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The Impact of Electron-phonon Coupling on the Benzene-like Quantum Dots Molecule Energy Gap.

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ABSTRACT

In this study, we developed a theoretical model to study the effect of electron-phonon coupling on the energy gap between the HOMO-LUMO levels in an artificial molecule composed of six quantum dots with a geometric shape similar to the benzene ring, where three different configurations of the benzene ring were studied (para, meta, and ortho) depending on the location of the donor and acceptor atoms, and the effect of different locations of the phonon bath was also taken into consideration. Our model is illustrated, through a comprehensive and compact Hamiltonian approach, that specifies the dynamics of electronic and phonon states within these quantum systems. Our results demonstrated the important role of phonon coefficients in modifying the electronic properties of molecules. Based on these results, we observed that the electron-phonon coupling strength and phonon energy can be manipulated to modulate the energy gap, providing promising ways to develop advanced nanoelectronics applications.

1. Introduction

The quantum confinement effect can be seen in quantum dots of any finite size, therefore making it potential to tune the energy gap very finely over a wide spectrum of environmental effects [1]. At the same time, the progress in quantum computing and nanotechnology is based on the special capacity of quantum dots to dramatically change size and discrete energy levels [2]. While quantum dots enjoy great interest nowadays due to a rich collection of experimental investigations, there is a rather new field in theoretical research related to the geometric configuration [3]. A characteristic basic feature that defines their behavior is the difference of energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), controlled by electron-phonon (e-ph) interaction over a wide energy range. The explanation for these processes lies in energy gap renormalization and is also the basis for the working of QD-based devices [5]. Probably most important to the majority of applications for nanostructures is their capacity for charge or energy transfer [6], [7]. In such systems, charge transfer involves quite complex interactions between orbital overlaps, energy alignments, and vibrational couplings of electronic states and lattice vibrations [8]. The relationship between the electronic states and vibrational dynamics in the electronic states of the

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nanomaterials needs to be further studied. In particular, in quantum dots, small gaps enhance physical properties such as electron-phonon (e-ph) coupling, which affects charge transfer and optical behaviors through the polaronic effect, and in return, the e-ph interactions tune both the effective mass of the electron and the quantum dot energy levels, thus modifying the HOMO-LUMO gap [9], [10].

Most in-depth, the e-ph coupling dynamics of QDs have been investigated with the use of ultrafast laser spectroscopy and temperature-dependent photoluminescence spectroscopy [11,12,13]. Such studies are quite important in the development of quantum dot technologies, since deeper understanding and control over e-ph coupling could dramatically enhance the efficiency of a device. One of the most important features of quantum dot properties is the tunning of the HOMO-LUMO gap due to e-ph interactions [14]. In this paper, we try to determine the relationship between e-ph coupling and the HOMO-LUMO gap of a benzene-like quantum dots molecule. We wish to learn in particular what the effects of the e-ph coupling may be on the efficiencies and performances of devices that may be built based on these structures.

2. Theoretical Model Calculation

Our investigation forms a theoretical framework that comprises two edge systems connected by atoms acting as donor and acceptor to them, and a central quantum dots molecule configured like the well-known benzene molecule. Fig. (1a–f) depicts these quantum dot systems. We selected the benzene-like case as the simplest, stable structure of a nanoscale system that can couple to phonon bath in different locations through these molecules.

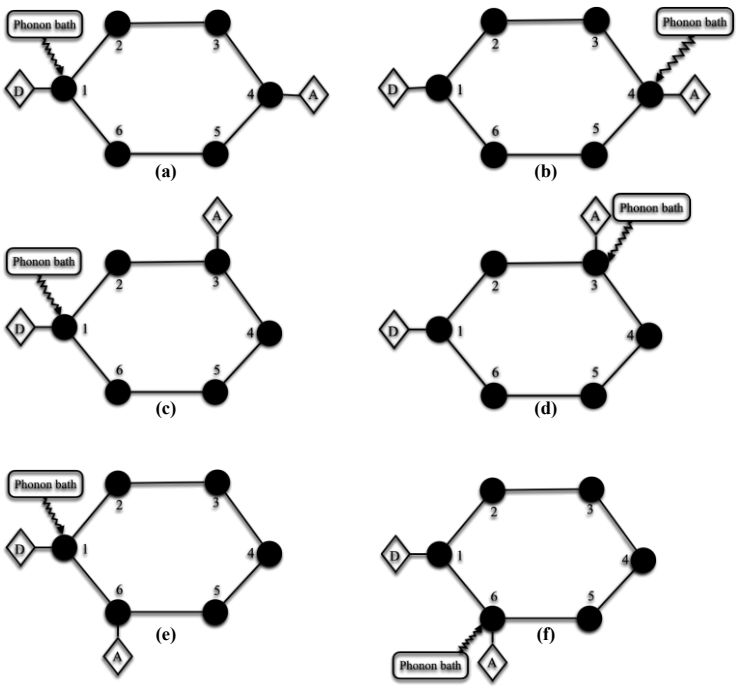

Fig. (1): Schematic illustration for the benzene shaped quantum dots-molecules in [**(a)** para-1 **(b)** para-2 **(c)** meta-1 **(d)** meta-2 **(e)** ortho-1 **(f)** ortho-2] configurations.

The Hamiltonian for the electronic part of the system is defined as:

$$\begin{aligned} H_e = & \sum_{j=1}^{6} E_j C_j^{\dagger} C_j + \sum_{\beta=D,A} E_\beta C_\beta^{\dagger} C_\beta \\ & + \sum_{j=1}^{6} \left(V_{j,j+1} C_j^{\dagger} C_{j+1} + V_{j+1,j} C_{j+1}^{\dagger} C_j \right) \\ & + \sum_{\beta=D,A} \left(V_{\beta,j} C_\beta^{\dagger} C_j + V_{j,\beta} C_j^{\dagger} C_\beta \right) \end{aligned} \quad (1)$$

where E_j denotes the on-site energy at the j-th quantum dot, and $C_j^{\dagger}, C_j$ are the creation and annihilation operators, respectively. E_β represents the energies at the donor and acceptor sites, with $V_{j,j+1}$ and $V_{j+1,j}$ indicating the couplings between adjacent quantum dots. This cyclic arrangement emulates a benzene-like structure, where the index $j+1$ returns to the first dot after the sixth, forming a closed loop.

The Hamiltonian for the phononic part is expressed as:

$$H_{ph} = \hbar\omega C_{ph}^{\dagger} C_{ph} \quad (2)$$

where $\hbar\omega$ denote to the phonon mode energy, and $C_{ph}^{\dagger}, C_{ph}$ the phonon state operators.

The interaction between the electronic and phononic states, particularly relevant for the quantum dot in the para-1 configuration, is captured by:

$$H_{e-ph} = V_{e-ph} C_1^{\dagger} C_1 \left(C_{ph}^{\dagger} + C_{ph} \right) \quad (3)$$

where V_{e-ph} signifies the strength of the electron-phonon coupling.

The dynamics of our theoretical model are governed by the Heisenberg equation of motion, which for our system is given by:

$$\frac{dC_j}{dt} = \frac{i}{\hbar} \frac{d\hat{H}}{dC_j^{\dagger}} \quad (4)$$

In the steady-state regime, where time-dependent properties stabilize, we implement a transformation of the operator coefficients to energy space. This is expressed by $C_j(E,t) = \bar{C}_j(E) e^{-i\frac{Et}{\hbar}}$, and we set the time derivatives of the phonon mode operator to zero $\left(\dot{C}_{ph} = 0\right)$. Consequently, we derive the following set of algebraic equations:

$$\left(E - E_1 + \frac{2V_{e-ph}^2 n_1}{\hbar\omega}\right) \bar{C}_1 - V_{12}\bar{C}_2 - V_{16}\bar{C}_6 - V_{1D}\bar{C}_D = 0 \quad (5)$$

$$(E - E_2)\bar{C}_2 - V_{21}\bar{C}_1 - V_{23}\bar{C}_3 = 0 \quad (6)$$

$$(E - E_3)\bar{C}_3 - V_{32}\bar{C}_2 + V_{34}\bar{C}_4 = 0 \quad (7)$$

$$(E - E_4)\bar{C}_4 - V_{43}\bar{C}_3 - V_{45}\bar{C}_5 - V_{4A}\bar{C}_A = 0 \quad (8)$$

$$(E - E_5)\bar{C}_5 - V_{54}\bar{C}_4 - V_{56}\bar{C}_6 = 0 \quad (9)$$

$$(E - E_6)\bar{C}_6 - V_{65}\bar{C}_5 - V_{61}\bar{C}_1 = 0 \quad (10)$$

$$(E - E_D)\bar{C}_D - V_{D1}\bar{C}_1 = 0 \quad (11)$$

$$(E - E_A)\bar{C}_A - V_{A4}\bar{C}_4 = 0 \quad (12)$$

These equations are conveniently represented in matrix form, which facilitates the systematic solution for eigenvalues. The matrix equation is defined as follows:

$$\begin{vmatrix} E - E_1 + \frac{2n_1 V_{e-ph}^2}{\hbar\omega} & -V_{12} & 0 & 0 & 0 & -V_{16} & -V_{D1} & 0 \\ -V_{21} & E - E_2 & -V_{23} & 0 & 0 & 0 & 0 & 0 \\ 0 & -V_{32} & E - E_3 & -V_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & -V_{43} & E - E_4 & -V_{45} & 0 & 0 & -V_{A4} \\ 0 & 0 & 0 & -V_{54} & E - E_5 & -V_{56} & 0 & 0 \\ -V_{61} & 0 & 0 & 0 & -V_{65} & E - E_6 & 0 & 0 \\ -V_{D1} & 0 & 0 & 0 & 0 & 0 & E - E_D & 0 \\ 0 & 0 & 0 & -V_{A4} & 0 & 0 & 0 & E - E_A \end{vmatrix} \begin{vmatrix} \bar{C}_1 \\ \bar{C}_2 \\ \bar{C}_3 \\ \bar{C}_4 \\ \bar{C}_5 \\ \bar{C}_6 \\ \bar{C}_D \\ \bar{C}_A \end{vmatrix} = 0 \quad ..(13)$$

By solving the (8×8) matrix equation, the energy spectrum for each configuration can be determined. The access to the energy gap would provide significant electronic properties for the most practical configuration of the three configurations that considered in our study.

We obtained the eigenvalues from a dimensional representation of the matrix in MATLAB. The well-known QR algorithm was used for that purpose [15].

3. Model Parametrization for HOMO-LUMO Gap Determination

Our first step is calculating the HOMO-LUMO gap of the fundamental three configurations in the absence of phonon bath. These results are shown in Table (1).

Table 1. HOMO-LUMO Gap Energies in Benzene Quantum Dots Molecules without Electron-Phonon Interaction

Configuration	HOMO-LUMO Gap (eV)
PARA	0.047813
META	0.80818
ORTHO	0.047791

The size of the molecular HOMO-LUMO energy gap is one of the most important features in developing mesoscopic devices. Electron-phonon interaction plays a significant role in electrical transport, thermal conductivity, and many-body phenomena. In low dimensions systems, the strength of this interaction is modified due to size effects in both electronic levels and the phonon frequencies. We have to develop a model for the strength of this interaction and understand how that model can be modified for structures vastly different from the bulk.
Our work aims to answer whether or not environmental factors have a beneficial influence on the HOMO-LUMO energy gap. We find the question especially fascinating because benzene-like quantum dots perform very well in the electrical arena. Exploring the internal workings of these dots as far as electron-phonon interactions are concerned allows us to see just how "tunable" the HOMO-LUMO gap happens to be. In the following, we will discuss how our model achieves this goal.
In our extended calculations, we found that the physical features of the para and ortho are concide, so the ortho configuration results will be not presented.
The gap is determined as a function of electron-phonon coupling across all three configurations. We consider phonon energies $\hbar\omega_{ph}$of 0.1 and 0.01 eV in Fig (2) and (3). We observe a notable increase in the HOMO-LUMO gap with the rise in V_{e-ph} values for para configuration. Conversely, the meta configuration exhibits a discernible decrease in the gap with increasing V_{e-ph}. This behavior becomes more pronounced upon adjusting the phonon energy mode, as depicted in Fig. (3). Additional investigations, shown in figures (4) and (5), explore how the offset in phonon energy affects the variation of the HOMO-LUMO gap for V_{e-ph}values of 0.4 eV and 0.04 eV, respectively. For the larger V_{e-ph} value set at 0.4 eV, the gap decreases appreciably as phonon energy is raised, with the exception of "meta" configurations. Here the HOMO-LUMO gap shrinks when the energy of a given phonon is increased, unconventionally "connecting" the dots. However, when the energy increases, the HOMO-LUMO gap in these "meta" configurations becomes almost identical to that of the original energy levels in the absence of electron-phonon coupling.

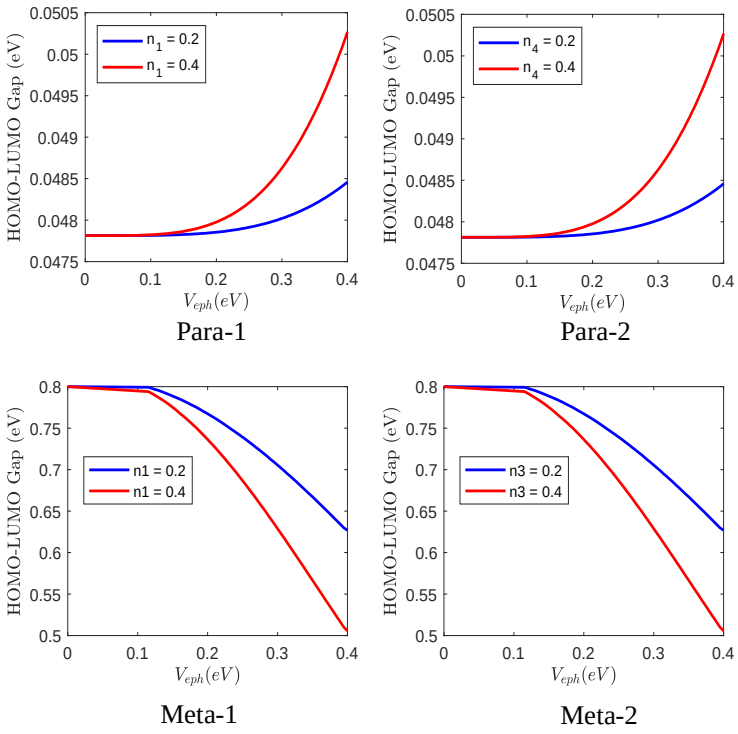

Fig. (2): Dependence of the HOMO-LUMO Gap on the Electron-Phonon Interaction Strength in Benzene Quantum Dots molecules with $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}$ and $\hbar\omega_{ph} = 0.1\text{eV}$.

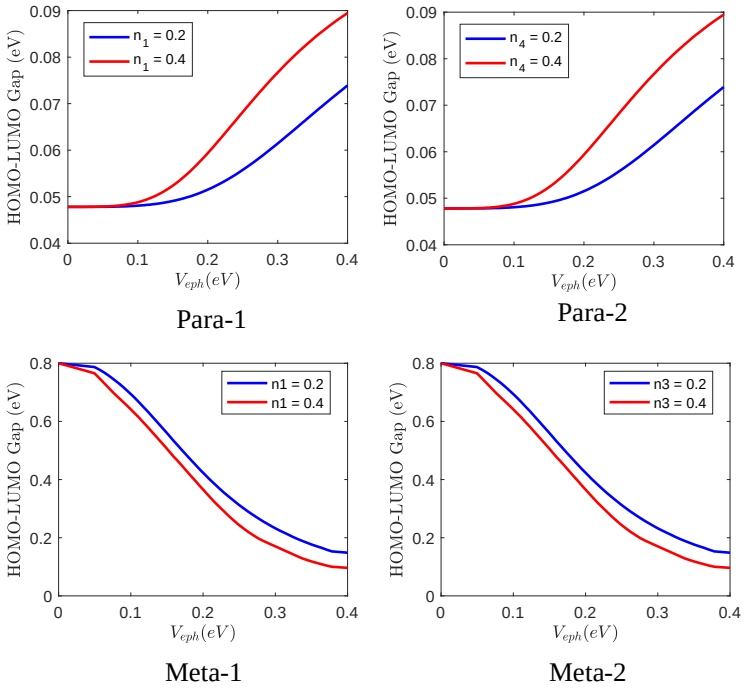

Fig. (3): Dependence of the HOMO-LUMO Gap on the Electron-Phonon Interaction Strength in Benzene Quantum Dots molecules with $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}$ and $\hbar\omega_{ph} = 0.01\text{eV}$.

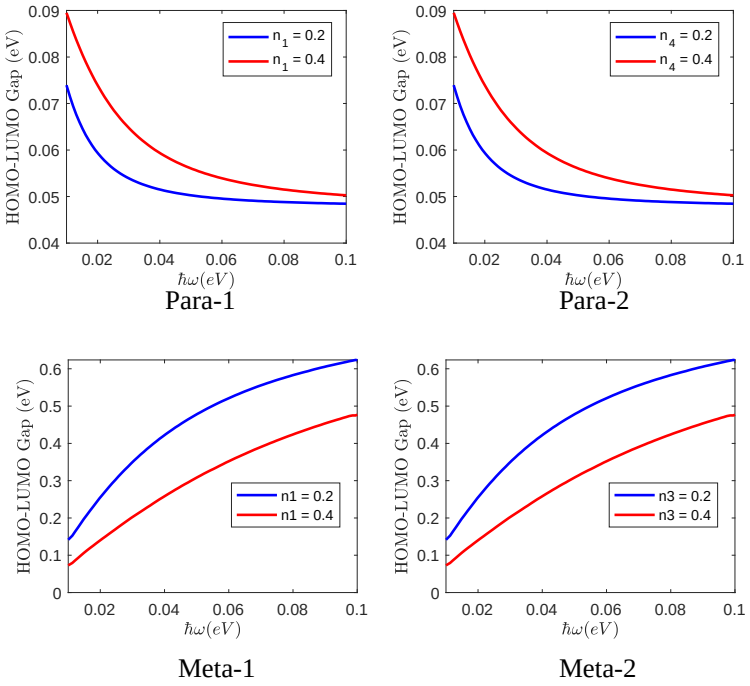

Fig. (4): HOMO-LUMO gap variation with phonon energy for benzene quantum dots molecules with $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}$, and $V_{eph} = 0.4eV$

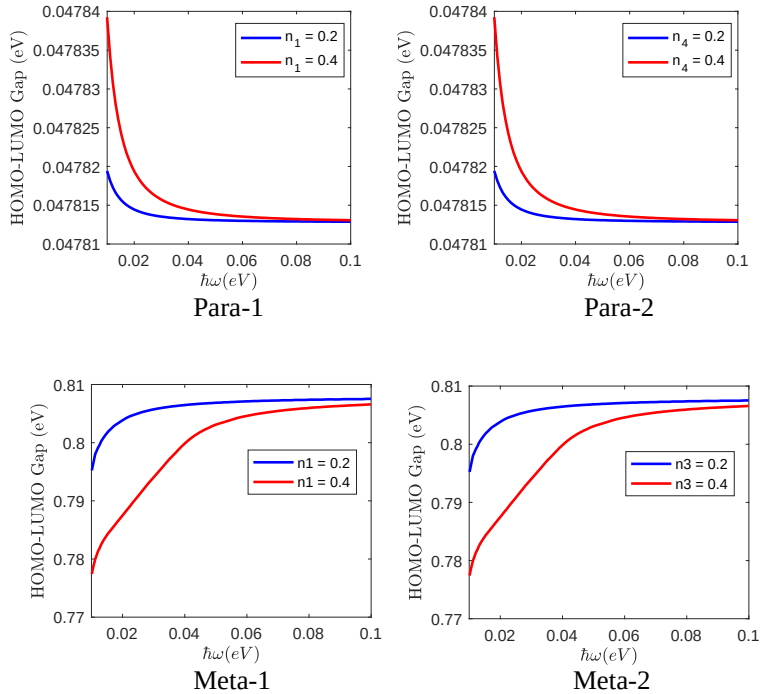

Fig. (5): HOMO-LUMO gap variation with phonon energy for benzene quantum dots molecules with $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}$, and $V_{eph} = 0.04eV$

Controlling the gap is experimentally achieved by applying gate voltage to the quantum dot that interacts with the phonon bath, as demonstrated in Figs. (6) to (7). In these illustrations, the quantum dot's occupation number, when associated with the phonon bath, dictates the energy gap values. This relationship inversely applies to meta configurations. The most significant changes in the energy gap are influenced by E_3, which can be easily adjusted in experimental settings. The electron-phonon coupling strength and the phonon mode predominantly determine these gap values. Figs. (6) and (7) highlight how the energy gap either increases or decreases as energy levels E_1, E_4, and E_3 are shifted to more positive values for para and vice versa for the meta configuration. According to Figs. (8) and (9), the position of these energy levels relative to the reference energy ($E = 0$) impacts the energy gap value. The effect of the effective energy levels of quantum contacts on the gap is also emphasized.

Notably, for high electron-phonon coupling values and when $E_{D(A)} \approx \hbar\omega_{ph}$, the energy gap mirrors its value in the absence of any environmental effects, as shown in Figs. (10) and (11). The dependency of the energy gap on occupation numbers (n_i, for $i = 1,4,3$) remains symmetrical across all configurations. When $E_{D(A)} > \hbar\omega_{ph}$, the HOMO-LUMO gap sustains a constant value for all configurations, although it reduces as the phonon energy decreases. Contrary, when $E_{D(A)} < 0$, we observe a different tendency: the energy gap increases (or decreases) with $|E_{D(A)}|$ in para and meta configurations. In terms of electron-phonon coupling, the occupation numbers, particularly at $\hbar\omega_{ph} = 0.1$eV, do not show any significant effect (Figs. (12) and (13)).

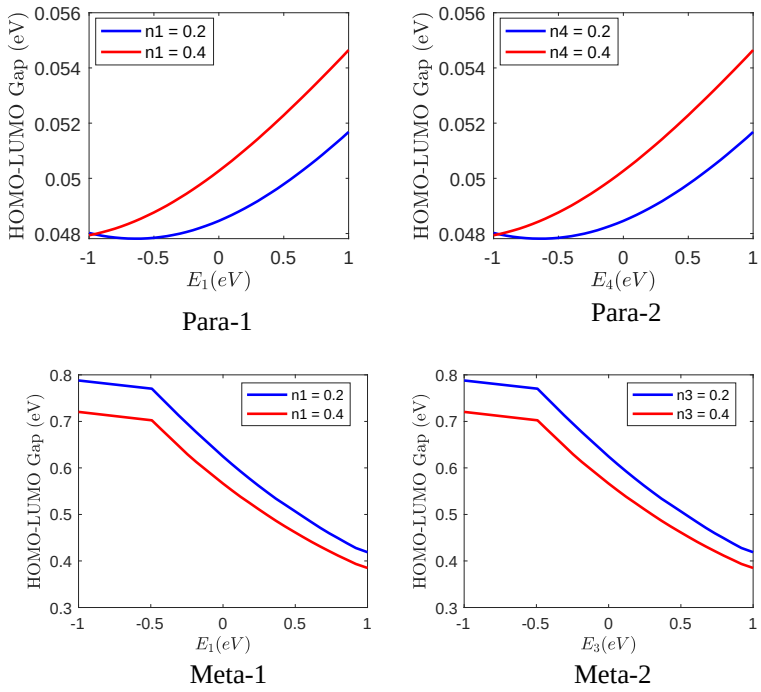

Fig. (6): correlation between the HOMO-LUMO gap and quantum dots energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.4eV$, and $\hbar\omega_{ph} = 0.1\text{eV}$

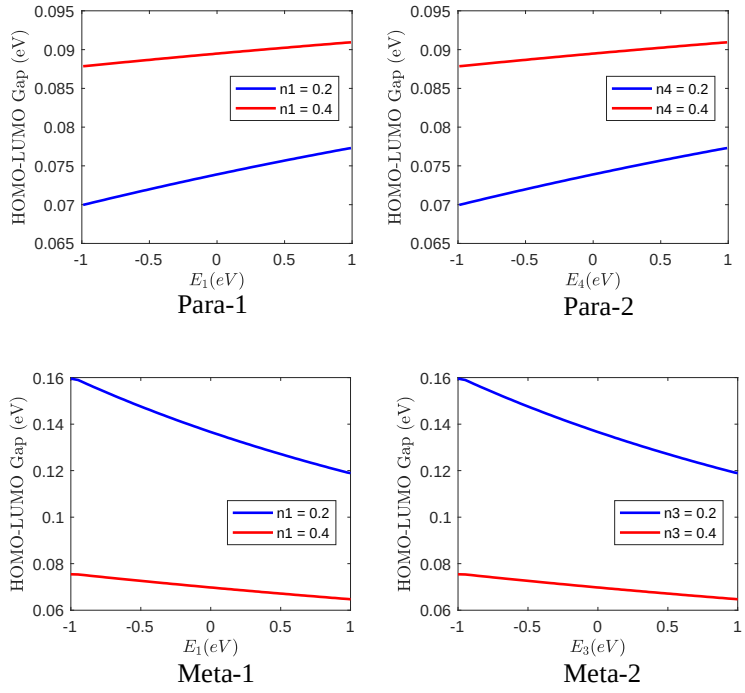

Fig. (7): correlation between the HOMO-LUMO gap and quantum dots energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.4eV$, and $\hbar\omega_{ph} = 0.01\text{eV}$

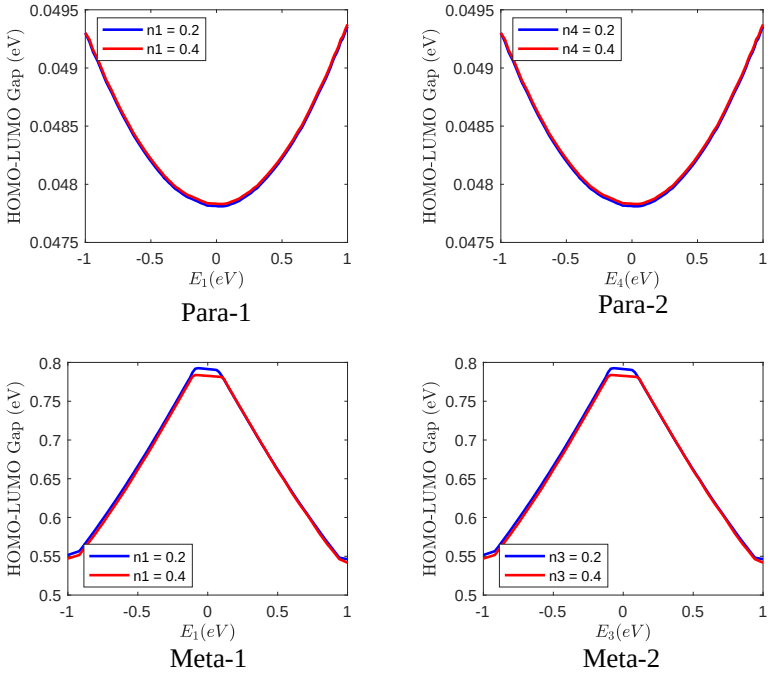

Fig. (8): correlation between the HOMO-LUMO gap and quantum dots energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.04eV$, and $\hbar\omega_{ph} = 0.1\text{eV}$

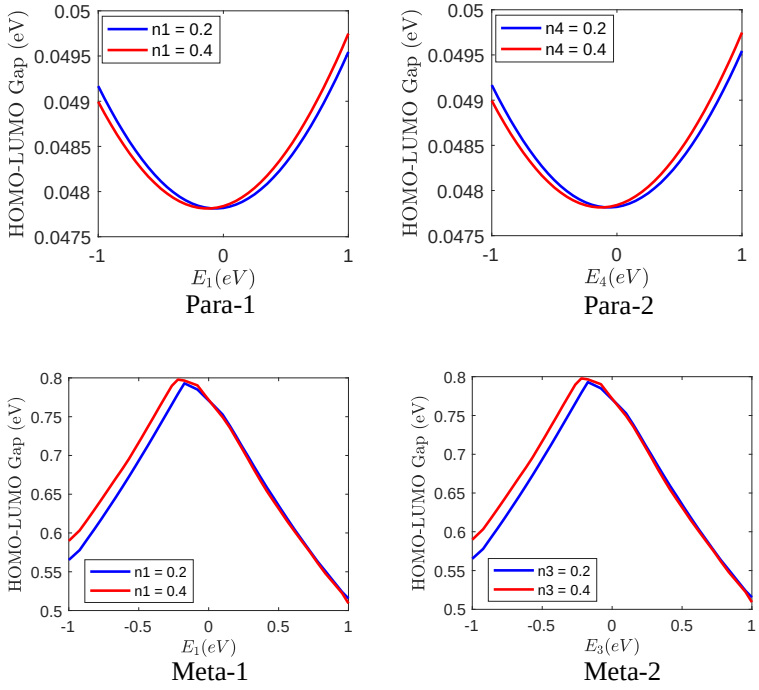

Fig. (9): correlation between the HOMO-LUMO gap and quantum dots energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.04eV$, and $\hbar\omega_{ph} = 0.01\text{eV}$

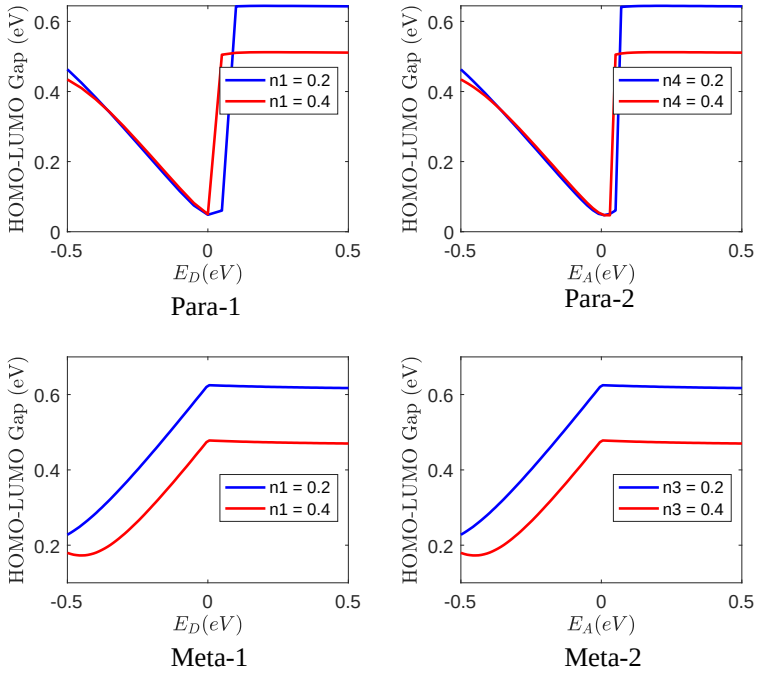

Fig. (10): correlation between the HOMO-LUMO gap and quantum contact energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.4eV$, and $\hbar\omega_{ph} = 0.1\text{eV}$

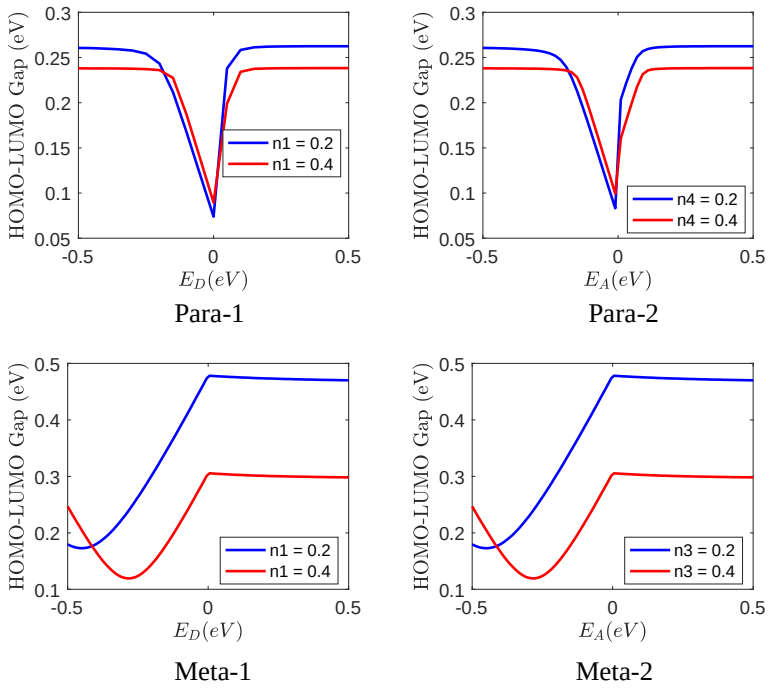

Fig. (11): correlation between the HOMO-LUMO gap and quantum contact energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.4eV$, and $\hbar\omega_{ph} = 0.01\text{eV}$

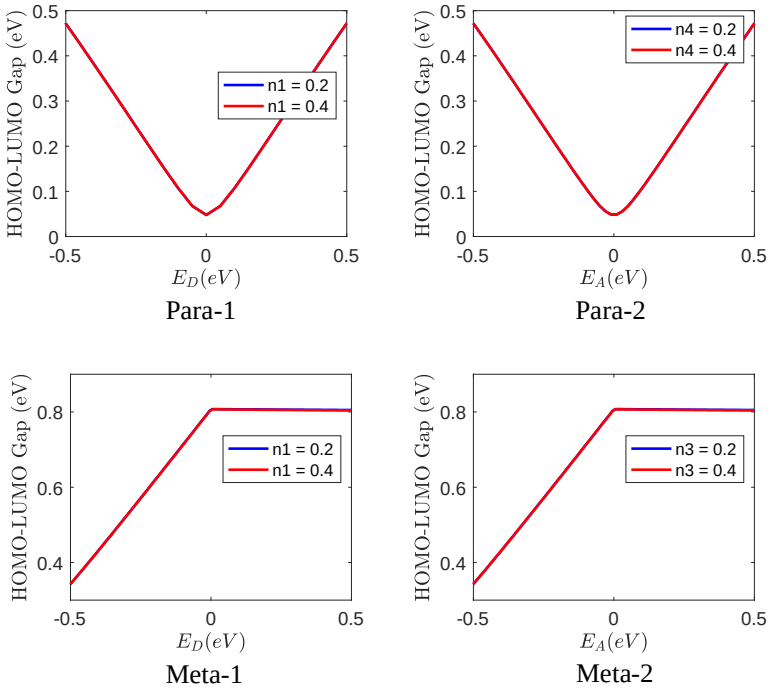

Fig. (12): correlation between the HOMO-LUMO gap and quantum contact energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.04eV$, and $\hbar\omega_{ph} = 0.1\text{eV}$

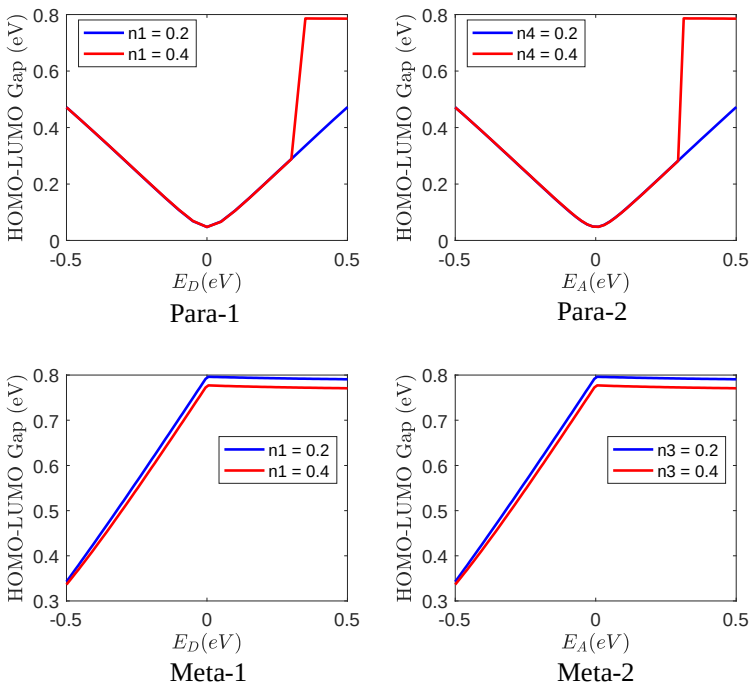

Fig. (13): correlation between the HOMO-LUMO gap and quantum contact energy levels in the presence of phonon path for benzene quantum dots molecules at $E_i = 0, V_{ij} = 0.8\text{eV}, V_{i\beta} = 0.2\text{eV}, V_{eph} = 0.04eV$, and $\hbar\omega_{ph} = 0.01\text{eV}$

4. Conclusions

To sum up, our investigation reveals the significance of electron-phonon interactions in the state of the-art parameterization of the energy difference between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap) within quantum dots of a benzene-like geometry. The tunability of the HOMO-LUMO gap, in that bifurcating interaction between electrons and phonons, was pushed to the limit and varied in its effect on the energy levels by applying different coupling strengths and energy settings. The role of the gate voltage and its effect on the energy gap was also explained and clarified.
The para and meta configurations have clear and separated reactions to phonon energy، the coupling strength and gate voltage. These situations are specific to the molecular structure and provide very enlightening knowledge about the way of the energy band varying in these systems. Finally, we hope that our study will contribute to increasing understanding of the behavior of nanosystems under the influence of environmental effects on electronic properties. The purpose is to obtain highly efficient nanodevices for various applications.

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تأثير اقتران الكترون-فونون على فجوة الطاقة لجزيئة نقاط كمية شبيهة بحلقة البنزين.

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معلومات البحث

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الكلمات المفتاحية

نقاط كمية، جزيئة البنزين، تفاعلات الكترون - فونون، فجوة الطاقة.

الملخص

في هذه الدراسة، قمنا باشتقاق انموذج نظري لدراسة تأثير اقتران الكترون-فونون على فجوة الطاقة بين المستويات HOMO-LUMO في جزيئة صناعية مكونة من ست نقاط الكمية ذات شكل هندسي يشبه حلقة البنزين، حيث تم دراسة ثلاث توزيعات مختلفة لحلقة البنزين (بارا، ميتا، و اورثو) اعتمادا على موقع الذرة المانحة والمستقبلة، وكذلك تم الاخذ بنظر الاعتبار تاثير مواقع مختلفة للحمام الفونوني. تم توضيح نموذجنا، من خلال نهج هاميلتوني شامل ومحكم، يحدد ديناميكيات الحالات الإلكترونية و الفونونية داخل هذه الأنظمة الكمية. أوضحت النتائج التي تم الحصول عليها الدور الهام لمعاملات الفونون في تعديل الخواص الإلكترونية للجزيئات. واستنادا الى هذه النتائج لاحظنا انه يمكن التعامل مع قوة اقتران الكترون-فونون وطاقة الفونون لتعديل فجوة الطاقة، مما يوفر طرقًا واعدة لتطوير تطبيقات الإلكترونيات النانوية المتقدمة.

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