

Time-dependent density functional theory and non-adiabatic Ehrenfest dynamics with localized basis sets : method and applications

Grigory Kolesov, Oscar Grånäs, Robert Hoyt, Dmitry Vinichenko, Efthimios Kaxiras

School of Engineering and Applied Sciences, Harvard University

Here we present the method of real-time propagation with time-dependent density functional theory (TDDFT) coupled to ionic motion through the mean-field Ehrenfest dynamics approach. The goal of our method is to treat large systems and complex processes, in particular photo-catalytic reactions and electron transfer events on surfaces and thin films. Due to the complexity of these processes, computational simulations are needed to provide insight into the underlying mechanisms and are therefore crucial for the rational design of new materials. Because of short time steps (below 20 *as*) required for electron propagation such simulations are computationally expensive. Our methodology is based on numerical atomic orbital basis sets which results in good computational efficiency. We have also augmented our framework with a number of additional methods and analysis tools such as spherically- averaged and rotationally-invariant DFT+U methods for efficient and accurate treatment of electron correlation in transition metal oxides; a Hirshfeld partitioning scheme for charge tracking and analysis of local dipole contributions and calculation of absorption spectra from real-time TDDFT. We demonstrate an application of our method to photo-catalytic and electron transfer processes on the (110) surface of rutile titanium dioxide. The latter is one of the most thoroughly studied photocatalytic materials with numerous proposed applications, ranging from water photo-oxidation for hydrogen production to cleanup of environmental pollutants and self-cleaning coatings. We apply our method to study methoxy to formaldehyde photo-catalytic conversion on the surface of titania[1] and electron transfer in a model dye-sensitized solar cell consisting of titania and a perylene chromophore. These simulations unveil the mechanism of the photo-catalytic reaction[2] and demonstrate the critical impact that formation of small polarons has in both examples. In both presented simulations polarons act as strong traps that facilitate the methoxy to formaldehyde conversion reaction and impede perylene-to-titania electron transfer while subsequently allowing for higher electron-hole recombination rates.

[1] Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO₂ (110). *Journal of the American Chemical Society* 135, 574-577 (2013).

[2] Kolesov G., Vinichenko D., Tritsarlis G.A., Friend, C. M. & Kaxiras E. Anatomy of the photochemical reaction: excited-state dynamics reveals the C–H acidity mechanism of methoxy photo-oxidation on titania. *Journal of Physical Chemistry Letters*, 6, 1624–1627 (2015).