Self-Consistent Electronic Propagator

7/9/21

- Objective: Increase the numerical stability by imposing self-consistency and time-reversal symmetry [Lian, Adv. Theo. Sim. 1, 1800055 ('18); Sato, JCP 143, 224116 ('15)].

- Self-consistent time propagation

Consider time-dependent Kohn-Sham (KS) Hamiltonian

$$\hat{H}(t) = \hat{T}[t; \mathbf{j}(\mathbf{r},t)] + \hat{V}[\rho(\mathbf{r},t)], \quad (1)$$

where kinetic energy $\hat{T}$ has both explicit time dependence through external vector potential $\mathbf{A}_{ext}(\mathbf{r},t)$ and implicit time dependence through current density $\mathbf{j}(\mathbf{r},t)$, whereas potential energy $\hat{V}$ only has implicit time dependence through electron density $\rho(\mathbf{r},t)$.

Time-propagation of n-th KS wave function $\psi_n(\mathbf{r},t)$ for small time-step, $\Delta = \Delta_{QD}$ (quantum-dynamics time step) is approximated in a time-reversible manner as

$$\psi_n(\mathbf{r},t+\Delta) \simeq \exp\left(-\frac{i\Delta}{\hbar}\hat{H}\left(t+\frac{\Delta}{2}\right)\right)\psi_n(\mathbf{r},t) \quad (2)$$

We further introduce another time-reversal approximation,

$$\hat{H}(t+\frac{\Delta}{2}) \simeq \frac{\hat{H}(t+\Delta) + \hat{H}(t)}{2}, \qquad (3)$$

so that

$$\psi_n(\mathbb{r}, t+\Delta) \simeq \exp\left(-\frac{i\Delta}{\hbar}\frac{\hat{H}(t+\Delta)+\hat{H}(t)}{2}\right)\psi_n(\mathbb{r}, t) \qquad (4)$$

or

$$\psi_n(\mathbb{r}, t+\Delta) = \exp\left(-\frac{i\Delta}{\hbar}\frac{\hat{H}[t;\rho(\mathbb{r},t+\Delta),\mathbb{j}(\mathbb{r},t+\Delta)]+\hat{H}[t;\rho(\mathbb{r},t),\mathbb{j}(\mathbb{r},t)]}{2}\right)$$

$$\times\ \psi_n(\mathbb{r}, t). \qquad (5)$$

Given $\psi_n(\mathbb{r},t)$, $\rho(\mathbb{r},t)$ & $\mathbb{j}(\mathbb{r},t)$, Eq.(5) is an implicit, self-consistent equation to determine unknown $\psi_n(\mathbb{r},t+\Delta)$, $\rho(\mathbb{r},t+\Delta)$ & $\mathbb{j}(\mathbb{r},t+\Delta)$.

- Kinetic energy

$$\hat{T}(t) = \frac{1}{2m}\left[\frac{\hbar}{i}\nabla + \frac{e}{c}\mathbb{A}(t)\right]^2 \tag{6}$$

$$\mathbb{A}(t) = \mathbb{A}_{ext}(t) + \mathbb{A}_{ind}(t) \tag{7}$$

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbb{A}_{ind}(t) = \frac{4\pi}{c}\mathbb{J}_{avg}(t) \tag{8}$$

$$\mathbb{J}_{avg}(t) = \frac{1}{\Omega}\int_{\Omega} d\mathbb{r}\, \mathbb{j}(\mathbb{r},t) \tag{9}$$

$$\begin{aligned}\mathbb{j}(\mathbb{r},t) &= -\frac{e}{m}\sum_n \mathrm{Re}\left[\psi_n^*(\mathbb{r},t)\frac{\hbar}{i}\nabla\psi_n(\mathbb{r},t)\right] f_n \\ &\quad - \frac{e^2}{mc}\mathbb{A}(t)\rho(\mathbb{r},t)\end{aligned} \tag{10}$$

$$\rho(\mathbb{r},t) = \sum_n |\psi_n(\mathbb{r},t)|^2 f_n \tag{11}$$

where f_n is occupation number for n-th KS orbital.

Instead of

$$\hat{T}\left(t+\frac{\Delta}{2}\right) \simeq \frac{\hat{T}(t+\Delta) + \hat{T}(t)}{2}, \tag{12}$$

we adopt an alternative time-reversible form,

$$\hat{T}\left(t+\frac{\Delta}{2}\right) \simeq \hat{T}\left(\frac{\mathbb{A}(t+\Delta) + \mathbb{A}(t)}{2}\right) \tag{13}$$

$$= \frac{1}{2m}\left[\frac{\hbar}{i}\nabla + \frac{e}{2c}\left(\mathbb{A}(t+\Delta) + \mathbb{A}(t)\right)\right]^2 \tag{14}$$

— Potential energy

$$\hat{V}(t) = v_{lpp}(\mathbb{r}) + v_H[\rho(\mathbb{r},t)] + v_{xc}[\rho(\mathbb{r},t)] \quad (15)$$

where v_{lpp} is local pseudopotential,

$$v_H[\rho(\mathbb{r},t)] = \int d\mathbb{r}' \frac{e^2}{|\mathbb{r}-\mathbb{r}'|} \rho(\mathbb{r},t) \quad (16)$$

is Hartree potential, and v_{xc} is exchange-correlation potential.

Time-reversible potential propagator is

$$\hat{V}(t+\frac{\Delta}{2}) \simeq \frac{\hat{V}[\rho(\mathbb{r},t+\Delta)] + \hat{V}[\rho(\mathbb{r},t)]}{2} \quad (17)$$

— Summary: mid-point approximation

$$\hat{H}(t+\frac{\Delta}{2}) \simeq \hat{T}\left(\frac{\mathbb{A}(t+\Delta) + \mathbb{A}(t)}{2}\right) + \frac{\hat{V}[\rho(\mathbb{r},t+\Delta)] + \hat{V}[\rho(\mathbb{r},t)]}{2} \quad (18)$$

Note $\mathbb{A}(t)$ is stored in Atot[3] array, whereas $\hat{V}[\rho(\mathbb{r},t)]$ is stored in v[Mstride].

– Time-reversible field propagation

To make vector-field propagation, we rewrite Eq. (8) as

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbb{A}_{ind}(t) = \frac{4\pi}{c}\,\frac{\mathbb{J}_{avg}(t+\Delta) + \mathbb{J}_{avg}(t)}{2}, \tag{19}$$

so that

$$\mathbb{A}_{ind}(t) \xmapsto[\frac{\mathbb{J}_{avg}(t+\Delta)+\mathbb{J}_{avg}(t)}{2}]{} \mathbb{A}_{ind}(t+\Delta) \tag{20}$$

Note $\mathbb{J}_{avg}(t)$ is stored in javg[3].

- When using dynamic simulated annealing (DSA) solver for Hartree potential, we solve

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) v_H(\mathbb{r},t) = 4\pi e^2 \rho(\mathbb{r},t) \tag{21}$$

Let us also make it time-reversible as

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) v_H(\mathbb{r},t) = 4\pi e^2\,\frac{\rho(\mathbb{r},t+\Delta)+\rho(\mathbb{r},t)}{2} \tag{22}$$

so that

$$v_H(\mathbb{r},t) \xmapsto[\frac{\rho(\mathbb{r},t+\Delta)+\rho(\mathbb{r},t)}{2}]{} v_H(\mathbb{r},t+\Delta) \tag{23}$$

– Time-reversible self-consistent propagator

$$\psi_n(\mathbf{r}, t+\Delta) = \exp\left(-\frac{i\Delta}{\hbar}\hat{H}\left(t+\frac{\Delta}{2}\right)\right)\psi_n(\mathbf{r}, t) \qquad (24)$$

$$\hat{H}\left(t+\frac{\Delta}{2}\right) \simeq \hat{T}\left(\overbrace{\frac{\mathbf{A}(t+\Delta)+\mathbf{A}(t)}{2}}^{\text{EM field}}\right) + \hat{V}\left[\overbrace{\frac{\rho(\mathbf{r}, t+\Delta)+\rho(\mathbf{r}, t)}{2}}^{\text{other electrons}}\right] \qquad (25)$$

$$= \frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{2c}\left(\mathbf{A}(t+\Delta)+\mathbf{A}(t)\right)\right)^2 + \hat{V}\left[\frac{\rho(\mathbf{r}, t+\Delta)+\rho(\mathbf{r}, t)}{2}\right] \qquad (26)$$

$$\mathbf{A}(t) = \mathbf{A}_{ext}(t) + \mathbf{A}_{ind}(t) \qquad (27)$$

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}_{ind}(t) = \frac{4\pi}{c}\,\overbrace{\frac{\mathbf{J}_{avg}(t+\Delta)+\mathbf{J}_{avg}(t)}{2}}^{\text{steady current}} \qquad (28)$$

$$\mathbf{J}_{avg}(t) = \frac{1}{\Omega}\int_{\Omega} d\mathbf{r}\,\mathbf{j}(\mathbf{r}, t) \qquad (29)$$

$$\mathbf{j}(\mathbf{r}, t) = -\frac{e}{m}\sum_n \mathrm{Re}\left[\psi_n^*(\mathbf{r}, t)\frac{\hbar}{i}\nabla\psi_n(\mathbf{r}, t)\right] - \frac{e^2}{mc}\mathbf{A}(t)\rho(\mathbf{r}, t) \qquad (30)$$

$$\rho(\mathbf{r}, t) = \sum_n |\psi_n(\mathbf{r}, t)|^2 f_n \qquad (31)$$

Optionally,

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) v_H(\mathbf{r}, t) = 4\pi e^2\,\overbrace{\frac{\rho(\mathbf{r}, t+\Delta)+\rho(\mathbf{r}, t)}{2}}^{\text{frozen electrons}} \qquad (32)$$

- Algorithm: single_step()

Input:

t (= start time), $\{\psi_n(\mathbf{r},t) \mid n = 0, N_{orb}-1\}$ → psi[Mstride·Norb], $\mathbb{A}_{ind}(t)$ → Aind[3], ($V_H(\mathbf{r},t)$) → vH[3Mstride] ← if DSA

Output:

$t \leftarrow t+\Delta$ → Dtgd, $\{\psi_n(\mathbf{r},t+\Delta) \mid n=0, N_{orb}-1\}$, $\mathbb{A}_{ind}(t+\Delta)$, $(V_H(\mathbf{r},t+\Delta))$

Procedure:

// Explicit propagation (predictor)

$\rho(\mathbf{r},t) \leftarrow \sum_n |\psi_n(\mathbf{r},t)|^2 f_n$ ~ compute_rho()
→ rho[Mstride]

$v_H(\mathbf{r},t) \leftarrow \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho(\mathbf{r},t')$ ~ field_solve|prop()

$v_{xc}(\mathbf{r},t) \leftarrow v_{xc}[\rho(\mathbf{r},t)]$ ~ compute_vxc()

$v(\mathbf{r},t) \leftarrow v_{lpp}(\mathbf{r}) + v_H[\rho(\mathbf{r},t)] + v_{xc}[\rho(\mathbf{r},t)]$ ~ compute_v()
→ v[Mstride] → vlpp[Mstride] → vxc[3Mstride]

$\mathbb{J}_{avg}(t) \leftarrow \mathbb{J}_{avg}[\{\psi_n(\mathbf{r},t)\}]$ ~ compute_cur()

$\mathbb{A}(t) \leftarrow \mathbb{A}_{ext}(t) + \mathbb{A}_{ind}(t)$
→ Atot[3] → Aext[3]

$$\hat{u}_T \leftarrow \exp\left(-\frac{i\Delta}{\hbar}\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \mathbb{A}(t)\right)^2\right) \tag{33}$$

~ set_prop()
input: Atot[] & V[]

$$\hat{u}_{V/2} \leftarrow \exp\left(-\frac{i\Delta}{2\hbar} v(\mathbf{r},t)\right) \tag{34}$$

$\{\psi_n^t(\mathbf{r}) \leftarrow \psi_n(\mathbf{r},t) \mid n=0, N_{orb}-1\}$, $\rho^t(\mathbf{r}) \leftarrow \rho(\mathbf{r},t)$, $\mathbb{J}_{avg}^t \leftarrow \mathbb{J}_{avg}(t)$

↳ psi_ini [Mstride·Norb] ↳ rho_ini [Mstride] ↳ javg_ini [3]

$\mathbb{A}_{ind}^t \leftarrow \mathbb{A}_{ind}(t)$, $\mathbb{A}^t \leftarrow \mathbb{A}(t)$, $t\_ini \leftarrow t$

↳ Aind_ini [3] ↳ Atot_ini [3]

$$\begin{cases} \psi_n(\mathbf{r},t+\Delta) \leftarrow \hat{\mathcal{U}}_{V/2}\, \hat{\mathcal{U}}_T\, \mathcal{U}_{V/2}\, \psi_n(\mathbf{r},t) \quad (n=0, N_{orb}-1) & (35) \\ \mathbb{A}_{ind}(t+\Delta) \leftarrow \mathbb{A}_{ind}(\mathbb{A}_{ind}(t), \mathbb{J}_{avg}(t), \Delta) \sim \text{vectp\_prop()} & (36) \end{cases}$$

<u>if (mode != 0) return ~ no self-consistency if imaginary-time</u>

$\rho_{old}^{t+\Delta}(\mathbf{r}) \leftarrow \rho(\mathbf{r}, t+\Delta) = \sum_n |\psi_n(\mathbf{r},t+\Delta)|^2 f_n$ ~ compute_rho()

↳ rho_fin_old [Mstride]

$\mathbb{J}_{avg,old}^{t+\Delta} \leftarrow \mathbb{J}_{avg}(t+\Delta) = \mathbb{J}_{avg}[\{\psi_n(\mathbf{r},t+\Delta)\}]$ ~ compute_cur()

~~↳ javg_ini_old [3]~~ // Don't use as convergence criterion

// Self-consistent corrector

for $i_{scp} = 1$, Maxscp

$\bar{\rho}(\mathbf{r}) \leftarrow \frac{1}{2}[\rho_{old}^{t+\Delta}(\mathbf{r}) + \rho^t(\mathbf{r})]$

$\bar{v}_H(\mathbf{r}) \leftarrow \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \bar{\rho}(\mathbf{r}')$ ~ field_solve | prop()

↳ OK to keep refining vH[] toward mid-point density when DSA

$\bar{v}_{xc}(\mathbf{r}) \leftarrow v_{xc}[\bar{\rho}(\mathbf{r})]$ ~ compute_vxc()

$\bar{v}(\mathbf{r}) \leftarrow v_{ipp}(\mathbf{r}) + \bar{v}_H(\mathbf{r}) + \bar{v}_{xc}(\mathbf{r})$ ~ compute_v()

$\bar{\mathbb{J}}_{avg} \leftarrow \frac{1}{2}[\mathbb{J}_{avg,old}^{t+\Delta} + \mathbb{J}_{avg}^t]$

$$\mathbb{A}(t+\Delta) \leftarrow \mathbb{A}_{ext}(t+\Delta) + \underbrace{\mathbb{A}_{ind}(t+\Delta)}_{\text{has been updated}}$$

$$\overline{\mathbb{A}} \leftarrow \frac{1}{2}[\mathbb{A}(t+\Delta) + \mathbb{A}^t]$$

$$\left\{\begin{array}{l} \hat{u}_T \leftarrow \exp\left(-\frac{i\Delta}{\hbar}\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \overline{\mathbb{A}}\right)^2\right) \\ \\ \hat{u}_{V/2} \leftarrow \exp\left(-\frac{i\Delta}{2\hbar} v(\mathbf{r})\right) \end{array}\right.$$

~ set_prop()
input: Atot[] & V[]

$$\left\{\begin{array}{l} \psi_n(\mathbf{r},t) \leftarrow \psi_n^t(\mathbf{r}) \quad (n = 0, N_{orb}-1) \\ \mathbb{A}_{ind}(t) \leftarrow \mathbb{A}_{ind}^t \end{array}\right.$$

$$\left\{\begin{array}{l} \psi_n(\mathbf{r},t+\Delta) \leftarrow \hat{u}_{V/2}\hat{u}_T\hat{u}_{V/2}\psi_n(\mathbf{r},t) \quad (n=0, N_{orb}-1) \\ \\ \mathbb{A}_{ind}(t+\Delta) \leftarrow \mathbb{A}_{ind}(\mathbb{A}_{ind}(t), \mathbb{J}_{avg}, \Delta) \end{array}\right.$$

$$\rho(\mathbf{r},t+\Delta) \leftarrow \sum_n |\psi_n(\mathbf{r},t)|^2 f_n$$ ~ compute_rho()

$$\mathbb{J}_{avg}(t+\Delta) \leftarrow \mathbb{J}_{avg}[\{\psi_n(\mathbf{r},t+\Delta)\}]$$ ~ compute_cur()

$$\text{if}\left(\|\rho(\mathbf{r},t+\Delta) - \rho_{old}^{t+\Delta}(\mathbf{r})\|_2 < \underbrace{\varepsilon}_{\text{Tolscp}}\rho_{avg}\right)$$ // Javg could be 0, not use it as convergence criterion

break

$$\rho_{old}^{t+\Delta}(\mathbf{r}) \leftarrow \rho(\mathbf{r},t+\Delta)$$

※ Note $t \mathrel{+}= \Delta_{QD}$ performed outside single_step().

- Self-consistency check

$$\left(\frac{1}{N_{xyz}} \sum_{ijk} \left| \rho(i\Delta x, j\Delta y, k\Delta z) - \rho_{old}^{t+\Delta}(i\Delta x, i\Delta y, i\Delta z) \right|^2 \right)^{1/2} \tag{37}$$

$< \text{Tolscp} \cdot \text{phoavg}$

– Observation

- Individual electrons propage in time interval $[t, t+\Delta]$ under frozen field

$$\overline{\mathbb{A}} = \frac{\mathbb{A}(t+\Delta) + \mathbb{A}(t)}{2} \tag{38}$$

and influence of frozen mean density (i.e., other electrons)

$$\overline{\rho}(\mathbb{r}) = \frac{\rho(\mathbb{r}, t+\Delta) + \rho(\mathbb{r}, t)}{2} \tag{39}$$

- Electromagnetic field propagates in time interval $[t, t+\Delta]$ with steady current

$$\overline{\mathbb{J}}_{avg} = \frac{\mathbb{J}_{avg}(t+\Delta) + \mathbb{J}_{avg}(t)}{2} \tag{40}$$