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Comparative assessment of density functionals for excited-state dipole moments

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Abstract

In this Letter, we report on the performance of density functionals in computing (π, π^*) excited-state dipole moments of several photochromic molecules. The studied set of theoretical approximations encompasses GGA, hybrid and long-range corrected hybrid functionals. The CC2 coupled-cluster model and a large, property-oriented basis set are used to determine the reference values. The preliminary results of calculations of geometric derivatives of dipole moment difference, between the (π, π^*) excited state and the ground state, are also presented.

Key words: excited-state dipole moment, photochromism, density functional theory, CC2 method

1. Introduction

High scaling of conventional *ab initio* electron correlation methods with respect to the number of basis functions prompts to develop computationally more efficient treatments. In particular, much effort has been made during last decade to implement density-fitting approximations to the electron repulsion integrals in popular quantum-chemistry packages [1, 2]. Analytic derivative methods combined with density fitting have made a great impact in computational chemistry, considerably extending the size of chemical systems which can be studied accurately. It is even possible to approach linear scaling by employing local correlation treatments [2]. Despite these advances, one witnesses an unabated interest in the application of Kohn-Sham formulation of density functional theory to virtually all chemistry-related problems at the molecular level [3]. This is certainly rationale behind huge effort in the development of new exchange-correlation functionals and improving the existing ones. Nowadays, GGA successors have a well-established reputation, *inter alia*, in thermochemistry and they are routinely used to determine equilibrium structures of molecules. However, they are known to be less successful in the field of electronic spectroscopy. It is particularly difficult to reliably predict the excitation energies to the charge-transfer and Rydberg states [4].

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