

Real-time time-dependent Hartree-Fock and density functional theory approach for optical response within Ehrenfest dynamics

Christine M. Isborn and Xiaosong Li

Department of Chemistry, University of Washington
Seattle, Washington, 98122

With increasing advances in laser pulse technology, there is great interest in understanding molecular phenomena at the femto and attosecond timescale. Accurate simulations of laser driven electron and nuclear dynamics remain a challenge. We have developed an implementation of Ehrenfest molecular dynamics, introduced in Ref [1], that incorporates electronic optical response based on real-time time-dependent Hartree-Fock (TDHF) and density functional theories (TDDFT) within a Gaussian basis framework. Instead of calculating the N -particle eigenstates directly, the response of the molecular system to a time-varying electric field is calculated in real time within a single Slater determinant framework. The exchange-correlation potential is continuously updated with the excited state charge density $\rho(\mathbf{r}, t)$, i.e., $V_{xc}(\mathbf{r}, t) = V_{xc}[\rho(\mathbf{r}, t)]$. In Ref [2] electronic optical response of conjugated molecules was studied with real time TDHF, CIS and CISD methods. We now extend the methodology to real-time TDDFT, including hybrid functionals. We examine the optical polarization that describes the distortion of the charges in response to an applied field, and the corresponding field free orbital occupations. We compare these results to the more expensive CISD and full CI (with minimal basis) dynamics to determine the importance of double excitations. .

- [1] C. M. Isborn and X. Li, *J. Chem. Phys.* **126**, 134307 (2007)
- [2] H. B. Schlegel, S. M. Smith and X. Li, *J. Chem. Phys.* **126**, 244110 (2007)