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

Nicholas J. Boyer,[†] Christopher Shepard,[†] Ruiyi Zhou,[†] Jianhang Xu,[†] and

Yosuke Kanai[*,†,‡]

[†]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

[‡]Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

E-mail: ykanai@unc.edu

Taylor Series Expansion

Using the Taylor series expansion directly is another way to propagate the moments. As done in classical MD simulation, the moments at a future time (i.e. $+\Delta t$) can be Taylor-expanded to the 2nd order,

$$\langle \mathbf{r}^i \rangle_j (t + \Delta t) = \langle \mathbf{r}^i \rangle_j (t) + \Delta t \frac{d \langle \mathbf{r}^i \rangle_j (t)}{dt} + \frac{1}{2}\Delta t^2 \frac{d^2 \langle \mathbf{r}^i \rangle_j (t)}{dt^2} + O(\Delta t^3), \qquad (S1)$$

where the time step Δt can be taken arbitrarily small so that $O(\Delta t^3)$ is negligible. This approach was used in our previous work with model Hamiltonians.[1] However, we found that

the direct application of this MD-like approach is highly susceptible to numerical noises from machine-learning first-principles simulation data. In this direct scheme, it is not possible to introduce the necessary correction (as we do to $\mathbf{Q}$ matrix elements) even when unphysical positive real values are observed (see Eq. 20). These positive values if uncorrected slowly cause the simulation to diverge over time as shown in Figure S1.
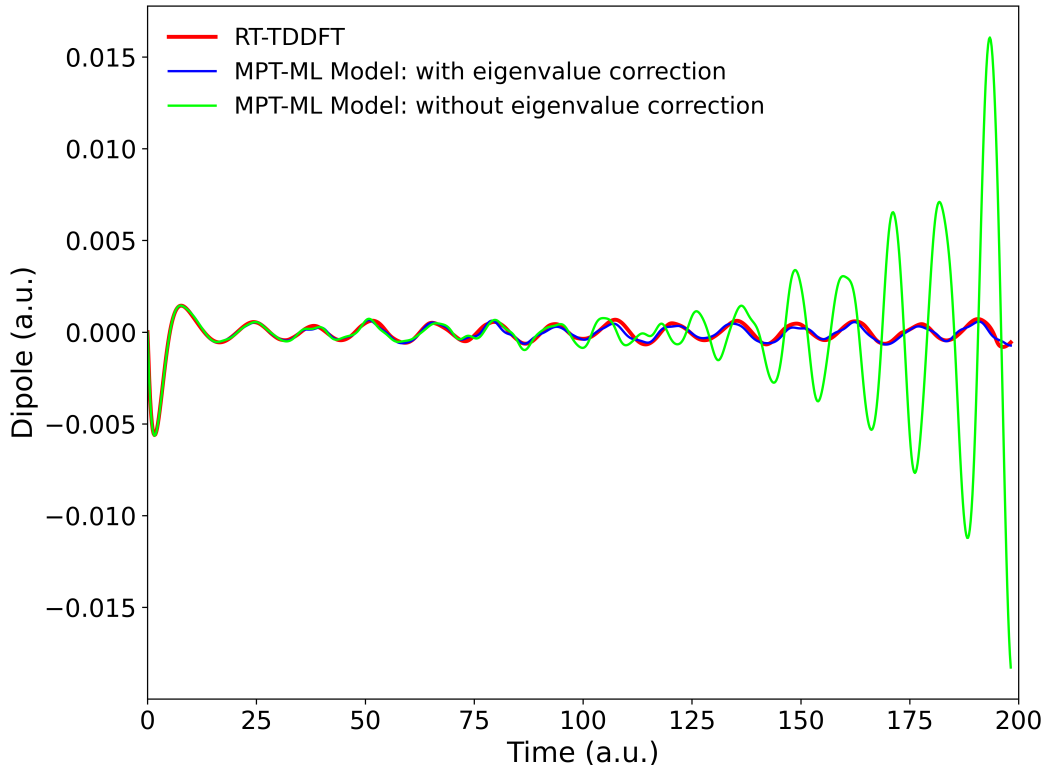

Figure S1: Electronic dipole of a single water molecule upon the "delta-kick" excitation. The electronic dipole diverges in the MPT-ML simulation if the real part of $\mathbf{Q}$ matrix is unphysically positive (i.e. without the egenvalue correction).

Close-up View of Excitation Peaks in Absorbance Spectra

For the optical absorption spectra of single molecules in the main text (Figures 3, 4, and 5), additional figures are include for a close-up view of the lower-energy excitation peaks in the spectra. Figures S2, S3, and S4 show the lower-energy region (25 eV and below) for each case. In particular, these figures further reemphasize the importance of including the second-order moments in the MPL-ML model.
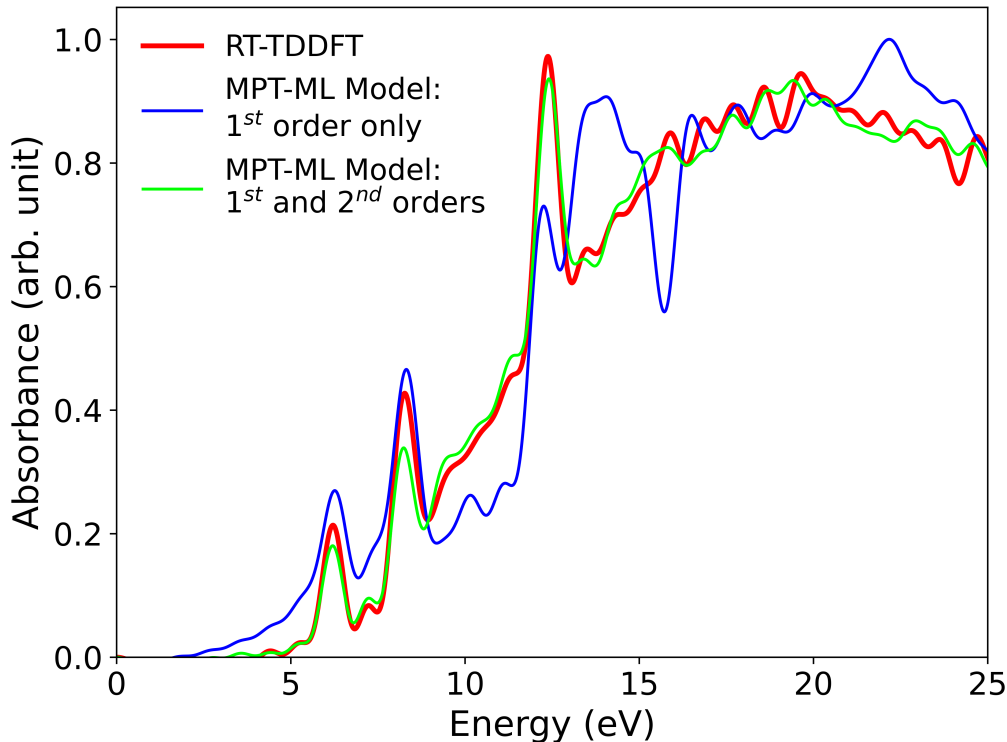

Figure S2: Close-up view of the low-energy region of the optical absorption spectrum (Figure 3 in the main text) for a single water molecule, using both RT-TDDFT and the MPT-ML methods.
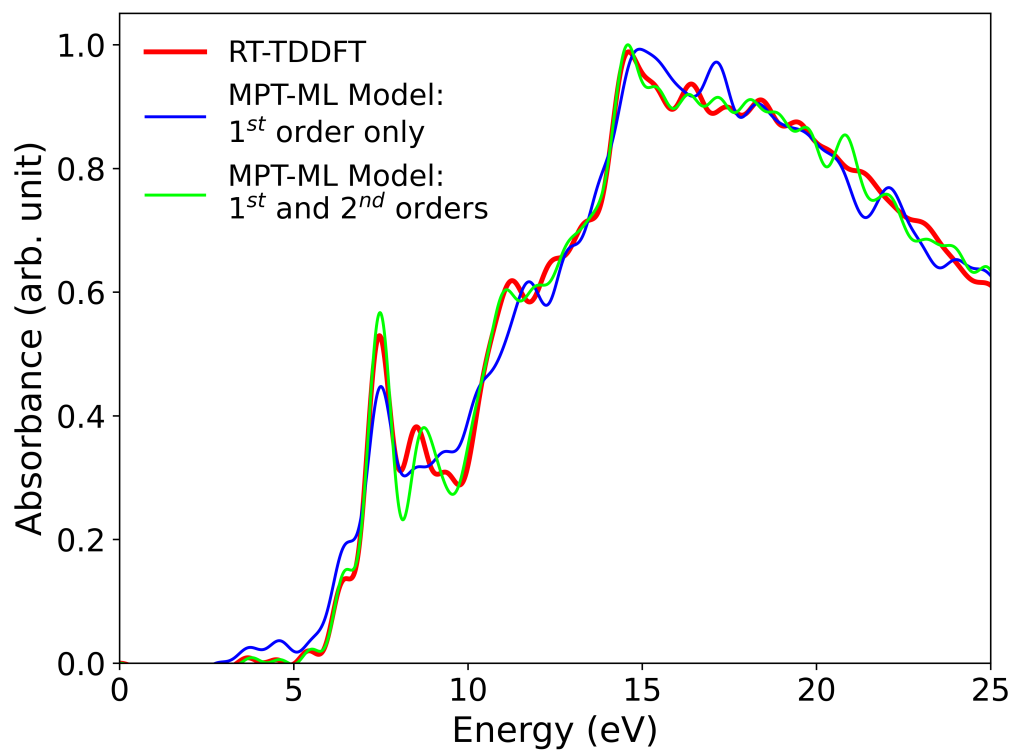
Figure S3: Close-up view of the low-energy region of the optical absorption spectrum (Figure 4 in the main text) for a single ethene molecule, using both RT-TDDFT and the MPT-ML methods.
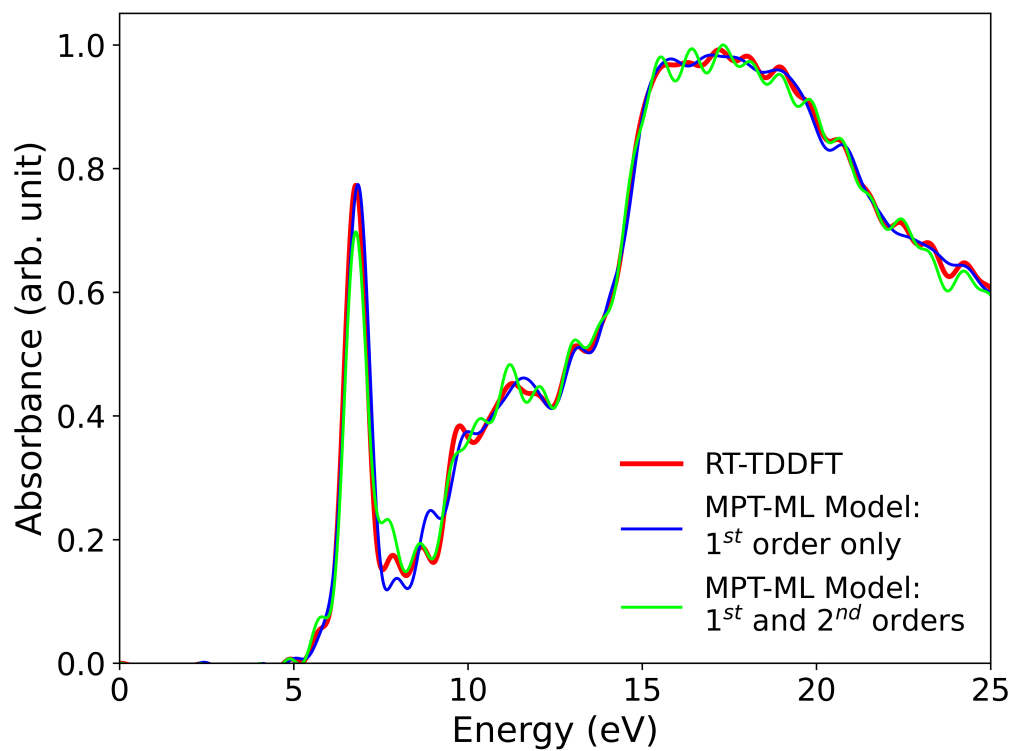
Figure S4: Close-up view of the low-energy region of the optical absorption spectrum (Figure 5 in the main text) for a single benzene molecule, using both RT-TDDFT and the MPT-ML methods.

References

(1) Boyer, N. J.; Shepard, C.; Zhou, R.; Xu, J.; Kanai, Y. Theory of moment propagation for quantum dynamics in single-particle description. *The Journal of Chemical Physics* **2024**, *160*.