Exciton Dynamics

8/14/21

- In orbital-based linear-response (LR) time-dependent density functional theory (TDDFT) [6/5/12], long-range corrected (LRC) exact-exchange kernel is required to describe exciton binding [Dreuw, JCP 119, 2943 ('03)]. However, it is computationally demanding to carry over the nonlocal exact-exchange kernel to real-time TDDFT (RT-TDDFT).

- Recently, a simple LRC exchange-correlation (xc) kernel was shown to describe exciton-dynamics contribution to optical responese adequately within RT-TDDFT [Sun, PRL 127, 077401 ('21)].

This is achieved through LRC-xc vector potential in the framework of time-dependent current density functional theory (TDCDFT) [Vignale, PRL 77, 2037 ('96); Maitra, PRB 68, 045109 ('03)] in the long-wavelength limit.

– LRC-xc kernel

Hartree kernel in atomic unit is

$$f_H(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{1}$$

in real space, and is

$$f_{H,\mathbf{G}\mathbf{G}'}(\mathbf{k}) = \frac{4\pi}{|\mathbf{k}+\mathbf{G}|^2}\delta_{\mathbf{G},\mathbf{G}'}(1-\delta_{\mathbf{G},0}) \tag{2}$$

in reciprocal space for periodic solid, where $\mathbf{G}$ & $\mathbf{G}'$ are reciprocal lattice vectors and $\mathbf{k}$ is a wave vector in first Brillouin zone.

Simple LRC-corrected xc kernel was adopted by Sun [PRL, 127, 077401 ('21)],

$$f_{xc,\mathbf{G}\mathbf{G}'}^{LRC}(\mathbf{k}) = -\frac{\alpha}{|\mathbf{k}+\mathbf{G}|^2}\underbrace{\delta_{\mathbf{G},0}\delta_{\mathbf{G}',0}}_{\text{Read-only}}, \tag{3}$$

where α is a material-dependent parameter.

Formally, Hartree to LRC-xc change can be symbolized as the substitution

$$4\pi \rightarrow -\alpha \tag{4}$$

– LRC-xc vector potential

The long-wavelength limit of LRC-xc effect needs be described by xc vector potential $A_{xc}(r,t)$ in TDCDFT. Time-dependent Kohn-Sham (KS) equation then reads

$$i\frac{\partial}{\partial t}\psi_n(r,t) = \left[\frac{1}{2}\left(\frac{\nabla}{i}+\frac{1}{c}A(r,t)\right)^2 + v_{ion}(r) + v_{Hxc}(r,t)\right]\psi_n(r,t) \quad (5)$$

where $\psi_n(r,t)$ is n-th KS orbital, $v_{ion}(r)$ is ionic potential, $v_{Hxc}(r,t)$ is Hartree-xc potential, and vector potential is

$$A(r,t) = A_{ext}(r,t) + A_{ind}(r,t) + A_{xc}(r,t). \quad (6)$$

In Eq. (6), Aext & Aind are external and induced vector potentials. In multiscale Maxwell-TDDFT approach [Yabana, PRB 85, 045134 ('12)], they are uniform within each periodic supercell, and their macroscopic spatial variation is parametrically represented through supercell positions. Specifically, $A_{ind\,R}(t)$ is obtained by solving

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial R^2}\right)A_{ind\,R}(t) = \frac{4\pi}{c}J_R(t) \quad (7)$$

where average current at R-th supercell is [6/25/20]

$$J_{IR}(t) = \frac{1}{\Omega_{IR}} \int_{\Omega_{IR}} dr\, j(r,t) \tag{8}$$

$$j(r,t) = -\sum_n Re\left[\psi_n^*(r,t)\left(\frac{\nabla}{i} + \frac{1}{c}A_{IR}(t)\right)\psi_n(r,t)\right] \tag{9}$$

For xc vector potential, there is no need to consider macroscopic coupling, and with the substitution (4),

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \cancel{\frac{\partial^2}{\partial R^2}}\right) A_{xc\,IR}(t) = -\frac{\alpha}{c} J_{IR}(t) \tag{10}$$

In DCMESH code, we introduce

$$\tilde{A}_{xc\,IR}(t) = -\frac{1}{c} A_{xc\,IR}(t), \tag{11}$$

for which Eq. (10) becomes

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \cancel{\frac{\partial^2}{\partial R^2}}\right) \tilde{A}_{xc\,IR}(t) = +\frac{\alpha}{c^2} J_{IR}(t) \tag{12}$$

or, by dropping IR-index,

$$\boxed{\frac{\partial^2}{\partial t^2}\tilde{A}_{xc}(t) = \alpha J_{avg}(t)} \tag{13}$$

- Data structures
  - Alpha_xc

    α (~ 0.1 default), defined in types_constants.h

  - std::vector<RealType> $A^{xc}_{x\ y\ z}$

    $A_{xc}[\alpha+0|1|2]$ ($\alpha = 0, 1, 2$) stores α-th vector element of $\tilde{A}_{xc}$ | $\dot{\tilde{A}}_{xc}\Delta_{FD}$ | $\ddot{\tilde{A}}_{xc}\Delta^2_{FD}/2$

- Initialization : LFD class initializer
  - Axc.resize(9)
  - Aind[i] $\leftarrow 0$ ($i = 0, 8$) $\times 2$ (before & after SCF())

- Time propagation : vectp_prop() & vectp_maxwell()

compute $\ddot{\hat{A}}_{xc} \leftarrow \frac{\Delta_{FD}^2}{2} \times \alpha \, J_{avg}$

for step = 1 to N_{FD}

$\dot{\hat{A}} \mathrel{+}= \ddot{\hat{A}}$

$\hat{A} \mathrel{+}= \dot{\hat{A}}$

$\dot{\hat{A}} \mathrel{+}= \ddot{\hat{A}}$

- Total vector potential

if IMAXWELL == 1

$A_{st}[i] \leftarrow A_{st\_ext}[i] + A_{st\_ind}[0+3i] + A_{xc}[0]$ (if $i = 2N_{em}$) in vectp_maxwell()

$A_{tot}[0] \leftarrow A_{st}[2N_{em}]$; $A_{tot}[1] = A_{tot}[2] = 0$

else

$A_{tot}[du] = A_{ext}[dir] + A_{xc}[dir]$

~ compute_cur(), single_step() x 2, single_step_spectral() x 2,
calc_energy()

- Print out Axc
  - print to cout & excfile before javg[0].

8/15/21

— Observation

- Adding A_{xc} without A_{ind} causes a run-away solution.

  ↓

  A_{ind} screens A_{ext}, while A_{xc} magnifies it (causing positive feedback); A_{xc} should be used along with A_{ind} so as to partially undo screening.

- LRC-xc works for weakly-bound, delocalized excitons, for which reduced screening results in enhanced exiton resonance peak in optical absorbtion.

- Algorithm

#if IMAXWELL == 1

Multiscale Maxwell + TDDFT method: Renormalize Coulombic kernel with LRC-xc.

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial \mathbb{R}^2}\right)\tilde{A}_{ind+xc\,\mathbb{R}}(t) = -\frac{4\pi-\alpha}{c^2}\,J_{\mathbb{R}}(t) \qquad (14)$$

or, for transverse geometry with surface-normal direction z,

$$\frac{\partial^2}{\partial t^2}\tilde{A}_{ind+xc,z}(t) = c^2\frac{\partial^2}{\partial z^2}\tilde{A}_{ind+xc,z}(t) - (4\pi-\alpha)J_z(t) \qquad (15)$$

Descritized form is

$$A_{st\_ind}[2+3i] = \frac{\Delta_{FD}^2}{2}\ddot{\tilde{A}}_{ind+xc,z}(t)$$

$$\leftarrow \underbrace{\left(\frac{\Delta_{FD}^2 c^2}{2\Delta_z^2}\right)}_{\text{Afac}}\left\{A_{st\_ind}[0+3(i-1)] - 2A_{st\_ind}[0+3i] + A_{st\_ind}[0+3(i+1)]\right\}$$

$$-\underbrace{\left(2\pi-\frac{\alpha}{2}\right)\Delta_{FD}^2}_{\text{Jfac.}} J_{st}[i] \qquad (16)$$

※ Note Ast_ind[] now stores $\tilde{A}_{ind+xc,z}(t)$.

~ vectp_maxwell()

#elif IMAXWELL == 0

Transverse-geometry surface-only approach, i.e.,

$$A_{tot}[] = A_{ext}[] \tag{17}$$

#else (IMAXWELL == -1)

Bulk exciton dynamics, i.e.,

$$A_{tot}[] = A_{ext}[] + A_{ind}[] + A_{xc}[] \tag{18}$$

~ compute_cur(), single_step()x2, single_step_spectral()x2, calc_energy().

In Eq. (18), $A_{ind|xc}[]$ for bulk exciton dynamics is obtained as

$$\frac{\partial^2}{\partial t^2} \tilde{A}^{ind}_{xc}(t) = \left\{ \begin{matrix} -4\pi \\ \alpha \end{matrix} \right\} J_z(t) \tag{19}$$

~ vectp_prop()

- Program change

  - if IMAXWELL = 1, print Ast[2Nem] = Aext + Aind + Axc
    else print Aext, Aind & Axc

  - For predictor-corrector method, Axc[] must be rolled back when repeating $[t, t+\Delta_{QD}]$ propagation:

    After predictor

    Std: vector<RealType> Axc_ini

    Axc_ini. resize(9)

    Axc_ini[i] ← Axc[i] (i = 0,8)

    Befor each corrector

    Axc[i] ← Axc_ini (i=0,8)

    ~ single_step(), single_step_spectral()