

Conical Intersections and Double excitations within Time-Dependent Density-Functional Theory

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Time-dependent density-functional theory (TDDFT) is a DFT theory for excited states, which can describe all many-body effects from the knowledge of only the time-dependent electronic density [1]. Though TDDFT is in principle exact, in practice we are obliged to make approximations, which limit its applicability. In this talk, we will focus on the long-standing problem of treating conical intersections and double excitations. These are fundamental for photochemistry simulations, but lacking in approximated TDDFT.

In quantum chemistry, we make extensive use of Casida's formulation of TDDFT [2]. In Casida's approach, all TDDFT approximations are done in the exchange-correlation (xc) kernel, a quantity alike to the xc-functional of DFT, that includes all many-body effects. Most TDDFT calculations apply the adiabatic approximation (AA) to the xc-kernel. The AA is responsible of the missing double excitations and the wrong conical intersections in TDDFT. During the talk, we will discuss why the AA misses these effects and we will present some extensions of TDDFT that can treat them.

First we will show how TDDFT can calculate conical intersections. TDDFT cannot be easily applied near the intersection region, because the Kohn-Sham approach fails (break down of the non-interacting v -representability.) It was proposed to use spin-flip TDDFT to work-around the v -representability problem [3, 4]. The spin-flip method is an extension over conventional TDDFT that couples excitations involving a change in the spin multiplicity. We will show how this property can be used to describe conical intersections for the particular case of oxirane's photochemical dissociation [5].

Second we will describe how to include double excitations in TDDFT. These are not present in any adiabatic xc-kernel. Maitra *et al.* proposed the dressed TDDFT method, a mixed TDDFT and many-body theory calculation that could include some double excitations [6]. Based on a formulation of the exact xc-kernel, we generalized it to any number of doubles [7, 8]. This allowed us to make extensive test of the dressed method, by comparing the quality dressed TDDFT excitation energies with benchmark results for 28 organic chromophores [9]. We will present the results of this test.

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