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ABSTRACT

A factorization of the matrix elements of the Dyll Hamiltonian in N -electron valence state perturbation theory allowing their evaluation with a computational effort comparable to the one needed for the construction of the third-order reduced density matrix at the most is presented. Thus, the computational bottleneck arising from explicit evaluation of the fourth-order density matrix is avoided. It is also shown that the residual terms arising in the case of an approximate complete active space configuration interaction solution and containing even the fifth-order density matrix for two excitation classes can be evaluated with little additional effort by choosing again a favorable factorization of the corresponding matrix elements. An analogous argument is also provided for avoiding the fourth-order density matrix in complete active space second-order perturbation theory. Practical calculations indicate that such an approach leads to a considerable gain in computational efficiency without any compromise in numerical accuracy or stability.

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I. INTRODUCTION

The complete active space self-consistent field (CASSCF) method¹ offers a possibility to account for static electron correlation in cases where the electronic state of a molecule cannot even be approximately described by a single Slater determinant. This happens if chemical bonds are broken and also in many transition metal complexes. The wave function resulting from this approach serves as a starting point for the treatment of dynamic electron correlation. However, the multiconfigurational nature of such wave functions leads to complications compared to the single reference case. Multireference configuration interaction (MRCI) based on uncontracted wave functions^{2,3} is, in general, far too expensive and shares the lack of size consistency with any limited configuration interaction (CI) approach. This, of course, also holds for the more efficient contracted MRCI versions^{4–10} where double excitation operators are applied to the reference wave function instead of individual

configuration state functions (CSFs). Multireference coupled cluster (MRCC)^{11–17} theory is complex from a theoretical point of view and still too expensive if applied to larger systems. Extensions of the coupled electron pair approximation (CEPA) to the multireference case have been proposed but have not yet reached the stage of practical applicability.^{18–24} Thus, one is left with multireference perturbation theory as a viable alternative for the treatment of dynamic electron correlation in the multireference case. The most popular methods in this context are complete active space second-order perturbation theory (CASPT2)^{25,26} and second-order N -electron valence state perturbation theory (NEVPT2).^{27–29} The computational bottleneck in the fully internally contracted (FIC) version of both of these methods is the appearance of the fourth-order density matrix in certain matrix elements. Apart from the possibility to avoid higher-order density matrices altogether by using an uncontracted ansatz for certain excitation classes,³⁰ time-dependent NEVPT2 theory equivalent to a Laplace transformation of energy denominators

and yielding uncontracted results,^{31,32} a stochastic approach in the context of strongly contracted NEVPT2 (SC-NEVPT2),³³ alternative post-CASSCF treatments such as the driven similarity renormalization group second-order perturbation theory (DSRG-PT2),^{34–37} or the multireference adiabatic connection (AC) formalism,³⁸ several approximations for the evaluation of the fourth-order density matrix have been suggested. The cumulant (CU) approximation has been applied for both CASPT2^{39–41} and NEVPT2.⁴² However, “false” intruder states arising from the application of this approximation to NEVPT2⁴² indicate a lack of reliability. Another possibility to approximate the fourth-order density matrix arises from prescreening (PS) and extended PS (EPS).⁴³ While this approach leads to computational savings and also to reliable quantitative results for sufficiently conservative thresholds, it does not change the unfavorable scaling behavior inherent in the construction of the fourth-order density matrix. A possibility to compute the terms involving the fourth-order density matrix with the same computational cost as those involving the third-order density matrix has been found by Kurashige and Yanai⁴⁴ for the CASPT2 method based on a density matrix renormalization group (DMRG) CASSCF reference function. Another strategy for the contraction of the Fock matrix with the fourth-order density matrix in the context of DMRG-CASPT2 has been suggested by Wouters *et al.*⁴⁵ An important and more general idea to reduce the computational effort for the evaluation of matrix elements involving the fourth-order density matrix without making any approximation has been presented by Chatterjee and Sokolov⁴⁶ for NEVPT2. The factorization suggested by these authors has also been used in the efficient implementation of internally contracted multireference configuration interaction theory,^{6,47} and it benefits from a shift of all creation and annihilation operators involved in the contraction with two-electron repulsion integrals toward the left end of the operator chain, thus reducing the computational effort to a level comparable to the one needed for the evaluation of the third-order density matrix. A modified version of this approach adapting to a formulation of the corresponding matrix elements in terms of excitation operators as given in the original paper of Angeli *et al.*²⁹ will be presented in the following. Another problem concerns only NEVPT2. As a consequence of the “rank reduction trick,” there is a residual with matrix elements involving even the fifth-order density matrix, which vanishes in the case of an exact complete active space configuration interaction (CASCI) solution but not for approximate solutions such as the density matrix renormalization group (DMRG),^{48–50} full configuration interaction Quantum Monte Carlo (FCIQMC),⁵¹ the semistochastic heat-bath configuration interaction (SHCI) method,⁵² selected CI methods (CIPSI: configuration interaction using a perturbative selection carried out iteratively),^{2,53–60} or the iterative configuration expansion (ICE),⁶¹ which are needed for large active spaces where an exact solution is no longer affordable. Such approximative solutions of the CASCI problem have been used with NEVPT2.^{62–66} Although false intruder states have been reported in this context,⁶⁴ their origin has been investigated only recently using the full rank NEVPT2 (FR-NEVPT2) method,⁶⁷ which takes into account the above-mentioned residual. It will be shown that this residual can also be factorized such that the computational effort becomes comparable to the one needed for the evaluation of the third-order density matrix. The same holds for the matrix elements involving the fourth-order density matrix in CASPT2 as will also be demonstrated.

II. AVOIDING THE EVALUATION OF THE FOURTH-ORDER AND FIFTH-ORDER DENSITY MATRICES IN THE MATRIX ELEMENTS OF THE DYALL HAMILTONIAN

Using indices $p, q, \dots, i, j, \dots, t, u, \dots$, and a, b, \dots for general, doubly occupied, active, and virtual orbitals, respectively, and defining electron and hole excitation operators summed up over spin (spin label: σ) as

$$\hat{E}_{pq} = \sum_{\sigma} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} \quad (1)$$

and

$$\hat{E}_{pq} = 2\delta_{pq} - \hat{E}_{qp}, \quad (2)$$

the Dyall Hamiltonian⁶⁸ used in NEVPT2 reads

$$\hat{H}^D = \hat{H}_i + \hat{H}_v \quad (3)$$

with

$$\hat{H}_i = \sum_{ij} F_{ij} \hat{E}_{ij} + \sum_{ab} F_{ab} \hat{E}_{ab} + C \quad (4)$$

and

$$\hat{H}_v = \sum_{tu} h_{tu}^{\text{eff}} \hat{E}_{tu} + \frac{1}{2} \sum_{tuvw} \langle tv|uw \rangle (\hat{E}_{tu} \hat{E}_{vw} - \delta_{uv} \hat{E}_{tw}), \quad (5)$$

where the Fock matrix is given by

$$F_{pq} = h_{pq}^{\text{eff}} + \sum_{tu} \langle \hat{E}_{tu} \rangle \left(\langle pt|qu \rangle - \frac{1}{2} \langle pt|uq \rangle \right) \quad (6)$$

with

$$h_{pq}^{\text{eff}} = h_{pq} + \sum_k (2 \langle pk|qk \rangle - \langle pk|kq \rangle). \quad (7)$$

The constant C in Eq. (4) is chosen such that

$$\hat{H}^D |\Psi^0\rangle = E^0 |\Psi^0\rangle \quad (8)$$

with $E^0 = \langle \Psi^0 | \hat{H} | \Psi^0 \rangle$. $|\Psi^0\rangle = \sum_I C_I |\Phi_I\rangle$ is a CASCI eigenfunction given as a linear combination of configuration state functions (CSFs) $|\Phi_I\rangle$ and E^0 is the corresponding eigenvalue.

In the following, we consider the fully internally contracted version of NEVPT2 (FIC-NEVPT2). The matrix elements of the Dyall Hamiltonian that require most of the computational effort are the ones involving doubly excited fully internally contracted wave functions $|\Psi_{tu}^{av}\rangle = \hat{E}_{at} \hat{E}_{vu} |\Psi^0\rangle$ and $|\Psi_{tu}^{tv}\rangle = \hat{E}_{ti} \hat{E}_{vu} |\Psi^0\rangle$. Using the abbreviation $\langle \hat{E}_{tu} \dots \rangle = \langle \Psi^0 | \hat{E}_{tu} \dots | \Psi^0 \rangle$ for the density matrices, the corresponding matrix elements can be written as

$$\begin{aligned}
 \langle \Psi_{i'v'}^{a'u'} | \hat{H}^D - E^0 | \Psi_{iu}^{tv} \rangle &= \langle \Psi^0 | (\hat{E}_{i't'} \hat{E}_{v'u'})^\dagger [\hat{H}^D, \hat{E}_{ti} \hat{E}_{vu}] | \Psi^0 \rangle + \langle \Psi^0 | (\hat{E}_{i't'} \hat{E}_{v'u'})^\dagger \hat{E}_{ti} \hat{E}_{vu} (\hat{H}^D - E^0) | \Psi^0 \rangle \\
 &= -F_{i't'} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vu} \rangle + \delta_{i't'} (K_{i't'v'u',tvu}^{1'} + R_{i't'v'u',tvu}^{1'}), \\
 \langle \Psi_{i'u'}^{a'u'} | \hat{H}^D - E^0 | \Psi_{iu}^{av} \rangle &= \langle \Psi^0 | (\hat{E}_{a't'} \hat{E}_{v'u'})^\dagger [\hat{H}^D, \hat{E}_{at} \hat{E}_{vu}] | \Psi^0 \rangle + \langle \Psi^0 | (\hat{E}_{a't'} \hat{E}_{v'u'})^\dagger \hat{E}_{at} \hat{E}_{vu} (\hat{H}^D - E^0) | \Psi^0 \rangle \\
 &= F_{a't'} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vu} \rangle + \delta_{a't'} (K_{i't'v'u',tvu}^{-1'} + R_{i't'v'u',tvu}^{-1'}).
 \end{aligned} \tag{9}$$

Equation (9) contains Koopmans matrices with the following elements:

$$\begin{aligned}
 K_{i't'v'u',tvu}^{-1'} &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \rangle + \sum_{wxy} \langle wx|vy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \hat{E}_{xy} \rangle - \sum_w h_{uw}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle \\
 &\quad - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{xy} \hat{E}_{vw} \rangle - \sum_w \left(h_{tw}^{eff} - \sum_x \langle xt|wx \rangle \right) \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle - \sum_{wxy} \langle xt|yw \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{xy} \hat{E}_{vw} \rangle
 \end{aligned} \tag{10}$$

and

$$\begin{aligned}
 K_{i't'v'u',tvu}^{1'} &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \rangle + \sum_{wxy} \langle wx|vy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \hat{E}_{xy} \rangle - \sum_w h_{uw}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle \\
 &\quad - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{xy} \hat{E}_{vw} \rangle + \sum_w h_{wt}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle + \sum_{wxy} \langle wx|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{xy} \hat{E}_{vw} \rangle.
 \end{aligned} \tag{11}$$

The expressions in Eqs. (10) and (11) differ from those given by Angeli *et al.*²⁹ by the order of the excitation operators in the operator chains with four excitation operators. This leads to a slightly more compact notation. The original form given by Angeli *et al.* can be restored by using the commutator relation

$$[E_{xy}, E_{vw}] = E_{xw} \delta_{vy} - E_{vy} \delta_{wx} \tag{12}$$

for shifting the excitation operators to appropriate positions. Equation (9) also illustrates the “rank reduction trick”⁶⁸ based on a shift of the Dyall Hamiltonian to the very right of the operator chain and resulting in residuals

$$R_{i't'v'u',tvu}^{-1'} = \langle \Psi^0 | \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vu} (\hat{H}^D - E^0) | \Psi^0 \rangle \tag{13}$$

and

$$R_{i't'v'u',tvu}^{1'} = \langle \Psi^0 | \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vu} (\hat{H}^D - E^0) | \Psi^0 \rangle, \tag{14}$$

which vanish for an *exact* solution of the CASCI problem within the CASSCF procedure because the corresponding CASCI wave function $|\Psi^0\rangle$ is also an exact eigenfunction of the Dyall Hamiltonian. Thus, the residuals that contain the fifth-order density matrix can be avoided in such a case. For large active spaces, however, it is often not possible to obtain an exact CASCI solution within a reasonably small period of time so that it becomes necessary to resort to approximations. However, the eigenvalue spectrum of the Dyall Hamiltonian

is very sensitive with respect to such approximations if the residual terms are neglected. Thus, even very small deviations from the exact CASCI solution can lead to a serious deterioration of the eigenvalue spectrum of the Dyall Hamiltonian, as indicated by “false” intruder states.⁴² The neglect of the residuals is then no longer possible. Both the factorization of the Koopmans matrices and the residuals will be considered in the following.

A. Factorization of the Koopmans matrices

Looking at the elements of the Koopmans matrices as given by Eqs. (10) and (11), it can be seen that they involve elements of the fourth-order density matrix, the evaluation of which, in general, represents the computational bottleneck in NEVPT2 calculations. It is, therefore, desirable to keep the computational cost for the evaluation of these matrix elements as low as possible. For a more favorable factorization of these matrix elements, we adopt an idea of Chatterjee and Sokolov⁴⁶ who shifted all operators in the operator chain of the density matrices with indices involved in the contraction with two-electron integrals to the left end of the chain. With the matrix elements given by Eqs. (10) and (11), we find it more convenient to shift these operators to the right end. Following this strategy, i.e., shifting the excitation operator involving two summation indices to the very right of the operator chain and the excitation operator involving one summation index to the neighboring position left of the former if necessary and using Eq. (2), one ends up with

$$\begin{aligned}
 K_{i't'v'u',tvu}^{-1'} &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \rangle + \sum_{wxy} \langle wx|vy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{wu} \hat{E}_{xy} \rangle - \sum_w h_{uw}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \hat{E}_{xy} \rangle \\
 &\quad - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} [\hat{E}_{xy}, \hat{E}_{vw}] \rangle - \sum_w \left(h_{tw}^{eff} - \sum_x \langle xt|wx \rangle \right) \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \rangle - \sum_{wxy} \langle xt|yw \rangle \langle \hat{E}_{u'v'} \hat{E}_{i't'} \hat{E}_{vw} \hat{E}_{xy} \rangle \\
 &\quad - \sum_{wxy} \langle xt|yw \rangle \langle \hat{E}_{u'v'} [\hat{E}_{i't'} \hat{E}_{xy}, \hat{E}_{vw}] \rangle
 \end{aligned} \tag{15}$$

and

$$\begin{aligned}
 K_{t'v'u',tvu}^I &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \rangle + \sum_{wxy} \langle wx|vy \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \hat{E}_{xy} \rangle - \sum_w h_{uw}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{t't} E_{vw} \rangle \\
 &\quad - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vw} \hat{E}_{xy} \rangle - \sum_{wxy} \langle ux|wy \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} [\hat{E}_{xy}, \hat{E}_{vw}] \rangle + \sum_w h_{wt}^{eff} \langle E_{u'v'} \hat{E}_{t'tw} E_{vu} \rangle \\
 &\quad + 2 \sum_{xy} \langle t'x|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{xy} \hat{E}_{vu} \rangle - \sum_{wxy} \langle wx|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{vw} \hat{E}_{wt'} \hat{E}_{xy} \rangle - \sum_{wxy} \langle wx|ty \rangle \langle \hat{E}_{u'v'} [\hat{E}_{wt'} \hat{E}_{xy}, \hat{E}_{vu}] \rangle.
 \end{aligned} \tag{16}$$

Defining the intermediates

$$\begin{aligned}
 X_{tu}^I &= \sum_{wxy} \langle \Phi_I | E_{wt} E_{xy} \rangle \langle wx|uy \rangle, \\
 Y_{tu}^I &= \sum_{wvw} \langle \Phi_I | E_{tw} E_{xy} \rangle \langle ux|wy \rangle,
 \end{aligned} \tag{17}$$

inserting the unit operator $\sum_I |\Phi_I\rangle \langle \Phi_I|$ in the CASCI space in front of the excitation operators involved in the contraction with two-electron repulsion integrals, and using the commutator relation in Eq. (12), one ends up with

$$\begin{aligned}
 K_{t'v'u',tvu}^{-1} &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \rangle + \sum_I \langle \hat{E}_{u'v'} \hat{E}_{t't} | \Phi_I \rangle X_{uv}^I - \sum_w \left(h_{uw}^{eff} - \sum_x \langle ux|xw \rangle \right) \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vw} \rangle \\
 &\quad - \sum_I \langle \hat{E}_{u'v'} \hat{E}_{t't} | \Phi_I \rangle Y_{vu}^I - \sum_{wx} \langle ux|wv \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{xw} \rangle - \sum_w \left(h_{tw}^{eff} - \sum_x \langle xt|wx \rangle \right) \langle \hat{E}_{u'v'} \hat{E}_{t'tw} \hat{E}_{vu} \rangle \\
 &\quad - \sum_I \langle \hat{E}_{u'v'} \hat{E}_{vu} | \Phi_I \rangle Y_{t't}^I - \sum_{wx} \langle xt|vw \rangle \langle \hat{E}_{u'v'} \hat{E}_{t'tw} \hat{E}_{xu} \rangle + \sum_{wy} \langle ut|yw \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vy} \rangle \\
 &\quad - \sum_{xy} \langle xt|yv \rangle \langle \hat{E}_{u'v'} \hat{E}_{t'tu} \hat{E}_{xy} \rangle + \delta_{t'u} \sum_{wxy} \langle xt|yw \rangle \langle \hat{E}_{u'v'} \hat{E}_{vw} \hat{E}_{xy} \rangle
 \end{aligned} \tag{18}$$

and

$$\begin{aligned}
 K_{t'v'u',tvu}^I &= \sum_w h_{wv}^{eff} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \rangle + \sum_I \langle \hat{E}_{u'v'} \hat{E}_{t't} | \Phi_I \rangle X_{uv}^I - \sum_w \left(h_{uw}^{eff} - \sum_x \langle ux|xw \rangle \right) \langle \hat{E}_{u'v'} \hat{E}_{t't} E_{vw} \rangle \\
 &\quad - \sum_I \langle \hat{E}_{u'v'} \hat{E}_{t't} | \Phi_I \rangle Y_{vu}^I - \sum_{wx} \langle ux|wv \rangle \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{xw} \rangle + \sum_w h_{wt}^{eff} \langle E_{u'v'} \hat{E}_{t'tw} E_{vu} \rangle + 2 \sum_{xy} \langle t'x|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{xy} \hat{E}_{vu} \rangle \\
 &\quad - \sum_I \langle \hat{E}_{u'v'} \hat{E}_{vu} | \Phi_I \rangle X_{t't}^I - \sum_{wx} \langle wx|tv \rangle \langle \hat{E}_{u'v'} \hat{E}_{wt'} \hat{E}_{xu} \rangle + \sum_{wy} \langle wu|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{wt'} \hat{E}_{vy} \rangle \\
 &\quad - \delta_{vt'} \sum_{wxy} \langle wx|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{wu} \hat{E}_{xy} \rangle + \sum_{xy} \langle ux|ty \rangle \langle \hat{E}_{u'v'} \hat{E}_{vt'} \hat{E}_{xy} \rangle.
 \end{aligned} \tag{19}$$

Writing the third-order density matrix as

$$\langle E_{u'v'} E_{t't} E_{vu} \rangle = \sum_I \langle E_{u'v'} E_{t't} | \Phi_I \rangle C_{vu}^I$$

with

$$C_{vu}^I = \langle \Phi_I | E_{vu} \rangle, \tag{20}$$

it can easily be seen that the terms containing the matrices X^I and Y^I in Eqs. (18) and (19) have the same structure so that the computational effort for their evaluation is reduced to a level comparable to the one needed for the evaluation of the third-order density matrix, which should thus lead to a considerable speed-up of NEVPT2 calculations. Note that these intermediates can be evaluated at a low computational cost. Their size of $N_{CSF} * N_{act}^2$ (N_{CSF} : number of CSF's, N_{act} : number of active orbitals) should not pose any memory problems because intermediates of the same size generally appear in the

evaluation of density matrices. The remaining terms in Eqs. (18) and (19) involve only the third-order density matrix, which has to be evaluated anyway. The intermediates in Eqs. (18) and (19) differ from the ones used by Chatterjee and Sokolov⁴⁶ insofar, as the latter contain a different number of creation and annihilation operators, whereas these numbers are, of course, equal in the present case. This is a consequence of using excitation operators instead of separate creation and annihilation operators.

B. Factorization of the residuals

The residuals Eqs. (13) and (14) can be analyzed in an analogous fashion. It is, of course, the active part \hat{H}_v of the Dyall Hamiltonian, which leads to the appearance of even fifth-order density matrix elements in the residuals. Inserting the unit operator $\sum_I |\Phi_I\rangle \langle \Phi_I|$ in the CASCI space in front of the Hamiltonian, the

relevant term in the residual Eq. (13) reads

$$\langle \Psi^0 | E_{u'v'} E_{t't} E_{vu} \hat{H}_v | \Psi^0 \rangle = \sum_I \langle E_{u'v'} E_{t't} E_{vu} | \Phi_I \rangle Z_I \quad (21)$$

with

$$Z_I = \langle \Phi_I | \hat{H}_v | \Psi^0 \rangle. \quad (22)$$

The structural analogy of Eq. (21) to the third-order density matrix as given by

$$\langle E_{u'v'} E_{t't} E_{vu} \rangle = \sum_I \langle E_{u'v'} E_{t't} E_{vu} | \Phi_I \rangle C_I \quad (23)$$

$$\begin{aligned} \langle \Psi_{t'u'}^{v'} | \hat{H}_0 - E^0 | \Psi_{iu}^{tv} \rangle &= -F_{ii'} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \rangle + \delta_{ii'} \left(\sum_w F_{wv} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \rangle - \sum_w F_{uw} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vw} \rangle + \sum_w F_{wt} \langle \hat{E}_{u'v'} \hat{E}_{t'w} \hat{E}_{vu} \rangle \right. \\ &\quad \left. + \sum_{ww'} F_{ww'} (\langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \hat{E}_{ww'} \rangle - \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \rangle \langle \hat{E}_{ww'} \rangle) \right), \\ \langle \Psi_{t'u'}^{a'} | \hat{H}_0 - E^0 | \Psi_{iu}^{av} \rangle &= F_{aa'} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \rangle + \delta_{aa'} \left(\sum_w F_{wv} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{wu} \rangle - \sum_w F_{uw} \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vw} \rangle - \sum_w F_{tw} \langle \hat{E}_{u'v'} \hat{E}_{t'w} \hat{E}_{vu} \rangle \right. \\ &\quad \left. + \sum_{ww'} F_{ww'} (\langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \hat{E}_{ww'} \rangle - \langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \rangle \langle \hat{E}_{ww'} \rangle) \right), \end{aligned} \quad (24)$$

where \hat{H}_0 is the zeroth-order Hamiltonian of CASPT2. Note that the excitation operators corresponding to Fock matrix elements have been shifted to the very right end of the operator chain in an analogy to the “rank reduction trick” in NEVPT2. The terms involving the fourth-order density matrices in Eq. (24) have the same structure as the corresponding term in Eq. (21) of the NEVPT2 residual and can be simplified analogously. One has

$$\sum_{ww'} F_{ww'} (\langle \hat{E}_{u'v'} \hat{E}_{t't} \hat{E}_{vu} \hat{E}_{ww'} \rangle) = \sum_I \langle E_{u'v'} E_{t't} E_{vu} | \Phi_I \rangle Z_I \quad (25)$$

with

$$Z_I = \sum_{ww'} F_{ww'} \langle \Phi_I | \hat{E}_{ww'} | \Psi^0 \rangle. \quad (26)$$

The structural analogy of Eq. (25) to the third-order density matrix is again obvious.

is again obvious.

III. AVOIDING THE EVALUATION OF THE FOURTH-ORDER DENSITY MATRICES IN CASPT2

The “trick” used in Sec. II B for the evaluation of the residual in NEVPT2 can also be applied to avoid the evaluation of the fourth-order density matrix in fully internally contracted CASPT2 (FIC-CASPT2). The most expensive matrix elements from a computational point of view are again those involving doubly excited fully internally contracted wave functions $|\Psi_{iu}^{av}\rangle = \hat{E}_{at} \hat{E}_{vu} |\Psi^0\rangle$ and $|\Psi_{iu}^{tv}\rangle = \hat{E}_{ti} \hat{E}_{vu} |\Psi^0\rangle$. These can be written as

IV. NUMERICAL RESULTS

The approach described in Secs. II and III has been implemented in the ORCA program package (version 5.0),⁶⁹ which has been used for the results presented in the following. *Trans*-stilbene with a relatively large (14,14) CAS has been chosen as an example. The calculations for this molecule have been carried out with a single core on a machine with four processors “Intel Xeon E7-8867 v3 @ 2.50 GHz” and a total of 3 TB available memory. The def2-TZVP basis set⁷⁰ has been used in combination with the RIJK⁷¹ approximation and the Def2/JK auxiliary basis.⁷² The geometry of the molecule is identical to the one given in a previous calculation⁴³ and also shown in the [supplementary material](#). The factorization described in Secs. II and III has been combined with the prescreening approach.⁴³ Table I shows the computation times for

TABLE I. Computation time for NEVPT2 and CASPT2 calculations of *trans*-stilbene with a (14,14) CAS in hours as a function of the threshold T^{PS} for the prescreening. The results are shown for the old default implementation of NEVPT2 in ORCA [NEVPT2 (old)] and the new factorization without (NEVPT2) and with inclusion of the residual (FR-NEVPT2) along with the results for the efficient ORCA implementation of CASPT2. Computation times for the terms involving the fourth-order density matrix (D4), for the residual in the case of FR-NEVPT2 (res), and for the iterative solution of a system of linear equations taking into account the interclass interaction for CASPT2 (iter) are given in addition to the total time for the respective perturbation calculation. The time for the CASSCF calculation preceding the perturbative treatment is also shown.

T^{PS}	CASSCF	NEVPT2 (old)		NEVPT2		FR-NEVPT2			CASPT2		
		D4	Total	D4	Total	D4	res	Total	D4	iter	Total
10^{-14}	8.28	130.55	132.31	3.59	5.01	3.59	1.56	6.57	2.55	0.66	4.59
10^{-12}	8.28	121.16	122.54	3.55	4.98	3.54	1.55	6.53	2.56	0.65	4.56
10^{-10}	8.28	75.95	77.32	3.20	4.62	3.21	1.46	6.08	2.57	1.11	5.04

various perturbation methods, i.e., NEVPT2 for both the old ORCA implementation and the new factorization described in this contribution, NEVPT2 including the residuals given by Eqs. (13) and (14) (FR-NEVPT2), and CASPT2 results for the efficient implementation avoiding the fourth-order density matrix. Apart from the total computation time for a distinct perturbation method, Table I also contains the time needed to evaluate the terms involving the elements of the fourth-order density matrix, i.e., their contraction with two-electron repulsion integrals (D4) and the time needed for the evaluation of the residual in the case of FR-NEVPT2 (res). Since CASPT2 takes into account the interclass interaction,^{25,26} it requires the iterative solution of a system of linear equations. The time consumed for this step is a function of the number of iteration cycles, which, in turn, depends on the prescreening parameter T^{PS} . Results for three different values of this parameter are given in Table I. Stable solutions are obtained for $T^{PS} = 10^{-14}$ and $T^{PS} = 10^{-12}$, whereas intruders in the sense of the appearance of negative energy denominators in the perturbation expansion are observed for $T^{PS} = 10^{-10}$ for both NEVPT2 and CASPT2. This increases the number of iteration cycles needed for the solution of the system of linear equations in the case of CASPT2 from seven ($T^{PS} = 10^{-14}$ and $T^{PS} = 10^{-12}$) to twelve ($T^{PS} = 10^{-10}$). Thus, the time consumed in this step is also given in Table I (iter). The computation time for the CASSCF calculation preceding the perturbation treatment shown in Table I is only intended to give a rough estimate because it can vary strongly depending on the initial guess for the orbitals, the methods used for the update of the orbitals and CASCI coefficients, and other parameters. Here, we used the super-CI-PT approach^{73,74} for the orbital update and MP2 natural orbitals as an initial guess, resulting in 38 CASSCF iterations. Looking at the numbers in Table I, one arrives at the following conclusions: (1) comparing NEVPT2 results, the gain in efficiency arising from the new factorization is impressive. The evaluation of the terms involving the fourth-order density matrix is still the most expensive step of the perturbation calculation, but the total time is now even lower than that of the preceding CASSCF calculation in this particular example. It should also be noted that no additional memory is needed for the new implementation compared to the old implementation. The peak memory usage was about 10 gigabyte in both cases for the stilbene example. (2) FR-NEVPT2 calculations including the residual are now affordable because the additional time needed for the evaluation of the latter is fairly small. (3) The dependence of the computation time on the prescreening parameter T^{PS} is strongly reduced for the new factorization of NEVPT2. Thus, one can use much smaller values for it, which increases the stability of the results.⁴³ In the case of CASPT2, this dependence is even negligible for this particular example. Without going into the details, we mention that this is due to the fact that the reduction in T^{PS} reduces the length of the CI expansion but has almost no effect on the size of the RI space needed for the evaluation of density matrices. The numbers in Table I even suggest an opposite effect, i.e., an increase in the computation time for the D4 terms with decreasing prescreening parameter, but this is the consequence of a certain spread in the determination of computation times that are never exactly reproducible.

Table II shows the errors of the total electronic energy as a function of the threshold T^{PS} . Contrary to what one would expect, one also observes that the errors due to prescreening are different for the old and the new approaches. This is a consequence of

TABLE II. Errors of the total electronic energy for a NEVPT2 calculation of *trans*-stilbene with a (14,14) CAS as a function of the threshold T^{PS} for the prescreening in μH . The results are shown for the old default implementation of NEVPT2 in ORCA [NEVPT2 (old)] and the new factorization without (NEVPT2) and with inclusion of the residual (FR-NEVPT2) along with the results for the efficient ORCA implementation of CASPT2.

T^{PS}	NEVPT2 (old)	NEVPT2	FR-NEVPT2	CASPT2
10^{-14}	0	-1	-1	0
10^{-12}	-1	4	4	6
10^{-10}	34	-26	-86	-49

the use of different working equations for the evaluation of the Koopmans matrices. While the old approach is based on the formulas given by Angeli *et al.* in their original paper,²⁹ the new approach employs Eqs. (18) and (19). Thus, the contraction of the elements of the fourth-order density matrix with the electron repulsion integrals is different in the two cases, leading to different results due to the limited accuracy of the mathematical operations performed by the computer. It is important to note in this context that the prescreening constant T^{PS} and, thus, the CASCI wave function are varied only for the evaluation of the fourth-order density matrix, and not, however, for the density matrices of lower order.

Further calculations have been performed for two transition metal complexes. First, a [Fe(II)-TPP] complex has been chosen for which a state-averaged CASSCF calculation for the triplet ground and three excited states with a (12,15) CAS comprising the Fe 3d, the equatorial sigma bonding ligand orbital, the empty Fe 4d orbitals, and the four Gouterman orbitals⁷⁵ has been performed. The subsequent perturbation theory calculations also involved these four states. They have been carried out with 8 cores on a machine with four processors “Intel Xeon E7-8867 v3 @ 2.50 GHz” and a total of 3 TB available memory, whereas 16 cores on the same machine have been used for the CASSCF calculation. The geometry of the molecule is shown in the [supplementary material](#). The second example is a spin-frustrated [Co(depa)Cl]₃ complex, the geometry of which is given in the [supplementary material](#). The calculations have been performed for the degenerate doublet ground state with a (21,15) CAS involving the Co 3d orbitals. 16 cores on a machine with four processors “Intel Xeon E7-8867 v4 @ 2.50 GHz” and a total of 3 TB available memory have been employed for this calculation. The def2-TZVP basis set⁷⁰ has been used for both complexes. In addition, the two-electron integrals entering the CASSCF gradient and the perturbation theory are approximated using the resolution of identity with the Def2-TZVP/C auxiliary basis set.⁷⁶ The Fock matrices are also approximated using the RIJCOSX approximation^{77,78} in conjunction with the Def2/J auxiliary basis set⁷⁹ in the case of the [Fe(II)-TPP] complex and the RIJK approximation⁷¹ with the Def2/JK⁷² auxiliary basis for [Co(depa)Cl]₃. The latter consists of 105 atoms with 2115 basis functions, whereas the former comprises 89 atoms with 1873 basis functions. It should be noted that the interclass interaction in the CASPT2 calculations had to be omitted (CASPT2-D) as the present (canonical) implementation requires substantial hard disk space for the storage of the wave function. The timings obtained with a prescreening constant of $T^{PS} = 10^{-14}$ are shown in Table III. One observes basically the same trends as for

TABLE III. Computation time for NEVPT2 and CASPT2 calculations of [Fe(II)-TPP] with a (12,15) CAS and [Co(depa)Cl]₃ with a (21,15) CAS in hours for $T^{PS} = 10^{-14}$. The results are shown for the old default implementation of NEVPT2 in ORCA [NEVPT2 (old)] and the new factorization without (NEVPT2) and with inclusion of the residual (FR-NEVPT2) along with results for the efficient ORCA implementation of CASPT2. Computation times for the terms involving the fourth-order density matrix (D4) and for the residual in the case of FR-NEVPT2 (res) are given in addition to the total time for the respective perturbation calculation. The time for the CASSCF calculation preceding the perturbative treatment is also shown.

	CASSCF	NEVPT2 (old)		NEVPT2		FR-NEVPT2			CASPT2-D	
		D4	Total	D4	Total	D4	res	Total	D4	Total
[Fe(II)-TPP]	10.88	319.69	325.79	6.50	12.69	6.51	0.01	12.71	4.42	11.45
[Co(depa)Cl] ₃	2.45	4.76	6.96	0.34	2.50	0.33	0.12	2.62	0.27	2.97

stilbene, i.e., large computational savings for the expensive D4 terms and negligible computational effort for the evaluation of the residual in FR-NEVPT2.

V. CONCLUSIONS

It has been shown that all relevant matrix elements in FIC-NEVPT2 can be calculated at a computational cost comparable to the one needed for the evaluation of the third-order density matrix at the most. In the case of prescreening, i.e., a truncated CASCI wave function, it will be somewhat higher for two reasons. First, the sum in Eq. (23) or Eq. (20) runs over the CSFs contained in the truncated CI space, whereas the corresponding sums for the intermediates X_{uv}^I , Y_{uv}^I , and Z^I run over the CI space needed for a resolution of the identity (RI), which is larger than the truncated CI space. Second, the RI space needed for the evaluation of the third-order density matrix comprises all CSFs obtained from $E_{tu}|\Phi_I\rangle$ with $|\Phi_I\rangle$ being CSFs in the truncated CI space. The corresponding RI space in the matrix elements $\sum_I \langle \hat{E}_{v'u'} \hat{E}_{t't} |\Phi_I\rangle X_{uv}^I$ and Eq. (21) is larger because it consists of all possible CSFs obtained from $E_{tu}E_{vv}|\Phi_I\rangle$. Thus, the evaluation of the terms involving the fourth-order density matrix still represents the most expensive part of the perturbation calculations. Nonetheless, the factorization given in this contribution leads to a total speed-up by almost two orders of magnitude compared to the old ORCA implementation for NEVPT2 calculations with a large CAS. It can even be faster than the preceding CASSCF calculation and can be applied to any approach based on the RI method for the evaluation of higher-order density matrices. Moreover, it can be used in conjunction with any CASCI eigensolver. In summary, we think that the factorization of matrix elements presented in this contribution represents an important step forward in the development of efficient multireference methods.

SUPPLEMENTARY MATERIAL

The Cartesian coordinates of the molecules treated in Sec. IV are given in the [supplementary material](#).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and the [supplementary material](#).

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