The Role of Symmetry in Molecular Electronic Conduction

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Molecular Electronics: Finding molecular signature: Inelastic Electron Tunnelling Spectroscopy (IETS)

MOLECULAR VIBRATION SPECTRA BY ELECTRON TUNNELING

R. C. Jaklevic and J. Lambe
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan
(Received 18 October 1966)

The conductance of metal–metal oxide–metal tunneling junctions has been observed to increase at certain characteristic bias voltages. These voltages are identified with vibrational frequencies of molecules contained in the barrier.
Application to molecules

![Graph showing applications to molecules](image1)

![Graph showing applications to molecules](image2)

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**References**

Our Aims:

• to use a priori computational methods to interpret the experimental results

• to identify simple ways of describing elastic and inelastic transport of electrons and holes through single molecules

  • through the role of molecular symmetry

  • through defining channels through which the charges pass
Observed and gDFTB-calculated IETS

Reed’s experiment

Calculations match and enhance experimental assignment

Methods for Calculating the Current

• Non-Equilibrium Green’s Function (NEGF) formalism
  • Implementation developed at Tor Vergata
  • Works at high voltage, allows for heating of molecule, etc.

• Landauer Formalism
  • Implementations developed at Tor Vergata & at Sydney
  • Good description of low-voltage elastic transport
Specifying the Electrode-Molecule-Electrode Hamiltonian Operator for the System Energy

\[
H = \begin{bmatrix}
H^L & J^L & 0 \\
(J^L)^\dagger & H^M & (J^R)^\dagger \\
0 & J^R & H^R
\end{bmatrix}
\]

Diagonal blocks are the energies of each part

Landauer Formalism

\[
H = \begin{bmatrix}
  H^L & J^L & 0 \\
  (J^L)^\dagger & H^M & (J^R)^\dagger \\
  0 & J^R & H^R 
\end{bmatrix}
\]

\[
I(V) = \int_{\mu_1}^{\mu_2} g(E,V) dE
\]

\[
T = g(E,V) = \text{Tr}(g(E,V))
\]

\[
g = \Gamma^L G^M \Gamma^R (G^M)^\dagger
\]

\[
\Gamma^L = -2 \text{Im}(\Sigma^L) = -2 J^L G^L (J^L)^\dagger
\]

\[
\text{Re}(\Sigma^L) = \text{Hilbert}_\text{Trans}(\text{Im}(\Sigma^L))
\]

\[
\Gamma^R = -2 \text{Im}(\Sigma^R) = -2 J^R G^R (J^R)^\dagger
\]

\[
\text{Re}(\Sigma^R) = \text{Hilbert}_\text{Trans}(\text{Im}(\Sigma^R))
\]

\[
G^L = \frac{1}{E - H^L} \quad G^R = \frac{1}{E - H^R} \quad G^M = \frac{1}{E - (H^M - \Sigma^L - \Sigma^R)}
\]

Major factors controlling conduction

- some properties are controlled by the **junctions**
  - Nature of conduction channels

- some properties are controlled by the **molecule**
  - Symmetry
  - connection between input and output channels
MOLECULAR SYMMETRY

• $G^M$ commutes with all molecular point-group symmetry operators

• $J^L$ and also $J^R$ only commute with operators that do not interchange the electrodes

• eg. Benzenedithiol (BDT): Full point group = $D_{2h}$
  conductance point group = $C_{2v}$

Lost operators: axes $C_{2x}$ and $C_{2y}$, inversion, Plane $\sigma_{xy}$
• The eigenvectors of $\mathbf{g} = \Gamma^L \mathbf{G}^M \Gamma^R (\mathbf{G}^M)\dagger$

  can be categorized as to their symmetry with respect to the conductance point group which knows all molecule and junction symmetry elements

• Asymmetric interactions with the electrodes are in general expected, but the intrinsic symmetry properties of the molecule will dominate conductivity. As a result, low symmetry of the conductance point group may be ignored and one use instead just the

MOLECULAR CONDUCTANCE POINT GROUP

Solomon, Gagliardi, Pecchia, Frauenheim, Di Carlo, Reimers, Hush J.C.P. 125 (2006) 184702
### Molecular-conductance point group

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetry</th>
<th>Symmetry Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au–Au–Au–Au</td>
<td>$D_{∞h}$</td>
<td>$C_{∞v}$</td>
</tr>
<tr>
<td><img src="image1" alt="structure 1" /></td>
<td>$D_{2h}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td><img src="image2" alt="structure 2" /></td>
<td>$D_{2h}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td><img src="image3" alt="structure 3" /></td>
<td>$\sim D_{2h}$</td>
<td>$\sim C_{2v}$</td>
</tr>
<tr>
<td><img src="image4" alt="structure 4" /></td>
<td>$C_{2h}$</td>
<td>$C_{s}$</td>
</tr>
<tr>
<td><img src="image5" alt="structure 5" /></td>
<td>$C_{2h}$</td>
<td>$C_{s}$</td>
</tr>
<tr>
<td><img src="image6" alt="structure 6" /></td>
<td>$C_{2v}$</td>
<td>$C_{s}$</td>
</tr>
<tr>
<td><img src="image7" alt="structure 7" /></td>
<td>$C_{s}$</td>
<td>$C_{s}$</td>
</tr>
</tbody>
</table>
BDT: Conduction channels of all symmetries

Black: total $A_1 + A_2 + B_1 + B_2$  
red: highest $g_{ii}$  
blue: second highest $g_{ii}$

When the junction symmetry is less than that of the Molecular Conductance Point Group

Black- 3 Au, exact
Green- 3 Au, using higher symmetry
Red- 25 Au, exact

Solomon, Gagliardi, Pecchia, Frauenheim, Di Carlo, Reimers, Hush J.C.P. 125 (2006) 184702
Why so few open channels?

• We can without loss of generality describe the electrodes in terms of their own molecular orbitals so that

\[
\Gamma^L_{ij} = 2 \sum_k J^L_{ik} J^L_{jk} G^L_{kk}
\]

• If only one mode of the electrode couples then

\[
\Gamma^L_{ij} = \sqrt{\Gamma^L_{ii} \Gamma^L_{jj}}
\]

• A matrix of this form has rank 1 independent of dimension

• Hence \( g = \Gamma^L G^M \Gamma^R (G^M)^\dagger \)

has rank 1 (ie, has only one nonzero eigenvalue \( g_{ii} \))

so there is only one open conductivity channel
JUNCTION-CONDUCTANCE ORBITALS

\[ g = \Gamma^L G^M \Gamma^R (G^M)^\dagger \]

\[ \text{Tr}(g) = \sum_i \sum_j \sum_k \sum_l \Gamma_{ij}^L G_{jk}^M \Gamma_{kl}^R (G_{il}^M)^* \]

Now, \( \Gamma^L \) can be diagonalized yielding the Junction-Conductance Orbitals \( \mathbf{D} \) (ignoring the overlap matrix \( \mathbf{S} \))

\[ g = \Gamma^{''L} G^{''M} \Gamma^{''R} (G^{''M})^\dagger \]

\[ G^{''M} = D_L^{-1} G^M D_R \]

\[ \Gamma^{''L} = D_L^\dagger \Gamma^L D_L \]

\[ \Gamma^{''R} = D_R^\dagger \Gamma^R D_R \]

\[ \text{Tr}(g) = \sum_{i,j} \Gamma^{''L}_{ii} \left| G^{''M}_{ij} \right|^2 \Gamma^{''R}_{jj} \]
Junction conductance orbital eigenvalues $\Gamma_{ii}$ for Au – benzenedithiol

<table>
<thead>
<tr>
<th>Eigenvalue</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.19</td>
<td>0.001</td>
<td>0.035</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>0.010</td>
<td></td>
<td>0.005</td>
<td>0.0004</td>
</tr>
<tr>
<td>3</td>
<td>0.0015</td>
<td></td>
<td>8\times10^{-8}</td>
<td>4\times10^{-10}</td>
</tr>
<tr>
<td>4</td>
<td>7\times10^{-5}</td>
<td></td>
<td></td>
<td>9\times10^{-14}</td>
</tr>
<tr>
<td>5</td>
<td>5\times10^{-8}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4\times10^{-9}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-1\times10^{-12}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Evaluated at the Fermi energy, in a.u. (Hartrees)

Elastic Transmission through $n^2$ channels

Inelastic scattering via molecule-weighted channels

\[ (\text{height})_q \propto \Gamma^L G^M \gamma_q (G^M)^\dagger \Gamma^R G^M \gamma_q (G^M)^\dagger = A^L \gamma_q A^R \gamma_q \]

\[ \gamma_q = \frac{dH}{dq} \]

\( q \) are the normal modes of vibration of the molecule

Now, \( A^L \) can be diagonalized as before yielding the **Molecule-weighted Junction-Conductance Orbitals** \( D \) (ignoring the overlap matrix \( S \))

**Through-molecule inelastic scattering**

**Weighted Left-junction interaction**

\[ \text{height}_q \propto \sum_{ij} A''^L_{ii} |\gamma''_{ij}|^2 A''^R_{jj} \]

**Weighted Right-junction interaction**

Weighted junction conductance orbital eigenvalues $\Gamma_{ii}$ for Au – benzenedithiol (in Hartrees)

<table>
<thead>
<tr>
<th>Eigenvalue</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.44</td>
<td>0.011</td>
<td>27.4</td>
<td>2.26</td>
</tr>
<tr>
<td>2</td>
<td>0.144</td>
<td></td>
<td>0.071</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.128</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• Now the $\pi B_1$ channel dominates!

• As only one $\hat{A}''_{ii}$ is large, the $i=j$ term dominates so that $\gamma''_{ij}$ must be totally symmetric and hence the $a_1$ modes dominate inelastic scattering:

$$height_q \propto \sum_{ij} A''_{ii} |\gamma''_{ij}|^2 A''_{jj}$$

Gagliardi, Solomon, Pecchia, Frauenheim, Di Carlo, Hush, Reimers *PRB 75* (2007) 174306
### Active channels for modes of different symmetry

<table>
<thead>
<tr>
<th>Vibration $q$</th>
<th>$I_q$</th>
<th>$g_q(E_F)$ exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
<td>$\omega$ (eV)</td>
<td>$\omega$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>30</td>
<td>0.014</td>
<td>112</td>
</tr>
<tr>
<td>29</td>
<td>0.028</td>
<td>228</td>
</tr>
<tr>
<td>26</td>
<td>0.043</td>
<td>346</td>
</tr>
<tr>
<td>25</td>
<td>0.045</td>
<td>365</td>
</tr>
<tr>
<td>24</td>
<td>0.057</td>
<td>462</td>
</tr>
<tr>
<td>23</td>
<td>0.072</td>
<td>583</td>
</tr>
<tr>
<td>21</td>
<td>0.088</td>
<td>713</td>
</tr>
<tr>
<td>20</td>
<td>0.098</td>
<td>790</td>
</tr>
<tr>
<td>19</td>
<td>0.102</td>
<td>826</td>
</tr>
<tr>
<td>18</td>
<td>0.104</td>
<td>836</td>
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<tr>
<td>17</td>
<td>0.125</td>
<td>1009</td>
</tr>
<tr>
<td>15</td>
<td>0.138</td>
<td>1114</td>
</tr>
<tr>
<td>13</td>
<td>0.161</td>
<td>1303</td>
</tr>
<tr>
<td>9</td>
<td>0.205</td>
<td>1656</td>
</tr>
</tbody>
</table>
Role of the molecule in determining amplitudes

\[ \text{height}_q \propto \sum_{ij} A''_{ii} |\gamma''_{ij}|^2 A''_{jj} \]

If the junction properties mean that only one \( ij \) term dominates the sum, what then is the physical origin of the inter-channel scattering amplitude \( |\gamma''_{ij}|^2 \)?
Interference between scattering off atoms and bonds


Conclusions

• Molecular symmetry can be used to provide a qualitative description of single-molecule conductivity—molecular conductance point group

• The electrode-molecule junctions allow only a few conductance pathways—junction conductance orbitals

• These must be weighted by their connection with the molecule at the energy of interest—molecule-weighted junction conductance orbitals

• Inelastic scattering is most intense through symmetric vibrations that couple the most active input junction orbital to the most active output junction orbital; junction channel symmetry provides high-level control.

• Inelastic scattering occurs off both atoms and bonds within molecules, determined by how the vibrations influence the input-junction and output-junction orbitals. Interference effects provide low-level control.

Reimers, Solomon, Gagliardi, Bic, Hish, Frauengruber, Di Carlo, Recchia JPCA 111 (2007) 5692
The End
Abstract

How Molecular Symmetry Controls Molecular Electronic Conduction

Jeffrey R. Reimers
School of Chemistry
The University of Sydney

The Greens Function Density-Functional Tight-Binding (gDFTB) method developed at Tor Vergata and Paderborn/Bremen is applied to determine the role that molecular symmetry plays in controlling single-molecule conductivity. Both coherent elastic electron transport processes and inelastic electron-tunnelling spectroscopy (IETS) are considered. Symmetry becomes manifest in various ways: through the molecular point-group symmetry of the conducting molecule ($D_{2h}$ for chemisorbed benzenedithiol between two gold electrodes), through the conductance point-group symmetry displayed by the gDFTB equations (this embodies junction asymmetry and may be very low and nominally non-existent), and through an approximate molecular-conductance point group ($C_{2v}$ for chemisorbed benzenedithiol) that makes manifest the non-equilibrium steady-state nature of conduction. Indeed, constraint of the gDFTB equations to operate within the restriction of molecular-conductance point-group symmetry is shown to have negligible affect on calculated conductivities for a range of relevant problems. This allows the complex $g(E)$ (transmission as a function of electron injection energy) curves calculated by many research groups to be dramatically simplified and partitioned into symmetry-depicted channels. Means are then introduced that isolate a very small number of component channels describing different aspects of single-molecule conductivity: input junction channels, through-molecule channels, and output-junction channels. For elastic transport, all through-molecule channels are totally symmetric and hence a rigorous selection rule appears that transport is allowed involving only input-junction and output-junction channels of the same symmetry. However, for IETS, the through-molecule channels have the symmetry of the scattering molecular vibration and hence the input-junction and output-junction channel symmetries may vary. In general, just one channel is expected to dominate the junctions, leading to the IETS propensity rule that totally symmetric transitions (linking the dominant input channel to the dominant output channel) are the most intense ones. Simple physical pictures are presented showing the input, vibrational scattering, and output channels for IETS, leading to predictions of how this effect can be controlled chemically. In general, IETS is shown to arise through non-trivial cancellation of intensity of electron waves scattered from both the atoms and the bonds of the conducting molecule.
Rigorously Defined Coherent Conductance Channels

\[ I(V) = \int_{\mu_1}^{\mu_2} g(E,V) dE \]

\[ T = g(E,V) = \text{Tr}(g(E,V)) \]

\[ g = \Gamma^L G^M \Gamma^R (G^M)^\dagger \]

• Büttiker showed that \( g \) may be diagonalized to introduce eigenchannels of conduction with eigenvalues \( g_{ii} \)

so that \( \text{Tr}(g) = \sum_i g_{ii} \)

where the eigenvalues have the property \( 0 \leq g_{ii} \leq 1 \)

Useful for Conduction Through Metal Filaments

Plane-wave Basis:

\[ e^{i \mathbf{k} \cdot \mathbf{r}} \sum_i t_{ij} e^{i \mathbf{k}_i \cdot \mathbf{r}} \]

Eigenchannel Basis:

\[ (U_{\text{in}})_i \rightarrow t_i (U_{\text{out}})_i \]

Conduction can be attributed to atomic orbitals


Can also make progress by restricting the number of atoms in the “molecule” (see Jacob & Palacios PRB 73 (2006) 075424)
But the eigenvectors reveal little about the role of non-metallic bridges

• “The associated eigenvectors turn out to be useless”
  
  Jacob & Palacios PRB 73 (2006) 075424

• They are dominated by the atom(s) connecting the molecule to the source electrode
  
  • What can be discovered about the role of the molecule ?

• The eigenvectors form a few nearly parallel sets
  
  • What are the natures of these sets ?

• Almost all channels have $g_{ii} \ll 1$ … only a few “open” channels
  
  • Why ?
Discontinuous nature of the Büttiker eigenvectors at a crossover point
MOLECULAR-CONDUCTANCE ORBITALS

\[ g = \Gamma^L G^M \Gamma^R (G^M)^\dagger \]

\[ \text{Tr}(g) = \sum_i \sum_j \sum_k \sum_l \Gamma^L_{ij} G^M_{jk} \Gamma^R_{kl} (G^M_{il})^* \]

Now, \( G^M \) can be diagonalized yielding the Molecular-Conductance Orbitals \( C \) given the overlap matrix \( S \)

\[ g = \Gamma'^L G'^M \Gamma'^R (G'^M)^\dagger \]

\[ G'^M = C^{-1} S^{-1} G^M C \]

\[ (G'^M)^\dagger = C^\dagger (G'^M)^\dagger S^{-1} (C^{-1})^\dagger \]

\[ \Gamma'^L = C^\dagger S \Gamma^L S C \]

\[ \Gamma'^R = C^{-1} \Gamma^R (C^{-1})^\dagger \]

\[ \text{Tr}(g) = \sum_i \Gamma'^L_{ii} \Gamma'^R_{ii} |G'^M_{ii}|^2 + \sum_i \sum_{j \neq i} \Gamma'^L_{ij} G'^M_{ii} \Gamma'^R_{ji} (G'^M_{jj})^* \]

Diagonal matrices

Revised electrode couplings

MOLECULAR-CONDUCTANCE ORBITALS

\[ \text{Tr}(g) = \sum_i \Gamma'_{ii}^L \Gamma'_{ii}^R | G_{ii}^M |^2 + \sum_i \sum_{j \neq i} \Gamma'_{ij}^L G_{ii}^M \Gamma'_{ji}^R (G_{jj}^M)^* \]

Current through each molecular-conductance orbital

Interference between molecular-conductance orbitals

Small if the eigenvalues are well separated in energy

A$_1$ Channels and Molecular-Conductance Orbitals
$A_1$ Channels and Molecular-Conductance Orbitals

$$T = \text{Tr}(g) = \sum_i \Gamma_{ii}^L \Gamma_{ii}^R |G_{ii}^M|^2 + \sum_i \sum_{j \neq i} \Gamma_{ij}^L G_{ii}^M \Gamma_{ji}^R (G_{jj}^M)^*$$
$B_1$ Channels and Molecular-Conductance Orbitals

![Graph showing the transmission $T$ and the modulus of the molecular conductance $|G'_{ii}|$ as functions of energy. The Fermi level $E_f$ is indicated.](image)
$T = \text{Tr}(g) = \sum_i \Gamma'_{ii} \Gamma^R_{ii} | G^M_{ii} |^2 + \sum_i \sum_{j \neq i} \Gamma'_{ij} G^M_{ii} \Gamma^R_{ji} (G^M_{jj})^*$
Inelastic scattering (IETS)

\[(\text{height})_q \propto \Gamma^L G^M \gamma_q (G^M)^\dagger \Gamma^R G^M \gamma_q (G^M)^\dagger = \Gamma^L \alpha_q \Gamma^R \alpha_q^\dagger\]

\[\gamma_q = \frac{dH}{dq}\]

\(q\) are the normal modes of vibration of the molecule

Now, \(\Gamma^L\) can be diagonalized as before yielding the Junction-Conductance Orbitals \(D\) (ignoring the overlap matrix \(S\))

Left-junction interaction \((\text{height})_q = \sum_{i,j} \Gamma^L_{ii} |\alpha_{ij}|^2 \Gamma^R_{jj}\)

Right-junction interaction

Weighted Through-
molecule inelastic scattering

Gagliardi, Solomon, Pecchia, Frauenheim, Di Carlo, Hush, Reimers \textit{PRB} (2007) submitted
Molecular Electronics: Measuring single molecule conduction

**Nanopore**

Wang et al. PRB 68 (2003) 035416

**Cross-wire**

Kushmerick et al. PRL 89 (2002) 086802

**STM Break Junction**

BN & NLJ The Science (2003) 301, 1221

**Scanning Probe**

Cui et al. Science 294 (2001) 571

**Electromigration**


**Nanocluster**


**Mechanical Break Junction**

Epstein et al. PRL 170804
Single-Molecule Conductivity

L ELECTRODE

MOLECULE

R ELECTRODE
Single-Molecule Conductivity

L ELECTRODE

MOLECULE

R ELECTRODE

Molecular Orbitals

Fermi energy
Single-Molecule Conductivity

L ELECTRODE

MOLECULE

R ELECTRODE

Molecular Orbitals

$V_e$

$I$

$V$

$V^0$

$V^e$

$e$
Shot noise measurements

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**Graphs and Figures:***

1. **Plot 1:**
   - Title: Number of counts vs. Electrode displacement (nm)
   - X-axis: Electrode displacement (nm)
   - Y-axis: Number of counts
   - Data points for Pt/H and Pt/H$_2$

2. **Plot 2:**
   - Title: Conductance vs. Electrode displacement (nm)
   - X-axis: Electrode displacement (nm)
   - Y-axis: Conductance (Ω$^{-1}$/cm)
   - Data points for Pt/H and Pt/H$_2$

3. **Plot 3:**
   - Title: Differential conductance vs. Bias voltage (mV)
   - X-axis: Bias voltage (mV)
   - Y-axis: Differential conductance (Ω$^{-1}$/cm)
   - Data points for Pt/H and Pt/H$_2$

4. **Plot 4:**
   - Title: Transmission vs. Energy (eV)
   - X-axis: Energy (eV)
   - Y-axis: Transmission
   - Data points for 8 k-points and Γ-point

5. **Plot 5:**
   - Title: Excess noise vs. Bias current (µA)
   - X-axis: Bias current (µA)
   - Y-axis: Excess noise ($10^{-2} Ω^2/Hz$)
   - Data points for Full shot noise

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**References:**

- Solomon, Gagliardi, Pecchia, Frauenheim, Di Carlo, Reimers, Hush Nano Lett. 6 (2006) 2431
Convergence of coherent $I(V)$ with respect to the number of atoms used to represent the electrodes

Varying the Extended-Molecule Size

No junction region  typical  converged

Convergence of coherent $I(V)$ with respect to the number of electrode atoms used in the extended molecule

Methods used to Calculate the Hamiltonian

• DFT is most common method used, but not by us

• Density-Functional Tight-Binding (DFTB)
  • Developed at Paderborn-Dresden

• Intermediate Neglect of Differential Overlap (INDO)
  • Implemented at Sydney, does ROHF and Multi-Reference CI

• Analytical Hückel Models (Tight Binding)
  • Mujica/Ratner type approaches
$\text{A}_2\text{ Channels and Molecular-Conductance Orbitals}$

![Graph showing the relationship between energy and conductance. The graph has a vertical axis labeled $T$ and a horizontal axis labeled $\text{Energy}$. There are two peaks at $E_f$, indicating conductance maxima.}
A$_2$ Channels and Molecular-Conductance Orbitals

\[ T = \text{Tr}(g) = \sum_i \Gamma'_{ii} \Gamma'_{ii} |G'^M_{ii}|^2 + \sum_i \sum_{j \neq i} \Gamma'_{ij} G'^M_{ii} \Gamma'_{ji} (G'^M_{jj})^* \]
B$_2$ Channels and Molecular-Conductance Orbitals
B₂ Channels and Molecular-Conductance Orbitals

\[ T = \text{Tr}(g) = \sum_i \Gamma^L_{ii} \Gamma^R_{ii} |G^M_{ii}|^2 + \sum_i \sum_{j \neq i} \Gamma^L_{ij} G^M_{ii} \Gamma^R_{ji} (G^M_{jj})^* \]
Including more atoms in the extended molecule

Au atoms per electrode in extended molecule:

Black - 3
Red - 25

Effect of the binding site on CH intensity

Wang, Loo, Ketzschmar & Red

Opt structure

Calculated IETS

Low energy

C-S Stretch

C-H Stretch

High Energy

CH, Rock

Sushmerick, Lazorcik, Patterson &