First-Principles Quantum Mechanical Simulation for Quantum Open Systems

Chen Guanhua

Department of Chemistry

The University of Hong Kong

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Principle Investigator :

Prof. Guanhua Chen

Research Assistant Professor:

Dr. Chi Yung Yam (PhD, HKU)

Research Associates / Postdocs :

Dr. L.Y. Meng Dr. J. Peng Dr. H. Cao
Dr. Jian Sun Dr. H. Xie

Graduate Students:

Mr. S. K. Koo Mr. S.G. Chen
Mr. C.L. Zhang Mr. Heng Tian
Mr. Z.Y. Yin Mr. Q. Zhang
Mr. Y. Zhang Miss J.Q. Zhang
Mr. Y. Huang Mr. K. Kwok

Former Members :

Prof. WanZhen Liang (U. Sci. & Tech. China)
Prof. Satoshi Yokojima (Tokyo U. Phar. & Life)
Prof. Xiujun Wang (S. China U. Tech.)
Prof. Fan Wang (Sichuan Univ.)
Dr. Andy Ng (NTU, Singapore)
Dr. Martin Ma (Ph.D., HKU)
Dr. Larry Wong (Ph.D., HKU)
Prof. Xiao Zheng (U. Sci. & Tech. China)
Prof. Yang Zhao (NTU, Singapore)
Dr. Yan Mo (Ph.D., HKUST)
Mr. Xiaobo Li (Mphil., HKU)
Dr. Xiaojing Ren (PetroChina)
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UC Riverside:	Prof. Q. Jiang
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Tsinghua Univ.:	Profs. Q.S. Zheng, Z.P. Xu
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Univ. Bremen:	Prof. T. Frauenheim
U. Regensburg:	Prof. T. Niehaus
Caltech:	Prof. W.A. Goddard

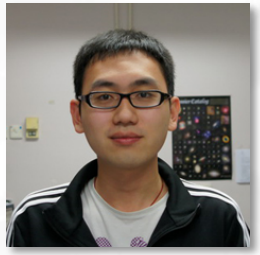
Xiao Zheng

Fan Wang

Jacky Yam

Heng TIAN

SG CHEN



Hang XIE

Open Systems

First-principles method for open systems ?

Quantum Dissipation Theory / Master Equation /

Liouville-von Neumann Equation: model systems

(one or two levels)

$$i\, d\rho/dt = [H, \rho] - i\, R\rho$$

ρ: density matrix of system

☸ Role of Electron Density Function ρ(**r**)

✓ **Ground-state density functional theory (DFT)**

HK Theorem P. Hohenberg & W. Kohn, *Phys. Rev.* **136**, B864 (1964)

ρ(r) ⟹ all system properties

✓ **Time-dependent DFT for excited states (TDDFT)**

RG Theorem E. Runge & E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984)

ρ(r,t) ⟹ Excited state properties

What do we solve usually?

Schrödinger Equation for electrons

$$\mathbf{H}\,\psi = \mathbf{E}\,\psi$$

Hamiltonian

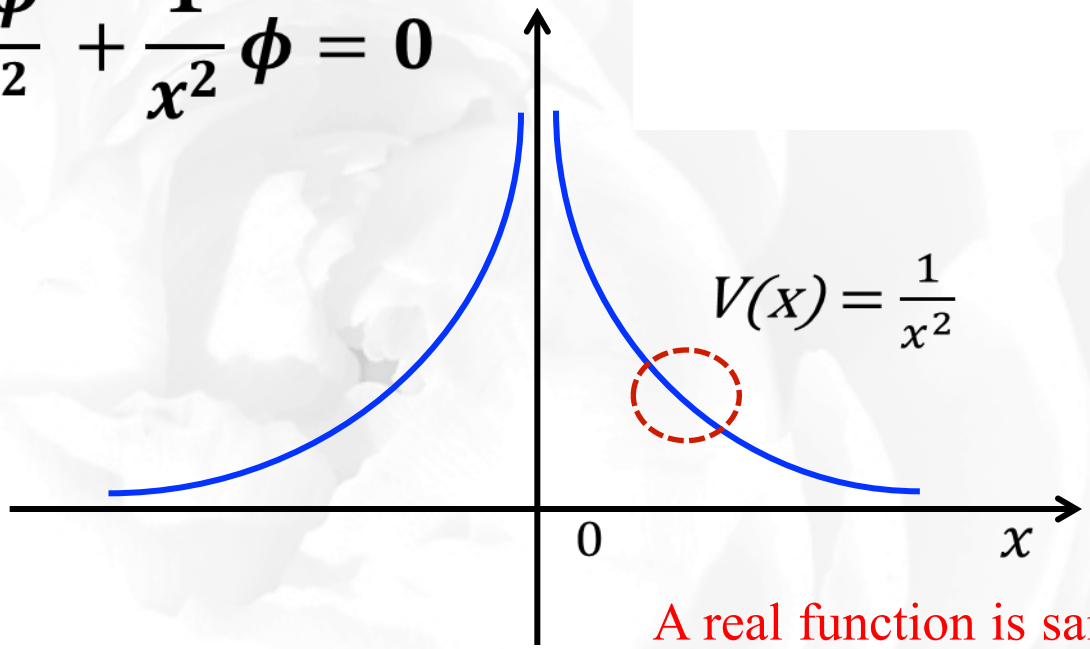
$$H = -(h^2/2m_e)\sum_i \nabla_i^2 - \sum_i \sum_\alpha Z_\alpha e^2/r_{i\alpha} + \sum_i \sum_j e^2/r_{ij}$$

Ψ is analytical except (i) $r_i = R_\alpha$; & (ii) $r_i = r_j$

ψ is real analytic in $\mathbf{R}^{3N} \setminus \Sigma$.

$$\Sigma = \left\{ \mathbf{x} \in \mathbf{R}^{3N} \;\middle|\; \left(\prod_{i=1}^{N} \prod_{l=1}^{L} |x_i - R_l| \right) \left(\prod_{1 \le i < j \le N} |x_j - x_i| \right) = 0 \right\}$$

$$-\frac{1}{2}\frac{d^2\phi}{dx^2}+\frac{1}{x^2}\phi=0$$



A real function is said to be **analytic** if it possesses derivatives of all orders and agrees with its **Taylor series** in the neighborhood of every point

Solution:

$$\phi=\frac{C}{x}\ :\ \ analytical\ except\ x=0$$

(C: a constant)

Commun. Math. Phys. 228, 401 – 415 (2002)

Communications in
Mathematical
Physics

The Electron Density is Smooth Away from the Nuclei *

Søren Fournais[1,**,***], **Maria Hoffmann-Ostenhof**[2],
Thomas Hoffmann-Ostenhof[1,3,†], **Thomas Østergaard Sørensen**[1,‡,♣]

[1] The Erwin Schrödinger International Institute for Mathematical Physics, Boltzmanngasse 9, 1090 Vienna, Austria
[2] Institut für Mathematik, Strudlhofgasse 4, Universität Wien, 1090 Vienna, Austria.
E-mail: mhoffman@esi.ac.at
[3] Institut für Theoretische Chemie, Währingerstrasse 17, Universität Wien, 1090 Vienna, Austria.
E-mail: thoffman@esi.ac.at

Received: 29 October 2001 / Accepted: 15 November 2001

Abstract: We prove that the electron densities of electronic eigenfunctions of atoms and molecules are smooth away from the nuclei.

Ark. Mat., **42** (2004), 87–106

Analyticity of the density of electronic wavefunctions

Søren Fournais, Maria Hoffmann-Ostenhof, Thomas Hoffmann-Ostenhof and Thomas Østergaard Sørensen

Abstract. We prove that the electronic densities of atomic and molecular eigenfunctions are real analytic in $\mathbf{R}^3$ away from the nuclei.

Theorem 1.1. *Let $\psi \in L^2(\mathbf{R}^{3N})$ satisfy the equation*

$$H\psi = E\psi,$$

with $E \in \mathbf{R}$ and H given by (1.1). *Let the density ϱ be defined as in* (1.6). *Then ϱ is a real analytic function in $\mathbf{R}^3 \setminus \{R_1, \dots, R_L\}$.*

Lett Math Phys (2010) 93:73–83
DOI 10.1007/s11005-010-0401-9

A New Proof of the Analyticity of the Electronic Density of Molecules

THIERRY JECKO
Département de mathématiques, site de Saint Martin, AGM, UMR 8088 du CNRS, Université de Cergy-Pontoise, 2 avenue Adolphe Chauvin, F-95000 Pontoise, France.
e-mail: thierry.jecko@u-cergy.fr; URL: http://www.u-cergy.fr/tjecko/

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Published online: 6 June 2010 – © Springer 2010

Holographic Electron Density Theorem

Steven G. Krantz
Harold R. Parks

A Primer of Real Analytic Functions

1992 Birkhäuser Verlag
Basel · Boston · Berlin

Corollary 1.2.5 *If f and g are real analytic functions on an open interval U and there is an open set $W \subset U$ such that*

$$f(x) = g(x), \qquad \text{for all } x \in W,$$

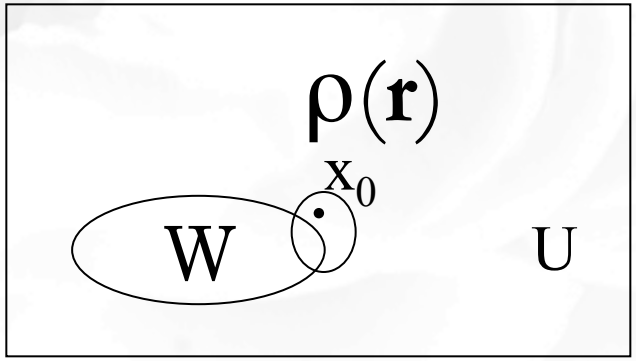
then

$$f(x) = g(x), \qquad \text{for all } x \in U.$$

☸ Holographic electron density theorem for time-independent systems

Lemma: If the electron density function $\rho(\mathbf{r})$ is real analytic on a connected physical space U with $\mathrm{W} \subseteq U$ being a subspace, $\rho(\mathbf{r})$ can be uniquely determined on entire U, provided that $\rho(\mathbf{r})$ is known for all $\mathbf{r} \in \mathrm{W}$

$\rho(\mathbf{r})$ is real analytical



Zheng, Wang, Yam, Mo & **GHC**, Phys. Rev. B75 195127 (2007)
Zheng, Wang Yam & **GHC**, Phys. Chem. Chem. Phys. 14, 4695 (2012)

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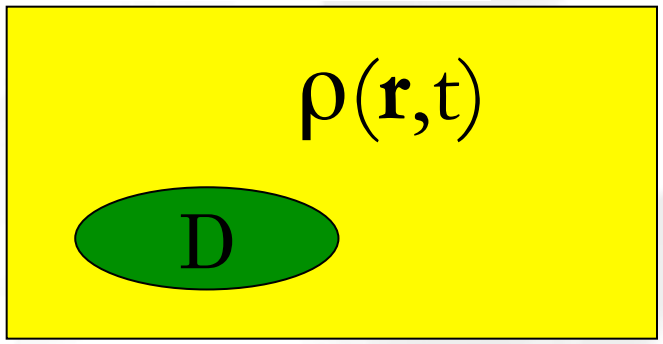
PHYSICAL REVIEW B 75, 195127 (2007)

Time-dependent density-functional theory for open systems

Xiao Zheng,[1] Fan Wang,[1] Chi Yung Yam,[1] Yan Mo,[1] and GuanHua Chen[1,2,*]
[1]*Department of Chemistry, The University of Hong Kong, Hong Kong, China*
[2]*Centre for Theoretical and Computational Physics, The University of Hong Kong, Hong Kong, China*
(Received 19 December 2006; revised manuscript received 23 March 2007; published 24 May 2007)

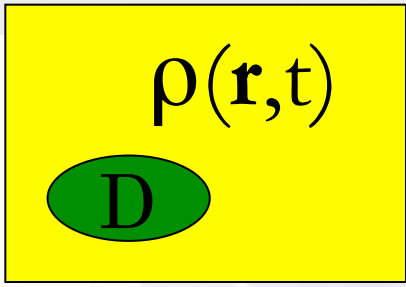
Theorem. If the electron density function of a real finite physical system at t_0, $\rho(\mathbf{r},t_0)$, is real analytic in $\mathbf{r}$ space, the corresponding wave function is $\Phi(t_0)$, and the system is subjected to a real analytic (in both t space and $\mathbf{r}$ space) external potential field $v(\mathbf{r},t)$, the time-dependent electron density function on any finite subspace D, $\rho_D(\mathbf{r},t)$, has a one-to-one correspondence with $v(\mathbf{r},t)$ and determines uniquely all electronic properties of the entire time-dependent system.

$\rho_D(\mathbf{r},t) \Longleftrightarrow v(\mathbf{r},t)$



Rung & Gross, Phys. Rev. Lett. (1985):

$$\left.\frac{\partial^{k+2}}{\partial t^{k+2}}[\rho(\mathbf{r},t)-\rho'(\mathbf{r},t)]\right|_{t=t_0} = -\nabla\cdot\mathbf{u}(\mathbf{r}),$$



where

$$\mathbf{u}(\mathbf{r}) = \rho(\mathbf{r},t_0)\,\nabla\left\{\left.\frac{\partial^{k}}{\partial t^{k}}[v(\mathbf{r},t)-v'(\mathbf{r},t)]\right|_{t=t_0}\right\}.$$

it is *impossible* to have $\nabla\cdot\mathbf{u}(\mathbf{r})=0$ on the entire $\mathbf{r}$ space.

Therefore it is also impossible that $\nabla\cdot\mathbf{u}(\mathbf{r})=0$ everywhere in D because of analytical continuation of $\nabla\cdot\mathbf{u}(\mathbf{r})$. Note that $\rho_D(\mathbf{r},t)=\rho(\mathbf{r},t)$ for $\mathbf{r}\in D$. We have thus

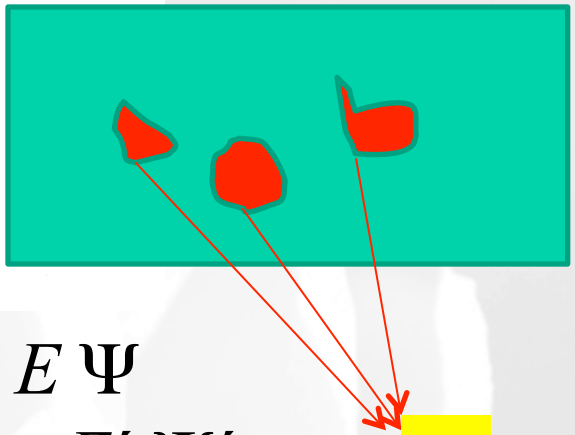
$$\left.\frac{\partial^{k+2}}{\partial t^{k+2}}[\rho_D(\mathbf{r},t)-\rho'_D(\mathbf{r},t)]\right|_{t=t_0} \neq 0 \qquad (4)$$

for $\mathbf{r}\in D$. This confirms the existence of a one-to-one correspondence between $v(\mathbf{r},t)$ and $\rho_D(\mathbf{r},t)$.

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†
École Normale Superieure, Paris, France
AND
W. KOHN‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California



The proof proceeds by *reductio ad absurdum*. Assume that another potential $v'(\mathbf{r})$, with ground state Ψ' gives rise to the *same* density $n(\mathbf{r})$. Now clearly [unless $v'(\mathbf{r})-v(\mathbf{r})=\text{const}$] Ψ' cannot be equal to Ψ since they satisfy different Schrödinger equations.

$$E'=(\Psi',H'\Psi')<(\Psi,H'\Psi)=(\Psi,(H+V'-V)\Psi),$$

so that

$$E'<E+\int[v'(\mathbf{r})-v(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \quad (6)$$

Interchanging primed and unprimed quantities, we find in exactly the same way that

$$E<E'+\int[v(\mathbf{r})-v'(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \quad (7)$$

Addition of (6) and (7) leads to the inconsistency

$$E+E'<E+E'. \quad (8)$$

$$\boldsymbol{H}\,\Psi = E\,\Psi$$
$$\boldsymbol{H}'\,\Psi' = E'\,\Psi'$$

If $\Psi' = \Psi$

$$(V\text{-}V')\,\Psi = (E\text{-}E')\Psi$$

thus

$$V\text{-}V' = E\text{-}E'$$

or

$\Psi = 0$ & $V\text{-}V' \neq$ const.

for subspaces, which is false:

Because $V\text{-}V'/\Psi$ is analytical

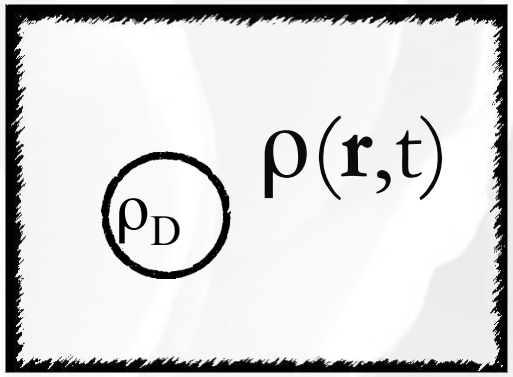
Riess & Munch, Theoret. Chim. Acta (Berl.) 58, 295 (1981)

Time-dependent holographic electron density theorem

Zheng, Wang, Yam, Mo & Chen, Phys. Rev. B (2007).

$\rho_D(\mathbf{r},t) \Longleftrightarrow v(\mathbf{r},t) \Longrightarrow$ system properties

The electron density distribution of a sub-system determines all physical Properties of the entire system!

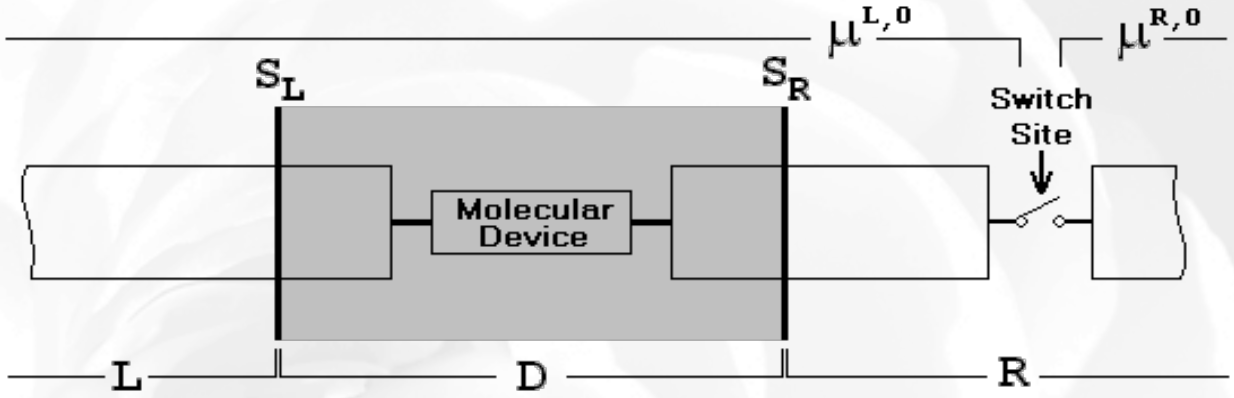


Existence of a rigorous TDDFT for Open System

X. Zheng and G.H. Chen, *arXiv:physics*/0502021 (2005)

Zheng, Wang, Yam, Mo & Chen, PRB 75, 195127 (2007)

What is the first-principles method for open system?



Liouvile-von Neumann Eq.

$$i\dot{\sigma}(t) = \left[h(t), \sigma(t)\right]$$

$$\sigma_{ij}(t) = \left\langle a_j^{\dagger}(t) a_i(t) \right\rangle$$

Density matrix

$$\sigma = \begin{bmatrix} \sigma_L & \sigma_{LD} & \sigma_{LR} \\ \sigma_{DL} & \sigma_D & \sigma_{DR} \\ \sigma_{RL} & \sigma_{RD} & \sigma_R \end{bmatrix}$$

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

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

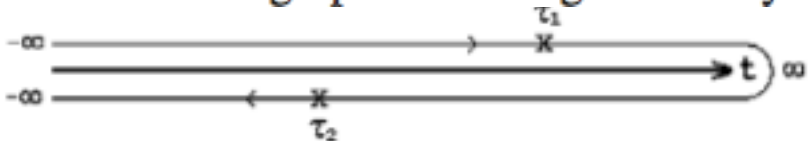
$$Q_{\alpha,nm}(t) = -\sum_{l \in D} \int_{-\infty}^{\infty} d\tau \left[G^{<}_{nl}(t,\tau)\Sigma^{a}_{\alpha,lm}(\tau,t) + G^{r}_{nl}(t,\tau)\Sigma^{<}_{\alpha,lm}(\tau,t) + \text{H.c.} \right]$$

Zheng, Wang, Yam, Mo & Chen, PRB 75, 195127 (2007)

In the Keldysh formalism,[30] the nonequilibrium single-electron Green's function $G_{k_\alpha m}(t,t')$ is defined by

$$G_{k_\alpha m}(t,t') \equiv -i\langle T_C\{a_{k_\alpha}(t)a_m^\dagger(t')\}\rangle, \qquad \text{(A1)}$$

T_C is the contour-ordering operator along the Keldysh contour



Dyson equation for $G_{k_\alpha m}(t,t')$

$$G_{k_\alpha m}(t,t') = \sum_{l\in D}\int_C d\tau g_{k_\alpha}(t,\tau)h_{k_\alpha l}(\tau)G_{lm}(\tau,t')$$

where $G_{lm}(\tau,t')$ and $g_{k_\alpha}(t,\tau)$ are the contour-ordered Green's

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

Applying the analytical continuation rules of Langreth,[31] we have

$$G^<_{mk_\alpha}(t',t) \equiv i\langle a^\dagger_{k_\alpha}(t)a_m(t')\rangle$$

$$= -[G^<_{k_\alpha m}(t,t')]^* = \sum_{l\in D}\int_{-\infty}^{\infty} d\tau h_{lk_\alpha}(\tau)$$

$$\times[g^<_{k_\alpha}(\tau,t)G^r_{ml}(t',\tau) + g^a_{k_\alpha}(\tau,t)G^<_{ml}(t',\tau)]$$

$$\Sigma^a_{\alpha,ln}(t,\tau) = \sum_{k_\alpha\in\alpha} h_{lk_\alpha}(t)g^a_{k_\alpha}(t,\tau)h_{k_\alpha n}(\tau)$$

$$\Sigma^<_{\alpha,ln}(t,\tau) = \sum_{k_\alpha\in\alpha} h_{lk_\alpha}(t)g^<_{k_\alpha}(t,\tau)h_{k_\alpha n}(\tau)$$

Langreth & Nordlander, PRB 43, 2541 (1991)
Zheng, Wang, Yam, Mo & GHC, PRB 75, (2007)

Exact TDDFT for Quantum Transport

Xiao Zheng, Guanhua Chen, Yan Mo, Siukong Koo, Heng Tian, ChiYung Yam, & YiJingYan, **"Time-dependent density functional theory for quantum transport"**, **Journal of Chemical Physics 133, 114101 (2010)**

$$i\dot{\boldsymbol{\sigma}}_{\mathrm{D}} = [\boldsymbol{h}_{\mathrm{D}}, \boldsymbol{\sigma}_{\mathrm{D}}] - \sum_{\alpha} [\boldsymbol{\varphi}_{\alpha}(t) - \boldsymbol{\varphi}_{\alpha}^{\dagger}(t)],$$

$i\mathbf{Q}_{\alpha}$

$$i\dot{\boldsymbol{\varphi}}_{\alpha}(\epsilon,t) = [\boldsymbol{h}_{\mathrm{D}}(t) - \epsilon - \Delta_{\alpha}(t)]\boldsymbol{\varphi}_{\alpha}(\epsilon,t)$$

$$\boldsymbol{\varphi}_{\alpha}(t) = \int d\epsilon \boldsymbol{\varphi}_{\alpha}(\epsilon,t)$$

1st-tier Auxiliary Density matrix

$$+ [f_{\alpha}(\epsilon) - \boldsymbol{\sigma}_{\mathrm{D}}]\boldsymbol{\Lambda}_{\alpha}(\epsilon) + \sum_{\alpha'} \int d\epsilon' \boldsymbol{\varphi}_{\alpha,\alpha'}(\epsilon,\epsilon',t),$$

$$i\dot{\boldsymbol{\varphi}}_{\alpha,\alpha'}(\epsilon,\epsilon'$$

2nd -tier Auxiliary Density matrix

Integration ➔ Summation

EXACT !!!!

$$\boldsymbol{\varphi}_{\alpha}(\epsilon,t) = i\int_{-\infty}^{t} d$$

$$\boldsymbol{\varphi}_{\alpha,\alpha'}(\epsilon,\epsilon',t)$$

$$= i\left[\int_{C} d\tau_1 \int_{C} d\tau_2 \boldsymbol{\Sigma}_{\alpha'}(t,\tau_1;\epsilon')\boldsymbol{G}_{\mathrm{D}}(\tau_1,\tau_2)\boldsymbol{\Sigma}_{\alpha}(\tau_2,t;\epsilon)\right]^{<}$$

Two Numerical Schemes

Hang XIE

Scheme One: **Lorentzian-Padé Decomposition**

Self-energy decomposition

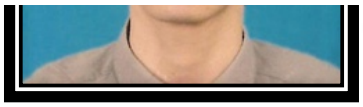
non-Markovian, finite temperatures

CPU Time $\propto O(N^3)$

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

Xie et. al. J. Chem. Phys. 137, 044113 (2012)

An efficient solution of Liouville-von Neumann equation that is applicable to zero and finite temperatures



Heng TIAN

CPU Time $\propto O(N^3)$

Tian and GHC, J. Chem. Phys. 137, 044113 (2012)

Scheme One: Lorentzian-Padé Decomposition

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

$$i\dot{\varphi}_{\alpha k} = \left[h_D(t) - i\gamma_{\alpha k} - \Delta_\alpha(t)\right]\varphi_{\alpha k}(t) + i\left[\sigma_D(t)A^>_{\alpha k} + \bar{\sigma}_D(t)A^<_{\alpha k}\right]$$

1st-tier Auxiliary Density matrix

$$+\sum_{\alpha'}\sum_{k'=1}^{N_k}\varphi_{\alpha k,\alpha' k'}(t)$$

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

2nd -tier Auxiliary Density matrix

Self-energy: Lorentzian expansion

Fermi function: Padé expansion

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

Xie et. al. JCP 137, 044113 (2012)

Scheme Two: Chebyshev Spectral Decomposition

Tian & GHC, JCP 137, 204114 (2012)

$$\bar{\omega} = \frac{\omega_{max} + \omega_{min}}{2}, \quad \Omega = \frac{\omega_{max} - \omega_{min}}{2},$$

$$i\dot{\boldsymbol{\sigma}}_{\mu\nu}(t) = [\boldsymbol{h}(t), \boldsymbol{\sigma}(t)]_{\mu\nu} - \sum_{\alpha} \Omega \int_{-1}^{1} \mathrm{d}x \left[\mathrm{e}^{i\Omega x(t-t_0)} \boldsymbol{\varphi}_{\alpha,\mu\nu}(x,t) - \mathrm{e}^{-i\Omega x(t-t_0)} \boldsymbol{\varphi}^{\dagger}_{\alpha,\mu\nu}(x,t) \right].$$

1st-tier auxiliary density matrix

$$i\dot{\boldsymbol{\varphi}}_{\alpha,\mu\nu}(x,t) = -\left[\Delta_{\alpha}(t) + \bar{\omega}\right] \boldsymbol{\varphi}_{\alpha,\mu\nu}(x,t) + \sum_{\mu'} \boldsymbol{h}_{\mu\mu'} \boldsymbol{\varphi}_{\alpha,\mu'\nu}(x,t)$$

$$- \sum_{\mu'} \boldsymbol{\sigma}_{\mu\mu'}(t) \boldsymbol{\Lambda}_{\alpha,\mu'\nu}(x,t) + f^{-}_{\alpha}(x) \boldsymbol{\Lambda}_{\alpha,\mu\nu}(x,t)$$

2nd-tier auxiliary density matrix

$$+ \Omega \sum_{\alpha'} \int_{-1}^{1} \mathrm{d}x' \, \mathrm{e}^{-i\Omega x'(t-t_0)} \boldsymbol{\psi}_{\alpha'\alpha,\mu\nu}(x', x, t).$$

$$\dot{\boldsymbol{\psi}}_{\alpha'\alpha,\mu\nu}(x', x, t)$$

$$= i\left[\Delta_{\alpha}(t) + \bar{\omega}\right] \boldsymbol{\psi}_{\alpha'\alpha,\mu\nu}(x', x, t) - i\left[\Delta_{\alpha'}(t) + \bar{\omega}\right] \boldsymbol{\varphi}_{\alpha'\alpha,\mu\nu}(x', x, t) + \mathrm{tr}_{\mathrm{T}}\left[\tilde{b}^{\dagger}_{\alpha\nu}(x,t)\, \tilde{b}_{\alpha'\mu}(x',t)\, \dot{\tilde{\boldsymbol{\rho}}}_{\mathrm{T}}(t)\right]$$

$$= i\left[\Delta_{\alpha}(t) - \Delta_{\alpha'}(t)\right] \boldsymbol{\psi}_{\alpha'\alpha,\mu\nu}(x', x, t) - i \sum_{\mu'} \boldsymbol{\Lambda}^{*}_{\alpha',\mu\mu'}(x', t) \boldsymbol{\varphi}_{\alpha,\mu'\nu}(x,t) + i \sum_{\mu'} \boldsymbol{\varphi}^{\dagger}_{\alpha',\mu\mu'}(x', t) \boldsymbol{\Lambda}_{\alpha,\mu'\nu}(x,t).$$

Scheme Two: Chebyshev Spectral Decomposition

Tian & GHC, JCP 137, 204114 (2012)

Jacobi-Anger identity

$$\bar{\omega} = \frac{\omega_{max} + \omega_{min}}{2}, \quad \Omega = \frac{\omega_{max} - \omega_{min}}{2},$$

$$\mathrm{e}^{-i\Omega x(t-t_0)} = J_0\left(\Omega(t-t_0)\right) + \sum_{n=1}^{\infty} 2(-i)^n J_n\left(\Omega(t-t_0)\right) T_n(x)$$

$J_n(t)$ is the Bessel function of the first kind of integer order

$T_n(x)$ is the Chebyshev polynomial of the first kind

$$i\dot{\boldsymbol{\sigma}}(t) = [\boldsymbol{h}(t), \boldsymbol{\sigma}(t)] - \sum_{\alpha}\sum_{k=0}^{\infty}\left[\Omega i^k J_k\left(\Omega(t-t_0)\right)\boldsymbol{\varphi}_{\alpha,k}(t) - \mathrm{H.C.}\right],$$

$$i\dot{\boldsymbol{\varphi}}_{\alpha,k}(t) = \left[\boldsymbol{h}(t) - \bar{\omega} - \Delta_\alpha(t)\right]\boldsymbol{\varphi}_{\alpha,k}(t) + (2-\delta_{k,0})\left[\boldsymbol{\Xi}_{\alpha,k}(t) - \boldsymbol{\sigma}(t)\boldsymbol{\Pi}_{\alpha,k}(t)\right]$$

1st-tier auxiliary density matrix

$$+\sum_{\alpha'}\sum_{k'=0}^{\infty}(-i)^{k'}\Omega J_{k'}(\Omega(t-t_0))\boldsymbol{\psi}_{\alpha'k',\alpha k}(t),$$

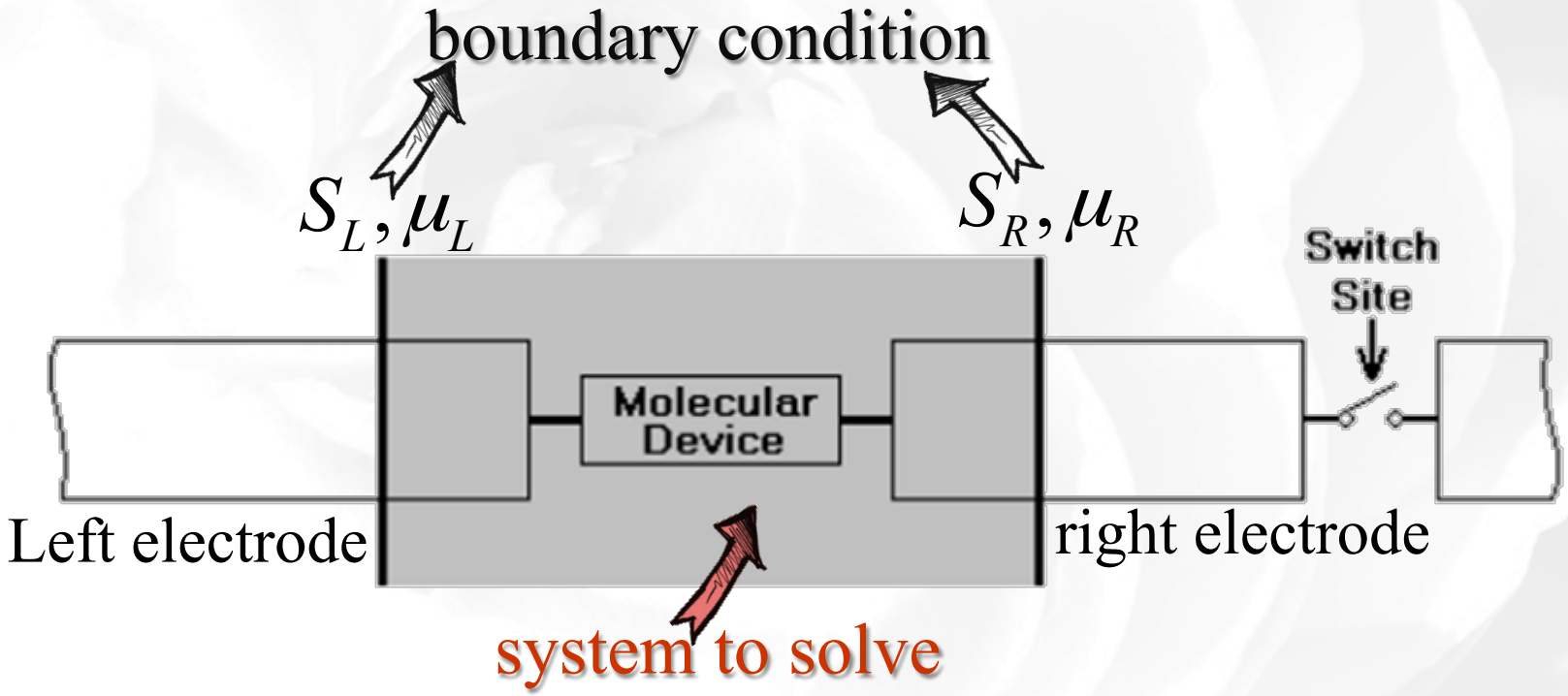
$$i\dot{\boldsymbol{\psi}}_{\alpha'k',\alpha k}(t) = (2-\delta_{k'0})\boldsymbol{\Pi}^*_{\alpha',k'}(t)\boldsymbol{\varphi}_{\alpha,k}(t) - (2-\delta_{k0})\boldsymbol{\varphi}^\dagger_{\alpha',k'}(t)\boldsymbol{\Pi}_{\alpha,k}(t)$$

2nd-tier auxiliary density matrix

$$+\left[\Delta_{\alpha'}(t) - \Delta_\alpha(t)\right]\boldsymbol{\psi}_{\alpha'k',\alpha k}(t),$$

$$\boldsymbol{\varphi}_{\alpha,k}(t) = (2-\delta_{k,0})\int_{-1}^{1}\mathrm{d}x T_k(x)\boldsymbol{\varphi}_\alpha(x,t) \qquad J_n(t) \sim \frac{1}{\sqrt{2\pi n}}\left(\frac{\mathrm{e}t}{2n}\right)^n \quad \text{as } n\to\infty$$

First-principles Liouville-von Neumann equation



$$i\dot{\sigma}_D = \left[h_D\left[t;\rho_D(\mathbf{r},t)\right],\sigma_D\right] - i\sum_{\alpha=L,R} Q_\alpha\left[t;\rho_D(r,t)\right]$$

Poisson Equation with *boundary condition via potentials at* S_L *and* S_R

Zheng, Wang, Yam, Mo & Chen, PRB 75, 195127 (2007)

Quantum Transport through Mesoscopic Devices

Quantum kinetic equation:

Quantum version of Boltzmann Transport Eq.

for Wigner function: f(R, k; t)

$\sigma(r,r';t)=\sigma(R,\Delta;t)$ → Wigner function: f(R, k; t)

Fourier Transformation *with* $R = (r+r')/2$; $\Delta = r-r'$

Our Theory: ***First-principles quantum kinetic equation for transport***

Simple Boundary Condition & Easy to Implement

PHYSICAL REVIEW B 75, 195127 (2007)

Time-dependent density-functional

Xiao Zheng,[1] Fan Wang,[1] Chi Yung Yam,[1] Y
[1]*Department of Chemistry, The University of*
[2]*Centre for Theoretical and Computational Physics, The U*
(Received 19 December 2006; revised manuscript receive

EUROPHYSICS LETTERS
Europhys. Lett., **67** (1), pp. 14–20 (2004)
DOI: 10.1209/epl/i2004-10043-7

Time-dependent quantum transport:
An exact formulation based on TDDFT

G. Stefanucci and C.-O. Almbladh
Department of Solid State Theory, Institute of Physics, Lund University
Sölvegatan 14 A, 223 62 Lund, Sweden

C. Solution for steady-state current

(if steady state current exists)

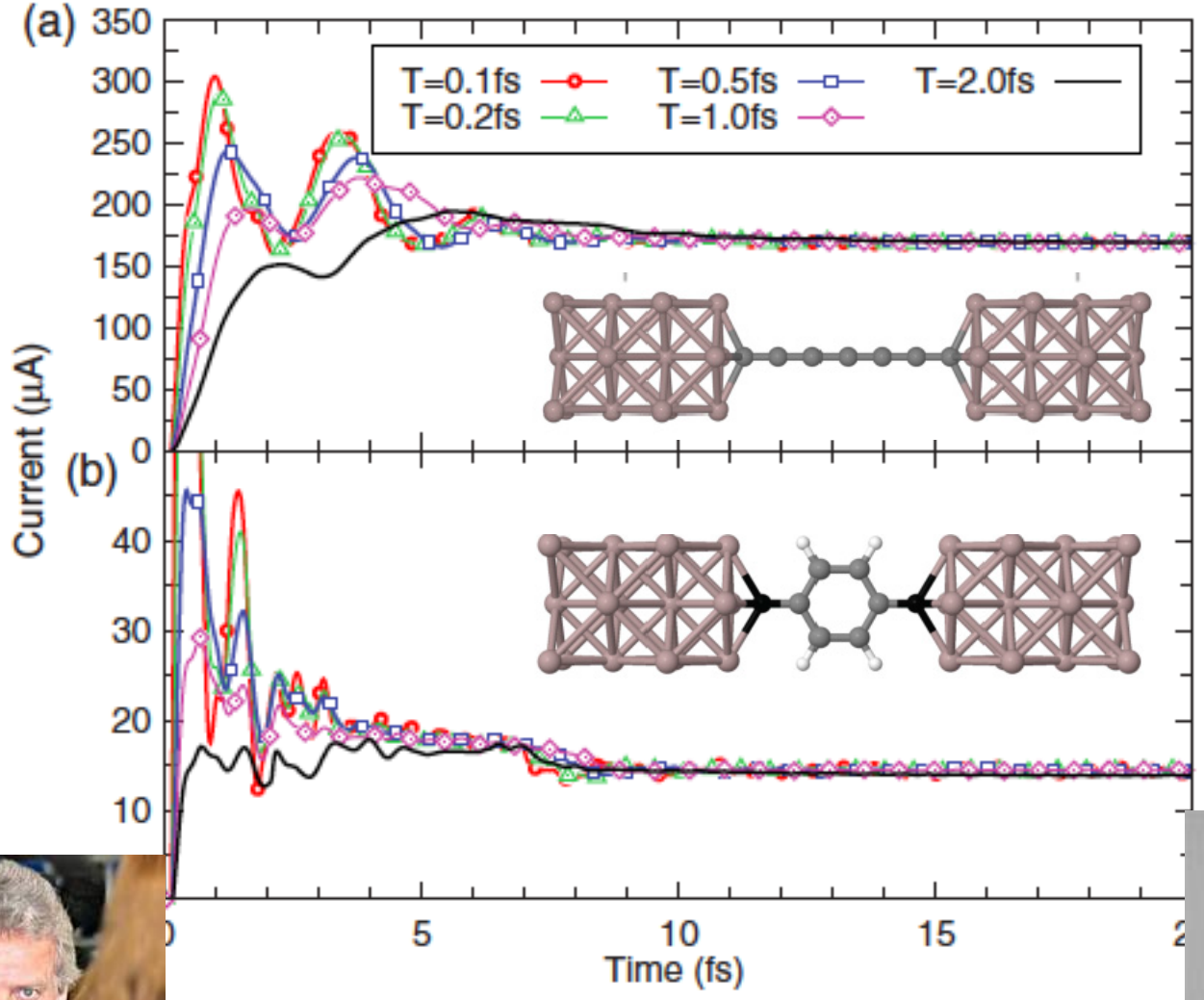
$$J_L(\infty) = -J_R(\infty) = -\sum_{n\in D} Q_{L,nn}(\infty)$$

$$= 2\pi\Bigg(\sum_{k\in L} f_k^L \sum_{l\in R} \delta(\epsilon_l^R - \epsilon_k^L)\mathrm{tr}[G_D^r(\epsilon_k^L)\Gamma^{l_R} G_D^a(\epsilon_k^L)\Gamma^{k_L}]$$

$$- \sum_{l\in R} f_l^R \sum_{k\in L} \delta(\epsilon_k^L - \epsilon_l^R)\mathrm{tr}[G_D^r(\epsilon_l^R)\Gamma^{l_R} G_D^a(\epsilon_l^R)\Gamma^{k_L}]\Bigg)$$

$$= \int [f^L(\epsilon) - f^R(\epsilon)]T(\epsilon)d\epsilon, \qquad (17)$$

formally analogous to the Landauer formula[36,37]



Thomas Frauenheim

TDLDA-NEGF

CECAM 2015

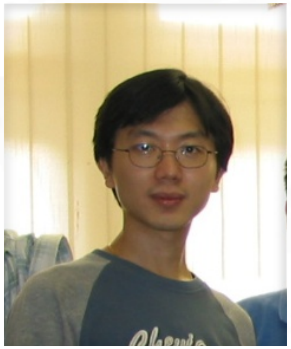
Thomas Niehaus

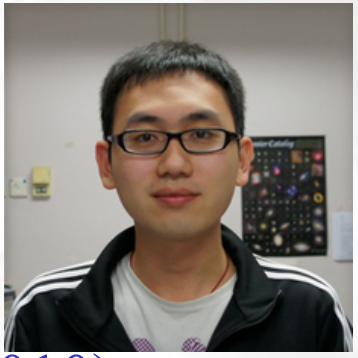
Wide-Band-Limit Approximation

$$\dot{\boldsymbol{\varphi}}_{\alpha}(t) = i[\boldsymbol{\sigma}_D - \frac{1}{2}]\boldsymbol{\Lambda}_{\alpha}(t) - \sum_k \boldsymbol{\varphi}_{\alpha,k}(t)$$

$$\dot{\boldsymbol{\varphi}}_{\alpha k}(t) = \frac{2}{\beta}\boldsymbol{\Lambda}_{\alpha}(t) - i[\mathbf{h}_D(t) - i\boldsymbol{\Lambda}(t) - z_{\alpha k}(t)]\boldsymbol{\varphi}_{\alpha k}(t)$$

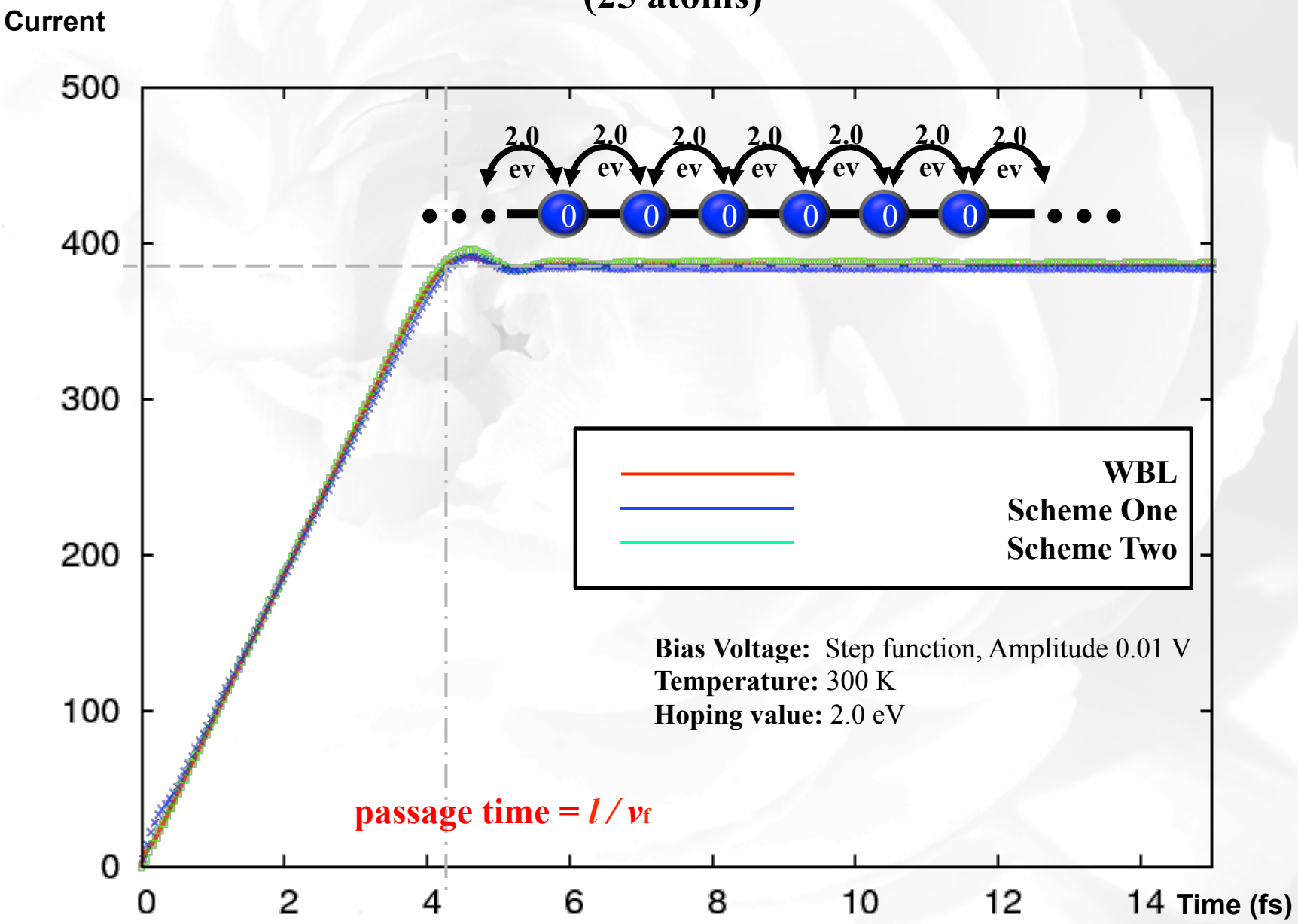
$$i\dot{\boldsymbol{\sigma}}_D(t) = [\mathbf{h}_D(t), \boldsymbol{\sigma}_D(t)] - \sum_{\alpha}[\boldsymbol{\varphi}_{\alpha}(t) - \boldsymbol{\varphi}_{\alpha}^{\dagger}(t)]$$



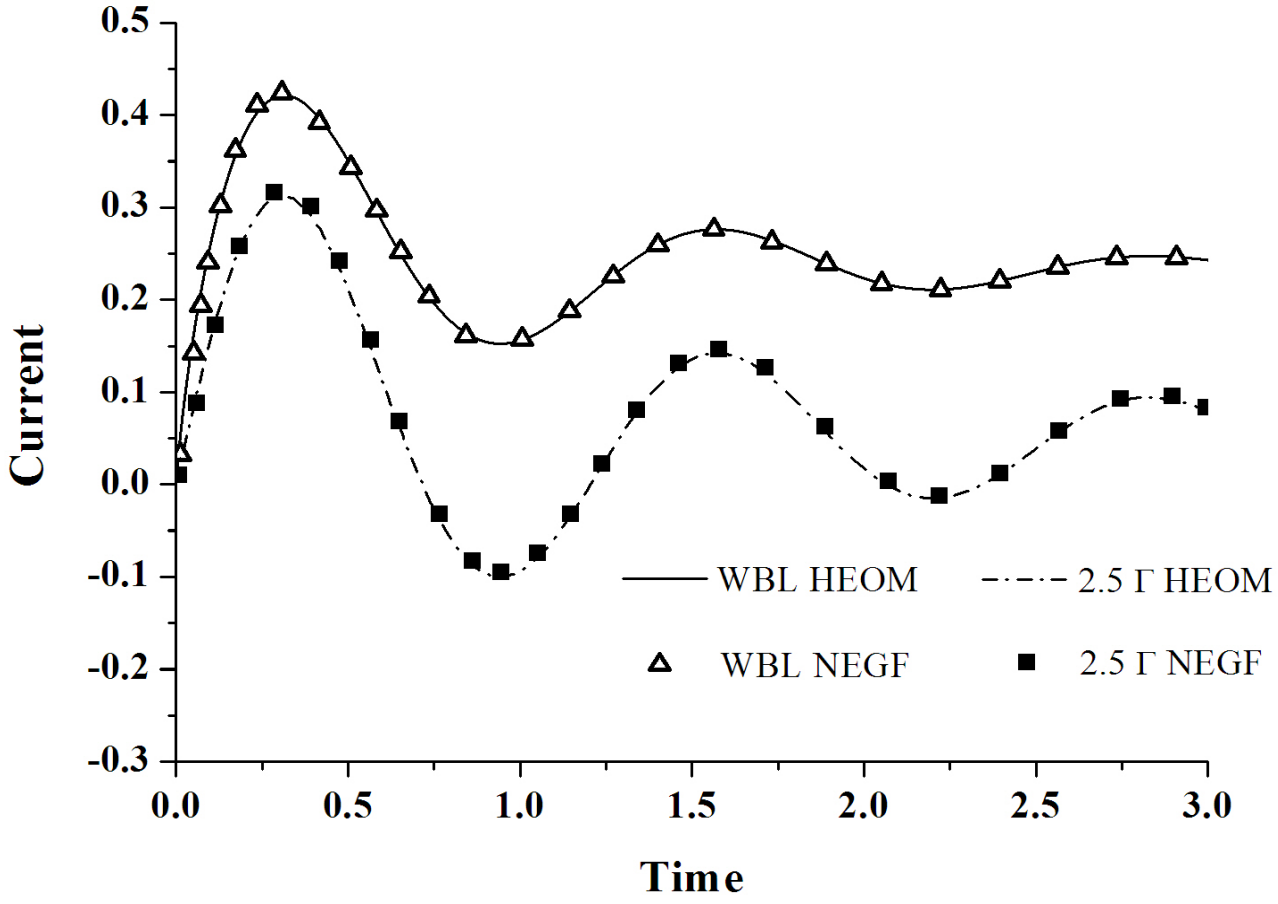


Zheng et. al. JCP 133, 114101 (2010)

Comparison between different schemes for spectrum expansion (25 atoms)



Single site model



$$\Sigma_{total} = \Sigma_{electrode} + \Sigma_{phonon} + \Sigma_{photon} + \Sigma_{electron\text{-}electron}$$

Environment has infinite numbers of states, $\mathbf{\Sigma} = \mathrm{Re}\,(\mathbf{\Sigma}) + i\,\mathrm{Im}(\mathbf{\Sigma})$

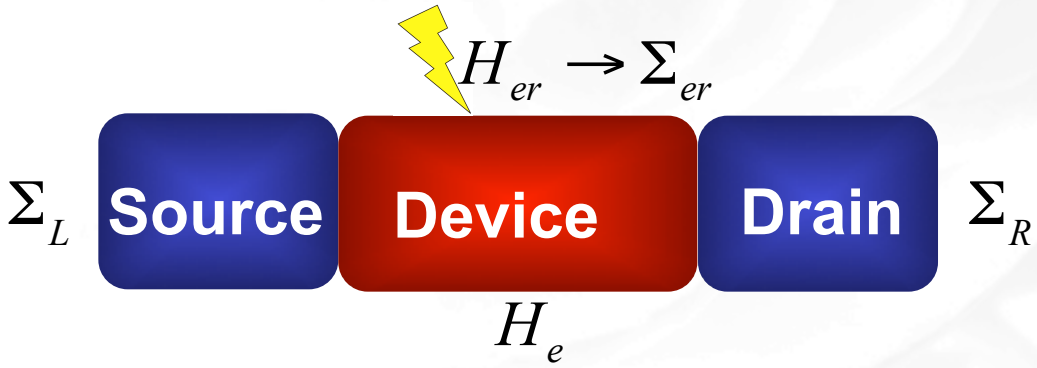
Quantum-Mechanical Prediction of Nanoscale Photovoltaics

Yu Zhang,[†] LingYi Meng,[‡,†] ChiYung Yam,[§,†] and GuanHua Chen*[,†]

$$H = \frac{1}{2m}(\boldsymbol{p} + e\boldsymbol{A})^2 + V(\boldsymbol{r}) = H_e + \frac{e}{m}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{2m}\boldsymbol{A}^2$$

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

$$H_{er} = \sum_{\mu\nu} e\left(\frac{\hbar\sqrt{\tilde{\mu}\tilde{\epsilon}}}{2N\omega\epsilon c}F_r\right)^{1/2}(be^{-i\omega t} + b^{\dagger}e^{i\omega t})\boldsymbol{a}\cdot\langle\mu|\frac{\boldsymbol{p}}{m}|\nu\rangle d_{\mu}^{\dagger}d_{\nu}$$



Yu Zhang

“无量无边诸国土，悉令共入一尘中”，
《华严经•Avatamsakasütra》

Auguries of Innocence

William Blake

To see a world in a grain of sand,
And a heaven in a wild flower,
Hold infinity in the palm of your hand,
And eternity in an hour...

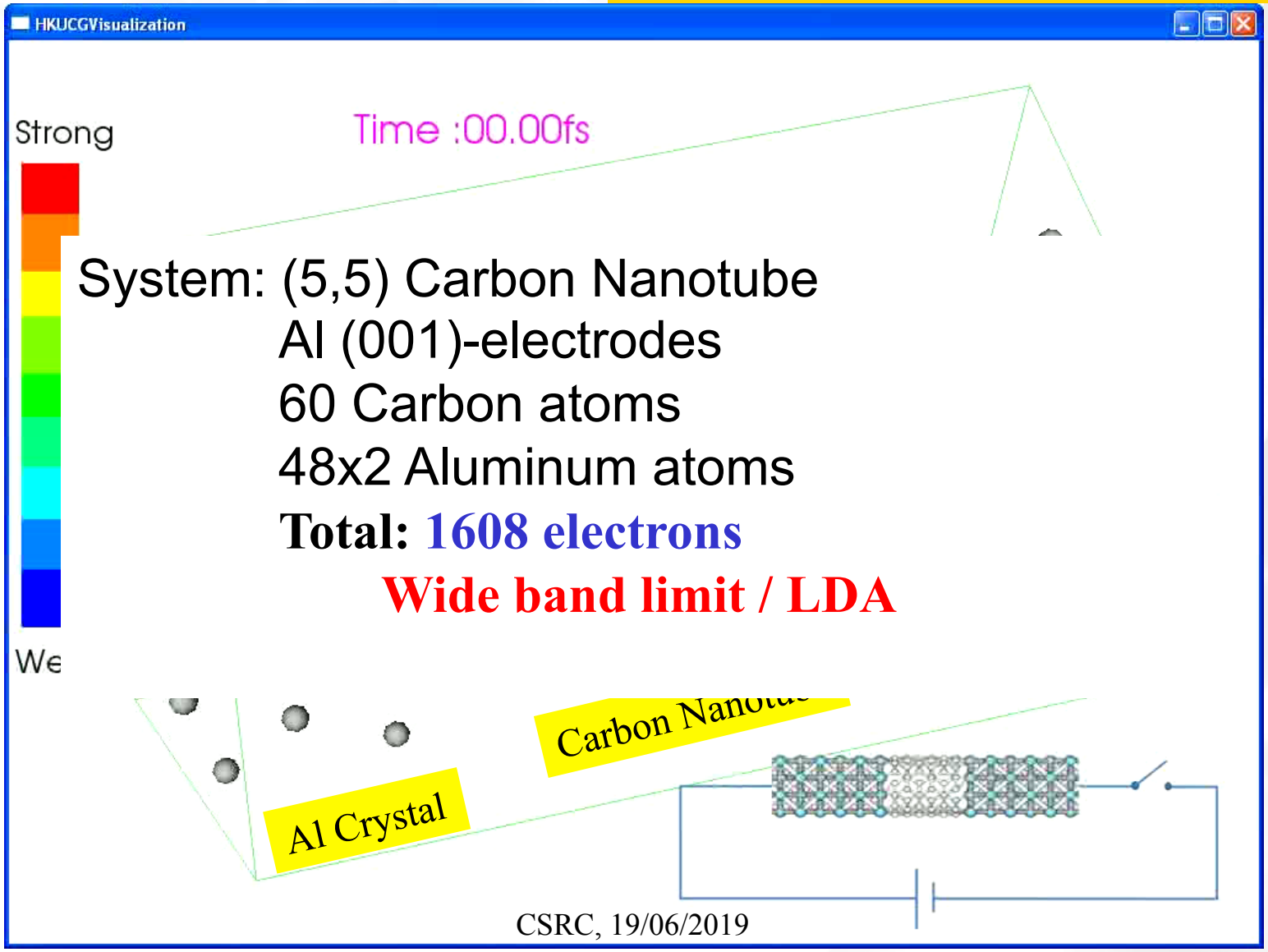
William Blake ***(1757–1827)***
English poet, painter

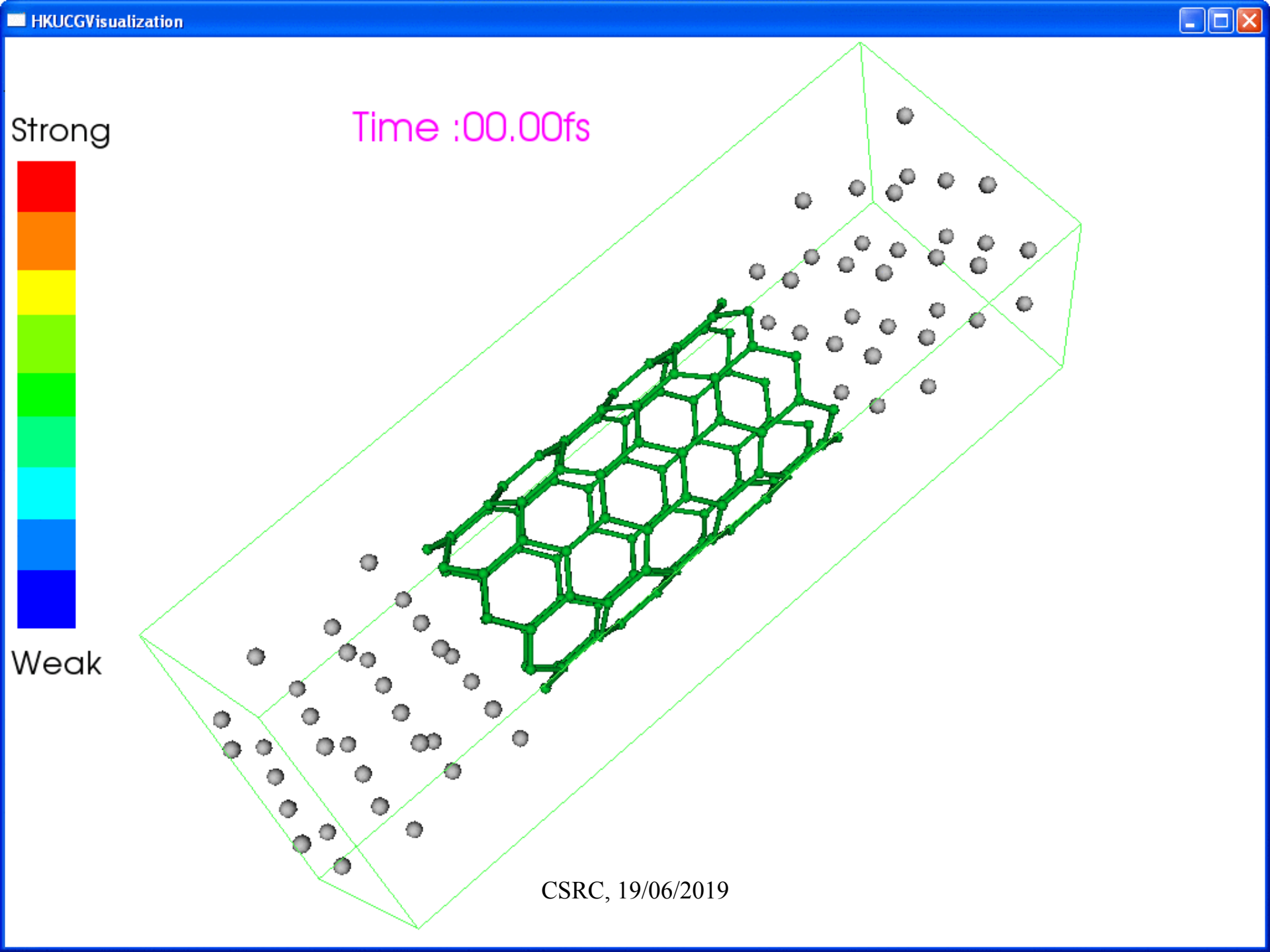
一沙一世界，一叶一菩提，
一花一天堂，一笑一尘缘。

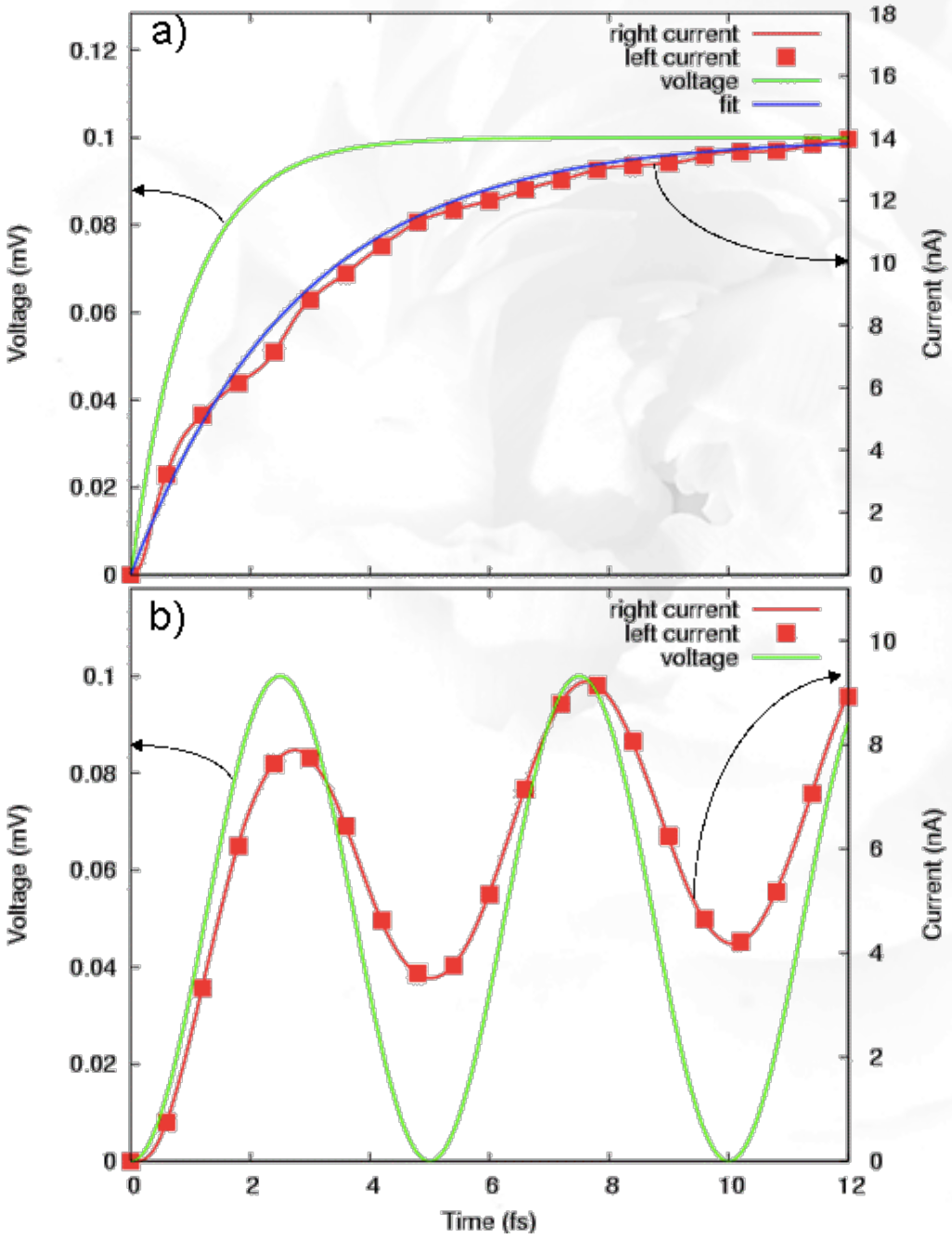
Transient Current Density Distribution through Al-CNT-Al Structure

Time dependent Density Func. Theory

Color: Current Strength
Yellow arrow: Local Current direction



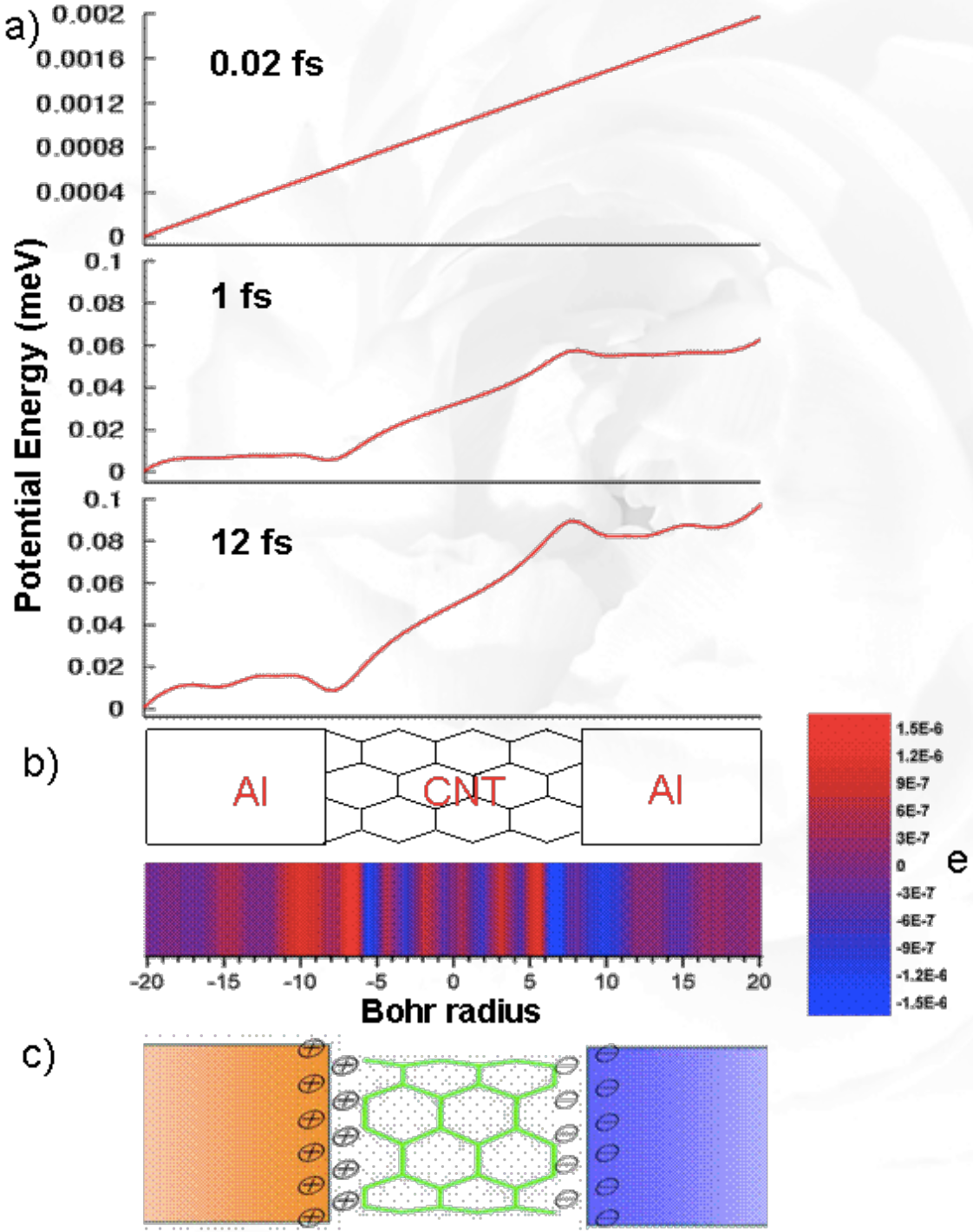

HKUCGVisualization
Strong
Time :00.00fs
Weak
CSRC, 19/06/2019



Transient current (red lines) & applied bias voltage (green lines) for the Al-CNT-Al system. (a) Bias voltage is turned on exponentially, Vb = V0 (1-$e^{-t/a}$) with V_0 = 0.1 mV & a = 1 fs. Blue line in (a) is a fit to transient current, $I_0(1-e^{-t/\tau})$ with τ = 2.8 fs & I_0 =13.9 nA. (b) Bias voltage is sinusoidal with a period of T = 5 fs. The red line is for the current from the right electrode & squares are the current from the left electrode at different times.

$V_b = V_0 (1-e^{-t/a})$
V_0 = 0.1 mV & a = 1 fs

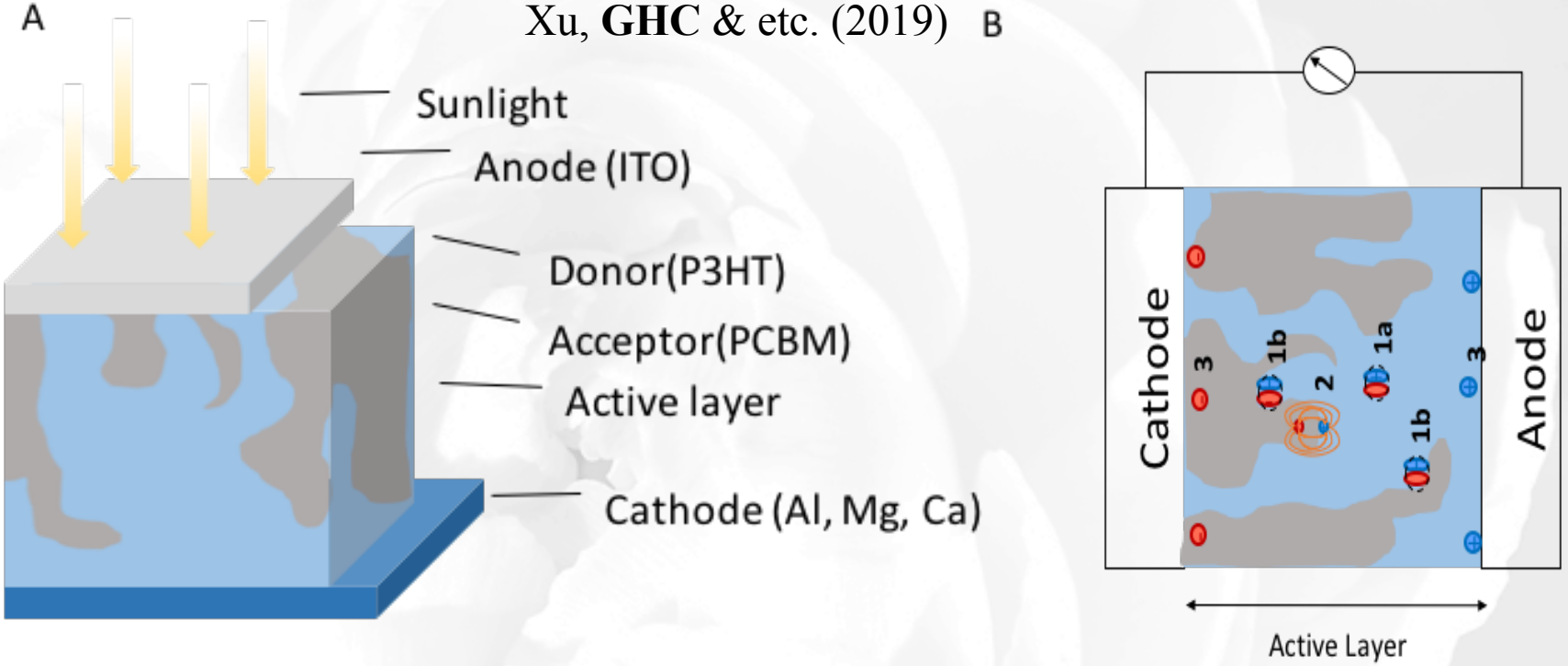
Switch-on time: ~ 10 fs

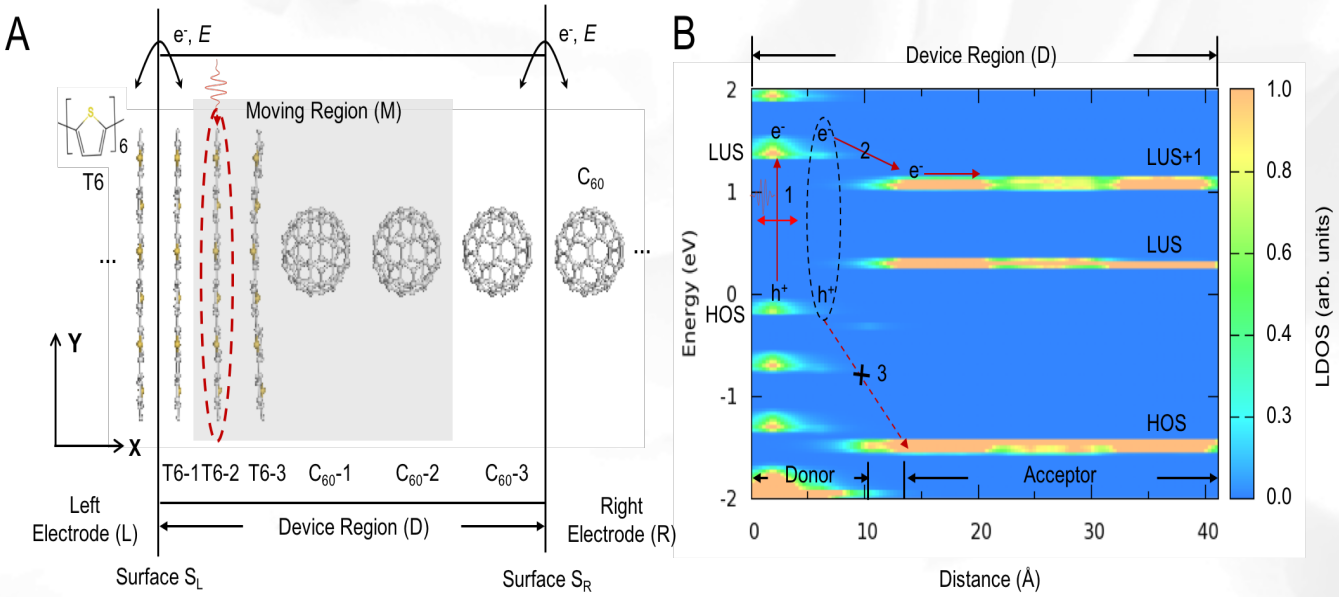


(a) Electrostatic potential energy distribution along the central axis at t = 0.02, 1 and 12 fs. (b) Charge distribution along Al-CNT-Al at t = 4 fs. (c) Schematic diagram showing induced charge accumulation at two interfaces which forms an effective capacitor.

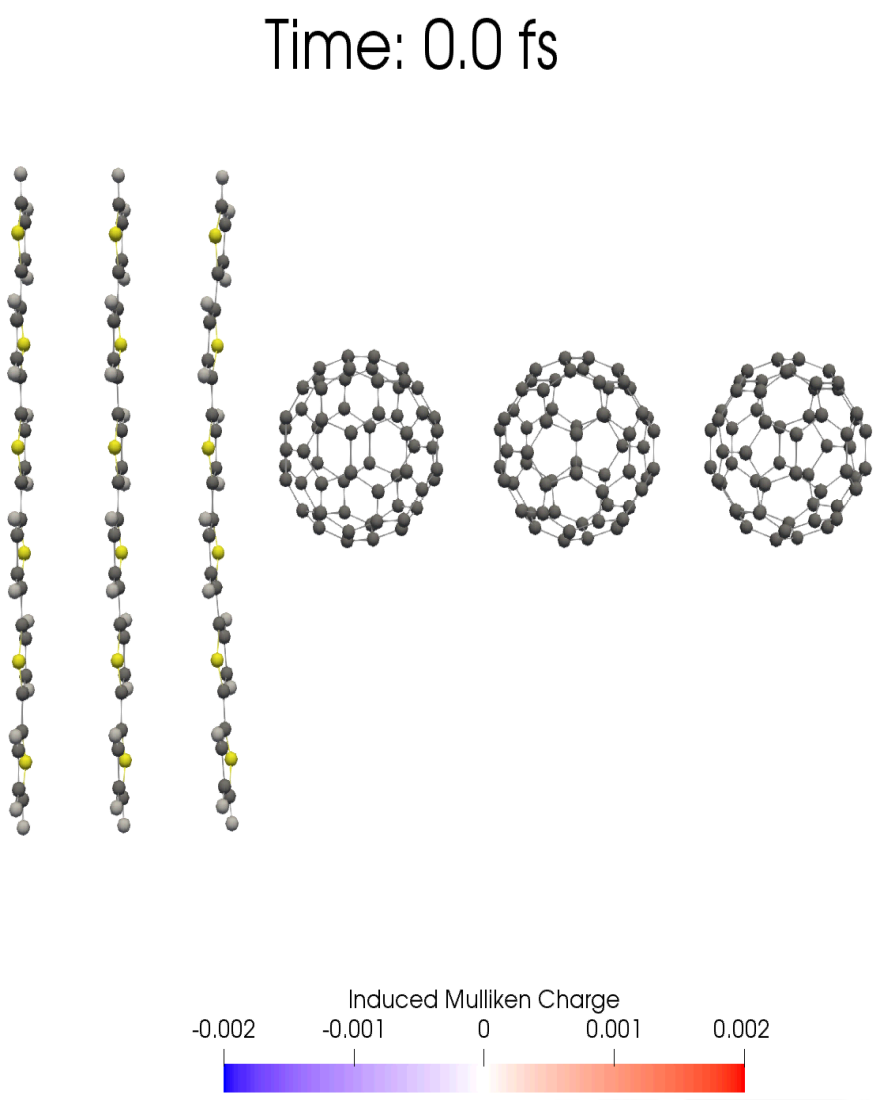
Direct simulation of organic optoelectronic device

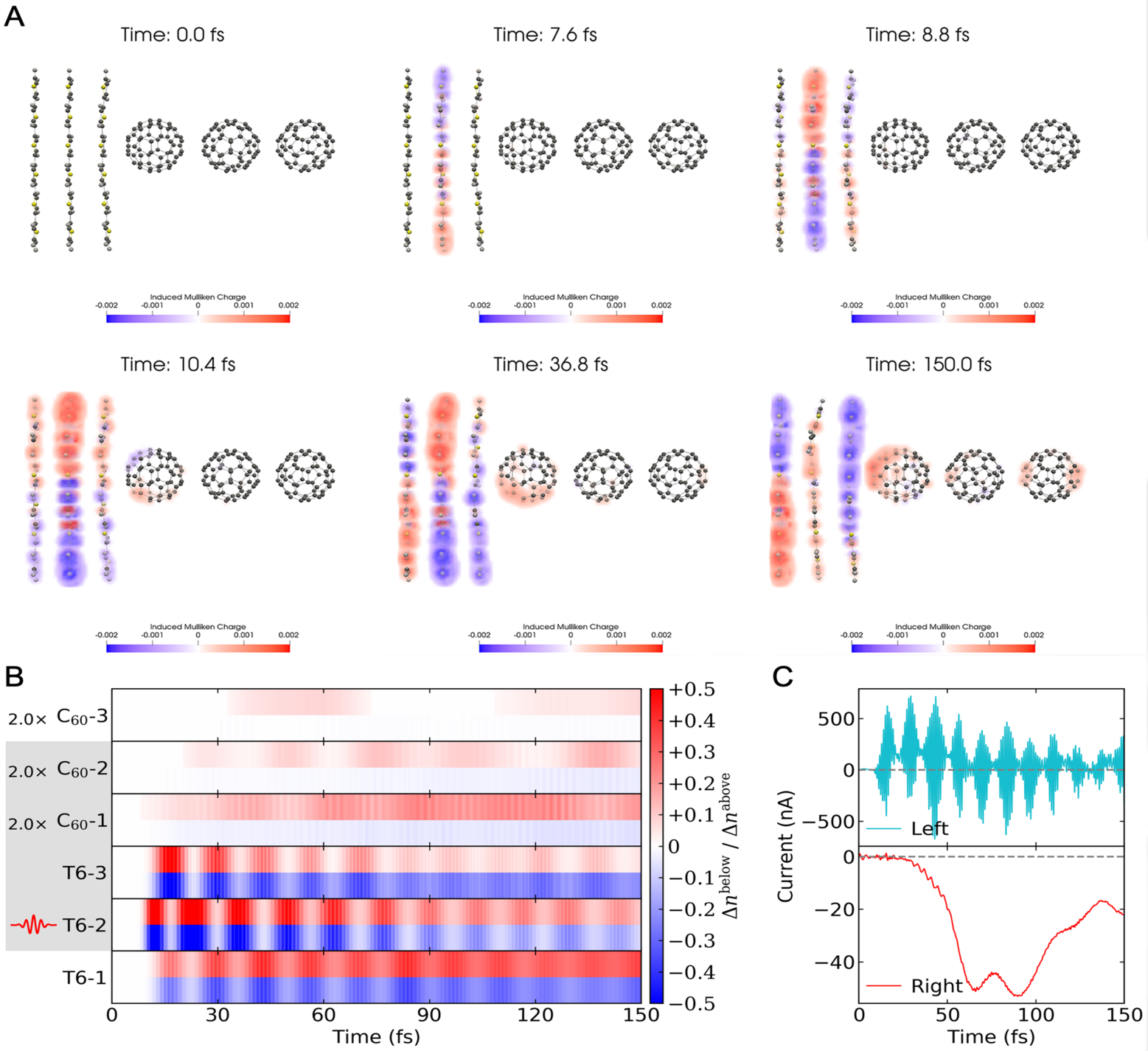
Xu, **GHC** & etc. (2019)

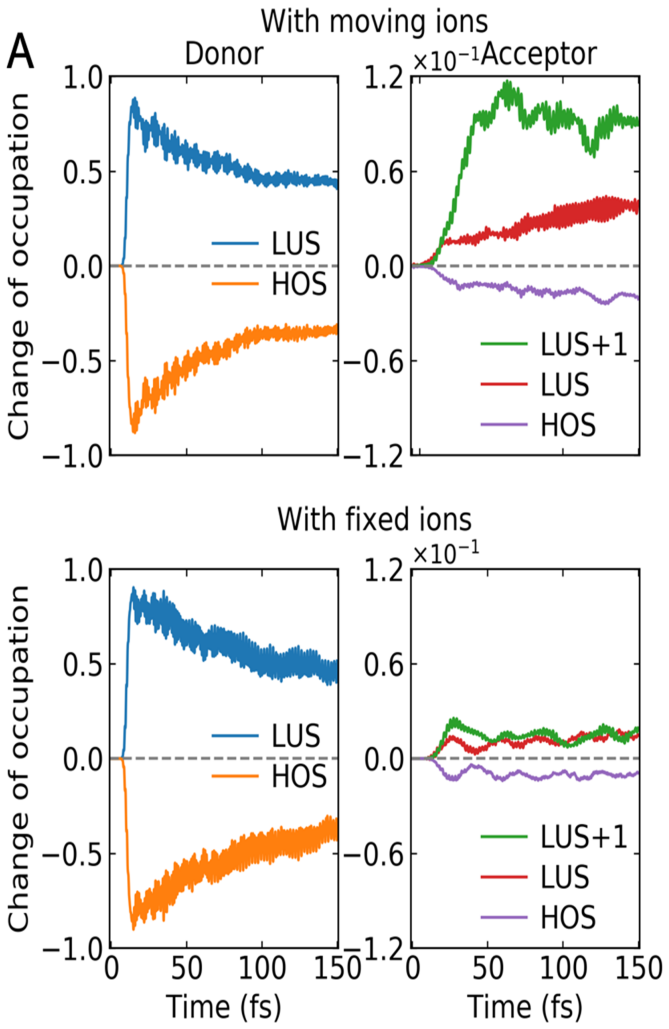


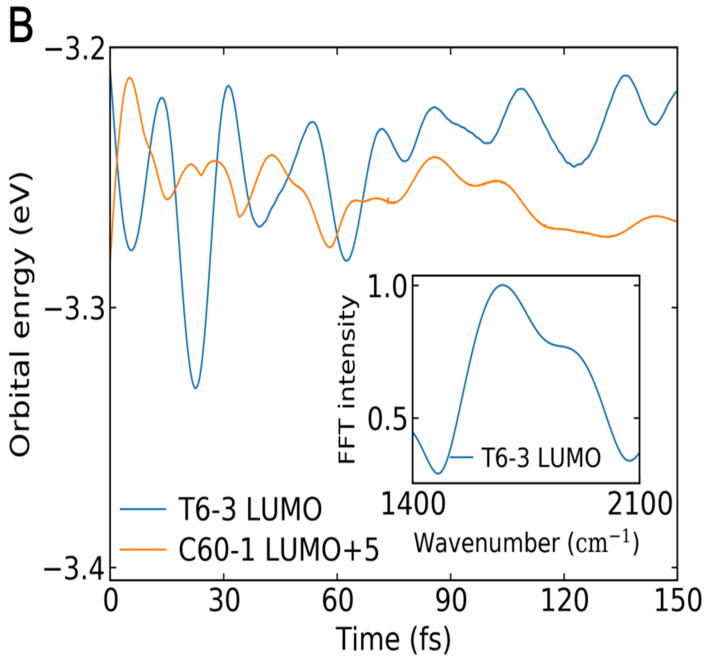


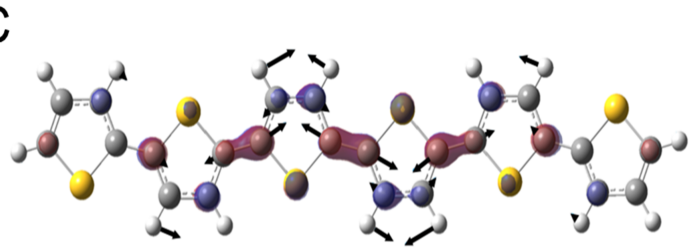
Induced Mulliken charge distributed onto real space




A
Time: 0.0 fs
Time: 7.6 fs
Time: 8.8 fs
Time: 10.4 fs
Time: 36.8 fs
Time: 150.0 fs
Induced Mulliken Charge
-0.002
-0.001
0
0.001
0.002
B
2.0× C60-3
2.0× C60-2
2.0× C60-1
T6-3
T6-2
T6-1
+0.5
+0.4
+0.3
+0.2
+0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
Δn^below / Δn^above
0
30
60
90
120
150
Time (fs)
C
500
0
−500
Left
0
−20
−40
Right
Current (nA)
0
50
100
150
Time (fs)


A
With moving ions
Donor
Acceptor
×10⁻¹
Change of occupation
LUS
HOS
LUS+1
With fixed ions
Time (fs)


B
Orbital enrgy (eV)
T6-3 LUMO
C60-1 LUMO+5
FFT intensity
Wavenumber (cm⁻¹)
Time (fs)


C

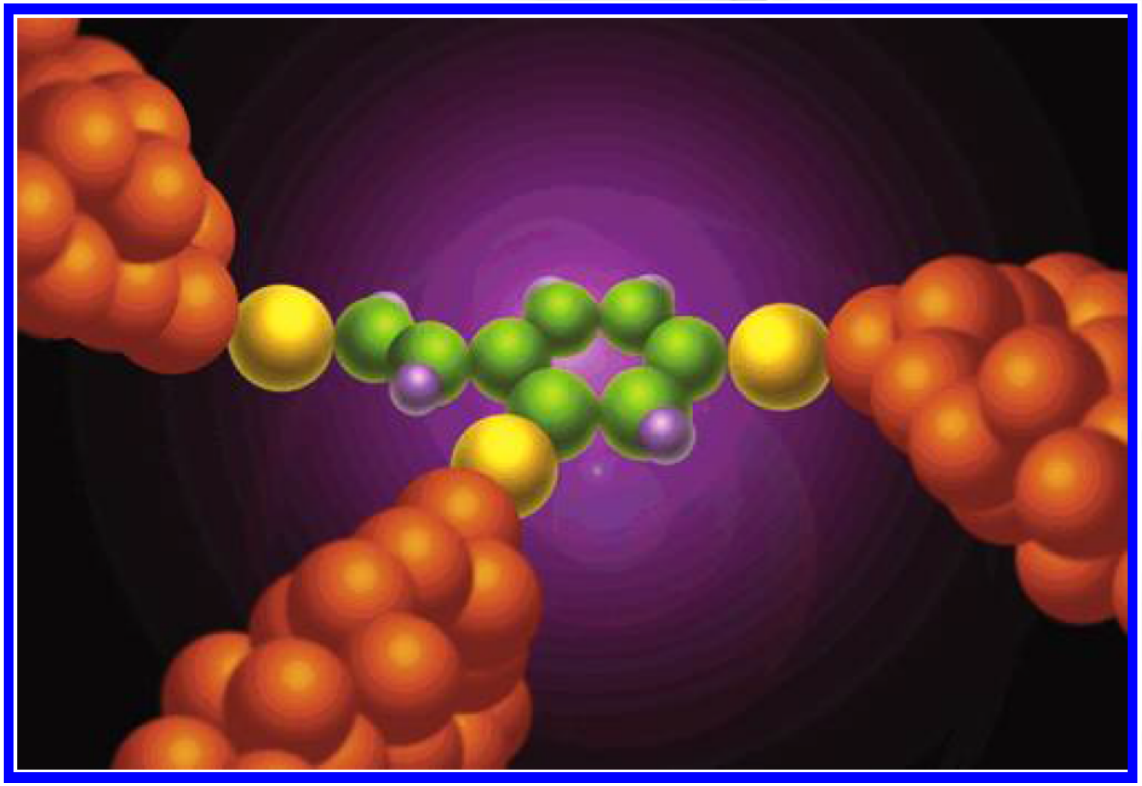
NANO LETTERS

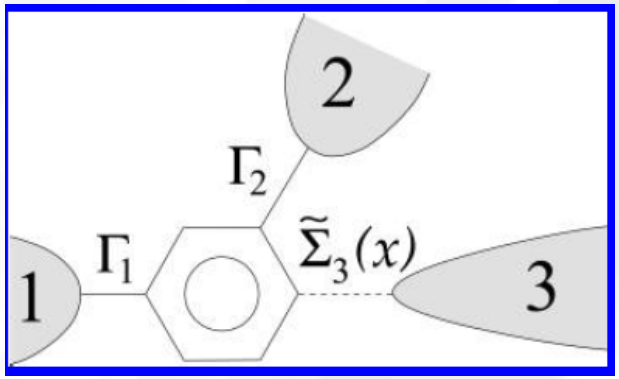
2006
Vol. 6, No. 11
2422−2426

Controlling Quantum Transport through a Single Molecule

David M. Cardamone,* Charles A. Stafford, and Sumit Mazumdar

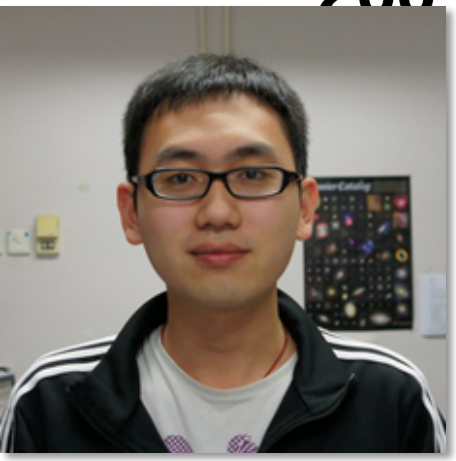
Department of Physics, University of Arizona, 1118 E. 4th Street, Tucson, Arizona 85721





An electron entering the molecule at the Fermi level has de Broglie wavevector $k_F = \pi/2d$, where $d = 1.397$ Å is the

interactions[22]). The two most direct paths through the ring have lengths $2d$ and $4d$, with a phase difference $k_F 2d = \pi$,



Fermi velocity

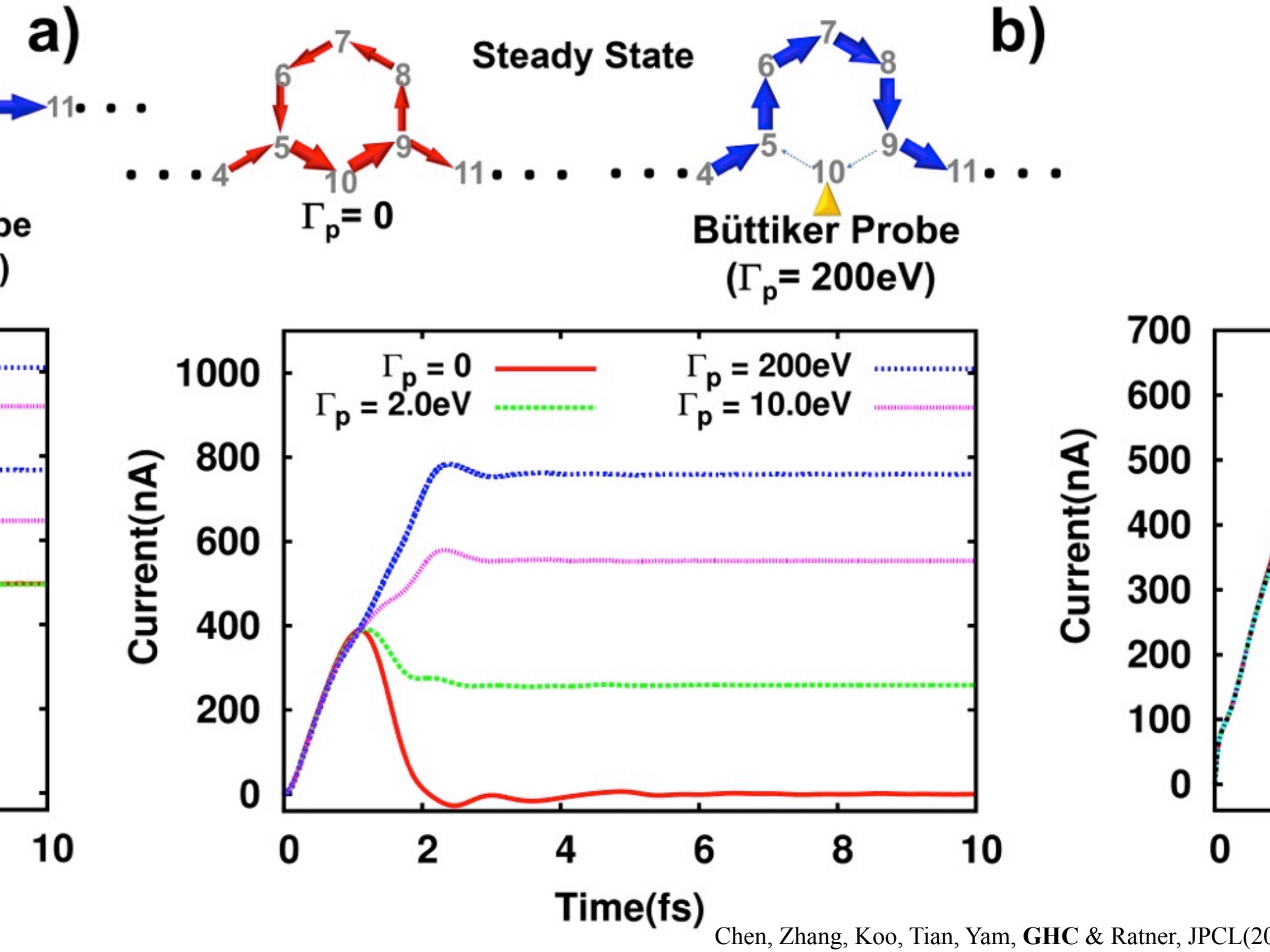
Chen, Zhang, Koo, Tian, Yam, **GHC** & Ratner, JPCL (2014)

ShuGuang CHEN

Buttiker Probe

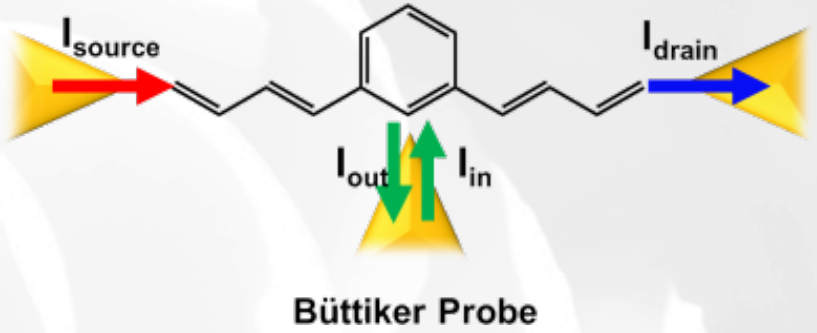
Net current = zero

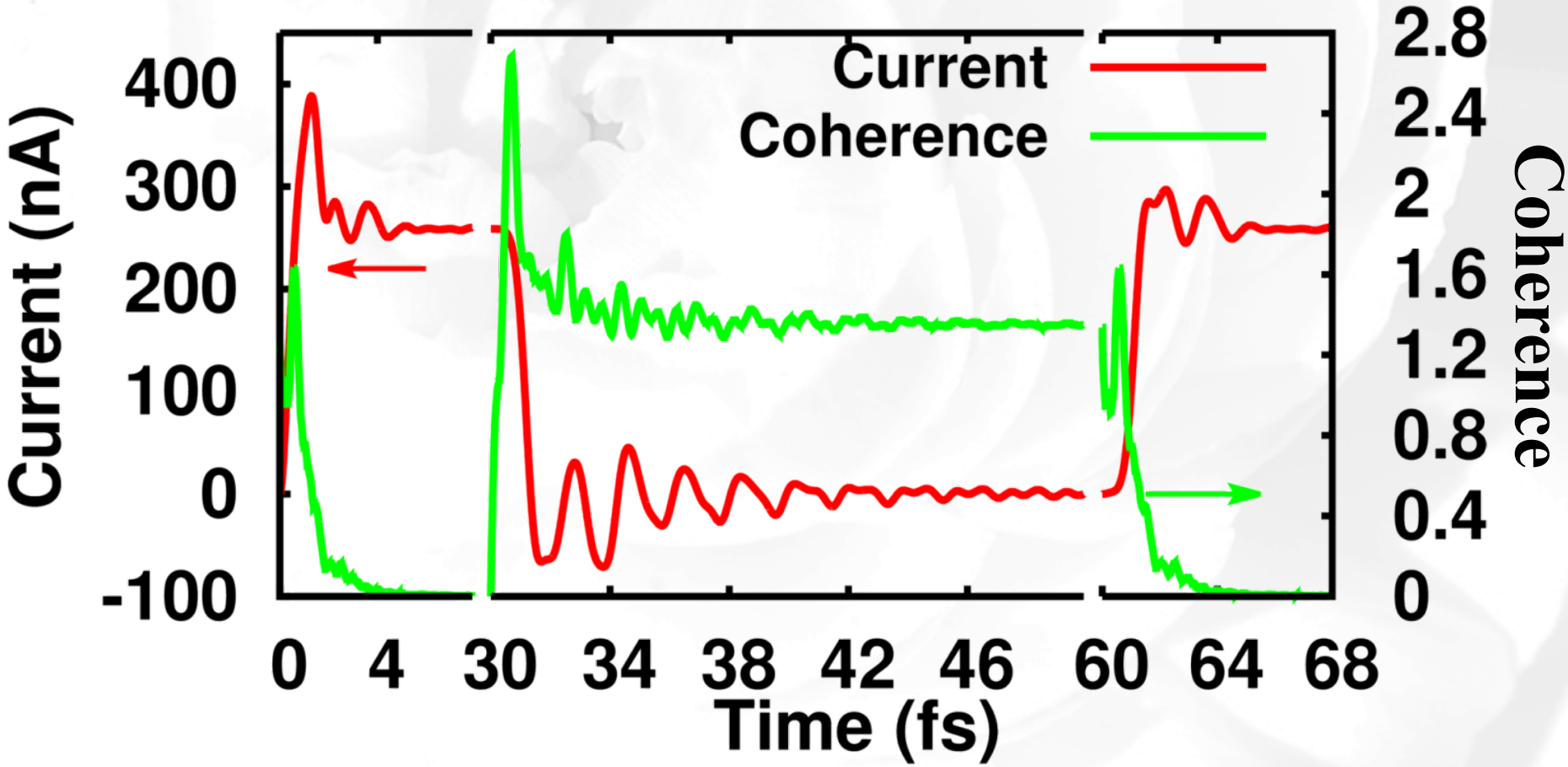
Dephasing



Chen, Zhang, Koo, Tian, Yam, **GHC** & Ratner, JPCL(20

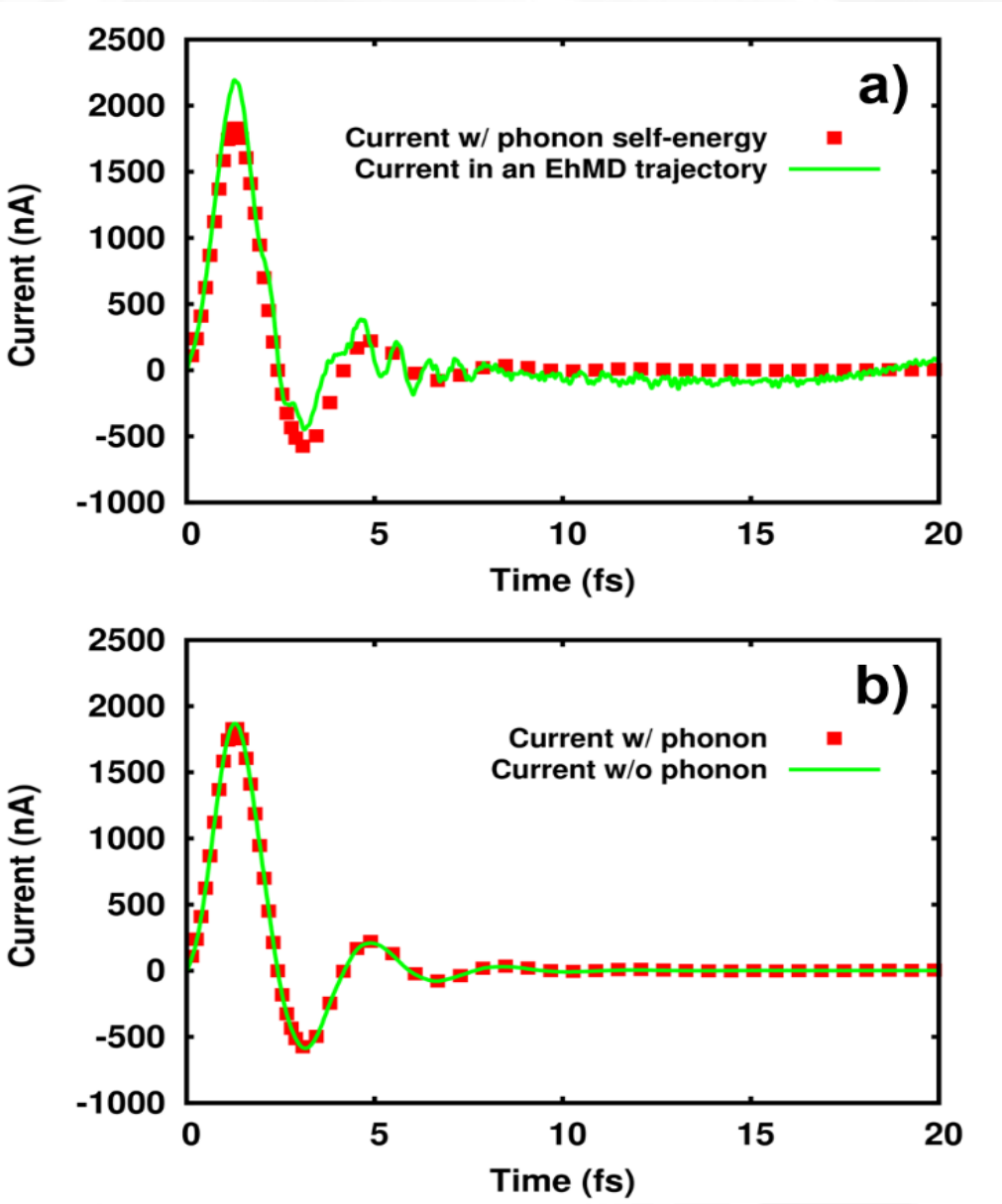
Disubstituted Benzenes





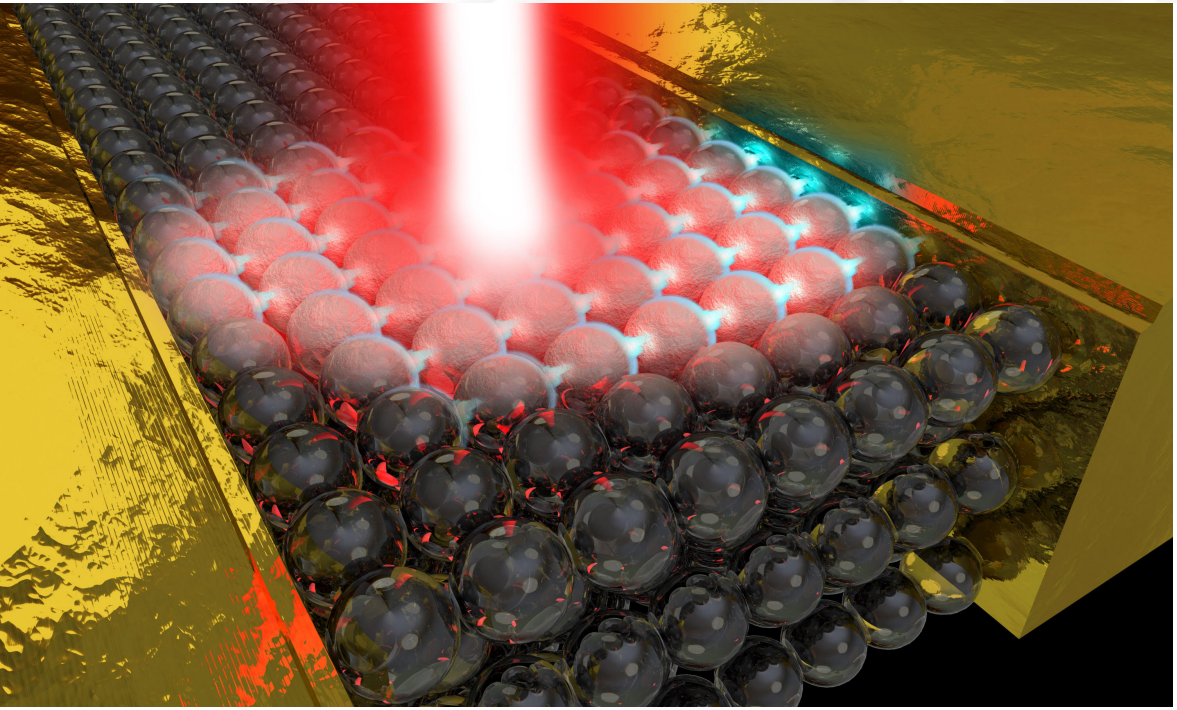
Chen, Zhang, Koo, Tian, Yam, **GHC** & Ratner, JPCL (2014)

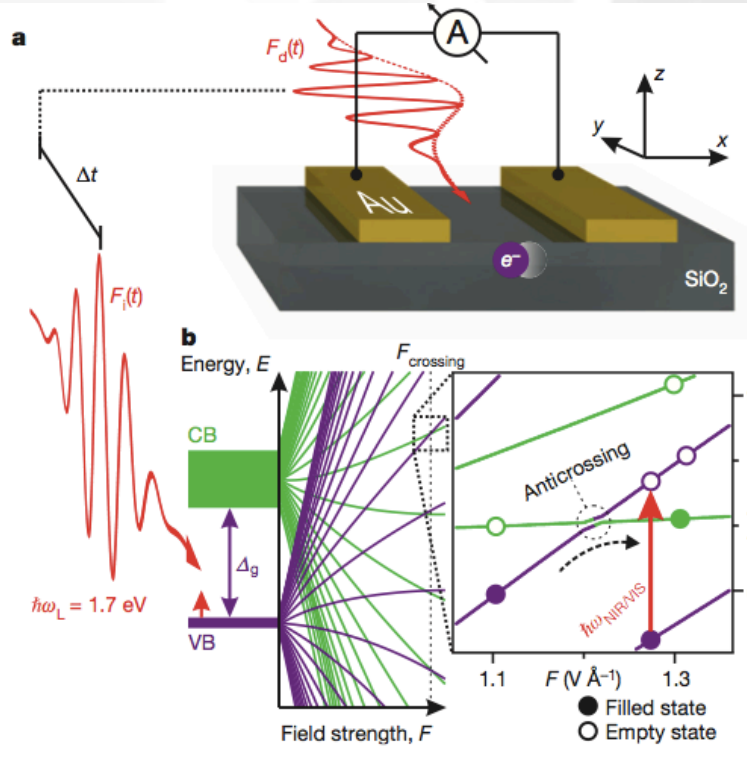
Can it survive the influences of phonon?



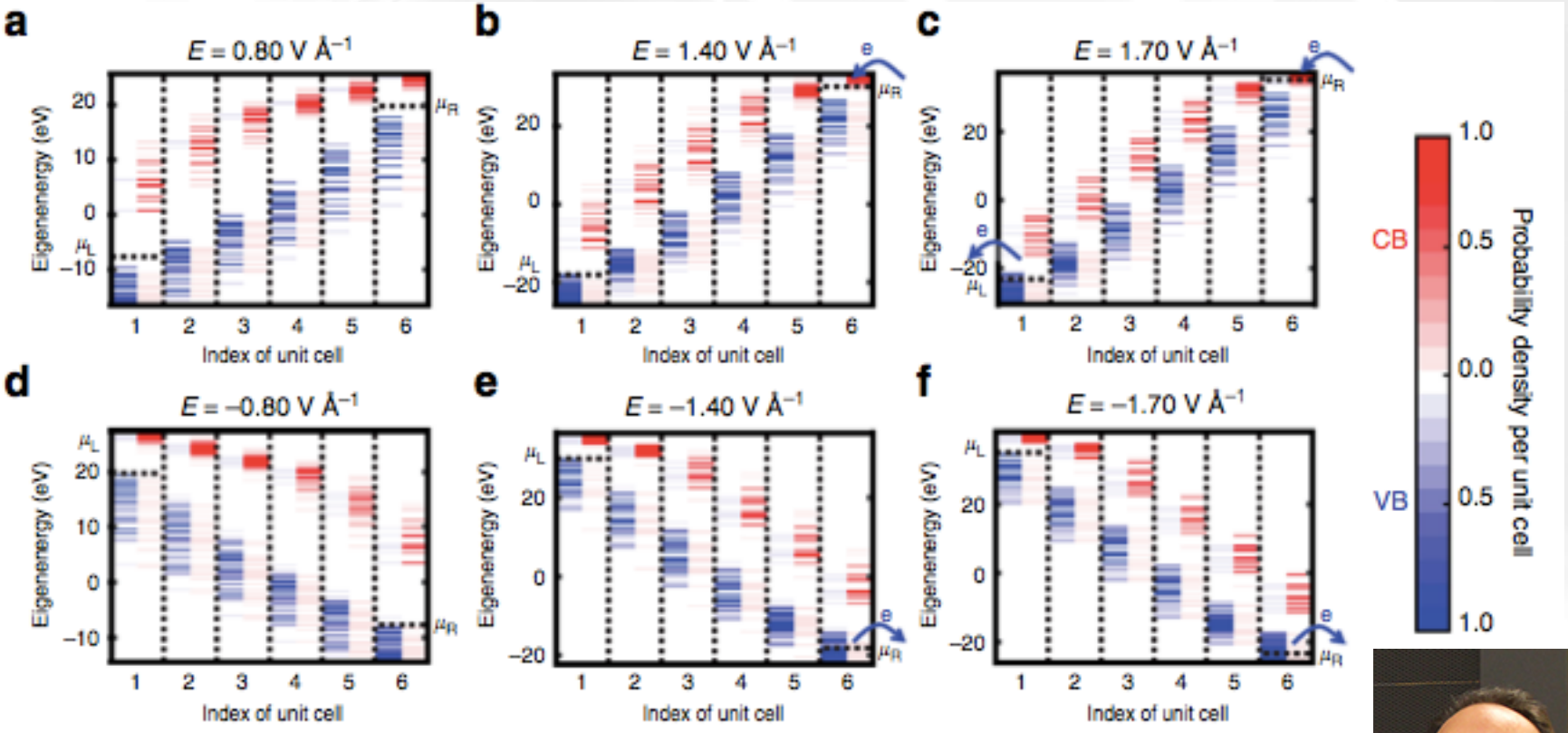
Chen, Zhou, **GHC** & Ratner, JPCL 2017

Schiffrin, A. et al. Optical-field-induced current in dielectrics. Nature 493, 70–74 (2013)



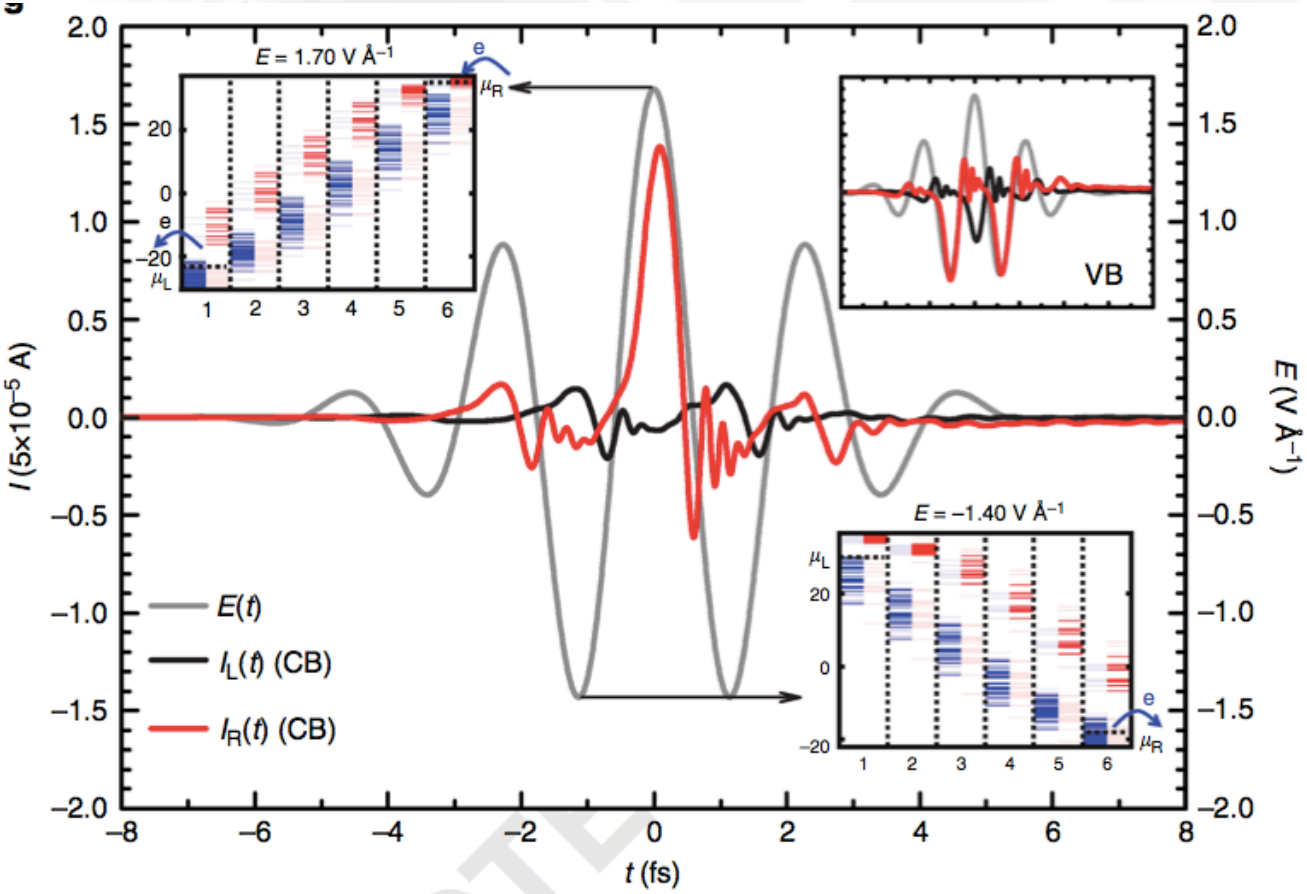


Courtesy of I. Franco



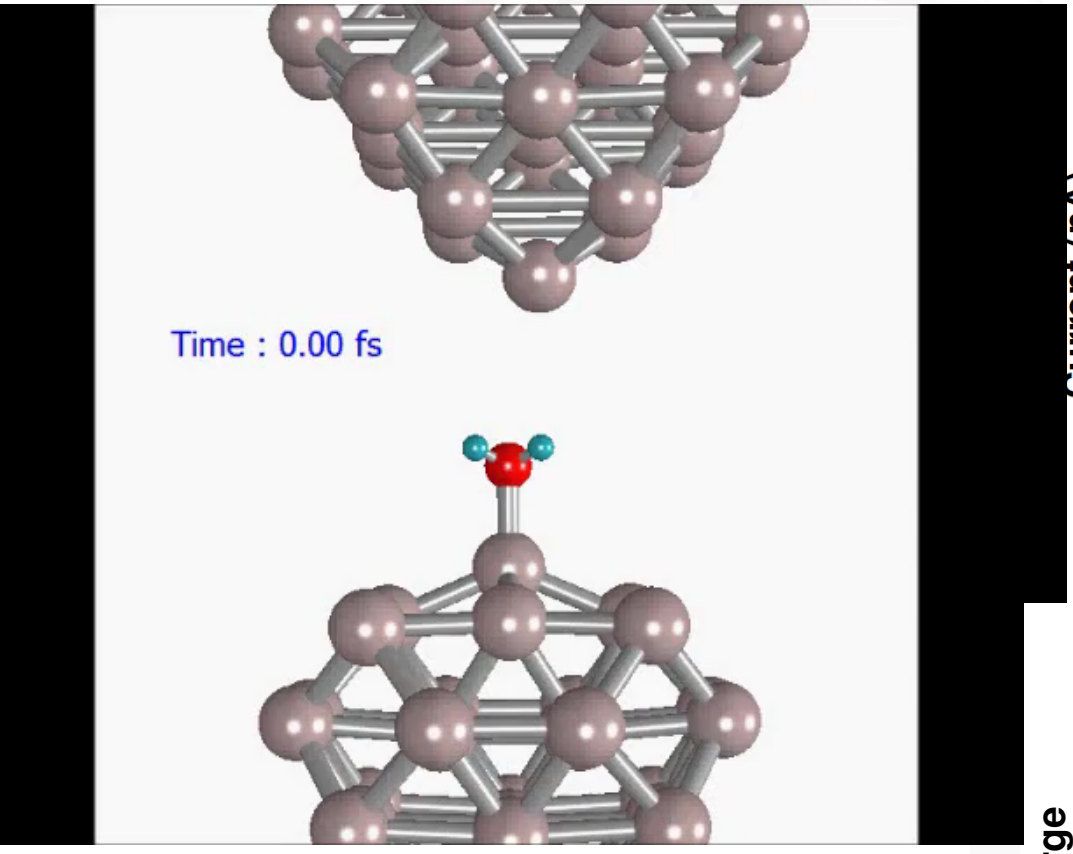
L. Chen, Y. Zhang, **GHC** & I. Franco, Nat. Comm. (2018)

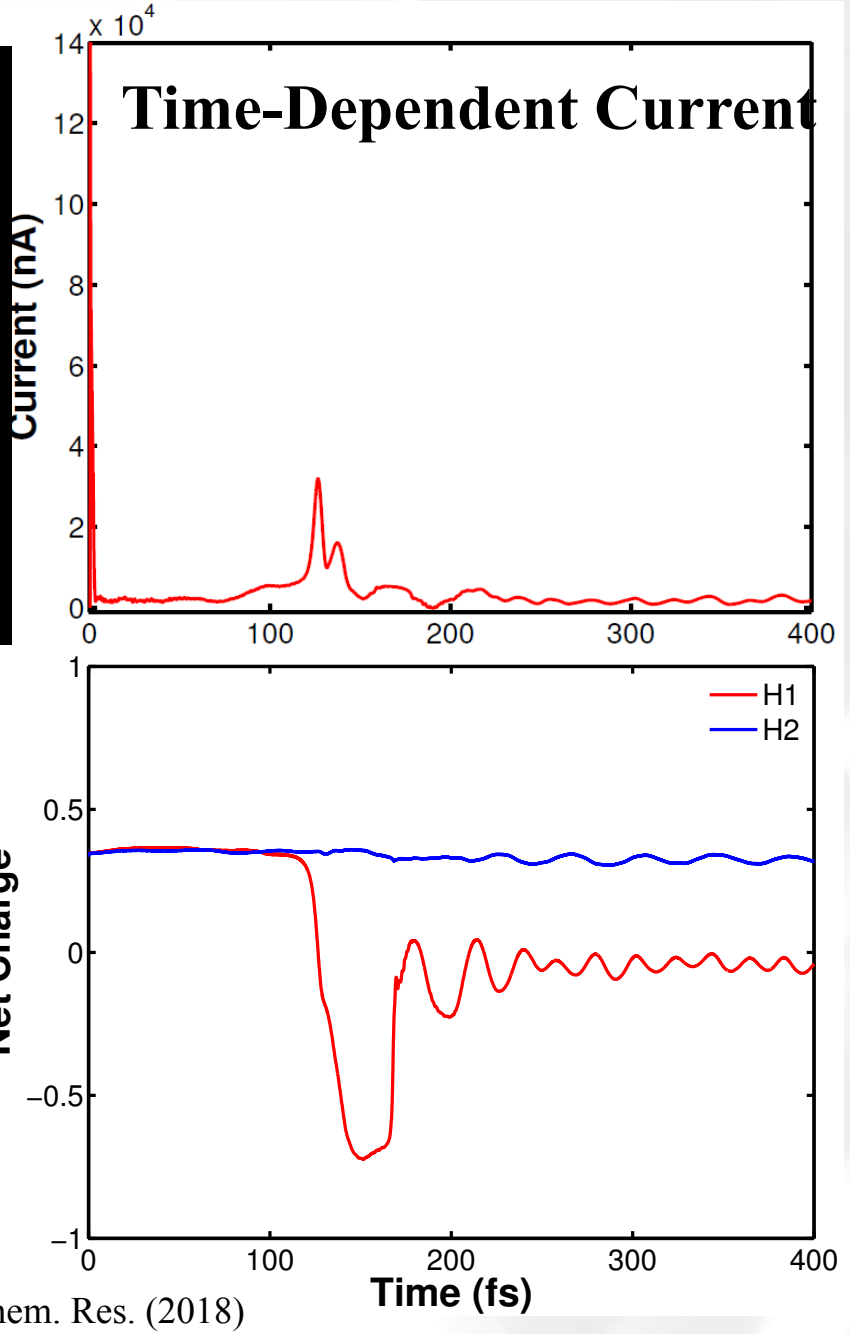
Stark control of electrons along nanojunction

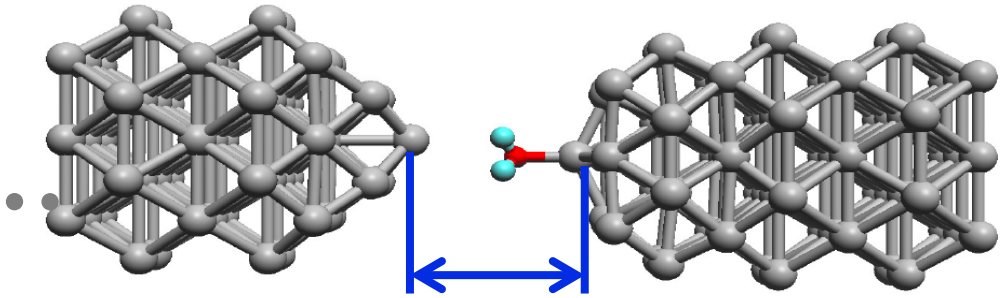


L. Chen, Y. Zhang, **GHC** & I. Franco, Nat. Comm. (2018)

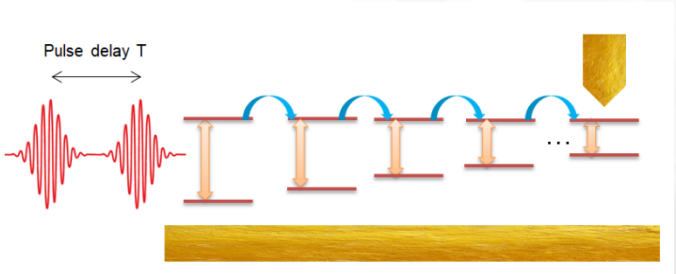
Water dissociation





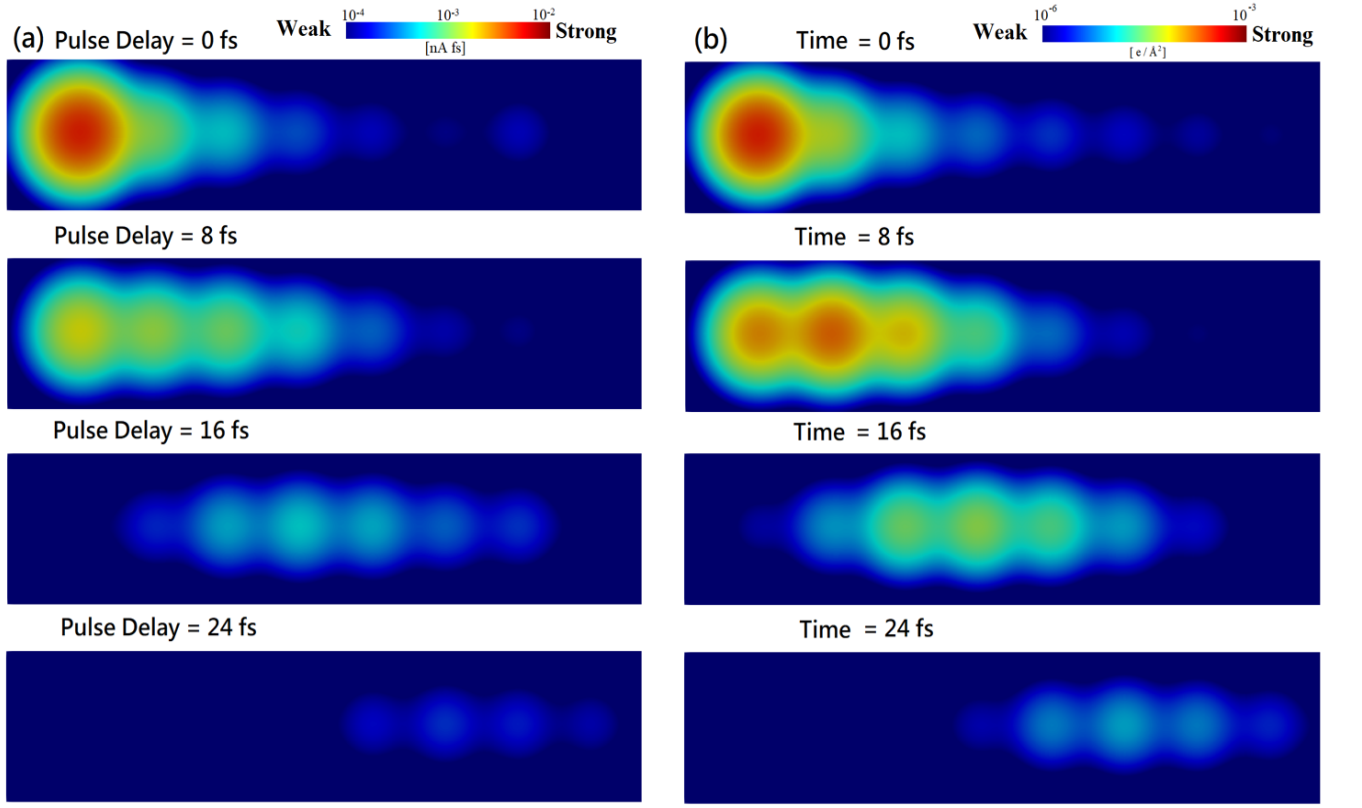


Chen, Kwok & **GHC**, Acc. Chem. Res. (2018)



Imaging of electron dynamics in real space and time (fs & atomic resolution)

Kwok, **GHC**, Mukamel, submitted



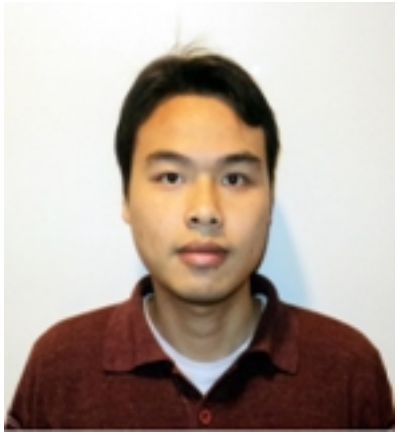
Left panel: pump-probe STM images with various pulse delays As indicated. Color reflects the magnitude of integrated current on a log scale (projected on real space). Right panel: electron density images (obtained by projecting occupation of LUMOs on real space) at the same times. Color reflects the magnitude of electron density on a log scale.

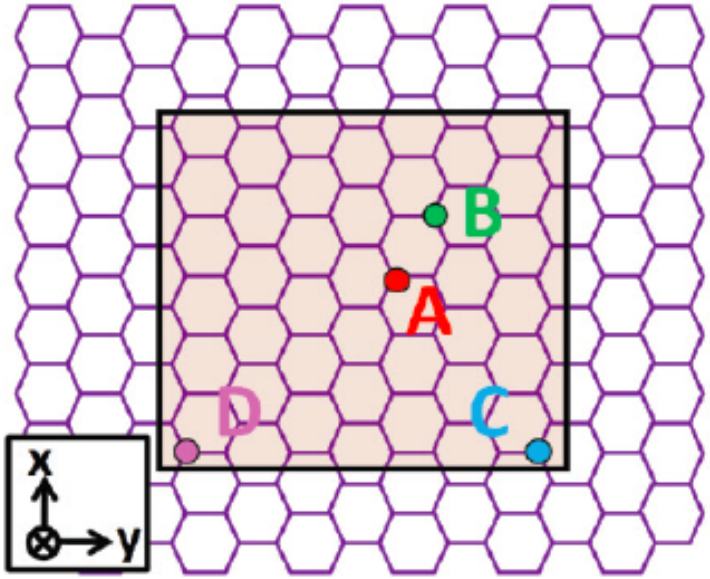
Transparent Boundary:
A drop of an electron onto graphene

PHYSICAL REVIEW B **88**, 205126 (2013)

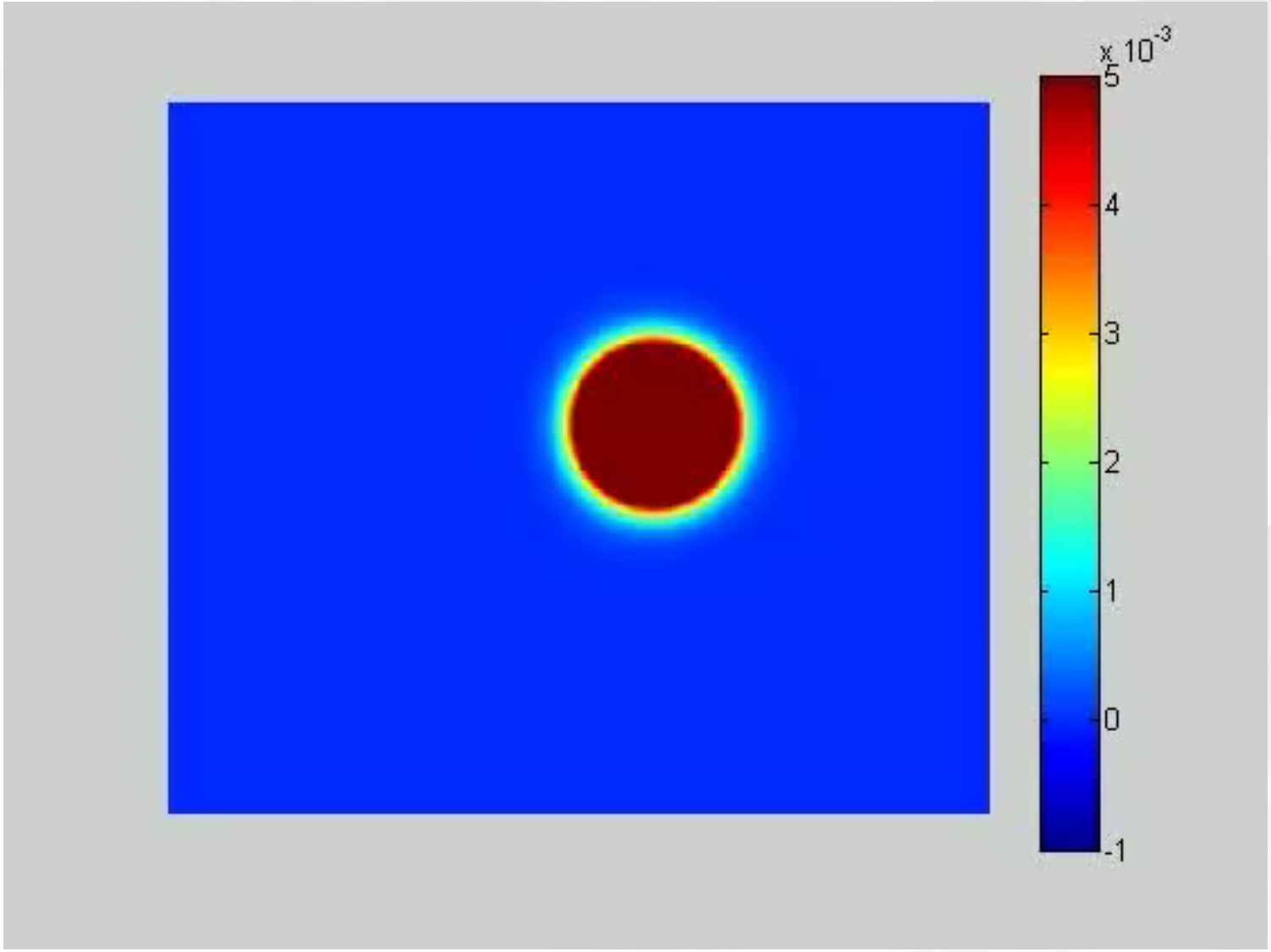
Time-dependent density-functional theory for real-time electronic dynamics on material surfaces

Rulin Wang,[1,2] Dong Hou,[1] and Xiao Zheng[1,*]
[1]*Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China*

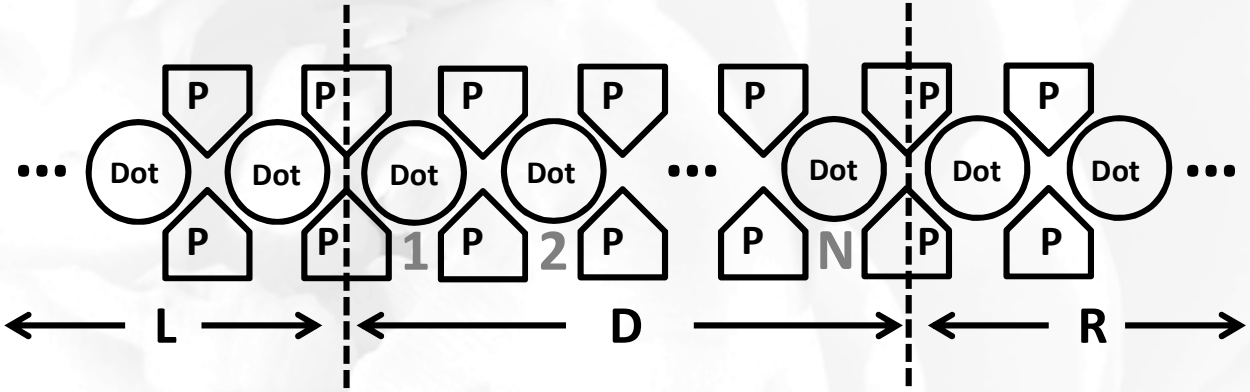




Open

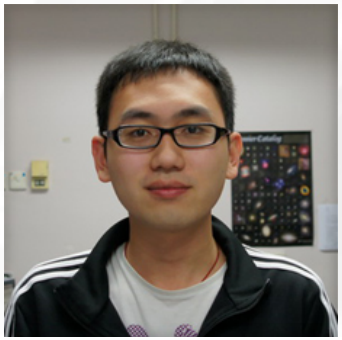


Tight-Binding Model



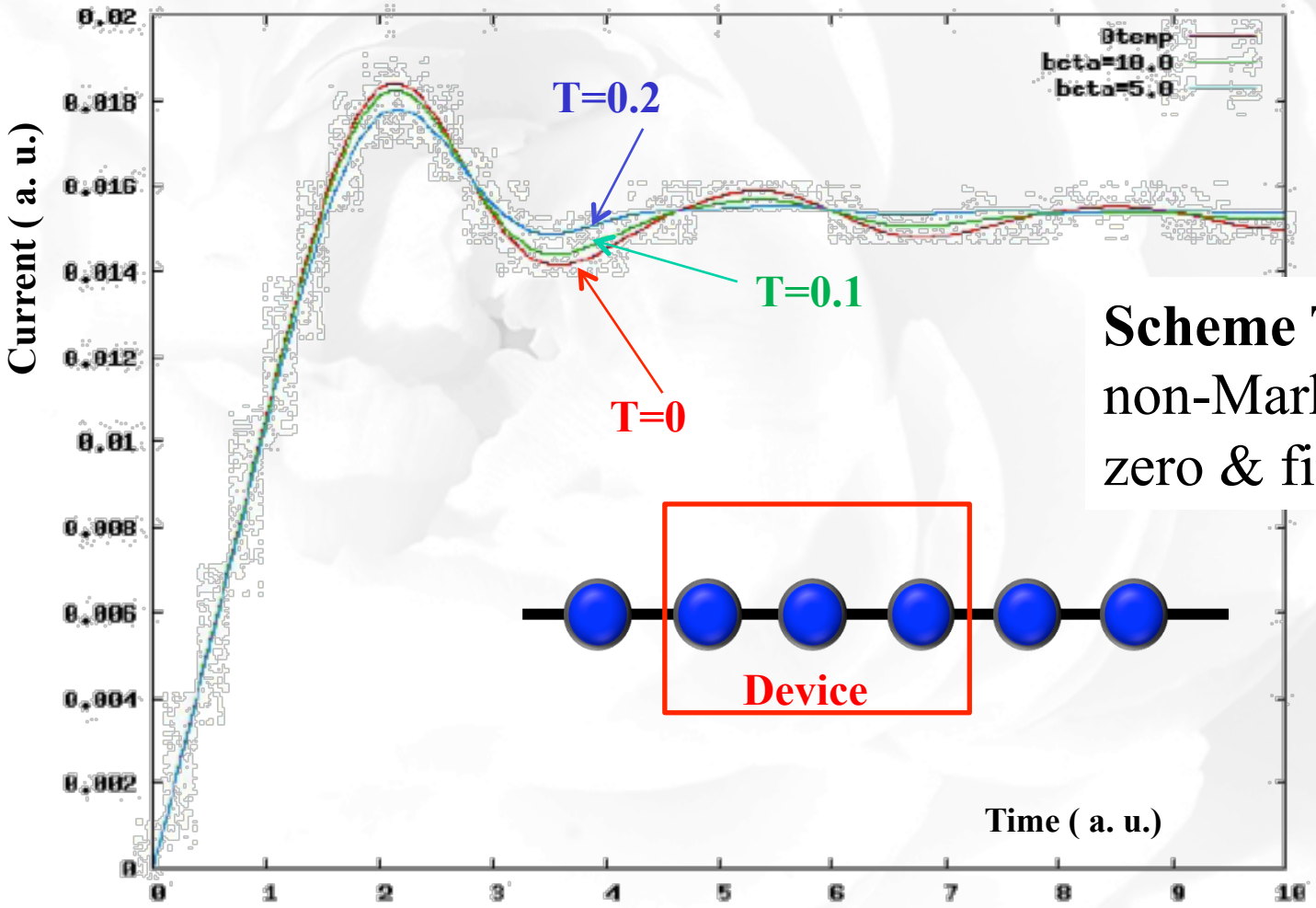
TIAN Heng

XIE Hang



CHEN Shuguang

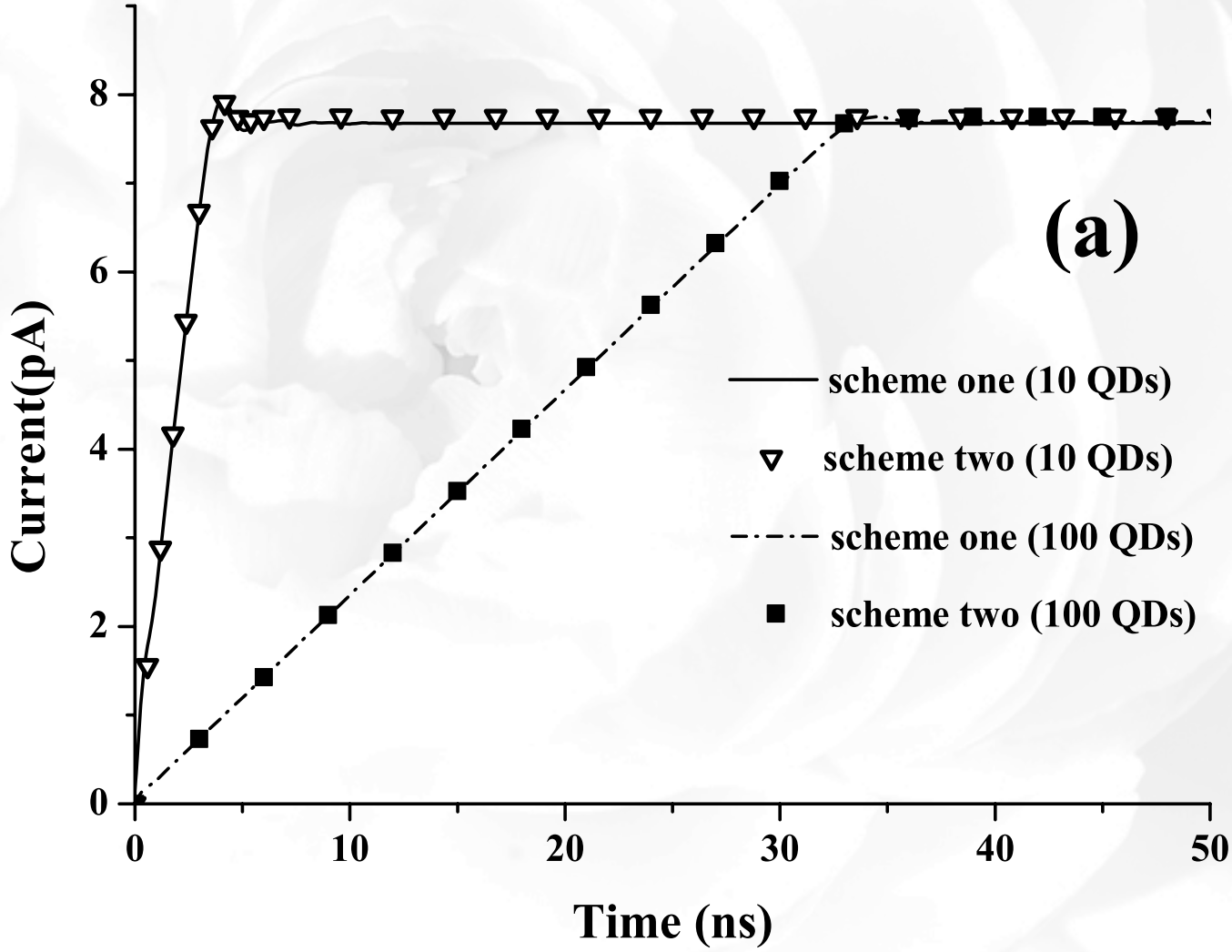
Currents at different temperatures



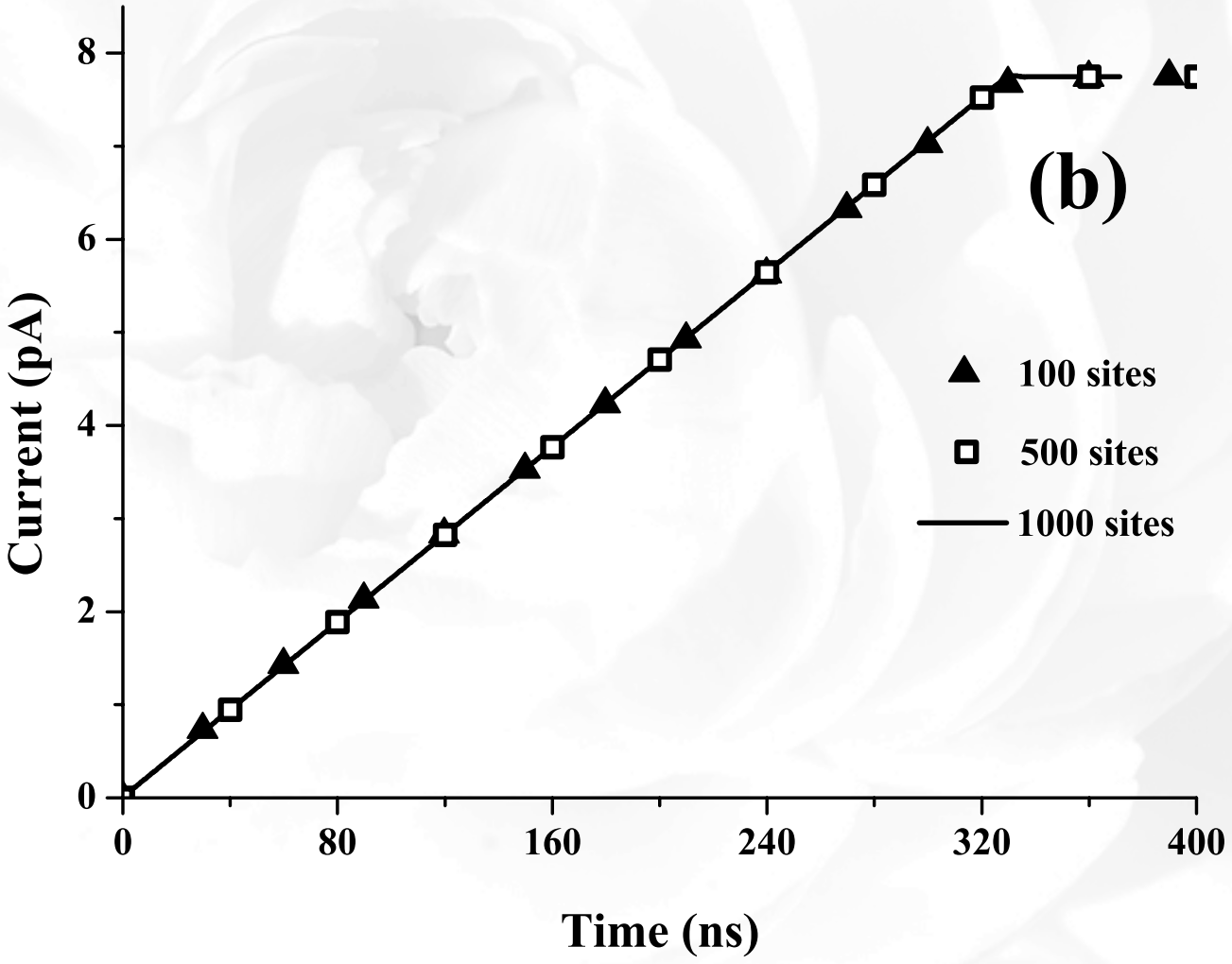
Scheme Two:
non-Markovian
zero & finite T

$\mu\downarrow 0 = 1.5$, $ampL = 0.05$, $ampR = -0.05$, $Tmax = 10.0$, $dt = 0.005$

Coupling matrix element: 2 μeV



Rescaled 100, 500 and 1000 Quantum Dots



$$E = \frac{1}{2} L I^2$$

$$P = IV = \frac{d}{dt} E = LI \frac{d}{dt} I(t)$$

$$\frac{d}{dt} I(t) = \frac{V}{L}$$

$$\tau_{switch} = \frac{I_{steady}}{dI/dt} = \frac{e^2 V/h}{V/L} = \frac{e^2 L}{h}$$

$$L = \frac{N\hbar^2 \pi}{e^2 \gamma}$$

$$\tau_{switch} = \frac{N\hbar}{2\gamma}$$

Kinetic inductance *L*: Yam et al. Nanotechnology 19, 495203 (2008)
Burke IEEE Trans. Nanotechnol. 2, 55 (2003)

Fermi velocity $V_f = \frac{2\gamma a}{\hbar}$

Passage time $\tau_d = \frac{Na}{V_f} = \frac{N\hbar}{2\gamma}$

$$\tau_{switch} = \tau_d$$