SALMON

http://salmon-tddft.jp

Practical Aspects of TDDFT Calculations

partly as an introduction to the afternoon tutorial session
using SALMON: Scalable Ab Initio Light-Matter simulator
for Optics and Nano-science

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Classifications of TDDFT calculations for optical responses that can be done in current SALMON

	Isolated Systems (Molecules, Nano-particles)	Periodic Systems (Crystalline solids)	Light propagation in bulk materials (Maxwell + TDDFT)
Weak fields (Linear response)	Polarizability $\alpha(\omega)$	Dielectric function $\varepsilon(\omega)$	1D light propagation E(x,t), J(x,t)
Strong fields (Nonlinear dynamics)	Excitation energy Atomic motion	Excitation energy Carrier density Atomic motion	

To be developed:
- spin degrees (at present, only spin-saturated system: LSDA, spin-orbit,…)
- 1D, 2D systems
- Electromagnetic field analyses with various options of electron dynamics

Basic features of light-matter interactions

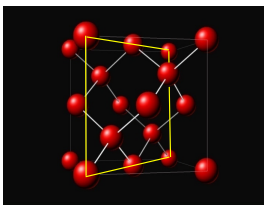
- **Interaction dominates between light electric field and electrons.**
- **For ordinary (weak) light, one may use perturbation theory in quantum mechanics.**
- **There are two spatial scales and single time scale ➔ Dipole approximation**

Laser pulse

$\hbar\omega \sim 1.55$ eV
$\lambda \sim 800$ nm

(Ti:Sapphire laser)

Electron dynamics

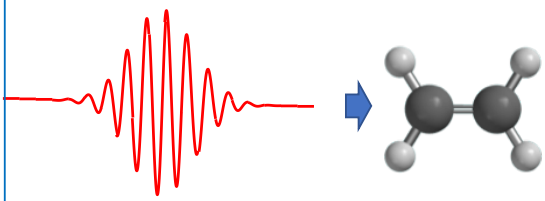


$E_{gap} \approx 1\sim10$ eV
$\Delta x\sim1$ Å

(Typical dielectric)

Linear optical response of molecule is characterized by polarizability in dipole approximation

Electric field $E_\nu(t)$



$\hbar\omega \sim 1.55$ eV
$\lambda \sim 800$ nm

$E_{gap} \approx 1\sim10$ eV
$\Delta x\sim1$ Å

Polarization

$$p_\mu(t) = \int d\vec{r}\,(-er_\mu)\,\rho(\vec{r},t)$$

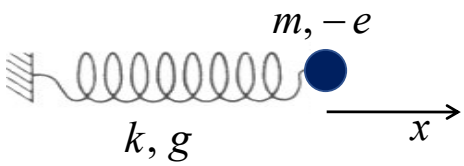
Polarizability (time domain)

$$p_\mu(t) = \sum_\nu \int dt' \alpha_{\mu\nu}(t-t')E_\nu(t')$$

Relation to frequency-dependent polarizability (polarizability for fixed-frequency field)

$$\alpha_{\mu\nu}(\omega) = \frac{\int dt e^{i\omega t} p_\mu(t)}{\int dt e^{i\omega t} E_\nu(t)}$$

Polarizability: a classical spring-mass model



Newton equation $m\ddot{x} + g\dot{x} + kx = -eE(t)$

Polarization and Polarizability $p(t) = -ex(t) = \int dt' \alpha(t - t')E(t')$

We can solve the equation for

Sinusoidal field

$$E(t) = E_0 e^{-i\omega t}$$

Impulsive field

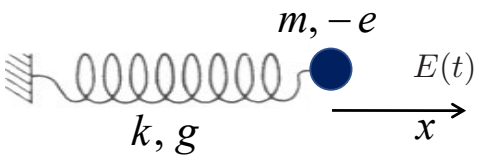
$$E(t) = \frac{I}{-e}\delta(t)$$

Sinusoidal external field (forced oscillator)

$$m\ddot{x} + g\dot{x} + kx = -eE_0 e^{-i\omega t}$$

$$x(t) = -\frac{e}{m}\frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2}E_0 e^{i\omega t}$$

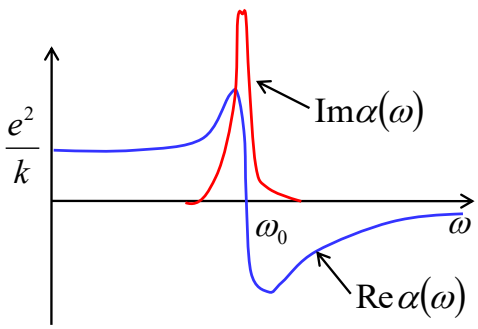
$$\omega_0^2 = \frac{k}{m} \quad \gamma = \frac{g}{m}$$



Polarization and polarizability

$$p(t) = -ex(t) = \alpha(\omega)E(t)$$

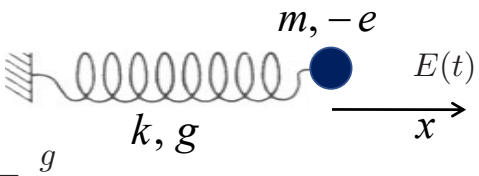
$$\alpha(\omega) = \frac{e^2}{m}\frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2}$$



Impulsive external field (Damped oscillation)

$$m\ddot{x} + g\dot{x} + kx = I\delta(t)$$

$$x(0) = 0 \quad \dot{x}(0) = \frac{I}{m}$$ Impulse

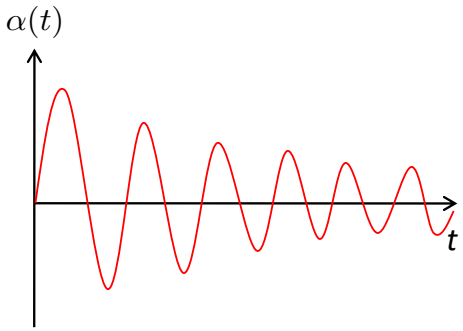


$$x(t) = \frac{I}{m} e^{-\gamma t/2} \frac{\sin\sqrt{\omega_0^2 - \gamma^2 t/4}}{\sqrt{\omega_0^2 - \gamma^2/4}} \qquad \omega_0^2 = \frac{k}{m} \quad \gamma = \frac{g}{m}$$

Polarization and polarizability

$$p(t) = -ex(t) = \int dt' \alpha(t - t') E(t')$$

$$\alpha(t) = \frac{e^2}{m} \theta(t) e^{-\gamma t/2} \frac{\sin\sqrt{\omega_0^2 - \gamma^2 t/4}}{\sqrt{\omega_0^2 - \gamma^2/4}}$$



A classical spring-mass model: Compare two descriptions

Polarizability as a function of time
= damped oscillation induced by an impulse

$$\alpha(t) = \frac{e^2}{m} \theta(t) e^{-\gamma t/2} \frac{\sin\sqrt{\omega_0^2 - \gamma^2 t/4}}{\sqrt{\omega_0^2 - \gamma^2/4}}$$

Polarizability as a function of frequency
= forced oscillation

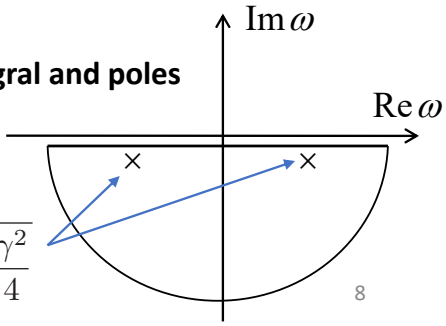
$$\alpha(\omega) = \frac{e^2}{m} \frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2}$$

$$\alpha(t) = \frac{1}{2\pi} \int_C d\omega \alpha(\omega) e^{-i\omega t}$$

Time and frequency domain Polarizabilities are related by Fourier transformation.

Two description involves the same physical information

Contour for integral and poles

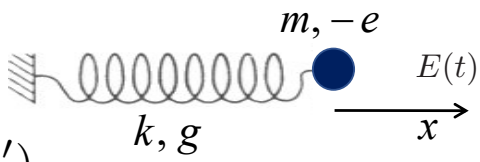


$$\omega = -\frac{i\gamma}{2} \pm \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$$

A classical spring-mass model: Photoabsorption cross section

$$F_{\text{ext}}(t) = -eE(t)$$

$$p(t) = -ex(t) = \int dt' \alpha(t-t')E(t')$$



Work done by light electric field = Energy absorbed by the spring

$$W = \int dt \dot{x}(t) F_{\text{ext}}(t) = \int dt \dot{p}(t) E(t) = \frac{1}{\pi}\int_0^\infty d\omega \omega \text{Im}\alpha(\omega)|E(\omega)|^2$$

Photoabsorption cross section is given by imaginary part of the polarizability

$$\sigma(\omega) = \frac{4\pi\omega}{c}\text{Im}\alpha(\omega)$$

A general (accurate) formula of polarizability for molecules

Electronic description for a molecule

Hamiltonian $$H = \sum_i \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_a \frac{Z_a e^2}{|\vec{r}_i - \vec{R}_a|} \right\} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Schroedinger eq. $$H\Phi_n = E_n \Phi_n$$

Dipole operator $$D = \sum_i z_i$$

Polarizability $$\alpha(\omega) = \frac{e^2}{m}\sum_n f_{n0} \frac{1}{-\omega^2 - i\gamma\omega + \left(\frac{E_n - E_n}{\hbar}\right)^2}$$

Oscillator strength $$f_{n0} = \frac{2m}{\hbar^2}(E_n - E_0)\left|\langle \Phi_n | D | \Phi_0 \rangle\right|^2$$

Each excited state contributes as a classical oscillator.

Polarizability of classical oscillator $$\alpha(\omega) = \frac{e^2}{m}\frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2}$$

Polarizability for molecules in TDDFT

TDDFT provides time-dependent density for a given external potential

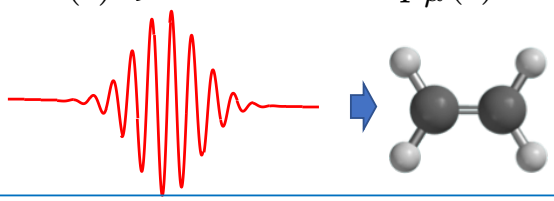
$$V_{\rm ext}(\vec{r},t) \Rightarrow \rho(\vec{r},t)$$

External potential of uniform electric field

$$V_{\rm ext}(\vec{r},t) = eE(t)r_\nu$$

Induced polarization in molecule

$$p_\mu(t) = \int d\vec{r} r_\mu \rho(\vec{r},t)$$



Polarizability is given by

$$p_\mu(t) = \int dt' \alpha_{\mu\nu}(t-t')E(t') \qquad \alpha_{\mu\nu}(\omega) = \frac{\int dt e^{i\omega t} p_\mu(t)}{\int dt e^{i\omega t} E_\nu(t)}$$

Calculation of Polarizability in TDDFT
Time-domain method

Time-Dependent Kohn-Sham equation

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

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

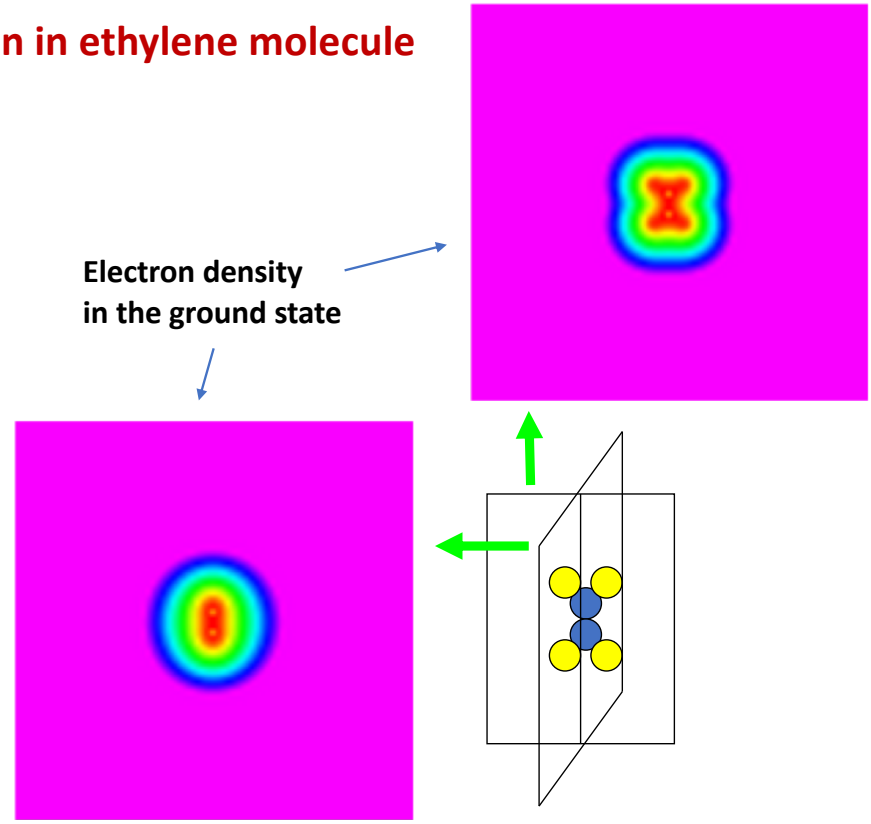
Computational procedure

Prepare ground state	$h_{KS}\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$
Apply impulsive external potential	$V_{ext}(\vec{r},t) = I\delta(t)z$
Orbitals immediately after the impulse	$\psi_i(\vec{r},t=0_+) = e^{iIz/\hbar}\phi_i(\vec{r})$
Calculate polarization	$p(t) = -e\int d\vec{r} z\rho(\vec{r},t)$
Fourier transformation Frequency-dependent polarizability	$\alpha(\omega) = \frac{1}{I}\int dt e^{i\omega t}p(t)$

Newton mechanics

$$\dot{x}(t=0_+) = \frac{I}{m}$$

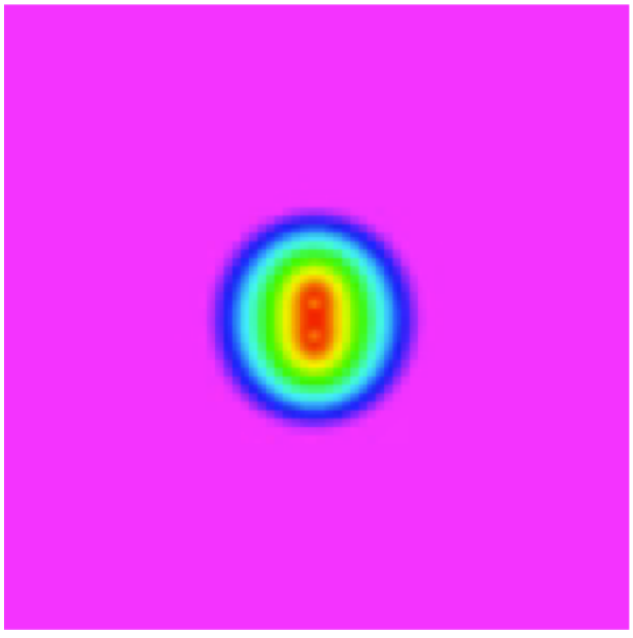
An example: photoabsorption in ethylene molecule



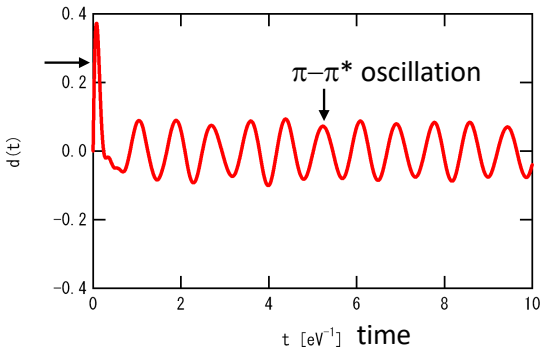
Electron density change
in ethylene molecule

Real-time response: Optical response of Ethylene (C_2H_4) molecule

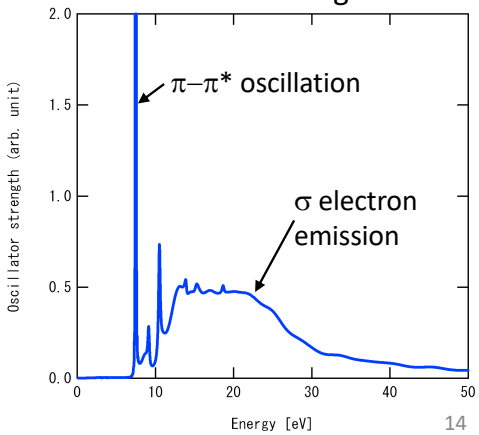
Electron density after impulsive kick



Dipole moment



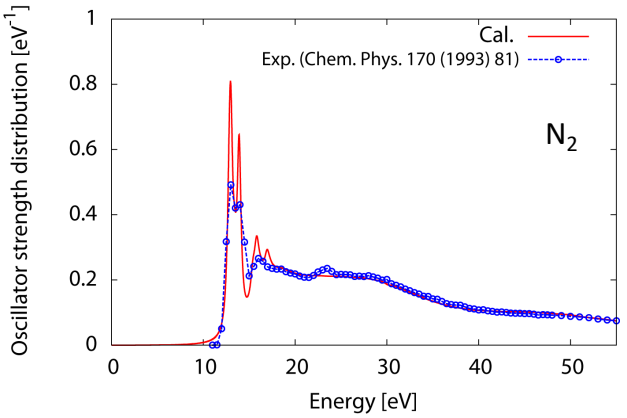
Oscillator strength

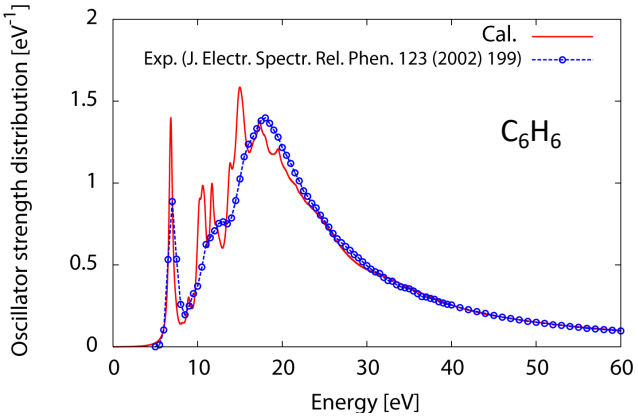


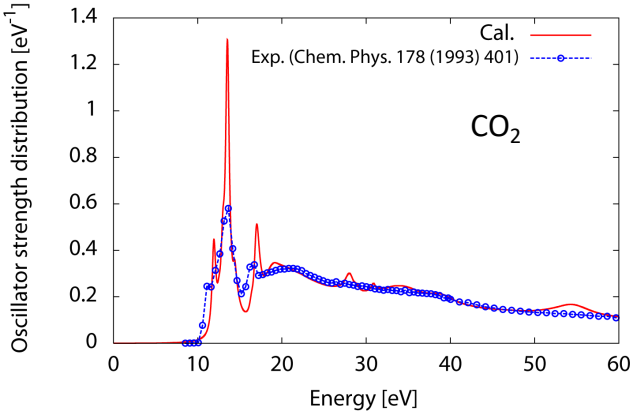
Excitation energy

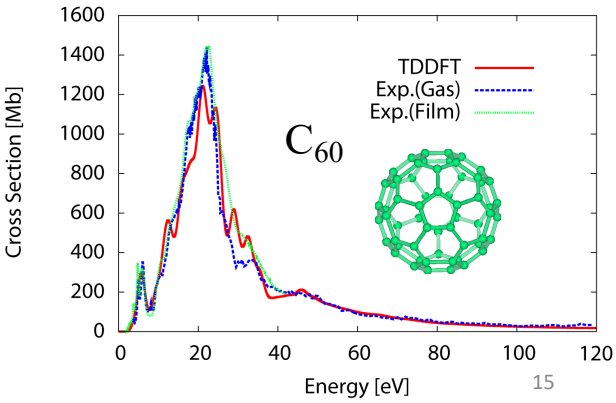
Photoabsorption cross section of typical molecules

K. Yabana et.al, Chap.4, Charged Particle and Photon Interactions with Matter, CRC Press, 2010.



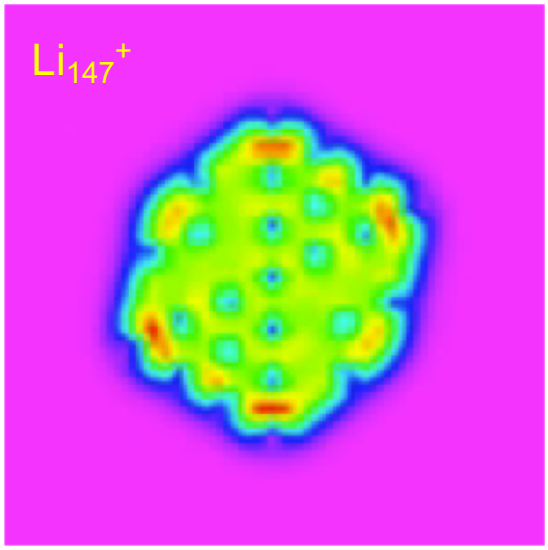




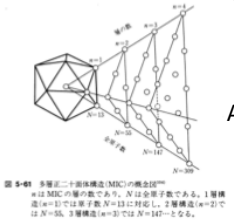


Surface plamons (Mie plasmon): Collective excitation in metallic cluster

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

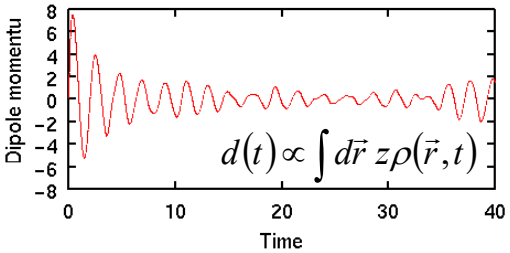


Electron density change from the ground state

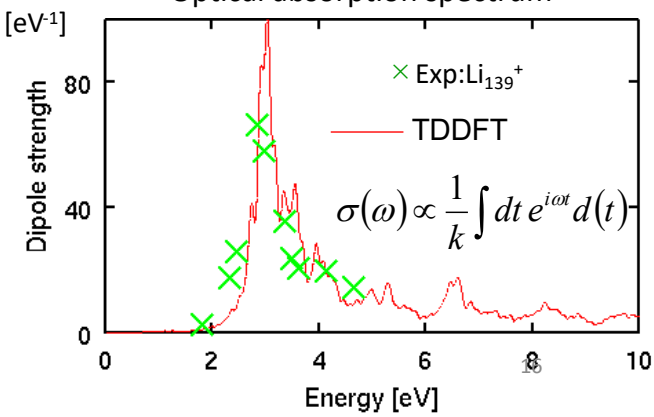


Assume icosahedral geometry

Time-dependence of dipole moment



Optical absorption spectrum

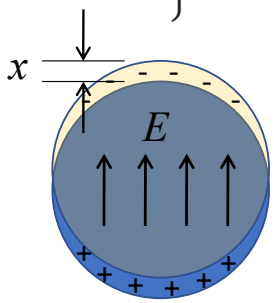


Dynamical screening effect: Time-dependence of the Kohn-Sham Hamiltonian

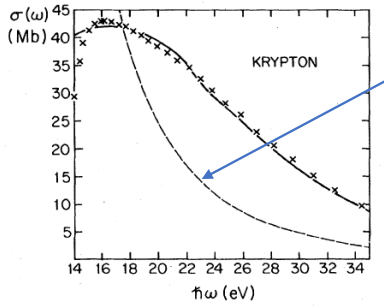
$$i\hbar\frac{\partial}{\partial t}\psi_i(\vec{r},t) = \left\{-\frac{\hbar^2}{2m}\nabla^2 - \sum_a \frac{Z_a e^2}{|\vec{r}-\vec{R}_a|} + \int d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}\rho(\vec{r}',t) + \mu_{xc}[\rho(\vec{r},t)] + V_{\rm ext}(\vec{r},t)\right\}\psi_i(\vec{r},t)$$

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

Change of Hartree potential by the motion of electrons



Photoabsorption of rare gas atom
Zangwill, Soven 1980

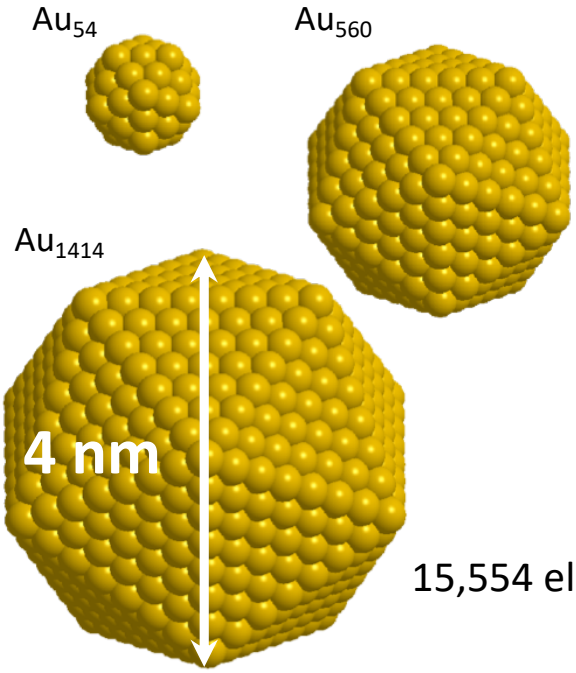


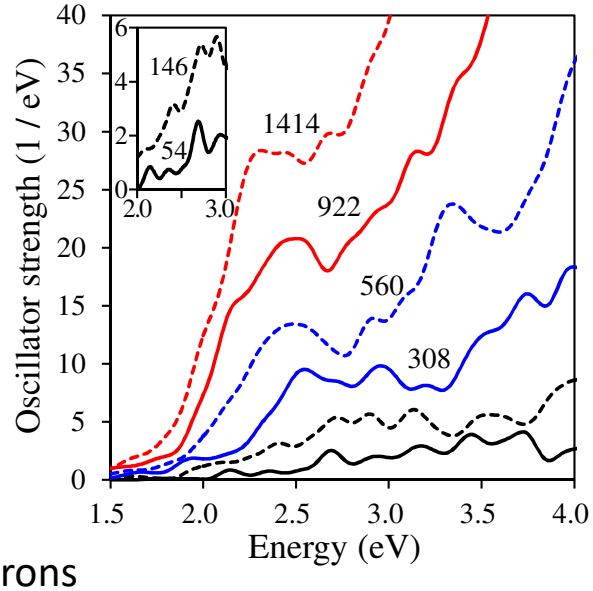
Without dynamical screening (Time-independent Hamiltonian)

Dynamical screening effect is important even for very small system (atom).

Calculation of large systems using massively parallel supercomputers

Surface plasmon resonance of Au clusters





15,554 electrons

K. Iida, M. Noda, K. Ishimura, K. Nobusada, JPCA, 118, 11317 (2014)

Thomas-Reiche-Kuhn (TRK) sum rule

Sum of oscillator strength over all excited states is equal to the number of electrons.

$$\int_0^\infty d\omega\sigma(\omega) = \frac{4\pi}{c}\int_0^\infty d\omega\omega \mathrm{Im}\alpha(\omega) = \frac{2\pi^2 e^2}{mc} N_e$$

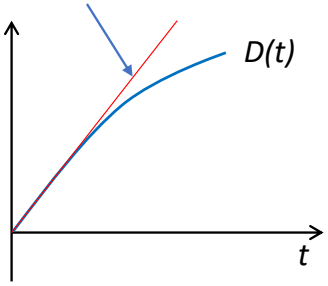
Number of electrons

TRK sum rule is related to the initial velocity after impulsive excitation

$$\alpha(t) = \int \frac{dt}{2\pi} e^{-i\omega t}\alpha(\omega) \qquad \left.\frac{d\alpha(t)}{dt}\right|_{t=0} = \frac{1}{\pi}\int_0^\infty d\omega\omega \mathrm{Im}\alpha(\omega)$$

Velocity immediately after the kick

$$\frac{dD(t)}{dt} = N_e\frac{I}{m}$$



Computational Schemes for linear response calculations

Orbital representation

- Real space grid with pseudpotential
- Plane wave with pseudopotential
- Basis functions referring to atomic positions

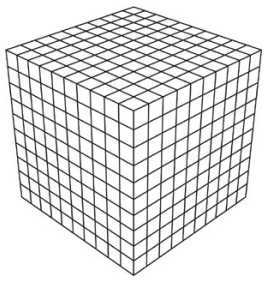
Solve linear response problem

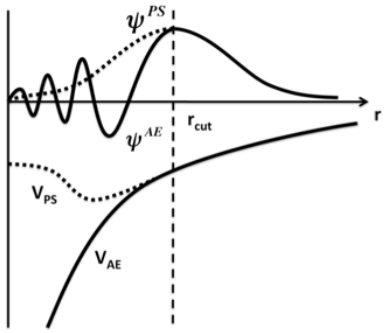
- Time domain method
  solve TDKS equation in real time
- Frequency domain method (Sternheimer method)
  linear algebraic equation
- Eigenvalue method
  an option of quantum chemistry methods

Merit of real-space + real-time

- Easy to parallelize by space division (real space)
- Good for excitations involving huge number of particle-hole excitations (real time)
- Only choice for nonlinear dynamics (real time)

SALMON adopts
Real-space grid +
norm conserving pseudopotential



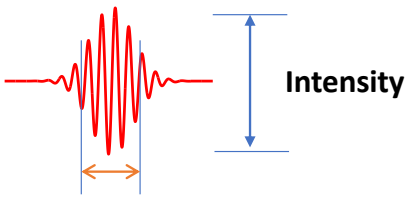


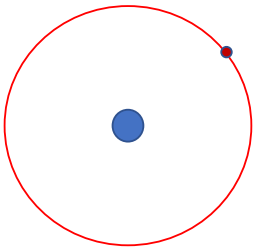
Classifications of TDDFT calculations for optical responses
that can be done in current SALMON

	Isolated Systems (Molecules, Nano-particles)	Periodic Systems (Crystalline solids)	Light propagation in bulk materials (Maxwell + TDDFT)
Weak fields (Linear response)	Polarizability $\alpha(\omega)$	Dielectric function $\varepsilon(\omega)$	1D light propagation E(x,t), J(x,t)
Strong fields (Nonlinear dynamics)	Excitation energy Atomic motion	Excitation energy Carrier density Atomic motion	

Interaction of intense and ultrashort laser pulses with matters

What is strong? What is ultrashort?



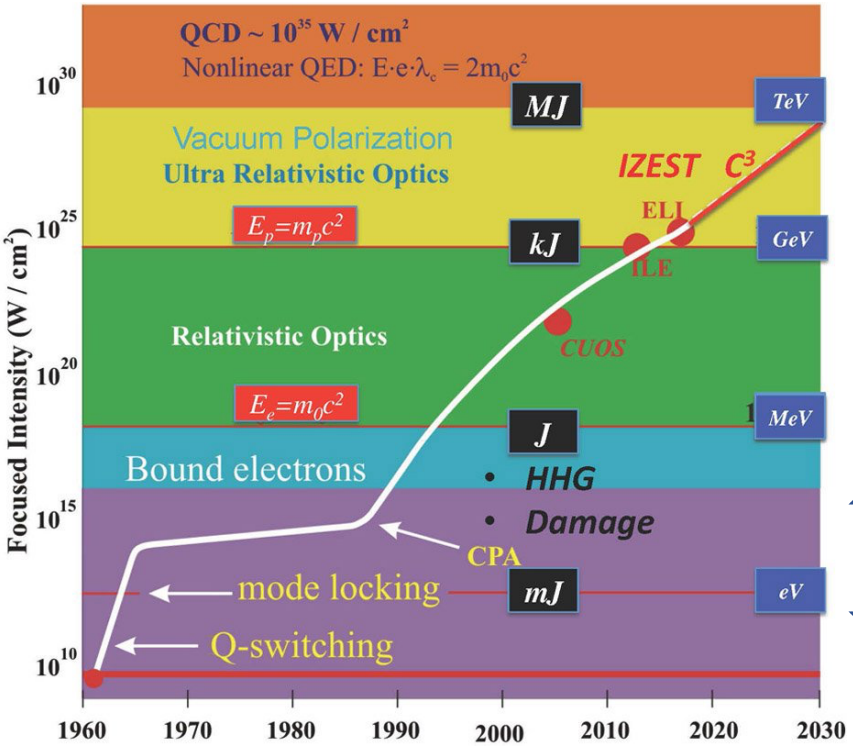


Bohr model for hydrogen atom

To be compared: atomic unit

- **Time: period of hydrogen atom = 2π**
- **Field strength: electric field felt by electron in classical hydrogen atom**

Development of Intense Laser Pulses



QED Vacuum breakdown

Nuclear reaction, Acceleration

Relativistic Classical

Nonlinear electron dynamics

Nonrelativistic Quantum

G. Mourou and T. Tajima, SPIE News

Extremely nonlinear optics --- Intense laser pulse ---

1 atomic unit I_{crit}: 3.51×10^{16}W/cm^2

Solar constant
$0.1366\ \mathrm{W/cm^2}$

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

Strongest laser pulse
$10^{22}\ \mathrm{W/cm^2}$

Linear optics
$\varepsilon(\omega)$

Nonlinear Optics (Perturbative)
$\chi^{(2)}(\omega_1,\omega_2),\ \chi^{(3)}(\omega_1,\omega_2,\omega_3)$

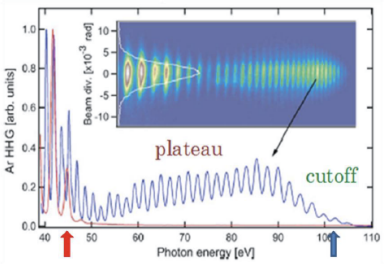
Nonlinear (Non-perturbative)

Laser acceleration

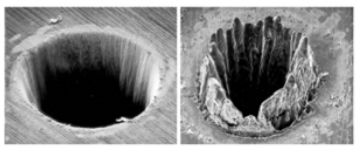
Vacuum breakdown

High harmonic generation

femtosecond laser processing

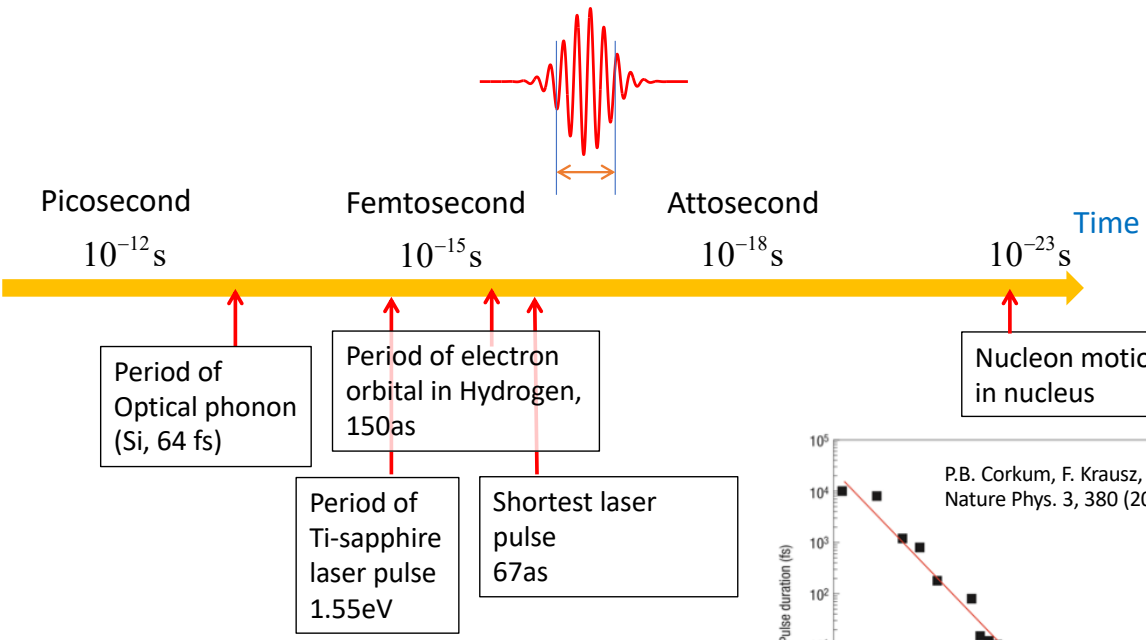


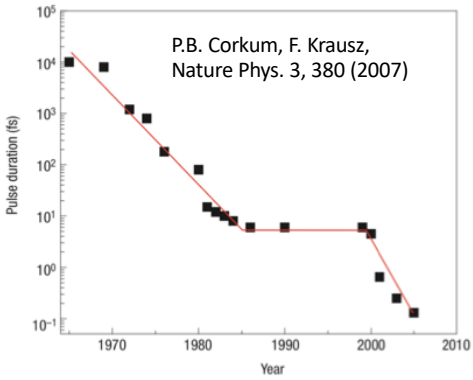
Takahashi et.al,
Appl. Phys. Lett. 93, 041111 (2008)



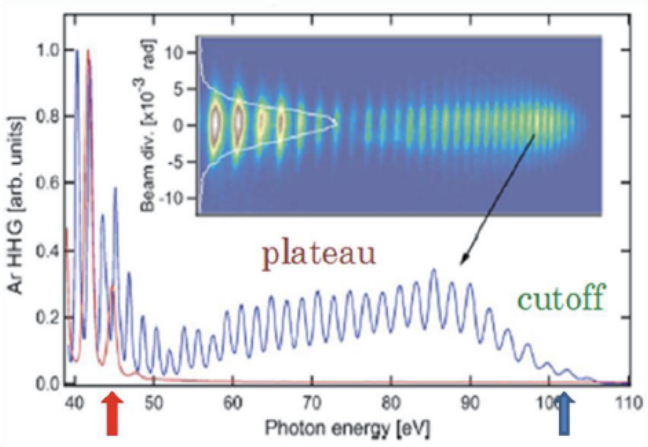
B.N. Chichkov et.al,
Appl. Phys. A63, 109 (1996)

Extremely nonlinear optics --- Ultrashort laser pulse ---





High harmonic generation spectrum from atom



Takahashi et.al,
Appl. Phys. Lett. 93, 041111 (2008)

I = 1.5 x 10^{14} W/cm^2

Red: 1400nm (0.88 eV)

Blue: 800nm (1.55 eV)

Three step model (Rescattering)

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

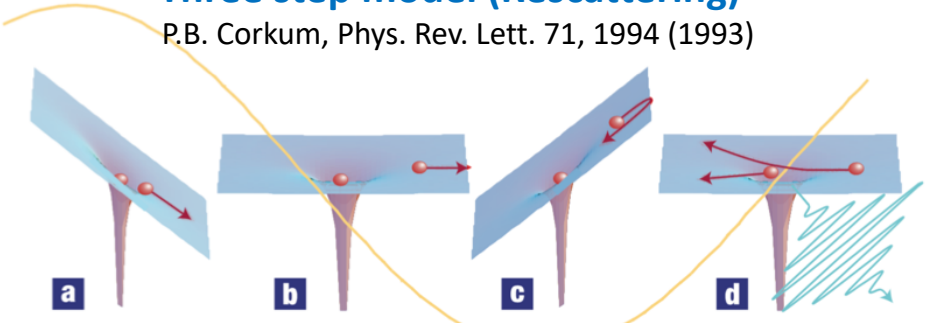
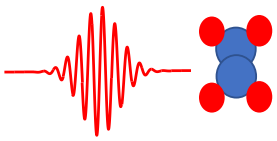


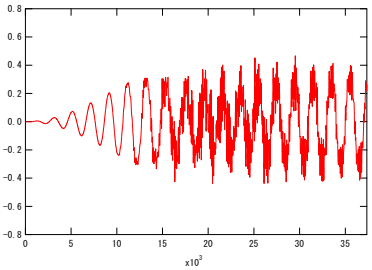
Figure taken from P.B. Corkum, F. Krausz, Nature Phys. 3, 380 (2007)

Rescattering by TDDFT

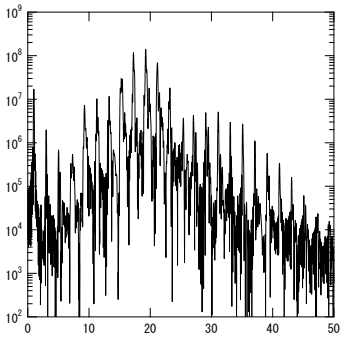
Ethylene molecule (C_2H_4)

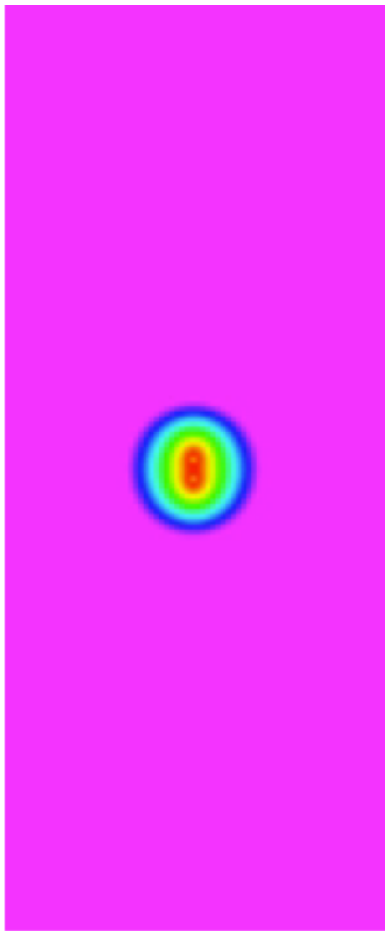


$$\frac{dD(t)}{dt} = \frac{d}{dt}\int d\vec{r} z\rho(\vec{r},t)$$

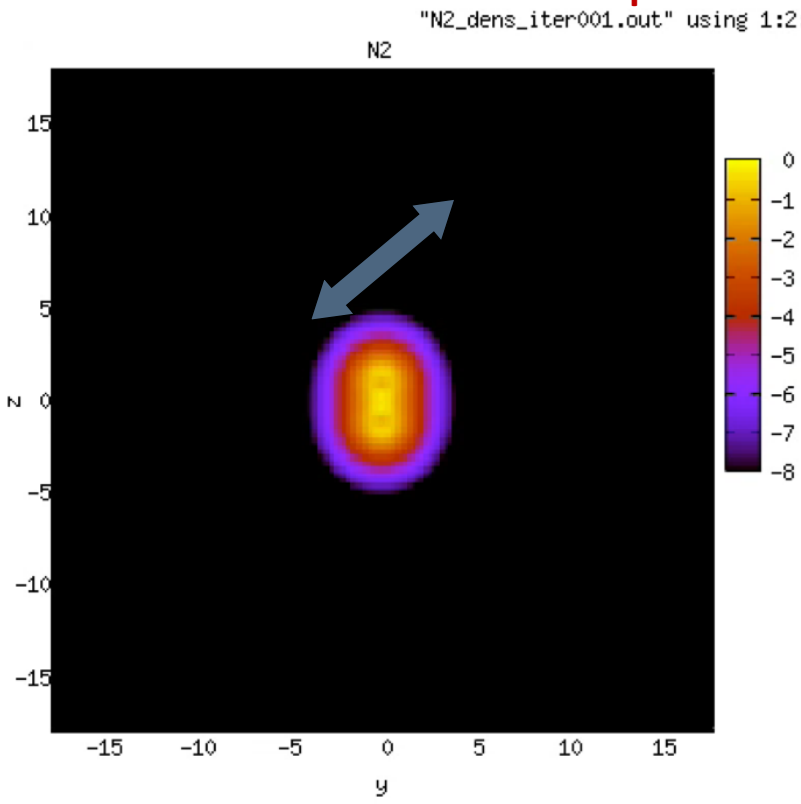


$$I(\omega) \propto \left|\int dt e^{i\omega t} d_A(t)\right|^2$$





Coulomb explosion of molecules under intense and ultrashort laser pulse



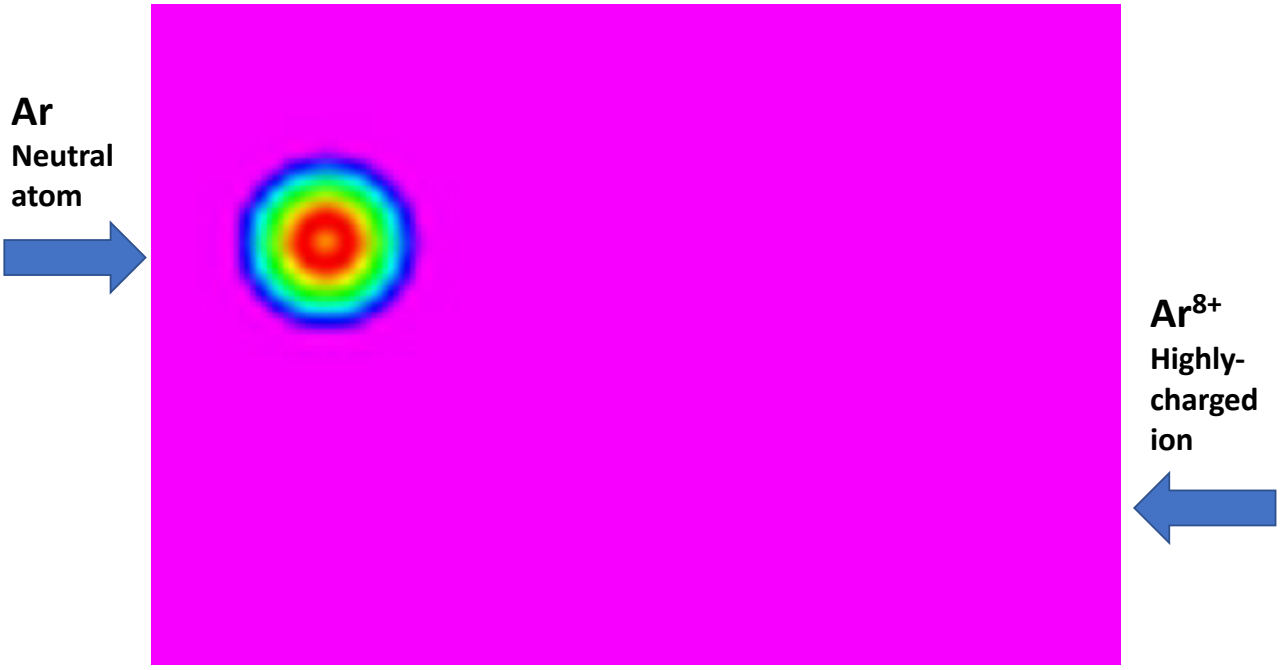
N_2 molecule
I=3.35x10^{15}W/cm^2, 27fs

Electron dynamics + Atomic motion (Ehrenfest dynamics)

Final charge states are fractional, and not simple to compare with measurements.

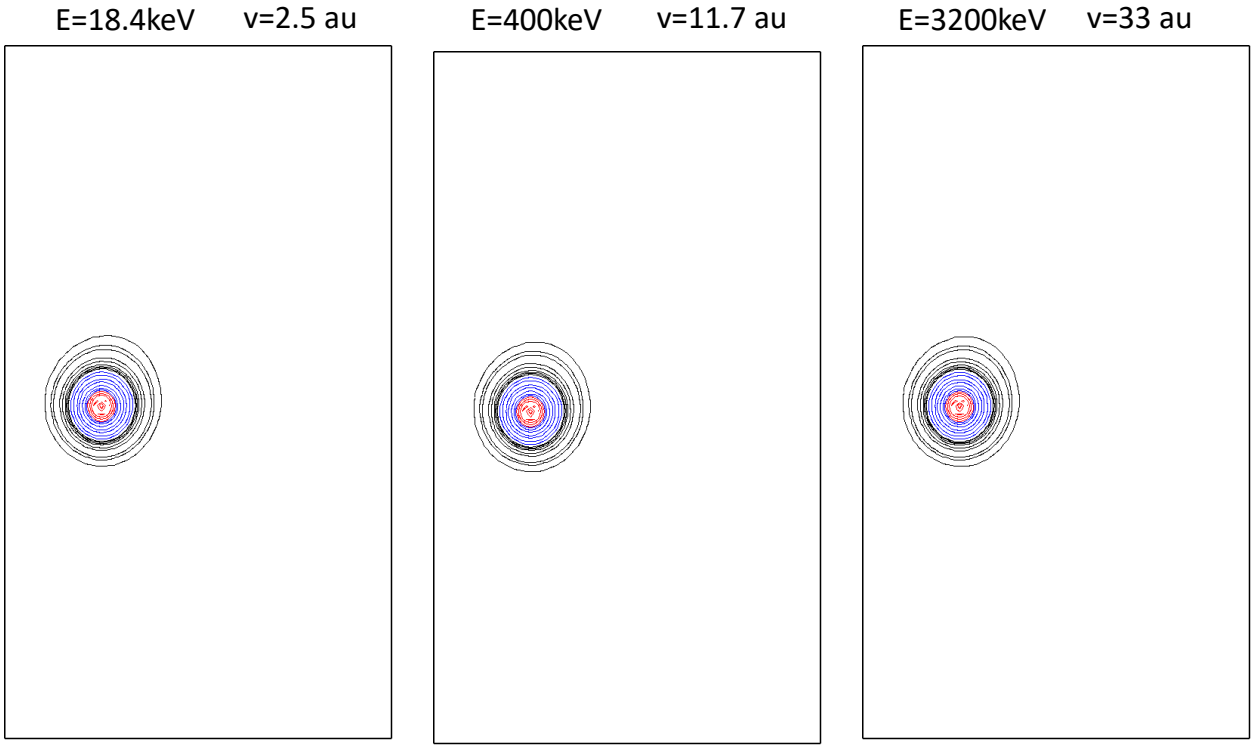
Collision of highly charged ion with atom

Ar^{8+} - Ar at 18 keV v=2.5 au

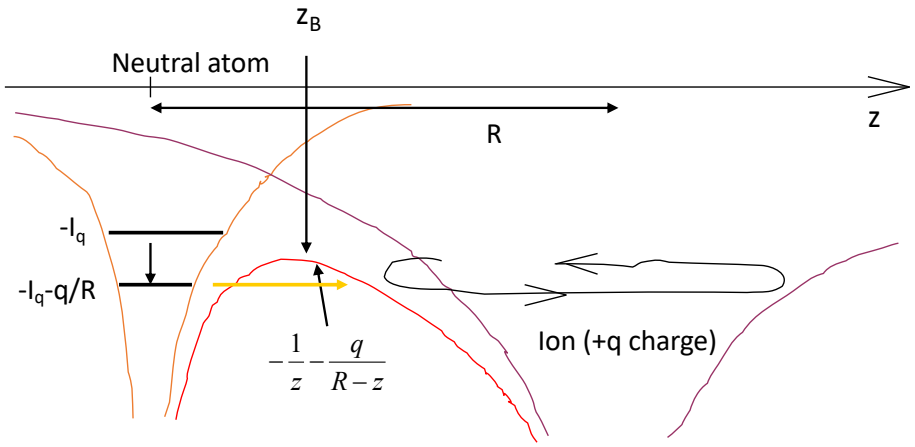


Ar^{8+} - Ar Collision

Nagano, Yabana, Tazawa, Abe, Phys. Rev. A62(2000)062721



Electron transfer to highly excited orbitals: Classical Overbarrier Model



Condition for charge transfer

$$-I_P-\frac{q}{R}=-\frac{1}{z_B}-\frac{q}{R-z_B}$$

SALMON

http://salmon-tddft.jp

TDDFT School and SALMON Hands-on Seminar
Center for Computational Sciences, University of Tsukuba
Nov. 11-12, 2018

Practical Aspects of TDDFT Calculations

partly as an introduction to the afternoon tutorial session using SALMON: Scalable Ab Initio Light-Matter simulator for Optics and Nano-science

Kazuhiro Yabana

Center for Computational Sciences
University of Tsukuba

筑波大学 計算科学研究センター Center for Computational Sciences

筑波大学 University of Tsukuba

Classifications of TDDFT calculations for optical responses
that can be done in current SALMON

	Isolated Systems (Molecules, Nano-particles)	Periodic Systems (Crystalline solids)	Light propagation in bulk materials (Maxwell + TDDFT)
Weak fields (Linear response)	Polarizability $\alpha(\omega)$	Dielectric function $\varepsilon(\omega)$	1D light propagation E(x,t), J(x,t)
Strong fields (Nonlinear dynamics)	Excitation energy Atomic motion	Excitation energy Carrier density Atomic motion	

Schrödinger equation in a periodic potential: Bloch's theorem

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right\}\phi_i(x)=\epsilon_i\phi_i(x) \qquad V(x+a)=V(x)$$

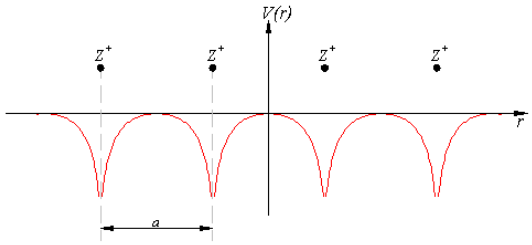
$$\phi_i(x)=e^{ikx}u_{nk}(x)$$

$$u_{nk}(x+a)=u_{nk}(x)$$

$$\left\{\frac{1}{2m}\left(-i\hbar\frac{d}{dx}+\hbar k\right)^2+V(x)\right\}u_{nk}(x)=\epsilon_{nk}u_{nk}(x)$$

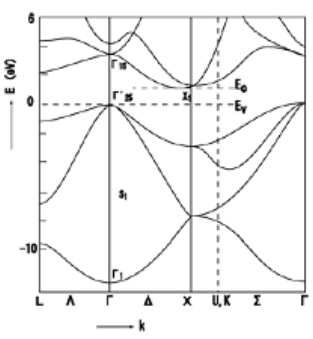
$$-\frac{\pi}{a}<k<\frac{\pi}{a}$$

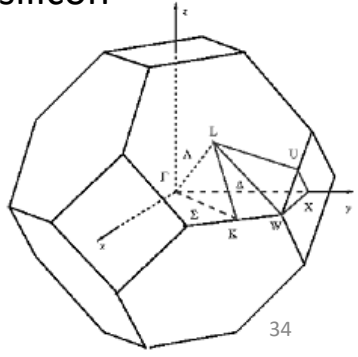
Brillouin zone (k-points)



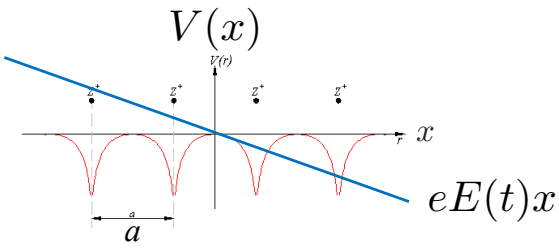
Energy band of crystalline silicon

$\epsilon_{n\vec{k}}$





Using potential ("length gauge"), lattice periodicity is violated



$$V(x+a) \neq V(x)$$

We make use of gauge freedom to overcome the problem.

A general scheme of gauge transformation

$$i\hbar\frac{\partial}{\partial t}\psi = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla}+\frac{e}{c}\vec{A}\right)^2+\phi\right\}\psi$$

$$\psi'(\vec{r},t) = \exp\left[\frac{ie}{\hbar c}f(\vec{r},t)\right]\psi(\vec{r},t)$$

$$i\hbar\frac{\partial}{\partial t}\psi' = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla}+\frac{e}{c}\vec{A}'\right)^2+\phi'\right\}\psi'$$

$$\vec{A}'(\vec{r},t) = \vec{A}(\vec{r},t) - \vec{\nabla}f(\vec{r},t)$$

$$\phi'(\vec{r},t) = \phi(\vec{r},t) - \frac{e}{c}\frac{\partial}{\partial t}f(\vec{r},t)$$

Physical quantities are invariant under the transformation.

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

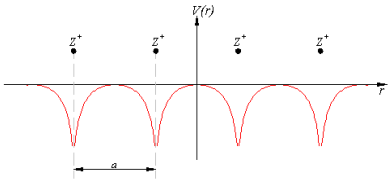
$$\rho(\vec{r},t) = |\psi(\vec{r},t)|^2$$

$$\vec{j}(\vec{r},t) = \mathrm{Re}\left\{\psi(\vec{r},t)\frac{1}{m}\left(-i\hbar\vec{\nabla}+\frac{e}{c}\vec{A}(\vec{r},t)\right)\psi(\vec{r},t)\right\}$$

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\phi(\vec{r},t) - \frac{1}{c}\frac{\partial\vec{A}(\vec{r},t)}{\partial t}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A}(\vec{r},t)$$

Gauge transformation: from "length gauge" to "velocity gauge"



Length gauge

$$i\hbar\frac{\partial}{\partial t}\psi = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla}\right)^2 + V(\vec{r}) + e\vec{E}(t)\cdot\vec{r}\right\}\psi$$

$$\psi' = \exp\left[\frac{ie}{\hbar c}\vec{A}(t)\cdot\vec{r}\right]\psi \qquad \vec{E}(t) = -\frac{1}{c}\frac{d\vec{A}(t)}{dt}$$

Velocity gauge

$$i\hbar\frac{\partial}{\partial t}\psi' = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \frac{e}{c}\vec{A}(t)\right)^2 + V(\vec{r})\right\}\psi'$$

Expressing the spatially-uniform electric field by a vector potential, Hamiltonian has the lattice periodicity.

$$h(\vec{r}+\vec{a}) = h(\vec{r})$$

Time-Dependent Kohn-Sham equation

$$i\hbar\frac{\partial}{\partial t}\psi_i(\vec{r},t) = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \frac{e}{c}\vec{A}(t)\right)^2 - \sum_a \frac{Z_a e^2}{|\vec{r}-\vec{R}_a|} + \int d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}\rho(\vec{r}',t) + \mu_{xc}[\rho(\vec{r},t)]\right\}\psi_i(\vec{r},t)$$

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

At each time, we may apply the Bloch's theorem

$$\psi_i(\vec{r},t) = e^{i\vec{k}\vec{r}}u_{n\vec{k}}(\vec{r},t) \qquad i \to (n\vec{k})$$

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

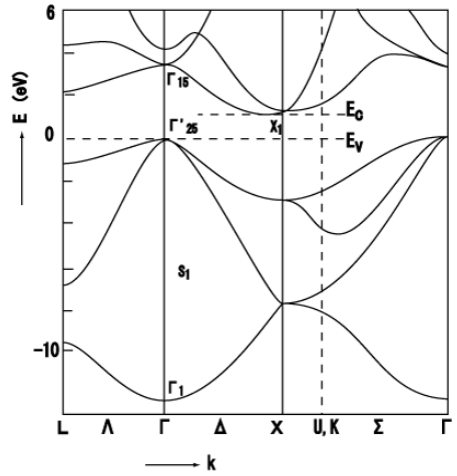
$$u_{n\vec{k}}(\vec{r}+\vec{a},t) = u_{n\vec{k}}(\vec{r},t)$$

Electron dynamics in a unit cell of solid (bulk silicon)

Ground state band structure
static Density Functional Theory (DFT)

$$\varepsilon_{nk} u_{nk}(r) = \left[\frac{1}{2m}(p+\hbar k)^2 + V_H(r) + V_{xc}(r)\right] u_{nk}(r)$$

Energy band of silicon

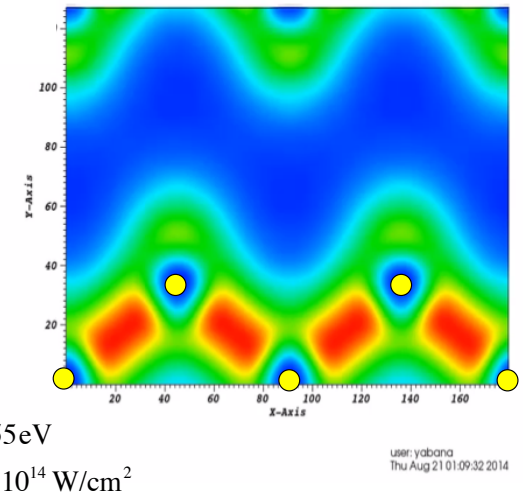


Electron dynamics in a unit cell
Time-dependent DFT (TDDFT)

$$i\hbar\frac{\partial}{\partial t} u_{nk}(r,t) = \left[\frac{1}{2m}\left(p+\hbar k+\frac{e}{c}A(t)\right)^2 + V_H(r,t) + V_{xc}(r,t)\right] u_{nk}(r,t)$$

$$A(t) = -c\int^t E(t')\mathrm{d}t'$$

Change of electron density in crystalline silicon



$\hbar\omega = 1.55\mathrm{eV}$

$I = 1.0\times10^{14}\ \mathrm{W/cm^2}$

Further gauge transformation is possible: "length gauge" in k-space

Already discussed

Length gauge

$$i\hbar\frac{\partial}{\partial t}\psi = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla}\right)^2 + V(\vec{r}) + e\vec{E}(t)\cdot\vec{r}\right\}\psi$$

$$\vec{E}(t) = -\frac{1}{c}\frac{d\vec{A}(t)}{dt}$$

Velocity gauge

$$i\hbar\frac{\partial}{\partial t}\psi' = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \frac{e}{c}\vec{A}(t)\right)^2 + V(\vec{r})\right\}\psi'$$

Time-dependent Bloch equation

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

New

$$u'_{n\vec{k}}(\vec{r},t) = \exp\left[-\frac{e}{\hbar c}\vec{A}(t)\vec{\nabla}_k\right]u_{n\vec{k}}(\vec{r},t)$$

Length gauge in k-space

$$i\hbar\frac{\partial}{\partial t}u'_{n\vec{k}} = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \hbar\vec{k}\right)^2 + V(\vec{r}) + ie\vec{E}(t)\vec{\nabla}_k\right\}u'_{n\vec{k}}$$

Coordinate operator in Bloch space $\vec{r} \to i\nabla_k$ $\qquad e\vec{E}(t)\cdot\vec{r}$

Modern theory of polarization using Berry's phase

R.D. King-Smith, D. Vanderbilt, Phys. Rev. B47, 1651 (1993)

$$\vec{P} = \frac{1}{V}\int d\vec{r}\ \ \vec{r}\rho(\vec{r})$$

$$\vec{P} = -e\frac{1}{(2\pi)^3}\sum_n \int_{BZ} d\vec{k}\langle u_{n\vec{k}}|i\vec{\nabla}_k|u_{n\vec{k}}\rangle \qquad \vec{r} \to i\nabla_k$$

Dynamical Berry theory

$$i\hbar\frac{\partial}{\partial t}u'_{n\vec{k}} = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \hbar\vec{k}\right)^2 + V(\vec{r}) + ie\vec{E}(t)\vec{\nabla}_k\right\}u'_{n\vec{k}}$$

Coordinate operator in Bloch space $\vec{r} \to i\nabla_k$ $\qquad e\vec{E}(t)\cdot\vec{r}$

I. Souza, J. Iniguez, D. Vanderbilt, Phys. Rev. B69, 085106 (2004)
C. Attaccalite, M. Gruening, Phys. Rev. B88, 235113 (2013)

Time-dependent Kohn-Sham equation for Bloch orbitals (implemented in SALMON)

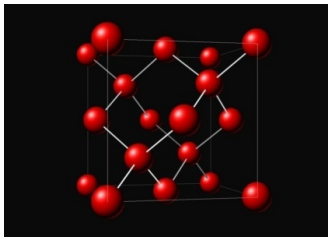
$$i\hbar\frac{\partial}{\partial t}u_{n\vec{k}}(\vec{r},t) = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \hbar\vec{k} + \frac{e}{c}\vec{A}(t)\right)^2 - \sum_a \frac{Z_a e^2}{|\vec{r}-\vec{R}_a|} + \int d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}\rho(\vec{r}',t) + \mu_{xc}[\rho(\vec{r},t)]\right\}u_{n\vec{k}}(\vec{r},t)$$

$$u_{n\vec{k}}(\vec{r}+\vec{a},t) = u_{n\vec{k}}(\vec{r},t) \qquad \vec{E}(t) = -\frac{1}{c}\frac{d\vec{A}(t)}{dt}$$

- **Calculation of dielectric function in real time**
- **Electron dynamics in crystalline solids under intense and ultrashort light pulse**

Electric field, Electric current density, Polarization density, Conductivity, Dielectric function

$E(t)$



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

Current density from Microscopic to Macroscopic

$$J(t) = \frac{1}{V}\int_V d\vec{r} j(\vec{r},t)$$

Electric field induces electric current in a unit cell of solid

$$J(t) = \int^t dt' \underline{\sigma(t-t')} E(t')$$

conductivity

Polarization is given as time-integral of the current

$$P(t) = \int^t dt' J(t')$$

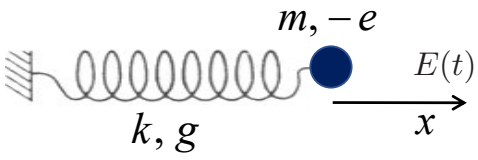
Dielectric function

$$D(t) = E(t) + 4\pi P(t) = \int^t dt' \underline{\epsilon(t-t')} E(t')$$

Dielectric function

Classical spring-mass model for dielectric function

Impulsive force



Sinusoidal field

Newtonian dynamics

$$m\ddot{x} + kx = I\delta(t)$$

$$x(0) = 0 \quad \dot{x}(0) = \frac{I}{m}$$

$$x(t) = \theta(t)\frac{I}{m\omega_0}\sin\omega_0 t \quad \omega_0^2 = \frac{k}{m}$$

Electric current

$$J(t) = -en\dot{x}(t) \quad n \text{ oscillator density}$$

Conductivity and dielectric function

$$\sigma(t) = \theta(t)\frac{e^2 n}{m}\cos\omega_0 t$$

$$\epsilon(t) = \delta(t) + \theta(t)\frac{4\pi e^2 n}{m\omega_0}\sin\omega_0 t$$

Newtonian dynamics

$$m\ddot{x} + kx = -eE_0 e^{-i\omega t}$$

$$x(t) = -\frac{e}{m}\frac{1}{-\omega^2+\omega_0^2}E_0 e^{-i\omega t}$$

Polarization

$$P(t) = -enx(t) = \frac{e^2 n}{m}\frac{1}{-\omega^2+\omega_0^2}E(t)$$

Dielectric function

$$D = E + 4\pi P = \epsilon(\omega)E$$

$$\epsilon(\omega) = 1 + \frac{4\pi e^2 n}{m}\frac{1}{-\omega^2+\omega_0^2}$$

Calculation of Dielectric function in TDDFT
Time-domain method

Time-dependent Kohn-Sham equation for Bloch orbitals (implemented in SALMON)

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

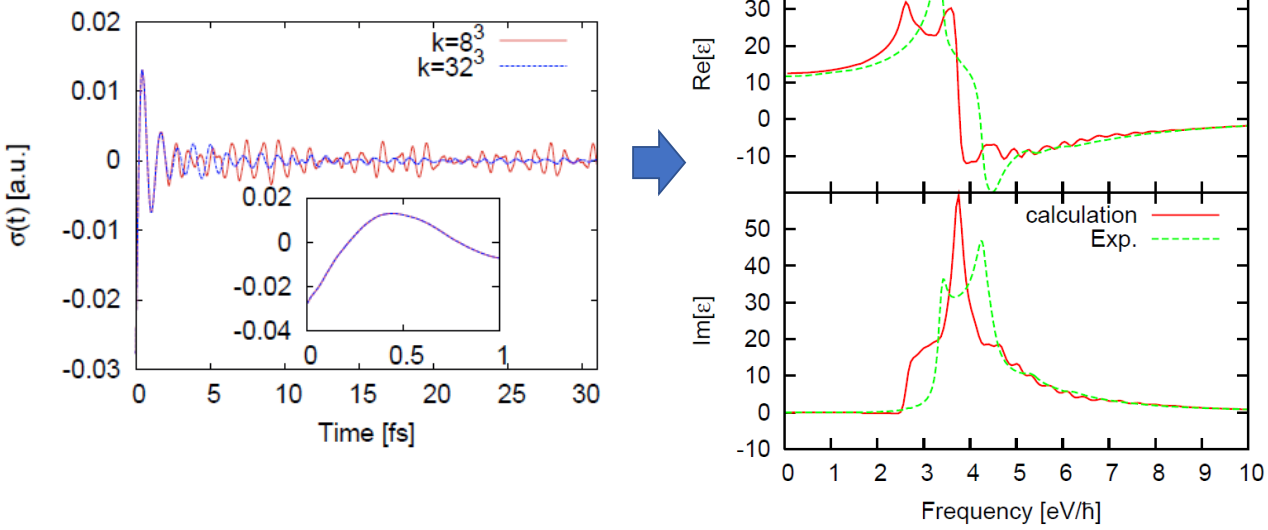
$$u_{n\vec{k}}(\vec{r}+\vec{a},t)=u_{n\vec{k}}(\vec{r},t)\qquad \vec{E}(t)=-\frac{1}{c}\frac{d\vec{A}(t)}{dt}$$

Computational procedure

Prepare ground state	$h_{KS}\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r})$
Apply impulsive external potential = shift of k-value	$E(t)=k\delta(t)\qquad A(t)=-ck\theta(t)$
Calculate electric current	$J(t)=\frac{1}{V}\int d\vec{r}j(\vec{r},t)\rightarrow k\sigma(t)$
Fourier transformation Conductivity and dielectric function	$\sigma(\omega),\quad \epsilon(\omega)=1+\frac{4\pi i\sigma(\omega)}{\omega}$

Dielectric function for bulk Si（TDDFT-ALDA）

$$E(t)=k\delta(t)\qquad A(t)=-kc\theta(t)$$



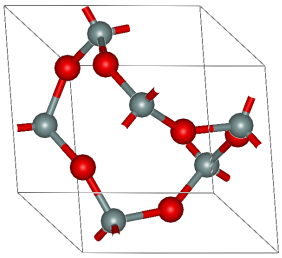
Results using LDA is rather poor.

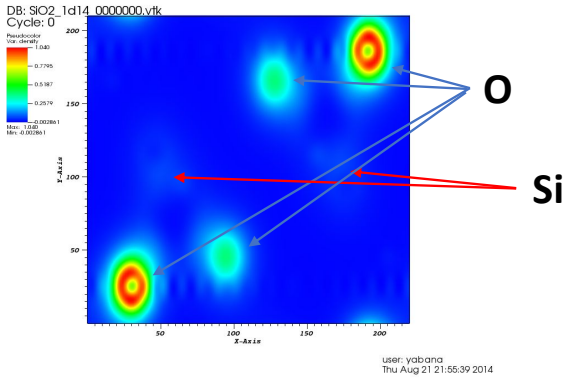
Classifications of TDDFT calculations for optical responses
that can be done in current SALMON

	Isolated Systems (Molecules, Nano-particles)	Periodic Systems (Crystalline solids)	Light propagation in bulk materials (Maxwell + TDDFT)
Weak fields (Linear response)	Polarizability $\alpha(\omega)$	Dielectric function $\varepsilon(\omega)$	1D light propagation E(x,t), J(x,t)
Strong fields (Nonlinear dynamics)	Excitation energy Atomic motion	Excitation energy Carrier density Atomic motion	

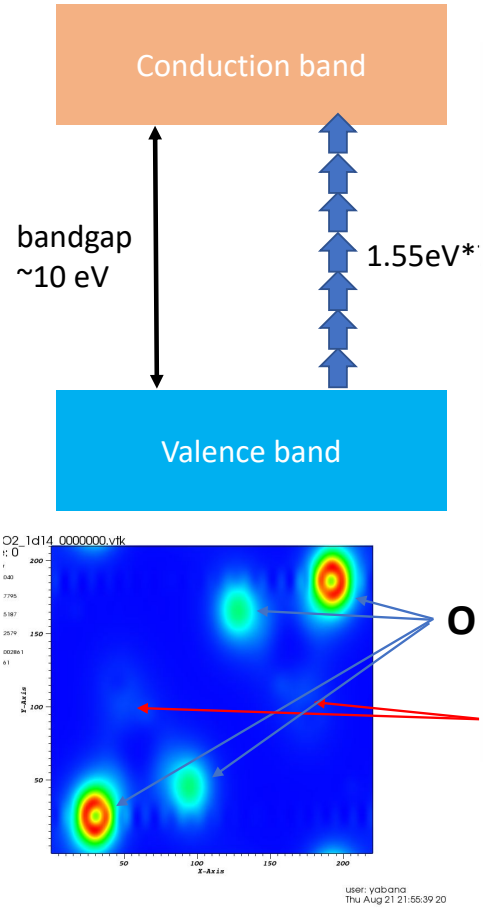
Electron dynamics in α-quartz (SiO_2)

Electron density in the ground state
In a plane containing two O atoms

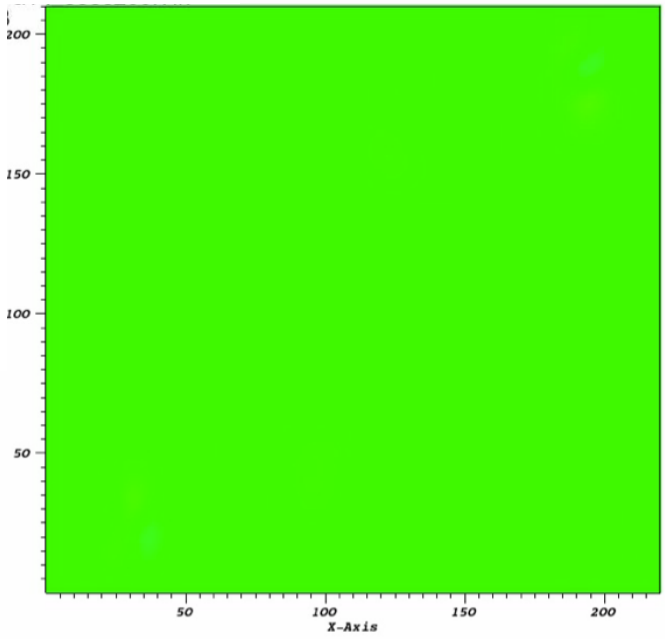




Multiphoton/Tunneling excitation



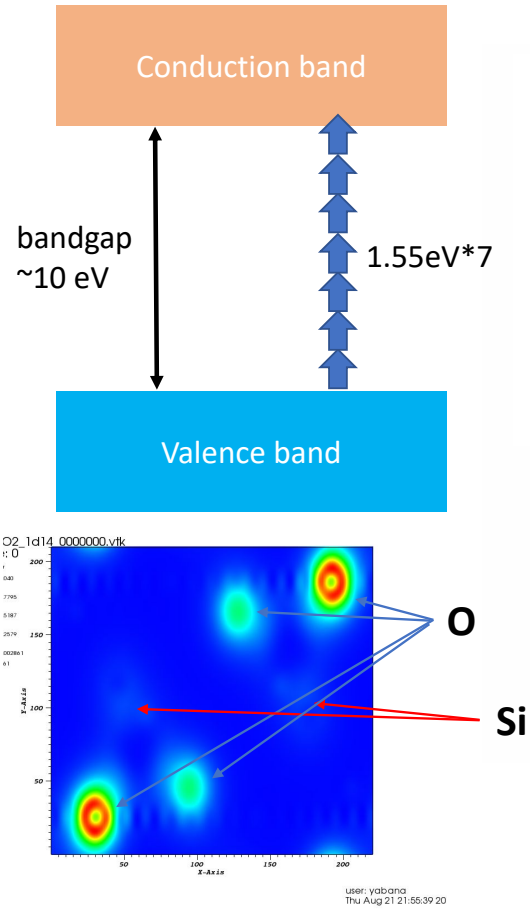
Electron density change
Laser pulse: 10^{13} W/cm^2, 800nm (1.55eV)



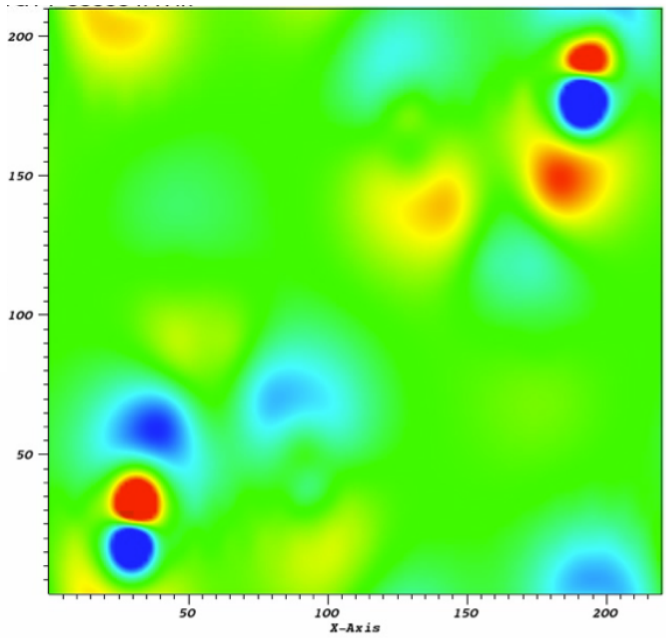
Red: increase, Blue: decrease

user: yaba
Thu Aug 2

Multiphoton/Tunneling excitation



Electron density change
Laser pulse: 10^{14} W/cm^2, 800nm (1.55eV)

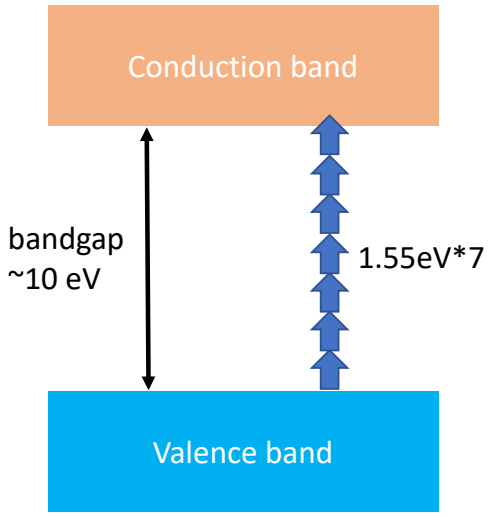


Red: increase, Blue: decrease

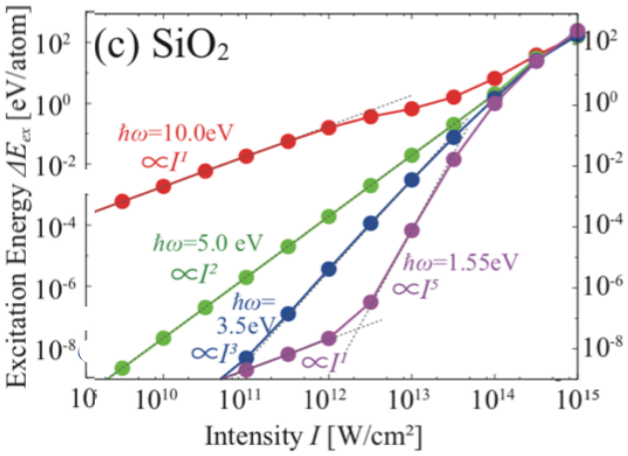
user: yabc
Thu Aug 2

Energy transfer from a pulsed electric field to electrons in solids

Multiphoton/Tunneling excitation



Pulse duration (FWHM) 5.5 fs

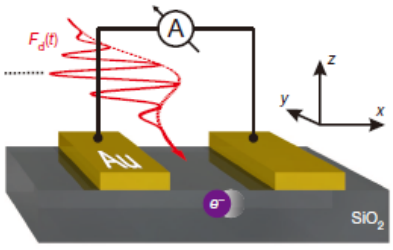


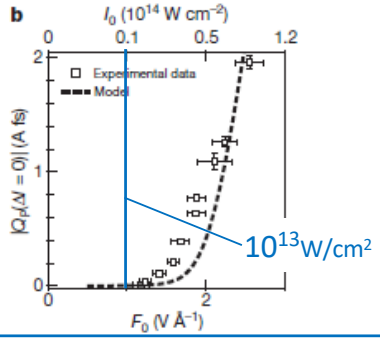
A. Yamada, K. Yabana, arXiv:1807.02733

Possible applications in forefront optical sciences

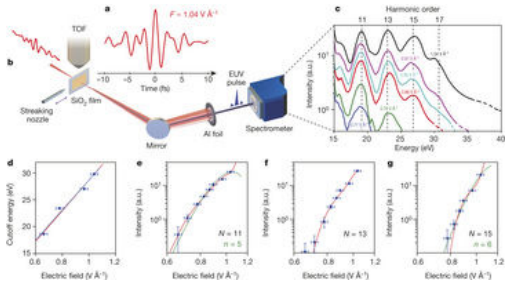
Optical field induced current in SiO_2

Experiment:
Schiffrin et.al,
Nature 493, 70 (2013).





High Harmonic Generation in solids

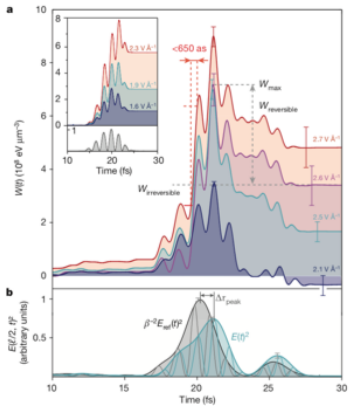


T.T. Luu et.al, Nature 521, 498 (2015)

Possible applications in forefront optical sciences

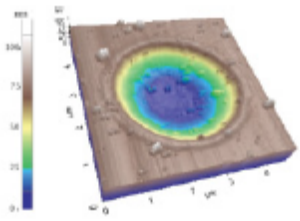
Ultrafast energy transfer from laser pulse to electrons in SiO_2

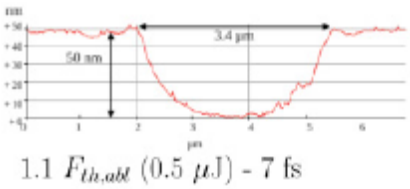
A. Sommer et.al, Nature 534, 86 (2016)



Creation of crator by strong laser pulse: Initial stage of nonthermal laser processing

B. Chimier et al, Phys. Rev. B84, 094104 (2011)





$1.1\ F_{th,abl}\ (0.5\ \mu\mathrm{J})$ - 7 fs

Classifications of TDDFT calculations for optical responses that can be done in current SALMON

	Isolated Systems (Molecules, Nano-particles)	Periodic Systems (Crystalline solids)	Light propagation in bulk materials (Maxwell + TDDFT)
Weak fields (Linear response)	Polarizability $\alpha(\omega)$	Dielectric function $\varepsilon(\omega)$	1D light propagation E(x,t), J(x,t)
Strong fields (Nonlinear dynamics)	Excitation energy Atomic motion	Excitation energy Carrier density Atomic motion	

“Calculations” of light-matter interaction

Macroscopic Electromagnetism (EM)

Light propagation description by Maxwell equations. Materials’ properties comes into through constitutive relations (dielectric constant).

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

$$D = \varepsilon E$$

Constitutive relation connects two theories

Quantum Mechanics (QM)

First-principles calculations for dielectric function.
Perturbation theory in quantum mechanics.

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

Constitutive Relation bridges EM and QM

$$D(r,t) = E(r,t) + 4\pi P(r,t)$$

Ordinary assumption: Local + Linear

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

General form (nonlocal, nonlinear)

$$\begin{aligned} P(r,t) &= P[E(r',t')] \\ &= \int dt' dr' \chi^{(1)}(r,r',t-t') E(r',t') \\ &\quad + \int dt' dt'' dr' dr'' \chi^{(2)}(r,r',r'',t-t',t-t'') E(r',t') E(r'',t'') + \cdots \end{aligned}$$

In recent optical sciences,

Nano-structure → nonlocal
Intense laser pulse → nonlinear

⇒ Require unified approach of EM and QM.

Propagation of light electromagnetic fields

Maxwell eq. + ”modelling for electron dynamics”

Empirical, computationally cheap

Drude or Lorentz model for dielectric function
electron dynamics = classical Newtonian motion

Empirical models
Rate equation for carriers, Two temperature model

Semiconductor Bloch Equation (SBE)
Time evolution of density matrix, with (ab-initio) band structure, empirically introducing dephasing, exciton, e-phonon,…

Ab-initio, computationally expensive

TDDFT in real time

Light propagation using dielectric constant

Incident pulse

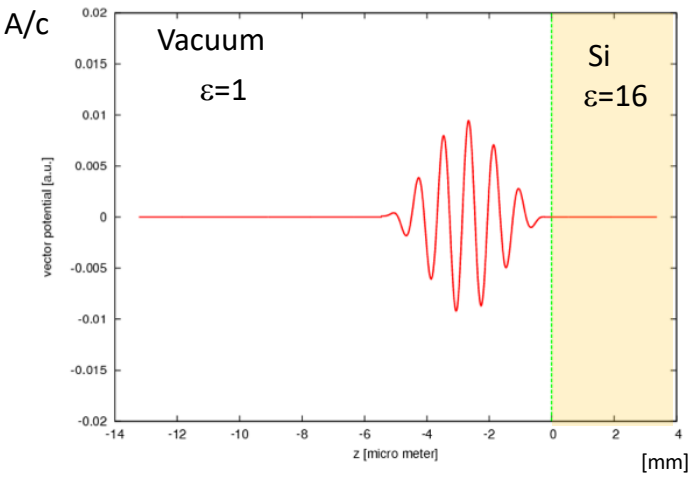
$\lambda = 800\text{nm},$

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

Wave equation

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

$$\varepsilon(z) = \begin{cases} 16 & (\text{Si}) \\ 1 & (\text{vacuum}) \end{cases}$$



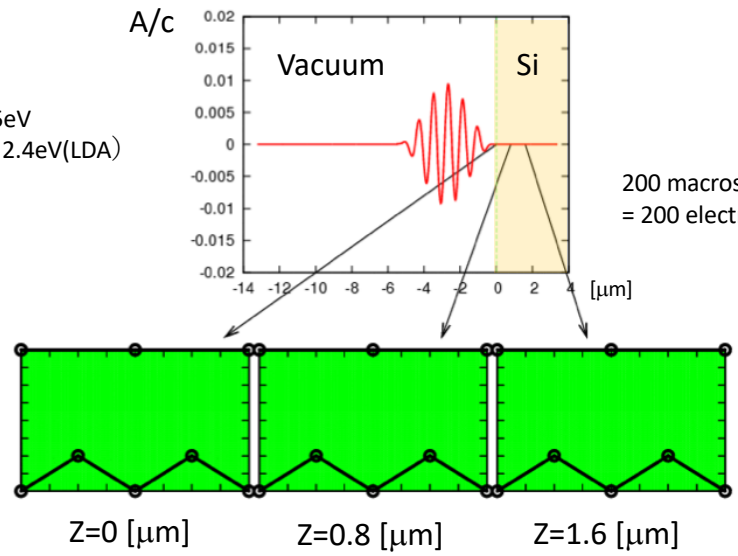
When light pulse is very strong, we cannot use dielectric function.

Maxwell + TDDFT multiscale simulation

Weak pulsed light irradiating on a surface of bulk Si

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

Frequency: 1.55eV
Direct bandgap: 2.4eV(LDA)



200 macroscopic grid ponts
= 200 electron dynamics in parallel

Z=0 [μm] Z=0.8 [μm] Z=1.6 [μm]