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Computational Analysis of Electric Field Effects on Frontier Orbitals of Simple Molecular Structures

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Abstract: In this article, acetonitrile, paranitroaniline, and trans-butadiene were chosen as simple molecular models for popular molecular systems, and the behaviour of the HOMO and LUMO orbitals of the molecules was studied under external electric fields using the B3LYP functional and the 6-31G basis set within density functional theory (DFT). Acetonitrile demonstrated first-order electronic perturbation; Paranitroaniline showed relatively higher orbital sensitivity; and finally, trans-butadiene demonstrated non-linear behaviour. Electronic perturbation theory is used to explain the behaviour of the molecules and highlight characteristics that might be favourable or unfavourable for applications in molecular electronics.

Keywords: *Single-Molecule Transistors, Density Functional Theory, HOMO-LUMO Orbital Tuning, Electronic Perturbation Theory, Hückel Molecular Orbital Theory, Effect of Electron-Donating or Withdrawing Substituents on Orbital Behaviour, Electric Field Effects on Conjugated Polyenes, Effects of A Permanent Dipole Moment.*

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I. INTRODUCTION

According to Moore's law [1], the number of transistors on a microchip doubles every two years. Chipmakers follow Moore's law to reduce transistor sizes and, consequently, the circuit sizes of electronic components, trying different methods to test the limits of device miniaturization. Molecular electronics is a branch of nanotechnology that proposes using single molecules or collections of molecules as wires, diodes, and other electrical components. Since the introduction of the idea of a molecular diode by Aviram and Ratner [2], molecular electronics has been considered as an alternative to conventional solid-state electronics, specifically for components like transistors, diodes, or wires, in light of Moore's law and decreasing circuit sizes.

Established literature has proposed and explored different types of molecular electronics components that work on different ideas and principles: Single electron transistors that use molecular quantum dots and coulomb blockade theory to establish controlled sequential electron tunnelling under a gate voltage[3]; molecular relays that replicate mechanical switching at a molecular scale using organic molecules with high conformational flexibility; highly conjugated molecules like polyenes that behave as wires, or the molecular equivalent of Field Effect Transistors that use an electric field to shift molecular orbitals to create conductive channels [4]. Frontier Molecular Orbital Theory can provide crucial insights into the behaviour of molecular orbitals of molecules under external electric fields. The Fermi Level of the attached electrodes, the Highest Occupied Molecular Orbital (HOMO), the Lowest Unoccupied Molecular Orbital (LUMO), and their energies relative to the electrode Fermi level are relevant to understanding the charge transfer and conductivity of a molecule.

Electrical conduction through a molecule requires a low energy gap between the Fermi level of the attached electrodes and the molecular orbitals. Generally, a low E_{LUMO} favours electron-dominated transport while a low E_{HOMO} favours hole-dominated transport. However, because the Fermi level can differ among electrodes, the behaviour of the energy gap (ΔE) often provides sufficient information about a molecule's conductivity. Conductors have a low or negligible energy gap, insulators have a high energy gap, and candidates for molecular electronics should exhibit a significant orbital response to an external electric field to enable orbital tuning.

$$E_{LUMO} = E_{LUMO} - E_F$$

$$E_{HOMO} = E_{HOMO} - E_F$$

$$\Delta E = E_{LUMO} - E_{HOMO}$$

The dipole moment, polarisability, charge distribution, and conjugation of molecules are a few important

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characteristics among many that describe orbital behaviour under external electric fields. A permanent dipole moment could indicate linear changes in energy levels; highly polarisable molecules are generally more sensitive to electric field effects, and the charge distribution and overlap of pi orbitals, often called conjugation, describe the delocalization of electrons and ease of charge transfer in molecules. Electronic perturbation theory is the quantum mechanical framework that uses these quantifiable properties to describe orbital behaviour and changes in orbital energies under external electric fields.

Density Functional Theory (DFT) is a quantum mechanical modelling method used in computational chemistry to study molecules and materials [5]. Unlike other computational methods like Hartree-Fock, which approximate individual electron behaviour in a multi-electron system, DFT is computationally inexpensive and uses charge density, making it suitable for simulating and analysing energy surfaces of most molecules. In this study, DFT has been used as the primary computation method to optimize molecular geometries and calculate HOMO and LUMO energies under external electric fields.

II. METHODOLOGY

The Gaussian 09 software has been used for all calculations. Within DFT, Becke's three-parameter hybrid functional (B3) [6] combined with the electron correlation functional of Lee, Yang, and Parr (B3LYP) [7] was used with the 6-31G basis set to optimize selected molecules to their lowest energy conformations and subsequently track orbital behaviour, the energy gap (ΔE), and dipole moments under an external electric field. The 6-31G basis set and B3LYP have been used due to the good balance between the computational cost and accuracy they offer. [8] Four different molecules, acetonitrile, para-nitroaniline, and butadiene, have been studied in this article. The molecules were selected based on varying molecular structure and properties: acetonitrile for its permanent dipole, para-nitroaniline for the donor-acceptor behaviour of its substituents, and butadiene for its linear conjugated backbone. After optimizing the molecules, they were reoriented in GaussView such that one or more Cartesian axes lay along a particular bond, the permanent dipole moment, or the backbone of the molecule. Then, electric fields ranging from 0.001 a.u to 0.009 a.u were applied in the positive and negative x, y, and z directions, and the resulting orbital behaviour and dipole moment were measured. Electronic perturbation theory was used as a qualitative framework to interpret the observed orbital behaviour and trends.

Although electrodes and anchor groups are often added in similar studies, the primary aim of this article is not to identify molecules that can be used to make molecular electronic components. That would require a lot more physical testing and analysis of current and voltage behaviour. Instead, this study hopes to investigate the behaviour of molecules due to their intrinsic characteristics within the context of frontier orbital theory and perturbation theory to identify certain characteristics or structures that might have potential applications in electronics. To this end, anchor groups and electrodes have been ignored to exclude additional effects such as electrode-induced gap renormalization, contact resistance, and interface effects of the anchor groups.

III. RESULTS AND DISCUSSION

- *Acetonitrile*

Acetonitrile is an organic nitrile, a hydrogen cyanide where the hydrogen is substituted by a methyl group. The methyl group is connected to the nitrile group by a sigma bond. The methyl carbon is sp^3 hybridized with a tetrahedral geometry, while the nitrile group is sp-hybridized, forcing the molecule into a linear shape.

The nitrile group is a strong electron-withdrawing group, pulling electron density through the C-C sigma bond using inductive effects. It polarises the molecule and generates a strong, permanent dipole moment of 3.92 D, with a partial negative charge on the nitrile group and a partial positive charge on the methyl group. Although acetonitrile has π electrons near the nitrile group, the absence of continuous π orbital overlapping prevents a conjugated system, localizing the electrons to the sp orbital. Acetonitrile was selected as a simple model system to investigate dipole–field interactions and the response of a highly polar molecule to an external electric field in the presence of a strong electron-withdrawing nitrile group. The main frontier orbitals of acetonitrile are located at the nitrile end of the molecule: The nitrogen lone pair, a non-bonding molecular orbital, acts as the HOMO, while a degenerate pair of π^* anti-bonding orbitals, formed by the linear combination of the p orbitals of the nitrile triple bond, act as the LUMO orbitals. The optimised structure of acetonitrile, shown in Figures 1 and 2, was reoriented in GaussView such that the X and Y axes formed a perpendicular plane centred at the nitrile carbon and the Z axis pointed along the molecular axis, towards the nitrogen, parallel to the permanent dipole of the molecule. Electric fields ranging from 0.001 a.u to 0.009 a.u were applied along all three axes.

As the electric field increases from 0.001 a.u. to 0.009 a.u., the dipole moment shows the greatest change in magnitude when applying the field in the Z-direction parallel to the permanent dipole. This is expected since the induced polarisation of the external electric field adds to the permanent dipole, however, it is evident from table 1 that even under the maximum electric field of 0.009 a.u., the net dipole moment shows negligible change increasing from 3.9 D to 4.666 D. Due to localised electrons and the absence of a conjugate backbone, the induced polarisation is relatively low compared to the permanent dipole and can be ignored. A strong permanent dipole with negligible induced polarisation is the condition under which first-order perturbation theory predicts purely linear orbital energy responses to an electric field. Consistent with this, Table 2 and Figure 3 demonstrate that the HOMO and LUMO energies scale linearly with field strength, confirming that second-order and higher contributions to the orbital energies are insignificant.

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The electron-withdrawing nature of the nitrile group has a stabilizing effect on the molecular backbone [9] and, consequently, the HOMO and LUMO orbitals located at the nitrile end. Increasing the electric field further stabilizes the electron density at the nitrile, lowering HOMO and LUMO orbital energies, explaining the decreasing trend in Figure 3. Moreover, owing to its linear structure and highly cylindrical charge distribution, electric fields applied in the x and y directions have similar effects on orbital energies.

Substituent groups are important in determining charge transport properties. Existing literature supports the idea that, while the values and behaviour of the fermi level, ΔE_{HOMO}, and ΔE_{LUMO} are required to identify the type of charge transport in a molecule, it is generally observed that electron withdrawing groups like the nitrile group decrease HOMO and LUMO orbital energies, moving the HOMO orbital energy away from the fermi level and the LUMO orbital energy toward the fermi level, promoting the likelihood of LUMO based electron-dominated transport. In acetonitrile, although the overall behaviour of the dipole moments, frontier orbitals, and nature of the substituent energies is in agreement with theoretical predictions, the localization of electron density and the restricted extent of intramolecular charge transfer led to an extremely weak response to the applied electric field, resulting in visibly negligible changes in both orbital energies and molecular polarisation. Therefore, despite certain favourable characteristics like an electron-withdrawing group, a strong dipole moment, or predictable linear orbital behaviour, it is seen that charge mobility, electron delocalization, and a conjugate framework are necessary to achieve effective orbital tuning for a molecular electronic component.

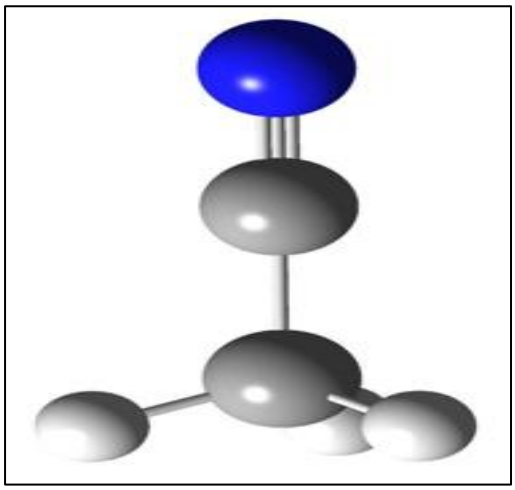

Fig 1 Optimised Structure of Acetonitrile

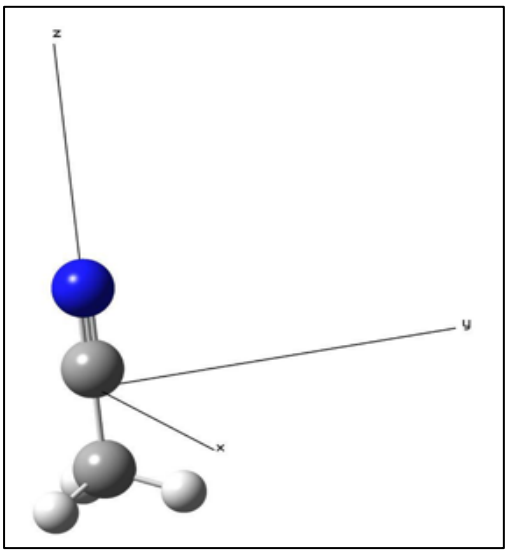

Fig 2 Orientation of Acetonitrile

Table 1 X, Y, Z, Dipole Moment Components of Acetonitrile on Applying a Positive Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)
0.000	0.000	0.000	-3.8831	0.000	0.000	-3.8831	0.000	0.000	-3.8831
0.001	-0.0424	0.0000	-3.8831	0.0000	-0.0424	-3.8831	0.0000	0.0000	-3.9698
0.002	-0.0847	0.0001	-3.8830	0.0000	-0.0848	-3.8830	0.0000	0.0000	-4.0565
0.003	-0.1271	0.0002	-3.8828	0.0000	-0.1273	-3.8828	0.0000	0.0000	-4.1433
0.004	-0.1694	0.0004	-3.8826	0.0000	-0.1698	-3.8826	0.0000	0.0000	-4.2302
0.005	-0.2118	0.0006	-3.8823	0.0000	-0.2124	-3.8823	0.0000	0.0000	-4.3171
0.006	-0.2542	0.0009	-3.8820	0.0000	-0.2551	-3.8820	0.0000	0.0000	-4.4042
0.007	-0.2965	0.0013	-3.8815	0.0000	-0.2978	-3.8815	0.0000	0.0000	-4.4914
0.008	-0.3389	0.0017	-3.8811	0.0000	-0.3406	-3.8810	0.0000	0.0000	-4.5786
0.009	-0.3813	0.0021	-3.8805	0.0000	-0.3834	-3.8805	0.0000	0.0000	-4.6660

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Table 2 HOMO, LUMO, and HOMO-LUMO Energy Gap for Acetonitrile on Applying a Positive Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)
0.000	-0.33176	0.03127	0.36303	-0.33176	0.03127	0.36303	-0.33176	0.03127	0.36303
0.001	-0.33172	0.03115	0.36287	-0.33172	0.03114	0.36286	-0.33226	0.0311	0.36336
0.002	-0.33167	0.03101	0.36268	-0.33168	0.03101	0.36269	-0.33276	0.0309	0.36366
0.003	-0.33163	0.03087	0.3625	-0.33164	0.03086	0.3625	-0.33325	0.03069	0.36394
0.004	-0.33159	0.03073	0.36232	-0.3316	0.03071	0.36231	-0.33373	0.03046	0.36419
0.005	-0.33154	0.03058	0.36212	-0.33157	0.03055	0.36212	-0.3342	0.03022	0.36442
0.006	-0.3315	0.03042	0.36192	-0.33153	0.03038	0.36191	-0.33467	0.02996	0.36463
0.007	-0.33145	0.03026	0.36171	-0.3315	0.0302	0.3617	-0.33513	0.02968	0.36481
0.008	-0.3314	0.03009	0.36149	-0.33148	0.03001	0.36149	-0.33558	0.02939	0.36497
0.009	-0.33136	0.02992	0.36128	-0.33145	0.02982	0.36127	-0.33602	0.02909	0.36511

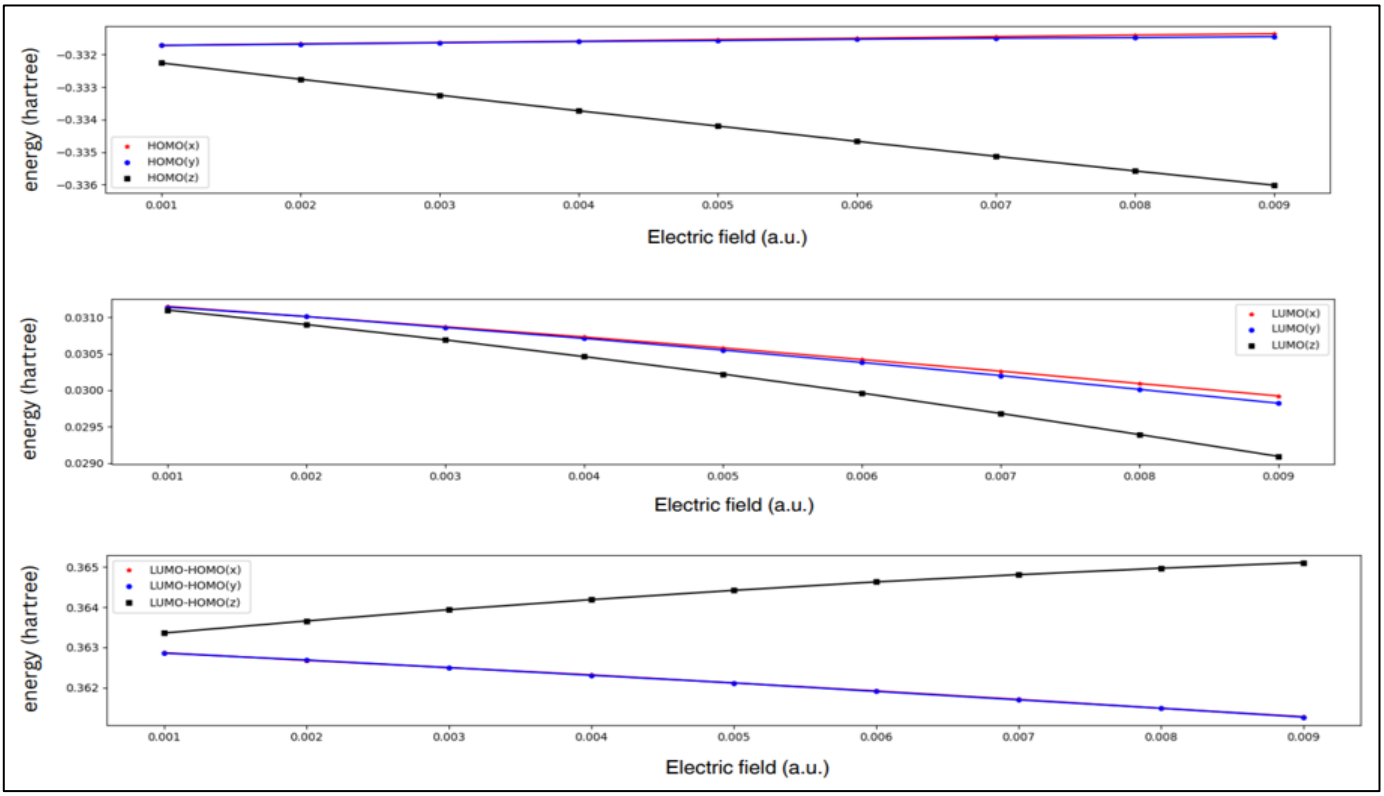

Fig 3 HOMO, LUMO, and the HOMO-LUMO Energy Gap Behavior of Acetonitrile on Applying an Electric Field in the Positive z Direction

➢ *Paranitroaniline*

Paranitroaniline is an organic compound that consists of a central benzene ring and two substituents, NH_2 and NO_2, attached to the para positions of the benzene ring, opposite to each other. NH_2 is a strong electron-donating group, whereas NO_2 is a strong electron-withdrawing group. The main frontier orbitals are located at either end of the benzene ring: the HOMO orbital is located near NH_2 and the LUMO orbital near NO_2. Due to the "push-pull" nature of both substituents, mesomeric effects result in a large permanent dipole moment of 8.29 D pointing from NH_2 to NO_2. The continuous, overlapping network of p-orbitals of benzene creates a conjugated system that promotes charge distribution and electron delocalisation across the molecule, acting as a bridge between the two substituents. [10]

The Aviram-Ratner diode, the foundational idea of molecular electronics, proposed a Donor-Bridge-Acceptor structure to model semiconductors at the molecular scale for applications in molecular electronics [11]. Although intended for rectification, the underlying ideas are relevant to tuning orbital energy levels, making them applicable to other electronic components as well. The design incorporates electron-donating and electron-accepting groups at opposite ends of the molecule, conjugated anchor groups to facilitate alignment with the electrode Fermi levels, and sigma-bond coupling between the donor and acceptor units to mechanically separate the frontier orbitals. Although the sigma bond effectively localizes the frontier orbitals at the molecular ends, it acts as an insulating barrier, reducing charge transport across the molecule.

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Work by Haiying He et al. uses a para-terphenyl system to describe frontier orbital tuning in highly conjugated Donor-Bridge-Acceptor systems [12]. Aiming to improve charge transfer and enhance orbital tuning, it proposes using a π-conjugated backbone as the bridge between the donor and the acceptor to delocalize electrons across the molecule and consequently create a stronger dipole moment from the donor to the acceptor. Instead of using sigma bond coupling to mechanically separate orbitals, it relies on this dipole moment to separate the orbitals without compromising the ease of charge transport. In this study, Paranitroaniline was selected as a model of conjugated structures like para-terphenyl. The electron-donating NH_2 group, π-conjugated benzene ring, and electron-withdrawing NO_2 group provide a simple donor-bridge-acceptor system to investigate donor-acceptor interactions and orbital tuning in conjugated systems with reduced structural complexity.

The optimised structure of paranitroaniline was oriented in GaussView such that the positive x-axis aligned antiparallel to the dipole moment and pointed toward the NH_2 group along the molecular axis, the y-axis lay within the molecular plane and perpendicular to the molecular axis, whereas the z-axis was oriented normal to the molecular plane. Positive electric fields ranging from 0.001 to 0.009 and negative electric fields ranging from -0.001 to -0.009 were applied along all three axes. Table 3 and Table 4 suggest that a negative field in the x-direction increases the dipole moment in magnitude, while a positive field decreases it. Due to the orientation of the axes used, a negative electric field in the x-direction is parallel to the dipole moment and enhances polarisation of the molecule, but a positive electric field in the x-direction is anti-parallel to the dipole moment and acts opposite the molecular polarisation. As the electric field increases from 0.001 a.u. to 0.009 a.u., the dipole moment remains around 8.3 D for fields along the y and z axes, which are perpendicular to the permanent dipole. Conversely, electric fields applied in the molecular axis in the x-direction result in larger changes of the dipole moment from 8.3 D to 11.83 D through enhanced molecular polarisation and charge transfer through the conjugated system.

On increasing the magnitude of the electric field in the -x direction along the permanent dipole, as evident in Table 5 and the trends in figure 5, induced polarisation of the molecule amplified by the charge transfer through the conjugate system from the donor to the acceptor stabilises the acceptor group, decreasing the LUMO orbital energy and destabilises the donor group, increasing the HOMO orbital energy, ultimately bringing the frontier orbitals together and decreasing the energy gap. In contrast, Figure 6 and Table 6 show that increasing electric fields in the + x direction, antiparallel to the permanent dipole, decreases the HOMO energy and increases the LUMO energy, widening the energy gap. This observed frontier orbital behaviour of para-nitroaniline under varying electric fields is consistent with the orbital responses reported for para-terphenyl systems by Haiying He et al.

Although considerable change in the dipole moment on applying the field along the molecular axis indicates second or higher order contributions to orbital energies, the linear graphs for the HOMO and LUMO orbital energies in figures 5 and 6 suggest that the strong permanent dipole in paranitroaniline, enhanced by the substituents and electron delocalisation across the molecule, results in a dominant linear response to electric fields, agreeing with first order electronic perturbation theory. Although higher-order contributions could affect the graph, the range of electric fields from 0.001 a.u. To 0.009 a.u. may be too small to observe any significant non-linear behaviour.

In most electronic components, it becomes necessary to tune the energies of the frontier HOMO and LUMO orbitals with respect to the Fermi level. Considering molecular transistors, for example, tuning ΔE_{LUMO} and ΔE_{HOMO} to achieve either hole-dominated or electron-dominated transport is analogous to a positive or negative gate voltage switching NPN or PNP transistors on or off. Supported by existing literature and the electric-field effects observed in paranitroaniline, a conjugated donor-acceptor system offers an easy way to tune orbital energies while preserving excellent charge-transport properties.

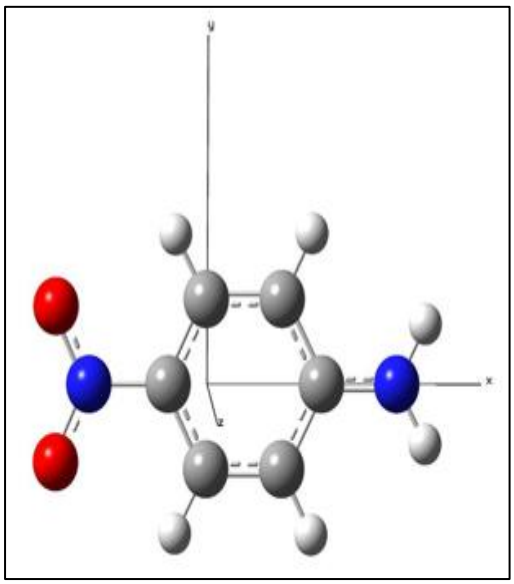

Fig 4 Optimised Structure of Paranitroaniline

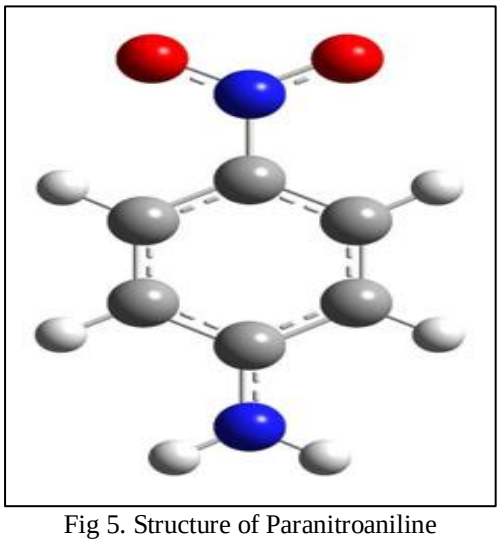

Fig 5. Structure of Paranitroaniline

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Table 3 X, Y, Z Dipole Moment Components of Paranitroaniline on Applying a Negative Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)
0.000	8.2979	0.0008	0.0025	8.2979	0.0008	0.0025	8.2979	0.0008	0.0025
-0.001	8.6703	0.0008	0.0025	8.2977	0.2278	0.0025	8.2979	0.0008	0.0655
-0.002	9.0477	0.0008	0.0025	8.2971	0.4547	0.0025	8.2979	0.0008	0.1285
-0.003	9.4302	0.0008	0.0025	8.2960	0.6816	0.0025	8.2979	0.0008	0.1916
-0.004	9.8179	0.0008	0.0025	8.2946	0.9086	0.0025	8.2978	0.0008	0.2546
-0.005	10.2108	0.0008	0.0025	8.2927	1.1356	0.0025	8.2977	0.0008	0.3176
-0.006	10.6092	0.0008	0.0025	8.2903	1.3626	0.0024	8.2976	0.0008	0.3806
-0.007	11.0129	0.0008	0.0025	8.2876	1.5897	0.0024	8.2975	0.0008	0.4437
-0.008	11.4220	0.0008	0.0025	8.2845	1.8168	0.0024	8.2974	0.0008	0.5067
-0.009	11.8366	0.0008	0.0025	8.2809	2.0440	0.0024	8.2972	0.0008	0.5697

Table 4 X, Y, Z Dipole Moment Components of Paranitroaniline on Applying a Positive Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)
0.000	8.2979	0.0008	0.0025	8.2979	0.0008	0.0025	8.2979	0.0008	0.0025
0.001	7.9304	0.0009	0.0025	8.2977	-0.2261	0.0025	8.2979	0.0009	-0.0605
0.002	7.5676	0.0009	0.0025	8.2971	-0.4530	0.0025	8.2979	0.0009	-0.1236
0.003	7.2092	0.0009	0.0025	8.2961	-0.6800	0.0025	8.2979	0.0009	-0.1866
0.004	6.8553	0.0009	0.0025	8.2946	-0.9069	0.0025	8.2978	0.0009	-0.2496
0.005	6.5055	0.0009	0.0025	8.2927	-1.1339	0.0025	8.2977	0.0009	-0.3126
0.006	6.1597	0.0009	0.0025	8.2904	-1.3609	0.0025	8.2976	0.0009	-0.3757
0.007	5.8178	0.0009	0.0025	8.2877	-1.5880	0.0025	8.2975	0.0009	-0.4387
0.008	5.4794	0.0009	0.0025	8.2845	-1.8151	0.0025	8.2974	0.0009	-0.5017
0.009	5.1445	0.0009	0.0025	8.2810	-2.0423	0.0025	8.2972	0.0009	-0.5648

Table 5 HOMO, LUMO, and HOMO-LUMO Energy Gap for Paranitroaniline on Applying a Positive Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)
0.000	-0.23026	-0.08614	0.14412	-0.23026	-0.08614	0.14412	-0.23026	-0.08614	0.14412
0.001	-0.23185	-0.08519	0.14666	-0.23026	-0.08614	0.14412	-0.23026	-0.08614	0.14412
0.002	-0.23345	-0.08423	0.14922	-0.23027	-0.08615	0.14412	-0.23026	-0.08614	0.14412
0.003	-0.23506	-0.08325	0.15181	-0.23027	-0.08617	0.1441	-0.23027	-0.08614	0.14413
0.004	-0.23667	-0.08226	0.15441	-0.23028	-0.08619	0.14409	-0.23027	-0.08614	0.14413
0.005	-0.2383	-0.08126	0.15704	-0.23029	-0.08621	0.14408	-0.23027	-0.08614	0.14413
0.006	-0.23992	-0.08025	0.15967	-0.2303	-0.08624	0.14406	-0.23027	-0.08615	0.14412
0.007	-0.24155	-0.07925	0.1623	-0.23031	-0.08628	0.14403	-0.23028	-0.08615	0.14413
0.008	-0.24318	-0.07825	0.16493	-0.23033	-0.08633	0.14400	-0.23028	-0.08615	0.14413
0.009	-0.24481	-0.07726	0.16755	-0.23035	-0.08638	0.14397	-0.23029	-0.08616	0.14413

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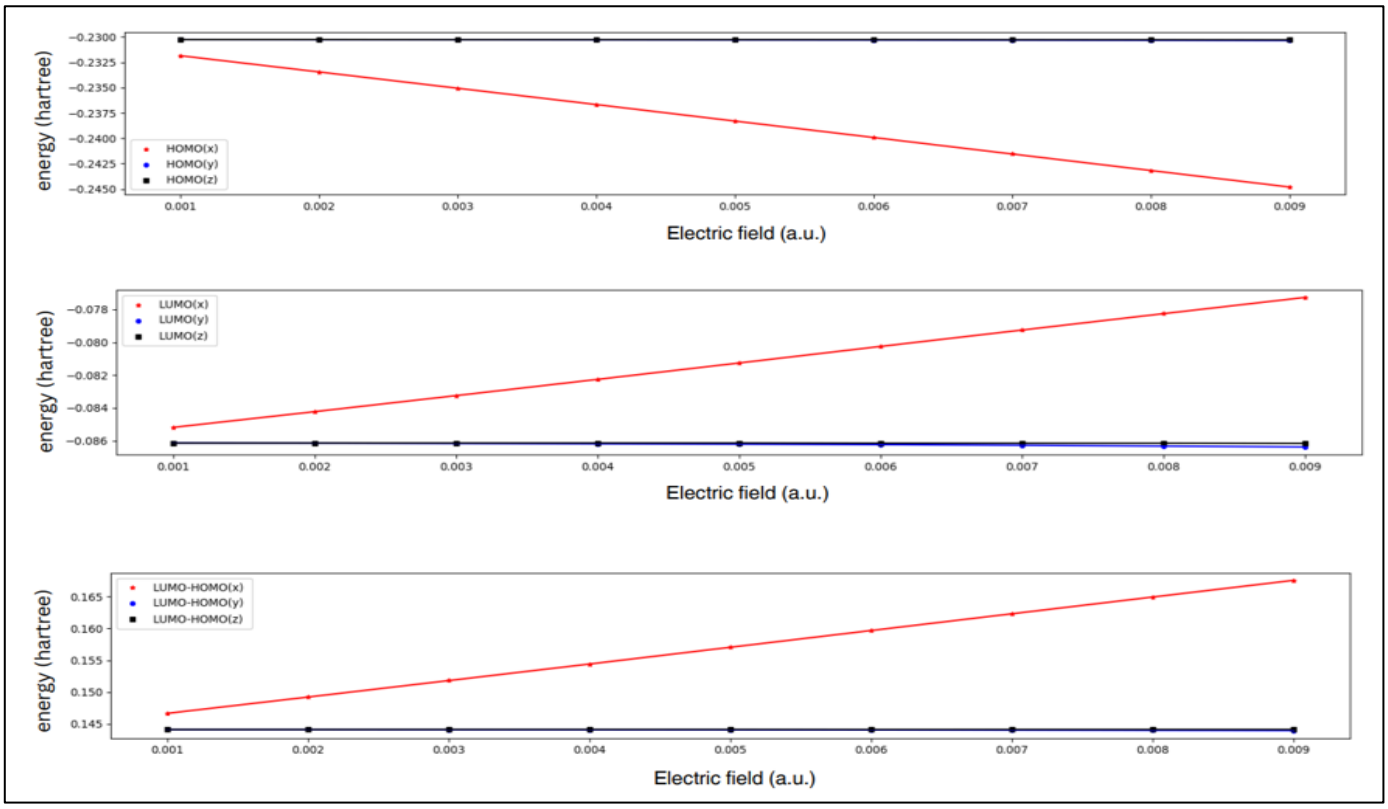

Fig 6 HOMO, LUMO, and HOMO-LUMO Energy Gap Behavior of Paranitroaniline on Applying an Electric Field in the Positive x Direction

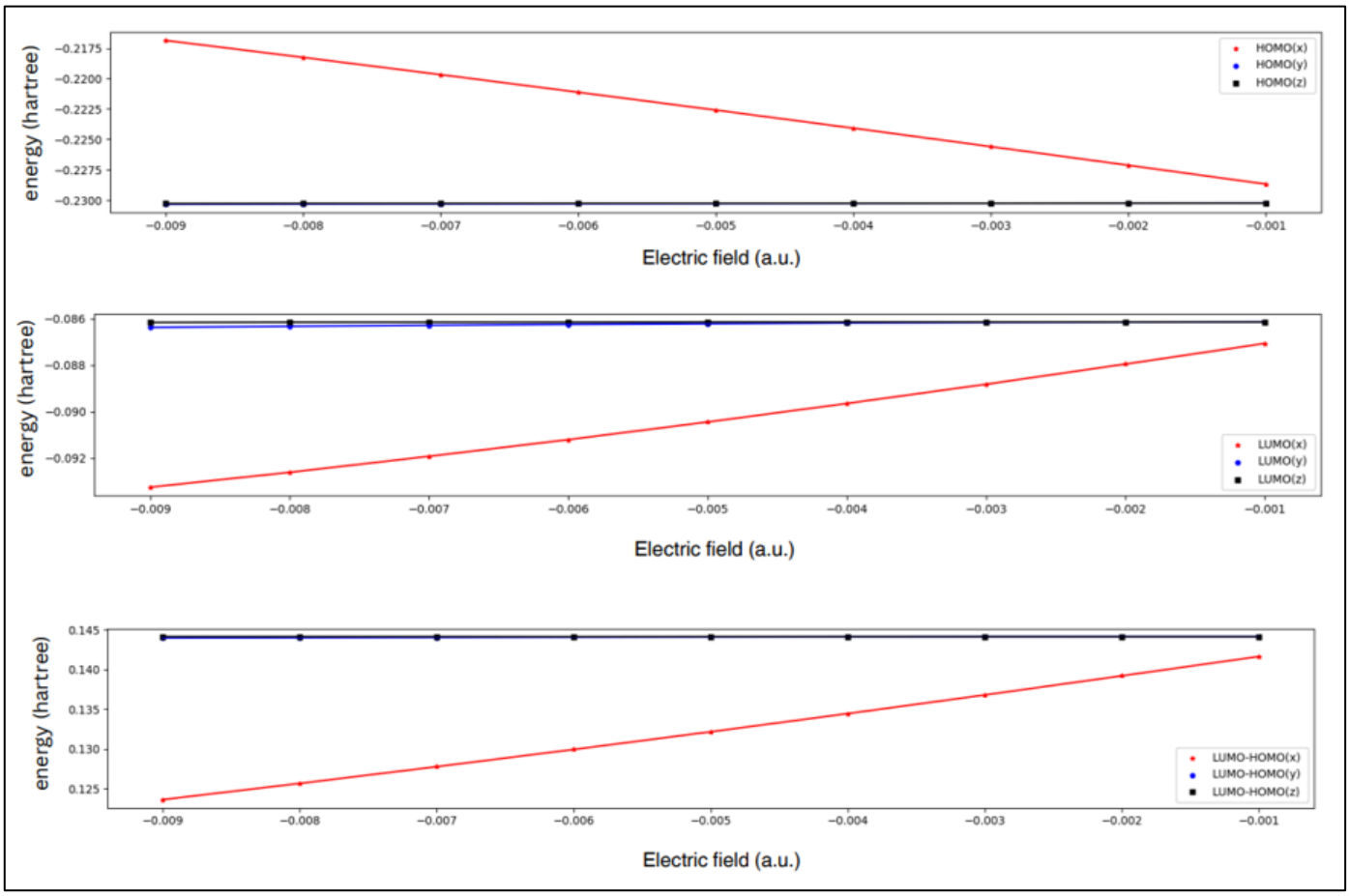

Fig 7 HOMO, LUMO and HOMO-LUMO Energy Gap Behaviour of Paranitroaniline on Applying an Electric Field in the Negative x Direction

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➢ *1,3 Trans - Butadiene*

Trans-butadiene is a planar polyene molecule made up of four carbon atoms arranged as two ethene-like double-bonded fragments connected by a sigma bond. Butadiene is found as both cis- and trans- isomers, the latter of which was chosen for this study due to the reduced steric hindrance, increased stability, and improved conjugation associated with the trans- isomer [13]. All four carbon atoms are sp^2 hybridized, leaving a pure p orbital on each carbon atom, perpendicular to the molecular plane. Overlapping of these p-orbitals creates a near-linear conjugated system along the molecular backbone, increasing electron delocalization and charge transfer. The four p-orbitals combine to create four molecular orbitals: 2 π^* Anti-Bonding Molecular Orbitals and 2π Bonding Molecular Orbitals. Due to its highly symmetric structure, trans-butadiene does not show a permanent dipole. According to Huckel Molecular Orbital theory [14], used to determine orbital energies and behaviour in conjugated systems such as aromatic compounds or polyenes, the frontier molecular orbitals of Butadiene are closer in energy to the outer molecular orbitals than to each other.

Conjugated molecules and structures such as polyenes, polyynes, and oligomers are preferred for molecular electronic applications such as wires and switches due to improved electron transfer and observable higher-order polarisability effects [15]. To induce a permanent dipole and improve orbital tuning, most studies add donor and acceptor substituents to polyenes to replicate a donor-bridge-acceptor system [16]. To investigate the orbital behaviour of non-polar conjugated polyenes, trans-1,3-butadiene was selected because of its high molecular symmetry, extensive π-electron delocalization, and structural simplicity. As an unsubstituted polyene with no permanent dipole moment, trans-butadiene exhibits negligible first-order electronic perturbation in an external electric field, allowing second- and higher-order field effects to be examined more clearly. These characteristics make it a useful model for understanding the electric-field response of more complex conjugated polyenes. The axis passing through the terminal carbons was considered the molecular axis, and the molecule was oriented in GaussView so that the y-axis aligned with the molecular axis and the x- and z-axes formed a plane perpendicular to the molecular backbone. (Figure 8).

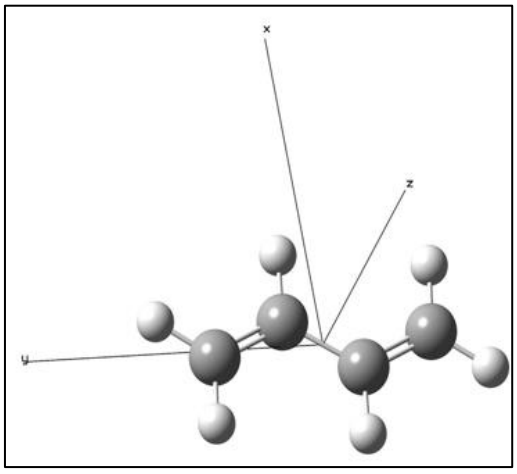

Fig 8 Orientation of Butadiene

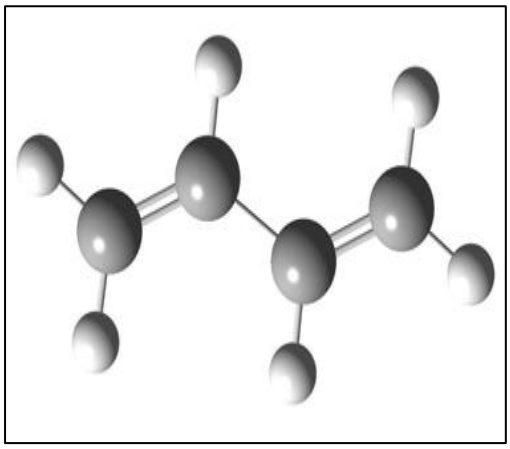
Fig 9 Optimized Structure of Butadiene

Electric fields ranging from 0.001 a.u. to 0.009 a.u. were applied in the positive and negative directions along all three axes. Due to the molecule's symmetry, positive and negative electric fields of equal magnitude induced equal dipole moments. Therefore, only the data corresponding to the dipole moment in the positive field are shown in Table 7. Admittedly, due to the trans- conformation of the molecular backbone, the electrons are not delocalized exactly along the straight molecular axis. Consequently, although increasing the electric field along the y-axis showed the greatest change in the y component, increasing it from 0 D to 1.78 D, it also induced polarisation in the x and z directions, increasing the x and z dipole components in magnitude.

According to Figure 9 and Table 6, the electric field applied along the x- and z-axes, perpendicular to the molecular backbone, has negligible effects on the frontier orbitals, since the conjugated system lies along the y-axis. However, orbital behavior as the electric field in the y-direction increases is non-linear, seemingly quadratic. This indicates expected behavior in the absence of a permanent dipole: there is no first-order linear perturbation of orbitals by the external electric field. Instead, higher-order contributions and second-order electronic perturbation theory can be used to explain orbital behavior. Increasing the electric field promotes orbital mixing and interactions among the molecular orbitals of butadiene. According to second-order electronic perturbation theory, when a higher-energy orbital interacts with a lower-energy orbital, the higher-energy orbital is pushed up in energy, and the lower-energy orbital is pushed down in energy. The magnitude of these energy shifts is inversely proportional to the initial energy difference between the orbitals. Closer orbitals show greater interactions and greater energy changes.

In Butadiene, the changes in the frontier orbital energies (Table 6 and Figure 9), although relatively small over a narrow range of electric fields (0.001 a.u to 0.009 a.u.), can be explained using these orbital interactions. Under an increasing electric field, the HOMO orbital interacts with the LUMO orbital and the closer Bonding Molecular Orbital, ultimately moving up in energy. Conversely, the LUMO orbital interacts with the HOMO orbital and the closer anti-bonding molecular orbital, ultimately decreasing in energy.

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LUMO energies show greater response to the electric field, likely due to the diffuse, field-sensitive nature of the anti-bonding orbitals. Therefore, the interactions of the orbitals result in an increasing HOMO, decreasing LUMO, and a consequent narrowing of the HOMO-LUMO energy gap, explaining the orbital energy trends in Figure 9 and Table 8.

Moreover, Table 7 and Table 8 show that orbital energies are equal in the positive and negative directions, owing largely to the symmetry and non-polarity of butadiene. Therefore, Figures 10 and 11 show a narrowing HOMO-LUMO energy gap under an electric field in positive and negative directions.

Table 6 X, Y, Z Dipole Moment Components of Butadiene on Applying a Positive Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)	μ_x (Debye)	μ_y (Debye)	μ_z (Debye)
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.001	-0.0984	0.0160	0.0000	0.0160	-0.1976	0.0000	0.0000	0.0000	-0.0350
0.002	-0.1969	0.0320	0.0000	0.0320	-0.3951	0.0000	0.0000	0.0000	-0.0701
0.003	-0.2953	0.0481	0.0000	0.0481	-0.5927	0.0000	0.0000	0.0000	-0.1051
0.004	-0.3938	0.0641	0.0000	0.0640	-0.7903	0.0000	0.0000	0.0000	-0.1401
0.005	-0.4923	0.0801	0.0000	0.0800	-0.9881	0.0000	0.0000	0.0000	-0.1751
0.006	-0.5908	0.0962	0.0000	0.0959	-1.1860	0.0000	0.0000	0.0000	-0.2102
0.007	-0.6893	0.1122	0.0000	0.1117	-1.3840	0.0000	0.0000	0.0000	-0.2452
0.008	-0.7878	0.1283	0.0000	0.1275	-1.5821	0.0000	0.0000	0.0000	-0.2802
0.009	-0.8864	0.1443	0.0000	0.1432	-1.7805	0.0000	0.0000	0.0000	-0.3153

Table 7 HOMO, LUMO, and HOMO-LUMO Energy Gap for Butadiene on Applying a Positive Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)
0.000	-0.2299	-0.02406	0.20593	-0.2299	-0.02406	0.20593	-0.2299	-0.02406	0.20593
0.001	-0.22999	-0.02406	0.20593	-0.22998	-0.02407	0.20591	-0.22999	-0.02406	0.20593
0.002	-0.22999	-0.02407	0.20592	-0.22996	-0.0241	0.20586	-0.22999	-0.02406	0.20593
0.003	-0.23	-0.02408	0.20592	-0.22994	-0.02415	0.20579	-0.22999	-0.02406	0.20593
0.004	-0.23001	-0.0241	0.20591	-0.2299	-0.02423	0.20567	-0.22999	-0.02407	0.20592
0.005	-0.23003	-0.02412	0.20591	-0.22985	-0.02432	0.20553	-0.22999	-0.02407	0.20592
0.006	-0.23005	-0.02415	0.2059	-0.22979	-0.02444	0.20535	-0.23	-0.02408	0.20592
0.007	-0.23007	-0.02419	0.20588	-0.22973	-0.02457	0.20516	-0.23	-0.02409	0.20591
0.008	-0.2301	-0.02423	0.20587	-0.22965	-0.02473	0.20492	-0.23	-0.02409	0.20591
0.009	-0.23013	-0.02427	0.20586	-0.22956	-0.0249	0.20466	-0.23001	-0.0241	0.20591

Although the behaviour of frontier orbitals in butadiene is theoretically valid, it is undeniable that the orbital responses are still too small for any practical purposes. This is supported by a large number of studies emphasizing the importance of donor-acceptor substituents in polyenes to increase first and higher-order polarisabilities, essentially using the donor-pi-acceptor system in conjugated polyenes to localize orbitals on opposite ends and achieve better orbital tuning. Besides possible applications in molecular field-effect transistors via electric-field-induced orbital tuning, the fundamental structure of the conjugated backbone of a polyene is relevant to other components as well. According to Huckel Molecular Orbital theory [17], increasing the length of the conjugated system decreases the energy gap. The enhanced charge transfer across conjugated polyenes, as well as the ability to use polyene length to control the energy gap, make conjugated polyenes applicable as molecular equivalents of conductive wires.

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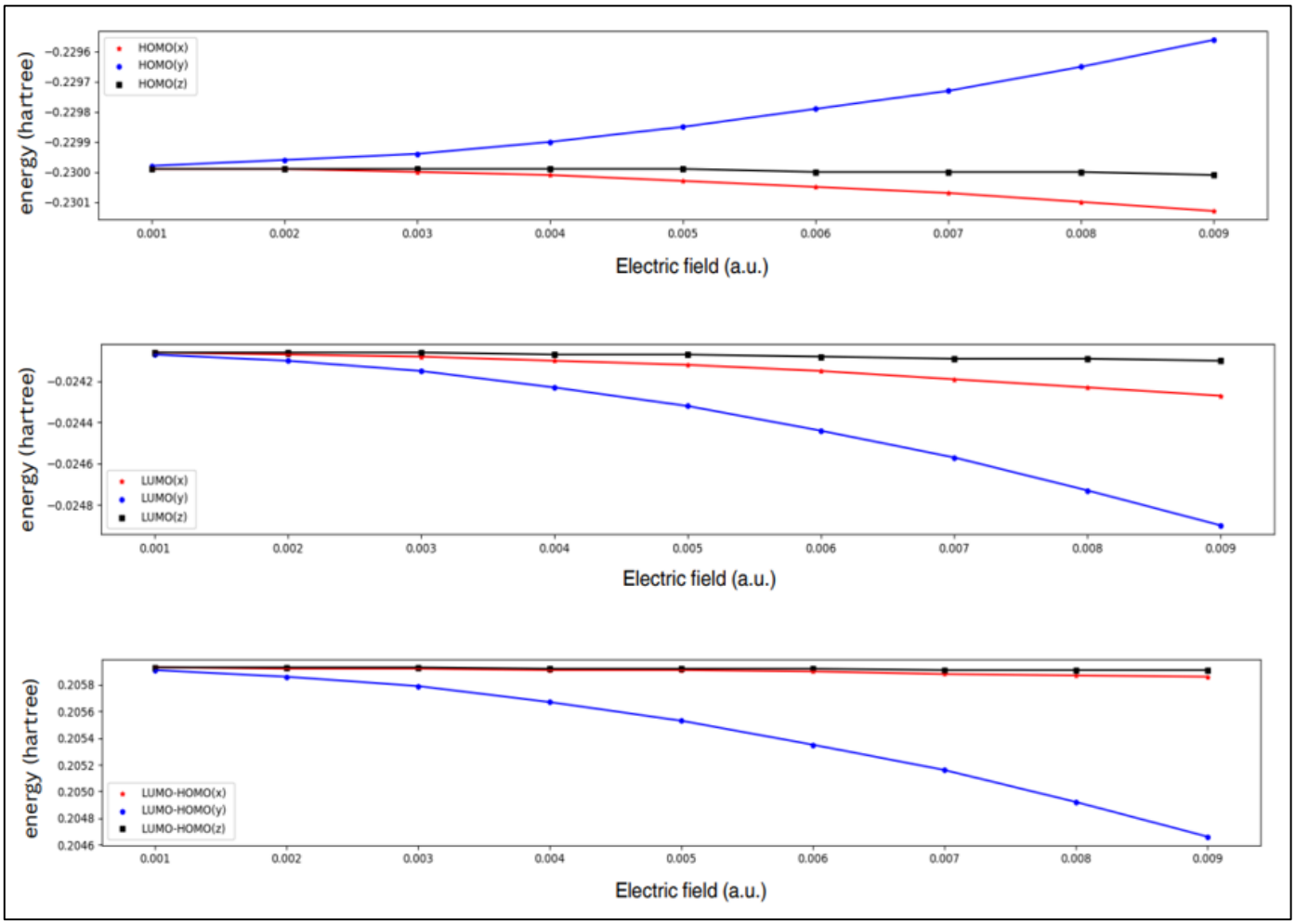

Fig 10 HOMO, LUMO, and HOMO-LUMO Energy Gap Behavior of Butadiene on Applying an Electric Field in the Positive y Direction

Table 8 HOMO, LUMO, and HOMO-LUMO Energy Gap for Butadiene on Applying a Negative Electric Field in Different Directions

	X - direction			Y-direction			Z-direction		
field (a.u)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)	HOMO (hartree)	LUMO (hartree)	ΔE (hartree)
0.000	-0.2299	-0.02406	0.20593	-0.2299	-0.02406	0.20593	-0.2299	-0.02406	0.20593
0.001	-0.22999	-0.02406	0.20593	-0.22998	-0.02407	0.20591	-0.22999	-0.02406	0.20593
0.002	-0.22999	-0.02407	0.20592	-0.22996	-0.0241	0.20586	-0.22999	-0.02406	0.20593
0.003	-0.23	-0.02408	0.20592	-0.22994	-0.02415	0.20579	-0.22999	-0.02406	0.20593
0.004	-0.23001	-0.0241	0.20591	-0.2299	-0.02423	0.20567	-0.22999	-0.02407	0.20592
0.005	-0.23003	-0.02412	0.20591	-0.22985	-0.02432	0.20553	-0.22999	-0.02407	0.20592
0.006	-0.23005	-0.02415	0.2059	-0.22979	-0.02444	0.20535	-0.23	-0.02408	0.20592
0.007	-0.23007	-0.02419	0.20588	-0.22973	-0.02457	0.20516	-0.23	-0.02409	0.20591
0.008	-0.2301	-0.02423	0.20587	-0.22965	-0.02473	0.20492	-0.23	-0.02409	0.20591
0.009	-0.23013	-0.02427	0.20586	-0.22956	-0.0249	0.20466	-0.23001	-0.0241	0.20591

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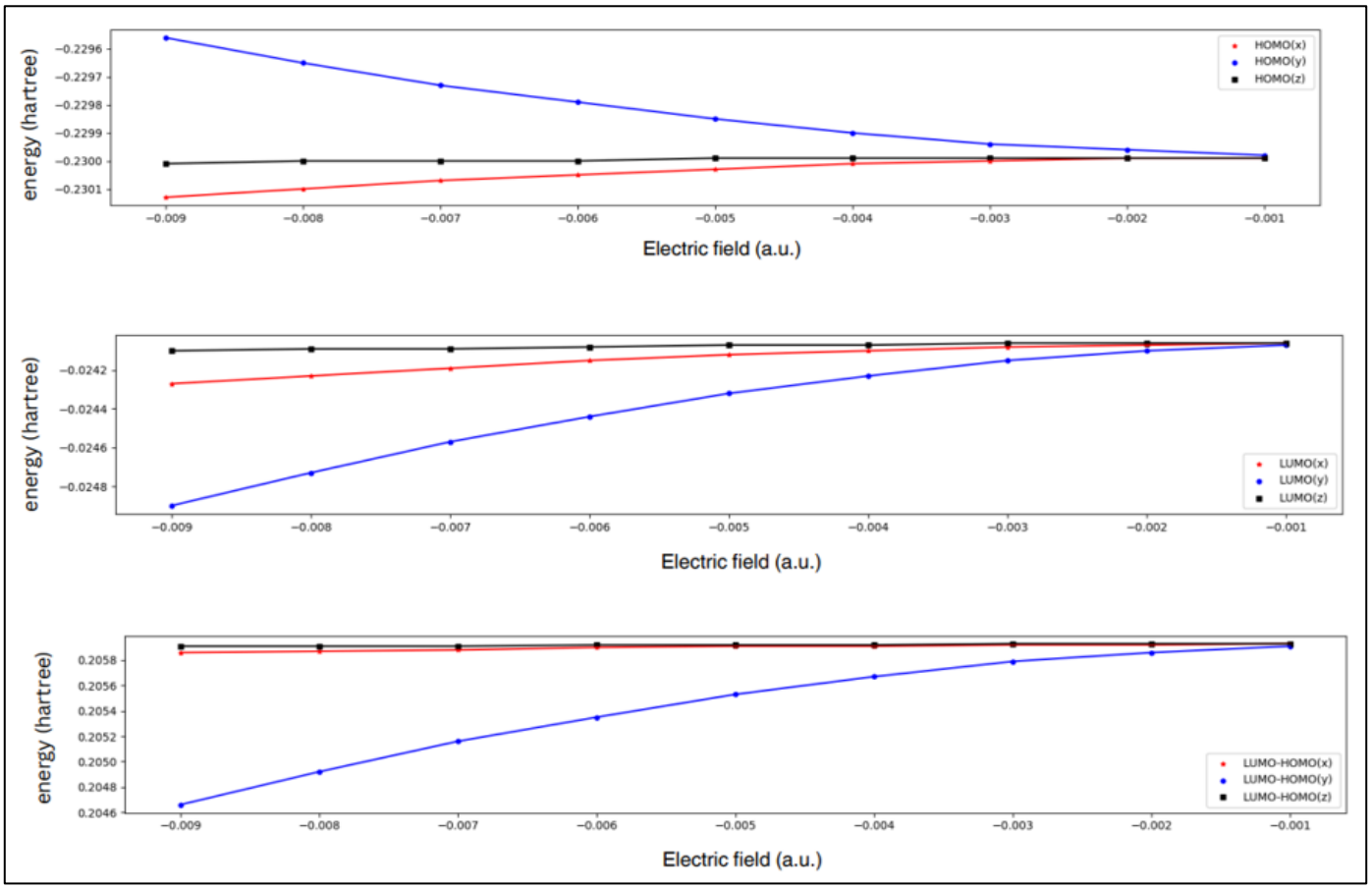

Fig 11 HOMO, LUMO, and HOMO-LUMO Energy Gap Behaviour of Butadiene on Applying an Electric Field in the Negative y Direction

IV. CONCLUSIONS

Using simple molecules that mimic the behaviour and structure of popular molecular systems, this paper analysed the behaviour of frontier molecular orbitals; used molecular orbital theory and perturbation theory for theoretical understanding [18],[19]; and ultimately identified certain intrinsic characteristics that may be favourable (or unfavourable) to specific applications in molecular electronics. Identifying molecules for practical applications requires a lot more than analyzing orbital energy trends, charge transfer, or dipole moments; however, that is not the primary goal of this article.

Acetonitrile, a highly polar molecule, exhibited a dominant first-order electronic perturbation, negligible orbital effects, and energy-level stabilization due to the electron-withdrawing nitrile group. Although the general orbital behaviour may be favourable for electron-dominated transport, the limited charge transfer in the absence of a conjugated system indicates the importance of electron mobility across molecules.

Hence, paranitroaniline, a polar molecule with a conjugated benzene ring, was chosen. The molecule also served as an excellent model for the popular donor-bridge-acceptor framework. Expectedly, the donor-acceptor framework increased the sensitivity of the orbitals. It showed a closing energy gap for fields applied along the permanent dipole and a widening gap for fields in the opposite direction. Consistent with other studies of similar systems, the enhanced charge transfer, polarity, and orbital behaviour of molecules such as paranitroaniline appear highly favourable for applications in molecular electronics. To assess the importance of polarity, 1,3-trans-butadiene, a symmetric, nonpolar polyene with a conjugated backbone, was also studied. In the absence of a permanent dipole, the orbitals showed expected non-linear trends; however, the orbital responses were too small. Although the linear and conjugated structure of butadiene is a favourable characteristic for components like wires, donor-acceptor substituents and a permanent dipole are necessary to achieve better orbital tuning in polyenes. Therefore, considering these three molecules, molecular structures or systems that provide a permanent dipole, a conjugated network, and enhanced charge transfer may be favourable for use in molecular electronics. =

There is no doubt that increased demand for faster, smaller, and more efficient electronics makes nano-electronics and molecular electronics a very important field. Although issues with manufacturing, testing, and implementation affect large-scale commercial application, the current rate of research and human development suggests that the application of molecular analogues of devices is unavoidable.

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