Electron transport through a molecular junction with a multiconfigurational description

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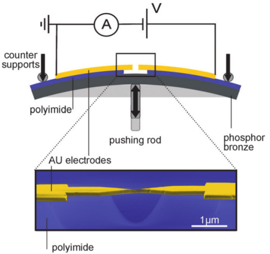
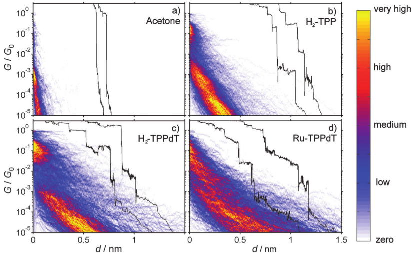
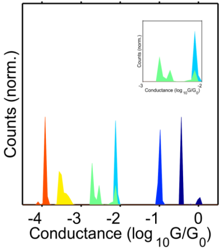
ENS DE LYON

Issues







- Experimental problems
  - Unknown geometry
  - Reproductibility
- Theoretical problems
  - Treat highly correlated systems
  - Coupling with electrodes

Ratner, M. A.; Aviram, A. ***Chem. Phys. Lett.*** 1974, ***29(2)***, **277–283**.

Herrmann, C.; Solomon, G. C.; Ratner, M. A. ***J. Am. Chem. Soc.*** 2010, ***132***, **3682–3684**.

Objectives

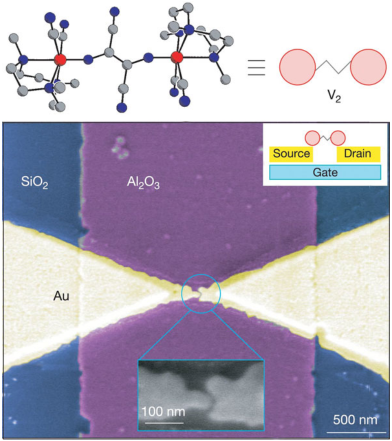
Aim

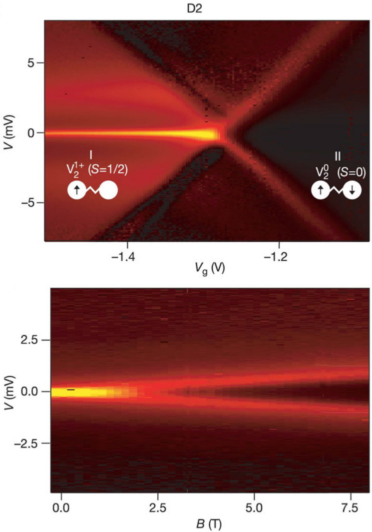
- Take into account an accurate spectroscopy,
- Demonstrate the importance of a **multi**reference description,
- Use a **multi**electronic state description rather than a **mono**electronic one,
- Estimate the influence of **many-body** parameters.

Tools

- Master equation,
- Many-body theory.

"V_2" between two gold electrodes





$$\frac{\partial I}{\partial V}$$

$$\frac{\partial I}{\partial V}$$

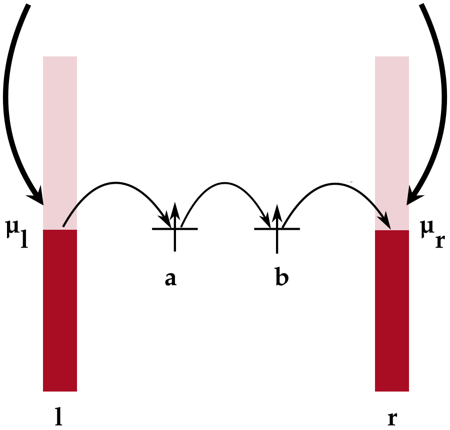
Liang, W. *et al.* ***Nature*** 2002, ***417***, **725-729**

Electronic description

$$\hat{H} = \hat{H}_l + \hat{H}_{fl} + \hat{H}_f + \hat{H}_{fr} + \hat{H}_r$$

tight binding

$$\frac{1}{1+\exp\left(\frac{E-\mu_\alpha}{k_B T}\right)}$$

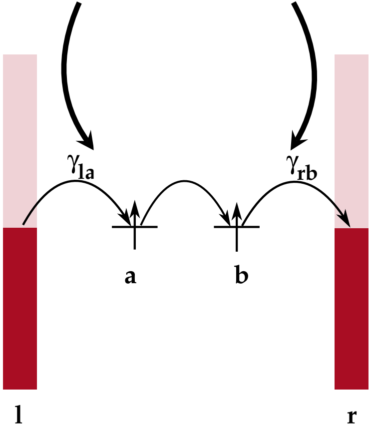


Electronic description

$$\hat{H} = \hat{H}_l + \hat{H}_{fl} + \hat{H}_f + \hat{H}_{fr} + \hat{H}_r$$

weak-coupling

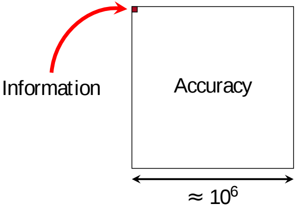
$$\gamma_{f\alpha} \ll k_{\mathrm{B}} T$$

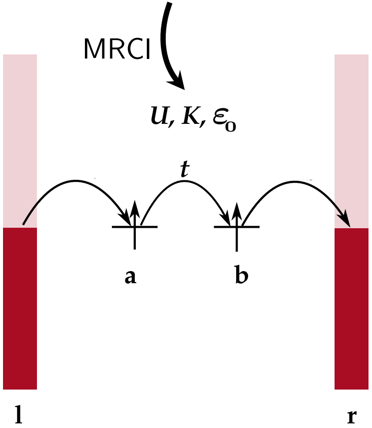


Electronic description

$$\hat{H} = \hat{H}_l + \hat{H}_{fl} + \hat{H}_f + \hat{H}_{fr} + \hat{H}_r$$

effective Hamiltonians





Calzado, C. J. *et al.* *J. Chem. Phys.* 2002, ***116***, **3985**

Vérot, M. *et al.* *Phys. Chem. Chem. Phys.* 2011, ***13***, **6657**

Electronic description

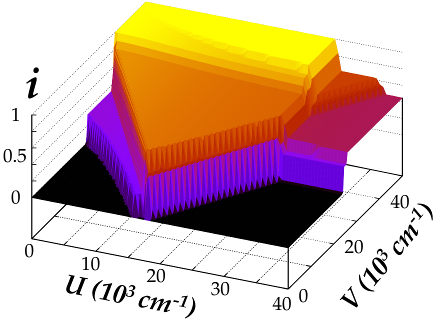
$$\frac{\mathrm{d}n_f}{\mathrm{d}t} = \left(w_{rf} + w_{lf}\right)\left(1 - n_f\right) - n_f\left(w_{fl} + w_{fr}\right) = 0$$

$$w_{\alpha f} = \frac{2\pi}{\hbar Z}\sum_{\Sigma\phi_\Gamma^N} \rho_\alpha\left(E_N - E_{N+1}\right)\left|\langle^{\Sigma'}\phi_{\Gamma'}^{N+1}|\hat{H}_{f\alpha}|^{\Sigma}\phi_\Gamma^N \otimes \phi_\alpha\rangle\right|^2 \exp\left(-\frac{E_{N+1}}{k_B T}\right)$$

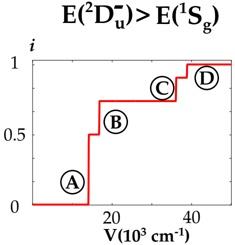
$$i(V) = e\left(w_{lf}\left(1 - n_f\right) - w_{fl} n_f\right)$$

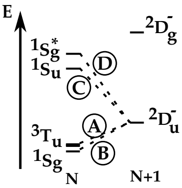
- Sequential tunneling,
- Elastic regime.

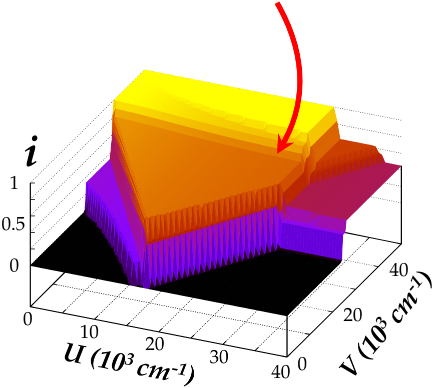
Impact of Coulomb repulsion



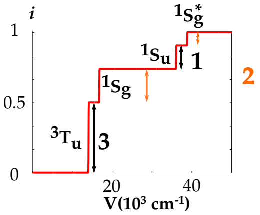
Impact of Coulomb repulsion

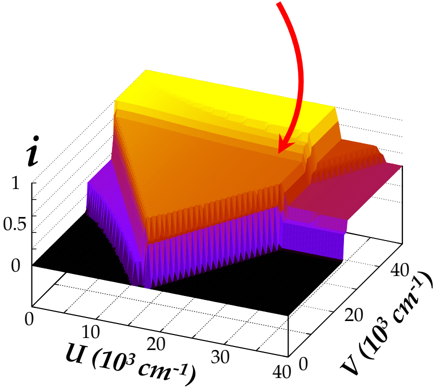






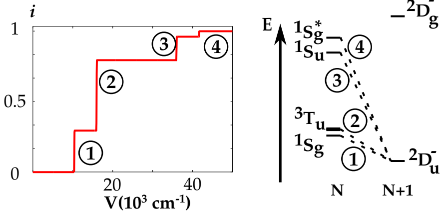
Impact of Coulomb repulsion

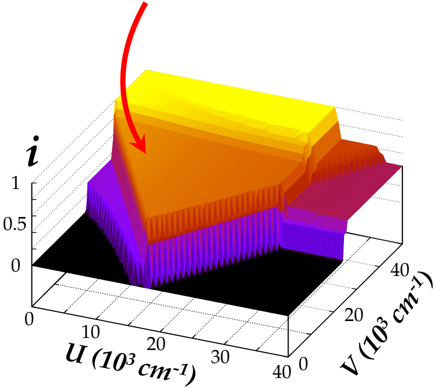




Impact of Coulomb repulsion

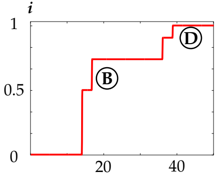
$E(^2D_u^-) < E(^1S_g^-)$

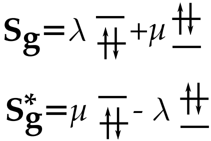




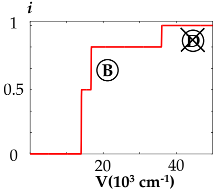
Impact of a multireference description

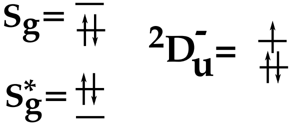
MRCI

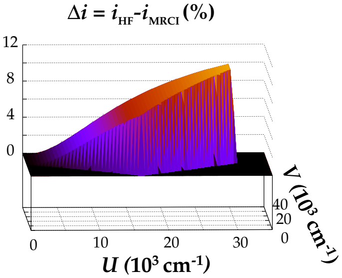


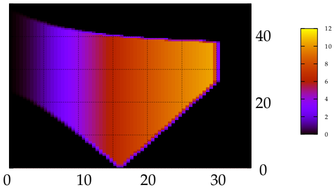


HF









Vérot, M. ; Borshch S. A. ; Robert, V. *Chem. Phys. Lett.* 2012, ***519-520***, 125–129

Conclusion

We showed

- How the I=f(V) curve is affected by a **multi**/**mono**-electronic description
- A strong link between the spectroscopy and the position of the peaks
- The importance of a multiconfigurational approach

We are

- Studying the influence of **external stimuli** (magnetic field, polarization of electrodes)

We plan to

- Study **anisotropy**

Thank you for your attention

Energy levels

^1S_g	$^1S_g^*$	^3T_u	^1S_u
$K + \dfrac{(U - \sqrt{U^2 + 16t^2})}{2}$	$K + \dfrac{(U + \sqrt{U^2 + 16t^2})}{2}$	$-K$	$-K + U$

$^2D_g^+$	$^2D_u^+$	$^2D_u^-$	$^2D_g^-$
$-\varepsilon_0 + t$	$-\varepsilon_0 - t$	$\varepsilon_0 + U + t - K$	$\varepsilon_0 + U - t - K$