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Communication: Extension of a universal explicit electron correlation correction to general complete active spaces

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We present the extension of a recently proposed universal explicit electron correlation (F12) correction for multi-reference perturbation theories to general complete active spaces and arbitrary choices of complete active space self-consistent field (CASSCF) orbitals. This F12 correction is applied to Mukherjee's multi-reference second-order perturbation theory (Mk-MRPT2). Pilot examples show the expected reduction of the basis sets incompleteness error of about two cardinal numbers.

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Post-Hartree-Fock methods represent the most accurate treatment in quantum chemistry. Albeit their effectiveness in the treatments of electron correlation, they provide a poor description of the electron-electron cusp when using a conventional expansion in terms of excited determinants.¹⁻³ This problem manifests itself in a very slow convergence with respect to one-electron basis set. One very effective way to accelerate this convergence is offered by explicitly correlated (F12) methods which are well tested and developed for single-reference systems.⁴⁻⁹ Some multi-reference analogues of the successful single-reference F12 corrections have been proposed and tested (MRMP2-F12,¹⁰ MR BW-CCSD-R12 and MR BW-CCSD-F12,¹¹ CASPT2-F12,¹² MRCISD-F12,¹³ MkCCSD-F12,¹⁴ Mk-MRPT2+F12, and Mk-MRPT2-F12¹⁵). Recently, Valeev and co-workers extended a F12 correction for arbitrary electronic states.^{16,17} Very recently, Booth *et al.* combined FCIQMC with F12 theory,¹⁸ and the internally contracted MRCCSD(F12*) has been presented.¹⁹ Most of the current explicitly correlated multi-reference approaches have been reviewed in Ref. 20.

Here, we report the extension of the universally applicable F12 correction “+F12” to general complete active spaces (CAS). This F12 correction is size-consistent and orbital-invariant; it is additive and compatible with any second-order multi-reference perturbation theory. We use this F12 correction in conjunction with a perturbative approximation to Mukherjee's state-specific multi-reference coupled cluster method (Mk-MRPT2).^{21,22} This combination is referred to as Mk-MRPT2+F12.¹⁵ We show application of Mk-MRPT2+F12 calculations to the dissociation curves of HF with CAS(2,2), H₂C=CH₂ with CAS(4,4), and H₆ arranged in a hexagon with CAS(6,6).

Since the employed methods have been described in detail elsewhere,^{15,21,22} we present only the changes we made to the previous F12 correction which was restricted to CAS(2,2) calculations using natural complete active space self-consistent field (CASSCF) orbitals. The general CAS version of the universal F12 correction using a spin-free formulation is given by

$$E_{\text{F12}} = \sum_{\mu, \nu} D_{\mu\nu} c_{\mu}^{(0)} c_{\nu}^{(0)}, \text{ where} \quad (1)$$

$$D_{\mu\nu} = \sum_{u, v, w, x} \frac{1}{2} \eta_{wx}^{\mu\nu} \Gamma_{wx, uv}^{\mu\nu} + \sum_i \sum_{v, x} (2\eta_{ix}^{iv} - \eta_{ix}^{vi}) \gamma_{vx}^{\mu\nu} + \sum_{i, j} \delta_{\mu\nu} (2\eta_{ij}^{ij} - \eta_{ji}^{ij}). \quad (2)$$

Here, the orbitals i and j (hereafter also referred as “core orbitals”) span the space of the orbitals doubly occupied in all model functions, excluding the frozen ones. Orbitals u, v, w , and x comprise the active space. In Eq. (1), $c_{\mu}^{(0)}$ and $c_{\nu}^{(0)}$ are the CASSCF CI coefficients, and $\gamma_{vx}^{\mu\nu}$ and $\Gamma_{wx, uv}^{\mu\nu}$ are one- and two-particle transition density matrices,

$$\gamma_{vx}^{\mu\nu} = \langle \phi_{\mu} | E_v^x | \phi_{\nu} \rangle, \quad (3)$$

$$\Gamma_{wx, uv}^{\mu\nu} = \langle \phi_{\mu} | E_{wu}^{xv} | \phi_{\nu} \rangle, \quad (4)$$

where ϕ_{μ} and ϕ_{ν} are model functions and E_v^x and E_{wu}^{xv} are spin-free one- and two-particle excitation operators. The matrix η is calculated from matrices \mathbf{B} and \mathbf{V} :⁵

$$\eta_{pq}^{rs} = V_{pq}^{rs} + \frac{1}{4} B_{pq}^{rs}, \quad (5)$$

$$V_{pq}^{rs} = \langle pq | f_{12} \hat{Q}_{12} r_{12}^{-1} | rs \rangle, \quad (6)$$

$$B_{pq}^{rs} = \langle pq | f_{12} \hat{Q}_{12} (\hat{F}_1 + \hat{F}_2) \hat{Q}_{12} f_{12} | rs \rangle, \quad (7)$$

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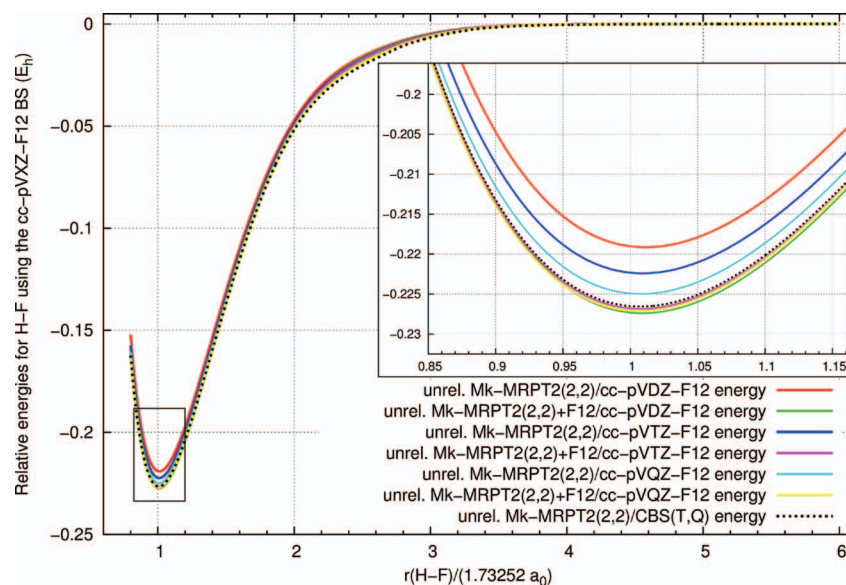


FIG. 1. Mk-MRPT2(2,2)/cc-pVXZ-F12 and Mk-MRPT2(2,2)+F12/cc-pVXZ-F12, $X = D, T,$ and Q , curves in hartree for the HF dissociation.

where $p, q, r,$ and s form the union of core and active space. In contrast to our earlier universal F12 correction,¹⁵ we use Ansatz 2 with the following strong orthogonality projector:

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \quad (8)$$

$$\hat{O}_\xi = \sum_p |\phi_p(\xi)\rangle \langle \phi_p(\xi)|, \quad (9)$$

$$\hat{V}_\xi = \sum_a |\phi_a(\xi)\rangle \langle \phi_a(\xi)|$$

with the union of core and active orbitals ϕ_p and virtual orbitals ϕ_a . This means that our universal F12 correction does not correspond in the dissociation limit to a standard ROHF-MP2-F12 calculation because we project out more orbitals in the multi-reference F12 treatment. The full active space is projected out which is, to some extent, part of the virtual space in a single-reference calculation. Thus, our universal F12 correction single-reference limit corresponds to a MP2-F12 calculation with Ansatz 2* A where the occupied and active orbitals (from the CASSCF) are used in \hat{O}_ξ while the external virtual orbitals are used for \hat{V}_ξ . Ten-no¹⁰ and Kong and Valeev¹⁷ proposed multi-reference F12 corrections very similar to ours. Except for technical details concerning integral evaluation, this universal F12 correction presented here is identical to the one by Ten-no.¹⁰ Both differ slightly from the version by Kong and Valeev¹⁷ because the latter includes the coupling between conventional and F12 contributions.

CASSCF calculations were performed using GAMESS-US²³ and Dalton 2011.²⁴ The conventional Mk-MRPT2 correction to the CASSCF energy was calculated using the SSMRPT2 program developed by Mao *et al.*²⁵ The F12 calculations were performed using a locally modified version of the RICC2 module of TURBOMOLE.²⁶ The cc-pVXZ-F12 series of basis sets, $X = D, T,$ ²⁷ with corresponding CBS²⁸ and RI basis sets were employed in this study.^{29,30} The geminal exponents $0.9 a_0^{-1}, 1.0 a_0^{-1},$ and $1.1 a_0^{-1}$ were used for

double-, triple-, and quadruple- ζ basis sets.²⁷ The $1s$ electrons of elements of the first octal row were kept frozen; all other electrons were correlated. All energies are relative to the corresponding fragment limits in hartree. The interatomic distances are provided as multiples of the equilibrium distance in the case of HF and $H_2C=CH_2$ ($r_e(\text{HF}) = 1.73252 a_0$ and $r_e(H_2C=CH_2) = 2.517 a_0$ were used).³¹ Unless stated otherwise, pseudo-canonical orbitals were used.

As a first example, we present the dissociation curve of HF using a CAS(2,2) reference in Figure 1. As we do not include a CABS-singles-like multi-reference correction,³² the complete basis set limit (CBS) estimate of the total energy is the sum of the CASSCF energy in the quadruple- ζ basis set and the CBS estimate of the correlation energy, $E^{\text{corr.}}(\text{CBS})$ from the two point extrapolation:³³

$$E^{\text{corr.}}(X) = E^{\text{corr.}}(\text{CBS}) + CX^{-3}, \quad (10)$$

fitting $E^{\text{corr.}}(\text{CBS})$ and C to energies $E^{\text{corr.}}(X)$ using cc-pVXZ-F12 with $X = (T = 3), (Q = 4)$. Equilibrium distances decrease when the basis set is enlarged. The conventional calculations show the usual slow convergence with basis set size in contrast to the F12-corrected curves. The F12-corrected double- and quadruple- ζ basis set curves are slightly below the CBS limit curve in the minimum region, while the F12-corrected triple- ζ basis set curve is indistinguishable from the CBS limit curve. A plot of the individual F12 contributions for HF dissociation is provided in Figure 2. Between three times of the equilibrium distance and the dissociation limit, the relative F12 corrections are negligible. At shorter distances, they are important in order to obtain a result within chemical accuracy even when the cc-pVQZ-F12 basis set is used.

The ethylene dissociation in Figure 3 is used as a second example. Here, we are breaking a double bond which requires a CAS(4,4) to obtain a qualitatively correct description of the dissociation curve. During the ethylene dissociation, we keep

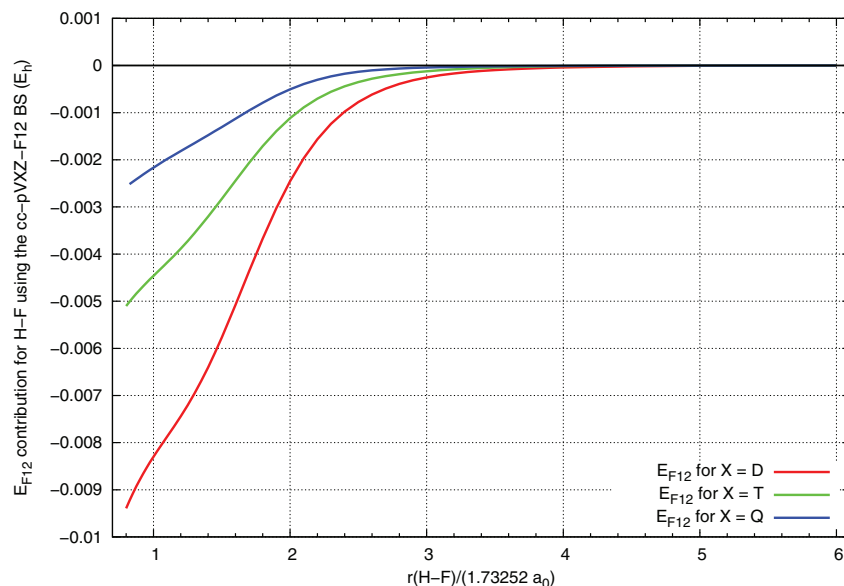


FIG. 2. E_{F12} correction curves using the cc-pVXZ-F12 basis set series, $X = D, T,$ and $Q,$ in hartree for the HF dissociation.

the C–H bond lengths fixed at $2.0417 a_0$ and the H–C–C bond angles at 121.35° . The F12-corrected triple- ζ basis set curve is slightly below the CBS limit curve in the minimum region, while the F12-corrected double- ζ and quadruple- ζ basis set curves are very close to the CBS limit curve.

As a final example, we present the dissociation of six hydrogen atoms arranged as a hexagon in Figure 4. All H–H distances are symmetrically increased starting from $1.2 a_0$ until $7.5 a_0$. An active space of six electrons in six orbitals is necessary to obtain a qualitatively correct reference function. All F12-corrected curves are very close together, slightly below the CBS limit curve.

The “+F12” correction presented here can also be combined with other multi-reference second-order perturbation methods. We decided to assess the F12 correction with Mk-MRPT2 because of its rigorous size extensivity that leads to

size consistency when the pseudo-canonical orbitals used in the calculations are localized to the fragments in the dissociation limit. The size-inconsistency error for HF and H_6 calculated at very large separations is essentially negligible, being close to the numerical accuracy due to convergence criteria of the CASSCF calculation. In the case of C_2H_4 , the pseudo-canonical orbitals in the dissociation limit are not uniquely determined as there can be arbitrary rotations within orbitals that are doubly degenerate due to the identity of the two fragments. While the size-inconsistency error obtained using explicitly fragment-localized pseudo-canonical orbitals is below the numerical accuracy, we should note that the Mk-MRPT2 energy is very sensitive to the orbital rotation: the energies between $2.5 r_e$ and $6 r_e$ plotted in the dissociation curve in Fig. 3, which were calculated without explicitly localizing the orbitals, are above the fragment limit by up to about $3.4 mE_h$.

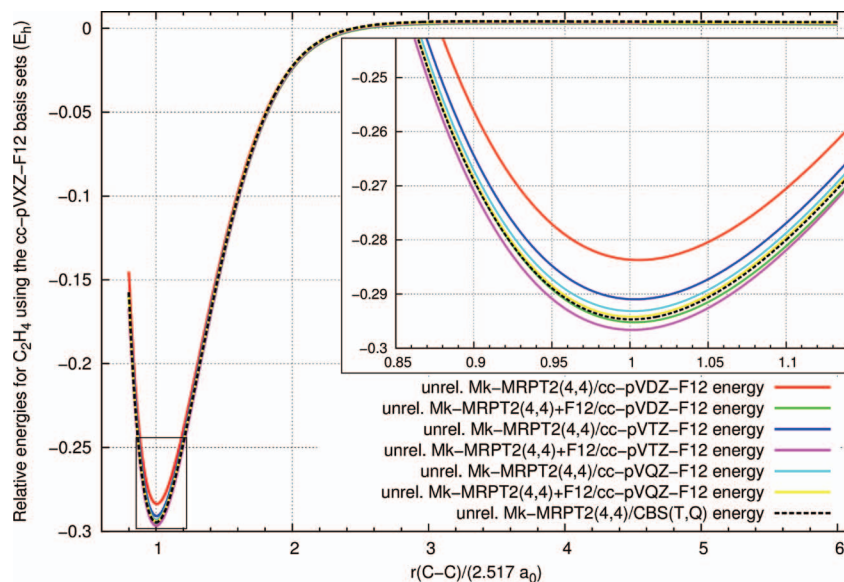


FIG. 3. Mk-MRPT2(4,4)/cc-pVXZ-F12 and Mk-MRPT2(4,4)+F12/cc-pVXZ-F12, $X = D, T,$ and $Q,$ curves in hartree for the $H_2C=CH_2$ dissociation.

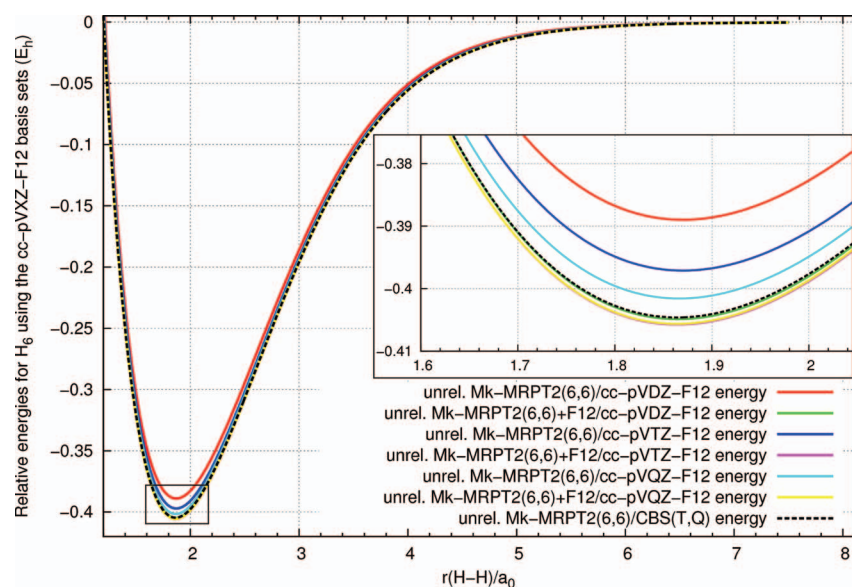


FIG. 4. Mk-MRPT2(6,6)/cc-pVXZ-F12 and Mk-MRPT2(6,6)+F12/cc-pVXZ-F12, $X = D, T,$ and $Q,$ curves in hartree for the dissociation of a H_6 hexagon.

This sensitivity of Mk-MRPT2 energies to the choice of orbitals warrants further research.

In summary, we have extended the universal F12 correction to multi-reference second-order perturbation methods to general complete active spaces and arbitrary orbital choices. The new version of the universal F12 correction has been applied to the dissociation curves of HF, $H_2C=CH_2$ and a H_6 hexagon. About two cardinal numbers are gained by the F12 correction, as known from single-reference F12 calculations. The examples shown here focus on the universal correction. Without further changes it is possible to introduce some coupling between F12 and conventional contributions by using $D_{\mu\nu}$ of Eq. (2) as described in Ref. 15 to obtain the “-F12” version. No significant change in performance should be expected from the “-F12” version for the examples shown here. We see an advantage of the uncoupled version as this provides a basis set correction independent of the employed MR-PT2 flavor.

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