SALMON

10th Time-Dependent Density-Functional Theory:
Prospects and Applications
Benasque Science Center, Spain
2025.4.14-16(15)

TDDFT for extremely nonlinear light propagation

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University of Tsukuba

Benasque, Telluride, and in Asia

Dr. Tomohito Otobe (QST, Kyoto) is organizing a School/Workshop in Nara.

Todaiji-temple: world heritage, largest wooden structure in the world

Combine Maxwell equations and TDDFT

Light propagation solving classical Maxwell's equations

$$\nabla \times \nabla \times \mathbf{A} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} = \frac{4\pi}{c}\mathbf{j}$$

Electron dynamics by TDDFT in real time

$$i\hbar\frac{\partial}{\partial t}\psi_i = \left\{\frac{1}{2m}\left(-i\hbar\nabla + \frac{e}{c}\mathbf{A}\right)^2 + V_{ion} + V_H + V_{xc}\right\}\psi_i$$

$$\mathbf{j} = -\frac{e}{2m}\left\{\psi_i^*\left(-i\hbar\nabla + \frac{e}{c}\mathbf{A}\right)\psi_i + c.c.\right\}$$

Contents

Extreme Optics

Frontiers of optical science using extreme pulsed light

Electric field

Nonlinear

Time

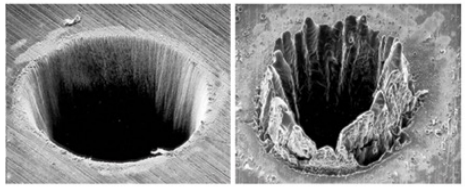
Ultrafast

Size

Nonlocal

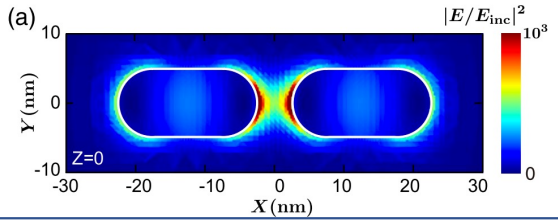
Intense field

High harmonic generation
Laser processing, surgery



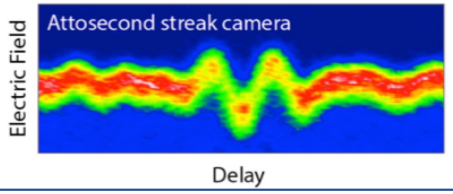
Nano-structure

Near field, plasmonics, meta-materials



Ultrashort pulse

Attosecond Science



In extreme optics, ordinary approach is not sufficient

Light propagation (Maxwell's)eq.

$$\nabla \cdot \boldsymbol{B} = 0$$
$$\nabla \times \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = \boldsymbol{0}$$
$$\nabla \cdot \boldsymbol{D} = \rho$$
$$\nabla \times \boldsymbol{H} - \frac{\partial \boldsymbol{D}}{\partial t} = \boldsymbol{j}$$

e.g, FDTD (Finite-difference time-domain method)

Constitutive relation

$$\boldsymbol{D}(\boldsymbol{r},\boldsymbol{t}) = \int_{-\infty}^{\boldsymbol{t}} \boldsymbol{dt'}\boldsymbol{\epsilon}(\boldsymbol{t}-\boldsymbol{t'})\boldsymbol{E}(\boldsymbol{r},\boldsymbol{t'})$$

$$\boldsymbol{D}(\boldsymbol{r},\boldsymbol{\omega}) = \boldsymbol{\epsilon}(\boldsymbol{\omega})\boldsymbol{E}(\boldsymbol{r},\boldsymbol{\omega})$$

First-principles quantum mechanics calculations of optical constants

$$\varepsilon_r = 1 + \frac{2Ne^2}{\varepsilon_0 \hbar} \sum_j \frac{\omega_{j0} \left| \langle 0|x|j \rangle \right|^2}{\omega_{j0}^2 - (\omega + i\gamma)^2}$$

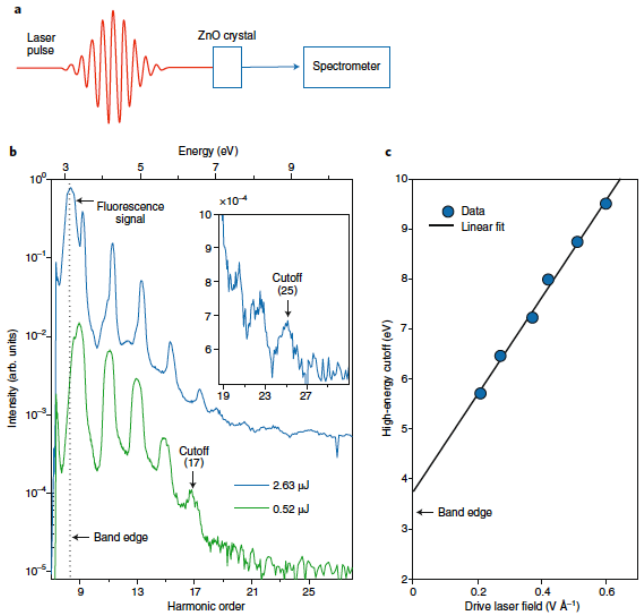
e.g, GW-BSE, TDDFT

Electromagnetism (EM)

Quantum Mechanics (QM)

Nonlinearity: strong laser pulse on materials

High harmonic generation from solids



S. Ghimire et al, Nat. Phys. 7, 138 (2011)
S. Ghimire, D.A. Reis, Nature Physics 15, 10 (2019)

$$P(\mathbf{r},t) = \int dt' \chi^{(1)}(t-t')E(\mathbf{r},t')$$

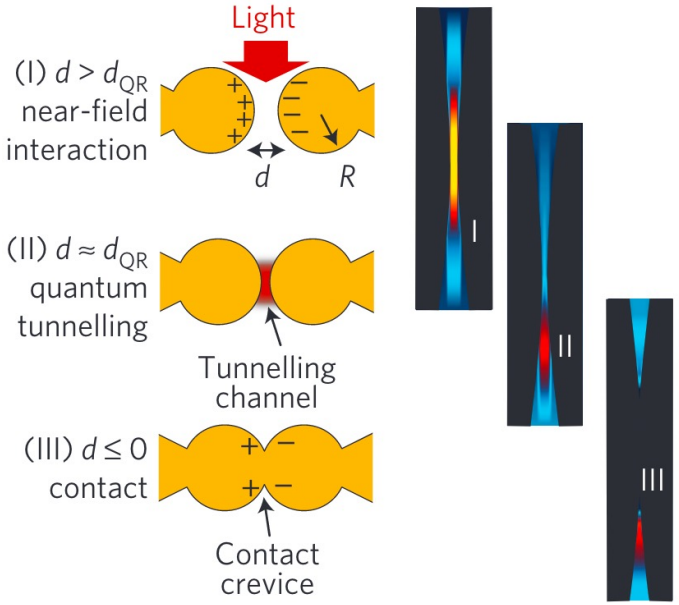
$$P(\mathbf{r},t) = \int dt' \chi^{(1)}(t-t')E(\mathbf{r},t') + \int dt'dt'' \chi^{(2)}(t-t',t-t'')E(\mathbf{r},t')E(\mathbf{r},t'') + \int dt'dt''dt''' \chi^{(3)}(t-t',t-t'',t-t''')E(\mathbf{r},t')E(\mathbf{r},t'')E(\mathbf{r},t''') + \cdots$$

Spatially local, but highly nonlinear

Explicit construction of nonlinear susceptibilities is difficult and useless.

Nonlocality: optical response in nano-material

Quantum Tunneling in Plasmonics



M.S. Tame et.al, Nature Phys. 9, 329 (2013)

$$P(\mathbf{r},t) = \int dt' \chi^{(1)}(t-t')E(\mathbf{r},t')$$

$$P(\mathbf{r},t) = \int dt' \int d\mathbf{r}' \chi^{(1)}(\mathbf{r},\mathbf{r}',t-t')E(\mathbf{r}',t')$$

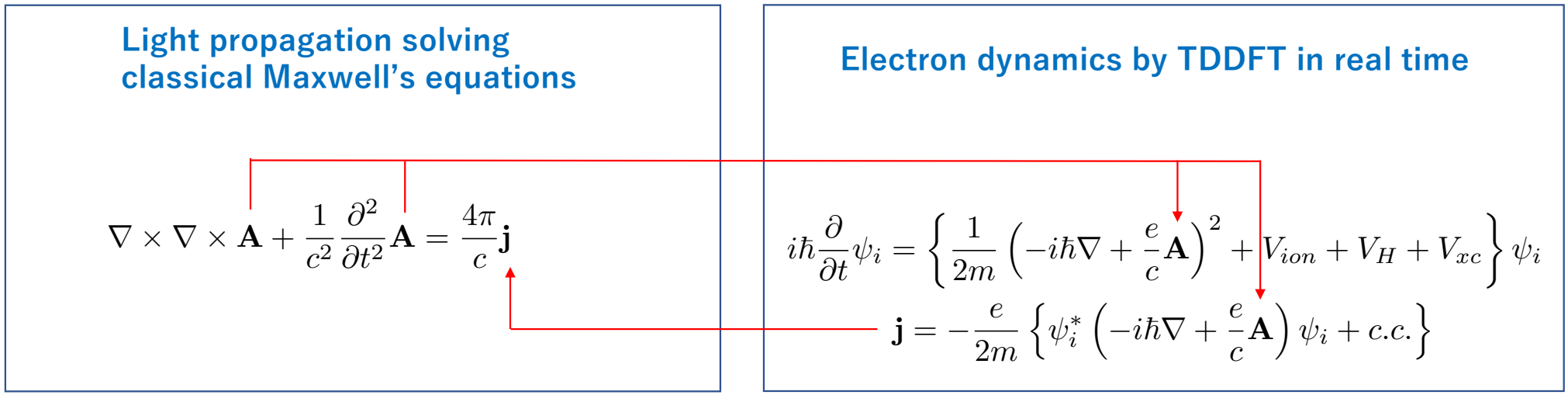
Linear, but spatially nonlocal

Explicit construction of nonlocal susceptibility is difficult and useless.

Contents

- About “Extreme Optics”
- Maxwell-TDDFT
- Some applications
- Maxwell-TDDFT at oblique incidence (under progress)
- Dephasing and density-matrix unfolding (under progress)

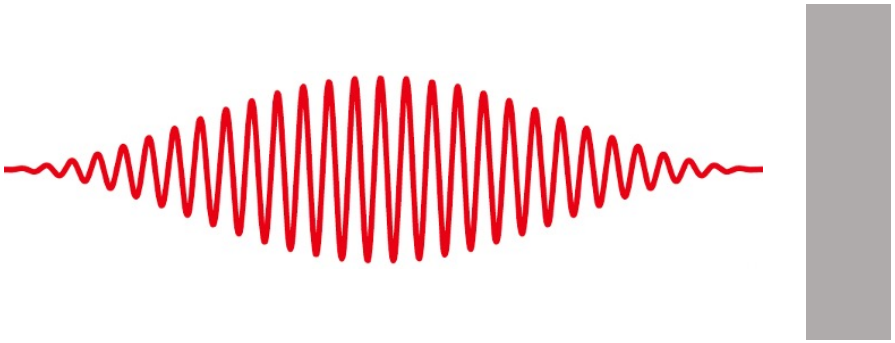
We combine EM and QM



We develop two connection methods, without/with coarse-graining.

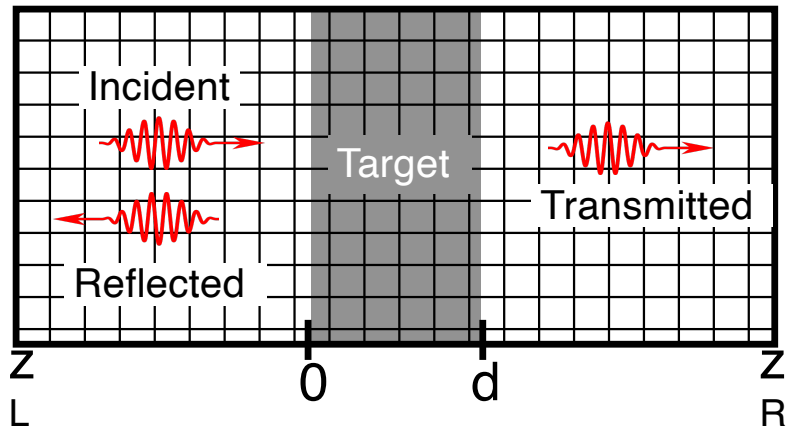
Microscopic (single-grid) vs Macroscopic (multi-grid)

Pulsed light on thin films at normal incidence



~~Microscopic~~ (Single-scale) vs. Macroscopic (Multi-scale)

Microscopic Maxwell+TDDFT



$$i\frac{\partial}{\partial t}u_{n\mathbf{k}} = \hat{H}_{\mathbf{k}+\frac{1}{c}A(\mathbf{r},t)}u_{n\mathbf{k}}$$

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\mathbf{A}(\mathbf{r},t) + \frac{1}{c}\nabla\dot{\phi}(\mathbf{r},t) = -\frac{4\pi}{c}\mathbf{j}_e(\mathbf{r},t)$$

$$\nabla^2\phi(\mathbf{r},t) = 4\pi n_e(\mathbf{r},t)$$

Single-scale approach using a **common** spatial grid

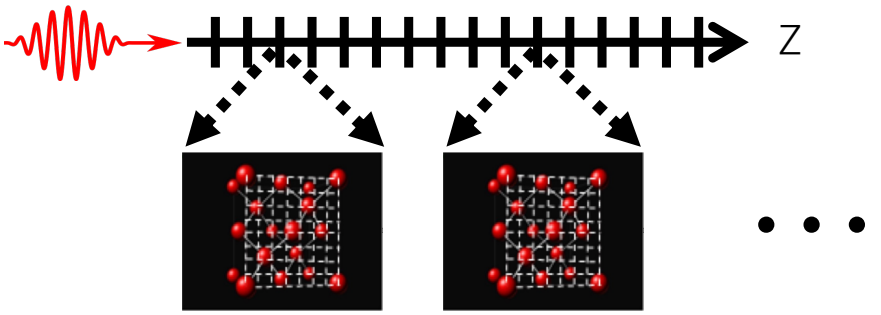
nonlocal + nonlinear

S. Yamada *et al*, PRB **98**, 245147 (2018).

Macroscopic Maxwell+TDDFT

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

grid spacing ~ 10 nm



nm-scale grid #1 nm-scale grid #2

$$i\frac{\partial}{\partial t}u_{n\mathbf{k},Z} = \hat{H}_{\mathbf{k}+\frac{1}{c}A_Z(t)}u_{n\mathbf{k},Z}$$

$$i\frac{\partial}{\partial t}u_{n\mathbf{k},Z} = \hat{H}_{\mathbf{k}+\frac{1}{c}A_Z(t)}u_{n\mathbf{k},Z}$$

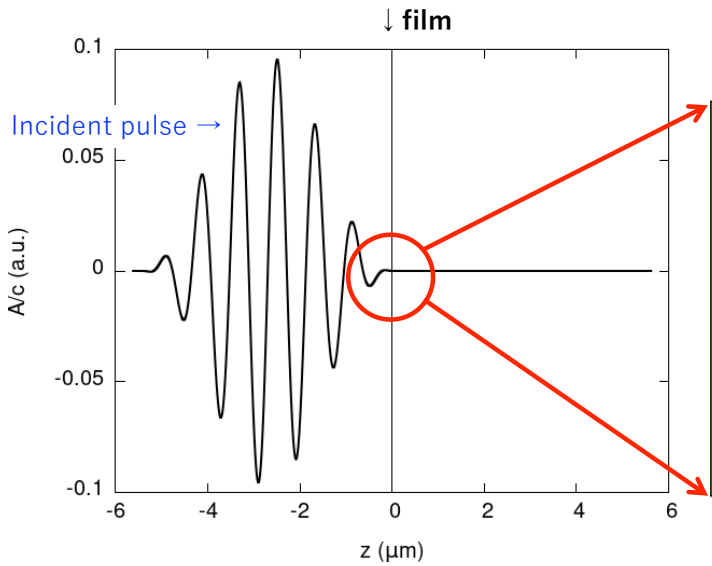
Multiscale approach using **different** spatial grid

nonlinear only

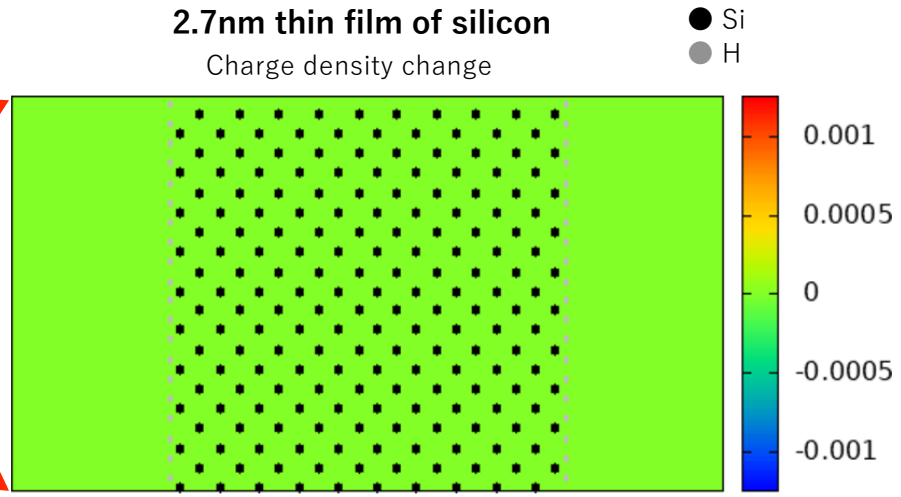
K. Yabana *et al.*, PRB **85**, 045134 (2012).

Microscopic (single-scale) Maxwell-TDDFT: pulsed light on Si nano-film

Shunsuke Yamada
Kansai Photon Sci. Inst



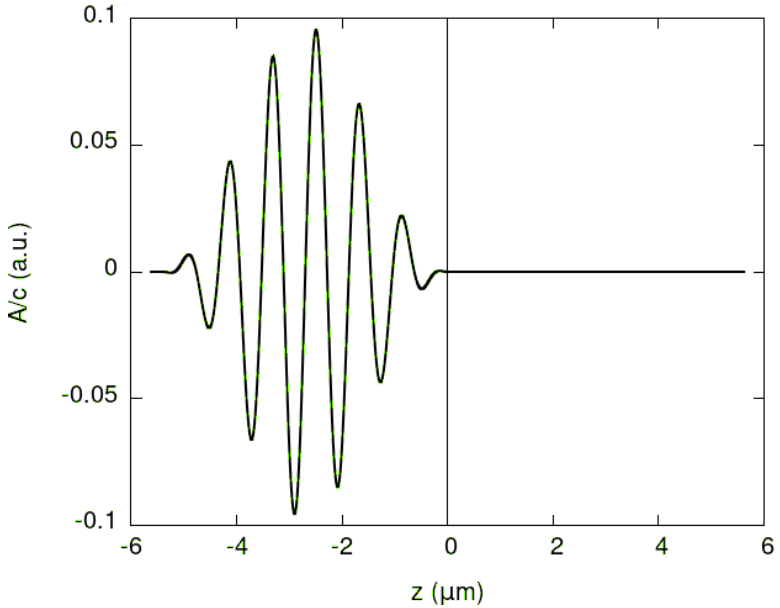
Light wavelength 800nm



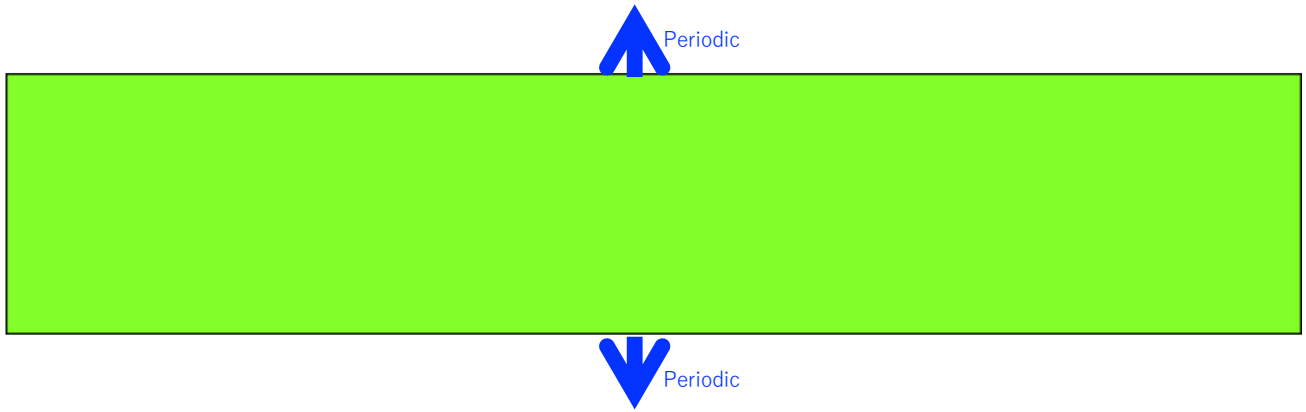
Nonlocal + Nonlinear

Thicker film（27.2nm）

Light pulse: $\hbar\omega = 1.5\mathrm{eV}, I = 10^{12}\mathrm{W/cm}^2, T = 18\mathrm{fs}$



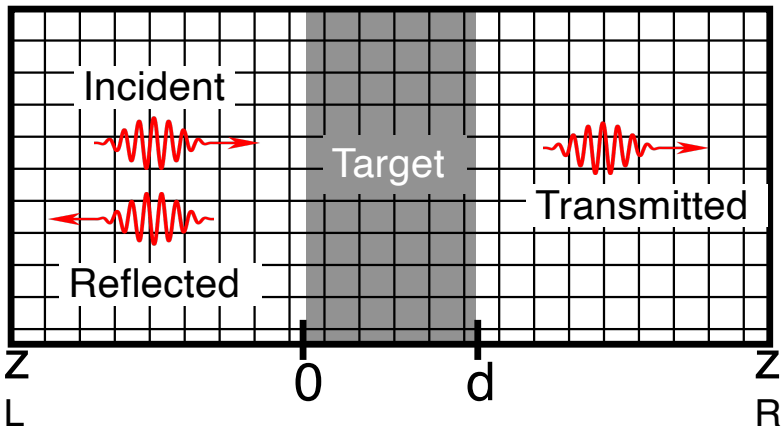
Charge density change



Max. possible thickness ~50nm
limited by computational capability

Microscopic (Single-scale) vs. Macroscopic (Multi-scale)

Microscopic Maxwell+TDDFT



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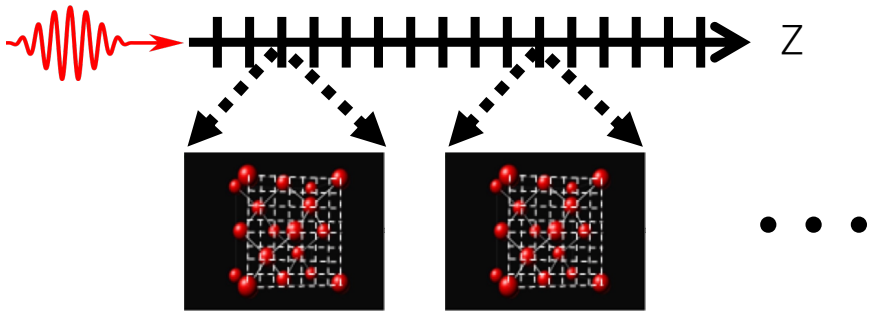

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Multiscale approach using **different** spatial grid

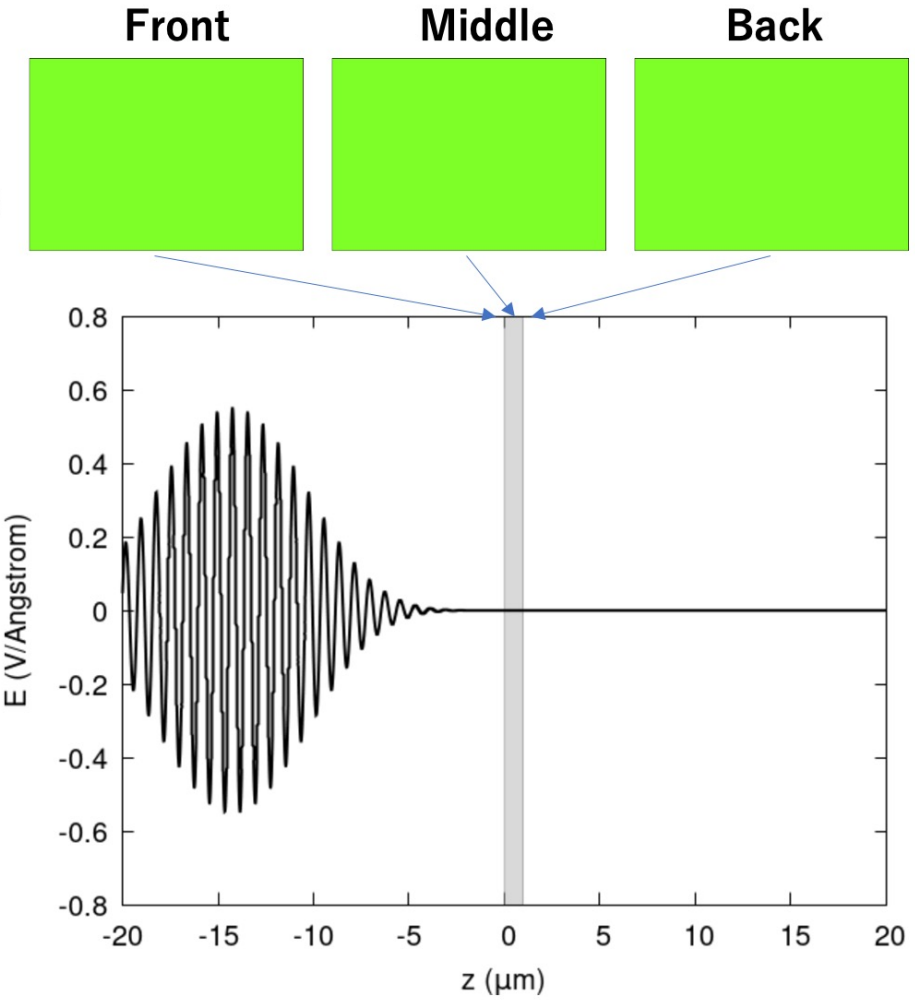
nonlinear only

K. Yabana *et al.*, PRB **85**, 045134 (2012).

Macroscopic (multi-scale) Maxwell-TDDFT: pulsed light on 1μm Si film

Change of electron density from ground state

$$\Delta n(\mathbf{r},t) = n(\mathbf{r},t) - n_{GS}(\mathbf{r})$$



~200 grid points for 1μm film

Thin film
Silicon, 1 μm thick

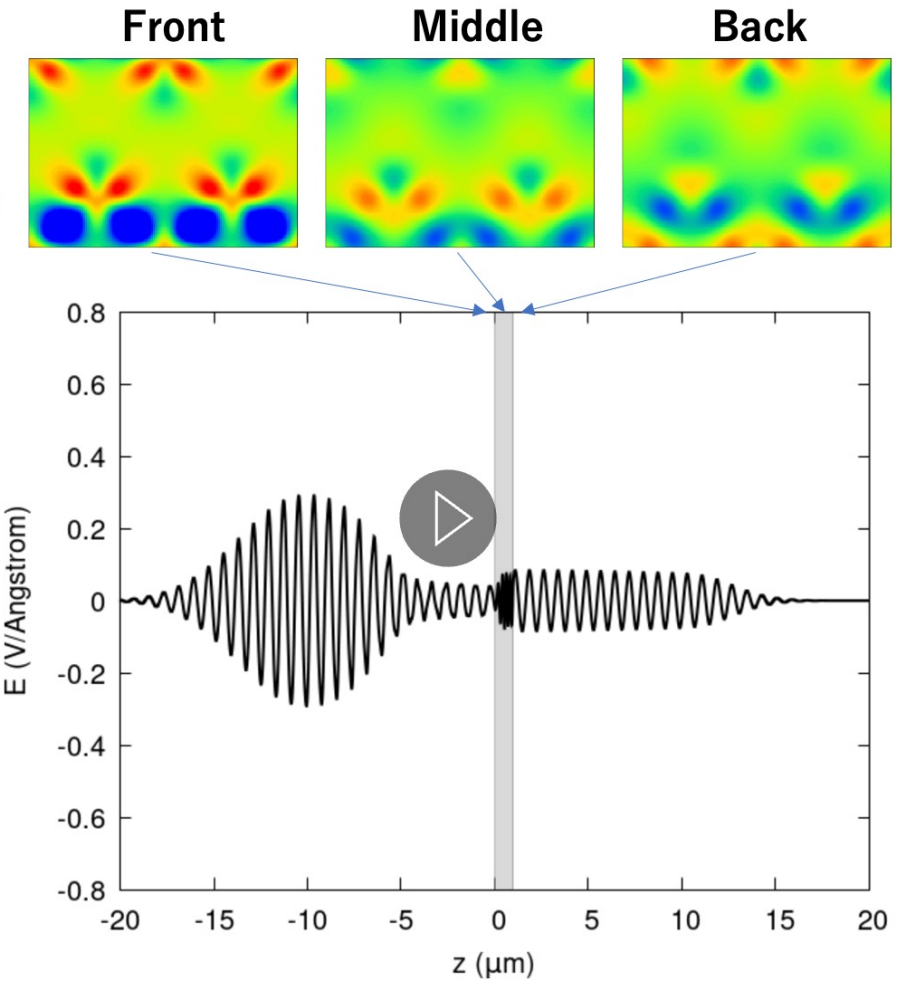
Laser pulse
800nm (1.55eV=below gap)
4×10^{12}W/cm^2

Nonlinear only

Macroscopic (multi-scale) Maxwell-TDDFT: pulsed light on 1μm Si film

Change of electron density from ground state

$\Delta n(\mathbf{r},t) = n(\mathbf{r},t) - n_{GS}(\mathbf{r})$



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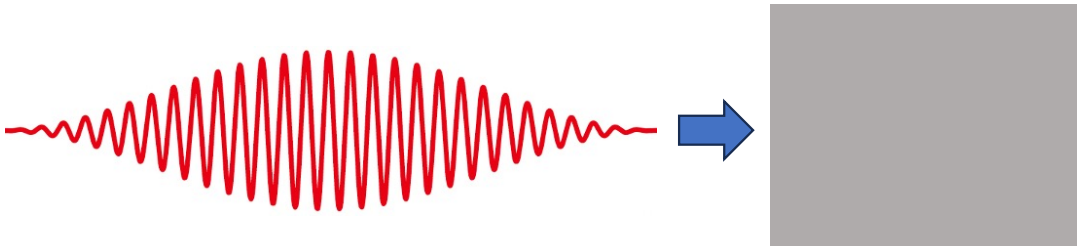
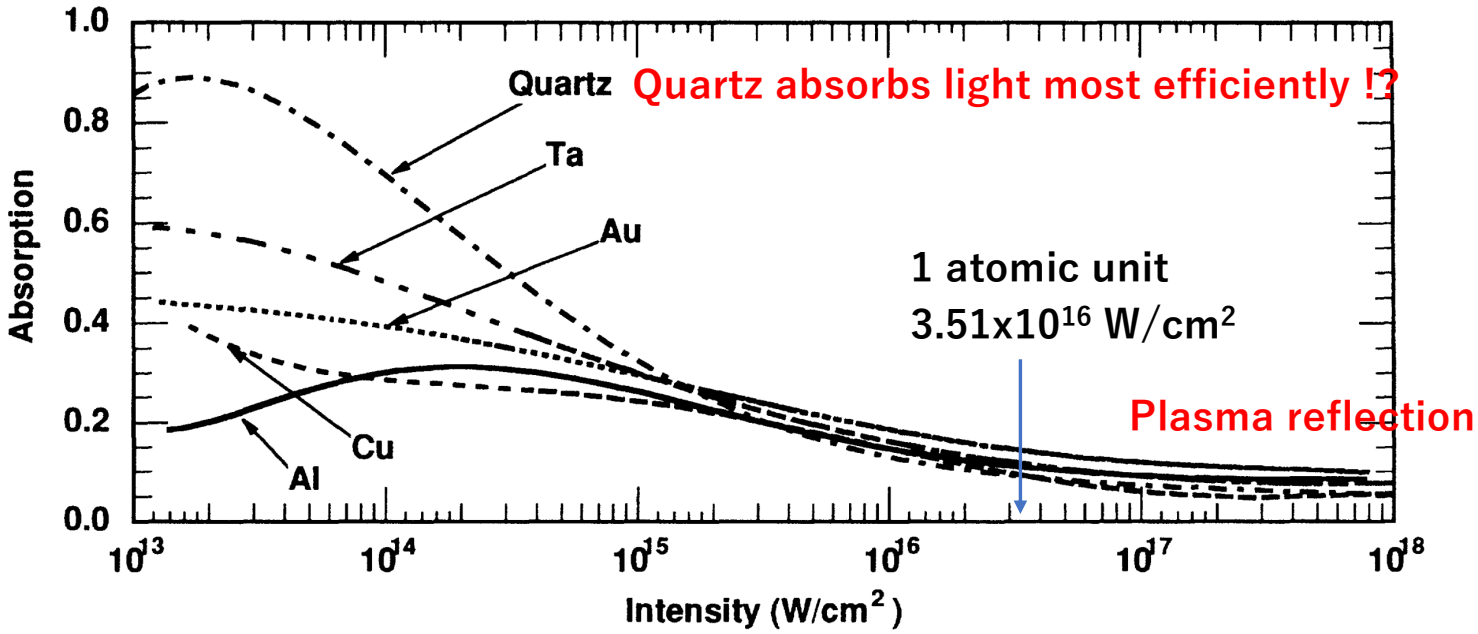
High intensity laser pulse on various materials : Systematics



Absorption
= 1 - Reflection



Experiment at LLNL, using 120fs pulse

D.F.Price et al., *Phys.Rev.Lett.***75**,252 (1995)

Atsushi Yamada
Defence Academy

High intensity laser pulse on various materials : Systematics

Experiment at LLNL, using 120fs pulse

D.F.Price et al., *Phys.Rev.Lett.***75**,252 (1995)

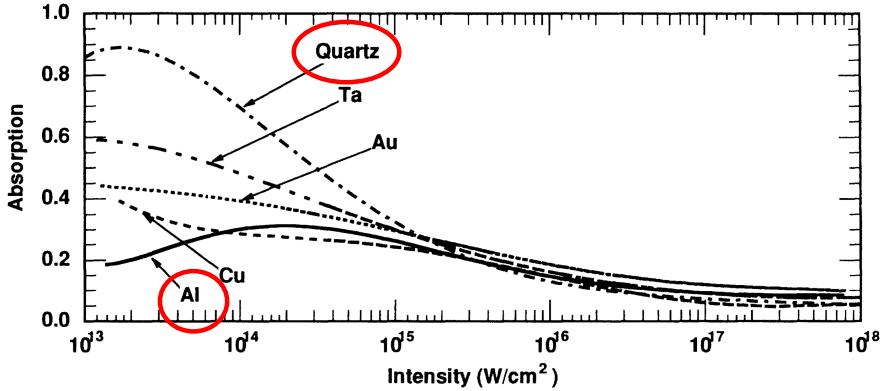
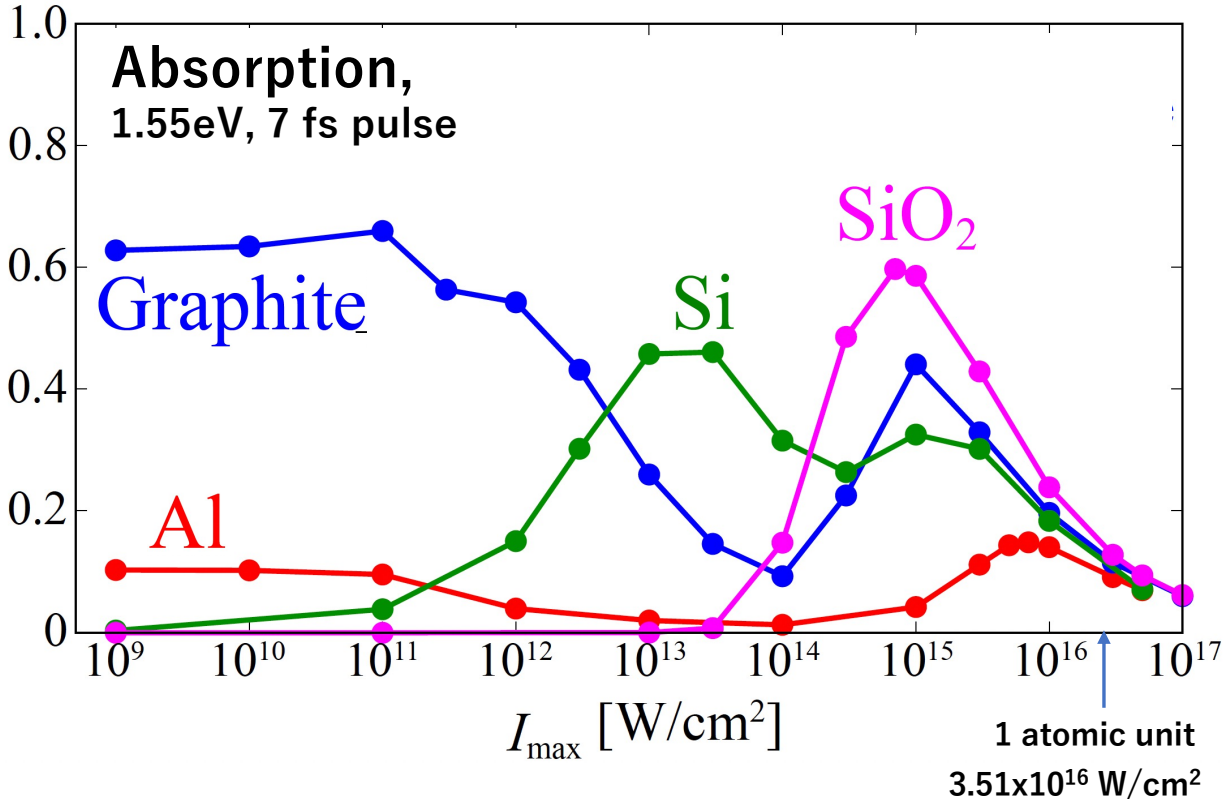


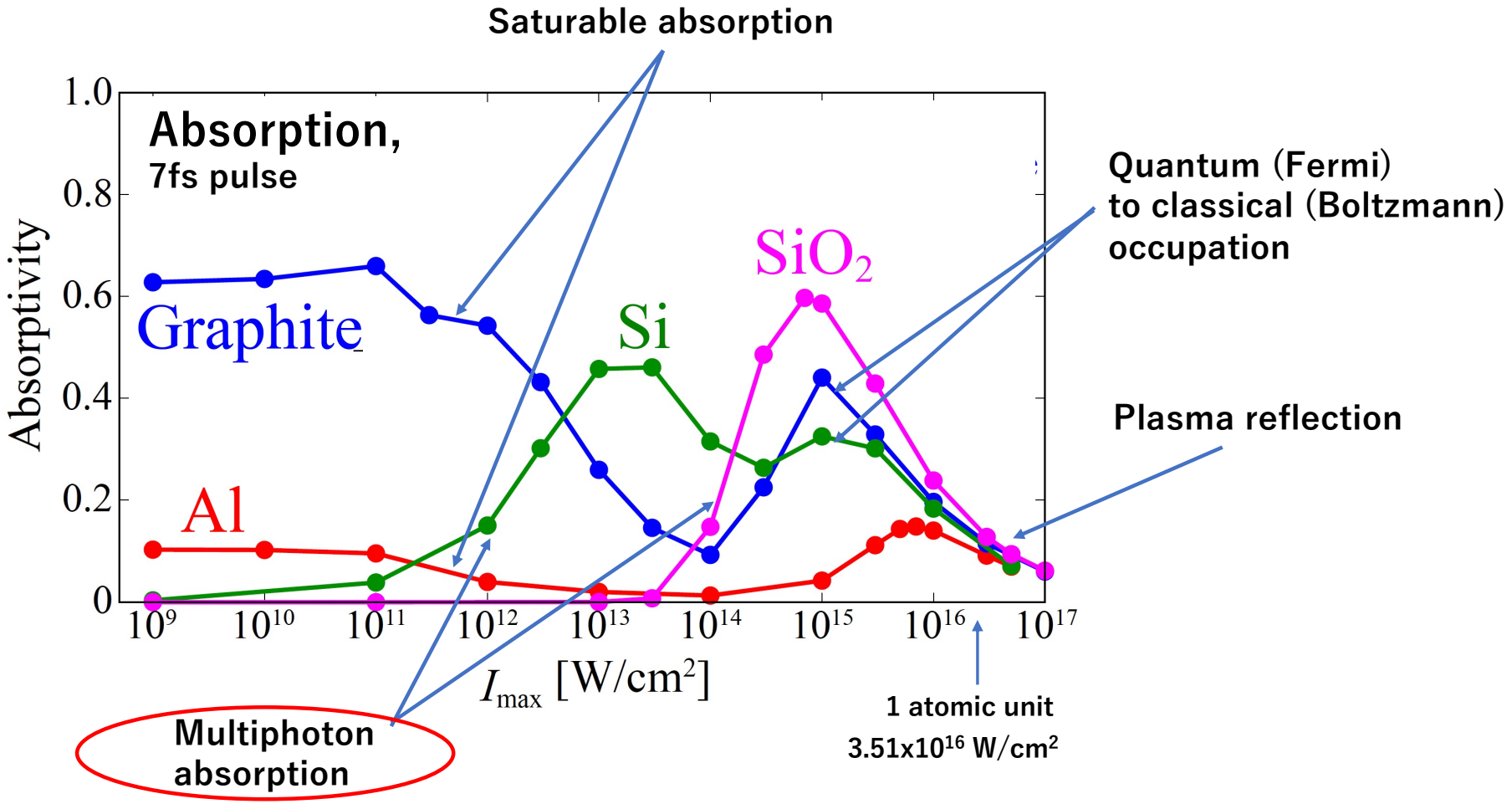
FIG. 1. Absorption fraction vs peak laser intensity for aluminum, copper, gold, tantalum, and quartz targets. In Figs. 1, 3, 4, and 5 laser intensity is the temporal and spatial peak value of the laser intensity.

Multiscale Maxwell-TDDFT calculation

A. Yamada, K. Yabana, Phys. Rev. B109, 245130 (2024)

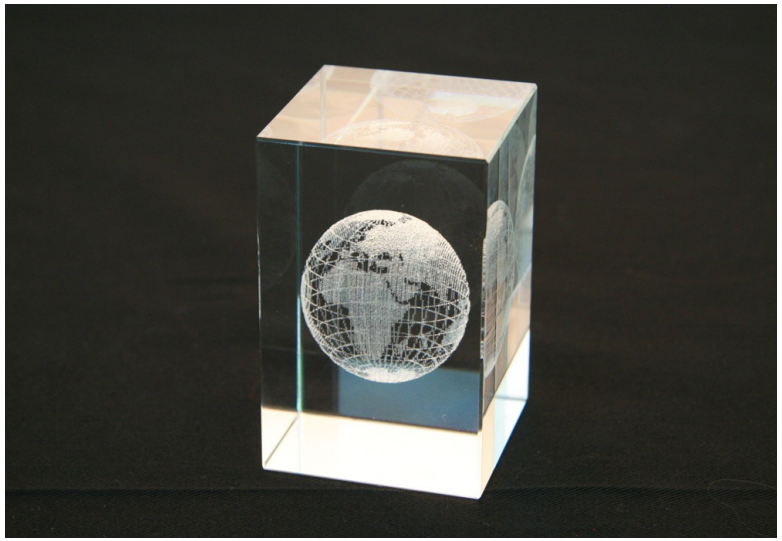


Nonlinear optical response: Mechanisms

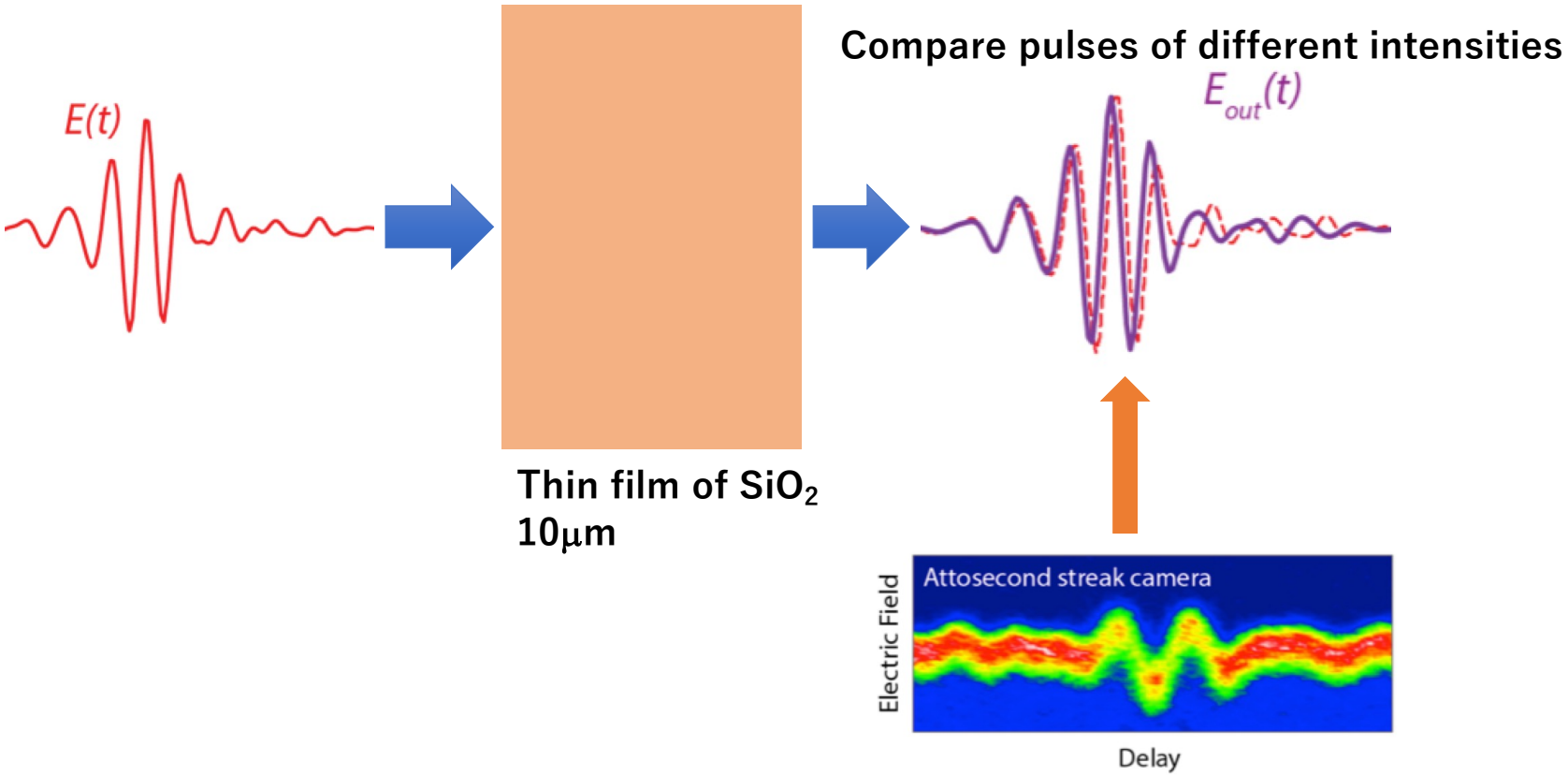


At which intensity of light, glass starts to absorb light?

Laser processing of dielectrics



Laser pulse propagation through SiO_2 10μm thin film

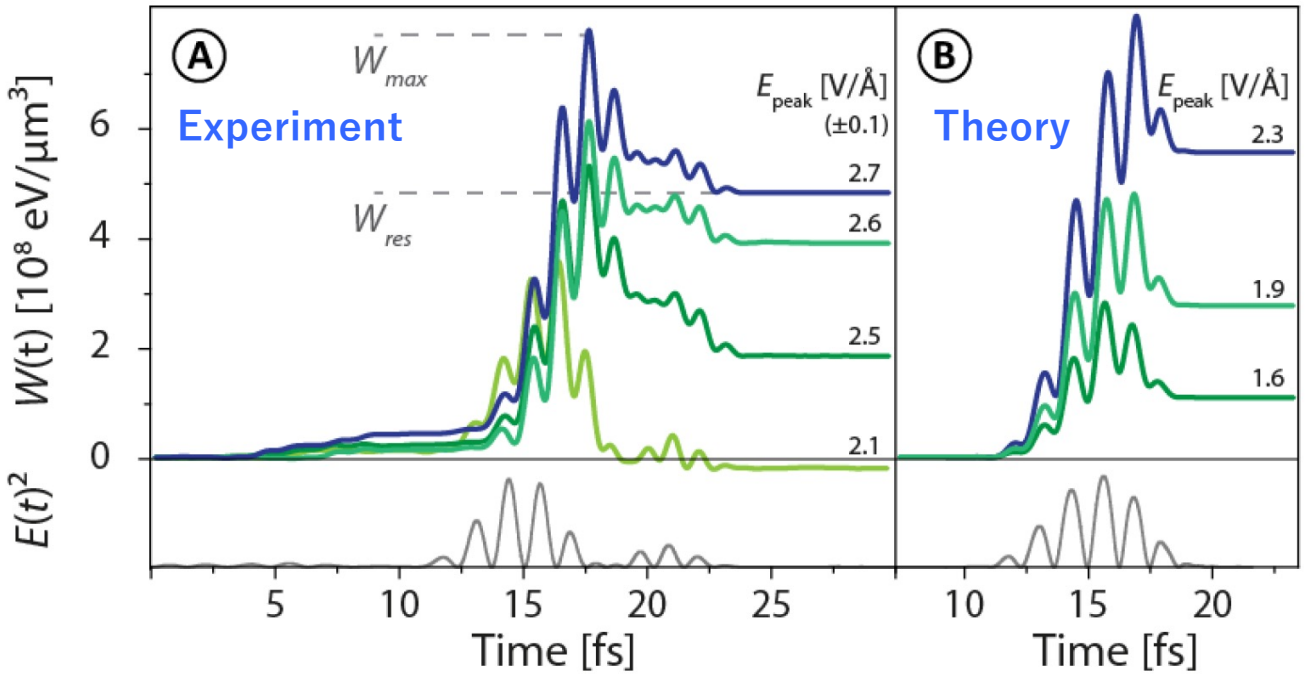


EXP: Attosecond streaking measurements
by Max Planck Inst. Quantum Optics

Shunsuke Sato
U. Tsukuba → Tohoku U.

Energy deposition from laser pulse to SiO_2 at mid point (5μm)

Comparison between theory and experiment



A. Sommer et.al, Nature 534, 86 (2016).
(exp: Max Planck Institute for Quantum Optics)

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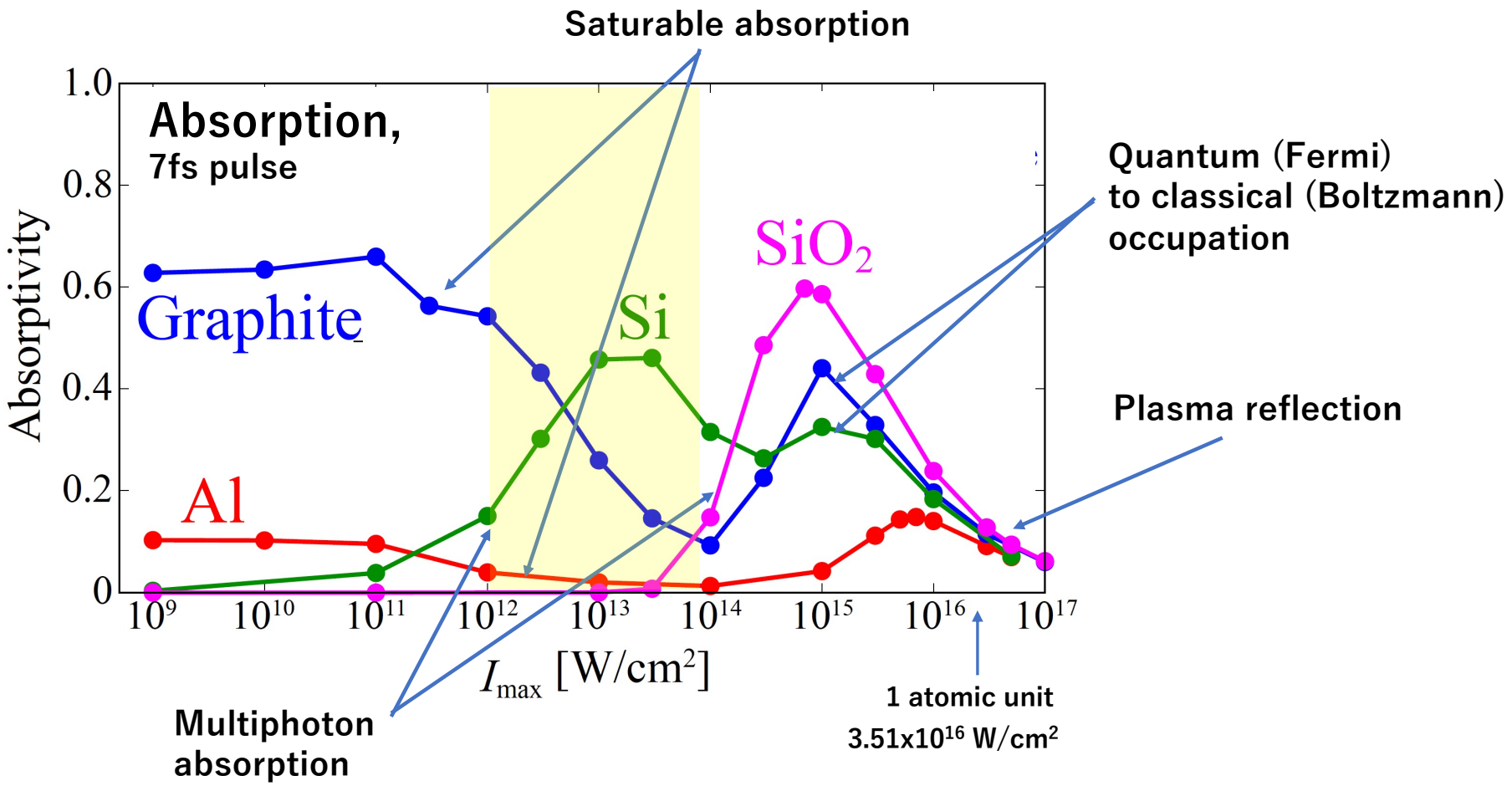
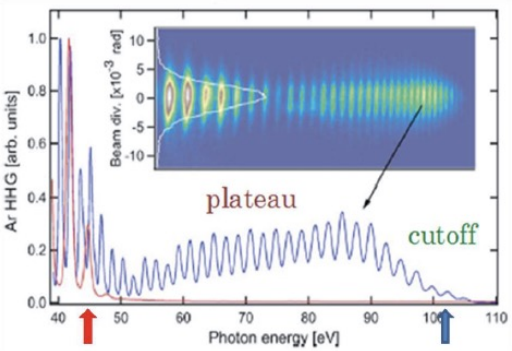


High harmonic generation (HHG)

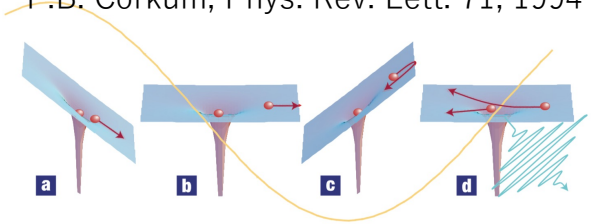
High harmonic generation from atoms

Soft X-ray from visible light



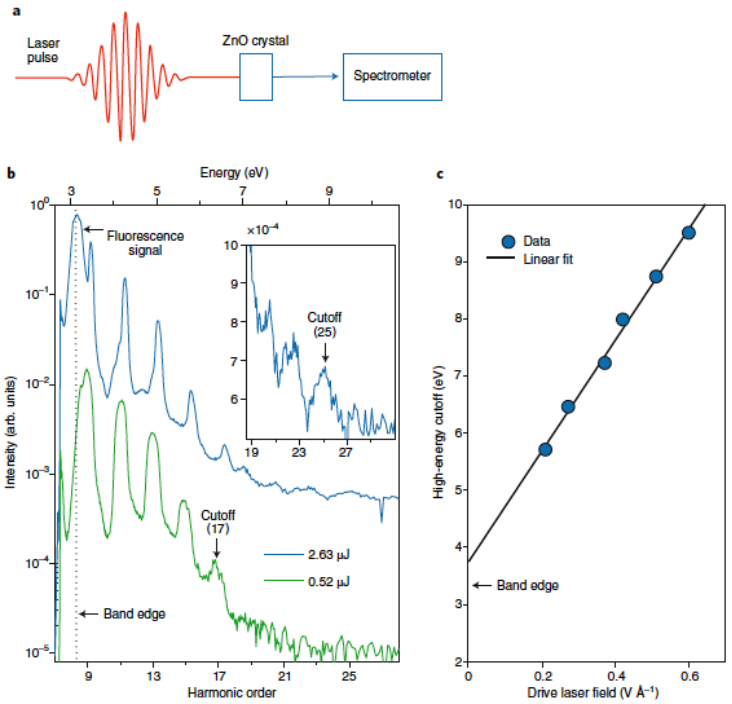
3 step model (electron rescattering)

P.B. Corkum, Phys. Rev. Lett. 71, 1994 (1993)



P.B. Corkum, F. Krausz, Nature Phys. 3, 380 (2007)

High harmonic generation from solids



S. Ghimire et al, Nat. Phys. 7, 138 (2011)

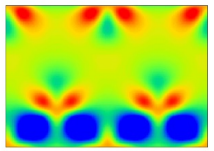
S. Ghimire, D.A. Reis, Nature Physics 15, 10 (2019)

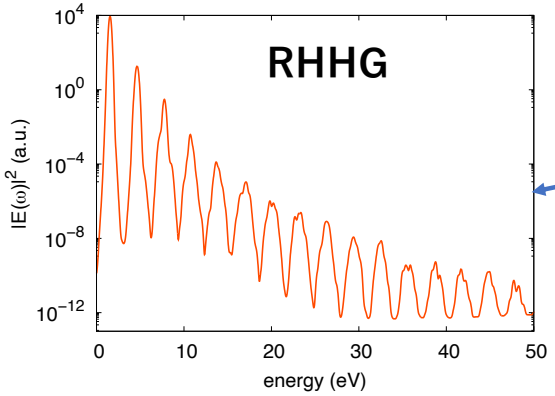
High harmonic components in transmission/reflection waves

S. Yamada et.al, Phys. Rev. B107, 035132 (2023)

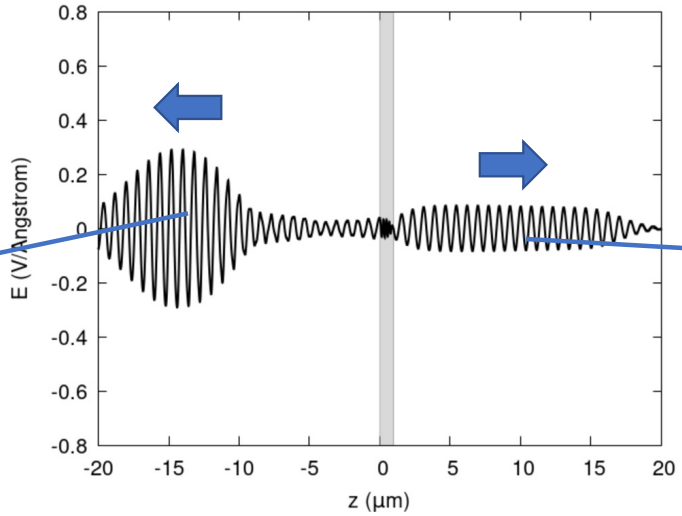
Thin film
Silicon, 1 μm thick

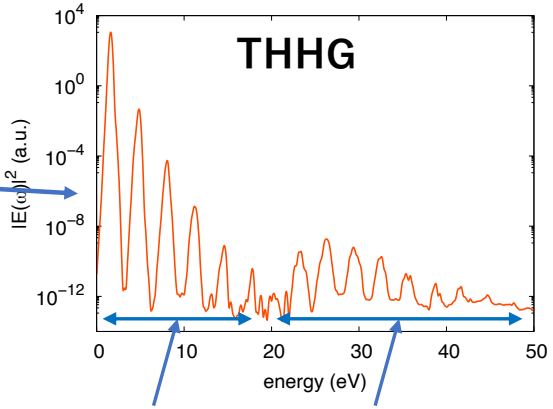
Laser pulse
800nm (1.55eV=below gap)
4×10^{12}W/cm^2





Generated at front surface





Back surface

Front surface

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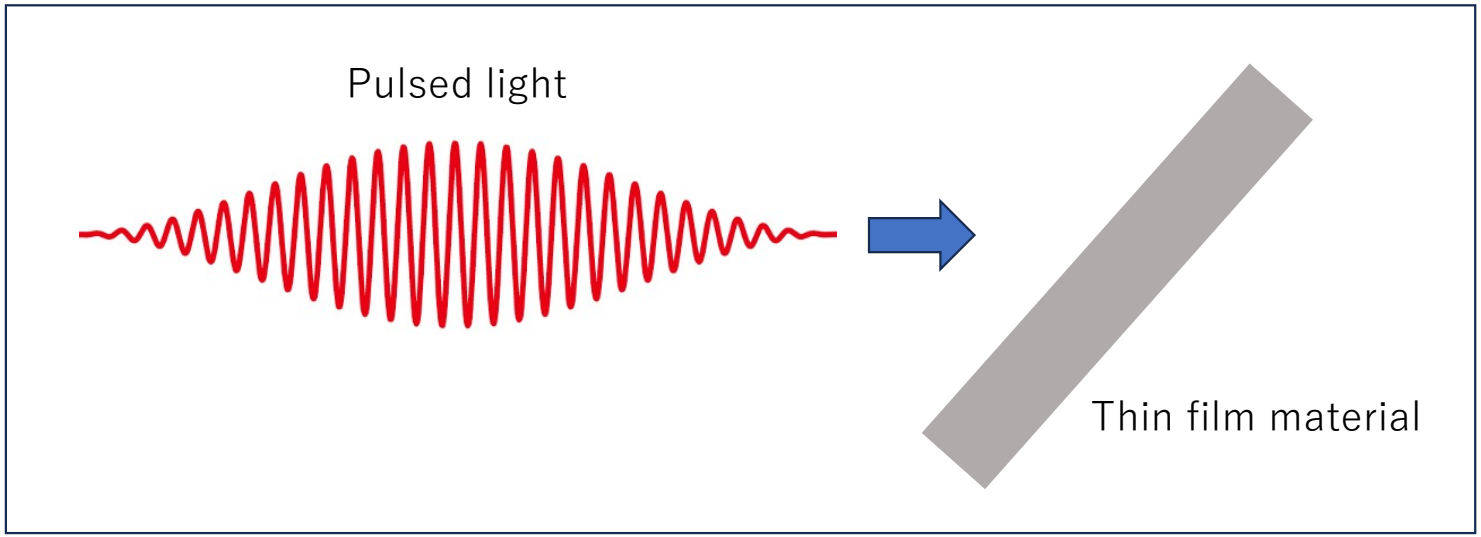
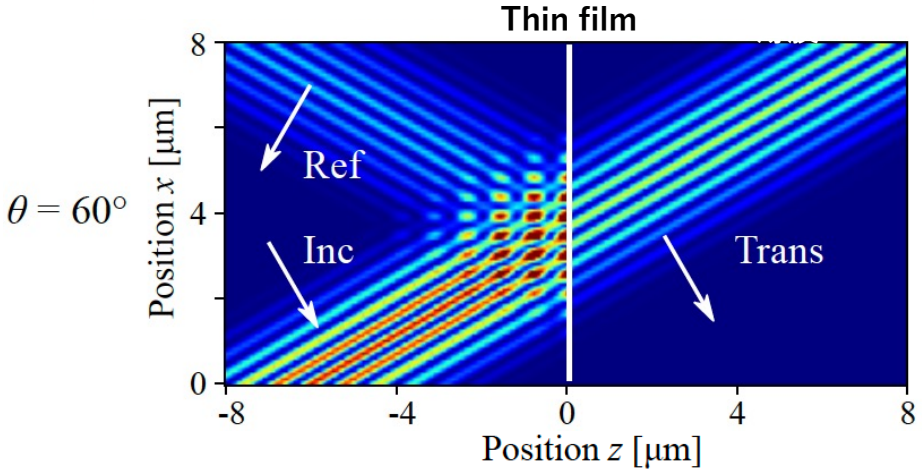
An irradiation of a thin material by a pulsed light at oblique incidence



Multiscale Maxwell-TDDFT calculation at oblique incidence

M. Uemoto, K. Yabana, Opt. Exp. 30, 23664 (2022), K. Yabana et.al, in preparation



Translational symmetry involving time and space

$$\boldsymbol{A}(\boldsymbol{R},t) = \boldsymbol{a}\left(Z, t - \frac{X\sin\theta}{c}\right)$$

$$\boldsymbol{J}(\boldsymbol{R},t) = \boldsymbol{j}\left(Z, t - \frac{X\sin\theta}{c}\right)$$

functions of z and t only

$$\nabla \times \boldsymbol{B} = \frac{4\pi}{c}\boldsymbol{J} + \frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{E},$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{B} = 0,$$

***s*-polarization**

$$\frac{\cos^2\theta}{c}\frac{\partial}{\partial t}e_y(z,t) = \frac{\partial}{\partial z}b_x(z,t) - \frac{4\pi}{c}j_y(z,t)$$

$$\frac{1}{c}\frac{\partial}{\partial t}b_x(z,t) = \frac{\partial}{\partial z}e_y(z,t)$$

***p*-polarization**

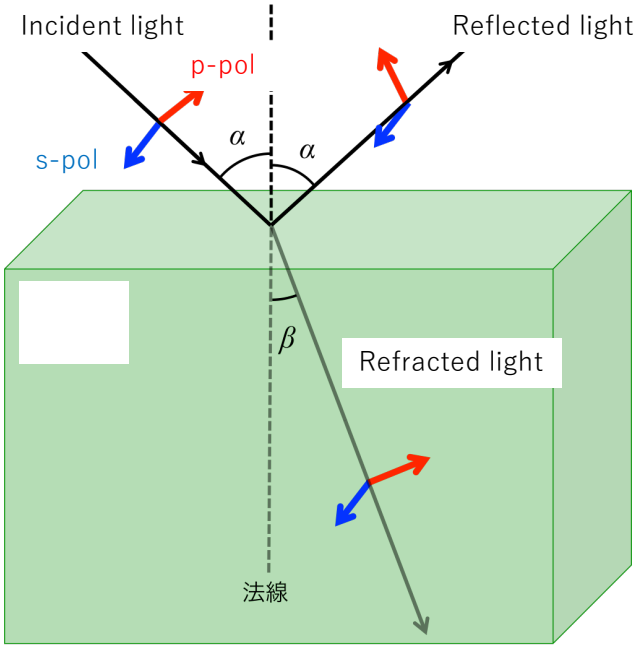
$$\frac{1}{c}\frac{\partial}{\partial t}e_x(z,t) = -\frac{\partial}{\partial z}b_y(z,t) - \frac{4\pi}{c}j_x(z,t)$$

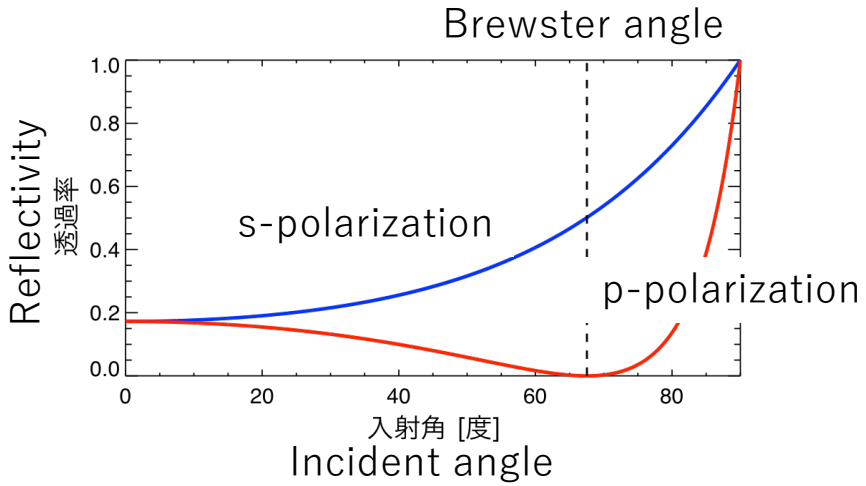
$$\frac{\cos^2\theta}{c}\frac{\partial}{\partial t}b_y(z,t) = -\frac{\partial}{\partial z}e_x(z,t) + \frac{4\pi}{c}\sin\theta j_z(z,t)$$

Oblique incidence can be calculated with the same computational cost as normal incidence.

Oblique-incident light propagation: linear optics

s- and p-polarizations

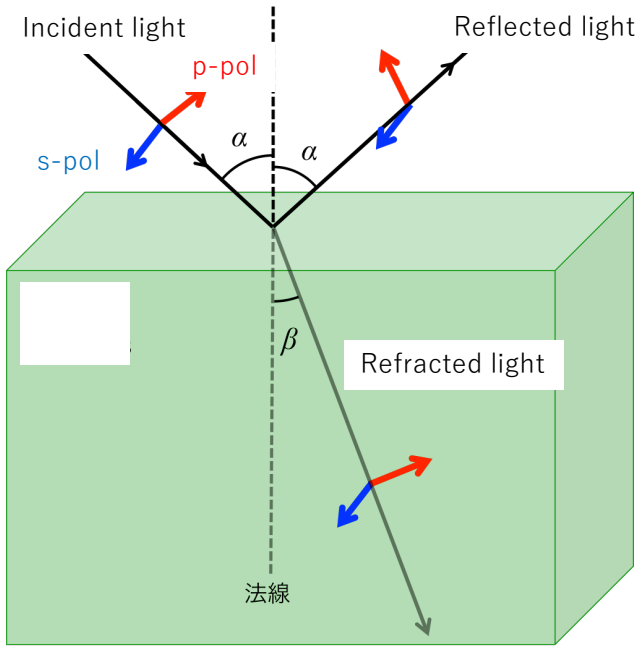




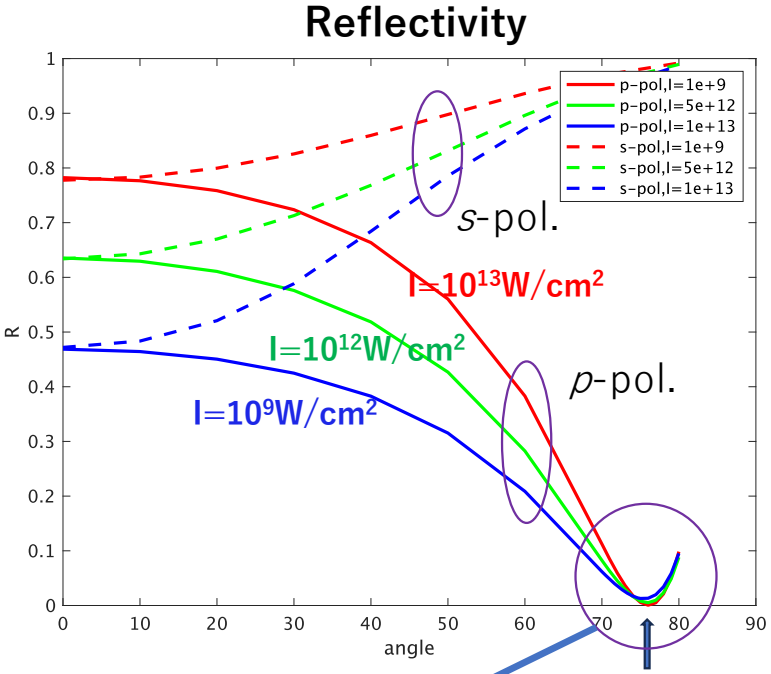
For p-polarization, zero-reflection (Brewster) angle appears.

Reflectivity for strong field : Si thin film (50nm)

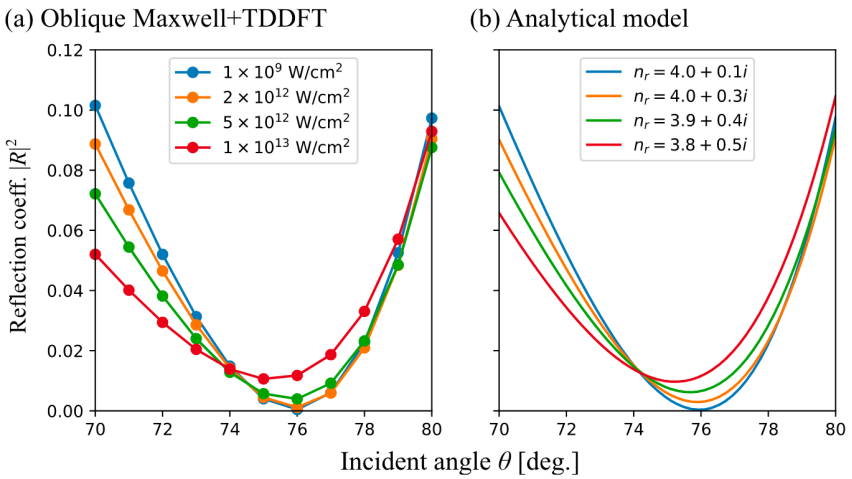
s- and p-polarizations



Brewster's angle appears robustly against intensity

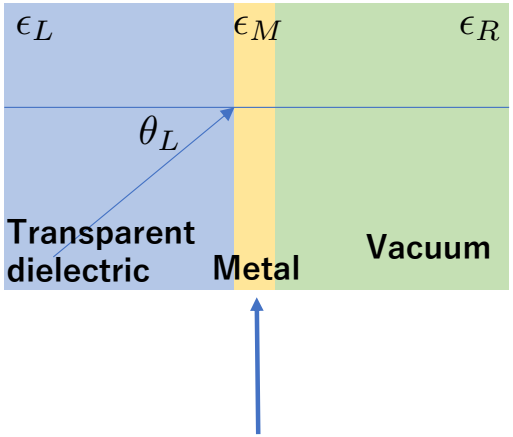


Brewster's angle



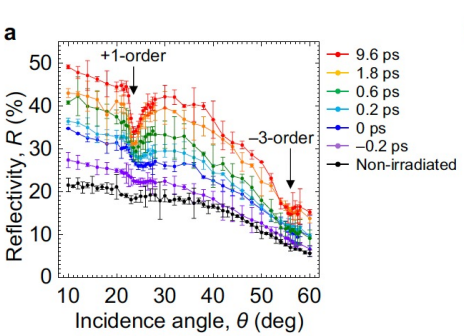
Nonlinearity described by the change of index of refraction

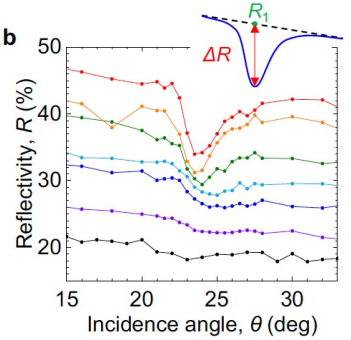
Nonlinearity in Surface Plasmon Polariton?



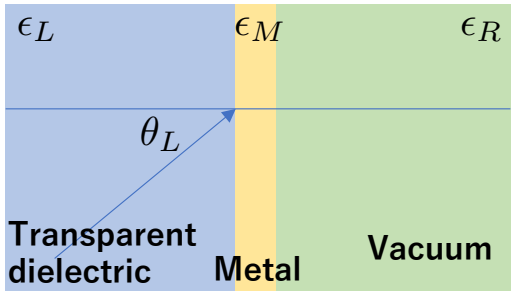
- **Nonlinearity in metals?**
- **Even dielectrics can produce SPP by metallization?**

Indication of SPP in Si
M. Tateda, Y. Iida, G. Miyaji, Sci. Rep. 13, 18414 (2023)





Surface Plasmon Polariton



Linear electromagnetism

$$R = \left| \frac{A^r}{A^i} \right|^2$$

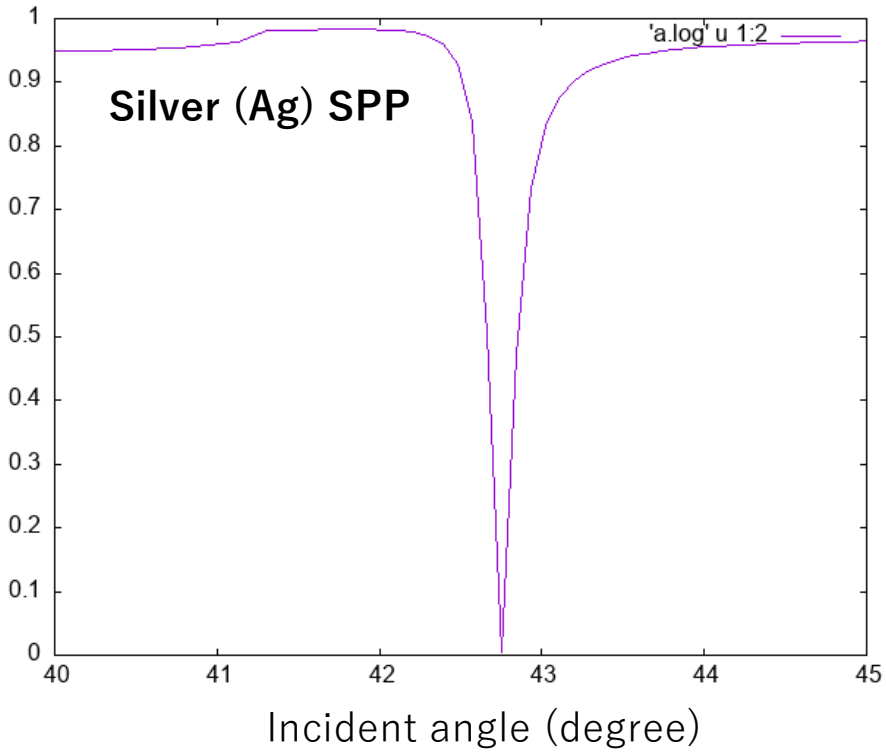
$$\frac{A^r}{A_i} = -\frac{r_{12} - r_{23} e^{2ik_M d}}{1 - r_{12} r_{23} e^{2ik_M d}}$$

$$r_{12} = \frac{f_{L,-}}{f_{L,+}}, \qquad r_{23} = \frac{f_{R,-}}{f_{R,+}} \qquad k_M = \frac{\omega}{c} \sqrt{\epsilon_M - n_L^2 \sin^2 \theta_L}$$

$$f_{(R,L),\pm} = n_{(R,L)} \left\{ \frac{\sqrt{\epsilon_{(R,L)} - \epsilon_L \sin^2 \theta_L}}{\epsilon_{(R,L)}} \pm \frac{\sqrt{\epsilon_M - \epsilon_L \sin^2 \theta_L}}{\epsilon_M} \right\}$$

$$\sqrt{\epsilon_R - \epsilon_L \sin^2 \theta_L} \to i \sqrt{\epsilon_L \sin^2 \theta_L - \epsilon_R}$$

$\epsilon_L = 2.3$, $\epsilon_R = 1.0$, $\epsilon_M = -18.23 + 0.482i$, $d = 1000$ au $= 52.9$ Å.

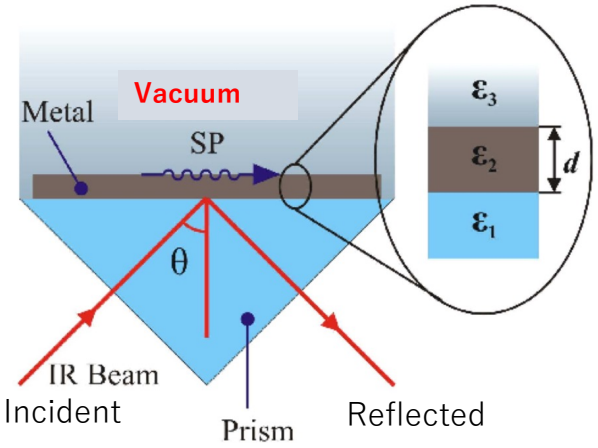


Nonlinear Surface Plasmon Polariton : Aluminum thin film (10nm)

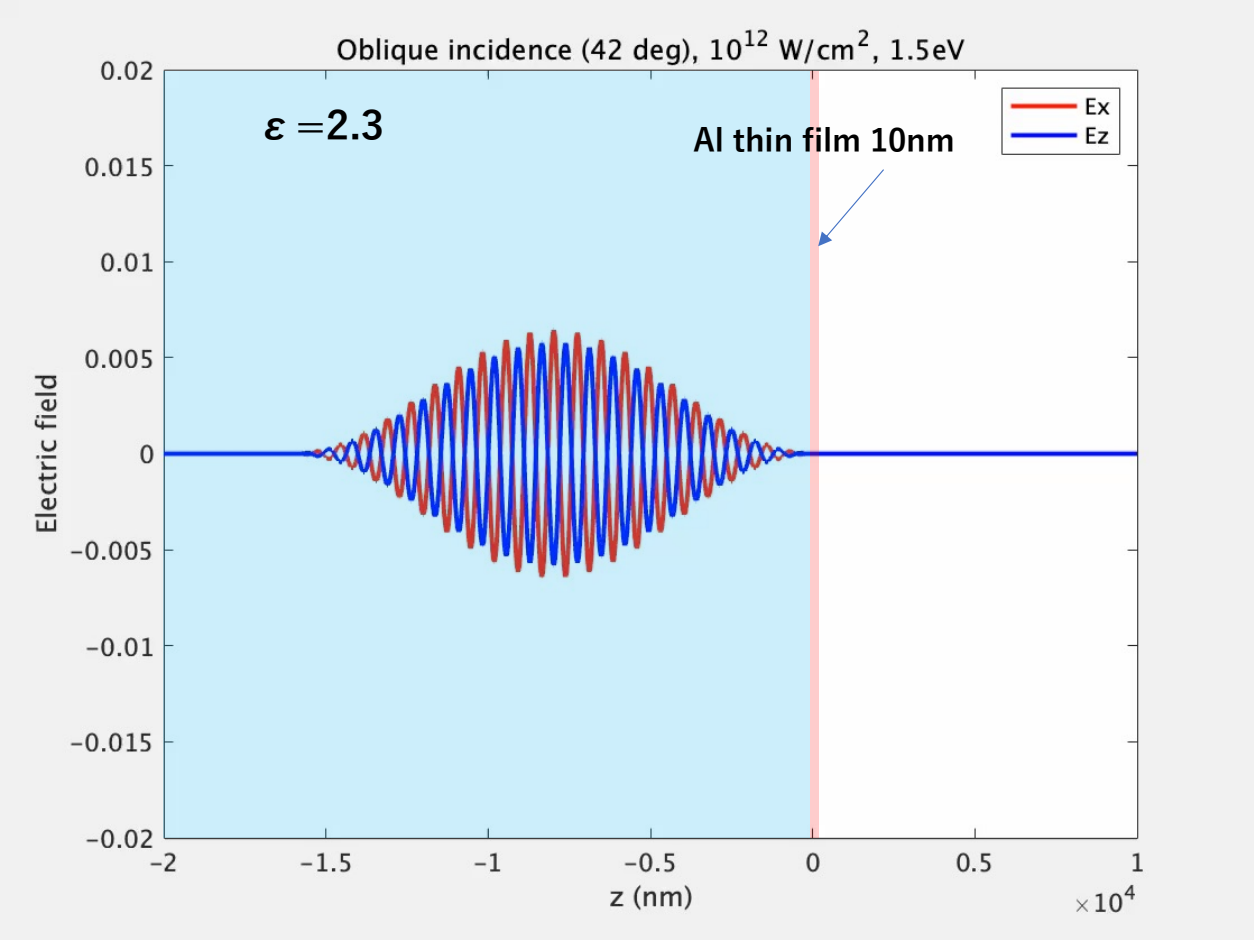
Multiscale Maxwell-TDDFT calculation at oblique incidence

Pulse information: I=10^{12} W/cm^2, hw=1.5eV, 42 deg., *p*-polarization

Kretchmann geometry



Surface plasmon mode appears when evanescent field appears in the vacuum region.

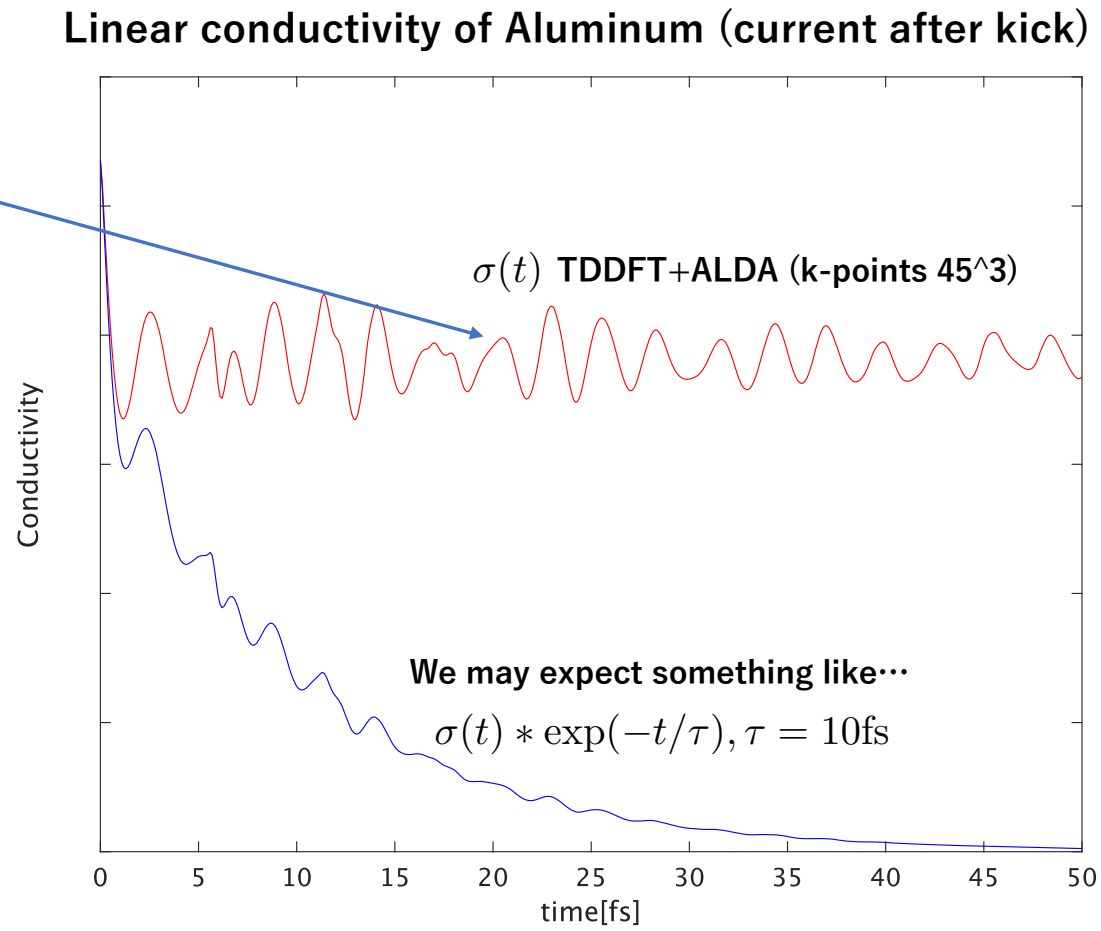


Contents

- About “Extreme Optics”
- Maxwell-TDDFT
- Some applications
- Maxwell-TDDFT at oblique incidence (under progress)
- Dephasing and density-matrix unfolding (under progress)

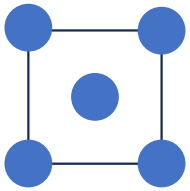
How reliable is TDDFT for metals?

TDDFT+ALDA lacks Drude damping

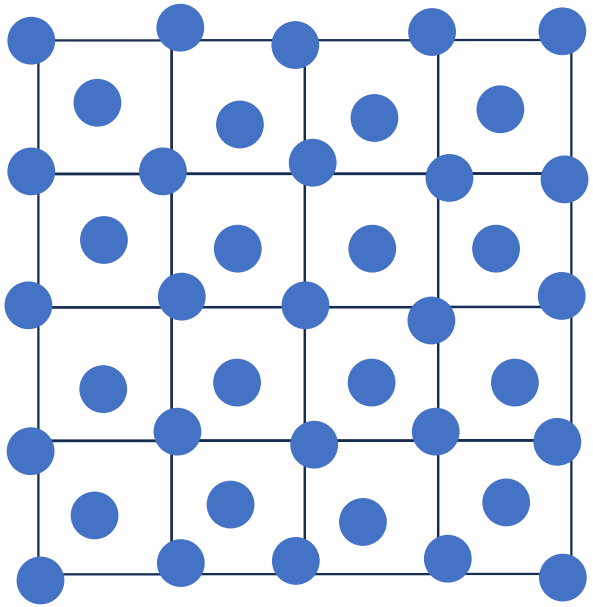


Simple method to incorporate electron-phonon scattering

Supercell calculation with thermally distorted (frozen) ionic positions



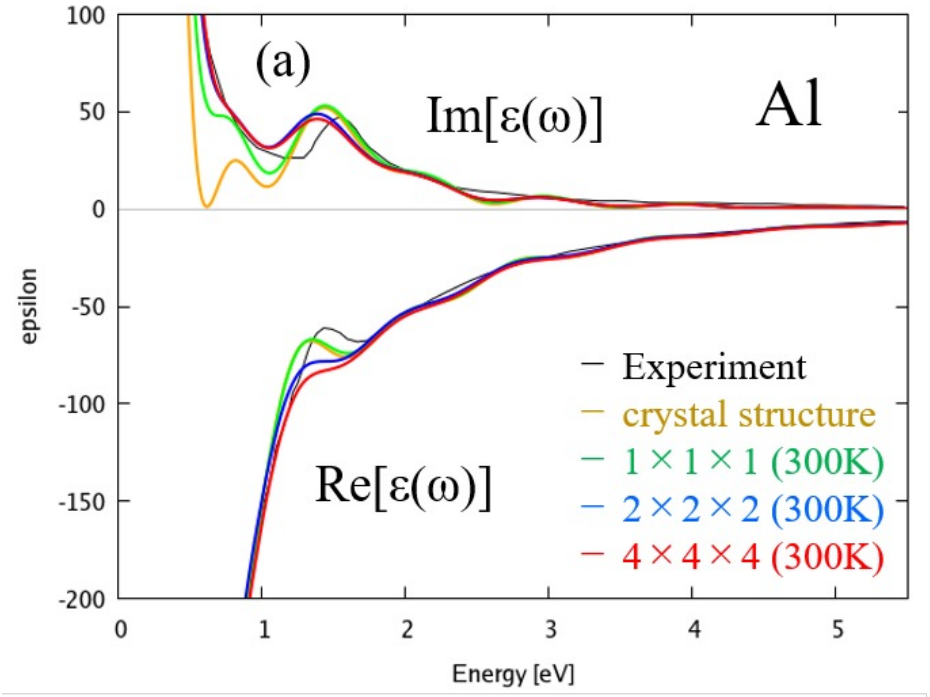
Primitive cell

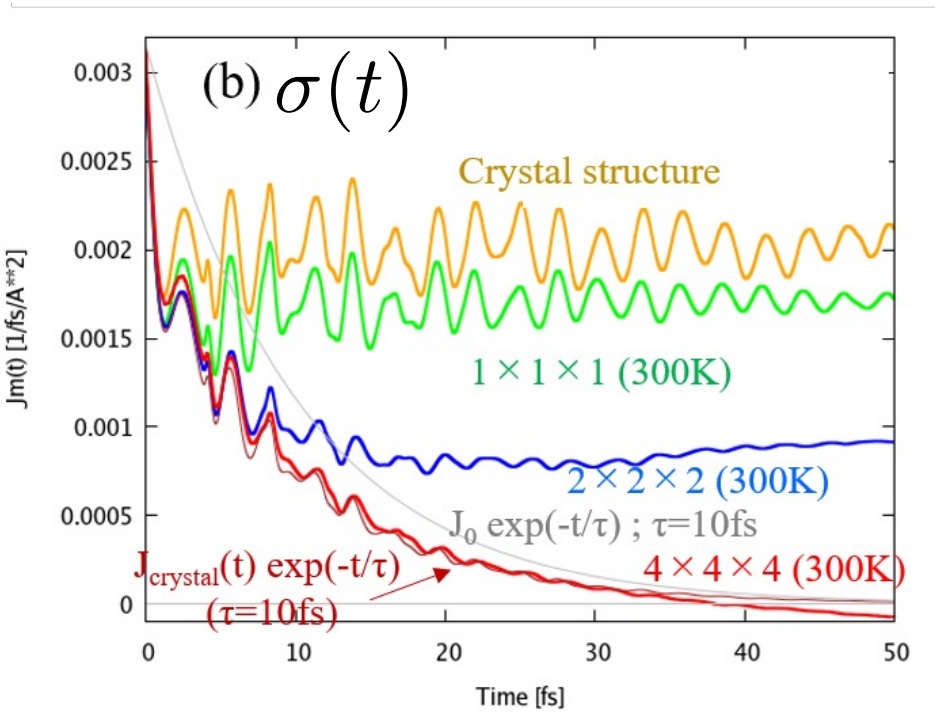


4x4 supercell

TDDFT for conductivity of Al: supercell calculations

with thermally distorted (frozen) ionic positions





4x4x4 supercell containing 256 atoms is sufficient to describe Drude damping

Dephasing in crystalline solids

- Supercell calculation with thermal distortion (frozen atomic position) explains Drude damping of 10 fs time scale.

- Single configuration is enough to describe damping (ensemble average not necessary).

Next question:

Is description of dephasing using T_2 term supported microscopically?

$$\left[i\frac{\partial}{\partial t} + \frac{i(1-\delta_{nn'})}{T_2} - \epsilon_{nn'\mathbf{k}}\right]\rho_{nn'\mathbf{k}}(t)$$
$$= \mathbf{E}(t)\sum_m (\rho_{nm\mathbf{k}}(t)d_{mn'\mathbf{k}} - d_{nm\mathbf{k}}\rho_{mn'\mathbf{k}}(t))$$

- Using density matrix, dephasing is often described as the attenuation of off-diagonal elements.

- Single-configuration supercell calculation is a pure state dynamics in folded k-space.

- Unfolding the density matrix into primitive-cell k-space, how damping looks like ?

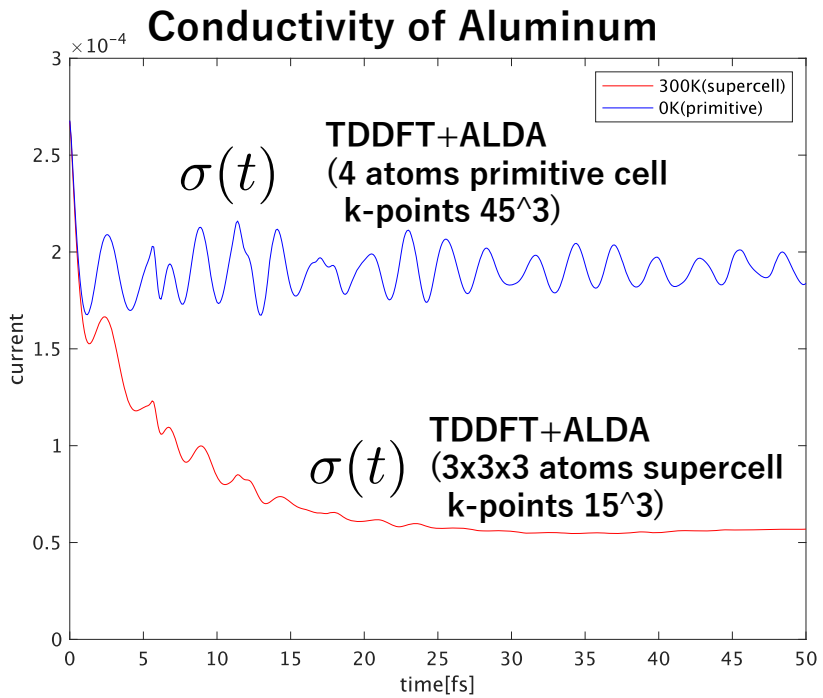
In unfolded density matrix, how Drude damping looks like?

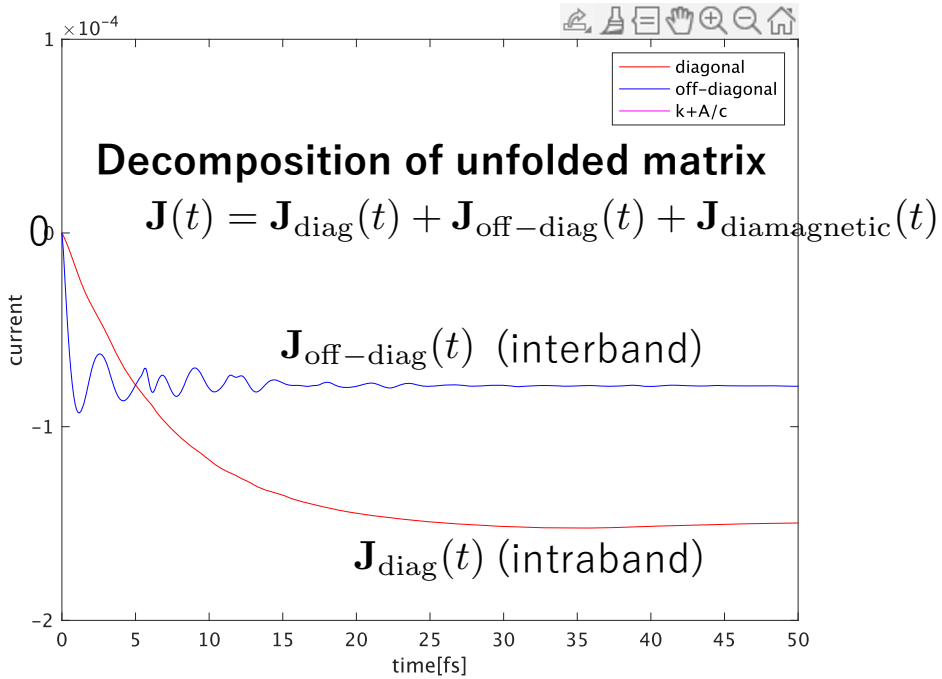
A. Yamada, K. Yabana, in preparation

Density-matrix unfolding $\rho_{mm'\mathbf{K}}(t) \rightarrow \rho_{nn'\mathbf{k}}(t)$

supercell primitive cell

$$\mathbf{J}(t) = \frac{1}{V}\sum_{nn'\mathbf{k}} \rho_{nn'\mathbf{k}}(t)\langle u_{n\mathbf{k}}|(\mathbf{p}+\mathbf{k}+\mathbf{A}(t)/c)|u_{n'\mathbf{k}}\rangle$$





Drude damping appears in diagonal elements of primitive-cell density matrix

Summary

In current frontier of optics characterized by ultrafast, nonlinear, and nonlocal,
traditional EM or QM approaches are not sufficient.

We develop first-principles electromagnetic analysis, combining EM and QM (Real-time TDDFT)

There are two connection methods: macroscopic (multiscale) and microscopic (single-scale)

Recent topics under progress includes oblique-incident Maxwell-TDDFT, dephasing description

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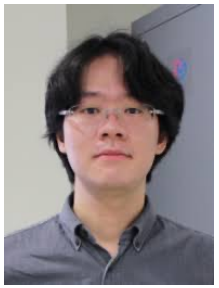

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