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Thermodynamic analysis of a molecular quantum Otto heat engine based on electronic energy state of ethylene

Ata Mehdizadeh
Azarbaijan Shahid Madani University
Jaber Jahanbin Sardroodi
jsardroodi@azaruniv.ac.ir

Azarbaijan Shahid Madani University

Article

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Abstract

One of the most paradigmatic models for exploring the performance of quantum heat engines at the nanoscale is represented by quantum Otto cycle. Here, a quantum Otto engine is designed based on the two-level electronic system composed from an ethylene molecule. In the considered engine the working substance is defined by the ground state (S_0) and the first excited state (S_1) of the ethylene molecule. The energies of this system are calculated using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT). An electric field was used as the thermal reservoir in high temperature in isochoric strokes and isothermal steps was set up by adsorption and emission of photons by the molecule that transport the molecule between ground and excited states. The differences in the ground state-excited state gap due to the application of electrical field is the source of work and can be considered as tunable parameter of the engine. considered engine was demonstrated quantitatively by evaluating the net-work, the exchanged heat, thermodynamics efficiency and other thermodynamics properties. The results show that the π system of ethylene, characterized by a tunable energy gap, allows us to construct a thermal engine operating within a specific frequency range of the thermal reservoirs. the efficiency varies nonlinearly with the work amount. Furthermore, it was observed that in specific values for electrical field, the proposed device transfers heat from cold reservoir to the hot bath and can be used as quantum refrigerator to decrease temperature of cold bath. From the results of this study, we can suggest the using of simple organic molecules as the building blocks for molecular-scale quantum thermal machines or quantum refrigerators for release work or transfer heat in order to cooling purposes.

1. INTRODUCTION

The study of thermodynamics has provided the foundation of energy and its transformations since the days of Carnot, who studied the efficiencies of macroscopic engines [1]. With the advent of quantum mechanics, however, energy exchange at the molecular level occurs through quantum leaps, coherence, and entanglement, phenomena that are absent in classical models. The combination of thermodynamics and quantum science has led to the development of quantum thermodynamics, one of the newest branches of physics, which aims to understand and harness energy conversion and transformation at the nanoscale [2–4]. In the initial phases of its development, researchers focused on atomic systems because their well-defined energy spectra offered a clear framework for discussing the underlying principles [4–6]. Atomic systems rely on sophisticated trapping and isolation techniques, such as optical lattices and ion traps, which limit ruggedness and impede scalability in realistic, decoherence-prone environments [7, 8]. On the other hand, molecular systems have distinct strengths for research and applications in quantum thermodynamics [8]. Molecular structure intrinsically combines quantization, stability, and tunability, yielding a scalable and controllable energy landscape under ambient conditions [8].

This work explores molecular energy levels as the working medium of an Otto quantum heat engine using ground-state and time-dependent DFT within a quantum thermodynamic framework [9–11]. In this research work, a two-level system derived from ethylene's electronic ground state and first excited state

functions as a qubit-type working substance in a quantum Otto engine. The first electronic excited state of ethylene, obtained by a $\pi \rightarrow \pi^*$ transition, is achieved by irradiation with photons of appropriate intensity and frequency. The $\pi \rightarrow \pi^*$ energy gap, Δ_{gap}, is changed by an electric field, Ef. The results of the present work and the published ones [12] show that the Δ_{gap} is reduced by the Ef. As a result, field-assisted excitation requires less energy than is recovered during relaxation to the ground state in the absence of the field. This difference can be converted to other types of energy, including mechanical work.

1.1 Quantum Heat Engines and the Otto Cycle

Here, we briefly introduce quantum heat engines (QHEs) and their role in the development and control of quantum devices [13]. QHEs are microscopic or nanoscale systems in which quantum interactions occur between their constituent components, or which operate under the rules of the quantum world [14, 15]. A survey of the literature indicates that the quantum Otto heat engine (QOHE) cycles have emerged as one of the most fundamental and extensively studied prototypes in the thermal-engines community, owing to their conceptual simplicity and their direct analogy to the classical Otto cycle [16, 17]. The thermodynamic cycle of the classical Otto heat engine (COHE) consists of four strokes: (i) adiabatic compression, (ii) isochoric heating, (iii) adiabatic expansion, and (iv) isochoric cooling [18]. It was established [15] that the following steps can be used to construct the quantum counterpart of the COHE.

1. adiabatic compression, during which the energy gaps are reduced while the occupation probabilities remain invariant.
2. hot isochor or heating at constant volume, where the system absorbs energy from a high-temperature thermal reservoir, resulting in excitation and variation in population.
3. adiabatic expansion, characterized by an increase in the energy-level spacing at constant relative occupations.
4. cold isochor or cooling at constant volume, in which heat is dissipated to a low-temperature thermal bath and the cycle is closed.

Here, the cycles of the molecular quantum Otto heat engine, MQOHE, are realized using the variations of the energy gap, Δ_{gap}, of π and π^* molecular orbitals of ethylene molecule, $C_2 H_4$, by applying an electric-field corresponded to work doing strokes (I and III), along with the population variations raised from photon absorption (ground to excited) and emission (excited to ground) resembled the heat-exchange steps (II and IV). A schema of the considered engine is presented as Fig. 1. Therefore, according to the above lines and Fig. 1, a brief explanation of the steps for design a molecular quantum Otto engine carried out in this research may be as followings.

- Utilization of electric field in order to tuning the energy levels for controlling the gap.
- Computation of the energies of the ground and excited states using the density functional theory, DFT, and its time dependent version.

- Comprehensive thermodynamic analysis across quantum-relevant temperature regime
- Optimization of field parameters and thermal baths' temperature for optimum values of the work output, efficiency, power output and other required quantities.

1.2 Molecular Systems as Working Substances:

Recent studies from multiple research groups have explored a variety of platforms for quantum heat engines (QHEs), including trapped ions, quantum dots, and molecular systems [19–22]. However, the use of single molecules offers a unique platform due to their well-defined, discrete energy levels and the vast chemical space for tenability [23]. Here, the electronic ground state ($|S_0\rangle$) and first singlet excited state ($|S_1\rangle$) of ethylene was define as an effective two-level working quantum substance for the considered quantum heat engine. The energies of these states are determined computationally using DFT for the ground state and TD-DFT for the excited state.

Then theses energy values were used for construction a Markovian process forming an quantum Otto cycle. This cycle including two energy level shifting derived by applying an electric field and two population variations via the adsorption and the emission of photons. In the latter two steps the system must be in contact with hot and cold baths to exchange energy with thermal environment in the form of heat flow into / out of itself. So, it is clear that these two steps are associated with dissipation and to elucidate the time evolution of the quantum mechanical quantities and the dynamics of the system, we need to solve the master Lindbladian equation.

2 Results and Discussion

2.1 The Results of DFT and TD-DFT:

The results of the high-level DFT and TD-DFT computations show that the planar structure of ethylene in its ground state is changed to a non-planar structure that is a gouache configuration, in its first singlet excited state. The obtained data including applied electric field, energy of the ground state and first excited state have been collected as Table S-1 in Supplementary Information. A brief procedure of computational methods have been presented in Supplementary Information, Section of S-2. If the reader needs detailed information or one of the used codes, please contact corresponding author, J. J. S by email. Figures <link rid="fig2">2</link>-a and 2-b express the DFT optimized geometry of the ethylene in its ground and first excited states, respectively. These figures show that the exciting an electron from π to π^* molecular orbitals leading to the reduction the bond order of C-C double bond to a value near to unity (). As a result, the energy barrier required for rotation of one of the CH2's around C-C bond in excited state is reduced compared to the ground state. Therefore, the repulsive interactions between opposing hydrogens overcome to this barrier and internal rotation occurs. On the other hand, this rotation causes the p atomic orbitals that had forming the π MO to move further apart, and the weakened π MO becomes bent and weaker. Figures 3a and 3b present the isosurfaces of MO's of ethylene in ground and excited states respectively. These figures clearly show the twisting and

weakening the π MO resulted from excitation. Finally, it must be noted that this cis-trans transformation resulted from excitation of one bonding electron that was located in the π MO to the ethylene's π^* MO of ethylene is with the population variation that does not satisfy Boltzmann equation.

To tune the π–π* energy gap via the DC Stark effect, a static electric field ranging from ± 0.01 to ± 0.039 atomic unit was applied along the C–C bond, parallel to the z-axis. The results of the computations performed in the presence of an external electric field are presented in Fig. 4. These figures reveal that both the ground- and excited-state energies decrease under the applied electric field; however, the unequal Stark shifts of the two states lead to a net reduction of the energy gap.

The temperature of the cold bath was varied according to the Eq. (1):

$$T_c = \frac{T_h \cdot \Delta_{gap_c}}{\Delta_{gap_h}}$$

1

to determine its optimum value so as to establish the optimal operating conditions for the considered QOHE. The hot-bath temperature was varied in the range of 0–20 K, ensuring that the kinetic energy and, consequently, the linear momentum of the molecular center of mass are effectively suppressed; therefore, trapping of the ethylene molecules—unlike in cold-atom–based engines—is not required.

Thermodynamic quantities over the QOHE cycle were evaluated using Python-based simulations with NumPy, SciPy, Matplotlib, and QuTiP. In strokes 1 and 3, the time evolution of the density matrix is obtained by solving the Lindblad master equation [15, 24]. Figures <link rid="fig5">5</link>-a, <link rid="fig5">5</link>-b and <link rid="fig5">5</link>-c present the work output, efficiency, and power in terms of the applied electric field in various hot-bath temperatures.

These figures show that as expected the amount of work output is increased when the field values are increased. The reduction of energy gap with electric field results the larger difference between energy required for excitation and energy released b relaxation of ethylene (field free state). A deep analysis of the energy exchanges between system and environment and also the sources of these energies that appear as heat and work, show that the heat output is resulted from the difference between the excitation energy needed in stroke 2 and the energy released in stroke 4 and the observed work can be attributed to the energy gap difference between stages 1 and 3. On the other hand, the efficiency is reduced with the electrical field and that is approximately independent from the hot temperature. This result show that there are factors wasting or dissipating energy like friction or widening the energy distribution between the levels which increases entropy. However, we have only two energy levels here and widening or sharpening of the energy distribution is not relevant here, but the electronic density and the geometry of molecular orbitals become more wide and this may increase the energy wasting or entropy. It is also possible that the observed trend is explained and understood with the help of uncertainty principle by develop relations between the energy gap, the spatial distribution of electronic

density and energy wasting. We probably develop such relations in our future researches and publications.

The dependency of efficiency to the work output in various hot temperatures is use full information. This diagram displays the values of energy that we received from the system as the work, per unit energy that absorbed by the system as heat. Such quantity similar other “per unit” quantities (molar and specific quantities) are independent from the system size or the amount of material or the volume of the system. When the amount of work per unit absorbed heat is reduced with the amount of work, we can elucidate that the rate of increasing work, is smaller than one belongs to the absorbed heat. This result can be expressed in other terms: applying changes in population of the levels is more difficult than the applying changes in energy levels. We can interpret this as a quantum world friction for population flow. Figure 6 is included the efficiency variations with work output in various hot temperatures that show the existence of quantum friction for the studied system.

Figure 7 presents the work output in terms of hot temperatures for selected electric fields 0, ± 0.015 and ± 0.030 au. We can see the work values are varied in low temperatures and it has a limiting value for temperatures greater than 5 K.

The present study establishes ethylene (C_2H_4) as a minimal yet physically rich molecular platform for quantum thermodynamic operation, in which its discrete electronic energy levels can be consistently mapped onto an effective two-level system (TLS). Within this reduced description, the electronic structure of ethylene assumes a dual role, simultaneously acting as a qubit-like quantum system and as the working substance of a quantum heat engine [25, 15]. This duality provides a natural conceptual bridge between quantum information science and quantum thermodynamics—two fields that have largely evolved in parallel despite sharing common quantum foundations [26, 19].

This work demonstrates that static electric-field control via the DC Stark effect provides a direct and experimentally realistic means of modulating the molecular Hamiltonian [27]. By tuning the external electric field, the HOMO–LUMO energy spacing of ethylene is continuously reshaped, thereby defining the work strokes of the quantum heat engine [14, 16]. In contrast to optically driven atomic platforms, which require complex laser configurations and stringent isolation for coherent control [28], electric-field tuning is intrinsically compatible with solid-state and on-chip architectures [29, 30]. This characteristic renders ethylene particularly attractive as a proof-of-concept molecular platform for surface-integrated quantum thermodynamic devices [30, 31].

From a thermodynamic perspective, the calculated work, power, and efficiency landscapes exhibit well-defined operational regimes that are governed primarily by the applied electric field [14, 16, 32]. The emergence of distinct high-efficiency and high-power regimes under specific electric-field configurations demonstrates that field-induced spectral deformation is the dominant mechanism responsible for work extraction in this molecular engine [32, 33, 34]. Importantly, the sharp transitions separating active and inactive regimes indicate that the engine can be effectively switched on and off through purely electrical

means, a feature that is highly desirable for functional nanoscale devices, where controllability and reversibility are essential [33].

A key conceptual contribution of this study emerges from the comparison between surface-anchored molecular qubits and trapped atomic qubits. Atomic qubits are well known for their long coherence times; however, maintaining such coherence relies on sophisticated trapping schemes and extreme isolation from the environment [28, 35]. By contrast, small molecules such as ethylene can be readily adsorbed or chemically anchored to solid substrates, eliminating the need for external trapping potentials [30, 31]. While surface coupling inevitably introduces decoherence and dissipation channels [36, 37], this does not constitute a limitation in the present thermodynamic context. Instead, it reflects the realistic operating conditions under which nanoscale engines must operate, where energy exchange with the environment is an intrinsic feature rather than an undesirable perturbation [14, 19]. In this sense, molecular platforms should be viewed not as inferior substitutes for atomic qubits, but as complementary systems specifically optimized for studying quantum energy conversion under non-ideal, physically relevant condition [26, 38].

By treating the HOMO–LUMO manifold of ethylene as an effective two-level system, this work deliberately avoids claims related to universal quantum computation [39]. Instead, it emphasizes a more immediate and experimentally accessible objective: demonstrating that qubit-like molecular states are capable of performing thermodynamic tasks [16, 25]. This restrained positioning prioritizes conceptual clarity and physical insight, underscoring that the value of the model lies in elucidating the essential mechanisms of quantum work extraction, rather than in advancing speculative scalability claims [19, 38].

Looking forward, the present study opens several avenues for future theoretical investigation. A natural extension involves relaxing the strict TLS approximation to incorporate multilevel electronic manifolds and vibronic degrees of freedom, thereby enabling an assessment of how molecular complexity modifies efficiency–power trade-offs under electric-field driving [34, 40]. Another promising direction is the development of finite-time thermodynamic cycles for molecular systems, in which decoherence and dissipation unfold on timescales comparable to that of the engine operation [32, 33].

From a device-oriented perspective, explicit modeling of surface-anchored molecular engines—including molecule–substrate hybridization and field-screening effects—represents a critical next step toward achieving chemically realistic quantum heat engines [29, 31, 36]. Such studies would enable a direct comparison between abstract TLS-based predictions and the actual performance of molecular systems operating under experimentally relevant conditions [37].

In a broader context, this work contributes to a growing effort to reframe molecular quantum heat engines as functional theoretical building blocks rather than purely abstract constructs [14, 26]. By combining discrete electronic spectra, chemical tunability, and compatibility with solid-state environments, small organic molecules occupy a unique and versatile position at the interface of chemistry, quantum information, and thermodynamics [19, 38].

Conclusion

In conclusion, we have designed and theoretically analyzed a photonic quantum Otto engine based on the S_0 and S_1 electronic states of the ethylene molecule. Using DFT and TD-DFT, we calculated the essential energy level structure and confirmed the optical accessibility of the transition. Our thermodynamic analysis revealed the conditions under which the engine performs positive work and quantified its efficiency, which is bounded by the fundamental Otto limit. While practical implementation faces challenges related to high operating temperatures and molecular dissipation channels, this work establishes a clear bridge between computational quantum chemistry and quantum thermodynamics. It paves the way for the design of more complex molecular machines with tailored quantum thermodynamic properties. The results demonstrate the feasibility of using the electronic states of a simple molecule like ethylene as the working substance for a quantum Otto engine. The significant $\pi \rightarrow \pi^*$ energy gap provides a robust two-level system for the cycle. The allowed nature of the transition is crucial, as it ensures efficient coupling to the photonic thermal bath during the isochoric strokes.

Declarations

Declaration of competing interest:

The authors declare that they have no known competing financial

Funding:

The authors have no financial or proprietary interests in any material discussed in this article.

Author Contribution

"A.M. wrote draft, Do the simulations, Develop python codes, Prepare figures and J.J.S. Supervision, Definition and Conceptualization, Declaration the idea and the protocol for overall work. All authors reviewed the manuscript."

Data Availability

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

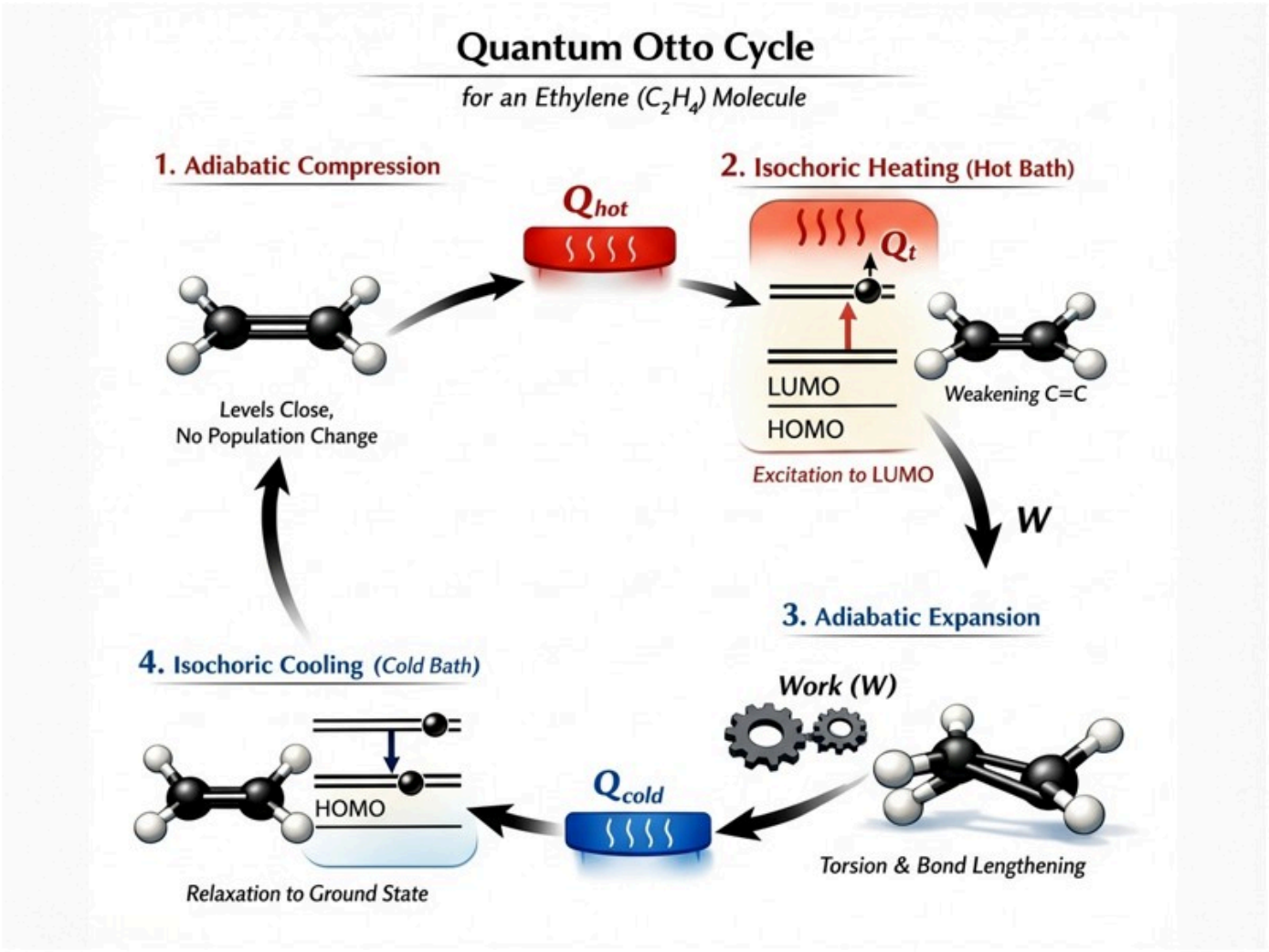
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Figures



1

Figure 1

schematic representation of molecular quantum Otto heat engine based on electronic states of ethylene

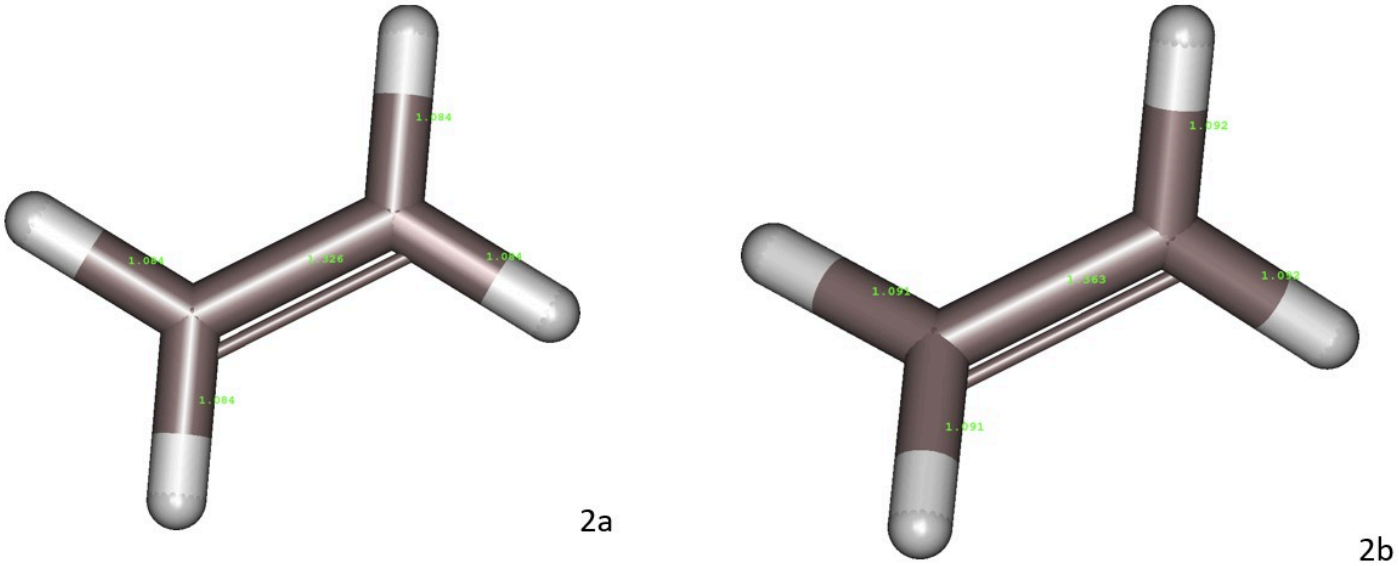


Figure 2

Optimized geometry of ethylene in the ground state (a) and in the first excited state (b)

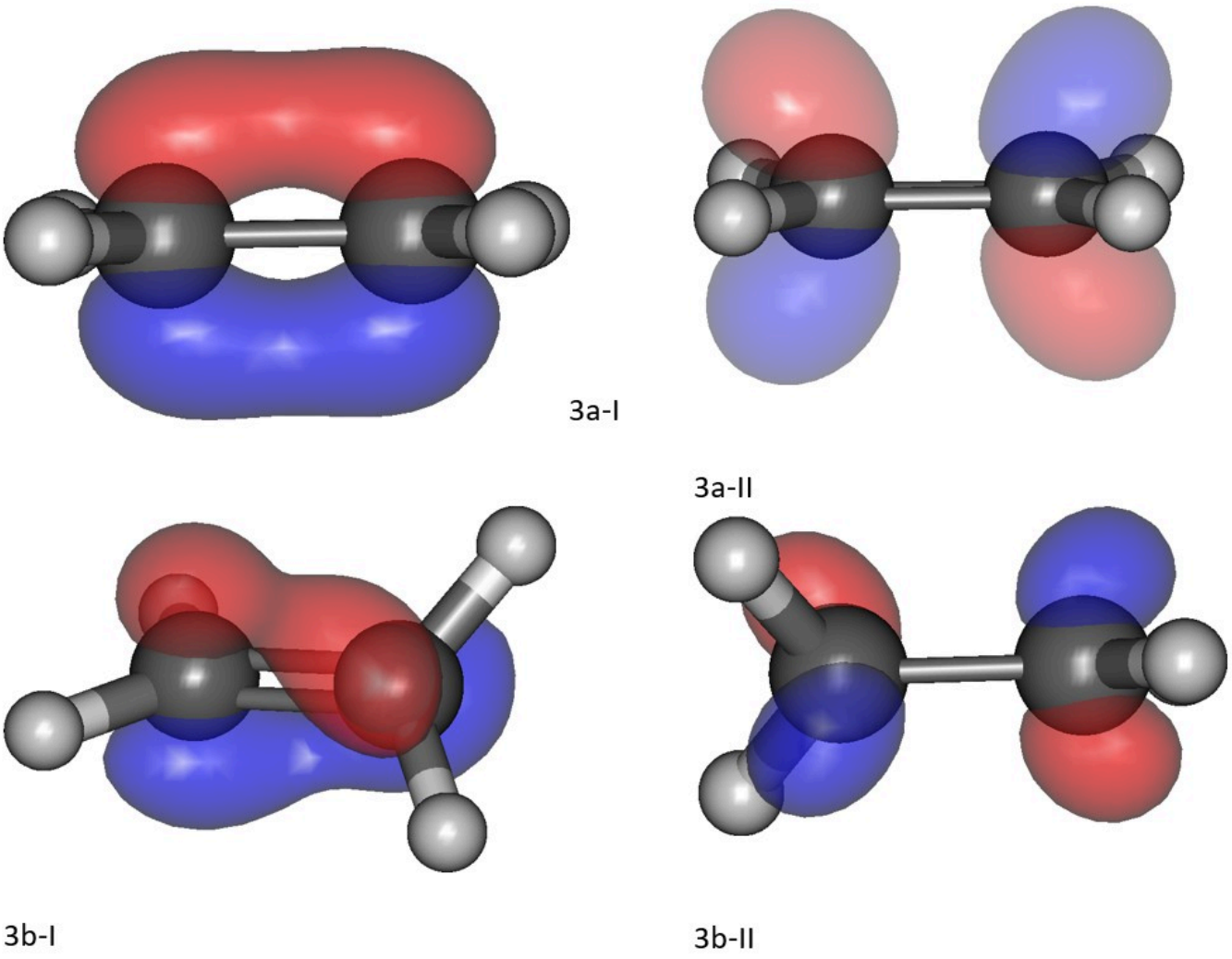
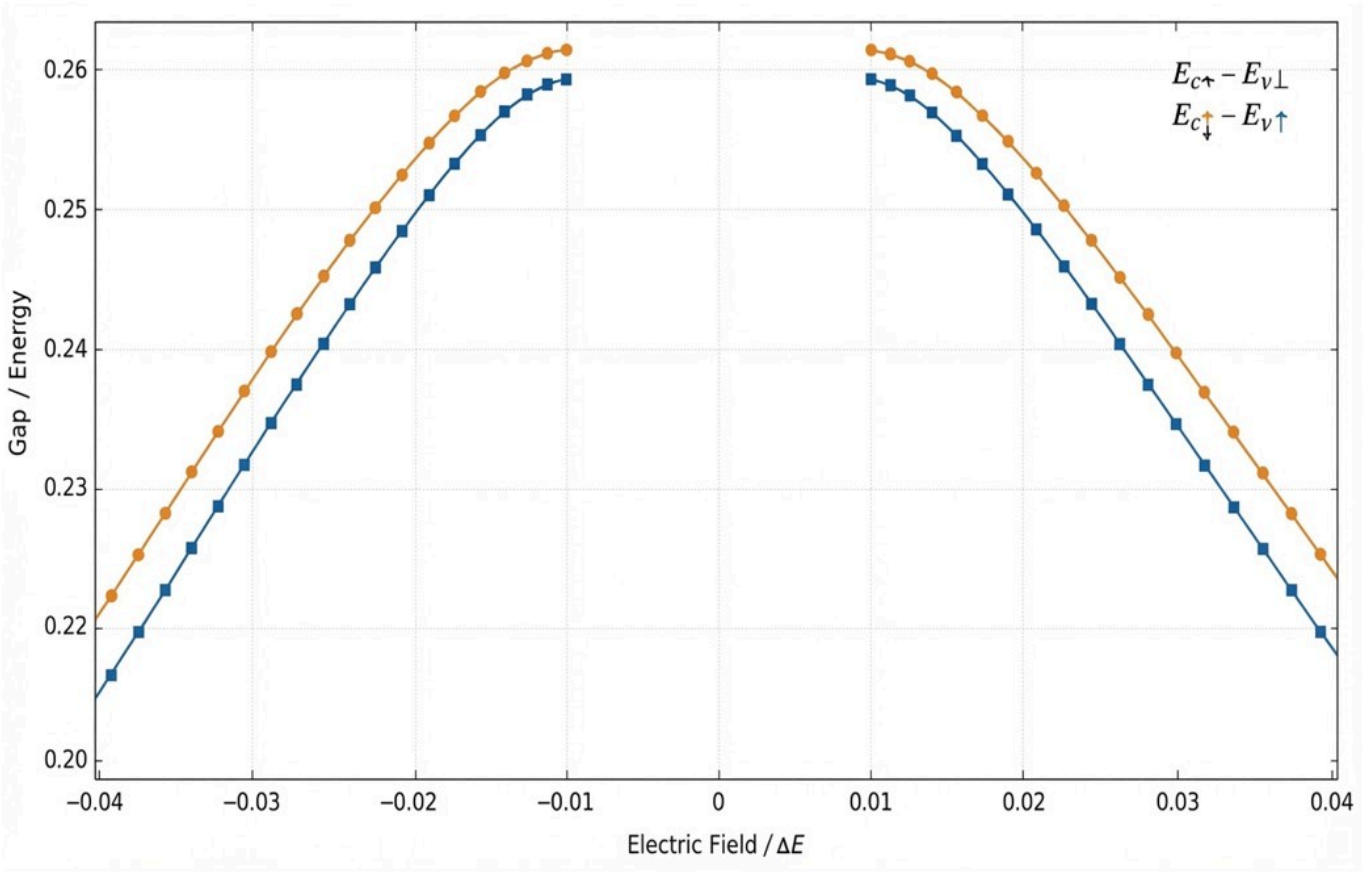


Figure 3

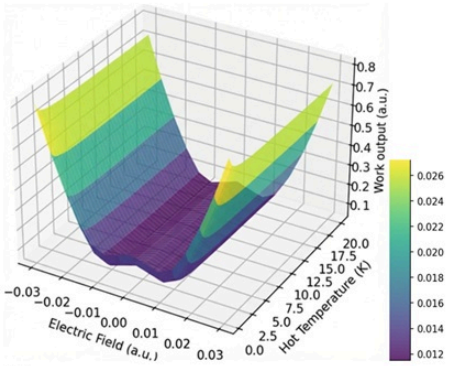
Frontier molecular orbitals of ethylene in the ground state (a; I: HUMO, II: LOMO) and in the excited state (b; I: HUMO, II: LOMO)



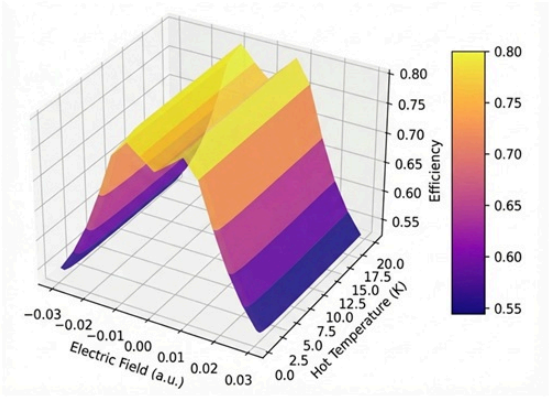
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Figure 4

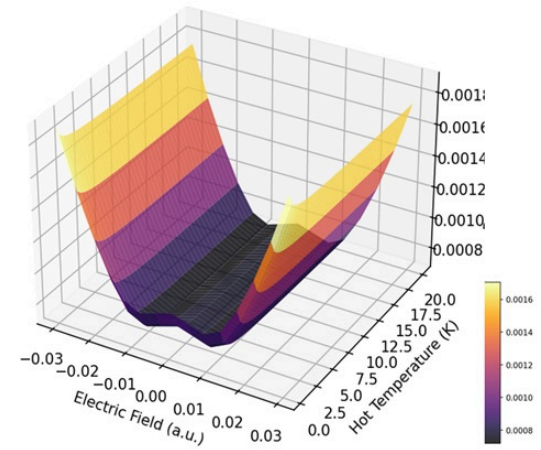
Energy gap between ground and first excited states of the ethylene vs. applied electric field



5-a



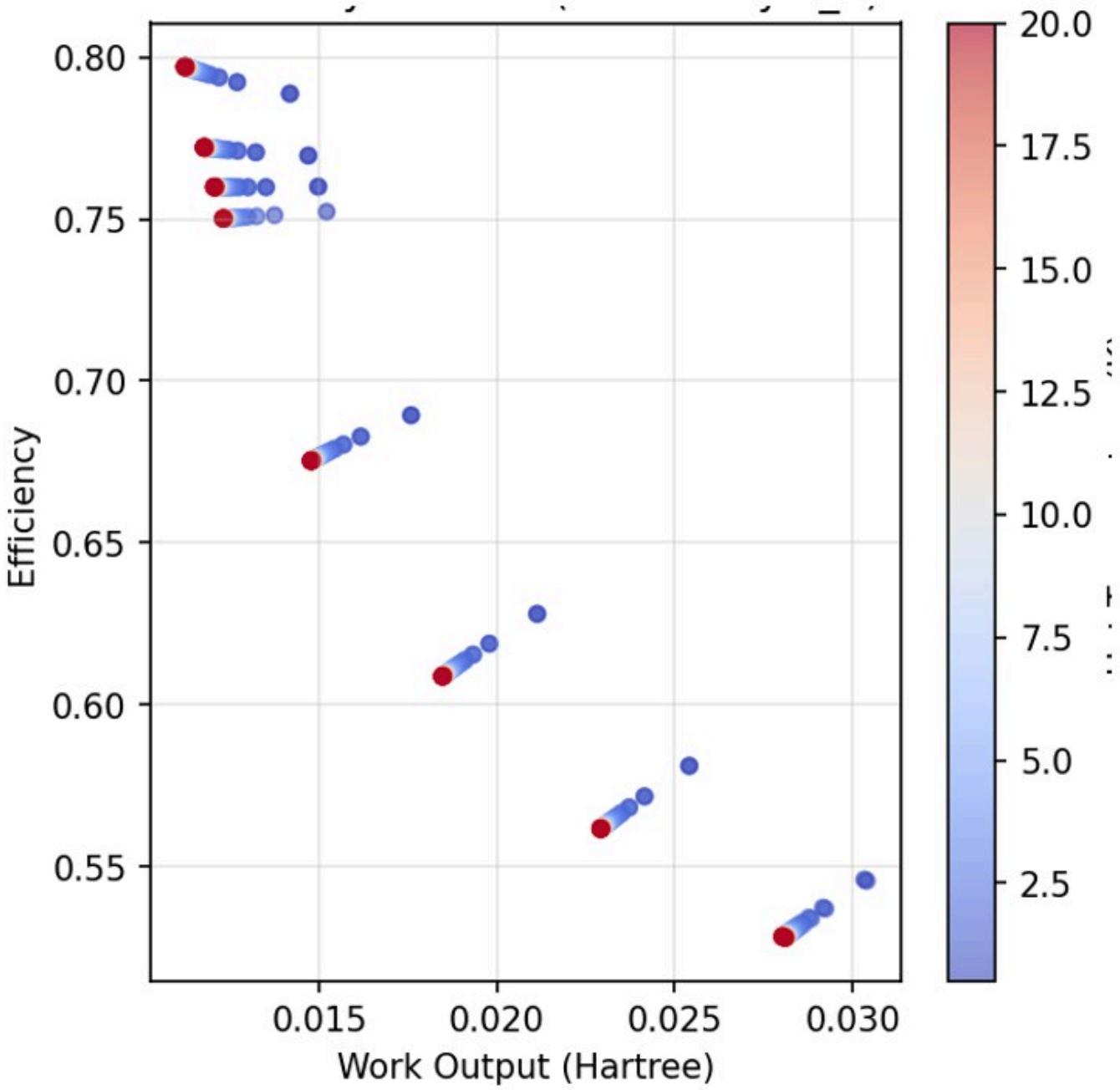
5-b



5-c

Figure 5

thermodynamics of studied molecular quantum Otto engine: a) work, b) efficiency, c) power vs. field and hot temperature



6

Figure 6

a) efficiency vs work output in terms of hot temperature, b) work output vs hot temperatures for selected electric fields.

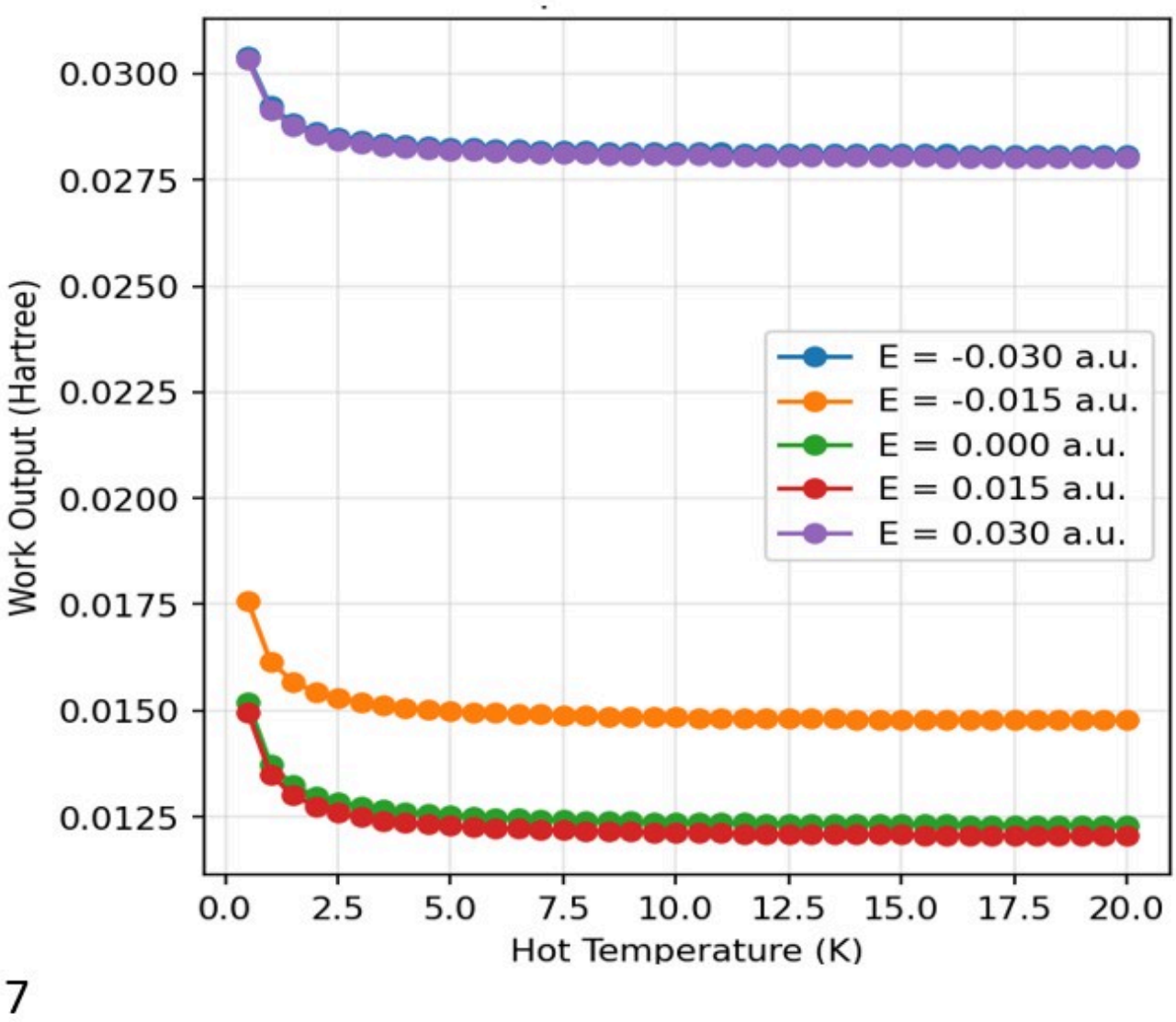


Figure 7

Legend not included with this version

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