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Long-range-corrected hybrids using a range-separated Perdew-Burke-Ernzerhof functional and random phase approximation correlation

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We build on methods combining a short-range density functional approximation with a long-range random phase approximation [B. G. Janesko, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **130**, 081105 (2009)] or second-order screened exchange [J. Paier *et al.*, *J. Chem. Phys.* **132**, 094103 (2010)] by replacing the range-separated local density approximation functional with a range-separated generalized gradient approximation functional in the short range. We present benchmark results that show a marked improvement in the thermodynamic tests over the previous local density approximation-based methods while retaining those methods' excellent performance in van der Waals interactions. © 2011 American Institute of Physics. [doi:10.1063/1.3630951]

I. INTRODUCTION

The random phase approximation (RPA) has been employed by many as an effective correlation energy correction to semilocal density functional theory in molecules and solids.¹⁻⁹ In these schemes, typically exact exchange and RPA correlation are evaluated as a one-shot calculation from Hartree-Fock (HF) or Kohn-Sham orbitals. These schemes have the advantages of being fairly accurate for the uniform electron gas in the high-density limit¹⁰ and treating long-range (LR) interactions accurately in molecules and solids,¹¹⁻¹⁴ but encounter difficulties in treating short-range (SR) interactions with reasonably sized basis sets.¹ Since this approach by itself underbinds a variety of systems,^{1,5,6,15-18} various corrections to this basic scheme can be added to ameliorate these issues. Among them are the RPA+ scheme,¹⁹ where short-range correlation from a semilocal functional is added; range-separated RPA,^{6-8,20} whereby the exact exchange and RPA correlation are used only in the long range, with semilocal methods being used in the short range; global hybrid functionals;^{21,22} and the use of hybrid reference states and single excitations.²³ We have favored a range-separated approach combining short-range semilocal density functional theory, long-range exact exchange, and long-range direct RPA (dRPA) correlation evaluated as a one-shot correction with the Kohn-Sham orbitals, where direct RPA refers to the neglect of exchange integrals in the particle-hole ring contractions in the correlation problem. Direct RPA has been used because the direct RPA correlation energy is unambiguously defined²⁴ and because it admits the use of the Cholesky decomposition to solve the equations more efficiently.²⁵ Furthermore, the addition of second-order screened exchange (SOSEX) (Refs. 8, 26, and 27) to direct RPA to fix one-electron self-interaction

error in the direct RPA correlation energy has been pursued because the reduction of this error has been argued to be significant for improving the description of many molecular properties,²⁸ although SOSEX also worsens the description of some static correlation compared to direct RPA.²⁹

In Ref. 6, it was shown that LC- ω LDA+dRPA, a range-separated functional combining local spin density approximation (LSDA) exchange-correlation in the short range with long-range HF exchange and long-range dRPA correlation, excels in a variety of thermochemistry benchmarks and gives an excellent description of a variety of weak interactions.⁶⁻⁸ To remedy the inherent one-electron self-interaction error in dRPA, one can augment dRPA correlation with SOSEX. Benchmarking the augmentation of LC- ω LDA+dRPA with SOSEX, which we call LC- ω LDA+SOSEX, has shown increased accuracy in describing free atoms compared to LC- ω LDA+dRPA but decreased accuracy in describing molecular properties;⁸ on the other hand, the fraction of Hartree-Fock exchange required is decreased.

Despite the success observed with this range-separated method, it is known that the local density approximation, by itself, is a very poor approximation for describing molecules in areas where the density varies rapidly. In addition, it has been observed that, for optimal results, LC- ω LDA+dRPA requires a relatively large range separation parameter ω , which increases basis set dependence and computational time.

Taking into account of these potential disadvantages of LC- ω LDA+dRPA, we have replaced the SR LSDA functional by a short-range Perdew-Burke-Ernzerhof (PBE) functional developed by Goll *et al.*^{30,31} These authors have demonstrated the utility of this functional in describing both noble gas-noble gas and alkali metal-noble gas dimers when combined with coupled cluster with singles, doubles, and perturbative triples in the long range. It has previously been demonstrated that results comparable to coupled cluster calculations can be attained using LC- ω LDA+dRPA for several systems.⁶⁻⁸ It is

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