Time-Dependent Density Functional Theory in Condensed Matter Physics

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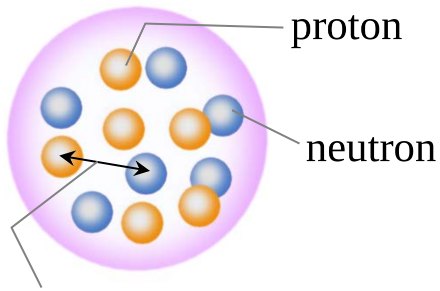
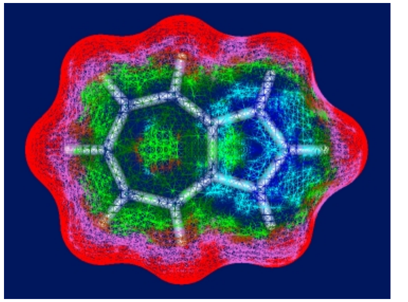
S.A. Sato	Univ. Tsukuba





	Nuclei Nucleon many-body system	Atoms, Molecules, Solids Electron many-body systems
Size	10^{-15}m	10^{-10}m
Energy	1MeV	1eV
Time	10^{-23}s	10^{-17}s
Mass	10^{9}eV	$5x10^{5}$eV
Interaction	Nuclear force (Strong interaction)	Coulomb force
Statistics	Fermion	Fermion

Time-Dependent Density Functional Theory

Successful for quantitative description of many-fermion dynamics

Nuclei (nucleon dynamics)	Atoms, Molecules, Solids (electron dynamics)

Linear response regime

- Giant resonances ((Q)RPA)	- Electronic excitaitons in molecules - Optical response of molecules and solids

Nonlinear regime, Initial value problem

- Heavy ion collision	- Laser science (Intense and ultra-short laser pulse)

We are developing real-time TDDFT computational method.

We pioneered the method, combining nuclear method developed in TDHF calculation with first-principles density functional Hamiltonian in condensed matter physics.

K. Yabana, G.F. Bertsch, Phys. Rev. B54, 4484 (1996).

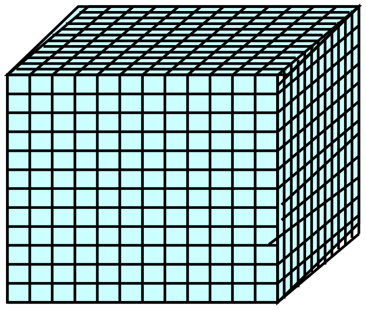
$$\left\{ -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \sum_a V_{ion}(\vec{r}-\vec{R}_a) + e^2 \int d\vec{r}\,' \frac{n(\vec{r}\,',t)}{|\vec{r}-\vec{r}\,'|} + \mu_{xc}(n(\vec{r},t)) + V_{ext}(\vec{r},t) \right\} \psi_i(\vec{r},t) = i\hbar \frac{\partial}{\partial t}\psi_i(\vec{r},t)$$

Hamiltonian for electrons
in First-principles DFT

$$n(\vec{r},t) = \sum_i |\psi_i(\vec{r},t)|^2$$

- High-order finite difference approximation for differential operators
- Taylor expansion method for time evolution

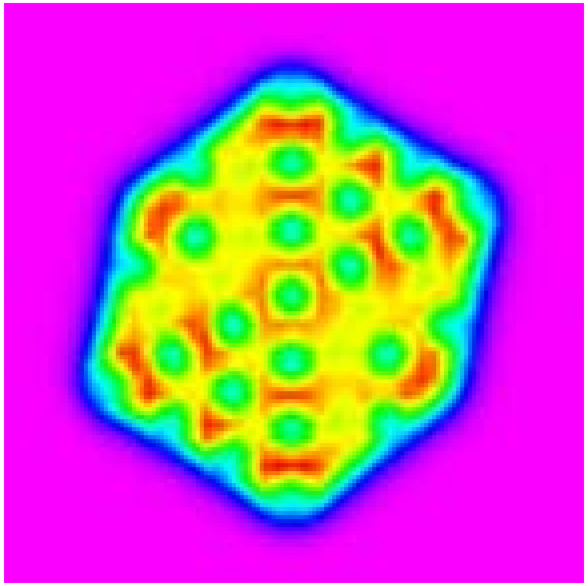
$$\psi_m(x_i, y_j, z_k, t_l)$$



Electron dynamics in metallic clusters by TDDFT

K. Yabana, G.F. Bertsch, Phys. Rev. B54, 4484 (1996).

Na_{147}^{+}



Assume
Icosahedral shape

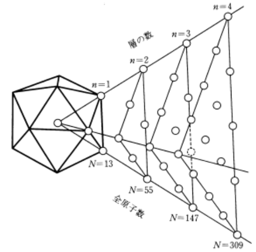
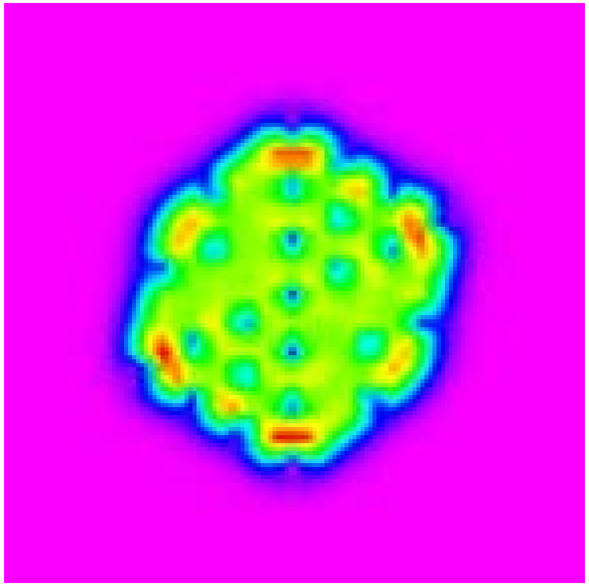
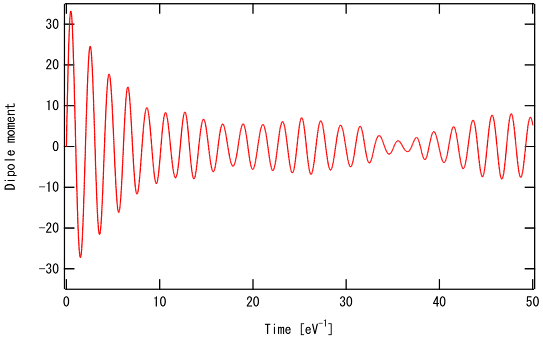


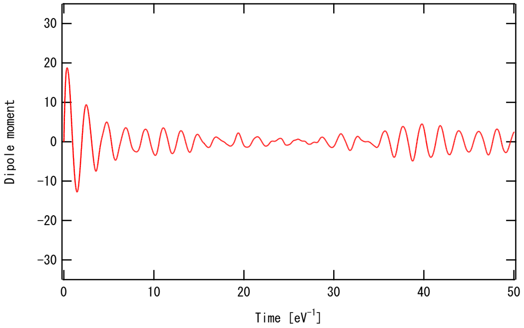
図 5・61　多層正二十面体構造(MIC)の概念図[104)]
n は MIC の層の数であり，N は全原子数である。1 層構造($n=1$)では原子数 $N=13$ に対応し，2 層構造($n=2$)では $N=55$，3 層構造($n=3$)では $N=147$…となる。

Li_{147}^{+}



Density change induced by impulsive force

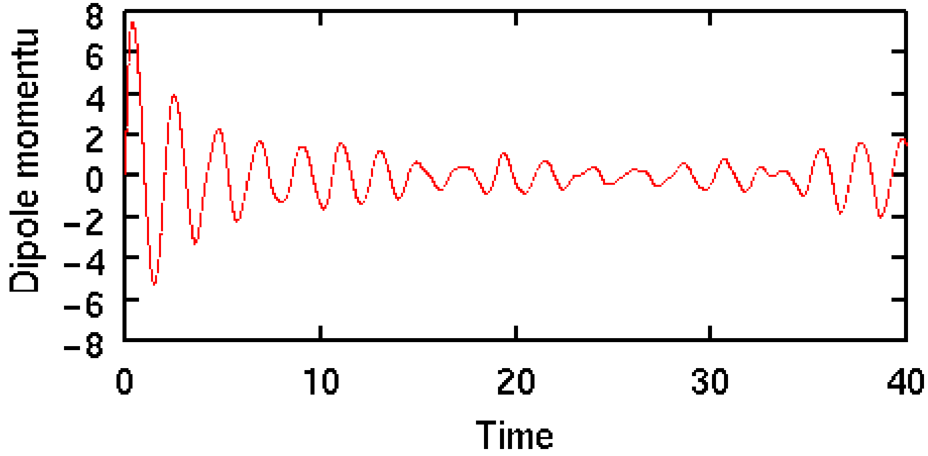




Dipole moment as function of time

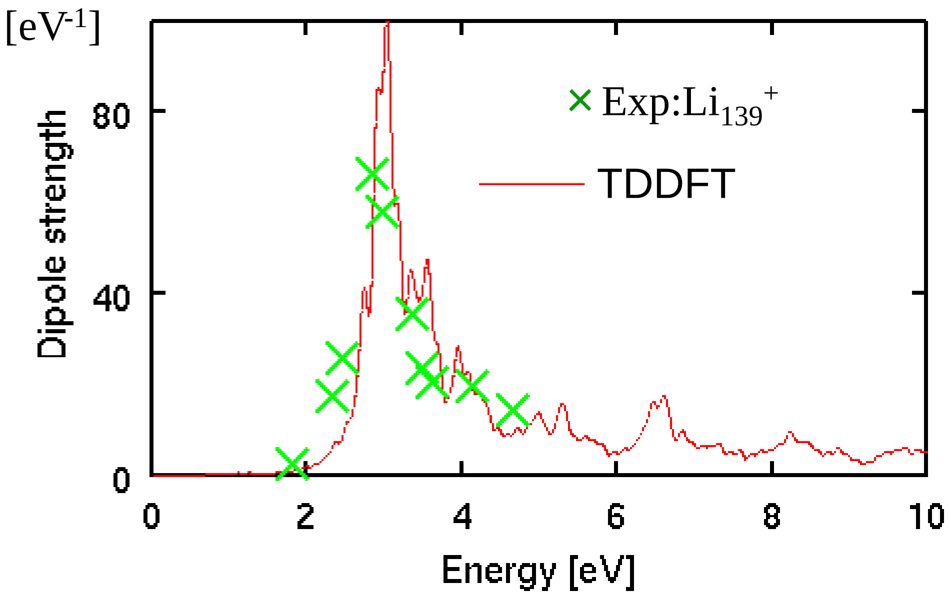
Real-time calculation for optical absorption spectrum of Li_{147}^{+}

K. Yabana, G.F. Bertsch, Phys. Rev. B54, 4484 (1996).



Real-time calculation
for autocorrelation function

$$\langle \hat{z}(t)\hat{z}(0)\rangle$$



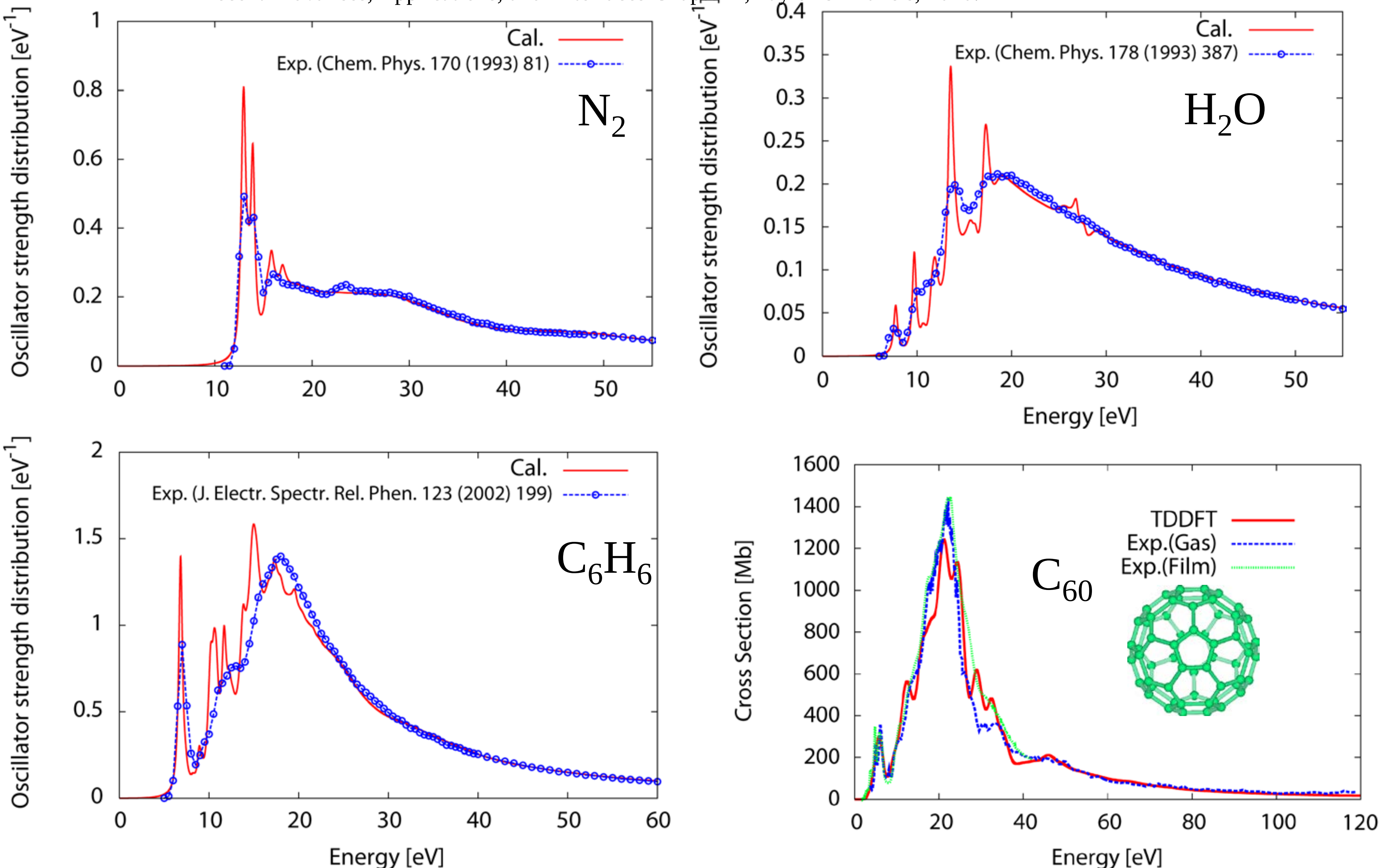
Fourier transformation
→ oscillator strength distribution

$$\sigma(\omega) \propto \frac{1}{k}\int dt\, e^{i\omega t}\langle \hat{z}(t)\hat{z}(0)\rangle$$

Photoabsorption of molecules by TDDFT (LB94 functional)

"Continuum RPA calculation for deformed system"

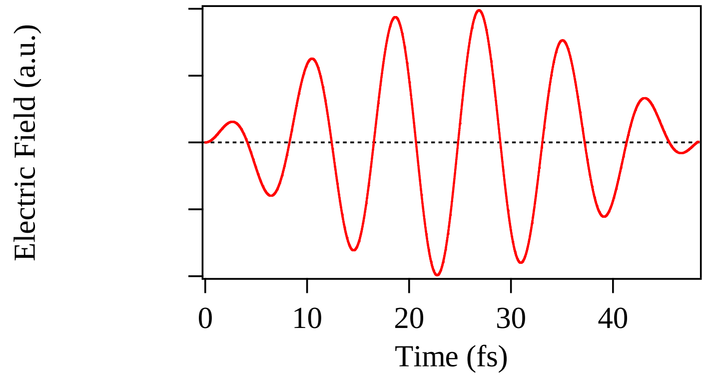
K. Yabana, Y. Kawashita, T. Nakatsukasa, J.-I. Iwata, Charged Particle and Photon Interactions with Matter: Recent Advances, Applications, and Interfaces Chapter 4, Taylor & Francis, 2010.

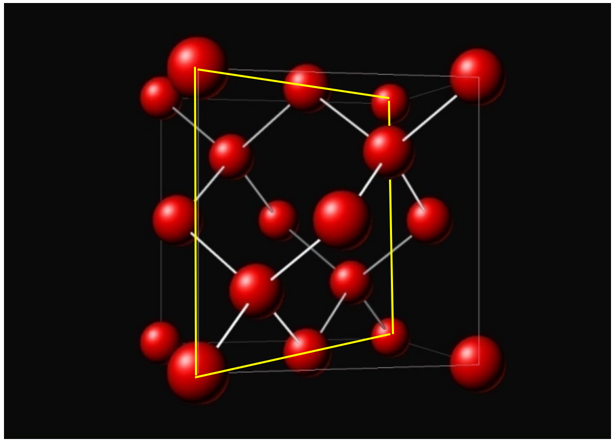


Electron dynamics in bulk Si under strong laser pulse

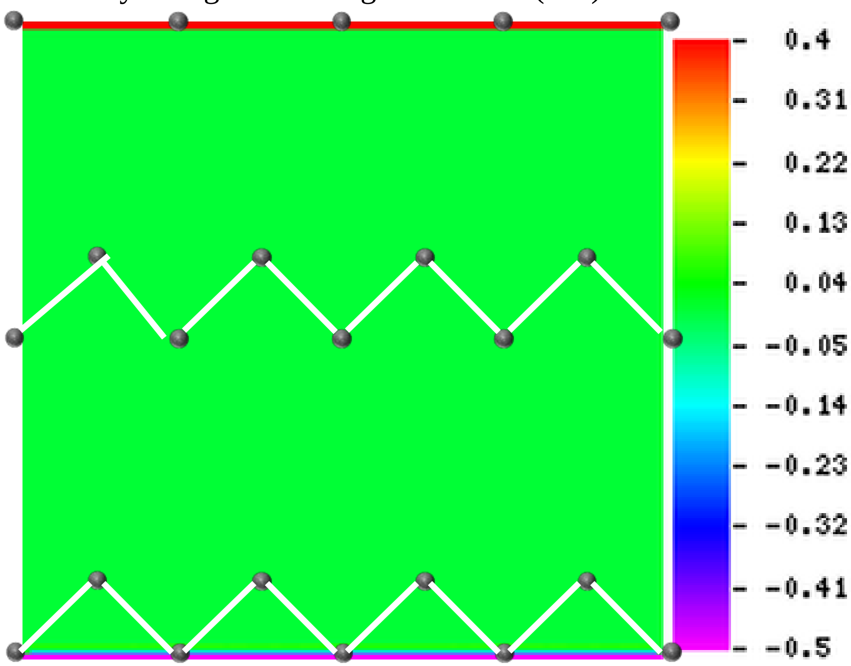
I= 3.5×10^{14} W/cm^2, T=50 fs, $\hbar\omega$=0.5 eV

Laser photon energy is much lower than direct bandgap.

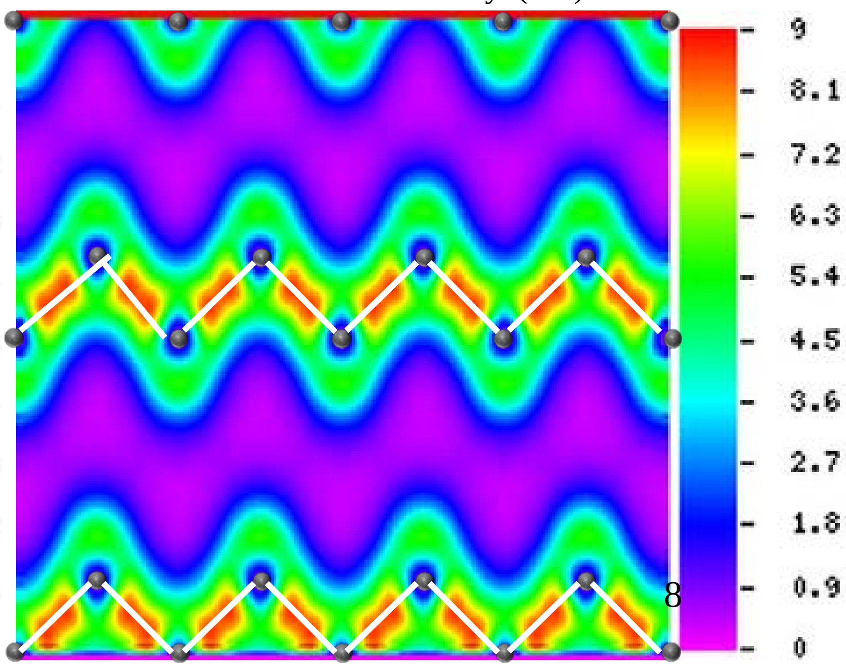




Density change from the ground state (110)



Ground state density (110)



Red +

Green 0

Blue -

Time-dependent extension of Bloch's band theory

$$i\hbar \frac{\partial}{\partial t} u_{n\vec{k}}(\vec{r},t) = \left[\frac{1}{2m}\left(\vec{p} + \vec{k} + \frac{e}{c}\vec{A}(t) \right)^2 + \int d\vec{r}\,' \frac{e^2}{|\vec{r}-\vec{r}\,'|} n(\vec{r}\,',t) + \mu_{xc}[n(\vec{r},t)] \right] u_{n\vec{k}}(\vec{r},t)$$

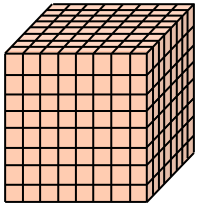
$$n(\vec{r},t) = \sum_{nk} \left| u_{n\vec{k}}(\vec{r},t) \right|^2$$

$$u_{nk}(\vec{r}+\vec{a},t) = u_{nk}(\vec{r},t)$$

Electron dynamics in crystalline solid (atomic positions are fixed)

Computational aspects

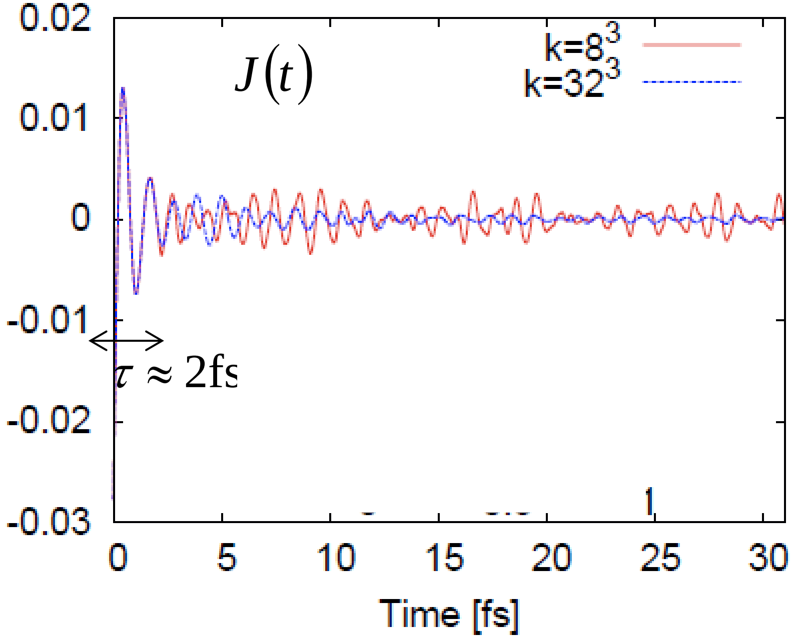
- 3D uniform gird for space, high-order finite difference for differentiation
- Taylor expansion for time evolution

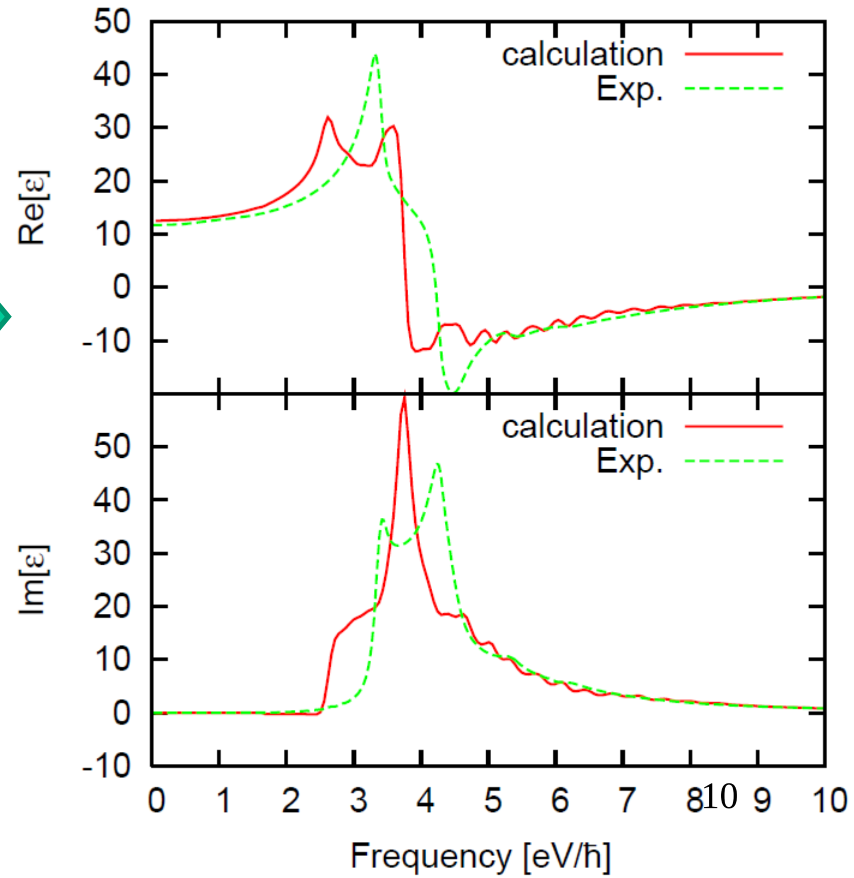


Dielectric function of Si from real-time TDDFT-ALDA

Instantaneous kick at t=0, then calculate current *J(t)*

$$\sigma(\omega)=\frac{1}{k}\int dt\, e^{i\omega t} J(t), \quad \varepsilon(\omega)=1+\frac{4\pi i\sigma(\omega)}{\omega}$$





Not very good in quality, however.

Frontiers of Laser Science

- Nonlinear electron dynamics induced by strong laser pulse
- Ultrafast electron dynamics – femto to attosecon -

Frontiers of Optical Sciences: Intense laser pulse on solid

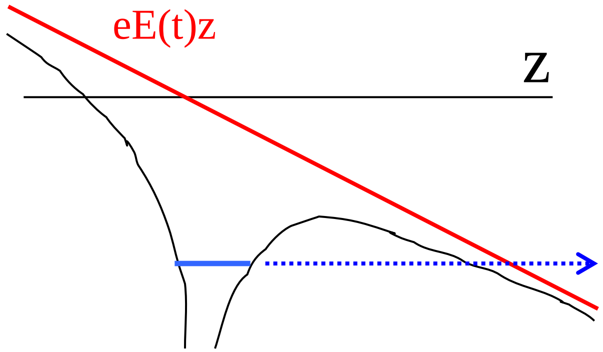
Laser intensity

$10^{13} - 10^{15}\,\mathrm{W/cm^2}$ $10^{22}\,\mathrm{W/cm^2}$

Nonlinear optics	Coherent phonon	HHG	Electron-hole plasma Optical breakdown Laser machining	Laser acceleration	Vacuum breakdown

Nonrelativistic
Quamtum mechanics

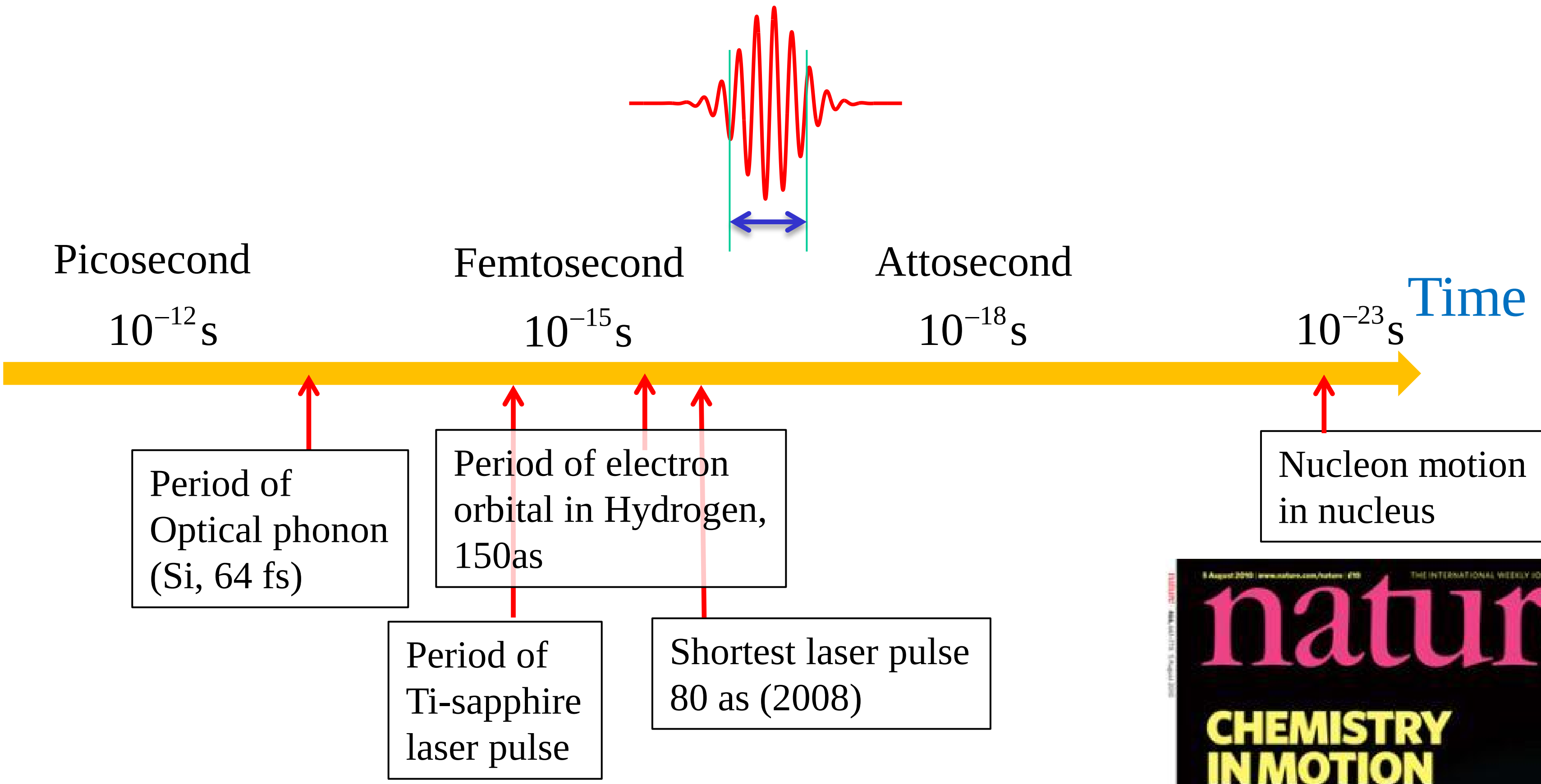
Relativistic
Classical mechanics

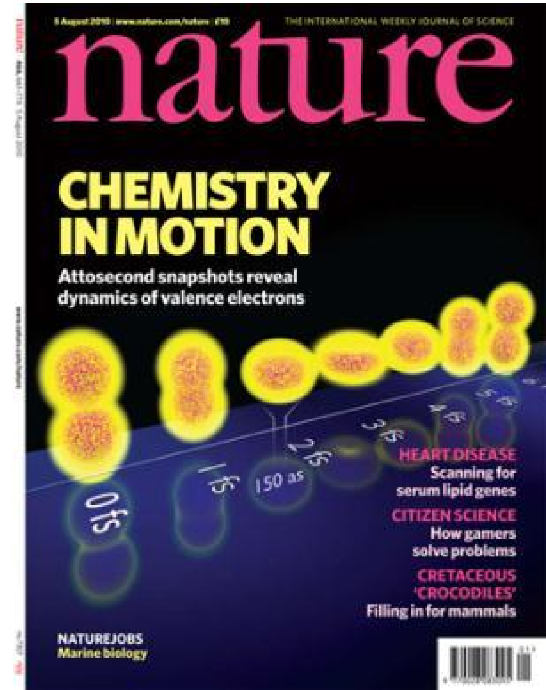


External electric field by laser pulse

≈ Internal electric field by nuclei

Frontiers in Optical Sciences: Ultra-short dynamics

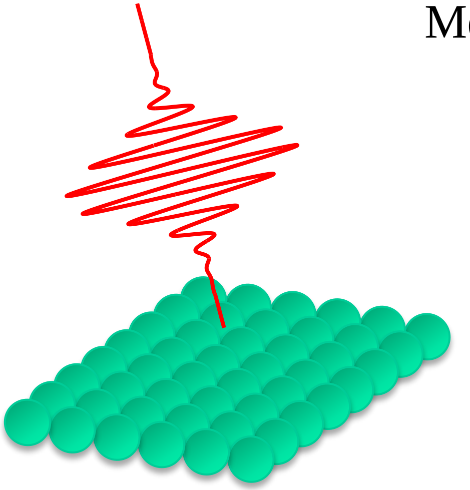




Real-time observation of valence electron motion

E. Goulielmakis et.al, Nature 466, 739 (2010).

Nonthermal Laser Machinery



Melting, ablation, filamentation on bulk surface

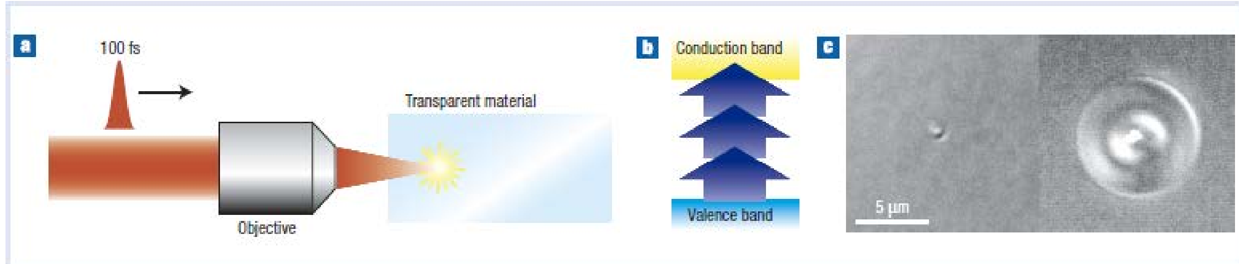
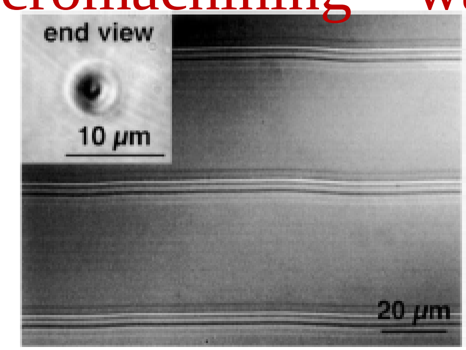


Figure B1 Femtosecond laser micromaching process. **a**, Schematic of the laser incident on a transparent material. **b**, Diagram of the excitation of electrons to the conduction band. **c**, Microscope images showing the large variation in the feature characteristics depending on the experimental conditions. Left: single 10-nJ pulse and right: 25,000 5-nJ pulses at a frequency of 25 MHz (both with the same focal spot).

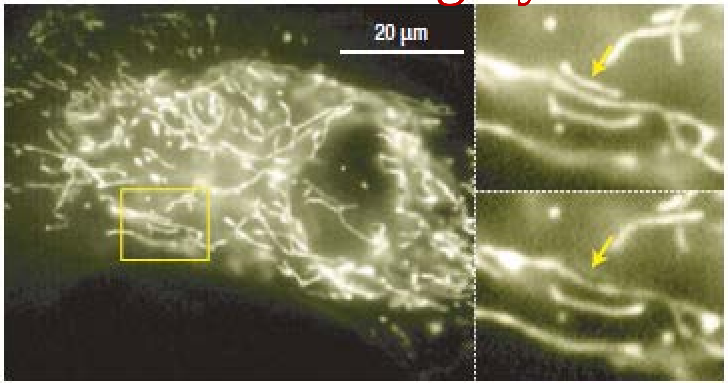
R.R. Gattass, E. Mazur, Nature Photonics 2, 220 (2008).

Micromachining – waveguide-



Optical microscope image of waveguides written inside bulk glass by a 25-MHz train of 5-nJ sub-100-fs pulses, C.B. Schaffer et.al, OPTICS LETTERS 26, 93 (2001)

Nanosurgery



Ablation of a single mitochondrion in a living cell.
N. Shen et.al, Mech. Chem. Biosystems, 2, 17 (2005).

Question: How to describe strong laser pulse propagation in solids?

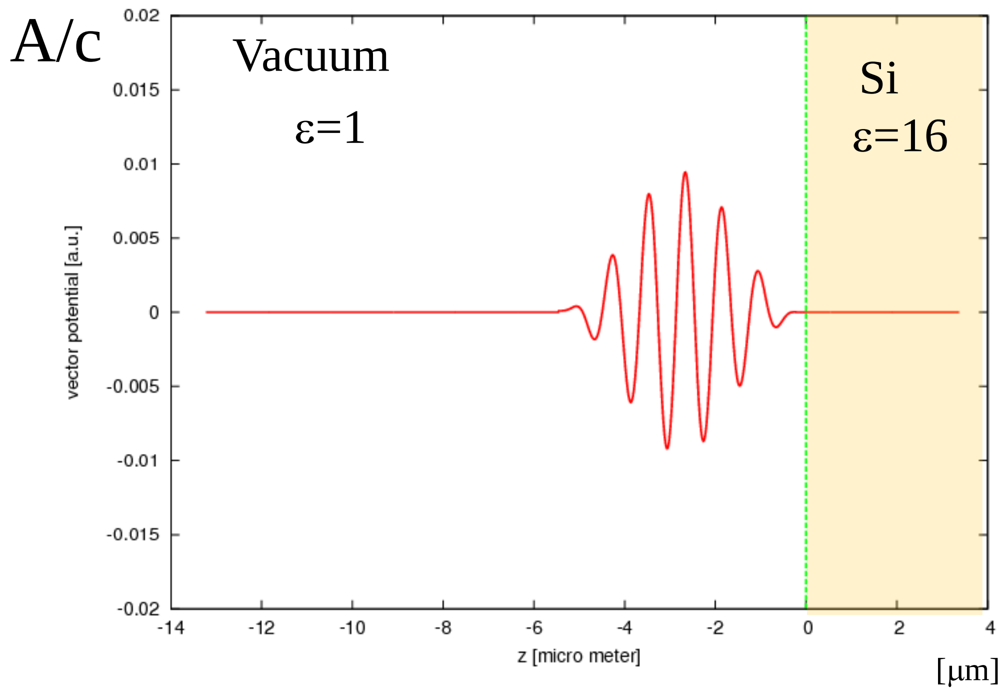
Assume constant dielectric function

$\lambda = 800\text{nm},$

$\hbar\omega = 1.55\text{eV}$ (below direct band gap)

Macroscopic Maxwell eq.

$$\frac{\varepsilon(z)}{c^2}\frac{\partial^2}{\partial t^2}A(z,t) - \frac{\partial^2}{\partial z^2}A(z,t) = 0$$



Weak field

Described solely by dielectric function (linear response)

Extremely strong field

Microscopically, nonlinear electron dynamics inside solid.

Macroscopically, electromagnetism need modification. How?

Question: How to describe strong laser pulse propagation in solids?

Our answer

It is necessary to combine electromagnetism and quantum mechanics by large scale computing

Real-time TDDFT for microscopic electron dynamics

+

Macroscopic Maxwell equation

Perturbation theory separates
macroscopic electromagnetism (EM) and quantum mechanics (QM)
through "Constitutive Relation".

$$D_\alpha(\vec{r},t) = E_\alpha(\vec{r},t) + 4\pi P_\alpha(\vec{r},t) = \int^t dt' \varepsilon_{\alpha\beta}(t-t') E_\beta(\vec{r},t')$$

Electromagnetism:
Maxwell equation for macroscopic fields,
E, D, B, H

Linear constitutive relation

$$D = D[E] = \varepsilon(\omega) E$$

Quantum Mechanics:
Perturbation theory to calculate linear susceptibilities,
$\varepsilon(\omega)$

As the field strength becomes large,
"nonlinear optics" becomes important.

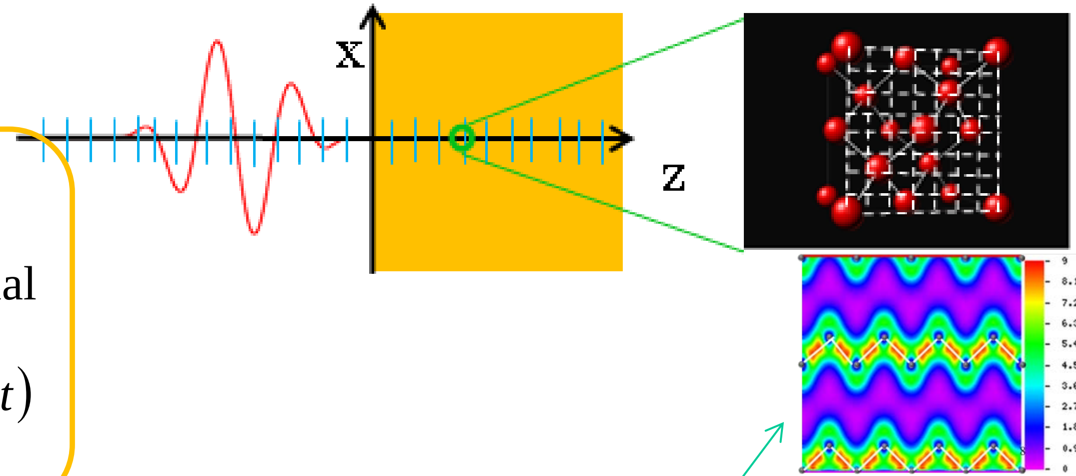
$$D_\alpha(\vec{r},t) = \int^t dt' \varepsilon_{\alpha\beta}(t-t') E_\beta(\vec{r},t') + 4\pi \int^t dt' \int^t dt'' \chi_{\alpha\beta\gamma}^{(2)}(t-t', t-t'') E_\beta(\vec{r},t') E_\gamma(\vec{r},t'') + \cdots$$

At extreme intense limit, EM and QM no more separate.

Multiscale simulation

K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe, G.F. Bertsch, Phys. Rev. B85, 045134 (2012).

At each macroscopic grid point,
We consider a unit cell and prepare microscopic grid.



Macroscopic grid points (μm)
to describe macroscopic vector potential

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}A(Z,t)-\frac{\partial^2}{\partial Z^2}A(Z,t)=\frac{4\pi}{c}J(Z,t)$$

$J(Z,t)$

Exchange of information by macroscopic current and macroscopic vector potential.

$A(Z,t)$

$$J(Z,t)=\int_\Omega d\vec{r}\,\vec{j}_{e,Z}$$

$$\vec{j}_{e,Z}=\frac{\hbar}{2mi}\sum_i\left(\psi^*_{i,Z}\vec{\nabla}\psi_{i,Z}-\psi_{i,Z}\vec{\nabla}\psi^*_{i,Z}\right)-\frac{e}{4\pi c}n_{e,Z}\vec{A}$$

At each macroscopic points, Kohn-Sham orbitals $\psi_{i,Z}$ are prepared, and described in microscopic grids.

$$i\hbar\frac{\partial}{\partial t}\psi_{i,Z}=\frac{1}{2m}\left(-i\hbar\vec{\nabla}+\frac{e}{c}\vec{A}\right)^2\psi_{i,Z}-e\phi_Z\psi_{i,Z}+\frac{\delta E_{xc}}{\delta n}\psi_{i,Z}$$

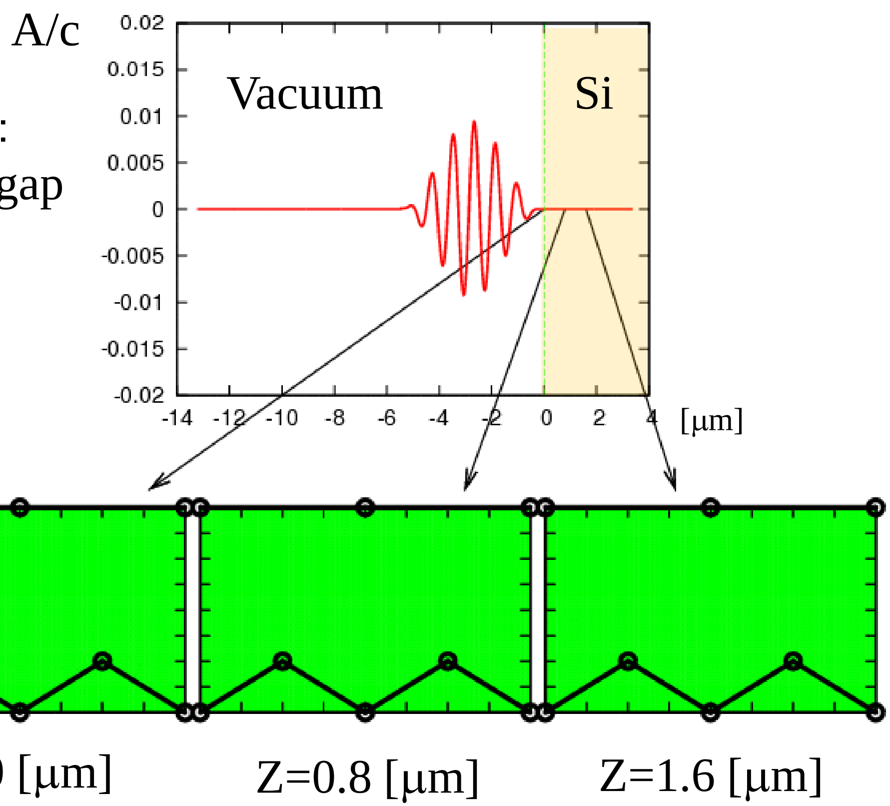
$$\vec{\nabla}^2\phi_Z=-4\pi\left\{en_{ion}-en_{e,Z}\right\}$$

Propagation of weak pulse

Ordinary electromagnetism is OK.

$I=10^{10}W/cm^2$

Laser frequency : 1.55eV :
lower than direct bandgap
2.4eV(LDA)

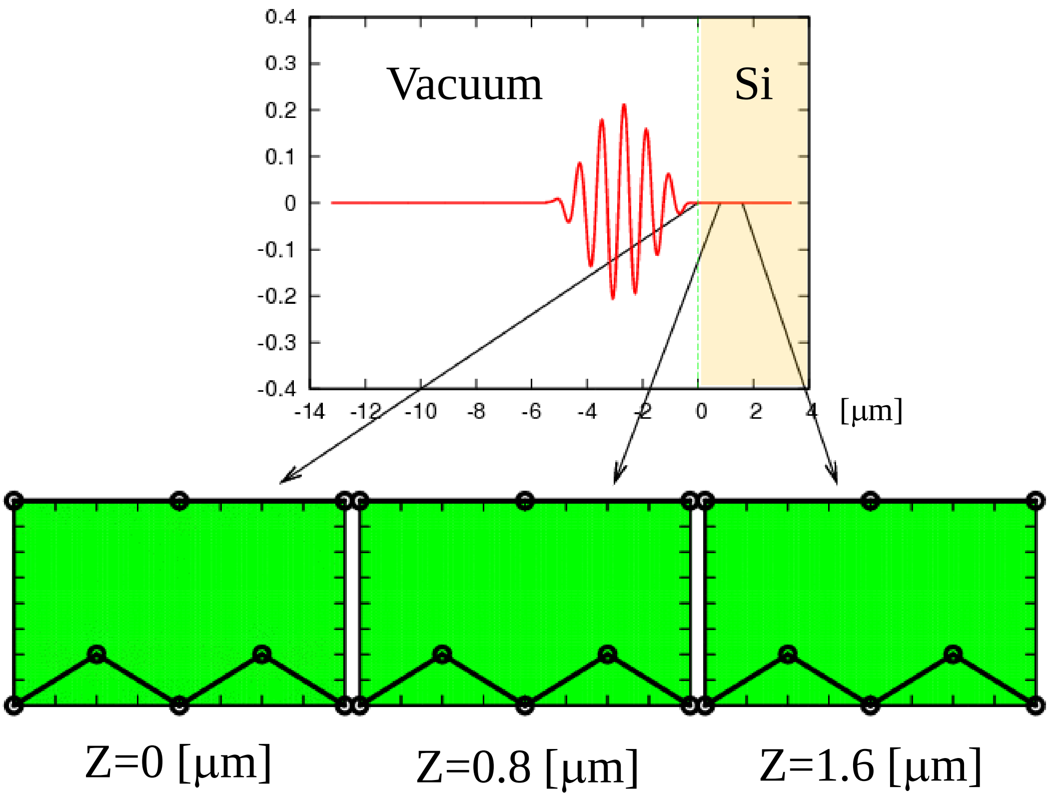


Coupled Maxwell + TDDFT simulation

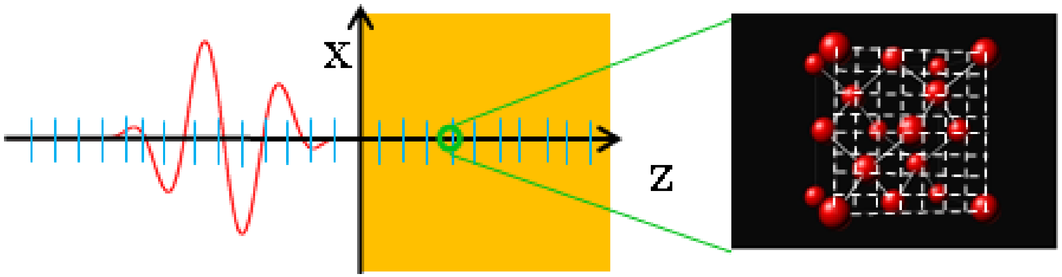
More intense laser pulse

Dynamics of electrons and macroscopic EM fields are no more separable.

$I = 5 \times 10^{12} W/cm^2$



Computationally challenging multiscale simulation



At present, 1-dim propagation (macroscopic grid)

Si, diamond:

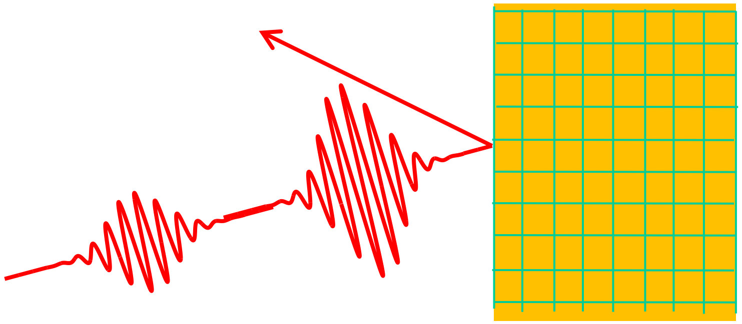
1,000 cores, 10 hours

20,000 cores, 20 min (K-computer, Kobe)

SiO_2 (α-quartz)

30,000 cores, 2 hours

Oblique incidence, 2-dim



×50

3-dim

- Self focusing
- Circular polarization

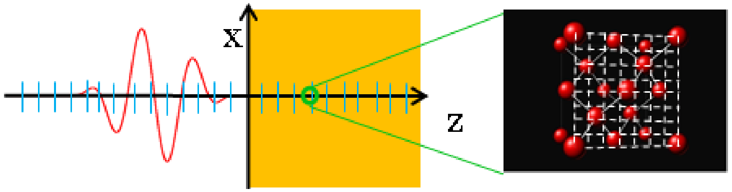
A million of macro-grid points

×1,000

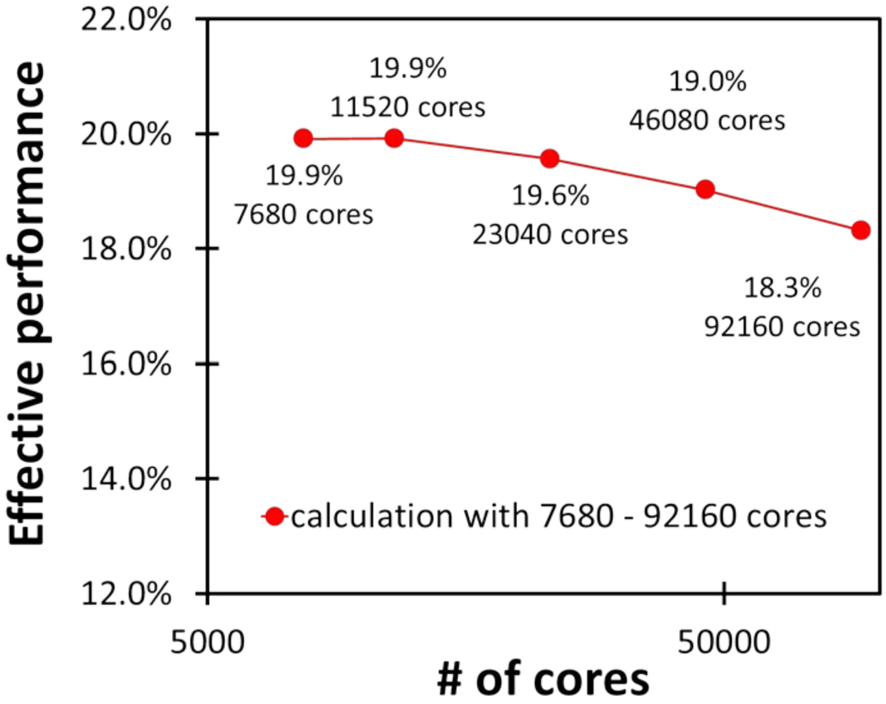
need to wait next generation supercomputers

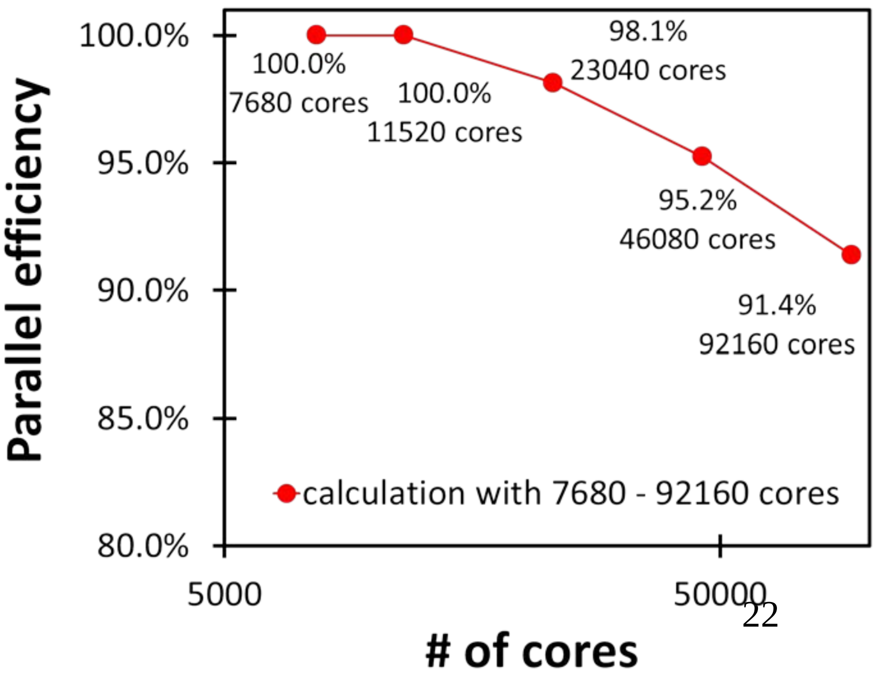
Computationally scalable simulation

1,000 cores, 10 hours
30,000 cores, 20 min (K-computer, Kobe)



Performance at K-Computer in Kobe (in early access)





We are granted 4M node-hours at K-computer for 2014 year.

Conclusion

TDDFT is a useful universal theory for many-Fermion dynamics.

	Nuclear Physics	Atoms, Molecules, Solids
Lineaar response	Giant resonances	Photoabsorption, Dielectric function
Initial value problem	Heavy ion collisions	Strong laser sciences

Interaction of strong laser pulse and solids require connection of two basic physics:
Macroscopic electromagnetism and quantum mechanics

We have developed a new multiscale simulation, Maxwell + TDDFT scheme, which runs only at the largest supercomputers available today.