Symmetry fingerprints of a benzene SET

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Benzene junction

Para configuration

- Weak coupling to the leads
- Low temperature

Coulomb blockade

Meta configuration

- Rotational symmetry
- Orbitally degenerate states

Interference
Weak coupling

- Gating of 2nm sized molecule
- Weak coupling realization with specific anchor groups

Conformation effects I
(within the molecule)

Conformation effects II
(at contacts)

Theory of Benzene junctions

Most of the theoretical literature on benzene junctions treats the strong coupling limit. The works which are closer to our investigation:

- **Interference effects through benzene junction:**
  - in strong coupling regime (coherent transport)
  - visible in the middle of the HOMO-LUMO gap
  - interaction only treated at Hartree-Fock level


- **Strong current suppression and NDC in the Coulomb blockade regime:**
  - in the para configuration
  - only in presence of an electromagnetic bath
  - master equation only for populations:
    - it does not describe interference effects

Anderson-molecule junction

\[ H_{PPP} = \sum_{i\sigma} \xi_{i\sigma} d_{i\sigma}^\dagger d_{i\sigma} + b \sum_{i\sigma} (d_{i\sigma}^\dagger d_{i+1\sigma} + d_{i+1\sigma}^\dagger d_{i\sigma}) \\
+ U \sum_i \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right) \\
+ V \sum_{\langle i< j \rangle} (n_{i\uparrow} + n_{i\downarrow} - 1)(n_{j\uparrow} + n_{j\downarrow} - 1) \]

The Pariser-Parr-Pople is an extended Hubbard Hamiltonian introduced to describe interaction effects in conjugated molecules.

Only \( \pi \)-electrons are taken into account. Ions are assumed to have the same spatial symmetry of the relevant electrons.
System dynamics

1. Write the Liouville equation:

\[ \frac{d\rho}{dt} = -\frac{i}{\hbar} [\mathcal{H}, \rho] \]

2. Restrict to 2nd order in the coupling to the electrical baths. Make the Markov approximations and trace out the leads:

\[ \dot{\sigma} = -\frac{1}{\hbar^2} \int_0^\infty d\tau \text{Tr}_B \{ [\hat{H}_1(t), [\hat{H}_1(t-\tau), \hat{\sigma}(t) \otimes \rho_B]] \} \]

3. Neglect coherences between states with different number of particles in the system: they are decoupled and damped.

4. KEEP coherences between (quasi-)degenerate energy states (Generalized Master Equation). Any other choice is (in general) arbitrary!!

5. Calculate the stationary solution of the GME and evaluate the expectation values of relevant observables.
Isolated Benzene

- The PPP Hamiltonian for isolated benzene reads:

\[
H_{\text{PPP}} = \xi \sum_{i,\sigma} d_{i\sigma}^\dagger d_{i\sigma} + b \sum_{i,\sigma} \left( d_{i\sigma}^\dagger d_{i+1\sigma}^\dagger + d_{i+1\sigma}^\dagger d_{i\sigma} \right) + U \sum_i (n_{i\uparrow} - \frac{1}{2})(n_{i\downarrow} - \frac{1}{2}) + V \sum_i (n_{i\uparrow} + n_{i\downarrow} - 1)(n_{i+1\uparrow} + n_{i+1\downarrow} - 1)
\]

- The **size** of the Fock space for the many-body system \(4^6 = 4096\) since for each site there are 4 possibilities: \(|0\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\)

- Within this Fock space we diagonalize exactly the Hamiltonian.
## The size of the problem

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Symmetry of the ground states

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Examples of A, B, and E symmetries

- $b_{2g}$
- $e_{2u}$
- $e_{1g}$
- $a_{2u}$
"even more" Reduced Density Matrix

- Diagonal in energy
- Diagonal in particle number
- RDM

- 15
- 924
- 4096
Generalized Master Equation

- We define the density matrix for fixed particle number and energy
  \[ \hat{\sigma}^{NE} = \mathcal{P}_{NE} \hat{\sigma} \mathcal{P}_{NE} \]

  where
  \[ \mathcal{P}_{NE} := \sum_{\ell \tau} |N E \ell \tau \rangle \langle N E \ell \tau | \]

- And write the set of coupled equations:

  \[ \dot{\hat{\sigma}}^{NE} = -\sum_{\alpha \tau} \frac{\Gamma_\alpha}{2} \left\{ d_{\alpha \tau} \left[ f^+(H_{PPP} - E) + \frac{i}{\pi} p_\alpha (H_{PPP} - E) \right] d_{\alpha \tau}^\dagger \hat{\sigma}^{NE} + \right. \]
  \[ + d_{\alpha \tau}^\dagger \left[ f^-(E - H_{PPP}) - \frac{i}{\pi} p_\alpha (E - H_{PPP}) \right] d_{\alpha \tau} \hat{\sigma}^{NE} + h.c. \right\} + \]
  \[ + \sum_{\alpha \tau E'} \Gamma_\alpha \mathcal{P}_{NE} \left\{ d_{\alpha \tau}^\dagger f_\alpha^+(E - E') \hat{\sigma}^{N-1E'} d_{\alpha \tau} + d_{\alpha \tau} f_\alpha^-(E' - E) \hat{\sigma}^{N+1E'} d_{\alpha \tau}^\dagger \right\} \mathcal{P}_{NE} \]

  where
  \[ f_\alpha^+(x) = \frac{1}{1 + e^{\beta(x - \mu_\alpha)}} \]
  \[ p_\alpha(x) = -\text{Re}\psi \left[ \frac{1}{2} + \frac{i\beta}{2\pi} (x - \mu_\alpha) \right] \]
  \[ f_\alpha^-(x) = 1 - f_\alpha^+(x) \]
Observables

- **Current**: using the GME we find the **operator**:

\[
\hat{I}_L = \Gamma_L \sum_{N \in \tau} P_{NE} \left[ d_{LT}^\dagger f_L^+(H_{PPP} - E) d_{LT}^\dagger - d_{LT}^\dagger f_L^-(E - H_{PPP}) d_{LT} \right] P_{NE}
\]

and thus calculate the **stationary current**:

\[
I_{\text{stat}} = \text{Tr}\{\hat{\sigma}_{\text{stat}} \hat{I}_L\}
\]

- Neglecting the energy non-conserving terms of the GME we can write an **analytical** formula for the **conductance**:

\[
G_{N,N+1}(\Delta E) = 2e^2 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{\sum_{nm\tau} \langle N, n | d_{LT} | N+1, m \rangle \langle N+1, m | d_{RT}^\dagger | N, n \rangle^2}{\sum_{nm\alpha\tau} |\langle N, n | d_{\alpha\tau} | N+1, m \rangle|^2} \left[ -\frac{f'(\Delta E)}{(S_{N+1} - S_N) f(\Delta E) + S_N} \right]
\]

**Overlap factor**
Para vs. Meta

Conductance suppression

Para

Meta

conserved

suppressed
Destructive interference

- The conductance is proportional to the overlap factor

\[ \Lambda = \left| \sum_{nm\tau} \langle N, n | d_{L\tau}^\dagger | N + 1, m \rangle \langle N + 1, m | d_{R\tau}^\dagger | N, n \rangle \right|^2 \]

- With the help of \( d_{R\tau}^\dagger = \mathcal{R}_\phi d_{L\tau}^\dagger \mathcal{R}_\phi \) it can be written:

\[ \Lambda = \left| \sum_{nm\tau} \langle N, n | d_{L\tau}^\dagger | N + 1, m \rangle^2 e^{i\phi_{nm}} \right|^2 \]

- Necessary condition for interference is that one of the two states involved in the transport is \textbf{orbitally degenerate}: A and B symmetry states are non-degenerate while E symmetry states are always doubly degenerate.
The 8 electrons “anomaly”

Mirror symmetry of the para-configuration

The tunnelling preserves this mirror symmetry: the lowest 8 electron state involved in transport is the mirror-symmetric (first excited) state with $E_{2g}$ symmetry.
NDC: the facts
NDC: the role of coherences

- The dynamics is restricted to a very limited number of states.
- The 7 particle ground state has spin and orbital degeneracies.
- The spin degeneracy is easily treated: $\hat{\sigma}_g^\uparrow = \hat{\sigma}_g^\downarrow$.
- The orbital degeneracy cannot be resolved.
- **Physical basis**: the basis that diagonalizes the stationary density matrix. It depends on the bias thus in whatever reference basis coherences are crucial for a correct description of the system.
- **A visualization tool**: the position resolved transition probability:

$$P(x, y; \ell \tau) = \lim_{L \to \infty} \sum_{\sigma} \frac{1}{2L} \int_{-L/2}^{L/2} \text{d}z |\langle 7g\ell\tau | \psi^\dagger_\sigma(\vec{r}) | 6g \rangle|^2$$
The "node" effect

![Graph showing the relationship between current and voltage, with labeled points a, b, c, d, e, and a diagram illustrating the node effect with labeled states a, b, c, d, and e, indicating backward and forward blocking states.](image-url)
Robustness

- We have tested the robustness of the effects against:
  - Residual potential drop on the benzene molecule (in weak coupling to the leads the potential drop is concentrated at the contacts)
  - On-site energy renormalization of the contact atom due to different anchor groups
  - Lifting of the electronic degeneracy due to deformation (static Jahn-Teller effect)

- Necessary condition for interference is only the presence of quasi-degenerate states:
  \[ \Delta E < k_B T \]
Conclusions

• Interplay electron-electron interaction and orbital symmetry are important to understand transport through benzene SETs.

• **Destructive interference** between degenerate states generates:

• **Semiempirical models** are useful tool study molecular electronics at an analytical level.

• **Coherences** between degenerate states play a crucial role in the generalized master equation approach to transport in benzene (molecular) junctions.
Thanks

Georg Begemann

Milena Grifoni

Dana Darau

...and you for your attention!