

Quantum-Mechanical Modeling of The Electronic Structure, Spatial Configuration, And Vibrational Dynamics of The Bis (Ethylenedithio) Tetraselenafulvalene (BEDT-TSF) Molecule

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Abstract: The bis (ethylenedithio) tetraselenafulvalene (BEDT-TSF) molecular system is a fundamental structural element from which low-dimensional organic conductors and superconductors are formed. In this work, a comprehensive study of the physical properties of an isolated neutral BEDT-TSF molecule in its ground state was conducted using density functional theory (DFT) methods. Within the framework of a consistent quantum-mechanical approach, the spectrum of single-electron states near the Fermi surface (frontier molecular orbitals) was initially determined, and the Kohn–Sham HOMO–LUMO orbital energy gap was calculated. Based on the electron density distribution, the spatial configuration of the nuclei was optimized, and the macroscopic thermodynamic characteristics of the system were calculated. Analysis of the matrix of second derivatives of the energy with respect to nuclear coordinates confirmed the dynamic stability of the structure (complete absence of imaginary frequencies) and allowed for a detailed description of the phonon spectrum of normal harmonic vibrations, which determines the parameters of the electron-phonon interaction in condensed phases of charge-transfer salts.

Keywords: BEDT-TSF molecule, density functional theory (DFT), quantum-mechanical modeling, electronic structure, HOMO–LUMO energy gap, molecular geometry optimization, vibrational spectrum, normal vibrational modes, thermodynamic properties, electron–phonon interaction.

Introduction:

Low-dimensional crystal structures based on quasi-two-dimensional organic compounds are of fundamental interest in solid-state physics due to their rich phase diagram of strongly correlated electronic phenomena. Such systems exhibit two-dimensional metallic conductivity, phase transitions

into states with charge or spin density waves, as well as superconductivity induced by an external magnetic field. The BEDT-TSF molecule is a modification of the classic organic donor BEDT-TTF, in which the four central sulfur atoms are replaced by selenium atoms. [1,8,9]

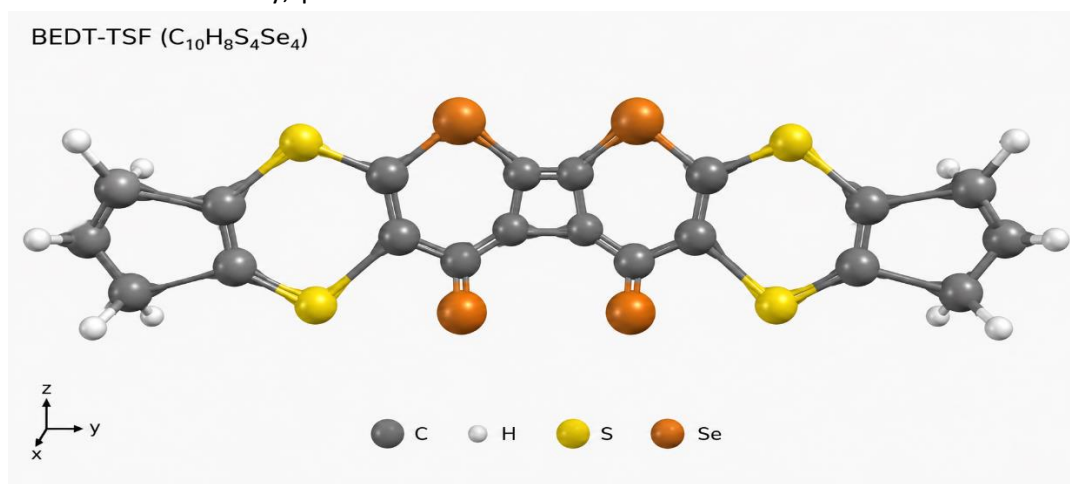


Fig. 1. The initial model of the BEDT-TSF molecule.

The physical rationale for this substitution is that the larger spatial extent and diffuse nature of selenium 4p orbitals ensure much more effective overlap of neighboring molecules' wave functions during translational packing into the crystal lattice. As a result, the electronic dimensionality of the subsystem increases, the conduction band expands, and ensures the formation of two-dimensional conducting planes.

To construct adequate theoretical models of electron transport and the phonon spectrum in the condensed state, we need a reliable basis of microscopic parameters for the isolated molecule. Quantum-mechanical modeling of a single neutral molecule in a vacuum makes it possible to obtain the fundamental characteristics of the electron spectrum and normal vibrations of the nuclear framework, free from perturbations of the crystal environment.

METHODOLOGY

All quantum-mechanical calculations of electron density, spatial geometry, and vibrational spectrum were performed using the density functional theory (DFT) method. To accurately describe the exchange and correlation interactions of electrons, the PBE0 hybrid functional was used, containing a fixed fraction of exact Hartree-Fock exchange, which is critical for minimizing the self-interaction error when calculating the energy gap.

Van der Waals dispersion forces were accounted for using the semi-empirical Grimme D3 correction with Becke-Johnson damping (D3BJ). Calculations were performed using a split-valence double-zeta quality def2-SVP basis set for all types of nuclei (H, C, S, Se).

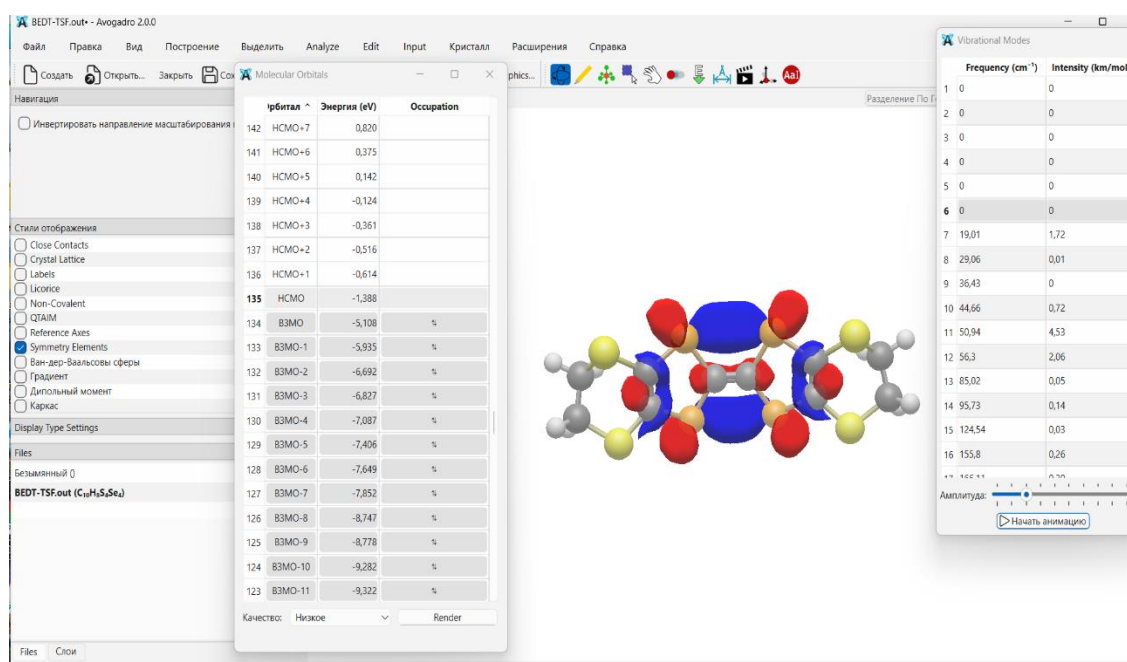
The self-consistent field (SCF) procedure was performed with strict control of density-matrix convergence. We determined the equilibrium nuclear configuration by full geometry relaxation until the forces on the atoms reached zero. The character of

the stationary point on the potential energy surface was verified by calculating the Hessian matrix (the matrix of second derivatives of energy with respect to nuclear coordinates): the absence of negative eigenvalues confirms that the found structure corresponds to a true local energy minimum.

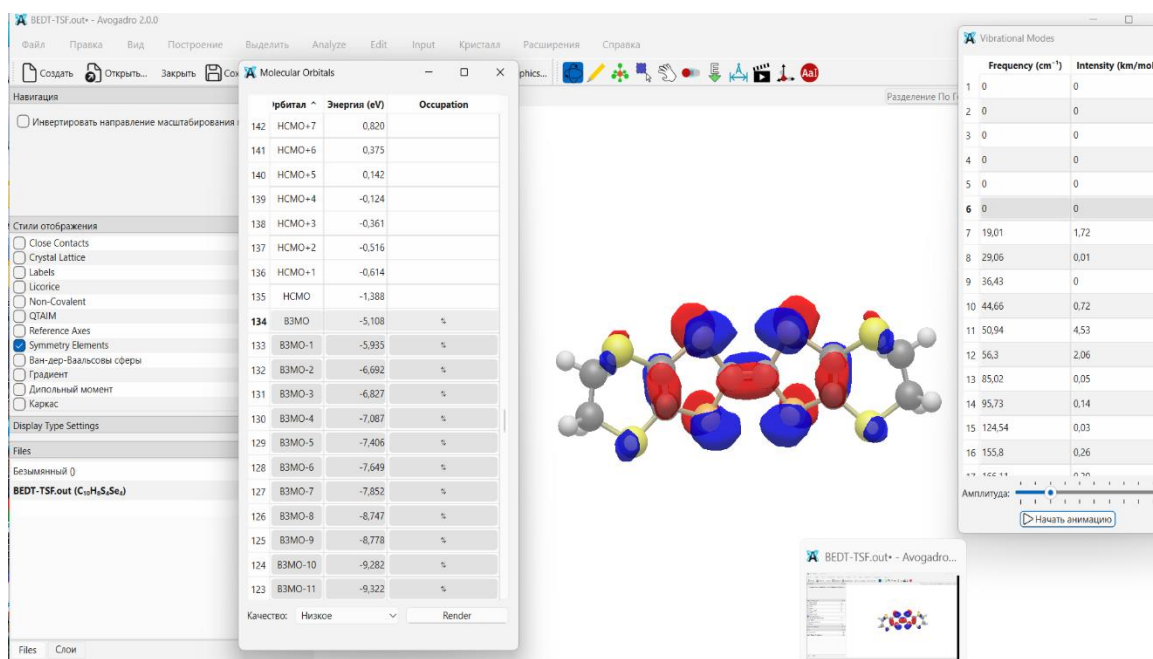
RESULTS AND DISCUSSION

1. Electronic spectrum and frontier energy levels

In accordance with the logic of quantum mechanics, the macroscopic properties of a system are determined by its electronic structure. In this regard, the spectrum of single-electron states of an isolated molecule near the hypothetical Fermi surface was initially investigated. [3]



a)



b)

Fig. 2. HOMO (a) and LUMO (b) orbitals of the BEDT-TSF molecule.

The main focus is on the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO)

quasiparticle levels, the parameters of which are presented in Table 1.

Table 1. Energy parameters of the frontier single-electron levels of the isolated BEDT-TSF molecule.

Energy level	Occupation number	Energy in atomic units (Eh)	Energy in electron-volts (eV)
Lowest unoccupied state (LUMO)	0.0000	-0.070567	-1.9202
Highest occupied state (HOMO)	2.0000	-0.191361	-5.2072
Fundamental energy gap (ΔE)	—	+0.120794	+3.2870

The highest occupied single-electron state of the BEDT-TSF molecule is localized at a relatively high energy level of -5.2072 eV.

According to Koopmans' theorem, the energy of this level, taken with the opposite sign, approximates the vertical ionization potential of the isolated system

with good accuracy ($I \approx 5.21$ eV). Such a low ionization potential indicates the lability of the molecule's electronic subsystem and its tendency toward effective delocalization of the electron density. In the solid state, when the HOMO wave functions of neighboring molecules overlap, this ensures the formation of two-dimensional conducting planes.

IR/Raman Assignment Table

Frequency, cm^{-1}	Main vibration	Atoms involved	Assignment
...	...	C=C	C=C stretching
...	...	Se-C-Se	skeletal vibration
...	...	C-S	stretching/bending
...	...	C-H	stretching

The separation between the frontier levels — the Kohn-Sham HOMO-LUMO orbital energy gap ($\Delta E_{HOMO-LUMO}$) — is 3.2870 eV (0.120794 Eh). [4]

This value indicates that the isolated molecule in a vacuum behaves as a wide-bandgap insulator with high quantum-mechanical stability of its electronic

ground state. This value establishes a rigorous reference basis for subsequent calculations of intermolecular transfer integrals and the modeling of the band structure in the condensed state, where discrete levels broaden into conduction bands. [3].

2. Spatial topology and thermodynamics of the ground state

The equilibrium spatial topology of the nuclear framework, formed under the influence of the calculated electron density of the ground state, is characterized by a specific spatial splitting. While the central C2 Se4 C2 fragment maintains almost strict coplanarity (flat shape), the outer ethylene

heterocycles exhibit a pronounced non-planar (bent) configuration.

Integral macroscopic thermodynamic functions accounting for electronic, vibrational, rotational, and translational contributions under standard physical conditions ($T=298.15$ K, $P=1.0$ atm) are provided in Table 2.

Table 2. Integral thermodynamic characteristics of the BEDT-TSF molecule.

Physical parameter	Value in atomic units (Eh)	Value in kcal/mol
Total electronic energy of the ground state (Eel)	11580.7724658	—
Total enthalpy of the system (H)	-11580.5946466	—
Entropy contribution at a given temperature ($-TS$)	-0.0705857	-44.29
Gibbs thermodynamic potential (G)	-11580.6652323	—
Total thermal correction (G-Eel)	0.1072335	+67.29

3. Vibrational spectrum (normal vibrational modes)

The dynamic properties of the nuclear framework of a molecular system consisting of

$N=28$ atoms are fully described by $3N-6=78$ normal harmonic vibrations. The calculated spectrum completely lacks imaginary or negative frequencies, which strictly confirms the dynamic stability of the identified geometric configuration.

The spectral density of normal modes (Fermi distribution of vibrational energies) is naturally divided into three distinct energy regions:

Low-frequency range ($19-400$ cm^{-1}): Collective bending vibrations of the skeletal framework, in which the kinetic energy of heavy selenium (SeSeSe) and sulfur (SSS) nuclei dominates. Modes in this region are critically important for condensed matter

physics, as they effectively hybridize with the intermolecular acoustic and optical phonons of the crystal lattice of an organic conductor, making a decisive contribution to the electron-phonon interaction.

Mid-frequency range ($1400-1620$ cm^{-1}): High-energy stretching vibrations of double carbon bonds $\text{C}=\text{CC}=\text{C}$ $\text{C}=\text{C}$. Characteristic discrete modes are localized at frequencies of 1580.56 cm^{-1} , 1584.35 cm^{-1} , and 1618.63 cm^{-1} .

The magnitude of the energy shift of the vibrational mode of the central bond $\text{C}=\text{CC}=\text{C}$ $\text{C}=\text{C}$ serves as a direct physical indicator of the degree of charge transfer to the molecule (charge state BEDT-TSF+ δ BEDT-TSF raised to the positive delta power BEDT-TSF+ δ) in crystalline phases with mixed valence.

High-frequency range (3079–3166 cm⁻¹): Stretching vibrations of light hydrogen nuclei on peripheral bonds C (sp³)–HC (sp)–H (sp³)–H, characterized by weak dispersion. [4,10–12]

CONCLUSION

Within the framework of first-principles quantum-mechanical modeling, a strictly consistent description of the physical characteristics of the isolated BEDT-TSF molecule was implemented. The established parameters of the single-electron spectrum (the high-lying HOMO level of –5.2072 eV and the energy gap of 3.2870 eV) form a fundamental basis of microscopic constants that determine the energetics of an isolated quasiparticle.

Based on the electron density, the equilibrium geometry, macroscopic thermodynamics of the ground state, and the phonon spectrum of normal vibrations of the backbone were determined. The obtained harmonic mode frequencies provide the necessary theoretical foundation for the unambiguous interpretation of experimental data from IR and Raman spectroscopy of low-dimensional crystals, as well as for subsequent many-body modeling of the energy band structure, effective carrier masses, and the conductivity tensor of organic superconductors.

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