Divide-Conquer-Recombine Nonadiabatic Quantum Molecular Dynamics (DCR-NAQMD) Revisited

5/19/20

— Goal: Dynamic correlations of electrons via divide-&-conquer

In Ehrenfest-hopping dynamics (EHD), we consider the effects of electron-electron & electron-phonon interactions on time-evolution of electron occupations. Using split-operator formalism, the former can be formulated as many-electron dynamics with fixed nuclear positions. The goal is to apply divide-&-conquer strategy to compute it on massively parallel computers.

— Electron-hole pair response function

We are interested in describing the response of electron-hole pairs to external potential, e.g., AC electric field. This is described by an electron-hole response function,

$$\chi(1,1';2) = \frac{\delta}{\delta\phi(2)} \sum_{\sigma} \langle T[\hat{\psi}_{\sigma}^{+}(1)\,\hat{\psi}_{\sigma}(1')] \rangle, \qquad (1)$$

where $1 \equiv (\mathbf{r}_1, t_1)$ is a shorthand notation for 3-dimensional position $\mathbf{r}_1$ and time t_1, $\hat{\psi}_{\sigma}^{+}(1)$ and $\hat{\psi}_{\sigma}(\mathbf{r})$ are creation and annihilation operators for an electron with spin σ, T is the time-ordering operator that orders operators in descending order in time, and $\langle\rangle$ denotes the expectation value for the ground state.

In Eq. (1), the external potential $\phi(2)$ couples to the electrons through a time-dependent potential energy

$$V(t_2) = \int d\mathbf{r}_2\, \hat{\rho}(2)\, \phi(2) \qquad (2)$$

where the density operator is

$$\hat{\rho}(2) = \sum_\sigma \hat{\psi}^+_\sigma(2)\, \hat{\psi}_\sigma(2). \qquad (3)$$

— Equation of motion

Equation of motion for χ is derived in [5/19/20] as

$$\begin{aligned}\chi(1',1;2) = &-\frac{2i}{\hbar}\, g(1,2)\, g(2,1') \\ &-\frac{2i}{\hbar}\, g(1,\bar{3})\, g(\bar{3},1')\, v(\bar{3},\bar{4})\, \chi(\bar{4}^+,\bar{4};2) \\ &+ g(1,\bar{3})\, g(\bar{3}',1')\, \Xi^{(2)}(\bar{3},\bar{3}';\bar{4},\bar{4}')\, \chi^{(2)}(\bar{4}',\bar{4};2) \qquad (4)\end{aligned}$$

where

$$g(1,1') = -\frac{i}{2} \sum_\sigma \langle T[\hat{\psi}_\sigma(1)\, \hat{\psi}^+_\sigma(1')] \rangle \qquad (5)$$

is the single-particle Green's function and $\Xi^{(2)}$ is the two-body correlation potential that represents the exchange-correlation contribution to the effective two-body interaction [see Eq. (13) in 5/19/20].

– Divide-&-conquer

In divide-&-conquer (DC) approaches, the 3D space Ω is decomposed into spatially-localized domains Ω_α:

$$\Omega = \bigcup_\alpha \Omega_\alpha \tag{6}$$

We focus on the behavior of electron-hole pairs in Ω_α. We thus consider

$$\chi^{(2)}_{\alpha\beta}(1,1';2) = \chi^{(2)}(1,1';2)$$

$$\text{where } \mathbf{r}_1, \mathbf{r}_1' \in \Omega_\alpha \text{ and } \mathbf{r}_2 \in \Omega_\beta \tag{7}$$

– Domain-projected EOM

$$\begin{aligned}\chi_{\alpha\beta}(1',1;2) = &-\frac{2i}{\hbar}\mathcal{G}(1,2)\mathcal{G}(2,1') \\ &-\frac{2i}{\hbar}\sum_\gamma \mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3},1')v(\bar{3},\bar{4})\,\chi_{\gamma\beta}(\bar{4},\bar{4}^+,2) \\ &+\sum_\gamma \mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3}',1')\,\Xi^{(2)}(\bar{3},\bar{3}';\bar{4},\bar{4}')\,\chi^{(2)}_{\gamma\beta}(\bar{4}',\bar{4};2)\end{aligned} \tag{8}$$

– Local approximation

Following [Nakano & Ichimaru, Phys. Rev. B 39, 4930 ('89)], we adopt a local approximation to $\Xi^{(2)}$,

$$\Xi^{(3)}(3,3';4,4') = \begin{cases} \tilde{\Xi}^{(3)}_{\alpha}(3,3';4,4') & \mathbf{r}_3, \mathbf{r}_3', \mathbf{r}_4, \mathbf{r}_4' \in \Omega_\alpha \\ 0 & \text{else} \end{cases} \tag{9}$$

Substituting Eq. (9) into (8), we obtain

$$\begin{aligned} \chi_{\alpha\beta}(1',1;2) = & -\frac{2i}{\hbar} g(1,2) g(2,1') \\ & -\frac{2i}{\hbar} \sum_\gamma g(1,\bar{3}) g(\bar{3},1') v(\bar{3},\bar{4}) \chi_{\gamma\beta}(\bar{4}^+,\bar{4};2) \\ & + g(1,\bar{3}) g(\bar{3},1') \tilde{\Xi}^{(3)}_{\alpha}(\bar{3},\bar{3}';\bar{4},\bar{4}') \chi_{\alpha\alpha}(\bar{4}',\bar{4};2) \delta_{\alpha\beta} \end{aligned} \tag{10}$$

To study short-term time evolution of electron-hole pairs in Ω_α, let us consider $\chi_{\alpha\alpha}(1',1;2)$. Its EOM reads

$$\begin{aligned} \chi_{\alpha\alpha}(1',1;2) = & \left. \begin{aligned} & -\frac{2i}{\hbar} g(1,2) g(2,1') \\ & -\frac{2i}{\hbar} g(1,\bar{3}) g(\bar{3},1') v(\bar{3},\bar{4}) \chi_{\alpha\alpha}(\bar{4}^+,\bar{4};2) \\ & + g(1,\bar{3}) g(\bar{3},1') \tilde{\Xi}^{(3)}_{\alpha}(\bar{3},\bar{3}';\bar{4},\bar{4}') \chi_{\alpha\alpha}(\bar{4}',\bar{4};2) \end{aligned} \right\} (\text{rhs})_\alpha \\ & -\frac{2i}{\hbar} \sum_\gamma^{\Omega\backslash\alpha} g(1,\bar{3}) g(\bar{3},1') v(\bar{3},\bar{4}) \chi_{\gamma\alpha}(\bar{4}^+,\bar{4};2) \end{aligned} \tag{11}$$

In Eq. (11), $(\text{rhs})_\alpha$ is the exact EOM within Ω_α, while the last term represents the mean-field Hartree potential contribution arising from the charge density in the all other domains but α, $\Omega \backslash \alpha$.

In DCR-NAQMD, we treat local electron dynamics at high level of approximation, e.g., real-time time-dependent density functional theory (RT-TDDFT) with long-range exact exchange correction (exx) to account for exciton binding [Dreuw, JCP 119, 2943 ('03)]. On the other hand, inter-domain electron interaction is treated at the level of random phase approximation (RPA).

DCR-NAQMD: Interpretation

5/20/20

– Divide-&-conquer Bethe-Salpeter equation

Let us rewrite the divide-&-conquer (DC) equation of motion (EOM) for electron-hole pair response function [Eq. (11) in 5/19/20] as

$$
\left.
\begin{aligned}
\chi_{\alpha\beta}(1',1;2) = & -\frac{2i}{\hbar}\mathcal{G}(1,2)\mathcal{G}(2,1')^{\textcircled{1}} \\
& -\frac{2i}{\hbar}\mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3},1')v(\bar{3},\bar{4})\chi_{\alpha\beta}(\bar{4}^{+}\bar{4};2)^{\textcircled{2}} \\
& +\mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3},1')\tilde{\Xi}^{(3)}_{\alpha}(\bar{3},\bar{3}';\bar{4}\bar{4}')\chi_{\alpha\beta}(\bar{4}',\bar{4};2)^{\textcircled{3}}
\end{aligned}
\right\} (\mathrm{rhs})_1
$$

$$
-\frac{2i}{\hbar}\sum_{\gamma}^{\Omega\backslash\alpha}\mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3},1')v(\bar{3},\bar{4})\chi_{\gamma\beta}(\bar{4}^{+},\bar{4},2) \quad (\mathrm{rhs})_2 \qquad (12)
$$

If we neglect $\tilde{\Xi}^{(3)}_{\alpha} = 0$, Eq. (1) describes the dynamics of electron-hole pairs within the random phase approximation (RPA). Else, $\tilde{\Xi}^{(\alpha)}$ describes local many-body effect beyond RPA only within the domain, which is <u>embedded</u> in the mean-field RPA description of the whole system Ω through $(\mathrm{rhs})_2$.

– Numerical integration

In practice, electron-hole pair dynamics is computed by numerically integrating EOM forward in time [5/1/88].

$$\left[\left(i\frac{\partial}{\partial t_1} + i\frac{\partial}{\partial t_{1'}}\right) + \frac{\hbar}{2m}(\nabla_1^2 - \nabla_{1'}^2)\right] \chi_{\alpha\beta}(1',1;2)$$

$$= -\frac{2i}{\hbar}[\delta(1,2) - \delta(1',2)]\, \mathcal{G}(1,1') \quad ①$$

$$-\frac{2i}{\hbar}\sum_{\gamma}[v(1,\bar{3}) - v(1',\bar{3})]\, \chi_{\gamma\beta}(\bar{3},2)\, \mathcal{G}(1,1') \quad ②$$

$$+ i\sum_{\gamma}[v(1^+,\bar{3}) - v(1'^-,\bar{3})]\, \chi^{(3)}_{\alpha\gamma\beta}(1',1;\bar{3}^+,\bar{3};2) \quad ③$$

$$(\mathbf{r}_1, \mathbf{r}_1' \in \Omega_\alpha;\ \mathbf{r}_2 \in \Omega_\beta;\ \mathbf{r}_3 \in \Omega_\gamma) \qquad (13)$$

Namely, $\chi_{\alpha\beta}(1',1;2)$ at positions $\mathbf{r}_1$ & $\mathbf{r}_1' \in \Omega_\alpha$ at times $[t_1, t_1+\Delta t]$ & $[t_1', t_1'+\Delta t]$ is computed (domain-by-domain), including the Hartree field (term ② in rhs) from all domains at the RPA level, while selectively including the three-body response (term ③ in rhs), locally within Ω_α according to Eq. (12).