Empowered by Innovation NEC

実用的シミュレーションに向けた、第一原理計算手法の開発
時間に依存する外場下での電子・格子ダイナミクス

NECナノエレクトロニクス研究所
宮本良之

謝辞

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Sichuan Univ. Prof. H. Zhang

U can change.

第12回コンピュテーショナル・マテリアルズ・デザイン
CMD®ワークショップ　2008年3月4日ー3月8日

outline

1. Application of the Time-dependent density functional theory
2. Ion collision to solid surface (Fabrication & Analysis using ion-beam)
3. Time-varying dielectric field (Pulse laser, dynamical conductivity)

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0. What's ab inito MD?

Molecular dynamics:
Electrons are under the ground (stationary) state
Atoms follow Newton's classical dynamics

$$H\psi_n = \varepsilon_n \psi_n$$

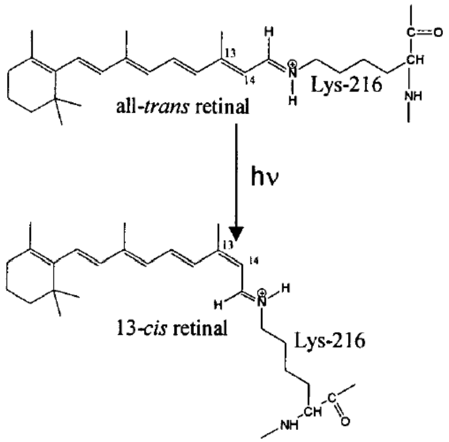
$$-\frac{\partial V}{\partial R_I} = M_I \frac{\partial^2 R_I}{\partial t^2}$$

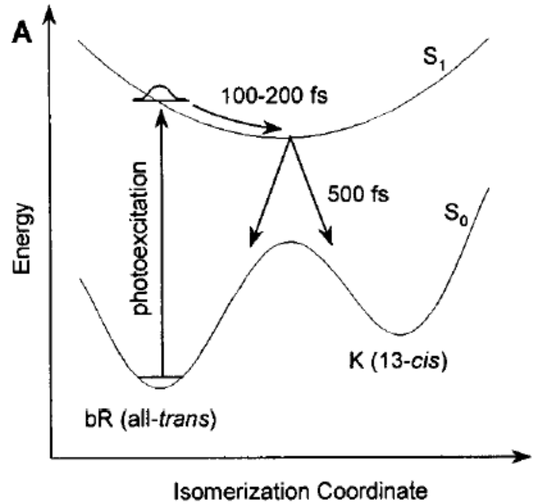
Thermodynamics、mechanics、reaction paths → Adiabatic approximation is a proper approach.

1. What's excited state dynamics?

Molecular dynamics under electronic excitation
ex). Photo-chemical reaction, high-energy atom/ion impact

Lifetime of excited state compared to time for atomic motion is a key factor





We need to treat electron dynamics!

$$i\hbar \frac{\partial \psi_n}{\partial t} = H\psi_n$$

F. Gai et al. Science 279, 1886 (1998)

Time-dependent version of the Density Functional Theory

E. Runge and E. K. U. Gross, PRL, 52, 997(1984).

Instead of total energy minimization, minimize an action given as,

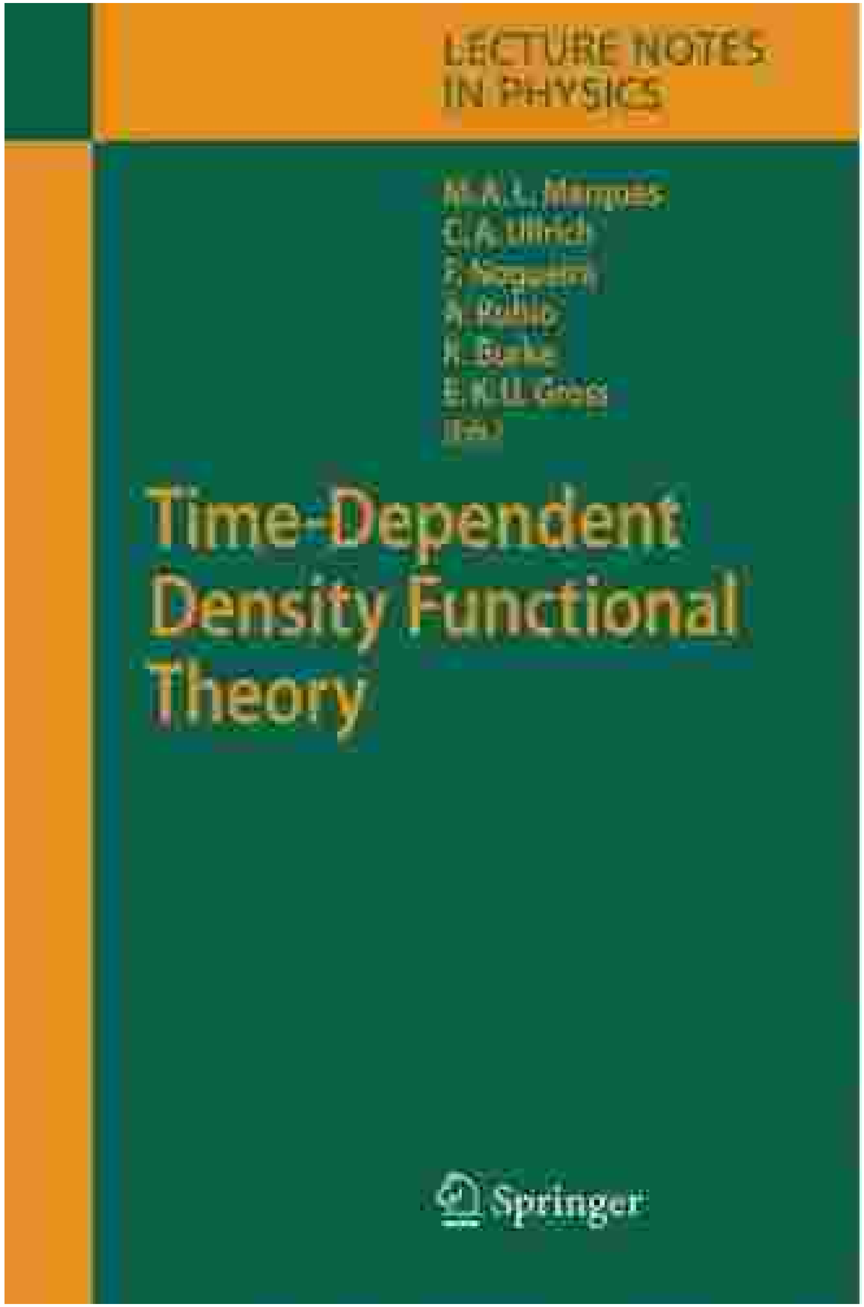
$$A = \int_{t_0}^{t_1} dt \langle \Phi(t) | i\partial/\partial t - \hat{H}(t) | \Phi(t) \rangle$$

Within DFT $\langle \phi \mid H \mid \phi \rangle = E_{tot}$ → $\delta A = 0$ gives

$$i\hbar \frac{d\psi_n(\vec{r},t)}{dt} = \left(-\nabla^2 + \int \frac{\rho(\vec{r}',t)}{|\vec{r}-\vec{r}'|} d\vec{r}' + \mu_{XC}[\rho(\vec{r},t)] + \sum_I \tilde{v}(\vec{r}' - \vec{R}_I(t), \vec{r} - \vec{R}_I(t)) + \sum_I \frac{Z_I(\vec{R}_I)}{|\vec{r} - \vec{R}_I(t)|} \right) \psi_n(\vec{r},t)$$

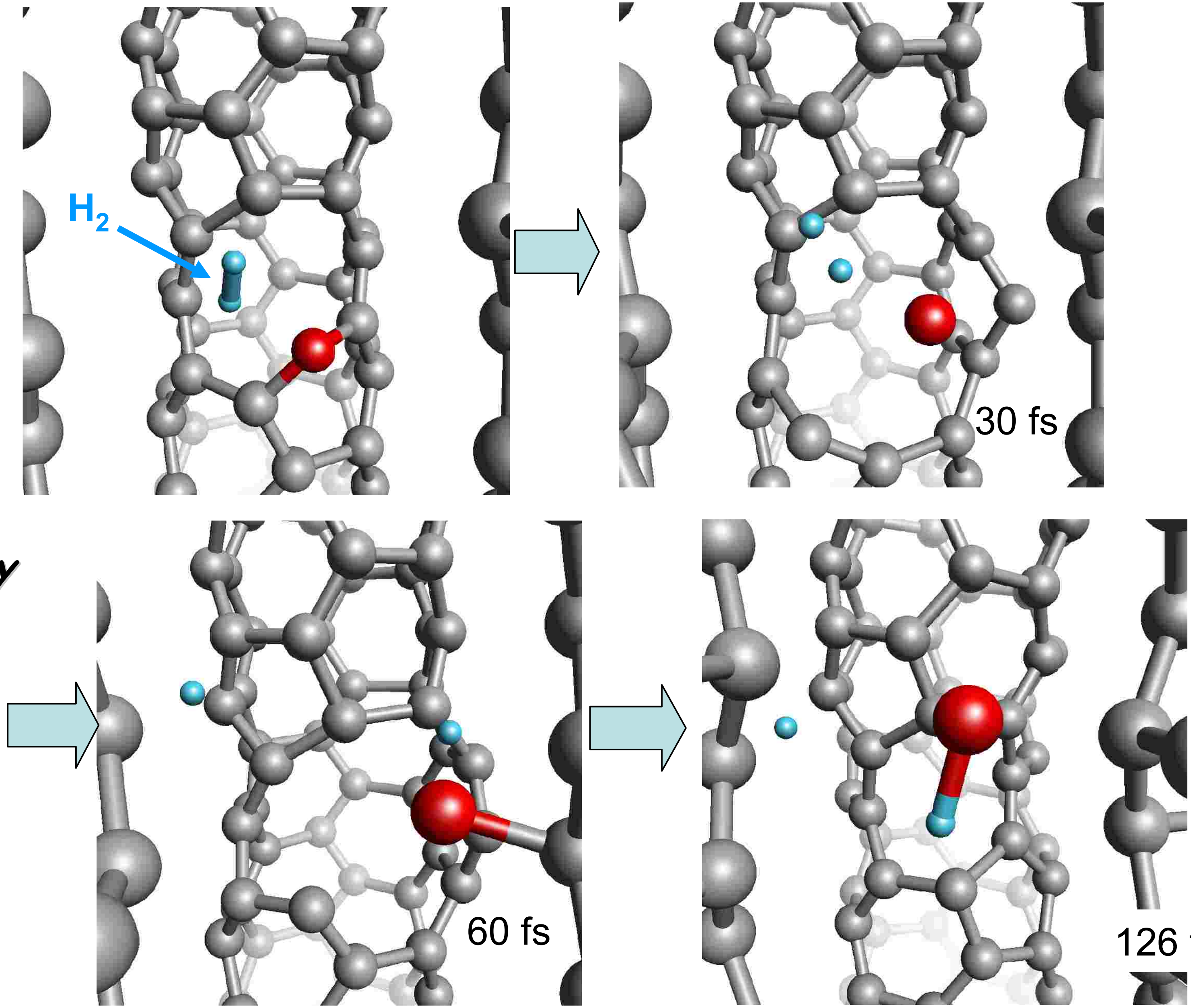
→ one-to-one relation with $v(\vec{r},t)$ and $\rho(\vec{r},t)$ with proper initial condition

Time-dependent Kohn-Sham equation


LECTURE NOTES
IN PHYSICS
Time-Dependent
Density Functional
Theory
Springer

80 €

Spontaneous O emission from CNT by electronic excitation!



Calculation was done by the Earth Simulator

Excited state dynamics within TDDFT-MD (Sugino, Miyamoto 1999, PRB)

TDDFT: plane wave and pseudopotentials

$$i\hbar \frac{\partial \psi_n}{\partial t} = H\psi_n$$

Classical MD with Hellman-Feynman forces

$$-\frac{\partial V}{\partial R_I} = M_I \frac{\partial^2 R_I}{\partial t^2}$$

Use of Hellman-Feynman forces based on Ehrenfest's framework. But we must seriously think about potential energy surface for ions at the moment of non-adiabatic transition.

$$F_I^{HF} = -\int \rho(r) \frac{\partial \sum_I V_I(r-R_I)}{\partial R_I} - \sum \frac{\partial E_{ion-ion}}{\partial R_I}$$

$$-2\,\mathrm{Re}\sum_n f_n \sum_{\alpha,\beta} C_\alpha^{n^*} C_\beta^n \langle \frac{\partial \phi_\alpha}{\partial R_I} | H - \varepsilon_n | \phi_\beta \rangle$$

$$\boxed{-2\,\mathrm{Re}\sum_n f_n \sum_{\alpha,\beta} \frac{\partial C_\alpha^{n^*}}{\partial R_I} C_\beta^n \langle \phi_\alpha | H - \varepsilon_n | \phi_\beta \rangle}$$

In case of TDDFT, ε_n is not the eigenvalue but expectation value.

Thanks to parallel computing

$$\psi_{1,k}(\mathbf{r}, t+\Delta t) = e^{\frac{\Delta t}{i\hbar} H_{KS}(t+\frac{\Delta t}{2})} \psi_{1,k}(\mathbf{r}, t)$$

$$|< \psi^*_{1,k}(\mathbf{r}, t) \mid \psi_{1,k}(\mathbf{r}, t) >|^2$$

$$\psi_{2,k}(\mathbf{r}, t+\Delta t) = e^{\frac{\Delta t}{i\hbar} H_{KS}(t+\frac{\Delta t}{2})} \psi_{2,k}(\mathbf{r}, t)$$

$H_{KS}(t+\Delta t)$

$H_{KS}(t+\Delta t)$

$$|< \psi^*_{2,k}(\mathbf{r}, t) \mid \psi_{2,k}(\mathbf{r}, t) >|^2$$

$$\rho(\mathbf{r}, t+\Delta t) = \sum_{n,k} |< \psi^*_{n,k}(\mathbf{r}, t+\Delta t) \mid \psi_{n,k}(\mathbf{r}, t+\Delta t) >|^2$$

$$H_{KS}(t+\Delta t) = -\frac{\hbar^2}{2m}\Delta + V_{HXC}[\rho(\mathbf{r}, t+\Delta t)] + v^{ps}_{l,\tau}$$

MPI_Allreduce

$$|< \psi^*_{n,k}(\mathbf{r}, t) \mid \psi_{n,k}(\mathbf{r}, t) >|^2$$

$H_{KS}(t+\Delta t)$

$$\psi_{n,k}(\mathbf{r}, t+\Delta t) = e^{\frac{\Delta t}{i\hbar} H_{KS}(t+\frac{\Delta t}{2})} \psi_{n,k}(\mathbf{r}, t)$$

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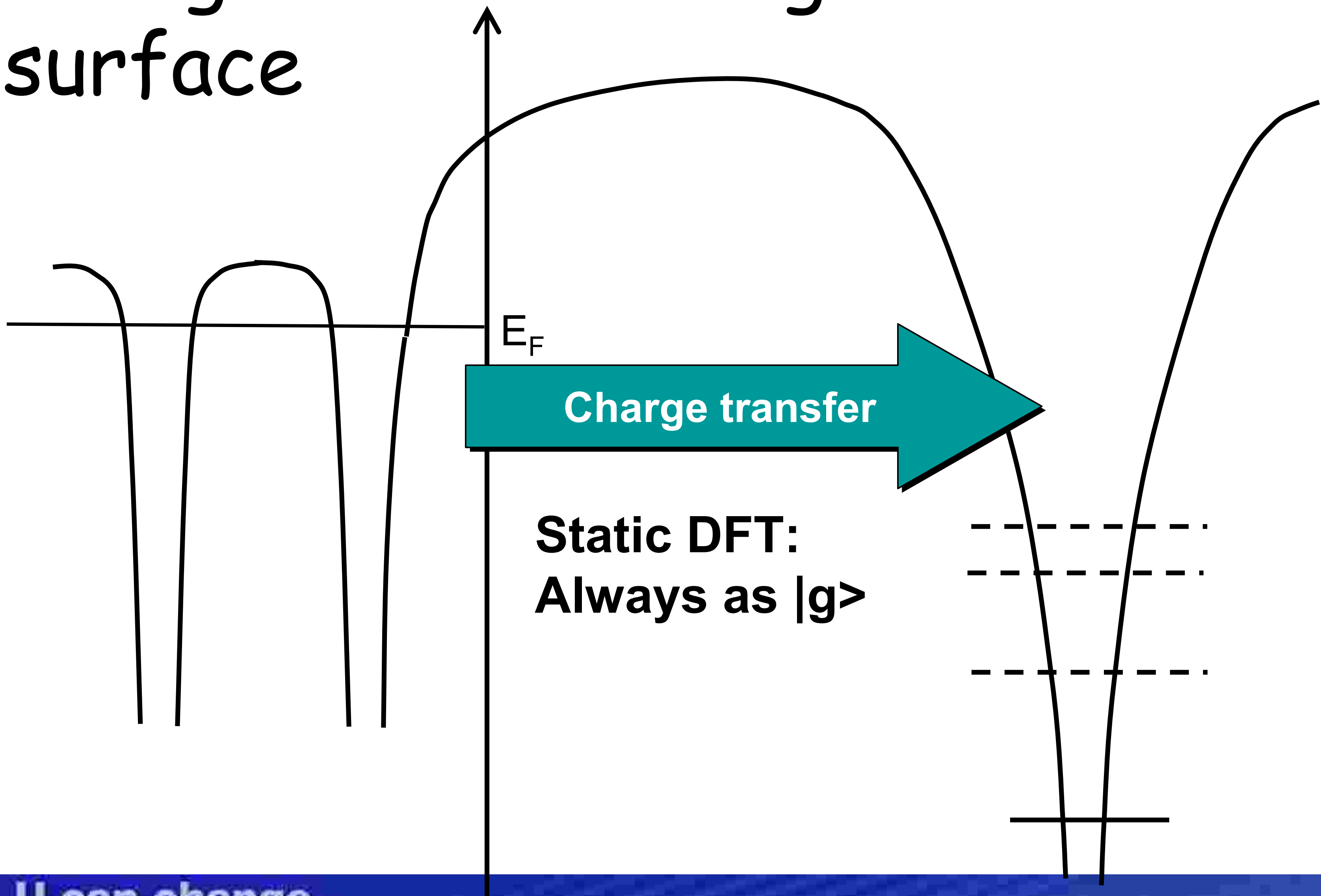
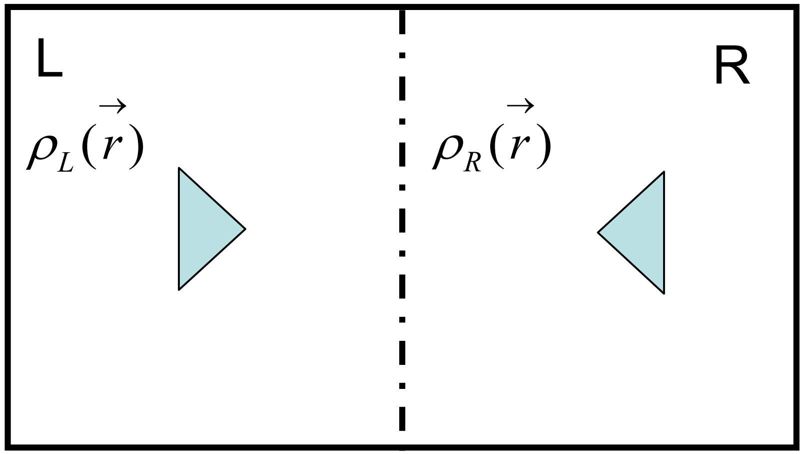
Simulating High-Speed Highly-Charged Ion colliding to a solid surface

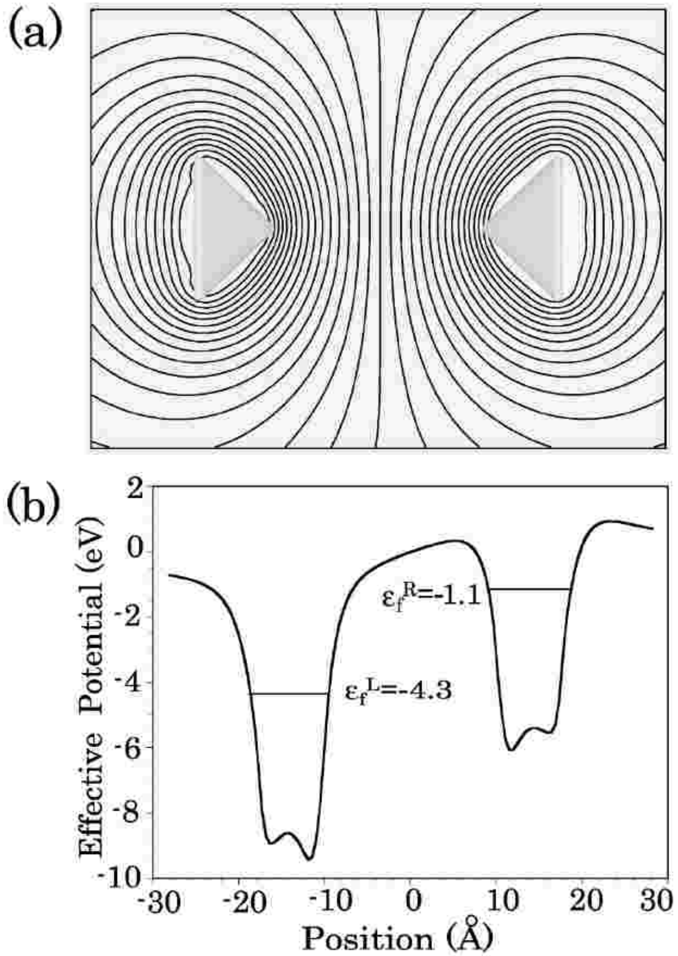


VOLUME 86, NUMBER 3 PHYSICAL REVIEW LETTERS 15 JANUARY 2001

Partitioned Real-Space Density Functional Calculations of Bielectrode Systems under Bias Voltage and Electric Field

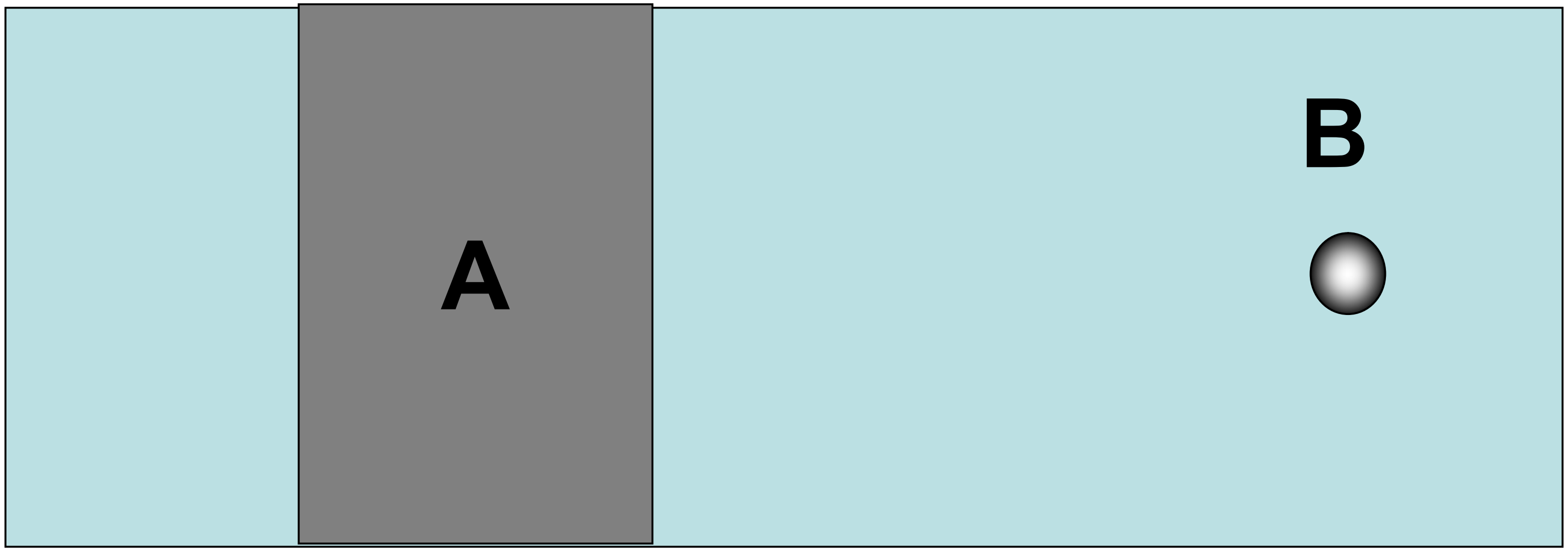
N. Nakaoka,[1] K. Tada,[1] S. Watanabe,[3,5] H. Fujita,[4,5] and K. Watanabe[1,2,5]





$$H_{KS}^{L}(\vec r) = -\frac{\hbar^2}{2m}\vec\nabla^2 + V_H[\rho_L(\vec r)+\rho_R(\vec r)] + V_{XC}[\rho_L(\vec r)] + V_{ION}^{L}(\vec r)$$

$$H_{KS}^{R}(\vec r) = -\frac{\hbar^2}{2m}\vec\nabla^2 + V_H[\rho_L(\vec r)+\rho_R(\vec r)] + V_{XC}[\rho_R(\vec r)] + V_{ION}^{R}(\vec r)$$



$$t = 0$$

$$\rho(r, t=0) = \rho_A(r) + \rho_B(r)$$

$$\{\psi_1(r, t=0), \psi_2(r, t=0), \ldots., \psi_N(r, t=0)\}$$

$$= \{\psi_1^A(r), \psi_2^A(r), \ldots, \psi_{N_A}^A(r), \psi_1^B(r), \psi_2^B(r), \ldots, \psi_{N_B}^B(r)\}$$

$$t > 0$$

$$i\hbar \frac{d\psi_n(\vec{r}, t)}{dt} = H[\rho(\vec{r}, t)]\psi_n(\vec{r}, t)$$

$$\vec{F}_I = M_I \frac{d\vec{R}_I}{dt}$$

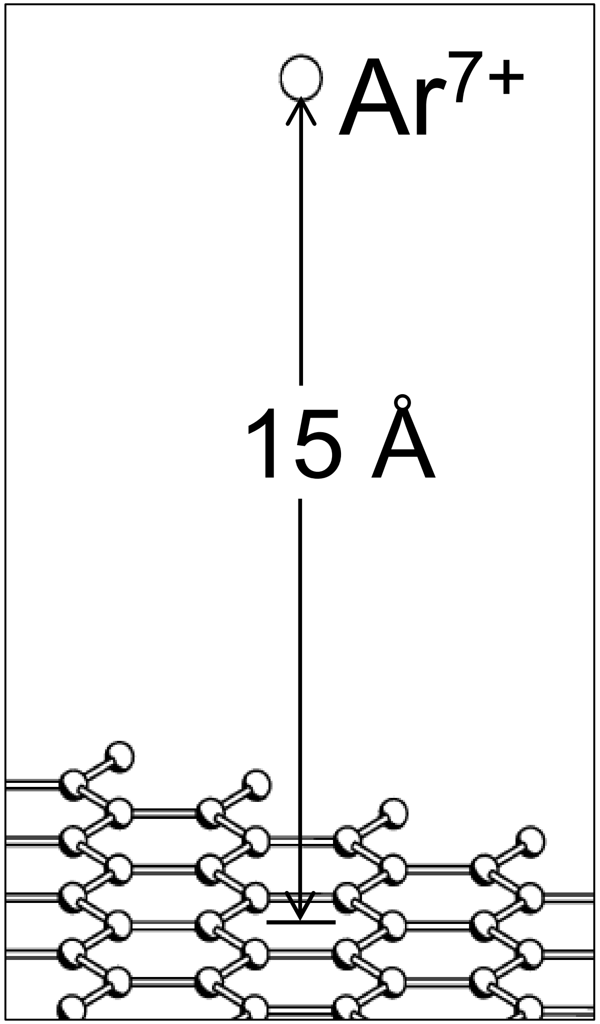
Demonstration: Ar^{7+} passing through a graphene sheet

Computational conditions (TDDFT-MD)

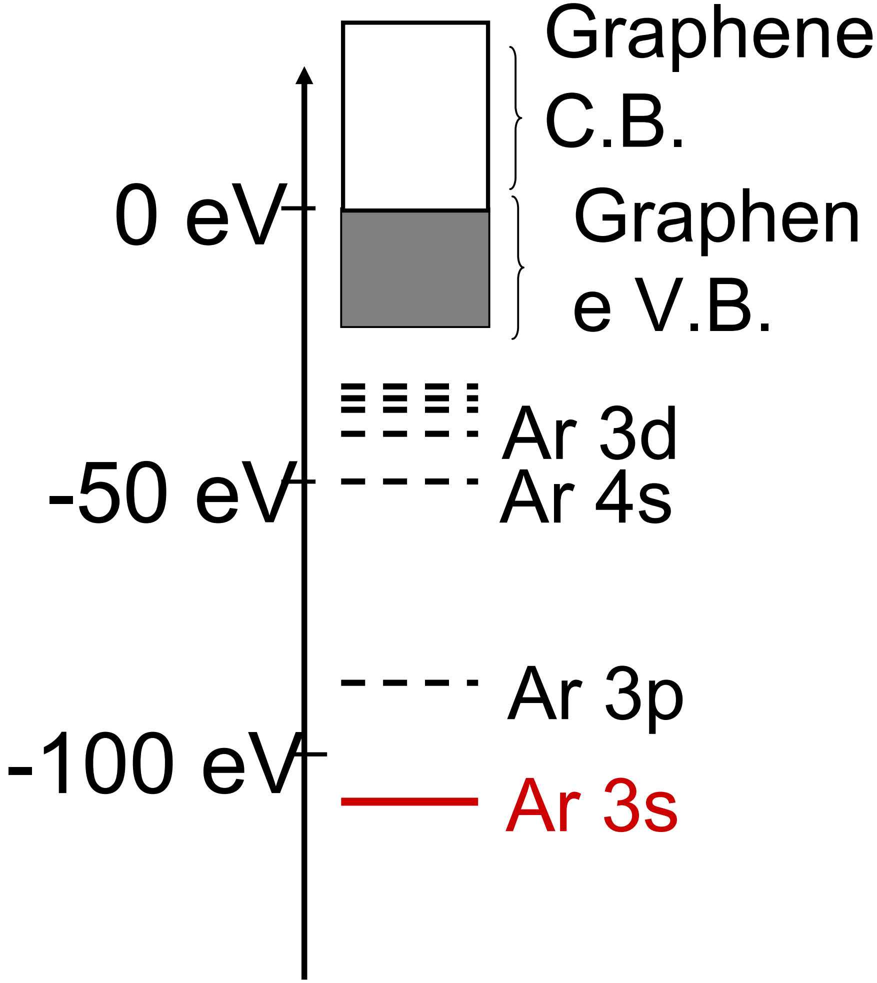
Computational conditions

1. Plane wave basis set (Ecut=60Ry)
2. Pseudo potentials (Troullier-Martins)
3. Γ -points with a 5x5 graphene layer (50 C atoms)
4. 30 Å for vacuum region
5. dt=0.02 a.u.(4.84×10^{-4} fs)

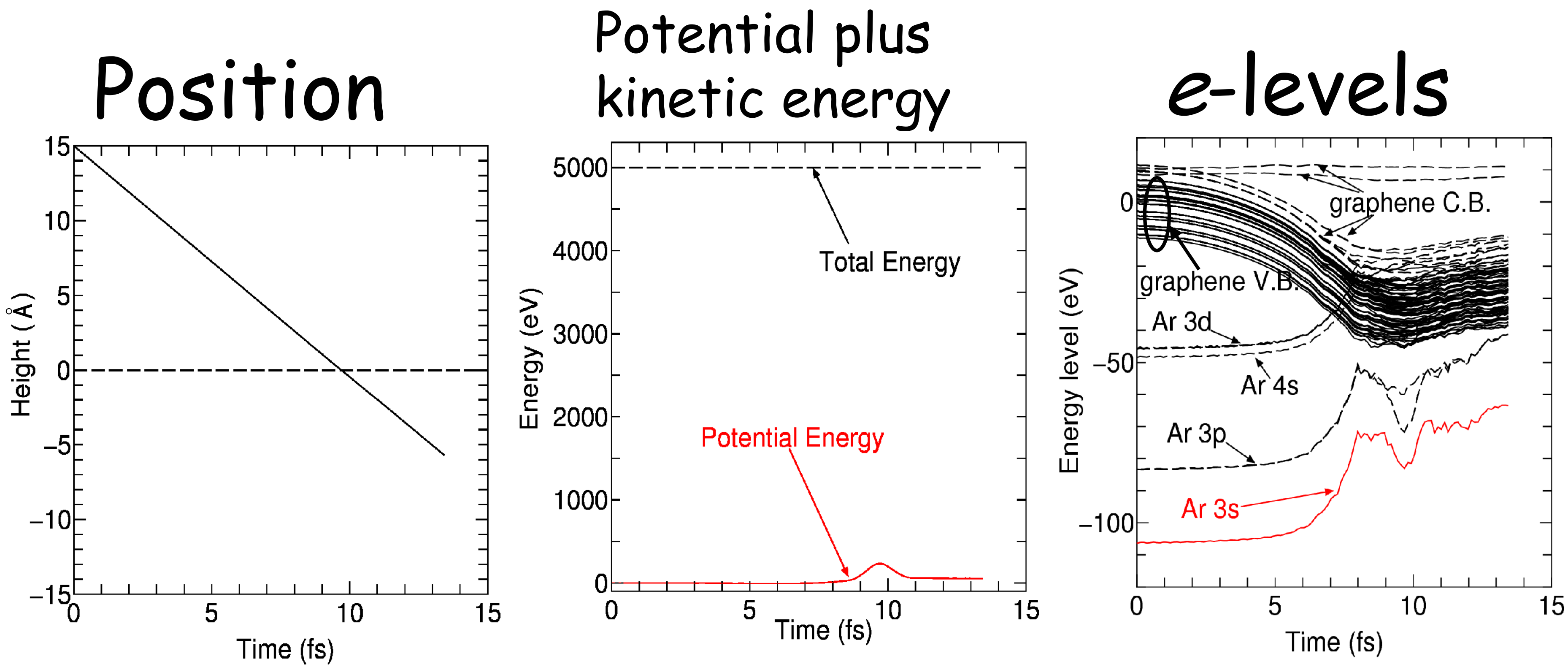
Computational condition



Energy levels



Ar^{7+} with incident energy of 5 KeV



Miyamoto, Zhang, PRB 77, 045433 (2008).

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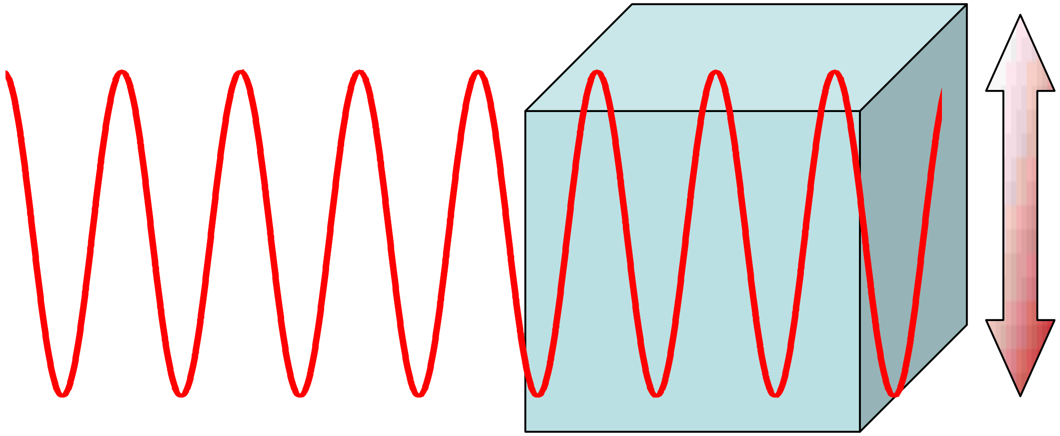
3. Time-varying dielectric field (Pulse laser, dynamical conductivity)

Pioneering works: 筑波大学　矢花先生

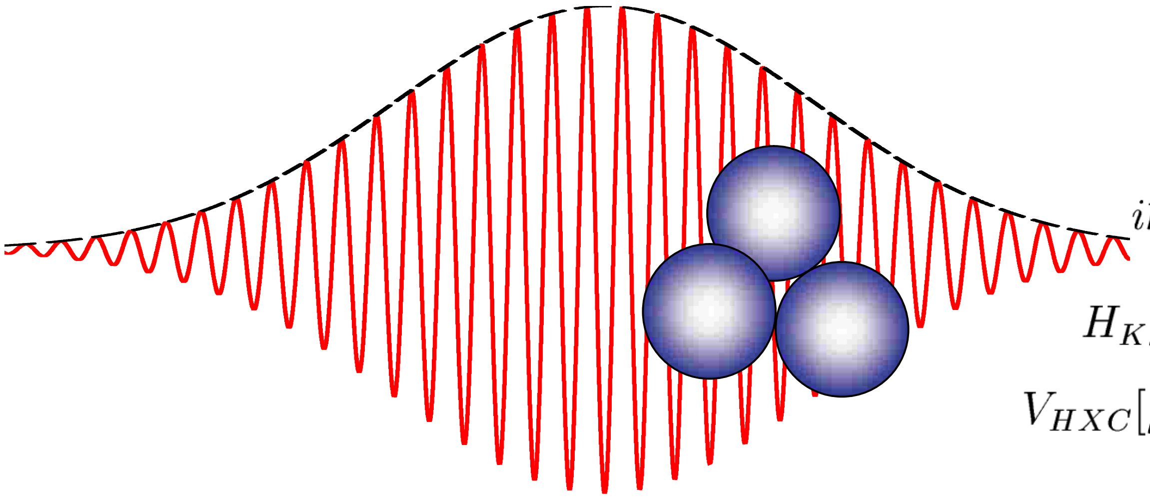


$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),\mathbf{A}(t)\right]$$

$$-\frac{\hbar^2}{2m}\left(\mathbf{P}-\frac{1}{c}\mathbf{A}(t)\right)^2$$

Bertsch, et al., PRB62 7998, (2000).



$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

$$H_{KS}\left[\rho(\mathbf{r},t)\right] \Rightarrow H_{KS}\left[\rho(\mathbf{r},t),V_{ext}(\mathbf{r},t)\right]$$

$$V_{HXC}[\rho(\mathbf{r},t)] \Rightarrow V_{HXC}[\rho(\mathbf{r},t)] + V_{ext}(\mathbf{r},t)$$

Castro et al., Eur. Phys. J. D 28, 211 (2004).

How can we know that the simulation goes numerically correct?

Let us use total-energy conservation rule.

In case of classical molecular dynamics (MD)

$$U(t) = \sum_I \frac{M_I}{2}\left(\frac{d\mathbf{R}_I}{dt}\right)^2 + V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)$$

$$\frac{dU(t)}{dt} = \sum_I \left(\frac{d\mathbf{R}_I(t)}{dt} \cdot M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{d\mathbf{R}_I(t)}{dt} \cdot \frac{V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)}{d\mathbf{R}_I(t)}\right) = 0$$

because $\boxed{-\frac{V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)}{d\mathbf{R}_I(t)} = M_I \frac{d^2\mathbf{R}_I(t)}{dt^2}}$

In case of combination of MD and TDDFT

$$V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right) \Rightarrow$$

$$\sum_i \left(\int \psi_i^*(\mathbf{r}, t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r}, t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}', t) v_{nl}(\mathbf{r}', \mathbf{r}) \psi_i(\mathbf{r}, t) d\mathbf{r}' d\mathbf{r} \right) + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}', t)\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$

$$+ \int E_{XC}[\rho(\mathbf{r}, t)] d\mathbf{r} + \sum_I Z_I \left(\int \frac{\rho(\mathbf{r}, t)}{|\mathbf{R}_I(t) - \mathbf{r}|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\mathbf{R}_I(t) - \mathbf{R}_J(t)|} \right) \equiv E_{tot}^{DFT}(\mathbf{r}, t)$$

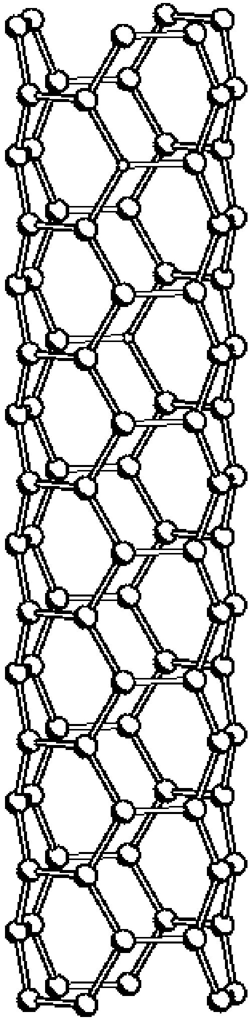
MD simulation must conserve

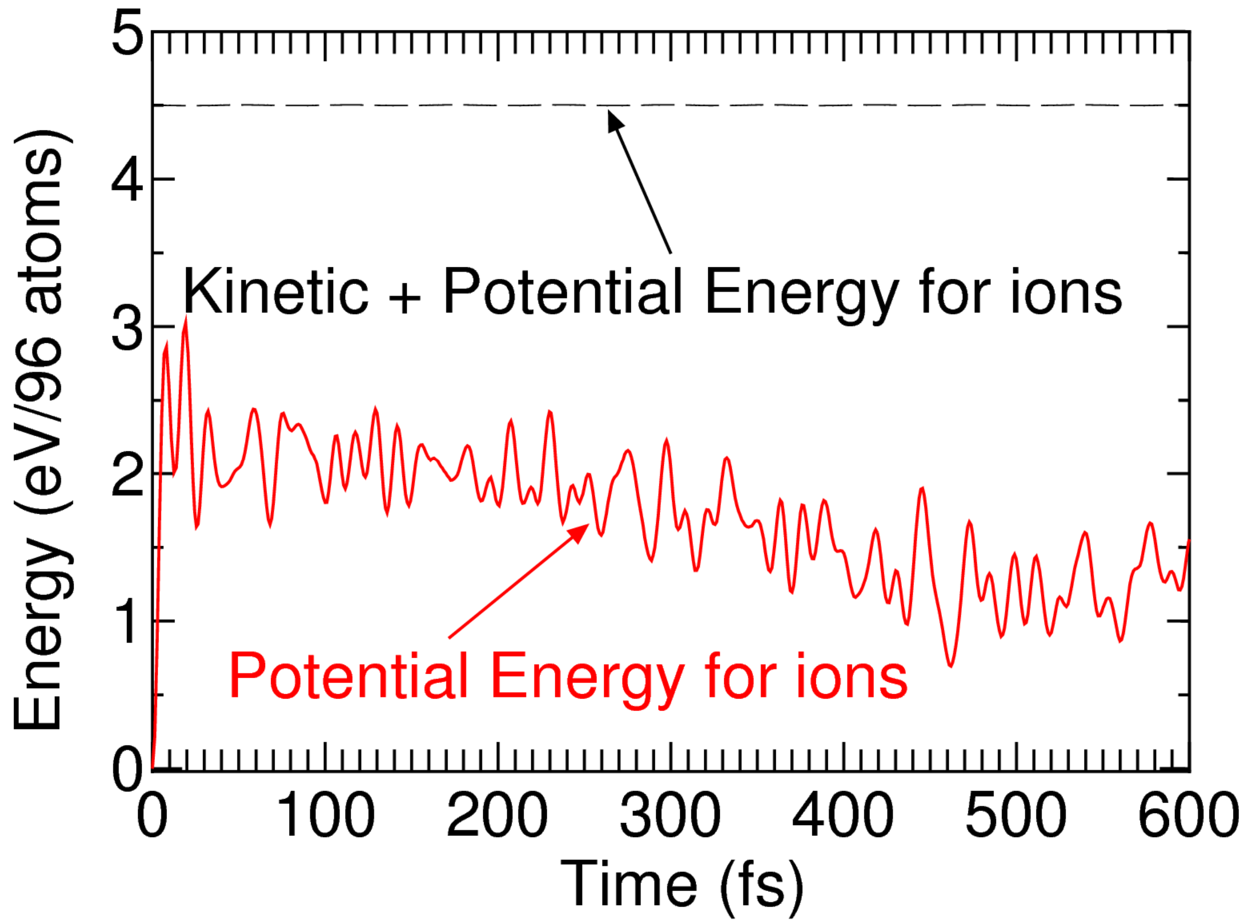
$$U(t) = \sum_I \frac{M_I}{2} \left(\frac{d\mathbf{R}_I}{dt} \right)^2 + E_{tot}^{DFT}(\mathbf{r}, t)$$

$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2 \mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r}, t)}{d\mathbf{R}_I(t)} \right) + \underbrace{\sum_i \left(\frac{d\psi_i^*(\mathbf{r}, t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r}, t)}{\delta \psi_i^*(\mathbf{r}, t)} + C.C. \right)}_{\text{TDDFT term}} = 0$$

$$\boxed{\begin{aligned} M_I \frac{d^2 \mathbf{R}_I(t)}{dt^2} &= -\frac{dE_{tot}^{DFT}(\mathbf{r}, t)}{d\mathbf{R}_I(t)} \\ \frac{\delta E_{tot}^{DFT}(\mathbf{r}, t)}{\delta \psi_i^*(\mathbf{r}, t)} &= H_{KS}(\mathbf{r}, t) \psi_i(\mathbf{r}, t) = i\hbar \frac{d\psi_i(\mathbf{r}, t)}{dt} \end{aligned}}$$

Example of TDDFT-MD 96 C atoms under R.T. and 173→231 excitation





Without time-varying external field

$$\sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}',t)\rho(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$+ \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r} + \sum_I Z_I \left(\int \frac{\rho(\mathbf{r},t)}{|\mathbf{R}_I(t)-\mathbf{r}|} d\mathbf{r} + \sum_{J\neq I} \frac{Z_J}{|\mathbf{R}_I(t)-\mathbf{R}_J(t)|} \right) \equiv E_{tot}^{DFT}(\mathbf{r},t)$$

With time-varying external field

$$V_{ext}(\mathbf{r},t) = \int \frac{\rho_{ext}(\mathbf{r}',t)}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}'$$

$$E_{tot}^{DFT}(\mathbf{r},t)$$
$$= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int\int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r}$$
$$+ \frac{1}{2} \int\int \frac{\left(\rho(\mathbf{r}',t)+\rho_{ext}(\mathbf{r}',t)\right)\left(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t)\right)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$+ \sum_I Z_I \left(\int \frac{\left(\rho(\mathbf{r},t)+\rho_{ext}(\mathbf{r},t)\right)}{|\mathbf{R}_I(t)-\mathbf{r}|} d\mathbf{r} + \sum_{J\neq I} \frac{Z_J}{|\mathbf{R}_I(t)-\mathbf{R}_J(t)|} \right)$$

$$E_{tot}^{DFT}(\mathbf{r},t)$$

$$= \sum_i \left(\int \psi_i^*(\mathbf{r},t) \frac{-\hbar^2}{2m} \Delta \psi_i(\mathbf{r},t) d\mathbf{r} + \int \int \psi_i^*(\mathbf{r}',t) v_{nl}(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r},t) d\mathbf{r}' d\mathbf{r} \right) + \int E_{XC}[\rho(\mathbf{r},t)] d\mathbf{r}$$

$$+ \frac{1}{2} \int \int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))\,(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\,\mathbf{r} - \mathbf{r}'\,|} d\mathbf{r}' d\mathbf{r}$$

$$+ \sum_I Z_I \left(\int \frac{(\rho(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t))}{|\,\mathbf{R}_I(t) - \mathbf{r}\,|} d\mathbf{r} + \sum_{J \neq I} \frac{Z_J}{|\,\mathbf{R}_I(t) - \mathbf{R}_J(t)\,|} \right)$$

$$U(t) = \sum_I \frac{M_I}{2} \left(\frac{d\mathbf{R}_I}{dt} \right)^2 + E_{tot}^{DFT}(\mathbf{r},t)$$

$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \overbrace{\left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right)}^{\text{Goes to zero!}}$$

$$+ \underbrace{\int \frac{d\rho_{ext}(\mathbf{r},t)}{dt} \int \left(\frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))}{|\,\mathbf{r}' - \mathbf{r}\,|} d\mathbf{r}' + \sum_I Z_I \frac{1}{|\,\mathbf{R}_I(t) - \mathbf{r}\,|} \right) d\mathbf{r}}_{\text{Remains as non-zero!}}$$

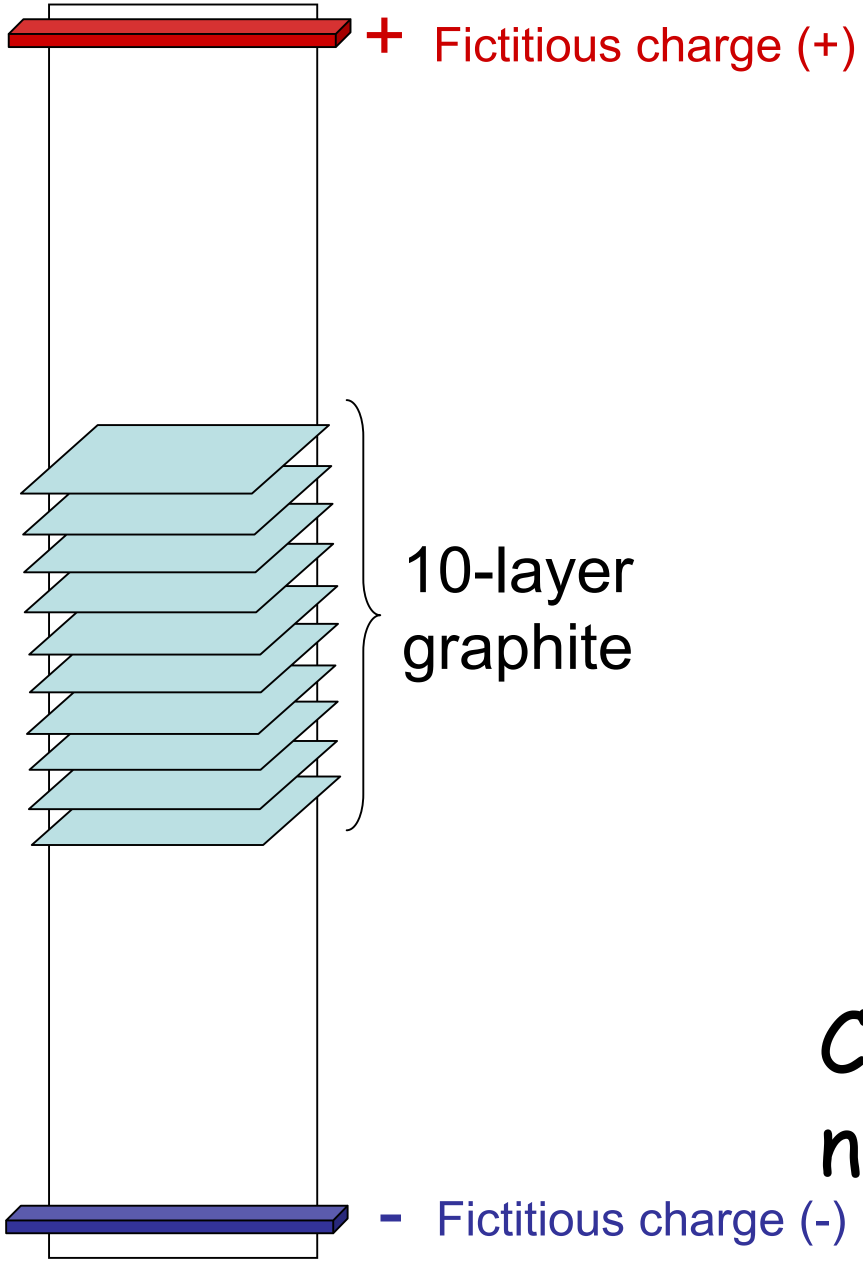
Work by external field is

$$W(t) = \int_{t_0}^{t} \frac{dU(t')}{dt'} dt' + W(t = t_0)$$

Thus a new conservation rule is

$$\frac{d\left(U(t) - W(t)\right)}{dt} = 0$$

Miyamoto, Zhang, submitted



Test calculation:

- ☑ AB-stacked graphite 2x2 cell in lateral directions
- ☑ under pulse E-field
- ☑ Ecut=60 Ry
- ☑ TM type pseudopotentials
- ☑ Single k-point
- ☑ dt=1.84 x 10^{-4} fs

Conservation rule was numerically confirmed

sumarries

1. Time-dependent density functional approach as a practical tool for nano-engineering
2. Ion-surface interaction
3. Irradiation with pulse shot

Some applications will be presented