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Explicitly correlated N-electron valence state perturbation theory (NEVPT2-F12)

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In this work, explicitly correlated second order N-electron valence state perturbation theory (NEVPT2-F12) has been derived and implemented for the first time. The NEVPT2-F12 algorithm presented here is based on a fully internally contracted wave function and includes the correction of semi-internal excitation subspaces. The algorithm exploits the resolution of identity (RI) approximation to improve the computational efficiency. The overall $O(N^5)$ scaling of the computational effort is documented. In Sec. III, the dissociation processes of diatomic molecules and the singlet-triplet gap of several systems are studied. For all relative energies studied in this work, the errors with respect to the complete basis set (CBS) limit for the NEVPT2-F12 method are within 1 kcal/mol. For moderately sized active spaces, the computational cost of a RI-NEVPT2-F12 correlation energy calculation for each root is comparable to a closed-shell RI-MP2-F12 calculation on the same system. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4996560>]

I. INTRODUCTION

It is well known that the electron correlation energy evaluated with determinantal wave functions converges slowly with respect to the basis set extension. To overcome this problem, Hylleraas first introduced a basis set that explicitly depended on the inter-electronic distance r_{12} more than 80 years ago.¹ Subsequently, in the 1980s, Kutzelnigg proposed the R12 method, which marks the most important step in explicit correlation theory.²⁻⁴ Kutzelnigg's seminal work has sparked many developments in the field of explicit electron correlation theory.⁵⁻¹⁰ Nowadays, the explicitly correlated R12/F12 methodology is well established for single reference (SR) methods.¹¹⁻¹⁴ Recently, F12 theory has been further extended to the linear or low scaling SR perturbation theory (PT) and coupled cluster (CC) theory.¹⁵⁻²⁰

The explicitly correlated method is applicable to multi-reference (MR) theories as well. Gdanitz developed the first explicitly correlated MR method, namely, the MR configuration interaction (MR-CI-R12) method.^{21,22} In the context of MRPT2, Ten-no²³ as well as Haunschild and co-workers²⁴ implemented the MR-MP2-F12 and Mk-MRPT2-F12 approaches, respectively. Explicitly correlated MRCC methods were independently proposed by Noga *et al.*,^{25,26} Yanai and Shiozaki,²⁷ and Köhn and co-workers.²⁸ However, many approaches, like the MR-F12 methods of Ten-no or Haunschild, do not consider the F12 correction for the semi-internal excitation subspaces. A series of explicitly correlated multireference methods were presented by Werner, Shiozaki, and Knizia, who applied the F12 theory to complete active space second-order perturbation theory

(CASPT2-F12),²⁹ and later to partially internally contracted MRCI.³⁰ In their approach, not only the doubly external spaces are considered but also the F12 corrections for semi-internal excitation spaces are included. In contrast to these method-specific MR-F12 theories, Valeev and co-workers developed a more general explicitly correlated formalism, applicable to all kinds of MR correlation methods.^{31,32} More detailed discussions of MR-F12 methods can be found in recent reviews.^{33,34}

Among the MR methods, MRPT is computationally the most attractive approach. The CASPT2 method developed by Roos and co-workers is a MRPT that is most widely used.^{35,36} However, CASPT2 suffers from the well-known intruder state problem and is not strictly size-extensive.³⁷ In an attempt to overcome some defects of CASPT2, Angeli, Malrieu, and co-workers proposed N-electron valence state perturbation theory (NEVPT2).^{38,39} NEVPT2 is a fully internally contracted MRPT method, which is computationally less expensive compared to uncontracted or partially internally contracted MR methods. Moreover, the NEVPT2 method is size consistent and virtually intruder state free. Because of these virtues, NEVPT2 has gained significant popularity and inspired many new developments in recent years.⁴⁰⁻⁴² For NEVPT2 calculations of large systems with moderate active spaces, the computational bottleneck is the treatment of the $S_{ij,ab}^{(0)}$ (two-hole/two-particle) subspace, which, in itself, is similar to SR-MP2. By using the basic idea of domain-based local pair natural orbitals (DLPNOs),⁴³⁻⁴⁵ we have developed a linear scaling NEVPT2 method, which can treat very large systems.⁴⁶ Subsequently, Werner and co-workers reported an efficient PNO-CASPT2 implementation.⁴⁷ Despite recent progress in the NEVPT2 methodology, the extension from NEVPT2 to NEVPT2-F12 has not yet been reported. In this short paper, we present our recent efforts on NEVPT2-F12.

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II. THEORY AND IMPLEMENTATION

Throughout this work, $\{i, j, k, l\}$ are used to denote the inactive MOs, $\{t, u, v, w\}$ denote the active MOs, and virtual MOs are labeled by $\{a, b, c, d\}$. The labels $\{\alpha', \beta', \gamma', \delta'\}$ and $\{p, q, r, s\}$ denote the orbitals in the complementary auxiliary basis set (CABS)⁸ and orbital basis set (OBS), respectively. Indices $\{\alpha, \beta, \gamma, \delta\}$ denote the (normalized) unoccupied orbitals in the CABS, which are orthogonal to the occupied space. Our formalism uses the spin traced excitation operators, given by $E_p^q = a_{q\uparrow}^+ a_{p\uparrow} + a_{q\downarrow}^+ a_{p\downarrow}$.

The 1st-order wave function used in NEVPT2-F12 is an extension of the single reference MP2-F12 method. It can generally be defined as

$$|1\rangle = |1_{NEVPT2}\rangle + |1_{NEVPT2-F12}\rangle, \quad (1)$$

in which $|1_{NEVPT2}\rangle$ is the 1st-order wave function of NEVPT2, and $|1_{NEVPT2-F12}\rangle$ is the 1st-order wave function of NEVPT2-F12. Similar to MP2-F12, the two electron integrals of projected geminals $W_{\alpha\beta}^{ij}$ have to be included in the definition of $|1_{NEVPT2-F12}\rangle$,

$$\begin{aligned} W_{\alpha\beta}^{ij} &= \langle \alpha\beta | Q_{12} \hat{f}_{12} | ij \rangle \\ &= \iint \varphi_\alpha(\mathbf{r}_1) \varphi_\beta(\mathbf{r}_2) Q_{12} \hat{f}_{12} \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (2)$$

Here, \hat{f}_{12} is the symmetric correlation factor and Q_{12} is the orthogonality projector, which has been defined previously⁴⁸ as

$$Q_{12} = 1 - \sum |ab\rangle \langle ab|. \quad (3)$$

Using $W_{\alpha\beta}^{ij}$ and E_p^q , the detailed definition of the NEVPT2-F12 1st-order wave function is given in Table I. Note that the $S_{i,a}^{(0)}$ and $S_a^{(-1)}$ subspaces contain Brillouin single excitations that must be projected out.³¹ This is due to the fact that the F12 terms are only designed to correct the basis set incompleteness of two-electron excitations.

For each subspace, the amplitudes of the 1st-order wave function must make the corresponding component of the Hylleraas functional stationary,

$$H_{yl} = \langle 1 | H^{Dyall} | 1 \rangle + 2 \langle 1 | H | 0 \rangle. \quad (4)$$

The 0th-order Hamiltonian is taken as the Dyal Hamiltonian H^{Dyall} .⁴⁹ Once the amplitudes have been determined, the NEVPT2-F12 energies correction can be computed. By varying the Hylleraas functional, two sets of residual equations are derived. One set comprises the canonical NEVPT2 equations; the other set defines the NEVPT2-F12 equations. The latter equations, involving the F12 intermediates, density matrices, and amplitudes, are much more complicated than their canonical NEVPT2 counterparts.

In general, the F12 equations derived from Eq. (4) must be solved iteratively. The computational cost for solving the F12 equations is larger than the cost of the canonical NEVPT2 calculation. In this work, the fixed amplitude approximation proposed by Ten-no is used, which fixes the F12 amplitudes T_{pq}^{rs} to fit the first order (natural) singlet and triplet cusp condition,⁶

$$T_{pq}^{rs} = \frac{3}{8} \delta_{pr} \delta_{qs} + \frac{1}{8} \delta_{ps} \delta_{qr}. \quad (5)$$

Inserting Eq. (5) into the Hylleraas functional, the F12 energy correction can directly be calculated (no iterations). More details about the NEVPT2-F12 equations derived and implemented in this work can be found in the [Appendix](#).

In the NEVPT2-F12 equations, all the involved density and Koopmans matrices are readily available from the preceding canonical NEVPT2 step. Therefore, the additional computational cost in NEVPT2-F12 solely arises from the computation of the F12 intermediates. All F12 integrals and intermediates are evaluated in the same way as the MP2-F12 algorithm in ORCA.⁵⁰ However, in contrast to MP2-F12, not only the diagonal V , B , and X matrix elements are needed¹⁰ but also the off-diagonal matrix elements, involving the active MO indices, have to be computed. For large systems with moderate active spaces, the bottleneck of NEVPT2-F12 is in the evaluation of two electron integrals and the ‘‘diagonal’’ elements of V , B , and X matrices.^{10,51} For such calculations, the computational cost of NEVPT2-F12 is comparable to its MP2-F12 counterpart.

Besides the F12 correction to the correlation energy, the correction for the basis set incompleteness of complete-active-space self-consistent field (CASSCF) calculation is considered in this work as well. Many efforts have been made in this

TABLE I. The definition of 1st-order wave functions for NEVPT2 and NEVPT2-F12. Einstein summation is implied, unless noted.

Subspace	$ 1_{NEVPT2}\rangle$	$ 1_{NEVPT2-F12}\rangle$
$S_{ij,ab}^{(0)}$	$\frac{1}{2} E_i^a E_j^b 0\rangle T_{ab}^{ij}$	$\frac{1}{2} W_{\alpha\beta}^{kl} E_i^\alpha E_j^\beta 0\rangle T_{kl}^{ij}$
$S_{i,ab}^{(-1)}$	$E_i^a E_t^b 0\rangle T_{ab}^{it}$	$W_{\alpha\beta}^{ju} E_i^\alpha E_t^\beta 0\rangle T_{ju}^{it}$
$S_{ab}^{(-2)}$	$E_t^a E_u^b 0\rangle T_{ab}^{tu}$	$W_{\alpha\beta}^{vw} E_t^\alpha E_u^\beta 0\rangle T_{vw}^{tu}$
$S_{ij,a}^{(1)}$	$E_i^a E_j^t 0\rangle T_{at}^{ij}$	$W_{\alpha t}^{kl} E_i^\alpha E_j^t 0\rangle T_{kl}^{ij}$
$S_{i,a}^{(0)}$	$E_i^a E_u^t 0\rangle T_{at}^{iu} + E_i^t E_u^a 0\rangle T_{ia}^{tu}$	$W_{\alpha t}^{ju} \left(E_i^\alpha E_u^t - \langle 0 E_u^t 0 \rangle E_i^\alpha \right) 0\rangle T_{ju}^{iu}$ $+ W_{t\alpha}^{ju} \left(E_i^t E_u^\alpha + \frac{1}{2} \langle 0 E_i^t 0 \rangle E_u^\alpha \right) 0\rangle T_{ju}^{iu}$
$S_a^{(-1)}$	$E_u^a E_v^t 0\rangle T_{at}^{uv}$	$W_{\alpha t}^{wx} \left(E_u^\alpha E_v^t - \sum_{xy} \frac{\langle 0 E_v^t E_u^\alpha 0 \rangle}{\langle 0 E_x^y 0 \rangle} E_y^\alpha \right) 0\rangle T_{wx}^{uv}$

area.^{52,53} To avoid an iterative process, the perturbative method proposed by one of the present authors is adopted here.⁵² The Dyll Hamiltonian is used as the 0th-order Hamiltonian. The original abbreviation $[2]_S$ is used to denote this CABS singles correction for the CASSCF.

III. RESULTS

The NEVPT2-F12 equations have been derived and implemented in a development version of ORCA. In all calculations shown below, the frozen core and resolution of identity (RI) approximations are used. In NEVPT2-F12 calculations, the cc-pVXZ-F12 ($X = D, T, Q$) basis sets with their matching Slater-type correlation factors $\hat{f}_{12} = (1 - \exp(-\gamma r_{12}))/\gamma$, CABS basis sets cc-pVXZ-F12/OptRI, and density fitting basis sets aug-cc-pVXZ are employed (abbreviated as “XZ-F12”).^{54,55} The cc-pVXZ-F12/OptRI basis set is a compact RI basis set optimized for explicitly correlated calculations by Peterson and co-workers.⁵⁵ The commonly used two point extrapolation schemes are utilized to estimate the CASSCF or NEVPT2 CBS limits, respectively. The extrapolation is based on cc-pV5Z and cc-pV6Z results. The CASPT2 and CASPT2-F12 calculations have been performed with MOLPRO.⁵⁶

Employing the NEVPT2-F12 method, the singlet and triplet states of CH_2 were computed (Table II). The geometries of the two states are taken from Werner’s CASPT2-F12 paper.²⁹ With a F12 optimized double- ζ basis set, the correlation energies produced by NEVPT2-F12 are already close to the CBS results. The deviation between NEVPT2-F12/DZ-F12 results and the CBS limit is around 1 mhartree, which is significantly more accurate than any of the results without the F12 correction. With larger basis sets, the NEVPT2-F12 method clearly comes very close to the CBS limit of the correlation energy.

We also studied the dissociation process of the O_2 molecule using the NEVPT2, NEVPT2-F12, and NEVPT2-F12+[2]_S methods. The state-averaged CASSCF wave functions of the $^3\Sigma^-$ ground and lowest $^1\Delta$ excited states are used as references. The errors of absolute and relative energies with respect to the CBS limit are given in Fig. 1. Figure 1(a) shows the absolute error of the different methods for the $^3\Sigma^-$ state of the O_2 molecule. The F12 correction improves the absolute energies substantially, especially for small basis set calculations. For the results with cc-pVDZ-F12, the $[2]_S$

TABLE II. The basis set convergence of NEVPT2 and NEVPT2-F12 correlation energies of the two lowest states of methylene.

State	Basis set	CASSCF(6,6) (a.u.)	NEVPT2 (a.u.)	NEVPT2-F12 (a.u.)
Singlet	DZ-F12	-38.953 690	-0.075 473	-0.097 323
	TZ-F12	-38.957 360	-0.087 261	-0.097 802
	QZ-F12	-38.958 105	-0.092 437	-0.097 891
	CBS	...	-0.097 803	...
Triplet	DZ-F12	-38.970 486	-0.077 616	-0.097 601
	TZ-F12	-38.973 413	-0.088 944	-0.098 319
	QZ-F12	-38.974 132	-0.093 646	-0.098 449
	CBS	...	-0.098 465	...

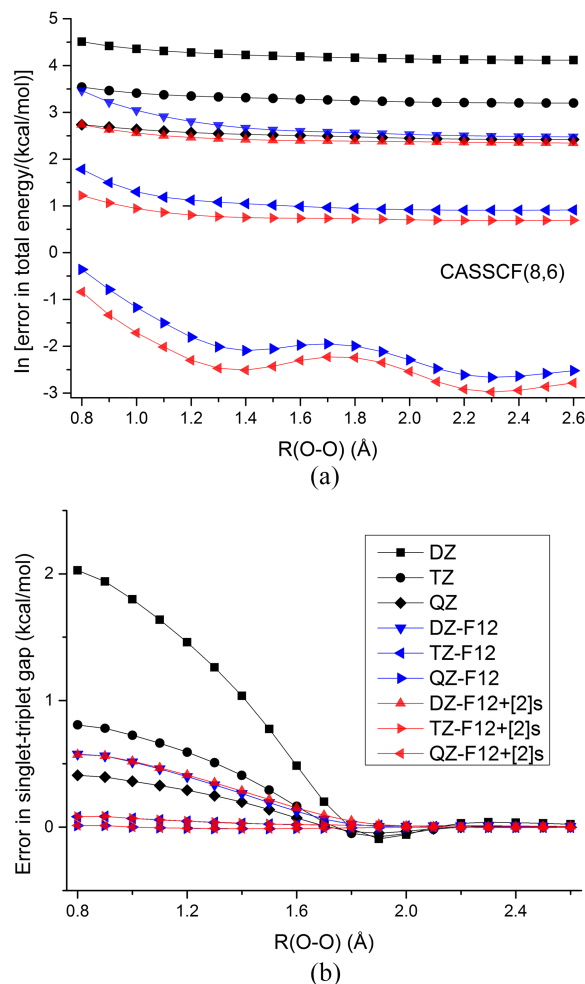


FIG. 1. (a) The basis set error of the total NEVPT2 energy for the ground state of the O_2 molecule along the PES. (b) The basis set error of the vertical singlet-triplet gap of O_2 molecule along the PES. The absolute correlation energies are given in Table S1 of the supplementary material (XZ are conventional NEVPT2 results with cc-pvXZ-F12 basis set, XZ-F12 are NEVPT2-F12 results, and XZ-F12+[2]_S are results with CABS singles corrections).

correction primarily reduces the error in the short-range region. The NEVPT2-F12+[2]_S approach, with a double- ζ basis set, predicts absolute energies comparable to NEVPT2 with the cc-pVQZ-F12 basis set. A similar trend is observed for the $^1\Delta$ excited state calculated by the same methods (see the supplementary material). The errors of the vertical excitation energies computed by the various NEVPT2 methods and different basis sets are shown in Fig. 1(b). The NEVPT2 calculations with the double- ζ basis set produce very large errors with respect to the CBS limit. With the F12 correction, the errors in the relative energy along the PES are consistently reduced to less than 1 kcal/mol. The $[2]_S$ correction does not improve the excitation energies, if state-averaged wave functions are used.

Finally, the adiabatic excitation energies of four molecules were studied. The ground and excited state geometries of the four molecules are taken from Ref. 57. For the NEVPT2 and NEVPT2-F12 calculations, state-specific CASSCF wave functions are used as reference. The results given in Table III demonstrate that the NEVPT2 results with small basis sets always underestimate the energy gaps. Without the F12

TABLE III. The low-lying adiabatic excitation energies (in eV) calculated by NEVPT2-F12 and CASPT2-F12 with different basis sets. The absolute energies are given in Table S2 of the [supplementary material](#).

Method	Basis sets	C ₂ H ₂ (¹ A ⁻¹ A)	C ₃ H ₄ O (³ A'' ⁻¹ A')	C ₆ H ₆ (¹ A ⁻¹ A)	C ₆ H ₈ (¹ A ⁻¹ A)
		CAS(4,4)	CAS(6,5)	CAS(6,6)	CAS(6,6)
NEVPT2	cc-pVDZ-F12	5.255	3.161	5.062	4.784
	cc-pVTZ-F12	5.264	3.175	5.093	4.791
	cc-pVQZ-F12	5.279	3.191	5.106	4.803
	CBS ^a	5.286	3.209	5.114	4.812
NEVPT2-F12	cc-pVDZ-F12	5.266	3.214	5.094	4.805
	cc-pVTZ-F12	5.288	3.213	5.119	4.814
	cc-pVQZ-F12	5.287	3.212	5.118	4.815
NEVPT2-F12+[2] _S	cc-pVDZ-F12	5.300	3.222	5.116	4.820
	cc-pVTZ-F12	5.286	3.214	5.120	4.816
	cc-pVQZ-F12	5.287	3.212	5.118	4.815
CASPT2	cc-pVDZ-F12	5.114	2.803	4.420	4.358
	cc-pVTZ-F12	5.118	2.806	4.432	4.353
CASPT2-F12 ^b	cc-pVDZ-F12	5.124	2.845	4.438	4.369
	cc-pVTZ-F12	5.142	2.840	4.453	4.373
Experiment	...	5.23	3.01	4.72	4.93

^aThe CASSCF energies in the CBS limit have been computed following Ref. 58.

^bFor the CASPT2 (CASPT2-F12) calculations on C₆H₆ and C₆H₈, a level shift of 0.2 Hartree is applied to both ground and excited states.

correction, the error between the double- ζ and CBS limits can exceed 0.05 eV, while with the NEVPT2-F12 correction, the CBS limit is predicted accurately. For all of these excitation energies, the deviations between DZ-F12 results and the CBS limit are less than 0.02 eV (0.5 kcal/mol). The energy gaps computed with the NEVPT2-F12+[2]_S method are also given. With the [2]_S correction, more accurate results are produced with the double- ζ basis set in most cases. However, when larger basis sets are employed, the [2]_S correction does not influence the excitation energies. The excitation energies calculated by CASPT2 and CASPT2-F12 are also given in Table III. Compared to the CASPT2 results, their F12 corrections increase the energy gaps as well. The final results predicted by NEVPT2-F12 and CASPT2-F12 are comparable.

For benzene, the detailed CPU time of NEVPT2-F12 for the ground state is shown in Table IV. All calculations are performed on one core of an Intel Xeon E5649 2.53GHz CPU and no advantage was taken of symmetry. The whole NEVPT2-F12 calculation can be divided into two parts: the evaluation of the

F12 matrices step and the Hylleraas functional evaluation step. The results show that the evaluation of the F12 matrices is the most time consuming step in NEVPT2-F12. The CPU time spent on the Hylleraas functional evaluation is negligible. For the conventional NEVPT2 calculation with the cc-pV6Z basis set, the NEVPT2 calculation takes less than 14 min, which is ten times faster than NEVPT2-F12 with the double- ζ basis set. However, with the sextuple- ζ basis set, the CASSCF step becomes the bottleneck of the overall calculation. By using the RIJK approximation (RI for both Coulomb and exchange matrices), the CASSCF calculations can be sped up significantly. Nevertheless, a large amount of CPU time can be saved for the NEVPT2-F12 calculations, since the CASSCF step is much faster for small basis sets. In Table IV, the CPU time for RI-MP2-F12 calculations is also given. The CPU time for NEVPT2-F12 and MP2-F12 is comparable (excluding the SCF step). The bottlenecks in both NEVPT2-F12 and MP2-F12 are the same, which is the evaluation of two electron integrals. If the number of active MOs is considered as a small constant, the overall algorithm of NEVPT2-F12 scales as $O(N^5)$.

TABLE IV. The detailed CPU time (in minutes) of NEVPT2-F12 and RI-MP2-F12 for C₆H₆.

	NEVPT2-F12			NEVPT2	
	DZ-F12	TZ-F12	QZ-F12	cc-pV5Z	cc-pV6Z
CASSCF/iteration ^a	1.6	9.3	299.3(2.1)	58.4	797.1(45.5)
F12 matrices evaluation	146.0	658.4	3465.8
Hylleraas functional evaluation	0.1	0.4	1.8	2.2	13.3
		MP2-F12			
Self-consistent-field (SCF)/iteration	1.2	7.8	65.3
MP2-F12	83.7	460.8	2940.1

^aThe number given in parentheses is the CPU time of CASSCF with the RIJK approximation.

IV. CONCLUSION

In this study, we have derived and implemented the explicitly correlated NEVPT2 method, which is able to predict NEVPT2 correlation energies close to the complete basis set limit. Our ansatz is based on a fully internally contracted wave function. In addition to the correlation energy corrections for the doubly external subspaces, the energy correction for semi-internal excitation subspaces is included as well. This is instrumental to obtain very accurate correlation energies already with double- ζ basis sets. The findings are supported by the bond dissociation processes and low lying excitation energies studied in this article. The relative energies predicted by NEVPT2-F12 with double- ζ basis sets are already very close to the CBS limit. The computational cost of NEVPT2-F12 increases significantly compared to the canonical approach, especially for the calculations with the QZ-F12 basis set. However, an explicitly correlated calculation with a double- ζ basis set is computationally much more efficient than a conventional calculation with a quintuple- ζ basis set (including the SCF step). The NEVPT2-F12 with a double- ζ basis set can already produce comparable results as basis set extrapolation with the quintuple and sextuple- ζ basis sets. Further progress can be made by combining the NEVPT2-F12 method with the concept of pair natural orbitals, as shown in our recent work on DLPNO-MP2-F12¹⁷ or the work of Werner and co-workers on PNO-MP2-F12.¹⁶ The promising combination of NEVPT2-F12 with the DLPNO methodology will be reported in due course.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for detailed absolute reference or correlation energies.

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APPENDIX: The NEVPT2-F12 EQUATIONS FOR $S_{i,ab}^{(-1)}$ AND $S_a^{(-1)}$ SUBSPACES

The 1st-order wave functions for both NEVPT2 and NEVPT2-F12 have been given in Table I. By inserting the 1st-order wave functions into the Hylleraas functional and minimizing it, one will get two sets of linear equations. One set of equations is corresponding to the conventional NEVPT2 energy equations, and the other set is the equations for F12 amplitudes. For the $S_{i,ab}^{(-1)}$ subspace, the two residues read as

$$R_{ab}^{it} = (ialub) \Gamma_u^t + (\varepsilon_a + \varepsilon_b) T_{ab}^{iu} \Gamma_u^t + T_{ab}^{iu} K_u^t - \varepsilon_i T_{ab}^{iu} \Gamma_u^t + T_{ju}^{it} C_{jw}^{ab} \Gamma_u^w, \quad (\text{A1})$$

$$R_{jv}^{it} = V_{it}^{ju} \Gamma_u^v + T_{ku}^{it} B_{jv}^{kw} \Gamma_u^w + T_{ku}^{it} X_{jv}^{kw} K_u^w - \varepsilon_i T_{ku}^{it} X_{jv}^{kw} \Gamma_u^w + C_{jw}^{ab} T_{ab}^{it} \Gamma_v^w. \quad (\text{A2})$$

In Eq. (A2), the intermediates are defined as

$$V_{it}^{ju} = (i\alpha|t\beta) W_{\alpha\beta}^{ju}, \quad (\text{A3})$$

$$B_{jv}^{kw} = W_{\alpha\beta}^{kw} (f_\alpha + f_\beta) W_{\alpha\beta}^{jv}, \quad (\text{A4})$$

$$X_{jv}^{kw} = W_{\alpha\beta}^{kw} W_{\alpha\beta}^{jv}, \quad (\text{A5})$$

$$C_{jw}^{\alpha\beta} = W_{\alpha\beta}^{kw} (f_\alpha + f_\beta), \quad (\text{A6})$$

where $f_\alpha = \langle \alpha | \hat{f} | \alpha \rangle$ is the Fock matrix. The intermediates given above are evaluated in the same way as the single reference case.¹⁰

In the NEVPT2 calculation, the amplitudes T_{0ab}^{it} have been computed according to a residue similar to Eq. (A1). However, the residue in canonical NEVPT2 calculations does not contain the last term in Eq. (A1). Under the fixed amplitude approximation, an extra iteration must be performed to get the converged T_{ab}^{it} to make R_{ab}^{it} vanish. To avoid the extra iteration, the final Hylleraas functional value (total correlation energy) is computed as

$$E_{Total}^{S_{i,ab}^{(-1)}} = \tilde{T}_{0ab}^{it} \left[(ialub) \Gamma_u^t + R_{ab}^{it} \right] + \tilde{T}_{jv}^{it} \left[V_{it}^{ju} \Gamma_u^v + R_{jv}^{it} \right] = E_{NEVPT}^{S_{i,ab}^{(-1)}} + \tilde{T}_{0ab}^{it} \left[T_{ju}^{it} C_{jw}^{ab} \Gamma_u^w \right] + \tilde{T}_{jv}^{it} \left[V_{it}^{ju} \Gamma_u^v + R_{jv}^{it} \right] = E_{NEVPT}^{S_{i,ab}^{(-1)}} + E_{F12}^{S_{i,ab}^{(-1)}}. \quad (\text{A7})$$

In Eq. (A7), the exact T_{ab}^{it} amplitudes in R_{ju}^{it} are calculated by T_{0ab}^{it} ,

$$T_{ab}^{it} = T_{0ab}^{it} - T_{ju}^{it} \tilde{C}_{ab}^{it} = T_{0ab}^{it} - T_{ju}^{it} S_\mu^u \frac{C_{j\mu}^{ab}}{\varepsilon_a + \varepsilon_b - \varepsilon_i + \varepsilon_\mu}. \quad (\text{A8})$$

In Eq. (A8), the S_μ^t matrix is the transformation matrix, which diagonalizes the Koopmans matrix K_v^w with the density matrix $\Gamma_v^w = \langle 0 | E_v^w | 0 \rangle$. The final F12 correction energy can be written as

$$E_{F12}^{S_{i,ab}^{(-1)}} = 2 \left[V_{it}^{ju} (2T_{ju}^{it} - T_{ju}^{ti}) \Gamma_u^t + C_{it}^{ab} T_{0ab}^{ju} (2T_{ju}^{it} - T_{ju}^{ti}) \Gamma_u^t - T_{it}^{kv} C_{it}^{ab} \tilde{C}_{ab}^{kv} T_{ju}^{it} (2T_{ju}^{it} - T_{ju}^{ti}) \Gamma_u^t + T_{it}^{kv} B_{jv}^{ju} (2T_{ju}^{it} - T_{ju}^{ti}) \Gamma_u^t + T_{it}^{kv} X_{kv}^{ju} (2T_{ju}^{it} - T_{ju}^{ti}) K_u^t - \varepsilon_i T_{it}^{kv} X_{kv}^{ju} (2T_{ju}^{it} - T_{ju}^{ti}) \Gamma_u^t \right]. \quad (\text{A9})$$

The final result $E_{F12}^{S_{i,ab}^{(-1)}}$ is invariant with respect to unitary rotations within the active space.

For the $S_a^{(-1)}$ subspace, we can also derive two residues for NEVPT2 and NEVPT2-F12 from the Hylleraas functional,

$$R_{at}^{uv} = (walxy) \Gamma_{uv}^{wxy} + F'_{wa} \Gamma_{uv}^{wv} + \varepsilon_a T_{aw}^{xy} \Gamma_{uv}^{wxy} + T_{aw}^{xy} K_{uv}^{wxy} + T_{xy} \Gamma_{uv}^{wxy} W_{aw}^{xy}, \quad (\text{A10})$$

$$R_{xy}^{uv} = W_{\alpha w}^{xy} \tilde{T}_{uv}^{wxy} (t\alpha|uv) + \varepsilon_a W_{\alpha w}^{xy} \tilde{T}_{uv}^{wxy} W_{\alpha t}^{uv} + W_{\alpha w}^{xy} \tilde{K}_{uv}^{wxy} W_{\alpha t}^{uv} + W_{aw}^{xy} \Gamma_{uv}^{wxy} T_{at}^{uv}, \quad (\text{A11})$$

where

$$\tilde{\Gamma}_{tuv}^{wxy} = \Gamma_{tuv}^{wxy} - \sum_{zz'} \Gamma_{tu}^{vz} \Gamma_{wx}^{yz'} (\Gamma^{-1})_z^{z'},$$

$$\begin{aligned} \tilde{K}_{tuv}^{wxy} &= A_{tuv}^{wxy} - \sum_{zz'} B_{tu}^{vz} \Gamma_{wx}^{yz'} (\Gamma^{-1})_z^{z'} - \sum_{zz'} \Gamma_{tu}^{vz} C_{wx}^{yz'} (\Gamma^{-1})_z^{z'} \\ &+ \sum_{z_1 z_2} D_{z_4}^{z_3} \Gamma_{tu}^{vz_1} \Gamma_{wx}^{yz_2} (\Gamma^{-1})_{z_1}^{z_3} (\Gamma^{-1})_{z_2}^{z_4}. \end{aligned}$$

By using the amplitudes T_{0at}^{uv} from the NEVPT2 calculation, the total correlation energy expression takes the following form:

$$\begin{aligned} E_{Total}^{(-1)} &= E_{NEVPT}^{S_a^{(-1)}} + T_{0t\alpha}^{uv} \left[T_{xy}^{uv} \Gamma_{uv}^{wxy} W_{aw}^{xy} \right] \\ &+ T_{xy}^{uv} \left[W_{\alpha w}^{xy} \tilde{\Gamma}_{uv}^{wxy} (t\alpha luv) + R_{xy}^{uv} \right] \\ &= E_{NEVPT}^{S_a^{(-1)}} + E_{F12}^{S_a^{(-1)}}. \end{aligned} \quad (\text{A12})$$

Since the energy corrections for semi-internal excitation subspaces are already very small, T_{0at}^{uv} is used as the approximation of converged T_{at}^{uv} in the last term of Eq. (A11).

In the above equations for both $S_{i,ab}^{(-1)}$ and $S_a^{(-1)}$, density and Koopmans matrices have been defined in our previous work.⁴⁶ The matrices A_{tuv}^{wxy} , B_{tu}^{vz} , C_{tu}^{vz} , $D_{z_4}^{z_3}$ have the same definition as $S_a^{(-1)}$ subspace in strongly contracted NEVPT2 (SC-NEVPT2).⁵⁹ The equations of other subspaces can be derived in the similar way.

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