Propagators for the Time Dependent Kohn-Sham Equations

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Theoretical Framework

- Kohn-Sham Equations

$$\epsilon_i|\phi_i\rangle = \hat{H}_{[n]}|\phi_i\rangle$$

$n(\mathbf{r}) = \sum_i \psi_i^\dagger(\mathbf{r})\psi_i(\mathbf{r})$

- Time-dependent Kohn-Sham Equations

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\phi_i\rangle = \hat{H}(t)_{[n(t)]}|\phi_i\rangle$$

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\phi_i\rangle = \left\{\hat{T} + \hat{V}^{\text{external}}(t) + \hat{V}^{\text{HXC}}_{[n(t)]}\right\}|\phi_i\rangle$$

$\hat{T} \rightarrow -\frac{\nabla^2}{2m}$
$\hat{V}^{\text{ext}}(t) \rightarrow$ ion potential $+ \mathbf{E}(t)\cdot\mathbf{r}$ (for example)
$\hat{V}^{\text{HXC}} \rightarrow \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V^{\text{XC}}[n(t)](\mathbf{r})$ (Adiabatic LDA)

Similar Problems

Time Dependent Kohn-Sham equations (TDKS)

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\phi_i\rangle = \hat{H}(t)_{[n(t)]}|\phi_i\rangle$$

Time Dependent Schrödinger Equation (TDSE)

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\phi\rangle = \hat{H}(t)|\phi_i\rangle$$

Non-linear Schrödinger Equation (NLSE)

$$i\partial_t\psi = -\frac{1}{2}\partial_x^2\psi + \kappa|\psi|^2\psi$$

Numerical Integration

Concerns

- Accuracy,
  e.g. method is order $\mathcal{O}(\Delta t)^4$
- Stability,
  e.g. numerical error increases as $exp(\gamma(\Delta t) T)$
- "Physical" properties,
  e.g. method conserves energy or norm exactly

Euler Method

A First Method

- Derivation

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\phi_i\rangle = \hat{H}|\phi_i\rangle$$

$$\mathrm{i}\hbar\frac{|\phi_i(t+\Delta t)\rangle - |\phi_i(t)\rangle}{\Delta t} + \mathcal{O}(\Delta t)^2 = \hat{H}|\phi_i(t)\rangle$$

$$|\phi_i(t+\Delta t)\rangle = |\phi_i(t)\rangle - \frac{\mathrm{i}}{\hbar}\Delta t\hat{H}|\phi_i(t)\rangle + \mathcal{O}_{\text{local}}(\Delta t)^2$$

- Integration Error (order)

$$\rightarrow |\phi_i(t)\rangle + \mathcal{O}_{\text{integration}}(\Delta t)$$

- Not Stable!

Second Order Differences (SOD), Part I

Second order in time

$$|\phi_i(t+\Delta t)\rangle = |\phi(t-\Delta t)\rangle - 2\mathrm{i}\Delta t \hat{H}[n(t)]|\phi_i(t)\rangle$$

- Integration Error (order)

$$\rightarrow |\phi_i(t)\rangle + \mathcal{O}_{\text{integration}}(\Delta t)^2$$

- Conditionally Stable of TDSE
- Unconditionally Unstable for TDKS

Von Neumann Stability Analysis

Criterion of Stability from Local Analysis

$$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2}$$

- Discretization (finite differences) in time **and space**

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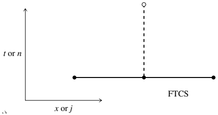

$$\frac{u_j^{n+1} - u_j^n}{\Delta t} = \alpha \frac{\left(u_{j+1}^n - 2u_j^n + u_{j-1}^n\right)}{\Delta x^2}$$

- Eigenmode analysis $u_j^n \to \xi(k)^n e^{\mathrm{i}kj\Delta x}$

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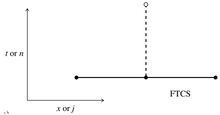

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$$\xi(k) = 1 - 4\frac{|\alpha|\Delta t}{\Delta x^2} \sin^2(k\Delta x/2)$$

- Stability Criterion $|\xi| \leq 1$

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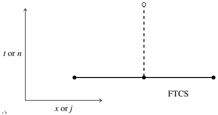

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$$\frac{2|\alpha|\Delta t}{\Delta x^2} \leq 1 \longrightarrow \frac{\Delta t \times E_{\text{cutoff}}^{\text{PW}}}{\pi^2 \hbar} \leq 1$$

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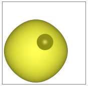
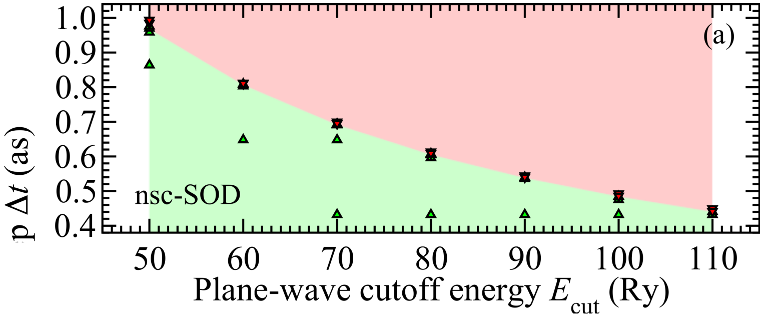
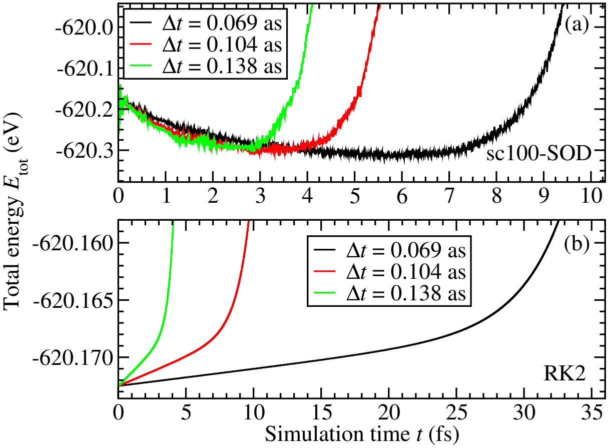




Analysis valid only for TDSE

Stabilizing SOD

The effect of the self consistent potential

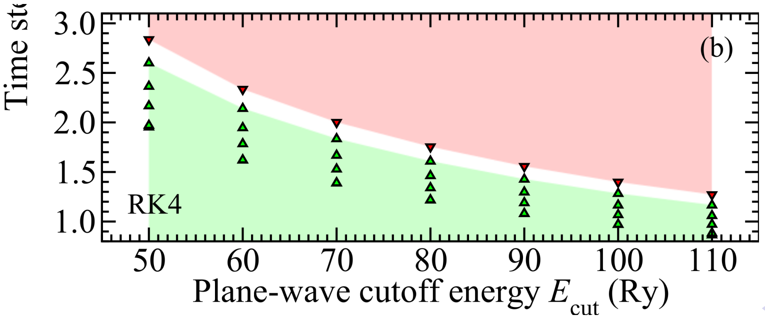


Updating the Hamiltonian once every several steps help stabilize the integration

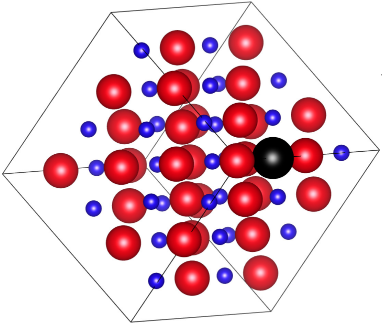
Runge-Kutta 4th Order

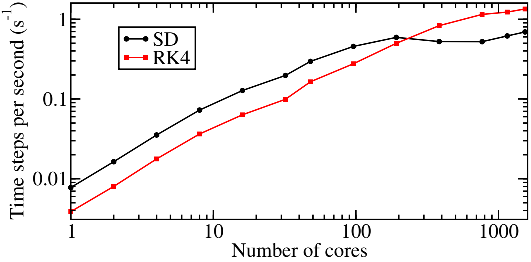
A conditionally stable, accurate method

$$|k_1\rangle = -\mathrm{i}\,\Delta t\,\hat{H}[n_{\phi(t)}]\,|\phi(t)\rangle\,,$$
$$|k_2\rangle = -\mathrm{i}\,\Delta t\,\hat{H}[n_{\phi(t)+0.5\cdot k_1}]|\phi(t)+0.5\cdot k_1\rangle,$$
$$|k_3\rangle = -\mathrm{i}\,\Delta t\,\hat{H}[n_{\phi(t)+0.5\cdot k_2}]|\phi(t)+0.5\cdot k_2\rangle,$$
$$|k_4\rangle = -\mathrm{i}\,\Delta t\,\hat{H}[n_{\phi(t)+k_3}]|\phi(t)+k_3\rangle,$$
$$|\phi(t+\Delta t)\rangle = |\phi(t)\rangle + \frac{1}{6}|k_1\rangle + \frac{1}{3}|k_2\rangle + \frac{1}{3}|k_3\rangle + \frac{1}{6}|k_4\rangle$$



Parallel Scalability





No orthogonalization bottleneck !

BO vs. TDKS+Ehrenfest, relative cost 500 → 50 → 25

$$\frac{\Delta t^{\mathrm{BOMD}}}{\Delta t^{\mathrm{TDKS}}} \sim 500, \quad \frac{\#SD}{\#MD} \sim 10, \quad \frac{\mathrm{Walltime}^{\mathrm{SD}}}{\mathrm{Walltime}^{\mathrm{TDKS}}} = 2$$

Cayley's Method (Crank Nicholson)

An Implicit Method

$$\left\{\hat{1} + \frac{1}{2}\mathrm{i}\hat{H}[n(t+\Delta t)]\Delta t\right\}|\psi_i(t+\Delta t)\rangle = \left\{\hat{1} - \frac{1}{2}\mathrm{i}\hat{H}[n(t)]\Delta t\right\}|\psi_i(t)\rangle \quad (1)$$

Future step is an implicit function of the previous step (need a non linear solution).
An approximation (use past density)

$$\left\{\hat{1} + \frac{1}{2}\mathrm{i}\hat{H}[n(t)]\Delta t\right\}|\psi_i(t+\Delta t)\rangle = \left\{\hat{1} - \frac{1}{2}\mathrm{i}\hat{H}[n(t)]\Delta t\right\}|\psi_i(t)\rangle \quad (2)$$

Still not very suitable for PW expansion.

Conclusions

- TDKS Propagators are subject to stability issues (like any PDE)
- Methods that work for TDSE may not work at all for TDKS
- RK4 presents good accuracy and stabiliry (at least for $T = 100\mathrm{fs}$)
- Plane-wave accuracy
- Parallel efficiecy up to 1500 cores for 450 electrons

References: Schleife et al., "Explicit integrators for the time-dependent Kohn-Sham equations within the plane-wave pseudopotential formalism",