How to Use SALMON-2: Periodic Systems

Overview

Mitsuharu UEMOTO

Center for Computational Sciences, University of Tsukuba

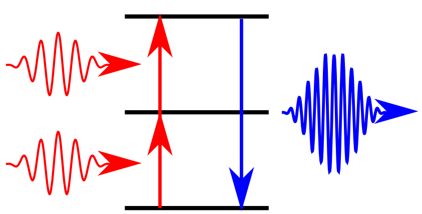
Introduction of RT-TDDFT for Solid

Real-Time TDDFT for “Nonlinear Optics” in Solid

- First-principle TDDFT-based electron dynamics simulation
- Light-matter interaction between **“strong laser pulse”** and “**solid crystal**”

Real-Time Calculation

- Linear response
  - Dielectric Function
- Nonlinear response:
  - SHG, THG, Kerr effects

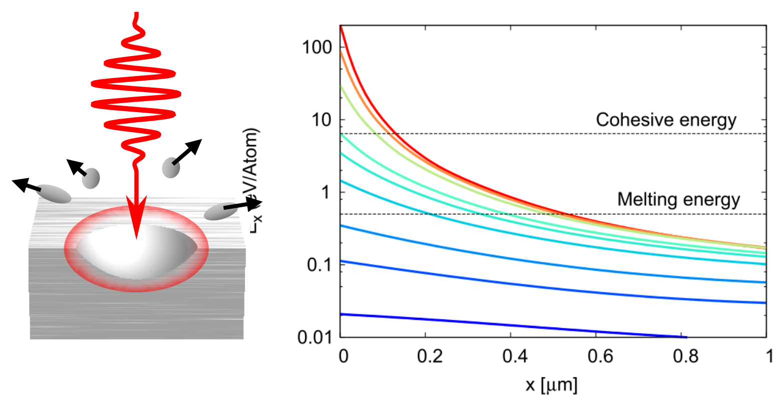


$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \cdots$$

- Light matter energy transfer

Multiscale calculation

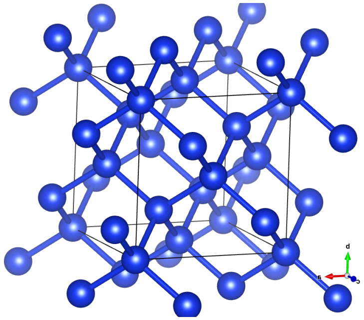
- Light Propagation
  - Damaging / Ablation
  - Non-thermal laser processing

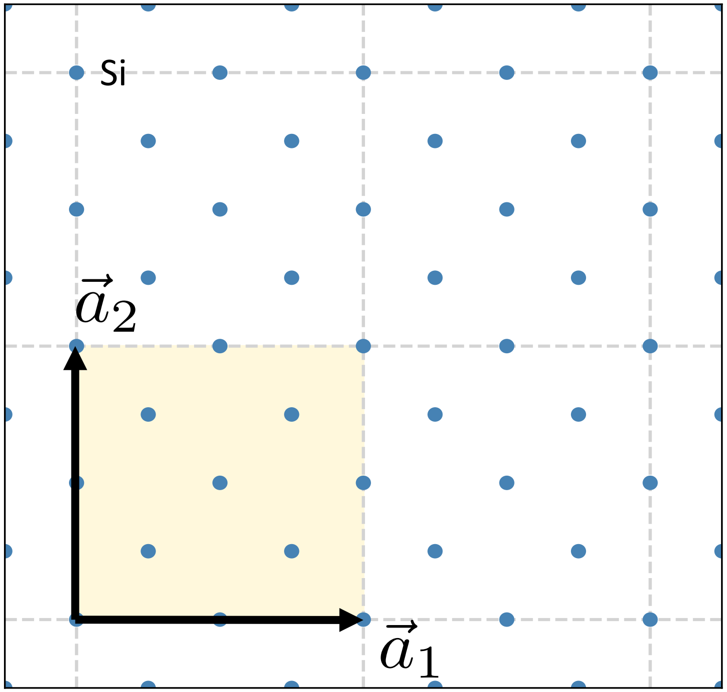


S.A. Sato, K. Yabana et al, PRB **92**, 1 (2015).

Solid Crystal


Silicon (Wikipedia.org)





- **Solid Crystal**
  - Periodic structure of atoms
  - Result is unmodified to the shift by the lattice vector:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

Periodic Condition and Bloch Wavefunction

$$[\mathcal{T}_{\mathbf{R}}, \mathcal{H}] = 0$$

- Hamiltonian is invariant to the shift by R

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) \;\rightarrow \hat{T}_{\mathbf{R}}$$ Translation Operator

Hamiltonian and Translation operator has common eigenstate:

$$\mathcal{H}\psi = \epsilon\psi \quad \mathcal{T}_{\mathbf{R}}\psi = \lambda\psi$$

Bloch's theorem

The electron's wavefuntion in periodic system satisfy:

$$\psi_{b,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{kR}}\psi_{b,\mathbf{k}}(\mathbf{r})$$

k: Bloch wavevector
b: Band Index

The Bloch wavefunction can rewritten by using the periodic function u_{bk} :

$$\psi_{b,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}u_{b,\mathbf{k}}(\mathbf{r})$$

Brillioun Zone and K points

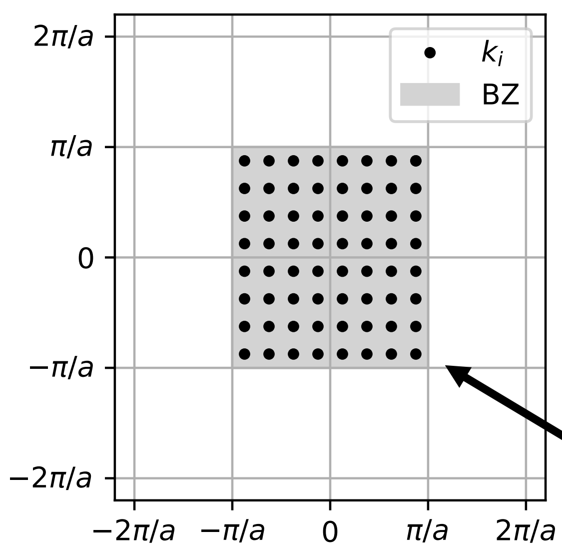
The ***k*** values with arbitrary integer *m* corresponds to the same eigenstate

$$\mathbf{k}' = \mathbf{k} + \left(\frac{2\pi m_1}{a_1}, \frac{2\pi m_2}{a_2}, \frac{2\pi m_3}{a_3}\right) \qquad u_{b,\mathbf{k}}e^{i\mathbf{k}\mathbf{R}} \leftrightarrow u_{b,\mathbf{k}'}e^{i\mathbf{k}'\mathbf{R}}$$

k-vectors are restricted in the region of the reciprocal space

$$\left(-\frac{\pi}{a_1} \le k_1 \le \frac{\pi}{a_1}\right), \left(-\frac{\pi}{a_2} \le k_2 \le \frac{\pi}{a_2}\right), \left(-\frac{\pi}{a_3} \le k_3 \le \frac{\pi}{a_3}\right)$$

→ Brillioun Zone (BZ)



Discretize BZ to finite number of ***k***-points:

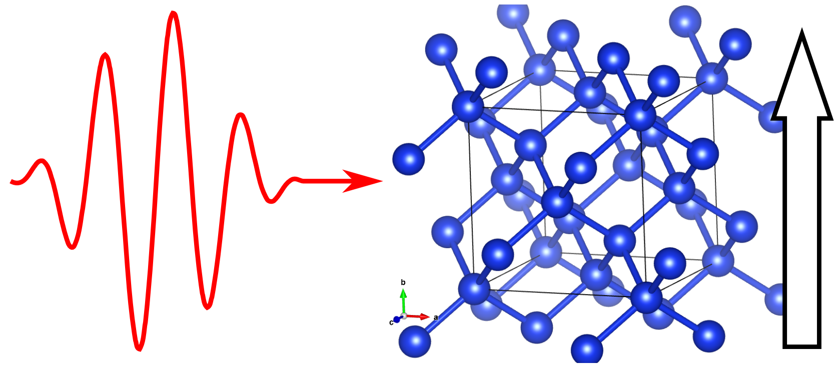
$$u_{b,\mathbf{k}} \rightarrow u_{b,\mathbf{k}_i}$$

$$\iiint \mathrm{d}\mathbf{k} f(\mathbf{k}) \rightarrow \sum_{\mathbf{k}_i} \omega(\mathbf{k}_i) f(\mathbf{k}_i)$$

Uniformly choose the k-points in the Brillioun Zone

Governing Equation in Periodic System

Incident Field $\mathbf{E}(t) = -\dot{\mathbf{A}}(t)/c$



$\mathbf{J}(t)$

Time-Dependent Kohn-Sham (TDKS) equation in Periodic System:

$$i\hbar \frac{\partial}{\partial t} u_{b,\mathbf{k}}(\mathbf{r},t) = \left[\frac{1}{2m} \left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}(t) \right)^2 + v_{\mathrm{ion}} + v_{\mathrm{H}} + v_{\mathrm{XC}} \right] u_{b,\mathbf{k}}(\mathbf{r},t)$$

KS orbit $u_{b,\mathbf{k}}$ Atomic potential v_{ion} Electron Interaction v_{H} v_{XC}

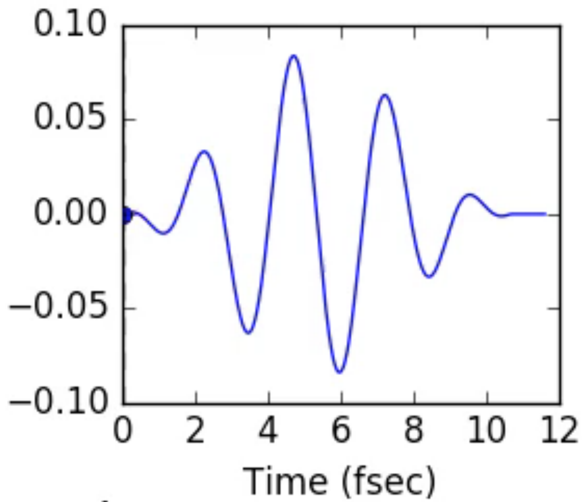
Compute TDKS equation by using Finite Difference Method on Real Space Grid

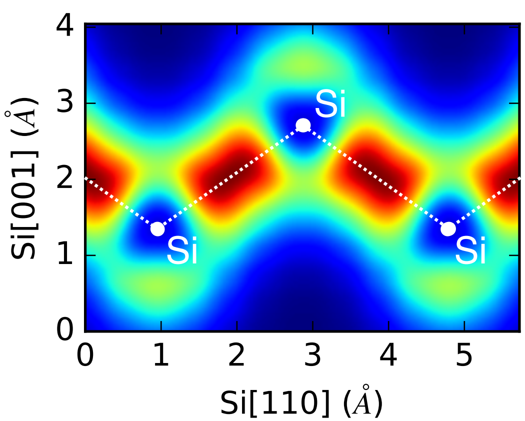
$$u_{b,\mathbf{k}}(\mathbf{r}) \rightarrow \texttt{zu(NL,NK,NB)}$$

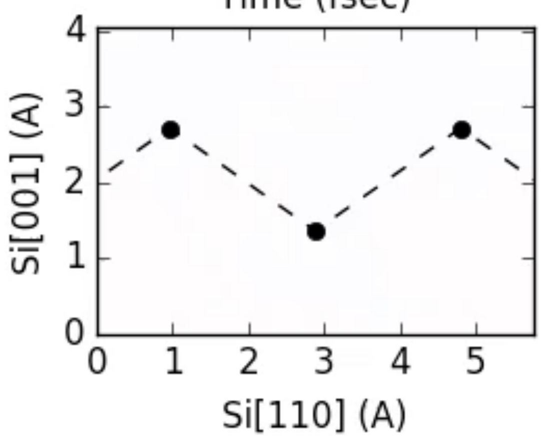
Example of RT-TDDFT Calculation

$$\mathbf{A}(t) = \mathbf{A}_0 \cos^2 \frac{\pi t}{T} \sin \omega_1 t$$

- Frequency = 1.55 [eV]
- Intensity = 10^9 [W/cm^2]
- Length = 10 [fs]







PART 1

Ground State Calculation

Ground State Calculation

Solve Kohn-Sham Equation

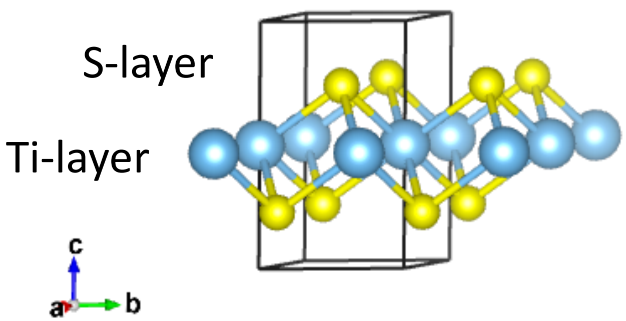
$$\varepsilon_{b,\mathbf{k}} u_{b,\mathbf{k}}(\mathbf{r}) = \left[\frac{1}{2m} \left(-\hbar\nabla + \hbar\mathbf{k}\right)^2 + v_{\mathrm{ion}} + v_{\mathrm{H}} + v_{\mathrm{XC}} \right] u_{b,\mathbf{k}}(\mathbf{r})$$

→ **Initial State of the real-time calculation**

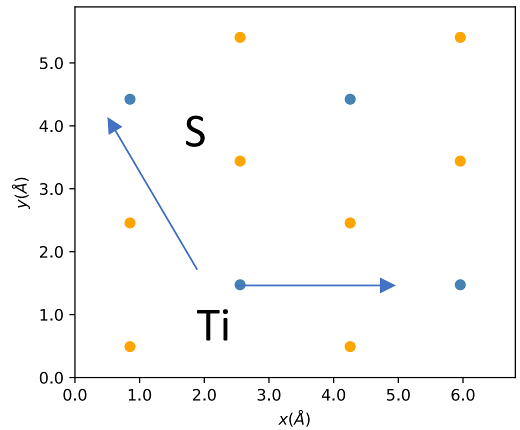
- Electron Single-particle Eigenenergy Spectra $\varepsilon_{b,\mathbf{k}}$
- Electron Density of States (DoS) $\rho(E) = \sum_{b,\mathbf{k}} \delta(E - \varepsilon_{b,\mathbf{k}}) f_{\mathbf{k}}$
- Charge Density Profile $n(\mathbf{r}) = \sum_{b,\mathbf{k}} |u_{b,\mathbf{k}}(\mathbf{r})|^2 f_{\mathbf{k}}$
- Total Energy E_{tot}

Example of Ground State Calculation

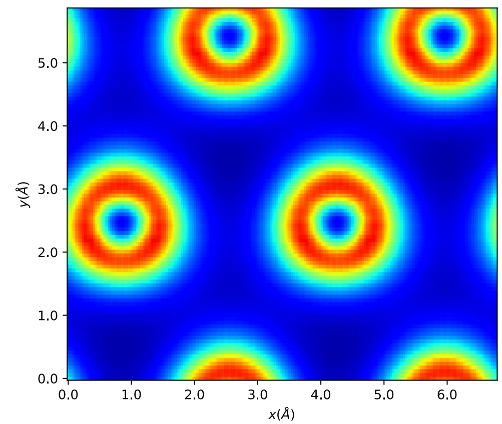
Crystal Structure

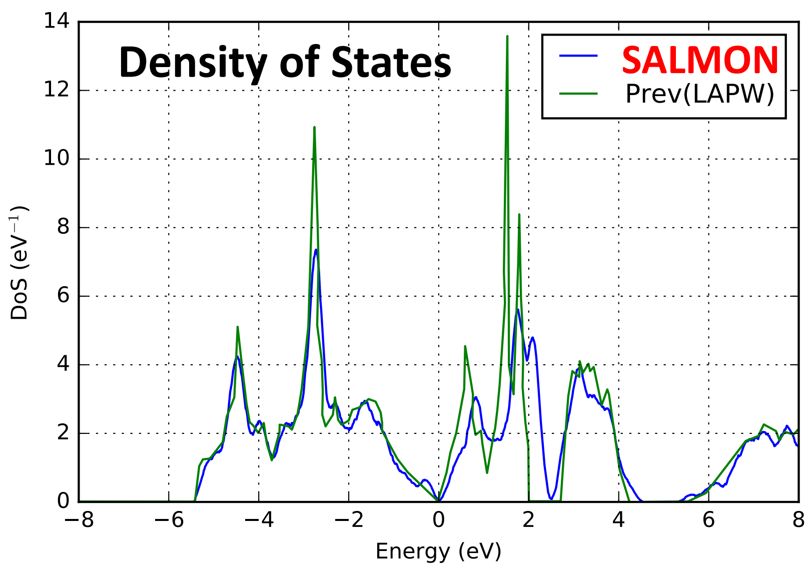


Top of View

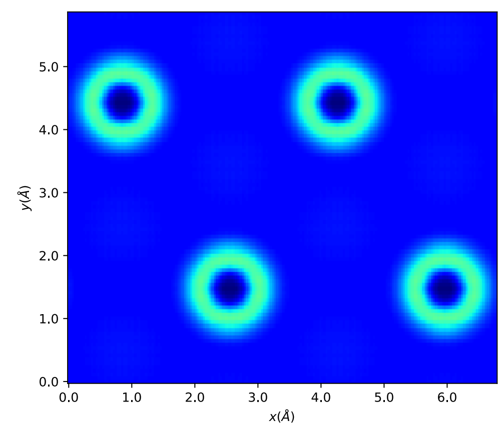


S-layer





Ti-layer



PART 2

Linear Response Calculation (Dielectric Function)

Linear Response Calculation

Solve Time-dependent Kohn-Sham Equation

$$i\hbar \frac{\partial}{\partial t} u_{b,\mathbf{k}}(\mathbf{r},t) = \left[\frac{1}{2m} \left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}(t) \right)^2 + v_{\mathrm{ion}} + v_{\mathrm{H}} + v_{\mathrm{XC}} \right] u_{b,\mathbf{k}}(\mathbf{r},t)$$

(with weak incident field: A(t), E(t))

$$\mathbf{A}(t) = \delta\mathbf{A}\ \theta(t)$$

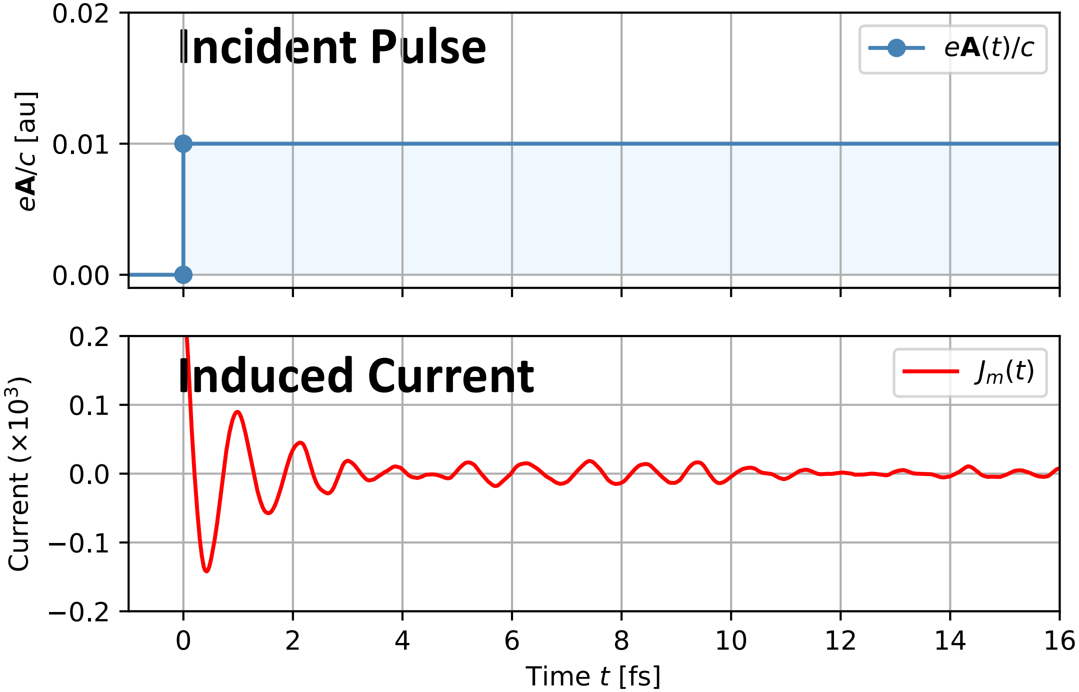
$$\mathbf{E}(t) = -\delta\mathbf{E}\ \delta(t)$$

- Impulse response $J(t)$
- Dielectric Function $\epsilon_{ij}(\omega)$ $\quad \mathbf{P}(\omega) = \frac{1}{4\pi}\left(\epsilon(\omega) - \mathbf{I}\right)\mathbf{E}(\omega)$
- Conductivity $\sigma_{ij}(\omega)$ $\quad \mathbf{J}(\omega) = \sigma(\omega)\mathbf{E}(\omega)$
- …

Linear Response (Dielectric Function)

Induced Current Density

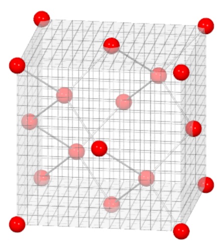
$$\mathbf{J}(t) = -\frac{e}{m}\sum_{b,\mathbf{k}}\frac{1}{\Omega}\int_{\Omega}\mathrm{Re}\, u^{\star}_{b,\mathbf{k}}(\mathbf{r},t)\left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}(t)\right)^{2} u_{b,\mathbf{k}}(\mathbf{r},t)\,\mathrm{d}\mathbf{r} + \mathbf{J}_{\mathrm{NL}}$$



Weak incident field

$$\mathbf{A}(t) = \delta\mathbf{A}\ \theta(t)$$

Response to weak incident

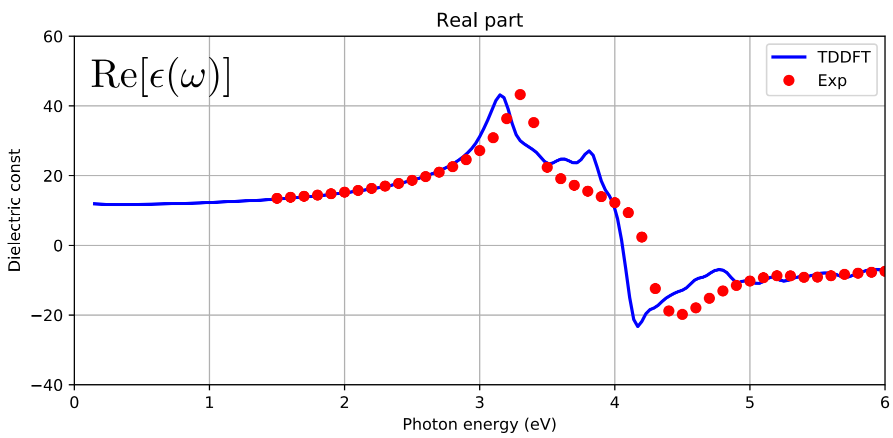


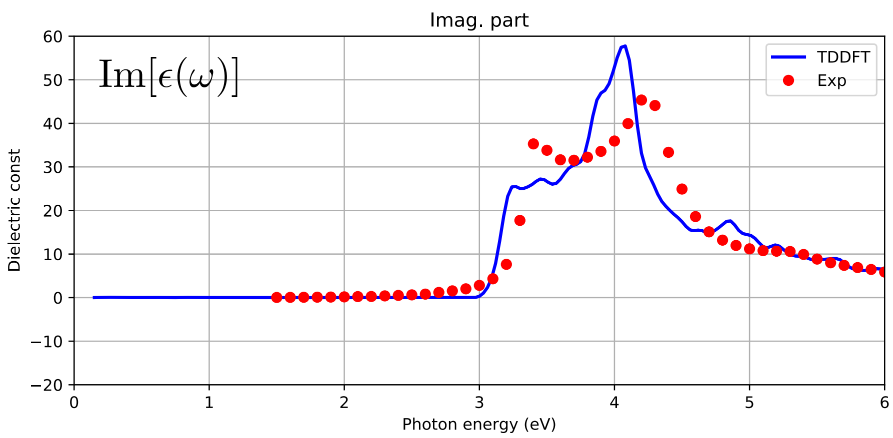
Linear Response (Dielectric Function)

Fourier transformed spectra

Conductivity $$\sigma(\omega) = \frac{\int J(t)e^{i\omega t}\,\mathrm{d}t}{\int E(t)e^{i\omega t}\,\mathrm{d}t} \longleftarrow E_0 \int \delta(t) e^{-i\omega t}\,\mathrm{d}t$$

Dielectric Const. $$\epsilon(\omega) = \frac{4\pi i}{\omega}\sigma(\omega)$$





(Experimental value from D. E. Aspnes et al. Phys. Rev. B, **27**, 2 (1983))

PART 3

Pulse Response Calculation

Pulse Response Calculation

Solve Time-dependent Kohn-Sham Equation

$$i\hbar\frac{\partial}{\partial t}u_{b,\mathbf{k}}(\mathbf{r},t)=\left[\frac{1}{2m}\left(-i\hbar\nabla+\hbar\mathbf{k}+\frac{e}{c}\mathbf{A}(t)\right)^2+v_{\mathrm{ion}}+v_{\mathrm{H}}+v_{\mathrm{XC}}\right]u_{b,\mathbf{k}}(\mathbf{r},t)$$

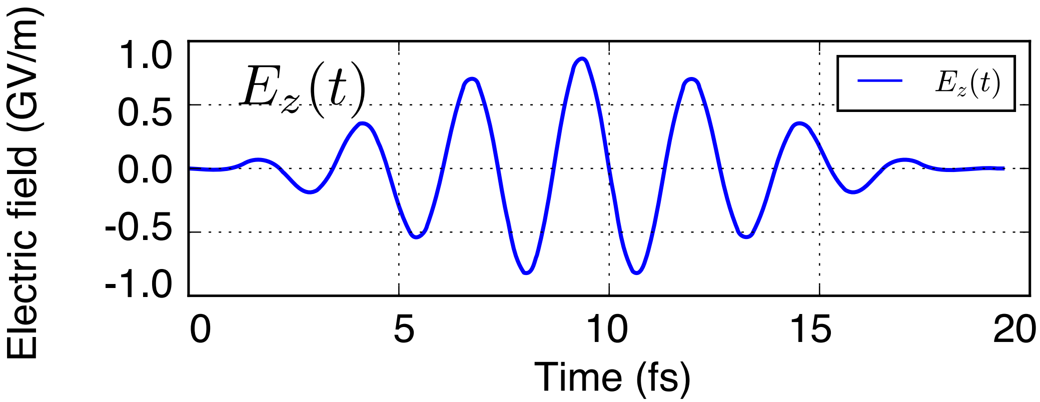
…with Strong Incident Pulse $\mathbf{A}(t)$

- **Induced Current, Polarization** $\mathbf{J}(t),\mathbf{P}(t)=\int\mathbf{J}(t)\,\mathrm{d}t$
- **Nonlinear optical constants** $\chi^{(2)},\chi^{(3)},\cdots$
- **Excitation Energy** $E_{\mathrm{ex}}(t)=E_{\mathrm{tot}}(t)-E_{\mathrm{tot}}(0)$
- **Projection to Ground State** and **Number of Excited Electrons**:

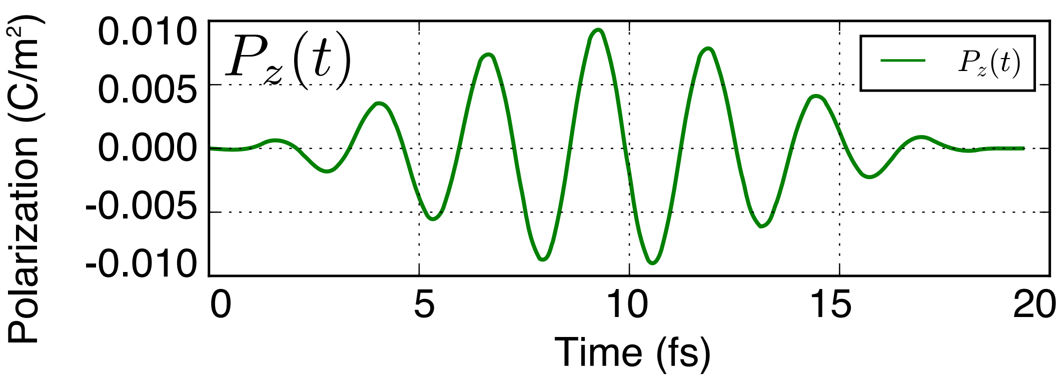
$$n_{\mathrm{ex}}=N_{\mathrm{elec}}-\sum_{\mathbf{k}}\sum_{b,b'}^{(\mathrm{occ})}\left|\left\langle u_{b,\mathbf{k}}^{\mathrm{GS}}\middle|u_{b',\mathbf{k}}(t)\right\rangle\right|^2 f_{\mathbf{k}}$$

Nonlinear Responses from SiO_2 Crystal

Applied electric field



Calculated polarization

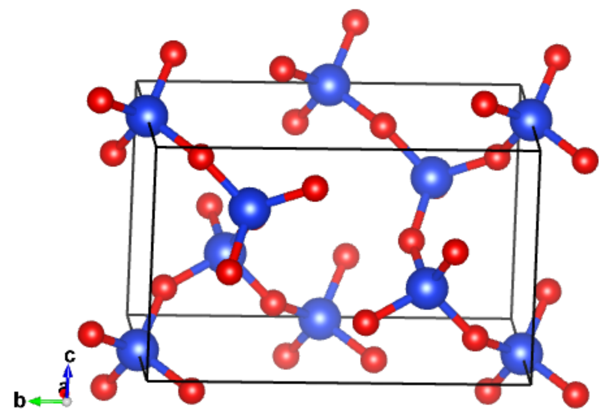


Incident pulse

- Pulse shape function

$$\mathbf{A}(t) = \mathbf{A}_0 \cos^2 \frac{\pi t}{T} \sin \omega_1 t$$

- Central frequency ω_1 = 1.55 eV
  Phase length T_p = 20 fs



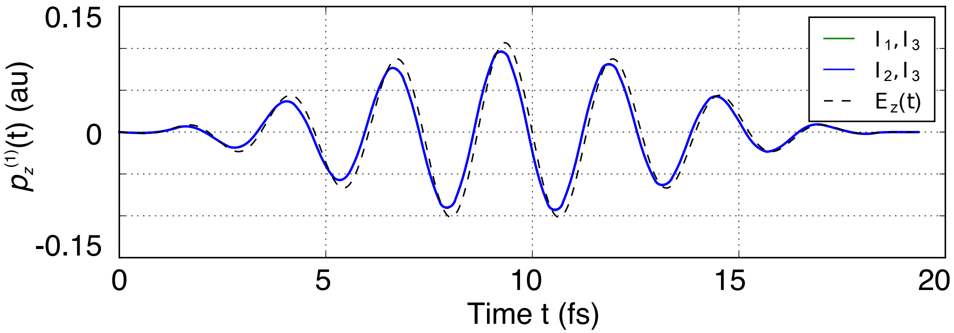
Nonlinear Responses from SiO_2 Crystal

- Numerically expanded the SiO_2 responses to the $\mathbf{p}^{(1)}$ and $\mathbf{p}^{(3)}$ components

$$\mathbf{P}(t) = \mathbf{p}^{(1)}(t)E + \cancel{\mathbf{p}^{(2)}(t)E^2} + \mathbf{p}^{(3)}(t)E^3 + \cdots$$

↑ Linear ↑ Second order ↑ Third order

$\mathbf{p}^{(1)}(t)$



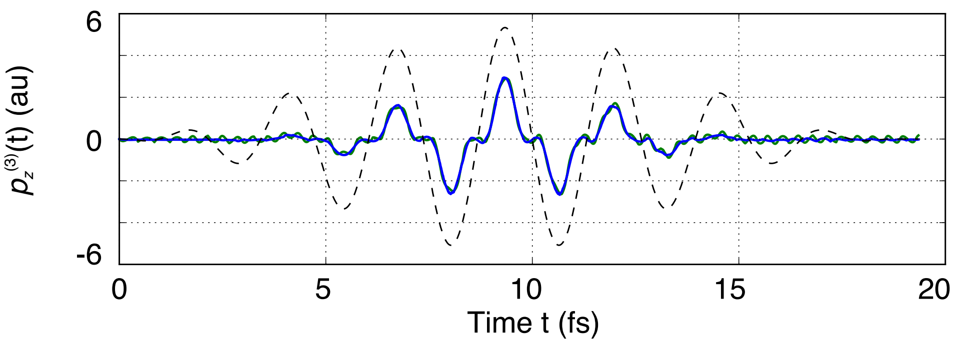
Pulse intensity

I_1 = 1 X 10^{10} W/cm2

I_2 = 5 X 10^{10} W/cm2

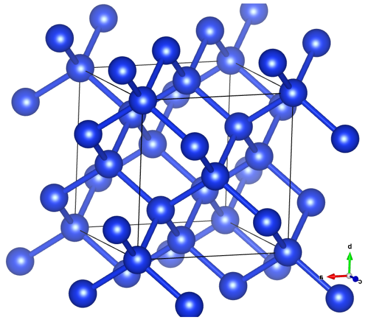
I_3 = 1 X 10^{11} W/cm2

$\mathbf{p}^{(3)}(t)$



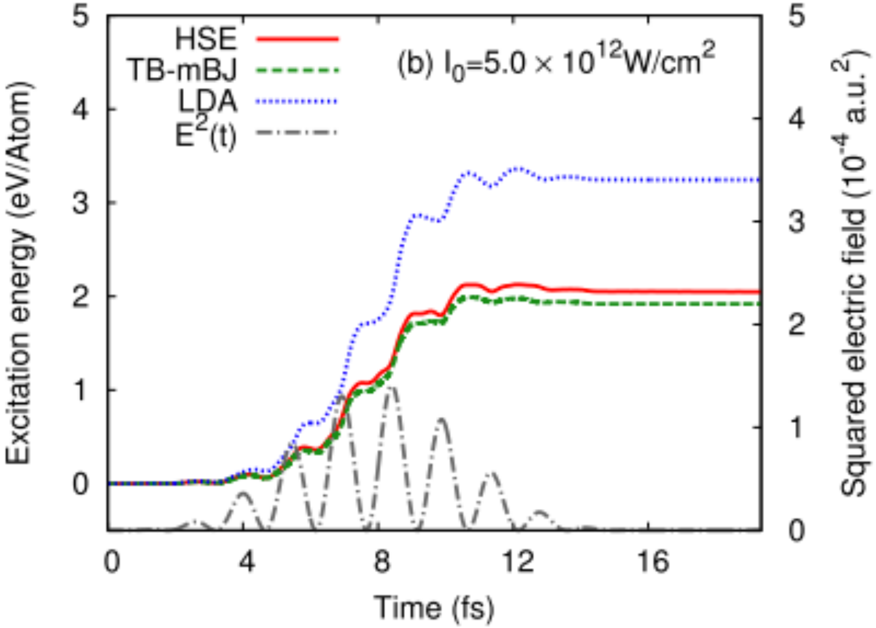
- $\chi^{(3)} = 4.32 \times 10^{-22}$ V^2/m^2 (LDA),
- $= 1.34 \times 10^{-22}$ V^2/m^2 (mGGA)
- Experiment $\chi^{(3)} = 2.5 \times 10^{-22}$ V^2/m

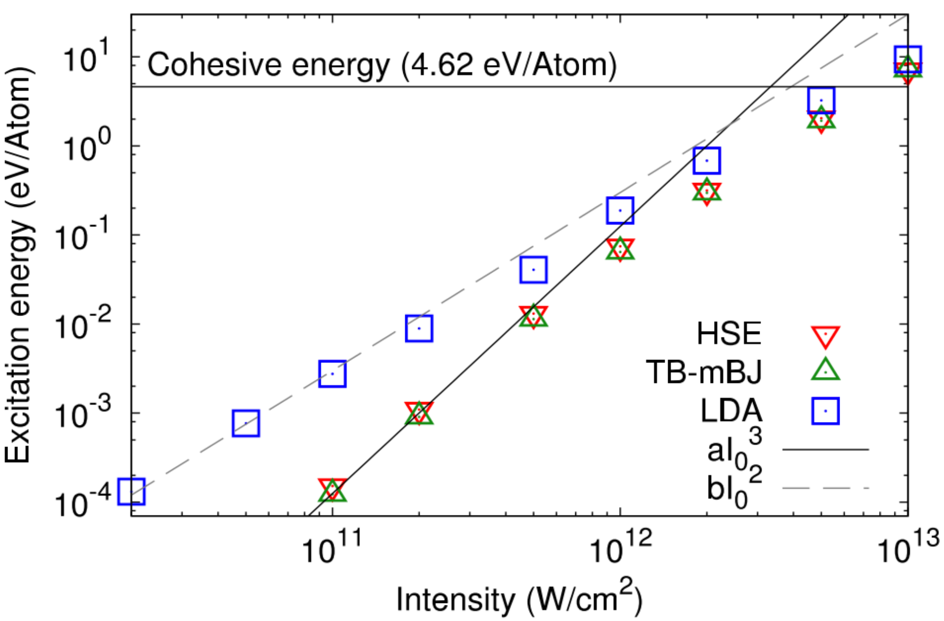
Excitation Energy of Silicon Crystal



Excitation energy

$$E_{\rm ex}(t) = E_{\rm tot}(t) - E_{\rm tot}(0) \quad \text{or} \quad \int^t \mathbf{J}(t')\mathbf{E}(t')\,\mathrm{d}t'$$





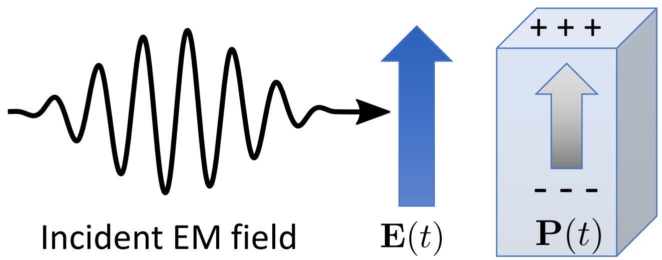
S. A. Sato, K. Yabana et al. J. Chem. Phys. **143**, (2015).

PART 4

Multiscale Maxwell+TDDFT Calculation

Light Propagation in Solid State Material

Consider the light irradiation into the solid material,



E(t) : Applied Electric Field
P(t) : Induced Polarization

Weak intensity light

- Dielectric response to applied field → **Linear Response**

$$\mathbf{P} = \chi^{(1)}\mathbf{E} = (\varepsilon - 1)/4\pi \cdot \mathbf{E}$$

- Light propagation in the solid media → **Maxwell's wave equation.**

$$-\nabla \times \nabla \times \mathbf{A}(\mathbf{r},t) - \frac{\varepsilon}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}(\mathbf{r},t) = 0$$

Strong intensity light

Light Propagation in Solid State Material

Induced current density in matter

$$\mathbf{J}(t) = -\frac{e}{m}\sum_{b,\mathbf{k}}\frac{1}{\Omega}\int_{\Omega} \mathrm{Re}\, u^{\star}_{b,\mathbf{k}}(\mathbf{r},t)\left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}(t)\right)^2 u_{b,\mathbf{k}}(\mathbf{r},t)\,\mathrm{d}\mathbf{r} + \mathbf{J}_{\mathrm{NL}}$$

- "**Constitution Relation**" of Electromagnetics:
  (Current density can be described as the functional of the EM field)

$$\mathbf{J} = \mathbf{J}[\mathbf{A}(t)]$$

Couple

Light propagation in the media

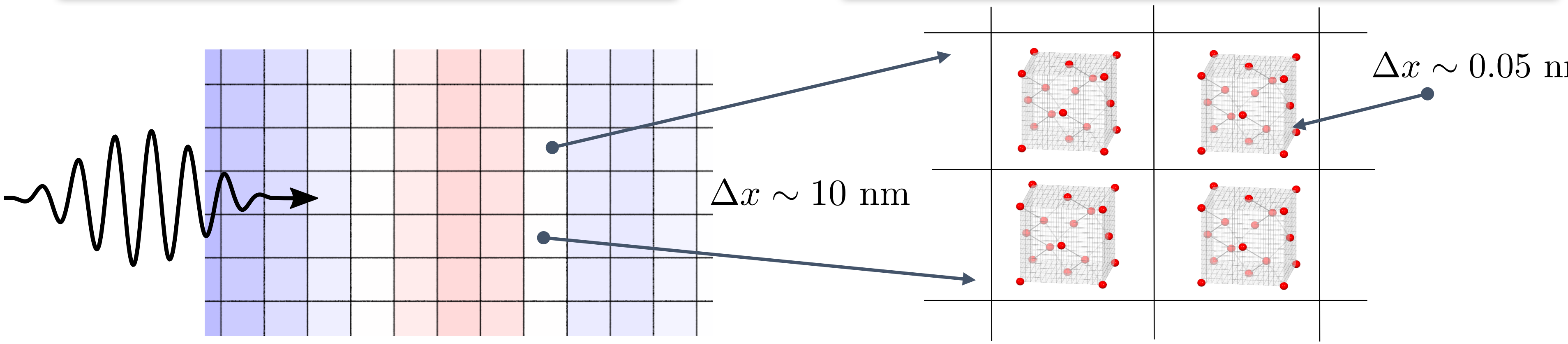
- Governing equation of EM field (Maxwell's wave eq.)

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

Multiscale Maxwell-TDDFT calculation

Macroscopic system (EM field)

Microscopic system (Electron dynamics)



Solve Maxwell's Eq. in Macroscopic grid:

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

FDTD-based EM calculation:

$$\mathbf{J}(t - \Delta t_i) \rightarrow \mathbf{A}(t)$$

Solve TD-KS Eq. in Microscopic Grid

$$\hat{E} u_{n\mathbf{k}} = \hat{\mathcal{H}}(k) u_{n\mathbf{k}}$$

RT-TDDFT calculation:

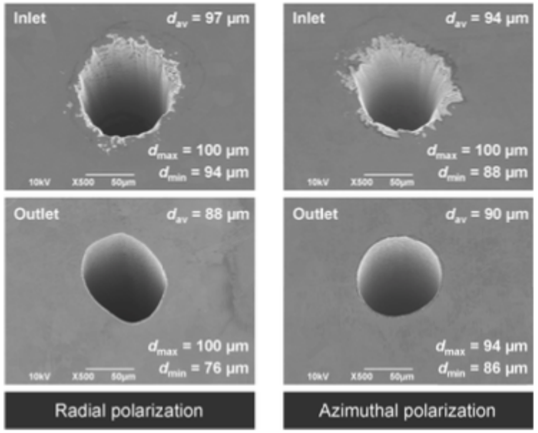
$$\mathbf{A}(t - \Delta t_i) \rightarrow \mathbf{J}(t)$$

Exchange J and A at every time step

Example of Multiscale Calculation

2 Dimensional problem

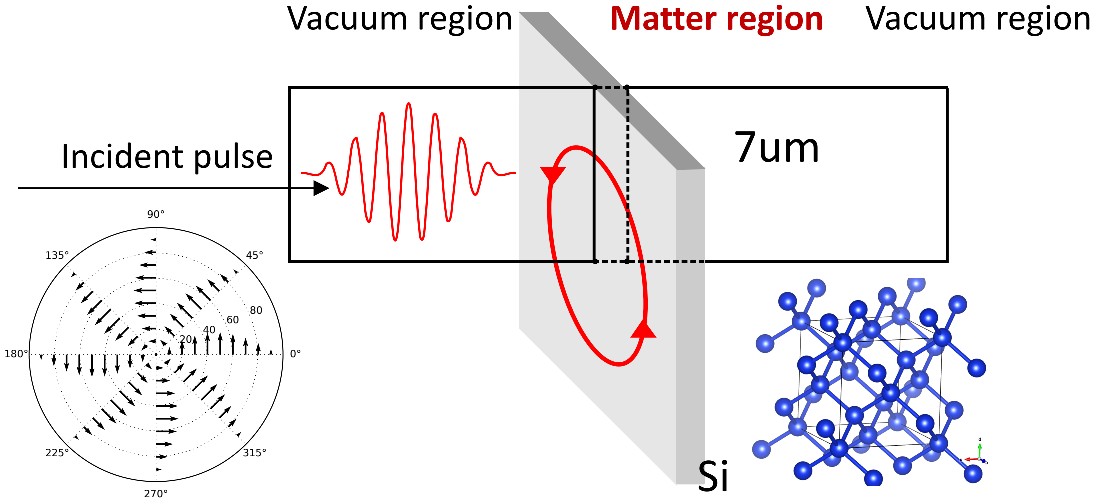
- Cylindrical symmetric case
  - Light propagation to thin film semiconductor
- Application
  - Simulation of Laser Processing by Cylindrical Vector Beam



Martin Kraus et al, OpEx, 18,. 21

Computation model

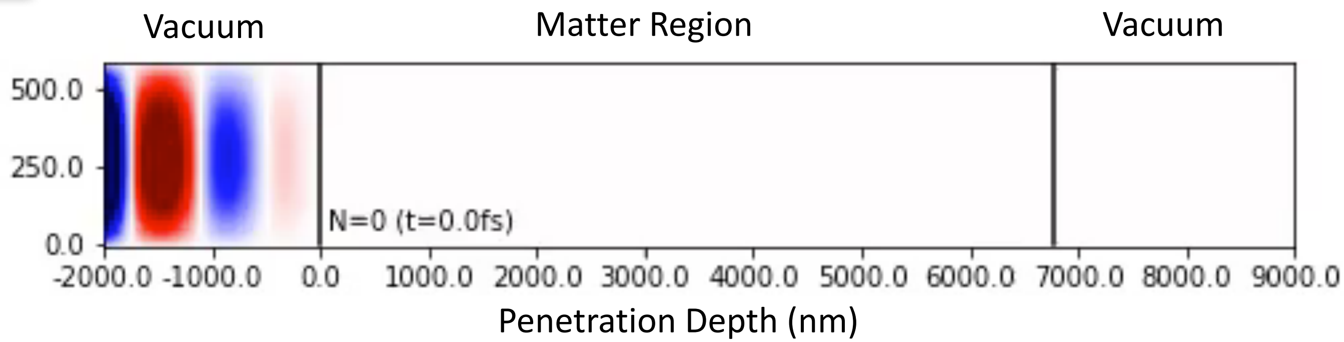
- Consider the laser pulse irradiation to thin-film (d~7µm) Silicon crystal



- Incident pulse
  - Frequency: 1.55 eV
  - Pulse length: 16 fs
  - Azimuth polarized beam
  - $I = 10^{12}$ W/cm^2

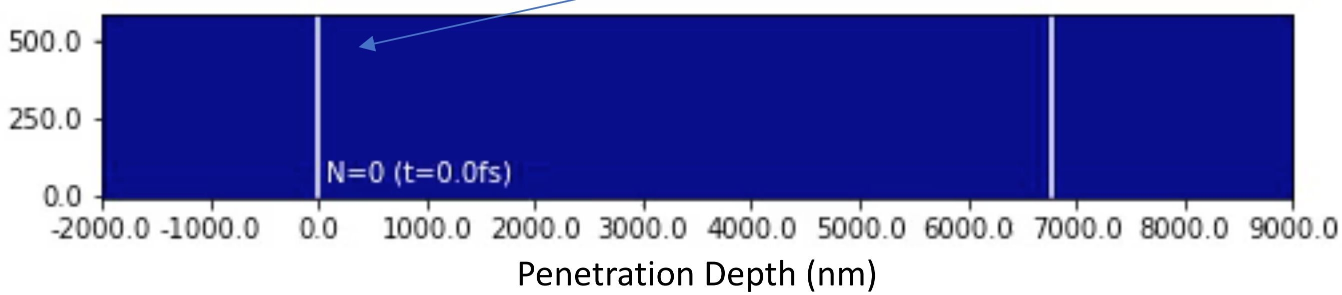
Example of Multiscale Calculation

EM Field



Electronic Excitation Energy

Energy absorption by the multi-photon excitation process



- 512 X 64 = 32768 macroscopic points

Conclusion

SALMON

Scalable Ab-initio Light-Matter simulator for Optics and Nanoscience

Isolated System (Molecule)	**Periodic System (Solid material)**
Ground State Calculation:	Total energy, DoS, Charge density profile …
Linear Response Calculation:	Dielectric function, Oscillator strength …
Pulse Reponse Calculation:	Nonlinear excitation, Energy transfer …
	Maxwell+TDDFT Multiscale Calculation

Let's enjoy your research life with SALMON !