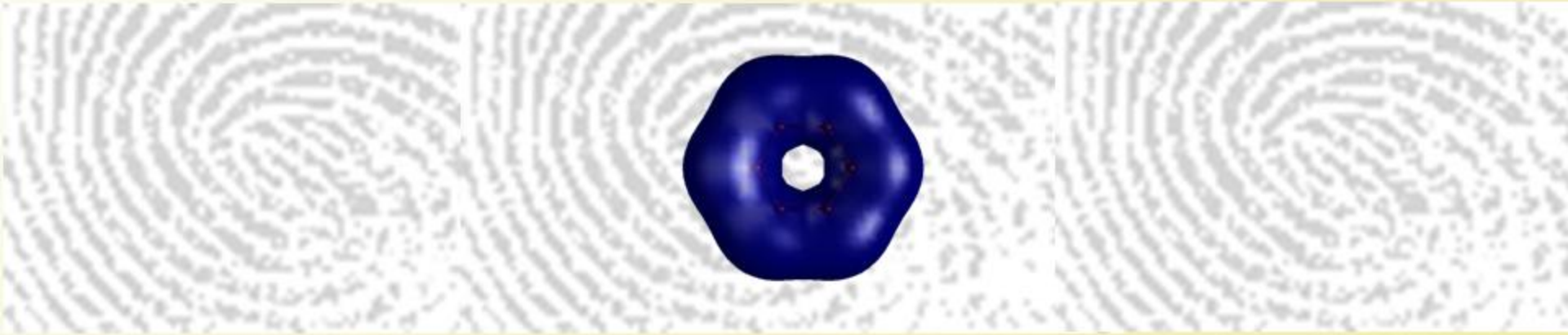
Symmetry fingerprints of a benzene SET

Andrea Donarini

Georg Begemann, Dana Darau, Milena Grifoni

University of Regensburg

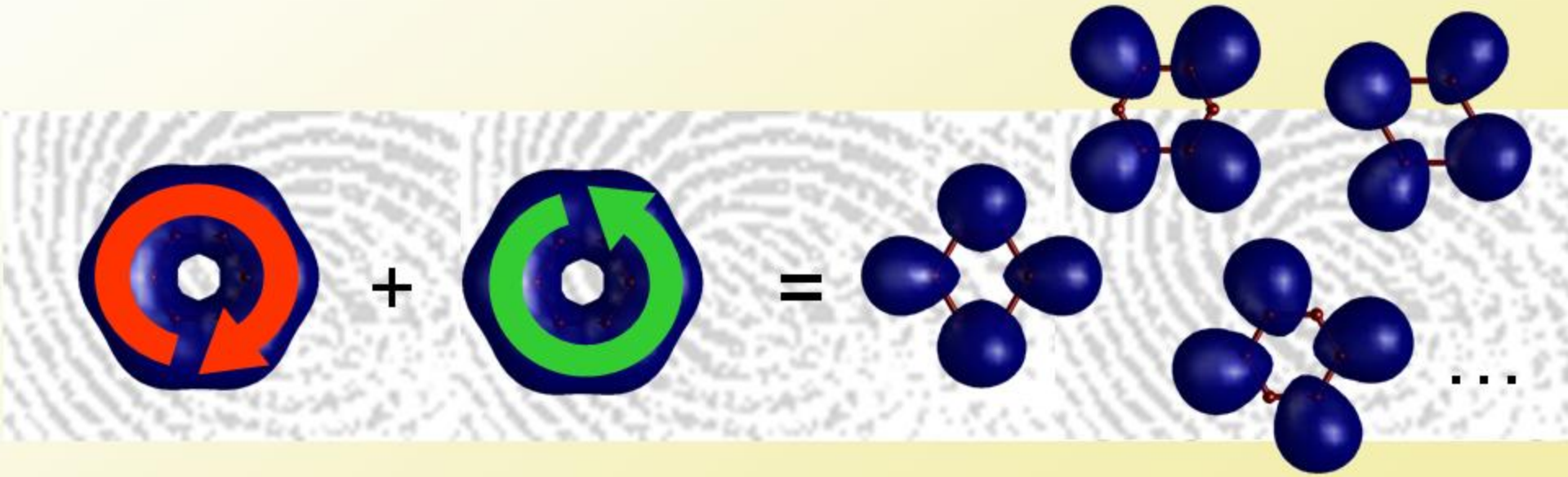


Symmetry fingerprints of a benzene SET

Andrea Donarini

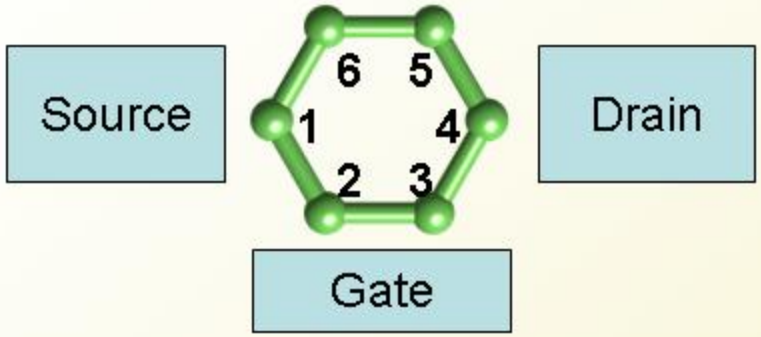
Georg Begemann, Dana Darau, Milena Grifoni

University of Regensburg



Benzene junction

Para configuration



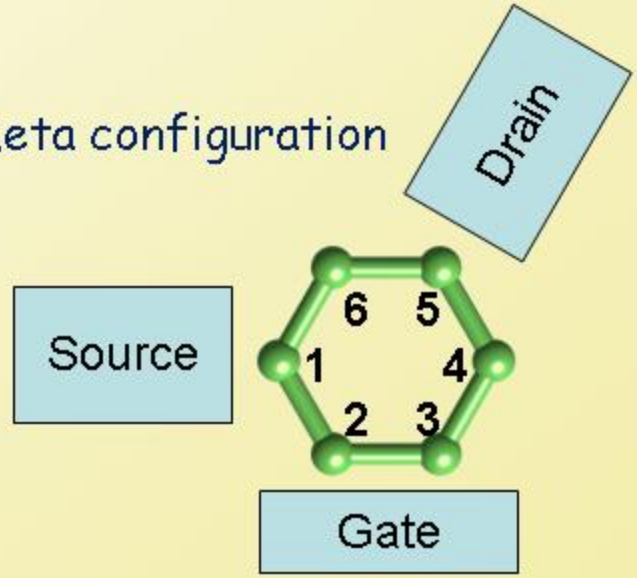
- Weak coupling to the leads
- Low temperature

Coulomb blockade

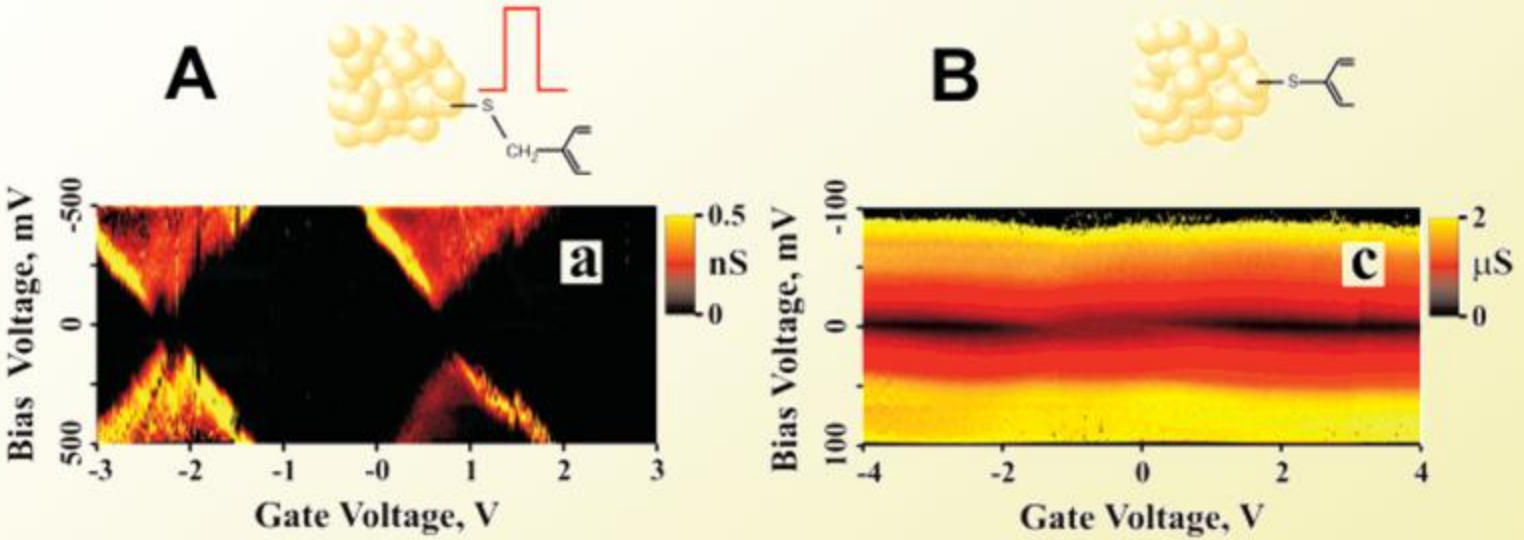
- Rotational symmetry
- Orbitally degenerate states

Interference

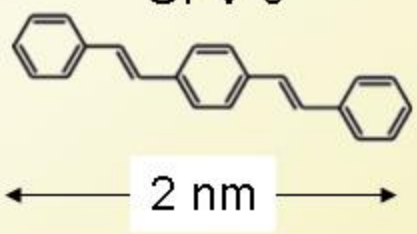
Meta configuration



Weak coupling



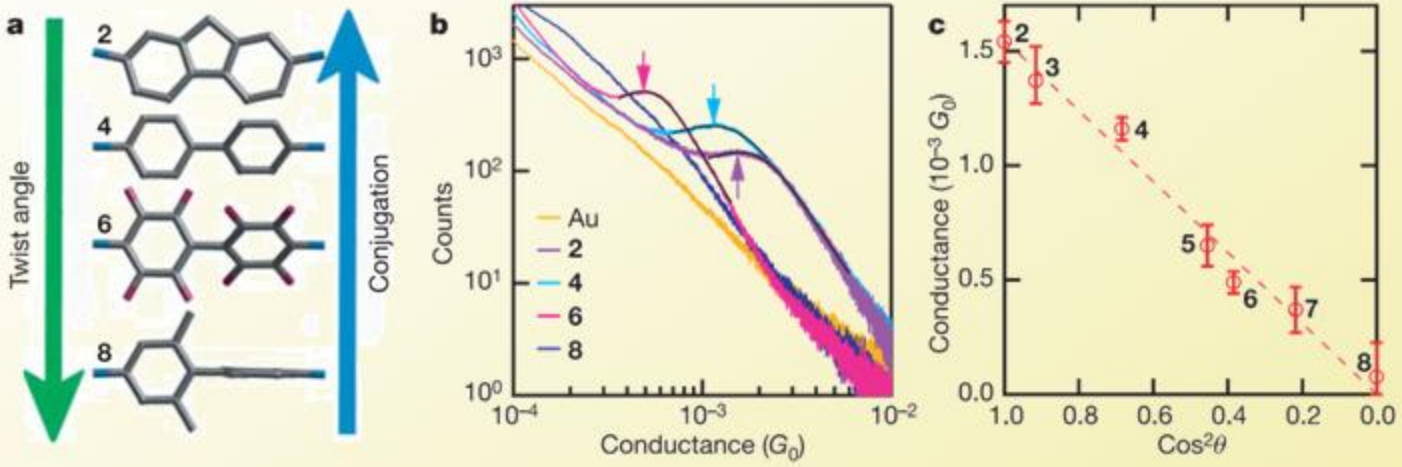
OPV-3



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

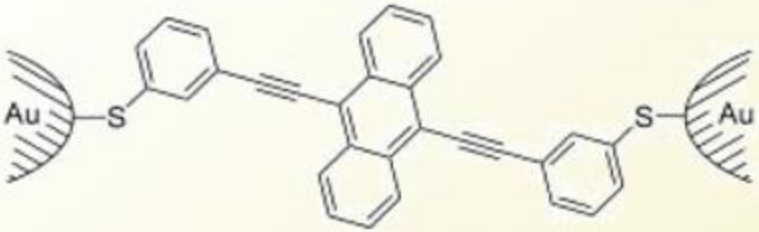
A. Danilov, S. Kubatkin, et al. Nanoletters **8**, 1 (2008)

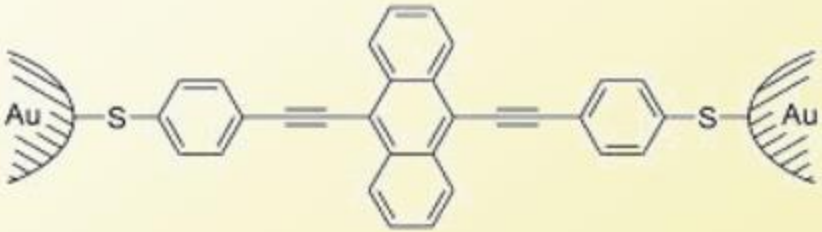
Conformation effects I
(within the molecule)

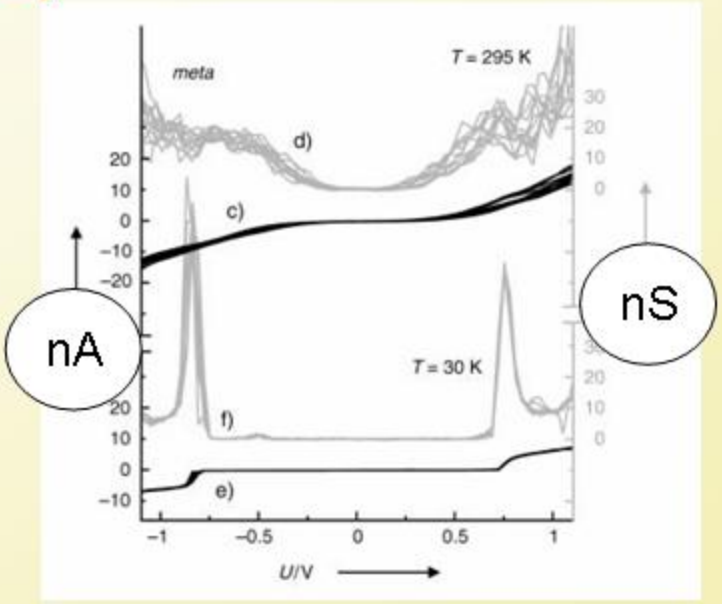


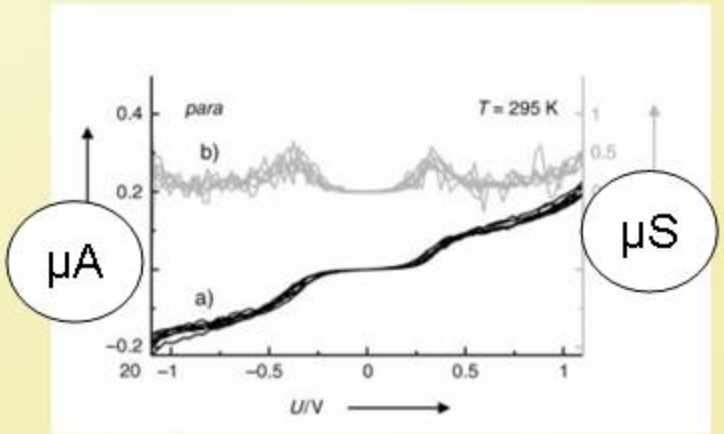
L. Venkataraman, J. E. Klare, et al. Nature, **424**, 904 (2006)

Conformation effects II
(at contacts)









M. Mayor, H. Weber, et al. Angew. Chem. Int. Ed. **42** 5843 (2003)

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

WE

- **Weak** coupling
- **At** the "HOMO" and "LUMO"
- **Exact** in interaction

D. V. Cardamone, C. A. Stafford *et al.*, Nano Lett. **6**, 2422 (2006).

- 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

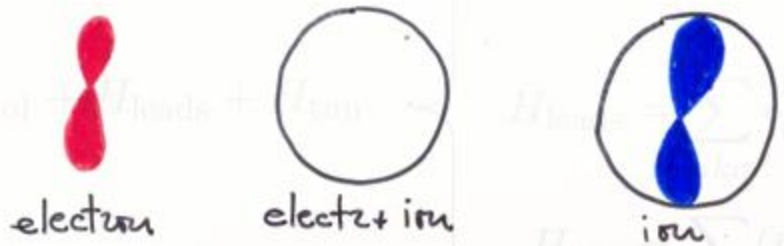
- NDC in **meta** configuration
- **Independent** from e.m.bath
- **Interference** effect captured thanks to coherences

M. Hettler, W. Wenzel *et al.* Phys. Rev. Lett. **90**, 076805 (2003)

Anderson-molecule junction

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

The **P**ariser-**P**arr-**P**ople is an **extended Hubbard** Hamiltonian introduced to describe interaction effects in **conjugated molecules**.



Only π-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:

$$\dot{\tilde{\sigma}} = -\frac{1}{\hbar^2}\int_0^\infty d\tau \mathrm{Tr}_\mathrm{B}\{[\tilde{H}_\mathrm{I}(t), [\tilde{H}_\mathrm{I}(t-\tau), \tilde{\sigma}(t)\otimes\rho_\mathrm{B}]]\}$$

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:

$$
\begin{aligned}
H_{\mathrm{PPP}} = & \xi \sum_{i\sigma} d_{i\sigma}^{\dagger} d_{i\sigma} + b \sum_{i\sigma} \left(d_{i\sigma}^{\dagger} d_{i+1\sigma} + d_{i+1\sigma}^{\dagger} d_{i\sigma} \right) + \\
& + U \sum_{i} \left(n_{i\uparrow} - \tfrac{1}{2} \right) \left(n_{i\downarrow} - \tfrac{1}{2} \right) + \\
& + V \sum_{i} \left(n_{i\uparrow} + n_{i\downarrow} - 1 \right) \left(n_{i+1\uparrow} + n_{i+1\downarrow} - 1 \right)
\end{aligned}
$$

- 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

N	# states
0	1
1	12
2	66
3	220
4	495
5	792
6	924
7	792
8	495
9	220
10	66
11	12
12	1
	4096

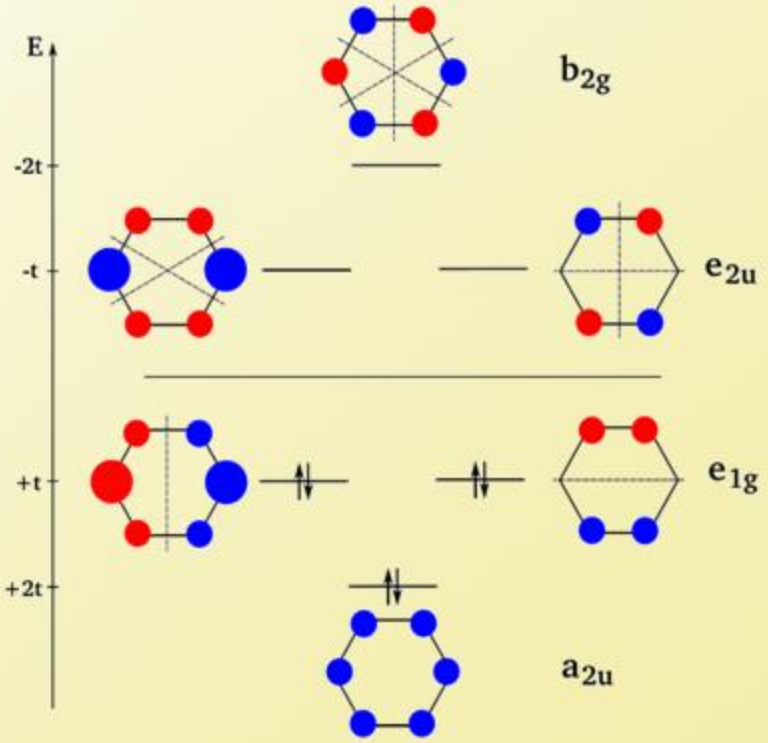
N	# ↑	# ↓	#states
5	5	0	6
	4	1	90
	3	2	300
	2	3	300
	1	4	90
	0	5	6
7	6	1	6
	5	2	90
	4	3	300
	3	4	300
	2	5	90
	1	6	6

N	# ↑	# ↓	#states
6	6	0	1
	5	1	36
	4	2	225
	3	3	400
	2	4	225
	1	5	36
	0	6	1

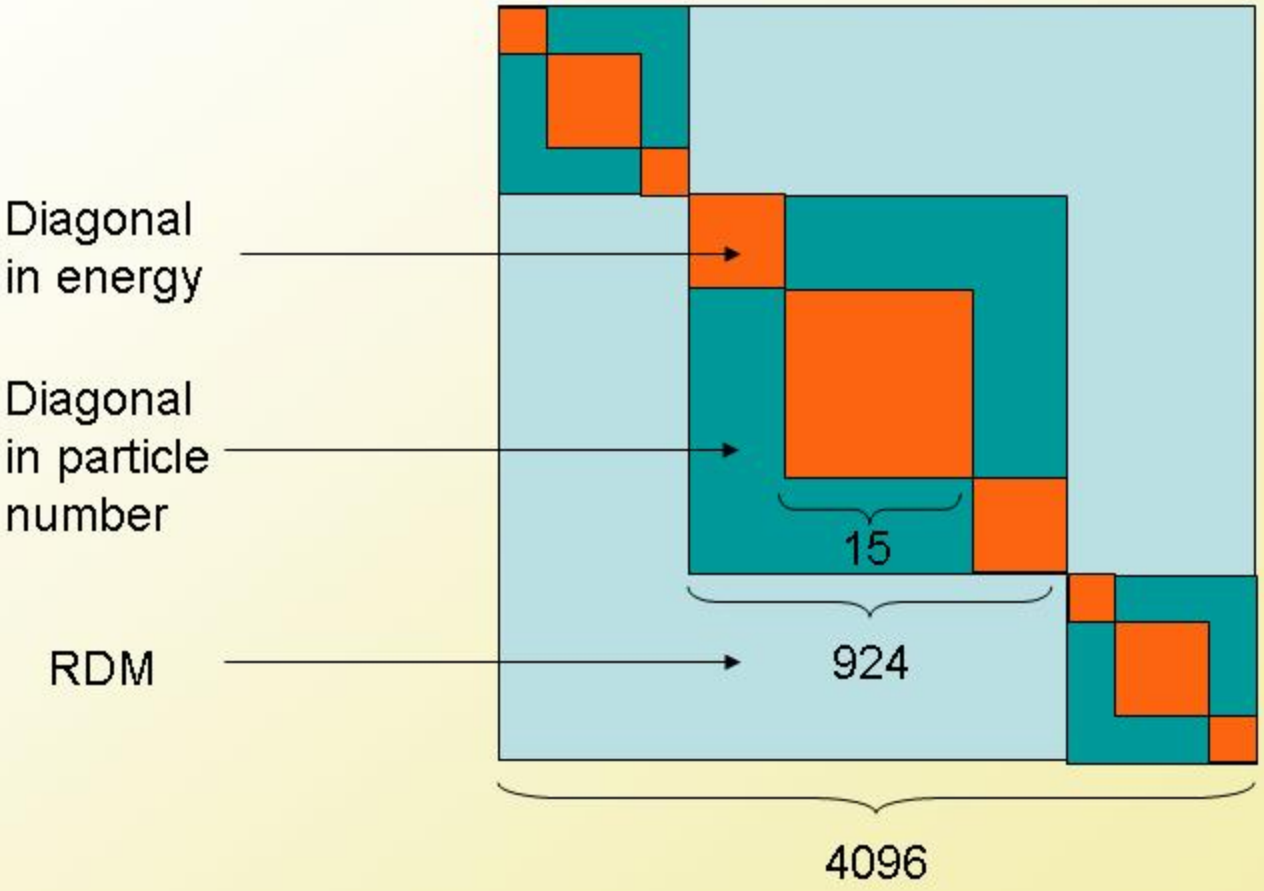
Symmetry of the ground states

N	Degeneracy	GS energy[eV] (at $\xi = 0$)	GS symmetry representation
0	1	0	A_{1g}
1	2	-22	A_{2u}
2	1	-42.25	A_{1g}
3	4	-57.42	E_{1g}
4	3	-68.875	A_{2g}
5	4	-76.675	E_{1g}
6	1	-81.725	A_{1g}
7	4	-76.675	E_{2u}
8	3	-68.875	A_{2g}
9	4	-57.42	E_{2u}
10	1	-42.25	A_{1g}
11	2	-22	B_{2g}
12	1	0	A_{1g}

Examples of A, B, and E symmetries



"even more" Reduced Density Matrix



Generalized Master Equation

- We define the density matrix for fixed particle number and energy

$$\hat{\sigma}^{NE} = \mathcal{P}_{NE}\,\hat{\sigma}\,\mathcal{P}_{NE} \qquad \text{where} \qquad \mathcal{P}_{NE} := \sum_{\ell\tau} |N\,E\,\ell\,\tau\rangle\langle N\,E\,\ell\,\tau|$$

- And write the set of coupled equations:

$$\begin{aligned}\dot{\hat{\sigma}}^{NE} = &-\sum_{\alpha\tau}\frac{\Gamma_\alpha}{2}\Bigg\{ d_{\alpha\tau}\left[f^{+}(H_{\mathrm{PPP}}-E)+\frac{i}{\pi}p_\alpha(H_{\mathrm{PPP}}-E)\right]d^{\dagger}_{\alpha\tau}\,\hat{\sigma}^{NE}+\\ &+ d^{\dagger}_{\alpha\tau}\left[f^{-}(E-H_{\mathrm{PPP}})-\frac{i}{\pi}p_\alpha(E-H_{\mathrm{PPP}})\right]d_{\alpha\tau}\,\hat{\sigma}^{NE}+h.c.\Bigg\}+\\ &+\sum_{\alpha\tau E'}\Gamma_\alpha\mathcal{P}_{NE}\Big\{ d^{\dagger}_{\alpha\tau}f^{+}_{\alpha}(E-E')\,\hat{\sigma}^{N-1E'}d_{\alpha\tau}+d_{\alpha\tau}f^{-}_{\alpha}(E'-E)\,\hat{\sigma}^{N+1E'}d^{\dagger}_{\alpha\tau}\Big\}\mathcal{P}_{NE}\end{aligned}$$

where

$$f^{+}_{\alpha}(x)=\frac{1}{1+e^{\beta(x-\mu_\alpha)}} \qquad f^{-}_{\alpha}(x)=1-f^{+}_{\alpha}(x) \qquad p_\alpha(x)=-\mathrm{Re}\psi\left[\tfrac{1}{2}+\tfrac{i\beta}{2\pi}(x-\mu_\alpha)\right]$$

Observables

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

$$\hat{I}_L = \Gamma_L \sum_{NE\tau} P_{NE}[d_{L\tau} f_L^+(H_{\mathrm{PPP}} - E) d_{L\tau}^\dagger - d_{L\tau}^\dagger f_L^-(E - H_{\mathrm{PPP}}) d_{L\tau}] P_{NE}$$

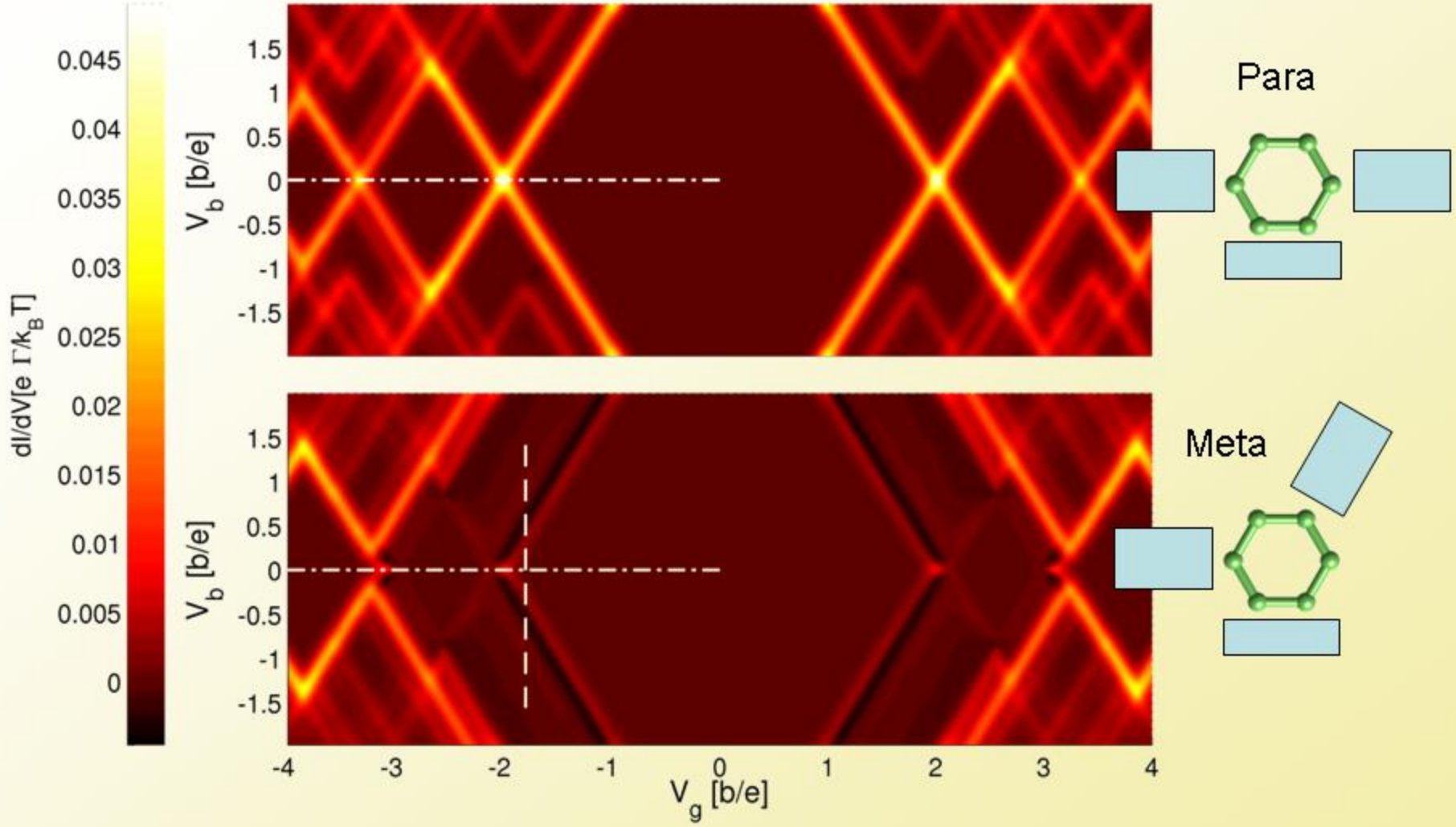
and thus calculate the **stationary current**:

$$I_{\mathrm{stat}} = \mathrm{Tr}\{\hat{\sigma}_{\mathrm{stat}} \hat{I}_L\}$$

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

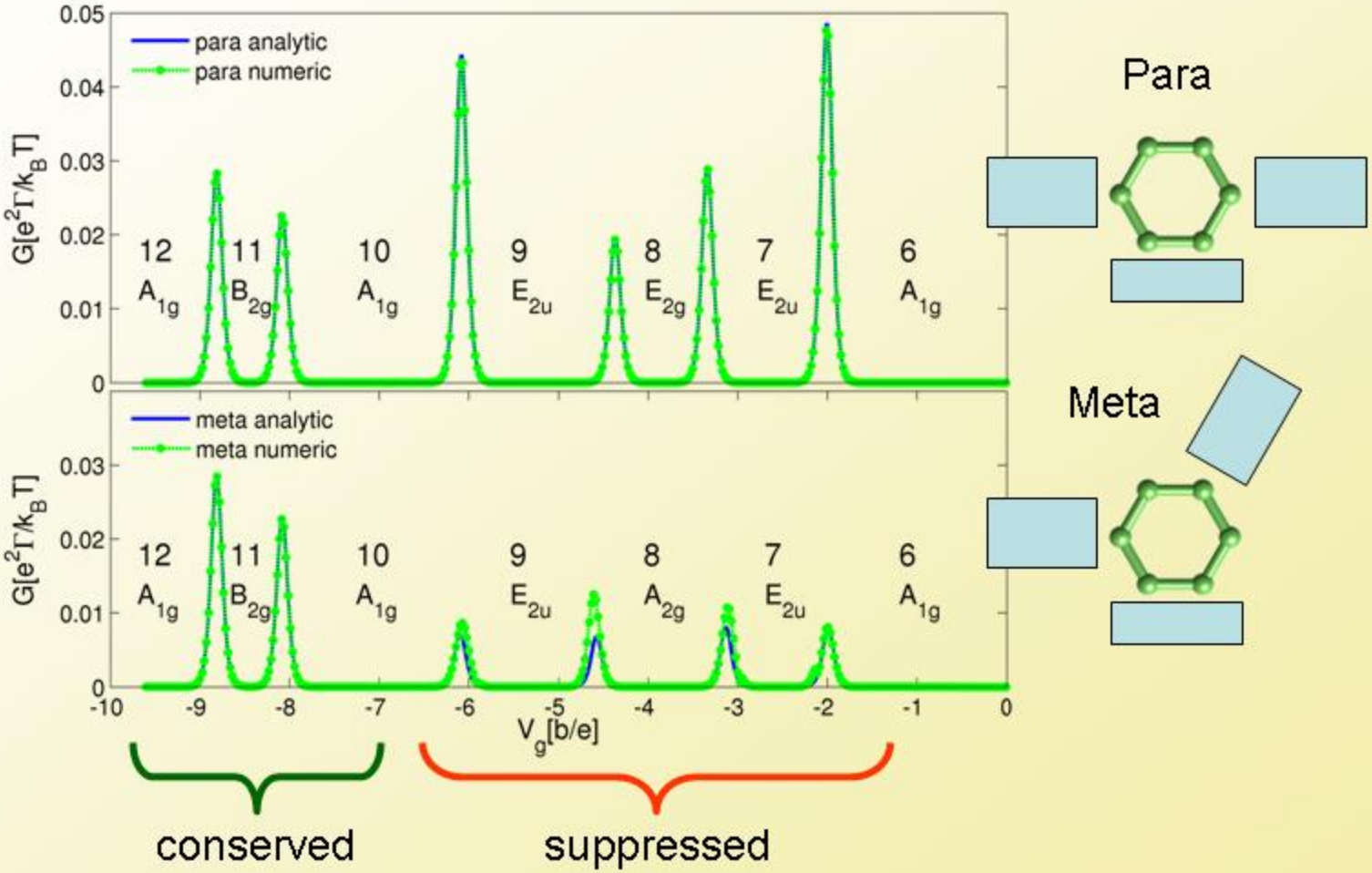
$$G_{N,N+1}(\Delta E) = 2e^2 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \underbrace{\frac{\left|\sum_{nm\tau} \langle N, n|d_{L\tau}|N+1, m\rangle\langle N+1, m|d_{R\tau}^\dagger|N, n\rangle\right|^2}{\sum_{nm\alpha\tau} |\langle N, n|d_{\alpha\tau}|N+1, m\rangle|^2}}_{\text{Overlap factor}} \left[-\frac{f'(\Delta E)}{(S_{N+1} - S_N) f(\Delta E) + S_N}\right]$$

Para vs. Meta



G. Begemann, D. Darau, **A. Donarini**, M. Grifoni, arXiv:0801.2961, to appear in PRB

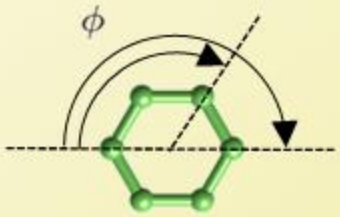
Conductance suppression



Destructive interference

- The conductance is proportional to the overlap factor

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

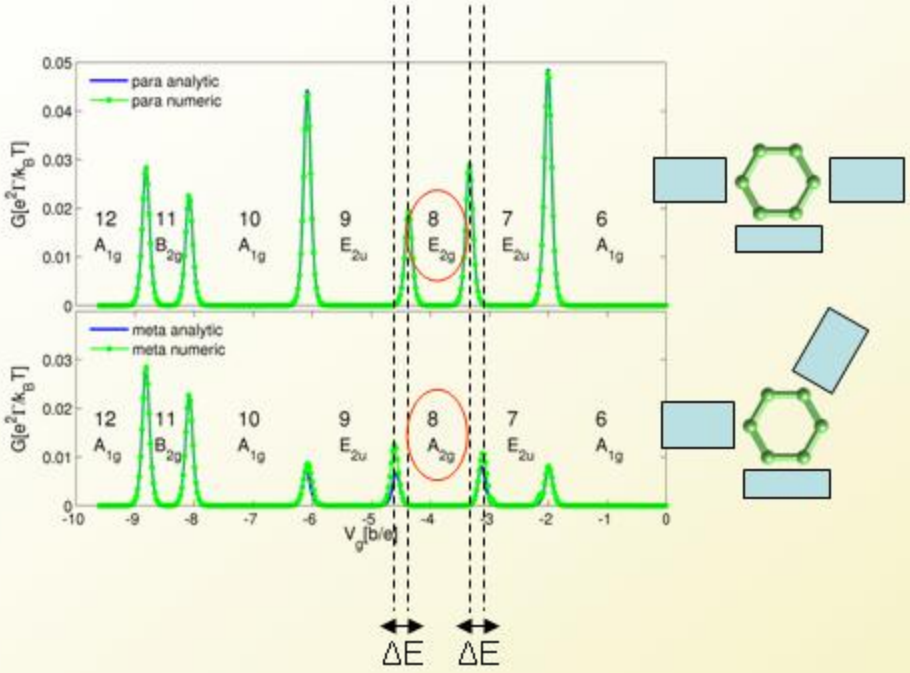


- With the help of $d^{\dagger}_{R\tau} = \mathcal{R}^{\dagger}_{\phi} d^{\dagger}_{L\tau} \mathcal{R}_{\phi}$ it can be written:

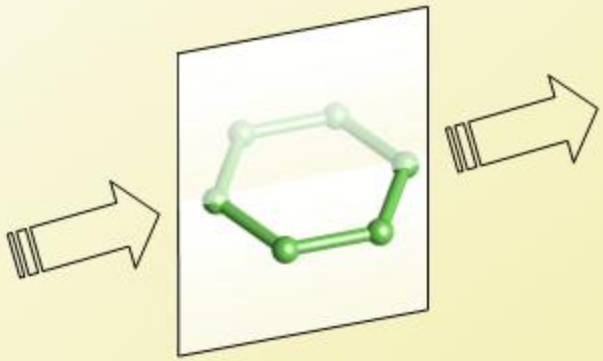
$$\Lambda = \left| \sum_{nm\tau} |\langle N, n | d_{L\tau} | N+1, m \rangle|^2 e^{i\phi_{nm}} \right|^2$$

- Necessary condition for interference is that one of the two states involved in the transport is orbitally degenerate: A and B symmetry states are non-degenerate while E symmetry states are always doubly degenerate.

The 8 electrons "anomaly"

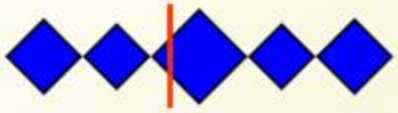


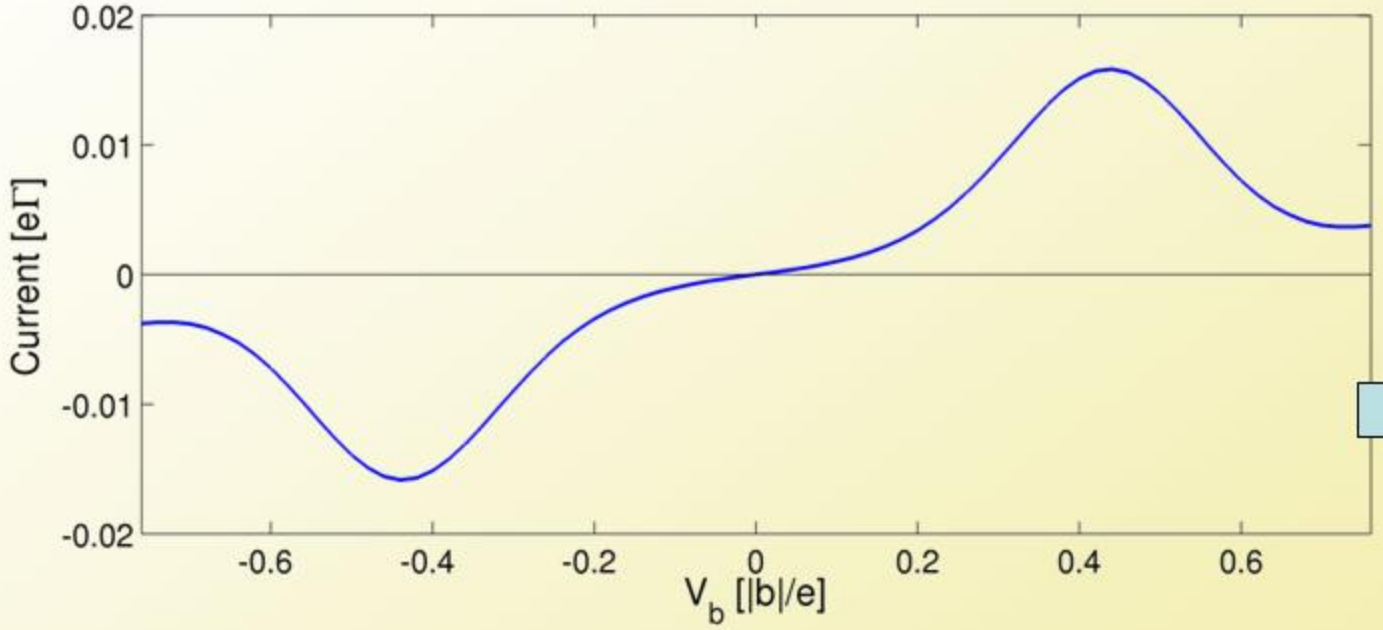
Mirror symmetry of the para-configuration

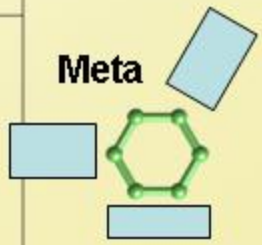


The tunnelling preserves this mirror symmetry: the lowest 8 electron state involved in transport is the mirror-symmetric (first excited) state with E_{2g} symmetry.

NDC: the facts

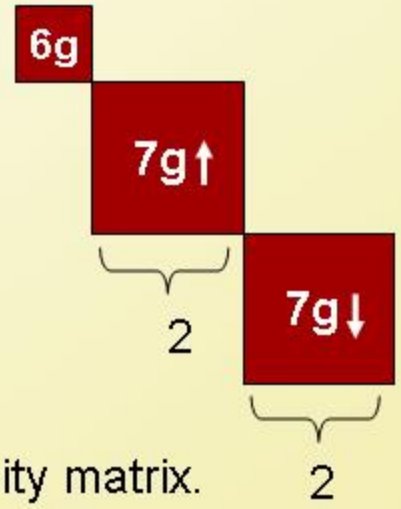






NDC: the role of coherences

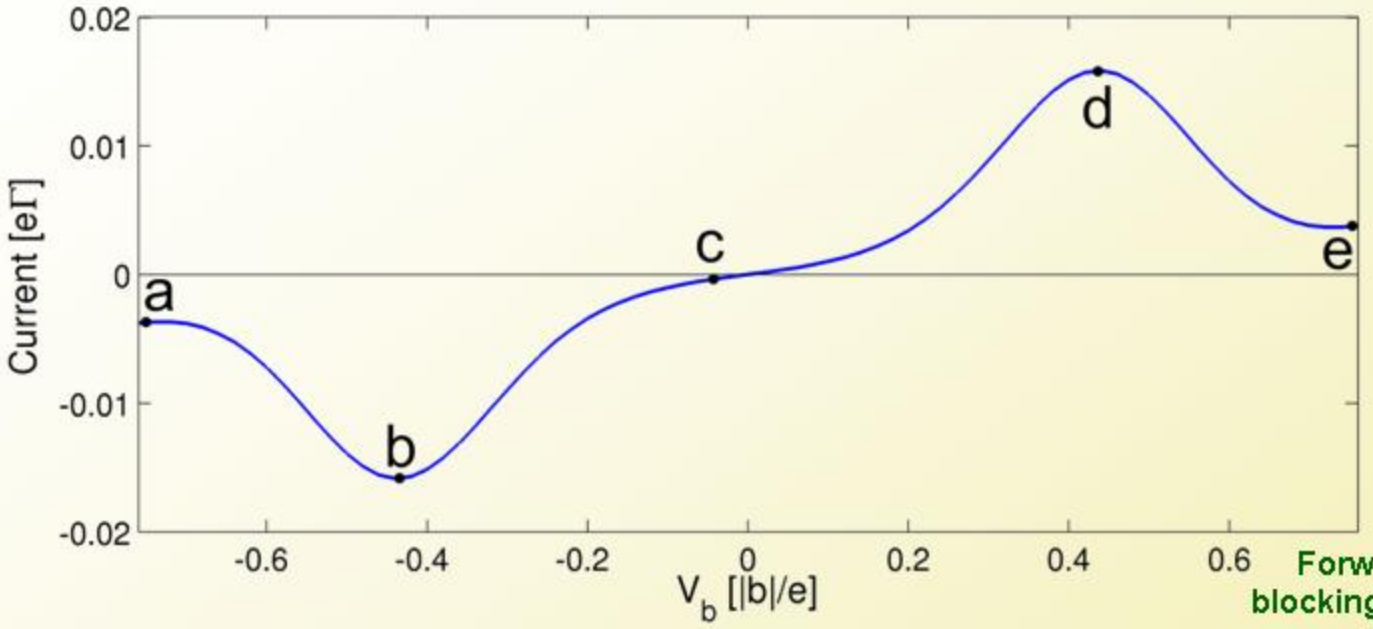
- The dynamics is restricted to a **very limited number** of states
- The 7 particle ground state has spin and orbital **degeneracies**
- The **spin** degeneracy is easily treated: $\hat{\sigma}_{7g\uparrow} = \hat{\sigma}_{7g\downarrow}$
- The **orbital** degeneracy cannot be resolved.

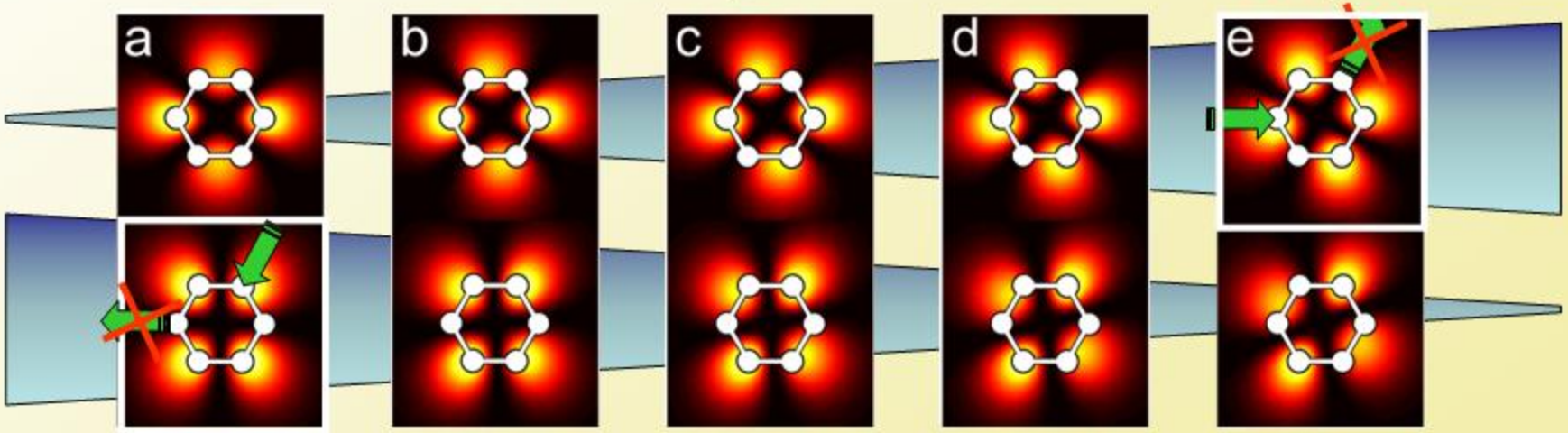


- **Physical basis**: the basis that diagonalizes the stationary density matrix. It depends on the bias thus in whatever reference basis coherences are crucial for a correct description of the system.
- A **visualization tool**: the position resolved **transition probability**:

$$P(x,y;\ell\tau) = \lim_{L\to\infty} \sum_{\sigma} \frac{1}{2L} \int_{-L/2}^{L/2} \mathrm{d}z |\langle 7g\ell\tau|\psi_{\sigma}^{\dagger}(\vec{r})|6g\rangle|^2$$

The "node" effect





Robustness

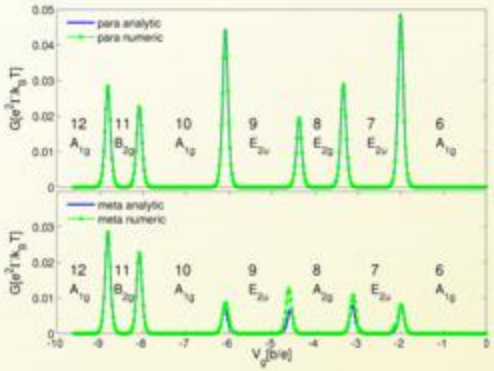
- We have tested the robustness of the effects against:
  - Residual potential drop on the benzene molecule (in weak coupling to the leads the potential drop is concentrated at the contacts)
  - On-site energy renormalization of the contact atom due to different anchor groups
  - Lifting of the electronic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

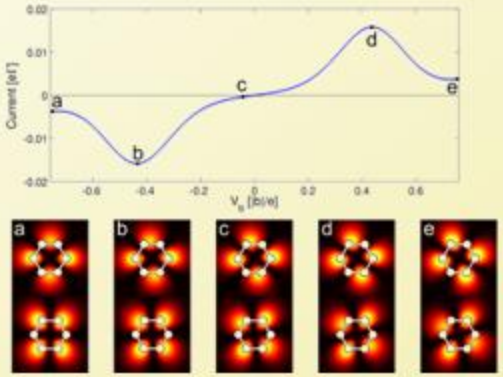
$$\Delta E < k_B T$$

Conclusions

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

- **Distructive interference** between degenerate states generates:





- **semiempirical models** are usefull 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!