Quantum Master Equation for the study of Electronic transport in organic systems

Pedro D Manrique*ϑϕ, **Rafael Gutierrez**ϑ, **Gotthard Seifert**ϕ **and G. Cuniberti**ϑ

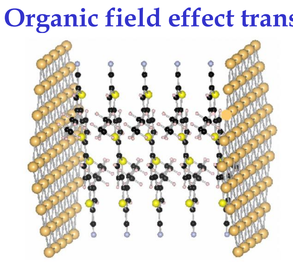
ϑ Institute for Materials Science and Max Bergmann Center of Biomaterials,
Dresden University of Technology, D-01062 Dresden, Germany.
ϕ Institute of Physical Chemistry and Electrochemistry,
Dresden University of Technology, D-01314 Dresden, Germany.

(*) pmanrique@nano.tu-dresden.de

We derive a non Markovian master equation for electronic transport through organic systems including the interaction of external bosonic degrees of freedom. Within this formalism we calculate the expression for the time dependent current (TDC) as the variation of the particle number of the electrodes (fermionic baths) at arbitrary temperatures. Some partial results for the TDC are shown for different values of boson coupling, in which we found significant changes at very short time evolution. In addition, for organic systems we calculate the total energy for different geometric configurations using density functional tight binding (DFTB) including the dispersion energy correction and contrast the results with MP2 methods finding a very good agreement.

MOTIVATION

Organic field effect transistors(OFETS)[1] → Develop low-cost storage and microelectronic devices.
→ High structural order.
→ High charge carrier mobilities and low resistive losses.



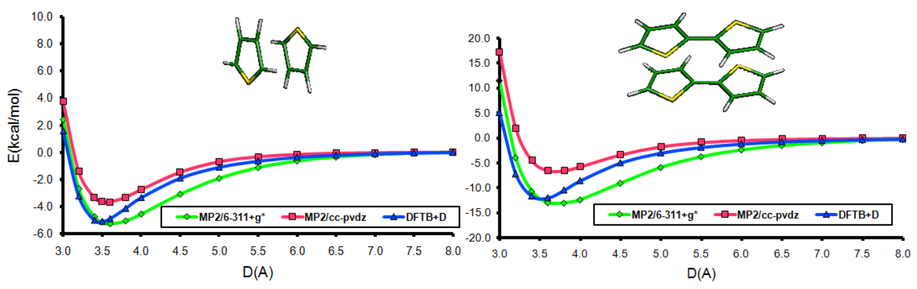
Oligothiophenes and their derivatives

→ Can form well-ordered stacks with a good π-orbital overlap

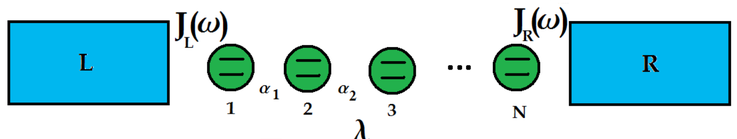
COMPUTATIONAL TOOLS [2]

DFTB+D (Self-consistent charge with the inclusion of London dispersion forces) is an approximate density-functional method, holds nearly the same accuracy but much lower computational cost, allowing investigation of the electronic structure of large systems which cannot be exploited with conventional *ab-initio* methods.

DFTB+D Accuracy (Geometry optimization)



HAMILTONIAN MODEL



Chain

$$H = \sum_i^N \omega_i d_i^\dagger d_i + \sum_i^{N-1}\left(\alpha_i d_i^\dagger d_{i+1} + \alpha_i^* d_i d_{i+1}^\dagger\right) + \sum_{jL(R)} \nu_{jL(R)} c_{jL(R)}^\dagger c_{jL(R)} + \sum_j \left(V_{jL(R)} c_{jL(R)}^\dagger d_{1(N)} + V_{jL(R)}^* c_{jL(R)}^\dagger d_{1(N)}\right)$$

Electrodes

$$+\ \Omega B^\dagger B + \sum_i^{N-1} \lambda (d_i^\dagger d_i - d_{i+1}^\dagger d_{i+1})(B + B^\dagger)$$

Phonon mode

$$\hat{H}_I(t) = e^{iH_0 t} H_I e^{-iH_0 t}$$ → **Interaction picture transformation**

Polaron transformation [3] →

$$\hat{\mathcal{H}}(t) = \hat{U} H_I(t) \hat{U}^{-1}$$
$$\hat{U} = e^{-\frac{\lambda}{\Omega}(B^\dagger - B)\sum_i^{N-1}\left(d_i^\dagger d_i - d_{i+1}^\dagger d_{i+1}\right)}$$

Renormalized coupling

$$\hat{\mathcal{H}}_I(t) = \sum_i^{N-1} \alpha_i \tilde{d}_i^\dagger(t)\tilde{d}_{i+1}(t) + \sum_j V_{jL(R)} c_{jL(R)}^\dagger(t)\tilde{d}_{1(N)}(t) + h.c \qquad \tilde{d}_n(t) = d_n e^{i\omega_n t} e^{-\frac{\lambda}{\Omega}\left(B^\dagger e^{i\Omega t} - B e^{-i\Omega t}\right)}$$

TIME CONVOLUTIONLESS FORMALISM

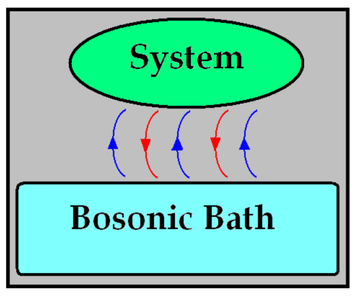
TCL generator [4]

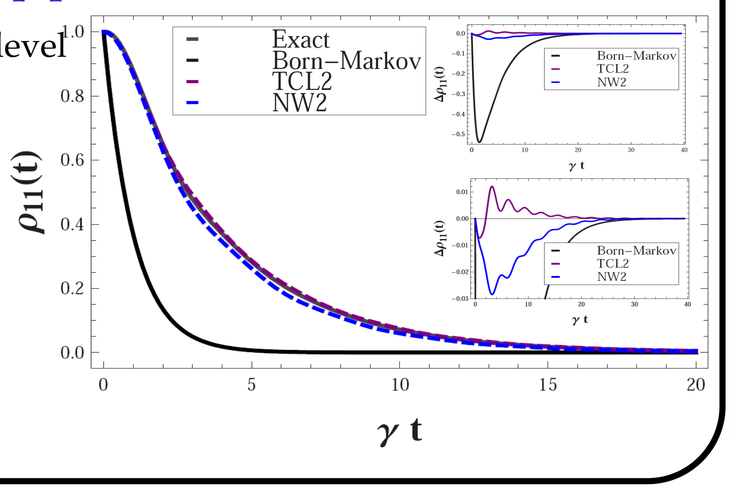
$$\frac{d}{dt}\rho_s(t) = \mathcal{K}(t)\rho_s(t) \qquad \mathcal{K}(t) = \alpha \sum_{n=0}^{\infty} \mathcal{PL}(t)\left[\Sigma(t)\right]^n \mathcal{P}$$

$$\Sigma(t) = \alpha \int_{t_0}^{t} ds \mathcal{G}(t,s)\mathcal{QL}(s)\mathcal{P}G(t,s)$$

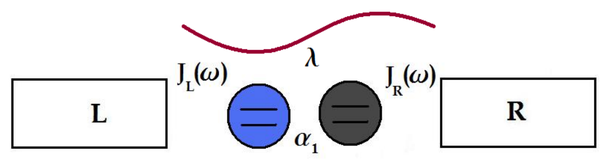
Example of accuracy [5]

Spontaneous decay of a two level system in a bosonic bath



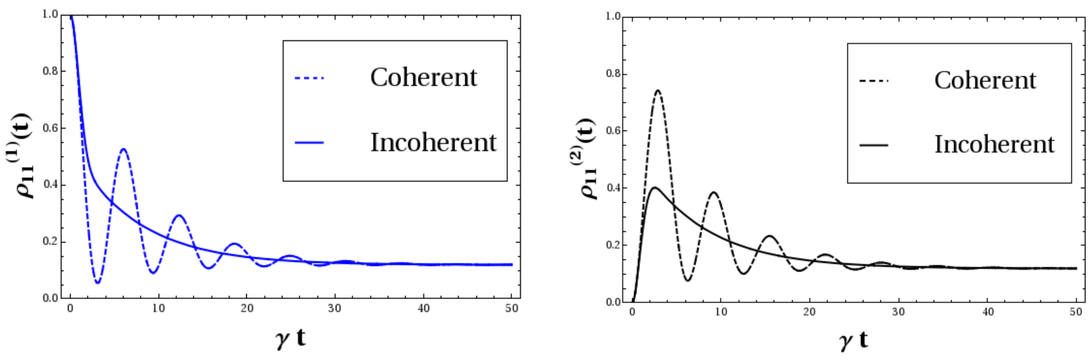


RESULTS



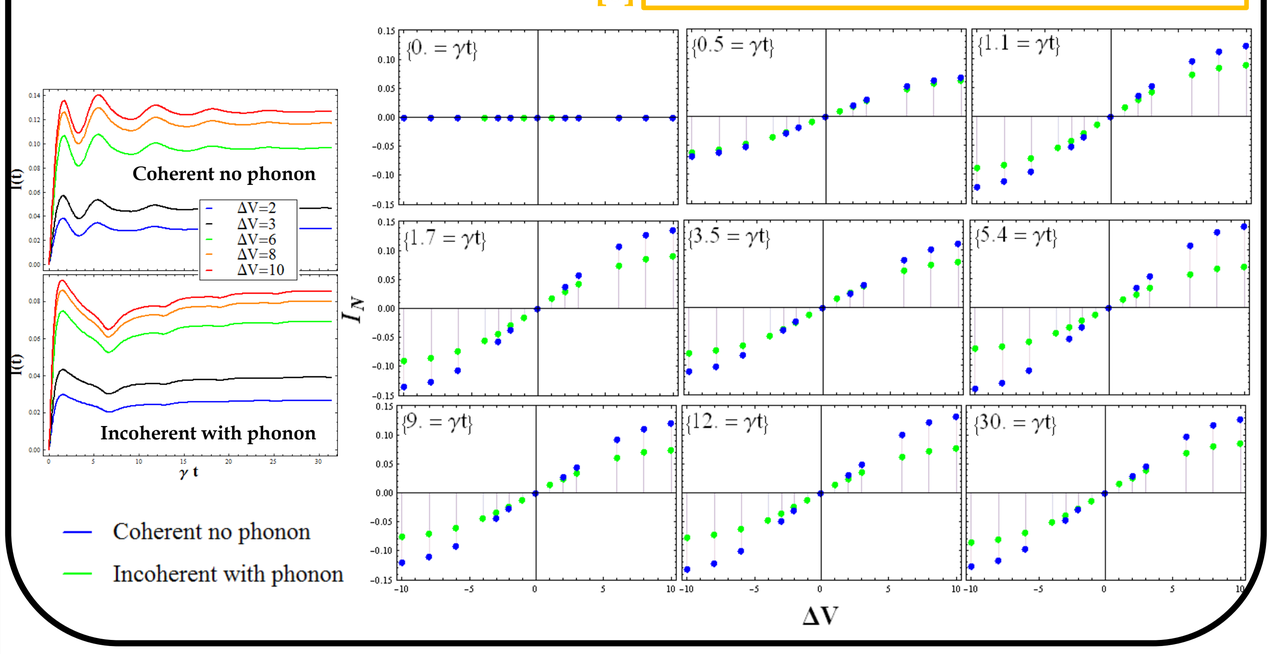
Dimer coupled with electrodes and a single phonon mode

Populations



Time dependent Current

[6] $$I_{L(R)}(t) = -e\langle \dot{N}_{L(R)} \rangle = -\frac{ie}{\hbar}\langle \left[\hat{\mathcal{H}}, N_{L(R)}\right] \rangle$$



CONCLUSIONS AND PERSPECTIVES

- ✓ Complete model for electronic transport in the density matrix formalism.
- ✓ Tested time dependent current expression for coherent and incoherent transport.
- ✓ Reduction in the transport properties in the incoherent limit
- ➢ Molecular dynamics simulations for velocities autocorrelation function in stacked Thiophene molecules.
- ➢ Parameter file (transfer integrals and on-site energies) calculation using DFTB+D.

REFERENCES

[1] K. Morawetz, S. Gemming, R. Luschtinetz, L.M Eng, G. Seifert, and A. Kenfack, New J. Phys. **10** (2008) 103014
[2] A. Oliveira, G. Seifert, T. Heine, H. Duarte, J. Braz. Chem. Soc. Vol 20, No 7, 1193- 1205, (2009)
[3] A. Nitzan, *Chemical Dynamics in Condensed Phases*, Oxford University Press, New York 2006
[4] H. P. Breuer and F. Petruccione. *The Theory of Open Quantum Systems.* Oxford University Press, 2006.
[5] Pedro D Manrique, F.Rodríguez. *Estudio de termalización no Markoviana en sistemas de qubits.* Master Thesis. Univesidad de los Andes. Bogota, Colombia (2009)
[6] A. Jauho, N. Wingreen, Y. Meir. Phys. Rev. B. **50,** 5528 (1994)