Characterizing Destructive Quantum Interference in Molecular Transport Junctions

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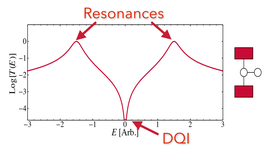
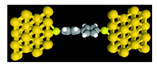
I. Background & Introduction

- Landauer-Büttiker theory is formulated around the transmission function $T(E)$ [1]
  - Provides probability that an electron tunnels from one electrode to the other
  - Value at the Fermi level relates to observables such as conductance $G = G_0 T(E_F)$
  - Peaks are resonances and some valleys are **destructive quantum interference (DQI)**





Molecular junction
(figure from [2])

- DQI provides an unconventional way for suppressing electric current
- DQI primarily depends on [3]
  - The isolated molecule's electronic structure
  - Where the electrodes couple to the molecule
- Energies where DQI occurs are described by the generalized eigenvalue problem [3]

$$[\mathbf{P}_R(\mathbf{H}_0 + \boldsymbol{\Sigma}_L + \boldsymbol{\Sigma}_R)\mathbf{P}_L]\,|\varphi_R\rangle = E\mathbf{P}_R\mathbf{P}_L\,|\varphi_R\rangle$$

Electrode couplings; Interference energy; Right eigenvector; Part of molecule not coupled to right electrode; Isolated molecule; Part of molecule not coupled to left electrode

- Only energies near the Fermi energy are experimentally observable
- The width of DQI in the transmission function leads to the idea of "robustness"
- The wider the width the more likely DQI can be observed experimentally

Key Questions
- How do we classify DQI?
- How do we predict the robustness of DQI?

II. Characterizing Destructive Quantum Interference

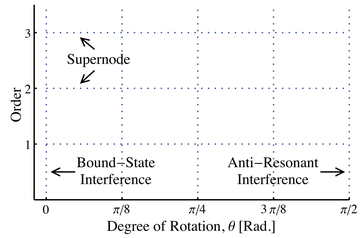
- The generalized eigenvalue problem (1) also produces right (and left) eigenvectors
- These eigenvectors will be called "**interference vectors**" and used to characterize DQI [4]

- DQI can be analyzed in terms of molecular orbitals (MOs) : An interference vector can be
  - an orbital of the molecule (single MO) $\Longrightarrow$ DQI is very sensitive to perturbation
  - a combination of multiple MOs $\Longrightarrow$ DQI is more robust

- Two key quantities from interference vectors
  1. **order** : describes the shape of the transmission around DQI
     order relates to the degeneracy of the eigenvalue = size of block in Kronecker form [5]
  2. **degree of rotation** : quantifies the nodal structure of the interference vectors where the electrodes couples to molecules

$$\theta = \sqrt{\arccos\left(\frac{|\langle\varphi_L|\mathbf{H}_0|\varphi_L\rangle|}{\||\varphi_L\rangle\|\,\|\mathbf{H}_0|\varphi_L\rangle\|}\right)\arccos\left(\frac{|\langle\varphi_R|\mathbf{H}_0|\varphi_R\rangle|}{\||\varphi_R\rangle\|\,\|\mathbf{H}_0|\varphi_R\rangle\|}\right)}.$$

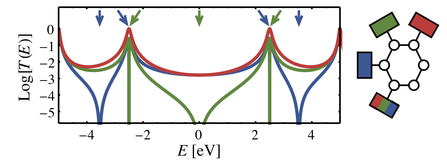
- Increased order and degree of rotation imply more robust DQI



- DQI is more robust when both left&right interference vectors are decoupled from the electrodes
- A bound state occurs when both electrodes couple to nodes in a MO

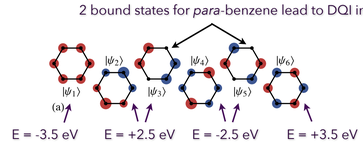
III. Benzene

- We can connect two electrodes to a benzene in 3 configurations: *ortho*-, *meta*-, and *para*-
- This results in 3 different transmission functions

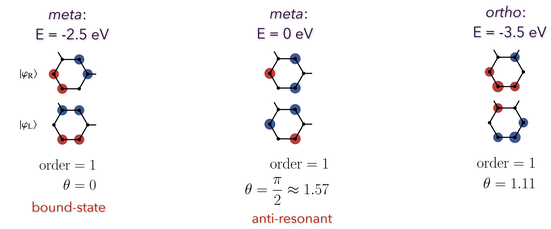


- Consider MOs, look for potential bound states

2 bound states for *para*-benzene lead to DQI in *ortho*- and *meta*-benzene



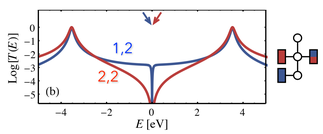
- Examine interference vectors



- In *meta*-configuration with E = 0 eV, both left and right interference vectors are decoupled from both electrodes, thus DQI is very robust

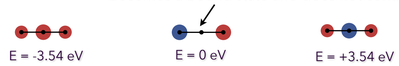
IV. Three-Site Model

- Consider a three-site model in 1,2 and 2,2 configurations
- Simplest model that shows a wide range of desired behavior. Not necessarily physically meaningful.

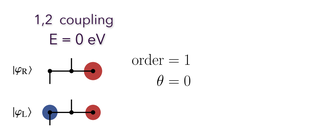


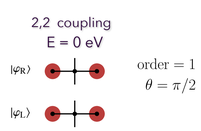
- 3 molecular orbitals

If both electrodes couple to the node (2,2 coupling), the MO becomes a bound state and does not contribute to transport



- Examine interference vectors





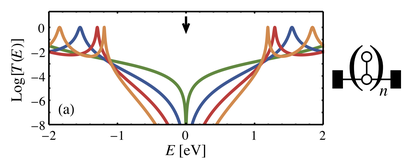
The left interference vector is an MO $\Longrightarrow$ DQI is less robust

- The left interference vector is a combination of MOs $\Longrightarrow$ DQI is more robust
- Both left and right interference vectors are decoupled from the electrodes. Therefore, DQI is very robust.

V. Cross-Conjugated Molecules

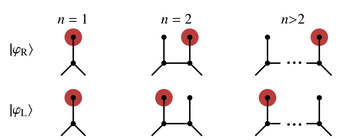
- Transmission functions for "comb" oligomers with n = 1 (green), 2 (blue), 3 (red), and 4 (orange)

coarse-grained models for cross-conjugated molecules



- The DQI at E = 0 eV is *n*-th order
- Higher-order DQI (resulting in supernodes) is more robust than lesser-order DQI

- Examine interference vectors



- All DQI in these comb oligomers is anti-resonant ($\theta = \pi/2$)

VI. Conclusions

- The "interference vectors" obtained from the generalized eigenvalue problem are the basis for our characterization scheme
- The interference vectors can be decomposed in MO basis, therefore revealing the participation of each MO in DQI
- Our characterization scheme can quantify DQI through the "order" and the "degree of rotation"
- Future work: apply group theory to better understand anti-resonances (DQI is a manifestation of substructure within molecular Hamiltonian)

References & Acknowledgements

(1) Cuevas & Scheer, *Molecular Electronics*, World Scientific (2010).
(2) **Reuter**, Solomon, Hansen, Seideman & Ratner J. Phys. Chem. Lett. **2**, 1667-1671 (2011).
(3) **Reuter** & Hansen, J. Chem. Phys. **141**, 181103 (2014).
(4) **Sam-ang** & **Reuter**, arXiv:1702.01341 (2017).
(5) Van Dooren, Lin. Alg. Appli. **27**, 103 (1979)

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