inner-shell electrons and  $\sigma$ -electrons are supposed to have their energies and distributions governed solely by the atomic orbital, or pair of orbitals, in which they move; and all effects depending on conjugation of unsaturation electrons, such as resonance energies and variations in bond order and electron density, are ascribed to the  $\pi$ -electrons as shown in Figure 4 .

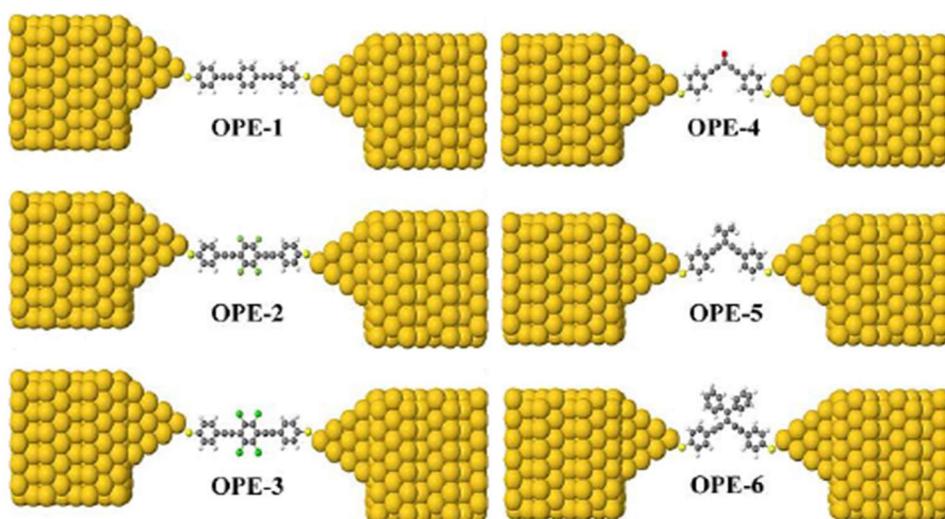


**Figure 4:** The optimized molecular junction of OPE-4, as an example.

a) The relaxed single molecule; b) The optimized extended molecule; c)

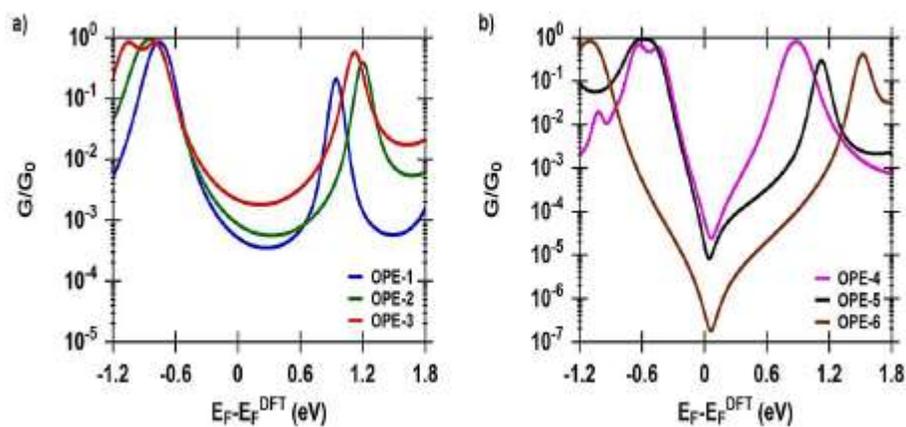
The relaxed pyramidal gold tips; d) The optimized molecular junction.

To provide further insight, and to better evaluate the properties and behavior of these molecular junctions, calculations using a combination of DFT and a nonequilibrium Green's function formalism were also carried out. Eight layers of (111)-oriented bulk gold with each layer consisting of  $6 \times 6$  atoms and a layer spacing of 0.235 nm were used to create the molecular junctions, as shown in figure 5 and described in detail elsewhere[35]



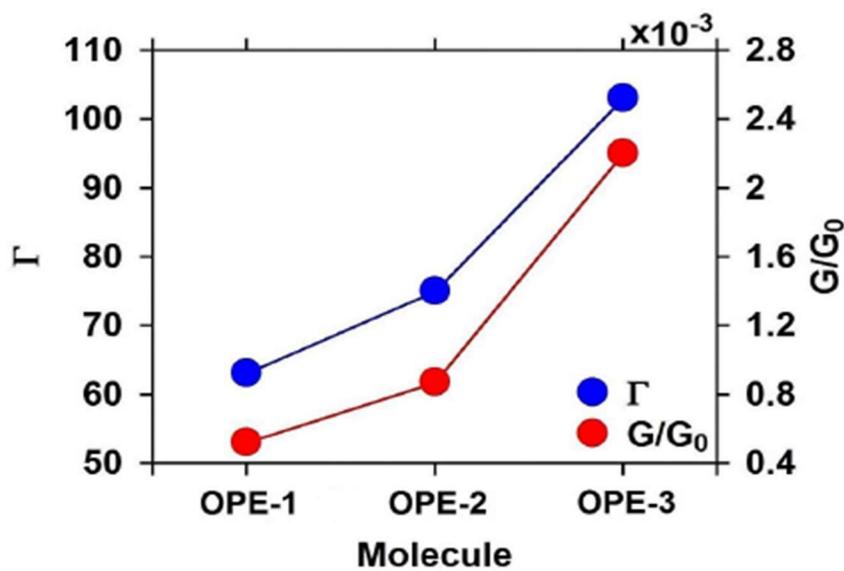
**Figure 5** :The optimized molecular junction of all structures.

The most important result of figure 6 a,b is the presentation of the relative contribution to the conductance from quantum interference (QI) in the central part of molecules, and it demonstrates that the QI is satisfied at the level of DFT.



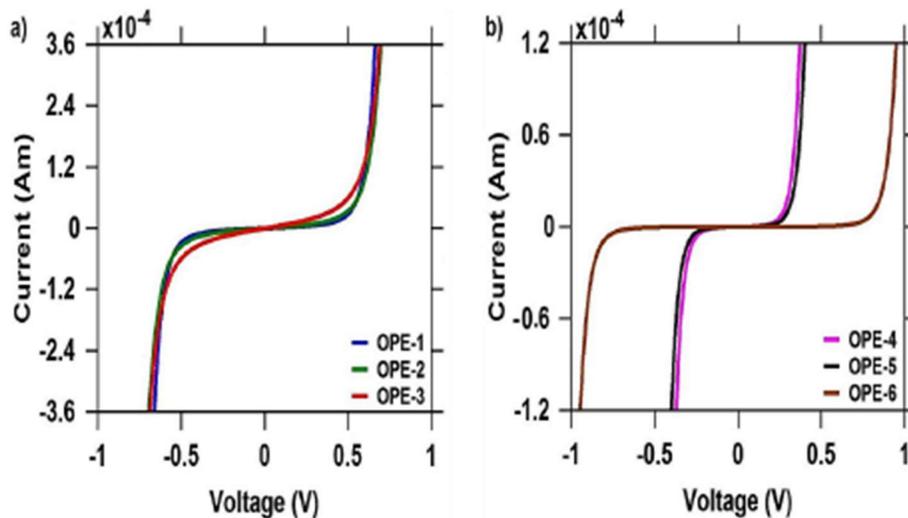
**Figure 6** :The electrical conductance of all structures.

figure 7 also shows that for a wide range of energies in the gap between the HOMO and LUMO, the ordering of the conductance is OPE-3 > OPE-2 > OPE-1 > OPE-4 > OPE-5 > OPE-6.



**Figure 7 :** The transferred electrons from molecule to the electrodes ( $\Gamma$ ), and the electrical conductance of OPE-1,2,3 molecular junctions.

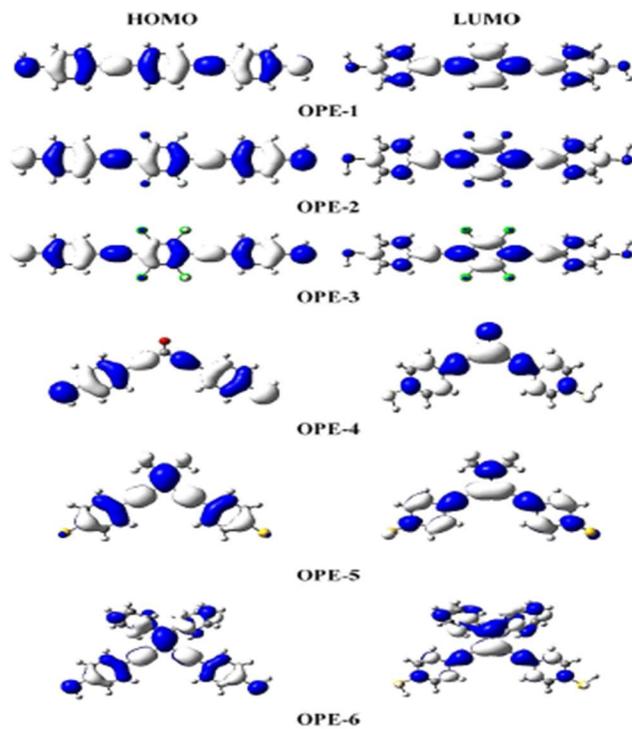
To elucidate above results of the conductance, Figure 8, shows a strong relationship between the number of electrons and the electrical conductance. In other words, high  $\Gamma$  leads to high  $G/G_0$ , and vice versa.



**Figure 8.** The current-voltage characteristics of all molecular junctions.

Figure 9 shows the plots of iso-surface orbitals (HOMOs and LUMOs) for all molecules. Almost, density functional theory calculations have shown that the orbitals for both HOMO and LUMO of all molecules are extended through linear  $\pi$  interactions. Although, the weight of HOMO is nearly equals that of the LUMO, and this could be consider as a sign of the  $\pi$ -conjugation electrons transport in these

molecules, but the HOMOs are concentrated on the C≡C bonds, while LUMOs are localized on the C–C bonds and shown less contribution than that of HOMOs.



**Figure 9.** Represents the electronic structure and the distribution of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for all molecules.

## 5. Conclusions

This thesis includes theoretical study of the electrical conductance, thermopower and emission oscillator strength of a family of OPEs with thiol linker groups, with different transport connection para and meta. Various side groups such as phenyl rings or a carbonyl functional group or propene side groups were distinguish structural aspects of molecules.

The conductance results showed well-defined conductance features of the junctions formed. Where, the presentation of the relative contribution to the conductance from quantum interference (QI) in the central part of molecules, and it demonstrates that the QI is satisfied at the level of DFT. It can be conclude that the QI is a powerful strategy to control and enhance the conductance and thermopower. For a wide range of Fermi energies, the meta connection in the medial of molecules leads to a destructive interference, which in turn leads not only to a low conductance value ( $0.17 \times 10^{-6}$ ) for molecule OPE-6, but also a high value for the thermopower ( $266 \mu\text{VK}^{-1}$ ) of this structure. In contrast, the molecule OPE-3 introduces a highest conductance  $22 \times 10^{-2}$ , and the lowest thermopower  $13 \mu\text{VK}^{-1}$ . The sign of thermopower for all compounds is positive, which confirms another important

conclusion, that the charge transport mechanism is a HOMO-dominated transport. The OPE-4,5,6 molecules have much smaller  $f_{em}$ , (0.96, 0.75, and 0.66 respectively), which directly leads to small  $\sigma_{em}$ , and therefore it can be concluded that any of these materials is not possible to serve as a good optical gain medium in practice. Whereas, the molecules with para linking (OPE-1,2,3) have a good emission oscillator strength ( $f_{em}$ ), since they owned  $f_{em} \approx 2$ , and that means those structures are promising candidates for laser gain medium.

### Acknowledgement

The authors wish to acknowledge the scientific support from University of Babylon, College of Sciences for Women Department of Laser Physics.

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