DCR-NAQMD: Embedded TDDFT

5/20/20

- Divide-conquer-recombine (DCR) nonadiabatic quantum molecular dynamics (NAQMD)

  DCR-NAQMD projects the equation of motion of the electron-hole pair equation-of-motion (EOM) to spatially-localized domains, selectively apply local approximations only to those terms that follow the quantum nearsightedness, and recombine the terms to obtain an approximate EOM.

- Time-dependent density functional theory (TDDFT)

  In order to implement numerical solution of DCR-NAQMD, we work in the framework of TDDFT, which is formally exact [Runge & Gross, PRL 52, 997 ('84)].

  Our target application is ultrafast electron dynamics induced by laser irradiation. Since a typical laser-spot size is micron or larger, which is larger the simulated system sizes, we model the laser field as a spatially uniform AC electric field.

- Time-dependent Kohn-Sham (TDKS) equations

In the TDKS formulation of TDDFT, exact dynamics of a many-electron system is described by. [10/6/89]

$$i\hbar\frac{\partial}{\partial t}\psi_{s\sigma}(\mathbf{r},t) = \left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{c}A_{ext}(t)\right)^2 + v_{nuc}(\mathbf{r}) + \int d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}',t) + v_{xc}(\mathbf{r},t)\right]\psi_{s\sigma}(\mathbf{r},t) \quad (1)$$

where $\psi_{s\sigma}(\mathbf{r},t)$ is the s-th KS orbital with spin σ, $v_{nuc}(\mathbf{r})$ is the potential energy arising from nuclei,

$$\rho(\mathbf{r},t) = \sum_{s\sigma} f_{s\sigma}|\psi_{s\sigma}(\mathbf{r},t)|^2 \quad (2)$$

is the electron density, with $f_{s\sigma} \in [0,1]$ being the occupation number of the orbital (s,σ), and the exchange-correlation potential $v_{xc}(\mathbf{r},t)$ is derived from the exchange-correlation (xc) action A_{xc} as

$$v_{xc}(\mathbf{r},t) = \frac{\delta A_{xc}}{\delta \rho(\mathbf{r},t)} \quad (3)$$

In Eq. (1), laser's electric field is derived from a vector potential [Nakano, PRB 43, 10928 ('91); Yabana, PRB 85, 045134 ('12); see 11/11/89] and

$$\mathbb{A}_{ext}(t) = \mathbb{A}^{(0)}_{ext} \cos(\omega_{ext} t - \vartheta_{ext}) \tag{4}$$

– Divide-&-conquer

We subdivide the physical space (Ω) into spatially-localized, overlapping domains,

$$\Omega = \bigcup_{\alpha} \Omega_{\alpha} . \tag{5}$$

The global electron density is a sum of domain densities $P_{\alpha}(\mathbb{r})$,

$$\rho(\mathbb{r}) = \sum_{\alpha} P_{\alpha}(\mathbb{r}) \rho_{\alpha}(\mathbb{r}) \tag{6}$$

$$\rho_{\alpha}(\mathbb{r}) = \sum_{s\sigma} f^{(\alpha)}_{s\sigma} |\psi^{(\alpha)}_{s\sigma}(\mathbb{r},t)|^2 \tag{7}$$

where $\{\psi^{(\alpha)}_{s\sigma}(\mathbb{r},t)\}$ are KS wave functions in Ω_{α}, $\{f^{(\alpha)}_{s\sigma}\}$ are their occupation numbers, and $P_{\alpha}(\mathbb{r})$ is a compactly-supported domain support function such that

$$P_\alpha(\mathbf{r}) = 0 \quad (\mathbf{r} \notin \Omega_\alpha), \tag{8}$$

which constitutes a partition of unity,

$$\sum_\alpha P_\alpha(\mathbf{r}) = 1 \tag{9}$$

– Local approximation

In DCR-NAQMD, the mean Hartree potential (3rd term in the right-hand side of Eq.(1)) is treated globally to form the random phase approximation (RPA), whereas the xc effect represented by $v_{xc}(\mathbf{r},t)$ is handled domain-by-domain based on the local approximation. The local KS equations in Ω_α thus reads

$$i\hbar\frac{\partial}{\partial t}\psi^{(\alpha)}_{s\sigma}(\mathbf{r},t) = \left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{c}A_{ext}(t)\right)^2 + v_{nuc}(\mathbf{r}) + \int d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}',t) + v_{xc}[\mathbf{r},t;\rho_\alpha(\mathbf{r},t)]\right]\psi^{(\alpha)}_{s\sigma}(\mathbf{r},t) \tag{8}$$

The xc potential v_{xc} in Eq.(8) is a functional of ρ_α. Eq.(8) amounts to the embedding of formally exact many-body system Ω_α in the global Hartree potential.

– Embedding-field approximation

The Hartree-potential contributions from the other domains vary smoothly in the domain, in a similar manner that far fields are computed using low-order multipoles in the fast multipole method (FMM) [Greengard & Rochlin, J. Comp. Phys. 73, 325 ('87)]. Similarly, far fields vary slowly in time. As a result, we employ a multiple time-step (MTS) approximation, in which the far fields are kept constant during N_{mts} time steps, as in the FMM-MTS scheme [Nakano, CPU 83, 197 ('94)].

(Multiple timescale, mutipole (MTMP) approximation)

$$v_H(\mathbf{r};t) = \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho(\mathbf{r}';t)$$

$$= \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho_\alpha(\mathbf{r}';t) + \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} [\rho(\mathbf{r}';t) - \rho_\alpha(\mathbf{r}';t)]$$

$$\simeq \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho_\alpha(\mathbf{r}';t) + e\mathbb{D}_{emb} \cdot \mathbf{r}^* \qquad (9)$$

*) Come back to the charge-neutrality issue — subtraction of far nuclei charges?

– MTMP-KS equations

Substituting the MTMP approximation, Eq. (9), in the DCR-TDKS equations, Eq. (8), we obtain

$$i\hbar\frac{\partial}{\partial t}\psi_{s\sigma}^{(\alpha)}(\mathbf{r},t) = \left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{c}A_{ext}(t) - e\mathbb{D}_{emb}t\right)^2 + v_{nuc}(\mathbf{r}) + \int d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho_\alpha(\mathbf{r}',t) + v_{xc}[\mathbf{r},t;\rho_\alpha(\mathbf{r},t)]\right]\psi_{s\sigma}^{(\alpha)}(\mathbf{r},t) \quad (10)$$

An example is range-separated hybrid exact-exchange functional to represent exciton binding, if there is only one exciton per domain.