Universal perturbative explicitly correlated basis set incompleteness correction

Martin Torheyden, and Edward F. Valeev

Citation: The Journal of Chemical Physics **131**, 171103 (2009); doi: 10.1063/1.3254836
View online: http://dx.doi.org/10.1063/1.3254836
View Table of Contents: http://aip.scitation.org/toc/jcp/131/17
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **131**, 171103 (2009)

Universal perturbative explicitly correlated basis set incompleteness correction

Martin Torheyden and Edward F. Valeev[a)]
Department of Chemistry, 107 Davidson Hall, Virginia Tech, Blacksburg, Virginia 24061, USA

(Received 31 August 2009; accepted 7 October 2009; published online 4 November 2009)

Basis set incompleteness error for an arbitrary approximate electronic wave function is robustly reduced using a second-order perturbative correction into a basis of explicitly correlated, internally contracted geminal functions. The Hylleraas functional for the second-order energy correction is evaluated algebraically involving at most a four-electron reduced density matrix and four-electron integrals. By using the *R12 technology* in combination with *screening approximations* such a correction only requires a two-electron reduced density matrix and two-electron integrals. Preliminary investigations of potential energy surfaces of hydrogen fluoride and nitrogen molecules at the multireference configuration interaction singles and doubles indicate that with the perturbative correction only an aug-cc-pVDZ basis is necessary to compute correlation energies of an aug-cc-pVQZ quality, or better. The proposed correction, dubbed $[2]_{\rm R12}$, can in principle be combined with any single reference and multireference method in use today. © *2009 American Institute of Physics*. [doi:10.1063/1.3254836]

The large, slowly converging basis set error of the electron correlation energy severely limits the relevance of many-body electronic structure methods to the majority of practicing chemists. The R12 (or F12) methods[1] overcome this slow convergence by modeling the two-particle correlation directly in terms of the interelectronic coordinates while avoiding nine-dimensional and higher-dimensional integrals. The "modern" R12 technology recently has been incorporated in an efficient manner into the standard coupled-cluster (CC) hierarchy,[2–5] with several production programs featuring CC-R12 methods. Only a triple-zeta quality basis is needed with R12 methods to match the precision of the standard quintuple-zeta energy.

To study systems with near degeneracies (most electronically excited states, ground states at stretched geometries, low-spin systems), true multireference methods are also desired. Gdanitz has developed the R12 versions of the multireference configuration interaction (MRCI) and averaged coupled-pair functional methods using the old R12 technology applicable to small systems.[6] Ten-no[7] has recently proposed the R12 extension of the MR-MP2 method that uses internal contraction and thus can be applied to larger systems.

Here we present an initial report on an internally contracted formulation of a perturbative R12 correction that can in principle be applied to *any electronic state for which the reduced density matrices are available*, e.g., general multideterminantal wave function. Our approach reduces to the R12 correction of the MP2-R12 method when a Hartree–Fock wave function is used as a reference. We demonstrate that the method robustly decreases the basis set error of the potential energy surfaces in prototypical bond-breaking scenarios.

We start with a general multiconfiguration reference wave function $|0\rangle$ expressed in a n-electron space obtained as a tensor product of a finite set of orbitals $\{p\}$. [Symbols κ, λ, and ζ represent functions from the formal complete basis set (CBS). Symbol α' denotes functions from CBS which are not part of the orbital basis set (OBS). All other symbols represent functions from OBS.] To correct for the two-electron basis set incompleteness we expand the first-order wave function in terms of strongly orthogonal geminal replacements

$$\psi^{(1)} = \tfrac{1}{4} t^{rs}_{pq} |\tilde{\Gamma}^{pq}_{rs}\rangle, \tag{1}$$

$$|\tilde{\Gamma}^{rs}_{pq}\rangle = \tfrac{1}{2} \hat{\mathcal{S}} \bar{R}^{rs}_{\kappa\lambda} \tilde{a}^{\kappa\lambda}_{pq} |0\rangle, \tag{2}$$

$$\hat{\mathcal{S}} = 1 - \sum_{t,\alpha'} |\Sigma^{\alpha'}_t\rangle\langle\Sigma^{\alpha'}_t|, \quad \text{where } |\Sigma^{\alpha'}_t\rangle = \tilde{a}^{\alpha'}_t |0\rangle. \tag{3}$$

Operators $\tilde{a}$ are the elementary normal-ordered operators in the Mukherjee–Kutzelnigg (MK) sense[8,9] (the covariant tensor notation is thoroughly explained elsewhere[10]). Although the use of MK operators is not essential, it conveniently ensures that the geminal functions are orthogonal to the reference. The role of projector $\hat{\mathcal{S}}$ is to ensure the strong-orthogonality condition

$$\langle \tilde{\Gamma}^{rs}_{pq} | a^{\lambda}_{\kappa} | 0 \rangle = 0, \quad \forall\, \kappa, \lambda \tag{4}$$

so that $|\tilde{\Gamma}^{rs}_{pq}\rangle$ describe purely two-electron effects. Neither the geminal functions nor the single replacements $|\Sigma^{\alpha'}_t\rangle$ are mutually orthonormal, hence the inverse metric is implicit in Eq. (3).

Matrix elements $\bar{R}^{rs}_{\kappa\lambda}$ are the antisymmetrized matrix elements of the correlation function $f(r_{12})$,

---

[a)] Electronic mail: evaleev@vt.edu.

$$R^{rs}_{\kappa\lambda} = \langle \kappa\lambda | \hat{Q}_{12} f(r_{12}) | rs \rangle, \tag{5}$$

with an optional projector $\hat{Q}_{12}$ invoked to simplify the formalism ($r^{rs}_{\kappa\lambda}$ will denote matrix elements without $\hat{Q}_{12}$). Setting $Q_{12}=1$ leads to very complicated equations that involve up to five-electron reduced density matrices (5-RDM) and will not be explored here. Projector

$$Q_{12} = (1-\hat{P}_1)(1-\hat{P}_2), \quad \text{where } \hat{P} = \sum_p |p\rangle\langle p|, \tag{6}$$

produces the simplest matrix elements of the Hamiltonian (only 3-RDM appear) and automatically ensures the strong orthogonality. For single-determinant references this choice leads to the expressions of MP2-R12 with projector **1**,[11] which is known to produce a relatively modest reduction in the basis set error. Our initial tests confirmed its poor performance and thus we used a less restrictive projector

$$Q_{12} = 1 - \hat{P}_1 \hat{P}_2, \tag{7}$$

which, for a single-determinant reference, leads to the R12 correction of MP2-R12 with modified projector **2**.[12]

A Rayleigh–Schrödinger perturbation expansion was then straightforwardly derived with Löwdin partitioning.[13] We selected a block-diagonal zeroth-order Hamiltonian, with its geminal block defined as $E^{(0)}+\hat{F}_N$, where $E^{(0)}$ is the reference energy and $\hat{F}_N = f^{\lambda}_{\kappa}\tilde{a}^{\kappa}_{\lambda}$, $f^{\lambda}_{\kappa} = h^{\lambda}_{\kappa} + \bar{g}^{\lambda q}_{\kappa p}\gamma^{p}_{q}$ is the normal-ordered Fock operator. The second-order energy is evaluated as a Hylleraas functional

$$H^{(2)} = \tfrac{1}{2}\langle 0 | \hat{H}_N | \tilde{\Gamma}^{rs}_{pq}\rangle t^{pq}_{rs} + \tfrac{1}{16} t^{vw}_{tu} \langle \tilde{\Gamma}^{vw}_{tu} | \hat{F}_N | \tilde{\Gamma}^{rs}_{pq}\rangle t^{pq}_{rs}. \tag{8}$$

The matrix elements, evaluated using the extended Wick's theorem,[9] involve up to 4-RDM and are relatively complicated. Therefore we made two additional approximations. (1) We neglected all terms that involve three-electron and four-electron cumulants[14] of the reduced density matrices, as well as terms quadratic in two-electron cumulants (similar approximations have appeared elsewhere[15]). (2) In the spirit of screening approximations[2] we omitted all diagrams in which two $\bar{r}$ matrix elements or a $\bar{r}$ and a Coulomb ($\bar{g}$) matrix elements are connected via a two-electron cumulant. We thus arrived at the final expressions

$$H^{(2)} = \tfrac{1}{2} V^{rs}_{pq} t^{pq}_{rs} + \tfrac{1}{16} t^{vw}_{tu} (B^{rs}_{vw}\gamma^{tu}_{pq} - X^{rs}_{vw}\phi^{tu}_{pq}) t^{pq}_{rs}, \tag{9}$$

with "R12" intermediates

$$V^{rs}_{pq} = \tfrac{1}{2}\Big(\tfrac{1}{2}\bar{g}^{\kappa\lambda}_{p_2p_3}\bar{r}^{rs}_{\kappa\lambda} - \bar{g}^{q_3\alpha'}_{p_2p_3}\gamma^{q_2}_{q_3}\bar{r}^{rs}_{q_2\alpha'} - \tfrac{1}{2}\bar{g}^{q_2q_3}_{p_2p_3}\bar{r}^{rs}_{q_2q_3}\Big)\gamma^{p_2p_3}_{pq}, \tag{10}$$

$$\begin{aligned} B^{rs}_{vw} = {} & -\bar{r}^{q_3p_3}_{vw} f^{q_2}_{q_3} \bar{r}^{rs}_{q_2p_3} - \bar{r}^{\alpha' p_3}_{vw} f^{q_2}_{\alpha'} \bar{r}^{rs}_{q_2p_3} - \bar{r}^{q_3p_3}_{vw} f^{\alpha'}_{q_3} \bar{r}^{rs}_{\alpha' p_3} \\ & + \bar{r}^{p_3\alpha'}_{vw} \gamma^{q_3}_{p_3} f^{q_2}_{q_3} \gamma^{p_2}_{q_2} \bar{r}^{rs}_{p_2\alpha'} - \bar{r}^{p_3\alpha'_3}_{vw} \gamma^{p_2}_{p_3} f^{\alpha'_2}_{\alpha'_3} \bar{r}^{rs}_{p_2\alpha'_2} \\ & - \bar{r}^{\kappa\alpha'}_{vw} f^{q_2}_{\kappa} \gamma^{p_2}_{q_2} \bar{r}^{rs}_{p_2\alpha'} - \bar{r}^{p_3\alpha'}_{vw} \gamma^{q_3}_{p_3} f^{\kappa}_{q_3} \bar{r}^{rs}_{\kappa\alpha'} + \bar{r}^{\xi\lambda}_{vw} f^{\kappa}_{\xi} \bar{r}^{rs}_{\kappa\lambda}, \end{aligned} \tag{11}$$

$$X^{rs}_{vw} = \tfrac{1}{2}\bar{r}^{\kappa\lambda}_{vw}\bar{r}^{rs}_{\kappa\lambda} - \bar{r}^{p_3\alpha'}_{vw}\gamma^{p_2}_{p_3}\bar{r}^{rs}_{p_2\alpha'} - \tfrac{1}{2}\bar{r}^{p_2p_3}_{vw}\bar{r}^{rs}_{p_2p_3}, \tag{12}$$

$$\begin{aligned} \phi^{tu}_{pq} = {} & P(pq)P(tu)\Big(\gamma^{t}_{p}\gamma^{q_3}_{q} f^{q_2}_{q_3}\gamma^{u}_{q_2} + \tfrac{1}{2}\gamma^{u}_{q_2} f^{q_2}_{q_3}\lambda^{tq_3}_{pq} \\ & + \tfrac{1}{2}\gamma^{q_3}_{p} f^{q_2}_{q_3}\lambda^{tu}_{q_2q} - \gamma^{t}_{p} f^{q_2}_{q_3}\lambda^{q_3u}_{q_2q}\Big), \end{aligned} \tag{13}$$

where $P(pq)$ is a permutation operator, acting on a given function as $P(pq)f(p,q)=f(p,q)-f(q,p)$. Instead of minimizing the Hylleraas functional we fixed the geminal amplitudes so that first-order cusp conditions are satisfied.[16] This approximation performs well for single-reference R12 methods[17] *and*, furthermore, has potential to alleviate the impact of other approximations, such as the neglect of higher rank cumulants, which can affect amplitude optimization by changing the spectrum of the zeroth-order Hamiltonian. Henceforth we will denote the explicitly correlated energy correction specified by Eqs. (9)–(13) with $[2]_{R12}$.

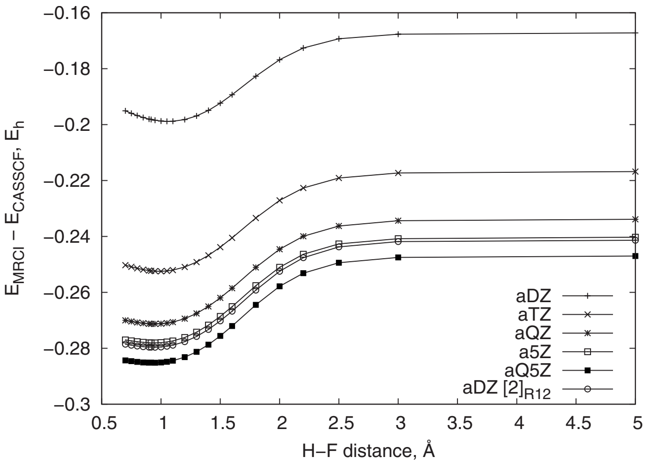

FIG. 1. MRCI correlation energy for the hydrogen fluoride molecule computed with the conventional and $[2]_{R12}$ approaches.

Intermediates V, B, and X were evaluated using the standard R12 technology[18,19] with an exponential correlation factor[20] (exponent $\gamma=1.5a_0^{-1}$) fit to six Gaussian geminals. The uncontracted cc-pV6Z basis set[21] supported the complementary auxiliary basis set (CABS) and the aug-cc-pVXZ basis sets,[22] abbreviated as aXZ, were used for orbital expansion. The two-point X^{-3} extrapolation[23] was used to estimate the CBS limit for correlation energies, denoted as aXYZ when obtained from aXZ and aYZ basis sets. The uncontracted MRCI singles and doubles wave function based on valence complete active space self-consistent field (CASSCF) were used. Core orbitals were frozen in MRCI. All R12 calculations utilized MPQC program,[24] with CI wave functions computed with PSI suite.[25]

To test our approach we investigated the ground-state potential energy surfaces of HF and N_2 molecules. These ground-state bond-breaking prototypes exhibit transitions between weak correlation and strong-correlation regimes which cannot be described by standard single-reference methods. The MRCI correlation energies, defined as $E_{MRCI}-E_{CASSCF}$, are plotted in Fig. 1 for hydrogen fluoride (HF) and Fig. 2 for N_2. The aDZ MRCI$[2]_{R12}$ correlation energy is comparable in quality with the conventional a5Z MRCI result for HF. In the more difficult case of N_2, the aDZ MRCI$[2]_{R12}$ is comparable to the conventional aQZ MRCI. Note that in N_2 the drastic underestimation of the correlation energy by the aDZ

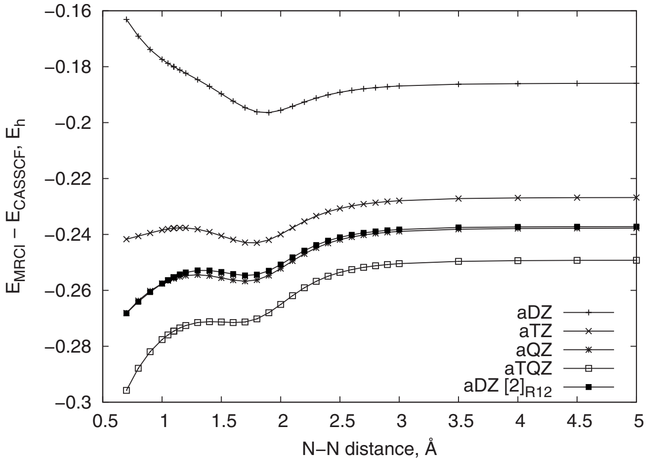

FIG. 2. MRCI correlation energy for the nitrogen molecule computed with the conventional and $[2]_{R12}$ approaches.

MRCI at the equilibrium and shorter distances is nicely corrected by the R12 correction.

To gauge the performance of the R12 correction for relative energies, we computed the electronic 0 K bond dissociation energies for the two molecules (see Table I). Although the basis set error of the correlation energy is the dominant source of error in small-basis conventional MRCI, the one-electron basis set error (i.e., the basis set error of CASSCF) dominates the MRCI$[2]_{R12}$ energies even when the smallest aDZ basis set is used. To account for this effect, the listed aXZ MRCI energies were obtained as E(a5Z CAS) $+E$(aXZ MRCI)$-E$(aXZ CAS). For the hydrogen fluoride the aDZ MRCI$[2]_{R12}$ energy is in an excellent agreement with the CBS MRCI estimate. The observed agreement with the "exact" reference D_e is not nearly as good, partially because of the residual method (FCI-MRCI) and basis set errors. For the nitrogen molecule the aDZ MRCI$[2]_{R12}$ dissociation energy is better than the aQZ MRCI dissociation energies. Overall, the significant improvement of relative energies from the $[2]_{R12}$ correction is undeniable.

In contrast to the MR-CI-R12 method of Gdanitz, the $[2]_{R12}$ method involves internal contraction and modern R12 technology, and introduces geminal functions perturbatively, not iteratively. The proposed correction bears resemblance to the MR-MP2-F12 method of Ten-no[7] in that it uses internally contracted geminal functions. [Note that "internally-contracted" in this context does not mean that internal contraction was used in computing the reference wave function. It refers to the fact that an entire multideterminantal reference function with fixed coefficients is used to generate geminal replacements in Eq. (2). In this paper we use uncontracted MRCI wave functions, but the geminal functions obtained from them are internally contracted.] Technically our methods are quite different and use different sets of approximations to arrive at the simple final expressions. Although our method assumes that all orbitals in $\{p\}$ are occupied (i.e., belong to the space spanned by occupied natural orbitals of the reference wave function), its generalization to active-space references, such as complete active space CI or density matrix renormalization group (DMRG), is straightforward.

TABLE I. The electronic dissociation energies of the HF and N_2 molecules (kJ/mol) [Dissociation energies computed as difference of the molecular energies $E(R_{HF}=10.0\ \text{Å})-E(R_{HF}=0.916808\ \text{Å})$ for the HF molecule and $E(R_{NN}=10.0\ \text{Å})-E(R_{NN}=1.097685\ \text{Å})$ for the N_2 molecule.]

	HF		N_2	
Basis set	CASSCF	MRCI[a]	CASSCF	MRCI[a]
aDZ	475.64	563.92	862.90	906.94
aTZ	481.49	575.79	886.20	920.51
aQZ	482.57	580.79	891.05	938.88
a5Z	482.56	581.81	891.53	
CBS extrapolation		582.87		952.29
aDZ $[2]_{R12}$		583.56		942.19
Reference[b]		593.03		955.50

[a] Computed as E_{CASSCF}(a5Z) plus ($E_{MRCI}-E_{CASSCF}$) in the given basis set.
[b] The nonrelativistic Born–Oppenheimer electronic energy from HEAT (Ref. 26) minus the core contribution to the atomization energy from Table 15.25 of Ref. 27.

We presented a novel approach to incorporate the explicitly correlated terms into highly correlated wave functions by perturbation theory. The resulting second-order correction for the two-electron basis set incompleteness can be computed for any reference state for which 1-RDM and 2-RDM are available. The performance of the method for the two prototypical diatomic potential energy surfaces is promising, with the double-zeta basis sufficient to match or exceed the precision of the conventional quadruple-zeta result. An in-depth investigation of this method seems warranted.

E.F.V. is grateful to the Donors of the American Chemical Society Petroleum Research Fund (Grant No. 46811-G6) and the U.S. National Science Foundation (CAREER Award No. CHE-0847295). E.F.V. is an Alfred P. Sloan Research Fellow.

[1] W. Klopper, F. R. Manby, S. Ten-No, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).
[2] E. F. Valeev, Phys. Chem. Chem. Phys. **10**, 106 (2008).
[3] T. B. Adler, G. Knizia, and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[4] D. P. Tew, W. Klopper, C. Neiss, and C. Hattig, Phys. Chem. Chem. Phys. **9**, 1921 (2007).
[5] D. Bokhan, S. Bernadotte, and S. Ten-no, J. Chem. Phys. **469**, 214 (2009).
[6] R. J. Gdanitz, Chem. Phys. Lett. **210**, 253 (1993).
[7] S. Ten-no, Chem. Phys. Lett. **447**, 175 (2007).
[8] D. Mukherjee, Chem. Phys. Lett. **274**, 561 (1997).
[9] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **107**, 432 (1997).
[10] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
[11] W. Klopper and C. C. M. Samson, J. Chem. Phys. **116**, 6397 (2002).
[12] E. F. Valeev and C. L. Janssen, J. Chem. Phys. **121**, 1214 (2004).
[13] M. Torheyden and E. F. Valeev, Phys. Chem. Chem. Phys. **10**, 3410 (2008).
[14] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **110**, 2800 (1999).
[15] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **120**, 7350 (2004).
[16] S. Ten-no, J. Chem. Phys. **121**, 117 (2004).
[17] E. F. Valeev, J. Chem. Phys. **125**, 244106 (2006).
[18] E. F. Valeev, Chem. Phys. Lett. **395**, 190 (2004).
[19] S. Kedžuch, M. Milko, and J. Noga, Int. J. Quantum Chem. **105**, 929 (2005).
[20] S. Ten-No, Chem. Phys. Lett. **398**, 56 (2004).
[21] A. K. Wilson, T. v. Mourik, and T. H. Dunning, J. Mol. Struct.: THEOCHEM **388**, 339 (1997).
[22] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[23] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).
[24] C. L. Janssen, I. B. Nielsen, M. L. Leininger, E. F. Valeev, and E. T. Seidl, *The Massively Parallel Quantum Chemistry Program (MPQC): Version 3.0 (alpha)* (Sandia National Laboratories, Livermore, 2009).
[25] T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Jannssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, J. Comput. Chem. **28**, 1610 (2007).
[26] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, J. Chem. Phys. **128**, 114111 (2008).
[27] T. Helgaker, P. Jørgensen, and J. Olsen, *Modern Electronic Structure Theory*, 1st ed. (Wiley, Chichester, 2000).