Ensemble Local Field Dynamics (E-LFD)

6/28/20

- Goal: Utilize multiple GPUs per computing node on A21 to run an ensemble of local field dynamics (LFD) instances to achieve higher accuracy.

- Occupation number integration

Consider an excited occupation numbers $\{f_n\}$, which is distinct from ground-state occupation $\{f_n^{(0)}\}$. Consider gradual promotion of electrons from ground- to excited-state configurations:

$$f_n^{(\lambda)} = f_n^{(0)} + \lambda \underbrace{[f_n - f_n^{(0)}]}_{\delta f_n} \quad (0 \le \lambda \le 1) \qquad (1)$$

Let us define a sum of Kohn-Sham (KS) orbital excitation energies:

$$\omega_{KS} = \sum_n \delta f_n \epsilon_n^{KS} \qquad (2)$$

where ϵ_n^{KS} is the energy of the n-th KS orbital.

According to Janak's theorem [PRB 18, 7165 ('78)], KS orbital energy is the derivative of the total energy w.r.t. occupation number:

$$\epsilon_n^{KS} = \frac{\partial E_{tot}}{\partial f_n} \tag{3}$$

Denoting the total energy of the system with KS occupation $f_n^{(\lambda)}$ as $E_{tot}(\lambda)$,

$$\frac{\partial E_{tot}(\lambda)}{\partial \lambda} = \sum_n \underbrace{\frac{\partial f_n^{(\lambda)}}{\partial \lambda}}_{\delta f_n} \underbrace{\frac{\partial}{\partial f_n} E_{tot}}_{\epsilon_n^{KS}} = \omega_{KS} \tag{4}$$

By integrating Eq.(4) from $\lambda = 0$ to 1,

$$\underbrace{\underbrace{E_{tot}(\{f_n\})}_{\text{excitation energy}} - \underbrace{E_{tot}(\{f_n^{(0)}\})}_{\text{ground-state energy}}}_{\text{Excitation energy}} = \int_0^1 d\lambda \underbrace{\omega_{KS}(\lambda)}_{\sum_n \delta f_n \epsilon_n^{KS}(\lambda)} \tag{5}$$

(Notes)

1. Even when $\epsilon_n^{KS}(\lambda)$ is evaluated with simple approximation, the excitation energy via occupation-number integration entails higher-order correlations [5/28/12 & Hu, PRA 74, 032508 ('06)]

2. Eq. (5) involves an ensemble of self-consistent calculations to produce $\{\epsilon_n^{KS}(\lambda)\}$ for different λ values, it is akin to ensemble density functional theory (E-DFT) [Gross, PRA 37, 2809 ('88)].

3. If we approximate λ-integration in Eq. (5) as one-point quadrature at $\lambda = 1/2$,

$$E_{tot}(\{f_n\}) - E_{tot}(\{f_n^{(0)}\}) = \omega_{KS}(\lambda=\tfrac{1}{2}), \qquad (6)$$

it is equivalent to Slater transition state [Slater, Adv. Quantum Chem. 6, 1 ('72); Liberman, PRB 62, 6851 ('00)].

– Trapezoidal Rule

We apply Eq. (5) to an ensemble of LFD instances. Let (M+1) be the number of quadrature points,

$$\lambda_M = \frac{1}{M} \quad (M = 0, 1, \ldots, M) \tag{7}$$

※ Using trapezoidal rule,

$$E_{tot}(\{f_n\}, t) - E_{tot}(\{f_n^{(0)}\}, t) = E_{ext}(t)$$

$$= \frac{1}{2M}\left[\omega_{KS}(\lambda=0) + 2\omega_{KS}(\lambda_1) + \cdots + 2\omega_{KS}(\lambda_{M-1}) + \omega_{KS}(1)\right] \tag{8}$$

where

$$\omega_{KS}(\lambda) = \sum_n \delta f_n \, \epsilon_n^{KS}(\lambda) \tag{9}$$

$$= \sum_n \delta f_n \cdot \left\langle \frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{c}A(t)\right)^2 \right\rangle_n$$

※ (M+1) LFD instances run concurrently on (M+1) GPUs, to better estimate excitation energy.