MC–srDFT triplet response

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Density functional theory (DFT) is one of the most widely used methods in the field of computational chemistry. However, DFT is only reliable when considering systems that are dominated by a single determinant. Molecules including transition metals are often unsatisfactorily described by single determinant methods, and thus need multi-configurational (MC) methods. Such state-of-the-art MC methods that includes both static and dynamic correlation, e.g. CASPT2 and NEVPT2, are often very computationally expensive.

As a promising alternative the dynamic correlation from DFT is combined with the static correlation from CASSCF in the framework of short-range DFT, giving the name MC–srDFT. In the short-range DFT framework the two electron operator is split into a short-range and a long-range contribution to avoid double counting of the electron interaction, and to make the method fully variational.

$$\frac{1}{r} \rightarrow \frac{f(\mu)}{r} + \frac{1 - f(\mu)}{r} \tag{1}$$

Due to the variational formulation of MC–srDFT, response theory is straightforwardly applicable to the model. Following the singlet response work of Fromager et. al.[1], we have extended MC–srDFT with triplet response from a singlet reference wave function. Due to the way the MC–srDFT model is constructed, the Hessian contribution to the response equation is a sum of the long-range and short-range contributions.

$$\left(\boldsymbol{E}^{[2],\mu} - \omega \boldsymbol{S}^{[2],\mu} \right) \Lambda\left(\omega\right) = i\boldsymbol{V}_x^{[1],\mu}, \qquad \boldsymbol{E}^{[2],\mu} = \boldsymbol{E}^{[2],\mathrm{lr}} + \boldsymbol{E}^{[2],\mathrm{sr}} \tag{2}$$

Furthermore, in an effort to improve the accuracy of the short-range functionals our implementation of the MC–srDFT model has been extended to include meta-GGAs. Meta-GGAs should in principle provide a more accurate short-range description, compared to srGGA and srLDA. This development has been utilizing the srTPPS meta-GGA from Goll et. al.[2]

The new code has been implemented in a development version of DALTON.

References

[1] E. FROMAGER, S. KNECHT, and H. J. A. JENSEN, *The Journal of Chemical Physics* **138**, 084101 (2013).

[2] E. GOLL, M. ERNST, F. MOEGLE-HOFACKER, and H. STOLL, *The Journal of Chemical Physics* **130**, 234112 (2009).