Supplemental material: First-principles interpretation of electron transport though single-molecule junctions using molecular dynamics of electron attached states

Dávid P. Jelenfi, Attila Tajti and Péter G. Szalay
ELTE Eötvös Loránd University, Institute of Chemistry, Laboratory of Theoretical Chemistry, P. O. Box 32, H-1518, Budapest 112, Hungary

ARTICLE HISTORY
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Email: tat@chem.elte.hu
Email: szalay@chem.elte.hu
1. The model system

**Table 1.** The structure of the single-molecule junction model built from the equilibrium structure of the BDA molecule and two gold clusters. The BDA is placed between the gold clusters so that the distance between the terminal gold and amino-nitrogen atoms is 2.38 Å, while the Au-N-C and Au-N-C-C angles are 112° and 87.5°, respectively.

| Fragment       | Notation | X     | Y     | Z     |
|----------------|----------|-------|-------|-------|
| **1. BDA molecule** |          |       |       |       |
| N              | 4.380    | -3.122| 0.000 |       |
| N              | -4.380   | 3.122 | 0.000 |       |
| C              | 2.148    | -1.642| 0.000 |       |
| C              | -2.148   | 1.642 | 0.000 |       |
| C              | 1.059    | -0.800| -2.284|       |
| C              | -1.059   | 0.800 | -2.284|       |
| C              | 1.059    | -0.800| 2.284 |       |
| C              | -1.059   | 0.800 | 2.284 |       |
| H              | 1.876    | -1.406| -4.091|       |
| H              | -1.876   | 1.406 | -4.091|       |
| H              | 1.876    | -1.406| 4.091 |       |
| H              | -1.876   | 1.406 | 4.091 |       |
| H              | 4.454    | -4.259| -1.557|       |
| H              | -4.454   | 4.259 | -1.557|       |
| H              | 4.454    | -4.259| 1.557 |       |
| H              | -4.454   | 4.259 | 1.557 |       |
| **2. Right electrode** |          |       |       |       |
| Au             | 8.090    | -0.580| 0.000 |       |
| Au             | 11.874   | -3.418| 2.731 |       |
| Au             | 11.874   | -3.418| -2.731|       |
| Au             | 13.288   | 1.095 | 0.000 |       |
| Au             | 17.072   | -1.743| -2.731|       |
| Au             | 17.072   | -1.743| 2.731 |       |
| **3. Left electrode** |          |       |       |       |
| Au             | -8.090   | 0.580 | 0.000 |       |
| Au             | -11.874  | 3.418 | 2.731 |       |
| Au             | -11.874  | 3.418 | -2.731|       |
| Au             | -13.288  | -1.095| 0.000 |       |
| Au             | -17.072  | 1.743 | -2.731|       |
| Au             | -17.072  | 1.743 | 2.731 |       |
1.1. Natural Transition Orbitals

Figure 1.: Natural transition orbitals of the electron attached states calculated SOS-ADC(2) in the equilibrium geometry.
2. Normal modes of the BDA molecule.

| \( \nu_1 \)       | \( \nu_2 \)       | \( \nu_3 \)       |
|-------------------|-------------------|-------------------|
| ![Image](image1.png)  | ![Image](image2.png)  | ![Image](image3.png)  |
| \( (\tau = 214.28 \text{ fs}) \) | \( (\tau = 133.05 \text{ fs}) \) | \( (\tau = 132.47 \text{ fs}) \) |

| \( \nu_4 \)       | \( \nu_5 \)       | \( \nu_6 \)       |
|-------------------|-------------------|-------------------|
| ![Image](image4.png)  | ![Image](image5.png)  | ![Image](image6.png)  |
| \( (\tau = 104.16 \text{ fs}) \) | \( (\tau = 91.74 \text{ fs}) \) | \( (\tau = 77.15 \text{ fs}) \) |

| \( \nu_7 \)       | \( \nu_8 \)       | \( \nu_9 \)       |
|-------------------|-------------------|-------------------|
| ![Image](image7.png)  | ![Image](image8.png)  | ![Image](image9.png)  |
| \( (\tau = 76.95 \text{ fs}) \) | \( (\tau = 70.78 \text{ fs}) \) | \( (\tau = 62.43 \text{ fs}) \) |

| \( \nu_{10} \)     | \( \nu_{11} \)     | \( \nu_{12} \)     |
|-------------------|-------------------|-------------------|
| ![Image](image10.png)  | ![Image](image11.png)  | ![Image](image12.png)  |
| \( (\tau = 50.69 \text{ fs}) \) | \( (\tau = 45.84 \text{ fs}) \) | \( (\tau = 45.38 \text{ fs}) \) |

| \( \nu_{13} \)     | \( \nu_{14} \)     | \( \nu_{15} \)     |
|-------------------|-------------------|-------------------|
| ![Image](image13.png)  | ![Image](image14.png)  | ![Image](image15.png)  |
| \( (\tau = 41.42 \text{ fs}) \) | \( (\tau = 40.56 \text{ fs}) \) | \( (\tau = 40.24 \text{ fs}) \) |
Normal modes of the BDA molecule

$\nu_{16}$ $(\tau = 38.75 \text{ fs})$ $\nu_{17}$ $(\tau = 38.21 \text{ fs})$ $\nu_{18}$ $(\tau = 35.1 \text{ fs})$

$\nu_{19}$ $(\tau = 35.02 \text{ fs})$ $\nu_{20}$ $(\tau = 32.81 \text{ fs})$ $\nu_{21}$ $(\tau = 30.91 \text{ fs})$

$\nu_{22}$ $(\tau = 29.15 \text{ fs})$ $\nu_{23}$ $(\tau = 29.03 \text{ fs})$ $\nu_{24}$ $(\tau = 28.16 \text{ fs})$

$\nu_{25}$ $(\tau = 25.97 \text{ fs})$ $\nu_{26}$ $(\tau = 25.74 \text{ fs})$ $\nu_{27}$ $(\tau = 24.64 \text{ fs})$

$\nu_{28}$ $(\tau = 24.63 \text{ fs})$ $\nu_{29}$ $(\tau = 22.5 \text{ fs})$ $\nu_{30}$ $(\tau = 21.53 \text{ fs})$

$\nu_{31}$ $(\tau = 20.5 \text{ fs})$ $\nu_{32}$ $(\tau = 20.18 \text{ fs})$ $\nu_{33}$ $(\tau = 20.08 \text{ fs})$
2 Normal modes of the BDA molecule

\[ \nu_{34} \quad \nu_{35} \quad \nu_{36} \]

\( (\tau = 19.94 \text{ fs}) \quad (\tau = 10.63 \text{ fs}) \quad (\tau = 10.63 \text{ fs}) \)

\[ \nu_{37} \quad \nu_{38} \quad \nu_{39} \]

\( (\tau = 10.58 \text{ fs}) \quad (\tau = 10.57 \text{ fs}) \quad (\tau = 9.67 \text{ fs}) \)

\[ \nu_{40} \quad \nu_{41} \quad \nu_{42} \]

\( (\tau = 9.67 \text{ fs}) \quad (\tau = 9.45 \text{ fs}) \quad (\tau = 9.45 \text{ fs}) \)
3. Results with the SOS-ADC(2) method

**Table 2.**: Statistics on the state SOS-ADC(2) energy differences ($\Delta E$, in eV) and hopping probabilities$^a$ ($p$, multiplied by 10$^3$) from 25 MD trajectories.

| T = 1 fs | Mean (SD$^a$ | Min. | Max. |
|------------------|--------------|------|------|
| $\Delta E (El_6, Mol_1)$ | 0.633 (0.214 | 0.312 | 0.971 |
| $p (El_6 \rightarrow Mol_1)$ | 0.05 (0.10 | 0.00 | 0.40 |
| $\Delta E (El_5, El_6)$ | 0.124 (0.074 | 0.016 | 0.244 |
| $p (El_6 \rightarrow El_5)$ | 0.15 (0.20 | 0.00 | 0.65 |
| $\Delta E (El_4, El_6)$ | 0.213 (0.066 | 0.127 | 0.353 |
| $p (El_6 \rightarrow El_4)$ | 0.00 (0.01 | 0.00 | 0.05 |
| $\Delta E (El_3, El_6)$ | 0.289 (0.097 | 0.156 | 0.478 |
| $p (El_6 \rightarrow El_3)$ | 0.01 (0.06 | 0.00 | 0.32 |

| T = 50 fs | Mean (SD$^a$ | Min. | Max. |
|------------------|--------------|------|------|
| $\Delta E (El_6, Mol_1)$ | 0.840 (0.248 | 0.367 | 1.086 |
| $p (El_6 \rightarrow Mol_1)$ | 0.03 (0.10 | 0.00 | 0.49 |
| $\Delta E (El_5, El_6)$ | 0.060 (0.042 | 0.002 | 0.147 |
| $p (El_6 \rightarrow El_5)$ | 0.57 (1.44 | 0.00 | 6.98 |
| $\Delta E (El_4, El_6)$ | 0.109 (0.084 | 0.014 | 0.327 |
| $p (El_6 \rightarrow El_4)$ | 0.19 (0.33 | 0.00 | 1.25 |
| $\Delta E (El_3, El_6)$ | 0.152 (0.083 | 0.042 | 0.341 |
| $p (El_6 \rightarrow El_3)$ | 0.00 (0.02 | 0.00 | 0.10 |

| T = 100 fs | Mean (SD$^a$ | Min. | Max. |
|------------------|--------------|------|------|
| $\Delta E (El_6, Mol_1)$ | 1.092 (0.278 | 0.553 | 1.284 |
| $p (El_6 \rightarrow Mol_1)$ | 0.00 (0.03 | 0.00 | 0.17 |
| $\Delta E (El_5, El_6)$ | 0.044 (0.027 | 0.010 | 0.105 |
| $p (El_6 \rightarrow El_5)$ | 1.48 (3.99 | 0.00 | 18.73 |
| $\Delta E (El_4, El_6)$ | 0.114 (0.079 | 0.024 | 0.337 |
| $p (El_6 \rightarrow El_4)$ | 1.58 (3.37 | 0.00 | 14.51 |
| $\Delta E (El_3, El_6)$ | 0.185 (0.115 | 0.052 | 0.519 |
| $p (El_6 \rightarrow El_3)$ | 1.27 (3.31 | 0.00 | 15.35 |

Entire trajectory$^b$

| T = 100 fs | Mean (SD$^a$ | Min. | Max. |
|------------------|--------------|------|------|
| $\Delta E (El_6, Mol_1)$ | 0.880 (0.238 | 0.389 | 1.280 |
| $p (El_6 \rightarrow Mol_1)$ | 0.14 (0.80 | 0.00 | 12.35 |
| $\Delta E (El_5, El_6)$ | 0.062 (0.044 | 0.003 | 0.184 |
| $p (El_6 \rightarrow El_5)$ | 1.74 (8.41 | 0.00 | 136.28 |
| $\Delta E (El_4, El_6)$ | 0.124 (0.063 | 0.020 | 0.473 |
| $p (El_6 \rightarrow El_4)$ | 0.80 (4.23 | 0.00 | 65.29 |
| $\Delta E (El_3, El_6)$ | 0.179 (0.076 | 0.051 | 0.361 |
| $p (El_6 \rightarrow El_3)$ | 0.47 (2.73 | 0.00 | 41.57 |

$^a$ Standard deviation
$^b$ Averages over all trajectories
4. The figures of selected properties along the MD trajectories.

In this section the figures of the energy gap (top panel, the equilibrium value marked with dashed line), the POS$_f$ values (middle panel, see main text for explanation) and the hopping probability (bottom panel) are shown as functions of the timestep for a pair of electron attached states in each MD trajectory.

4.1. Figures from El$_6$ and Mol$_1$ electron attached states.
4.1 Figures from \( El_6 \) and \( Mol_1 \) electron attached states

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4.1 Figures from $E_{6}$ and $Mol_{1}$ electron attached states
4.1 Figures from El$_6$ and Mol$_1$, electron attached states

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4.1 Figures from $E_{6}$ and $Mol_{1}$ electron attached states

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Electron attached states
4.1 Figures from \( E_{\text{El}_6} \) and \( \text{Mol}_1 \) electron attached states
4.1 Figures from $E_{l_6}$ and $M_{l_1}$ electron attached states

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4.1 Figures from El₆ and Mol₁ electron attached states

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4.1 Figures from El₆ and Mol₁ electron attached states

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4.2. Figures from El₆ and El₅ electron attached states.
4.2 Figures from El$_6$ and El$_5$ electron attached states
4.2 Figures from $E_{l_6}$ and $E_{l_5}$ electron attached states
4.2 Figures from El$_6$ and El$_5$ electron attached states
4.2 Figures from $E_{L_6}$ and $E_{L_5}$ electron attached states

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4.2 Figures from El₆ and El₅ electron attached states

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4.2 Figures from $E_{l_6}$ and $E_{l_5}$ electron attached states
4.2 Figures from $E_{l_6}$ and $E_{l_5}$ electron attached states
4.2 Figures from $E_{\text{L}_6}$ and $E_{\text{L}_5}$ electron attached states
4.3. Figures from El\textsubscript{6} and El\textsubscript{4} electron attached states.
4.3 Figures from El₆ and El₄ electron attached states
4.3 Figures from El₆ and El₄ electron attached states
4.3 Figures from El₆ and El₄ electron attached states
4.3 Figures from El₆ and El₄ electron attached states

[Graphs showing data from El₆ and El₄ electron attached states]
4.3 Figures from El\(_6\) and El\(_4\) electron attached states

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4.3 Figures from $E_{6}$ and $E_{4}$ electron attached states
4.3 Figures from $E_{l_6}$ and $E_{l_4}$ electron attached states

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4.3 Figures from \( El_6 \) and \( El_4 \) electron attached states

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4.4. Figures from El\textsubscript{6} and El\textsubscript{3} electron attached states.
4.4 Figures from $E_{6}$ and $E_{3}$ electron attached states

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4.4 Figures from $\text{El}_0$ and $\text{El}_3$ electron attached states
4.4 Figures from $\text{El}_6$ and $\text{El}_3$ electron attached states

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures}
\caption{\textbf{Figures from $\text{El}_6$ and $\text{El}_3$ electron attached states}}
\end{figure}
4.4 Figures from El$_6$ and El$_3$ electron attached states
Figures from $E_{L_{6}}$ and $E_{L_{3}}$ electron attached states
Figures from El₆ and El₃ electron attached states

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4.4 Figures from El$_6$ and El$_3$ electron attached states

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Figures from El$_6$ and El$_3$ electron attached states.}
\end{figure}
4.4 Figures from $E_{l_6}$ and $E_{l_3}$ electron attached states