Acceleration of basis set convergence of ACFDT-RPA and MP2 correlation energies using effective energy techniques

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Evaluation of total energies using correlated methods, such as the adiabatic-connection fluctuation-dissipation theorem method within the random phase approximation (ACDFT-RPA), are receiving more and more interest in the computational materials community. However, the applicability of ACFDT-RPA is to a large extent limited by the cost of evaluating the response function where many unoccupied bands need to be included to obtain sufficiently converged results. This issue is equivalent to the slow convergence encountered in standard quantum chemistry methods, such as coupled cluster or Møller-Plesset perturbation theory (MP). In fact, second order of the ACFDT-RPA expression corresponds to the so-called direct MP2 energy term [1]. A promising way to speed-up the convergence is to use the resolution of identity (ROI) and replace the sum over an infinite number of unoccupied states by an effective correction [2, 3]. However, the available schemes have been formulated only for norm-conserving pseudopotentials and lead to spurious errors when ultrasoft pseudopotentials (US-PPs) or the projector augmented-wave (PAW) method are used. We present and evaluate two modifications that allow to use the ROI correction within US-PPs or the PAW schemes. Furthermore, we show how the convergence of one of the schemes, the so-called effective-energy technique given in Ref. [3], can be further improved. Finally, the efficiency of the methods for ACFDT-RPA calculations and the prospect of using them to speed-up the convergence of other methods, such as MP2, are discussed.

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