Empowered by Innovation NEC

民間企業でもやっている、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

東大物性研　杉野　修　准教授
Sichuan Univ. Prof. H. Zhang
地球シミュレータセンター

U can change.

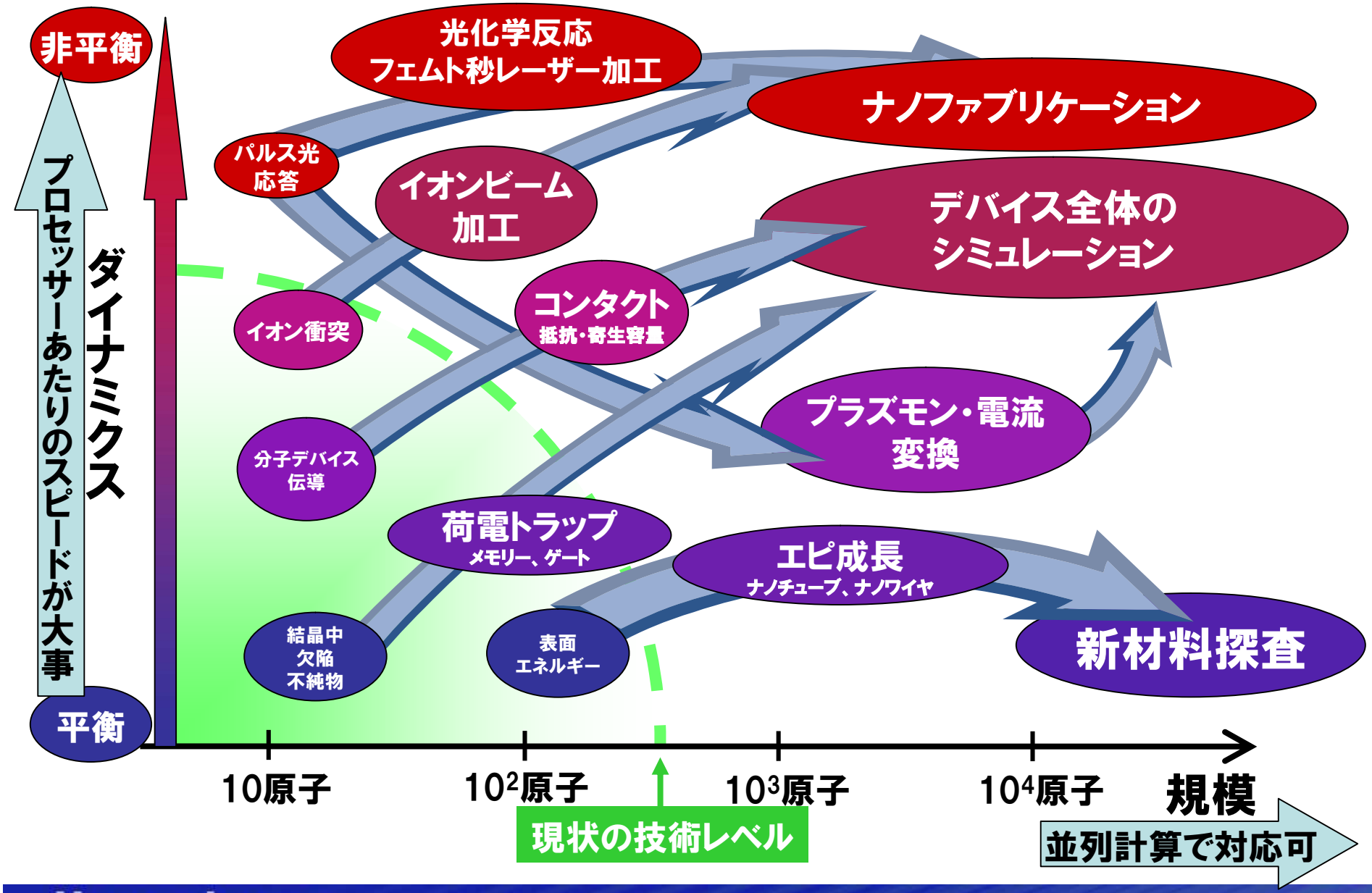
第13回コンピュテーショナル・マテリアルズ・デザイン
CMD®ワークショップ　2008年9月10日

outline

1. Motivation
2. Time-Dependent Density Functional Theory
3. Energy conservation rule throughout the simulation
4. Some applications

1. Motivation
2. Time-Dependent Density Functional Theory
3. Energy conservation rule throughout the simulation
4. Some applications

1. Motivation



2. 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

$$i\hbar \frac{d\psi_n(\vec{r},t)}{dt}$$

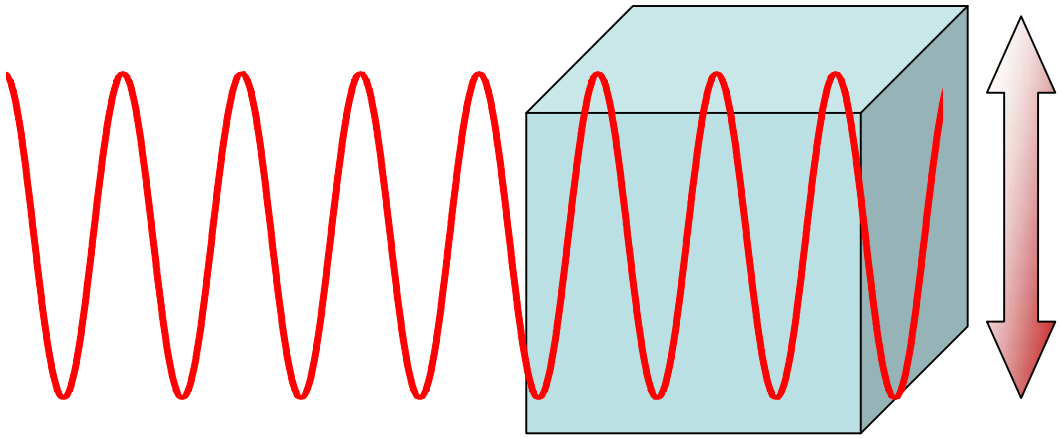
$$= \left(-\nabla^2 + \int \frac{\rho(\vec{r'},t)}{|\vec{r}-\vec{r'}|} d\vec{r'} + \mu_{XC}[\rho(\vec{r},t)] + \sum_I \tilde{v}(\vec{r'}-\vec{R}_I(t), \vec{r}-\vec{R}_I(t)) + \sum_I \frac{Z_I(\vec{R}_I)}{|\vec{r}-\vec{R}_I(t)|} \right) \psi_n(\vec{r},t)$$

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

Time-dependent Kohn-Sham equation

Influence of optical perturbation!

Pioneering works: **筑波大学　矢花先生**

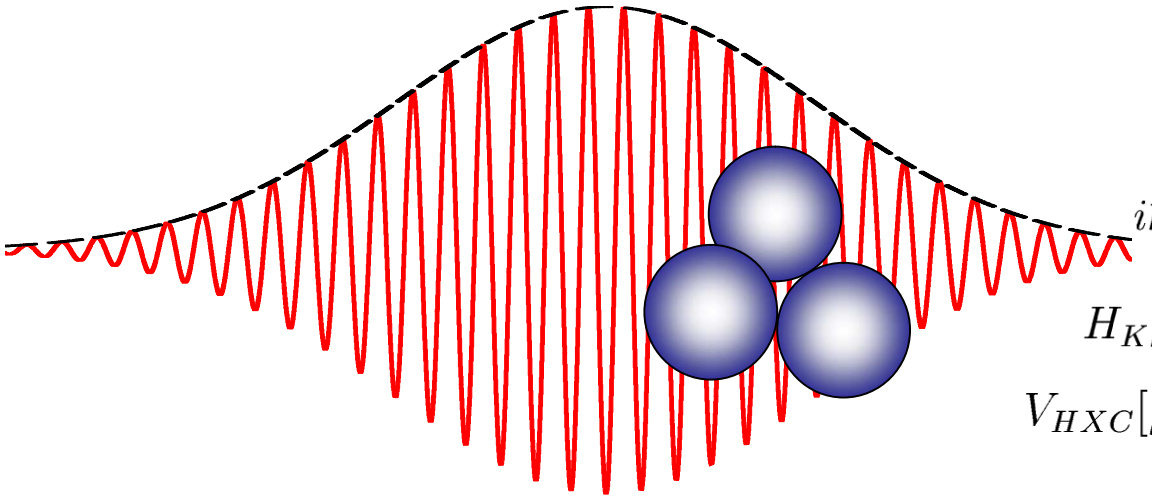


$$i\hbar\frac{d\psi_{n,k}(\mathbf{r},t)}{dt} = H_{KS}\left[\rho(\mathbf{r},t)\right]\psi_{n,k}(\mathbf{r},t)$$

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

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

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's us re-visit the 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 $$-\frac{V\left(\mathbf{R}_1(t), \mathbf{R}_2(t), , , , \mathbf{R}_N(t)\right)}{d\mathbf{R}_I(t)} = M_I \frac{d^2\mathbf{R}_I(t)}{dt^2}$$

In case of combination of MD and TDDFT

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

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

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

MD simulation must conserve

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

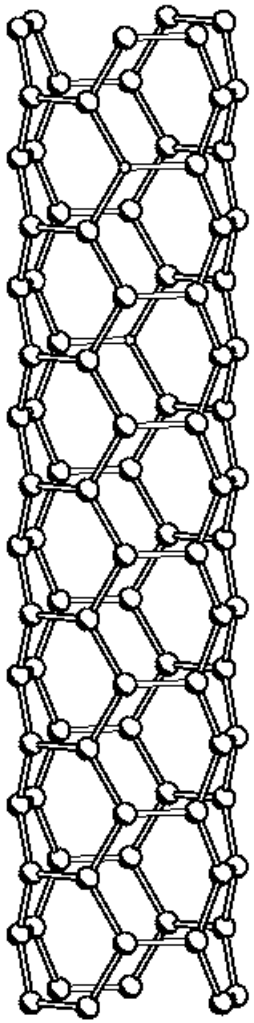
TDDFT term

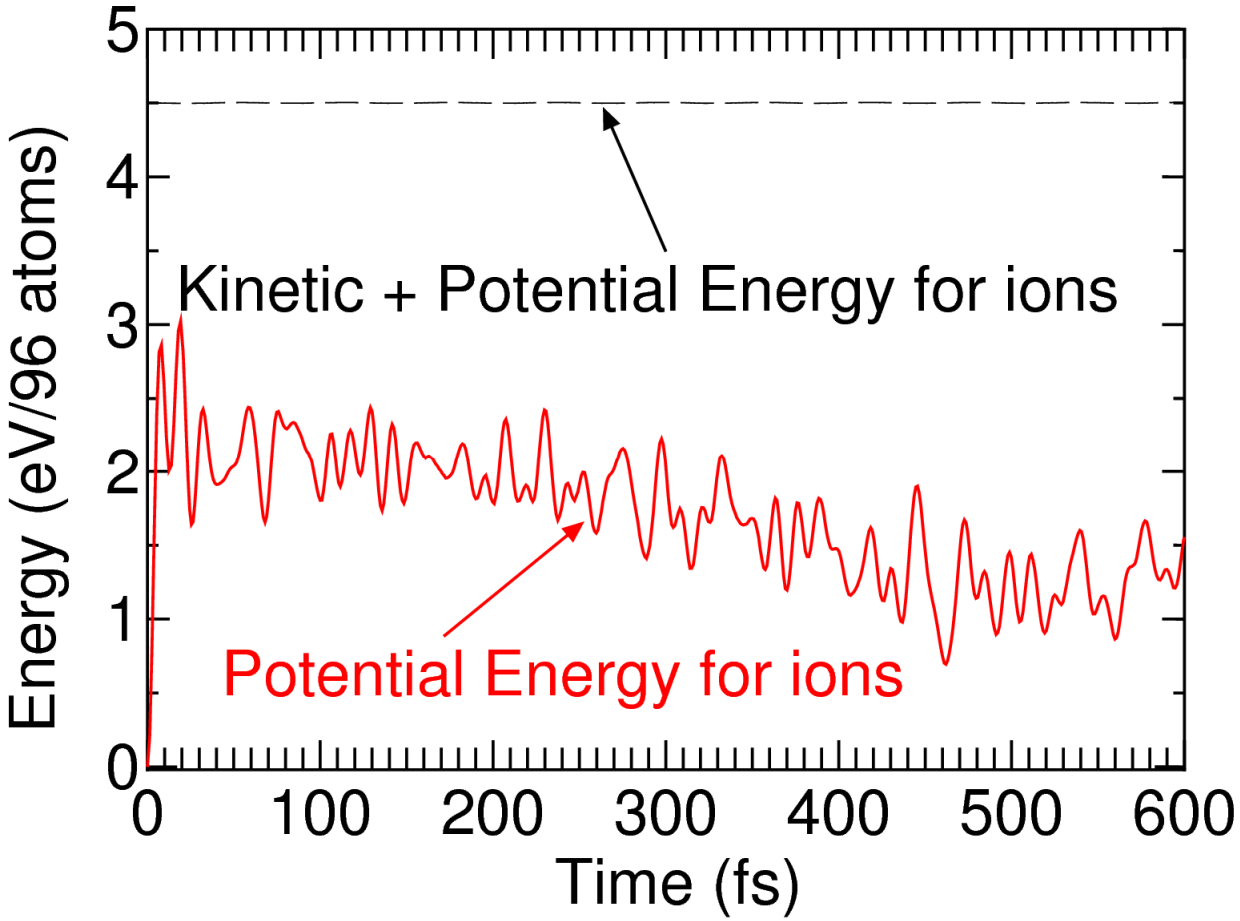
$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right)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

$$M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} = -\frac{dE_{tot}^{DFT}(\mathbf{r},t)}{d\mathbf{R}_I(t)}$$

$$\frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} = H_{KS}(\mathbf{r},t)\psi_i(\mathbf{r},t) = i\hbar \frac{d\psi_i(\mathbf{r},t)}{dt}$$

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

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

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

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

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

Goes to zero!

$$\frac{dU(t)}{dt} = \sum_I \frac{d\mathbf{R}_I(t)}{dt} \cdot \left(M_I \frac{d^2\mathbf{R}_I(t)}{dt^2} + \frac{dE_{tot}^{KS}(\mathbf{r},t)}{d\mathbf{R}_I(t)} \right) + \sum_i \left(\frac{d\psi_i^*(\mathbf{r},t)}{dt} \frac{\delta E_{tot}^{DFT}(\mathbf{r},t)}{\delta \psi_i^*(\mathbf{r},t)} + C.C. \right)$$
$$+ \int \frac{d\rho_{ext}(\mathbf{r},t)}{dt} \left(\int \frac{(\rho(\mathbf{r}',t) + \rho_{ext}(\mathbf{r}',t))}{|\,\mathbf{r}' - \mathbf{r}\,|} d\mathbf{r}' + \sum_I Z_I \frac{1}{|\,\mathbf{R}_I(t) - \mathbf{r}\,|} \right) d\mathbf{r}$$

Remains as non-zero!

Work by external field is

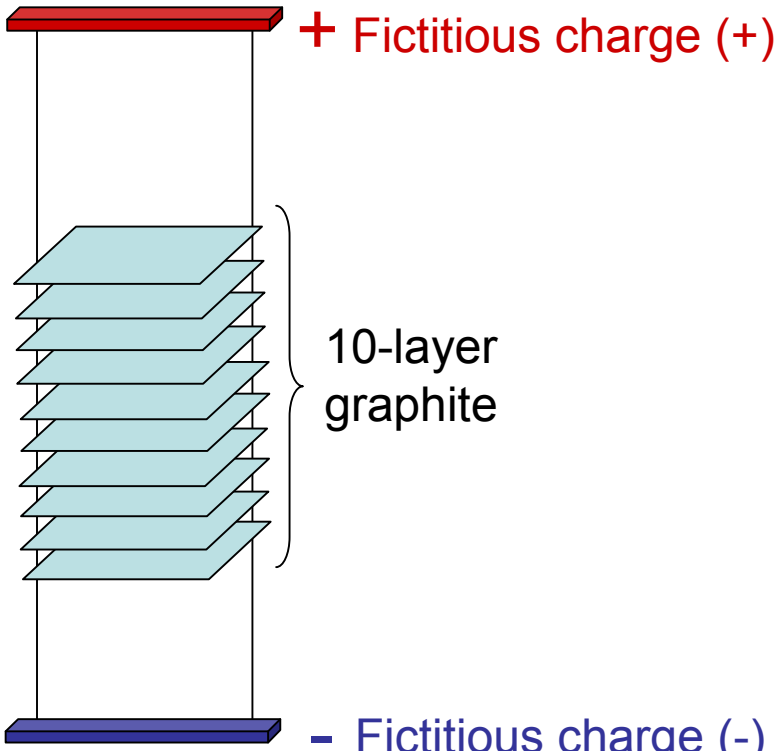
$$W(t) = \int_{t_0}^{t} \frac{dU(t')}{dt'} dt' + W(t = t_0)$$

Thus a new conservation rule is

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

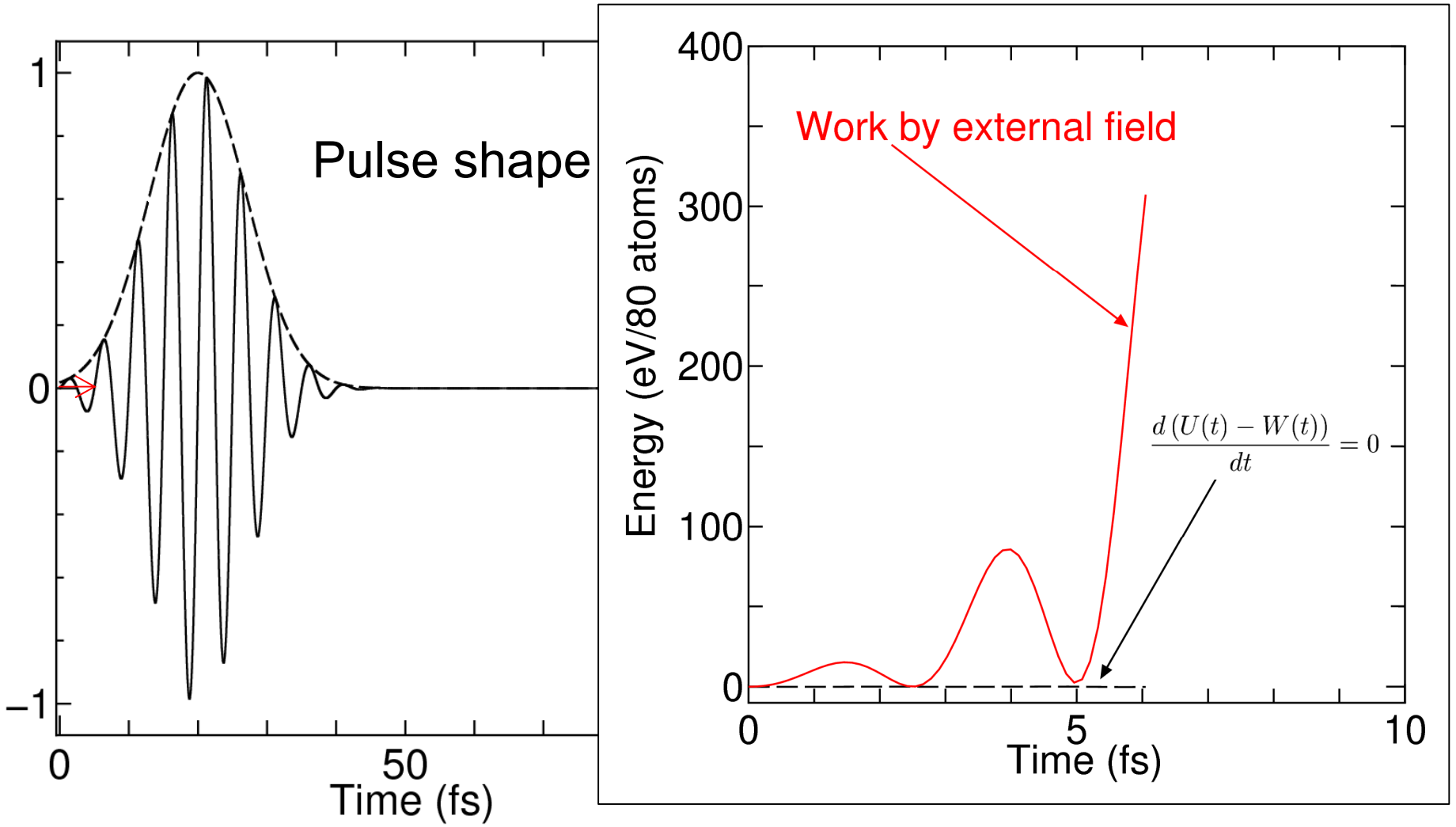
Miyamoto, Zhang, Phys. Rev. B77, 165123 (2008)

1. This holds regardless to xc-functional form (but within adiabatic xc-functional)
2. Inductance has not been included ($j \rightarrow B \rightarrow j_{ind}$) →current density functional theory



Test calculation:

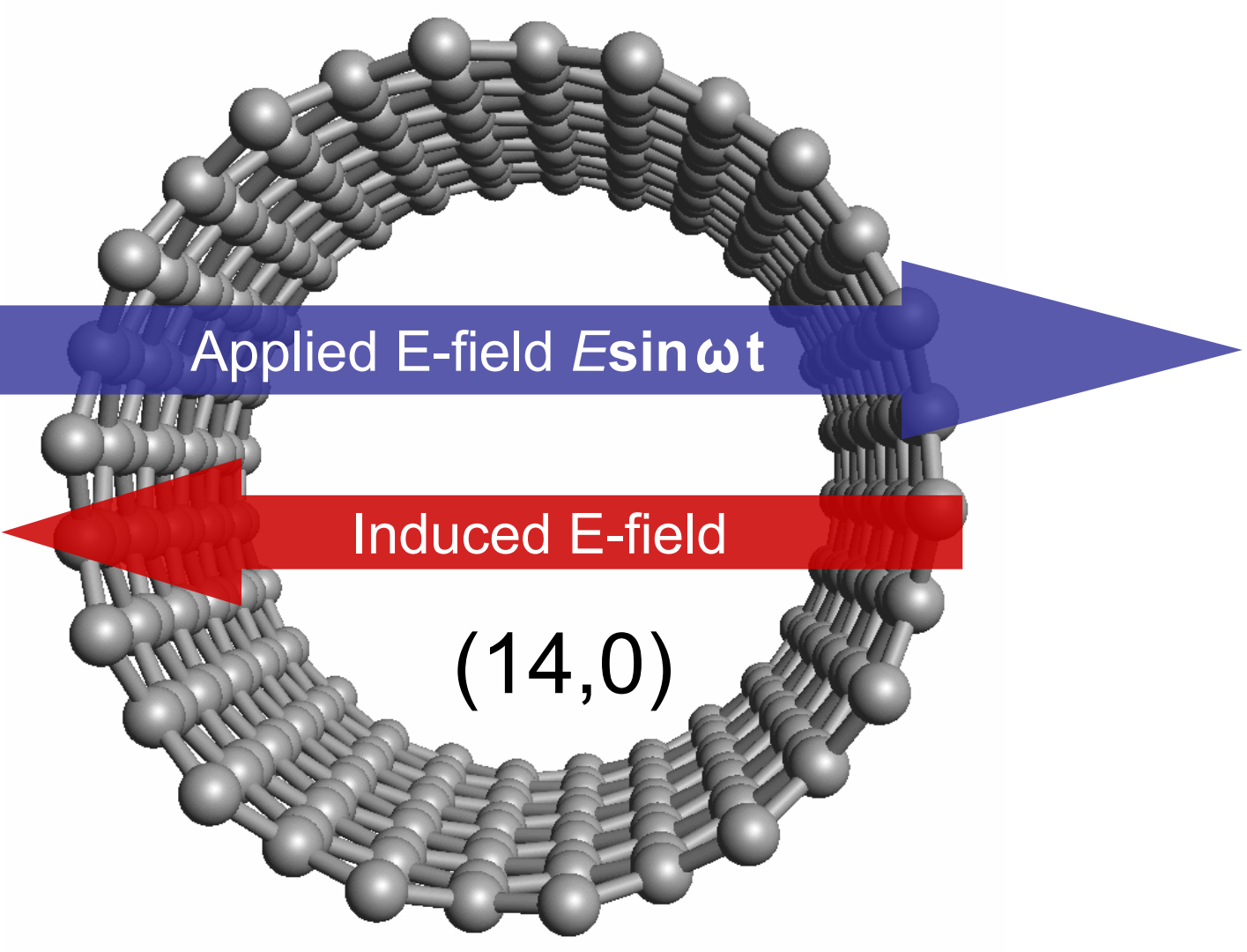
- ☑ AB-stacked graphite 2x2 cell in lateral directions
- ☑ under pulse E-field
- ☑ Ecut=60 Ry
- ☑ TM type pseudopotentials
- ☑ Single k-point
- ☑ dt=1.84 x 10^{-4} fs



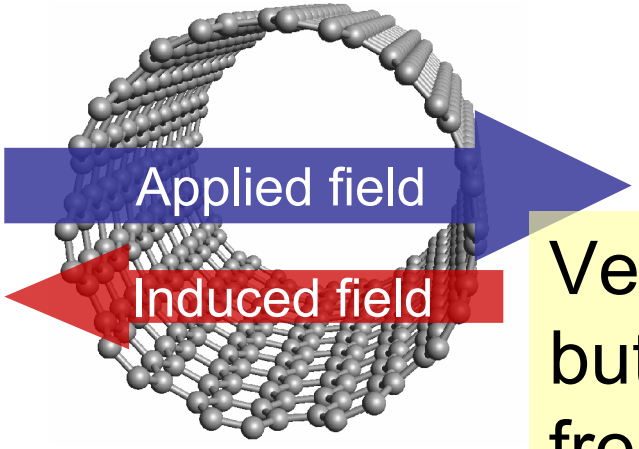
Application 1**は現在論文執筆中です**

配布資料化はなにとぞご容赦を

Application 2: optical-field inside nanotube

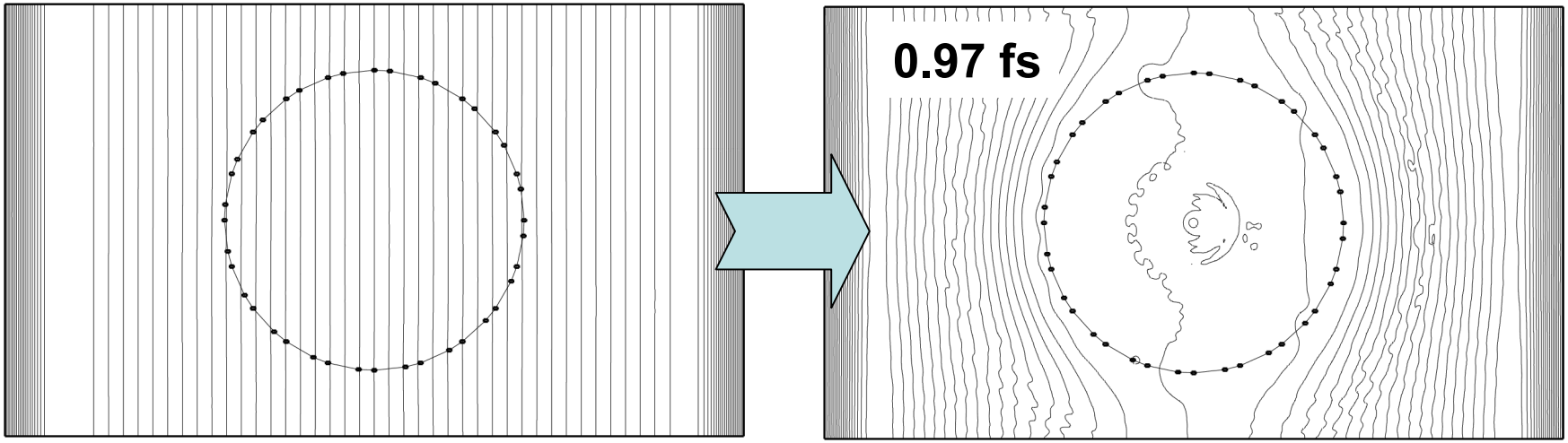


Demonstration: Screening against static E-field

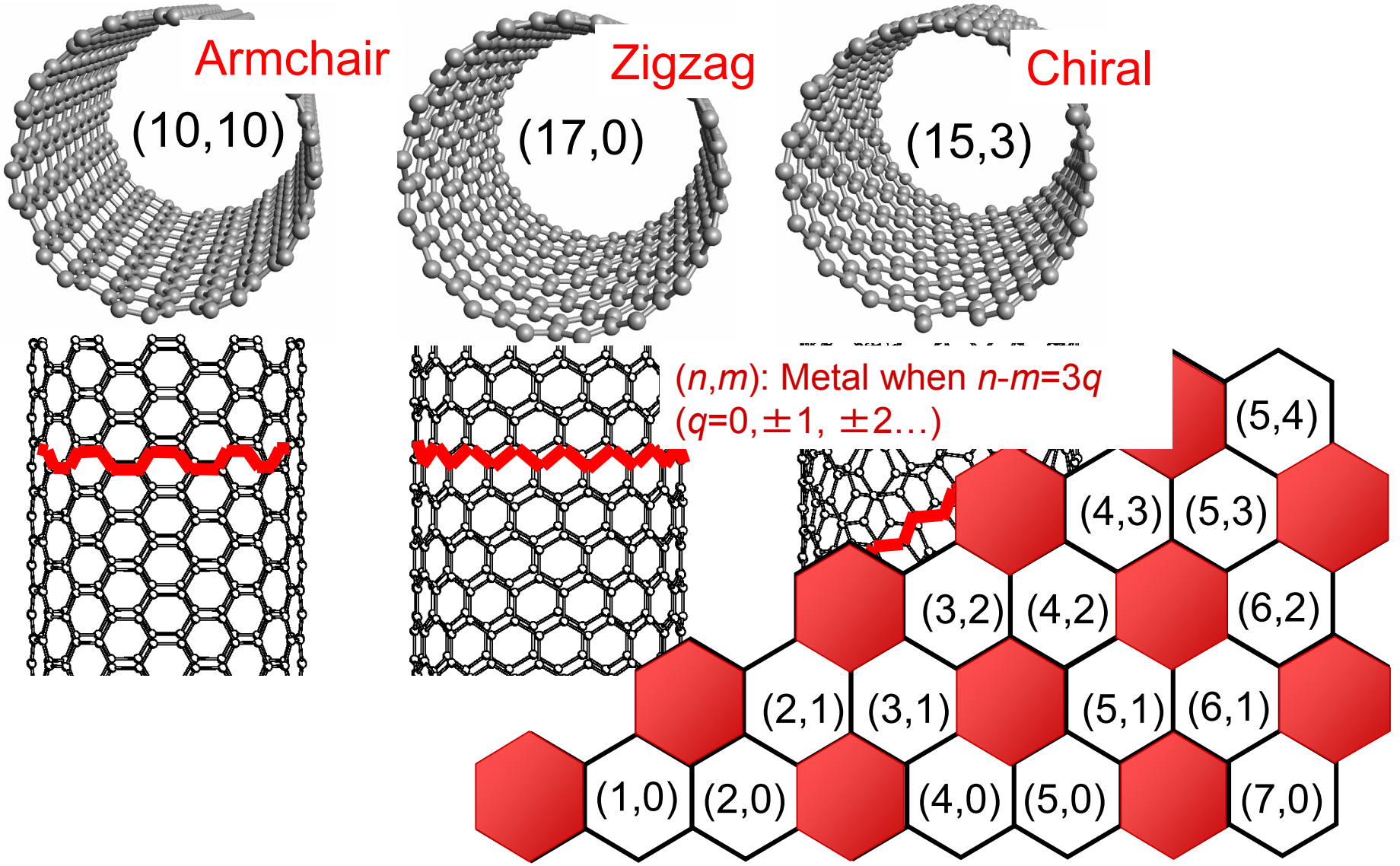


$$V_{HXC}^{TDDFT}(\vec{r},t;V_{appl})+V_{appl}(\vec{r})-V_{HXC}^{DFT}(\vec{r})$$

Very fast screening by depolarization, but still takes a time comparable to a frequency of E-field of light



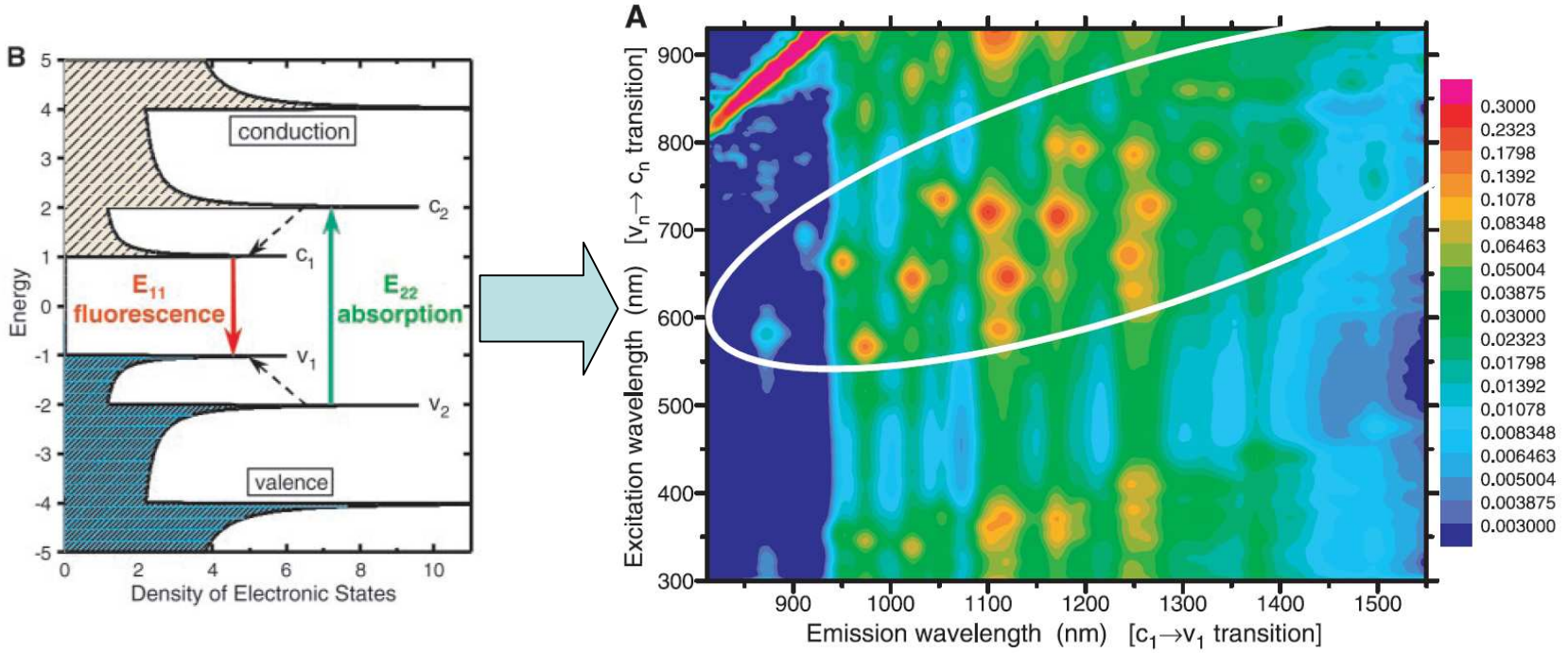
Nanotube's structures and electronic properties.



Identification of nanotube chirality (*n,m*) by optical transition

H. Kataura *et al*., Synthetic Metals 103, 2555 (1999), relation between (*n,m*) and optical absorption peak position

S. M. Bachilo et al., Science 298, 2361 (2002), photo luminescence to identify (*n,m*) available by dispersion technique of nanotubes.



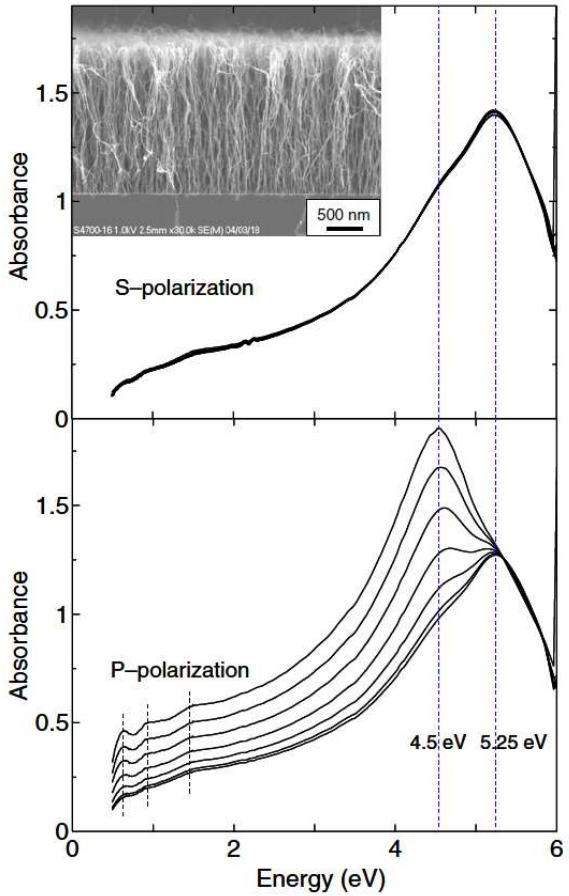
But this is a consideration under optical field parallel to tube axis!

Can nanotubes completely screen cross-polarized light?

Cross-excitations is atctually measured, so let's say NO!

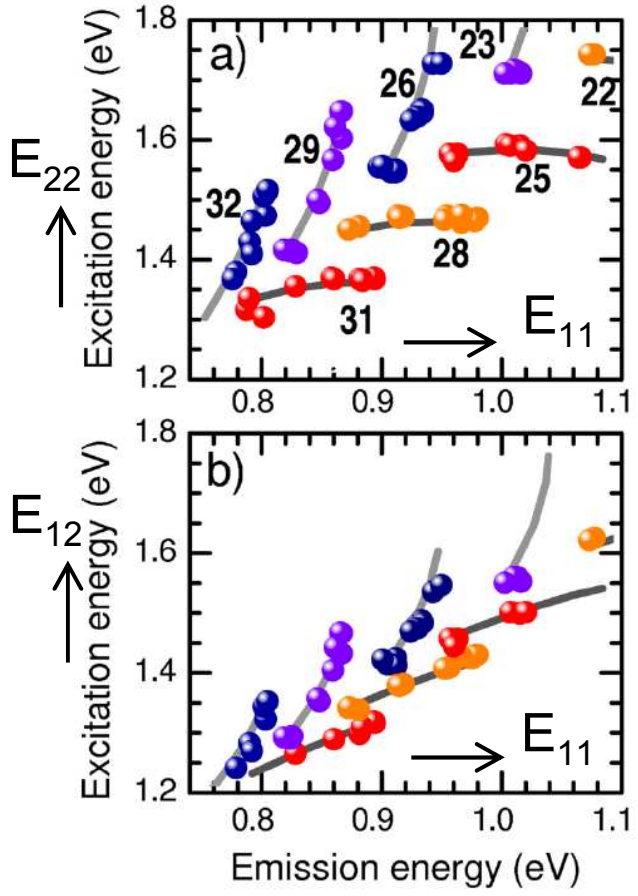
Applied E-field is no longer static!

Absorption



Murakami et al., PRL 94, 087402 (2005)

Absorption & luminescence



Lefebvre and Finnie, PRL 98, 167406 (2007)

Cross-polarization of CNT did not take attentions due to smaller oscillator strength and depolarization effect, which was considered in early famous AB-effect works!

H. Ajiki and T. Ando, Jpn. J. Appl. Phys. 34, Suppl, 34-1, 107 (1994).
H. Ajiki and T. Ando, Physica B 201, 349 (1994).

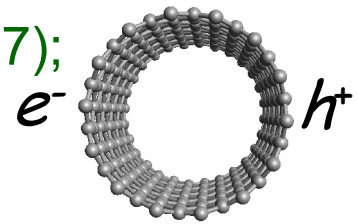
Question for theorists:
Why E-field with cross-polarization can survive?
What suppresses depolarization?

Exciton has been suggested to weaken depolarization.

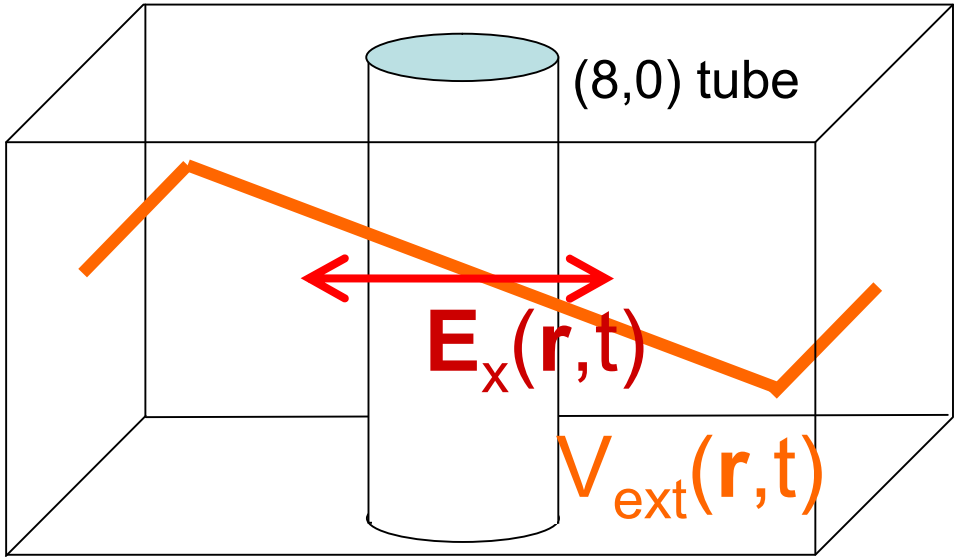
S. Uryu and T. Ando, PRB 74, 155411 (2006).

While excitons with cross-polarization are not strongly localized as those with parallel polarization.

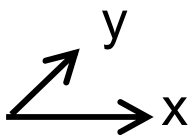
S. Kilina *et al.*, Adv. Funct. Mater, 17, 3405 (2007);
PNAS 105, 6797 (2008).



Free from adjustable parameters: *ab-inito* approach for response of nanotube against time-varying E-field



Periodic boundary conditions:
inter-wall 10 Å in x
6 Å in y



Combination with TDDFT and time-varying sawtooth-type external field

Plane-wave, TM-type pps. (Sugino-Miyamoto code)

O. Sugino, Y. Miyamoto PRB 59, 2579 (1999), 66, 089901(E) (2002).

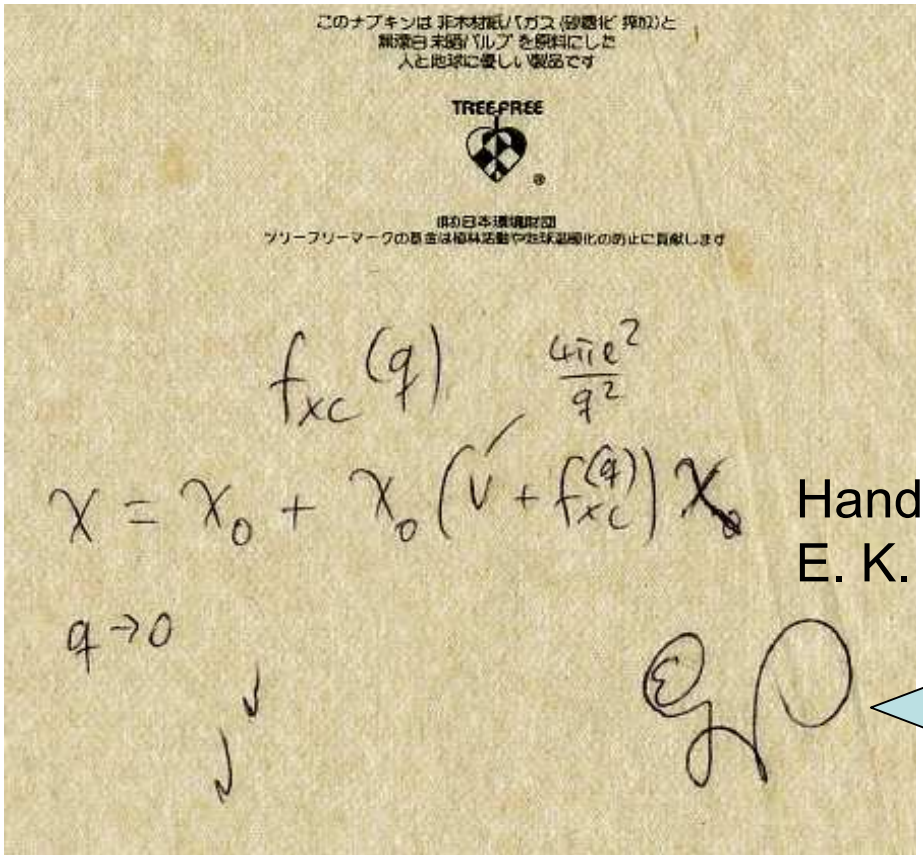
Checking energy conservation rule (Total Energy – Work)

Y. Miyamoto, H. Zhang, PRB 77, 165123 (2008)

Please let me remark

This approach does not correctly include excitonic effect.

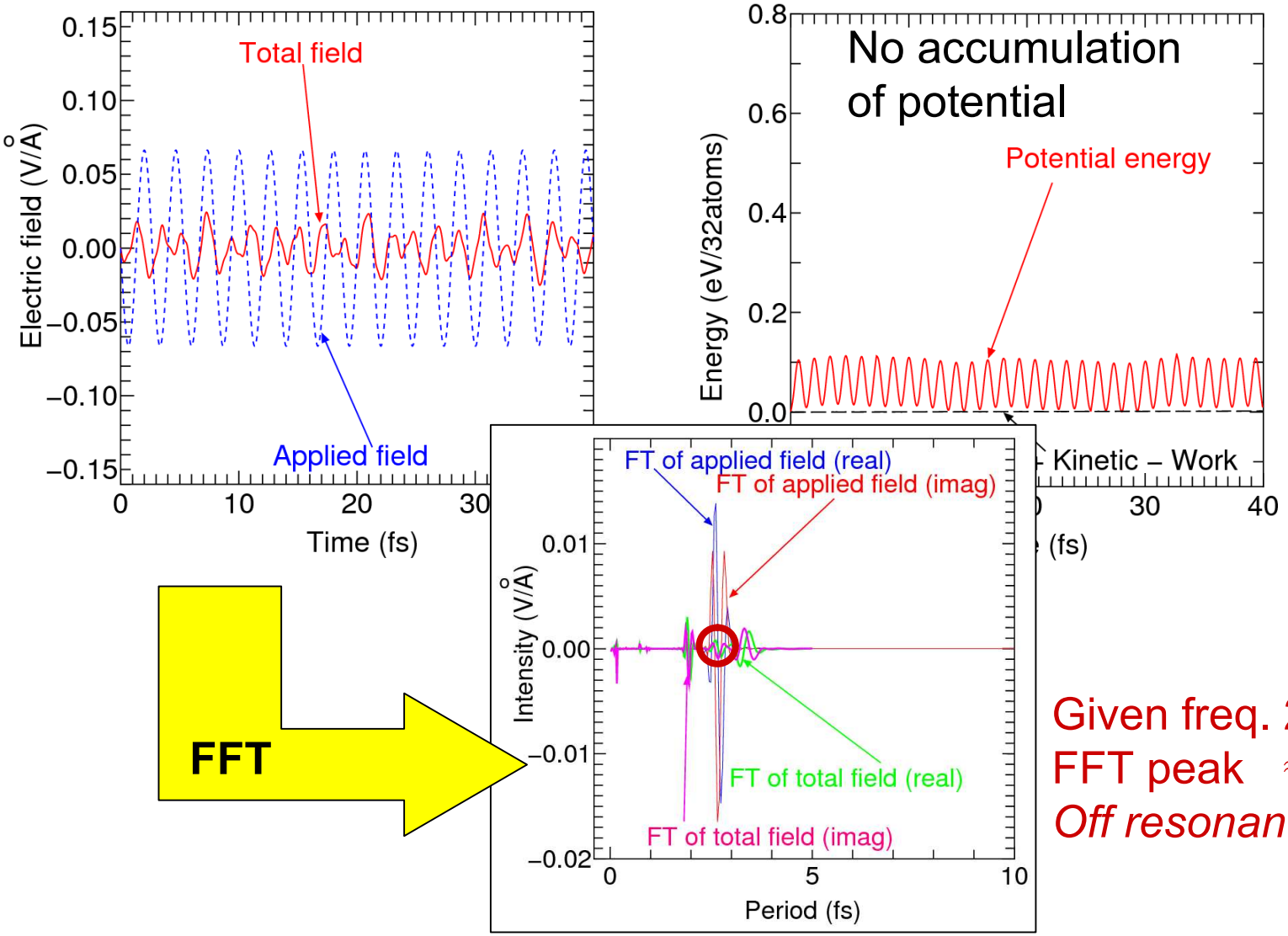
Should we still have strong depolarization?



Hand writing by
E. K. U. Gross

Result $E_{applied}$ vs. $E_{total}(=E_{applied} + E_{induced})$

800 nm light to (8.0) nanotube with cross-polarization



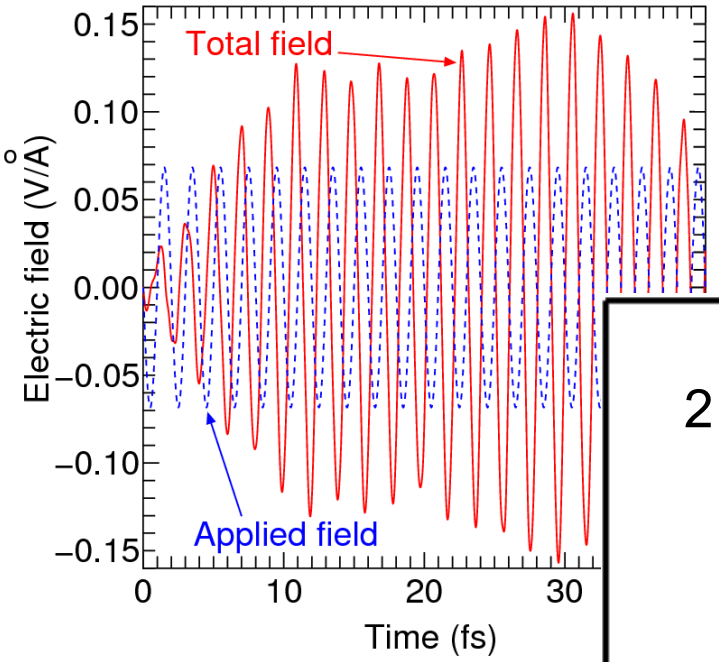
Given freq. 2.688 fs

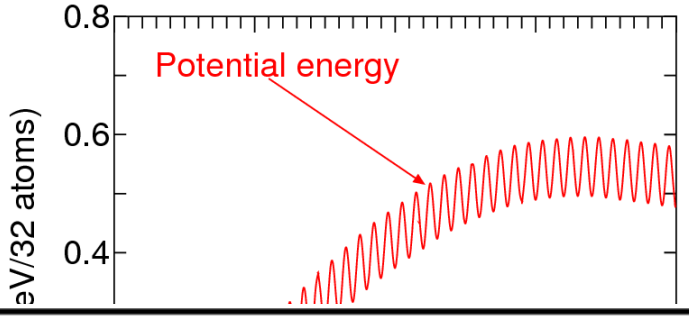
FFT peak ≈ 2 fs

Off resonance!

Result $E_{applied}$ vs. $E_{total}(=E_{applied} + E_{induced})$

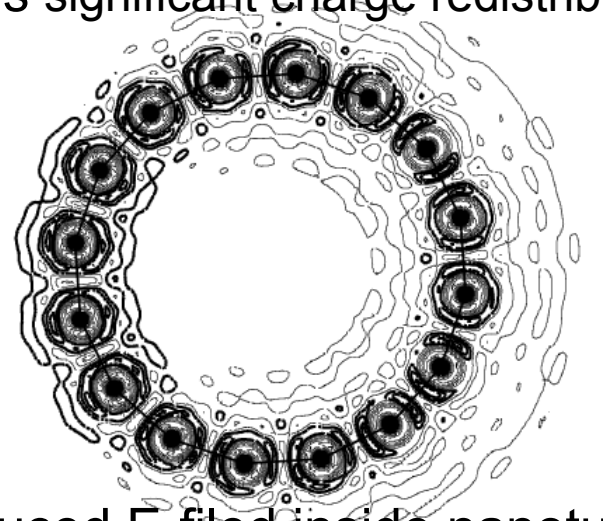
600 nm light to (8,0) nanotube with cross-polarization





Enhancement of E-field inside nanotube!

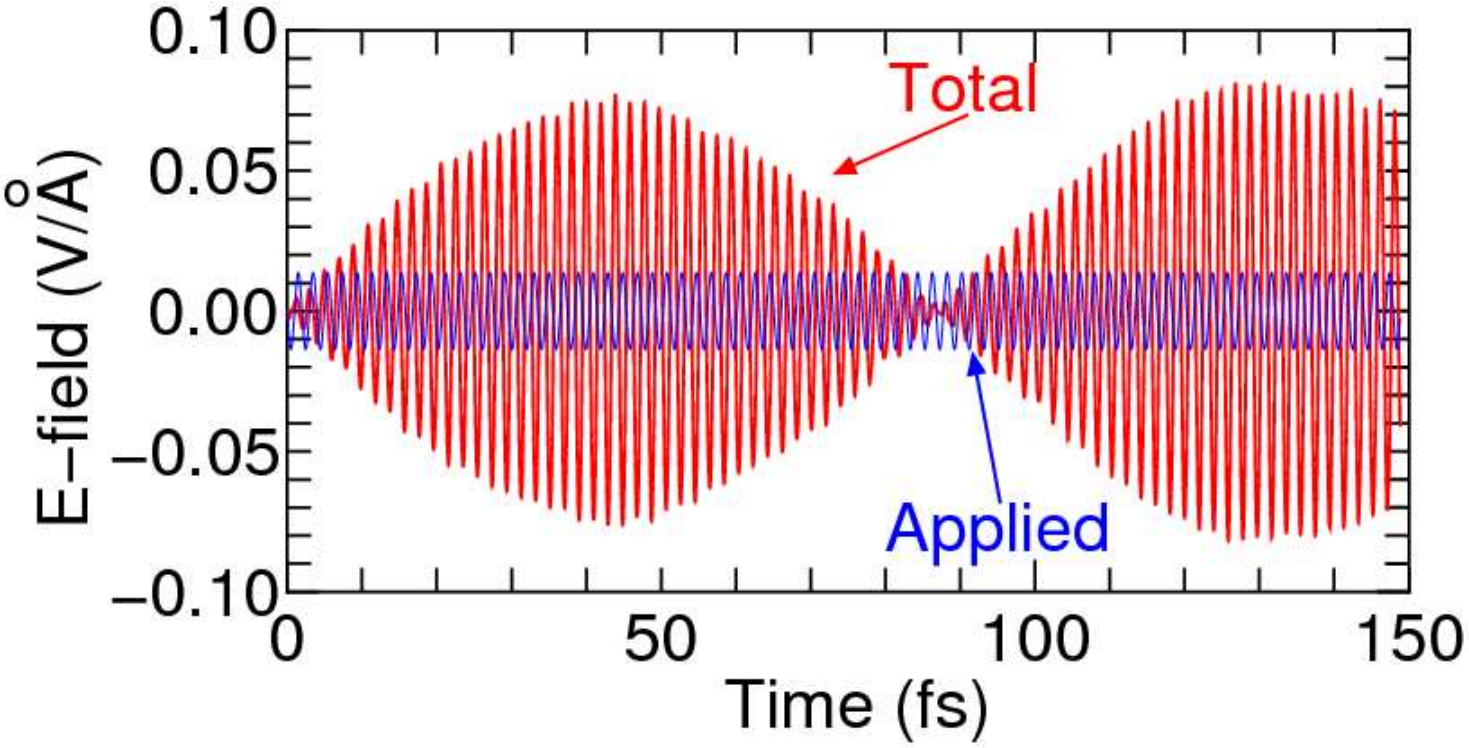
21.79 fs significant charge redistribution!



Induced E-filed inside nanotube exceeds applied E-field.

Further adjustment of frequency gives significant E-field enhancement!

Period = 1.952 fs =585nm=2.11 eV



The resonant energy 2.11 eV is similar to E_{21} energy of (8,0) tube.
(Cf. LDA gap is 1.75 eV.)

Please let me remark again

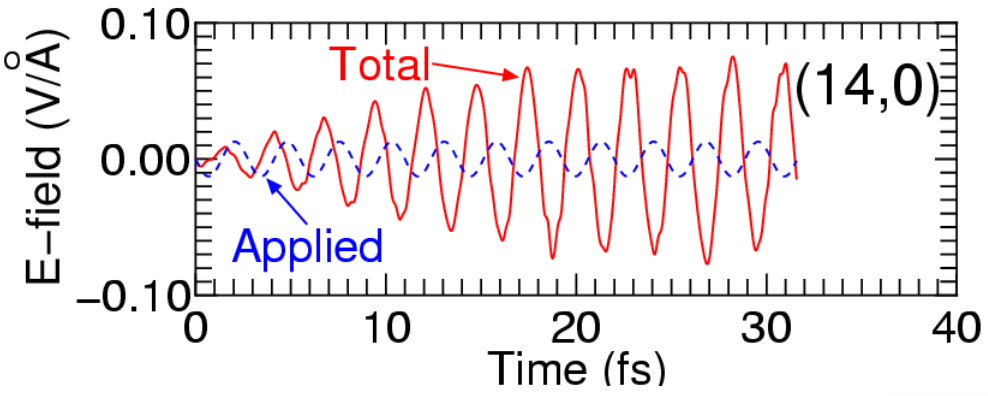
This approach does not correctly include excitonic effect.

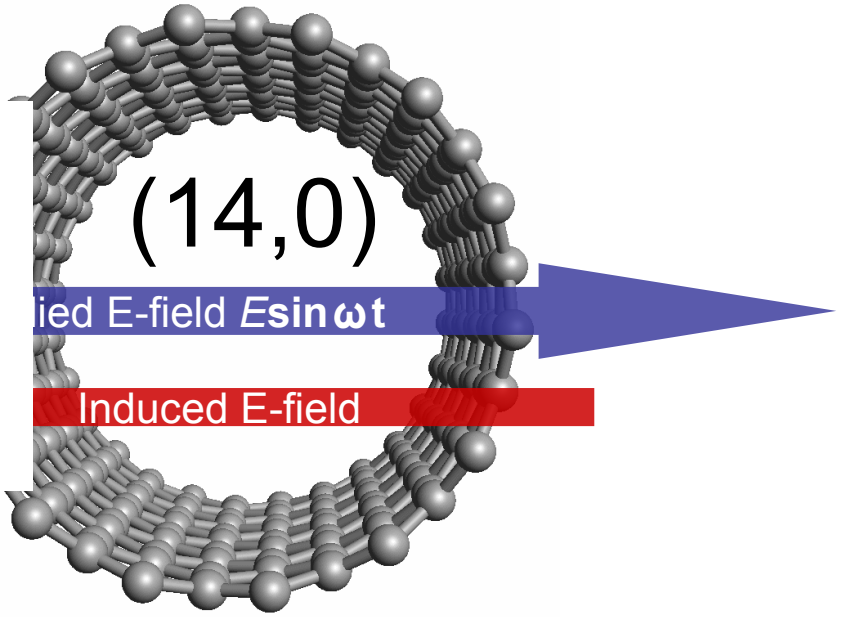
Should we still have strong depolarization?

No!

Instead, E-filed enhancement occurs in resonance!

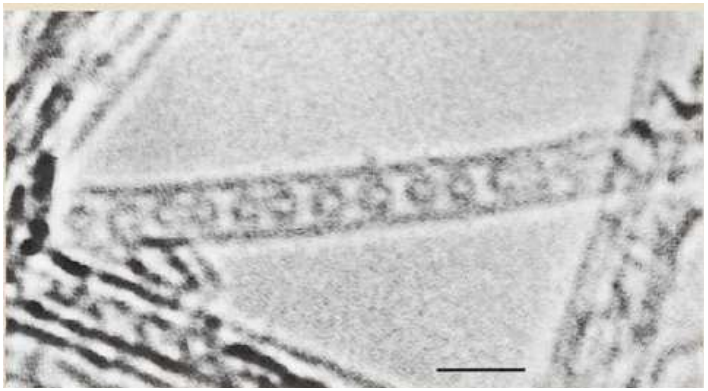
The diameter of (8,0) nanotube is only 6.8 Å, what about bigger diameter tube?





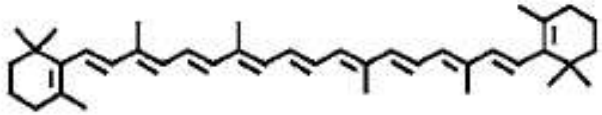
H. Zhang, YM, APL95, 053109 (2009).

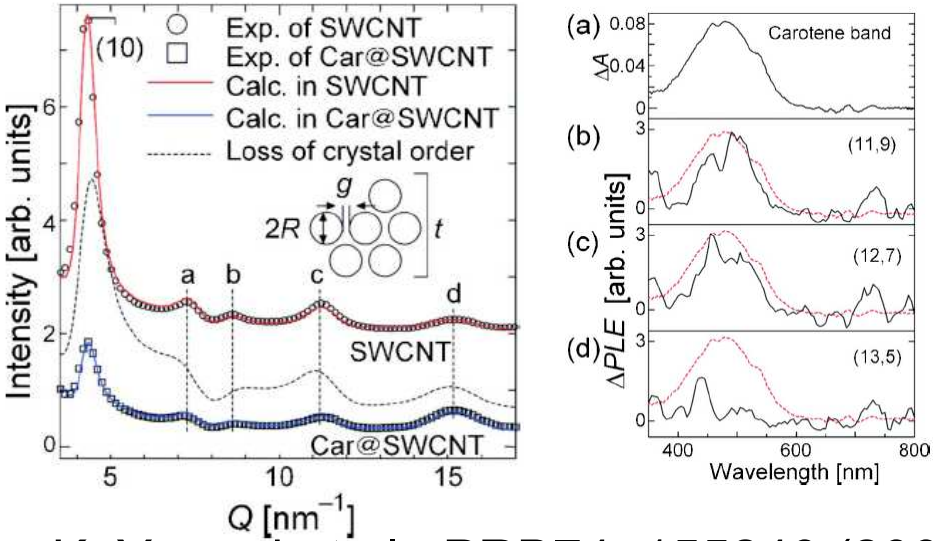
Application of E-field enhancement



B. W. Smith, M. Monthloux, and D. E. Luzzi Nature 396, 323 (1998)

β-carotene inside nanotube





K. Yanagi et al., PRB74, 155240 (2006)

Q: Can we shed light on molecules@CNT stronger?
A: Maybe yes with frequency of light of resonances.

sumarries

1. Time-dependent density functional approach as a practical tool for electron-ion dynamics under time-varying field
2. Energy conservation rule
3. Applications *(exfoliation of mono-graphene sheet from graphite: E-field enhancement inside CNT.)*