Poorman's Multiscale Maxwell + TDDFT

7/18/21

- Goal: Use DCMESH code structure to mimick Maxwell + TDDFT approach [Yabana, PRB <u>85</u>, 045134 ('12)].

- Observation: Non-self-consistent transverse-geometry surface interpretation (i.e., $\mathbb{A}(t) = \mathbb{A}_{ext}(t)$) has zero induced vector-potential feedback [Sato, JCP <u>143</u>, 224116 ('15)]

  $\downarrow$

  Presence of its & neighbor bulk supercells may somewhat screen external laser pulse even for surface supercell.

- Approach: Linear interpolation of recent $\mathbb{A}(t)$ vs. $\mathbb{J}_{avg}(t)$ history of the surface supercell to emulate the optical response (or constitutive equation) of bulk supercells as effective medium that satisfies

$$\mathbb{J}_{avg}(t) = \sigma \mathbb{E}(t) \qquad (1)$$

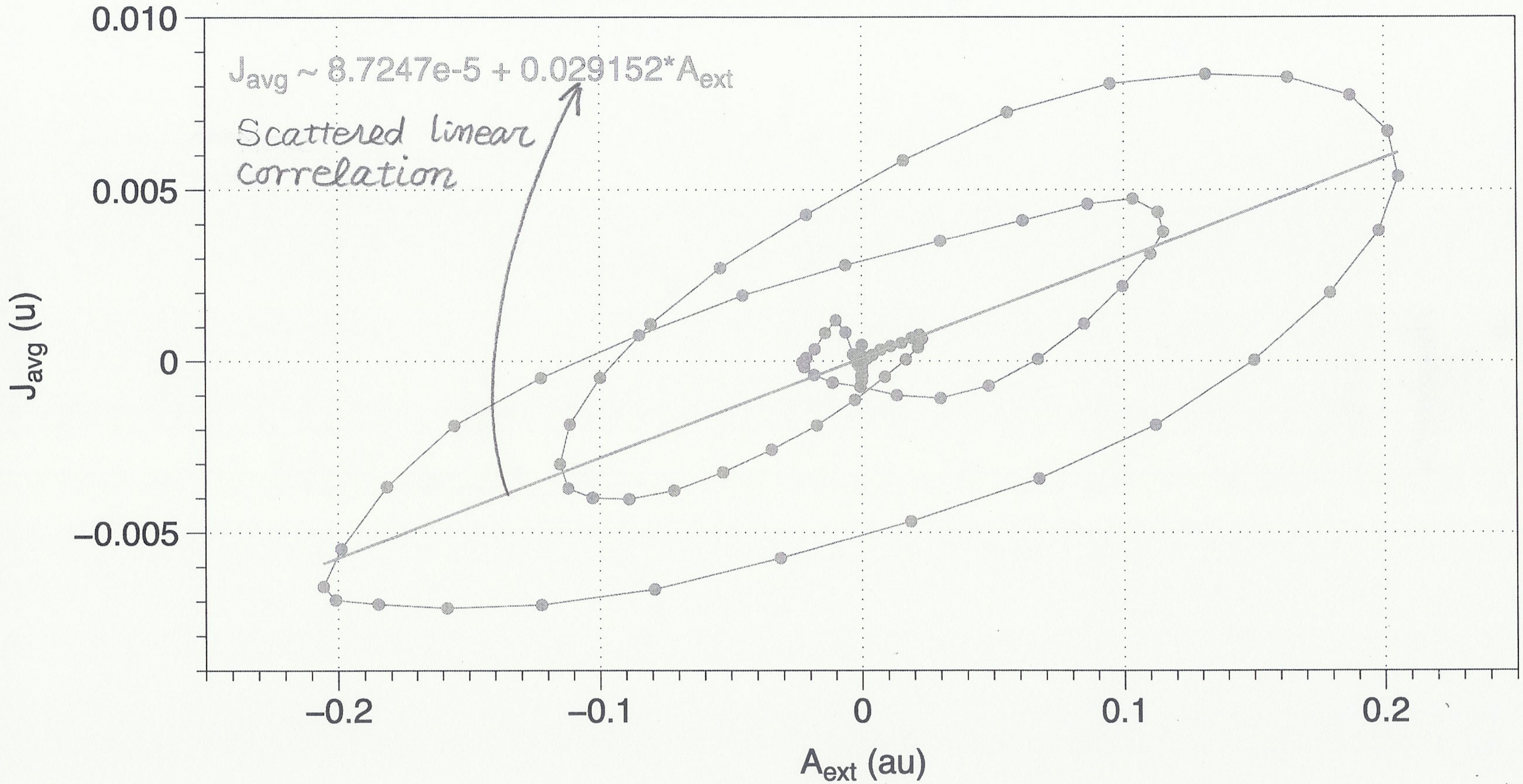
where $\mathbb{J}_{avg}(t)$ is supercell-averaged current, and electric field is obtained from vector potential $\mathbb{A}(t)$ as

$$\mathbb{E}(t) = -\frac{1}{c}\frac{\partial}{\partial t}\mathbb{A}(t) \qquad (2)$$

cf. $\mathbb{J}_{avg}(t)$ and $\mathbb{A}_{ext}(t)$ shows high correlation [PTO200nm-trns-sm-d005-071721].

* While some spectral analysis of $\sigma(\omega)$ is possible, we initially assume similar spectral components in recent history, hence simple prefactor scaling, for simplicity.

PTO 200nm - trns-sm-d005-071721/



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- Macroscopic Maxwell equation

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial \mathbb{R}^2}\right) \mathbb{A}_{\mathbb{R}}(t) = \frac{4\pi}{c} \mathbb{J}_{\mathbb{R}}(t) \tag{3}$$

where $\mathbb{R}$ is macroscopic position, and $\mathbb{A}_{\mathbb{R}}(t)$ & $\mathbb{J}_{\mathbb{R}}(t)$ are macroscopic vector potential & current.

We introduce

$$\tilde{\mathbb{A}}_{\mathbb{R}}(t) = -\frac{1}{c} \mathbb{A}_{\mathbb{R}}(t) \tag{4}$$

which satisfies

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial \mathbb{R}^2}\right) \tilde{\mathbb{A}}_{\mathbb{R}}(t) = -\frac{4\pi}{c^2} \mathbb{J}_{\mathbb{R}}(t) \tag{5}$$

or

$$\frac{\partial^2}{\partial t^2} \tilde{\mathbb{A}}_{\mathbb{R}}(t) = c^2 \frac{\partial^2}{\partial \mathbb{R}^2} \tilde{\mathbb{A}}_{\mathbb{R}}(t) - 4\pi \mathbb{J}_{\mathbb{R}}(t) \tag{6}$$

In terms of $\tilde{\mathbb{A}}_{\mathbb{R}}(t)$,

$$\mathbb{E}(t) = \frac{\partial}{\partial t} \tilde{\mathbb{A}}_{\mathbb{R}}(t) \tag{7}$$

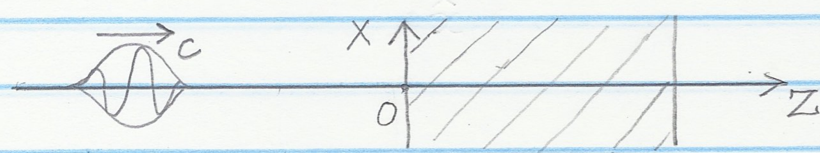
- Transverse geometry

We consider lineary-polarized vector potential incident normal to flat surface in xy-plane,

$$\tilde{\mathbb{A}}_{\mathbb{R}}(t) = \hat{x}\,\tilde{A}_Z(t), \tag{8}$$

for which current is

$$\mathbb{J}_{\mathbb{R}}(t) = \hat{x}\,J_Z(t). \tag{9}$$



Maxwell equation thus becomes

$$\frac{\partial^2}{\partial t^2}\tilde{A}_Z(t) = c^2\frac{\partial^2}{\partial Z^2}\tilde{A}_Z(t) - 4\pi J_Z(t) \tag{10}$$

※ We take $Z \geq 0$ to be material.

- Laser pulse [6/18/20]

At $t \leq 0$, let

$$\tilde{A}_Z(t) = \frac{D_{ext}}{\omega_{ext}} \sin\left[\omega_{ext}\left(t - \frac{Z}{c}\right) - \cancel{\varphi_{ext}}\right]$$

$$\times \sin^2\left[\frac{\pi}{T_{0ext}}\left(t - \frac{Z}{c}\right)\right] \Theta\left(0 < t - \frac{Z}{c} < T_{0ext}\right) \quad (11)$$

Let

$$Z_0 \equiv c\,T_{0ext}, \quad (12)$$

then, at $t=0$, $\tilde{A}_Z(t=0)$ is nonzero at

$$-Z_0 < Z < 0,$$

namely, the front of laser pulse just reached surface.

※ For PTO400nm.in, $T_{0ext} = 220.46$ au, thus

$$Z_0 = \underbrace{c}_{137.036\text{ au}} T_{0ext} = 30,210.96\text{ au} = 15987\,\text{Å} = 1.5987\,\mu\text{m}$$

- Time derivative (omit ext-subscript)

$$\frac{\partial \tilde{A}_z}{\partial t} = D\cos\left(\omega\left(t-\frac{z}{c}\right)\right)\sin^2\left(\frac{\pi}{T_0}\left(t-\frac{z}{c}\right)\right)$$

$$+\frac{D}{\omega}\sin\left(\omega\left(t-\frac{z}{c}\right)\right)\times 2\sin\left(\frac{\pi}{T_0}\left(t-\frac{z}{c}\right)\right)\frac{\pi}{T_0}\cos\left(\frac{\pi}{T_0}\left(t-\frac{z}{c}\right)\right)$$

$$= \sin\left(\frac{2\pi}{T_0}\left(t-\frac{z}{c}\right)\right)$$

$$\therefore \frac{\partial \tilde{A}_z}{\partial t} = D\cos\left(\omega\left(t-\frac{z}{c}\right)\right)\sin^2\left(\frac{\pi}{T_0}\left(t-\frac{z}{c}\right)\right)$$

$$+\frac{\pi D}{\omega T_0}\sin\left(\omega\left(t-\frac{z}{c}\right)\right)\sin\left(\frac{2\pi}{T_0}\left(t-\frac{z}{c}\right)\right) \qquad (13)$$

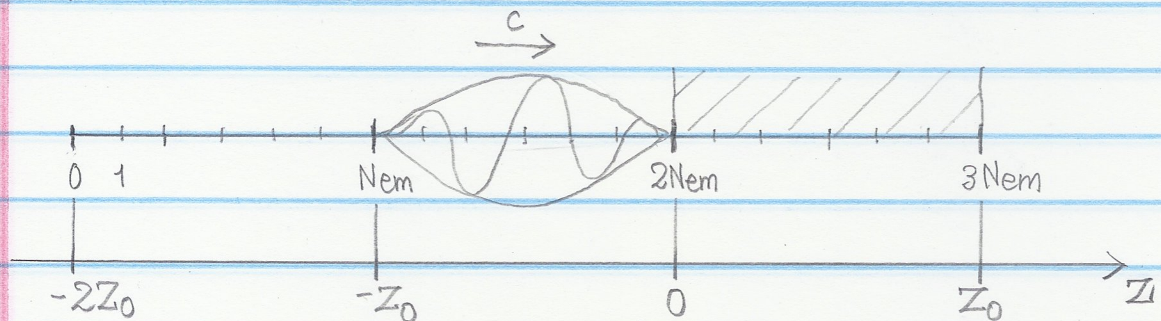
$$\left(0 < t-\frac{z}{c} < T_0\right)$$

– Spatial discretization: finite difference

We discritize Z_0-long pulse into Nem mesh points. Computational domain is defined as a range $Z \in [-2Z_0, Z_0]$. The mesh size is

$$\Delta_Z = \frac{Z_0}{N_{em}} \tag{14}$$

and there are $3N_{em}+1$ mesh points, including the both ends.



Data structure:

$A_{st}[3(3N_{em}+1)]$: $A_{st}[0|1|2+3\cdot i]$ stores $\tilde{A}_Z \,|\, \Delta_{QD}\dot{\tilde{A}}_Z \,|\, \frac{\Delta_{QD}^2}{2}\ddot{\tilde{A}}_Z$ (see below)

at $i \in [0, 3N_{em}]$ mesh point

where Δ_{FD} is time discretization unit for time propagation (10^{-3} au in lfd-PTO400nm.in).

$J_{st}[3N_{em}+1]$: $J_{st}[i]$ stores $J_Z(t)$ at i-th mesh point

Note i-th mesh point is

$$Z_i = -2Z_0 + i\Delta_Z \quad (i = 0, 3\cdot N_{em}) \tag{15}$$

※ If we take

$$N_{em} = 128$$

for PTO 400 nm case,

$$\Delta_Z = \frac{30,210.96}{128} = 236.02 \text{ au},$$

and it takes

$$\frac{\Delta z}{c} = \frac{236.02}{137.036} = 1.72 \text{ au}$$

for light to travel one mesh point. $\Delta_{FD} = 10^{-3}$ au is an overkill.

↓

Let's us Δ_{QD} as time-propagation unit instead.

- Dirichlet boundary condition

We set

$$A_{st}[01112 + 3\cdot 0] = A_{st}[011121 + 3\cdot(3N_{em})] = 0 \quad (16)$$

※ Note the supercell for electron dynamics is located at 2Nem-th mesh point, i.e.,

$$z_{2N_{em}} = -2z_0 + 2\cancel{N_{em}} \cdot \frac{z_0}{\cancel{N_{em}}} = 0$$

— Constitutive relation

We need to infer current at inner material mesh points from the surface-supercell value, Javg[0], following Eq. (1), or

$$J_Z(t) = \sigma \dot{\tilde{A}}_Z(t) \tag{17}$$

For free pulse, $\dot{\tilde{A}}_Z$ in Eq. (13) is bounded by

$$\dot{\tilde{A}}_Z^{max} = D_{ext}\left[1 + \frac{\pi}{\omega_{ext} \underbrace{T_{0ext}}_{N_{cycle}\,(\#\text{ of periods in pulse}) \times \frac{2\pi}{\omega_{ext}}}}\right] \tag{18}$$

$$= D_{ext}\left[1 + \frac{\cancel{\pi}}{\cancel{\omega_{ext}} \cdot N_{cycle} \cdot \frac{2\cancel{\pi}}{\cancel{\omega_{ext}}}}\right]$$

$$= D_{ext}\left[1 + \frac{1}{2N_{cycle}}\right] \tag{19}$$

Rough estimate of maximum Ast[] value, which stores $\Delta_{QD}\dot{\tilde{A}}_Z$ is thus

$$A_{stmax} \sim \Delta_{QD} D_{ext} \tag{20}$$

To avoid numerical divergence, we define

$$\mathrm{Astcut} = \underbrace{\mathrm{SMALL}}_{10^{-2}} \cdot \mathrm{Astmax} = \mathrm{SMALL} \cdot \Delta_{QD} D_{ext} \quad (21)$$

and estimate

$$\underbrace{\sigma}_{\text{CONDUCTIVITY}} = \frac{\mathrm{Javg}[\overset{\to x \text{ component}}{0}]}{\max(\underbrace{\mathrm{Ast}[1+2\cdot N_{em}]}_{\Delta_{QD}\dot{\tilde{A}}_{Z=0}(t)}, \mathrm{Astcut})} \quad (22)$$

then

$$\underbrace{J_{Z_i}(t)}_{\mathrm{Jst}[i]} \leftarrow \sigma \underbrace{\Delta_{QD} \dot{\tilde{A}}_{Z_i}(t)}_{\mathrm{Ast}[1+3i]} \quad (23)$$

— Algorithm: vectp_maxwell()

Time propagate vector potential for single quantum-dynamics time step, Δ_{QD}

Given Javg[], compute conductivity.

$$\sigma = \frac{Javg[0]}{\max(Ast[1+2\cdot Nem], \underbrace{Astcut}_{SMALL\cdot \Delta_{QD} Dext,\ SMALL = 10^{-3}})}$$

for $i = 1, 3Nem$

  if $i = 2\cdot Nem$

    $Jst[i] \leftarrow Javg[0]$

  else if $i > 2\cdot Nem$

    $Jst[i] \leftarrow \sigma\, Ast[1+3i]$

  else

    $Jst[i] \leftarrow 0$

for $i = 1,\ 3N_{em}-1$

$$A_{st}[2+3i] = \frac{\Delta_{QD}^2}{2}\ddot{\tilde{A}}_Z(t)$$

absorb $\quad$ Afac

$$\leftarrow \frac{\Delta_{QD}^2}{2}\left\{ c^2\,\frac{A_{st}[0+3(i-1)] - 2A_{st}[0+3i] + A_{st}[0+3(i+1)]}{\Delta_Z^2} + 4\pi J_{st}[i] \right\} \quad // \text{ compute acceleration}$$

Jfac

$A_{st}[1+3i] \mathrel{+}= A_{st}[2+3i]$ // 1st half kick

$A_{st}[0+3i] \mathrel{+}= A_{st}[1+3i]$ // position update

for $i = 1,\ 3N_{em}-1$

$A_{st}[2+3i] \leftarrow \frac{\Delta_{QD}^2}{2}\left\{ \;//\; \right\}$ // Recompute acceleration

$A_{st}[1+3i] \leftarrow A_{st}[2+3i]$ // 2nd half kick

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- Safer constitutive relation

For energy-absorbing laser irradiation, we take a numerically-more-stable alternative, i.e., spatially-decaying surface current.

$$J_Z(t) = J_{avg}[0] \exp(-Z/\lambda) \qquad (24)$$

where λ is optical decay length

$$\underbrace{\lambda}_{\text{DecayLength}} \sim 1{,}000 \text{ au} \sim 4\Delta_Z$$

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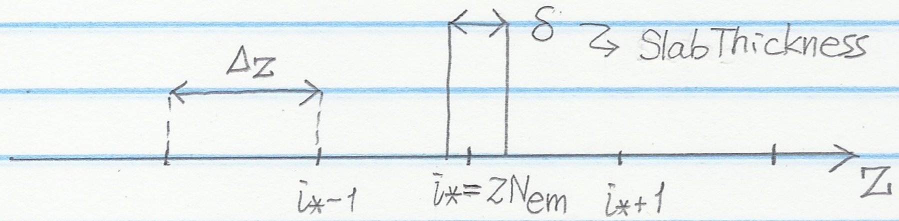
– Thin slab option (most gentle)



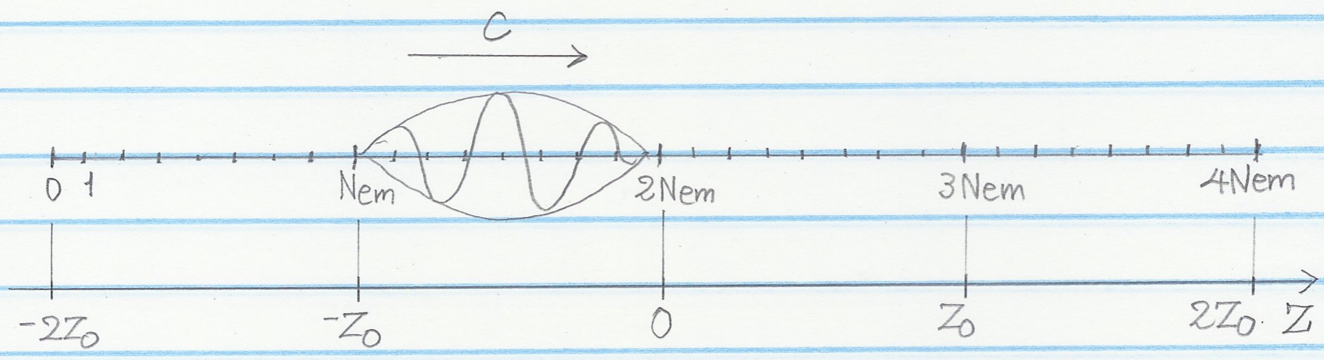
$$J_z(t) = \begin{cases} \dfrac{\delta}{\Delta z} J_{avg}[0] & (i = 2 \cdot N_{em}) \\ 0 & (\text{else}) \end{cases} \qquad (25)$$

Let $\delta = 80$ au (10 unit cells) $< \Delta z = 236$ au.

- $\delta = 0$ will recover non-self-consistent, transverse-field surface simulation, i.e., IMAXWELL $= 0$.

— Program change: symmetric computational cell

- To avoid reflection from the upper edge, macroscopic computational cell has been extended one more laser-pulse width upstream.



- Extended data structures:

  Ast [3(4Nem+1)]

  Jst [4Nem+1]

1D Maxwell Green's Function

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— 1D Maxwell equation [7/18/21]

$$\left(\frac{\partial^2}{\partial t^2} - c^2\frac{\partial^2}{\partial Z^2}\right)\tilde{A}_Z(t) = -4\pi J_Z(t) \tag{26}$$

where

$$\tilde{A}_Z(t) = -\frac{1}{c}A_Z(t) \tag{27}$$

is vector potential and $J_Z(t)$ is current density.

— Delta-function current

Let us consider delta-function current

$$J_Z(t) = \gamma\,\delta(z) \tag{28}$$

and Green's function G_Z that satisfies

$$-c^2\frac{\partial^2}{\partial Z^2}G_Z = -4\pi\gamma\,\delta(Z) \tag{29}$$

$\int dZ \times (29)$

$$\frac{\partial}{\partial Z}G_Z\Big|_{z=0-}^{z=0+} = -\frac{4\pi\gamma}{c^2} \tag{30}$$

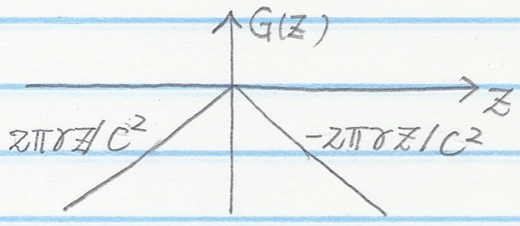
We adopt a symmetric solution,

$$\frac{\partial G_Z}{\partial z} = \begin{cases} 2\pi\gamma/c^2 & (z<0) \\ -2\pi\gamma/c^2 & (z>0) \end{cases} \tag{31}$$

$\int dZ \times (31)$

With integration constant to make $G_{Z=0} = 0$,

$$G_Z = \begin{cases} 2\pi\gamma Z/c^2 & (Z<0) \\ -2\pi\gamma Z/c^2 & (Z>0) \end{cases} \tag{32}$$



— Time-dependent solution

Consider a function

$$G_Z(t) = \begin{cases} 2\pi\gamma(Z-ct)/c^2 & (Z<0) \\ -2\pi\gamma(Z-ct)/c^2 & (Z>0) \end{cases} \tag{33}$$

This describes a vector potential at position Z at time t, which was created by the current at orgin at time 0.

— Net-neutralizing backflow

Charge sheet, Eq. (28), produces a diverging vector potential, Eq. (33), at long distance.

To avoid numerical divergence, we associate each current flow with symmetrically-placed neutralizing backflow.

$$J_Z(t) = \begin{cases} \dfrac{\delta}{\Delta z} J_{avg}[0] & (i = 2N_{em}) \\ \dfrac{\delta}{2\Delta z} J_{avg}[0] & (i = 2N_{em} \pm 1) \\ 0 & (\text{else}) \end{cases} \tag{34}$$

→ Up to hear, dcehd072221backflow/