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Kinetic Approach to Quantum Transport

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A kinetic approach to quantum transport

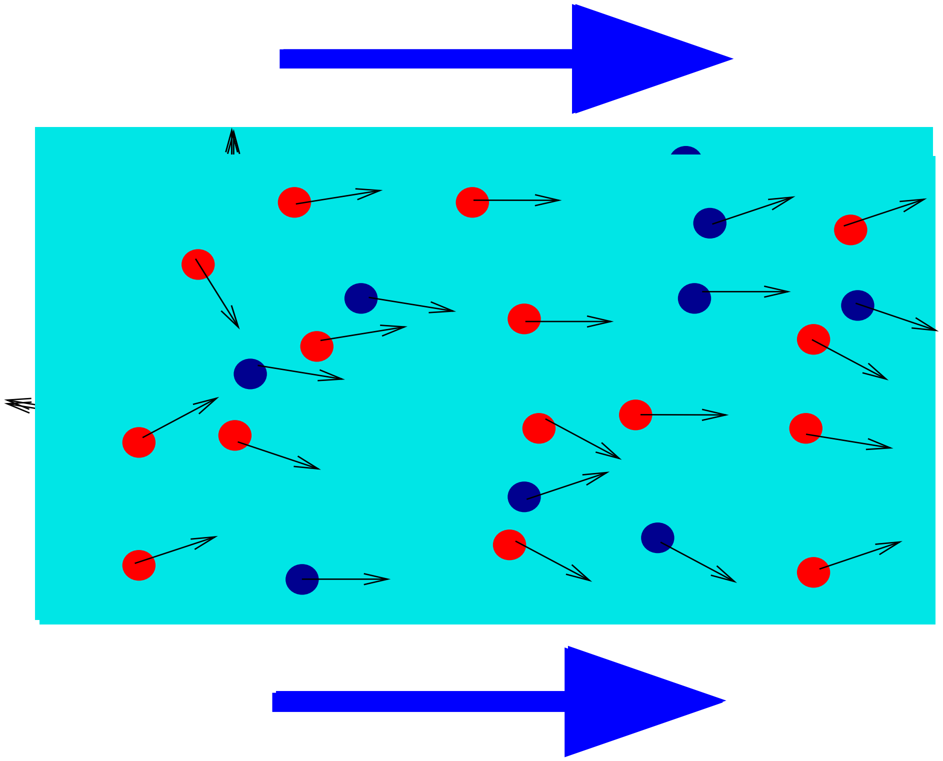
Ralph Gebauer

- The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste
- INFM DEMOCRITOS National Simulation Center, Trieste

Overview

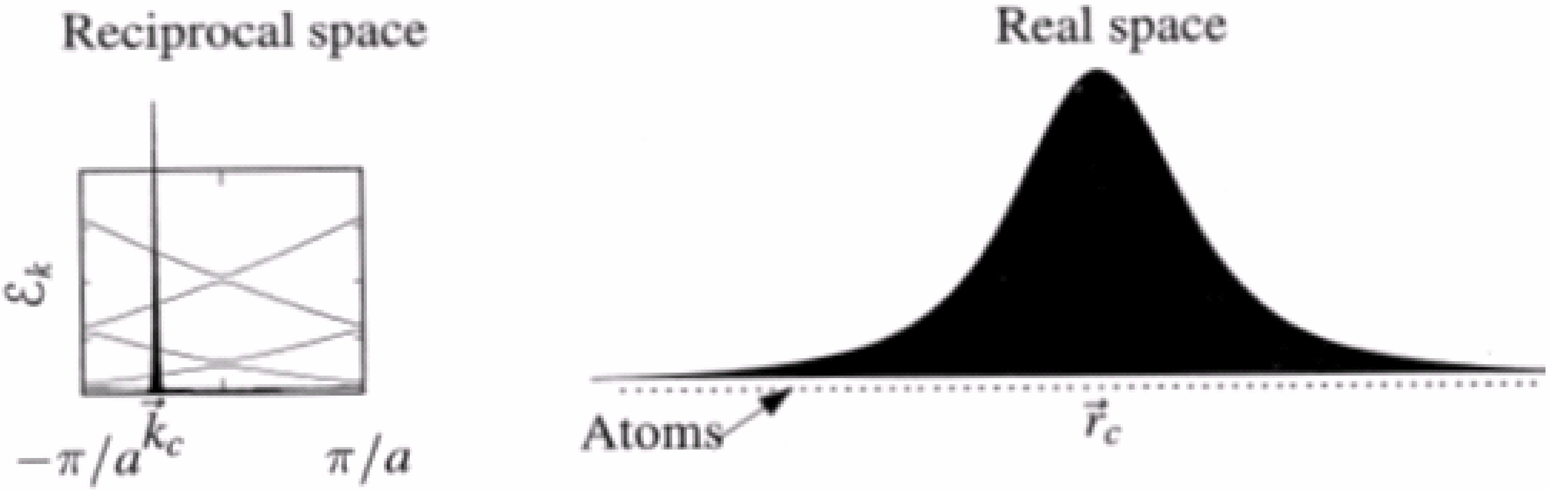
- What is a kinetic model?
  (look at classical and semiclassical models)
- Which are the key ingredients?
- Density matrices, master equations, coherence, etc.
- Develop the formalism
- How can we use all this?
- Look in detail at an example

Transport properties from classical molecular dynamics



$$m_i \ddot{\mathbf{x}}_i + \gamma \dot{\mathbf{x}}_i = \mathbf{F}_i^{int} + \mathbf{F}_i^{ext}$$

Transport properties from semi-classical models



Example of a wavepacket:

$$W_{\mathbf{r}_c,\mathbf{k}_c} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} w(\mathbf{k},\mathbf{k}_c)\; e^{-i\mathbf{k}\cdot\mathbf{r}_c}\; \psi_{\mathbf{k}}(\mathbf{r})$$

Equations of motion for a wavepacket

- Dynamics of the wavepackets are given by Hamilton's equations:

$$\dot{\mathbf{r}}_c = \frac{\partial \mathcal{H}}{\partial \mathbf{p}} = \frac{\partial E}{\partial \hbar \mathbf{k}_c}$$

$$\dot{\mathbf{p}} = \hbar \dot{\mathbf{k}}_c = \mathbf{F}_{ext} = -e\mathcal{E} - \frac{e\mathbf{v}}{c} \times \mathbf{B}$$

- Introduce a distribution function f(**r**,**k**) that gives the number of electrons at position **r** and with momentum **k**.

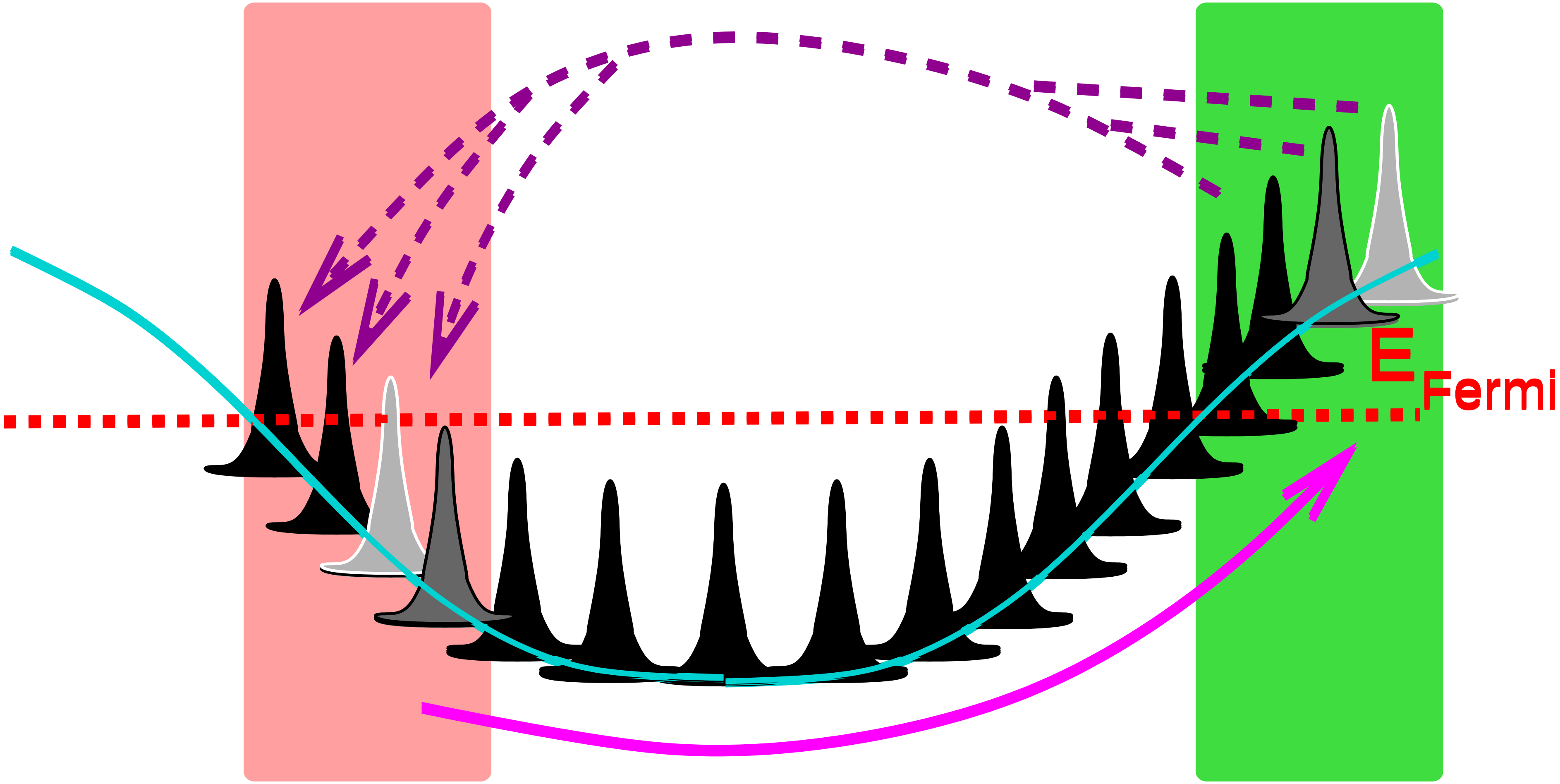
The Boltzmann equation

- Requesting that the number of particles is locally conserved, one can derive the Boltzmann equation for f:

$$\frac{\partial f}{\partial t} = -\dot{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} f - \dot{\mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{k}} f + \left.\frac{d\, f}{dt}\right|_{coll}$$

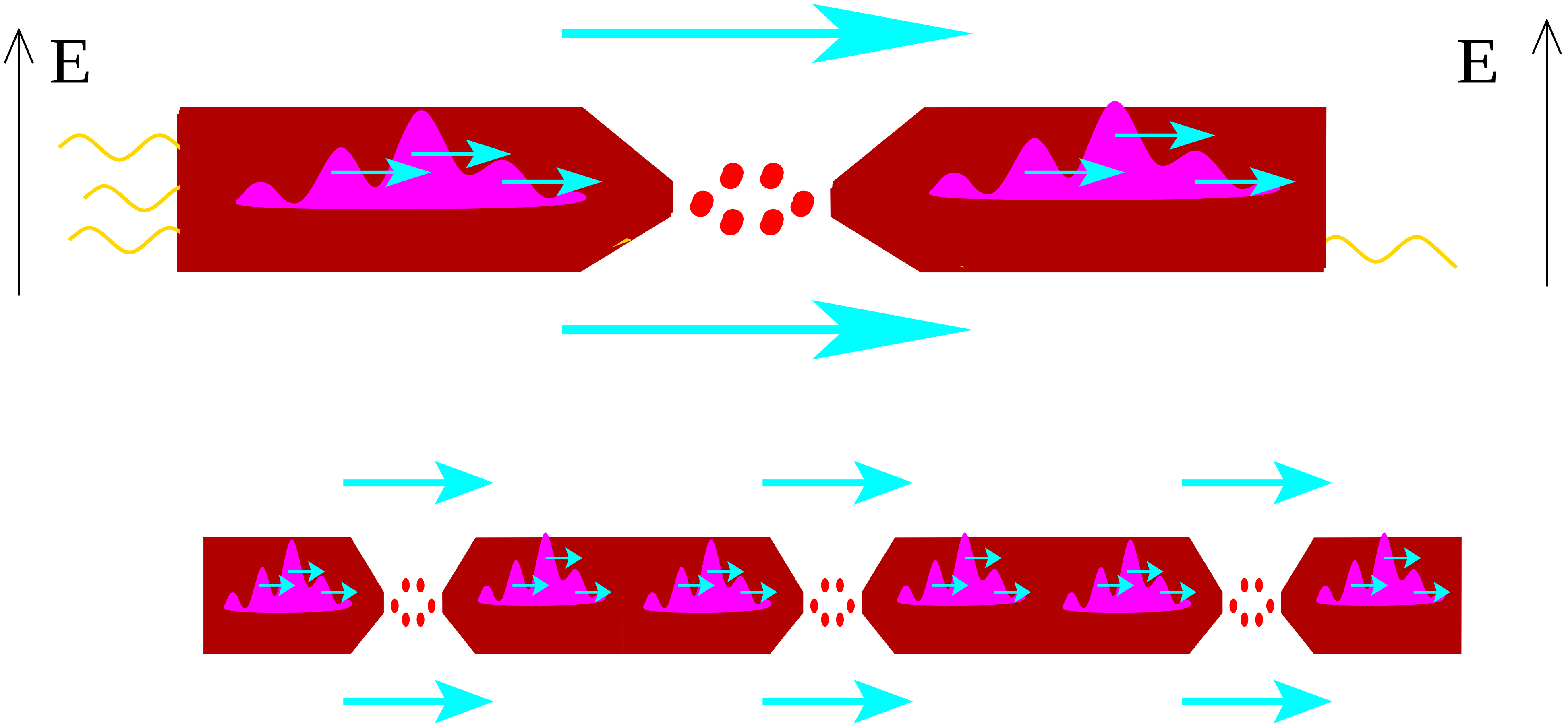
$$\begin{aligned} \left.\frac{d\, f(\mathbf{r}, \mathbf{k})}{dt}\right|_{coll} \quad = \quad & -f(\mathbf{r}, \mathbf{k}) \sum_{\mathbf{r}', \mathbf{k}'} \gamma_{(\mathbf{r}', \mathbf{k}'), (\mathbf{r}, \mathbf{k})} \left(1 - f(\mathbf{r}', \mathbf{k}')\right) \\ & + \left(1 - f(\mathbf{r}, \mathbf{k})\right) \sum_{\mathbf{r}', \mathbf{k}'} \gamma_{(\mathbf{r}, \mathbf{k}), (\mathbf{r}', \mathbf{k}')} f(\mathbf{r}', \mathbf{k}') \end{aligned}$$

Boltzmann equation in a simple metal



$$\left.\frac{d\,f(\mathbf{r},\mathbf{k})}{dt}\right|_{coll} = -f(\mathbf{r},\mathbf{k})\sum_{\mathbf{r}',\mathbf{k}'}\gamma_{(\mathbf{r}',\mathbf{k}'),(\mathbf{r},\mathbf{k})}\,(1-f(\mathbf{r}',\mathbf{k}')) + (1-f(\mathbf{r},\mathbf{k}))\sum_{\mathbf{r}',\mathbf{k}'}\gamma_{(\mathbf{r},\mathbf{k}),(\mathbf{r}',\mathbf{k}')}\,f(\mathbf{r}',\mathbf{k}')$$

What can we do for nano-scale transport ?



Ingredients for a quantum model

Instead of wavepackets, use wavefunctions.

Instead of the distribution function f, use the density matrix S.

Instead of the Boltzmann equation, use the Schrödinger equation.

But how can we describe dissipation in quantum mechanics ?????

Coupling to a heat bath, thermal equilibrium, and all that

In the absence of external perturbations, a coupling to a heat bath should bring the electrons towards thermal equilibrium.

Given a set of eigenstates $\{\Psi_i\}$ ıd corresponding energies , we know $\{\varepsilon_i\}$t thermal equilibrium is defined as:

$$S^{eq} = \sum_i \bar{n}\left(\varepsilon_i; T\right) \left|\Psi_i\right\rangle \left\langle\Psi_i\right|$$

This indicates that we need to use a formalism in terms of electronic *density matrices*!

More on density matrices

Consider first a pure state:

Wavefunction	Density Matrix
$\lvert\Psi\rangle$	$S = \lvert\Psi\rangle\langle\Psi\rvert$
$\langle\Psi\lvert\mathcal{A}\rvert\Psi\rangle$	$\mathrm{Tr}\left[\mathcal{A}\mathcal{S}\right]$
$N_e \times M$	$M \times M$

Let us determine the equation of motion:

$$i\frac{d}{dt}\lvert\Psi\rangle = H(t)\lvert\Psi\rangle$$

$$\begin{aligned}\frac{d}{dt}S = \frac{d}{dt}\lvert\Psi\rangle\langle\Psi\rvert &= \frac{d\lvert\Psi\rangle}{dt}\langle\Psi\rvert + \lvert\Psi\rangle\frac{d\langle\Psi\rvert}{dt}\\ &= -iH(t)\lvert\Psi\rangle\langle\Psi\rvert + i\lvert\Psi\rangle\langle\Psi\rvert H(t)\\ &= -i\left[H(t), S\right]\end{aligned}$$

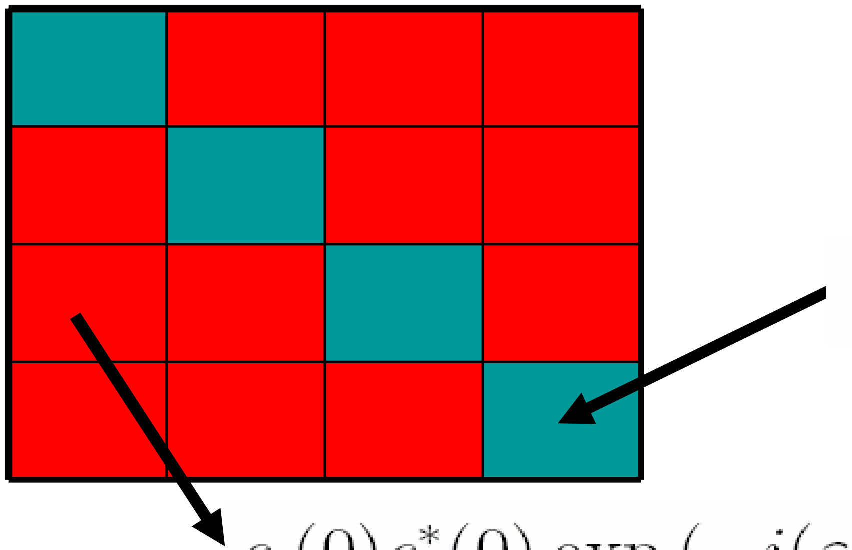
Can this be enough ??

Master equation: $\frac{d}{dt}S(t) = -i\,[H(t), S(t)]$

Take a general wfc: $|\Phi(t)\rangle = c_0(t)\,|\Psi_0\rangle + c_1(t)\,|\Psi_1\rangle + c_2(t)\,|\Psi_2\rangle + \cdots$

Then: $c_i(t) = c_i(0)\exp(-i\varepsilon_i t)$

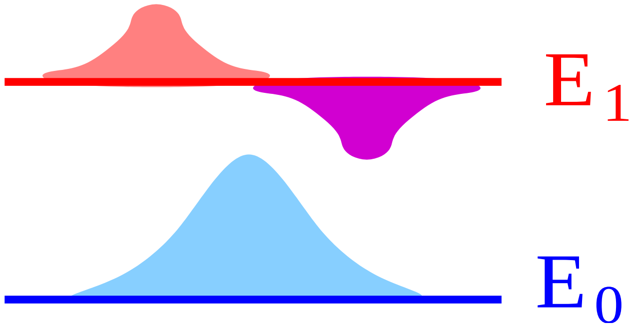
S =



$|c_i(0)|^2$

$c_i(0)c_j^*(0)\exp(-i(\varepsilon_i - \varepsilon_j)t)$

What about a time-dependent perturbation in H ??



$$H(t) = \begin{pmatrix} E_0 & V_{01} e^{i(E_1 - E_0)t} \\ V_{01} e^{-i(E_1 - E_0)t} & E_1 \end{pmatrix}$$

$$|\psi(t)\rangle = \sin\left(V_{01} t\right)\, e^{-iE_0 t}\, |0\rangle \,+\, \cos\left(V_{01} t\right)\, e^{-iE_1 t}\, |1\rangle$$

The system will come back to the excited state (recurrence).

The density matrix will not remain diagonal.

Dissipative master equation approach

$$\frac{d}{dt}S(t) = -i\,[H(t), S(t)] + \mathcal{C}[S(t)]$$

In the following we'll try to find an explicit form for the collision term in the master equation.

This approach is very commonly used e.g. in quantum optics.

See for example:

- William H. Louisell, *Quantum Statistical Properties of Radiation*, Wiley (1973).
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Dissipative master equation approach

$$S^1 = \sum_{\lambda\mu} f_{\lambda\mu} \left|\lambda\right\rangle \left\langle\mu\right| \qquad f_{\lambda\mu} = \mathrm{Tr}\; S\, c_\mu^\dagger\, c_\lambda$$

$$\frac{\partial S}{\partial t} = \frac{1}{i\hbar}[H, S] - \sum_{\alpha,\beta} g(\beta, \alpha) \times \\ \Big(L_{(\alpha\beta)} L_{(\beta\alpha)} S + S L_{(\alpha\beta)} L_{(\beta\alpha)} - 2 L_{(\beta\alpha)} S L_{(\alpha\beta)}\Big)$$

Master equation for the reduced density matrix

The final equations of motion for the $f_{\alpha\beta}(t)$ read:

$$\begin{aligned}
\dot{f}_{\alpha\beta} \quad = \quad & -i \sum_{\lambda} \left(H_{\alpha\lambda} f_{\lambda,\beta} - f_{\alpha\lambda} H_{\lambda,\beta} \right) \\
& + \left(\delta_{\alpha\beta} - f_{\alpha\beta} \right) \sum_{\lambda} \frac{1}{2} \left(\gamma_{\alpha\lambda} + \gamma_{\beta\lambda} \right) f_{\lambda\lambda} \\
& - f_{\alpha\beta} \sum_{\lambda} \frac{1}{2} \left(\gamma_{\lambda\alpha} + \gamma_{\lambda\beta} \right) \left(1 - f_{\lambda\lambda} \right) .
\end{aligned}$$

This equation ensures the following properties of the reduced density matrix:

1. the trace is invariant
2. $\dot{f}_{\alpha\beta}$ is hermitian
3. diagonal elements are between 0 and 1
4. off-diagonal elements tend to zero
5. stationary solution is given by the Fermi-Dirac distribution

How can this approach be used ?

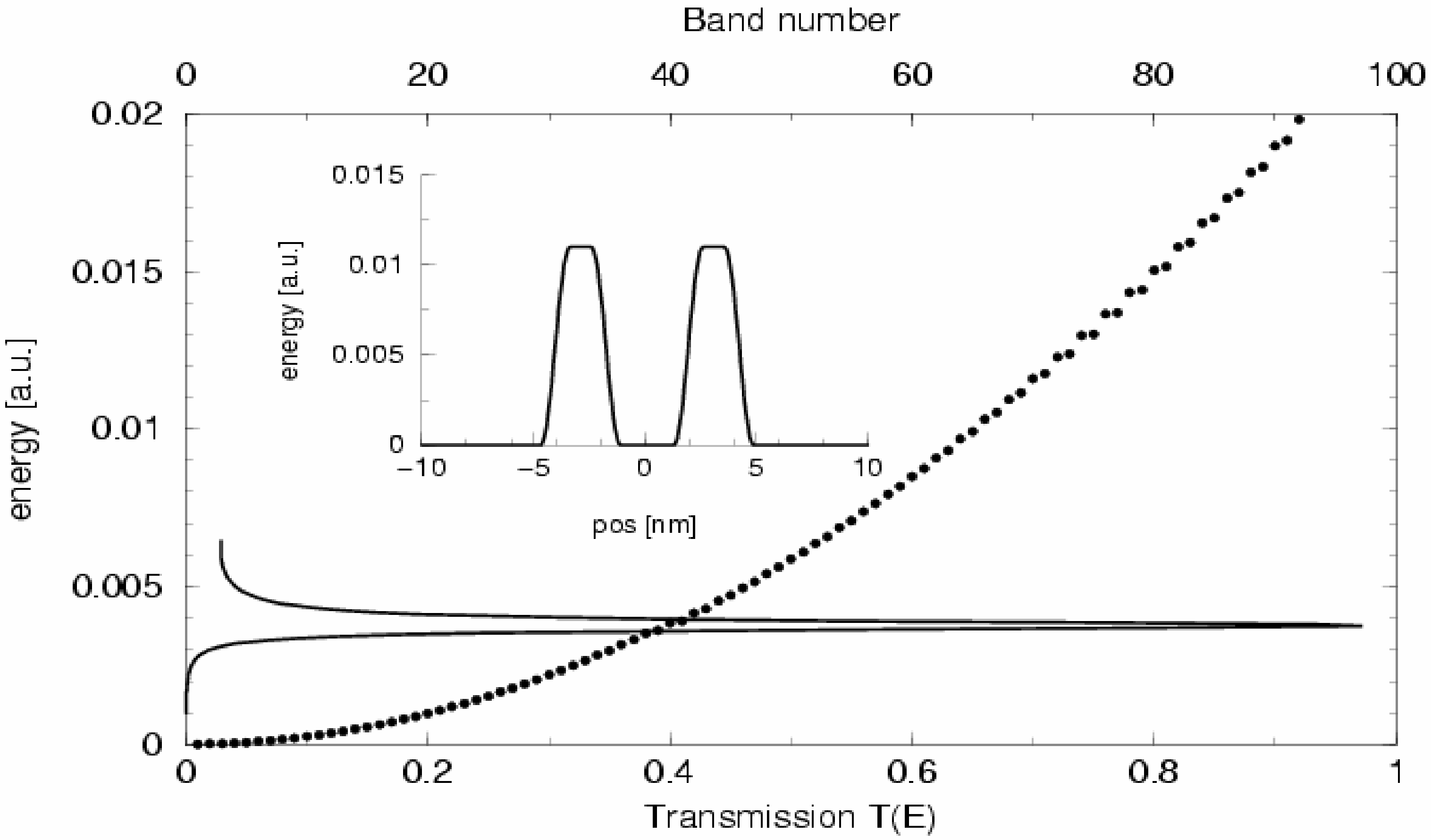
The quantum kinetic scheme can be used in various types of calculations:

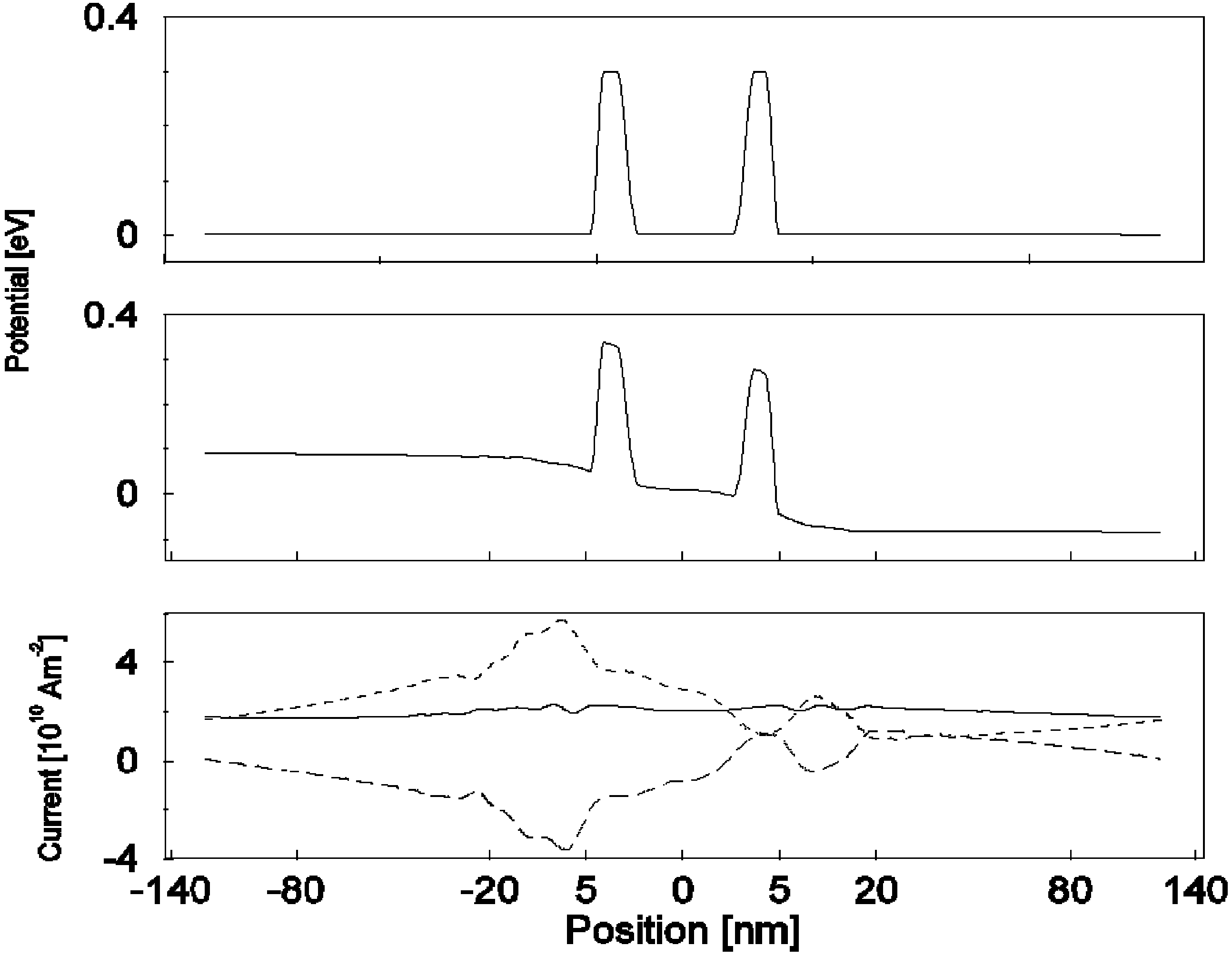
- Planewave density-functional pseudopotential calculations
- Self-consistent tight-binding calculations
- Effective-mass equations

↑ Increasing complexity

Application: Tunneling double barrier

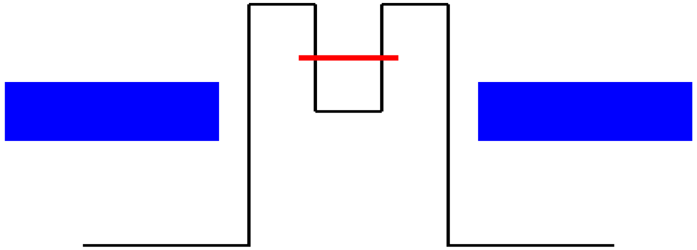
System setup:



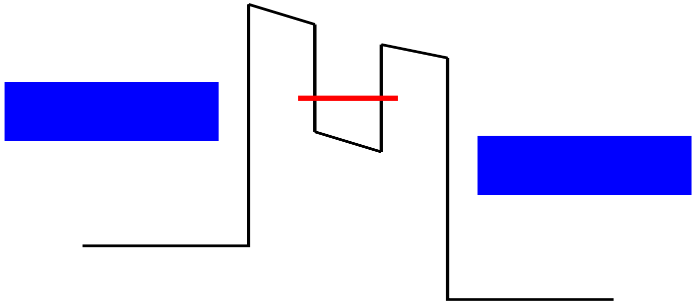

0.4
0
Potential [eV]
0.4
0
Current [10^{10} Am^{-2}]
4
0
-4
-140
-80
-20
5
0
5
20
80
140
Position [nm]

Trying to understand the physics of double-barrier tunneling

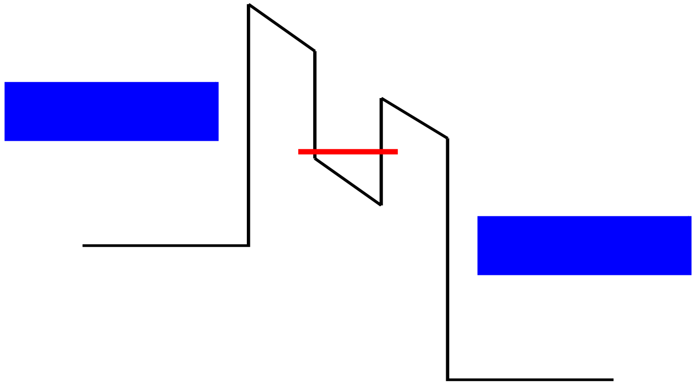
1) Equilibrium, no current



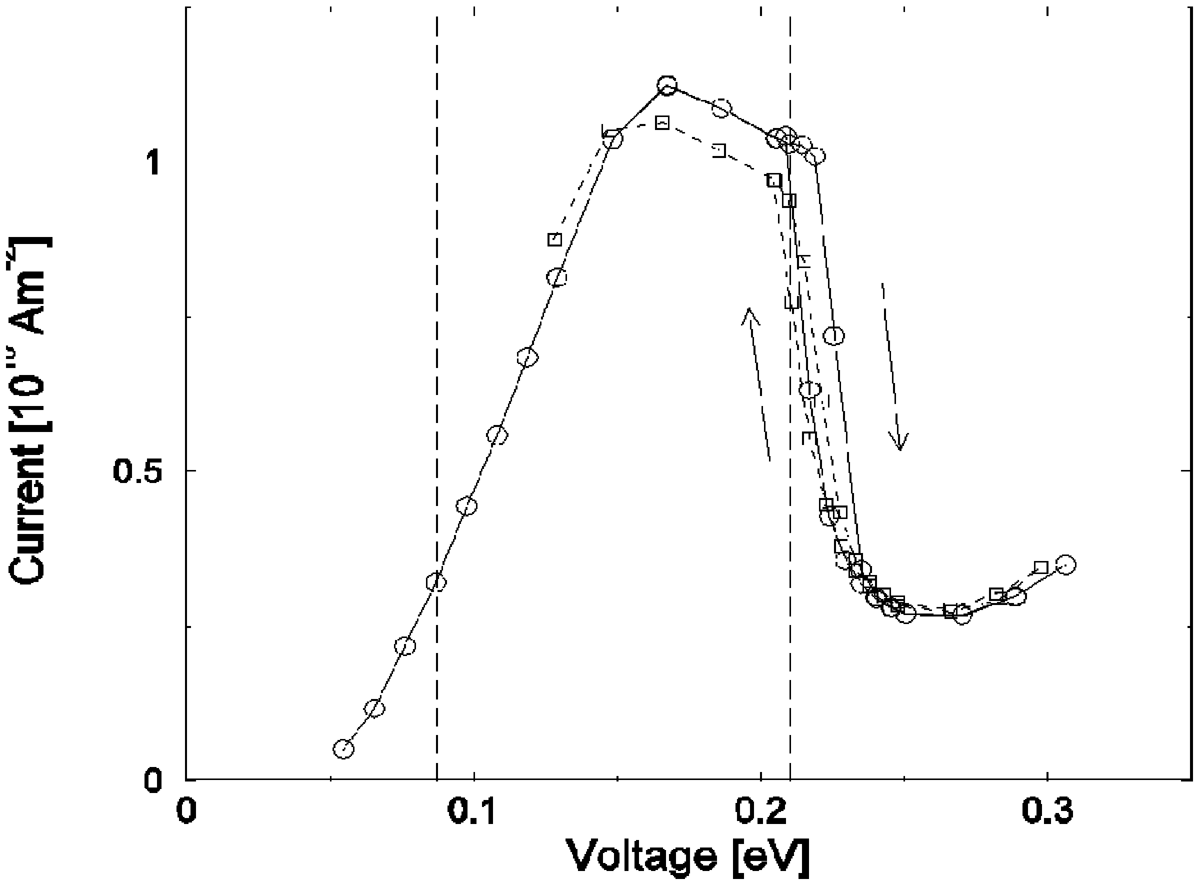
2) External bias,current



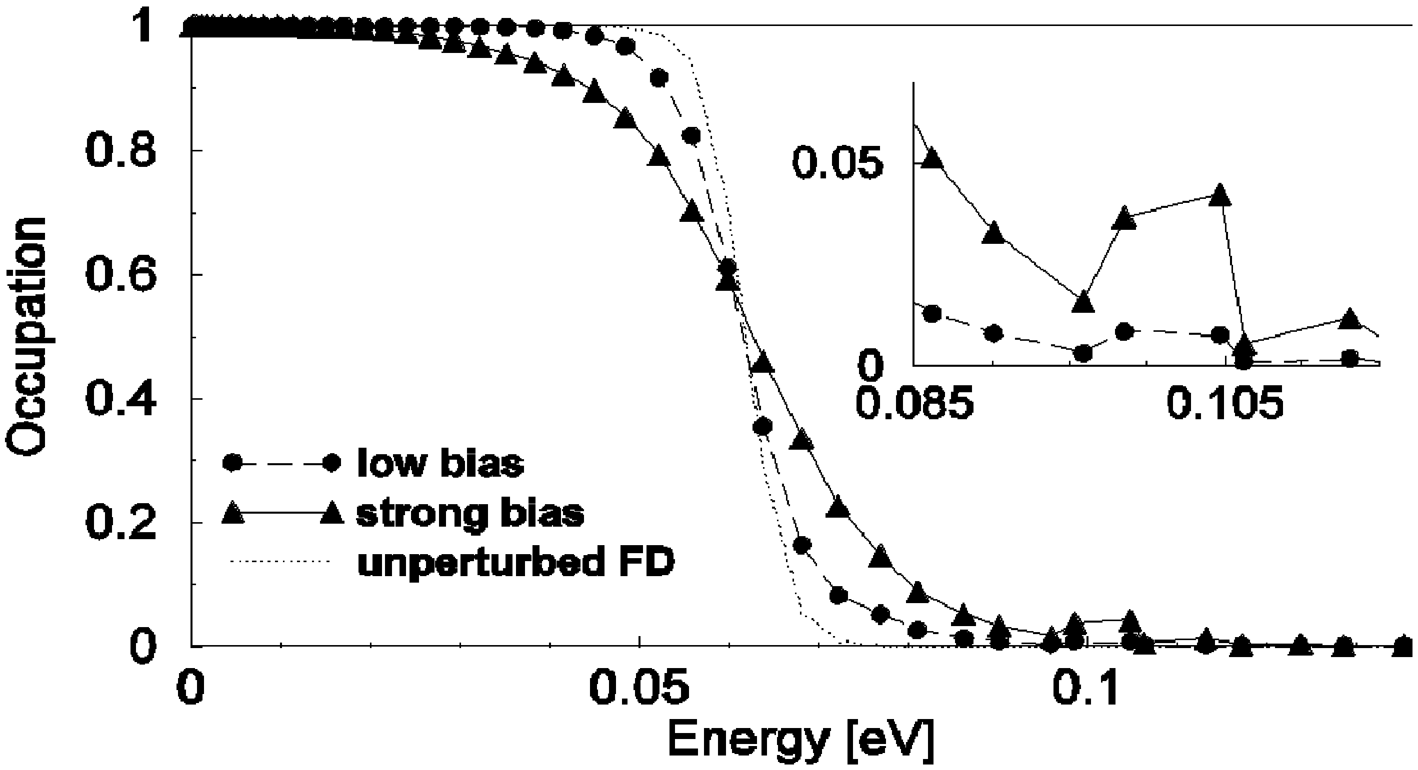
1) Strong bias



I-V characteristics of the DBRTS



Level occupations



Dissipative master equation approach

$$\frac{d}{dt}S(t) = -i\,[H(t), S(t)] + \mathcal{C}[S(t)]$$

In the following we'll try to find an explicit form for the collision term in the master equation.

This approach is very commonly used e.g. in quantum optics.

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Dissipation: Role of the external bath

Consider the electronic system coupled to an external (phonon) bath:

$$H_T = H + R + V = H_0 + V$$

(for example: $R = \sum_j \hbar\omega_j b_j^\dagger b_j$)
Equation of motion for the complete density operator:

$$i\hbar \frac{\partial \rho}{\partial t} = [H_T, \rho] = [H + R + V, \rho] \, .$$

We are interested in the electronic subsystem: $S(t) = \mathrm{Tr}_R \rho(t)$.
Define ρ and S in the interaction picture:

$$\begin{aligned} \rho(t) &= e^{-i/\hbar H_0 (t-t_0)} \chi(t) e^{i/\hbar H_0 (t-t_0)} \\ S(t) &= e^{-i/\hbar H (t-t_0)} s(t) e^{i/\hbar H (t-t_0)} \end{aligned}$$

Perturbation theory

Two crucial approximations are made in order to obtain the final master equation for the damped electronic subsystem.

2nd order perturbation theory in V

$$\begin{aligned}\chi(t) &= \chi(t_0) + \frac{1}{i\hbar}\int_{t_0}^{t} [V(t'-t_0), \chi(t_0)]\,\mathrm{d}t' \\ &+ \frac{1}{(i\hbar)^2}\int_{t_0}^{t}\mathrm{d}t' \int_{t_0}^{t'}\mathrm{d}t''\,[V(t'-t_0), [V(t''-t_0), \chi(t_0)]] + \ldots\end{aligned}$$

Assume V of the form: $V = \sum_i L_i F_i$

where the $\begin{matrix} L_i \\ F_i \end{matrix}$ act on $\begin{matrix} \text{electrons} \\ \text{bath} \end{matrix}$ only.

Markov Approximation

The equation of motion of $s(t)$ reads then:

$$\begin{aligned}
s(t) & -s(t_0) \equiv \Delta s = \\
= & -\sum_{i,j} \int_0^{t-t_0} \mathrm{d}\xi \Big\{ \left[L_i L_j s(t_0) - L_j s(t_0) L_i\right] \int_0^{t-t_0-\xi} \mathrm{d}\tau e^{i\omega_i \tau} \left\langle F_i(\tau) F_j(0) \right\rangle_R \\
& - \left[L_i s(t_0) L_j - s(t_0) L_j L_i\right] \int_0^{t-t_0-\xi} \mathrm{d}\tau e^{i\omega_i \tau} \left\langle F_j(0) F_i(\tau) \right\rangle_R \Big\} e^{i(\omega_i+\omega_j)\xi}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial S}{\partial t} & = e^{-iH(t-t_0)} \left\{ -i\left[H, s(t)\right] + \frac{\partial s}{\partial t} \right\} e^{iH(t-t_0)} \\
& \approx e^{-iH(t-t_0)} \left\{ -i\left[H, s(t)\right] + \frac{\Delta s}{\Delta t} \right\} e^{iH(t-t_0)}
\end{aligned}$$

Master equation for the density matrix

After the Markov Approximation:

$$\begin{aligned}\frac{\partial S}{\partial t} &= \frac{1}{i\hbar}[H, S] - \sum_{\alpha,\beta} \gamma_{\beta,\alpha} \times \\ &\left(L_{(\alpha\beta)} L_{(\beta\alpha)} S + S L_{(\alpha\beta)} L_{(\beta\alpha)} - 2 L_{(\beta\alpha)} S L_{(\alpha\beta)} \right) .\end{aligned}$$

Master equation for the density matrix

After the Markov Approximation:

$$\begin{aligned}\frac{\partial S}{\partial t} &= \frac{1}{i\hbar}\left[H, S\right] - \sum_{\alpha,\beta} \gamma_{\beta,\alpha} \times \\ & \left(L_{(\alpha\beta)} L_{(\beta\alpha)} S + S L_{(\alpha\beta)} L_{(\beta\alpha)} - 2 L_{(\beta\alpha)} S L_{(\alpha\beta)}\right).\end{aligned}$$

The numbers $\gamma_{\alpha,\beta}$ are defined by

$$\gamma_{\alpha,\beta} = \begin{cases} \left|\langle\alpha\left|V_{e-ph}\right|\beta\rangle\right|^2 \left(\bar{n}\left(e_\beta - e_\alpha\right) + 1\right) & e_\alpha < e_\beta \\ \left|\langle\alpha\left|V_{e-ph}\right|\beta\rangle\right|^2 \left(\bar{n}\left(e_\alpha - e_\beta\right)\right) & e_\alpha > e_\beta \end{cases}$$

$$\text{and} \qquad \bar{n}(\omega) = 1/\left(e^{\frac{\omega}{kT}} - 1\right).$$

Going to the 1-particle reduced density matrix

$$S^1 = \sum_{\lambda\mu} f_{\lambda\mu} \, |\lambda\rangle \langle\mu| \qquad\qquad f_{\lambda\mu} = \mathrm{Tr}\; S \, c_\mu^\dagger \, c_\lambda$$

$$\begin{aligned}\frac{\partial S}{\partial t} \quad &= \frac{1}{i\hbar} [H, S] - \sum_{\alpha,\beta} g(\beta,\alpha) \times \\ &\big(L_{(\alpha\beta)} L_{(\beta\alpha)} S + S L_{(\alpha\beta)} L_{(\beta\alpha)} - 2 L_{(\beta\alpha)} S L_{(\alpha\beta)}\big)\end{aligned}$$

$$\begin{aligned}\frac{\partial S}{\partial t} \quad &= \frac{1}{i\hbar} [H, S] - \sum_{\alpha,\beta} g(\beta,\alpha) \times \\ &\Big(c_\alpha^\dagger \, c_\beta \, c_\beta^\dagger \, c_\alpha \, S + S \, c_\alpha^\dagger \, c_\beta \, c_\beta^\dagger \, c_\alpha - 2 c_\beta^\dagger \, c_\alpha \, S \, c_\alpha^\dagger \, c_\beta\Big) .\end{aligned}$$

Use: $Tr \, S \, c_\alpha^\dagger \, c_\beta^\dagger \, c_\gamma c_\delta = f_{\delta\alpha} f_{\gamma\beta} - f_{\delta\beta} f_{\gamma\alpha}$

Master equation for the reduced density matrix

The final equations of motion for the $f_{\alpha\beta}(t)$ read:

$$\begin{aligned}\dot{f}_{\alpha\beta} &= -i\sum_{\lambda}\left(H_{\alpha\lambda}f_{\lambda,\beta} - f_{\alpha\lambda}H_{\lambda,\beta}\right)\\ &\quad +\left(\delta_{\alpha\beta} - f_{\alpha\beta}\right)\sum_{\lambda}\frac{1}{2}\left(\gamma_{\alpha\lambda} + \gamma_{\beta\lambda}\right)f_{\lambda\lambda}\\ &\quad -f_{\alpha\beta}\sum_{\lambda}\frac{1}{2}\left(\gamma_{\lambda\alpha} + \gamma_{\lambda\beta}\right)\left(1 - f_{\lambda\lambda}\right).\end{aligned}$$

This equation ensures the following properties of the reduced density matrix:

1. the trace is invariant
2. $\dot{f}_{\alpha\beta}$ is hermitian
3. diagonal elements are between 0 and 1
4. off-diagonal elements tend to zero
5. stationary solution is given by the Fermi-Dirac distribution

How the time-propagation is done: Electric field

A Potential $V_{\mathbf{E}}(\mathbf{x}) = -\mathbf{E}\cdot\mathbf{x}$ is incompatible with pbc.
Choose a particular gauge:

$$\mathbf{A}(\mathbf{x},t) = -\mathbf{E}t \qquad \mathbf{E}(\mathbf{x},t) = -\nabla V_{\mathbf{E}}(\mathbf{x},t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{x},t)$$

$$\mathbf{V}_{\mathbf{E}}(\mathbf{x}) = 0 \qquad \mathbf{B}(\mathbf{x},t) = \nabla\times\mathbf{A}(\mathbf{x},t)$$

The price to pay in this description is that the Hamiltonian becomes explicitly time-dependent:

$$H_{\mathbf{k}}(t) = \frac{1}{2m}\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}\mathbf{x}} + \hbar\mathbf{k} - e\mathbf{E}t\right)^2 + V(\mathbf{x})$$

Gauge transformations:

It is possible to perform a gauge transformation: One can add ΔA to a vector potential, if at the same time the wavefunctions are multiplied by a planewave $\exp\left(-i\Delta A \cdot x\right)$.

The planewave is compatible with pbc if ΔA is an integer multiple of $2\pi/L$.

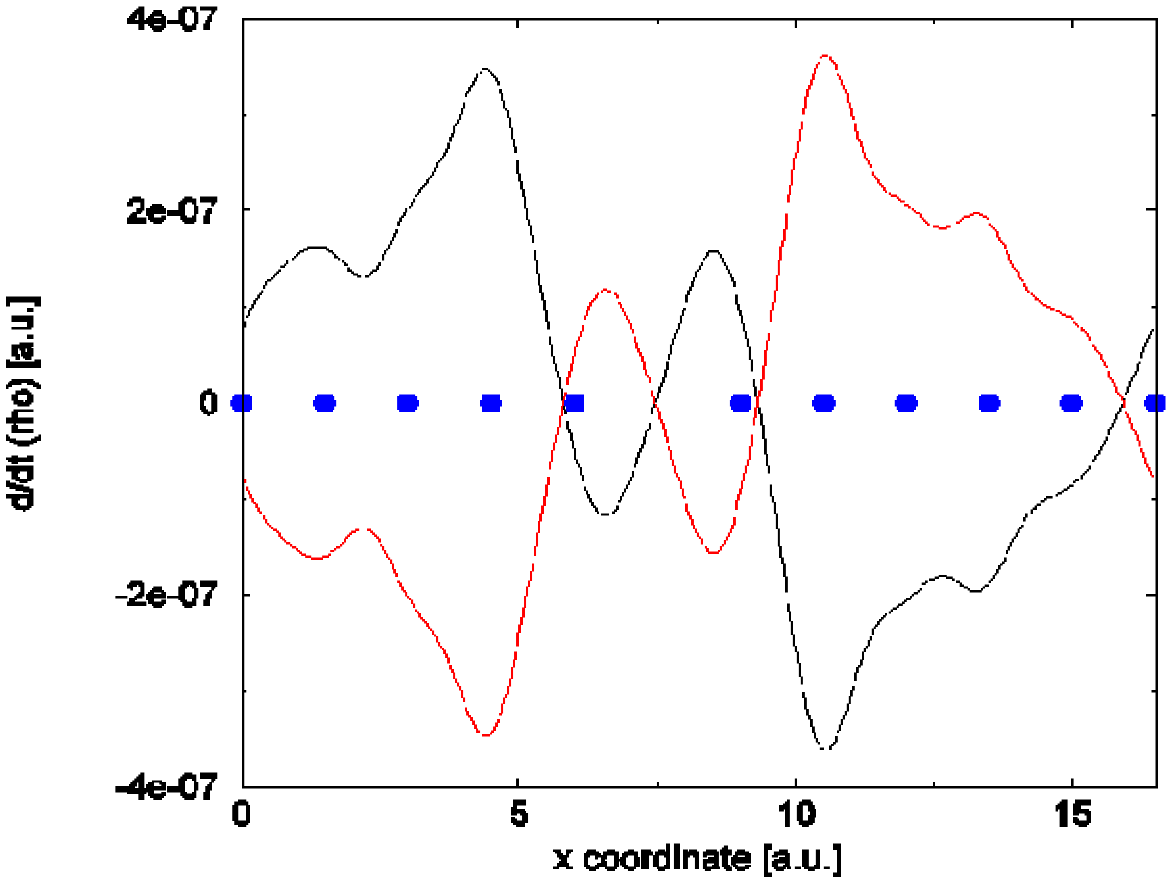
The minimal time τ_E to pass before a gauge transformation can be applied to a system is therefore

$$\tau_E = \frac{2\pi}{LeE}$$

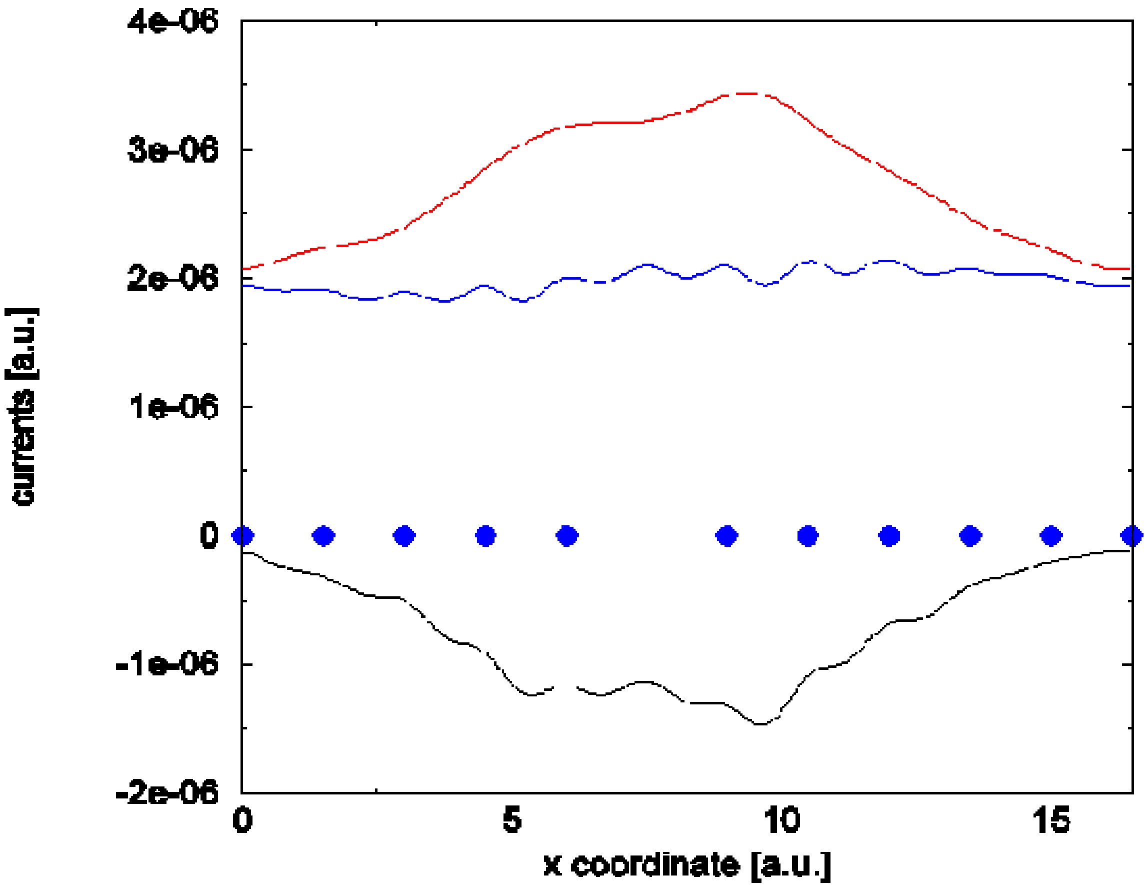
This introduces a natural propagation time step τ_E.

In practice, the propagator is split, and propagations for τ_E of the dissipative dynamics and the Hamiltonian dynamics are alternated.

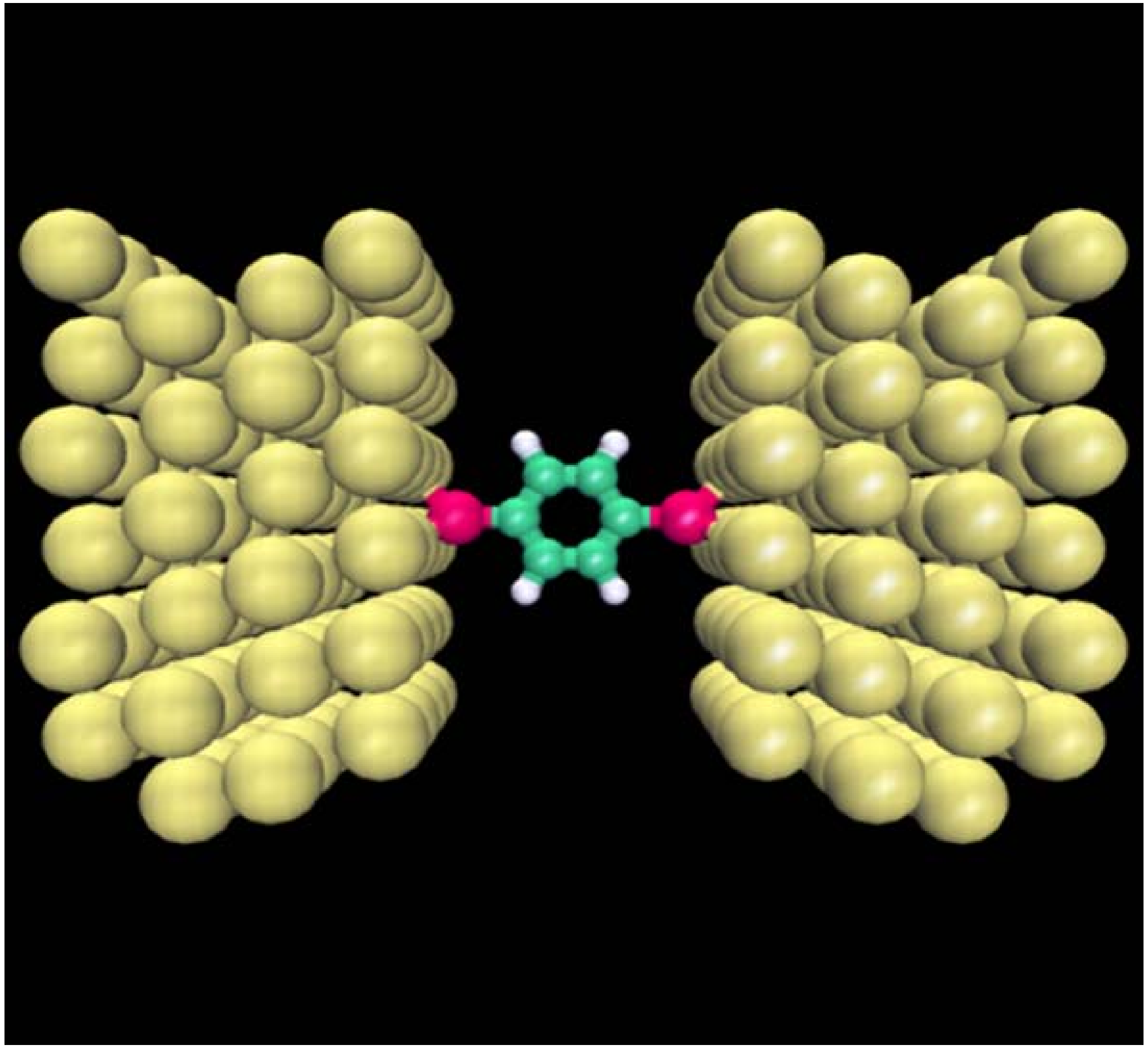
Next application example: DFT implementation



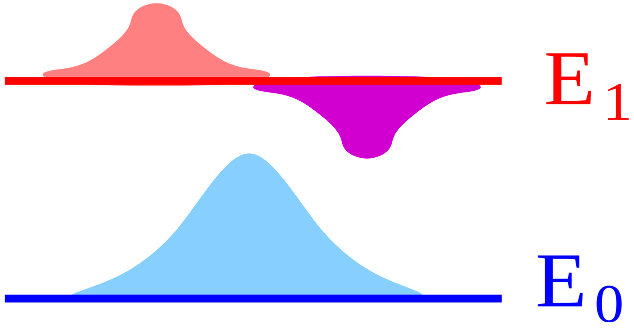
DFT implementation: Currents



DFT implementation: Present project



The dissipative current



$$
\begin{aligned}
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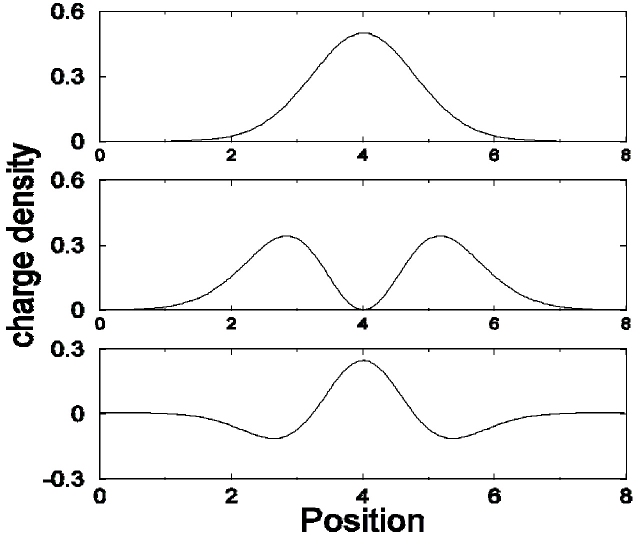
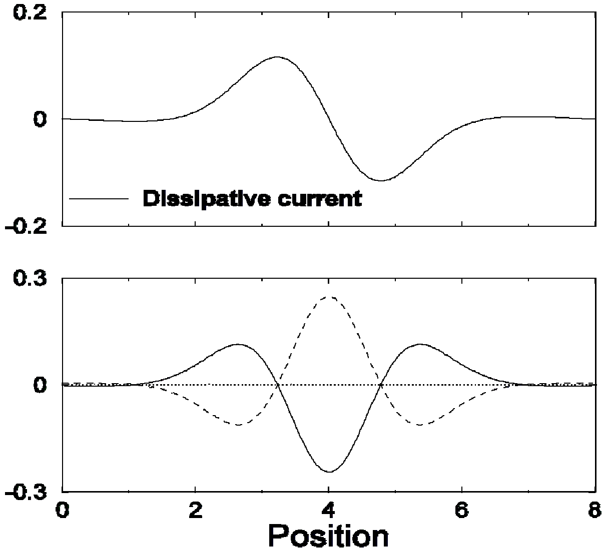
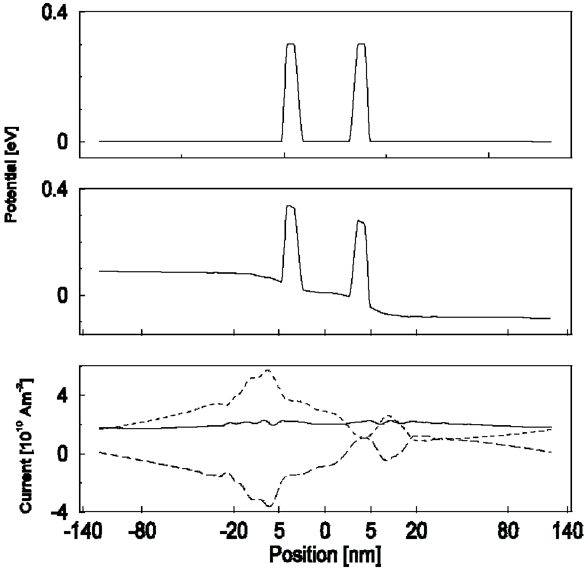
&+\left(\delta_{\alpha\beta} - f_{\alpha\beta}\right)\sum_{\lambda}\frac{1}{2}\left(\gamma_{\alpha\lambda} + \gamma_{\beta\lambda}\right) f_{\lambda\lambda}\\
&-f_{\alpha\beta}\sum_{\lambda}\frac{1}{2}\left(\gamma_{\lambda\alpha} + \gamma_{\lambda\beta}\right)\left(1 - f_{\lambda\lambda}\right).
\end{aligned}
$$







Another possible field of application: SCF tight binding models

Tight binding schemes present an intermediate between full DFT implementations and effective-mass approaches.

A crucial ingredient is charge (potential) self-consistency in order to correctly describe the charging at the contacts.

$$\begin{aligned} H &= \sum_{n,\gamma,n',\gamma'} |\phi_{n\gamma}\rangle \, H_{n\gamma,n'\gamma'} \, \langle \phi_{n'\gamma'}| \\ &= \sum_{n,n'} |\phi_n\rangle \, H_{n,n'} \, \langle \phi_{n'}| \end{aligned}$$

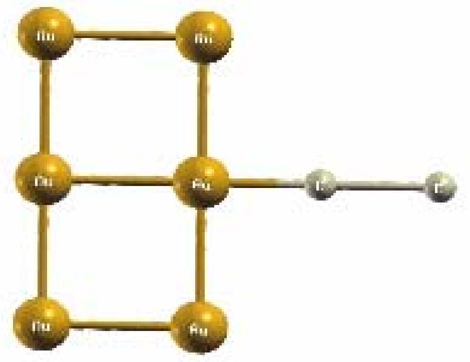
$$H_{nn'} = \begin{cases} t_{nn'} & \text{if } n, n' \text{ are nearest neighbors} \\ h_n^0 + V_n^{scf} & \text{if } n = n' \\ 0 & \text{otherwise.} \end{cases}$$

The case of carbon and gold

One possible application of this tight binding scheme is the gold – carbon nanotube – gold system.

Carbon nanotubes are relatively well described using one p-orbital per C atom.

The on-site energy must reflect that the workfunction of gold and the workfunction of carbon nanotubes differ by 0.8 eV.



Definition of the current in tight-binding schemes

Let us define a projection operator on site n:

$$P_n = \sum_\gamma |\phi_{n\gamma}\rangle \langle\phi_{n\gamma}| = |\phi_n\rangle \langle\phi_n|$$

Then we have $\sum_n P_n = 1$.

If the system is in a state $|\psi(t)\rangle$, then the occupation of site n is given by $P_n(t) = \langle\psi(t)| P_n |\psi(t)\rangle$.

The equation of motion for $P_n(t)$ is

$$\dot{P}_n(t) = -i \langle\psi(t)| [P_n, H] |\psi(t)\rangle .$$

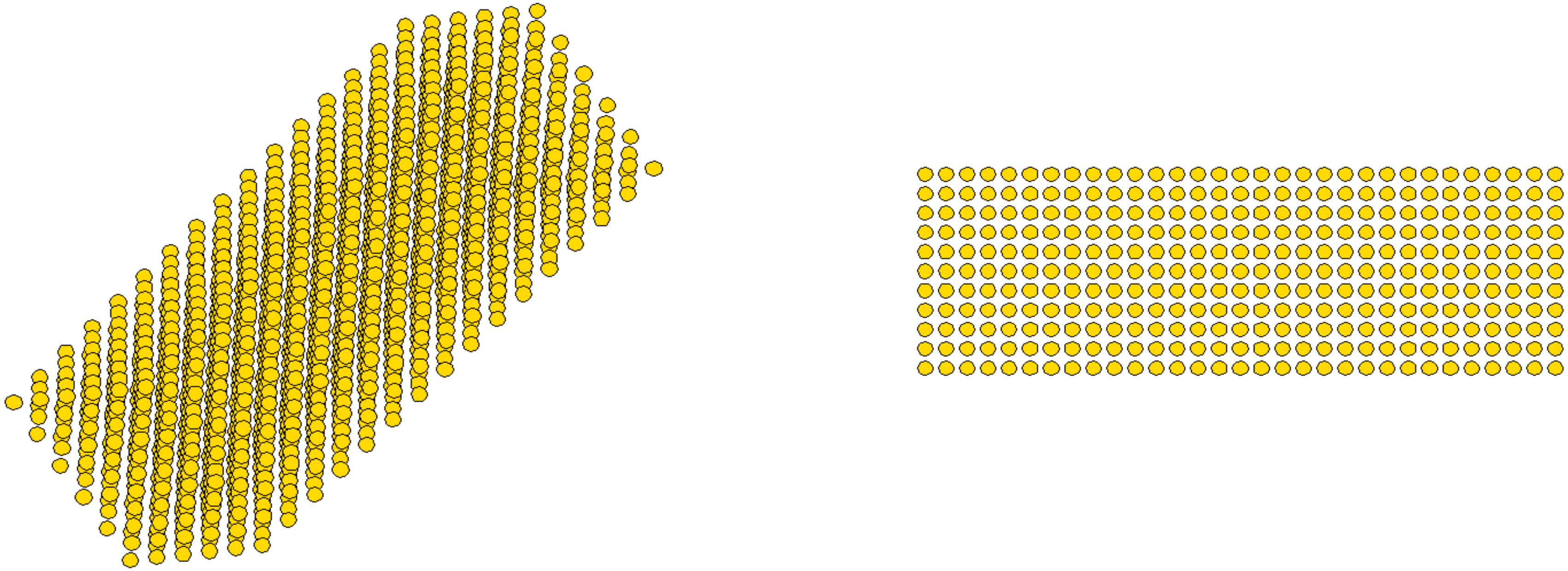
Define J_n as the rate of change of the occupation at site n.

$$J_n = -i [P_n, H] = -i \sum_{n' \neq n} (P_n H P_{n'} - P_{n'} H P_n) .$$

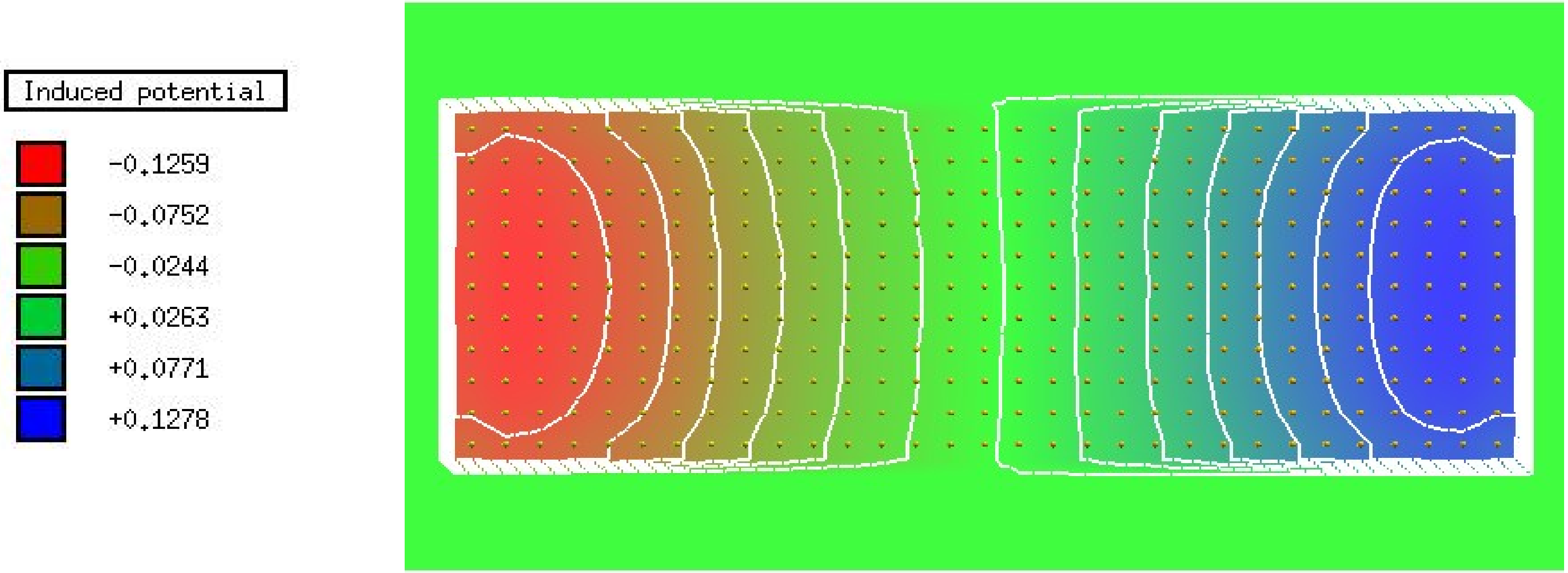
Therefore, we can identify $J_{n'n}$ as an operator representing the particle current from site n' to site n:

$$\begin{aligned} J_{n'n} &= -i (P_n H P_{n'} - P_{n'} H P_n) \\ &= -i \sum_{\gamma,\gamma'} (|\phi_{n\gamma}\rangle H_{n\gamma,n'\gamma'} \langle\phi_{n'\gamma'}| - |\phi_{n'\gamma'}\rangle H_{n'\gamma',n\gamma} \langle\phi_{n\gamma}|) . \end{aligned}$$

Use of the SCF tight binding model



Induced potential



Conclusions

- Kinetic model that can describe all quantum features of nano-scale transport.
- Interaction with an external (phonon) bath as a key ingredient.
- Interplay between dissipation and external acceleration (E-field) leads to a steady state.
- Possible to study the influence of inelastic electron-phonon scattering.
- Time- or history dependent (hysteresis) effects can be described.
- Applications are possible using models of various degrees of sophistication (effective mass, tight-binding, DFT pseudopotential ...).

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