Nonlocal Pseudopotential Correction Revisited

7/28/21

— Objective: Explicitly suppress excitation to above-bandgap states [Wang, JPCM 31, 214002 ('19)].

— Definitions [cf. 12/7/20]

Let $\{\epsilon_n^{nl} | n=0,\ldots,N_{orb}-1\}$ be Kohn-Sham (KS) energies of Norb KS orbitals incorporating nonlocal pseudopotential (NLP), which are passed from main Maxwell-Ehrenfest-surface hopping (MESH) Fortran code at time $t=0$.

$$\left[-\frac{\nabla^2}{2} + \hat{v}_{loc} + \hat{v}_{nl}\right] |\psi_n^{nl}\rangle = \overbrace{\epsilon_n^{nl}}^{\texttt{enl[]}} |\psi_n^{nl}\rangle, \tag{1}$$

where $\hat{v}_{loc}$ & $\hat{v}_{nl}$ are local & nonlocal potentials and $\{|\psi_n^{nl}\rangle | n=0,\ldots,N_{orb}-1\}$ are KS wave functions.

Local field dynamics (LFD) is initiated by solving self-consistent field (SCF) iterations using only (unscreened) local pseudopotential to obtain shadow orbitals $\{|\psi_n\rangle | n=0,\ldots,N_{orb}-1\}$ that satisfy

$$\left[-\frac{\nabla^2}{2} + \hat{v}_{loc}\right] |\psi_n\rangle = \underbrace{\epsilon_n^{shadow}}_{\texttt{eshadow\_gamma[]}} \overbrace{|\psi_n\rangle}^{\texttt{psi0[]}} \tag{2}$$

where $\{\epsilon_n^{shadow} | n=0,\ldots,N_{orb}-1\}$ are shadow KS energies.

- LFD with NLP correction

Consider time propagation of shadow wave functions

$$i\frac{\partial}{\partial t}|\psi_n(t)\rangle = \hat{h}(t)\,|\psi_n(t)\rangle \qquad (3)$$

↳ psi[]

where $|\psi_n(t=0)\rangle = |\psi_n\rangle$. Time-dependent Hamiltonian in Eq.(3) is defined as

$$\hat{h}(t) = \frac{1}{2}\left(\frac{\nabla}{i} + \frac{1}{c}\mathbb{A}(t)\right)^2 + v_{loc}(\mathbb{r},t) + \hat{v}_{nl}. \qquad (4)$$

$$= \hat{h}_{loc}(t) + \hat{v}_{nl} \qquad (5)$$

where $\mathbb{A}(t)$ is spatially-uniform vector potential and $v_{loc}(\mathbb{r},t)$ reflects the change of Hartree & exchange-correlation (xc) potentials due to time evolution of electron density.

- Time propagator

Time evolution of shadow wave function during quantum-dynamics (QD) time step, Δ_{QD}, is achieved by Trotter expansion,

$$|\psi_n(t+\Delta_{QD})\rangle = e^{-i\hat{v}_{nl}\Delta_{QD}/2}\, e^{-i\hat{h}_{loc}(t+\Delta_{QD}/2)\Delta_{QD}}\, e^{-i\hat{v}_{nl}\Delta_{QD}/2} \times |\psi_n(t)\rangle. \tag{6}$$

While local propagator, $e^{-i\hat{h}_{loc}(t+\Delta_{QD}/2)\Delta_{QD}}$, is handled by self-consistent unitary propagator [7/9/21], we use a simple Euler propagator for nonlocal time propagator [Vlcek, JCP 150, 184118 ('19)],

$$e^{-i\hat{v}_{nl}\Delta_{QD}/2}|\psi\rangle \simeq \frac{1-i\hat{v}_{nl}\Delta_{QD}/2}{\|(1-i\hat{v}_{nl}\Delta_{QD}/2)|\psi\rangle\|}|\psi\rangle \tag{7}$$

– NLP correction by projection

We operate $\hat{v}_{nl}$ approximately by projecting wave functions to vector space $\mathcal{V}$ spanned by $\{|\psi_n\rangle\}$.

Let the projection operator to $\mathcal{V}$ be

$$\mathcal{P} \equiv \sum_{n=0}^{Norb-1} |\psi_n\rangle\langle\psi_n| = \sum_{n=0}^{Norb-1} |n\rangle\langle n|. \tag{8}$$

Then, for $\forall|\psi\rangle$,

$$\begin{aligned}\hat{v}_{nl}|\psi\rangle &= \hat{v}_{nl}[\mathcal{P}+(1-\mathcal{P})]|\psi\rangle \\ &= \sum_n \hat{v}_{nl}|n\rangle\langle n|\psi\rangle + \underbrace{\hat{v}_{nl}(1-\mathcal{P})|\psi\rangle}_{\simeq 0} \\ &= \sum_n \hat{v}_{nl}|n\rangle\langle n|\psi\rangle \end{aligned} \tag{9}$$

We introduce a scissor-like approximation,

$$\begin{aligned}\hat{v}_{nl}|\psi\rangle &= \sum_n \hat{v}_{nl}|n\rangle\langle n|\psi\rangle \\ &\simeq \sum_n (\epsilon_n^{nl} - \epsilon_n^{shadow})|n\rangle\langle n|\psi\rangle \end{aligned} \tag{10}$$

- Scissor correction

With Iscissor > 0 in dcmesh code, we adopt scissor-correction scheme [12/9/20], such that

$$\tilde{\epsilon}_n^{nl} = \begin{cases} \epsilon_n^{shadow} + \Delta_{sci} & (n \geq n_{LUMO}) \\ \epsilon_n^{shadow} & (n \leq n_{HOMO}) \end{cases} \quad (11)$$

replaces ϵ_n^{nl} in Eq. (10), where scissor shift is

$$\boxed{\Delta_{sci} = (\epsilon_{LUMO}^{nl} - \epsilon_{HOMO}^{nl}) - (\epsilon_{LUMO}^{shadow} - \epsilon_{HOMO}^{shadow}) \quad (12)}$$

and LUMO/HOMO denote lowest-unoccupied/highest-occupied molecular orbitals.

With scissor approximation, NLP operator becomes

$$\hat{v}_{nl}|\psi\rangle = \Delta_{sci} \sum_{n_{LUMO}}^{Norb-1} |n\rangle\langle n|\psi\rangle \quad (13)$$

The energy correction is

$$\epsilon_{nlc} = \sum_{n=0}^{Norb-1} f_n \langle\psi_n|\hat{v}_{nl}|\psi_n\rangle$$

$$= \sum_n f_n \Delta_{sci} \sum_{m \geq LUMO} \sum_{m' \geq LUMO} \langle\psi_n|m\rangle \underbrace{\langle m|m'\rangle}_{\delta_{mm'}} \langle m'|\psi\rangle$$

$$\boxed{\therefore \epsilon_{nlc} = \Delta_{sci} \sum_{n=0}^{Norb-1} \underbrace{f_n}_{\text{occ[]}} \sum_{m=n_{LUMO}}^{Norb-1} |\langle \underbrace{m}_{\text{psi0[]}} | \underbrace{\psi_n}_{\text{psi[]}} \rangle|^2 \quad (14)}$$

- Time propagation

According to Eq. (7), NLP time propagation is

$$|\psi_n\rangle \leftarrow (1 - i\hat{v}_{nl}\Delta_{QD}/2)|\psi_n\rangle$$

$$= \underbrace{|\psi_n\rangle}_{\text{psi[]}} - \frac{i\Delta_{sci}\Delta_{QD}}{2}\sum_{m=n_{LUMO}}^{N_{orb}-1}|m\rangle\underbrace{\langle m|\psi_n\rangle}_{\text{psi0[]}} \quad (15)$$

$$|\psi_n\rangle \leftarrow \frac{1}{\sqrt{\langle\psi_n|\psi_n\rangle}}|\psi_n\rangle \quad (16)$$

※ Excited components of $|\psi_n\rangle$ will acquire fast phase rotation, to be suppressed; thus excitation will be suppressed without resonance with above-bandgap optical phase rotation.

※ For PTO400nm,

$$\Delta_{QD} = 0.02\,\text{au}$$

$$\Delta_{sci} = \underbrace{(0.3793 - 0.2406)}_{\epsilon_{gap}^{nl} = 0.1387} - \underbrace{(0.6371 - 0.6017)}_{\epsilon_{gap}^{shadow} = 0.0354}$$

$$= 0.1033\,\text{au}$$

$$\therefore \frac{\Delta_{sci}\Delta_{QD}}{2} = \frac{0.1033 \times 0.0\cancel{2}^{1}}{\cancel{2}_{1}} = 1.033 \times 10^{-3} \ll 1$$

- Single QD step algorithm

```
nlp_prop()   // Half-time NLP propagation, Eqs. (15) & (16)
pot_prop()   // Half-time potential propagation
kin_prop_spectral() // Full-time kinetic propagation
  ~ or series of space-splitting method (SSM) propagators
pot_prop()
nlp_prop()
```

- Electric current

Paramagnetic current is computed as [6/25/20],

$$\mathbf{j}^P(\mathbf{r}) = -\sum_n f_n \,\mathrm{Re}[\psi_n^*(\mathbf{r})\frac{\nabla}{i}\psi_n(\mathbf{r})].$$

Consider the action of current operator on wave function,

$$\frac{\nabla}{i}|\psi\rangle = \frac{\nabla}{i}[P + (1-P)]|\psi\rangle \tag{17}$$

$$= \underbrace{\frac{\nabla}{i}\sum_{m=0}^{Norb-1}|m\rangle\langle m|\psi\rangle}_{\simeq \sum_{l=0}^{Norb-1}|l\rangle\langle l|\frac{\nabla}{i}|m\rangle\langle m|\psi\rangle} + \frac{\nabla}{i}(1-P)|\psi\rangle \tag{18}$$

$$= \sum_{l=0}^{Norb-1}\sum_{m=0}^{Norb-1}|l\rangle\langle l|\frac{\nabla}{i}|m\rangle\langle m|\psi\rangle + \frac{\nabla}{i}(1-P)|\psi\rangle \tag{19}$$

$\langle\psi| \times$ Eq. (19)

$$\mathbb{P} \equiv \mathrm{Re}\langle\psi|\frac{\nabla}{i}|\psi\rangle \tag{20}$$

$$= \sum_{l,m}\langle\psi|l\rangle\underbrace{\mathrm{Re}\langle l|\frac{\nabla}{i}|m\rangle}_{\equiv \mathbb{P}_{lm}}\langle m|\psi\rangle + \langle\psi|\frac{\nabla}{i}(1-P)|\psi\rangle \tag{21}$$

$$= \sum_{l,m}\langle\psi|l\rangle\mathbb{P}_{lm}\langle m|\psi\rangle + \langle\psi|\frac{\nabla}{i}(1-P)|\psi\rangle \tag{22}$$

Following Eq. (22) in Wang'19, we apply scissor correction to current matrix element,

$$\tilde{\mathbb{P}}_{lm} = \frac{\tilde{\epsilon}_l^{nl} - \tilde{\epsilon}_m^{nl}}{\epsilon_l^{shadow} - \epsilon_m^{shadow}} \mathbb{P}_{lm} = \frac{\tilde{\epsilon}_{lm}^{nl}}{\epsilon_{lm}^{shadow}} \mathbb{P}_{lm} \qquad (23)$$

Accordingly, change of current due to NLP correction is

$$\delta\mathbb{P} = \langle\psi|\frac{\tilde{\nabla}}{i}|\psi\rangle - \langle\psi|\frac{\nabla}{i}|\psi\rangle \qquad (24)$$

$$= \sum_{l,m} \langle\psi|l\rangle \left(\frac{\tilde{\epsilon}_{lm}^{nl}}{\epsilon_{lm}^{shadow}} - 1\right) \mathbb{P}_{lm} \langle m|\psi\rangle \qquad (25)$$

With scissor correction, Eq. (11),

$$\tilde{\epsilon}_{lm}^{nl} = \begin{cases} \epsilon_{lm}^{shadow} + \Delta_{sci} & (l \geq n_{LUMO}, m \leq n_{HOMO}) \\ \epsilon_{lm}^{shadow} - \Delta_{sci} & (l \leq n_{HOMO}, m \geq n_{LUMO}) \end{cases} \qquad (26)$$

Substituting Eq. (26) into (25),

$$\delta\mathbb{P} = \sum_{l \geq n_{LUMO}} \sum_{m \leq n_{HOMO}} \langle\psi|l\rangle \frac{\Delta_{sci}}{\epsilon_{lm}^{shadow}} \mathbb{P}_{lm} \langle m|\psi\rangle$$

$$+ \underbrace{\sum_{l \leq n_{HOMO}} \sum_{m \geq n_{LUMO}} \langle\psi|l\rangle \frac{\Delta_{sci}}{\epsilon_{lm}^{shadow}} \mathbb{P}_{lm} \langle m|\psi\rangle}_{l \leftrightarrow m} \qquad (27)$$

$$\sum_{m \leq n_{HOMO}} \sum_{l \geq n_{LUMO}} \langle\psi|m\rangle \frac{\Delta_{sci}}{\underbrace{\epsilon_{ml}^{shadow}}_{= +\epsilon_{lm}^{shadow}}} \mathbb{P}_{ml} \langle l|\psi\rangle$$

$$\therefore \delta \mathbb{P} = \sum_{l \geq n_{LUMO}} \sum_{m \leq n_{HOMO}} \frac{\Delta sci}{\epsilon^{shadow}_{lm}} \left[\langle \psi | l \rangle \mathbb{P}_{lm} \langle m | \psi \rangle + \langle \psi | m \rangle \mathbb{P}_{ml} \langle l | \psi \rangle \right] \tag{28}$$

Note the current operator is in fact [6/25/20]

$$\mathbb{P}_{ml} = \frac{1}{2} \int d\mathbf{r} \left[m^*(\mathbf{r}) \frac{\nabla}{i} l(\mathbf{r}) - \left(\frac{\nabla}{i} m^*(\mathbf{r}) \right) l(\mathbf{r}) \right]$$

$$= \frac{1}{2} \int d\mathbf{r} \left[l^*(\mathbf{r}) \frac{\nabla}{i} m(\mathbf{r}) - \left(\frac{\nabla}{i} l^*(\mathbf{r}) \right) m(\mathbf{r}) \right]^*$$

$$= \mathbb{P}^*_{lm} \tag{29}$$

Substituting Eq. (29) to (28),

$$\delta \mathbb{P} = \sum_{l \geq n_{LUMO}} \sum_{m \leq n_{HOMO}} \frac{\Delta sci}{\epsilon^{shadow}_{lm}} \underbrace{\left[\langle \psi | l \rangle \mathbb{P}_{lm} \langle m | \psi \rangle + \langle \psi | l \rangle^* \mathbb{P}^*_{lm} \langle m | \psi \rangle^* \right]}_{2 \operatorname{Re} \langle \psi | l \rangle \mathbb{P}_{lm} \langle m | \psi \rangle.}$$

$$\therefore \delta \mathbb{P} = 2 \sum_{l \geq n_{LUMO}} \sum_{m \leq n_{HOMO}} \frac{\Delta sci}{\epsilon^{shadow}_{lm}} \operatorname{Re} \left[\langle \psi | l \rangle \mathbb{P}_{lm} \langle m | \psi \rangle \right] \tag{30}$$

where

$$\mathbb{P}_{lm} = \frac{1}{2} \int d\mathbf{r} \left[l^*(\mathbf{r}) \frac{\nabla}{i} m(\mathbf{r}) - \left(\frac{\nabla}{i} l^*(\mathbf{r}) \right) m(\mathbf{r}) \right] \tag{31}$$

Consider paramagnetic current

$$\mathbf{j}^P(\mathbf{r}) = -\sum_n f_n \operatorname{Re}[\psi_n^*(\mathbf{r}) \frac{\nabla}{i} \psi_n(\mathbf{r})] \tag{32}$$

and its contribution to average current

$$\mathbb{J}_{avg}^P \equiv \frac{1}{\Omega}\int_\Omega d\mathbf{r}\, \mathbf{j}^P(\mathbf{r}) \tag{33}$$

$$= -\frac{1}{\Omega}\sum_n f_n \int_\Omega d\mathbf{r} \operatorname{Re}[\psi_n^*(\mathbf{r}) \frac{\nabla}{i} \psi_n(\mathbf{r})] \tag{34}$$

Substituting Eq. (30) to (34), NLP correction to average current is

$$\boxed{\begin{aligned} \delta\mathbb{J}_{avg} &= -\frac{2}{\Omega}\sum_n f_n \sum_{l \geq n_{LUMO}} \sum_{m \leq n_{HOMO}} \frac{\Delta_{sci}}{\epsilon_{lm}^{shadow}} \\ &\times \operatorname{Re}[\langle\psi_n|l\rangle \mathbb{P}_{lm} \langle m|\psi_n\rangle] \quad (35) \\ &\text{where} \\ \mathbb{P}_{lm} &= \frac{1}{2}\int d\mathbf{r}\,[l^*(\mathbf{r}) \frac{\nabla}{i} m(\mathbf{r}) - (\frac{\nabla}{i} l^*(\mathbf{r}))\, m(\mathbf{r})] \quad (36) \end{aligned}}$$

※ The ground-state orbitals $\{l(\mathbf{r}) | l = 1, \ldots, N_{orb}-1\}$ are all real, thus (if Γ-point)

$$\boxed{\mathbb{P}_{lm} = -\frac{i}{2}\int d\mathbf{r}\,[l(\mathbf{r}) \nabla m(\mathbf{r}) - (\nabla l(\mathbf{r}))\, m(\mathbf{r})] \quad (37)}$$

is pure imaginary.

Ground-State Start

7/30/21

- Since we now only consider ground-state start,

$$\underbrace{f_n}_{\text{occ[]}} = \begin{cases} 2 & (n \le \text{nhomo}) \\ 0 & (n \ge \text{nlumo}) \end{cases} , \tag{38}$$

we are able to simplify NLP-correction computation.

- Energy correction

$$\boxed{\epsilon_{nlc} = \Delta_{sci} \sum_{n=0}^{\text{nhomo}} \underbrace{f_n}_{\text{occ[n]}=2} \sum_{m=n_{LUMO}}^{\text{Norb}-1} |\underbrace{\langle m|}_{\text{psi0[]}} \underbrace{\psi_n\rangle}_{\text{psi[]}}|^2} \tag{39}$$

- Time propagation

if $n \le \text{nhomo}$

$$|\psi_n\rangle \longleftarrow (1 - i\hat{v}_{nl}\Delta_{QD}/2)|\psi_n\rangle$$

$$= |\psi_n\rangle - \frac{i\Delta_{sci}\Delta_{QD}}{2} \sum_{m=\text{nlumo}}^{\text{Norb}-1} \underbrace{|m\rangle\langle m|}_{\text{psi0[]}}\psi_n\rangle \tag{15}$$

$$|\psi_n\rangle \longleftarrow \frac{1}{\sqrt{\langle\psi_n|\psi_n\rangle}}|\psi_n\rangle \tag{16}$$

— Current

For occupied state n ($\leq$ nhomo), overlap with initial orbital $\langle m|\psi_n\rangle$ is dominated by that with itself in Eq. (35). Hence, we only retain $m=n$ term in m-sum.

$$\boxed{\begin{aligned}&\delta \mathbb{J}_{avg} = -\frac{2}{\Omega}\sum_{n=0}^{\text{nhomo}} f_n \sum_{l \geq n_{LUMO}} \frac{\Delta_{sci}}{\epsilon_{ln}^{shadow}} \mathrm{Re}[\langle\psi_n|l\rangle \mathbb{P}_{ln} \langle n|\psi_n\rangle] \qquad (40)\\ &\text{where}\\ &\mathbb{P}_{ln} = \frac{1}{2}\int d\mathbf{r}\left[l^*(\mathbf{r})\frac{\nabla}{i}n(\mathbf{r}) - \left(\frac{\nabla}{i}l^*(\mathbf{r})\right)n(\mathbf{r})\right] \qquad (41)\end{aligned}}$$

※ While $\mathbb{J}_{avg}$ can be used for computing optical conductivity [Wang, JPCM 31, 214002 ('19)], its effect on electron dynamics through induced vector potential is very small in current multiscale Maxwell-solver setting [7/24-26/21]. In fact, for slab thickness = 0, there is no effect by $\mathbb{J}_{avg}$ on electron propagation.

↓

Temporalily disable NLP correction on current.