Auxiliary-Field Electron-Dynamics Solver

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— Local-pseudopotential/exchange-correlation electron propagator.

multi-scale, multi-physics (ee & en) method

In the Ehrenfest-hopping dynamics (EHD), the innermost loop (to be accelerated on GPU) propagates Kohn-Sham wave functions in time only using local pseudopotential & local density/gradient exchange-correlation potential.

$$\boxed{\begin{aligned} &\psi_{i\sigma}(\mathbf{r}, t+\Delta) \leftarrow \exp\left(-\frac{i\Delta}{\hbar}\hat{h}_{loc}\right)\psi(\mathbf{r}, t) && (1) \\ &\hat{h}_{loc} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - e\mathbb{D}t\right)^2 + v_{localpp}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^{loc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \end{aligned}}$$

(2)

— Auxiliary-field Hartree-potential solver.

We introduce an auxiliary field that represents the Hartree potential [Car & Parrinello, Solid State Commun. 62, 403 ('87)], which is solved with a dynamical simulated annealing (DSA) method [Nakano et al., CPC 83, 181 ('94)].

In the Lorentz gauge, the electrostatic potential $\phi(\mathbf{r}, t)$ obeys a hyperbolic partial differential equation,

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\phi(\mathbf{r}, t) = -4\pi e\rho(\mathbf{r}, t) \quad (3)$$

The Hartree potential $v_H(\mathbf{r}, t) = -e\phi(\mathbf{r}, t)$ thus obeys

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)v_H(\mathbf{r}, t) = 4\pi e^2\rho(\mathbf{r}, t) \quad (4)$$

While the Kohn-Sham wave functions, hence the electron density $\rho(\mathbf{r},t)$, have characteristic time of

$$\tau_e = \hbar^3/me^4 = 2\times10^{-17}\ \mathrm{sec}$$

while the intrinsic time scale of Eq. (4) is

$$\tau_c = \underbrace{(\hbar^2/me^2)}_{\text{Bohr length}}/c = 2\times10^{-19}\ \mathrm{sec} = 10^{-2}\times\tau_e$$

Car & Parrinello replaced Eq. (4) by Lagrangian dynamics involving a fictitious mass of v_H, which is equivalent to introducing a fictitious velocity $b \ll c$ such that

$$\boxed{\left(\frac{1}{b^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) v_H(\mathbf{r},t) = 4\pi e^2 \rho(\mathbf{r},t) \qquad (5)}$$

as long as the electrons adiabatically follow $v_H(\mathbf{r},t)$.

Eqs. (1) & (5) will be concurrently solved on GPU.

— Electron solver : space-splitting method (SSM)

$$\hat{h}_{loc} = \hat{k} + v(\mathbf{r}) \tag{6}$$

where the kinetic-energy operator is

$$\hat{k} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{\hbar e t}{mi}\mathbb{D}\cdot\nabla + \frac{e^2 D^2 t^2}{2m} \tag{7}$$

$$\begin{aligned} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar e t}{mi} D_x \frac{\partial}{\partial x} + \frac{e^2 D^2 t^2}{6m} \sim \hat{k}_x \\ &\quad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar e t}{mi} D_y \frac{\partial}{\partial y} + \frac{e^2 D^2 t^2}{6m} \sim \hat{k}_y \\ &\quad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} - \frac{\hbar e t}{mi} D_z \frac{\partial}{\partial z} + \frac{e^2 D^2 t^2}{6m} \sim \hat{k}_z \end{aligned} \tag{8}$$

whereas the potential-energy propagator is

$$v(\mathbf{r}) = v_{localpp}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^{loc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \tag{9}$$

Using Trotter expansion, Eq. (1) is decomposed to

$$e^{-i\hat{h}_{loc}\Delta/\hbar} = e^{-iv\Delta/2\hbar}\, e^{-i\hat{k}_x\Delta/\hbar}\, e^{-i\hat{k}_y\Delta/\hbar}\, e^{-i\hat{k}_z\Delta/\hbar}\, e^{-iv\Delta/2\hbar} + O(\Delta^3) \tag{10}$$

We will use 2x2 block-diagonal SSM to implement the kinetic propagators.

The wave function is discretized on a finite-difference grid as

$$\psi_{jkl}^{(i\sigma)} = \psi_{i\sigma}(j\Delta_x, k\Delta_y, l\Delta_z) \tag{11}$$

where Δ_x, Δ_y & Δ_z are grid spacing in the x, y & z directions.

$$\begin{aligned}
\hat{h}_x \psi_{jkl}^{(i\sigma)} &= -\frac{\hbar^2}{2m\Delta_x^2}\left(\psi_{j-1,k,l}^{(i\sigma)} - 2\psi_{j,k,l}^{(i\sigma)} + \psi_{j+1,k,l}^{(i\sigma)}\right) \\
&\quad - \frac{\hbar e D_x t}{2i m\Delta_x}\left(\psi_{j+1,k,l}^{(i\sigma)} - \psi_{j-1,k,l}^{(i\sigma)}\right) \\
&\quad + \frac{e^2 D^2 t^2}{6m}\psi_{j,k,l}^{(i\sigma)} \\
&= \left(\underbrace{-\frac{\hbar^2}{2m\Delta_x^2} - i\frac{\hbar e D_x t}{2m\Delta_x}}_{b}\right)\psi_{j-1,k,l}^{(i\sigma)} \\
&\quad + \left(\underbrace{\frac{\hbar^2}{m\Delta_x^2} + \frac{e^2 D^2 t^2}{6m}}_{2a}\right)\psi_{j,k,l}^{(i\sigma)} \\
&\quad + \left(\underbrace{-\frac{\hbar^2}{2m\Delta_x^2} + i\frac{\hbar e D_x t}{2m\Delta_x}}_{b^*}\right)\psi_{j+1,k,l}^{(i\sigma)}
\end{aligned} \tag{12}$$

$$= b\,\psi_{j-1,k,l}^{(i\sigma)} + 2a\,\psi_{j,k,l}^{(i\sigma)} + b^*_{j+1,k,l}\,\psi_{j+1,k,l}^{(i\sigma)} \tag{13}$$

The tridiagonal kinetic-energy operator is split into even & odd 2×2 block diagonal matrices; the following is done to mix j-indices for each (k,l) pair.

$$\hat{k}_x = \begin{bmatrix} 2a & b^* & & & & \\ b & 2a & b^* & & & \\ & b & 2a & b^* & & \\ & & \ddots & \ddots & \ddots & \\ & & & b & 2a & b^* \\ & & & & b & 2a \end{bmatrix} = \frac{1}{2}\begin{bmatrix} a & b^* & & & & \\ b & a & & & & \\ & & a & b^* & & \\ & & b & a & & \\ & & & & \ddots & \\ & & & & & a \; b^* \\ & & & & & b \; a \end{bmatrix}$$

$$+ \begin{bmatrix} a & & & & & \\ & a & b^* & & & \\ & b & a & & & \\ & & & a & b^* & \\ & & & b & a & \\ & & & & & \ddots & \\ & & & & & & a \end{bmatrix} + \frac{1}{2}\begin{bmatrix} a & b^* & & & & \\ b & a & & & & \\ & & a & b^* & & \\ & & b & a & & \\ & & & & \ddots & \\ & & & & & a \; b^* \\ & & & & & b \; a \end{bmatrix} \qquad (14)$$

Using Trotter expansion, the kinetic propagator is

$$\exp\left(-\frac{i\Delta}{\hbar}\hat{P}_x\right)$$

$$= \begin{bmatrix} \epsilon_2^0 & \epsilon_2^+ & & & & & \\ \epsilon_2^- & \epsilon_2^0 & & & & & \\ & & \epsilon_2^0 & \epsilon_2^+ & & & \\ & & \epsilon_2^- & \epsilon_2^0 & & & \\ & & & & \ddots & & \\ & & & & & \epsilon_2^0 & \epsilon_2^+ \\ & & & & & \epsilon_2^- & \epsilon_2^0 \end{bmatrix} \times \begin{bmatrix} \epsilon_1^0 & & & & & & \\ & \epsilon_1^0 & \epsilon_1^+ & & & & \\ & \epsilon_1^- & \epsilon_1^0 & & & & \\ & & & \epsilon_1^0 & \epsilon_1^+ & & \\ & & & \epsilon_1^- & \epsilon_1^0 & & \\ & & & & & \ddots & \\ & & & & & & \epsilon_1^0 \end{bmatrix} \times \begin{bmatrix} \epsilon_2^0 & \epsilon_2^+ & & & & & \\ \epsilon_2^- & \epsilon_2^0 & & & & & \\ & & \epsilon_2^0 & \epsilon_2^+ & & & \\ & & \epsilon_2^- & \epsilon_2^0 & & & \\ & & & & \ddots & & \\ & & & & & \epsilon_2^0 & \epsilon_2^+ \\ & & & & & \epsilon_2^- & \epsilon_2^0 \end{bmatrix}$$

$$+ O(\Delta^3) \tag{15}$$

where

$$\epsilon_n^0 = \frac{1}{2}\left[\exp\left(-\frac{i\Delta}{n\hbar}(a+|b|)\right) + \exp\left(-\frac{i\Delta}{n\hbar}(a-|b|)\right)\right] \tag{16}$$

$$\epsilon_n^+ = \frac{b^*}{2|b|}\left[\exp\left(-\frac{i\Delta}{n\hbar}(a+|b|)\right) - \exp\left(-\frac{i\Delta}{n\hbar}(a-|b|)\right)\right] \tag{17}$$

$$\epsilon_n^- = \frac{b}{2|b|}\left[\exp\left(-\frac{i\Delta}{n\hbar}(a+|b|)\right) - \exp\left(-\frac{i\Delta}{n\hbar}(a-|b|)\right)\right] \tag{18}$$

$$a = \frac{\hbar^2}{2m\Delta_x^2} + \frac{e^2D^2t^2}{12m} \tag{19}$$

$$b = -\frac{\hbar^2}{2m\Delta_x^2} - i\,\frac{\hbar e D_x t}{2m\Delta_x}$$

Field solver : velocity Verlet

We discretize the Hartree potential as

$$v^H_{jkl} = v_H(j\Delta_x, k\Delta_y, l\Delta_z) \tag{20}$$

Then, Eq. (5) is discretized as

$$\frac{1}{b^2}\frac{\partial^2}{\partial t^2} v^H_{jkl} = \frac{1}{\Delta_x^2}\left(v^H_{j-1\,kl} - 2v^H_{jkl} + v^H_{j+1\,kl}\right) + \frac{1}{\Delta_y^2}\left(v^H_{j\,k-1\,l} - 2v^H_{jkl} + v^H_{j\,k+1\,l}\right)$$
$$+ \frac{1}{\Delta_z^2}\left(v^H_{jk\,l-1} - 2v^H_{jkl} + v^H_{jk\,l+1}\right) + 4\pi e^2 \rho_{jkl}$$

or

$$\underbrace{\frac{(\Delta_x\Delta_y\Delta_z)^{2/3}}{b^2}}_{\equiv M}\frac{\partial^2}{\partial t^2} v^H_{jkl} = \left.\begin{aligned}&\left(\frac{\Delta_y\Delta_z}{\Delta_x^2}\right)^{2/3}\left(v^H_{j-1\,kl} - 2v^H_{jkl} + v^H_{j+1\,kl}\right)\\ &+ \left(\frac{\Delta_z\Delta_x}{\Delta_y^2}\right)^{2/3}\left(v^H_{j\,k-1\,l} - 2v^H_{jkl} + v^H_{j\,k+1\,l}\right)\\ &+ \left(\frac{\Delta_x\Delta_y}{\Delta_z^2}\right)^{2/3}\left(v^H_{jk\,l-1} - 2v^H_{jkl} + v^H_{jk\,l+1}\right)\\ &+ 4\pi e^2(\Delta_x\Delta_y\Delta_z)^{2/3}\rho_{jkl}\end{aligned}\right\} \equiv F_{jkl} \tag{21}$$

Namly, the field dynamics is governed by Newtonian dynamics.

$$M \frac{d^2}{dt^2} v^H_{jkl} = F_{jkl} \tag{22}$$

$$M = \frac{(\Delta_x \Delta_y \Delta_z)^{2/3}}{b^2} \tag{23}$$

$$\begin{aligned} F_{jkl} = & \left(\frac{\Delta_y \Delta_z}{\Delta_x^2}\right)^{2/3} \left(v^H_{j-1\,kl} - 2v^H_{jkl} + v^H_{j+1\,kl}\right) \\ & + \left(\frac{\Delta_z \Delta_x}{\Delta_y^2}\right)^{2/3} \left(v^H_{jk-1\,l} - 2v^H_{jkl} + v^H_{jk+1\,l}\right) \\ & + \left(\frac{\Delta_x \Delta_y}{\Delta_z^2}\right)^{2/3} \left(v^H_{jk\,l-1} - 2v^H_{jkl} + v^H_{jk\,l+1}\right) \\ & + 4\pi e^2 (\Delta_x \Delta_y \Delta_z)^{2/3} \rho_{jkl} \end{aligned} \tag{24}$$

— Split-operator formalism: velocity-Verlet algorithm

The Newtonian equation (22) is cast into the Hamiltonian form by introducing the conjugate momenta π_{jkl}: Time evolution of the system

$$\Gamma = \{\pi_{jkl}, v^H_{jkl}\} \tag{25}$$

is then dictated by the Liouville operator [Tuckerman, JCP 97, 1990 ('92)].

$$\Gamma(t+\delta) = \exp\left(i\hat{\mathcal{L}}\delta\right)\Gamma(t) \tag{26}$$

where the Liouville operator is

Time derivative ; $\Pi_{jkl} = M\dot{V}^H_{jkl}$

$$i\hat{\mathcal{L}} = \sum_{jkl}\left[\dot{V}^H_{jkl}\frac{\partial}{\partial V^H_{jkl}} + F_{jkl}\frac{\partial}{\partial \Pi_{jkl}}\right] \tag{27}$$

$$= \quad i\hat{\mathcal{L}}_1 \qquad + \qquad i\hat{\mathcal{L}}_2 \tag{28}$$

Using Trotter expansion,

$$\exp(i\hat{\mathcal{L}}\delta) = e^{i\hat{\mathcal{L}}_2\delta/2}\, e^{i\hat{\mathcal{L}}_1\delta}\, e^{i\hat{\mathcal{L}}_2\delta/2} + O(\delta^3) \tag{29}$$

This expansion amounts to velocity Verlet algorithm:

(Verocity-Verlet field propagation)

$\delta = \Delta/N_f$: Field time step is N_f-times smaller than Δ

$\dot{V}^H_{jkl} \leftarrow 0$

Given initial V^H_{jkl}, compute F_{jkl} (Eq. 24)

for step = 1 to N_f

$$\dot{V}^H_{jkl} \longleftarrow \dot{V}^H_{jkl} + F_{jkl}\delta/2 \tag{30}$$

$$V^H_{jkl} \longleftarrow V^H_{jkl} + \dot{V}^H_{jkl}\delta \tag{31}$$

Recompute F_{jkl} with new V^H_{jkl} (Eq. 24)

$$\dot{V}^H_{jkl} \longleftarrow \dot{V}^H_{jkl} + F_{jkl}\delta/2 \tag{30}$$

— Remark

① While both SSM-electron & DSA-field propagators achieved high percentage of peak floating-point performance on SIMD machines like MasPar, advanced performance tuning will be required on GPU.

② Both SSM & DSA solvers are stencil computations, and techniques like register blocking [Dursun, JSC 62, 946 ('12)] may work.

③ We will develop GPU kernel for the local electron propagator first; later will be incorporated into Fuyuki's DCR-NAQMD code through hand-shaking, $\{\psi_{io}(\mathbf{r})\}$ & $v_{\text{local}pp}(\mathbf{r})$.

④ Do this in single precision.