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Communication: Second-order multireference perturbation theory with explicit correlation: CASPT2-F12

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An explicitly correlated complete active space second-order perturbation (CASPT2-F12) method is presented which strongly accelerates the convergence of CASPT2 energies and properties with respect to the basis set size. A Slater-type geminal function is employed as a correlation factor to represent the electron-electron cusp of the wave function. The explicitly correlated terms in the wave function are internally contracted. The required density matrix elements and coupling coefficients are the same as in conventional CASPT2, and the additional computational effort for the F12 correction is small. The CASPT2-F12 method is applied to the singlet-triplet splitting of methylene, the dissociation energy of ozone, and low-lying excited states of pyrrole.
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Electronic structure methods based on wave functions suffer from a very slow convergence of the correlation energy with basis set size. This is due to the poor description of the wave function around the coalescence point of two electrons by expansions of antisymmetrized orbital products (Slater determinants). The problem can be much alleviated by introducing terms into the wave function expansion that depend explicitly on the electron-electron distance (called geminal functions).[1] In the past decade much progress has been made in developing such explicitly correlated (so-called F12) methods, which are efficient, reliable, and numerically robust. For details we refer to recent reviews.[2,3] Unfortunately, so far most of these methods are limited to wave functions with single-determinant (Hartree–Fock) reference functions in the electronic ground states.

In many applications it is necessary, however, to employ multireference (MR) methods, which use a complete active space self-consistent field (CASSCF) or other multiconfiguration wave function as zeroth-order approximation. MR methods are needed in all near degeneracy situations, as for example to describe bond-breaking processes. Furthermore, many electronically excited states have multiconfiguration character. Avoided crossings or conical intersections of nearly degenerate states play an important role in photochemistry, and for a theoretical description of such processes MR methods are mandatory. One of the simplest and most popular MR methods is complete active space second-order perturbation theory (CASPT2). However, as any other conventional electron correlation method, CASPT2 suffers from the slow convergence of the dynamical correlation energy with basis set size.

In this communication, we develop an efficient explicitly correlated CASPT2-F12 method by combining the modern F12 techniques and the CASPT2 method.[4–10] This not only allows for near complete basis-set (CBS) limit accuracy in CASPT2 calculations with affordable computational cost, but also paves the road to more advanced explicitly correlated MR methods for the treatment of strongly correlated systems [MR configuration interaction (MRCI-F12) and coupled-cluster (MRCC-F12) methods]. In addition, the CASPT2-F12 method is useful as an excited-state electronic-structure theory; the usual single-reference F12 methods have difficulties to obtain a balanced description of the ground and excited states through the equation-of-motion CC-F12 approaches, owing to the biased parameterization of the wave functions towards the ground state.[11]

Gdanitz[12,13] has been the first to implement explicitly correlated MR methods using the so-called standard approximation and a linear r_{12} correlation factor (called R12-MRACPF). More recently, Ten-no[14] has studied a simple F12 theory with the MR Møller–Plesset perturbation theory (MRMP) method,[6] in which the correction to semi-internal contributions is neglected and an approximate diagonal Fock operator along with the so-called approximation A is used to simplify the formalism. Furthermore, an *a posteriori* F12 approach for arbitrary correlation models has been proposed by Torheyden and Valeev.[15] Varganov and Martínez[16] have proposed to augment the CASSCF method with a geminal factor (G-CASSCF).

The CASPT2-F12 method proposed in the present study is based on the MR methods of Werner and Knowles,[17,18] in which internally contracted configurations are used for the doubly external space, while the singly external configurations remain uncontracted to avoid the diagonalization of the third-order reduced density matrix (3RDM) in the active space. The extension of this work to the more elaborate contraction scheme of Celani and Werner[8] will be considered later. Apart from the usual resolution of the identity approximations, we assume no other approximations in the F12 treatment and use the full Fock matrix including off-diagonal parts. Thus, our method has the same orbital invariance properties as the CASSCF reference function and the standard CASPT2 wave function. It is not restricted to CASSCF reference functions but also allows to use restricted active space

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(RAS) or arbitrary other reference functions. The F12 corrections to the semi-internal contributions to the CASPT2 energy are included in the formalism. Their contributions become important especially when large active spaces are used.

We use the following notation for indices: i,j,k,l,m,n label correlated valence orbitals, o all occupied orbitals in the reference function including the uncorrelated core orbitals, a,b external (unoccupied in the reference) orbitals represented by the orbital basis set (OBS), r,s all orbitals represented by the OBS, x,y external orbitals in the complementary auxiliary basis set (CABS),[19] and α,β external orbitals in the complete space. Furthermore, κ,λ label any orbitals in the complete space. We employ the usual spin-free excitation operators $\hat{E}_i^l$, $\hat{E}_{ij}^{lm}$, and $\hat{E}_{ijk}^{lmn}$. Doubly external configurations are internally contracted[7,8,17] as $|\Phi_{ijp}^{ab}\rangle=\frac{1}{2}(\hat{E}_{ij}^{ab}+p\hat{E}_{ji}^{ab})|0\rangle$, where $|0\rangle$ is the reference wave function, which is a linear combination of N-electron configuration state functions (CSFs). The parity p is ± 1 for singlet and triplet coupling of the two external electrons, respectively. In addition, we define orthonormal uncontracted internal and singly external CSFs, $|I\rangle$ and $|S^a\rangle$, in which I and S label internal N- and $(N-1)$-electron functions, respectively, which are constructed from occupied orbitals only.[17,18] The RDMs with valence orbital indices that appear in our formulation are defined as $\Gamma_i^l=\langle 0|\hat{E}_i^l|0\rangle$, $\Gamma_{ij}^{lm}=\langle 0|\hat{E}_{ij}^{lm}|0\rangle$, and $\Gamma_{ijk}^{lmn}=\langle 0|\hat{E}_{ijk}^{lmn}|0\rangle$.

The wave function of the CASPT2-F12 method is parametrized as

$$|\Psi\rangle = t^I|I\rangle + t_a^S|S^a\rangle + t_{ab}^{ijp}|\Phi_{ijp}^{ab}\rangle + \hat{Q}\hat{F}|0\rangle, \tag{1}$$

where $\hat{F}$ is a geminal excitation operator and the projector $\hat{Q}$ keeps the explicitly correlated terms orthogonal to the conventional first-order wave function (which is described by the first three terms). The internal configuration space $|I\rangle$ includes the reference configurations. Here and in the following, repeated indices imply summation over them. When the indices correspond to singlet or triplet pairs, restrictions such as $t_{ab}^{ijp}\hat{E}_{ijp}^{ab}\rightarrow\Sigma_{i\leq j,p}\Sigma_{ab}t_{ab}^{ijp}\hat{E}_{ijp}^{ab}$ are implied.

The geminal excitation operator is defined as

$$\hat{F} = \frac{1}{2}\mathcal{F}_{\alpha\beta}^{ij}\hat{E}_{ij}^{\alpha\beta} + \mathcal{F}_{xm}^{ij}\{\hat{E}_{ij}^{xm}\}, \tag{2}$$

where a curly bracket denotes (extended) normal ordering of the operator[20]

$$\{\hat{E}_{ij}^{xm}\} = \hat{E}_{ij}^{xm} - \Gamma_j^m\hat{E}_i^x + \frac{1}{2}\Gamma_i^m\hat{E}_j^x. \tag{3}$$

The normal ordering retains (in an approximate manner) only the two-electron excitation part of the geminal excitation operator. $\mathcal{F}_{\alpha\beta}^{ij}$ is the two-electron integral of F_{12} combined with the geminal amplitudes, $\mathcal{F}_{\alpha\beta}^{ij}=\langle\alpha\beta|F_{12}|kl\rangle t_{kl}^{ij}$. A Slater-type geminal,[21] $F_{12}=-\gamma^{-1}\exp(-\gamma r_{12})$, with $\gamma=1.0a_0^{-1}$ is used throughout this work. In this study, we employ the SP ansatz of Ten-no,[22] which fixes the geminal amplitudes to the values determined by the first-order cusp condition for singlet and triplet pairs as $t_{kl}^{ij}=\frac{3}{8}\delta_k^i\delta_l^j+\frac{1}{8}\delta_l^i\delta_k^j$.[23]

In the CASPT2-F12 theory, the projector $\hat{Q}$ in Eq. (1) is defined in the N electron space, which is

$$\hat{Q} = \hat{P}_{\alpha\beta,ij} - \hat{P}_{ab,ij} + \hat{P}_S. \tag{4}$$

Here, $\hat{P}_{\alpha\beta,ij}$ is a projector onto the complete (infinite) space spanned by nonorthogonal internally contracted configurations $|\Phi_{ij}^{\alpha\beta}\rangle$, and $\hat{P}_{ab,ij}$ removes the subspace which is included in the conventional CASPT2 wave function. The operator $\hat{P}_S$, which is usually neglected in the single-reference MP2-F12 theory, projects onto the space of uncontracted singly external configurations with one electron in the CABS space, $\hat{P}_S=\Sigma_S\Sigma_x|S^x\rangle\langle S^x|$. The restriction of these excitations to CABS orbitals is necessary in order to avoid many-electron integrals. This is justifiable since, in atomic cases, the basis-set truncation error of semi-internal contributions saturates with auxiliary functions of angular momentum quantum numbers up to $3l_{\mathrm{val}}$ where l_{val} is the maximum angular momentum quantum number in the valence space. In the supplementary material[23] it is demonstrated that the convergence of the correlation energy with the size of the CABS basis is indeed similar to single-reference MP2-F12.

The conventional amplitudes are determined by minimizing the Hylleraas functional

$$E_2 = \langle\Psi^{(1)}|\hat{H}^{(0)}|\Psi^{(1)}\rangle + 2\langle\Psi^{(1)}|\hat{H}|0\rangle. \tag{5}$$

The zeroth-order Hamiltonian is the projected normal-ordered Fock matrix, $\hat{H}^{(0)}=\hat{P}_0\hat{f}\hat{P}_0+(1-\hat{P}_0)\hat{f}(1-\hat{P}_0)$, with $\hat{f}=f_\kappa^\lambda\hat{E}_\lambda^\kappa-E_0$ and $\hat{P}_0=|0\rangle\langle 0|$. This definition of $\hat{H}_0$ ensures that the reference $|0\rangle$ is an eigenvector of $\hat{H}_0$ with an eigenvalue equal to 0. Amplitude equations are obtained by taking the functional derivatives of the Hylleraas functional with respect to the conventional amplitudes. This leads to the standard CASPT2 residuals,[7] augmented by the F12 coupling terms

$$C_{ab}^{ijp} = \frac{1}{2}(f_a^x\mathcal{F}_{xb}^{kl} + \mathcal{F}_{ax}^{kl}f_b^x)\langle 0|\hat{E}_{kl}^{ij} + p\hat{E}_{kl}^{ji}|0\rangle, \tag{6}$$

$$C_a^S = f_a^x\mathcal{F}_{xk}^{ij}\langle S^a|\{\hat{E}_{ij}^{ak}\}|0\rangle + \mathcal{F}_{ax}^{ijp}f_k^x\langle S^a|\hat{E}_x^k|\Phi_{ijp}^{ax}\rangle, \tag{7}$$

$$C^I = f_k^x\mathcal{F}_{xl}^{ij}\langle I|\hat{E}_x^k|S^x\rangle\langle S^x|\{\hat{E}_{ij}^{xl}\}|0\rangle \tag{8}$$

for pairs, singles, and internals, respectively. These terms are analogous to the C_{ab}^{ijp} coupling terms in MP2-F12. Here and in the following, the density matrices and coupling coefficients such as $\langle S^a|\hat{E}_x^k|\Phi_{ijp}^{ax}\rangle$ or $\langle S^x|\{\hat{E}_{ij}^{xl}\}|0\rangle$ are the same as needed in conventional CASPT2; in the latter quantities a and x are dummy labels for virtual or CABS orbitals, that is, the coupling coefficients are independent of these indices.

The CASPT2-F12 energy is evaluated by the Hylleraas functional, which can be written as a sum of the conventional CASPT2 energy expression (E_{CASPT2}) and additional F12 energy contributions: $E_{\text{CASPT2-F12}}=E_{\mathrm{CASPT2}}+E_{\mathrm{F12}}$. Note that E_{CASPT2} differs from the conventional CASPT2 value, since due to the additional coupling terms in the residuals the optimized amplitudes are not the same. The additional F12 energy contribution is

TABLE I. The reference and second-order energies of methylene ($^1A_1$ and $^3B_1$) in E_h computed by CASPT2 and CASPT2-F12 with the full-valence active space and different basis sets.

State	OBS	CASSCF	CASPT2	CASPT2-F12
$^1A_1$	VDZ-F12	−38.953 68	−0.082 33	−0.106 04
	VTZ-F12	−38.957 35	−0.095 54	−0.106 40
	VQZ-F12	−38.958 10	−0.101 11	−0.106 68
	CBS	−38.958 2	−0.106 7	⋯
$^3B_1$	VDZ-F12	−38.970 48	−0.088 14	−0.109 42
	VTZ-F12	−38.973 41	−0.100 90	−0.110 62
	VQZ-F12	−38.974 13	−0.106 05	−0.110 96
	CBS	−38.974 2	−0.111 0	⋯

TABLE II. $^1A_1-{}^3B_1$ separation of methylene in kcal/mol obtained by CASSCF, CASPT2, and CASPT2-F12 methods.

Active space	OBS	CASSCF	CASPT2	CASPT2-F12
(3,2,1,0)	VDZ-F12	10.55	14.19	12.67
	VTZ-F12	10.08	13.44	12.73
	VQZ-F12	10.06	13.16	12.75
	CBS	10.0	12.8	⋯
(7,4,3,1)	VDZ-F12	11.21	11.00	9.74
	VTZ-F12	10.61	10.23	9.72
	VQZ-F12	10.53	10.00	9.71
	CBS	10.5	9.7	⋯

$$\begin{aligned} E_{\text{F12}} = {} & 2(t^{ijp}_{ab}C^{ijp}_{ab} + t^S_a C^S_a + t^I C^I) \\ & + \tfrac{1}{2}(\mathcal{B}^{ij}_{kl} - E_0 \mathcal{X}^{ij}_{kl} + 2\mathcal{V}^{ij}_{kl})\Gamma^{kl}_{ij} \\ & + \tfrac{1}{2}\mathcal{X}^{ij}_{lm}\Gamma^{lmn}_{ijk} f^k_n + 2\mathcal{F}^S_x p^S_x \\ & + 2\mathcal{F}^S_x (f^a_k \mathcal{F}^{ijp}_{xa} + f^y_k \mathcal{F}^{ijp}_{xy})\langle S^x|\hat{E}^k_a|\Phi^{xa}_{ijp}\rangle \\ & + \mathcal{F}^S_x[f^y_x \delta^S_T + f^i_j \langle S^a|\hat{E}^j_i|T^a\rangle \delta^y_x - E_0 \delta^S_T \delta^y_x]\mathcal{F}^T_y. \end{aligned} \tag{9}$$

Here, $\mathcal{F}^S_x=\langle S^x|\hat{F}|0\rangle$ and $p^S_x=\langle S^x|\hat{H}|0\rangle$. The F12 intermediates $\mathcal{B}$, $\mathcal{X}$, and $\mathcal{V}$ are the usual B, X, and V intermediates, as in MP2-F12, combined with the geminal amplitudes, e.g. $\mathcal{B}^{kl}_{ij}=t^{kl}_{mn}B^{mn}_{m'n'}t^{ij}_{m'n'}$. For an efficient implementation of these intermediates, which involve the two-electron projector $\hat{Q}_{12}=1-|rs\rangle\langle rs|-|ox\rangle\langle ox|-|xo\rangle\langle xo|$, see Ref. 24.

The described CASPT2-F12 method has been implemented in the MOLPRO package.[25] The implementation is based in part on the codes developed in the former studies.[7,17,26] The coupling constants and RDMs have been taken from the existing CASPT2 code in MOLPRO. An efficient algorithm for computing them has been detailed in Ref. 18. The storage of the 3RDM occurring in Eq. (9) is avoided by directly computing its contraction with the Fock matrix elements as described in Ref. 17. All the F12 integrals are evaluated using density fitting,[27,28] and approximating the Slater-type geminal function to a weighted[24] linear combination of six Gaussian-type geminal functions.[29] The CABS is constructed from the union of OBS and auxiliary basis sets by projecting out the OBS components.[19,30] For the B intermediate, we have used the so-called approximation C,[31] whose working equations can be found, for instance, in Ref. 24.

As a first example, we calculated the adiabatic $^1A_1-{}^3B_1$ separation of methylene (CH_2). For all calculations reported in this paper, we employed the cc-pVXZ-F12 orbital basis sets[32] along with the corresponding cc-pVXZ-F12/OPTRI CABS basis sets.[33] Further computational details such as geometries and fitting basis sets can be found in the supplementary material.[23] The basis-set dependence of the CASPT2 and CASPT2-F12 energies with the full-valence active space [six electrons in three a_1, two b_2, one b_1 orbitals, denoted (3,2,1,0)] is summarized in Table I. Using the cc-pVDZ-F12 basis set the CASPT2-F12 second-order energies are already within 2 mE_h of the CBS values (obtained by extrapolation[23,34]), while the conventional CASPT2 energies are off by 25 mE_h. With cc-pVTZ-F12 basis set, more than 99% of the second-order energies at the CBS limits are recovered for both states, attesting a similar efficiency of the CASPT2-F12 method for multi-reference cases to that of the MP2-F12 method for single-reference systems.

Table II in the supplementary material lists the CASPT2 and CASPT2-F12 energies of CH_2 at the same geometries computed with an extended (7,4,3,1) active space [formally full valence space+C($3s3p3d$)]. In contrast to the CASPT2 method, which captures with the cc-pVDZ-F12 basis set less than 50% of the CBS second-order correlation energies, the CASPT2-F12 method reproduces ≈107% and 104% of them for $^1A_1$ and $^3B_1$ states, respectively. The slight overshooting in small basis sets appears to be an intrinsic feature of the CASPT2 method; it is due to the contributions of semi-internal configurations and is also observed if a standard CASPT2 calculation is carried out using the union of the orbital and CABS basis sets (using CASSCF reference functions optimized with the OBS only).

The computed singlet-triplet separations are presented in Table II. Although the agreement of the CASPT2-F12 values at the cc-pVDZ-F12 level with the CBS limit seems partly fortuitous (as judged from the basis-set convergence of CASSCF contributions and that of CASPT2-F12), we obtain near CBS limit accuracy already with the cc-pVTZ-F12 basis set. The experimental value corrected for the effects of zero-point vibrational energy and relativity is 9.12 ± 0.20 kcal/mol.[35] The difference between the experimental and computed CBS values should be ascribed to the higher-order dynamical correlation contributions that are neglected in CASPT2. The use of larger active spaces helps to capture these effects.

To demonstrate that calculations with general reference spaces are possible, we performed RASPT2 calculations in which only up to two electrons were allowed in the nine orbitals that do not belong to the valence space. The results can be found in the supplementary material.[23]

As another example, the dissociation energy of the ground-state of ozone, $O_3(^1A_1)\rightarrow O_2(^3\Sigma_g^-)+O(^3P)$, has been computed using the full valence active space. Already with the triple-ζ basis set, the CASPT2-F12 dissociation energy is within 0.5 kcal/mol of the CBS limit. In contrast, the basis-set truncation error of the conventional CASPT2 method amounts about 3 and 1.3 kcal/mol with the triple-ζ and

TABLE III. Vertical excitation energies (in eV) for low-lying A_1 and B_2 states of pyrrole with six electrons in four b_1 and three a_2 active orbitals.

OBS	A_1 $1a_2 \rightarrow 3p_x$	A_1 $2b_1 \rightarrow 3p_x$	B_2 $1a_2 \rightarrow 3p_x$	B_2 $2b_1 \rightarrow 3p_x$	B_2 $\pi \rightarrow \pi^*$
		CASSCF			
VDZ-F12+	5.57	5.68	4.87	6.34	8.00
VTZ-F12+	5.59	5.70	4.88	6.37	8.00
VQZ-F12+	5.58	5.70	4.88	6.36	7.99
		CASPT2			
VDZ-F12+	6.69	6.81	6.00	7.61	6.03
VTZ-F12+	6.86	6.98	6.16	7.79	5.98
VQZ-F12+	6.92	7.04	6.21	7.85	5.97
		CASPT2-F12			
VDZ-F12+	6.96	7.09	6.26	7.90	5.99
VTZ-F12+	6.98	7.11	6.27	7.92	5.98
VQZ-F12+	6.98	7.10	6.27	7.92	5.97

quadruple-ζ basis sets, respectively. More details can be found in the supplementary material.[23]

Finally, the vertical excitation energies for low-lying states in the A_1 and B_2 symmetries of pyrrole (C_{2v} symmetry) have been computed with an active space of six electrons in four b_1 and three a_2 orbitals. The considered states have Rydberg $3p$ character except for the $\pi \rightarrow \pi^*$ valence state in B_2 symmetry.[36,37] Another valence state in A_1 symmetry[36,37] does not appear with this relatively small CAS. In order to describe the Rydberg states properly, the cc-pVXZ-F12 basis sets of C and N have been augmented by one even-tempered diffuse p function[23] (denoted as VXZ-F12+ in Table III). Due to the more compact electronic structure of the ground state, dynamical electron correlation increases the excitation energies of the Rydberg states, and to recover this effect with conventional CASPT2 large basis sets are needed. At the double-ζ level, the standard CASPT2 method underestimates the excitation energies of the Rydberg states by 0.2–0.3 eV. In contrast, the F12 correction captures almost all of the basis-set error in the Rydberg excitation energies already with the double-ζ basis set, yielding a remarkably good accuracy of 0.03 eV (as compared to the CBS limit) for all states considered here. The basis-set convergence of the valence excitation energy in the B_2 symmetry is already good with the CASPT2 method and the F12 correction plays only a minor role.

In conclusion, we have developed a CASPT2-F12 method which combines modern F12 techniques with the CASPT2 method to accelerate the basis-set convergence of second-order energies. The CASPT2-F12 method has been applied to the singlet-triplet separation of methylene, the dissociation energy of ozone, and the vertical excitation energies of pyrrole. The convergence of these quantities with basis set size is greatly accelerated by the F12 correction. The additional cost for the F12-treatment is modest: for example, a CASPT2-F12 calculation for pyrrole with the VTZ-F12 basis takes about 1.5 times longer than the corresponding standard CASPT2 calculation. As in the single-reference F12 theory, the cost-accuracy performance of the F12 methods relative to the conventional correlation models will become even more favorable when combined with higher-level correlation models. The development of an internally contracted MRCI-F12 method is currently in progress.

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