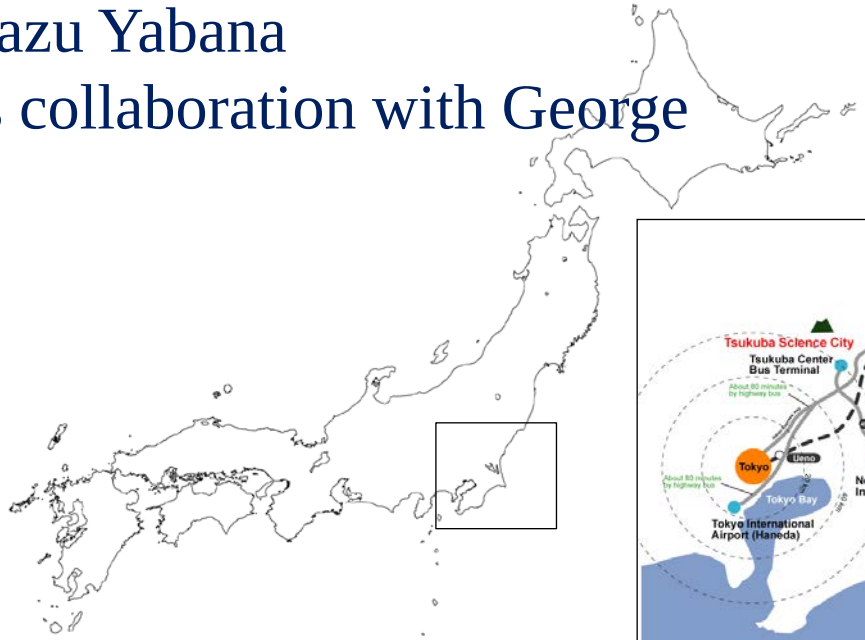
BERTSCHFEST
UW, Seattle
Sept. 7-9, 2012

Time-Dependent Density Functional Theory for Electron Dynamics

Kazu Yabana
based on 20 years collaboration with George



1991, I started to work with George when I visited MSU supported by Nishina fellowshop

Before my visit, George suggested me 3 possible subjects to work with him,

(1) ultrarelativistic collisions and the quark-gluon plasma,
(2) dynamics of large-amplitude shape changes in nuclei, and
(3) alkali metal clusters and C_{60}.

I chose #3 subject,
"alkali metal clusters and C_{60}"

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East Lansing, MI 48824-1321 USA

April 2, 1991

Dr. Kazuhiro Yabana
Department of Physics
Niigata University
Ikarashi 2
Niigata 950-21
Japan

Dear Dr. Yabana:

I am very pleased that you will join our group starting in October. I am sure you will find it stimulating to work here, and it is quite likely that we could find funds to support an extension of your stay after the first year.

subjects as well. I am always looking for open questions that are amenable to theoretical methods at our disposal.

It is probably wise to reserve University housing for you to live in. I believe my secretary, Shari Conroy, sent you housing information, which you should return at your earliest convenience as they fill these units in the order they receive requests.

Don't hesitate to ask me if there is something I can do to facilitate your stay.

Sincerely,

George F. Bertsch

George F. Bertsch
Professor of Physics

GFB/sbc
bertsch@MSUNSCL = e-mail

MSU is an Affirmative Action/Equal Opportunity Institution

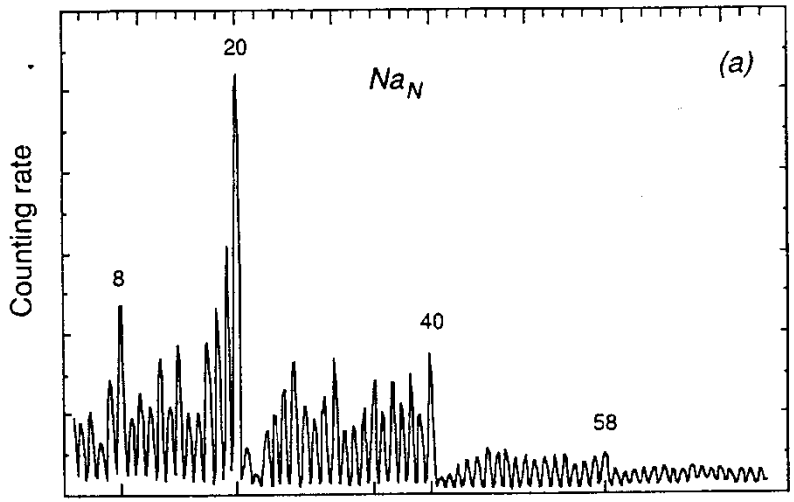
1991-
From Nuclear Physics to Atomic Clusters

Metal clusters show properties similar to atomic nucleus as many-fermion systems.

Magic number of Na cluster
Knight et.al.(1984)

Metal cluster： 2,8,20,40,58,92,138、...

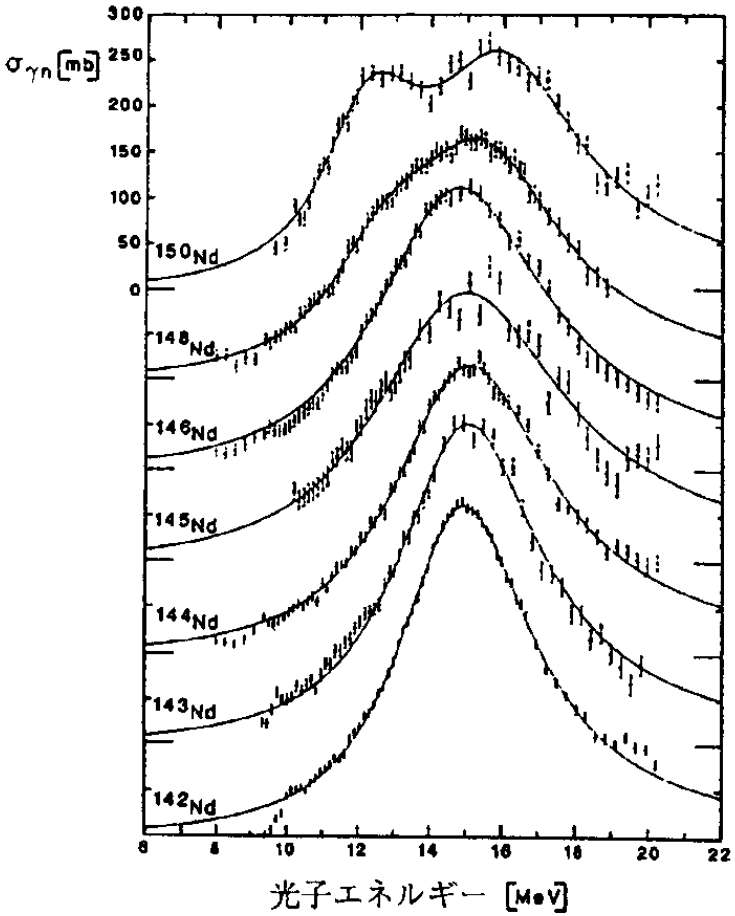
Atomic nucleus: 2,8,20,28,50,82,126、...

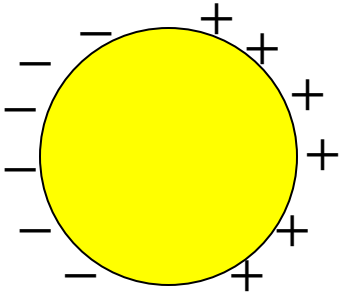


# of Na atoms

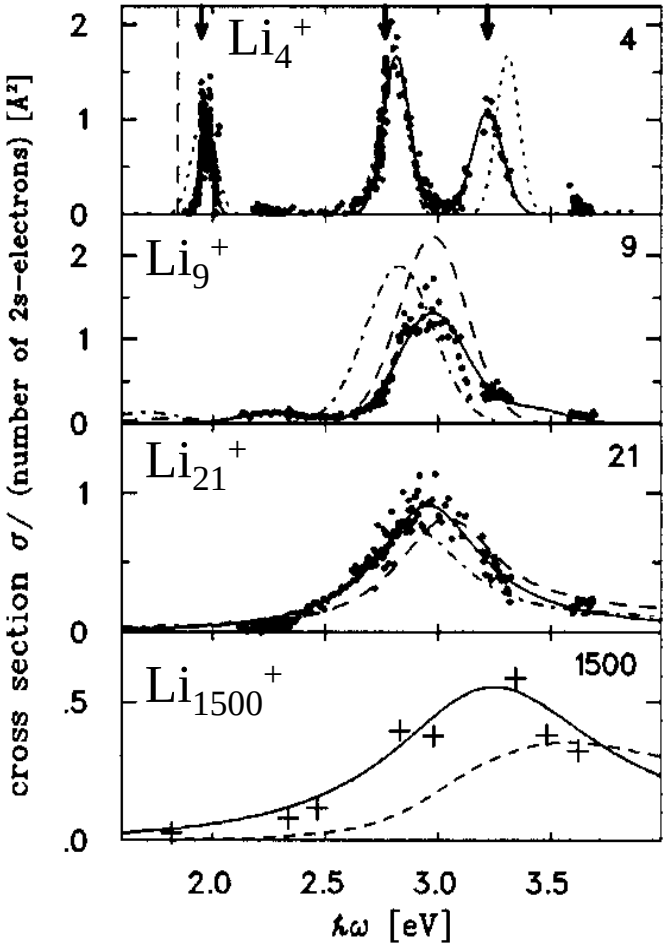
Giant Dipole Resonance

Atomic Nuclei





Metallic Clusters



How to describe many-electron dynamics in atomic clusters?

Combine nuclear TDHF method
with
Density functional calculation 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

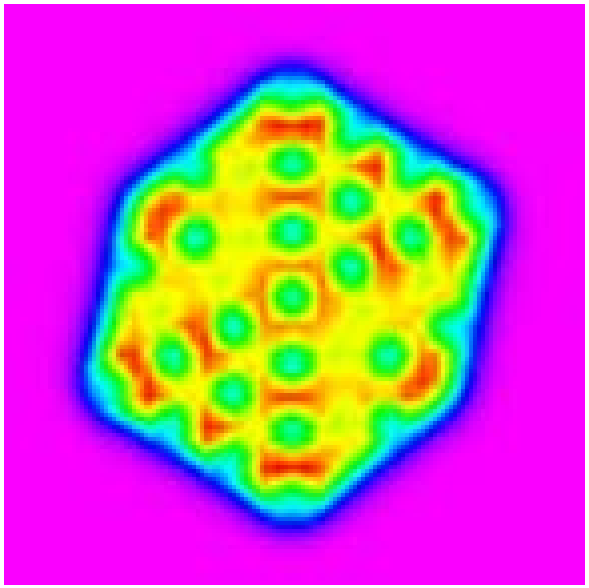
$$n(\vec{r},t)=\sum_i|\psi_i(\vec{r},t)|^2$$

Solve the equation in real-time and real-space

Electron dynamics in metallic clusters by TDDFT

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

Na_{147}^{+}



Assume
Icosahedral shape

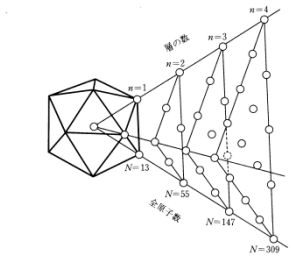
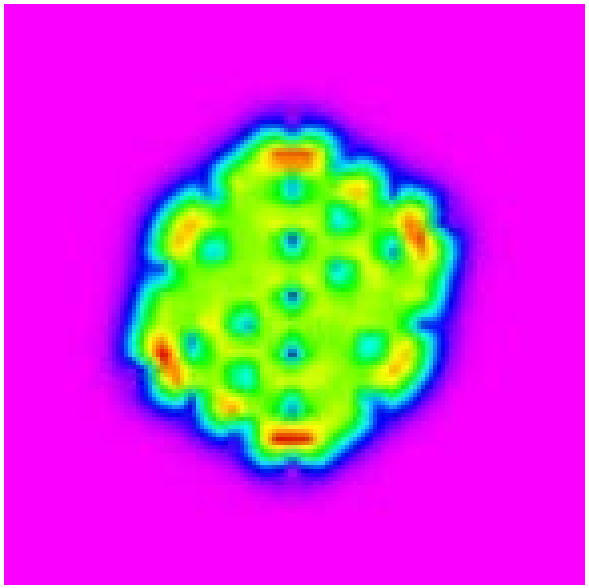
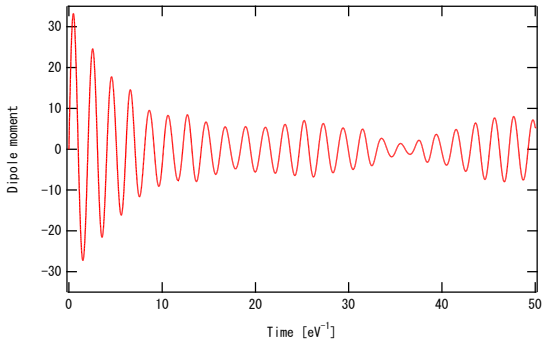


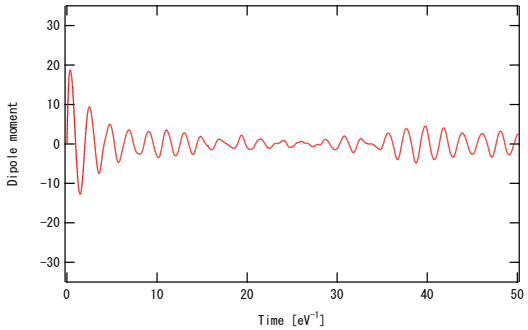
図 5·61 多層正二十面体構造(MIC)の概念図[104]
n は MIC の層の数であり，N は全原子数である。1 層構造($n=1$)では原子数 $N=13$ に対応し，2 層構造($n=2$)では $N=55$，3 層構造($n=3$)では $N=147$…となる。

Li_{147}^{+}



Density change induced by impulsive force

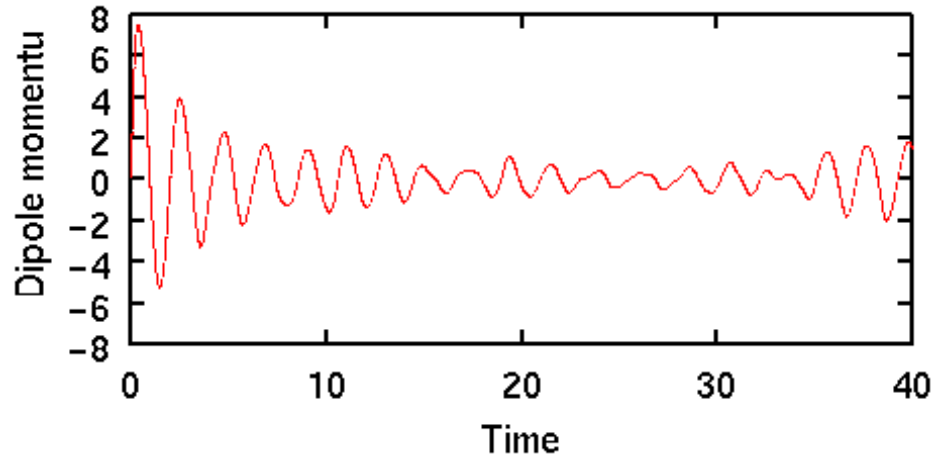




Dipole moment as function of time

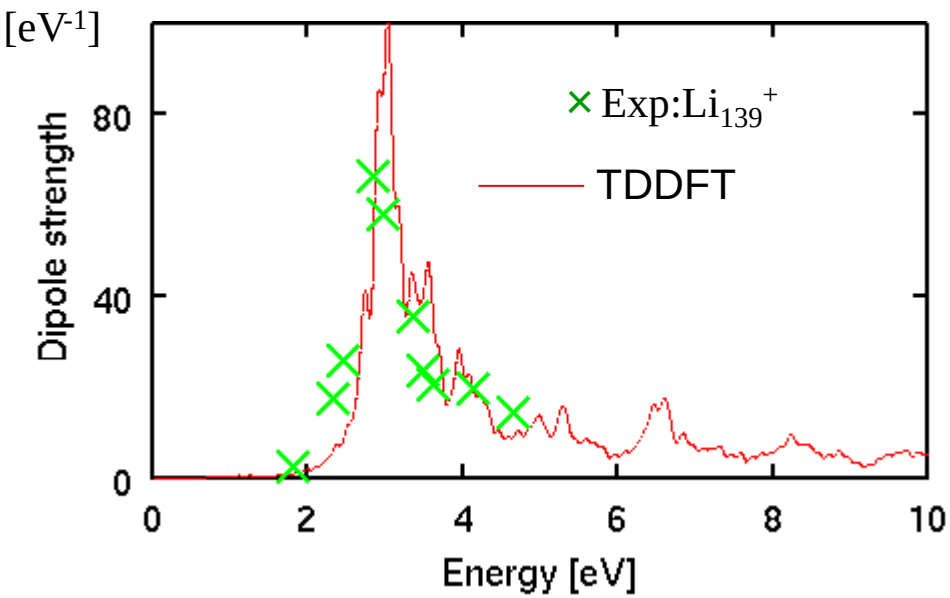
Real-time calculation for optical absorption spectrum of Li_{147}^{+}

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



Real-time calculation
for autocorrelation function

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

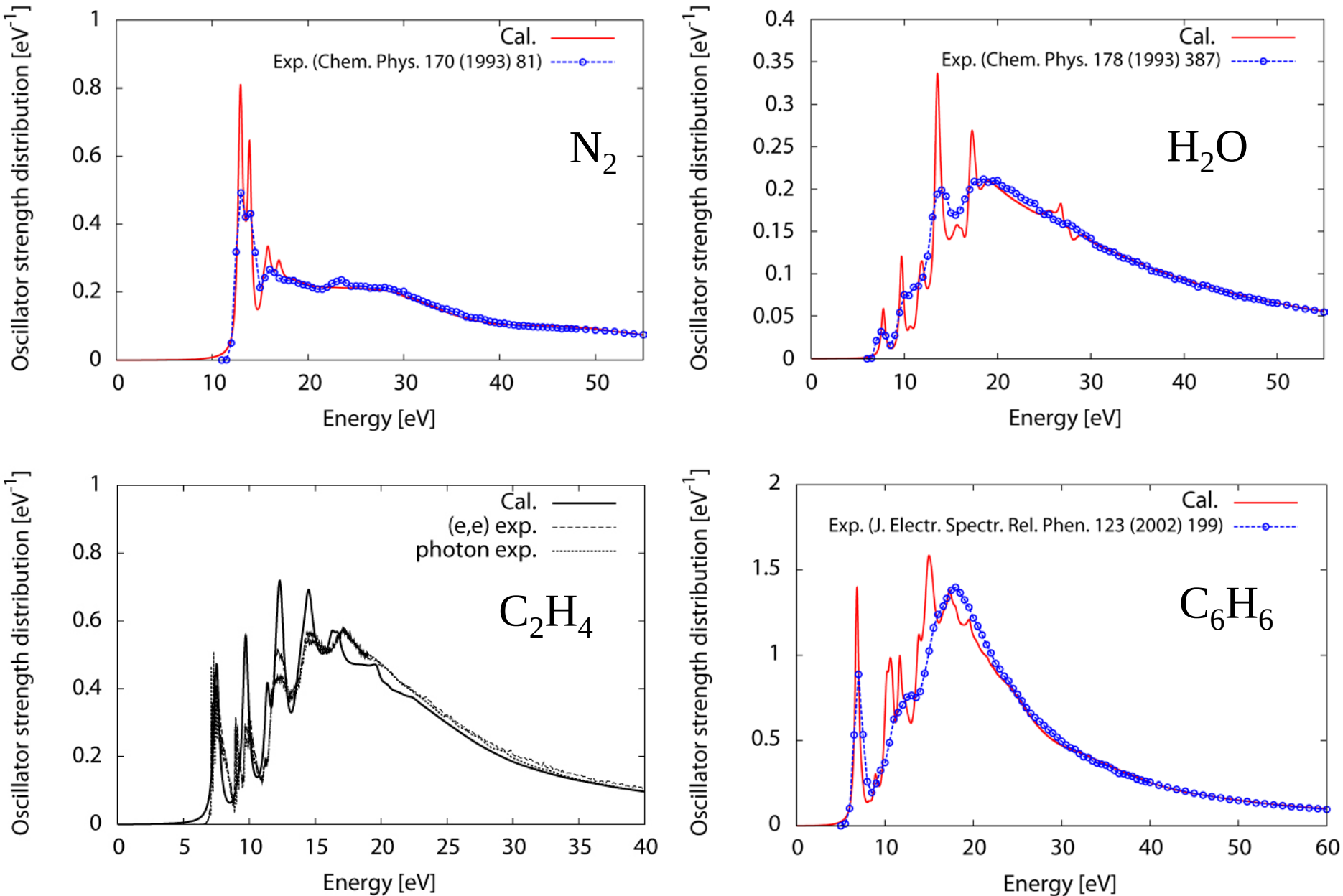


Fourier transformation
→ oscillator strength distribution

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

Oscillator strength distribution by TDDFT (LB94 functional)

"Continuum RPA calculation for deformed system"



1999 -
From Atomic Clusters to Solid State Physics

One day in 1999, George suggested me
" Calculate dielectric function in real-time ! "

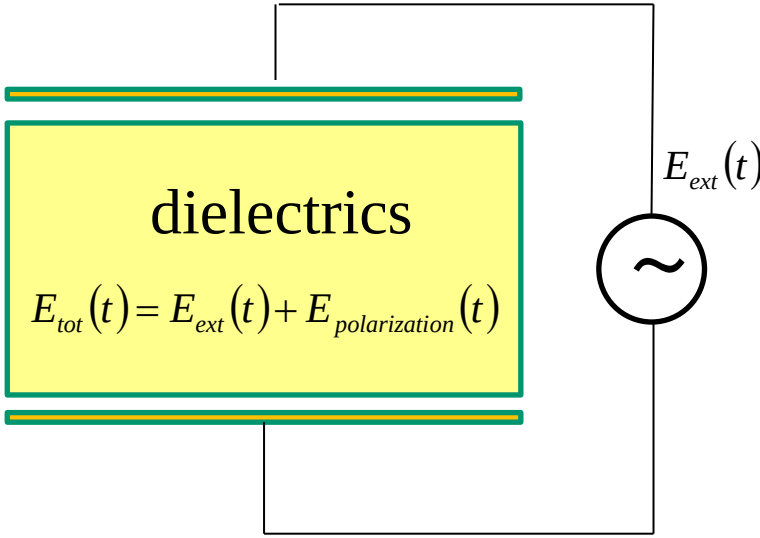
Consider electron dynamics under spatially-uniform electric field.
Treat the electric field by vector potential.

$$E(t) = -\frac{1}{c}\frac{dA(t)}{dt}$$

Time-dependent Kohn-Sham equation for Bloch orbitals
"Time-dependent band theory"

$$i\hbar\frac{\partial}{\partial t}u_{n\vec{k}}(\vec{r},t) = \left[\frac{1}{2m}\left(\vec{p} + i\vec{k} - \frac{e}{c}\vec{A}_{tot}(t)\right)^2 + V(\vec{r},t)\right]u_{n\vec{k}}(\vec{r},t)$$

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



Electric field inside the solid is a sum of
externally applied and induced polarization fields

$$\vec{A}_{tot}(t) = \vec{A}_{ext}(t) + \vec{A}_{polarization}(t)$$

Polarization field (surface charge) is generated
from the current flowing inside the solid

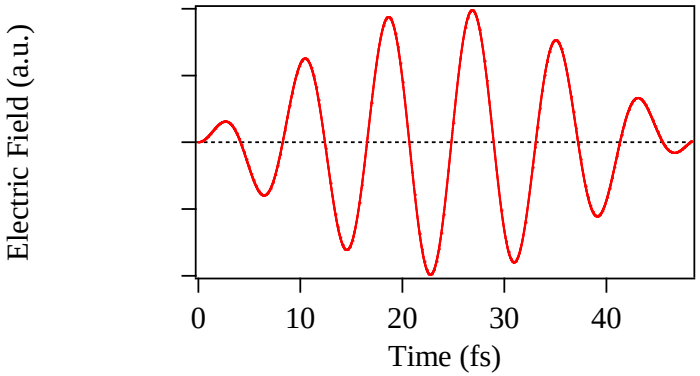
$$\frac{d^2\vec{A}_{polarization}(t)}{dt^2} = \frac{4\pi}{\Omega}\int_{\Omega(cell)} d\vec{r}\ \vec{j}(\vec{r},t)$$

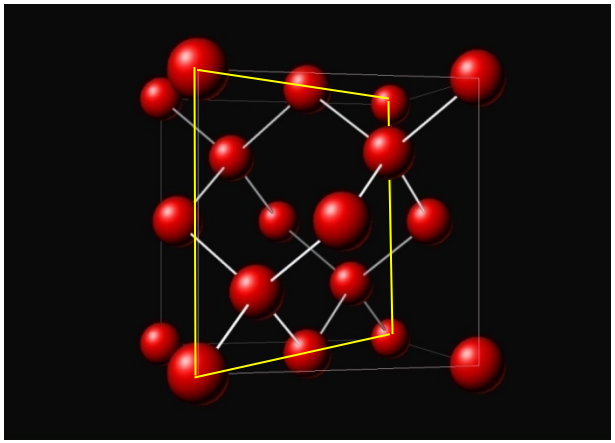
Bertsch, Iwata, Rubio, Yabana,
Phys. Rev. B62(2000)7998.

Electron dynamics in bulk silicon under pulse light

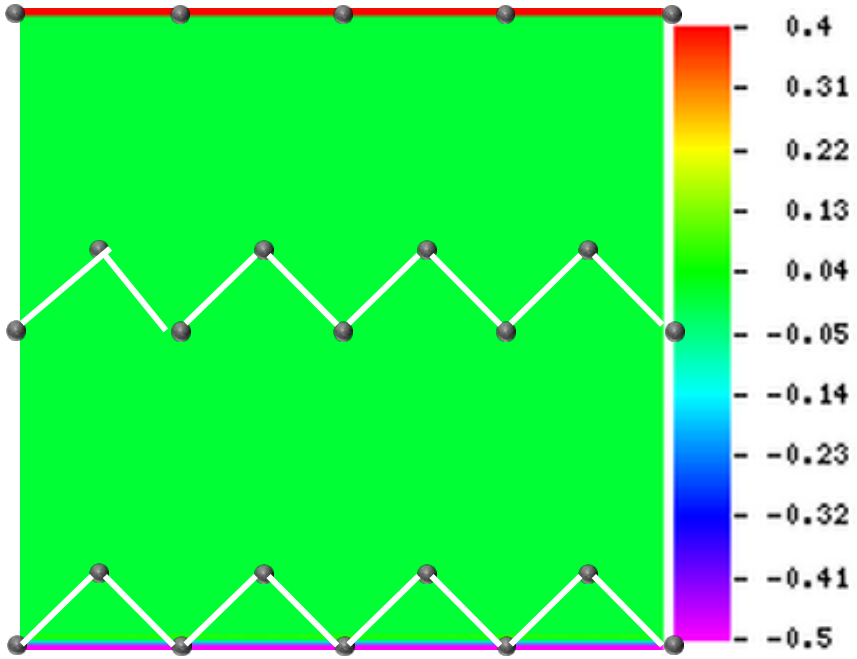
$I = 3.5 \times 10^{14}$ W/cm^2, T=50 fs, $\hbar\omega$=0.5 eV

Laser photon energy is much lower than direct bandgap.

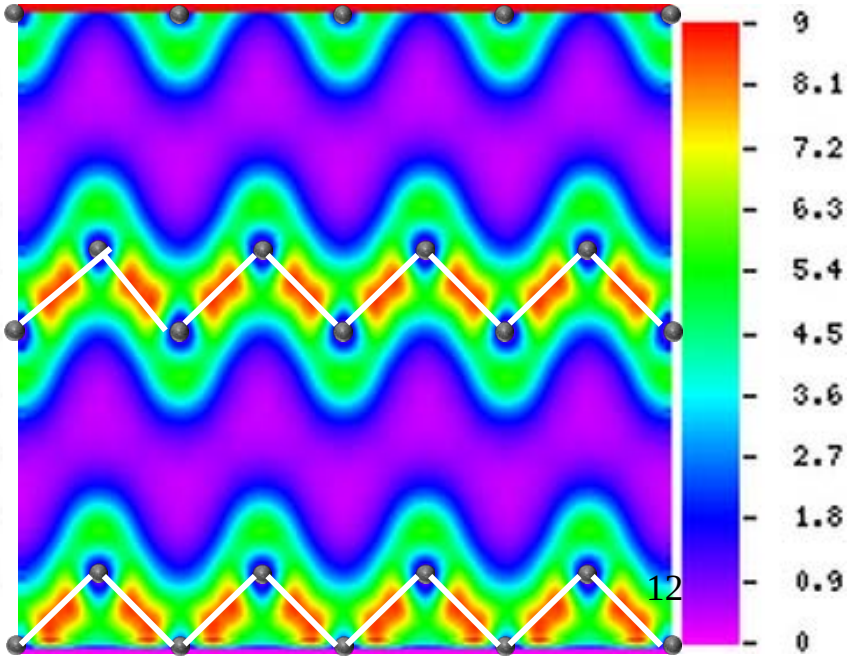




Density change from the ground state (110)



Ground state density (110)



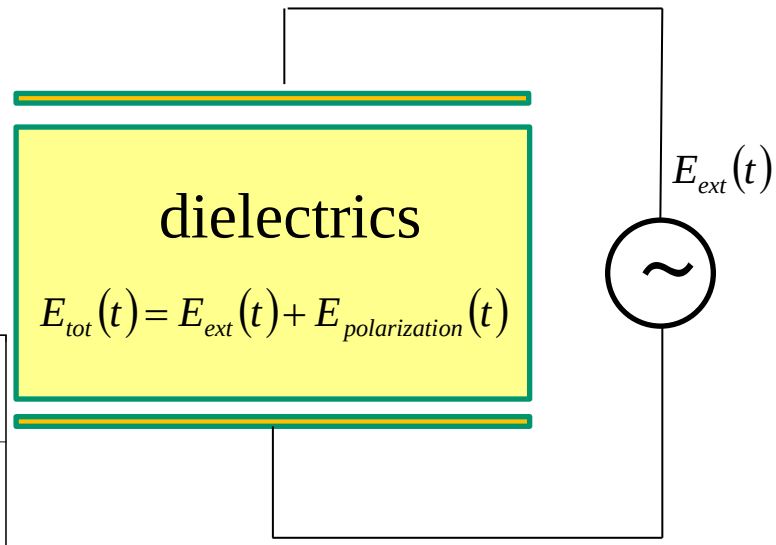
Red +

Green 0

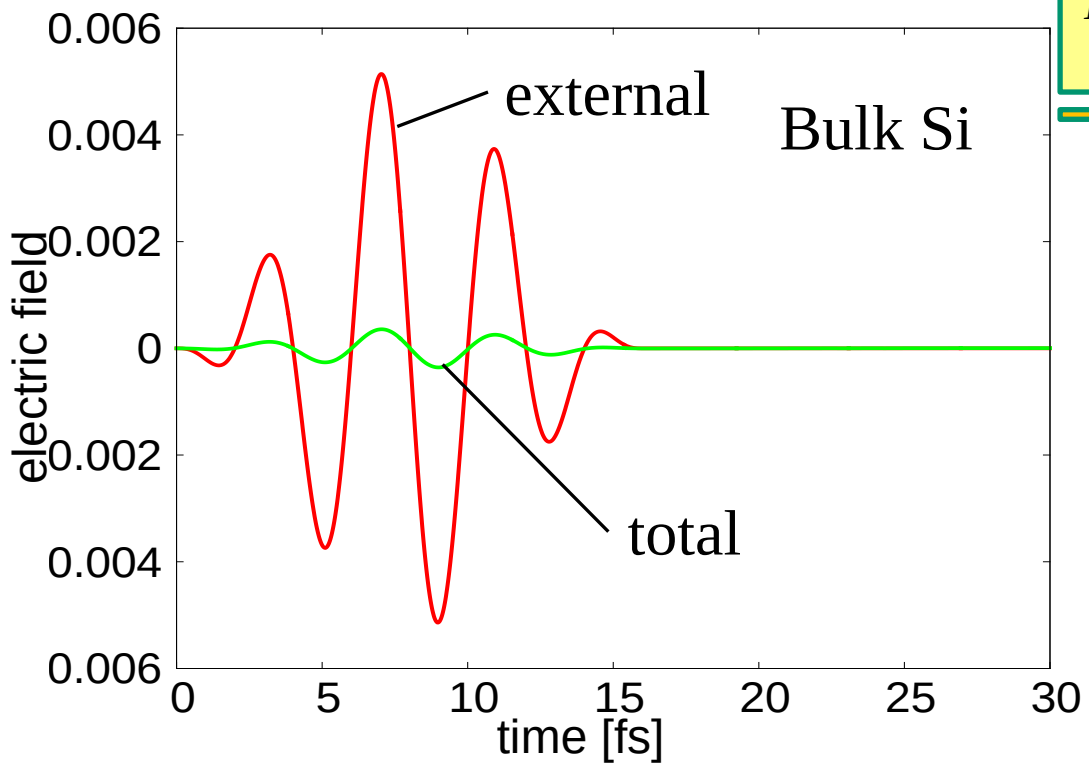
Blue -

$E_{ext}(t)$ and $E_{tot}(t)$ are related by dielectric function

$$E_{tot}(t) = \int^{t} dt' \, \varepsilon^{-1}(t-t') E_{ext}(t')$$



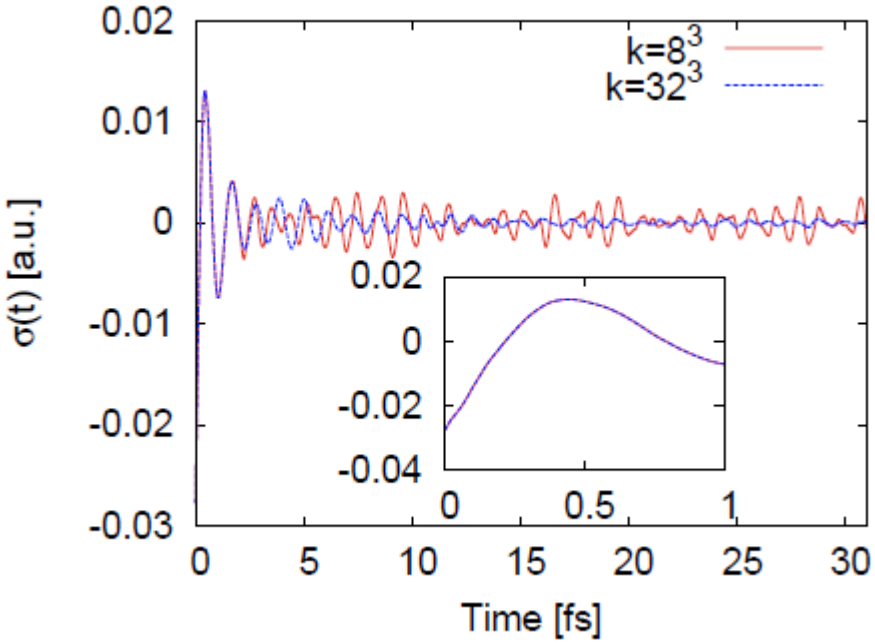
Calculations: $I=10^{12}$W/cm^2, $\hbar\omega$=1.03eV

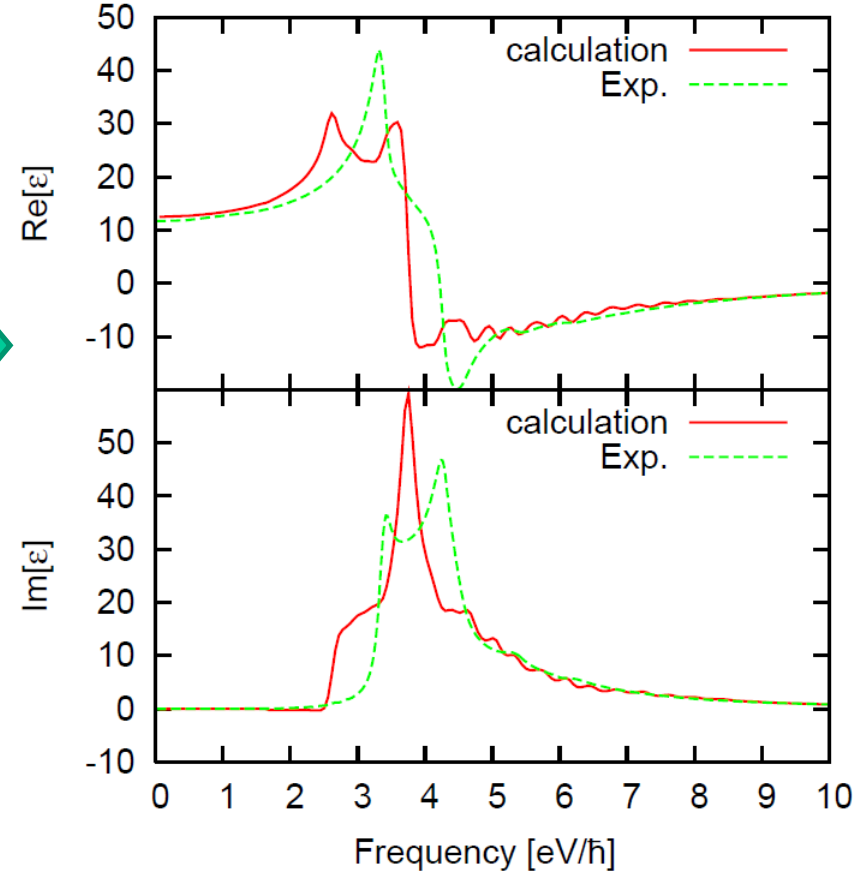


$\varepsilon \approx 14$ for Si

Dielectric function of Si in TDDFT (ALDA)

Instantaneous pulse field is applied at t=0, the induced current as a function of time.





Dielectric function by TDDFT (ALDA) is not very good.
Too small bandgap (common problem with LDA).

Many other theories have been developed,
GW+Bethe-Salpeter eq. is the most successful.

GW approx. + Bethe-Salpeter

Most successful but Beyond Kohn-Sham framework

Dots: experiment
Dash-dotted: RPA
Solid: Bethe-Salpeter

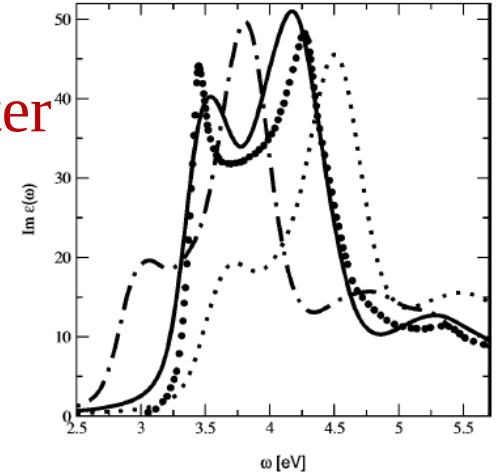
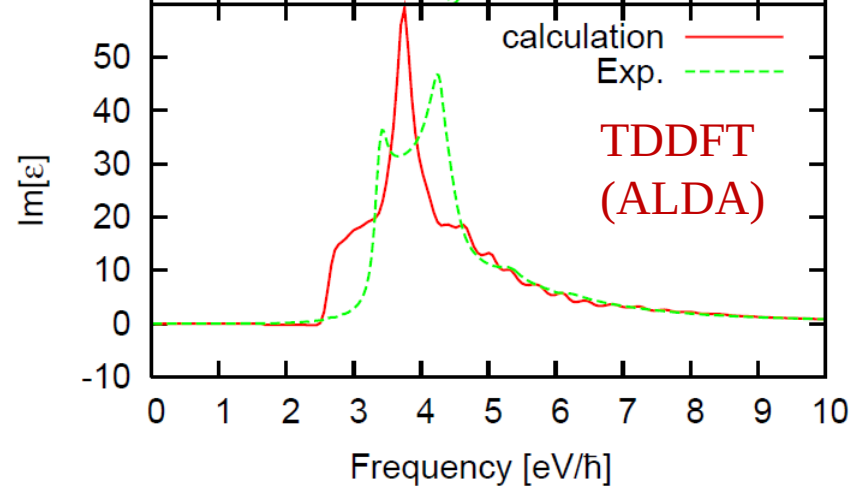
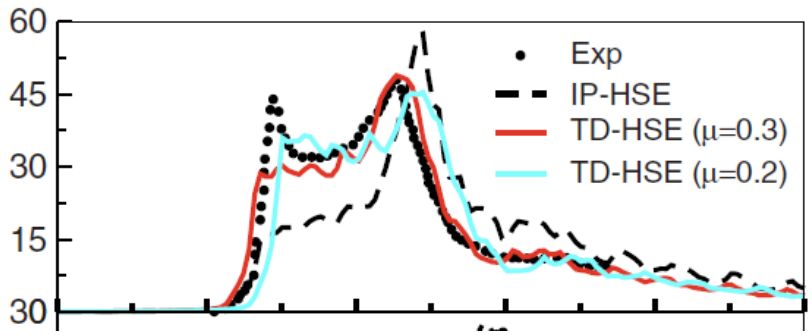


FIG. 5. Silicon absorption spectrum [Im(ε_M)]: ●, experiment (Lautenschlager *et al.*, 1987); dash-dotted curve, RPA, including local field effects; dotted curve, *GW*-RPA; solid curve, Bethe-Salpeter equation.

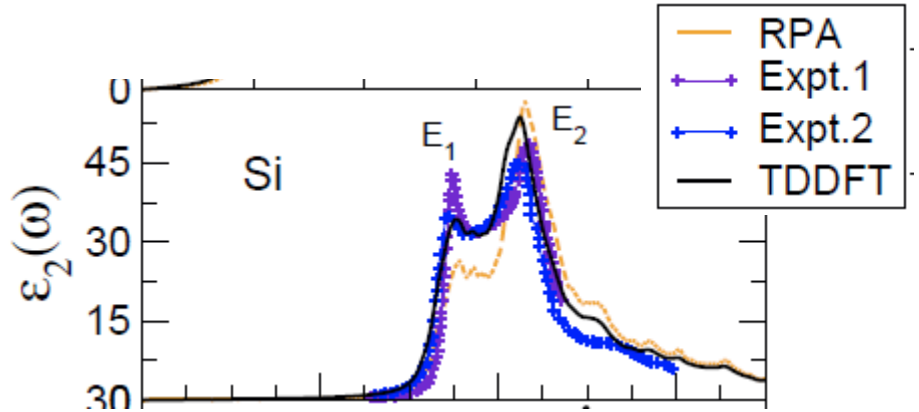
G. Onida, L. Reining, A. Rubio,
Rev. Mod. Phys. 74(2002)601.



TDDFT with hybrid (nonlocal) functional



Good results for small gap materials,
Less satisfactory for large gap materials.
J. Paier, M. Marsman, G. Kresse,
Phys. Rev. B78,121201 (2008)



PRL107, 186401 (2011)
S. Sharma, J.K. Dewhurst, A. Sanna, E.K.U. Gross,
Bootstrap approx. for the exchange-correlation kernel of time-dependent density functional theory

Limited to linear response regime.

2007-
From Solid State Physics to Laser Science

Frontiers of Optical Sciences: Intense laser pulse on solid

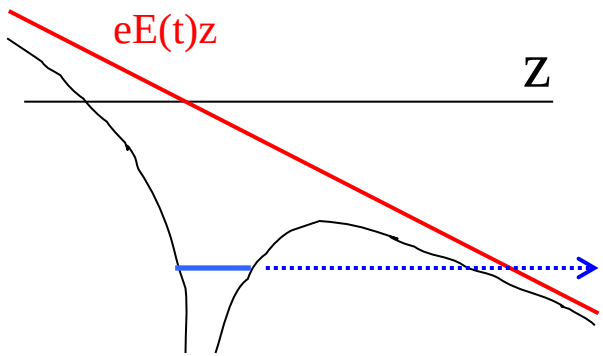
Laser intensity

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

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

Nonrelativistic
Quamtum mechanics

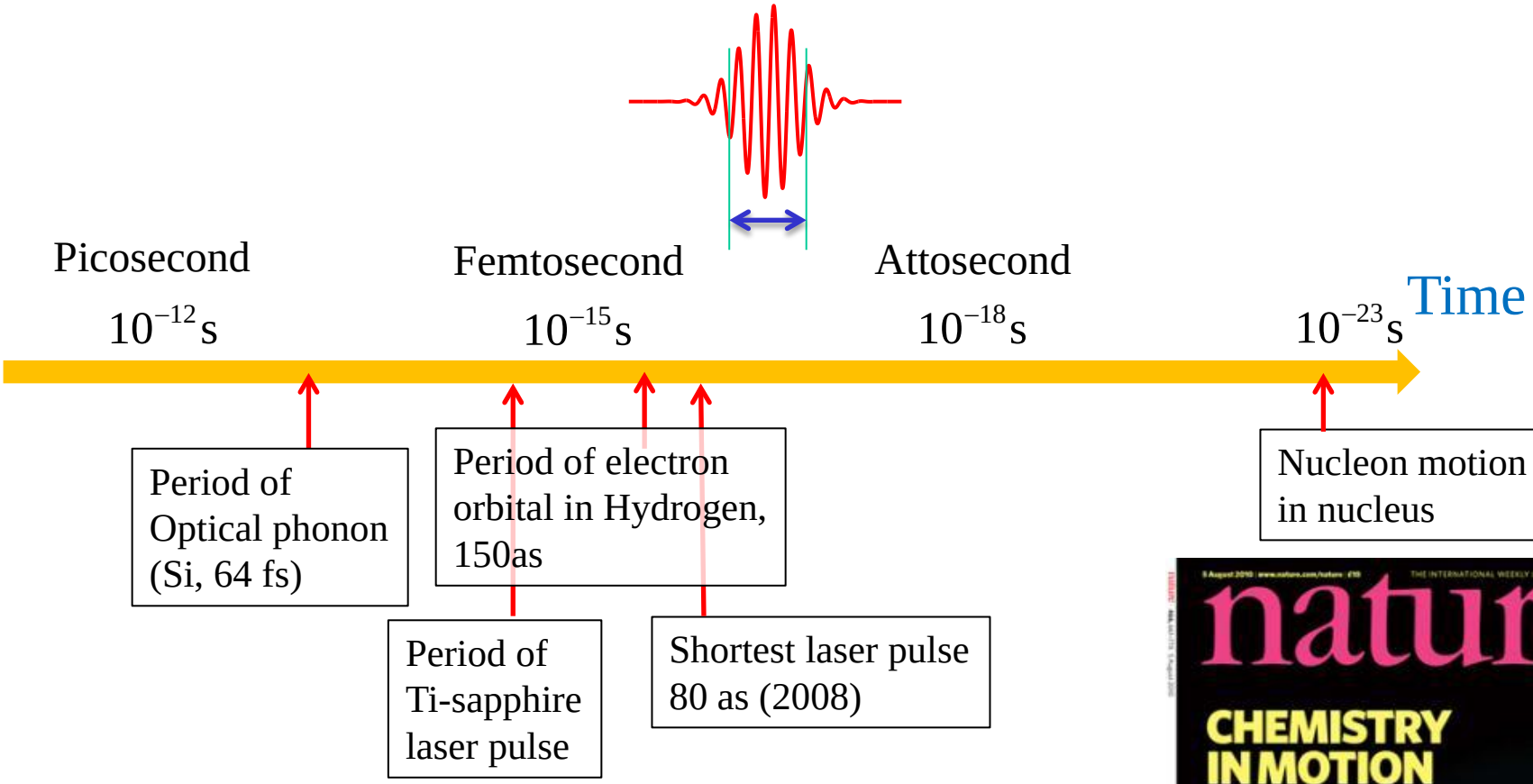
Relativistic
Classical mechanics

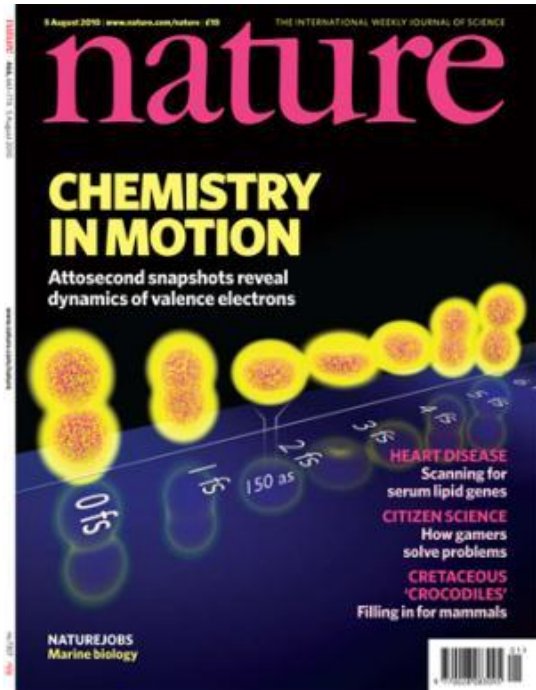


External electric field by laser pulse

≈ Internal electric field by nuclei

Frontiers in Optical Sciences: Ultra-short dynamics





Real-time observation of valence electron motion

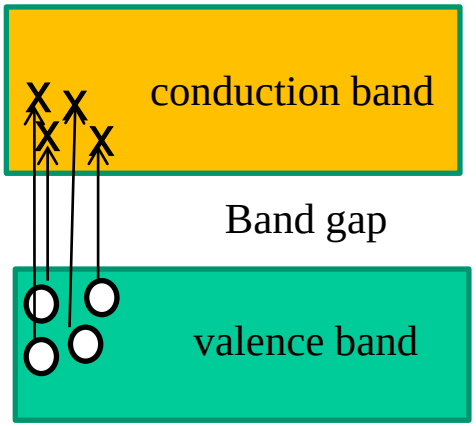
E. Goulielmakis et.al, Nature 466, 739 (2010).

As the laser intensity increases,

Calculation for diamond
laser frequency: 3.1eV,
below bandgap (4.8 eV)

At a certain intensity, optical breakdown is observed.

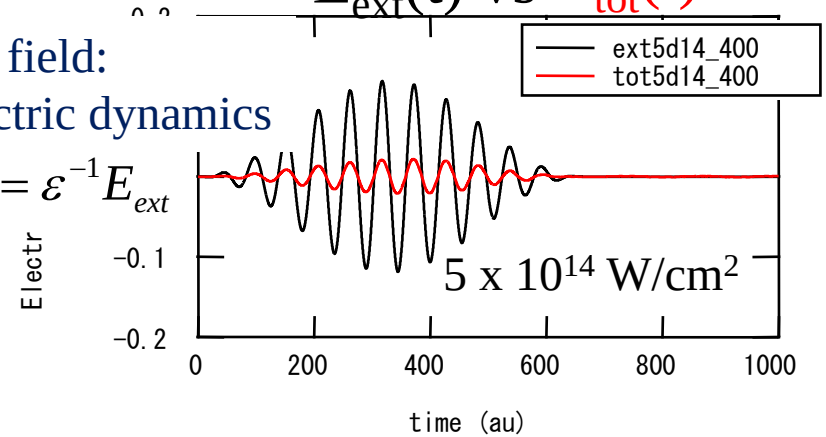
T. Otobe, M. Yamagiwa, J.-I. Iwata, K.Y. T. Nakatsukasa, G.F. Bertsch, Phys. Rev. B77, 165104 (2008)



$E_{ext}(t)$ vs $E_{tot}(t)$

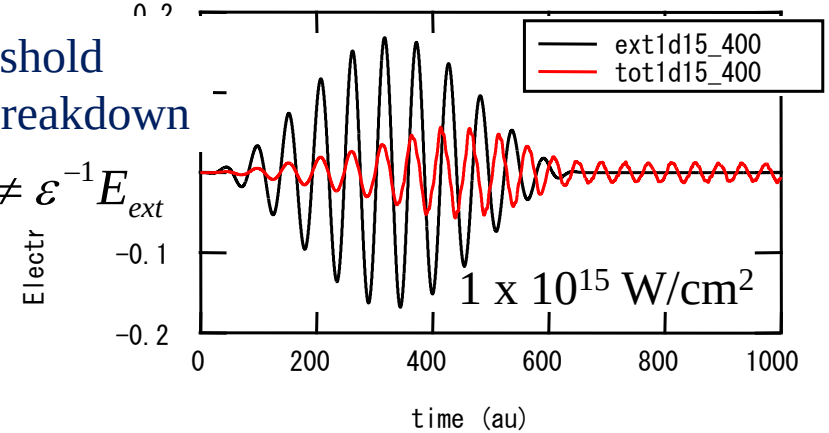
Weak field:
Dielectric dynamics

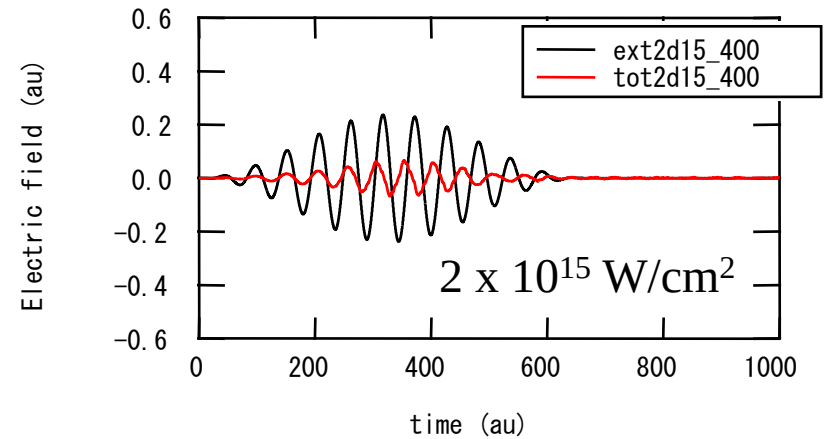
$$E_{tot} = \varepsilon^{-1} E_{ext}$$



Threshold
for breakdown

$$E_{tot} \neq \varepsilon^{-1} E_{ext}$$





Above a certain critical intensity, transparent materials (eg. diamond, quartz) absorb and/or reflect light pulse due to nonlinear electronic response to laser light.

This requires treatment beyond ordinary macroscopic electromagnetism for light-matter interaction.

2011-
From Microscopic Quantum Mechanics To Macroscopic Electromagnetism

Usually, light-matter interaction is described by

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

Constitution relation

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

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

As the light intensity increases, nonlinear effects appear

Quantum mechanics is useful to calculate nonlinear susceptibilities as well.

$$D = D[E] = \varepsilon(\omega)E + 4\pi\chi^{(2)}E^2 + 4\pi\chi^{(3)}E^3 + \cdots$$

Extreme intensity of laser pulse

⇩

We need to solve couple Maxwell + Schroedinger dynamics.

We need to solve couple Maxwell + Schroedinger dynamics.

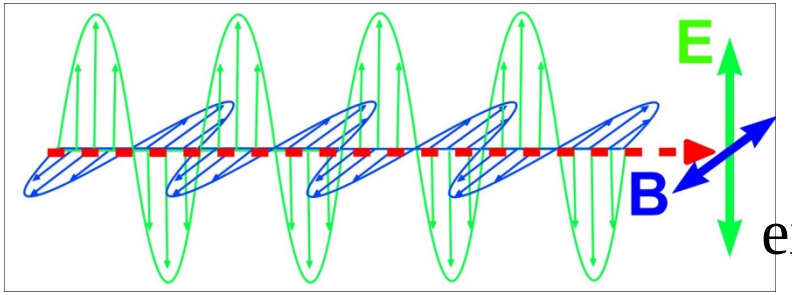
Two spatial scales

Maxwell equation
describing electromagnetic field

$$E(\vec{r},t), \quad B(\vec{r},t)$$

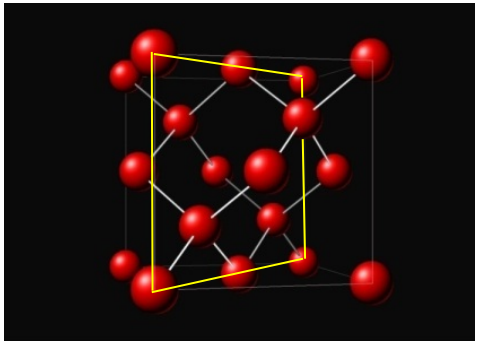
Time-dependent density-functional theory
describing electron dynamics

$$\psi_i(\vec{r},t)$$



polarization

external field



[μm]

Different spatial scales

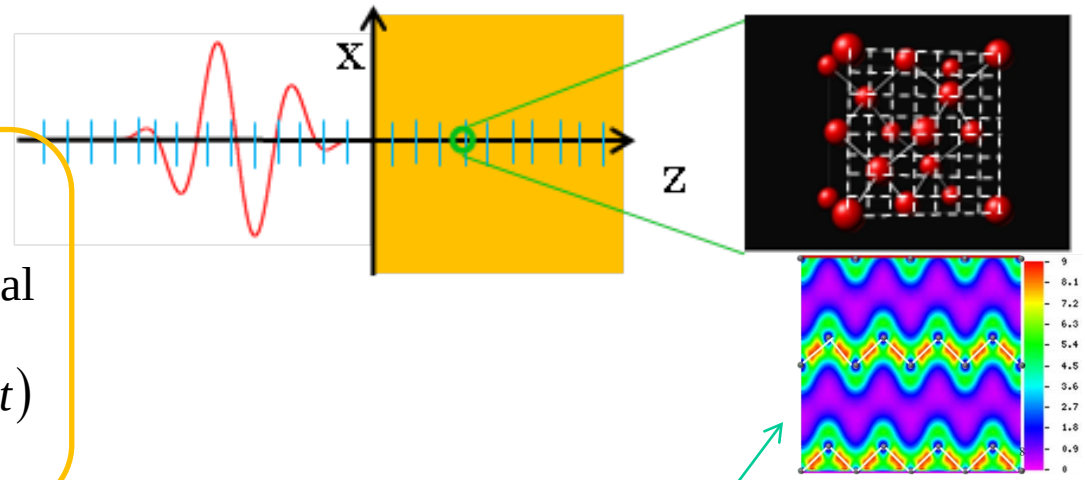
[nm]

We introduce two spatial grids and achieve “multiscale simulation”

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.

$A(Z,t)$

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

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

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

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

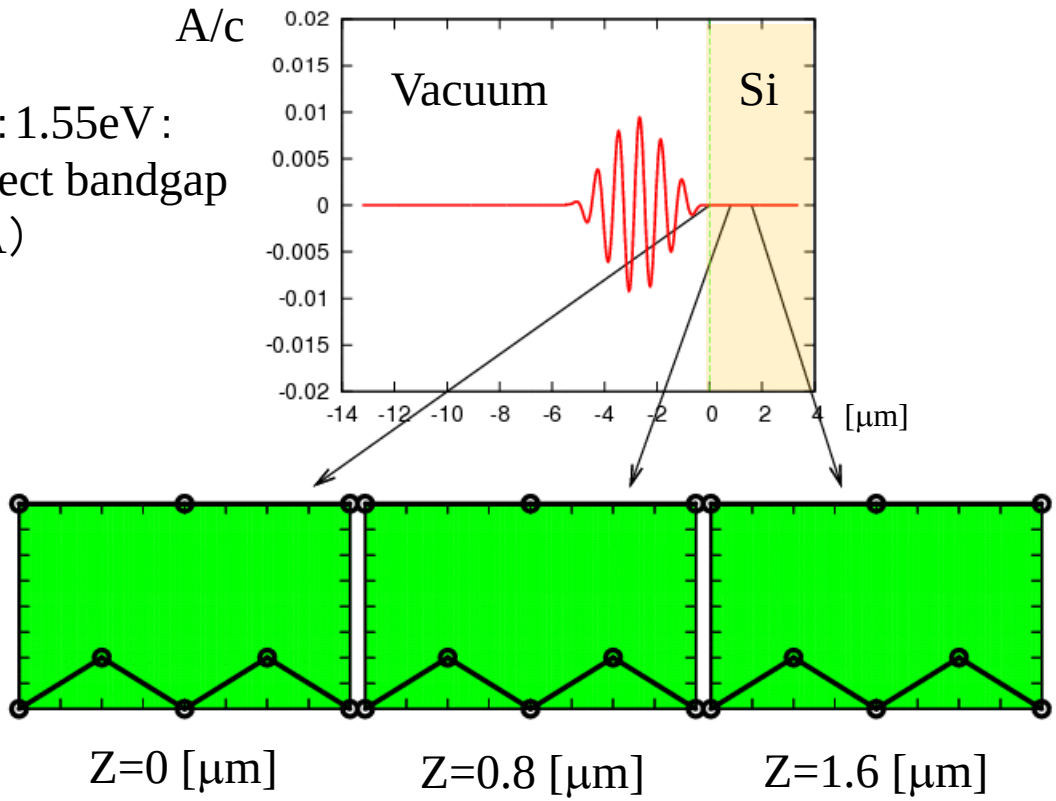
$$\vec{j}_{e,Z}=\frac{\hbar}{2mi}\sum_i\left(\psi_{i,Z}^*\vec{\nabla}\psi_{i,Z}-\psi_{i,Z}\vec{\nabla}\psi_{i,Z}^*\right)-\frac{e}{4\pi c}n_{e,Z}\vec{A}$$

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)

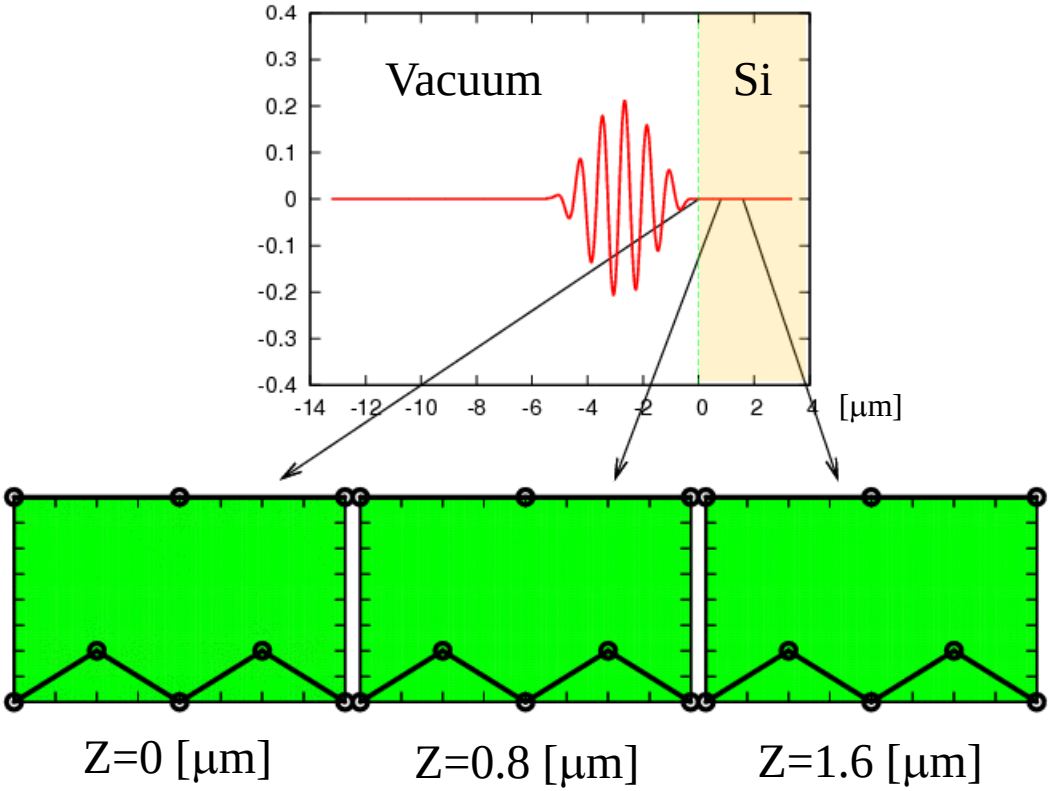


Coupled Maxwell + TDDFT simulation

More intense laser pulse

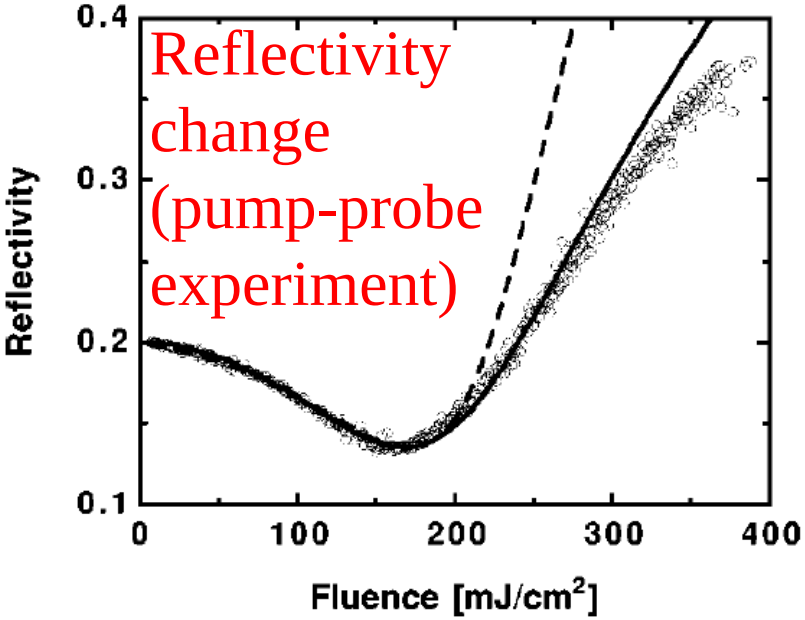
Dynamics of electrons and macroscopic EM fields are no more separable.

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



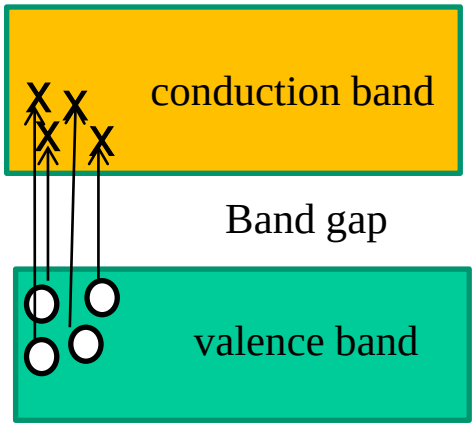
Dense electron-hole excitations modifies the dielectric properties of solid at the surface

K. Sokolowski-Tinten, D. von der Linde, Phys. Rev. B61, 2643 (2000)



Laser intensity

Change of reflectivity explained by free-electron (Drude) model



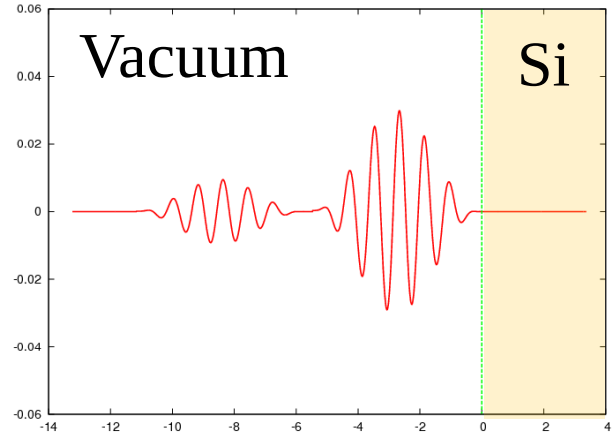
$$\varepsilon(n_{ph}) = \varepsilon_{gs} - \frac{4\pi e^2 n_{ph}}{m^*} \frac{1}{\omega\left(\omega + \frac{i}{\tau}\right)}$$

m^*=0.18, τ=1fs

$$\text{Reflectivity} = \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^2$$

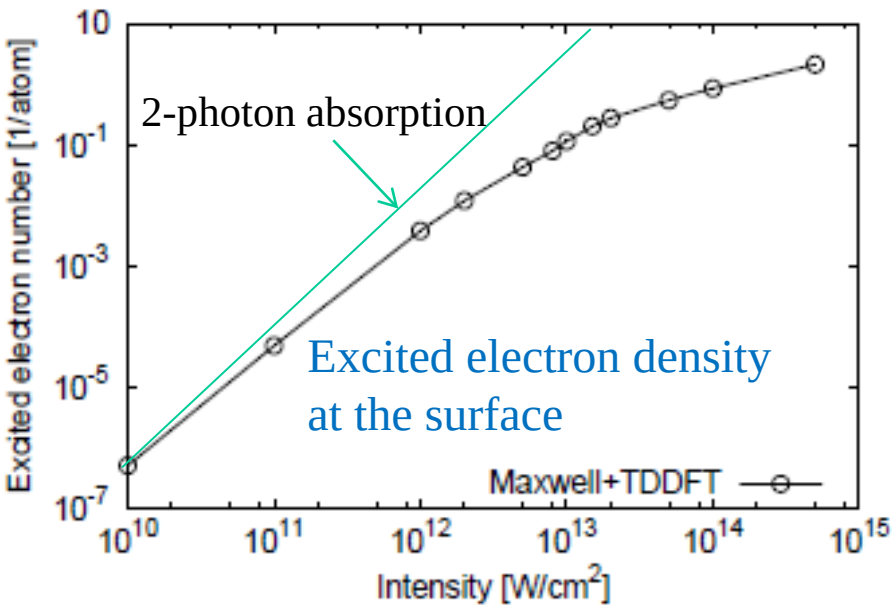
“Numerical Pump-Probe Experiment”

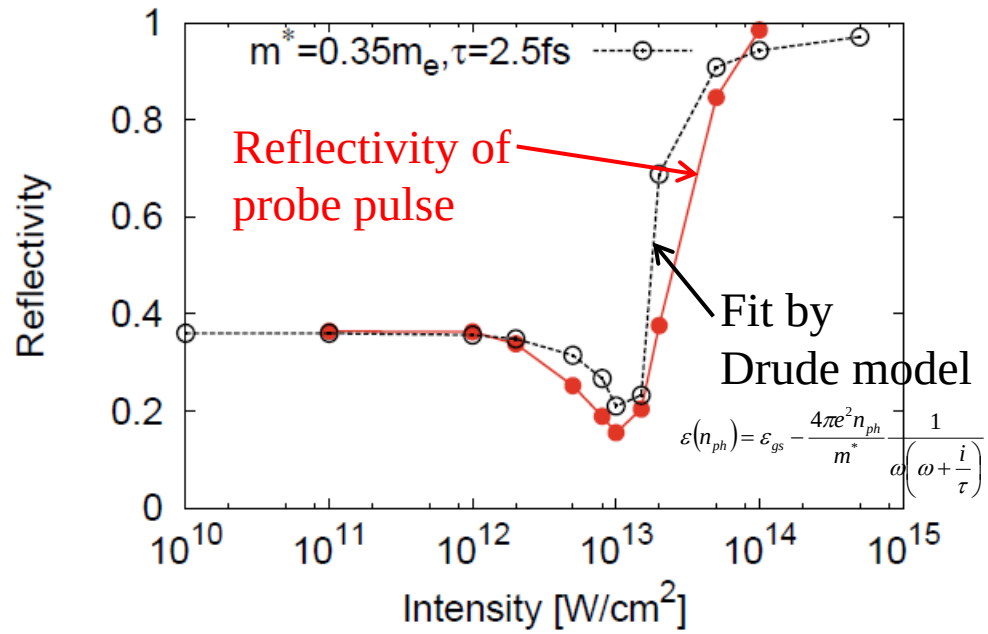
I=1x10^{11}W/cm^2,
$h\nu$=1.55eV



We can calculate

excited electron density at the surface by pump-pulse / reflectivity of probe pulse

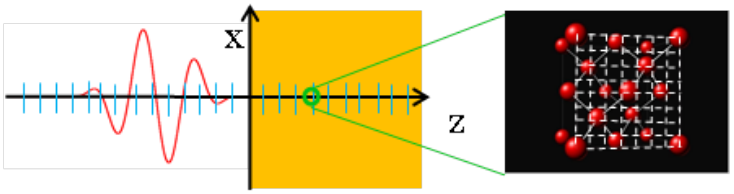




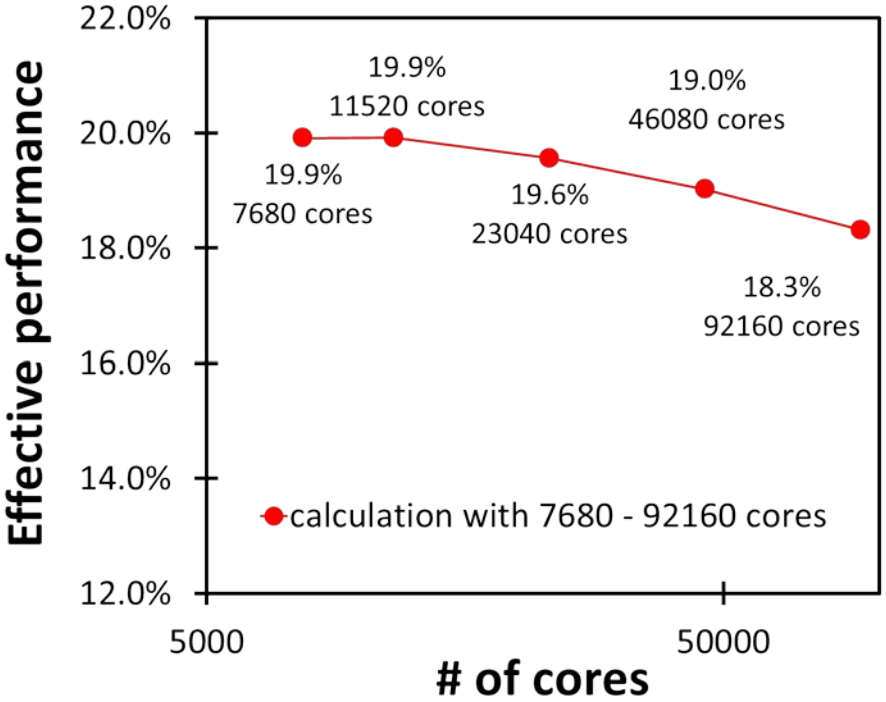
Computational Aspects

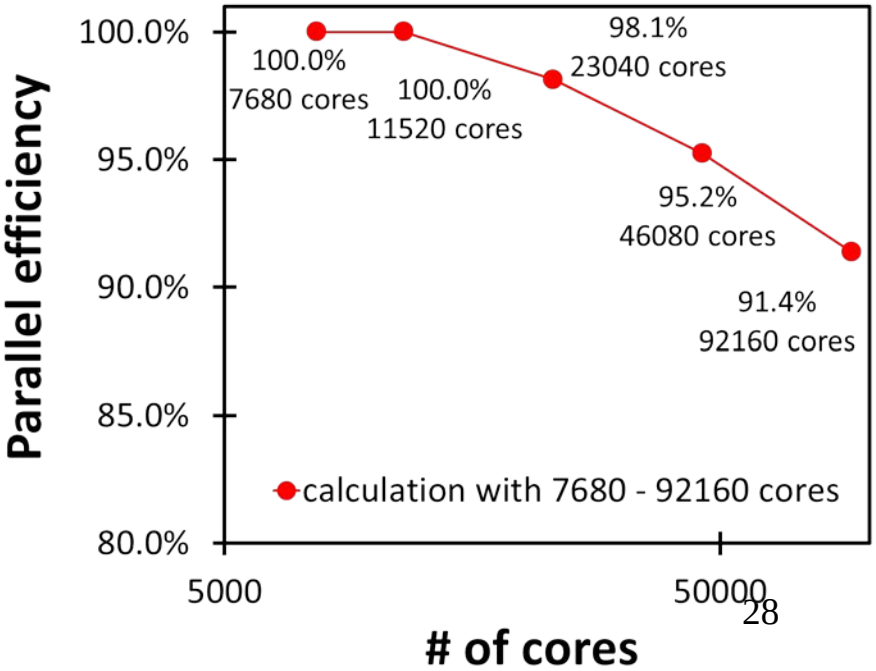
Large computational resources required for multi-scale calculation

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



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





Conclusion

Time-dependent mean-field theory is now widely used for electron dynamics. There are a number of linear and nonlinear applications in frontiers of optical sciences.

I have been enjoying a fantastic journey extending time-dependent mean-field approach to many fields.
I am much thankful to George to guide me the journey,
and hoping to further extend it.