

Shadow Ehrenfest-Hopping Dynamics

6/14/20

- Motivation

The crux of Ehrenfest-hopping dynamics (EHD) is:

Electrons interact with

(1) External laser field through field equations that are inherently local — hence, local-field dynamics (LFD)
— on one hand

(2) Ions chemically through nonlocal pseudopotential on the other hand.

Description of LFD can be described by smooth Kohn-Sham (KS) orbitals $\{\tilde{\psi}_{no}(r)\}$, which are solutions of local KS equations as a basis:

$$\underbrace{\left\{ \frac{\hbar^2}{2m} \nabla^2 + U_{\text{local-pp}}(r) + \int d\mathbf{r}' \frac{e^2 P(r')}{|r-r'|} + U_{xc}[P(r)] \right\} \tilde{\psi}_{no}(r)}_{\equiv U_{\text{loc}}(r)} = \tilde{E}_{no} \tilde{\psi}_{no}(r) \quad (1)$$

where $U_{\text{local-pp}}(r)$ is the local part of ionic pseudopotential, $P(r)$ is the electron density, and U_{xc} is the exchange-correlation (xc) potential.

The local KS orbitals have corresponding full KS orbitals $\{\psi_{no}(r)\}$, which are solutions of nonlocal KS equations:

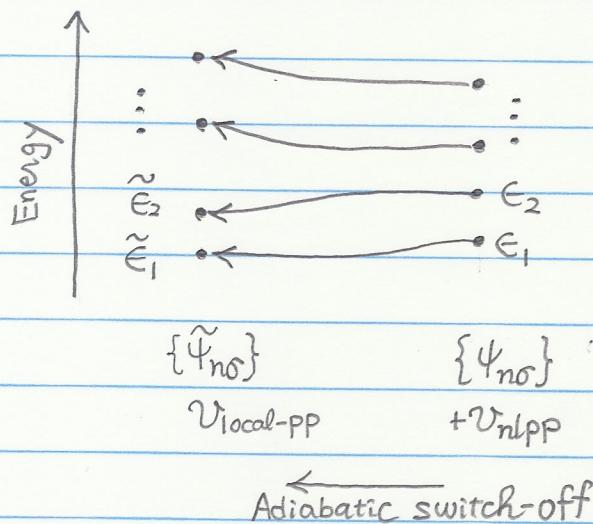
(2)

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{local-PP}}(ir) + \hat{V}_{\text{nlpp}} + \int d\mathbf{r}' \frac{e^2 P(ir')}{|ir - ir'|} + V_{xc}[P(ir)] \right\} \psi_{no}(ir) = E_{no} \psi_{no}(ir) \quad (2)$$

where \hat{V}_{nlpp} is the nonlocal pseudopotential.

- Smoothening (low-pass) filter transition

We assume, by adiabatic switch-off of \hat{V}_{NL} , $\{\psi_{no}\}$ can be mapped to $\{\tilde{\psi}_{no}\}$ one-to-one, similarly to Landau's Fermi-liquid theory [Landau, Sov. Phys. JETP 3, 920 ('57)].



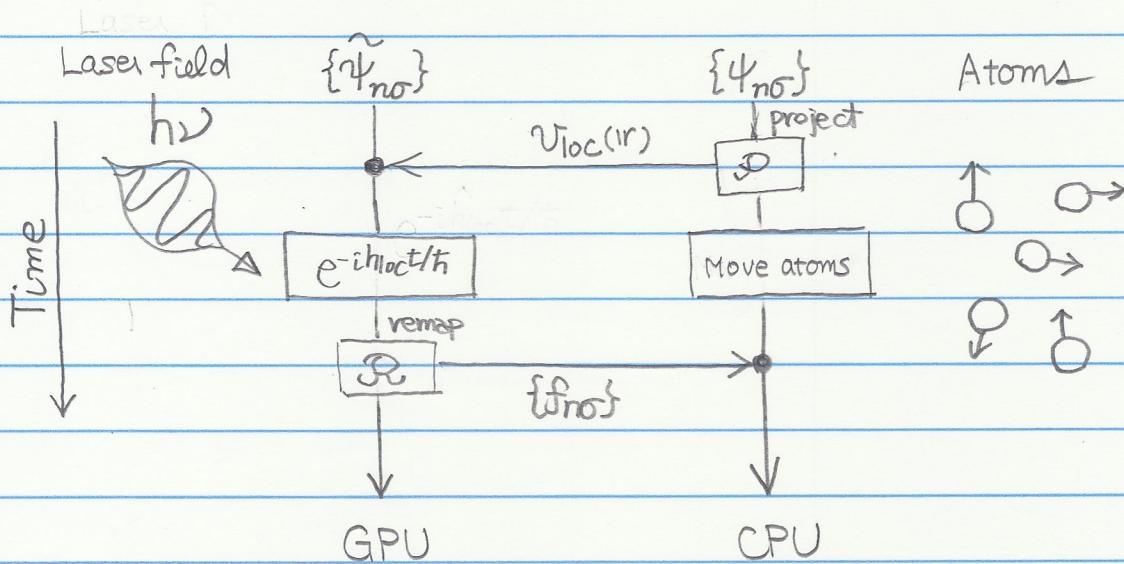
We define the local projection operator as

$$\tilde{\psi}_{no}(ir) = \mathcal{P} \psi_{no}(ir) \quad (3)$$

- Shadow EHD (SEHD)

We use $\{\tilde{\psi}_{no}\}$ as shadow proxy of $\{\psi_{no}\}$ to interact with laser field. In addition to simulate attosecond many-electron dynamics, time-propagated $\{\tilde{\psi}_{no}\}$ will be re-mapped to change in occupation numbers $\{f_{no}\}$ of $\{\psi_{no}\}$.

On the other hand, $\{\psi_{no}\}$ and $\{f_{no}\}$ describe chemistry and dictate atomic motions through Hellmann-Feynman theorem.



On heterogeneous parallel computers consisting of CPUs & GPUs, simple LFD operations on $\{\tilde{\psi}_{no}\}$ are handled by GPUs, while complex chemical operations by CPUs.

(4)

- Asynchronous shadow EHD (asEHD)

- At time 0, $\{\Psi_{no}\}$ & $\{f_{no}\}$, along with $V_{loc}(r)$, are passed from CPU to GPU.

- GPU performs projection, $\tilde{\Psi}_{no} \leftarrow \mathcal{P}\{\Psi_{no}\}$, i.e., self-consistly relax KS orbitals in imaginary time

$$\tilde{\Psi}_{no} = T \exp\left(-\frac{i}{\hbar} \int_0^{\infty} dt h(t)\right) \Psi_{no} \quad (4)$$

while performing Gram-Schmidt orthonormalization.

- Time-propagate $\tilde{\Psi}_{no}$ for one molecular-dynamics (MD) step, Δ_{MD} .

$$\tilde{\Psi}_{no}(\Delta_{MD}) = T \exp\left(-\frac{i}{\hbar} \int_0^{\Delta_{MD}} dt h(t)\right) \tilde{\Psi}_{no} \quad (5)$$

- Remap $\{\tilde{\Psi}_{no}(\Delta_{MD})\}$ to new $\{f_{no}\}$ and send to CPU.

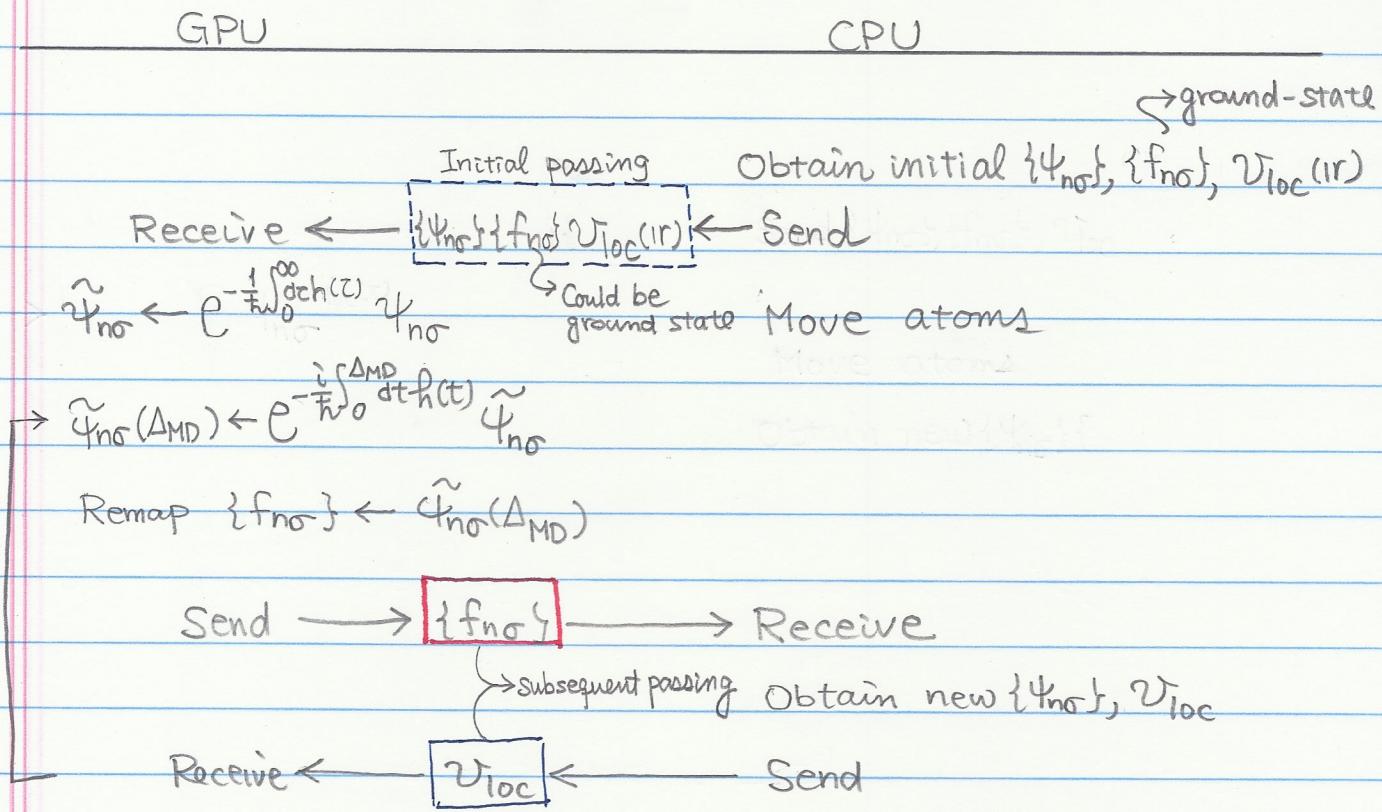
- CPU computes Hellmann-Feynman forces to move atoms.

6. Once atoms are moved, new $\{\tilde{\psi}_{no}(A_{t0})\} \neq \psi_{loc}(r)$ could be obtained and passed to GPU (synchronous EHD), by returning to 1
- or
- 6'. Assuming the $\tilde{\psi}_{no} - \psi_{no}$ correspondence has not been broken, GPU keeps time-propagating the old $\tilde{\psi}_{no}$, but only receiving new $\psi_{loc}(r)$ from CPU; call it step 1'.

* Self-consistent projection may be unstable (or level switch could occur). Let the initial $\tilde{\psi}_{no}$ be ground state.

(6)

- as EHD algorithm



- * As long as CPU is concerned, it only needs excited $\{f_{no}\}$, just as RT-TDDFT initializes constrained-DFT in sequential Ehrenfest-hopping dynamics in [Lee, NanoLett. 19, 3939 ('19)].