Enhancement of Thermoelectric Properties of Porphyrin-based Molecular Junctions by Fano Resonances

Rasool M. Al-Utayjawee¹, Oday A. Al-Owaedi²

¹,²Department of Laser Physics, College of Science for Women, University of Babylon, Hilla 51001, Iraq.

*Assistant Prof. Email: oday.alowaedi@uobabylon.edu.iq

Abstract. Single-molecule porphyrin applications gain attention by using molecules as elementary blocks of electronic components involving metallic atoms. Theoretically, one type of molecular-scale porphyrin device is used in this article, consisting of organometallic single molecules with different metals (Zn, Mg, Cu and Fe), sandwiched between gold electrodes bound by thiol anchor groups. The transmission and Seebeck coefficients for Au|molecule|Au configurations were computed by using density functional theory (DFT). The findings show that there is a robust Fano resonance in the transport behaviour around the Fermi energy, only for the porphyrin-based device with Fe metal. This result is attributed to the destructive quantum interference between continuous and discrete states. This work not only indicates that there is a relationship between the electrical conductance and thermopower but also it introduces a promising strategy to affect and control these characteristics via creation of Fano phenomenon.

1. Introduction
The subject of heat energy and electricity and their relation has attracted a wide research attention and become one of the most interesting fields for the promising applications of converting waste heat into electricity [1-2]. Achievement of such remarkable goal requires finding the appropriate material and exploring its electronic and thermoelectric properties such as the spin degree of freedom of electrons [3-4]. Also, it has been mentioned that the utilizing of nanoscale-thermoelectric devices can greatly promote the transformation efficiency between heat and electricity [5]. In this context, the individual molecules could be promising candidates to establish new field and structures called thermoelectric materials [6-7]. The Seebeck coefficient is one of the most important factors to evaluate the performance of thermoelectric devices [7]. Consequently, the investigation of different strategies to change Seebeck coefficient has become an attractive target for many researchers [5]. One of these strategies is the tuning of Seebeck coefficient by using different transition metal atoms [8]. Further, Li et al have reported that the manipulation in some of structural properties of molecular junctions such as linkage sites can change the thermopower [9]. The most robust way to modulate the characteristics of Seebeck coefficient is the creation of Fano resonance property [10-11]. Furthermore, it has been reported that the Fano resonances can noticeably enhance the spin thermoelectric characteristics of graphene nanoribbon-CACs junctions [10]. Porphyrin molecules are not only well known as promising components for spin-polarized currents production, but also they have used excessively in designing of molecular spintronic devices [12-13].
Here, we are focusing to explore the thermoelectric properties of porphyrin single molecules with different transition metals. For this goal porphyrin-based molecular junctions are designed by contact a set of porphyrin molecules to two gold electrodes using density functional theory methods with SIESTA code [14], and the transport properties are theoretically calculated using nonequilibrium Green’s function formalism with Gollum code [15].

2. Quantum Chemical Modeling and DFT Calculations
To gain a deeper understanding of the electrical and electronic behavior of molecular junctions, the electronic, electrical and thermoelectric properties were examined using DFT-based methods. Initial studies of the electronic structures were carried out at B3LYP level of theory [16] with LANL2DZ basis set for all molecules [17] to study the influence of the central metals on the properties of these devices. Plots of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are given in Figure 2. To obtain the optimized geometries of all systems under investigation in this work, and to compute the electrical conductance and thermopower, the density functional theory (DFT) methods (the SIESTA code), and a non-equilibrium Green’s function formalism [14, 15], were utilized. For the transmission and Seebeck coefficients calculations, the molecular junction was created by attaching the relaxed molecule to 35-atom pyramidal gold electrodes (see Figure 1), with 8 base layers, each layer consisting of 6x6 atoms and a layer spacing of 0.235. For more details see [18-22]. From these model junctions the conductance and thermopower, were calculated using the GOLLUM code [15].

![Figure 1. The optimized molecular junctions.](image)

3. Results and Discussion
The electronic structure calculation of any system is an important tool to explore and understand the different properties of molecular junctions. Therefore, we have calculated the charge distribution, energies, and molecular orbitals (HOMOs and LUMOs), for all molecules using the Gaussian package [16], as shown in Figure 2. Significantly, the value of HOMO-LUMO gap has been varied from 0.085 eV for Pr-Cu to 0.083 eV for Pr-Zn. Then, it dramatically shrunked from 0.081 eV for Pr-Mg to 0.063 eV for Pr-Fe. This results can be ascribed to the influence of the metal centres type. An important point that can be observed from Figure 2, that the HOMOs and LUMOs of the structure with Fe-centre are more metal in character than that of the rest structures. This result may aids to put a suitable interpretation of the electronic and thermoelectric results shown in figures 3 and 4. In addition, both of them HOMOs and LUMOs are not extended over the backbone of the molecule. Instead they are delocalized on the porphyrin unites. Furthermore, figure 2 indicates to a considerable result that the transport mechanism of charges is HOMO-dominated transport, which is consistent with transmission spectra and previous studies [23-25].
Figure 2. The iso-surfaces ($\pm 0.02$ (e/bohr$^3$)$^{1/2}$) of the HOMOs and LUMOs for all molecules.

Finally, iso-surface calculations of the structure with Fe metal show distinguished points that may aid to interpret the appearance of Fano resonance in the transmission spectra of this molecule. It is clear that the narrowest HOMO-LUMO gap is presented by Fe-based molecular junction, which can be ascribed to the highest atomic force as shown in Figure 4c. The second point is the exotic electronic structure of this system, which may lead to a destructive quantum interference between continuous and discrete states, which resulted to lowest conductance as shown in Figures 4a,b.

Table 1. The electrical conductance ($G/G_0$), thermopower ($S$), electronic figure of merit ($ZT_e$), and HOMO-LUMO gaps for all molecules at $E_F = 0.09$ eV.

| Molecule | $G/G_0$ | $S$ (µVK$^{-1}$) | $ZT_e$ | HOMO-LUMO Gap (eV) |
|----------|--------|-----------------|--------|-------------------|
| Pr-Zn    | 0.21   | 129             | 0.69   | 0.083             |
| Pr-Cu    | 0.14   | 134             | 0.64   | 0.085             |
| Pr-Mg    | 0.23   | 127             | 0.69   | 0.081             |
| Pr-Fe    | 0.1    | 169             | 1.5    | 0.063             |

In terms of low electrical conductance yields high thermopower, our results presented in table 1 show that the lowest conductance is introduced by Pr-Fe, which leads to a significant raising of figure of merit value, and the highest value of Seebeck coefficient. On the other hand, it is obvious that there is a strong link between the HOMO-LUMO gap and electronic and thermoelectric properties of these structures, which definitely needs more investigation. Figure 3 shows a promise strategy to influence and control the thermoelectric properties of single-molecule junctions. The creation of Fano resonance is a useful strategy to lower the conductance and raise the thermopower. It is obvious this phenomenon leads to decrease the transmission coefficient over a wide range of electron energy (-0.6 - 0.6 eV) as shown in Figure 3a.
Specifically, there is one Fano resonance peak in the transport spectra for the structure with Fe-metal centre, and this is a result of a destructive quantum interference between the discrete and continuous states. In addition, the position of Fano resonance peak helps us to determine the theoretical Fermi energy, which is 0.09 eV. This value of Fermi energy is used in all theoretical calculations in this work.

Electrical conductance and thermopower are the most important properties for the electronic applications. Here we are demonstrate that there is a strong relation between these properties, since the high conductance yields low thermopower and vice versa, as shown in figures 3b,d. Another important point can be observed from Figure 3c, which exhibits by the distinguish enhancement of the figure of merit for the molecule with Fe-metal centre. This result proves that the existence of Fano resonance decreases the electrical conductance as shown in Figure 3d, and improves the thermoelectric properties dramatically as shown in Figure 3b. Noteworthy to mention that the HOMO peak of all molecules in figure 3a is splitted into two broad peaks. This result can be attributed to the spin effect.

### Table 2. The total number of electrons on the metal (Q), the number of electrons transferred from the metal to electrodes (Γ), atomic forces (eV/A0), and total energy (eV) of all molecular junctions.

| Molecule | Q  | Γ      | Atomic Force (eV/A0) | Total Energy (eV) |
|----------|----|--------|---------------------|------------------|
| Pr-Zn    | 30 | 18.3   | 0.000299            | -78903           |
| Pr-Cu    | 29 | 18.1   | 0.000172            | -78624           |
| Pr-Mg    | 12 | 10.5   | 0.000254            | -77490           |
| Pr-Fe    | 26 | 18.1   | 0.002873            | -77965           |
The investigation of thermoelectric properties of single molecule devices is one of the most modern branches in the field of thermoelectric materials. Particularly, thermopower and electrical conductance, which picture the conversion efficiency of thermal energy into electrical energy. Figure 4a shows that the lowest conductance is presented by Pr-Fe, and the same structure introduces the highest thermopower, while Pr-Mg offers the highest conductance and the lowest thermopower. This outcome proves in somehow there is an interplay relationship between the electrical conductance and Seebeck coefficient. On the other hand, Figure 4b illustrates that an increasing in number of electrons transfer from metal centre to the electrodes increases the electrical conductance. The highest Γ (87%), is displayed via Pr-Mg, which leads to the highest conductance. In contrast, Pr-Cu shows the lowest Γ (61%) and a low conductance, which is 0.14. Although, the Pr-Fe structure exhibits a high Γ (70%), it offers the lowest conductance, and this attributed the Fano resonance effect. Figures 4c,d show the atomic forces and total energy of all molecular junctions. The order of atomic force is Pr-Fe > Pr-Zn > Pr-Mg > Pr-Cu. These results may explain the narrowest HOMO-LUMO gap that introduced via Pr-Fe structure as shown in Figure 2.

4. Conclusions

In conclusion, this work provides a considerable body of information about the design of thermoelectric materials and control the thermoelectric properties of single molecule devices. By using the density functional theory and a non-equilibrium Green’s function, we have investigated the thermoelectric properties of porphyrin-based molecular junctions with different metals (Zn, Mg, Cu and Fe). Although the existence of destructive quantum interference as a Fano resonance decreases the electrical conductance sharply, but it is a powerful strategy to enhance the thermopower and figure of merit. The position of the Fano resonance is not only an important factor to determine the sign of Seebeck coefficient, but also it is a useful technique to predicate the value of Fermi energy. Further, the electrons transfer ratio from molecule to the electrodes can be a support factor to promote or decrease the electrical conductance and thermopower respectively.
5. References

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