

Time reversible Born Oppenheimer molecular dynamics

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(time dependent) Born-Oppenheimer approximation

Nuclear-electronic Schrödinger equation

$$i\partial_t \Psi(x, R) = -\frac{1}{2}\Delta_x \Psi(x, R) - \frac{1}{2M}\Delta_R \Psi(x, R) + V(x, R)\Psi(x, R)$$

Born-Oppenheimer (adiabatic) approximation

$$\varepsilon = \sqrt{1/M} \ll 1 \quad (M \approx 1836 \text{ for hydrogen})$$

Assume that the wave function takes

$$\Psi(x, R) = \psi(R)\Phi_0(x; R)$$

where $\Phi_0(\cdot; R)$ is the ground state for electronic Hamiltonian

$$\left[-\frac{1}{2}\Delta_x + V(x, R)\right]\Phi_0(x; R) = E_0(R)\Phi_0(x; R)$$

Semiclassical limit

Nuclear Schrodinger equation

$$i\partial_t\psi(R) = -\frac{1}{2M}\Delta_R\psi(R) + E_0(R)\Psi(x, R)$$

We are interested in long time dynamics for nuclei, hence we rescale to the time scale $\mathcal{O}(\sqrt{M})$ and get (recall $\varepsilon = \sqrt{1/M}$)

$$i\varepsilon\partial_t\psi(R) = -\frac{\varepsilon^2}{2}\Delta_R\psi(R) + E_0(R)\Psi(x, R)$$

Semiclassical approximation ($\varepsilon \ll 1$) gives Newton's equation of motion

$$M\ddot{R} = -\nabla_R E_0(R).$$

Mathematical works by Combes, Hagedorn, Jecko, Joye, Markowich, Martinez, Maslov, Panati, Paul, Spohn, Teufel, ...

Born-Oppenheimer molecular dynamics

BOMD equation of motion

$$M\ddot{R} = -\nabla_R E_0(R);$$
$$E_0(R) = \inf_{\Phi} \langle \Phi | H(x; R) | \Phi \rangle.$$

Force can be calculated using Hellmann-Feynman theorem

$$\nabla_R E_0(R) = \langle \Phi_0(x; R) | \nabla_R H(x; R) | \Phi_0(x; R) \rangle.$$

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Unfortunately, the variational problem is **too difficult to solve practically**.

- **Curse of dimensionality** ($d = 3N$, where N is the number of electrons);
- Symmetry restrictions of Φ due to Pauli's exclusion principle

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N);$$

- Φ has complicated singularity structure.

Density functional theory

Approximate solutions are given by electronic structure models.

The most popular choice is the density functional theory

[Hohenberg-Kohn 1964, Kohn-Sham 1965]

The energy is a functional of the one-body electron density $\rho : \mathbb{R}^3 \rightarrow \mathbb{R}_+$

$$\rho(x) = N \int |\Phi|^2(x, x_2, \dots, x_N) dx_2 \cdots dx_N.$$

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Levy-Lieb constrained variational principle [Levy 1979, Lieb 1983]:

$$E_0 = \inf_{\Phi} \langle \Phi | H | \Phi \rangle = \inf_{\rho} \inf_{\Phi: \Phi \mapsto \rho} \langle \Phi | H | \Phi \rangle$$

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The energy functional takes the general form

$$E_{\text{DFT}}(\rho; R) = T_s(\rho) + \int \rho V_{\text{ext}}(x; R) + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} + E_{\text{xc}}(\rho)$$

$T_s(\rho)$: Kinetic energy of non-interacting electrons;

$E_{\text{xc}}(\rho)$: **Exchange-correlation energy**, which encodes the many-body interaction.

Kohn-Sham density functional theory

Kohn-Sham density functional theory introduces one-particle orbitals to better approximate the kinetic and exchange-correlation energies.

It is the most widely used electronic structure theory, which achieves the best compromise between accuracy and cost.

The energy functional is minimized for N orbitals $\{\psi_i\} \subset H^1(\mathbb{R}^3)$.

$$E_{\text{KS}}(\{\psi_i\}; R) = \frac{1}{2} \sum_{i=1}^N \int |\nabla \psi_i|^2 + \int \rho V_{\text{ext}}(x; R) + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} + E_{\text{xc}}(\rho)$$

where the electron density is given by

$$\rho(x) = \sum_{i=1}^N |\psi_i|^2(x).$$

Remark: spin degree of freedom is neglected

Kohn-Sham density functional theory

Kohn-Sham DFT can be understood as a mean field type theory, as electrons interact through an effective potential.

The electron density satisfies the following consistent relation:

$$H_{\text{eff}}(\rho)\psi_i = E_i\psi_i, \quad \text{and} \quad \rho(x) = \sum_{i=1}^N |\psi_i|^2(x)$$

where the effective Hamiltonian contains the interactions of electrons:

$$H_{\text{eff}}(\rho) = -\frac{1}{2}\Delta + V_{\text{eff}}(\rho);$$
$$V_{\text{eff}}(\rho) = V_{\text{ext}} + V_c(\rho) + \frac{\delta}{\delta\rho}E_{xc}(\rho).$$

Note that this gives a fix point equation

$$\rho = F_{\text{KS}}(\rho).$$

BOMD with Kohn-Sham DFT

Equation of motion

$$M\ddot{R} = -\nabla_R E_{0,\text{KS}}(R);$$
$$E_{0,\text{KS}}(R) = \inf_{\{\psi_i\}} E_{\text{KS}}(\{\psi_i\}; R).$$

Straightforward application of Hellmann-Feynman type argument gives

$$\nabla_R E_{0,\text{KS}}(R) = \int \rho_{\text{KS}}(x; R) \frac{\partial}{\partial R} V_{\text{ext}}(x; R) dx$$

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Straightforward application of Hellmann-Feynman type argument gives

$$\nabla_R E_{0,KS}(R) = \int \rho_{KS}(x; R) \frac{\partial}{\partial R} V_{\text{ext}}(x; R) dx$$

We can then write

$$M\ddot{R} = - \int \rho_{KS}(x; R) \frac{\partial}{\partial R} V_{\text{ext}}(x; R) dx$$
$$\rho_{KS}(x; R) = \arg \min_{\rho} E_{KS}(\rho; R)$$

where (with some abuse of notation)

$$E_{KS}(\rho; R) = \inf_{\{\psi_i\}; \{\psi_i\} \mapsto \rho} E_{KS}(\{\psi_i\}; R)$$

for math justification, see [Ambrosio-Figalli-Friesecke-Giannoulis-Paul 2011]

Self-consistent field iteration

The challenge is now to find the ground state electron density

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Self-consistent field iteration

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$$\rho_{\text{KS}}(x; R) = \arg \min_{\rho} E_{\text{KS}}(\rho; R).$$

The common (and efficient) way to find ρ_{KS} is to use a nonlinear iteration scheme to solve the fix point equation

$$\rho = F_{\text{KS}}(\rho).$$

This is known as the [self-consistent field \(SCF\) iteration](#) in literature.

An example of the mixing scheme is:

1. $\tilde{\rho} = F_{\text{KS}}(\rho^n)$
2. $\rho^{n+1} = \rho^n + \alpha P(\tilde{\rho} - \rho^n)$

where α is a mixing parameter and P a preconditioner, e.g.

$P = \text{Id}$ for simple mixing,

$P = \frac{-\Delta}{4\pi\gamma - \Delta}$ for Kerker mixing.

Simple mixing:

$$\rho^{n+1} = \rho^n + \alpha(F_{\text{KS}}(\rho^n) - \rho^n).$$

Kerker mixing:

$$\rho^{n+1} = \rho^n + \alpha \frac{-\Delta}{4\pi\gamma - \Delta} (F_{\text{KS}}(\rho^n) - \rho^n)$$

We will not go into the details of more advanced SCF iteration scheme here, but just make two remarks for discussions in the sequel:

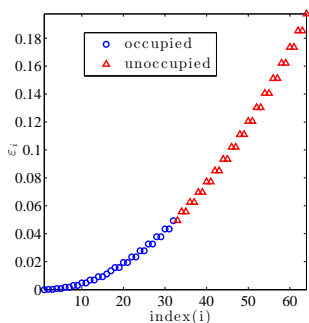
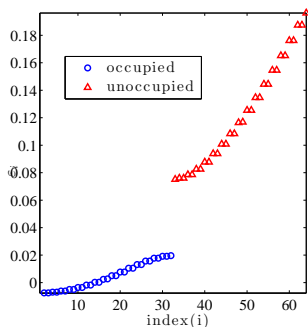
1. As usual for iterative schemes, the SCF iteration starts with an **initial guess** ρ^0 , which greatly affects the number of iterations;
2. As the system has huge number of degrees of freedom, in practice, the SCF iteration can take a long time to converge. This is the **bottleneck** of BOMD simulations.

A simple example

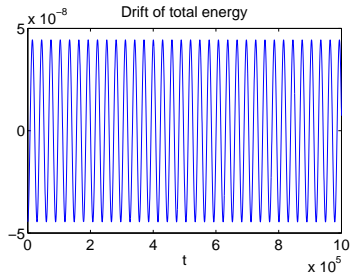
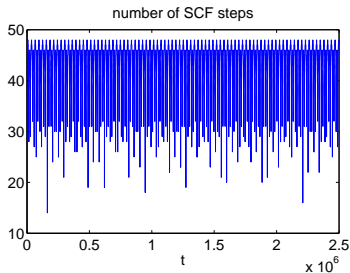
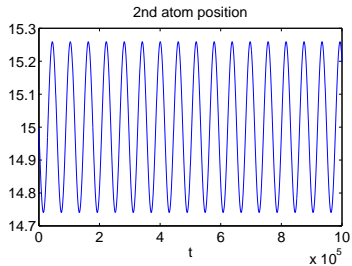
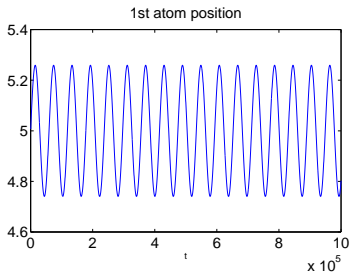
Let us use as example the dynamics of an one-dimensional chain of atoms.

$$E_{\text{KS}}(\psi, R) = \sum_i \int |\nabla \psi_i|^2 + \frac{1}{2} \iint (\rho(x) - m(x; R)) v(|x-y|) (\rho(y) - m(y; R))$$

where $m(x; R) = \sum_I m_{\text{ion}}(x - R_I)$. By different choice of ionic background charge m_{ion} , we have either insulating or metallic systems.



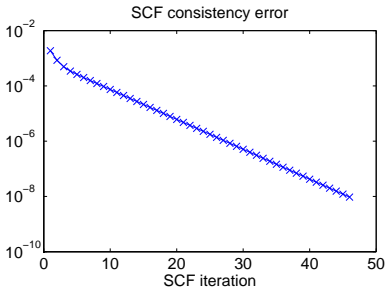
We use BOMD to study the phonon frequency of the system.



How to accelerate BOMD?

Since the bottleneck is SCF, we try to reduce the number of steps:

- Use ρ from last atom position R as initial guess (already used);
- Terminate the SCF iteration before convergence (who need 10^{-9}) ...

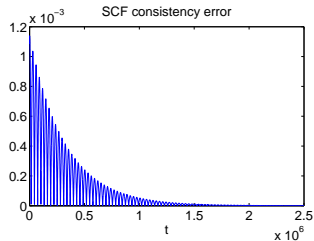
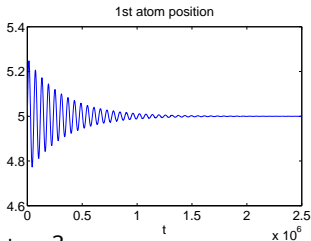


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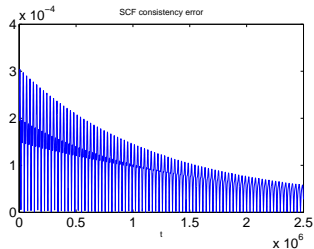
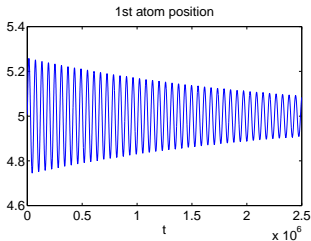
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- Use ρ from last atom position R as initial guess (already used);
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Unfortunately, it does not work ...



More SCF steps?



Recall the Born-Oppenheimer molecular dynamics

$$M\ddot{R} = - \int \rho_{\text{KS}}(x; R) \partial_R V_{\text{ext}}(x; R) dx$$
$$\rho_{\text{KS}}(x; R) = \arg \min_{\rho} E_{\text{KS}}(\rho; R)$$

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We have introduced a dependence on the initial guess ρ (superscript dropped), which is superficial now, since ρ_{KS} is the minimizer (assuming uniqueness, at least locally ...)

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When we use **non-convergent** SCF iteration, let us denote $\rho_{\text{SCF}}(x; R, \rho)$ the output density from **initial guess** ρ of the non-convergent SCF iteration.

$$M\ddot{R} = - \int \rho_{\text{SCF}}(x; R, \rho) \partial_R V_{\text{ext}}(x; R) dx$$
$$\rho(t+) \leftarrow \rho_{\text{SCF}}(x; R, \rho(t))$$

where we update the initial guess for the next time step using the current output.

Loss of time-reversible symmetry

BOMD with non-convergent SCF iteration

$$M\ddot{R} = - \int \rho_{\text{SCF}}(x; R, \rho) \partial_R V_{\text{ext}}(x; R) dx$$
$$\rho(t+) \leftarrow \rho_{\text{SCF}}(x; R, \rho(t))$$

Due to the dependence on the initial guess of the SCF iteration, the dynamics is no longer **time-reversible** nor **symplectic**.

The loss of structure leads to instability and drift behavior.

We note that irreversibility also arises if SCF is accelerated using

- linear scaling algorithm (uncontrolled error due to cut-off), or
- adaptive basis sets (Pulay force).

Time-reversible Born-Oppenheimer molecular dynamics

Key idea: Restore the **time reversibility** by treating the initial guess of electron density as dynamical variables.

[Niklasson-Tymczak-Challacombe 2006, Niklasson 2008]

Time-reversible Born-Oppenheimer molecular dynamics (TRBOMD)

$$M\ddot{R} = - \int \rho_{\text{SCF}}(x; R, \rho) \partial_R V_{\text{ext}}(x; R) dx$$
$$\ddot{\rho} = \omega^2 (\rho_{\text{SCF}}(x; R, \rho) - \rho)$$

Here ω^2 is a frequency parameter for the artificial dynamics of ρ .

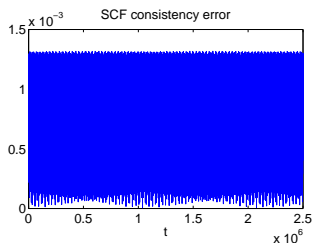
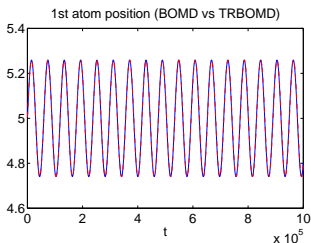
The dynamics apparently has **time reversal symmetry**, however it is not symplectic (no “energy” conservation in general).

Remark: other than the second order dynamics for ρ , we might also consider time-reversible first order stochastic dynamics.

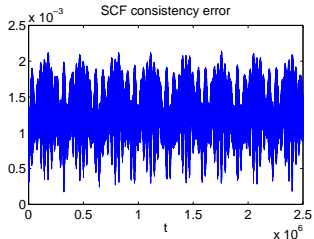
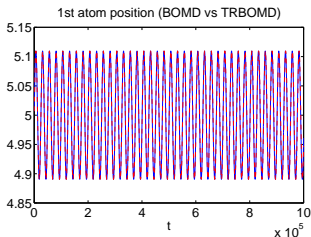
Numerical examples for TRBOMD

Back to the original phonon example, we use SCF step = 3.

Metal system:



Insulator system:



Questions:

- When does and how does TRBOMD work?
- How to choose the parameter ω^2 ?
- How does the performance depend on the system and choice of ρ_{SCF} ?

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To answer these (at least partially), we first do a linear stability analysis of the dynamics.

Denote R^* and $\rho^* = \rho_{\text{KS}}(R^*)$ the reference equilibrium state.

Write $R = R^* + \tilde{R}$ and $\rho = \rho^* + \tilde{\rho}$, we have (after dropping tildes)

$$M\ddot{R} = - \int \rho_{\text{SCF}}(x; R^* + R, \rho^* + \rho) \partial_R V_{\text{ext}}(x; R^* + R) dx$$
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$$\ddot{\rho} = \omega^2 (\rho_{\text{SCF}}(R^* + R, \rho^* + \rho) - \rho^* - \rho)$$

Assumption: consistency of the SCF map

$$\rho_{\text{SCF}}(R, \rho_{\text{KS}}(R)) = \rho_{\text{KS}}(R), \quad \text{in particular } \rho_{\text{SCF}}(R^*, \rho^*) = \rho^*.$$

Linearization gives (all derivatives evaluated at R^* and ρ^*)

$$M\ddot{R} = -\left(\int \frac{\partial V_{\text{ext}}}{\partial R} \frac{\partial \rho_{\text{SCF}}}{\partial R} + \rho^* \frac{\partial^2 V_{\text{ext}}}{\partial R^2}\right)R - \int \frac{\partial V_{\text{ext}}}{\partial R} \frac{\partial \rho_{\text{SCF}}}{\partial \rho} \rho$$
$$\omega^{-2}\ddot{\rho} = \frac{\partial \rho_{\text{SCF}}}{\partial R}R + \left(\frac{\partial \rho_{\text{SCF}}}{\partial \rho} - \text{Id}\right)\rho$$

By consistency of the SCF map, we have

$$\frac{\partial \rho_{\text{SCF}}}{\partial R} = \left(\text{Id} - \frac{\partial \rho_{\text{SCF}}}{\partial \rho}\right) \frac{\partial \rho_{\text{KS}}}{\partial R}$$

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$$\frac{\partial \rho_{\text{SCF}}}{\partial R} = \left(\text{Id} - \frac{\partial \rho_{\text{SCF}}}{\partial \rho}\right) \frac{\partial \rho_{\text{KS}}}{\partial R} =: \mathcal{K} \frac{\partial \rho_{\text{KS}}}{\partial R}$$

We arrive at

$$M\ddot{R} = -M\mathcal{D}R - \int \frac{\partial V_{\text{ext}}}{\partial R} (\mathcal{K} - \text{Id}) \left(\frac{\partial \rho_{\text{KS}}}{\partial R}R - \rho\right)$$
$$\omega^{-2}\ddot{\rho} = \mathcal{K} \left(\frac{\partial \rho_{\text{KS}}}{\partial R}R - \rho\right)$$

where \mathcal{D} is the [dynamical matrix for atoms](#)

$$M\mathcal{D} = \left(\int \frac{\partial V_{\text{ext}}}{\partial R} \frac{\partial \rho_{\text{KS}}}{\partial R} + \rho^* \frac{\partial^2 V_{\text{ext}}}{\partial R^2}\right)$$

Linearized TRBOMD

$$M\ddot{R} = -M\mathcal{D}R - \int \frac{\partial V_{\text{ext}}}{\partial R} (\mathcal{K} - \text{Id}) \left(\frac{\partial \rho_{\text{KS}}}{\partial R} R - \rho \right)$$
$$\omega^{-2} \ddot{\rho} = \mathcal{K} \left(\frac{\partial \rho_{\text{KS}}}{\partial R} R - \rho \right)$$

Note that $M\ddot{R} = -M\mathcal{D}R$ agrees with the linearization of BOMD, which gives the (Born-Oppenheimer) phonon frequency of the atoms.

Observations:

1. $\mathcal{K} = \text{Id} - \partial \rho_{\text{SCF}} / \partial \rho$ must be **diagonalizable with positive eigenvalues**, otherwise, the ρ dynamics is unstable.
2. Denote the characteristic frequency of R as Ω , we have

$$\frac{\Omega - \Omega(\mathcal{D})}{\Omega(\mathcal{D})} = \omega^{-2} \left(\int \frac{\partial V_{\text{ext}}}{\partial R} (\text{Id} - \mathcal{K}^{-1}) \frac{\partial \rho_{\text{KS}}}{\partial R} + \mathcal{O} \left(\frac{\Omega(\mathcal{D})^2}{\omega^2 \lambda_{\min}(\mathcal{K})} \right) \right)$$

under the **non-resonance condition**: $\omega^{-2} \ll \lambda_{\min}(\mathcal{K}) / \Omega(\mathcal{D})^2$.

Accuracy of TRBOMD

Accuracy from linear response analysis:

$$\frac{\Omega - \Omega(\mathcal{D})}{\Omega(\mathcal{D})} = \omega^{-2} \left(\int \frac{\partial V_{\text{ext}}}{\partial R} (\text{Id} - \mathcal{K}^{-1}) \frac{\partial \rho_{\text{KS}}}{\partial R} + \mathcal{O}\left(\frac{\Omega(\mathcal{D})^2}{\omega^2 \lambda_{\min}(\mathcal{K})}\right) \right)$$

Hence, to improve the accuracy, we want to increase ω ; however, larger ω gives stiffness of the equation, which requires more computational cost.

We have a trade off between accuracy and cost.

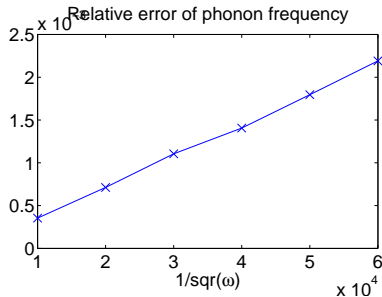
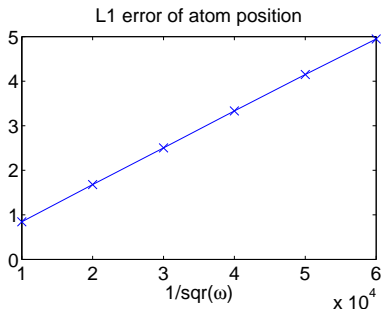
We also see that the prefactor decreases if the spectrum of \mathcal{K} is close to Id. Recall that $\mathcal{K} = \text{Id} - \frac{\partial \rho_{\text{SCF}}}{\partial \rho}$. We would want to choose SCF map so that

$$\left\| \frac{\partial \rho_{\text{SCF}}}{\partial \rho} \right\| \ll 1$$

This means that the output does not depend much on the initial guess, in other words, we would like to choose an effective SCF consistent iteration.

Numerical validation: Error as a function of ω^{-2} for metallic system

ω^{-2}	$\ R^{\text{BO}} - R^{\text{TR}}\ _{L^1}$	$\ R^{\text{BO}} - R^{\text{TR}}\ _{L^\infty}$	$ \Omega^{\text{TR}}/\Omega(\mathcal{D}) - 1 $
1e4	0.84367	0.87842e - 3	0.35399e - 3
2e4	1.67923	1.74862e - 3	0.71191e - 3
3e4	2.50381	2.60483e - 3	1.10521e - 3
4e4	3.33255	3.46855e - 3	1.40545e - 3
5e4	4.14935	4.31790e - 3	1.79543e - 3
6e4	4.94810	5.14452e - 3	2.19074e - 3



Summary of the linear response analysis

- Linear stability requires $\lambda(\mathcal{K}) > 0$ (requirement of SCF map).
- Accuracy $\mathcal{O}(\omega^{-2})$ provided non-resonance $\omega^{-2} \ll \lambda_{\min}(\mathcal{K})/\Omega(\mathcal{D})^2$.
- Performance depends on $\partial\rho_{\text{SCF}}/\partial\rho$, the effectiveness of SCF iteration.

More on the stability condition $\lambda(\mathcal{K}) > 0$:

Lemma

If ρ_{SCF} is given by simple mixing or Kerker mixing, \mathcal{K} is diagonalizable and its eigenvalues are real. The condition $\lambda(\mathcal{K}) > 0$ can be satisfied with suitable choice of preconditioner and the mixing parameter.

Sketch of Proof.

For simple or Kerker mixing, $\partial\rho_{\text{SCF}}/\partial\rho$ is a polynomial of $P\partial\rho_{\text{KS}}/\partial\rho$.

Claim: $P\partial\rho_{\text{KS}}/\partial\rho$ is diagonalizable with real eigenvalues.



How about nonlinear regime?

$$M\ddot{R} = - \int \rho_{\text{SCF}}(x; R, \rho) \partial_R V_{\text{ext}}(x; R) dx$$
$$\ddot{\rho} = \omega^2 (\rho_{\text{SCF}}(R, \rho) - \rho)$$

For $\omega^2 \gg 1$, we have time scale separation: ρ changes much faster compared to R .

Formal two-scale asymptotic expansion ($\tau = \omega t$):

$$R = R(t) \quad \text{and} \quad \rho = \rho(t, \tau)$$

To the leading order, we obtain

$$M\ddot{R}(t) = - \int \rho_{\text{SCF}}(x; R(t), \rho(t, \tau)) \partial_R V_{\text{ext}}(x; R(t)) dx$$
$$\partial_\tau^2 \rho(t, \tau) = \rho_{\text{SCF}}(R(t), \rho(t, \tau)) - \rho(t, \tau)$$

Averaging perspective of TRBOMD

To the leading order in ω

$$M\ddot{R}(t) = - \int \rho_{\text{SCF}}(x; R(t), \rho(t, \tau)) \partial_R V_{\text{ext}}(x; R(t)) dx$$
$$\partial_\tau^2 \rho(t, \tau) = \rho_{\text{SCF}}(R(t), \rho(t, \tau)) - \rho(t, \tau)$$

$R(t)$ is frozen in the leading order equation for ρ .

Assumption: The limit of the time average exists

$$\bar{\rho}(x; R(t)) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \rho_{\text{SCF}}(R(t), \rho(t, \tau)) d\tau$$

As ρ_{SCF} can be fairly nonlinear and complicated, it seems difficult to justify the assumption in general.

Average of R equation over τ , we have

$$M\ddot{R}(t) = - \int \bar{\rho}(x; R(t)) \partial_R V_{\text{ext}}(x; R(t)) dx$$

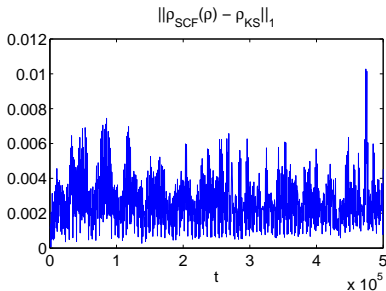
Effective equation of TRBOMD for R :

$$M\ddot{R}(t) = - \int \bar{\rho}(x; R(t)) \partial_R V_{\text{ext}}(x; R(t)) dx$$

Compared with BOMD

$$M\ddot{R}(t) = - \int \rho_{\text{KS}}(x; R(t)) \partial_R V_{\text{ext}}(x; R(t)) dx$$

The pathwise accuracy is determined by the difference $\rho_{\text{KS}} - \bar{\rho}$.
In the limit $\omega \rightarrow \infty$, TRBOMD may still have an error compared to BOMD.
It is affected by the SCF map ρ_{SCF} and the long time dynamics of $\rho(\tau)$.

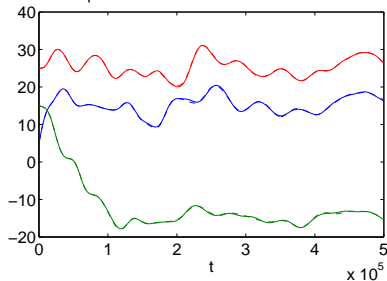


non-equilibrium metallic system, $\omega^{-2} = 62500$, SCF step = 7

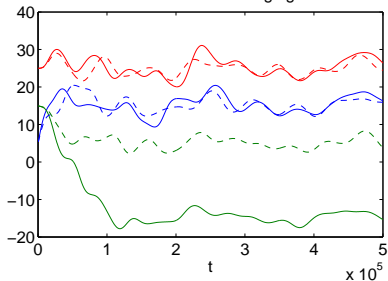
Numerical example: non-equilibrium case, metal system

At time 0, we “kick” the first atom, so that $\dot{R}_1(0) = 1e - 3$.

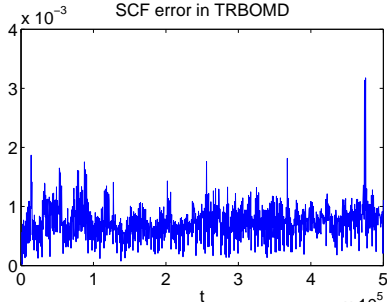
Comparison between TRBOMD and BOMD



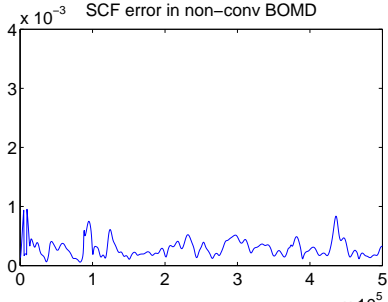
BOMD with non-converging SCF



SCF error in TRBOMD



SCF error in non-conv BOMD



Car-Parrinello molecular dynamics

Key idea: Undo the adiabatic limit by introducing (artificial) classical dynamics for electrons. It can be viewed as a relaxation scheme.

[Car-Parrinello 1985]

Car-Parrinello equation of motion

$$M\ddot{R} = -\frac{\partial E_{\text{KS}}(\psi, R)}{\partial R} = -\int \rho_{\psi}(x) \frac{V_{\text{ext}}(x; R)}{\partial R} dx$$
$$\mu\ddot{\psi}_i = -\frac{\partial E_{\text{KS}}(\psi, R)}{\partial \psi_i} + \sum_j \psi_j \Lambda_{ji}$$

Here Λ 's are Lagrange multipliers for the orthonormality constraints.

CPMD is a Hamiltonian system (on the manifold $\int \psi_i \psi_j = \delta_{ij}$) with Lagrangian given by

$$\mathcal{L}(R, \dot{R}, \psi, \dot{\psi}) = M|\dot{R}|^2 + \mu \sum_i \|\dot{\psi}_i\|^2 - E_{\text{KS}}(\psi, R).$$

Analysis of CPMD

The stability is guaranteed by the energy conservation.

Following the similar strategy, we have

1. **Adiabatic condition:** $\mu \ll \lambda_{\min}(\mathcal{H})/\Omega(\mathcal{D})^2$ where $\mathcal{H} = \partial^2 E_{\text{KS}}/\partial\psi^2$ and $\lambda_{\min}(\mathcal{H}) = E_{\text{gap}}$; **Fails for gapless system.**
2. Accuracy of phonon frequency:

$$\left| \frac{\Omega - \Omega(\mathcal{D})}{\Omega(\mathcal{D})} \right| \lesssim \frac{\mu}{E_{\text{gap}}^2}.$$

The analysis can be extended to the nonlinear regime (a classical adiabatic type result), thanks to the symplectic structure:

Theorem (Bornemann-Schütte 1998)

For insulating systems (with spectral gap), for a finite time T small enough that the gap persists, we have

$$\left\| R^{\text{BO}} - R^{\text{CP}} \right\|_{L^\infty(0,T)} \leq C(T)\mu^{1/2}.$$

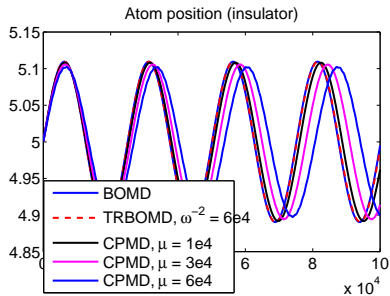
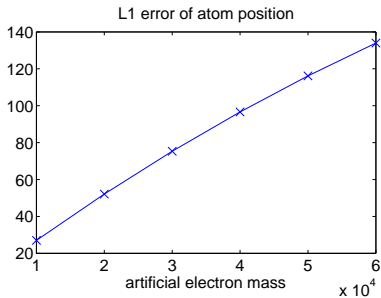
Comparison between TRBOMD and CPMD

	TRBOMD	CPMD
structure	time-reversible	symplectic
tuning parameter	ω^{-2}	μ
non-resonance condition	$\omega^{-2} \ll \lambda_{\min}(\mathcal{K})/\Omega^2$	$\mu \ll \lambda_{\min}(\mathcal{H})/\Omega^2$
	$\mathcal{K} = I - \frac{\partial \rho_{\text{SCF}}}{\partial \rho}$	$\mathcal{H} = \frac{\partial^2 E_{\text{KS}}}{\partial \psi^2}$
insulator	yes (if $\lambda(\mathcal{K}) > 0$)	yes
metal	yes (if $\lambda(\mathcal{K}) > 0$)	no

- TRBOMD works for metal
- TRBOMD offers more flexibility to improve accuracy (i.e. using better SCF maps)
- TRBOMD is NOT guaranteed to be long-time stable

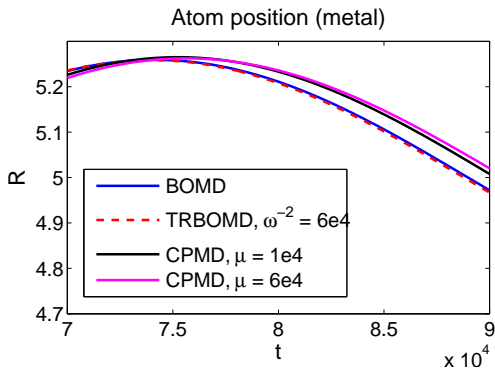
Numerical comparison of TRBOMD and CPMD: Insulating system

μ	$\ R^{\text{BO}} - R^{\text{CP}}\ _{L^1}$	$\ R^{\text{BO}} - R^{\text{CP}}\ _{L^\infty}$	$ \Omega^{\text{CP}}/\Omega(\mathcal{D}) - 1 $
$1e4$	$0.27009e + 2$	$0.32930e - 1$	$1.24227e - 2$
$2e4$	$0.52117e + 2$	$0.60463e - 1$	$2.42788e - 2$
$3e4$	$0.75312e + 2$	$0.85131e - 1$	$3.58139e - 2$
$4e4$	$0.96623e + 2$	$1.09253e - 1$	$4.68517e - 2$
$5e4$	$1.16149e + 2$	$1.31137e - 1$	$5.14133e - 2$
$6e4$	$1.33986e + 2$	$1.49472e - 1$	$5.95193e - 2$



Numerical comparison of TRBOMD and CPMD: Metallic system

μ	$\ R^{\text{BO}} - R^{\text{CP}}\ _{L^1}$	$\ R^{\text{BO}} - R^{\text{CP}}\ _{L^\infty}$	$ \Omega^{\text{CP}}/\Omega(\mathcal{D}) - 1 $
$1e4$	34.6848	$3.60028e - 2$	$1.43067e - 2$
$2e4$	38.8461	$4.19386e - 2$	$1.67889e - 2$
$3e4$	40.9346	$4.43534e - 2$	$1.82828e - 2$
$4e4$	42.3424	$4.57893e - 2$	$1.80796e - 2$
$5e4$	43.6062	$4.70760e - 2$	$1.87239e - 2$
$6e4$	44.8588	$4.83539e - 2$	$1.89897e - 2$



Conclusion and future directions

Conclusion

- BOMD can be accelerated by using the time-reversible Born-Oppenheimer molecular dynamics.
- TRBOMD is time-reversible, and hence has better long-time stability; however, it is not symplectic.
- TRBOMD requires effective self-consistent field iterations to work.
- The tuning parameter ω offers a trade-off of efficiency and accuracy.

Some future directions

- Canonical ensemble (NVT) case (thermostat).
- Long-time behavior and nonlinear stability of TRBOMD.
- Time-reversible stochastic version of TRBOMD.
- Explore symplectic BOMD with non-convergent SCF iterations.
- Better understanding of SCF iterations (e.g. \mathcal{K}).
- CPMD for metallic systems.

Thank you for your attention

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