Transport through Anderson Molecules

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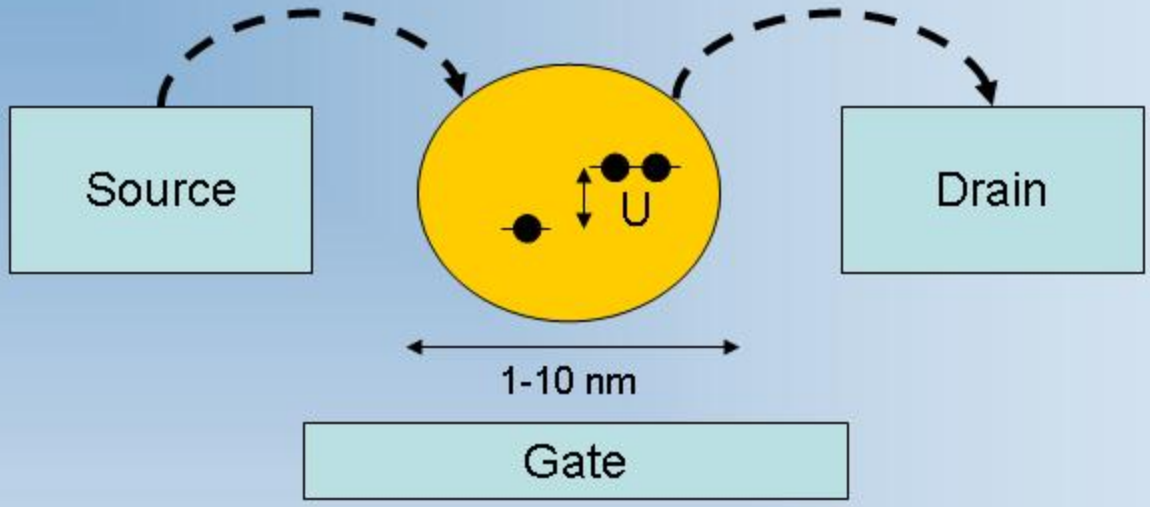
Anderson Impurity (AI)



$$H = H_{\rm dot} + H_{\rm leads} + H_{\rm tun}$$

$$H_{\rm dot} = \sum_{\sigma} \xi_\sigma d^\dagger_\sigma d_\sigma + U\left(n_\uparrow - \frac{1}{2}\right)\left(n_\downarrow - \frac{1}{2}\right)$$

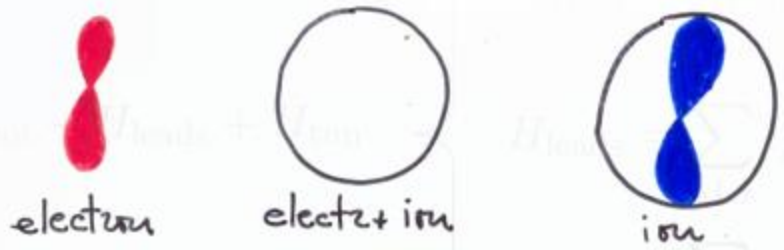
$$H_{\rm leads} = \sum_{\alpha k \sigma} \epsilon_{\alpha k \sigma} c^\dagger_{\alpha k \sigma} c_{\alpha k \sigma}$$

$$H_{\rm tun} = \sum_{\alpha k \sigma} (t_{\alpha k \sigma} c^\dagger_{\alpha k \sigma} d_\sigma + t^*_{\alpha k \sigma} d^\dagger_\sigma c_{\alpha k \sigma})$$

Anderson Molecules

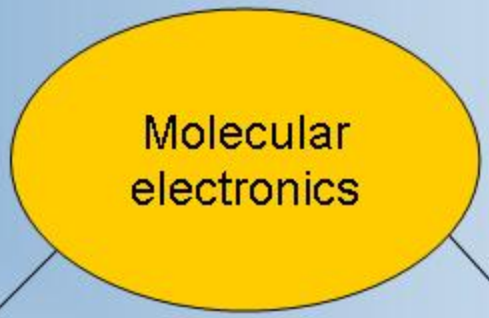
$$H_{\mathrm{PPP}} = \sum_{i\sigma} \xi_\sigma d^\dagger_{i\sigma} d_{i\sigma} + b \sum_{i\sigma} (d^\dagger_{i\sigma} d_{i+1\sigma} + d^\dagger_{i+1\sigma} d_{i\sigma}) + U \sum_i \left(n_{i\uparrow} - \frac{1}{2}\right)\left(n_{i\downarrow} - \frac{1}{2}\right) + V \sum_{\langle i<j \rangle} (n_{i\uparrow}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

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..

Why studying them?



Ab-initio methods

- Detailed structure
- Electron-electron interaction poorly treated (substantially mean field)
- Coherent transport

Anderson

Molecules

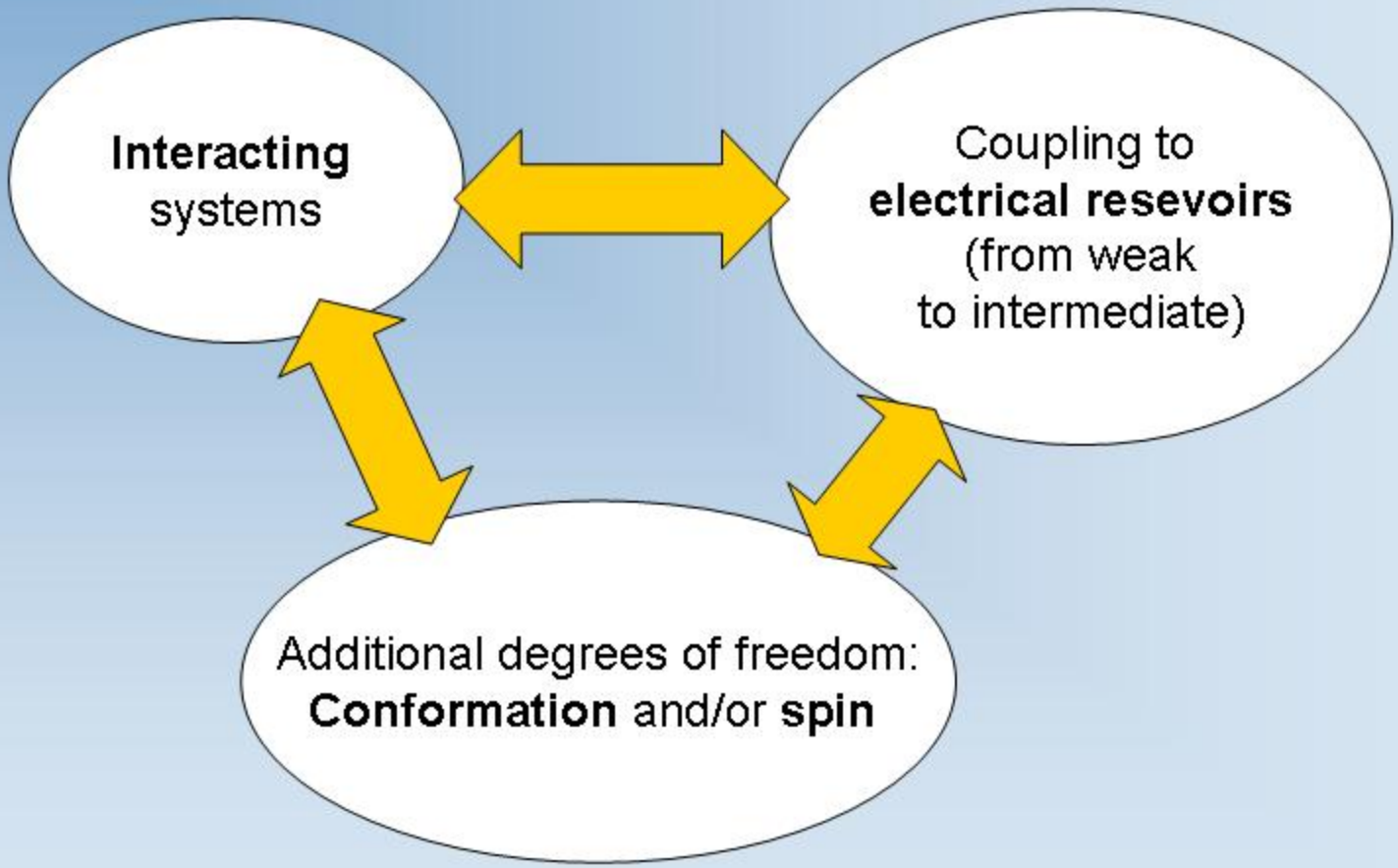
Modellistic approach

- Oversimplified structure: "a molecule is a Quantum Dot"
- Very good description of electron-electron interaction
- Coulomb Blockade – Kondo – Coherent transport regimes

Goals

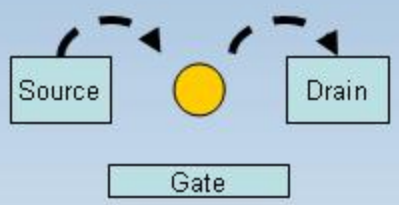
- Stability diagram through an Anderson Molecule **weakly** coupled to leads;
- Electrical conductance through an AM for **intermediate coupling**;
- Role played by the conformational degree of freedom in the electron transport.

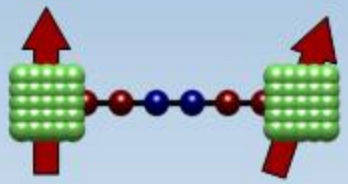
Problems

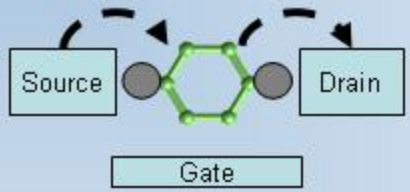

Interacting systems
Coupling to **electrical resevoirs** (from weak to intermediate)
Additional degrees of freedom: **Conformation** and/or **spin**

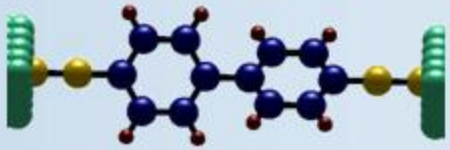
Roadmap to complexity

1, 2, 6, …many

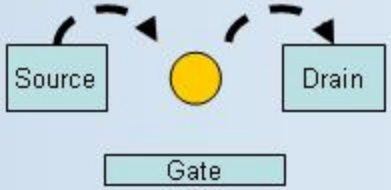






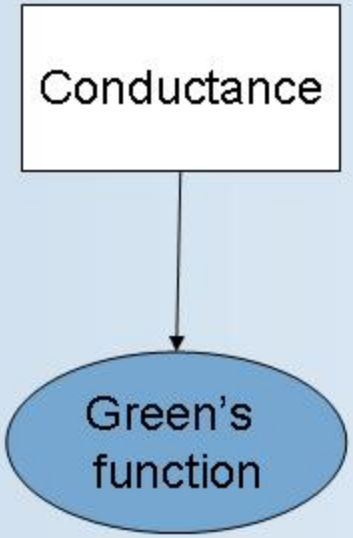


The conductance for the AI



The conductance through an AI can be written as:

$$G = \frac{e^2}{h} \sum_{\sigma} \int \frac{d\omega}{2\pi} \frac{\Gamma_{L\sigma}(\omega)\Gamma_{R\sigma}(\omega)}{\Gamma_{L\sigma}(\omega) + \Gamma_{R\sigma}(\omega)} A_{\sigma}(\omega;\xi) \left(-\frac{\partial n_F}{\partial \omega}\right)$$

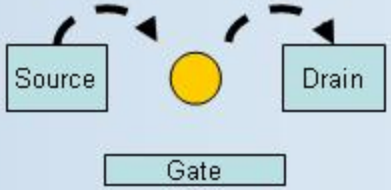


where

$A_{\sigma}(\omega;\xi) = -2\mathrm{Im}[\mathcal{G}^r_{\sigma}(\omega;\xi)]$ is the **spectral function** of the impurity

$\Gamma_{\alpha\sigma}(\omega) = 2\pi \sum_{k\in\alpha} |t_{\alpha k\sigma}|^2 \delta(\omega - \epsilon_{\alpha k\sigma})$ are the **tunnelling rates** to the leads.

Anderson Impurity



- **Test model** for transport through an interacting region in the weak to intermediate coupling regime;

- In the **intermediate coupling** we apply the Green's function method in the Equation of Motion (EoM) technique.

Equation of motion technique (i)

The first step is to apply the **time derivative** to the single particle retarded Green's function:

$$\mathcal{G}^r_\sigma(t;\xi) \equiv -\mathrm{i}\theta(t)\langle\{d_\sigma(t), d^\dagger_\sigma(0)\}\rangle$$

Error! There is +!

$$\mathrm{i}\partial_t \mathcal{G}^r_\sigma(t;\xi) = \delta(t)\langle\{d_\sigma(0), d^\dagger_\sigma(0)\}\rangle - \mathrm{i}\theta(t)\langle\{[H, d_\sigma(t)], d^\dagger_\sigma(0)\}\rangle$$

The commutator with the Hamiltonian generates, in general, **other kind of Green's functions** which once again we differentiate. For example for the AI:

$$\left(\omega^+ - \xi_\sigma + \frac{U}{2}\right)\langle\langle d_\sigma, d^\dagger_\sigma\rangle\rangle = 1 + U\langle\langle n_{\bar\sigma} d_\sigma, d^\dagger_\sigma\rangle\rangle + t^*_{\alpha k\sigma}\sum_{\alpha k}\langle\langle c_{\alpha k\sigma}, d^\dagger_\sigma\rangle\rangle$$

where we have used the notation $\langle\langle A, B\rangle\rangle \equiv \int_{-\infty}^{+\infty} dt\, \mathrm{e}^{\mathrm{i}\omega t}(-\mathrm{i})\theta(t)\langle\{A(t), B(0)\}\rangle$

Equation of motion technique (ii)

- In general, for an AM the **number of different kind** of GF that one generates is **infinite** and the system of equations does **NOT** close.

- We introduce a **mean-field approximation** and reduce the problem to an effective single particle problem;

- We develop a **truncation scheme**.

Is there a reliable EoM ?

The truncation scheme must be scalable and respect the symmetries.

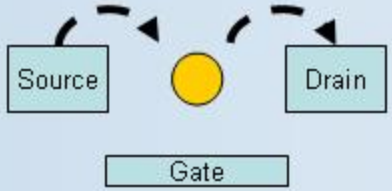
Mean field: Highly scalable since it reduces the problem to an effective single particle problem. It is introducing ***spurious spin polarization*** and treats poorly correlation.

"Cut off " approximation: Still on reasonable scaling level and respects major symmetries.

Wingreen-Meir-Lee: Starts to challenge scalability and ***violates particle-hole symmetry***.

System-bath correlation

Cut-off approximation



$$\left(\omega^+ - \xi_\sigma + \tfrac{U}{2}\right)\langle\langle d_\sigma, d_\sigma^\dagger\rangle\rangle = 1 + U\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + \sum_{\alpha k} t^*_{\alpha k\sigma}\langle\langle c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle$$

$$\left(\omega^+ - \xi_\sigma - \tfrac{U}{2}\right)\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle n_{\bar\sigma}\rangle + \sum_{\alpha k}\left(t^*_{\alpha k\sigma}\langle\langle n_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle + t^*_{\alpha k\bar\sigma}\langle\langle d^\dagger_{\bar\sigma} c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle - t_{\alpha k\bar\sigma}\langle\langle c^\dagger_{\alpha k\bar\sigma} d_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle\right)$$

$$(\omega^+ - \epsilon_{\alpha k\sigma})\langle\langle c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle = t_{\alpha k\sigma}\langle\langle d_\sigma, d_\sigma^\dagger\rangle\rangle$$

$$(\omega^+ - \epsilon_{\alpha k\sigma})\langle\langle n_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle = t_{\alpha k\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + \sum_{\beta k'}\left(t^*_{\beta k'\sigma}\langle\langle d^\dagger_{\bar\sigma} c_{\beta k'\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle - t_{\beta k'\sigma}\langle\langle c^\dagger_{\beta k'\bar\sigma} d_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle\right)$$

$$(\omega^+ - \epsilon_{\alpha k\bar\sigma} + \xi_{\bar\sigma} - \xi_\sigma)\langle\langle d^\dagger_{\bar\sigma} c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle d^\dagger_{\bar\sigma} c_{\alpha k\bar\sigma}\rangle + t_{\alpha k\bar\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle +$$

$$+ \sum_{\beta k'}\left(t^*_{\beta k'\sigma}\langle\langle d^\dagger_{\bar\sigma} c_{\alpha k\bar\sigma} c_{\beta k'\sigma}, d_\sigma^\dagger\rangle\rangle - t_{\beta k'\bar\sigma}\langle\langle c^\dagger_{\beta k'\bar\sigma} c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle\right)$$

$$(\omega^+ + \epsilon_{\alpha k\bar\sigma} - \xi_{\bar\sigma} - \xi_\sigma)\langle\langle c^\dagger_{\alpha k\bar\sigma} d_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle c^\dagger_{\alpha k\bar\sigma} d_{\bar\sigma}\rangle - t^*_{\alpha k\bar\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle +$$

$$+ \sum_{\beta k'}\left(t^*_{\beta k'\bar\sigma}\langle\langle c^\dagger_{\alpha k\bar\sigma} c_{\beta k'\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + t^*_{\beta k'\sigma}\langle\langle c^\dagger_{\alpha k\bar\sigma} d_{\bar\sigma} c_{\beta k'\sigma}, d_\sigma^\dagger\rangle\rangle\right)$$

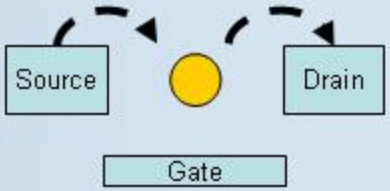
Summarizing, the cut-off approximation:

- Neglects Green's functions containing two or more operators of the leads
- Replaces the effect of the leads with a constant damping:

$$\sum_{\alpha k} t^*_{\alpha k\sigma}\langle\langle c_{\alpha k\sigma}\mathcal{O}_{0d}, d_\sigma^\dagger\rangle\rangle \approx -\mathrm{i}\Gamma_\sigma\langle\langle d_\sigma\mathcal{O}_{0d}, d_\sigma^\dagger\rangle\rangle$$

$$\sum_{\alpha k} t_{\alpha k\sigma}\langle\langle c^\dagger_{\alpha k\sigma}\mathcal{O}_{2d}, d_\sigma^\dagger\rangle\rangle \approx -\mathrm{i}\Gamma_\sigma\langle\langle d^\dagger_\sigma\mathcal{O}_{2d}, d_\sigma^\dagger\rangle\rangle$$

Cut-off approximation



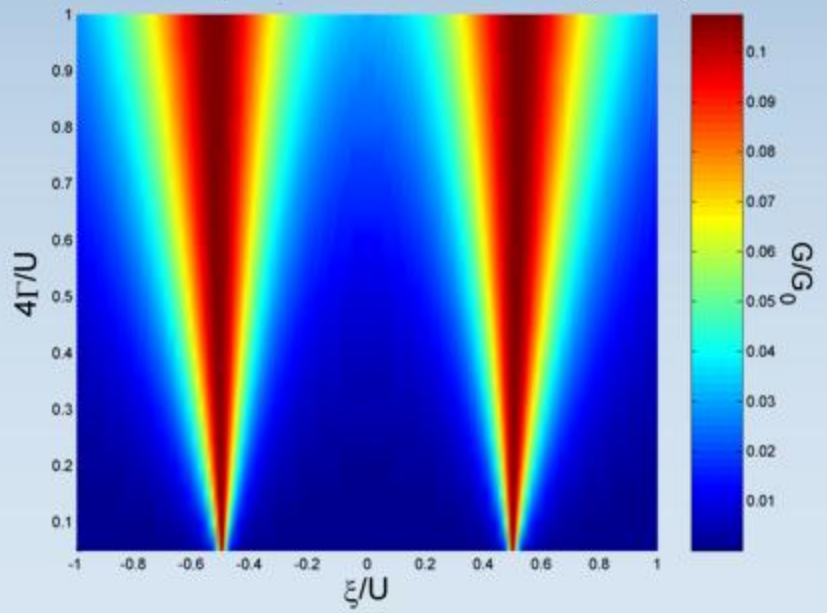
$$\left(\omega^{+}-\xi_{\sigma}+\frac{U}{2}+\mathrm{i}\Gamma_{\sigma}\right)\langle\langle d_{\sigma},d_{\sigma}^{\dagger}\rangle\rangle=1+U\langle\langle n_{\bar{\sigma}}d_{\sigma},d_{\sigma}^{\dagger}\rangle\rangle$$

$$\left(\omega^{+}-\xi_{\sigma}-\frac{U}{2}+\mathrm{i}\Gamma_{\sigma}\right)\langle\langle n_{\bar{\sigma}}d_{\sigma},d_{\sigma}^{\dagger}\rangle\rangle=\langle n_{\bar{\sigma}}\rangle$$

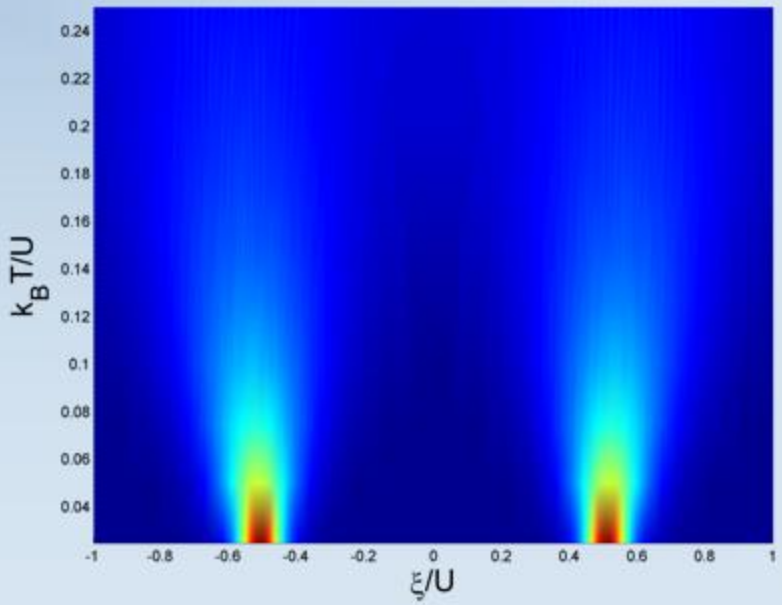
$$\Gamma_{\sigma}=\Gamma_{L\sigma}+\Gamma_{R\sigma}$$

A single broadening

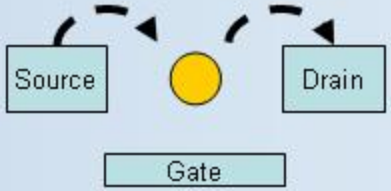
Low temperature conductance ($T < \Gamma$)

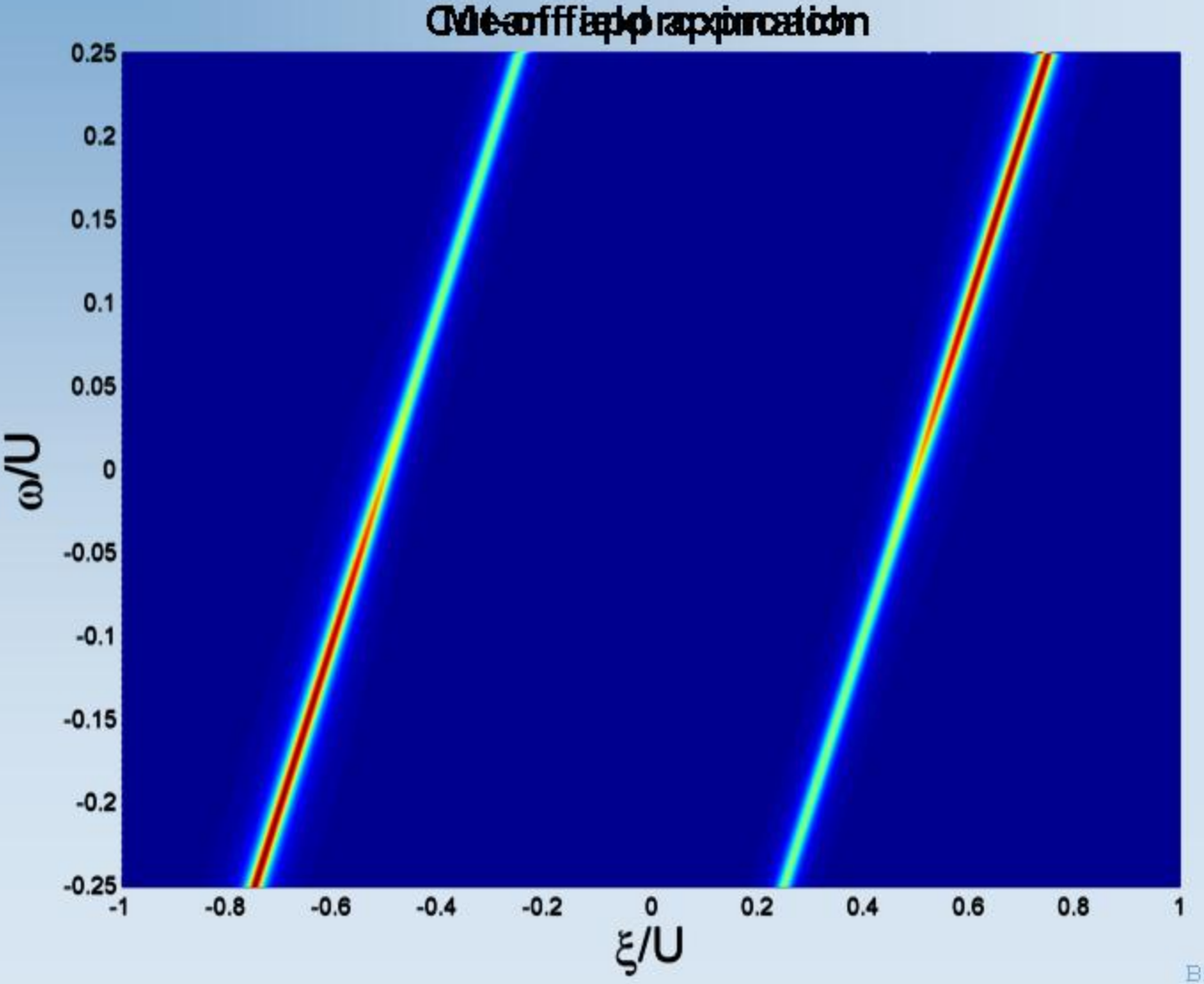


Temperature effects ($T > T_k$)

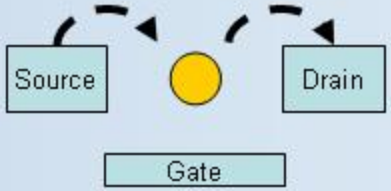


Spectral functions





Wingreen-Meir-Lee '91*



$$\left(\omega^+ - \xi_\sigma + \tfrac{U}{2}\right)\langle\langle d_\sigma, d_\sigma^\dagger\rangle\rangle = 1 + U\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + \sum_{\alpha k} t^*_{\alpha k\sigma}\langle\langle c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle$$

$$\left(\omega^+ - \xi_\sigma - \tfrac{U}{2}\right)\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle n_{\bar\sigma}\rangle + \sum_{\alpha k}\left(t^*_{\alpha k\sigma}\langle\langle n_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle + t^*_{\alpha k\bar\sigma}\langle\langle d_{\bar\sigma}^\dagger c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle - t_{\alpha k\bar\sigma}\langle\langle c_{\alpha k\bar\sigma}^\dagger d_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle\right)$$

$$(\omega^+ - \epsilon_{\alpha k\sigma})\langle\langle c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle = t_{\alpha k\sigma}\langle\langle d_\sigma, d_\sigma^\dagger\rangle\rangle$$

$$(\omega^+ - \epsilon_{\alpha k\sigma})\langle\langle n_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle = t_{\alpha k\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + \sum_{\beta k'}\left(t^*_{\beta k'\sigma}\langle\langle d_{\bar\sigma}^\dagger c_{\beta k'\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle - t_{\beta k'\bar\sigma}\langle\langle c_{\beta k'\bar\sigma}^\dagger d_{\bar\sigma} c_{\alpha k\sigma}, d_\sigma^\dagger\rangle\rangle\right)$$

$$(\omega^+ - \epsilon_{\alpha k\bar\sigma} + \xi_{\bar\sigma} - \xi_\sigma)\langle\langle d_{\bar\sigma}^\dagger c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle d_{\bar\sigma}^\dagger c_{\alpha k\bar\sigma}\rangle + t_{\alpha k\bar\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle +$$

$$+ \sum_{\beta k'}\left(t^*_{\beta k'\sigma}\langle\langle d_{\bar\sigma}^\dagger c_{\alpha k\bar\sigma} c_{\beta k'\sigma}, d_\sigma^\dagger\rangle\rangle - t_{\beta k'\bar\sigma}\langle\langle c_{\beta k'\bar\sigma}^\dagger c_{\alpha k\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle\right)$$

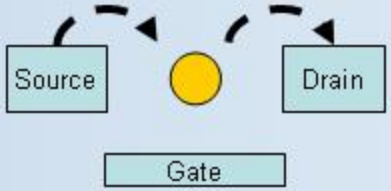
$$(\omega^+ + \epsilon_{\alpha k\bar\sigma} - \xi_{\bar\sigma} - \xi_\sigma)\langle\langle c_{\alpha k\bar\sigma}^\dagger d_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle = \langle c_{\alpha k\bar\sigma}^\dagger d_{\bar\sigma}\rangle - t^*_{\alpha k\bar\sigma}\langle\langle n_{\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle +$$

$$+ \sum_{\beta k'}\left(t^*_{\beta k'\bar\sigma}\langle\langle c_{\alpha k\bar\sigma}^\dagger c_{\beta k'\bar\sigma} d_\sigma, d_\sigma^\dagger\rangle\rangle + t^*_{\beta k'\sigma}\langle\langle c_{\alpha k\bar\sigma}^\dagger d_{\bar\sigma} c_{\beta k'\sigma}, d_\sigma^\dagger\rangle\rangle\right)$$

$$\vdots$$

*PRL **66** 3048 (1991) – 223 citations to now: most of them PRL and PRB

Essence of the WML



The essence of the WML approximation consists in 2 steps

- **Neglect** **equal time** correlators that do **NOT conserve** at the same time the particle number in the lead and impurity separately. (Kondo correlators)

$$\langle d_\sigma^\dagger c_{\alpha k\sigma}\rangle = 0$$

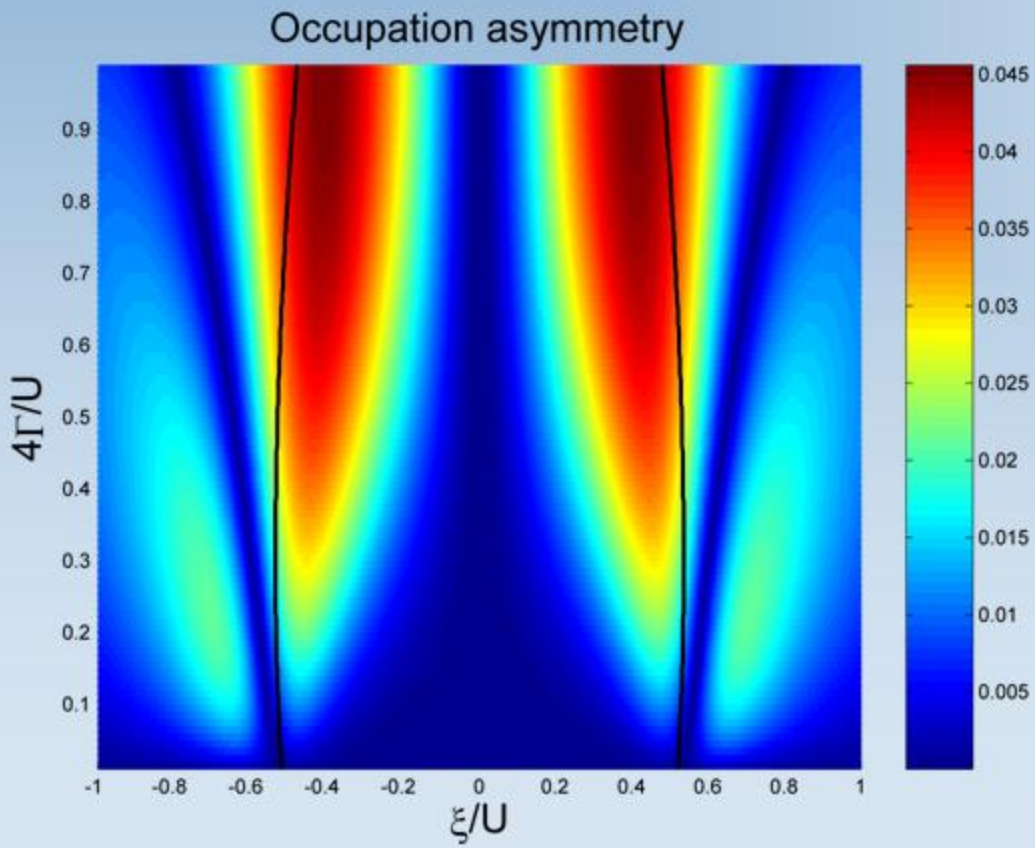
- **Factorize** all Green's functions containing **2 operators of the leads** as:

$$\langle\langle c_{\alpha k\sigma}^\dagger c_{\beta k'\sigma'} d_\sigma, d_\sigma^\dagger\rangle\rangle = \delta_{\alpha\beta}\delta_{kk'}\delta_{\sigma\sigma'} n_F(\epsilon_{\alpha k\sigma})\langle\langle d_\sigma, d_\sigma^\dagger\rangle\rangle$$

Symmetry violation of the WML

We demonstrate (see poster for details) analytically **particle hole symmetry violation**. Namely:

$$\langle n(\xi)\rangle \neq 1 - \langle n(-\xi)\rangle$$

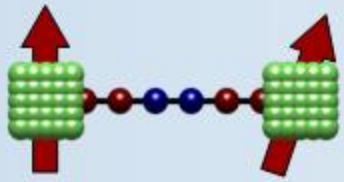


$$\langle n(\xi)\rangle \neq 1 - \langle n(-\xi)\rangle$$

$$\int \frac{d\omega}{2\pi} A(\omega;\xi) \neq 1$$

$$G(\xi) \neq G(-\xi)$$

The conductance formula for AM

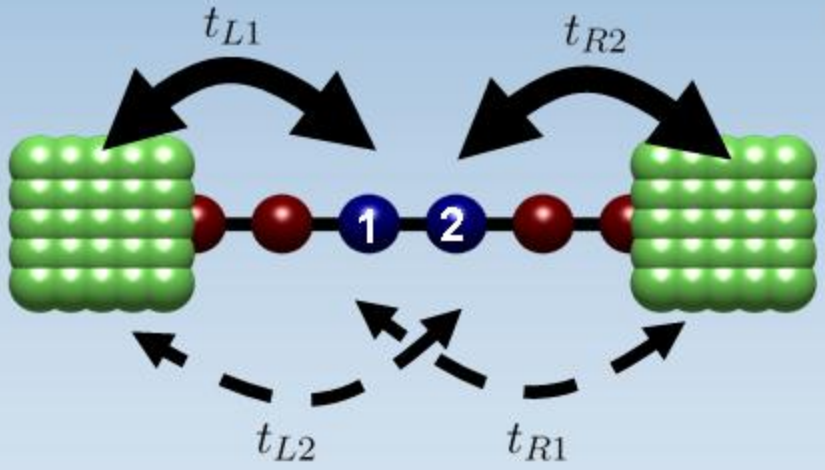


The conductance formula for AI is extendable to AM for proportional coupling

$$\mathbf{\Gamma}_{L\sigma}(\omega) = \lambda \mathbf{\Gamma}_{R\sigma}(\omega)$$

typically **violated** in Anderson Molecules even if they are symmetrically coupled:

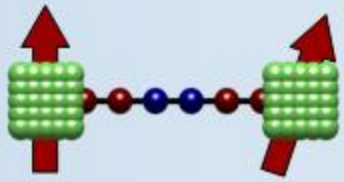
$$[\Gamma_{\alpha\sigma}(\omega)]_{ij} = 2\pi \sum_{k\in\alpha} t^*_{\alpha k\sigma i} t_{\alpha k\sigma j} \delta(\omega - \epsilon_{\alpha k\sigma})$$



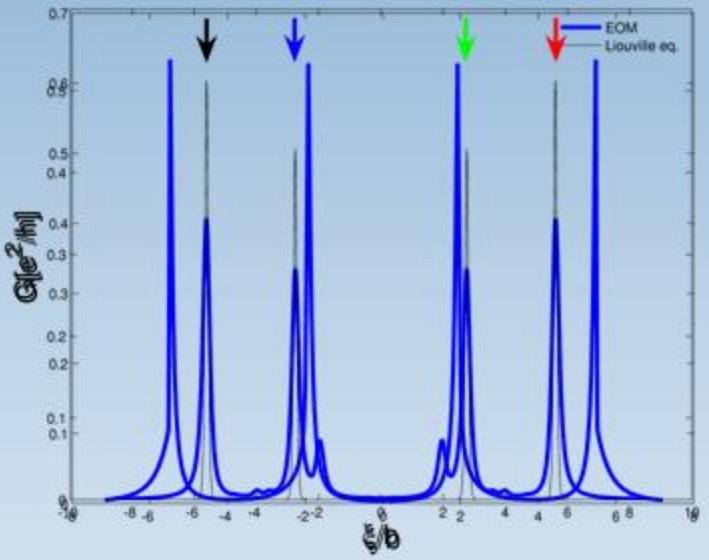
$$\mathbf{\Gamma}_L \approx \begin{pmatrix} \Gamma_L & 0 \\ 0 & 0 \end{pmatrix} \qquad \mathbf{\Gamma}_R \approx \begin{pmatrix} 0 & 0 \\ 0 & \Gamma_R \end{pmatrix}$$

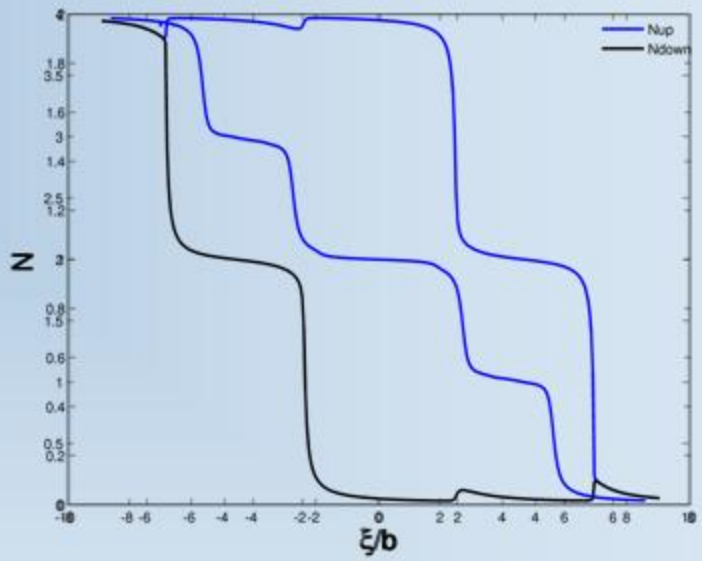
Small-intermediate coupling: consistently with the approximation scheme adopted for the calculation of the molecule spectral function.

Weak vs. intermediate coupling

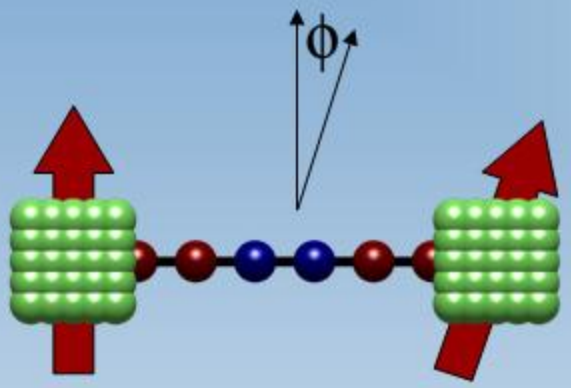


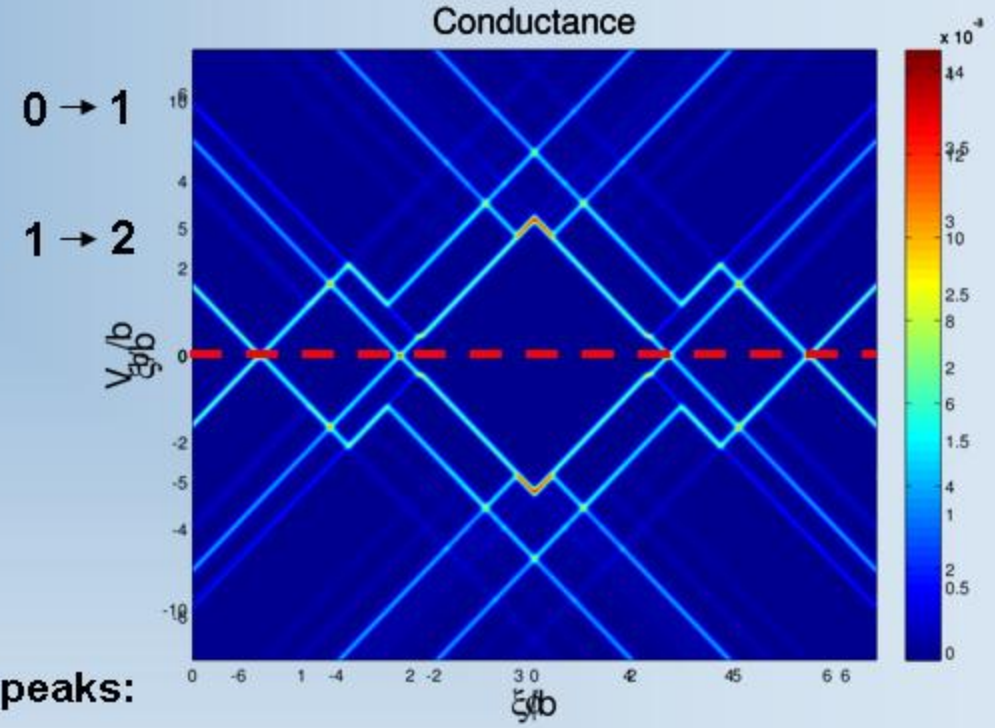
Cut off approximation





Transport with polarized leads



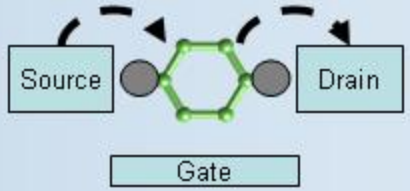


Analytical solution for conductance peaks:

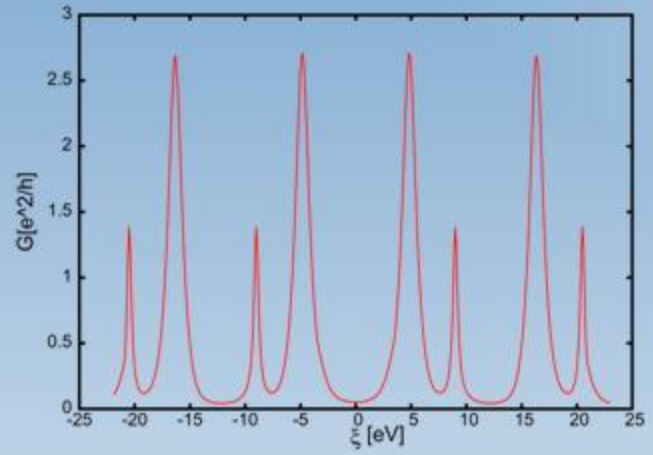
$$I_{0\to 1}(\Theta) = \frac{\Gamma}{2} e^2 \beta \left|\langle 1g|d^\dagger|0\rangle\right|^2 \left|\frac{f(\mu_1)f(-\mu_1)}{f(-\mu_1)-2}\right| \left(1 - \frac{P^2 sin^2(\frac{\Theta}{2})}{1 + A_{01} cos^2(\frac{\Theta}{2})}\right) V_{bias}$$

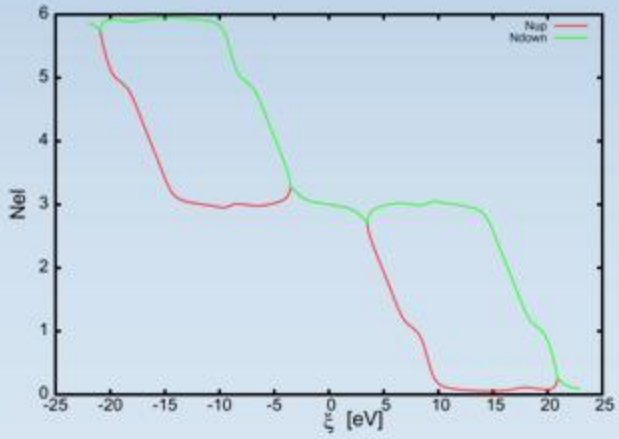
$$I_{1\to 2}(\Theta) = \frac{\Gamma}{2} e^2 \beta \left|\langle 2g|d^\dagger|1g\rangle\right|^2 \left|\frac{f(\mu_2)f(-\mu_2)}{f(-\mu_2)+1}\right| \left(1 - \frac{P^2 sin^2(\frac{\Theta}{2})}{1 + A_{12} cos^2(\frac{\Theta}{2})}\right) V_{bias}$$

Benzene

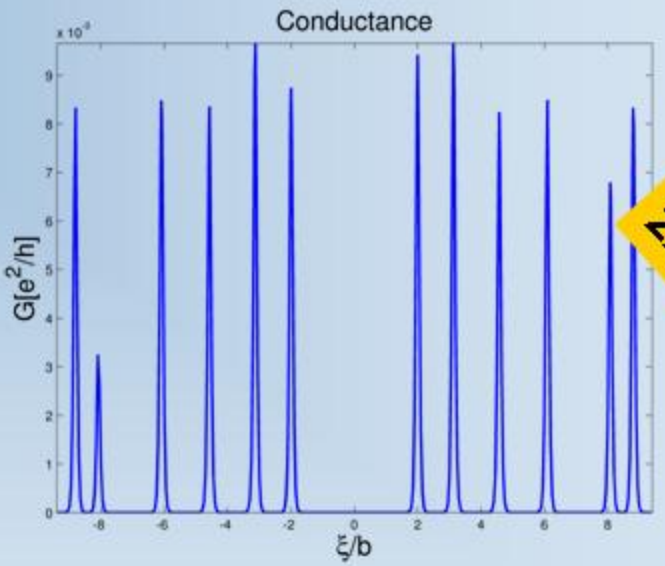


Mean-Field approach





Weak coupling



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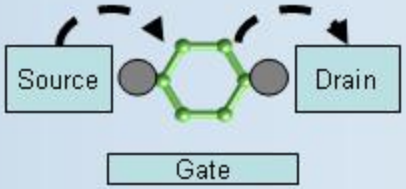
12 peaks corresponding to the **exact** Bohr frequencies

Symmetry of Many-body Eigenstates (i)



- The many body Fock space of benzene has dimension:

$$4^6 = 4096$$

- We exploit the **D_{6h} symmetry** of the system in order to separate the Hamiltonian in diagonal blocks with different symmetry and simplify the diagonalization procedure.

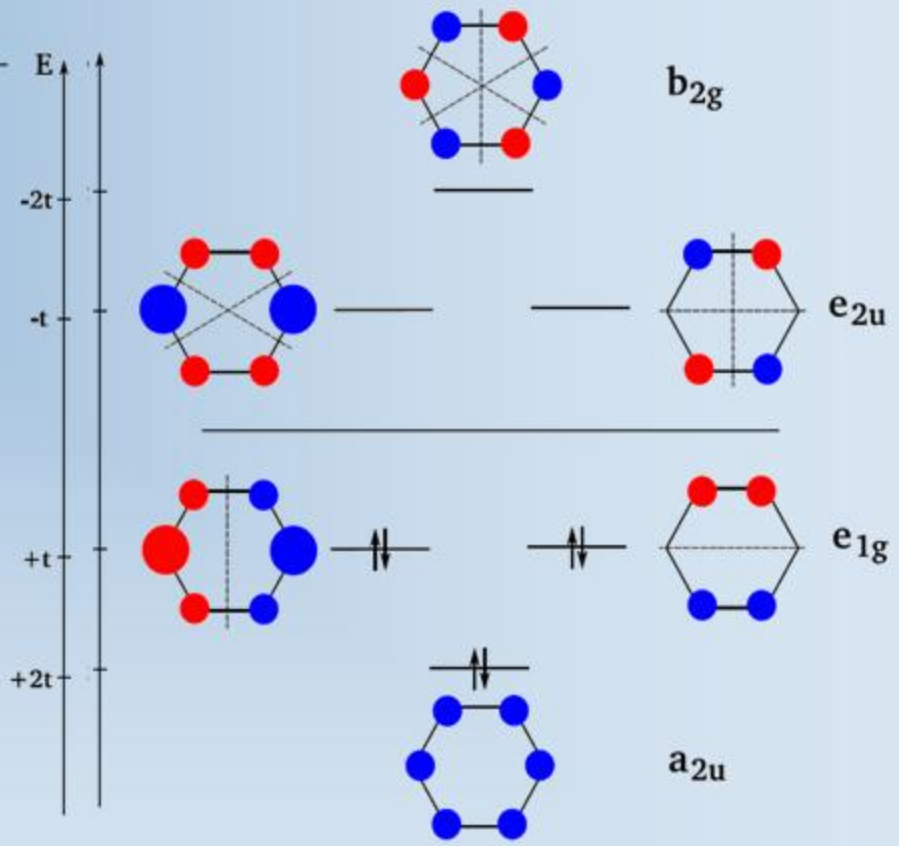
- Eventually we can associate a particular symmetry to **each** eigenstate.

- The symmetry of the ground state in the many-particle description is **not** the symmetry of the corresponding HOMO.

See poster

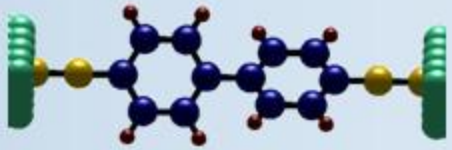
Symmetry of Many-body Eigenstates (ii)

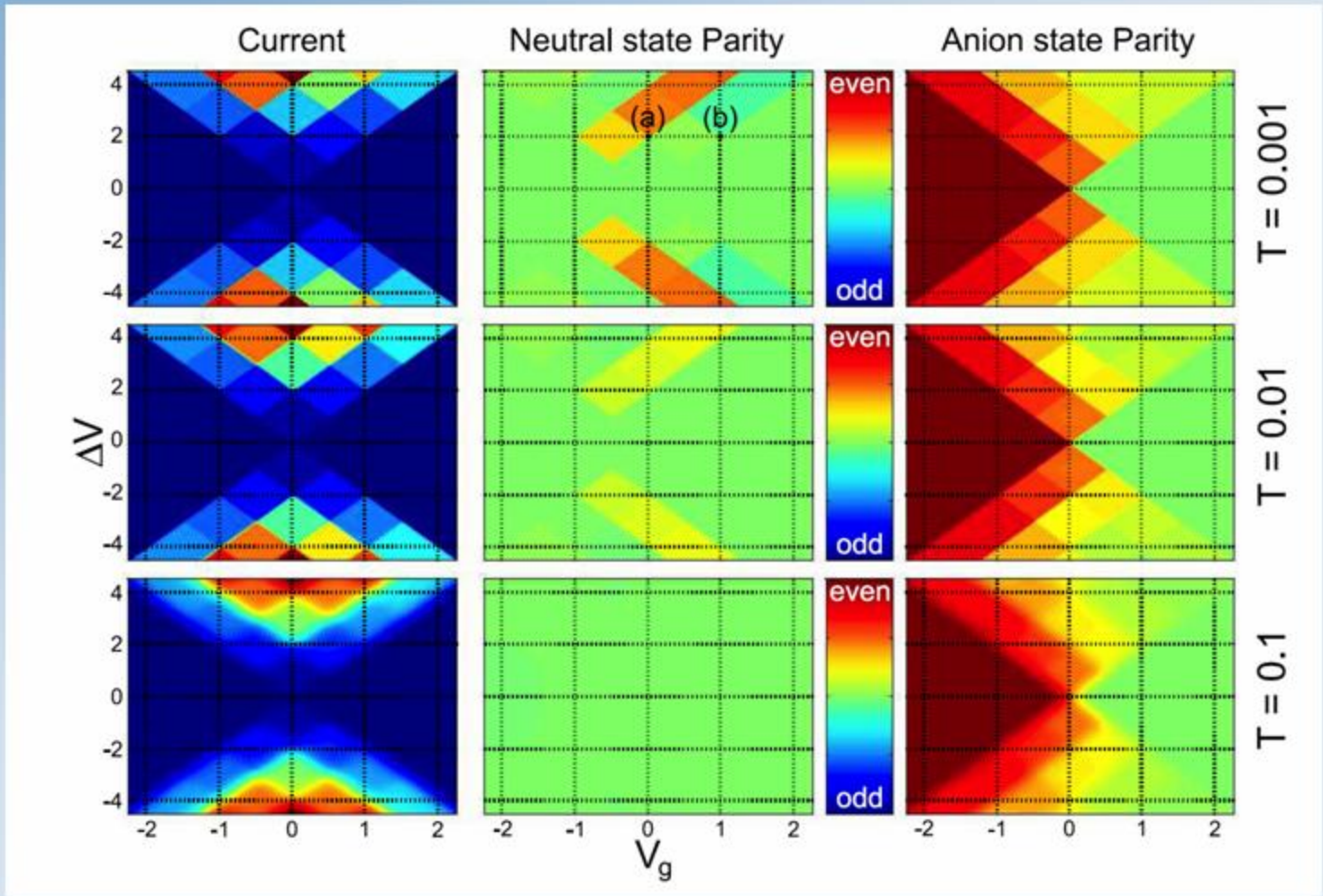
# particles	Symmetry of the ground state
12	A_{1g}
11	B_{2g}
10	A_{1g}
9	E_{2u}
8	A_{2g}
7	E_{2u}
6	A_{1g}
5	E_{1g}
4	A_{2g}
3	E_{1g}
2	A_{1g}
1	A_{2u}



Useful for the identification of states relevant in transport.

Biphenyl





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Outlook and Conclusions

- We describe transport through **interacting** molecular junctions in **weak to intermediate coupling** to the leads;

- We study systems with **growing level of complexity**;

- We use the **Anderson impurity Model** to test system the Equation of Motion technique with a range of different approximations and identify a **reliable truncation scheme;**

- In the **Pariser-Parr-Pople dimer** we studied the effect of polarized leads on the In the weak coupling regime we have studied the angular dependence

- We analyze transport characteristics in **Benzene** in mean-field approximation and in weak coupling to the leads.

- We solve the interacting PPP hamiltonian of benzene by means of **group theoretical methods**. The classification of the states with respect of their symmetries allows us a more efficient choice of the ones relevant for future transport calculations.