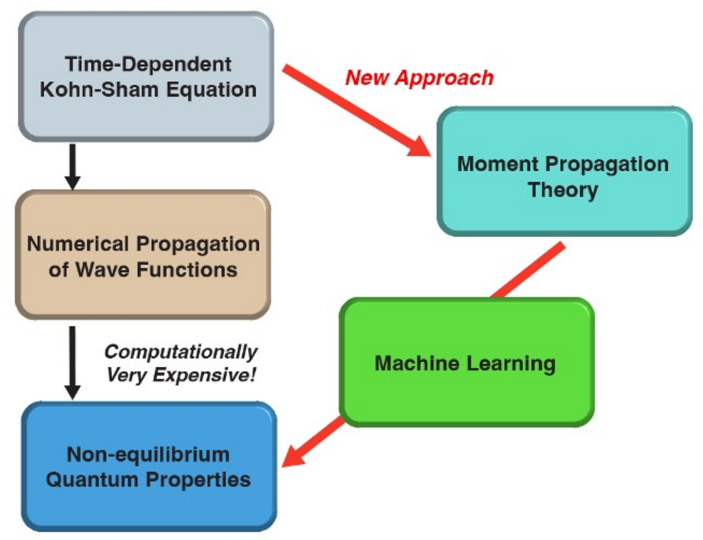
Machine-Learning Electron Dynamics with Moment Propagation Theory: Application to Optical Absorption Spectrum Computation using Real-Time TDDFT

Nicholas Boyer, Christopher Shepard, Ruiyi Zhou, Jianhang Xu, and Yosuke Kanai
Dept. of Chemistry, University of North Carolina at Chapel Hill
Dept. of Physics and Astronomy, University of North Carolina at Chapel Hill

Introduction

Recent development of real-time time-dependent density functional theory (RT-TDDFT) in maximally-localized Wannier functions (MLWF) gauge [1] and the use of machine learning (ML) for modeling quantum dynamics have motivated us to employ our newly formulated moment propagation theory (MPT) [2] for efficiently simulating quantum dynamics of electrons. Theoretical formalism for the moment propagation is presented and numerical details for using the theoretical formalism for ML models is demonstrated. Results for single molecules and a condensed matter system are presented.



Moments with increasing orders of the position operator with the particle density are

$$\langle x^a y^b z^c\rangle(t) \equiv \iiint x^a y^b z^c\, n(x,y,z,t)\,dxdydz$$

Theoretical Formulation

According to time-dependent Schrödinger equation in the single-particle description, the first and second order time derivatives can be written as [2],

$$\frac{d\langle x^a y^b z^c\rangle(t)}{dt} = -\frac{i}{2}\int\left[\nabla^2\left(x^a y^b z^c\right)n + 2\nabla\left(x^a y^b z^c\right)\cdot\nabla\psi\psi^*\right]d^3r$$

$$\frac{d^2\langle x^a y^b z^c\rangle(t)}{dt^2} = \int \mathrm{Re}\left[-\nabla(x^a y^b z^c)\cdot\nabla V n + \frac{1}{4}\nabla^4\left(x^a y^b z^c\right)n - \left(\nabla\otimes\nabla\left(x^a y^b z^c\right)\cdot(\nabla\otimes\nabla\psi)\right)\psi^*\right]d^3r$$

The EOM for the moments can be expressed as a function *F* that depends on the moments and their time derivatives:

$$\frac{d^2}{dt^2}\langle x^a y^b z^c\rangle(t) = \boldsymbol{F}\left(\{\langle x^d y^e z^f\rangle(t)\},\{\tfrac{d}{dt}\langle x^d y^e z^f\rangle(t)\}\right)$$

However, it's analytical form is very complicated for the use in first-principles electronic structure theory [2].

Using a simple linear model, the second order time derivatives of the quantum-particle j with the order of moments (a,b,c) is given by

$$\frac{d^2}{dt^2}\langle x^a y^b z^c\rangle_j(t) = \sum_k\left(B^{j,k}_{a,b,c} + \sum_{d,e,f} C^{j,k}_{a,b,c,d,e,f}\langle x^d y^e z^f\rangle_k(t) + \sum_{d,e,f} D^{j,k}_{a,b,c,d,e,f}\tfrac{d}{dt}\langle x^d y^e z^f\rangle_k(t)\right)$$

Using the matrix notation, the moments are represented as

$$\ddot{\mathbf{X}}(t) = \mathbf{C}\mathbf{X}(t) + \mathbf{D}\dot{\mathbf{X}}(t) + \mathbf{B}$$

Y defines the moments and their time derivative, as we have

$$\dot{\mathbf{Y}}(t) = \mathbf{A}\mathbf{Y}(t) + \mathbf{E}$$

$$\mathbf{Y}(t) \equiv \begin{bmatrix}\mathbf{X}(t)\\ \dot{\mathbf{X}}(t)\end{bmatrix}$$

$$\mathbf{A} \equiv \begin{bmatrix}\mathbf{0} & \mathbf{I}\\ \mathbf{C} & \mathbf{D}\end{bmatrix}$$

$$\mathbf{E} \equiv \begin{bmatrix}\mathbf{0}\\ \mathbf{B}\end{bmatrix}$$

Then,

$$\mathbf{Y}(t) = e^{\mathbf{A}t}\mathbf{V} - \mathbf{A}^{-1}\mathbf{E}$$

$$\mathbf{V} \equiv \mathbf{Y}(0) + \mathbf{A}^{-1}\mathbf{E}$$

$$\mathbf{Y}(t) = \mathbf{P}e^{\mathbf{Q}t}\mathbf{P}^{-1}\mathbf{V} - \mathbf{A}^{-1}\mathbf{E}$$

where P is the eigenvalue matrix and Q is the eigenvector matrix of A.

In this analytical formulation, unphysical behavior stemming from noises in the ML can be removed conveniently.

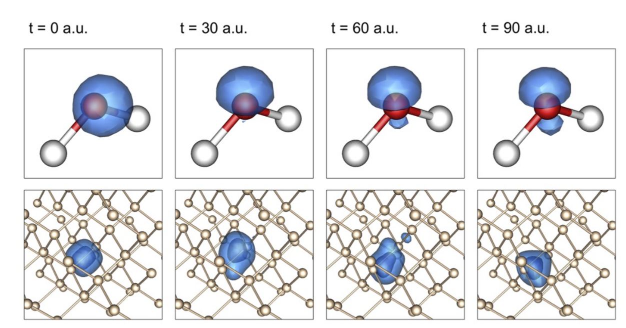
RT-TDDFT in Wannier Function Gauge

$$i\hbar\frac{d}{dt}|w_l(t)\rangle = \left\{\hat{A}^{ML} + \frac{1}{2m}[-i\hbar\nabla]^2 + \hat{v}_{ext} + \hat{v}_{HXC}[\rho]\right\}|w_l(t)\rangle$$

$\hat{A}^{ML}$ Ensures the maximal localization of the gauge invariant orbitals.

Example :

Time-evolution of a single $n_i(\mathbf{r};t) = |w_i(\mathbf{r};t)|^2$



Definitions of moments with periodic boundary conditions:

$$\langle\mathbf{r}\rangle = \frac{\mathbf{L}}{2\pi}\,\mathrm{Im}\ln\langle e^{i\frac{2\pi}{\mathbf{L}}\cdot\mathbf{r}}\rangle$$

$$\langle(r-\langle r\rangle)^2\rangle = \left(\frac{L_r}{2\pi}\right)^2\left(1 - |\langle e^{i\frac{2\pi}{L_r}r}\rangle|^2\right)$$

$$\langle(r-\langle r\rangle)(r'-\langle r'\rangle)\rangle = \frac{L_r L_{r'}}{16\pi^2}\left(\ln|\langle e^{i\frac{2\pi}{L_r}r}e^{-i\frac{2\pi}{L_{r'}}r'}\rangle|^2 - \ln|\langle e^{i\frac{2\pi}{L_r}r}e^{i\frac{2\pi}{L_{r'}}r'}\rangle|^2\right)$$

Dielectric function:

$$\epsilon(\omega) = 1 + \frac{4\pi i}{3\omega}\mathrm{Tr}\left[\sigma_{\mu\nu}(\omega)\right] \qquad \sigma_{\mu\nu}(\omega) = \frac{1}{\delta_\nu}\int dt\, e^{i\omega t}\sum_j\langle r_\mu\rangle_j(t)$$

Dipole strength function:

$$S(\omega) = \frac{4\pi\omega}{3c}\mathrm{Tr}\left[\mathrm{Im}\,\sigma_{\mu\nu}(\omega)\right]$$

1. Propagation of Maximally Localized Wannier Functions in Real-Time TDDFT
D.Yost, Y. Yao, Y. Kanai J. Chem. Phys., 150, 194113 (2019)

2. Theory of Moment Propagation for Quantum Dynamics in Single-Particle Description
N. Boyer, C. Shepard, R. Zhou, J. Xu, Y. Kanai J. Chem. Phys. 160, 064113 (2024)

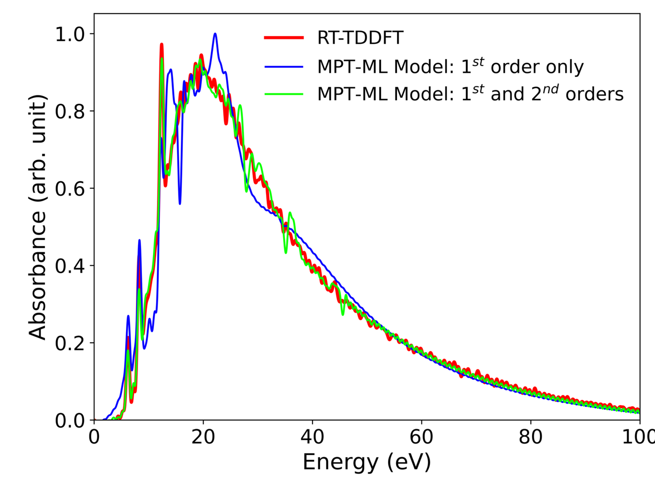
Results and Discussion

As a proof-of-principle application of the MPT-ML approach to quantum dynamics, optical absorption spectra are computed.

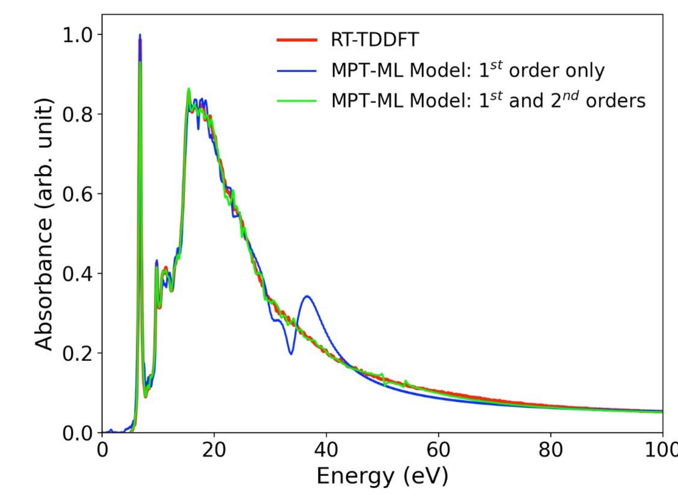
RT-TDDFT simulation is performed using Qball code and collect moments of TD-MLWFs. → Machine learning models are developed for learning the quantum dynamics via MPT. → EOM for the MPT-ML is solved to obtain the optical absorption spectrum from the moments.

Training Set : RT-TDDFT in Wannier gauge for a 200 a.u. simulation with Δt of 0.2 a.u.
Plane-wave basis set with 40 Ryd. Cutoff using Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotential pseudopotentials.

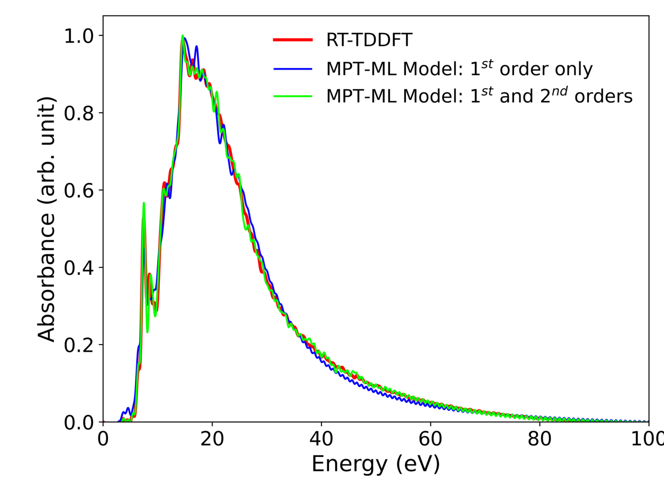
Water Molecule



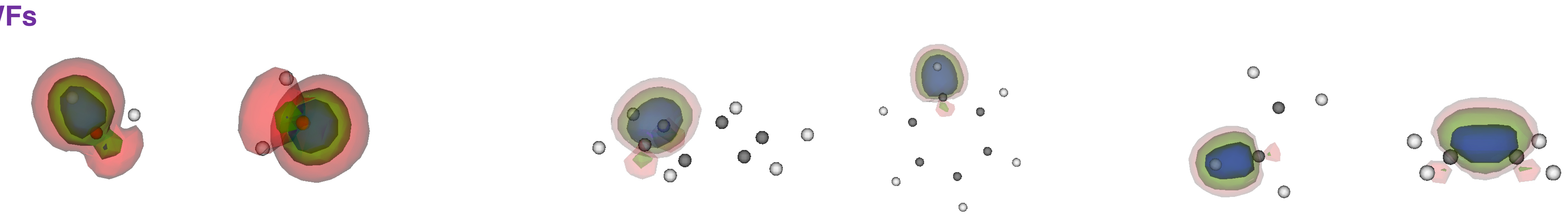
Benzene Molecule



Ethene Molecule

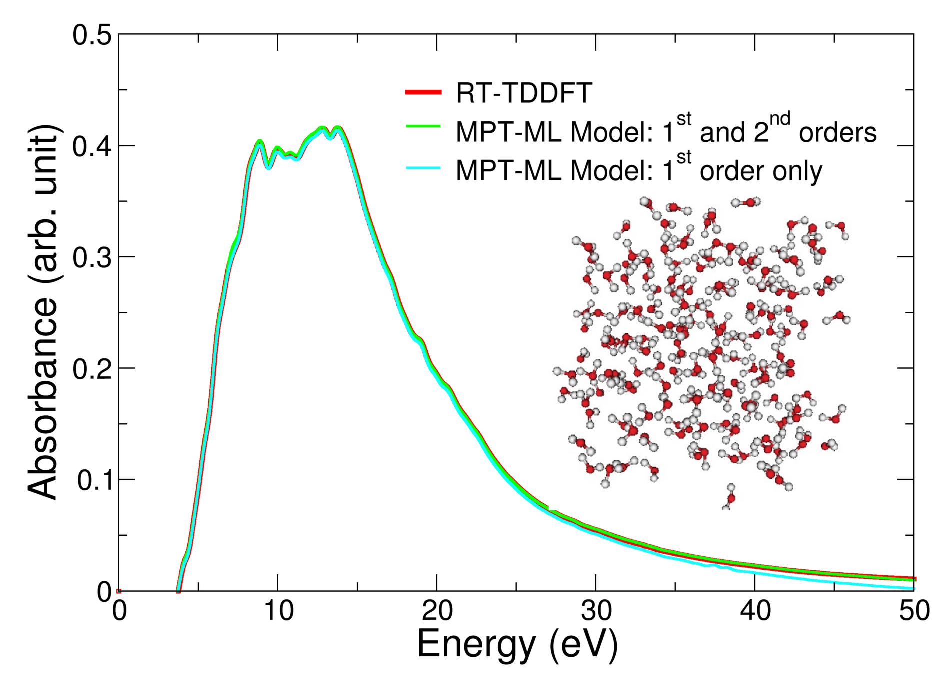


MLWFs



Training Set : RT-TDDFT (PBE) in Wannier gauge : 162 H_2O w/ PBC : 250 a.u. simulation with Δt of 0.1 a.u.
Plane-wave basis set with 50 Ryd. Cutoff using HSCV pseudopotentials.

Liquid Water

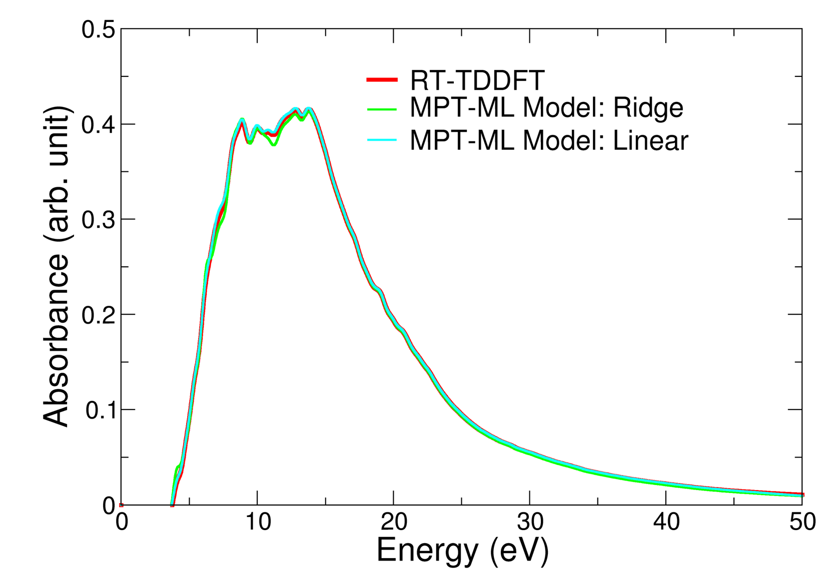


Using the MPT-ML model with up to 2nd order moments, the Ridge regression technique is also employed for preventing the overfitting problem.

The loss function, *L*, is minimized

$$L = \alpha * \sum_i LM_i^2 + \sum_j (y_j - LM(x_j))^2$$

where *LM* is the linear model

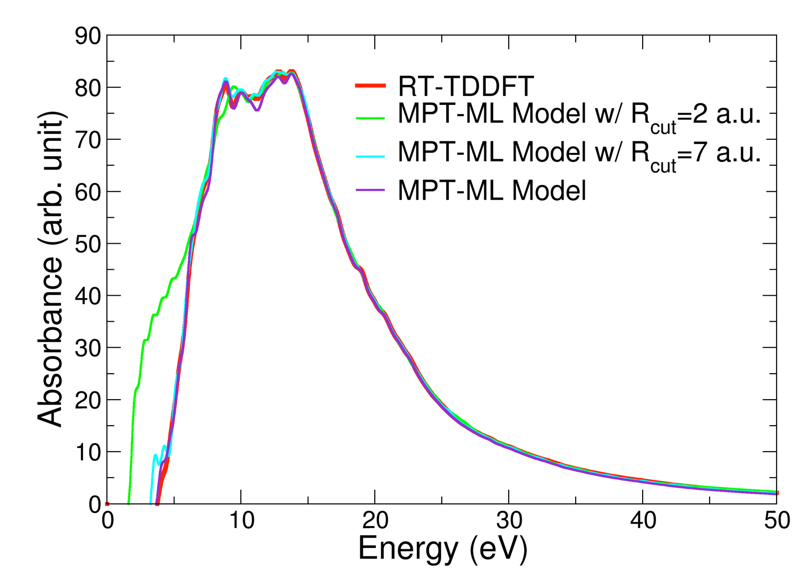


Application of Nearsightedness Principle of Electronic Matter with MPT-ML [3]

"local electronic properties, such as the density n(r), depend significantly on the effective external potential only at nearby points. Changes of that potential, *no matter how large*, beyond a distance R have limited effects on local electronic properties, which rapidly tend to zero as function of R"

3. E. Prodan and W. Kohn, PNAS, 102 , 11635 (2005)

$$\frac{d^2}{dt^2}\langle x^a y^b z^c\rangle_j(t) = \sum_{k\in|\langle r\rangle_j-\langle r\rangle_k|<R_{cut}}\left(B^{j,k}_{a,b,c} + \sum_{d,e,f} C^{j,k}_{a,b,c,d,e,f}\langle x^d y^e z^f\rangle_k(t) + \sum_{d,e,f} D^{j,k}_{a,b,c,d,e,f}\tfrac{d}{dt}\langle x^d y^e z^f\rangle_k(t)\right)$$



Acknowledgment: This work was supported by the SURF and by the National Science Foundation, under No. OAC-2209858 and No. CHE-1954894.