Exact adiabatic approximation in TDDFT

Jeiran Jokar and Nicole Helbig
Motivation

Rabi oscillation: Oscillation between the ground state and an excited state laser frequency close to resonance

Large change in the density $\rightarrow$ Problems with adiabatic approximations in TDDFT

\[ \Delta \begin{align*} \epsilon_e \\
\epsilon_g \end{align*} \]

$\omega$
Model system

Two electrons in the one dimensional external potential

\[ V_{\text{ext}}(x) = \frac{-2}{\sqrt{x^2 + 1}} \]

\[
H = -\frac{d^2}{dx_1^2} - \frac{d^2}{dx_2^2} - \frac{2}{\sqrt{x_1^2 + 1}} - \frac{2}{\sqrt{x_2^2 + 1}} + \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}
\]

We have two initial states

\{ Singlet, Triplet \}
Rabi oscillations

Exact calculation

\[ n_g \quad n_e \]

ALDA

Resonant Singlet

Resonant Triplet

Detuned Triplet
**Adiabatic approximation**

\[ V_{xc}[\rho(r,t')](r,t) \rightarrow \text{Depends on the density for all } t' < t \]

Potential at time \( t \) only depends on the density at time \( t \)

Example: LDA exchange:

\[ V_{x}^{LDA}(r) = - \left( \frac{3}{\pi} \right)^{1/3} \rho(r)^{1/3} \]

Adiabatic LDA exchange:

\[ V_{x}^{ALDA}(r, t) = - \left( \frac{3}{\pi} \right)^{1/3} \rho(r, t)^{1/3} \]

Exact adiabatic approximation:

We need to calculate the exact static potential
Exact static potential

Two particles in a singlet state in 1D

One occupied orbital

\[ \rho(x) = 2 \left| \varphi_1(x) \right|^2 \]

Finding KS potential by inverting the KS equation

\[ V_s(x) = \frac{1}{\varphi_1(x)} \left[ \frac{\nabla^2}{2} \varphi_1(x) + \epsilon_1 \varphi_1(x) \right] \]

\[ = \frac{\nabla^2 \sqrt{\rho(x)}}{2 \sqrt{\rho(x)}} + \epsilon_1 \]

Hartree potential

\[ V_H(x) = \int d^3x' \frac{\rho(x')}{|x - x'|} \]
Exact static potential

Exchange correlation potential

\[ V_{xc}(x) = V_s(x) - V_{ext}(x) - V_H(x) \]
Exact static potential

More than one occupied orbital — Find $V_s$ iteratively

\[ V_s(x) = \frac{1}{\rho(x)} \sum_{j=1}^{2} \varphi_j^*(x) \left( \frac{\nabla^2}{2} + \epsilon_j \right) \varphi_j(x) \]

\[ V_s(x)^{k+1} = \frac{1}{\rho(x)} \sum_{j=1}^{2} \varphi_j^k(x) \left( \frac{\nabla^2}{2} + \epsilon_j^k \right) \varphi_j^k(x) \]

\[ V_s^{k+1}(x) = \frac{\rho^k(x)}{\rho(x)} V_s^k(x) \]
Exact static potential

In 1 dimension\(^1\)

\[ V_{s}^{k+1}(x) = V_{s}^{k}(x) + \alpha |x|^\beta (\rho_{s}^{k}(x) - \rho(x)) \]

Alternative idea\(^2\)

\[ V_{s}^{k+1}(x) = V_{s}^{k}(x) + \alpha \frac{\rho_{s}^{k}(x) - \rho(x)}{\rho(x) + \beta} \]

\[ \Delta \rho(x) = \rho_{s}^{k}(x) - \rho(x) \]

Target density

\(^1\)M. Thiele et al., PRL 100, 153004 (2008)
\(^2\)L. Stella, M.J. Verstraete private communication
Use the second potential \( \alpha = 1 \) \( \beta = 10^{-5} \)
Convergence

Change $\beta$ in each iteration

$$\beta = \frac{Max \Delta \rho}{10}$$

![Graph showing the convergence of the Singlet with different values of $\alpha$ and $\beta$.](image)

- **Legend**:
  - Black line: $\alpha = 1$, $\beta = 1e-5$
  - Blue line: $\alpha = 1$, $\beta$ tuned

**Axes**:
- Y-axis: Max $\Delta \rho$ (a.u.)
- X-axis: Iteration
Exchange correlation potential

Singlet

Potentials/Density (a.u.)

x (a.u.)

PRL 100, 153004

L. Stella

Exact calculation

Density
Conclusion

We have three ways to construct $V_s$

Two iterative ways

Exact way (only for 2 electron singlet)

Problem in asymptotic region because of the small density

Outlook

Use static potential in adiabatic TDDFT

Apply exact adiabatic approximation for Rabi oscillations
Thank you for your attention!
Exact adiabatic approximation

With the given ground-state density at each time

We can calculate exact static $V_{xc}$ for that specific time

1. Find $V_{s}^{adia}(r,t)$ from inversion of static KS equation

With $\rho_{gs}$ of the system at each time, We can construct $V_s$

2. Find $V_{ext}^{adia}(r,t)$ from inversion of many-body Schrödinger equation

3. Obtain $V_{xc}^{adia}(r,t)$ from

$$V_{xc}^{adia}(r,t) = V_{s}^{adia}(r,t) - V_{ext}^{adia}(r,t) - V_{H}(r,t)$$

4. Propagate with

$$V_{s}(r,t) = V_{ext}(r,t) + V_{H}(r,t) + V_{xc}^{adia}(r,t)$$