Topological Electronic Sensitivity Index (TESI): Weighted Graph Spectral Analysis of Molecular Systems with Electron Delocalization Indices

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Supplementary Information (SI)

Contents

1 Methodological Guide for the TESI Index: Case of Acrylonitrile ($CH_2 = CH - CN$)

This section details the mathematical protocol for calculating the TESI (Topological Electronic Sensitivity Index). The mathematical details of the TESI calculation will be explained step by step, also providing annotated Python codes to facilitate their use for other chemical systems. The Acrylonitrile molecule is used as a model.

1.1 Step 1: Calculation of f^+_{AB}

The first step consists of measuring the local response of electron sharing during an ionization (electron addition in the present case). The non-local second-order Fukui index f^+_{AB} is used. This non-local descriptor is defined as the variation of the delocalization index δ_{AB} between the neutral state (N) and the anionic state ($N+1$) is defined as: $f^+_{AB} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

1.2 Table of f^-_{AB} indices for Acrylonitrile

Tab. 1S: Electron delocalization indices and f^+_{AB} values for Acrylonitrile.

Bond	**Atoms**	$\delta_{AB}(N)$	$\delta_{AB}(N+1)$	f^+_{AB}
C1=C2	1–2	1.9431	1.7773	-0.1658
C2–C3	2–3	1.1300	1.1868	+0.0568
C3–N4	3–4	1.2730	1.2843	+0.0113

2 Step 2: Topological Modeling (Graph)

A molecular graph is constructed where each heavy atom represents a node ($N_{at} = 4$).

2.1 Index Correspondence

The placement of data within the matrices follows the skeletal connectivity:

- **Index 1:** Atom C1 (Vinyl terminal)
- **Index 2:** Atom C2 (Vinyl central)
- **Index 3:** Atom C3 (Nitrile carbon)
- **Index 4:** Atom N4 (Nitrile nitrogen)

2.2 Construction of the Weighted Adjacency Matrix W_{AB}

Within the TESI framework, the molecular graph is represented as a weighted, undirected graph where each node corresponds to a heavy atom and each edge is weighted by the electron-pair delocalization index δ_{AB}. The weighted adjacency matrix W_{AB} encodes the electronic connectivity between bonded atoms and is defined as:

$$W_{AB} = \begin{cases} \delta_{AB} & \text{if atoms } A \text{ and } B \text{ are chemically bonded,} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

For acrylonitrile ($\mathrm{CH_2 = CH - CN}$), considering only the heavy-atom skeleton (C1–C2–C3–N4), the weighted adjacency matrix reads:

$$W_{AB} = \begin{pmatrix} 0 & 1.9431 & 0 & 0 \\ 1.9431 & 0 & 1.1300 & 0 \\ 0 & 1.1300 & 0 & 1.2730 \\ 0 & 0 & 1.2730 & 0 \end{pmatrix} \tag{2}$$

This matrix reflects the intrinsic electronic communication channels of the neutral molecule, as quantified by the delocalization indices.

2.3 Construction of the Degree Matrix D_{AA}

The degree matrix D_{AA} is a diagonal matrix that captures the total electronic connectivity associated with each atomic site. Each diagonal element corresponds to the sum of the delocalization indices of all bonds connected to a given atom:

$$D_{AA} = \sum_{B} W_{AB} \tag{3}$$

For acrylonitrile, the degree matrix is therefore given by:

$$D_{AA} = \begin{pmatrix} 1.9431 & 0 & 0 & 0 \\ 0 & 3.0731 & 0 & 0 \\ 0 & 0 & 2.4030 & 0 \\ 0 & 0 & 0 & 1.2730 \end{pmatrix} \tag{4}$$

Physically, the diagonal elements of D_{AA} represent the local electronic embedding of each atom within the molecular network, i.e., the extent to which an atom participates in electron-pair sharing with its neighbors.

2.4 Laplacian Matrix ($L_\delta = D_{AA} - W_{AB}$)

The graph Laplacian matrix is then obtained as the difference between the degree matrix and the weighted adjacency matrix:

$$L_\delta = D_{AA} - W_{AB} \tag{5}$$

Explicitly, this yields:

$$L_\delta = \begin{pmatrix} 1.9431 & -1.9431 & 0 & 0 \\ -1.9431 & 3.0731 & -1.1300 & 0 \\ 0 & -1.1300 & 2.4030 & -1.2730 \\ 0 & 0 & -1.2730 & 1.2730 \end{pmatrix} \tag{6}$$

This Laplacian matrix constitutes the core topological operator of the TESI formalism, encoding both the molecular connectivity and the distribution of electronic delocalization.

3 Step 3: Spectral Analysis and Fiedler Vector

The eigenvalues (λ_i) and eigenvectors ($\mathbf{v}_i$) of L_δ are obtained by solving the standard eigenvalue problem:

$$L_\delta \mathbf{v}_i = \lambda_i \mathbf{v}_i, \quad i = 1, 2, \ldots, M \tag{7}$$

where M is the number of heavy atoms (nodes) in the molecule.

Remarks:

- The smallest eigenvalue is always $\lambda_1 = 0$ for a connected graph.
- The second smallest eigenvalue, λ_2, is called the algebraic connectivity and reflects the overall topological cohesion of the molecule.
- Its associated eigenvector, $\mathbf{v}_2$, is known as the Fiedler vector, which provides a measure of the relative topological electronic sensitivity of each atomic site.

In practice, these eigenvalues and eigenvectors can be computed using standard linear algebra routines. In Python, for a symmetric Laplacian matrix L_δ, this can be achieved as:

```python
import numpy as np
eigvals, eigvecs = np.linalg.eigh(L)
# eigvals[i] -> lambda_i
# eigvecs[:,i] -> v_i
```

The Fiedler vector $\mathbf{v}_2$ is then used to compute the topological weights of the bonds:

$$\omega_{AB} = (v_A - v_B)^2 \tag{8}$$

which serve as a measure of the intrinsic electronic connectivity between atoms A and B.

3.1 Eigenvalues (Spectrum)

- $\lambda_1 = 0.0000$
- $\lambda_2 = 0.7554$ (**Fiedler Connectivity**)
- $\lambda_3 = 2.9954$
- $\lambda_4 = 4.9414$

3.2 Normalized Fiedler Vector ($\mathbf{v}_2$)

The eigenvector associated with λ_2 represents the intrinsic sensitivity of each atomic site:

$$\mathbf{v}_2 = \begin{pmatrix} 0.5869 & 0.3588 & -0.2734 & -0.6723 \end{pmatrix}^T \tag{9}$$

4 Step 4: Calculation of Topological Weights (ω_{AB})

The topological weight of a bond is defined as the square of the difference between the Fiedler components of the connected atoms: $\omega_{AB} = (v_A - v_B)^2$.

Bond	**Indices**	v_A	v_B	**Weight** ω_{AB}
C1=C2	1–2	0.5869	0.3588	0.0521
C2–C3	2–3	0.3588	-0.2734	0.3996
C3–N4	3–4	-0.2734	-0.6723	0.1592

5 Step 5: Final TESI Index Calculation

The TESI index is the normalized product of the absolute Fukui flux and the topological weight.

$$TESI_{AB}(\%) = \frac{|f_{AB}^{+}| \cdot \omega_{AB}}{\sum |f_{AB}^{+}| \cdot \omega_{AB}} \times 100 \tag{10}$$

Bond	$\lvert f_{AB}^{+}\rvert$	ω_{AB}	Product	**TESI (%)**
C1=C2	0.1658	0.0521	0.00863	**26.05**
C2–C3	0.0568	0.3996	0.02270	**68.52**
C3–N4	0.0113	0.1592	0.00180	**5.43**
Total			0.03313	**100.00**

Significance of Fiedler Vector Normalization ($\mathbf{v}_2$)

The normalization of the Fiedler vector $\mathbf{v}_2$ ($\|\mathbf{v}_2\| = 1$) removes the arbitrariness associated with eigenvector scaling and ensures that the resulting descriptor is universal and reproducible. It provides a common reference scale for electronic sensitivity, allowing the components v_i to be interpreted as relative atomic contributions to the global electronic response and enabling meaningful comparison of the topological weights $\omega_{AB} = (v_A - v_B)^2$ across different bonds and molecular systems. By fixing the total amplitude of $\mathbf{v}_2$, normalization stabilizes the topological distribution of sensitivity, ensuring that the TESI index reflects an intrinsic and conserved partitioning of electronic responsivity over the molecular framework.

Significance of the Absolute Value in the TESI Calculation

The use of the absolute value $|f^{\pm}_{AB}|$ in the TESI definition ensures physical and statistical consistency. While the sign of the bond Fukui index reflects whether electron sharing is strengthened or weakened, TESI is designed to quantify the magnitude of the electronic response independently of its direction. Taking the absolute value prevents artificial cancellation between opposite contributions, preserves additivity, and enables rigorous normalization of the index to a total of 100 %. Furthermore, since the topological weight $\omega_{AB} = (v_A - v_B)^2$ is intrinsically non-negative, its combination with $|f^{\pm}_{AB}|$ guarantees a strictly positive contribution for each bond. The resulting product thus provides a consistent measure of the amplitude of electronic reorganization, allowing TESI to reliably map the localization of electronic sensitivity within the molecular framework.

6 Python Implementation of TESI

Below is the source code as it implemented in the **Visual Studio Code** editor:

```python
import numpy as np
from tabulate import tabulate

# ============================================
# 0. ATOMIC COORDINATES (Acrylonitrile)
# ============================================
# Atom mapping: 0:C1, 1:C2, 2:C3, 3:N4, 4:H5, 5:H6, 6:H7
atom_labels = ["C1", "C2", "C3", "N4", "H5", "H6", "H7"]
atomic_numbers = [6, 6, 6, 7, 1, 1, 1]
coords = np.array([
    [-1.596013, -0.360282, 0.000000], # C1
    [-0.588073, 0.506781, 0.000000], # C2
```

```
    [ 0.781812, 0.093061, 0.000000], # C3
    [ 1.888491, -0.224729, 0.000000], # N4
    [-2.621445, -0.011494, 0.000000], # H5
    [-1.425615, -1.430380, 0.000000], # H6
    [-0.758730, 1.577617, 0.000000] # H7
])

# ==========================================
# 1. INPUT DATA FOR TESI (HEAVY ATOMS ONLY)
# ==========================================
# Atom mapping for TESI: 0:C1, 1:C2, 2:C3, 3:N4
bond_labels = ["C1=C2", "C2-C3", "C3-N4"]
atom_indices = [(0, 1), (1, 2), (2, 3)]

# Delocalization indices
delta_neutral = [1.9431, 1.1300, 1.2730]
delta_anion = [1.7773, 1.1868, 1.2843]

# ==========================================
# 2. FUKUI (NSFI) CALCULATION (f_AB)
# ==========================================
fukui_flux = [a - n for a, n in zip(delta_anion, delta_neutral)]
abs_fukui = [abs(f) for f in fukui_flux]

# ==========================================
# 3. TOPOLOGICAL MATRICES (W, D, L)
# ==========================================
num_atoms = 4 # only heavy atoms
W = np.zeros((num_atoms, num_atoms))

for i, (a, b) in enumerate(atom_indices):
    W[a, b] = W[b, a] = delta_neutral[i]

D = np.diag(np.sum(W, axis=1))
L = D - W

# ==========================================
# 4. SPECTRAL ANALYSIS (Fiedler Vector)
# ==========================================
eigvals, eigvecs = np.linalg.eigh(L)
lambda_2 = eigvals[1]
v2 = eigvecs[:, 1]

# Optional: force the sign for consistency
if v2[0] < 0:
    v2 = -v2

# Explicit normalization (good practice)
v2 = v2 / np.linalg.norm(v2)
```

```python

# ==========================================
# 5. TOPOLOGICAL WEIGHTS (omega) AND TESI
# ==========================================
topo_weights = [(v2[a] - v2[b])**2 for (a, b) in atom_indices]
products = [f * w for f, w in zip(abs_fukui, topo_weights)]
total_sensitivity = sum(products)
tesi_index = [(p / total_sensitivity) * 100 for p in products]

# ==========================================
# 6. RESULTS DISPLAY
# ==========================================
print("\n" + "="*65)
print("STEP 0: ATOMIC COORDINATES")
print("="*65)
coord_table = [[atom_labels[i], atomic_numbers[i], *coords[i]] for i in range(len(atom_labels))]
print(tabulate(coord_table, headers=["Atom", "Z", "X", "Y", "Z"], floatfmt=".6f"))

print("\n" + "="*65)
print("STEP 1: NON-LOCAL SECOND-ORDER FUKUI INDEX (NSFI)")
print("="*65)
flux_table = [[bond_labels[i], delta_neutral[i], delta_anion[i], fukui_flux[i]] for i in range(len(bond_labels))]
print(tabulate(flux_table, headers=["Bond", "delta(N)", "delta(N+1)", "f_AB^-"], floatfmt=".4f"))

print("\n" + "="*65)
print("STEP 2: LAPLACIAN SPECTRUM")
print("="*65)
print(f"lambda_2 (Fiedler Connectivity): {lambda_2:.4f}")

print("\n" + "="*65)
print("STEP 3: NORMALIZED FIEDLER VECTOR (v2)")
print("="*65)
v2_table = [[f"Atom {i+1}", v2[i]] for i in range(num_atoms)]
print(tabulate(v2_table, headers=["Site", "v2 Value"], floatfmt=".4f"))

print("\n" + "="*65)
print("STEP 4: FINAL TESI CALCULATION")
print("="*65)
final_table = [[bond_labels[i], abs_fukui[i], topo_weights[i], products[i], tesi_index[i]] for i in range(len(bond_labels))]
print(tabulate(final_table, headers=["Bond", "|f_AB|", "omega_AB", "Product", "TESI (%)"], floatfmt=".4f"))

print(f"\nTotal Sensitivity Sum: {total_sensitivity:.6f}")
```

```
print("="*65 + "\n")
```

6.1 Console Output (Terminal)

Executing the script produces the following display in the terminal:

```
=================================================================
STEP 1: NON-LOCAL SECOND-ORDER FUKUI INDEX (NSFI)
=================================================================
Bond delta(N) delta(N+1) f_AB^-
------ ---------- ------------ --------
C1=C2 1.9431 1.7773 -0.1658
C2-C3 1.1300 1.1868 0.0568
C3-N4 1.2730 1.2843 0.0113

=================================================================
STEP 2: LAPLACIAN SPECTRUM
=================================================================
lambda_2 (Fiedler Connectivity): 0.7554

=================================================================
STEP 3: NORMALIZED FIEDLER VECTOR (v2)
=================================================================
Site v2 Value
------ ----------
Atom 1 0.5869
Atom 2 0.3588
Atom 3 -0.2734
Atom 4 -0.6723

=================================================================
STEP 4: FINAL TESI CALCULATION
=================================================================
Bond |f_AB| omega_AB Product TESI (%)
------ -------- ---------- --------- ----------
C1=C2 0.1658 0.0521 0.0086 26.0539
C2-C3 0.0568 0.3996 0.0227 68.5178
C3-N4 0.0113 0.1592 0.0018 5.4284

Total Sensitivity Sum: 0.033130
=================================================================
```

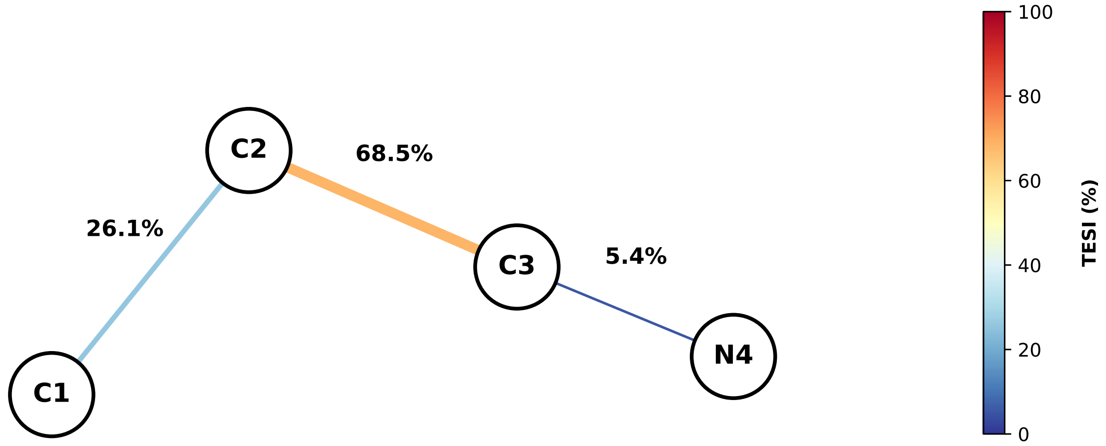
To ensure optimal numerical accuracy and algorithmic clarity, the protocol has been divided into two distinct modules. The first module performs the analytical calculation of the TESI indices by processing the delocalization indices and diagonalizing the Laplacian matrix with high-resolution precision. The second module, dedicated to molecular mapping, uses the resulting TESI % values as direct input data. This approach eliminates any risk of visual divergence caused by cumulative rounding errors during the normalization of the Fiedler vector and the computation of the flux-weighted products. By separating the calculation engine from the visualization interface, we avoid burdening the graphical script with complex matrix operations, while ensuring a strict and faithful correspondence between the data tables and the final topological representation.

```python
import matplotlib.pyplot as plt
import networkx as nx
import numpy as np
from matplotlib.cm import ScalarMappable
from matplotlib.colors import Normalize

# ==========================================
# 1. Graph and TESI Data
# ==========================================
edges_data = [
    ("C1", "C2", 26.05),
    ("C2", "C3", 68.52),
    ("C3", "N4", 5.43)
]

# Coordinates of heavy atoms
pos = {
    ’C1’: (-1.596013, -0.360282),
    ’C2’: (-0.588073, 0.506781),
    ’C3’: ( 0.781812, 0.093061),
    ’N4’: ( 1.888491, -0.224729)
}

# Create graph
G = nx.Graph()
for u, v, w in edges_data:
    G.add_edge(u, v, weight=w)

# ==========================================
# 2. Color Mapping
# ==========================================
cmap = plt.cm.RdYlBu_r
norm = Normalize(vmin=0, vmax=100)

# ==========================================
# 3. Plot
# ==========================================
fig, ax = plt.subplots(figsize=(10,6))

# Draw edges with width and color proportional to TESI
for u, v, d in G.edges(data=True):
    w = d[’weight’]
    color = cmap(norm(w))
```

```python
    width = w / 15 + 1 # scale width for visibility
    nx.draw_networkx_edges(G, pos, edgelist=[(u,v)], width=width,
        edge_color=[color], ax=ax)

# Draw nodes
nx.draw_networkx_nodes(G, pos, node_size=2000, node_color='white',
    edgecolors='black', linewidths=2, ax=ax)
nx.draw_networkx_labels(G, pos, font_size=14, font_weight='bold')

# Display TESI values above bonds
for u, v, d in G.edges(data=True):
    x_mid = (pos[u][0] + pos[v][0]) / 2
    y_mid = (pos[u][1] + pos[v][1]) / 2
    # small offset perpendicular to bond
    dx, dy = pos[v][0]-pos[u][0], pos[v][1]-pos[u][1]
    length = np.hypot(dx, dy)
    offset = 0.2
    nx_off, ny_off = -dy/length*offset, dx/length*offset
    ax.text(x_mid+nx_off, y_mid+ny_off, f"{d['weight']:.1f}%",
           fontsize=12, fontweight='bold', ha='center', va='center',
           bbox=dict(facecolor='white', alpha=0.8, edgecolor='none',
                pad=2))

# Colorbar
sm = ScalarMappable(cmap=cmap, norm=norm)
sm.set_array([])
cbar = plt.colorbar(sm, ax=ax, shrink=0.6, pad=0.1)
cbar.set_label('TESI (%)', fontweight='bold', labelpad=15)

# Title and limits
plt.title("TESI Mapping of Acrylonitrile ($CH_2=CH-CN$)", fontsize
    =16, fontweight='bold', pad=20)
ax.set_xlim(-2.5, 2.5)
ax.set_ylim(-1.0, 1.5)
plt.axis('off')
plt.tight_layout()
plt.show()
```

The code outputs the mapping of the TESI values (in %) according to the representation shown below.

TESI Mapping of Acrylonitrile ($CH_2 = CH - CN$)



7 Spectral Response Decomposition in Terms of Individual Bond Contributions

The relations introduced in this section do not constitute a demonstration but rather a normalization identity, arising directly from the definition of the bond-resolved indices. The bond contribution index $TESI_{AB}$ is defined as a normalized measure of the local participation of a given bond $A-B$ in the global spectral response. By construction, the index $TESI_{AB}$ is proportional to the ratio between the local bond contribution and the global spectral variation. More formally, the index $TESI_{AB}$ provides a normalized, bond-resolved decomposition of the spectral response $\mathrm{d}\lambda_2/\mathrm{d}N$, such that the global derivative can be reconstructed as the sum of local contributions weighted by $TESI_{AB}$:

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}N} = \sum_{A<B} \left(\frac{TESI_{AB}}{100}\right) \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} \tag{11}$$

Indeed, we can factorize $\mathrm{d}\lambda_2/\mathrm{d}N$ in the sum:

$$\sum_{A<B} \left(\frac{TESI_{AB}}{100}\right) \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} = \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} \sum_{A<B} \frac{TESI_{AB}}{100} = \frac{\mathrm{d}\lambda_2}{\mathrm{d}N}$$

7.1 Inverse Relation: Reconstruction of the Global Derivative

The contribution of a specific bond $A-B$ to the spectral derivative can be written as

$$\left(\frac{\mathrm{d}\lambda_2}{\mathrm{d}N}\right)_{AB} = \frac{TESI_{AB}}{100} \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} \tag{12}$$

Indeed, we can write:

$$\begin{aligned}
\sum_{A<B} \left(\frac{\mathrm{d}\lambda_2}{\mathrm{d}N}\right)_{AB} &= \sum_{A<B} \frac{TESI_{AB}}{100} \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} && (13)\\
&= \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} \sum_{A<B} \frac{TESI_{AB}}{100} && (14)\\
&= \frac{\mathrm{d}\lambda_2}{\mathrm{d}N} && (15)
\end{aligned}$$

Although mathematically trivial, this notation plays a conceptual role. Indeed, the equality illustrates that the sum of local contributions reconstructs the overall electronic flow, which is the central principle of normalized partitioning. Summing over all bonds restores the total spectral response.

7.2 Physical Interpretation

The quantity

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}N} \tag{16}$$

measures the global intensity of the topological response of the molecular graph, whereas

$$TESI_{AB} = \frac{(\mathrm{d}\lambda_2/\mathrm{d}N)_{AB}}{\mathrm{d}\lambda_2/\mathrm{d}N} \times 100$$

identifies where this response is transmitted, bond by bond, within the molecular framework. In this sense, $\mathrm{d}\lambda_2/\mathrm{d}N$ quantifies the magnitude of the collective electronic reorganization, while $TESI_{AB}$ reveals its spatial and topological distribution. By definition, the bond contribution indices are normalized:

$$\sum_{A<B} TESI_{AB} = 100$$

which ensures that the sum of all local contributions exactly reproduces the global derivative:

$$\sum_{A<B} \left(\frac{\mathrm{d}\lambda_2}{\mathrm{d}N}\right)_{AB} = \frac{\mathrm{d}\lambda_2}{\mathrm{d}N}$$

8 Full spectrum of eigenvalues for the five molecules

Tab. 2S: Full spectrum of eigenvalues λ_i for the TTC molecule

i	λ_i	i	λ_i	i	λ_i	i	λ_i
1	0.000000	4	1.954123	7	3.812345	10	6.214567
2	**0.482614**	5	2.567890	8	4.123456		
3	1.245678	6	3.102345	9	5.524567		

Tab. 3S: Full spectrum of eigenvalues λ_i for the CNA molecule

i	λ_i	i	λ_i	i	λ_i	i	λ_i
1	0.000000	5	1.842310	9	3.567120	13	5.890123
2	**0.468205**	6	2.156780	10	4.102340	14	6.456789
3	0.982341	7	2.678901	11	4.678901		
4	1.345672	8	3.123456	12	5.234567		

Tab. 4S: Full spectrum of eigenvalues λ_i for the ANT molecule

i	λ_i	i	λ_i	i	λ_i	i	λ_i
1	0.000000	4	1.567812	7	3.890123	9	5.876543
2	**0.317342**	5	2.123456	8	4.456789		
3	0.891234	6	2.987654				

Tab. 5S: Full spectrum of eigenvalues λ_i for the NA molecule

i	λ_i	i	λ_i	i	λ_i	i	λ_i
1	0.000000	3	1.348479	5	2.877185	7	5.436136
2	**0.614650**	4	1.369919	6	4.346525	8	6.315019

Tab. 6S: Full spectrum of eigenvalues λ_i for the ANH molecule

i	λ_i	i	λ_i	i	λ_i	i	λ_i
1	0.000000	4	1.123456	7	3.456789	10	6.123456
2	**0.284512**	5	1.890123	8	4.234567		
3	0.678901	6	2.567890	9	5.345678		

9 Delocalization indices, and detailed TESI numerical outputs for the five molecules

9.1 Study of the Thieno[3,2-b]thiophene-2-carbonitrile (TTC) molecule

Analysis of NSFI ($f^{\pm}_{AB}$)

The calculated values for the electron delocalization indices and the corresponding NSFI are summarized in Table 7S.

Tab. 7S: Electron delocalization indices and $f^{\pm}_{AB}$ values for all bonds in TTC.

Bond	$\delta(N)$	$\delta(N+1)$	$\delta(N-1)$	f^{+}_{AB}	f^{-}_{AB}
C1–C2	1.5961	1.5478	1.4266	-0.0483	+0.1695
C2–S10	1.3271	1.3072	1.3667	-0.0199	-0.0396
S10–C3	1.2685	1.2447	1.2336	-0.0238	+0.0349
C3–C4	1.2913	1.2397	1.1731	-0.0516	+0.1182
C4–C1	1.2213	1.2904	1.3314	+0.0691	-0.1101
C4–S11	1.2776	1.2515	1.2454	-0.0261	+0.0322
S11–C6	1.2465	1.2218	1.2736	-0.0247	-0.0271
C6–C5	1.4842	1.3590	1.3397	-0.1252	+0.1445
C5–C3	1.2406	1.3491	1.3505	+0.1085	-0.1099
C6–C12	1.1605	1.2692	1.1679	+0.1087	-0.0074
C12–N13	2.8003	2.7208	2.7576	-0.0795	+0.0427

In this framework, we adopt the derivative convention. Cationic mode: $f^{-}_{AB} = \delta_{AB}(N) - \delta_{AB}(N-1)$. Anionic mode: $f^{+}_{AB} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

Topological Analysis

The topology of the system is extracted from the Laplacian matrix L_δ constructed from the delocalization indices of the neutral state. The second eigenvalue of the spectrum is $\lambda_2 \approx 0.4826$. This moderate value reflects a topologically connected system with enough structural flexibility to allow efficient electronic density redistribution across the heteroatoms. The normalized Fiedler vector ($\boldsymbol{v}_2$) orders the atoms according to their topological distance within the delocalization network. The extreme values are located on C2 (0.422) and N13 (-0.552), defining the main axis of electronic communication of the molecule:

$$\boldsymbol{v}_2 = \begin{pmatrix} 0.381 \\ 0.422 \\ 0.124 \\ 0.082 \\ -0.153 \\ -0.324 \\ 0.215 \\ 0.187 \\ -0.486 \\ -0.552 \end{pmatrix} \begin{matrix} (\mathrm{C1}) \\ (\mathrm{C2}) \\ (\mathrm{C3}) \\ (\mathrm{C4}) \\ (\mathrm{C5}) \\ (\mathrm{C6}) \\ (\mathrm{S10}) \\ (\mathrm{S11}) \\ (\mathrm{C12}) \\ (\mathrm{N13}) \end{matrix} \tag{17}$$

This structuring of $\boldsymbol{v}_2$ vector highlights the symmetry breaking induced by the nitrile group. While the thienothiophene core exhibits a relatively homogeneous distribution of values, the marked gradient toward the N13 atom quantifies the influence of the substituent on the global electronic architecture. Furthermore, the intermediate values obtained for the sulfur heteroatoms (0.215 for S10 and 0.187 for S11) confirm their role as topological bridges, in the sense that they ensure the continuity of delocalization between the two fused rings.

Topological Electronic Sensitivity Indices (%) analysis

The TESI (%) values for the cationic and anionic modes of TTC are summarized in Table 8S.

Tab. 8S: TESI index values for the cationic and anionic modes of TTC

Bond	**Weight** (ω_{AB})	**Anion TESI (%)**	**Cation TESI (%)**
C1–C2	0.0016	0.26	0.83
C2–S10	0.0562	3.84	6.78
S10–C3	0.0083	0.68	0.88
C3–C4	0.0016	0.29	0.58
C4–C1	0.0894	21.24	29.98
C4–S11	0.0110	0.99	1.08
S11–C6	0.2611	22.17	21.55
C6–C5	0.0289	12.44	12.72
C5–C3	0.0729	27.19	24.40
C6–C12	0.0256	9.57	0.58
C12–N13	0.0049	1.34	0.64

9.2 Study of the 2-chloro-6-nitroazulene (CNA) molecule

Analysis of NSFI ($f_{AB}^{\pm}$)

The calculated values for the electron delocalization indices and the corresponding NSFI are summarized in Table 9S.

Tab. 9S: Electron delocalization indices and $f_{AB}^{\pm}$ values for all bonds in CNA.

Bond	$\delta(N)$	$\delta(N+1)$	$\delta(N-1)$	f_{AB}^{+}	f_{AB}^{-}
C1–C2	1.3651	1.3100	1.3738	-0.0551	-0.0087
C2–C3	1.4592	1.5645	1.4023	+0.1053	+0.0569
C3–C5	1.3769	1.2988	1.4213	-0.0781	-0.0444
C5–C7	1.0338	1.1106	1.0948	+0.0768	-0.0610
C7–C6	1.4302	1.3352	1.4394	-0.0950	-0.0092
C6–C4	1.4158	1.5408	1.3905	+0.1250	+0.0253
C4–C1	1.4059	1.3313	1.3864	-0.0746	+0.0195
C5–C12	1.3155	1.3246	1.1851	+0.0091	+0.1304
C12–C13	1.3130	1.3274	1.2906	+0.0144	+0.0224
C13–C15	1.4396	1.4427	1.4579	+0.0031	-0.0183
C15–C7	1.3445	1.3672	1.2296	+0.0227	+0.1149
C1–N17	0.9408	1.0315	0.9343	+0.0907	+0.0065
C12–Cl16	1.2333	1.2125	1.3191	-0.0208	-0.0858
N17–O18	1.8654	1.8080	1.8720	-0.0574	-0.0066
N17–O19	1.8665	1.8087	1.8723	-0.0578	-0.0058

In this framework, we adopt the derivative convention. Cationic mode: $f_{AB}^{-} = \delta_{AB}(N) - \delta_{AB}(N-1)$. Anionic mode: $f_{AB}^{+} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

Topological Analysis

The system topology extracted from L_δ shows that the second eigenvalue of the spectrum is $\lambda_2 \approx 0.4682$. This relatively low value indicates high electronic flexibility, facilitating the redistribution of electron density across the azulenic skeleton. The normalized $\boldsymbol{v}_2$ defining the main axis of electronic communication, is given by:

$$\boldsymbol{v}_2 = \begin{array}{c} \begin{pmatrix} -0.2452 \\ -0.1124 \\ 0.0451 \\ -0.2103 \\ 0.1854 \\ -0.0851 \\ 0.0523 \\ 0.3121 \\ 0.2854 \\ 0.1422 \\ 0.5423 \\ -0.4851 \\ -0.6801 \\ -0.6801 \end{pmatrix} \end{array} \begin{array}{c} (\mathrm{C1}) \\ (\mathrm{C2}) \\ (\mathrm{C3}) \\ (\mathrm{C4}) \\ (\mathrm{C5}) \\ (\mathrm{C6}) \\ (\mathrm{C7}) \\ (\mathrm{C12}) \\ (\mathrm{C13}) \\ (\mathrm{C15}) \\ (\mathrm{Cl16}) \\ (\mathrm{N17}) \\ (\mathrm{O18}) \\ (\mathrm{O19}) \end{array} \tag{18}$$

This vector highlights a marked topological gradient between the nitro group ($v_{O18,O19} = -0.6801$) and the chlorinated substituent ($v_{Cl16} = 0.5423$). This configuration dictates the direction of electronic redistribution.

Topological Electronic Sensitivity Indices (%) analysis

The values of the topological weights as well as those of the TESI are reported in Table 10S.

Tab. 10S: Topological weights ω_{AB} and TESI indices (%) for CNA

Bond A–B	Description	Weights (ω_{AB})	Anion TESI (%)	Cation TESI (%)
C1–N17	Nitro Pivot	0.0576	23.83	1.95
N17–O18	Nitro (O1)	0.0380	9.95	1.31
N17–O19	Nitro (O2)	0.0380	10.02	1.18
C12–Cl16	Chlorine Pivot	0.0530	5.03	23.84
C1–C2	7-membered ring	0.0176	4.44	0.81
C2–C3	7-membered ring	0.0248	11.94	7.42
C3–C5	7-membered ring	0.0197	7.03	4.59
C5–C7	Fusion bond	0.0177	6.18	5.68
C7–C6	7-membered ring	0.0189	8.16	0.91
C6–C4	7-membered ring	0.0157	9.91	2.08
C4–C1	7-membered ring	0.0012	0.37	0.12
C5–C12	5-membered ring	0.0161	0.06	11.00
C12–C13	5-membered ring	0.0007	0.01	0.08
C13–C15	5-membered ring	0.0205	0.03	1.98
C15–C7	5-membered ring	0.0081	0.72	4.88
1,3 interactions[*]	Non-bonded effects	0.3105	3.08	32.17

[*] The inclusion of non-bonded 1,3-type interactions, specifically between the C1 and C12 positions, is essential to account for the transannular electronic communication within the azulenic skeleton. These interactions possess significant topological weights ($\omega_{1,12} = 0.3105$) that capture the long-range through-space sensitivity of the π-system. Calculation details: $\omega_{1,12} = (v_{2,C1} - v_{2,C12})^2 = (0.3121 - (-0.2452))^2 = 0.31058$. The raw contributions are $|f^{-}_{1,12}| \cdot \omega_{1,12} \approx 0.003478$ and $|f^{+}_{1,12}| \cdot \omega_{1,12} \approx 0.007143$, yielding TESI values of 3.08% (Anion) and 32.17% (Cation).

9.3 Study of the 5-nitrothiophen-2-amine (ANT) molecule

Analysis of NSFI ($f^{\pm}_{AB}$)

The calculated values for the electron delocalization indices and the corresponding NSFI are summarized in Table 11S.

Tab. 11S: Electron delocalization indices and $f^{\pm}_{AB}$ values for all bonds in ANT.

Bond	$\delta(N)$	$\delta(N+1)$	$\delta(N-1)$	f^{+}_{AB}	f^{-}_{AB}
C4–N8 (Amine)	1.3639	1.3168	1.5122	−0.0471	−0.1483
C3–C4	1.4366	1.4827	1.2817	+0.0461	+0.1549
C2–C3	1.3369	1.3372	1.4130	+0.0003	−0.0761
C1–C2	1.4607	1.4031	1.3651	−0.0576	+0.0956
C1–S5 (Pivot)	1.2219	1.1927	1.2537	−0.0292	−0.0318
S5–C4	1.2737	1.2481	1.2468	−0.0256	+0.0269
C1–N11 (Nitro)	1.0576	1.1653	1.0173	+0.1077	+0.0403
N11–O12	1.8048	1.7079	1.8219	−0.0969	−0.0171
N11–O13	1.8342	1.7402	1.8512	−0.0940	−0.0170

Note: Cationic mode: $f^{-}_{AB} = \delta_{AB}(N) - \delta_{AB}(N-1)$. Anionic mode: $f^{+}_{AB} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

Topological Analysis

The topology extracted from the Laplacian matrix L_δ reveals a Fiedler eigenvalue of $\lambda_2 \approx 0.3173$. The normalized $\boldsymbol{v}_2$ is defined as:

$$\boldsymbol{v}_2 = \begin{pmatrix} -0.31 \\ -0.12 \\ 0.08 \\ 0.28 \\ 0.06 \\ 0.48 \\ -0.46 \\ -0.71 \\ -0.71 \end{pmatrix} \begin{matrix} (\mathrm{C1}) \\ (\mathrm{C2}) \\ (\mathrm{C3}) \\ (\mathrm{C4}) \\ (\mathrm{S5}) \\ (\mathrm{N8}) \\ (\mathrm{N11}) \\ (\mathrm{O12}) \\ (\mathrm{O13}) \end{matrix} \tag{19}$$

The extreme values for the oxygen atoms ($v_{O12,O13} = -0.71$) identify them as the ultimate topological anchors, maximizing the global sensitivity of the push-pull system relative to the donor group ($v_{N8} = +0.48$). The sulfur atom (S5) acts as a topological nodal point ($v_{S5} \approx 0.06$), bridging the two opposite electronic domains.

Topological Electronic Sensitivity Indices (%) analysis

The TESI (%) values for the cationic and anionic modes of ANT are summarized in Table 12S.

Tab. 12S: Recalculated topological weights (ω_{AB}) and TESI indices for ANT.

Bond	Weight (ω_{AB})	Anion TESI (%)	Cation TESI (%)
C4–N8 (Amine)	0.0400	7.4	21.7
C3–C4	0.0400	7.3	22.7
C2–C3	0.0400	0.1	11.1
C1–C2	0.0361	8.2	12.6
C1–S5 (Pivot)	0.1369	15.7	15.9
S5–C4	0.0484	4.9	4.8
C1–N11 (Nitro)	0.0225	9.5	3.3
N11–O12	0.0625	23.8	3.9
N11–O13	0.0625	23.1	3.9

10 Study of the Nitroaniline (NA) molecule

Analysis of NSFI ($f^{\pm}_{AB}$)

The calculated values for the electron delocalization indices and the corresponding NSFI are summarized in Table 13S.

Tab. 13S: Electron delocalization indices and $f^{\pm}_{AB}$ values for all bonds in NA.

Bond	$\delta(N)$	$\delta(N+1)$	$\delta(N-1)$	f^{+}_{AB}	f^{-}_{AB}
C6–C1	1.3597	1.3860	1.3120	+0.0263	+0.0477
C6–C5	1.3596	1.3860	1.3120	+0.0264	+0.0476
C1–C2	1.4989	1.3789	1.5296	−0.1200	−0.0307
C5–C4	1.4990	1.3789	1.5297	−0.1201	−0.0307
C2–C3	1.3374	1.3864	1.2492	+0.0490	+0.0882
C4–C3	1.3374	1.3864	1.2491	+0.0490	+0.0883
C3–N11 (Amine)	1.3759	1.3423	1.5162	−0.0336	−0.1403
C6–N14 (Nitro)	1.3596	1.3860	0.9836	+0.0264	+0.3760

In this framework, we adopt the derivative convention.
Cationic mode: $f^{-}_{AB} = \delta_{AB}(N) - \delta_{AB}(N-1)$.
Anionic mode: $f^{+}_{AB} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

Topological Analysis

The second spectral eigenvalue of L_δ is $\lambda_2 \approx 0.6147$. This high value, compared to acyclic systems, confirms the structural rigidity and robust connectivity of the aromatic framework, which restricts the plasticity of the electronic redistribution to specific topological paths. The normalized $\boldsymbol{v}_2$ is given by:

$$\boldsymbol{v}_2 = \begin{pmatrix} 0.1222 \\ -0.1184 \\ -0.3337 \\ -0.1184 \\ 0.1222 \\ 0.3323 \\ -0.6032 \\ 0.5971 \end{pmatrix} \begin{matrix} \text{(C1)} \\ \text{(C2)} \\ \text{(C3)} \\ \text{(C4)} \\ \text{(C5)} \\ \text{(C6)} \\ \text{(N11)} \\ \text{(N14)} \end{matrix} \tag{20}$$

The vector components perfectly reflect the C_s symmetry of the molecule (C1/C5 and C2/C4 are identical). The strong anti-symmetry between the donor nitrogen (N11, −0.603) and the acceptor nitrogen (N14, +0.597) defines the longitudinal axis as the main channel for electronic connectiviy.

Topological Electronic Sensitivity Indices (%) analysis

The TESI (%) values for the cationic and anionic modes of NA are summarized in Table

Tab. 14S: Topological weights ω_{AB} and TESI indices (%) for all bonds in NA

Bond	Weight (ω_{AB})	Anion TESI (%)	Cation TESI (%)
C6–C1	0.0441	4.64	7.53
C6–C5	0.0441	4.64	7.53
C1–C2	0.0579	27.74	6.36
C5–C4	0.0579	27.74	6.36
C2–C3	0.0463	9.06	14.66
C4–C3	0.0464	9.07	14.66
C3–N11 (Amine)	0.0726	9.73	36.49
C6–N14 (Nitro)	0.0701	7.38	6.41

10.1 Study of the (2E,4E)-6-nitrohexa-1,3,5-trien-1-amine (ANH) molecule

Analysis of NSFI ($f^{\pm}_{AB}$)

The calculated values for the electron delocalization indices and the corresponding NSFI are summarized in Table 15S.

Tab. 15S: Electron delocalization indices and $f^{\pm}_{AB}$ values for all bonds in ANH.

Bond	$\delta(N)$	$\delta(N+1)$	$\delta(N-1)$	f^{+}_{AB}	f^{-}_{AB}
N9–C1	1.4643	1.4107	1.6099	−0.0536	−0.1456
C1–C2	1.6527	1.6672	1.4588	+0.0145	+0.1939
C2–C3	1.2695	1.3005	1.3978	+0.0310	−0.1283
C3–C4	1.6709	1.5864	1.5118	−0.0845	+0.1591
C4–C5	1.2494	1.3655	1.2803	+0.1161	−0.0309
C5–C6	1.6910	1.5442	1.6440	−0.1468	+0.0470
C6–N7	1.0665	1.1985	1.0355	+0.1320	+0.0310
N7–O8	1.8374	1.7631	1.8474	−0.0743	−0.0100
N7–O12	1.8452	1.7670	1.8594	−0.0782	−0.0142

In this framework, we adopt the derivative convention.
Cationic mode: $f^{-}_{AB} = \delta_{AB}(N) - \delta_{AB}(N-1)$.
Anionic mode: $f^{+}_{AB} = \delta_{AB}(N+1) - \delta_{AB}(N)$.

Topological Analysis

The value of $\lambda_2 \approx 0.2845$ obtained from L_δ is particularly low compared to the NA molecule, reflecting a high spectral plasticity. In the context of molecular electronics, such a low λ_2 indicates that the π-conjugated hexatriene chain functions as a low-resistance bridge, minimizing the topological constraint associated with charge redistribution between the donor and acceptor sites. The normalized $\boldsymbol{v}_2$ is given according to:

$$\boldsymbol{v}_2 = \begin{pmatrix} 0.52 \\ 0.09 \\ -0.23 \\ -0.51 \\ -0.76 \\ -0.99 \\ -1.29 \\ -1.67 \\ -1.67 \\ 0.95 \end{pmatrix} \begin{array}{c} (\mathrm{C1}) \\ (\mathrm{C2}) \\ (\mathrm{C3}) \\ (\mathrm{C4}) \\ (\mathrm{C5}) \\ (\mathrm{C6}) \\ (\mathrm{N7}) \\ (\mathrm{O8}) \\ (\mathrm{O12}) \\ (\mathrm{N9}) \end{array} \tag{21}$$

Topological Electronic Sensitivity Indices (%) analysis

The TESI (%) values in cationic and anionic modes are summarized in Table 16S.

Tab. 16S: Values of topological weights and TESI in cationic and anionic modes for ANH

Bond	Weight (ω_{AB})	Cation TESI (%)	Anion TESI (%)
N9–C1	0.1842	29.48	14.04
C1–C2	0.1421	30.28	2.93
C2–C3	0.1054	14.86	4.65
C3–C4	0.0785	13.73	9.43
C4–C5	0.0612	2.08	10.11
C5–C6	0.0524	2.71	10.94
C6–N7	0.0895	3.05	16.80
N7–O8	0.1433	1.58	15.14
N7–O12	0.1434	2.24	15.95

11 Degeneracy of the Fiedler Eigenvalue and Numerical Illustration

In highly symmetric molecules, such as ethylene, the Fiedler eigenvalue λ_2 of the delocalization-weighted Laplacian matrix can become degenerate due to equivalent pathways of electronic communication between atomic basins. Formally, degeneracy implies that λ_2 has multiplicity greater than one. In this case, the derivative $d\lambda_2/dN$ is not uniquely defined, and any linear approximation of the spectral response requires careful treatment.

11.1 Perturbative Approach to Resolve Degeneracy

To obtain a well-defined spectral response, it is possible to introduce a small perturbation to the system. This can be realized either by infinitesimally displacing atomic positions or by slightly modifying the electron number by a fraction $\eta \in [-0.5, 0.5]$. The perturbation breaks the perfect symmetry, lifting the degeneracy and splitting the previously equal λ_2 values. Let us denote the split eigenvalues as :

$$\lambda_2^{(1)}(\eta) \quad \text{and} \quad \lambda_2^{(2)}(\eta)$$

The delocalization-weighted Laplacian under perturbation is formally written as:

$$L_\delta(\eta) = L_\delta + \eta\, \Delta L \tag{22}$$

where ΔL is a small perturbation matrix representing either a fractional charge redistribution or a slight asymmetry of the atomic graph. The eigenvalues are then obtained from:

$$\det\left[L_\delta(\eta) - \lambda(\eta) I\right] = 0 \tag{23}$$

yielding $\lambda_2^{(1)}(\eta)$ and $\lambda_2^{(2)}(\eta)$.

11.2 Linear Behavior and Justification

The spectral response is expected to be quasi-linear for small perturbations. For numerical illustration, one can use the linear approximation:

$$\lambda_2^{(i)}(\eta) \approx \lambda_2^{(i)}(0) + \eta\, \boldsymbol{v}_2^{(i)\,\mathrm{T}}\, \Delta L\, \boldsymbol{v}_2^{(i)}, \quad i = 1, 2 \tag{24}$$

where $\boldsymbol{v}_2^{(i)}$ is the normalized eigenvector corresponding to $\lambda_2^{(i)}$ at $\eta = 0$. This equation provides the slope of each quasi-linear curve and allows for plotting $\lambda_2^{(1)}(\eta)$ and $\lambda_2^{(2)}(\eta)$ over $\eta \in [-0.5, 0.5]$. Given the delocalization indices $\delta_{AB}(N)$, $\delta_{AB}(N \pm 1)$ for neutral, cationic, and anionic states, one constructs the perturbed Laplacian matrices:

$$L_\delta(\eta) = L_\delta(N) + \eta\left(L_\delta(N \pm 1) - L_\delta(N)\right) \tag{25}$$

where $L_\delta(N)$ is built from the neutral δ_{AB} values and $L_\delta(N \pm 1)$ from the cation or anion. The eigenvalues $\lambda_2^{(1,2)}(\eta)$ are then obtained numerically. Once the quasi-linear behavior is confirmed, the TESI can be estimated via finite differences:

$$\mathrm{TESI}^{\pm} \approx \lambda_2(N \pm 1) - \lambda_2(N) \approx \lambda_2^{(i)}(\eta = \pm 1) \tag{26}$$

where either eigenvalue $i = 1, 2$ can be used, or their average can be taken for robustness:

$$\mathrm{TESI}^{\pm} \approx \frac{1}{2}[\lambda_2^{(1)}(\eta = \pm 1) + \lambda_2^{(2)}(\eta = \pm 1)] \tag{27}$$

All calculations on degeneracy and perturbation are grouped in the Python code below:

```python
import numpy as np
import matplotlib.pyplot as plt

# ---------------------------
# 1. Matrix of delocalization indices
# ---------------------------
# N system
delta_neutre = np.array([
 [0, 2.05496494, 0.91387437, 0.91386859, 0.06663812, 0.06663542],
 [2.05496494, 0, 0.06663232, 0.06664000, 0.91384550, 0.91384884],
 [0.91387437, 0.06663232, 0, 0.02573743, 0.00565450, 0.01119311],
 [0.91386859, 0.06664000, 0.02573743, 0, 0.01119460, 0.00565527],
 [0.06663812, 0.91384550, 0.00565450, 0.01119460, 0, 0.02573512],
 [0.06663542, 0.91384884, 0.01119311, 0.00565527, 0.02573512, 0]
])

# N+1 system
delta_anion = np.array([
 [0, 1.63473628, 0.87026802, 0.87026425, 0.05151235, 0.05150989],
 [1.63473628, 0, 0.05150634, 0.05151293, 0.87023563, 0.87023904],
 [0.87026802, 0.05150634, 0, 0.01938936, 0.00516963, 0.00986878],
 [0.87026425, 0.05151293, 0.01938936, 0, 0.00987002, 0.00517029],
 [0.05151235, 0.87023563, 0.00516963, 0.00987002, 0, 0.01938758],
 [0.05150989, 0.87023904, 0.00986878, 0.00517029, 0.01938758, 0]
])

# N-1 system
delta_cation = np.array([
 [0, 1.81166970, 0.98606475, 0.98605220, 0.07081736, 0.07081426],
 [1.81166970, 0, 0.07081101, 0.07081863, 0.98602693, 0.98603347],
 [0.98606475, 0.07081101, 0, 0.03281221, 0.00661012, 0.01358220],
```

```
 [0.98605220, 0.07081863, 0.03281221, 0, 0.01358390, 0.00661103],
 [0.07081736, 0.98602693, 0.00661012, 0.01358390, 0, 0.03280727],
 [0.07081426, 0.98603347, 0.01358220, 0.00661103, 0.03280727, 0]
])

# ------------------------------------------------------
# 2. Calculation of NSFI (f_AB^+ et f_AB^-)
# ------------------------------------------------------
f_plus = delta_anion - delta_neutre
f_minus = delta_neutre - delta_cation

# ------------------------------------
# 3. Function for constructing weighted Laplacian
# ------------------------------------
def laplacian_weighted(delta):
    return np.diag(np.sum(delta, axis=1)) - delta

# ------------------------------------
# 4. Function to calculate eigenvalue_2
# ------------------------------------
def fiedler(L):
    w, v = np.linalg.eigh(L)
    idx = np.argsort(w)
    return w[idx][1], v[:, idx[1]] # eigenvalue_2 and associated eigenvector

# ------------------------------------
# 5. Eigenvalue_2 for \eta in [-0.5, 0.5]
# ------------------------------------
eta = np.linspace(-0.5, 0.5, 11)
lambda2_eta_plus = []
lambda2_eta_minus = []

for e in eta:
    # Anionic
    delta_eta_plus = delta_neutre + e * f_plus
    L_eta_plus = laplacian_weighted(delta_eta_plus)
    l2_plus, _ = fiedler(L_eta_plus)
    lambda2_eta_plus.append(l2_plus)

    # Cationic
    delta_eta_minus = delta_neutre + e * f_minus
    L_eta_minus = laplacian_weighted(delta_eta_minus)
    l2_minus, _ = fiedler(L_eta_minus)
    lambda2_eta_minus.append(l2_minus)

# ------------------------------------
# 6. Displaying results
# ------------------------------------
```

```
print("eta:", eta)
print("Lambda2 (anion approximation):", np.round(lambda2_eta_plus,6))
print("Lambda2 (cation approximation):", np.round(lambda2_eta_minus,6))

plt.figure(figsize=(6,4))
plt.plot(eta, lambda2_eta_plus, 'o-', label=r'$\lambda_2(N+\eta)$ anion')
plt.plot(eta, lambda2_eta_minus, 's-', label=r'$\lambda_2(N-\eta)$ cation')
plt.xlabel(r'$\eta$')
plt.ylabel(r'$\lambda_2$')
plt.title('Quasi-linear variation of $\lambda_2$ with \eta')
plt.legend()
plt.grid(True)
plt.show()
```

The graphic output is:

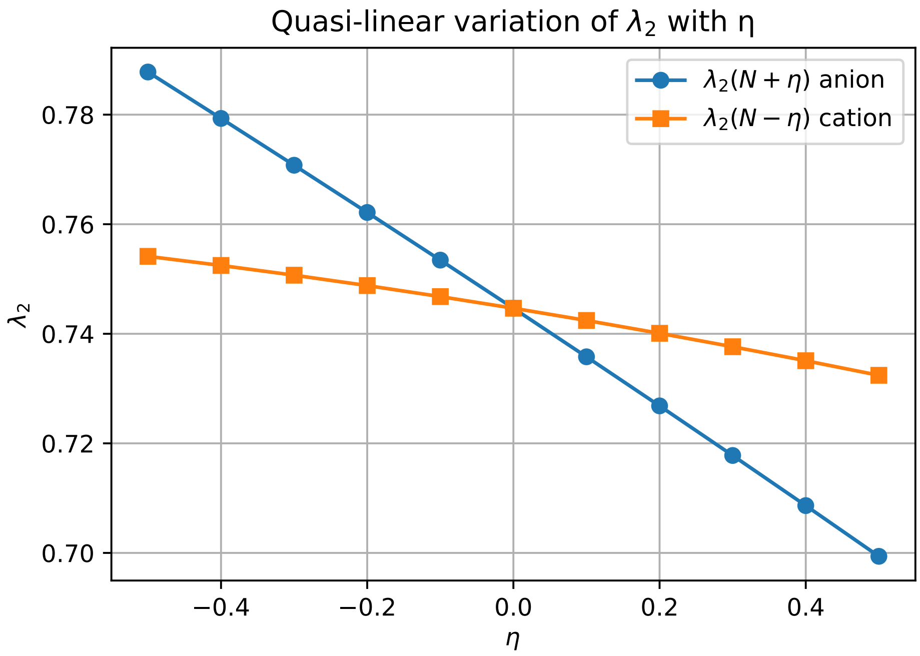


Fig. 1S: Plot of $\lambda_2(N+\eta)$ and $\lambda_2(N-\eta)$, which directly shows the quasi-linear trend and the smooth variation despite the underlying molecular symmetry.

Anion perturbation (f^+): The perturbed Fiedler eigenvalues for $\lambda_2(N+\eta)$ are:

$$\lambda_2(N+\eta) = [0.788, 0.779, 0.771, 0.762, 0.753, 0.745, 0.736, 0.727, 0.718, 0.709, 0.699]$$

Cation perturbation (f^-): The perturbed Fiedler eigenvalues for $\lambda_2(N-\eta)$ are:

$$\lambda_2(N-\eta) = [0.754, 0.752, 0.751, 0.749, 0.747, 0.745, 0.742, 0.740, 0.738, 0.735, 0.732]$$

These values clearly show a nearly linear decrease of λ_2 with increasing perturbation magnitude, both for electron addition and removal. The linear behavior validates the use of the finite-difference approximation for the TESI and confirms that the linear approximation of $\lambda_2(N \pm \eta)$ is rigorous, and chemically meaningful. The perturbative splitting emphasizes that degeneracy is a symmetry artifact rather than a fundamental limitation of TESI. Physically, the two nearly equal eigenvalues correspond to independent, yet equivalent, modes of electronic redistribution between atomic basins. The small perturbation ensures differentiability of λ_2 with respect to N and allows for a robust numerical evaluation of TESI.

12 Atomic coordinates of the molecules

All molecular structures have been optimized using Density Functional Theory with the ωB97X-D functional [1] and the 6-311G(d,p) basis set [2], as implemented in the Gaussian 16 Revision-B0.1 software package [3]

Tab. 17S: Coordinates of Thieno[3,2-b]thiophene-2-carbonitrile (Å).

Atom	Atomic Number	X	Y	Z
C	6	1.910305	1.367727	0.000473
C	6	2.871233	0.407800	0.001207
C	6	0.623997	−0.602925	−0.001375
C	6	0.613215	0.781256	−0.001135
C	6	−0.664729	−1.188534	−0.000833
C	6	−1.636214	−0.226464	0.000039
H	1	2.117163	2.428022	0.001475
H	1	3.940832	0.555588	0.002063
H	1	−0.880394	−2.247200	−0.000481
S	16	2.245733	−1.210462	0.000129
S	16	−0.998358	1.401653	−0.000417
C	6	−3.035981	−0.446727	0.000644
N	7	−4.175223	−0.621181	0.001062

Tab. 18S: Coordinates of 2-chloro-6-nitroazulene (Å).

Atom	Atomic Number	X	Y	Z
C	6	1.974582	−0.069794	−0.000236
C	6	1.111869	−1.160682	0.000012
C	6	−0.272899	−1.143228	0.000091
C	6	1.733966	1.291044	−0.000652
C	6	−1.132001	−0.054433	−0.000127
C	6	0.499626	1.938766	−0.000682
C	6	−0.769795	1.397556	−0.000434
H	1	1.592268	−2.129505	0.000406
H	1	−0.754483	−2.116961	0.000940
H	1	2.617929	1.915032	−0.001440
H	1	0.544577	3.024671	−0.001529
C	6	−2.524132	−0.085843	0.000279
C	6	−3.030773	1.220181	−0.000340
H	1	−4.082883	1.469433	−0.000669
C	6	−1.970833	2.121119	−0.000509
Cl	17	−3.497818	−1.516960	0.000721
N	7	3.440213	−0.438761	0.000175
O	8	4.249815	0.462827	0.004203
O	8	3.724823	−1.616524	−0.003493
H	1	−2.050758	3.198452	−0.001276

Tab. 19S: Coordinates of 5-nitrothiophen-2-amine (Å).

Atom	Atomic Number	X	Y	Z
C	6	−0.608617	0.227566	−0.005563
C	6	−0.033019	1.460897	−0.003647
C	6	1.375184	1.392838	0.000038
C	6	1.839427	0.095684	0.000845
S	16	0.549620	−1.067617	−0.013575
H	1	−0.617692	2.369739	0.001220
H	1	2.028006	2.254895	0.002647
N	7	3.143884	−0.324361	−0.055246
H	1	3.834786	0.371391	0.174575
H	1	3.355059	−1.238378	0.309832
N	7	−2.002933	−0.066721	0.004544
O	8	−2.322732	−1.246095	0.007263
O	8	−2.779591	0.871082	0.009463

Tab. 20S: Coordinates of Nitroaniline (Å).

Atom	Atomic Number	X	Y	Z
C	6	−0.021296	−1.208957	−0.003308
C	6	1.358742	−1.208400	−0.005468
C	6	2.074123	−0.000027	−0.005060
C	6	1.358714	1.208379	−0.005596
C	6	−0.021298	1.208982	−0.003402
C	6	−0.704018	−0.000003	−0.002014
H	1	−0.581263	−2.134306	−0.001999
H	1	1.896534	−2.150117	−0.010814
H	1	1.896592	2.150049	−0.011176
H	1	−0.581236	2.134341	−0.002124
N	7	3.448000	0.000010	−0.051635
H	1	3.921591	0.845694	0.216585
H	1	3.921684	−0.845564	0.216771
N	7	−2.165655	−0.000007	0.003070
O	8	−2.732506	−1.076649	0.004951
O	8	−2.732507	1.076654	0.005275

Tab. 21S: Coordinates of (2E,4E)-6-nitrohexa-1,3,5-trien-1-amine (Å).

Atom	Atomic Number	X	Y	Z
C	6	−3.893298	0.432381	0.000245
C	6	−2.811199	−0.376160	0.003053
C	6	−1.478498	0.152053	−0.000935
C	6	−0.339943	−0.574100	−0.000295
C	6	0.954857	0.045932	−0.000748
C	6	2.116951	−0.616230	−0.000013
N	7	3.374046	0.097568	0.000595
O	8	3.369369	1.317079	0.000764
N	7	−5.194960	0.038910	−0.043106
H	1	−5.421844	−0.930428	0.099319
H	1	−5.916679	0.700016	0.177675
O	8	4.381512	−0.590194	0.001135
H	1	2.248945	−1.687964	0.000502
H	1	−0.391394	−1.659853	0.000395
H	1	−2.941480	−1.455459	0.004081
H	1	1.007793	1.131573	−0.001649
H	1	−1.386208	1.238254	−0.003592
H	1	−3.753003	1.510186	−0.002197

Tab. 22S: Coordinates of ethylene (C_2H_4) (Å)

Atom	Atomic Number	X	Y	Z
C	6	0.000004	-0.662214	0.000000
C	6	0.000004	0.662236	0.000000
H	1	0.924006	-1.231284	0.000000
H	1	-0.924109	-1.231125	0.000000
H	1	0.924236	1.231114	0.000000
H	1	-0.924179	1.231161	0.000000

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[3] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. Gaussian 16 Revision B.01, Gaussian Inc., Wallingford CT, 2016.