Time-Dependent Density Functional Theory for Open Systems

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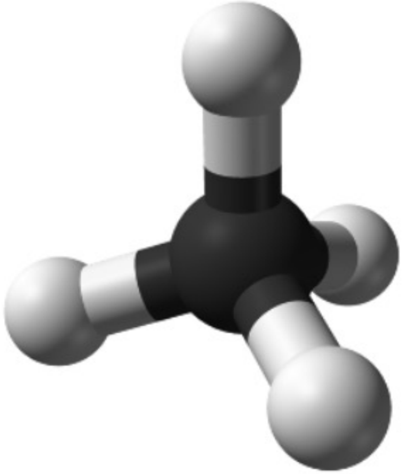
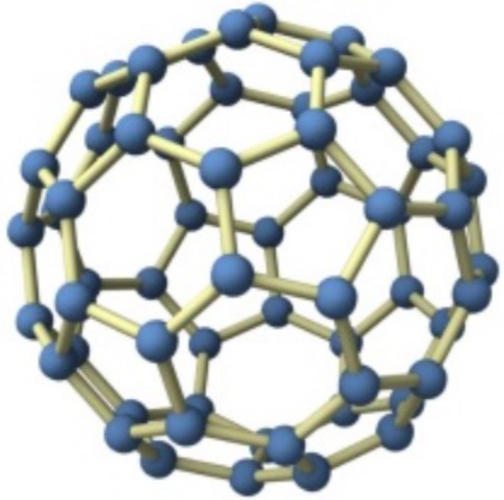
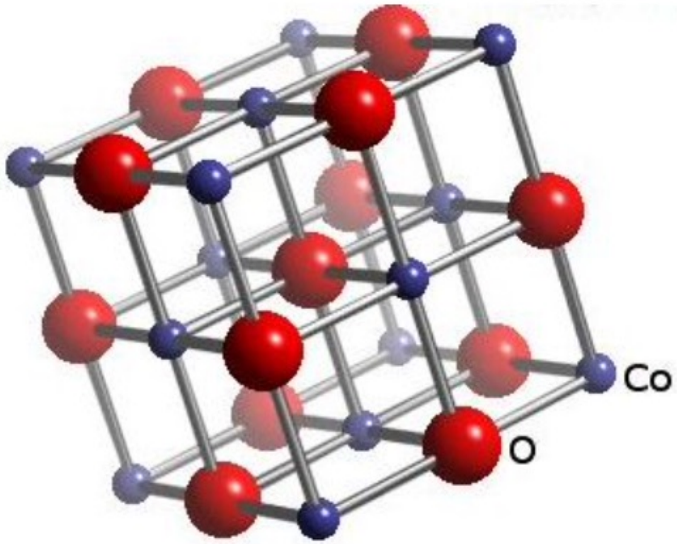
CSRC, Beijing, 2024-05-14

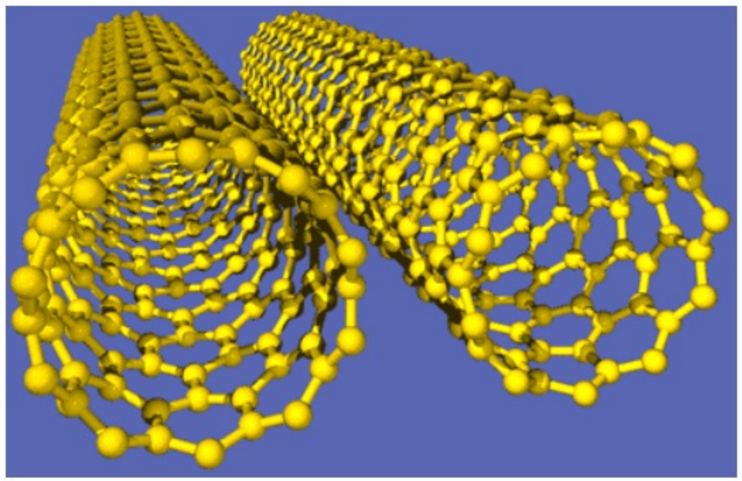
isolated systems



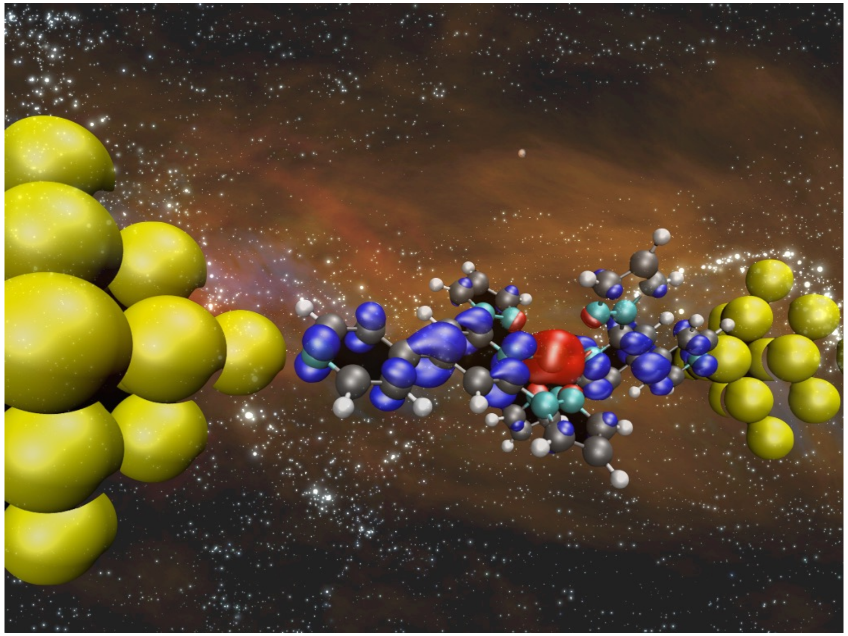


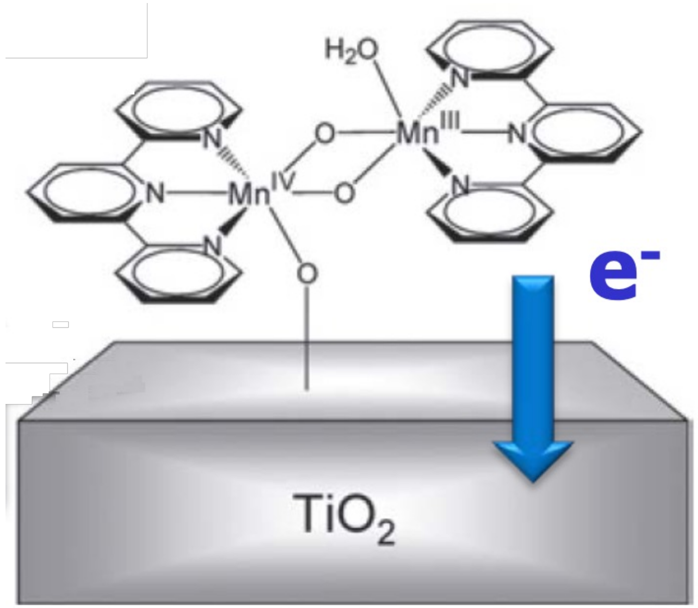
periodic systems

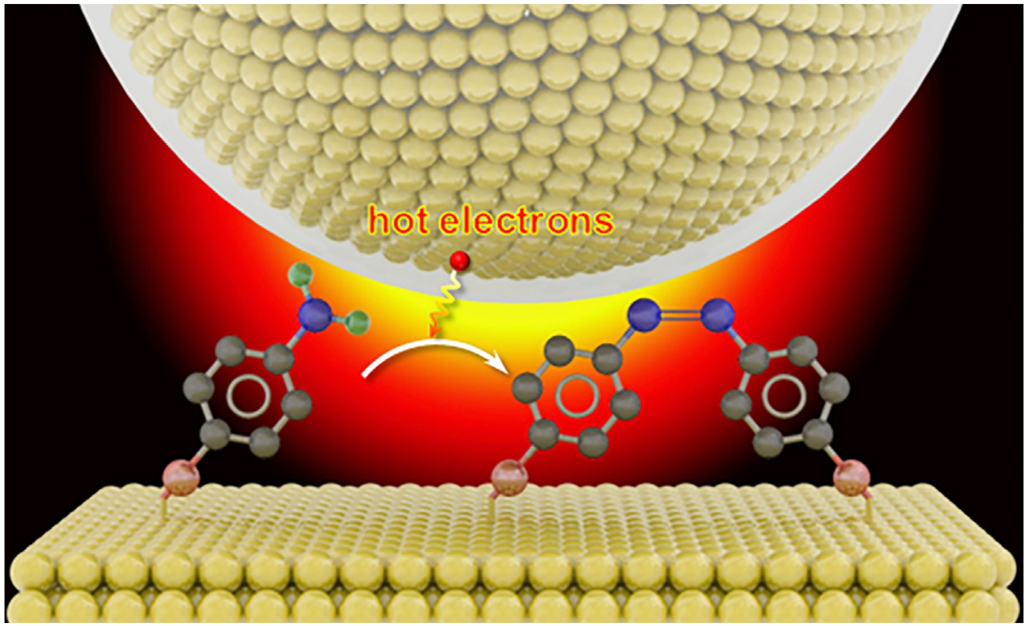


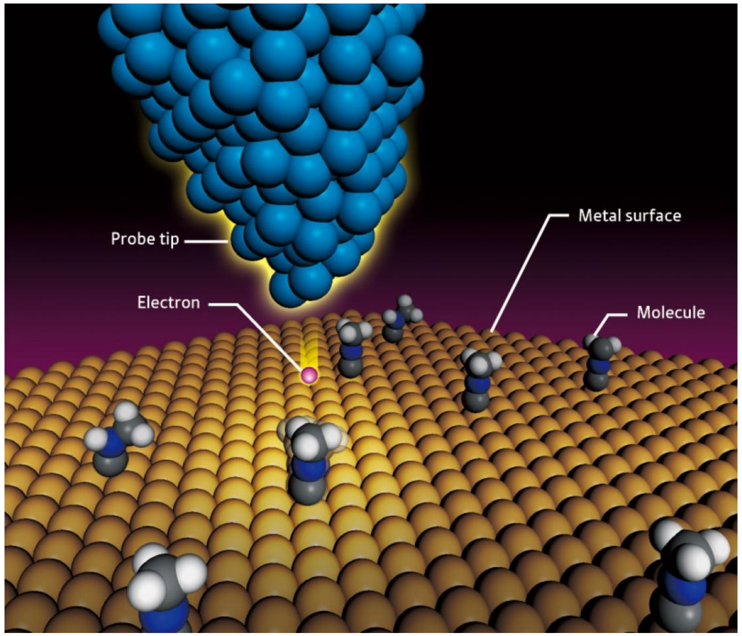


Open Systems

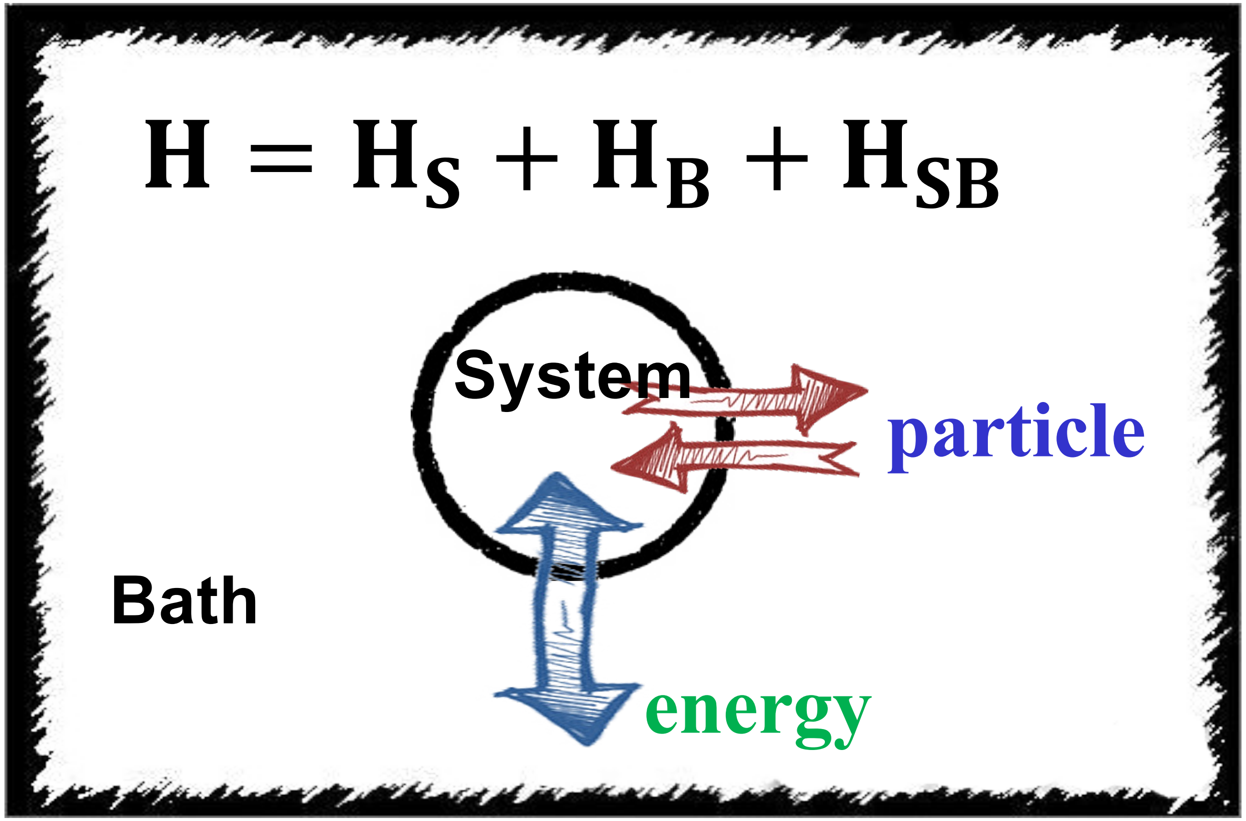






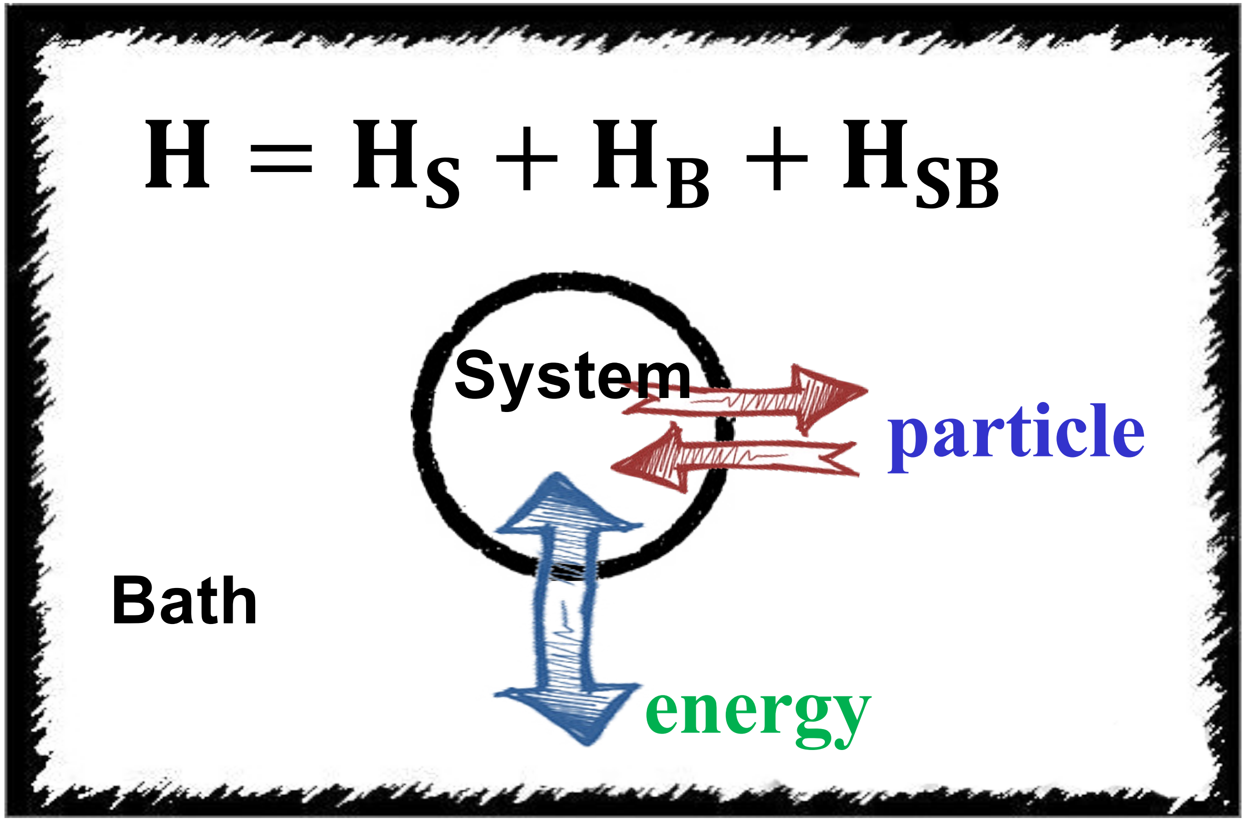


Open Systems



Quantum Dissipation Theory / Master Equation / Liouville-von Neumann Equation: model systems

Open Systems

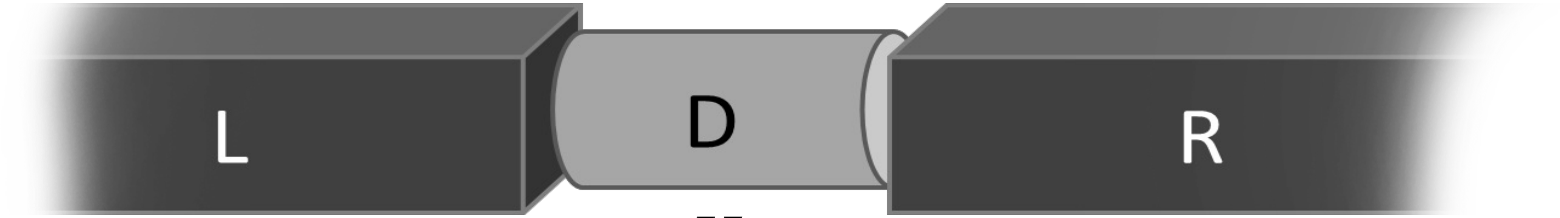


$$\begin{bmatrix} ES_S - H_S & ES_{SB} - H_{SB} \\ ES_{SB}^{+} - H_{SB}^{+} & ES_B - H_B \end{bmatrix} \times \begin{bmatrix} G_S & G_{SB} \\ G_{BS} & G_B \end{bmatrix} = \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix}$$

Green's function: $G_S(E) = \{ES_S - [H_S + \Sigma_B(E)]\}^{-1}$

Self-energy: $\Sigma_B(E) = (ES_{SB} - H_{SB})^{+} G_B (ES_{SB} - H_{SB})$

Environment



Green's Function (*G*) :

- **Charge density**

$$\rho = \frac{i}{2\pi}\int dE\left[G^{<}(E)\right]$$

- **DOS**

$$D(E) = -\frac{1}{\pi}\mathrm{Im}[G^{r}(E)]$$

- **Potential**

$$\nabla^2 V = -4\pi\rho$$

Self-energy (Σ) :

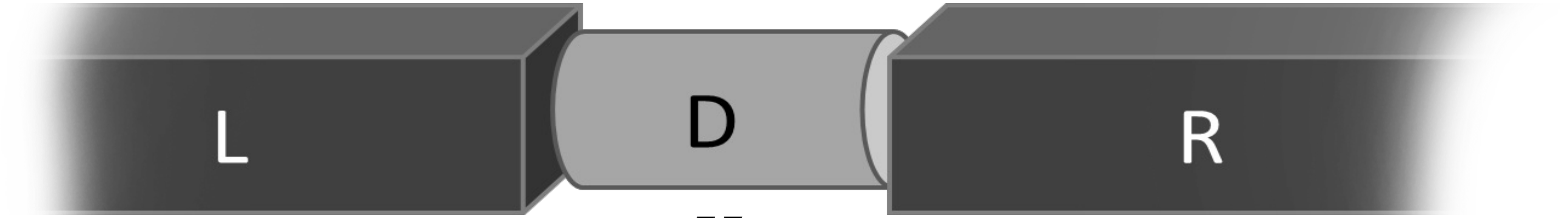
- **Current**

$$I = \frac{2e}{h}\int\frac{dE}{2\pi}\mathrm{Tr}[\Sigma^{<}(E)G^{>}(E) - \Sigma^{>}(E)G^{<}(E)]$$

- **Transmission**

$$T(E) = \mathrm{Tr}\left[\Gamma_L(E)G_D^{r}(E)\Gamma_R(E)G_D^{\dagger}(E)\right]$$

Environment



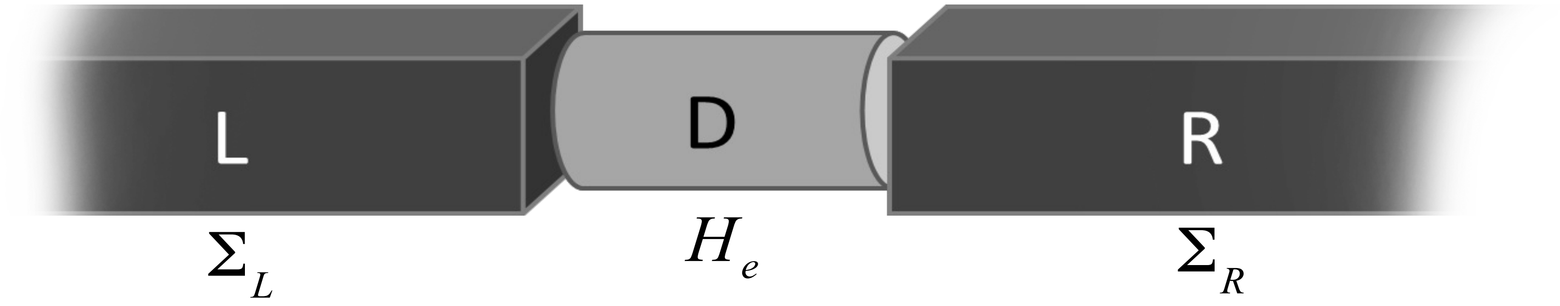
Σ_L H_e Σ_R

$$[EI - H]g = I$$

$$\begin{pmatrix} E\mathbf{I}_{1,1} - \mathbf{H}_{1,1} & -\mathbf{H}_{1,2} & \mathbf{0} & \cdots \\ -\mathbf{H}_{1,2}^{\dagger} & E\mathbf{I}_{2,2} - \mathbf{H}_{2,2} & -\mathbf{H}_{2,3} & \cdots \\ \mathbf{0} & -\mathbf{H}_{2,3}^{\dagger} & E\mathbf{I}_{3,3} - \mathbf{H}_{3,3} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \mathbf{g} = \begin{pmatrix} \mathbf{g}_{1,1} & \mathbf{g}_{1,2} & \mathbf{g}_{1,3} & \cdots \\ \mathbf{g}_{2,1} & \mathbf{g}_{2,2} & \mathbf{g}_{2,3} & \cdots \\ \mathbf{g}_{3,1} & \mathbf{g}_{3,2} & \mathbf{g}_{3,3} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\Sigma_L^r(E) = H_{DL} g_L^r(E) H_{LD}$$

Environment



$$(\omega - H_{00})G_{00} = I + H_{01}G_{10}$$
$$(\omega - H_{00})G_{10} = H_{01}^{+}G_{00} + H_{01}G_{20}$$
$$\vdots$$
$$(\omega - H_{00})G_{n0} = H_{01}^{+}G_{n-1,0} + H_{01}G_{n+1,0}$$

$$(\omega - \varepsilon_{1s})G_{00} = I + \alpha_1 G_{20}$$

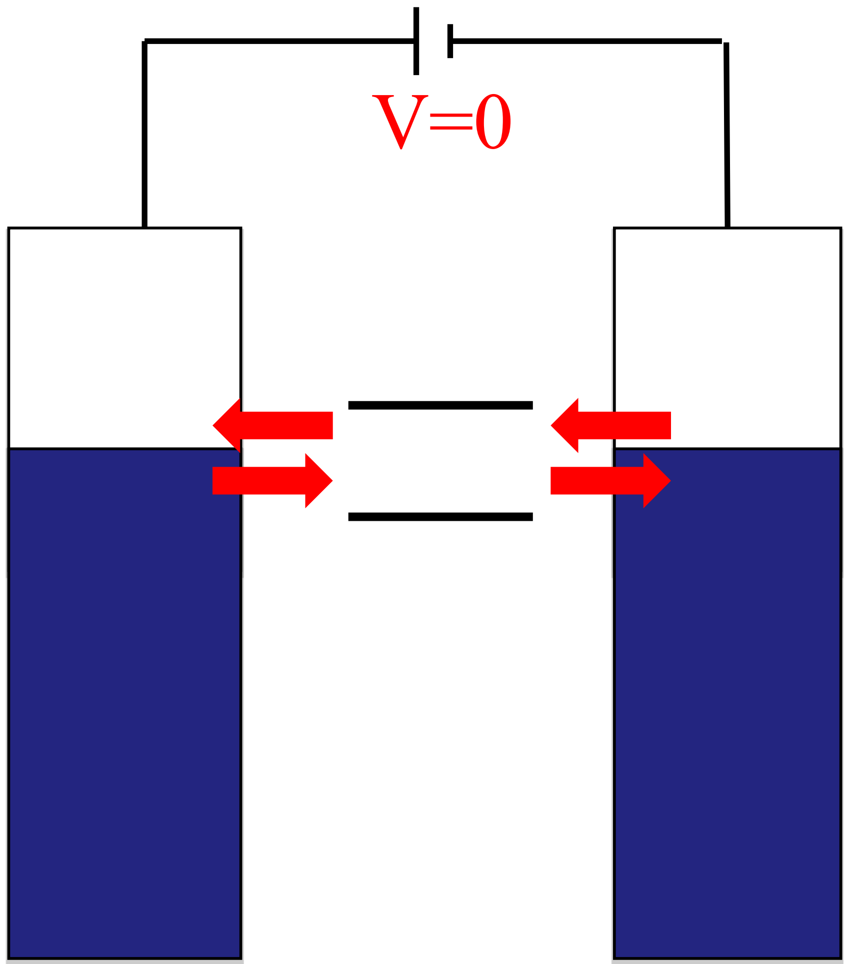
$$(\omega - \varepsilon_1)G_{2n,0} = \beta_1 G_{2(n-1),0} + \alpha_1 G_{2(n+1),0}$$

$$(\omega - \varepsilon_1)G_{2n,2n} = I + \beta_1 G_{2(n-1),2n} + \alpha_1 G_{2(n+1),2n}.$$

$$\begin{cases} \boldsymbol{\alpha}_{n+1} = \boldsymbol{\alpha}_n - \boldsymbol{\beta}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\gamma}_n, \\ \boldsymbol{\beta}_{n+1} = -\boldsymbol{\beta}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\beta}_n, \\ \boldsymbol{\gamma}_{n+1} = -\boldsymbol{\gamma}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\gamma}_n, \\ \boldsymbol{\lambda}_{n+1} = \boldsymbol{\lambda}_n - \boldsymbol{\gamma}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\beta}_n - \boldsymbol{\beta}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\gamma}_n, \\ \boldsymbol{\eta}_{n+1} = \boldsymbol{\eta}_n - \boldsymbol{\beta}_n \boldsymbol{\lambda}_n^{-1} \boldsymbol{\gamma}_n. \end{cases}$$

Quantum Transport

$$I = \frac{2e}{h}\int \frac{dE}{2\pi}\,\mathrm{Tr}[\Sigma^{<}(E)G^{>}(E) - \Sigma^{>}(E)G^{<}(E)]$$



Quantum Transport

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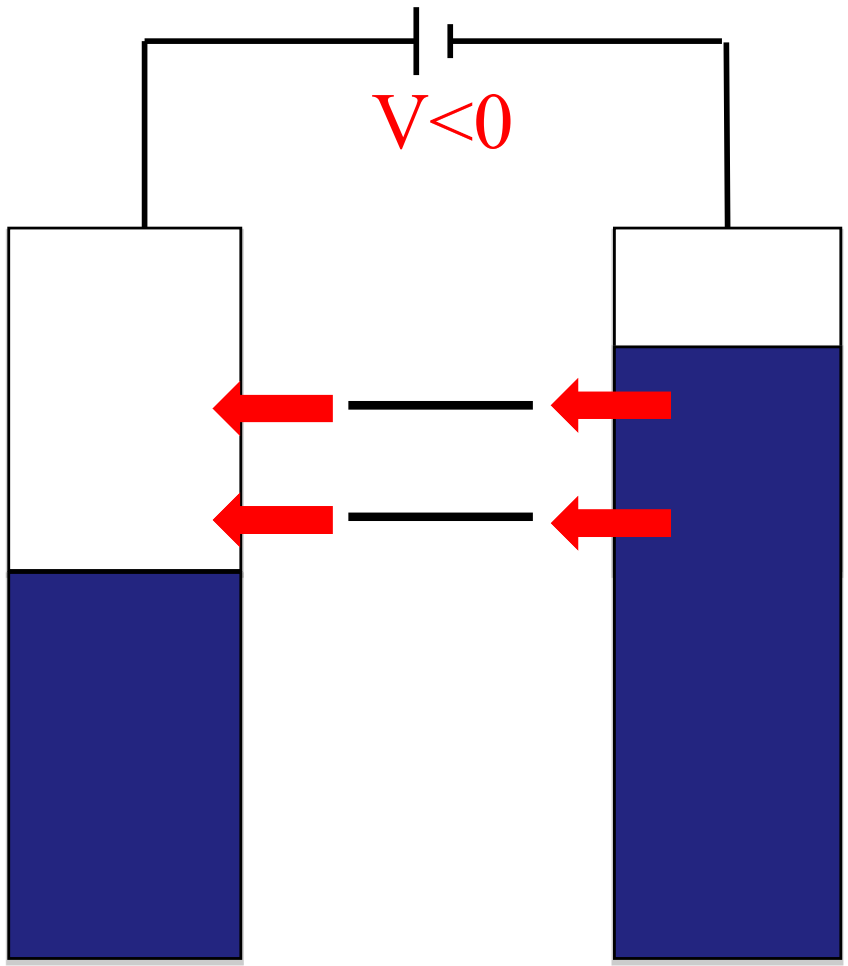
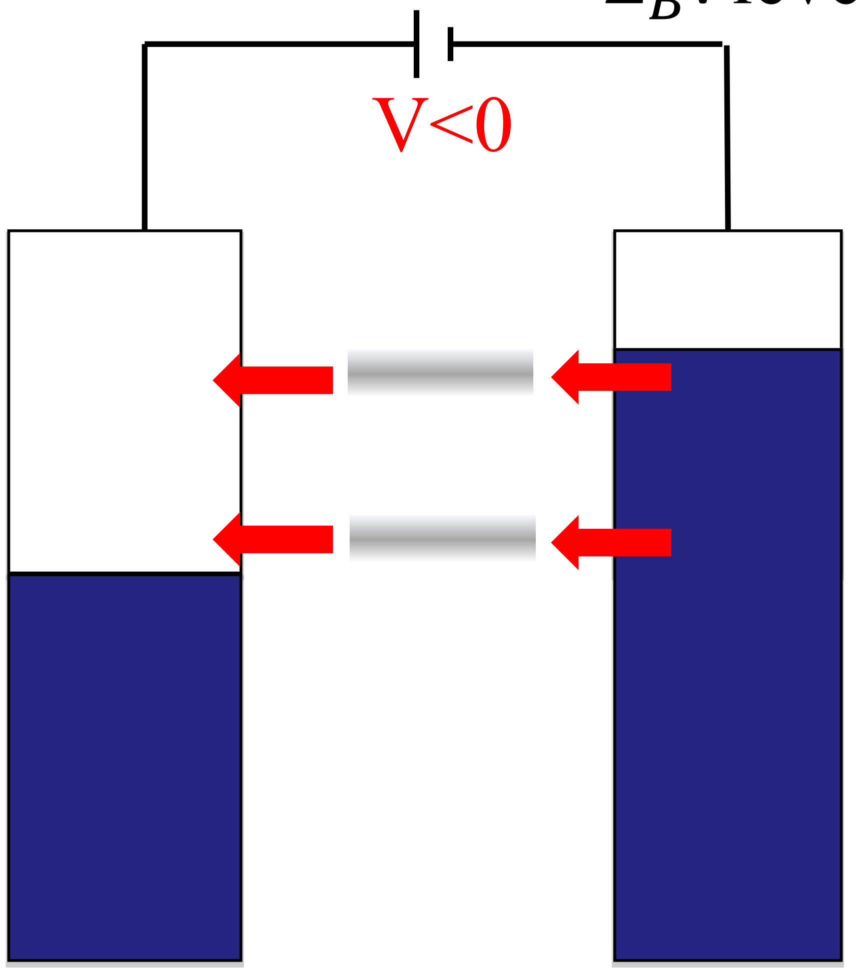


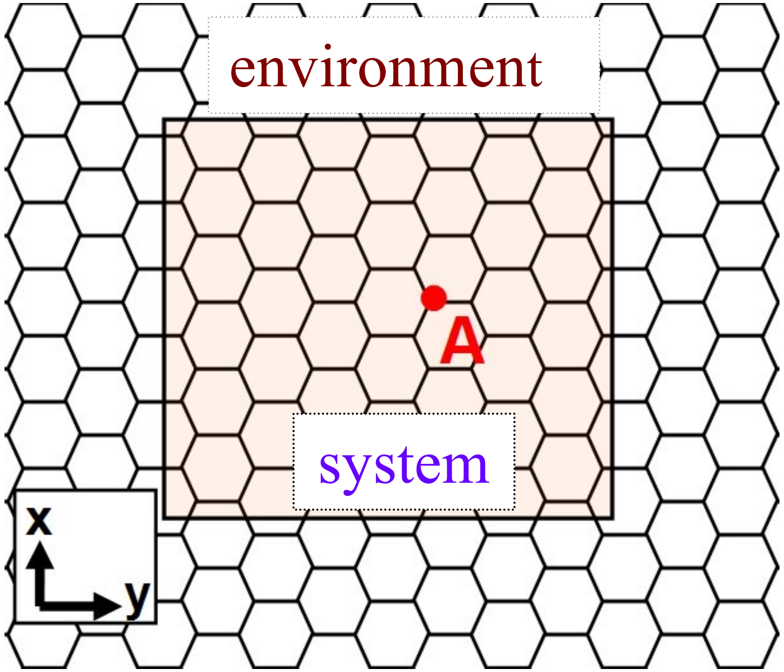
Quantum Transport

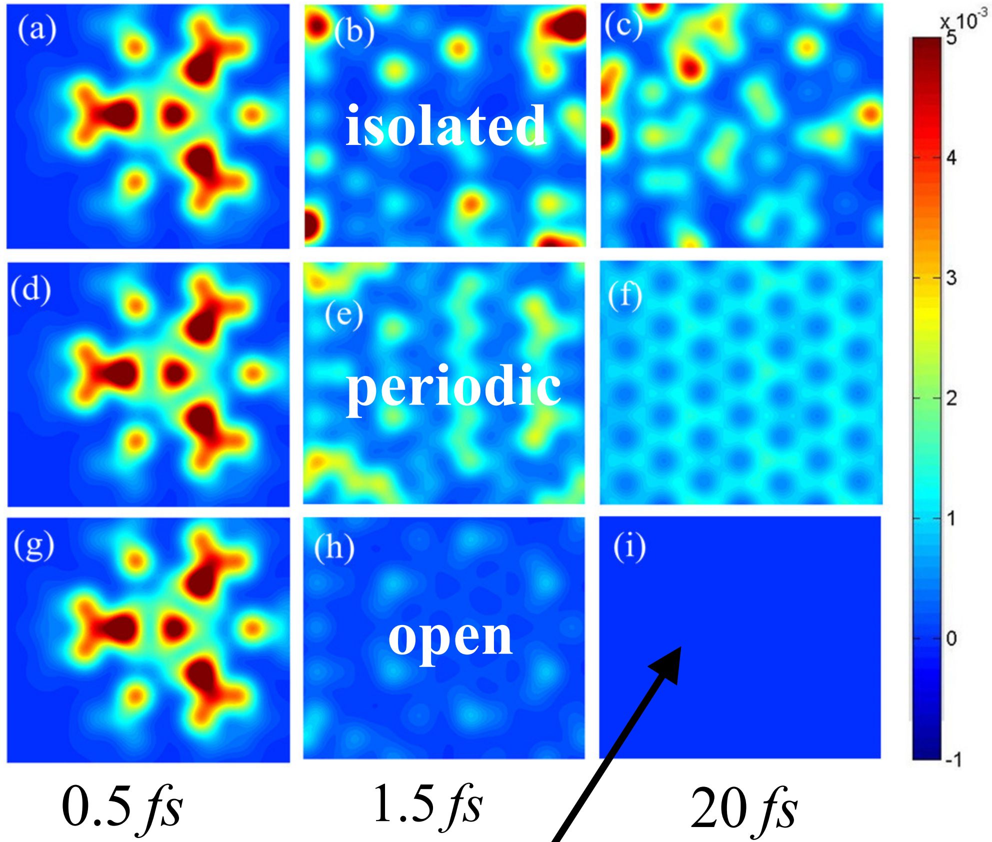
$$I = \frac{2e}{h}\int \frac{dE}{2\pi}\,\mathrm{Tr}[\Sigma^{<}(E)G^{>}(E) - \Sigma^{>}(E)G^{<}(E)]$$

Σ_B: level shift, broadening



Molecules on Surface





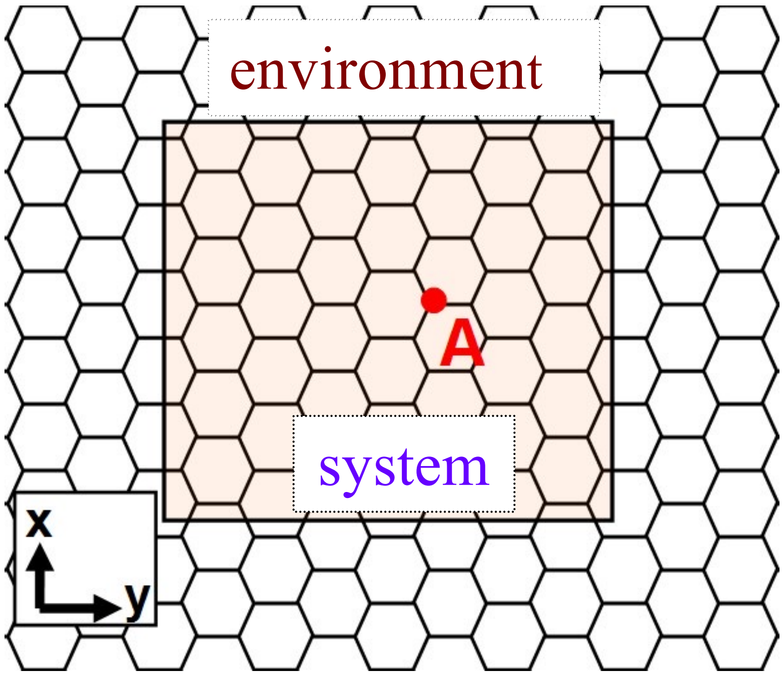
electron not conserved

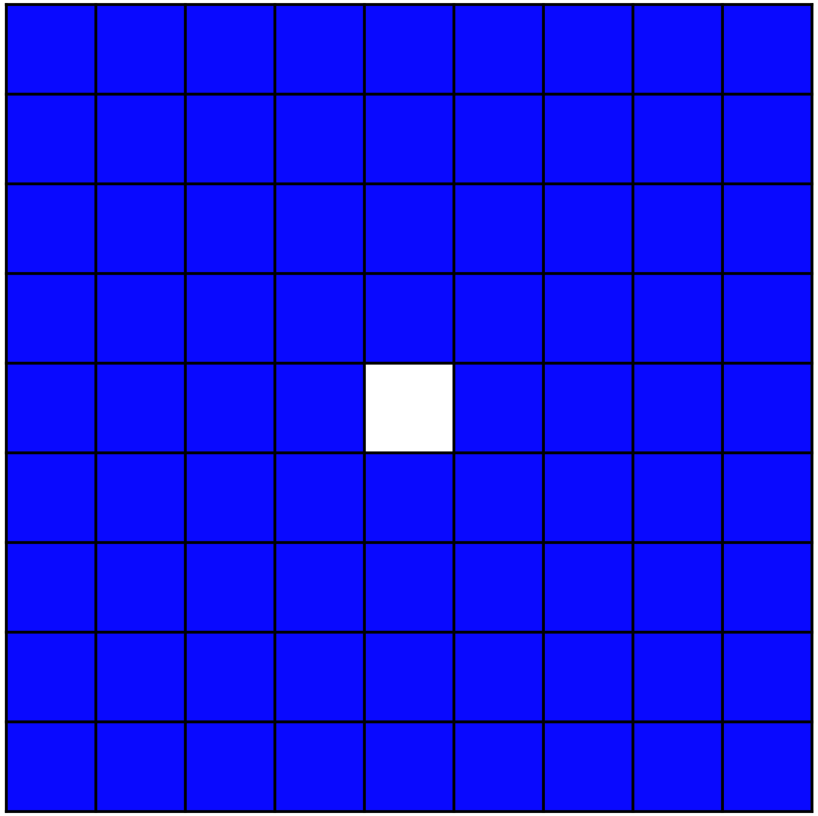
- tight-binding Hamiltonian
- an excess electron is injected onto atom A

Wang, Hou, Zheng Phys. Rev. B (2013)

Wang, Zheng, Chen and Yam. J. Chem. Phys. (2015)

Molecules on Surface





$$G^r_{\boldsymbol{R}_0}(\boldsymbol{R}_1,\boldsymbol{R}_2;\epsilon) = G^r_0(\boldsymbol{R}_2-\boldsymbol{R}_1;\epsilon) - \Delta G_{\boldsymbol{R}_0}(\boldsymbol{R}_1,\boldsymbol{R}_2;\epsilon),$$

$$\Delta G_{\boldsymbol{R}_0}(\boldsymbol{R}_1,\boldsymbol{R}_2;\epsilon) = G^r_0(\boldsymbol{R}_0-\boldsymbol{R}_1;\epsilon)[G^r_0(\boldsymbol{0};\epsilon)]^{-1} \times G^r_0(\boldsymbol{R}_2-\boldsymbol{R}_0;\epsilon),$$

External Field

$$\vec{A} = \vec{a}\left(\frac{\hbar\sqrt{\tilde{\mu}\tilde{\varepsilon}}}{2N\omega\varepsilon c}F_r\right)^{1/2}\left(be^{-i\omega t} + b^{\dagger}e^{i\omega t}\right)$$

$$H_{ep} = \sum_{\mu\nu}\frac{e}{m}\left\langle\mu\middle|\vec{A}\cdot\vec{p}\middle|\nu\right\rangle d_{\mu}^{*}d_{\nu} = \sum_{\mu\nu}M_{\mu\nu}(be^{-i\omega t} + b^{*}e^{i\omega t})d_{\mu}^{*}d_{\nu}$$

$$\Sigma_{ep}(\tau,\tau') = iM\left[D(\tau,\tau')G(\tau,\tau')\right]M$$

Photon Green's Function:

$$D^{>}(t,t') = [Ne^{i\omega(t-t')} + (N+1)e^{-i\omega(t-t')}]$$

$$D^{<}(t,t') = [Ne^{-i\omega(t-t')} + (N+1)e^{i\omega(t-t')}]$$

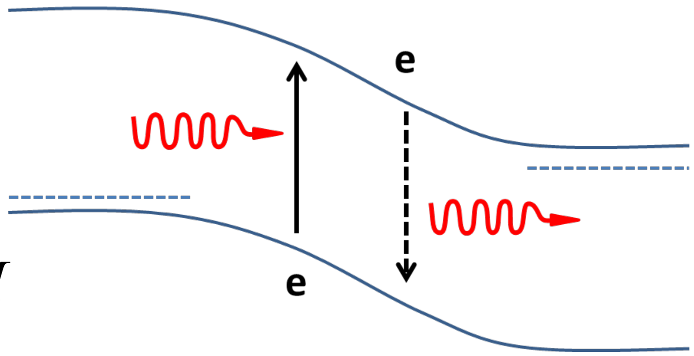
Fourier transform:

$$\Sigma_{ep}^{<,>}(E) = M\left[NG^{<,>}(E\mp\hbar\omega) + (N+1)G^{<,>}(E\pm\hbar\omega)\right]M$$

absorption emission

External Field

$$F(\omega) = \frac{1}{\hbar}\int \frac{dE}{2\pi}\mathrm{Tr}\left[\Sigma_{ep}^{<}(E)G^{>}(E) - \Sigma_{ep}^{>}(E)G^{<}(E)\right]$$



$$\Sigma_{ep}^{<,>}(E) = M\left[NG^{<,>}(E \mp \hbar\omega) + (N+1)G^{<,>}(E \pm \hbar\omega)\right]M$$

Absorption of photon

$$\frac{1}{\hbar}\int \frac{dE}{2\pi}\mathrm{Tr}N\left[MG^{<}(E-\hbar\omega)MG^{>}(E)\right]$$

hole density at E

electron density at E - $\hbar\omega$

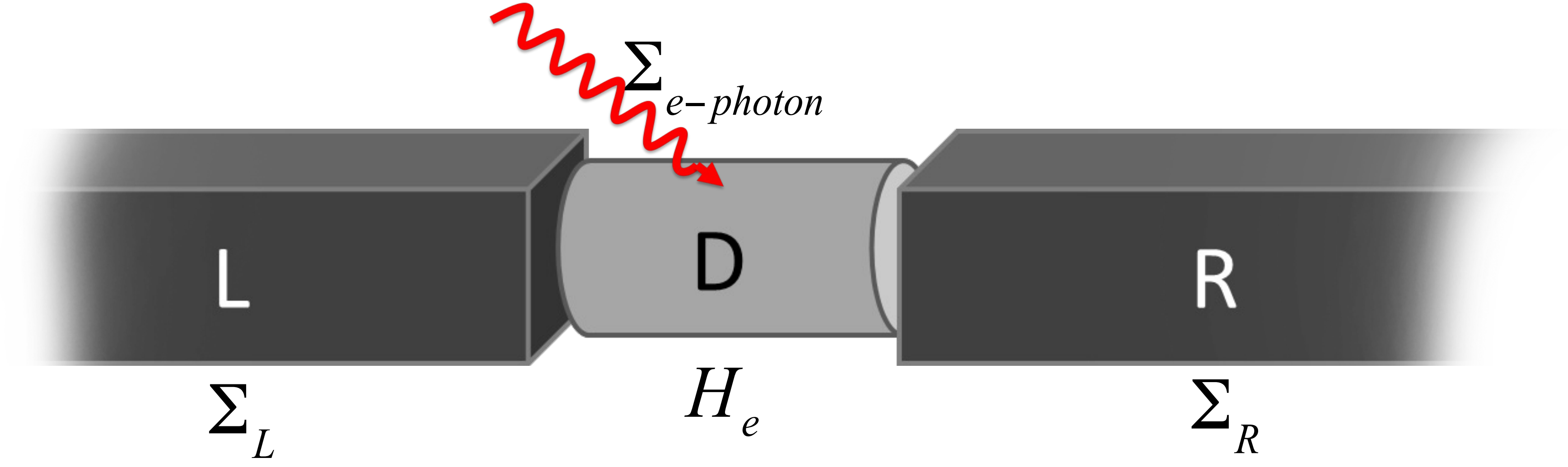
Emission

$$\frac{1}{\hbar}\int \frac{dE}{2\pi}\mathrm{Tr}\left[MG^{>}(E-\hbar\omega)MG^{<}(E)\right]$$

Absorption flux:

$$F_a(\hbar\omega) = \frac{1}{\hbar}\int \frac{dE}{2\pi}\mathrm{Tr}N\left[MG^{<}(E-\hbar\omega)MG^{>}(E) - MG^{>}(E-\hbar\omega)MG^{<}(E)\right]$$

External Field



Self-energy:

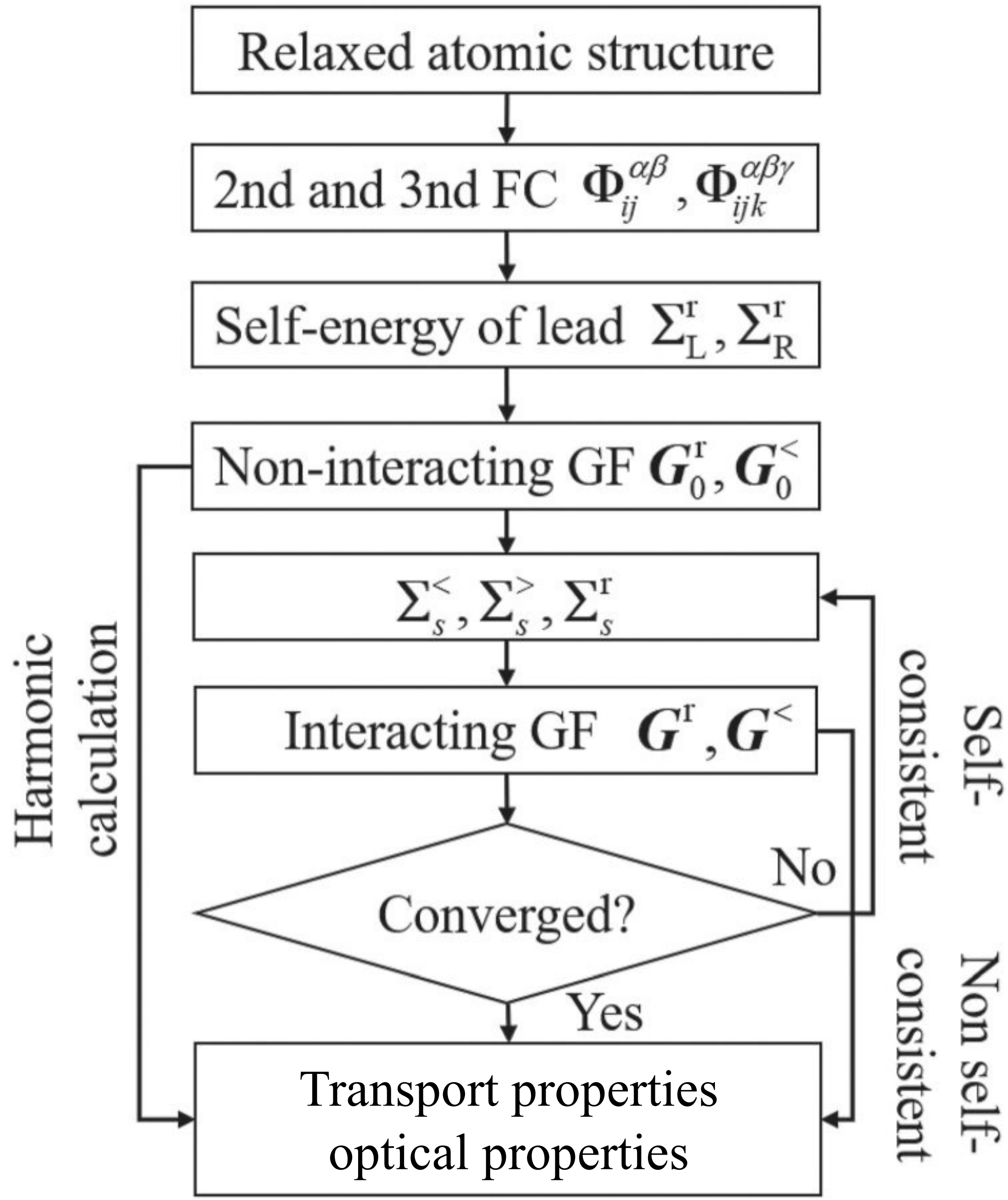
$$G^r(E) = \left[ES - H - \Sigma^r_L(E) - \Sigma^r_R(E) - \Sigma^r_{ep}(E)\right]^{-1}$$

- electronic structure includes effect from e-p interaction

Current:

- elastic part: $I^{el}_{\alpha} = \frac{2e}{\hbar}\int \frac{dE}{2\pi}\left(f_{\alpha} - f_{\beta}\right)\mathrm{Tr}\left[\Gamma_{\alpha}(E)G^r(E)\Gamma_{\beta}(E)G^a(E)\right]$
- inelastic part: $I^{inel}_{\alpha} = \frac{2e}{\hbar}\int \frac{dE}{2\pi}\mathrm{Tr}[\Gamma_{\alpha}(E)G^r(E)\Gamma_{eff}(E)G^a(E)]$

Workflow


Relaxed atomic structure
2nd and 3nd FC $\Phi_{ij}^{\alpha\beta}, \Phi_{ijk}^{\alpha\beta\gamma}$
Self-energy of lead Σ_L^r, Σ_R^r
Non-interacting GF $G_0^r, G_0^<$
$\Sigma_s^<, \Sigma_s^>, \Sigma_s^r$
Interacting GF $G^r, G^<$
Converged?
No
Yes
Transport properties
optical properties
Harmonic calculation
Self-consistent
Non self-consistent

Time-Dependent Case

VOLUME 52, NUMBER 12 PHYSICAL REVIEW LETTERS 19 MARCH 1984

Density-Functional Theory for Time-Dependent Systems

Erich Runge and E. K. U. Gross
Institut für Theoretische Physik, Johann Wolfgang Goethe-Universität, D-6000 Frankfurt, Federal Republic of Germany
(Received 16 August 1983)

Theorem – With a fixed initial state $\Phi(t_0) = \Phi_0$, the time-dependent electron density $\rho(\boldsymbol{r}, t)$ uniquely determines the external potential $v(\boldsymbol{r}, t)$ [apart from a time-dependent constant $C(t)$] .

Runge-Gross Theorem

$$\rho(r,t) \xrightarrow{\text{Runge-Gross}} v(r,t) \xrightarrow{\text{Schrodinger Eq.}} \Psi(r_1 \cdots r_N, t)$$

Time-dependent Kohn-Sham Theorem

$$v_{ext}(r,t) \xleftrightarrow{\text{interacting}} \rho(r,t) \xleftrightarrow{\text{non-interacting}} v_{KS}(r,t)$$

true system Kohn-Sham system

TDDFT in time domain

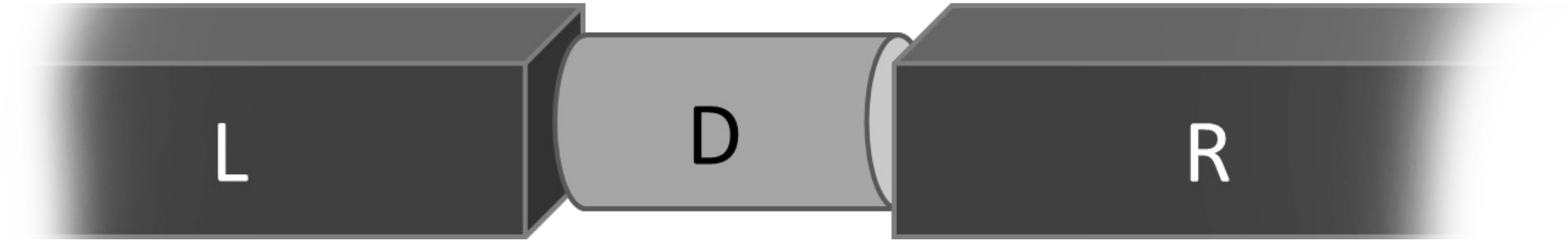
Time–dependent Kohn-Sham equation:

$$i\hbar\frac{\partial\psi_i}{\partial t} = h_{KS}\psi_i = \left(-\frac{1}{2}\nabla^2 + \upsilon_{\text{eff}}(t)\right)\psi_i$$

EOM for one-electron density matrix:

$$i\hbar\dot{\rho} = [h, \rho]$$

TDDFT in time domain



$$i\hbar\dot{\rho}(t) = [h(t), \rho(t)]$$

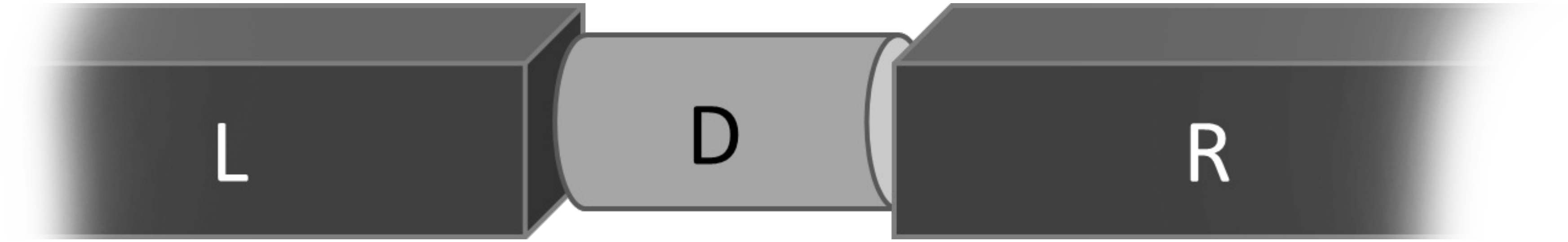
$$\rho_{ij}(t) = \langle a_j^+(t) a_i(t) \rangle$$

$$\rho = \begin{bmatrix} \rho_L & \rho_{LD} & \rho_{LR} \\ \rho_{DL} & \rho_D & \rho_{DR} \\ \rho_{RL} & \rho_{RD} & \rho_R \end{bmatrix}$$

$$i\dot{\rho}_{nm}(t) = \sum_{l\in D} (h_{nl}\rho_{lm} - \rho_{nl}h_{lm}) - i \sum_{\alpha=L,R} Q_{\alpha,nm}$$

$$Q_{\alpha,nm} = i \sum_{k_\alpha \in \alpha} \left(h_{nk_\alpha}\rho_{k_\alpha m} - \rho_{nk_\alpha} h_{k_\alpha m} \right)$$

TDDFT in time domain

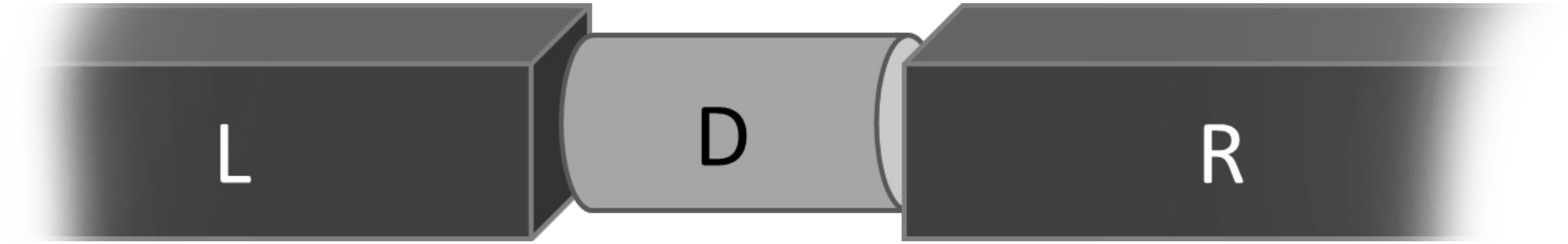


$$Q_{\alpha,nm} = i \sum_{k_\alpha \in \alpha} \left(h_{nk_\alpha} \rho_{k_\alpha m} - \rho_{nk_\alpha} h_{k_\alpha m} \right)$$

$$J_\alpha(t) = -\sum_{k_\alpha \in \alpha} \frac{d}{dt} \rho_{k_\alpha k_\alpha}(t) = i \sum_{l \in D} \sum_{k_\alpha \in \alpha} \left(h_{k_\alpha l} \rho_{l k_\alpha} - \rho_{k_\alpha l} h_{l k_\alpha} \right)$$

$$= -\sum_{l \in D} Q_{\alpha,ll} = -\mathrm{Tr}[Q_\alpha(t)]$$

Time-dependent Quantum Transport

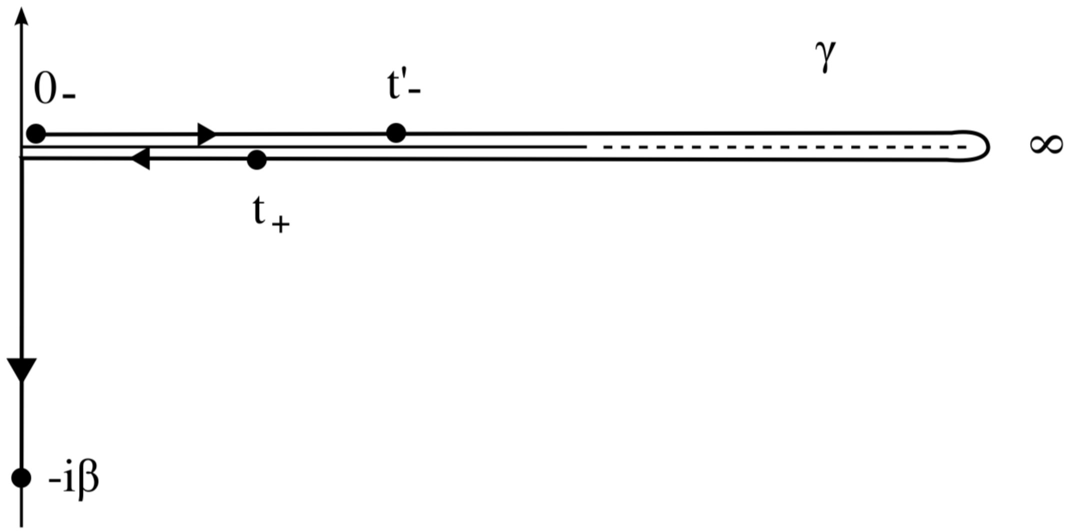


$$\boldsymbol{\rho} = \begin{bmatrix} \rho_L & \rho_{LD} & \rho_{LR} \\ \rho_{DL} & \rho_D & \rho_{DR} \\ \rho_{RL} & \rho_{RD} & \rho_R \end{bmatrix} \qquad \boldsymbol{H} = \begin{bmatrix} h_L & h_{LD} & h_{LR} \\ h_{DL} & h_D & h_{DR} \\ h_{RL} & h_{RD} & h_R \end{bmatrix}$$

$$i\dot{\rho_D}(t) = [h_D(t), \rho_D(t)] - i\sum_{\alpha} Q_{\alpha}$$

$$Q_{\alpha,nm}(t) = -\sum_{l\in D}\int_{-\infty}^{\infty} d\tau\left[G_{nl}^{r}(t,\tau)\Sigma_{\alpha,lm}^{<}(\tau,t) + G_{nl}^{<}(t,\tau)\Sigma_{\alpha,lm}^{a}(\tau,t) + \mathrm{H.c.}\right]$$

Keldysh Formalism

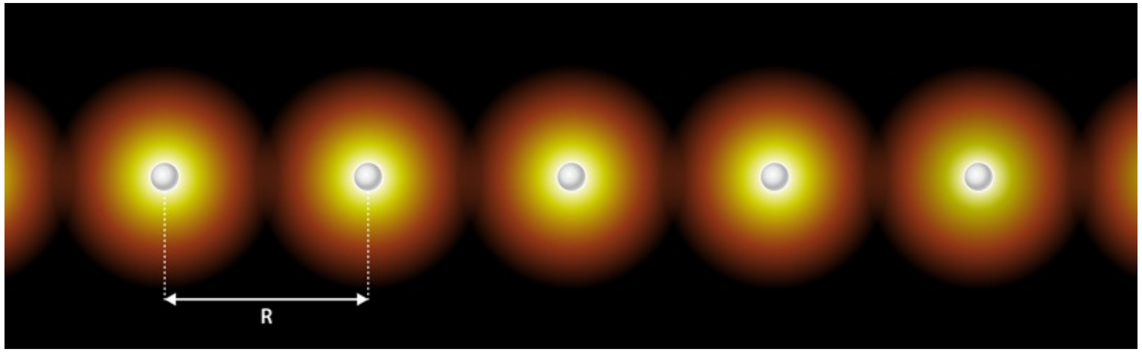


$$G_{k_\alpha m}(t,t') \equiv -i\left\langle T_C\left\{a_{k_\alpha}(t)a_m^+(t')\right\}\right\rangle$$

$$G^<_{k_\alpha m}(t,t') \equiv -i\left\langle a_m^+(t')a_{k_\alpha}(t)\right\rangle$$

$$\Sigma^<_{\alpha,ln}(t,t') = \sum_{k_\alpha \in \alpha} h_{lk_\alpha}(t)g^<_{k_\alpha}(t,\tau)h_{k_\alpha n}(\tau)$$

Time-dependent Quantum Transport



$$G^r(t_1, t_2) = G_0^r(t_1, t_2) + \iint dt_3 dt_4\, G_0^r(t_1, t_3) \sum_\alpha V_\alpha(t_3, t_4)\, G^r(t_4, t_2)$$

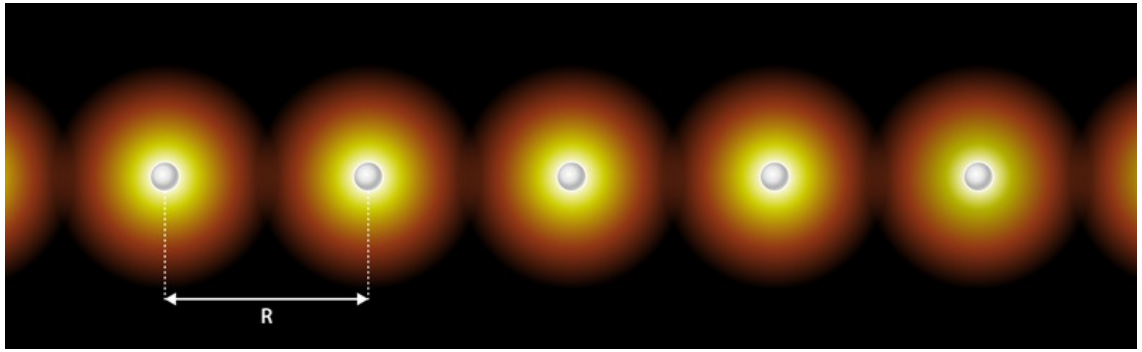
$$G^<(t_1, t_2) = \iint dt_3 dt_4\, G^r(t_1, t_3) \sum_\alpha \Sigma_\alpha^<(t_3, t_4)\, G^a(t_4, t_2)$$

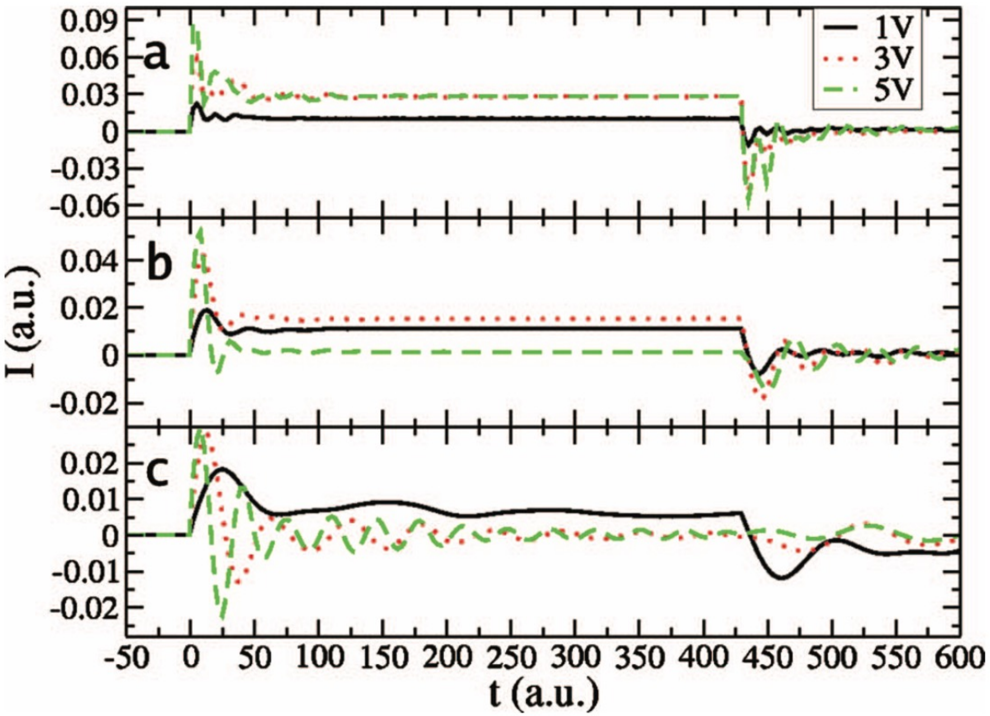
$$V_\alpha(t_1, t_2) = \Sigma_{0\alpha}^r(t_1 - t_2)\left(e^{i \int_{t_1}^{t_2} \Delta_\alpha(t) dt} - 1\right)$$

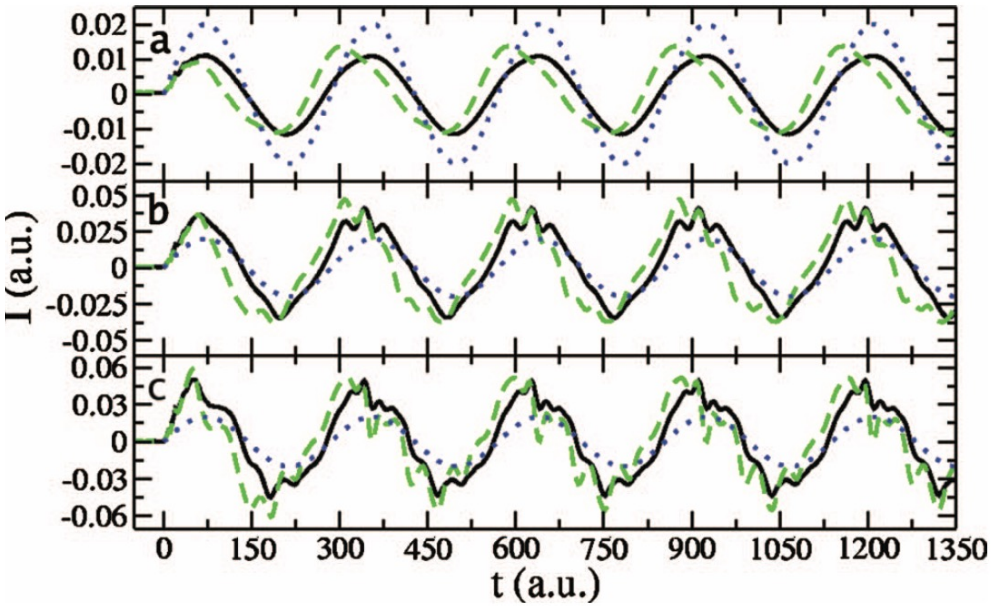
time meshs: ~200-600 points

Ke *et al*. *J. Chem. Phys* **132**, 234105 (2010)

Time-dependent Quantum Transport







Ke *et al*. *J. Chem. Phys* **132**, 234105 (2010)

TDDFT-NEGF

$$i\dot{\rho_D}(t) = [h_D(t), \rho_D(t)] - i\sum_{\alpha}[\varphi_\alpha(t) - \varphi_\alpha^{+}(t)]$$

auxiliary density matrix:

$$\varphi_\alpha(t) = i\int_{-\infty}^{t} d\tau[G^{<}(t,\tau)\Sigma_\alpha^{>}(\tau,t) - G^{>}(t,\tau)\Sigma_\alpha^{<}(\tau,t)]$$

outgoing incoming

self energies:

$$\Sigma_\alpha^{<,>}(\tau,t) = \pm 2i\int \frac{d\epsilon}{2\pi} f_\alpha^{\pm}(\epsilon) e^{i\int_\tau^t [\epsilon + \Delta_\alpha(t_1)]dt_1} \Lambda_\alpha(\epsilon)$$

$\Lambda_\alpha(\epsilon)$: line width function

$$I_\alpha(t) = i\mathrm{Tr}[\varphi_\alpha(t) - \varphi_\alpha^{\dagger}(t)]$$

TDDFT-NEGF

$$\boldsymbol{Q}_\alpha(t) = -i[\boldsymbol{\varphi}_\alpha(t) - \boldsymbol{\varphi}_\alpha^\dagger(t)] = -i\int d\epsilon[\boldsymbol{\varphi}_\alpha(\epsilon,t) - \boldsymbol{\varphi}_\alpha^\dagger(\epsilon,t)]$$

equation of motions of auxiliary density matrix:

$$i\dot{\varphi}_\alpha(\epsilon,t) = [h(t) - \epsilon - \Delta_\alpha(t)]\varphi_\alpha(\epsilon,t)$$
$$+[f_\alpha(\epsilon) - \rho]\Lambda_\alpha(\epsilon) + \sum_{\alpha'}\int d\epsilon'\,\varphi_{\alpha,\alpha'}(\epsilon,\epsilon',t)$$

$$i\dot{\varphi}_{\alpha,\alpha'}(\epsilon,\epsilon',t) = -[\epsilon + \Delta_\alpha(t) - \epsilon' - \Delta_{\alpha'}(t)]\,\varphi_{\alpha,\alpha'}(\epsilon,\epsilon',t)$$
$$+\Lambda_{\alpha'}(\epsilon')\,\varphi_\alpha(\epsilon,t) - \varphi_\alpha^+(\epsilon',t)\Lambda_\alpha(\epsilon)$$

solve: $\rho, \varphi_\alpha, \varphi_{\alpha,\alpha'}$

Wide Band Approximation

$$\Sigma_\alpha^{<,>}(\tau,t) = \pm 2i \int \frac{d\epsilon}{2\pi} f_\alpha^{\pm}(\epsilon) e^{i\int_\tau^t [\epsilon+\Delta_\alpha(t_1)]dt_1} \Lambda_\alpha$$

Padé expansion of Fermi-Dirac distribution:

$$f_\alpha^{\pm}(\epsilon) \approx \frac{1}{2} \mp \sum_k^N \left[\frac{\eta_k}{\beta(\epsilon-\mu_\alpha)+i\zeta_k} + \frac{\eta_k}{\beta(\epsilon-\mu_\alpha)-i\zeta_k} \right]$$

Wide Band Approximation

$$\varphi_\alpha(t) = i[\rho(t) - 1/2]\Lambda_\alpha + \sum_k^N \varphi_{\alpha k}(t)$$

$$\varphi_{\alpha k}(t) = -i\int_{-\infty}^{\infty} d\tau\, G^r(t,\tau)\Sigma_{\alpha k}^{+}(\tau,t)$$

$$\Sigma_{\alpha k}^{+}(\tau,t) = \frac{2}{\beta}\eta_k e^{i\int_\tau^t \epsilon_{\alpha k}^{\pm}(t_1)dt_1}\Lambda_\alpha$$

$\epsilon_{\alpha k}^{\pm}$ relates to *k*th Padé poles and time-dependent external bias voltage

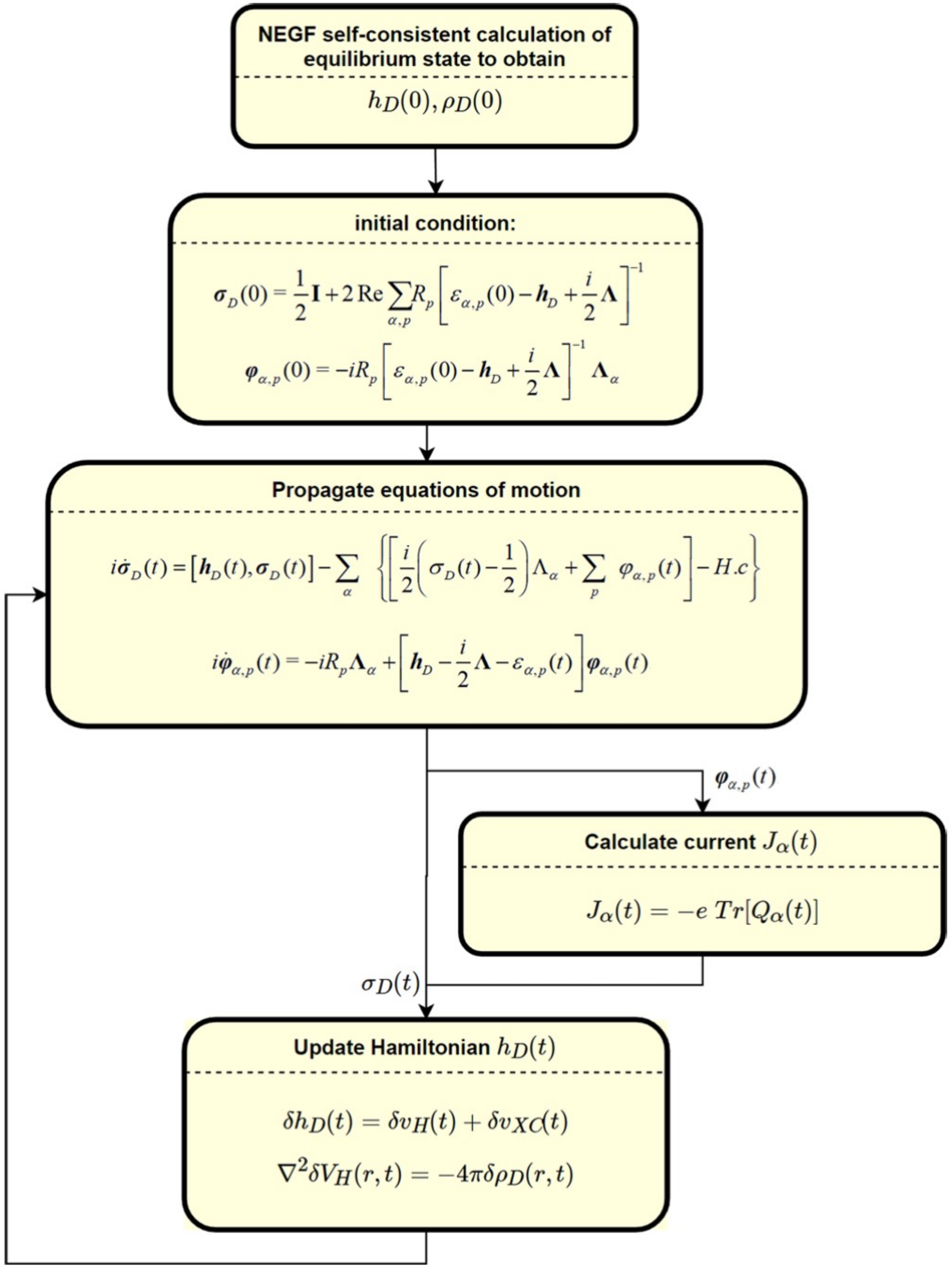
equation of motion for the auxiliary density matrix:

$$i\dot{\varphi}_{\alpha k}(t) = -\frac{2i\eta_k}{\beta}\Lambda_\alpha - [\epsilon_{\alpha k}^{+}(t) - h(t) + i\Lambda]\varphi_{\alpha k}(t)$$

with initial condition:

$$0 = -\frac{2i\eta_k}{\beta}\Lambda_\alpha - [\epsilon_{\alpha k}^{+}(0) - h(0) + i\Lambda]\varphi_{\alpha k}(0)$$

Wide Band Approximation



Lorentzian Decomposition

$$Q_\alpha(t) = \int d\varepsilon \int_{-\infty}^{t} dt_1 \sum_{\upsilon'\in D} \{[G^{<}_{\mu\upsilon'}(t,t_1)\Sigma^{>}_{\upsilon'\upsilon}(t_1,t;\varepsilon) - G^{>}_{\mu\upsilon'}(t,t_1)\Sigma^{<}_{\upsilon'\upsilon}(t_1,t;\varepsilon)] - H.c.\}$$

$$\Sigma^{<,>}_{\alpha}(t,\tau;\varepsilon) = \pm i e^{-i\int_{\tau}^{t}\Delta_\alpha(\xi)d\xi} e^{-i\varepsilon(t-\tau)} f_\alpha^{\pm}(\varepsilon)\Lambda_\alpha(\varepsilon)$$

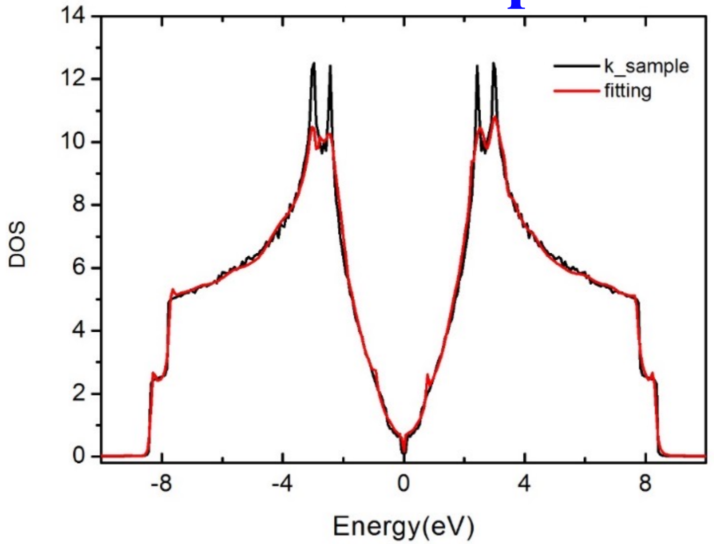
$f_\alpha^{\pm}(\varepsilon)$: ***Fermi distribution function***

$\Lambda_\alpha(\varepsilon)$: ***Linewidth function due to α lead***

$f_\alpha^{\pm}(\varepsilon)$: Padé expansion

$$f_\alpha^{\pm}(\varepsilon) \approx \frac{1}{2} \pm \sum_{k}^{N} [\frac{\eta_k}{\beta(\varepsilon-\mu_\alpha)+i\zeta_k} + \frac{\eta_k}{\beta(\varepsilon-\mu_\alpha)-i\zeta_k}]$$

Lorentzian Decomposition



Zheng, Chen, Mo, Koo, Tian, Yam & Yan, JCP 133, 114101 (**2010**)

Lorentzian Decomposition

$$i\dot{\sigma}_D = \left[h_D, \sigma_D\right] - i\sum_{\alpha=L,R} Q_\alpha(t) \qquad Q_\alpha(t) = i\sum_{k=1}^{N_k}\left[\varphi_{\alpha k}(t) - \varphi^\dagger_{\alpha k}(t)\right]$$

$$i\dot{\varphi}_{\alpha k} = \left[h_D(t) - i\gamma_{\alpha k} - \Delta_\alpha(t)\right]\varphi_{\alpha k}(t)$$
$$+i\left[\sigma_D(t)A^>_{\alpha k} + \bar{\sigma}_D(t)A^<_{\alpha k}\right]$$
$$+\sum_{\alpha'}\sum_{k'=1}^{N_k}\varphi_{\alpha k,\alpha' k'}(t)$$

1st-tier auxiliary matrix

$$i\dot{\varphi}_{\alpha k,\alpha' k'} = -\left[i\gamma_{\alpha k} + \Delta_\alpha(t) - i\gamma_{\alpha' k'} - \Delta_{\alpha'}(t)\right]\varphi_{\alpha k,\alpha' k'}(t)$$
$$+i\left(A^>_{\alpha' k'} - A^<_{\alpha' k'}\right)\varphi_{\alpha k}(t)$$
$$-i\varphi^\dagger_{\alpha' k'}(t)\left(A^>_{\alpha k} - A^<_{\alpha k}\right)$$

2nd -tier auxiliary matrix

Zheng et. al. JCP 133, 114101 (2010)

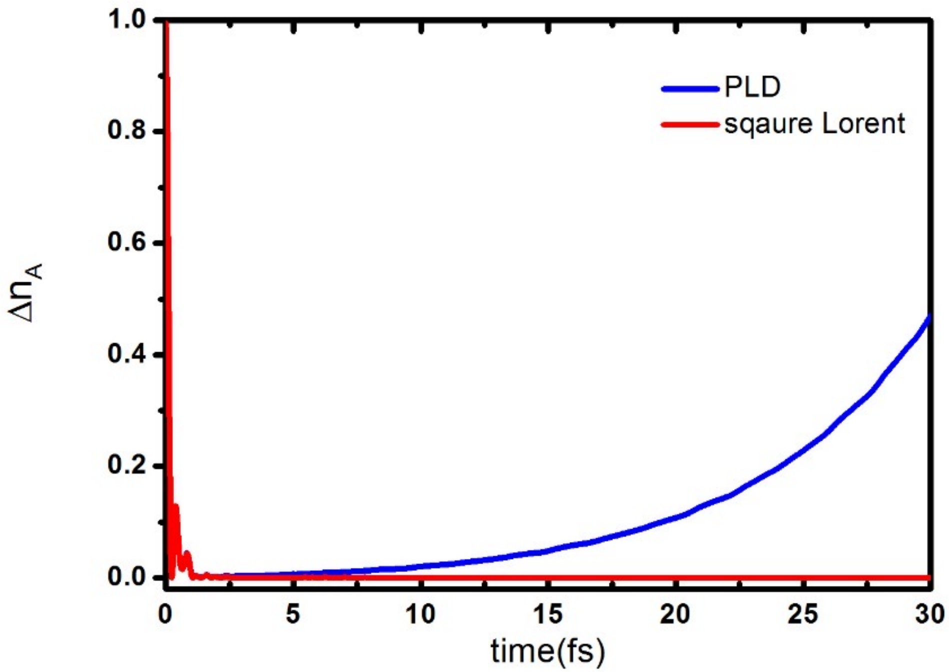
Self-energy: Lorentzian expansion
Fermi function: Padé expansion

Lorentzian Decomposition

Squared-Lorentzian decomposition

$$\Lambda_\alpha(\acute{U}) = \sum_{d=1}^{N_d}\sum_{d'=1}^{N_{d'}} \frac{\eta_d}{(\acute{U}-\Omega_d)^2 + W_d{}^2} \times \frac{\eta_{d'}}{(\acute{U}-\Omega_{d'})^2 + W_{d'}{}^2} \bar{\Lambda}_{\alpha,d}\bar{\Lambda}_{\alpha,d'}$$

maintain the positivity of spectral function



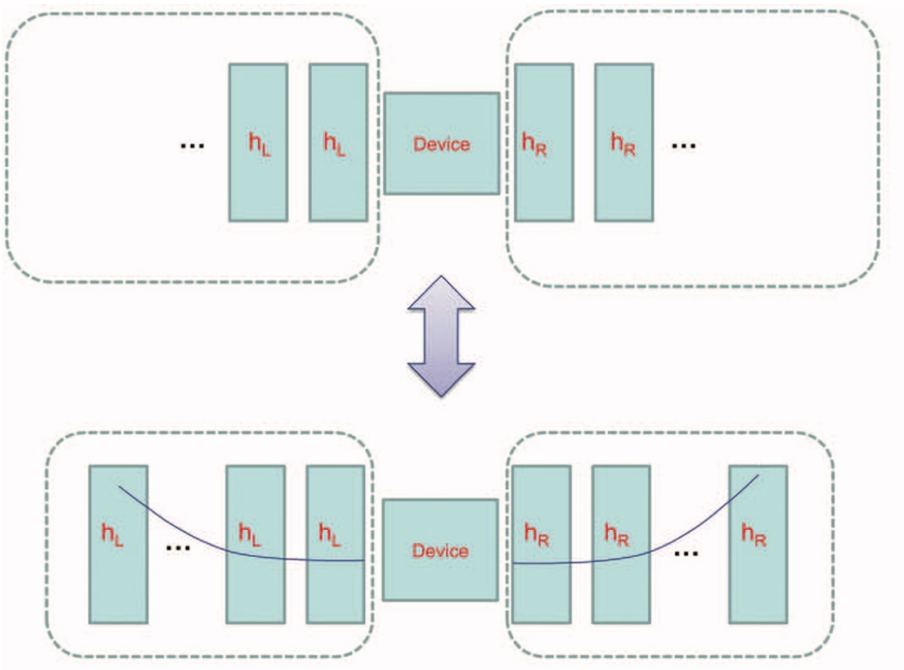
Wang, Zheng, Chen and Yam. J. Chem. Phys. (2015)

Complex Absorbing Potential

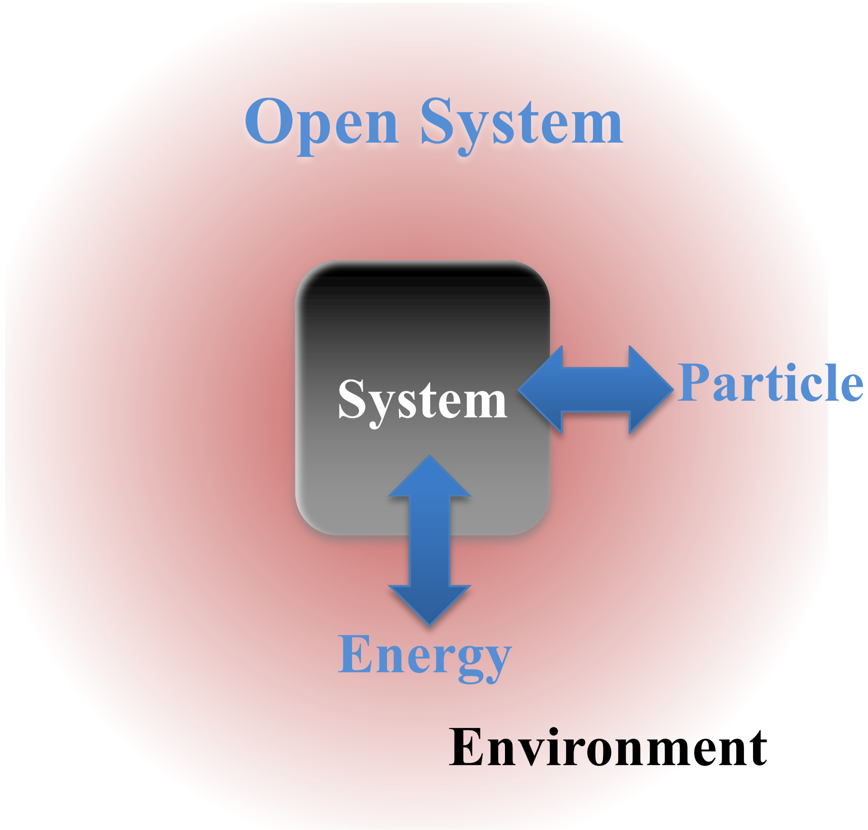
$$W(r) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{r_1}\right)^2 \frac{4}{c^2}\left[\frac{r_1^2}{(r_1 - r)^2} + \frac{r_1^2}{(r_1 + r)^2} - 2\right]$$

$$\boldsymbol{\Sigma}^r(\epsilon) = \sum_{c=1}^{N_c} \frac{\boldsymbol{H}_{DE}\varphi_c\phi_c^\dagger \boldsymbol{H}_{ED}}{\epsilon - \epsilon_c} = \sum_{c=1}^{N_c} \frac{\boldsymbol{B}_c}{\epsilon - \epsilon_c}$$

r_1: define the size of absorbing region

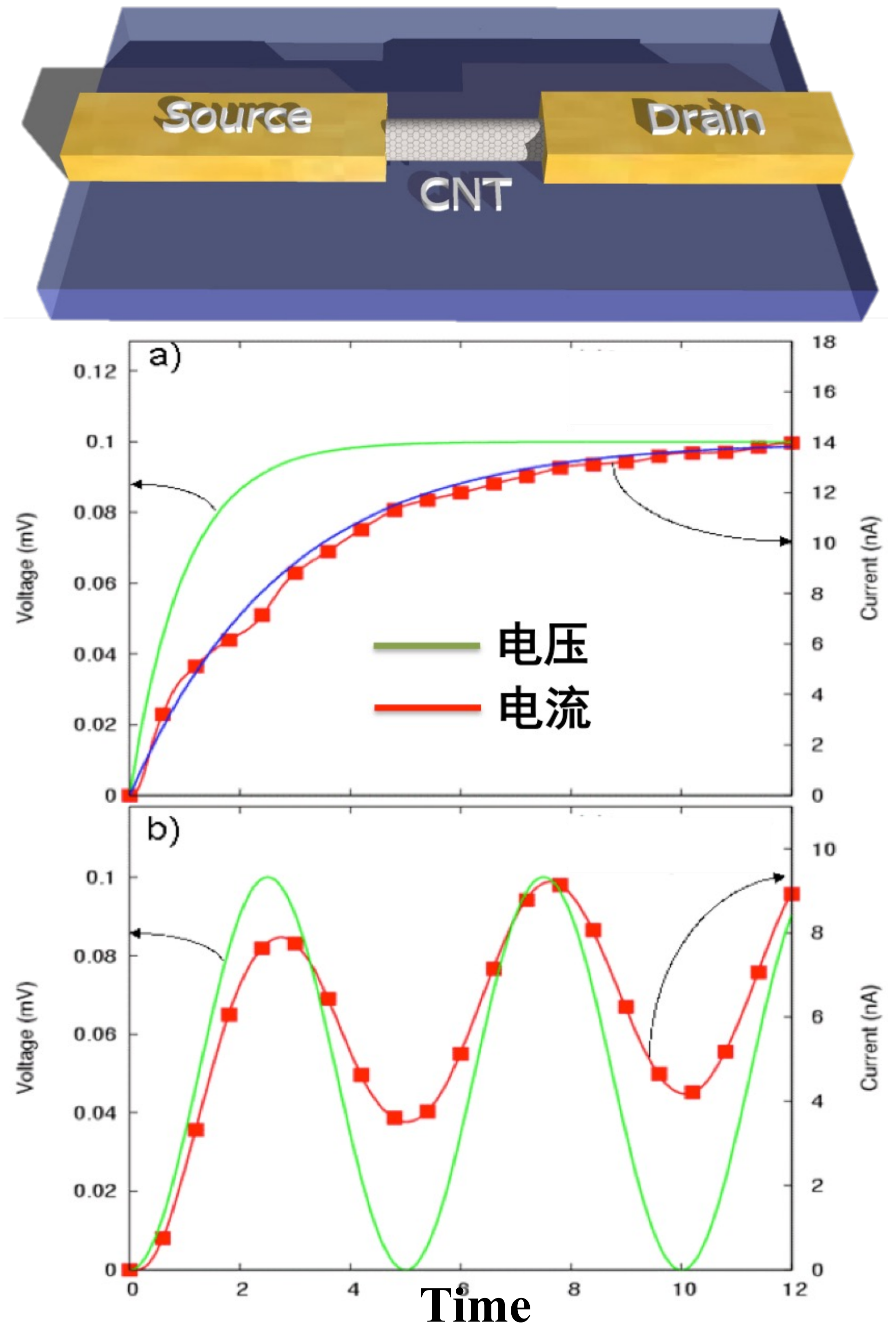


CNT Molecular Electronics

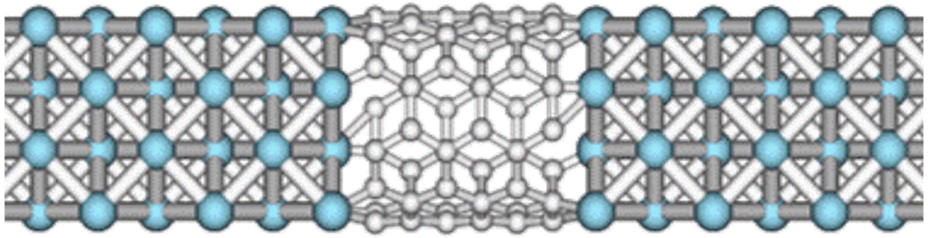


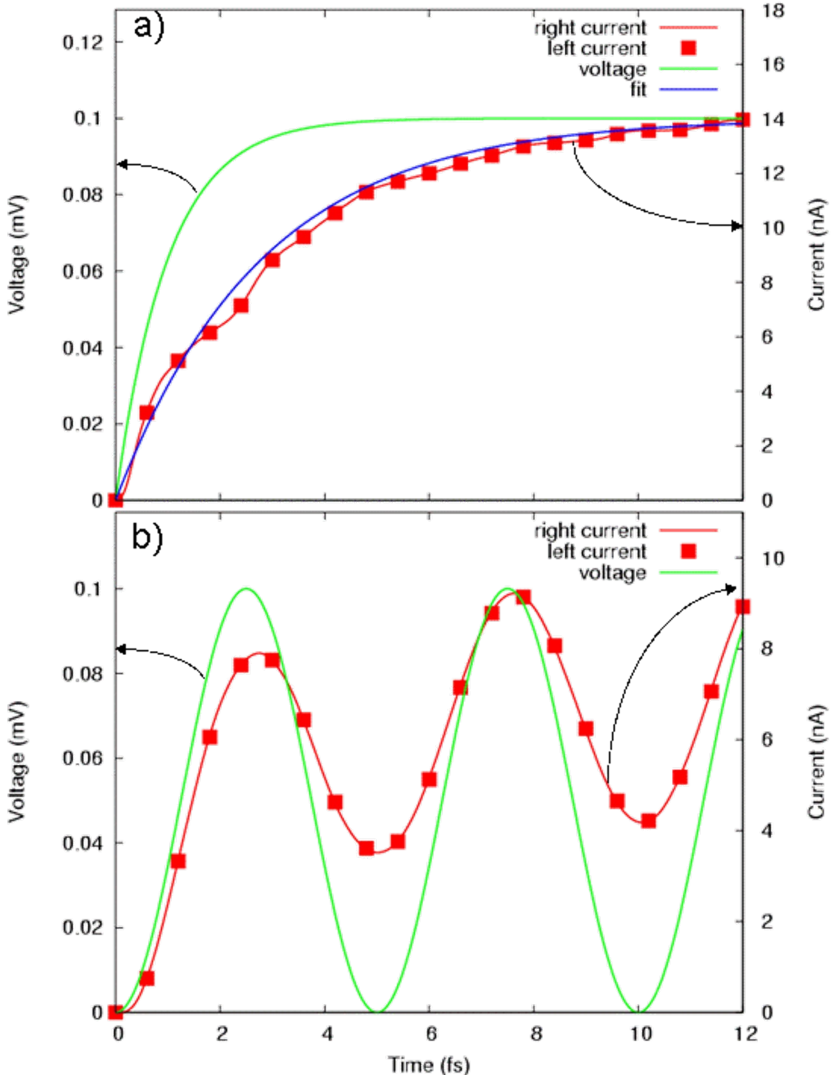
$$i\hbar\dot{\rho}_D(t) = [h_D(t), \rho_D(t)] - i\sum_{\alpha} Q_\alpha(t)$$

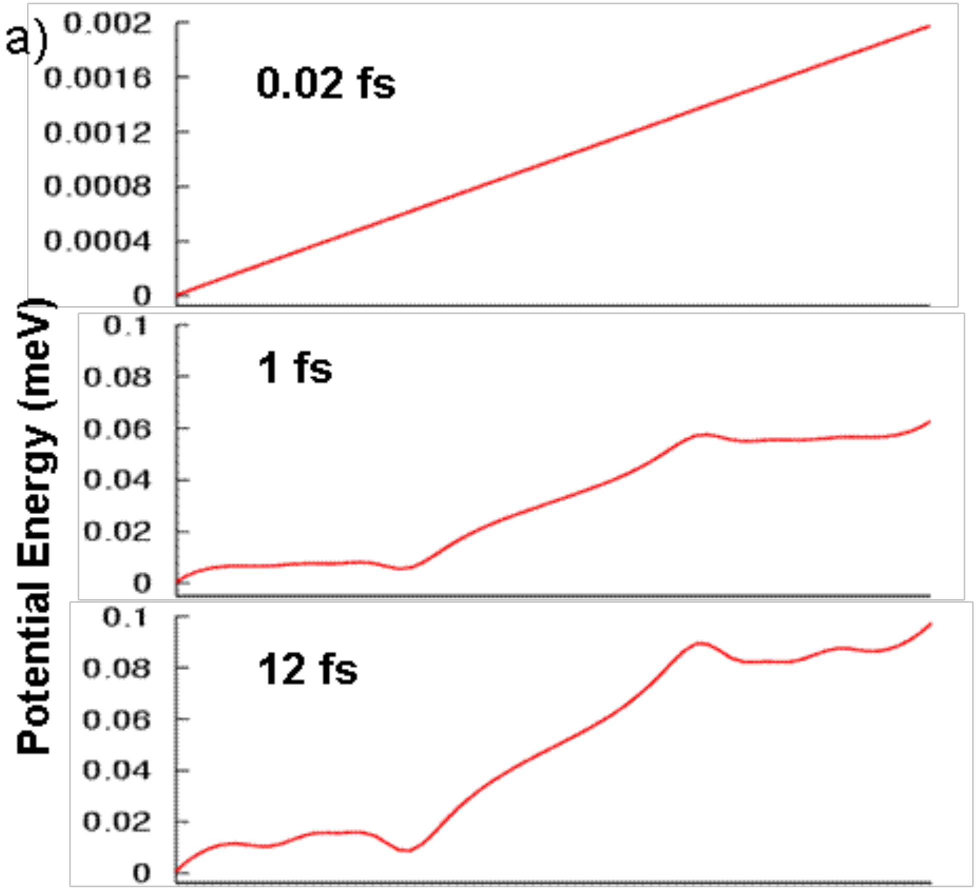
$$I_\alpha(t) = -\mathrm{Tr}[Q_\alpha(t)]$$



Dynamic Admittance

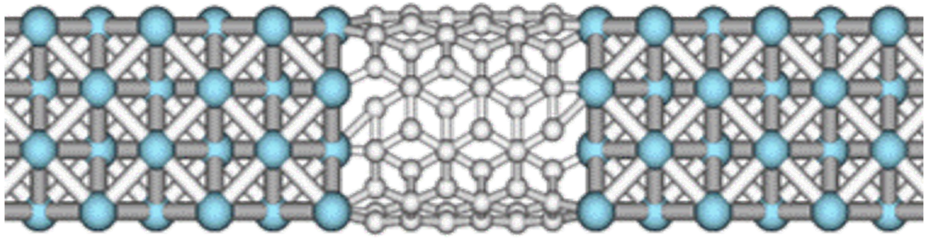


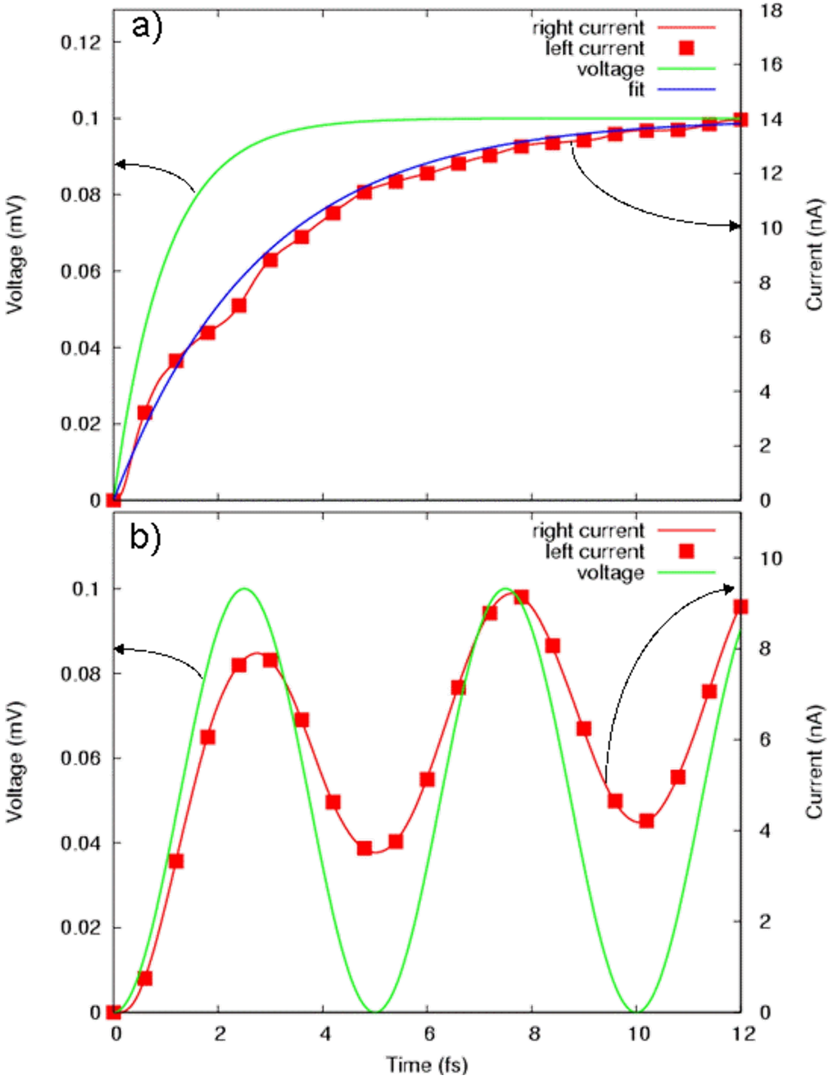


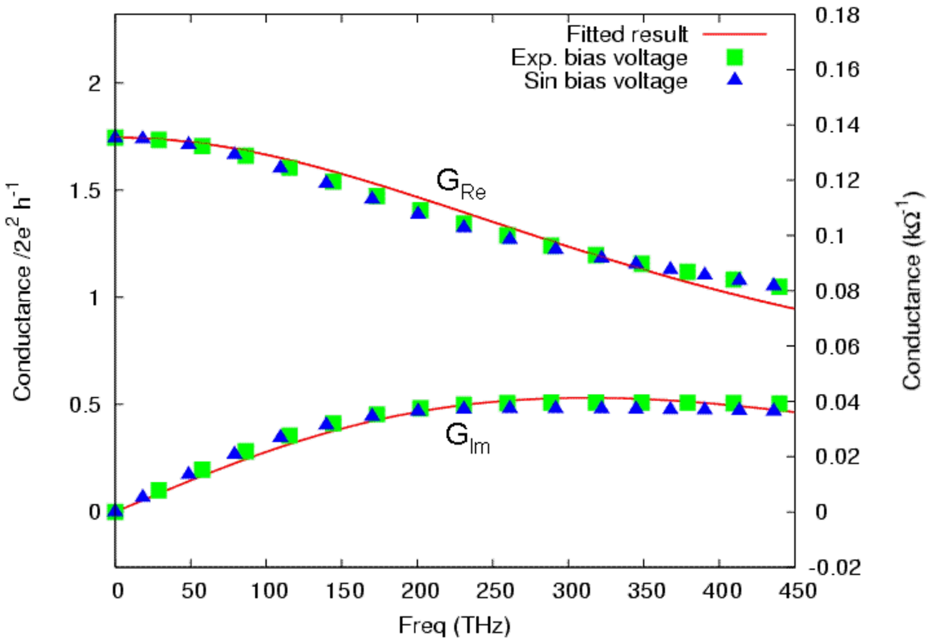


Yam, Mo, Wang, Li, Chen, Zheng, Matsuda, Tahir-Kheli & Goddard (2008)

Dynamic Admittance



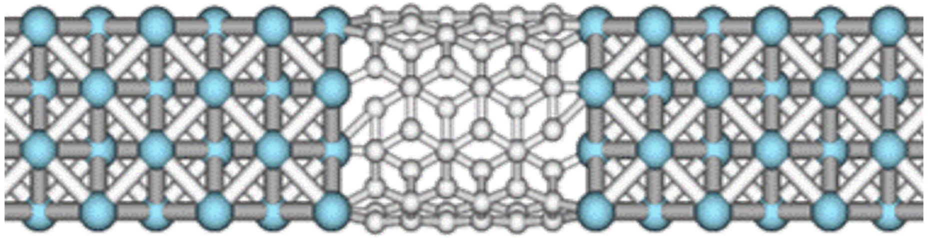


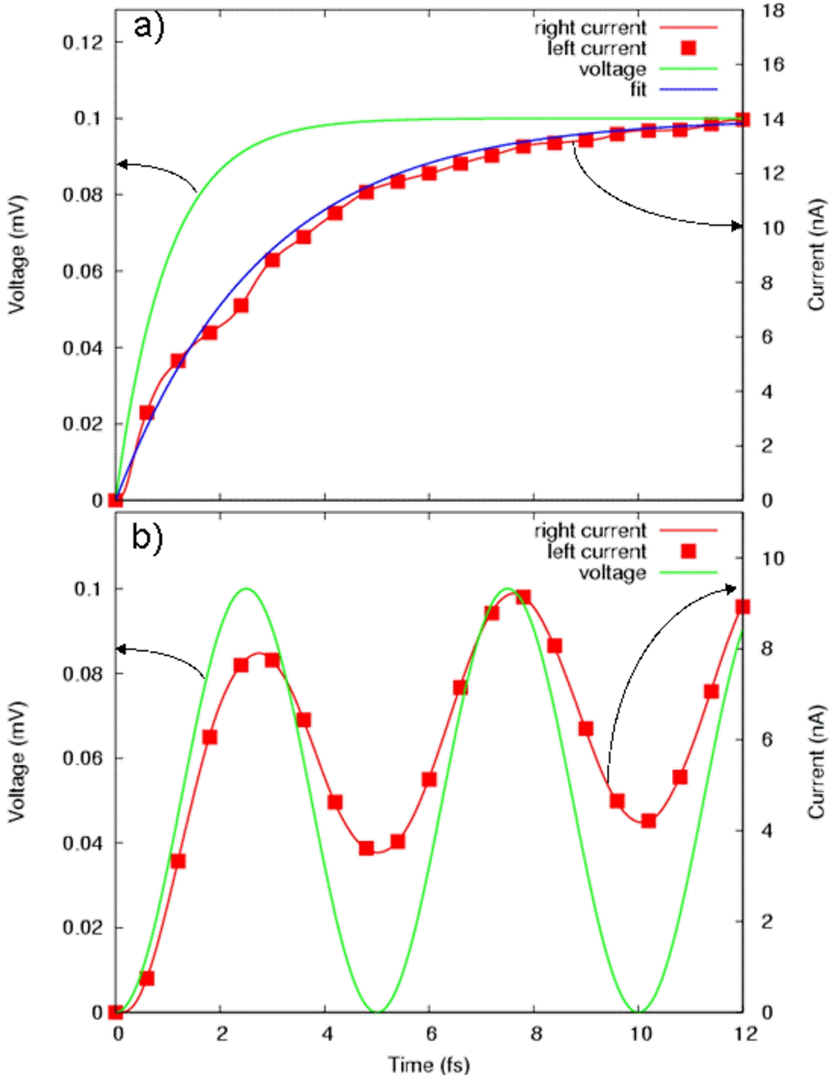


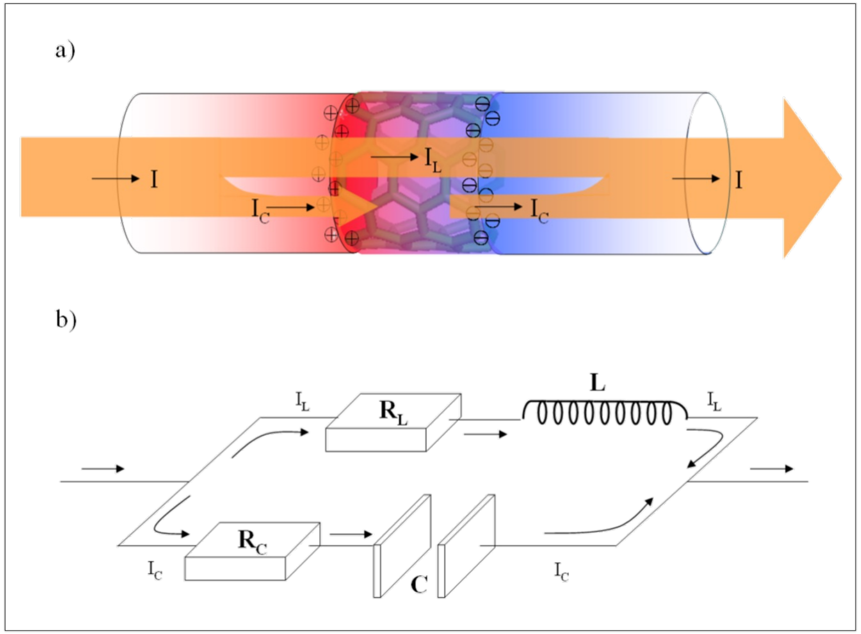
Switch-on time: ~ 10 fs

Yam, Mo, Wang, Li, Chen, Zheng, Matsuda, Tahir-Kheli & Goddard (2008)

Equivalent Circuit







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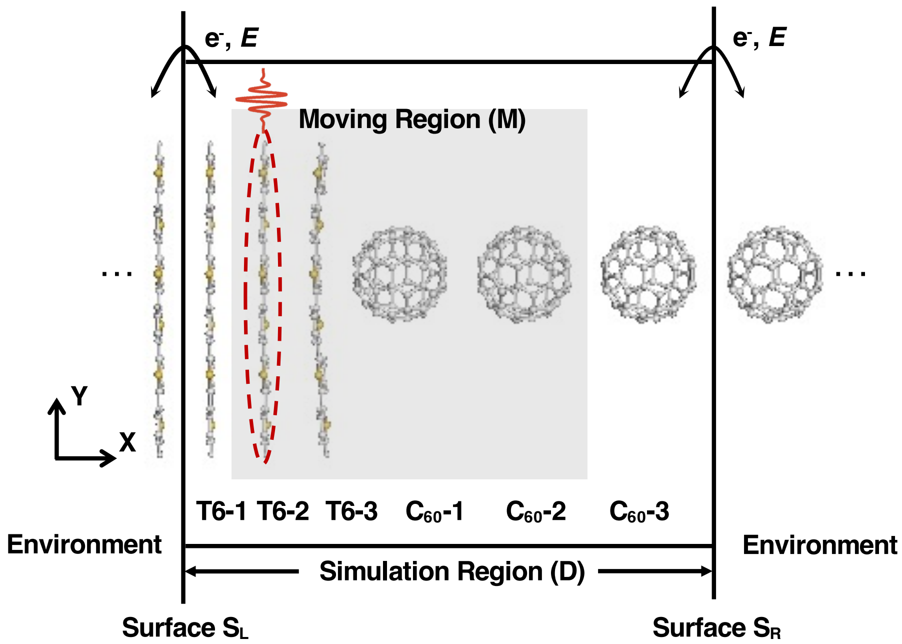
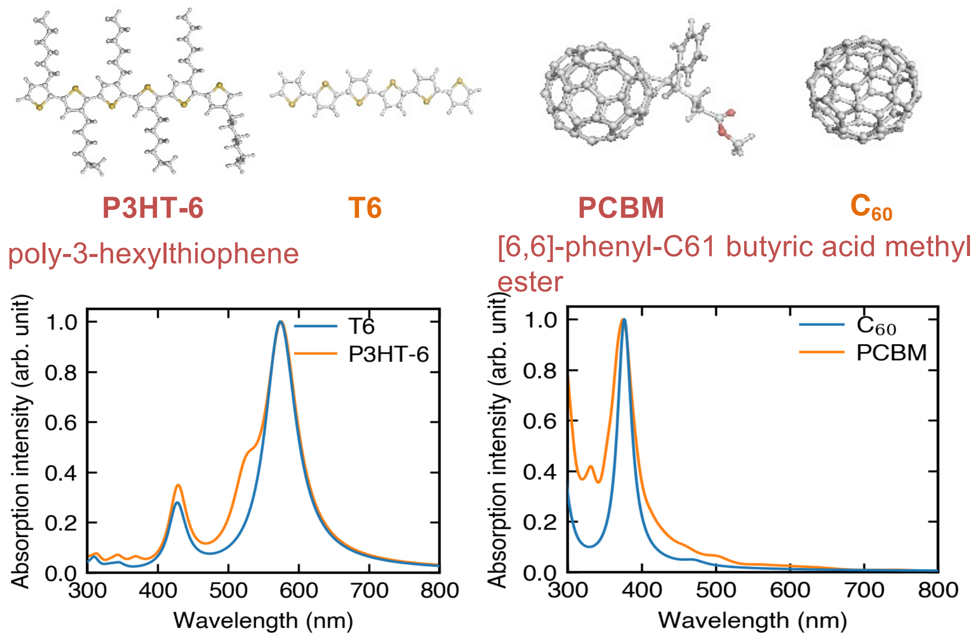
Yam, Mo, Wang, Li, Chen, Zheng, Matsuda, Tahir-Kheli & Goddard (2008)

Organic Solar Cell: Model

- six-ring oligothiophene (T6) as donor and C_{60} as acceptor
- simulation region is sandwiched between semi-infinite T6 and C_{60} molecular units



Absorption



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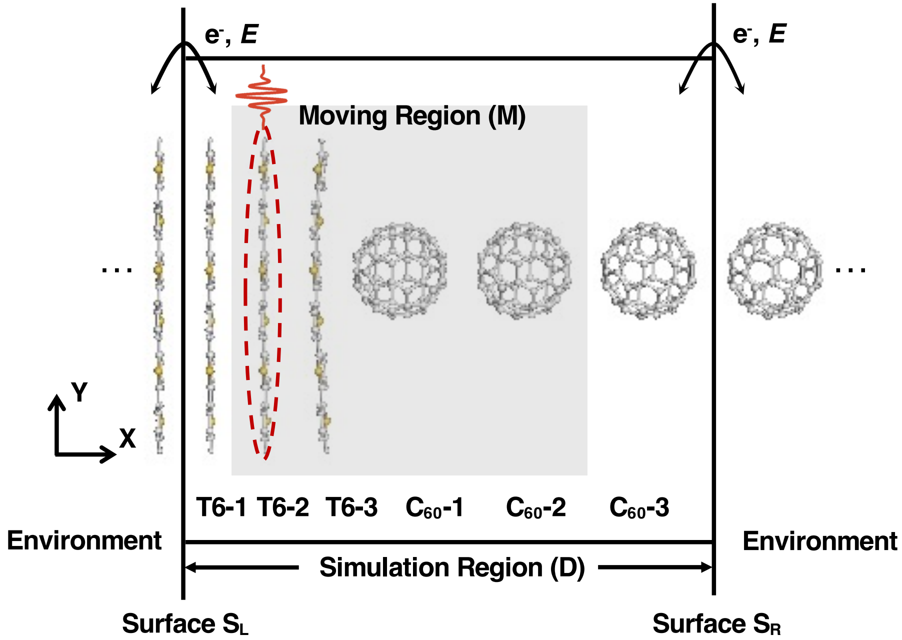
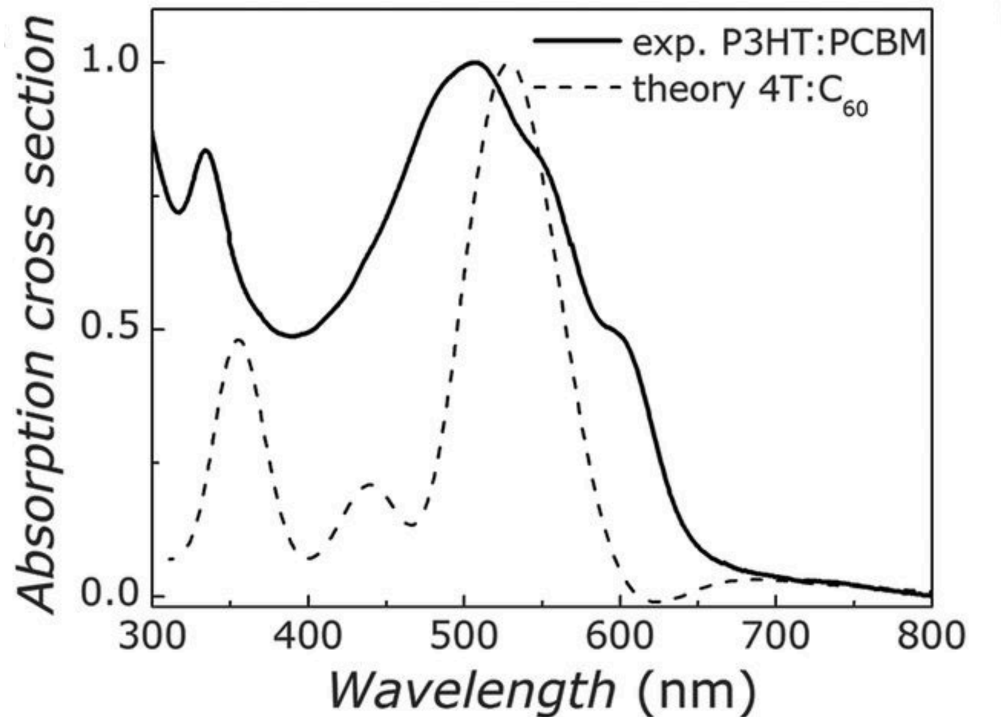


Absorption



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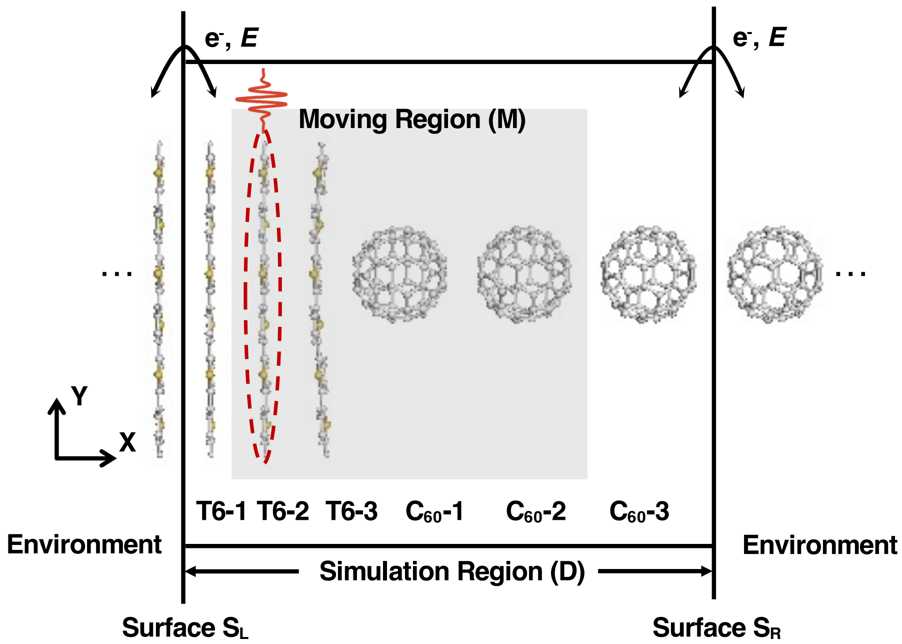
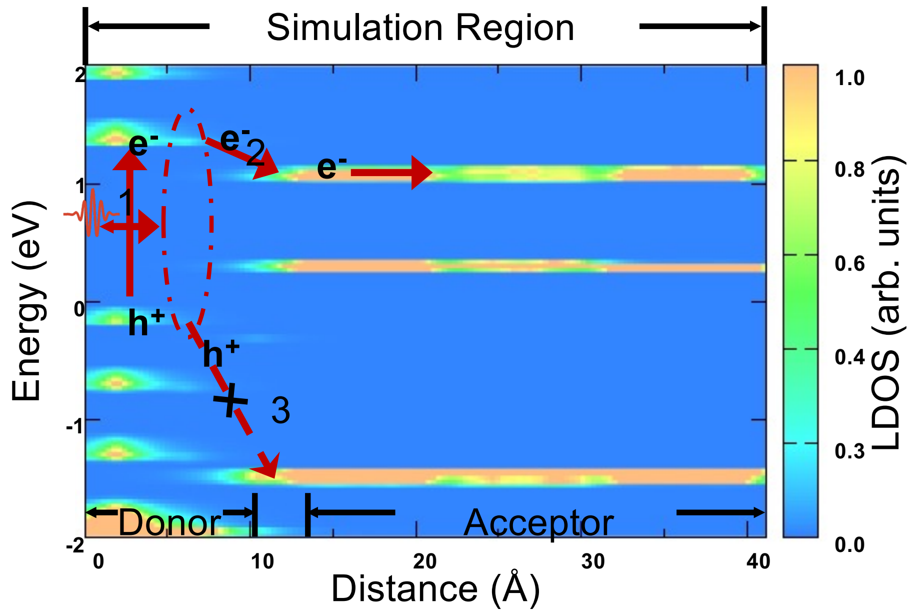
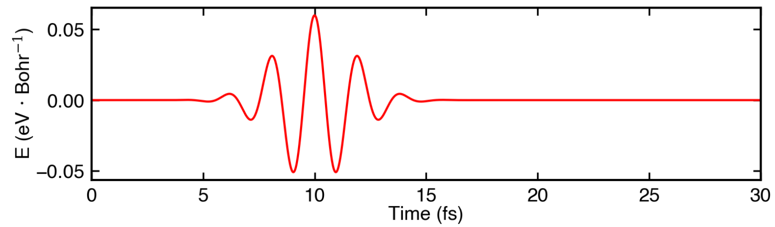
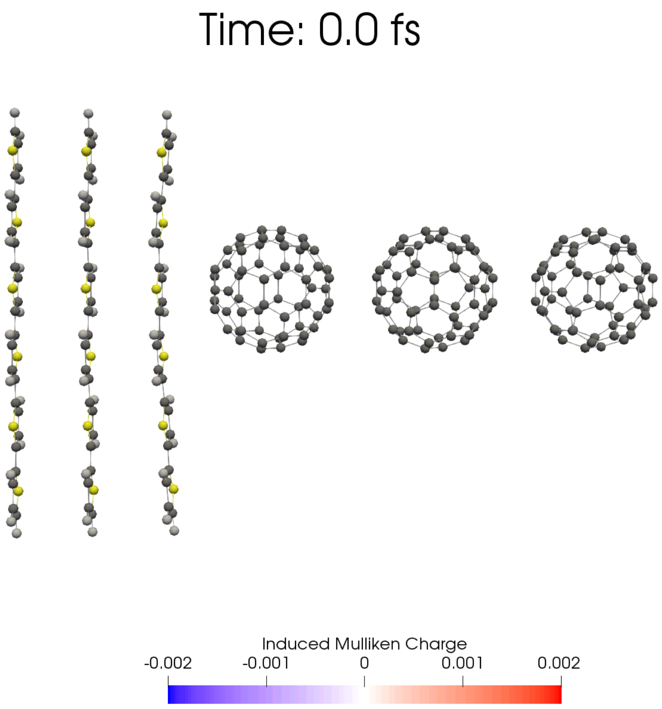


DOS



Light-induced charge carrier dynamics

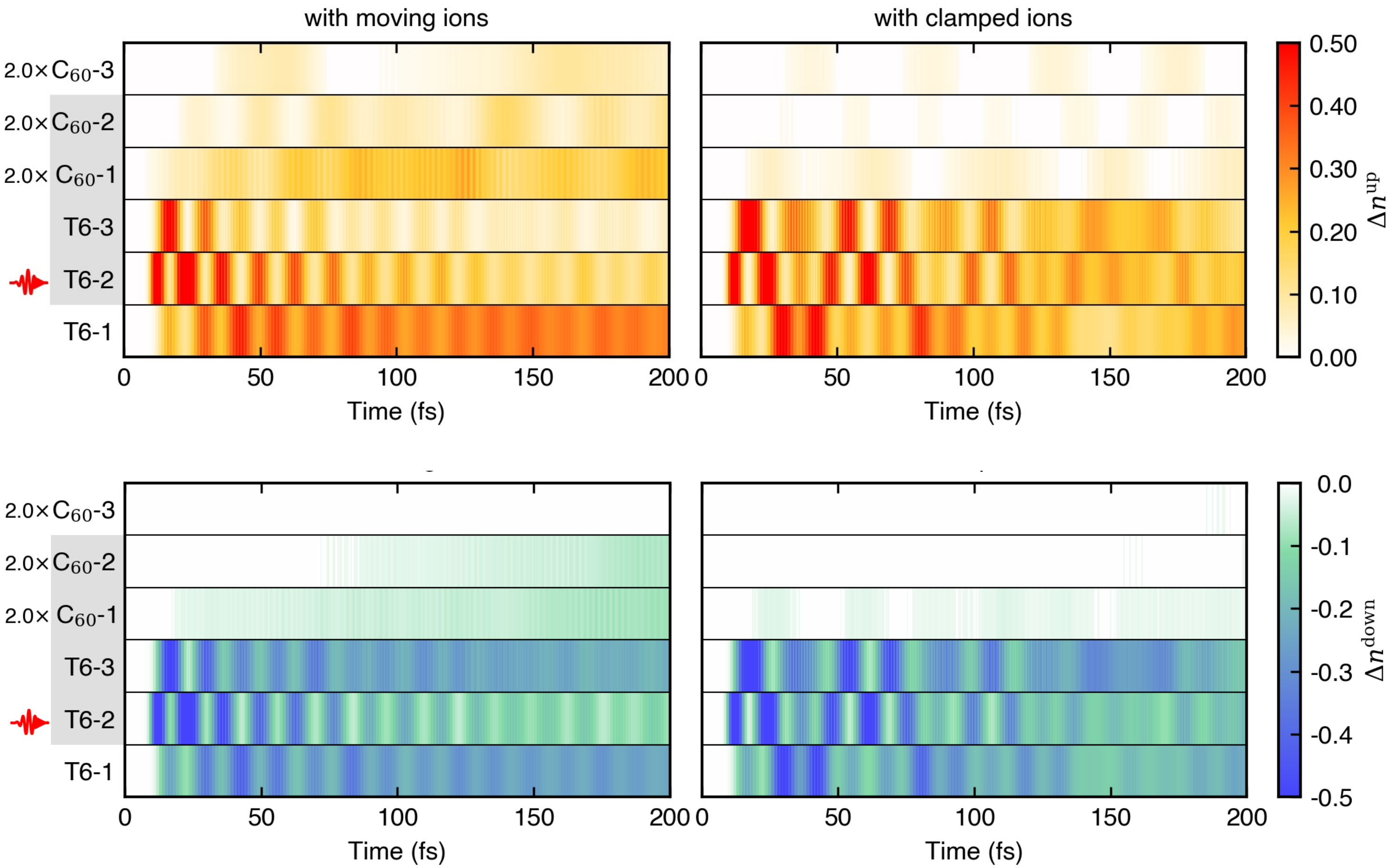




Dynamics of induced Mulliken charge in real space

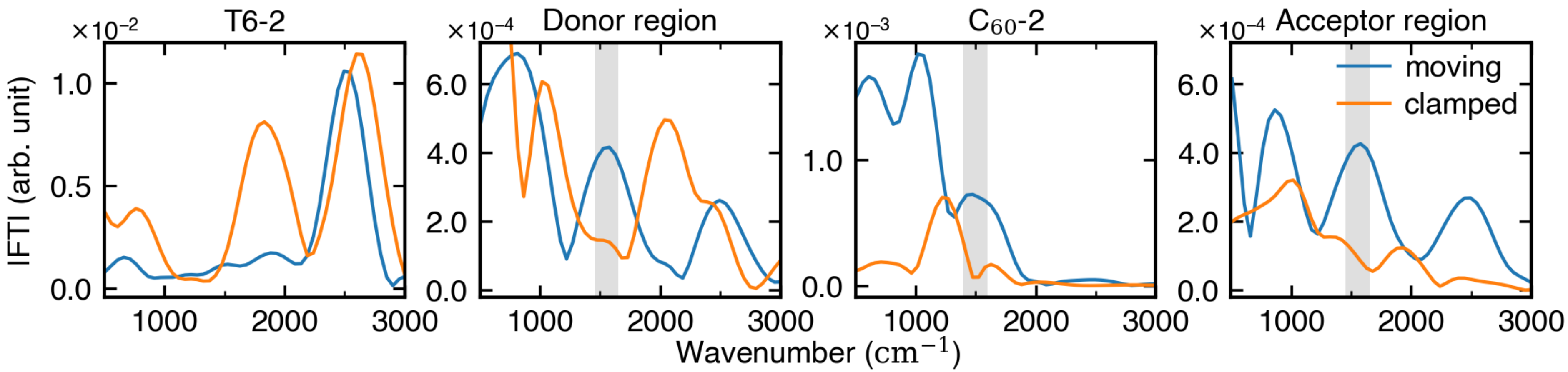
- Red: induced electron
- Blue: induced hole
- External field applied on T6-2 only.
- The ground state Mulliken charge is deducted to illustrate charge dynamics due to the excitation.
- The induced Mulliken charge is integrated within a 0.4 fs time interval to properly display the the excitation effect.

Light-induced Charge Dynamics in Blend



- **Identical** dynamics of the electron and hole in the donor region;
- Same oscillations of the electron and hole: excitonic nature of the transport of optical excitation.
- Hole transfer from T6 to C_{60} is mostly **suppressed**

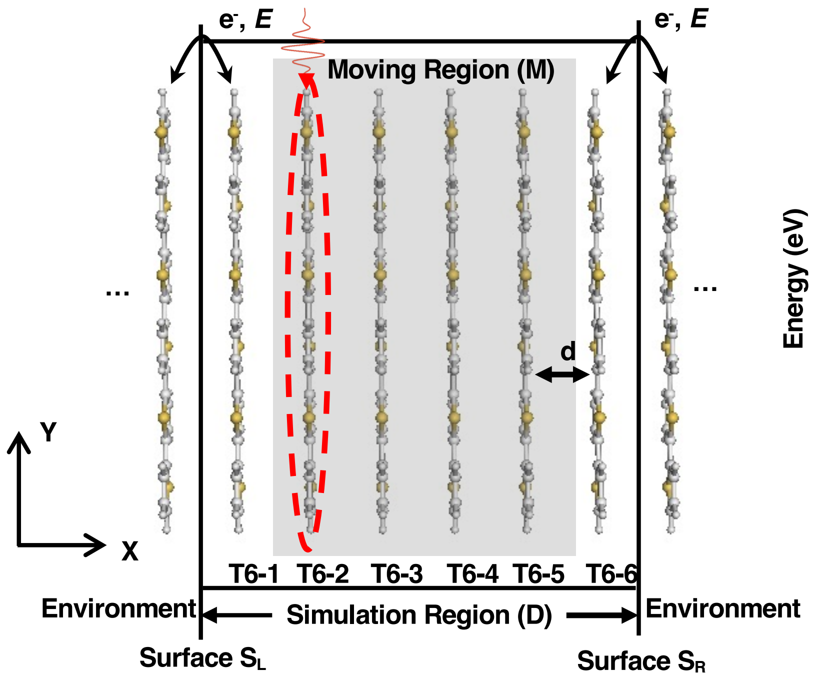
Light-induced Charge Dynamics in Blend

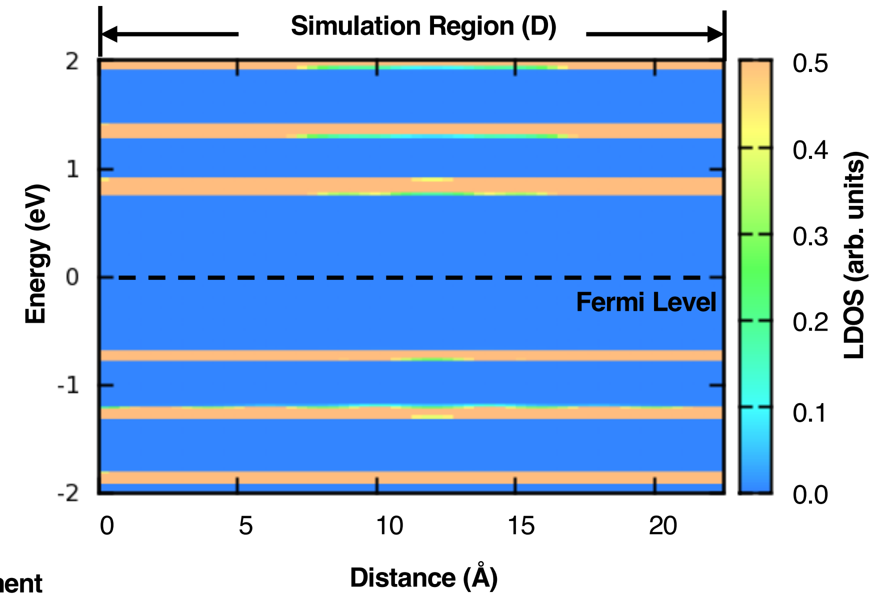


Fourier transform (FT) of Δn^{up} for T6-2, donor region (all three T6 molecular units), C_{60}-2, and acceptor region (all three C_{60} molecular units) with moving (blue) and clamped ions (orange), respectively.

Wavenumber	Region	Moving/Clamped	Attribution
2500 cm^{-1}	T6-2	Both	Electronic couplings between neighboring T6-units
1800 cm^{-1}	T6-2	Clamped ions	Electronic couplings between neighboring T6-units
1600 cm^{-1}	Donor	Moving ions	The C=C stretching vibrational mode
1000 cm^{-1}	C_{60}-2	Both	Electronic couplings between neighboring C_{60}-units
1600 cm^{-1}	C_{60}-2, Acceptor	Moving ions	Vibronic-enhanced charge transfer

Induced Charge Dynamics in ordered T6

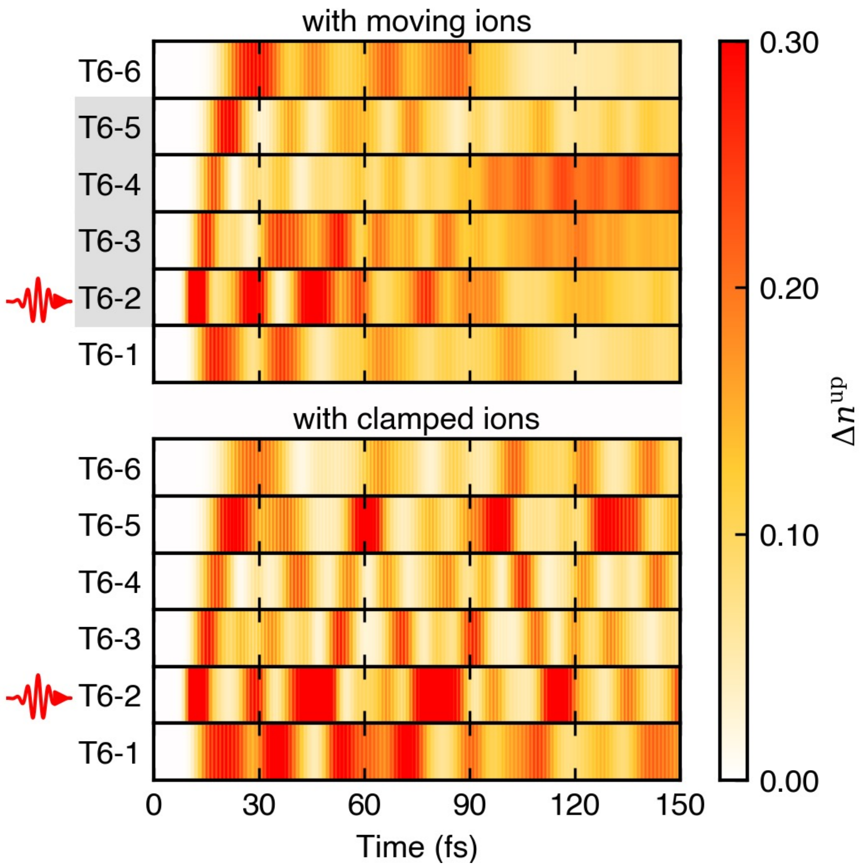


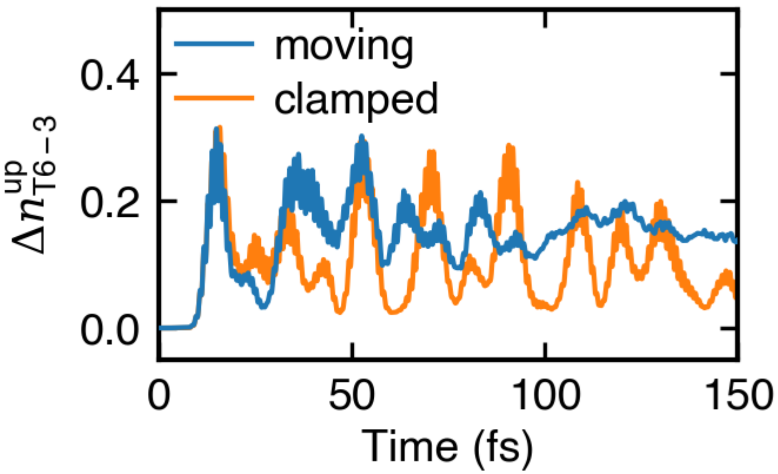


Well-ordered: Molecular structures are exactly same and highly ordered along the transport direction

LDOS: Occupied and unoccupied states span the entire simulation region

Induced Charge Dynamics in ordered T6





- 0 - 20 fs: identical oscillations for both cases;
- 20 - 150 fs: vibrational motions set in, wash out the oscillation periodicity in the case of moving ions;
- Occupation oscillations over the entire simulation region and time interval;
- More pronounced oscillation in the case of clamped ions;

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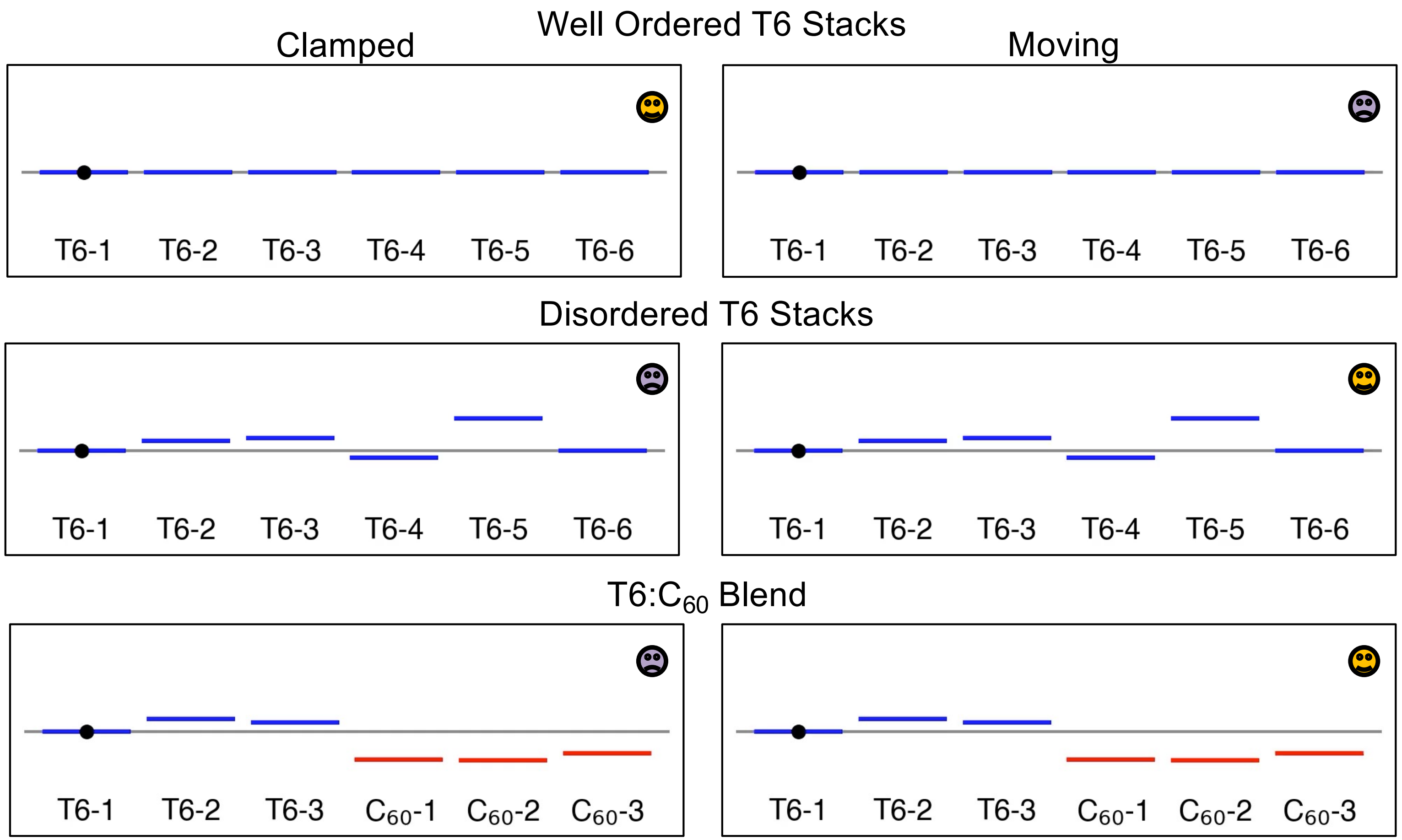
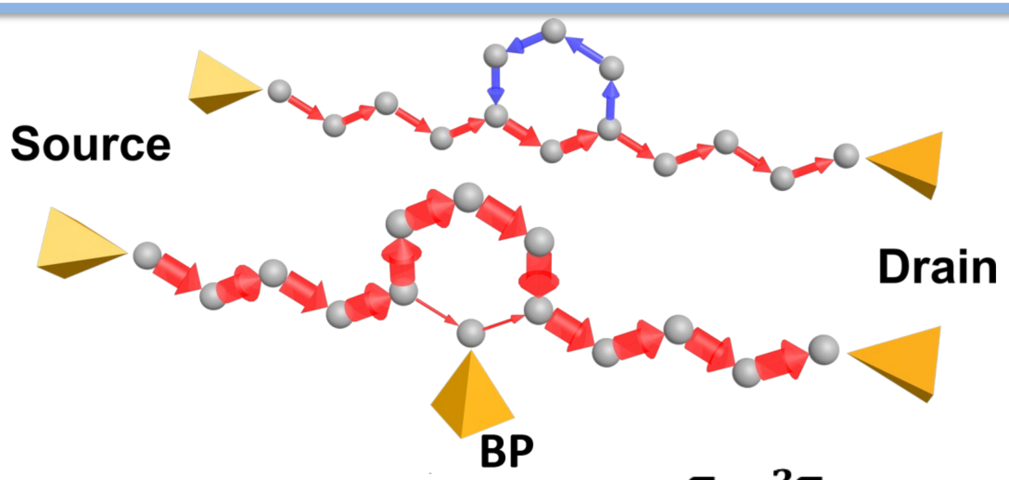
- More pronounced oscillation in the case of clamped ions;

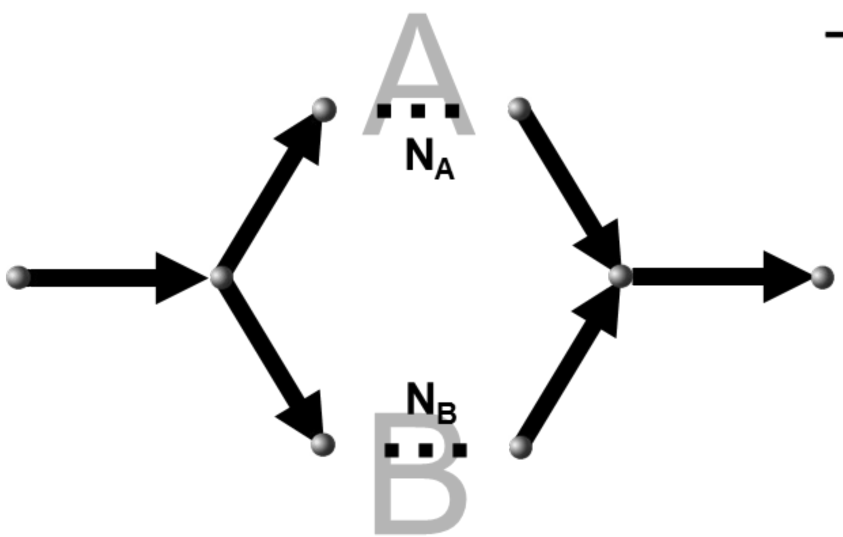
Light-induced Charge Dynamics in Blend



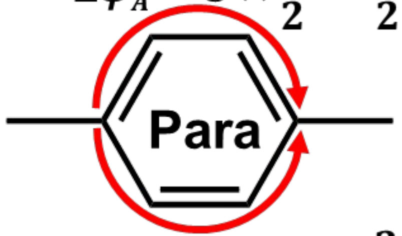
- Vibrational mode (C=C) modulates the electronic couplings between the donor units by detuning the electronic states
- In disordered systems: the coupling of electrons to selected vibrational modes may promote coherent charge transport

Interference and Molecular Transport





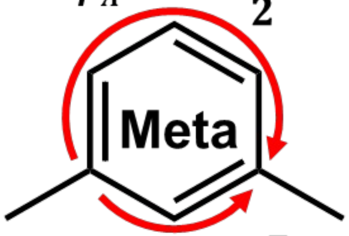
$$\Delta\varphi_A = 3 \times \frac{\pi}{2} = \frac{3\pi}{2}$$



Constructive Interference

$$\Delta\varphi_B = 3 \times \frac{\pi}{2} = \frac{3\pi}{2}$$

$$\Delta\varphi_A = 4 \times \frac{\pi}{2} = 2\pi$$



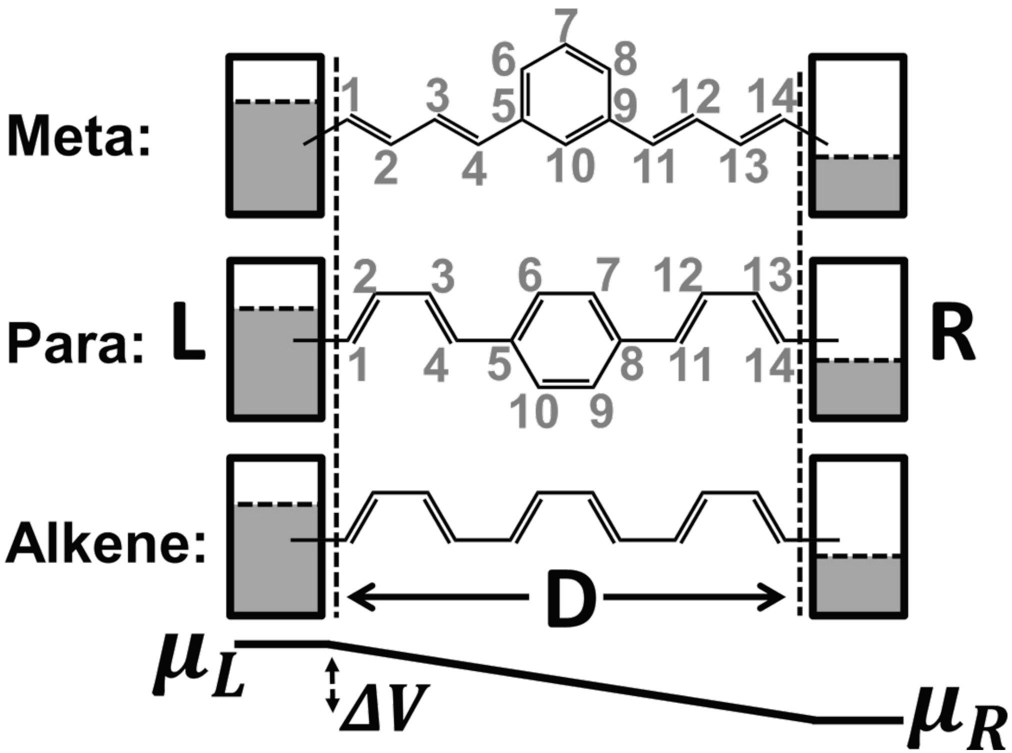
Destructive Interference

$$\Delta\varphi_B = 2 \times \frac{\pi}{2} = \pi$$

Model

Tight-binding Hamiltonian:

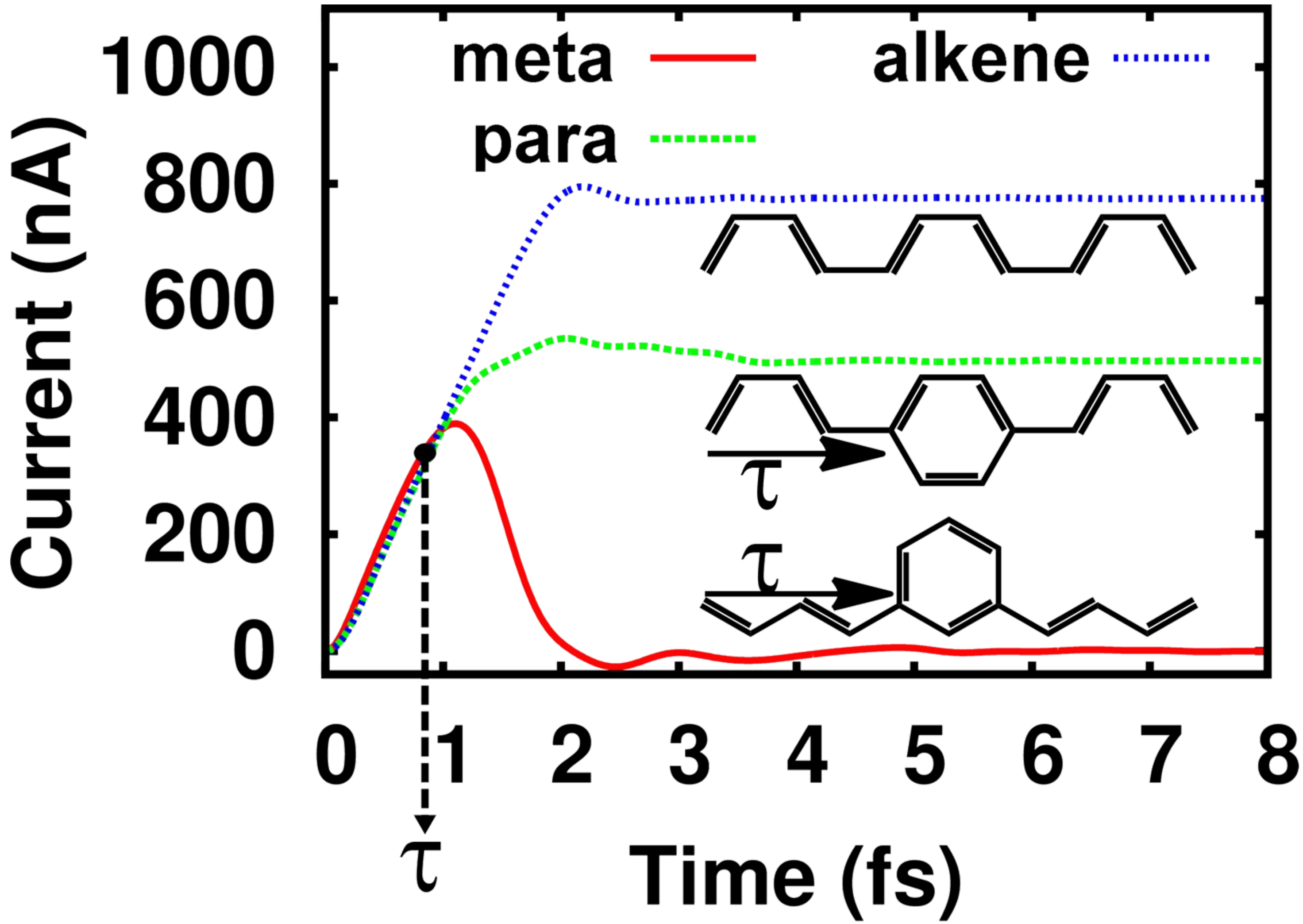
$$H = \sum_{\mu} \varepsilon d_{\mu}^{\dagger} d_{\mu} + \sum_{\mu,\upsilon=\mu\pm 1} \gamma d_{\mu}^{\dagger} d_{\upsilon} + \sum_{k_\alpha} \varepsilon_{k_\alpha} c_{k_\alpha}^{\dagger} c_{k_\alpha} + \sum_{\alpha,k_\alpha,\mu} (V_{k_\alpha \mu} c_{k_\alpha}^{\dagger} d_{\mu} + H.c.)$$



$\gamma = 2eV$

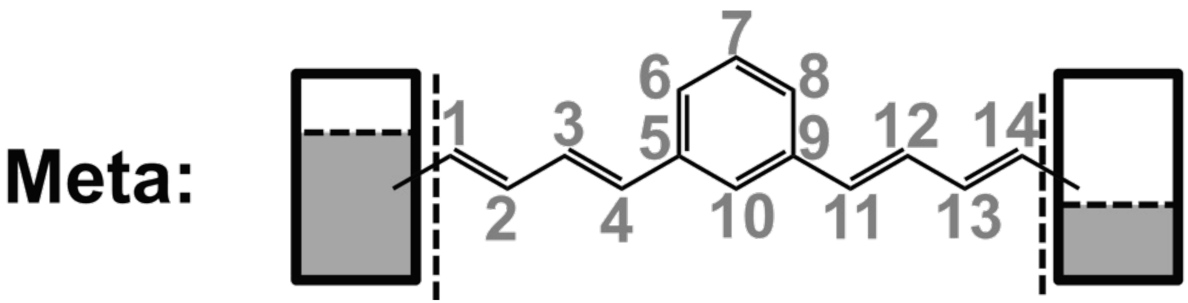
$(t \geq 0) = 0.01V$

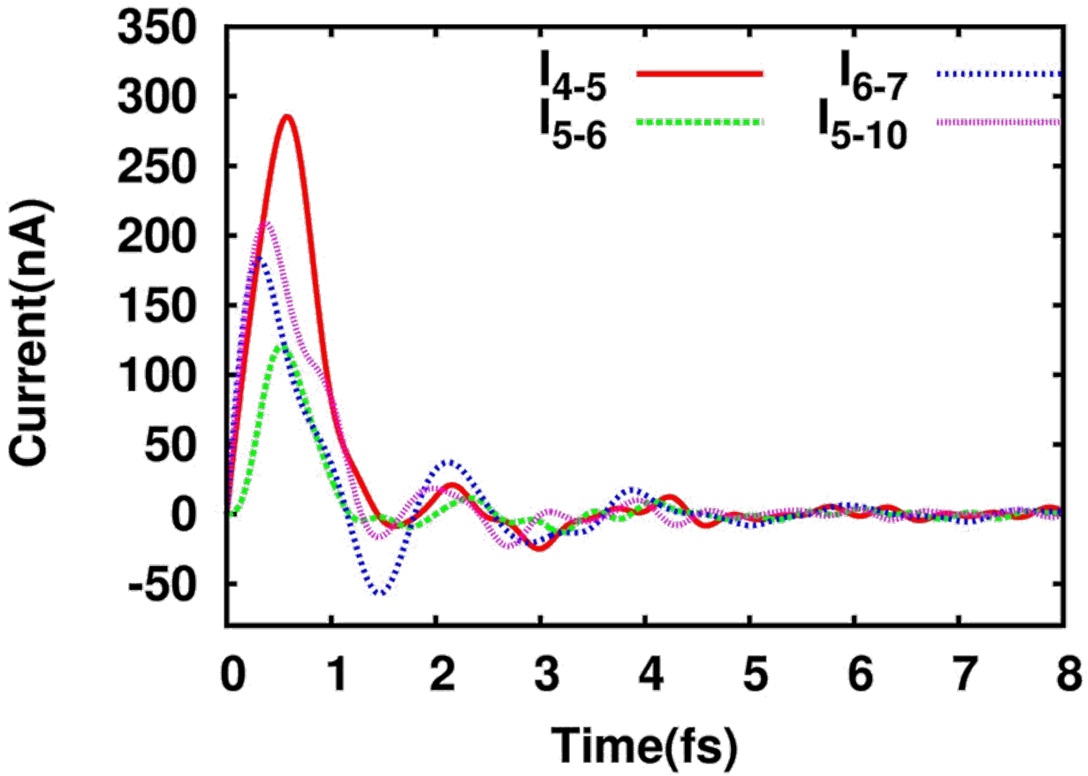
Transient Current



Chen, Zhang, Koo, Tian, Yam, Chen, Ratner JPCL (**2014**)

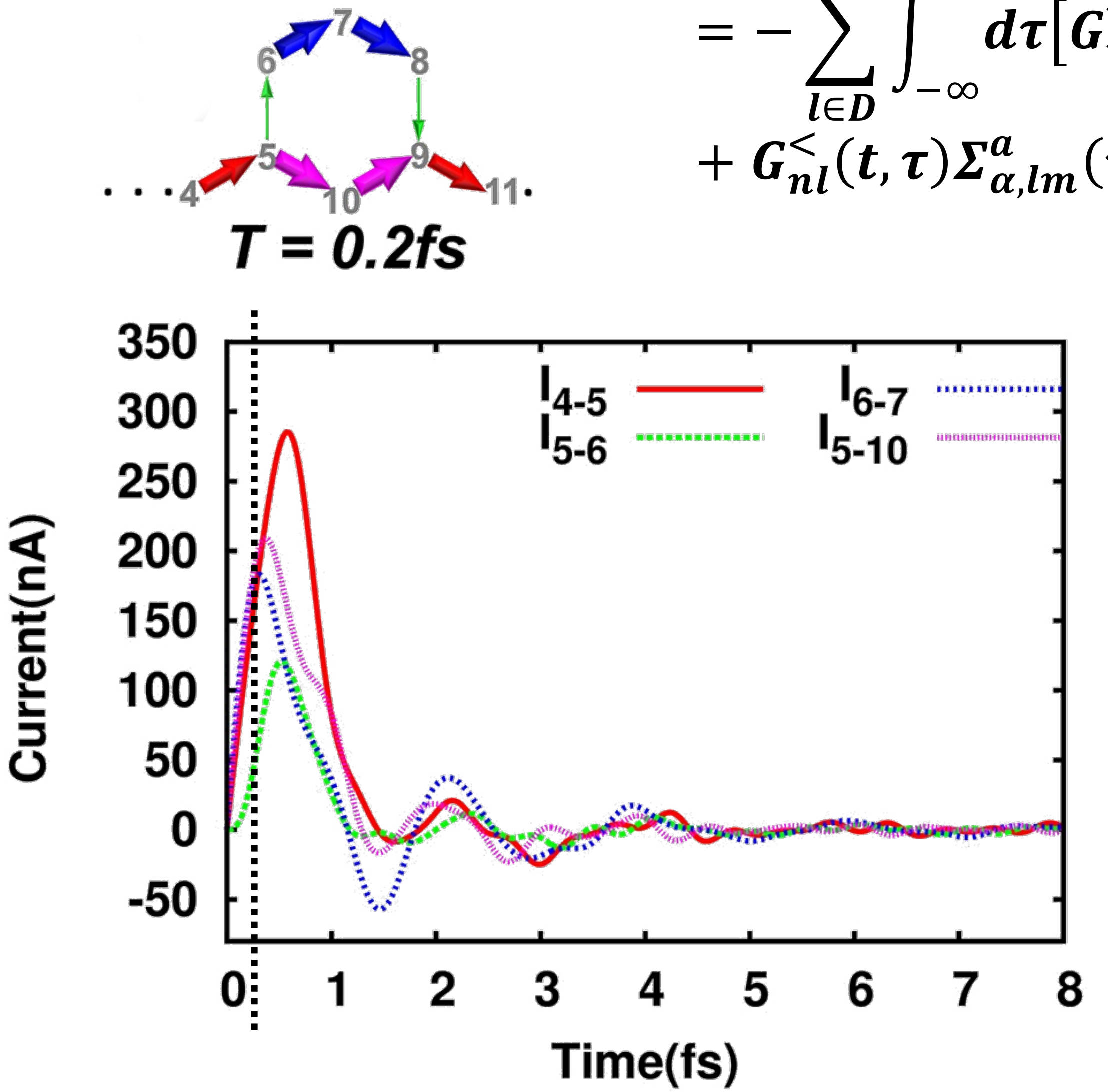
Transient Current – meta



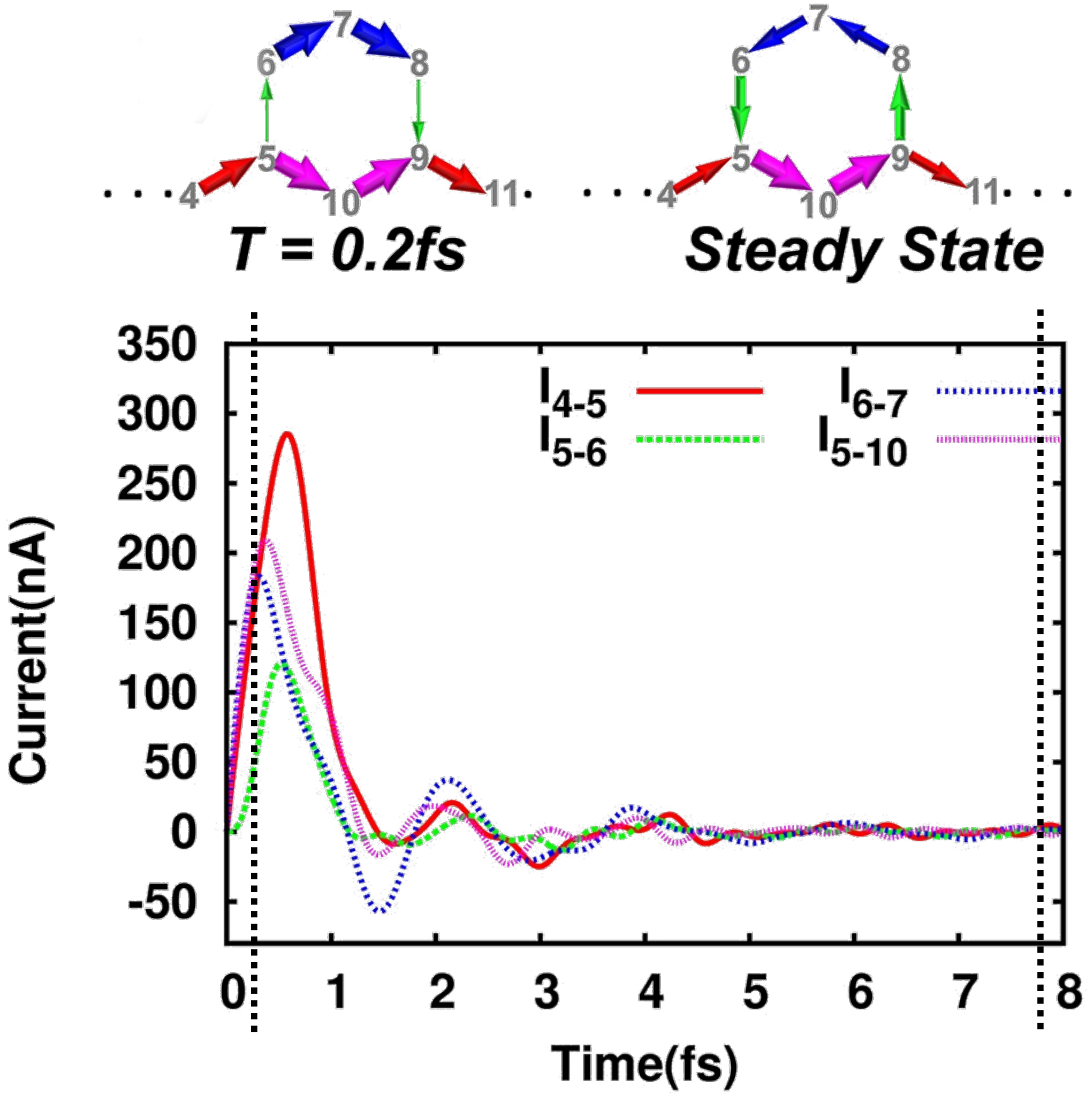


Transient Current – meta

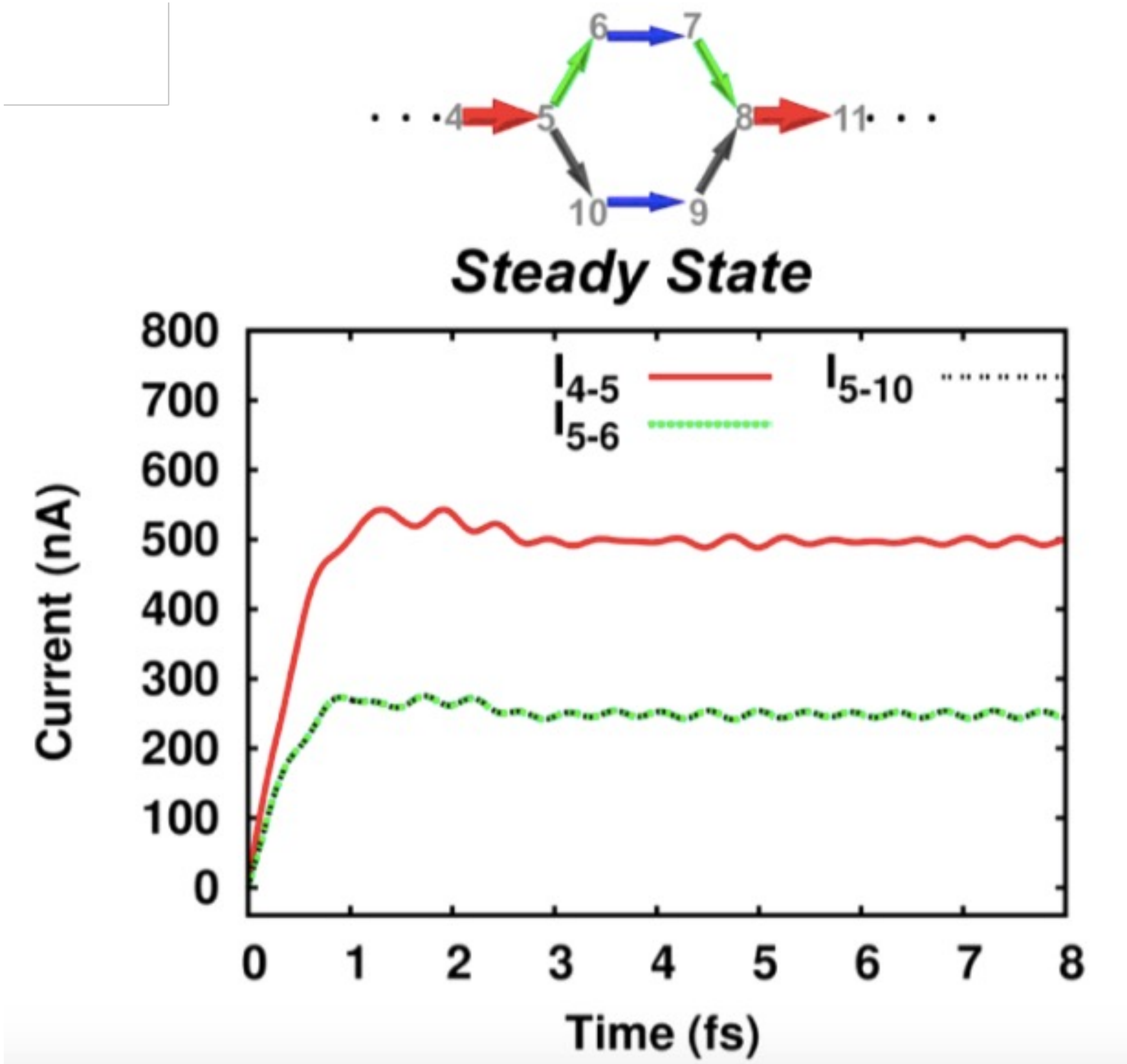
$$Q_{\alpha,nm}(t) = -\sum_{l\in D}\int_{-\infty}^{\infty} d\tau \left[G^{r}_{nl}(t,\tau)\Sigma^{<}_{\alpha,lm}(\tau,t) + G^{<}_{nl}(t,\tau)\Sigma^{a}_{\alpha,lm}(\tau,t) + \mathrm{H.c.} \right]$$



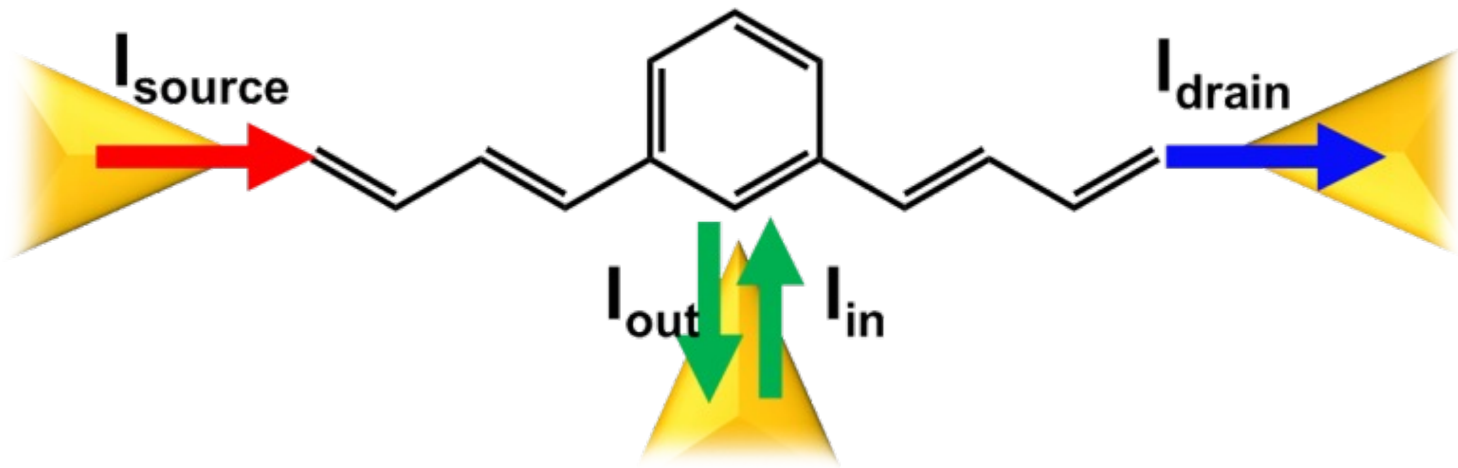
Interference



Transient Current – para case

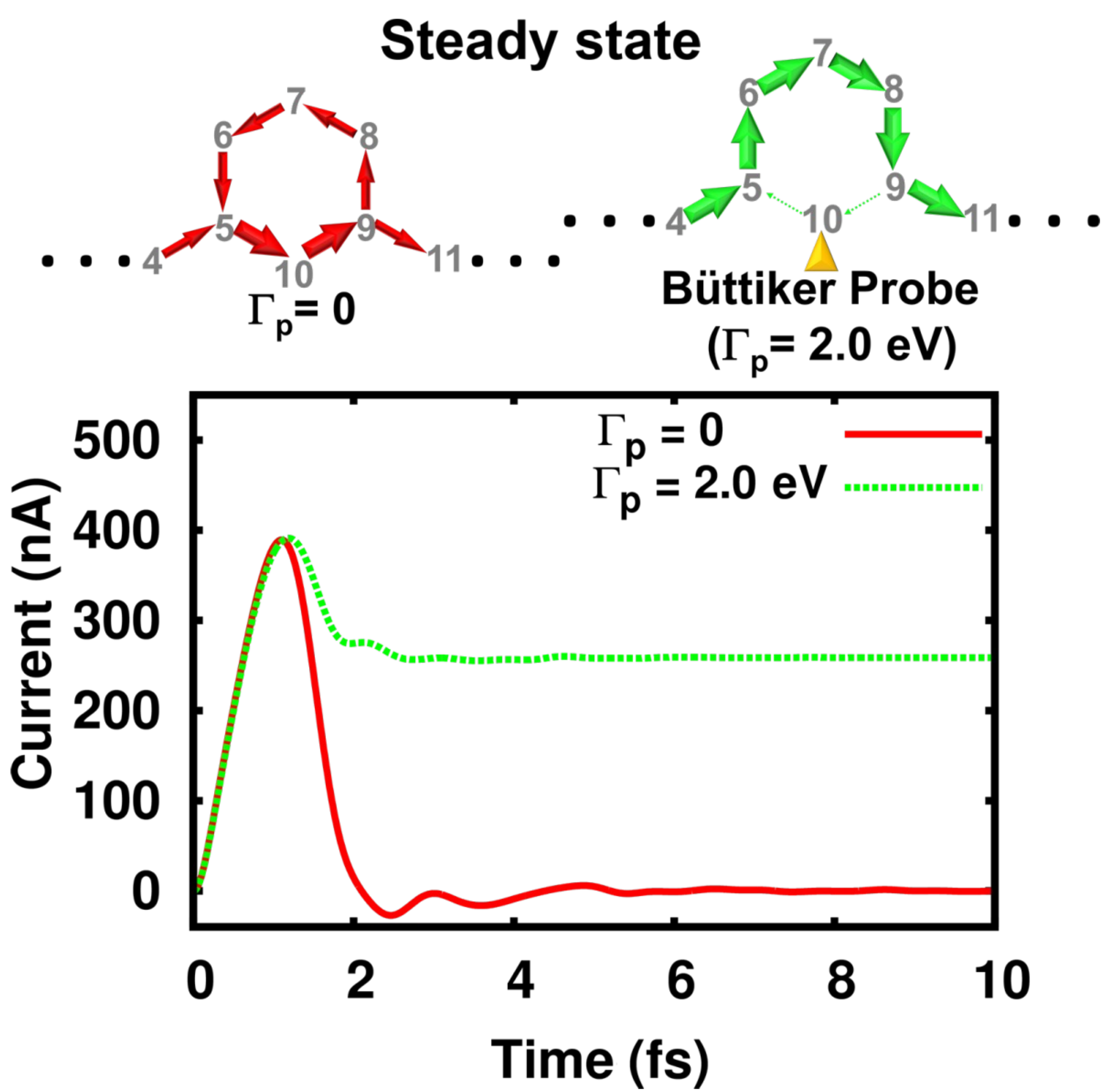


Buttiker probe - Decoherence



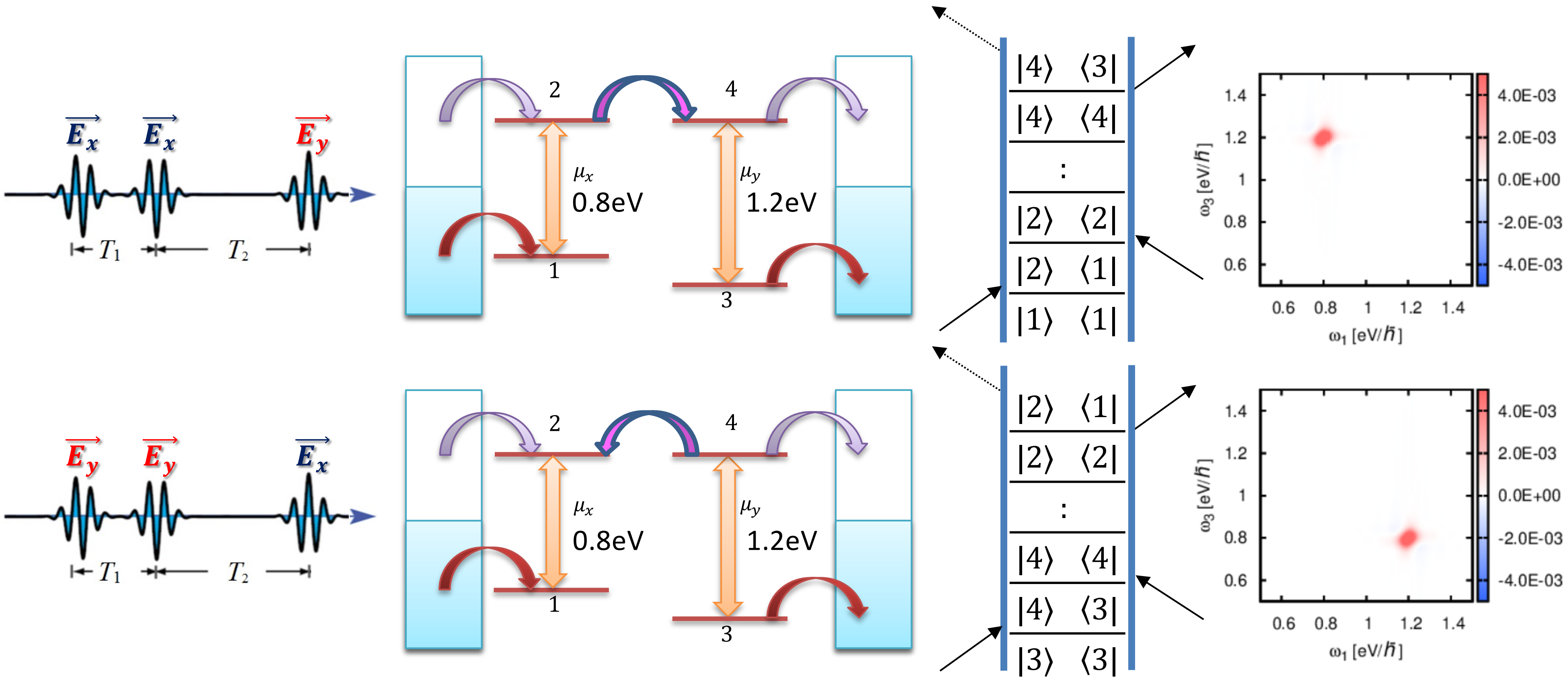
Büttiker Probe

Decoherence



Photoinduced Charge Transfer

Charge flow results in coherent peaks in 2-D electronic spectra



Phonon-Assisted Charge Transfer

- Equations of motion
  $i\hbar\dot{\sigma}(t)$
  $= [h(t), \sigma(t)] - \sum_{\alpha=L,R} \left[\varphi_\alpha(t) - \varphi_\alpha^\dagger(t)\right] - \left[\varphi_{Ph}(t) - \varphi_{Ph}^\dagger(t)\right]$
- Electron-Phonon Interaction (EPI) Self-Energy

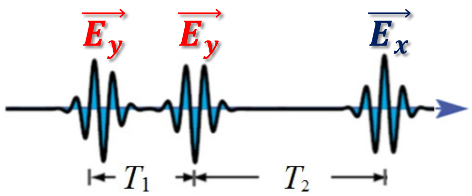
$$\Sigma_{Ph}(t,\tau) \approx i\hbar \sum_q \gamma_q d_{0,q}(t,\tau) G_{DD}(t,\tau)\gamma_q$$

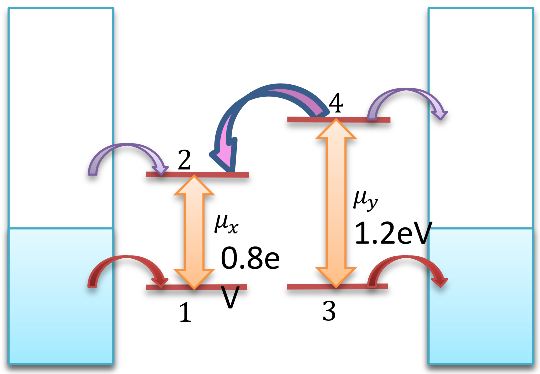
$$\varphi_{Ph}(t) \equiv i\hbar \int_{-\infty}^{t} d\tau \, [G_D^<(t,\tau)\Sigma_{Ph}^>(\tau,t) - G_D^>(t,\tau)\Sigma_{Ph}^<(\tau,t)]$$

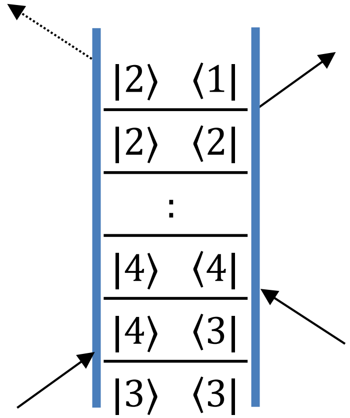
J. Chem. Phys. 2013. 138, 164121

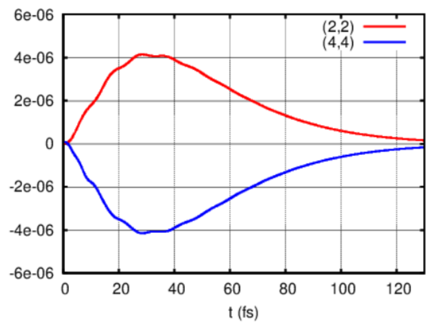
Phonon-Assisted Charge Transfer

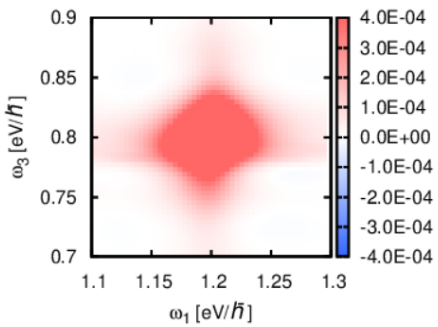
- Energy transmission between phonon and excited electrons



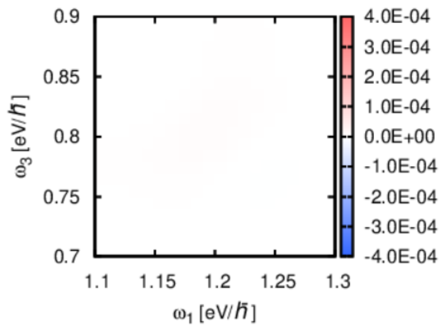






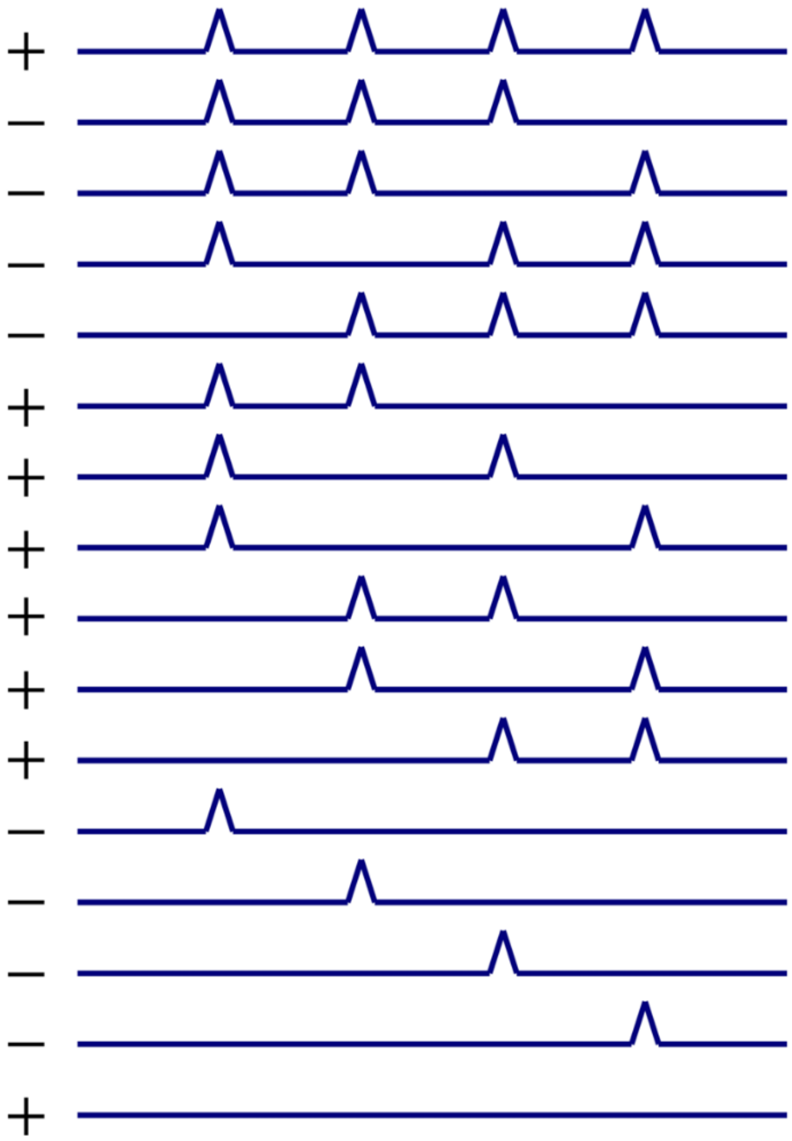


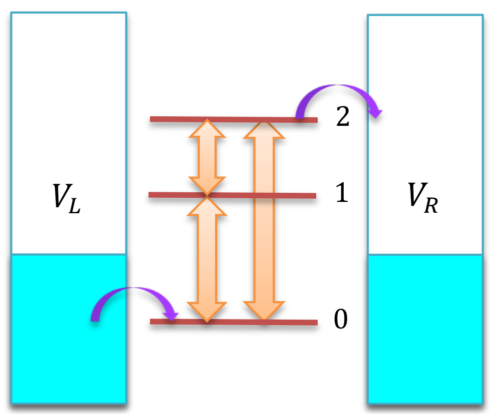
$\omega_q = 0.4\text{eV}/\hbar$



No Phonon

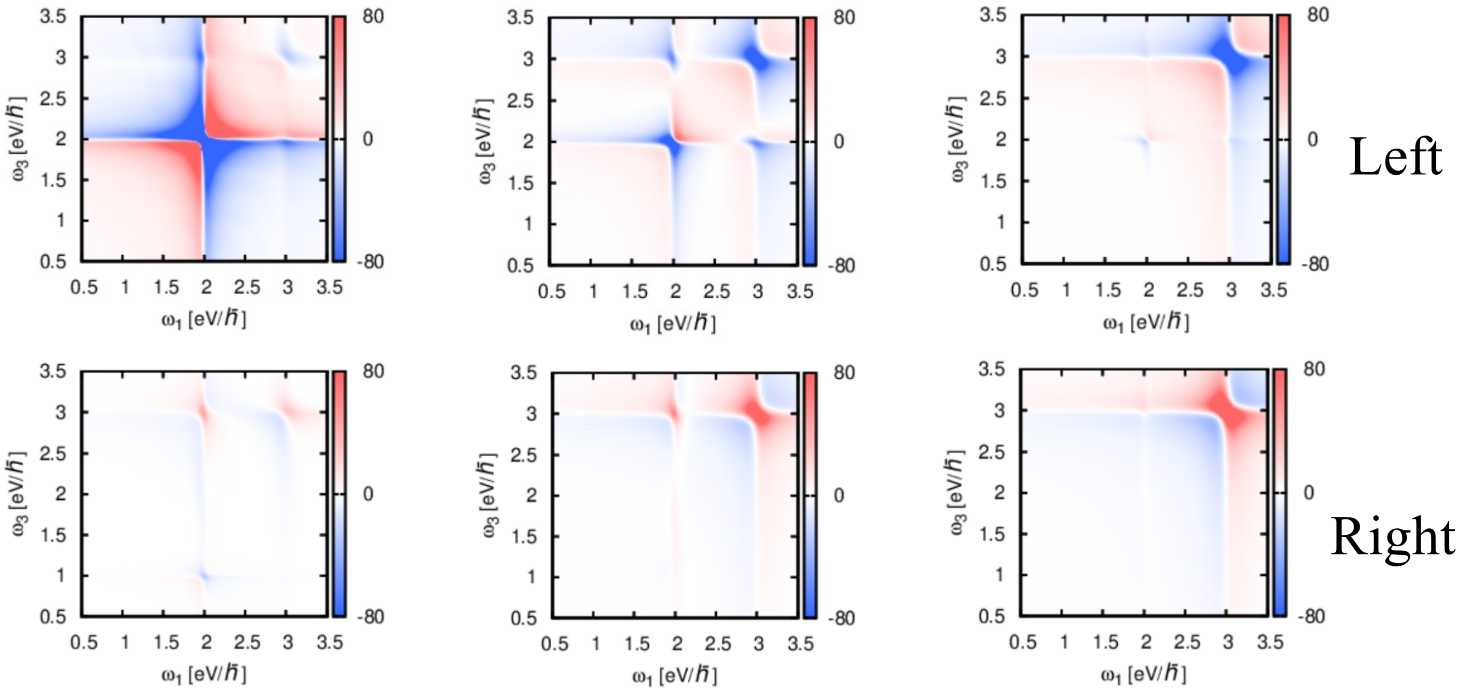
Two-dimensional Photocurrent Spectra



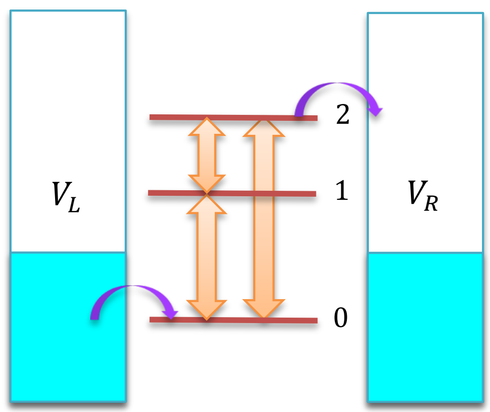


Two-dimensional Photocurrent Spectra

Pulse Frequency and System-Electrode Coupling



$\omega_E = 2.0\mathrm{eV}/\hbar$ $\omega_E = 2.5\mathrm{eV}/\hbar$ $\omega_E = 3.0\mathrm{eV}/\hbar$



Thank you for your attention