DYNAMICAL ANALYSIS OF ELECTRON-PHONON INTERACTIONS IN QUANTUM DOT MOLECULAR SYSTEMS

ANÁLISIS DINÁMICO DE LAS INTERACCIONES ELECTRÓN-FONÓN EN SISTEMAS MOLECULARES DE PUNTOS CUÁNTICOS

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Abstract

Theoretically, we analyze the effect of electron-phonon interaction in the dynamics of an electron trapped in a benzene-shaped quantum dots-molecule. The molecule consists of six small quantum dots coupled locally to a phonon bath. The tight binding model is used to write the model Hamiltonian and to derive the set of equations of motion of different types of benzene quantum dots-molecules. The time-dependent model has a numerically exact solution producing rich dynamics. The values of time-dependent occupations strongly depend on the electron-phonon coupling. A notable result of the present work is that one can tune the energy levels of quantum dots, the quantum contacts energy levels, and the benzene quantum dots-molecule configuration to enhance or diminish the heat flow between electrons and phonons in molecular junctions. This study contributes to the dynamic and expanding field of quantum dot molecular systems, providing insights for broader technological applications.

Keywords: quantum dot molecule, electron-phonon coupling, quantum state occupancies, electron transfer, benzene-shaped structures.

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Resumen

Teóricamente, analizamos el efecto de la interacción electrón-fonón en la dinámica de un electrón atrapado en una molécula de puntos cuánticos con forma de benceno. La molécula está compuesta por seis pequeños puntos cuánticos acoplados localmente a un baño de fonones. Se utiliza el modelo de unión fuerte para escribir el Hamiltoniano del modelo y para derivar el conjunto de ecuaciones de movimiento de diferentes tipos de moléculas de puntos cuánticos de benceno. El modelo dependiente del tiempo proporciona una solución numéricamente exacta, revelando una dinámica compleja. Los valores de ocupación dependientes del tiempo dependen considerablemente del acoplamiento electrón-fonón. Un hallazgo notable de este estudio es la posibilidad de ajustar los niveles de energía de los puntos cuánticos, los contactos cuánticos y la configuración de la molécula de puntos cuánticos de benceno para modular el flujo de calor entre electrones y fonones en uniones moleculares. Este estudio contribuye al campo en expansión de los sistemas moleculares de puntos cuánticos, proporcionando ideas para aplicaciones tecnológicas más amplias.

Palabras clave: molécula de puntos cuánticos, acoplamiento electrón-fonón, ocupaciones de estados cuánticos, transferencia de electrones, estructuras de forma benceno.

Introduction

In the rapidly growing field of molecular electronics, the focus has shifted toward using individual atoms or molecules to create electronic devices, marking the beginning of a new era in device miniaturization and functionality [1]. This approach has generated a keen interest in understanding the complex electronic properties of these devices, where interactions may arise from electron-electron, electron-phonon, and ion-ion dynamics, as well as electron hopping between orbitals [2]. The effort to build innovative nanoelectronic devices has resulted in the development of molecular electronic transistors, quantum wires, rectifiers, switches, and storage devices, all characterized by their transmission probabilities, I-V characteristic curves, thermal transport properties, and tunnel magnetoresistance, among other features [3].

Particularly, semiconductor quantum dots (QDs) have become a significant focus due to their wide range of applications, from nanojunctions to quantum information processing [4]. This growing interest is partially due to the crucial role of electron transfer within molecules, a fundamental phenomenon in chemical, electrochemical, and biological processes. Recent advances allow for the detailed study of electron movement within individual molecules, enhancing our understanding of molecular dynamics [5, 6].

The field of quantum electronics, which includes both molecular systems and artificial constructs like QDs, is a natural extension of the trend toward electronic device miniaturization [7]. This movement promises to increase computing power and reduce costs while revealing the rich physics of these systems, including phenomena like the Kondo effect, Fano resonance, Coulomb blockade, and Aharonov-Bohm oscillations [8].

Recent advancements in nanofabrication enable the precise creation of QD structures and the detailed study of electron transport mechanisms. Additionally, manipulating electrical properties in molecular rings opens new paths for innovative structures in scientific applications, emphasizing the importance of electron transfer between molecular systems—a key concept in chemistry, physics, and biology, as described by Marcus theory and its applications to molecular electronics [9]. Understanding electron-phonon coupling is crucial for comprehending various phenomena in physics, where recent theoretical efforts address the challenges of charge qubit decoherence in double-dot systems caused by electron-phonon interactions [10].

Our study will examine two-terminal systems consisting of linkers (donor and acceptor) and central quantum dots-molecules. The choice of the donor and acceptor, which are connected to the active region, are regarded as quantum contacts. This involves exploring various geometrical structures of donor-quantum dots benzene molecules-acceptor configurations. The benzene quantum dots-molecule is designed with a hexagonal ring, consisting of six quantum dots. The phonon bath is locally coupled to a single quantum dot. Three configurations of the benzene-shaped quantum dots-molecule—para, meta, and ortho—will be examined and studied. Figure (1) illustrates all the configurations and cases of phonon bath connection sites that are considered in our study.

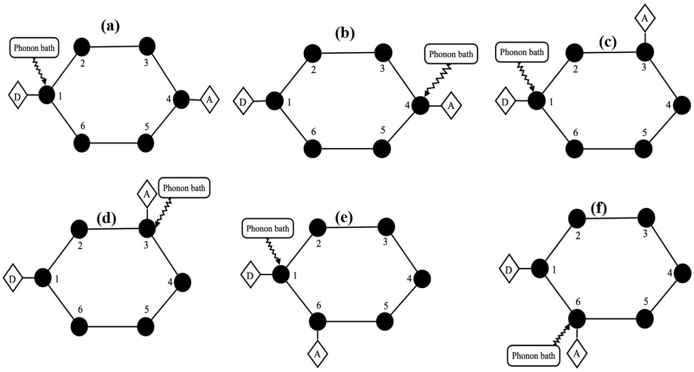


FIGURE 1. *Schematic illustration for the benzene shaped quantum dots-molecules in [(*a) para-1 (b) para-2 (c) meta-1 (d) meta-2 (e) ortho-1 (f) ortho-2] configurations.

Theoretical framework

The dynamical features of our quantum dot systems are mathematically encapsulated by the tight-binding model. The Hamiltonian of our system is divided into three essential components: the electronic, phononic, and electron-phonon interaction Hamiltonians. These three components are combined in the total Hamiltonian of our quantum dot system, represented as:

$$H = H_e + H_{ph} + H_{e-ph} \tag{1}$$

By delving into the holistic Hamiltonian, we aim to extract the complex dynamics underlying the interaction between electrons and phonons within our quantum dots system. The electronic component of the Hamiltonian, expressed in terms of various variables, considers the energy states of the quantum dots along with those of the donor and the acceptor, as well as the coupling interactions among these entities.

$$\begin{aligned} H_\mathrm{e} = & \sum_{i=1}^{6} E_i C_i^\dagger C_i + \sum_{\beta=D,A} E_\beta C_\beta^\dagger C_\beta \\ & + \sum_{i=1}^{6} \left(V_{i,i+1} C_i^\dagger C_{i+1} + V_{i+1,i} C_{i+1}^\dagger C_i \right) \\ & + \sum_{\beta=D,A} \left(V_{\beta i} C_\beta^\dagger C_i + V_{i\beta} C_i^\dagger C_\beta \right) \end{aligned} \tag{2}$$

Within this framework, E_i represents the on-site energy of the i-th quantum dot within the benzene-shaped quantum dots ring. The creation and annihilation operators for these dots are represented by $C_i^\dagger$ and C_i, respectively. Similarly, E_β denotes the on-site energies for the donor (D) and acceptor (A) sites, with their respective creation and annihilation operators given by $C_\beta^\dagger$ and C_β. The term $V_{i,i+1}$ and its harmonic conjugate $V_{i+1,i}$ describe the coupling between adjacent quantum dots. In the context of our benzene-shaped configuration, which comprises six quantum dots, it is important to note that the index $i+1$ in the coupling terms is considered cyclic. This implies that for the sixth quantum dot (where $i = 6$), the $i+1$ term effectively refers back to the first quantum dot, thereby ensuring a closed-loop configuration consistent with the benzene-shaped structure. Additionally, the coupling interactions between the donor and acceptor sites and specific quantum dots in the ring are efficiently encapsulated by the terms $V_{i\beta}$ and $V_{\beta i}$.
The energy related to phonons, or the quantized pattern of lattice vibrations, is quantified by the phonon Hamiltonian H_ph it is described as follows:

$$H_\mathrm{ph} = \hbar\omega C_\mathrm{ph}^\dagger C_\mathrm{ph} \tag{3}$$

$\hbar$ represents the reduced Planck's constant, ω symbolizes the phonon frequency and the creation and annihilation operators for the phonon state are denoted by $C_\mathrm{ph}^\dagger$ and C_ph respectively. The Hamiltonian for the electron-phonon interaction, $H_\text{e-ph}$, represents the coupling between the electronic and phononic states. In our model, we assume that this interaction is dominant only on quantum dot number 1 for the para-1 configuration. It can be expressed as:

$$H_{\text{e-ph}} = V_{\text{e-ph}} C_1^\dagger C_1 \left(C_{\text{ph}}^\dagger + C_{\text{ph}} \right) \tag{4}$$

where $V_{\text{e-ph}}$ represents the electron-phonon interaction strength. Likewise, as shown in Figure (2-2), every alternate configuration Hamiltonian has been methodically created to reflect the distinct electronic properties associated to these systems. Based on the foundation of the Heisenberg equation and with our system's Hamiltonian established, we can understand the temporal evolution of all components in our quantum dot system. The equations of motion for each component, derived using the Heisenberg equation, are presented as follows, for quantum dot 1 when it is coupled to the phonon bath:

$$\dot{C}_1 = \frac{-i}{\hbar} \left(E_1 C_1 + V_{D1} C_D + V_{12} C_2 + V_{16} C_6 + V_{\text{e-ph}} C_1 \left(C_{\text{ph}} + C_{\text{ph}}^\dagger \right) \right) \tag{5}$$

for the other quantum dots.

$$\dot{C}_2 = \frac{-i}{\hbar} \left(E_2 C_2 + V_{21} C_1 + V_{23} C_3 \right) \tag{6}$$

$$\dot{C}_3 = \frac{-i}{\hbar} \left(E_3 C_3 + V_{32} C_2 + V_{34} C_4 \right) \tag{7}$$

$$\dot{C}_4 = \frac{-i}{\hbar} \left(E_4 C_4 + V_{A4} C_A + V_{43} C_3 + V_{45} C_5 \right) \tag{8}$$

$$\dot{C}_5 = \frac{-i}{\hbar} \left(E_5 C_5 + V_{54} C_4 + V_{56} C_6 \right) \tag{9}$$

$$\dot{C}_6 = \frac{-i}{\hbar} \left(E_6 C_6 + V_{61} C_1 + V_{65} C_5 \right) \tag{10}$$

for the quantum contacts.

$$\dot{C}_D = \frac{-i}{\hbar} \left(E_D C_D + V_{D1} C_1 \right) \tag{11}$$

$$\dot{C}_A = \frac{-i}{\hbar} \left(E_A C_A + V_{A4} C_4 \right) \tag{12}$$

And for the phonon subsystem.

$$\dot{C}_{\text{ph}} = \frac{-i}{\hbar}\left(\hbar\omega C_{\text{ph}} + V_{\text{e-ph}} C_1^{\dagger} C_1\right) \tag{13}$$

Our numerical simulations to examine the behavior of the system under various conditions will be based on these equations. Notably, a set of equations of motion is derived for each geometry presented in Figure 1.

Computational Analysis

The present manuscript describes the dynamic effects of dissipation by a phononic bath for a benzene-type molecule. For this, the coupled system of equations is analyzed, and the effects of these dynamics on the thermodynamics of the system are described. It involves resolving the system's equations of motion using the MATLAB language and the Runge-Kutta numerical method. Initial states and key parameters are defined, with a focus on electron-phonon interactions.

The solutions obtained through this method provide a comprehensive representation of the time evolution of each component in the system. Further processing of these solutions computes the occupation numbers (n_1 to n_6) associated with the six quantum dots $n_i = C_i^{\dagger} C_i$ ($i = 1 \to 6$), the phonon population count $n_{\text{ph}} = C_{\text{ph}}^{\dagger} C_{\text{ph}}$, and the donor and acceptor occupation numbers $n_{\beta} = C_{\beta}^{\dagger} C_{\beta}$. These values essentially indicate the likelihood of finding an electron at each site and the quantity of phonons present at any given time. These occupation numbers, along with the phonon count, are graphically plotted versus time to give a thorough insight into the state of the system. This graph illustrates the time evolution of the quantum dot system and highlights the dynamics of the electron transfer process, as well as the role of electron-phonon coupling in the system.

In the initial step of our calculations, specific parameters were chosen: the coupling between any two tightly bound quantum dots, V_{ij}, is fixed at 0.8 eV. The interaction coupling between the molecule and quantum contacts (donor and acceptor), $V_{i\beta}$, is set to 0.2 eV, where $i = 1(4)$ and $\beta = D(A)$ for para-1 configurations. Meanwhile, the electron-phonon coupling, $V_{\text{e-ph}}$, is fixed at 0.4 eV; i.e., $V_{i\beta} < V_{\text{e-ph}} < V_{ij}$. All energy levels of the dots and quantum contacts, (E_i and E_{β}), are controlled by a gate voltage to be at 0 eV, while $\hbar\omega_{\text{ph}} = 0.1$ eV. The occupation numbers of the six quantum dots, n_i (for $i = 1, \ldots, 6$) and n_{β} (where $\beta = D, A$), are calculated as a function of time.

These calculations are crucial as they provide a clear understanding of the charge transfer in the quantum dots-molecule from donor to acceptor. Furthermore, we also focus on the phonon bath parameters, specifically the phonon number, n_{ph}, and the heat flow between electrons and phonons, Q, which will be presented in detail. Our calculations cover all cases of molecule diagrams displayed in Fig. (1). The results are shown in Fig. 2 (a-f) as a function of time. Notably, the occupation numbers of the six quantum dots are not shown in these figures.

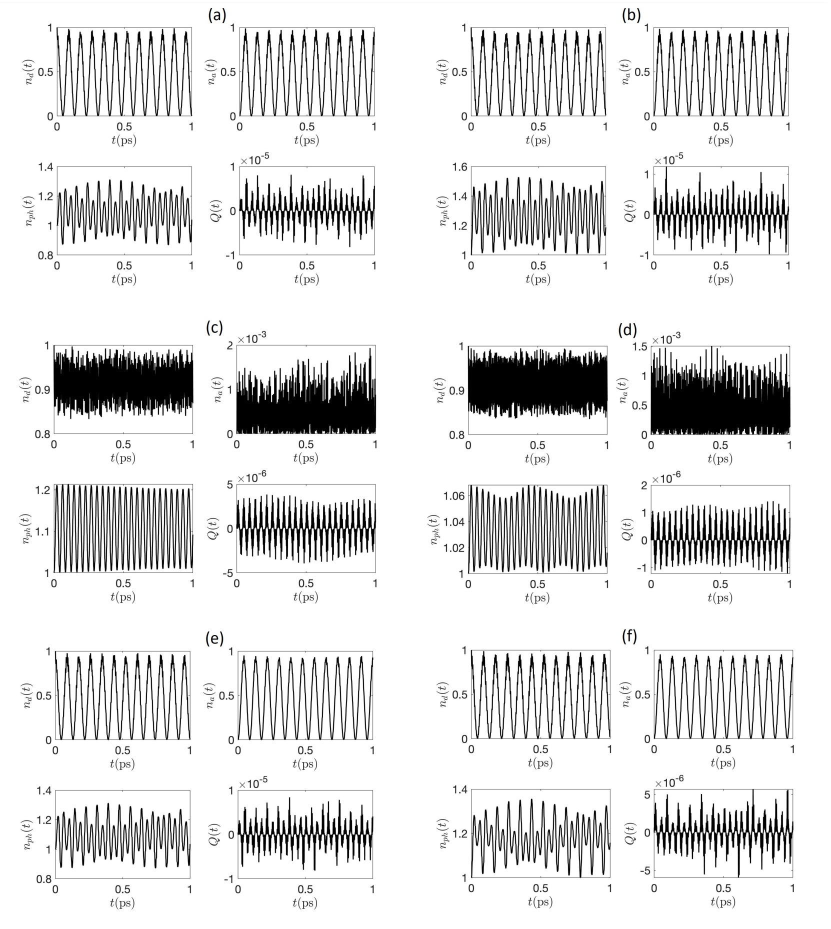


FIGURE 2. *The occupation numbers of the quantum contacts, as well as the phonon number and heat flow as a function of time for [(**a**) para-1, (**b**) para-2, (**c**) meta-1, (**d**) meta-2, (**e**) ortho-1, (**f**) ortho-2] quantum dots-molecules with* $V_{ij} = 0.8\,eV, V_{i\beta} = 0.2\,eV, E_i = 0,$ *and* $\hbar\omega_{ph} = 0.1\,eV$.

Based on the data presented in these figures, we can deduce several important physical features for the para-1, para-2, meta-1, meta-2, ortho-1, and ortho-2 molecules. The occupation numbers of the dots and quantum contacts in these benzene-shaped molecules exhibit consistent behavior over time, as illustrated in Figure 2. These occupation numbers, particularly for the donor and acceptor, highlight the phenomenon of single-electron transfer. Interestingly, in these figures, the sites where the phonon bath is coupled do not demonstrate a significant role. A different behavior is observed in Figures (2c) and (2d), where the electron charge accumulates on the donor, yet no charge transfer to the acceptor occurs.

Regarding the phonon number, it remains relatively similar across all these quantum dot molecules. However, the heat flow between electrons and phonons, which may result from either the emission or absorption of phonons, shows notably higher values for the meta-1 and ortho-2 molecules. Given these observations for this specific set of parameters, it is advisable to exclude meta-1 and ortho-2 quantum dot molecules to avoid excessive heat flow between electrons and phonons.

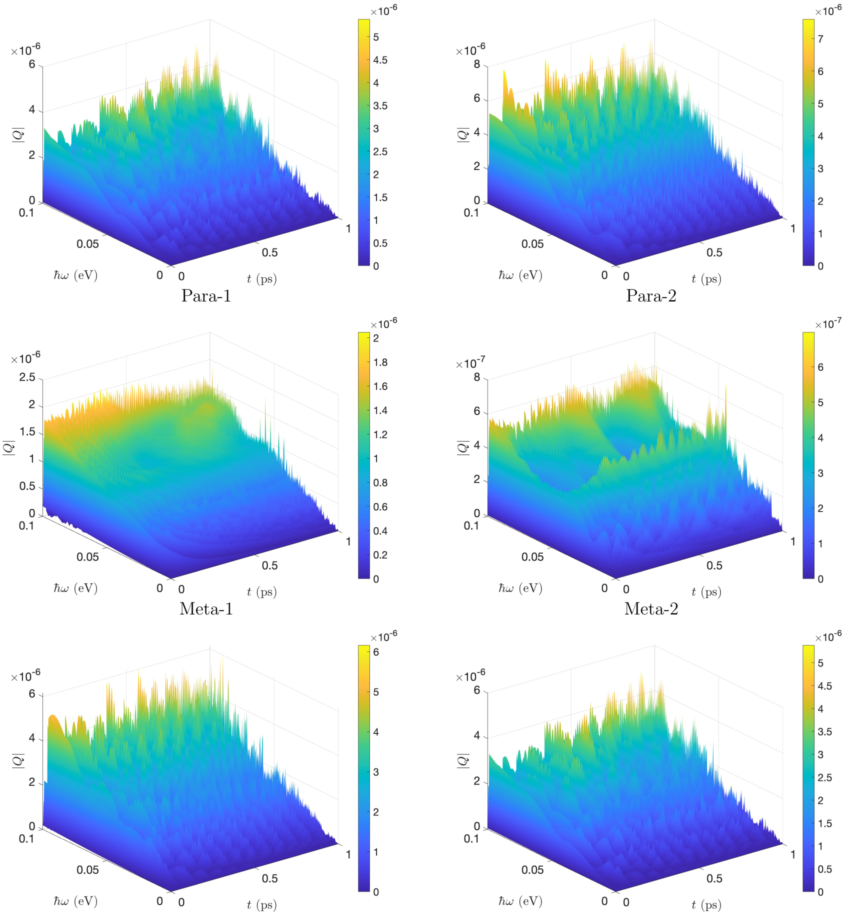
Experimentally, the gate voltage coupled to any site in the molecular junction is considered the most important factor to dominate the molecular electronics features of the device [11]. The role of gate voltage linked to molecular sites that are coupled to the phonon bath (i.e., E_1 in the case of para-1, ortho-1, and meta-quantum dot molecules; and E_4, E_6, and E_3 in the case of para-2, ortho-2, and meta-2 quantum dot molecules, respectively) is investigated but not introduced where $V_{\text{e-ph}} = 0.4\,\text{eV}$ and $\hbar\omega_{\text{ph}} = 0.1\,\text{eV}$. In general, the phonon number is relatively small, and it increases for $0 < E_1 < 2\,\text{eV}$ for para-1, ortho-1, and meta-1 quantum dot molecules, as well as for para-2 and ortho-2 molecules when $0 < E_4 < 2\,\text{eV}$ and $0 < E_6 < 2\,\text{eV}$, respectively. In meta-2 quantum dot molecules, the phonon number increases when $-1\,\text{eV} < E_3 < 2\,\text{eV}$. The gate voltage may also link to the donor for type-1 quantum dot molecules and to the acceptor for type-2 quantum dot molecules. Our results show a definite physical feature confirming that the phonon number significantly increases for $-2\,\text{eV} < E_D < -1\,\text{eV}$ in type-1 quantum dot molecules. No role can be noticed for the cases of type-2 molecules.

Understanding the underlying processes that control the efficiency and functionality of nanoelectronics and molecular junction devices requires a thorough understanding of the microscopic heat transfer mechanisms within these devices [12]. The primary source of heating in these devices is the intricate dynamics of inelastic scattering, namely electron-electron and electron-phonon interactions. Through interaction to electron reservoirs and phononic environments, these interactions play a crucial role in the energy exchange processes that take place between the nanostructured system and its surroundings.

Regarding systems like quantum dots and molecular junction devices interfaced with electron reservoirs, the phenomenon of quantized energy transport—in which phonons function as discrete quanta of energy—represents an important theoretical prediction within the field of quantum mechanics. Understanding heat transfer at the quantum level has been made possible by theoretical frameworks that predict quantized flow of energy via phonons, and these predictions have been validated by thorough experimental research [13]. Notably, these microscopic models of heat transfer have been empirically supported by experiments showing quantized heat flow in systems such as quantum wells coupled to electron reservoirs. Furthermore, the investigation of local heating effects caused by current, as demonstrated by Huang et al. [14, 15] on single molecules, underscores the intricate relationship between electronic excitation and phononic heat dissipation in molecular junction devices.

To quantitatively analyze the heat flow dynamics between electrons and phonons in these advanced devices, $Q(t) = \hbar\omega_{\text{ph}}\frac{dn_{\text{ph}}}{dt}$ is calculated and investigated. This relation highlights the significant role of phonons in mediating energy exchange between the electronic and vibrational states of nanoelectronics and molecular junction devices, providing a foundation for understanding the microscopic mechanism of heat transfer. In Figure (3), our findings are elaborated upon by presenting the behavior of heat flow as a function of time and phonon energy for electron-phonon coupling strengths of $V_{\text{e-ph}} = 0.4\,\text{eV}$. It is important to highlight that the relationship between phonon numbers and their energy diverges from the correlation between heat flow and phonon energy. This distinction emphasizes that heat flow is decisively influenced by electron-phonon interactions, with para-2 and meta-2 quantum dot molecules consistently exhibiting the maximum and minimum heat flow values, respectively.

Further scrutiny, as depicted in Figure (4), establishes a linkage between the energy level E_1 and the gate voltage for type-1 quantum dot molecules, which notably enhances the heat flow within the energy range of $-1\,\text{eV} < E_1 < 1\,\text{eV}$. On the contrary, the minimum heat flow values for type-2 quantum dot molecules are observed within the energy range of $-1\,\mathrm{eV} < E_i < 0$ (where $i = 4, 3, 6$ corresponds to para-2, meta-2, and ortho-2 benzene-shaped molecules, respectively). As demonstrated in Figure (5), adjusting the gate voltage in relation to the donor or the acceptor can substantially diminish the heat flow in both type-1 and type-2 quantum dot molecules, respectively.

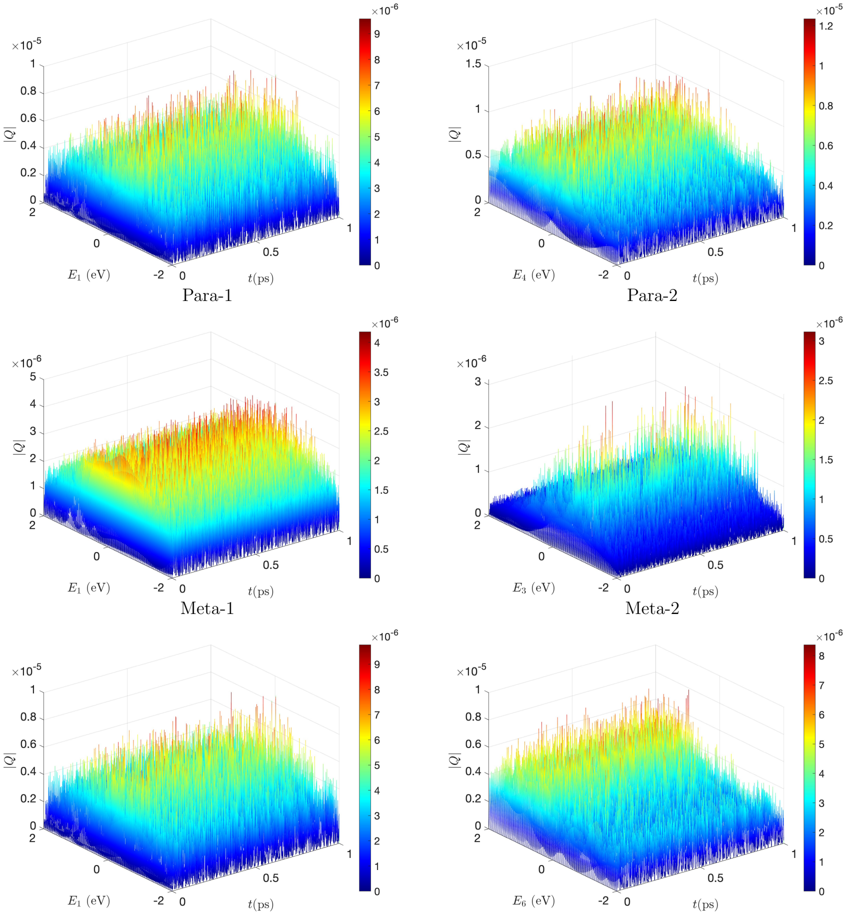


Para-1 Para-2

Meta-1 Meta-2

Ortho-1 Ortho-2

FIGURE 3. *Heat flow as a function of time and $\hbar\omega_{ph}$ when $V_{e\text{-}ph} = 0.4\ eV$ for para, meta, and ortho-quantum dots molecules when $V_{ij} = 0.8\ eV$, $V_{i\beta} = 0.2\ eV$.*



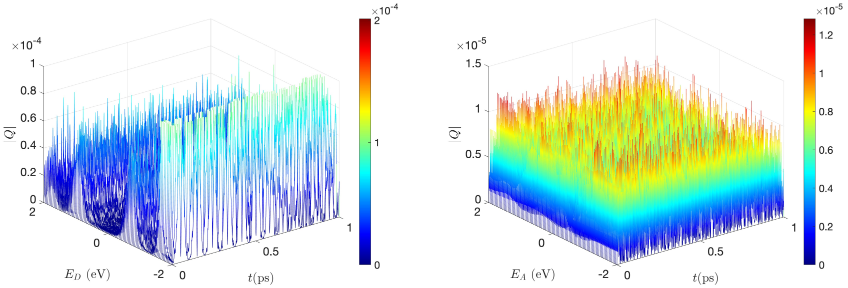
Para-1 Para-2

Meta-1 Meta-2

Ortho-1 Ortho-2

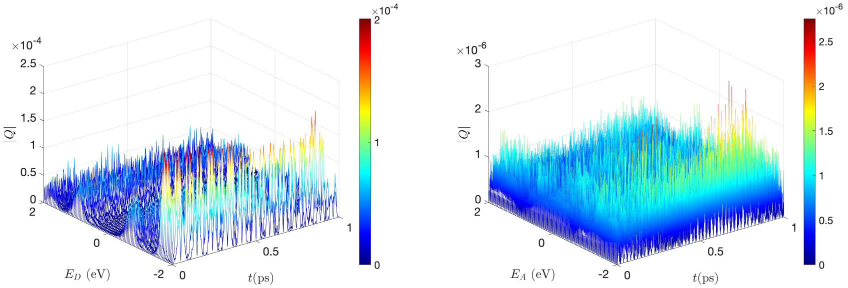
FIGURE 4. *Heat flow as a function of time and gate voltage coupled to E_i when $V_{e\text{-}ph} = 0.4\,eV$, $\hbar\omega_{ph} = 0.1\,eV$ for para, meta, and ortho-quantum dot molecules when $V_{ij} = 0.8\,eV$, $V_{i\beta} = 0.2\,eV$.*

Finally, we must write down our observations about the quantum transfer of charge through the six systems presented in our study. Without the influence of electron-phonon interaction, it is expected that the calculated results for the para configuration differ from the meta and ortho configurations, because only in the para configuration there are two symmetrical channels for the electron to reach the acceptor, while for the meta and ortho configurations, the two channels for the electron to reach the acceptor are asymmetrical. In the presence of



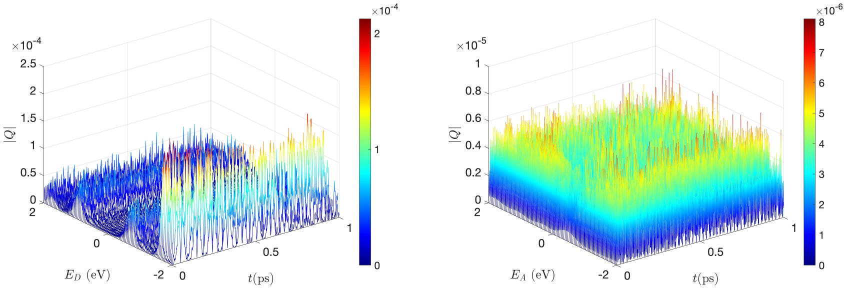
Para-1

Para-2



Meta-1

Meta-2



Ortho-1

Ortho-2

FIGURE 5. *Heat flow as a function of time and gate voltage coupled to* E_β *when* $V_{e\text{-}ph} = 0.4\,eV$, $\hbar\omega_{ph} = 0.1\,eV$ *for para, meta, and ortho-quantum dot molecules when* $V_{ij} = 0.8\,eV$, $V_{i\beta} = 0.2\,eV$.

electron-phonon interaction, the environmental effects play a role in determining the results, in addition to quantum interference effects due to the symmetry or asymmetry of the electron access channels to the acceptor, as is evident from our calculations. These observations will be highlighted extensively in the future to calculate the transmission coefficient and transport characteristics for the whole systems.

Conclusion

In conclusion, the obtained results are a contribution to the understanding of electron-phonon interaction in benzene-shaped quantum dots molecules and its influence on electron transfer dynamics. A model that estimates basic parameters of the population evolutions of both electrons and phonons clearly expresses the nature of the most pronounced processes in the dynamics of phonons and electron-phonon coupling, using the MATLAB language and Runge-Kutta. These results indicate the importance of appropriate selection of quantum dot molecules for minimizing these undesired thermal effects, and further that manipulation of the gate voltage is of utmost importance in controlling molecular electronics. This study suggests that tuning the energy level is crucial to control the thermal energy for proper performance and efficiency in quantum dot applications. As such, it contributes to the understanding of the dynamics of quantum dot systems and demonstrates the power of computational approaches in optimizing nanoelectronic devices, as well as guiding further studies on thermal management and operational optimization in nanoelectronics.

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