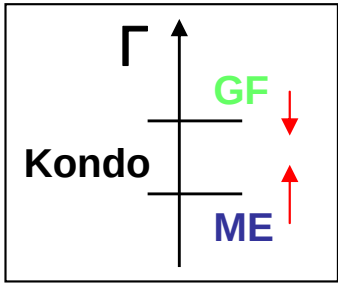
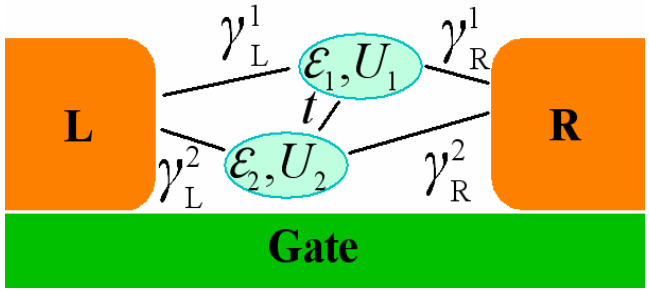
Molecular junctions in the Coulomb blockade regime

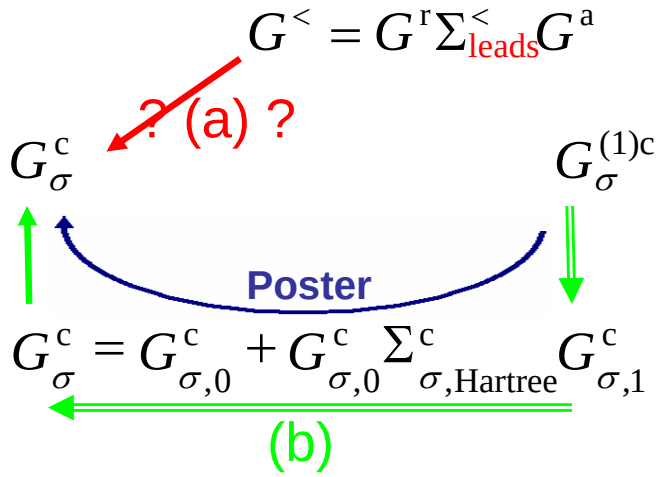
Bo Song, Dmitry A. Ryndyk, and Gianaurelio Cuniberti



- **Single and double site junctions in Coulomb blockade regime**

- **System and methods**

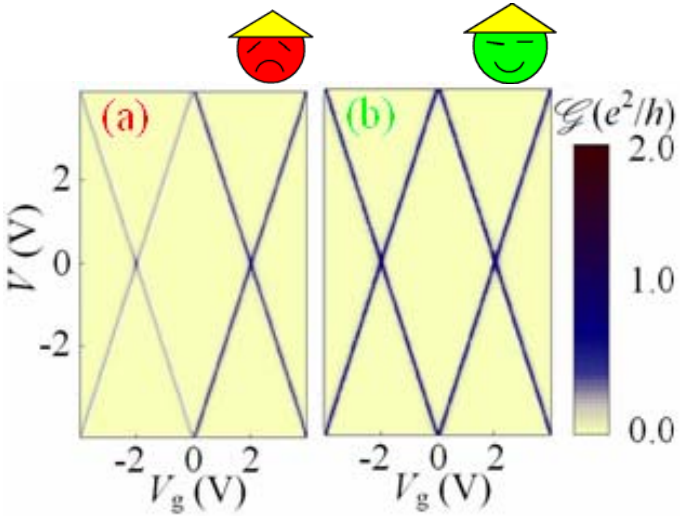


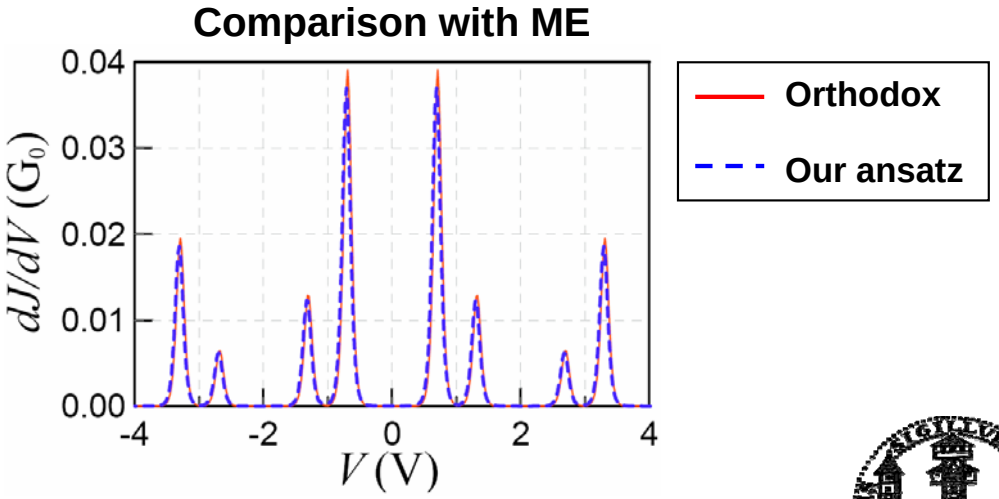


EOM

Dyson

- **Some results**





Molecular junctions in the Coulomb blockade regime: rectification and nesting

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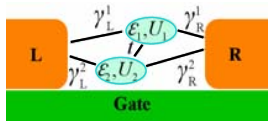
Quantum transport through single molecules is very sensitive to the strength of the molecule-electrode contact. Here, we investigate the behavior of a model molecular junction weakly coupled to external electrodes in the case where charging effects do play an important role (Coulomb blockade regime). As a minimal model, we consider a molecular junction with two spatially separated donor and acceptor sites. Depending on their mutual coupling to the electrodes, the resulting transport observables show well defined features such as rectification effects in the I-V characteristics and nesting of the stability diagrams. To be able to accomplish these results, we have developed a theory which allows to explore the charging regime via the non-equilibrium Green function formalism parallel to the widely used master equation technique. Our results, beyond their experimental relevance, offer a transparent framework for the systematic and modular inclusion of a richer physical phenomenology.

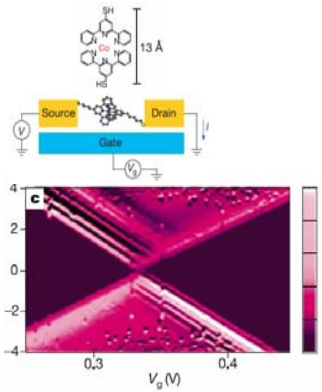
Motivation

Molecular junctions

A double site donor/acceptor molecular junction. The level $\varepsilon_{1,2}$ with charging energies $U_{1,2}$ are connected via t and coupled to the electrodes via the linewidth injection rates γ^{α}_{ν}.

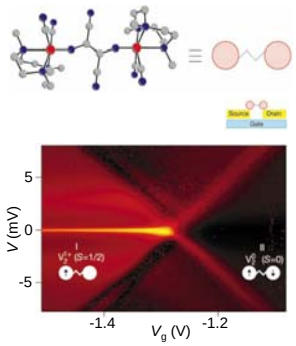


Weak coupling to the leads: Coulomb blockade (CB)



J. Park *et al*. Nature **417**, 722 (2002)

Intermediate coupling to the leads: Kondo effect

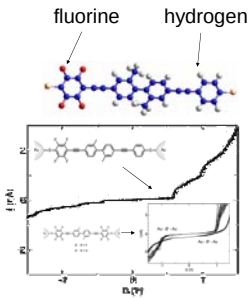


W. Liang *et al*. Nature **417**, 725 (2002)

Molecular diode

diode-like behavior due to different tunneling thresholds for positive and negative bias

- contacted via break junctions
- separation by reduced overlap of π-systems
- different donor/acceptor properties: substitution of hydrogen by fluorine
- control experiments: no rectification for symmetric molecules (H/H) or (F/F)

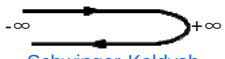


M. Elbing *et al*. Proc. Natl. Acad. Sci. USA **102**, 8815 (2005)

Methodology: EOM for NEGF

Non-equilibrium (Keldysh) Green function (NEGF)

- Along the time contour path, introducing the contour Green function $\check{G}$ and the corresponding self energy $\check{\Sigma}$



Schwinger-Keldysh time contour

- Dyson equation is $\check{G} = \check{G}_0 + \check{G}_0\check{\Sigma}\check{G}$
- By the help of Langreth theorem, the lesser Green function is obtained

$$G^< = G_0^< + G_0^r\Sigma^r G^< + G_0^r\Sigma^< G^a + G_0^<\Sigma^a G^a$$
$$\Rightarrow G^< = (1+G^r\Sigma^r)G_0^<(1+\Sigma^a G^a) + G^r\Sigma^< G^a$$

- If $G_0^<$ can be written in the form $G_0^< = G_0^r\Sigma_0^< G_0^a$, we then obtain

$$G^< = G^r(\Sigma_0^< + \Sigma^<)G^a = G^r\Sigma_{\text{eff}}^< G^a \qquad (1)$$

which is widely used for first-principle and model Hamiltonian calculations.

Introducing NEGF to EOM

Let us consider a double-level (spin-up/spin-down) Anderson impurity model as an example.

- ***Mapping on the retarded GF: equilibrium case***

There are two ways to obtain the retarded Green function:

- EOM approach and a truncation at the CB level
- Dyson-equation approach, the second-order truncation and Hartree-like self energy

$$G^r = G^r_{\sigma,0} + G^r_{\sigma,0}\Sigma^r_{\sigma,\text{Hartree}}G^{(1)r}_{\sigma} \qquad \text{EOM}$$
$$\updownarrow \qquad\qquad \updownarrow$$
$$G^r_{\sigma} = G^r_{\sigma,0} + G^r_{\sigma,0}\Sigma^r_{\sigma,\text{Hartree}}G^r_{\sigma,1} \qquad \text{Dyson}$$

where

$$G^r_{\sigma,0} = \frac{1}{\omega - \varepsilon_\sigma - \Sigma^r_{\sigma,\text{leads}}},\quad G^{(1)r}_{\sigma} = \frac{1}{\omega - \varepsilon_\sigma - U - \Sigma^r_{\sigma,\text{leads}}}$$
$$G^r_{\sigma,1} = G^r_{\sigma,0} + G^r_{\sigma,0}\Sigma^r_{\sigma,\text{Hartree}}G^r_{\sigma,0},\quad \Sigma^r_{\sigma,\text{Hartree}} = \langle n_{\bar{\sigma}}\rangle U$$

The mapping above prompts a way to include further many-particle effects into the Dyson equation, by replacing the *Dyson-first-order* $G^r_{\sigma,1}$ with the *EOM* $G^{(1)r}_{\sigma}$.

- ***Mapping on the contour GF: non-equilibrium case***

Similar to the mapping in the equilibrium case, we perform an *Ansatz* consisting in substituting the *Dyson-first-order* $G^{r/a/<}_{\sigma,1}$ with the *EOM one* $G^{(1)r/a/<}_{\sigma}$ to consider more many-particle correlations

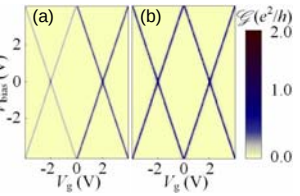
$$\check{G}_{\sigma} \qquad\qquad \check{G}^{(1)}_{\sigma} \qquad \text{EOM}$$
$$\updownarrow \qquad\qquad \downarrow$$
$$\check{G}_{\sigma} = \check{G}_{\sigma,0} + \check{G}_{\sigma,0}\check{\Sigma}_{\sigma,\text{Hartree}}\check{G}_{\sigma,1} \qquad \text{Dyson}$$

Then applying the Langreth theorem, one can obtain the lesser GF working well in the Coulomb blockade regime.

Some results in the CB regime

Single site junction (SSJ)

The stability diagram of a SSJ with
$\varepsilon_\sigma = 2.0\ eV$
$U = 4.0\ eV$
$\Gamma_L = \Gamma_R = 0.05\ eV$

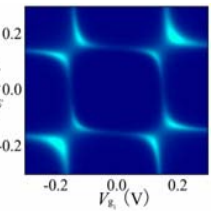


(a) The incorrect result obtained by means of the widely used formula in Eq. (1) with $\Sigma^<_{\text{eff}} = \Sigma^<_{\text{leads}}$ for the lesser GF is not symmetric for the levels ε_σ and $\varepsilon_\sigma + U$.

(b) Results obtained by means of our *Ansatz* shows correctly symmetric for the two levels.

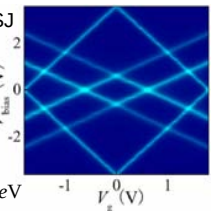
Serial configuration of double site junction (S-DSJ)

The stability diagram of S-DSJ
$\varepsilon_{1,\sigma} = \varepsilon_{2,\sigma} = -0.15\ eV$
$U_1 = U_2 = 0.3\ eV$
$t = 0.05\ eV$
$\gamma^1_L = \gamma^2_R = 0.02\ eV$
$\gamma^2_L = \gamma^1_R = 0.0\ eV$
$V_b = 0.005\ eV$



Parallel configuration of double site junction (P-DSJ)

Nested stability diagram of P-DSJ
$\varepsilon_{1,\sigma} = -1.8\ eV$
$\varepsilon_{2,\sigma} = -0.3\ eV$
$U_1 = 3.6\ eV$
$U_2 = 0.6\ eV$
$t = 0.001\ eV$
$\gamma^1_L = \gamma^1_R = 0.04\ eV$
$\gamma^2_L = \gamma^2_R = 0.05\ eV$

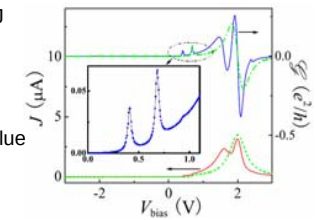


Simulation of molecular diode

Current and conductance vs. bias-voltage of S-DSJ

$\varepsilon_{1,\sigma} = -\varepsilon_{2,\sigma} = 0.5\ eV$ $\quad U_1 = U_2 = 0.3\ eV$
$t = 0.07\ eV$ $\quad \gamma^1_L = \gamma^2_R = 0.03\ eV$
$V_{g2} = -V_{g1} = V_{bias}/4$ $\quad V_R = -V_L = V_{bias}/2$

The red curve represents the current, while the blue the conductance



Conclusions and Outlook

- ✓ Powerful Ansatz for NEGF.
- ✓ Correct stability diagrams for SSJ, S-DSJ and P-DSJ.
- ✓ Agreement with master equation results in the CB regime.
- ✓ Pseudo-peak and a dip for molecular diode, due to charging effects.

- ? Could this approach work in the Kondo regime?
- ? How to introduce vibron-effects to the CB and Kondo regime?
- ? Is it possible to introduce photon-electron interaction?
- ? Ultimate goal: LDA+U+NEGF.

Related paper

Bo Song, Dmitry A. Ryndyk, and Gianaurelio Cunniberti, cond-mat/0611190.