

Implementation of the CCSD(T)-F12 method using hybrid QD/RI approach

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Introduction

Explicitly correlated methods have become very popular recently, since the inclusion of geminal functions can significantly improve the accuracy of standard methods of electronic structure theory without dramatic increase of the computational costs. Recent results obtained with MP2-F12 show high level of accuracy for the correlation energies even for relatively small bases, if the standard approximation (SA) is not used[1]. In the case of CCSD(T)-F12 method use of the SP *Ansatz* allows to shrink computational time and avoid numerical instabilities in the equations for the geminal amplitudes. Some approximate methods were implemented by Alder *et.al*[4] and Tew *et.al*[2]. More recently, we implemented the full CCSD(T)-F12 method using the SP *Ansatz* within the SA[3]. Numerical results for total energies have shown the possibility to predict electronic contributions to reaction enthalpies by the use of quadruple- ζ bases[3]. To achieve the same accuracy with triple- ζ bases it is necessary to go beyond the SA[6, 5]. In this work we implement CCSD(T)-F12 method without SA by the use of numerical quadratures (QD)[6]. The correlation energies and chemical reaction enthalpies will be reported.

Theory

An implementation of the explicitly correlated coupled-cluster singles and doubles with perturbative triples method (CCSD(T)-F12) is performed by the use of the hybrid approach, which utilizes both numerical quadratures and resolution of identity (QD/RI) techniques. The approach is based on so-called SP *Ansatz*, which is based on cusp-conditions for the electronic wave functions at the coalescence point. The corresponding CCSD(T)-F12 energy functional is expressed as:

$$E_{CCSD-F12} = \langle 0 | (1 + \Lambda') e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle \quad (1)$$

where the operator \hat{T} consists of regular \hat{T}_1 and \hat{T}_2 operators and \hat{T}'_2 , which is defined in the following way:

$$\hat{T}'_2 = \frac{1}{2} \sum_{ijkl} t_{kl}^{ij} \left(\sum_{\alpha\beta} \langle \alpha\beta | f_{12} | kl \rangle \hat{E}_{\alpha i} \hat{E}_{\beta j} - \sum_{ab} \langle ab | f_{12} | kl \rangle \hat{E}_{a i} \hat{E}_{b j} \right) \quad (2)$$

The Λ' operator is defined as:

$$\hat{\Lambda}' = \frac{1}{2} \sum_{ijkl} \lambda_{ij}^{kl} \left(\sum_{\alpha\beta} \langle \alpha\beta | f_{12} | kl \rangle \hat{E}_{i\alpha} \hat{E}_{j\beta} - \sum_{ab} \langle ab | f_{12} | kl \rangle \hat{E}_{ia} \hat{E}_{jb} \right) \quad (3)$$

where f_{12} is the Slater-type geminal in our implementation

$$f_{12}(r_{12}) = -\frac{1}{\gamma} e^{-\gamma r_{12}}. \quad (4)$$

The corresponding amplitudes are defined, using the cusp conditions[3]

$$t_{ii}^{ii} = \lambda_{ii}^{ii} = \frac{1}{2}, \quad (5)$$

$$t_{ij}^{ij} = \lambda_{ij}^{ij} = \frac{3}{8}, \quad (6)$$

$$t_{ij}^{ji} = \lambda_{ij}^{ji} = \frac{1}{8}. \quad (7)$$

Table 1: Hartree-Fock and correlation energies from different methods (in a.u.).

| | SCF | MP2 | | CCSD | | CCSD(T) | |
|-------------------------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | IJKL | SP | IJKL | SP | IJKL | SP |
| H ₂ | -1.334629 | -0.034220 | -0.034197 | -0.040813 | -0.040747 | | |
| HF | -100.069492 | -0.385476 | -0.384944 | -0.379659 | -0.379359 | -0.388095 | -0.387794 |
| H ₂ O | -76.066515 | -0.362688 | -0.362215 | -0.360413 | -0.360186 | -0.369914 | -0.369687 |
| NH ₃ | -56.224135 | -0.323233 | -0.322785 | -0.328733 | -0.328517 | -0.337793 | -0.337573 |
| CH ₄ | -40.216468 | -0.274394 | -0.274016 | -0.289418 | -0.289229 | -0.296564 | -0.296371 |
| CO ₂ | -187.723173 | -0.866081 | -0.864473 | no conv | -0.840214 | no conv | -0.872466 |
| CH ₂ | -38.895616 | -0.210067 | -0.209658 | -0.230698 | -0.230495 | -0.236434 | -0.236219 |
| CH ₂ O | -113.921987 | -0.565561 | -0.564648 | no conv | -0.564842 | no conv | -0.583367 |
| F ₂ | -198.770561 | -0.743301 | -0.741891 | -0.732910 | -0.731767 | -0.754919 | -0.753776 |
| N ₂ | -108.991679 | -0.538622 | -0.537430 | -0.526606 | -0.526079 | -0.547480 | -0.546952 |
| CO | -112.789504 | -0.521174 | -0.520141 | no conv | -0.513954 | no conv | -0.533174 |
| HCN | -92.914774 | -0.500708 | -0.499662 | -0.495387 | -0.494906 | -0.515420 | -0.514943 |
| C ₂ H ₂ | -76.854879 | -0.455774 | -0.454785 | -0.459453 | -0.459110 | -0.477774 | -0.477434 |
| HNO | -129.848153 | -0.616594 | -0.615235 | no conv | -0.608992 | no conv | -0.631717 |
| C ₂ H ₄ | -78.069798 | -0.483230 | -0.482387 | -0.498786 | -0.498420 | -0.515629 | -0.515259 |
| H ₂ O ₂ | -150.849224 | -0.693375 | -0.692183 | -0.686448 | -0.685643 | -0.708325 | -0.707521 |

An implementation, based on the SP *Ansatz*, is much cheaper computationally, since the optimization of the geminal amplitudes is not required and many intermediates are fixed outside CC iterations. Also it avoids numerical instabilities of the corresponding IJKL *Ansatz* - based method.

Numerical results

In the present work numerical tests for a set of 16 molecules have been performed and significant improvement is found for the total energies compared to the method with the regular RI. This improvement is caused by the use of numerical quadratures for the evaluation of three- and four - electron integrals, which are necessary for the explicitly - correlated part of CCSD(T)-F12 method. We also perform benchmark calculations on 13 chemical reactions with the cusp-condition QD/RI CCSD(T)-F12 method can reproduce experimental enthalpies within 2 kJ/mol. This accuracy can be achieved with significantly smaller basis sets, than the requirement in the CCSD(T)-F12 method with RI.

References

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