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## Communication: Orbital instabilities and triplet states from time-dependent density functional theory and long-range corrected functionals

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Long-range corrected hybrids represent an increasingly popular class of functionals for density functional theory (DFT) that have proven to be very successful for a wide range of chemical applications. In this Communication, we examine the performance of these functionals for time-dependent (TD)DFT descriptions of triplet excited states. Our results reveal that the triplet energies are particularly sensitive to the range-separation parameter; this sensitivity can be traced back to triplet instabilities in the ground state coming from the large effective amounts of Hartree-Fock exchange included in these functionals. As such, the use of *standard* long-range corrected functionals for the description of triplet states at the TDDFT level is not recommended. © 2011 American Institute of Physics. [doi:10.1063/1.3656734]

### I. INTRODUCTION

Density functional theory (DFT) and its time-dependent extension (time-dependent density functional theory; TDDFT) have become the methods of choice for quantum-mechanical applications in many areas of chemistry. Recently, long-range corrected (LRC) hybrid functionals have generated a significant amount of attention in the literature.<sup>1</sup> Indeed, they have been shown to improve upon the standard hybrid functionals for numerous properties of particular interest; examples include: fundamental gaps and ionization potentials (IPs),<sup>2,3</sup> bond-length alternations in  $\pi$ -conjugated materials,<sup>4</sup> molecular polarizabilities and hyperpolarizabilities,<sup>5</sup> or vibrational frequencies and IR/Raman intensities.<sup>6</sup> Primarily, however, it is the outstanding performance of LRC-hybrids for charge-transfer excitations that makes this new class of functionals particularly interesting for TDDFT applications in organic electronics.<sup>7-9</sup>

The central premise underlying all LRC functionals is a separation of the Coulomb operator into short-range (SR) and long-range (LR) components that can be treated separately. For instance, a semilocal exchange-correlation functional can be used for the SR and Hartree-Fock for LR. The most popular approach to the range separation (and the one employed in this work) is to partition the Coulomb operator via the standard error function:

$$\frac{1}{r} = \frac{\text{erf}(\omega r)}{r} + \frac{\text{erfc}(\omega r)}{r}. \quad (1)$$

The range-separation parameter  $\omega$  determines the separation/partitioning of the SR and LR components. Initial work in this area assumed a single, system-independent range-separation parameter dependent only upon the underlying exchange-correlation functional.<sup>10</sup> However, recent work has

revealed that  $\omega$  should depend primarily on the electronic structure of the system and only to a much lesser extent on the particulars of the semilocal exchange-correlation functional employed.<sup>11</sup> In this work, as has been done previously by others as well,<sup>2</sup> we will use the “IP-tuning” to determine the optimal range-separation parameter. This is done by minimizing the difference between the highest occupied orbital eigenvalue and the computed ionization potential, i.e.,

$$\Delta_{IP}(\omega) = \left| -\varepsilon_{HOMO}^{\omega} - (E_{gs}(\omega, N) - E_{gs}(\omega, N - 1)) \right|. \quad (2)$$

The range-separation parameters determined by minimization of Eq. (2) have been shown to improve the description of properties related to the IP and the fundamental gap for a series of systems.<sup>2,3</sup> The IP-tuning procedure is completely self-consistent and non-empirical as it simply requires that the resultant generalized Kohn-Sham solution obey a property that is identically satisfied for an exact Kohn-Sham (and generalized Kohn-Sham) approach.

While a complete description of the TDDFT machinery has been presented elsewhere,<sup>12-14</sup> it is important to note that linear-response TDDFT comprises a generalization of ground-state DFT whereby the determination of the excitation spectra can be reduced to the solution of an eigenvalue problem. Casida *et al.*<sup>15</sup> have shown that, for the case of a simple two-state model system, the solutions to the TDDFT equations for the singlet ( $S$ ) and triplet ( $T$ ) excitation energies  $v_S$  and  $v_T$  simplify to

$$v_S = \sqrt{\Delta\varepsilon[\Delta\varepsilon + 2(K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow})]}, \quad (3)$$

$$v_T = \sqrt{\Delta\varepsilon[\Delta\varepsilon + 2(K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow})]}. \quad (4)$$

Here,  $\Delta\varepsilon$  denotes the difference in the occupied and virtual orbital energies (this difference is always positive due to the aufbau principle);  $K_{\uparrow,\uparrow}$  and  $K_{\uparrow,\downarrow}$  represent the same-spin and opposite-spin occupied-virtual coupling matrix

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