THE LAPLACE TRANSFORM PERTURBATIVE TRIPLES CORRECTION ANSATZ

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

We describe the implementation of the spin-unrestricted Laplace transform fourth-order perturbative triples correction. A reduction in the computational scaling with respect to canonical implementations is attained without relying on the large molecule asymptote. The intrinsic scaling difficulties that the Laplace equations exhibit upon increasing the size of the basis sets are properly addressed. The method is suited for medium-size molecules.
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The complexity and computational cost of electron correlation theories increase rapidly with the level of approach and the size of the systems considered. Configuration interaction (CI)[1] and coupled cluster (CC)[2,3] theories must include at least up to triple excitations in the accurate treatment of atoms and molecules[4–6]. Denoting by N the measure of a system size, *e.g.* the number of basis functions, the computational cost scales in principle as $\mathcal{O}(N^8)$ in an iterative-equation-solving procedure[7,8]. This high computational cost has spurred the development of a number of augmented techniques[7,9–11]. These techniques correct the energies from the singles and doubles wavefunctions with a perturbative, non-iterative triples contribution, which scales as $\mathcal{O}(N^7)$. Among the augmented approaches, the CCSD(T) method[12], which includes the connected coupled cluster singles and doubles and a fourth- and fifth-order triples correction, is regarded as possibly the best balance between efficiency and accuracy. It should be mentioned that recently much work has also been carried out in the development of so-called linear scaling coupled cluster methods[13–15].

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Many-body perturbative expansions have been historically formulated in the canonical spin-orbital basis, *i.e.*, the basis that diagonalizes the Fock operator. The resulting equations are simpler and exhibit a lower computational prefactor. The perturbative triples expression consists formally of a series of $\mathcal{O}(N^{10})$ terms. Each term is composed of a product of two integrals and two amplitudes that are divided by a sum of six diagonal Fock elements. Conveniently arranged, the summation over the ten-index series can be performed in $\mathcal{O}(N^7)$ steps. Häser and Almlöf first noted that a more advantageous $\mathcal{O}(N^6)$ arrangement is still attainable provided the energy denominators are factorized[16]. The factorization is feasible if the denominators are substituted by a Laplace transform quadrature. An alternative factorization based on the Cholesky decomposition of the denominators has also been proposed recently[17].

The introduction of the Laplace ansatz not only simplifies the sequences of tensor contractions. Once the Laplace kernel is factorized and included as part of attenuated integrals and amplitudes, the canonical constraint is lifted. The resulting equations are invariant under unitary orbital transforms, although they keep the simplicity and closed form of the canonical formulation. The advantages of these transforms have already been demonstrated in early works on low-order perturbation theory[16,18,19]. Indeed, localized, atomic representations have produced accurate linear scaling approaches to MP2 energies[20]. The energy invariance under unitary transforms of the virtual spin-orbitals facilitates removing an intrinsic inefficiency in the factorized, fourth-order triples correction[21]. Although the whole set of equations scales as $\mathcal{O}(N^6)$ as much, they exhibit an unfavorable dependency on large basis sets. Some contributions specifically scale as $\mathcal{O}(OV^5)$, for O being the number of occupied orbitals and V the number of virtuals. The projection of the attenuated integrals and amplitudes into a generalized natural orbital basis permits an efficient screening that reduces to $\mathcal{O}(OV^4)$ the computation of these contributions.

The present article extends our previous implementation[21] of the Laplace factorization of the perturbative triples to the unrestricted, open-shell case. It focuses on the derivation of the fourth-order terms and on the analysis of their accuracy and performance. The number of Laplace fifth-order terms is substantially reduced. The most expensive ones exhibit only an $\mathcal{O}(O^3V^3)$ scaling. Although their contribution is important for the accuracy of most (T) methods, the implementation is left to a separate paper.

The article is organized as follows. The section *Triple Substitutions in Fourth-Order Perturbation Theory* introduces first the canonical triples equations. In the subsection *Laplace Factorization*, the Laplace transform quadrature is applied, triples terms are rearranged and integrated. Then, subsection *Large Basis Sets* introduces the generalized natural orbital projection and subsection *Screening* presents improved techniques that simplify intermediate computations. The next section, *Benchmarks*, focuses on the two main performance-related issues, *i.e.*, efficiency and accuracy. While computational efficiency is centered on the CCSD(T) method, accuracy is also analyzed for BD(T)[22], QCISD(T)[23–25] and MP4(T)[9,26]. The subsection *Effective Scalings* presents an illustrative, practical approach to the triples complexity. In subsection *Accuracy*, Laplace triples energy deviations are analyzed. The subsection *Naphthalene, an Illustrative Computation* treats together efficiency and accuracy from an applied point of view. Final remarks are presented in the *Conclusions* section.

TRIPLE SUBSTITUTIONS IN FOURTH-ORDER PERTURBATION THEORY

The fourth-order contribution to triple substitution presents the general form[9]

$$E_{\mathrm{T}}^{[4]} = -\frac{1}{36}\sum_{ijk}\sum_{abc} |W_{ijk}^{abc}|^2 / D_{ijk}^{abc} . \qquad (1)$$

Triple excitations W_{ijk}^{abc} factorize as products of the two-electron quantities t_{rs}^{pq} and v_{rs}^{pq},

$$W_{ijk}^{abc} = P_{ij}^{k} P_{ab}^{c}\left[\sum_{f} t_{ij}^{af} v_{kf}^{cb} - \sum_{m} t_{im}^{ac} v_{bm}^{jk}\right]. \qquad (2)$$

Quantities t_{rs}^{pq} are the amplitudes for the converged singles and doubles wavefunctions and v_{rs}^{pq} are integrals antisymmetrized according to

$$v_{rs}^{pq} = \langle rs||pq\rangle = \langle rs|pq\rangle - \langle rs|qp\rangle . \qquad (3)$$

Operators P_{qr}^{p} perform the antisymmetric permutations of index p with indices q and r,

$$P_{qr}^{p}(\bullet) = \bullet_{pqr} - \bullet_{qpr} - \bullet_{rpq} . \qquad (4)$$

Denominators D_{ijk}^{abc} in Eq. (*1*) are given by the difference of diagonal elements of the considered reference determinant

$$D_{ijk}^{abc} \equiv f_{aa} + f_{bb} + f_{cc} - f_{ii} - f_{jj} - f_{kk} \,. \tag{5}$$

As usual, indices *p*, *q*, *r*, *s*, ... refer to unspecified spin-orbitals. Indices *i*, *j*, *k*, ..., (*a*, *b*, *c*, ...) specifically refer to occupied (unoccupied) spin-orbitals in the reference configuration. The number of occupied (unoccupied) orbitals will be denoted as O_α and O_β (V_α and V_β), according to spin cases. Number *N* will refer to the number of correlated orbitals, without specifying spin or their occupied or virtual nature, thus simply representing a size measure of the electronic system.

The augmented methods CCSD(T) and QCISD(T) include an additional correction to properly balance the contribution of single and double excitations. This particular, fifth-order addition, $E_{\mathrm{ST}}^{[5]}$, is given by[12,23]

$$E_{\mathrm{ST}}^{[5]} = -\sum_{ijk} \sum_{abc} V_{ijk}^{abc} W_{ijk}^{abc} \, / \, D_{ijk}^{abc} \,, \tag{6}$$

with V_{ijk}^{abc} being

$$V_{ijk}^{abc} = P_{ij}^{k} P_{ab}^{c} [t_i^a v_{jk}^{bc}]. \tag{7}$$

The triples (T) correction is finally computed as

$$E_{(\mathrm{T})} = E_{\mathrm{T}}^{[4]} + E_{\mathrm{ST}}^{[5]} \tag{8}$$

in a non-iterative, $\mathcal{O}(O^3V^4 + O^4V^3)$ procedure.

Laplace Factorization

The Laplace transform of the denominators D_{ijk}^{abc} in Eq. (*1*) gives the fourth-order triples contribution $E_{\mathrm{T}}^{[4]}$ as the integral

$$E_{\mathrm{T}}^{[4]} = -\frac{1}{36} \int_0^\infty \sum_{ijk} \sum_{abc} |W_{ijk}^{abc}|^2 \, \mathrm{e}^{-D_{ijk}^{abc} s} \mathrm{d}s \,. \tag{9}$$

Expanding integral (*9*) in a finite series yields the formula

$$E_{\mathrm{T}}^{[4]} = \frac{1}{36}\sum_{l} w_l \sum_{ijk}\sum_{abc} |W_{ijk}^{abc}|^2 \, \mathrm{e}^{-D_{ijk}^{abc} s_l} , \qquad (10)$$

where w_l are appropriate quadrature weights. The factorization of the Laplace kernel permits to express the energy $E_{\mathrm{T}}^{[4]}$ in terms of attenuated amplitudes and integrals $\bar{t}(s_l)$ and $\bar{v}(s_l)$,

$$E_{\mathrm{T}}^{[4]} = \frac{1}{36}\sum_{l} w_l \, | P_{ij}^{k} P_{ab}^{c} \Big[\bar{t}_{ij}^{af} \bar{v}_{kf}^{cb} - \bar{t}_{im}^{ac} \bar{v}_{bm}^{jk} \Big] |^2 . \qquad (11)$$

Summation over repeated indices is assumed and the s_l dependence of the amplitudes and integrals is removed for notation simplicity. Barred quantities $\bar{t}_{ij}^{af}$, $\bar{v}_{kf}^{cb}$, $\bar{t}_{im}^{ac}$ and $\bar{v}_{bm}^{jk}$ are, respectively, $t_{ij}^{af} e^{s_l (f_{ii} + f_{jj} - f_{aa})/2}$, $v_{kf}^{cb} e^{s_l (f_{kk} - f_{bb} - f_{cc})/2}$, $t_{im}^{ac} e^{s_l (f_{ii} - f_{aa} - f_{cc})/2}$ and $v_{bm}^{jk} e^{s_l (f_{jj} + f_{kk} - f_{bb})/2}$.

Denoting by o any of the occupied indices i, j, k, and by v any of the a, b, c virtuals, the complete expansion of Eq. (*11*) leads to 9^2 terms for each of the three sets characterized by templates $\bar{t}_{oo}^{vf} \bar{t}_{oo}^{vg} \bar{v}_{of}^{vv} \bar{v}_{og}^{vv}$, $\bar{t}_{om}^{vv} \bar{t}_{on}^{vv} \bar{v}_{vm}^{oo} \bar{v}_{vn}^{oo}$ and $\bar{t}_{oo}^{vf} \bar{t}_{om}^{vv} \bar{v}_{of}^{vv} \bar{v}_{vm}^{oo}$. Hereafter these sets will be denoted by $\{fg\}$, $\{mn\}$ and $\{fm\}$, respectively.

Thus, there are in total 243 spin-orbit terms contributing to the $E_{\mathrm{T}}^{[4]}$ energy. For the sake of computational efficiency, these terms are classified and computed according to spin cases. Each expanded term implies a summation over 8 indices. In turn, each index runs over the spin alpha and beta cases. Splitting the above 243 terms according to spin cases leads to a total of 243 2^8, *i.e.*, 62 208 terms. After checking for spin orthogonalities, this amount is reduced to 1314 non-zero terms for each set. The redundancies arising from having 8 different indices on a four-factor product of four-index arrays permit additional simplifications. Accordingly, sets $\{fg\}$ and $\{mn\}$ each posses 34 non-redundant terms, while group $\{fm\}$ has 44 different contributions. In summary, after expanding and simplifying Eq. (*11*), the unrestricted Laplace $E_{\mathrm{T}}^{[4]}$ energy is reduced to a total of 112 terms.

A representative term, denoted by $e_1^{\{fg\}}$, *i.e.*, the first term in set $\{fg\}$, is

$$e_1^{\{fg\}} = (\bar{t}_{i\alpha j\alpha}^{a\alpha f\alpha} \bar{t}_{i\alpha j\alpha}^{c\alpha g\alpha})(\bar{v}_{k\alpha f\alpha}^{b\alpha c\alpha} \bar{v}_{k\alpha g\alpha}^{a\alpha b\alpha}) . \qquad (12)$$

The parentheses indicate its lowest scaling contraction. Amplitudes are contracted by summing over i and j, while integrals over k and b. The contribution $e_1^{\{fg\}}$ is then evaluated by summing up f, g, a and c. In this way, the eight-index summation scales as $O(O_\alpha^2 V_\alpha^4 + O_\alpha V_\alpha^5)$, or, in short, as $O(N^6)$. Although there is a combinatorial number of possible summation schemes for $e_1^{\{fg\}}$, the lowest, $O(N^6)$ one is unique. This same property applies to the complete set of $E_T^{[4]}$ terms. The lowest scaling Laplace arrangement has then 88 terms scaling as $O(N^6)$ and 24 ones scaling as $O(N^5)$.

According to this set classification of terms, the energy expression reads

$$E_T^{[4]} = \frac{1}{36} \sum_l w_l [e^{\{fg\}}(s_l) + e^{\{mn\}}(s_l) - 2e^{\{fm\}}(s_l)], \qquad (13)$$

where each contribution $e^{\{pq\}}$ is the sum of all the terms in the set. In our implementation indices *fg*, *mn*, and *fm* are taken as the outermost loops. For each of those pairs, the inner tensor contractions are performed as matrix multiplications. Thus, the two contractions in Eq. (*12*) are done for each *f* and *g*, as a summation over *ij* for all *a* and *c*, and a summation over *kb* for all *a* and *c*. The result are two $V_\alpha V_\alpha$ matrices, $\mathbf{t}_{(fg)}$ and $\mathbf{v}_{(fg)}$, coming from the amplitude and integral contractions, respectively. The *fg* portion of term $e_1^{\{fg\}}$ is then the trace $\mathrm{Tr}[\mathbf{t}_{(fg)}\mathbf{v}_{(fg)}]$. Although the complete number of terms is 112 and each term considers two tensor contractions, the number of different intermediate matrices is only 132. If Eq. (*13*) is evaluated according to the spin blocks in the sets *fg*, *mn* and *fm*, storage of no more than six matrices suffices for a complete reuse of intermediates. In addition, using few appropriate permutations of the intermediates, the portions *fg* and *mn* of the sums $e^{\{fg\}}$ and $e^{\{mn\}}$ are symmetric, *i.e.*, $e_{fg}^{\{fg\}} = e_{gf}^{\{fg\}}$ and $e_{mn}^{\{mn\}} = e_{nm}^{\{mn\}}$.

The numerical integration of the Laplace transform, Eq. (*9*), is simple yet accurate[21]. The integration is over a series of exponential functions that is monotonically decreasing and positive everywhere. Substituting variable *s* by the logarithm transformation

$$s = \frac{-1}{D_{\min}} \ln x \qquad (14)$$

the integrand becomes a power series, formally

$$E_T^{[4]} = \frac{-1}{D_{\min}} \int_0^1 \sum_\nu z_\nu x^{\frac{D_\nu}{D_{\min}} - 1} \mathrm{d}x. \qquad (15)$$

Series coefficients z_ν and powers D_ν are readily identifiable from Eq. (*9*). Parameter D_{min} is the triples gap, *i.e.*, the minimum denominator. Such a choice minimizes the series slope and, therefore, the error bounds in the quadrature. Quadrature is easily and conveniently performed using the Gauss–Legendre open rule. This integration scheme is accurate. It produces triple corrections within mE_h to μE_h accuracy using few, no more than two to four quadrature points.

Large Basis Sets

The efficient implementation of the triples Laplace ansatz needs to address an intrinsic large basis set penalty. Of the complete set of 132 different tensor contractions, there are 8 that scale as $\mathcal{O}(OV^5)$ for increasing basis sets. This introduces a serious disadvantage of the method with respect to the canonical $\mathcal{O}(O^3V^4)$ implementation.

The invariance of the Laplace energy, Eq. (*11*), upon unitary transformations of the attenuated virtual (occupied) spin-orbitals facilitates, however, the evaluation of those contractions. As pointed by Klopper *et al.*[27] the convergence to complete basis set for triple excitations is fast enough to permit reliable truncations of the virtual space. Natural orbitals (NO) provide such a convenient way to fasten convergence.

Generalized NOs are here defined as the set that diagonalizes the second-order probability density matrix $D^{(2)}$, of elements

$$D^{(2)}_{a\alpha b\alpha} = t^{a\alpha c\alpha}_{i\alpha j\alpha} t^{b\alpha c\alpha}_{i\alpha j\alpha} + 2t^{a\alpha c\beta}_{i\alpha j\beta} t^{b\alpha c\beta}_{i\alpha j\beta} , \tag{16}$$

$$D^{(2)}_{a\beta b\beta} = t^{a\beta c\beta}_{i\beta j\beta} t^{b\beta c\beta}_{i\beta j\beta} + 2t^{a\beta c\alpha}_{i\beta j\alpha} t^{b\beta c\alpha}_{i\beta j\alpha} \tag{17}$$

and

$$D^{(2)}_{a\alpha b\beta} = D^{(2)}_{a\beta b\alpha} = 0 , \tag{18}$$

constructed through the converged, doubles amplitudes. The spin-block diagonalization of $D^{(2)}$ produces two unitary matrices R_α and R_β which define the transformation to the natural virtual orbital basis. The transformation R_α or R_β is then applied, respectively, to each virtual index α or β, to project integrals $\bar{v}$ and amplitudes $\bar{t}$ at each quadrature point. Upon this basis change, the matrix $\mathbf{e}^{\{fg\}}$ of elements $e^{\{fg\}}_{fg}$ or in short e_{fg} is best suited for screening.

Screening

The computation of the contributions $e^{\{fg\}}(s_l)$, in Eq. (*13*), is performed according to an ordered procedure, from the smallest value of s to the largest. The summation over the indices f and g is done according to spin blocks, *i.e.*, first over $f_\alpha g_\alpha$ or $f_\beta g_\beta$ and then over $f_\alpha g_\beta$. Screening criteria are applied to identify negligible e_{fg} elements. Being matrix $\mathbf{e}^{\{fg\}}$ positive definite, the inequality

$$e_{fg}^2 \le e_{ff} e_{gg} - \frac{1}{e_{hh}} (e_{ff}^{1/2} e_{gh} - e_{gg}^{1/2} e_{fh})^2 \qquad (19)$$

holds for all indices f, g and h. Inequality proof follows from the positiveness of all principal minors of $\mathbf{e}^{\{fg\}}$ and from the Cauchy–Schwarz inequality[28]. The sequence to complete the summation $e^{\{fg\}}(s_1)$ begins by evaluating the elements e_{11} and e_{22}. Then, e_{21} is evaluated only if the product $e_{11}e_{22}$ is greater than a threshold τ. Next in the sequence is the computation of element e_{33}. Element e_{32} is computed provided $e_{22}e_{33} > \tau$. The evaluation of e_{31} is then decided through the improved Cauchy–Schwarz criterion, inequality (*19*), using the off-diagonal elements e_{31} and e_{21}. In this way, the non-negligible terms are computed and summed, for f equal 1 to V and for g equal f to 1. Computed nondiagonal elements e_{gh} and e_{fh} are successively incorporated to sharpen the inference criteria. The improvement over a simple Cauchy–Schwarz screening appears to be dependent on the system and the basis set considered.

The effectiveness of the screening increases with the basis set size. Figures 1 and 2 show the $\mathbf{e}^{\{fg\}}$ matrix density plots for benzene molecule, in CCSD(T) = fc/cc-pVDZ and CCSD(T) = fc/aug-cc-pVDZ computations, respectively, performed trough a two-point quadrature. In black are depicted the matrix elements such that $|e_{fg}| > 10^{-6}$. In white, the elements inferred to be smaller than 10^{-6} by inequality (*19*). Grey elements are smaller than this threshold though undetected by rule (*19*). The diagonal elements are always computed. They appear either black or grey, accordingly.

At the quadrature point s_1, the whole $\mathbf{e}^{\{fg\}}$ needs to be computed for the smallest basis set cc-pVDZ, Fig. 1. At the point s_2, computational savings start being notorious. Figure 2 visualizes the fact of the increasing number of negligible e_{fg} elements as basis sets are enlarged. Matrix density plots are also reported for benzene computations running through the closed- and open-shell implementation. Screening patterns are similar in both implementations. The peculiarities of these patterns, *i.e.*, the sparsity shown at the low *f*, *g* values, are a consequence of ordering the eigenvalues and eigenvectors of the generalized density matrix $D^{(2)}$. Upon the rotation of the virtual orbitals, the diagonal elements of the $\mathbf{e}^{\{fg\}}$ matrix appear in an approximate ascending order. The off-diagonal elements with low *f* or *g* indices are thus smaller and most likely inferred to be negligible.

Suitable additional speedup is available by assuming the inequality

$$|e_{fg}(s_{l+1})| \leq |e_{fg}(s_l)| \qquad (20)$$

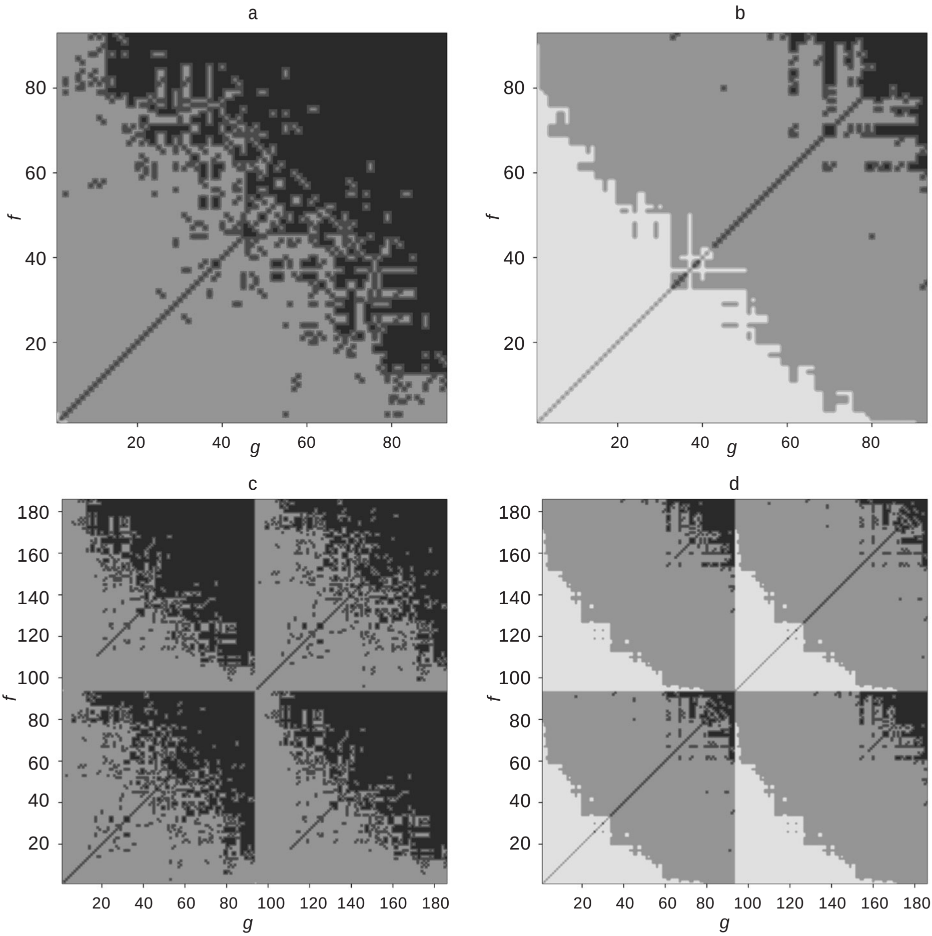

FIG. 1
Matrix $\mathbf{e}^{\{fg\}}(s_i)$ density plots for the benzene CCSD(T) = fc/cc-pVDZ computation at quadrature points a s_1 and b s_2; c and d are the corresponding open-shell code $\mathbf{e}^{\{fg\}}(s_i)$ density plots

for all $s_{l+1} \geq s_l$. Computed off-diagonal terms that appear to be below τ at the point s_l are disregarded from computation at the next point s_{l+1}. The exponential attenuation of the integrals and amplitudes introduced by the Laplace weights permits a significant reduction in the number of elements to be computed. Figures 1 and 2 also illustrate the Laplace attenuation. Gray, computed elements at point s_1 are no longer evaluated at point s_2.

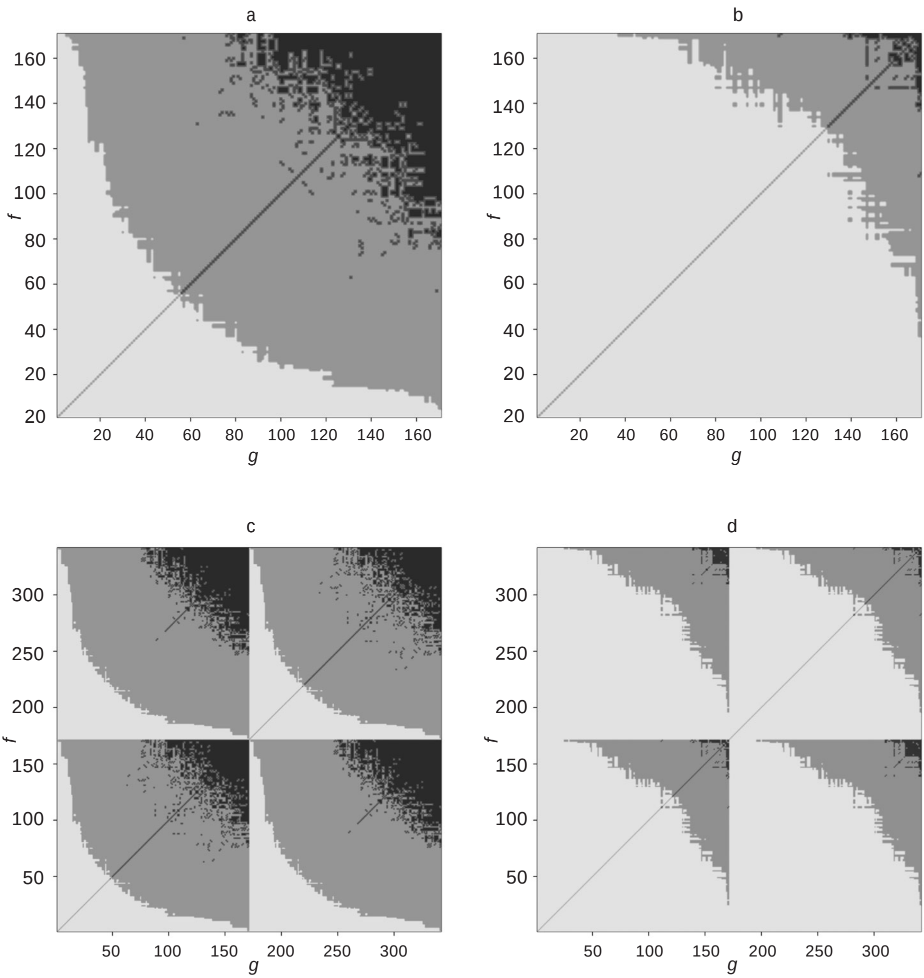

FIG. 2
Matrix $\mathbf{e}^{\{fg\}}(s_i)$ density plots for the benzene CCSD(T) = fc/aug-cc-pVDZ computation at quadrature points a s_1 and b s_2; c and d are the corresponding open-shell code $\mathbf{e}^{\{fg\}}(s_i)$ density plots

BENCHMARKS

The performance of the implemented Laplace ansatz for the triples correction is being analyzed in a series of benchmark computations. The implementation is tested and included in the *Gaussian* development version[29]. All computations are performed on a single processor of an IBM-p690 Power4 machine. The screening threshold τ is set to 10^{-6} in all computations. This is a rather conservative value that keeps truncation errors below the ones intrinsic to the two- and three-point integrations used here.

Effective Scalings

The actual scaling behavior of the Laplace triples ansatz is complicated by the complexity of its 112 terms and by the applied screenings. The following series of computations provide a practical illustration. Triples timings *versus* size results are plotted in Figs 3 and 4 for Laplace and canonical computations running on closed- and open-shell codes. A two-point quadrature is used in all these Laplace computations. Figure 3 presents time variations as the number of virtuals V increases while the number of occupied orbitals O is kept constant. Computations are performed for the neon atom at the CCSD(T) = full/cc-pV*n*Z levels, with n ranging from double to sextuple polarization. By fitting time values to a power curve $t(V) = aV^b$, the determined scalings b are approximately 3.8 in all four sets of computations. Thus, the $\mathcal{O}(OV^5)$ penalty on Laplace CCSD(T) and UCCSD(T) is completely removed by the proposed screening.

Figure 4 presents time variations with respect to the number of virtuals at a constant V/O ratio. Chains of 2, 4, 6, 8 and 10 neon atoms are considered. Atoms are placed at distance d_{NeNe} equal to 2.5 Å. Computations are performed at the CCSD(T) = fc/cc-pVDZ level. The fitted b parameter is here 5.5 for the open- and closed-shell Laplace curves. The corresponding canonical implementations present a scaling of 6.7, clearly one order of magnitude more. Crossover between Laplace and canonical lies between three and four Ne atoms.

An analogous procedure is used to estimate the effective scaling varying occupied orbitals with a fixed number of virtuals. The four-atom chains Ne[4] and $\mathrm{Ne[4]}^{2-}$ are used, at the levels CCSD(T) = fc/cc-pVDZ and CCSD(T) = full/cc-pVDZ. The scaling with respect to the number of occupied orbitals O is 2.4 and 3.5 for the Laplace and canonical implementations, respectively. This dependency clearly favors the Laplace implementation on core-valence correlation computations.

Accuracy

The Laplace implementation of the perturbative triples correction includes two numerical approaches. The Laplace transform itself is numerically computed and the matrix elements in $\mathbf{e}^{\{fg\}}$ are screened to either reduce the prefactor and the effective scaling. Thus the scaling advantages of the Laplace implementation with respect to the canonical one have to be con-

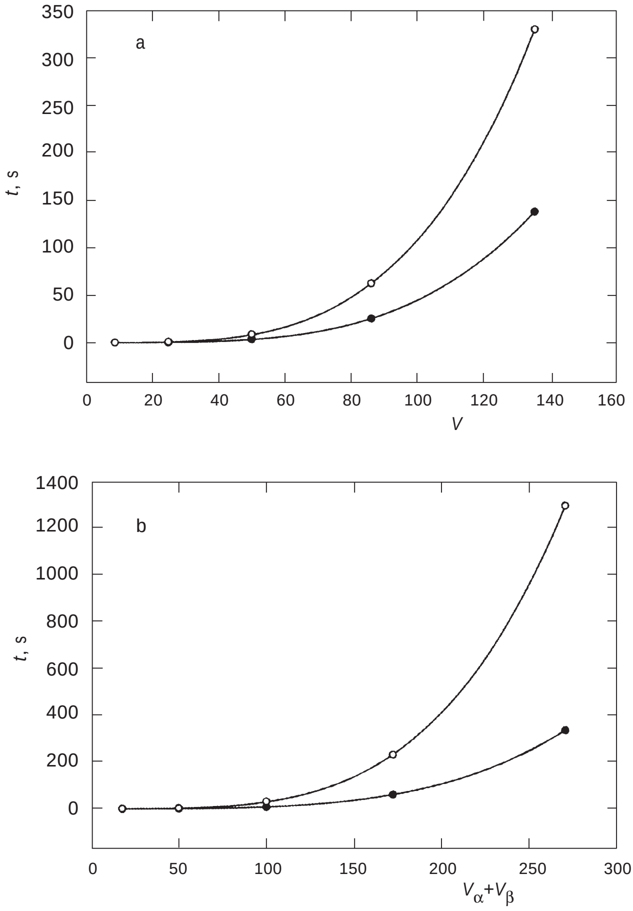

FIG. 3

Triples timing *versus* the number of virtuals V (O = *const.*) for the neon atom, at CCSD(T) = full/cc-pVnZ, n = 2, 6, using a two-point quadrature and a threshold $\tau = 10^{-6}$. a closed-shell, b open-shell codes. Open marks indicate the timings for the Laplace computations while solid marks correspond to canonical computations. The fitted parameter b – see text – is 3.8 for all four curves trasted by the attainable level of accuracy. In order to assess the Laplace triples accuracy, the G2/97 test set of molecules[30,31] is considered. For simplicity, only the Dunning's cc-pVDZ basis set with frozen core orbitals is used here. Molecules containing Li, Be, Na or Mg atoms are excluded from the G2/97 test set. Also excluded are the species ^4N and $^4O^+$ due to an extremely short triples gap that complicates the logarithm transform used in

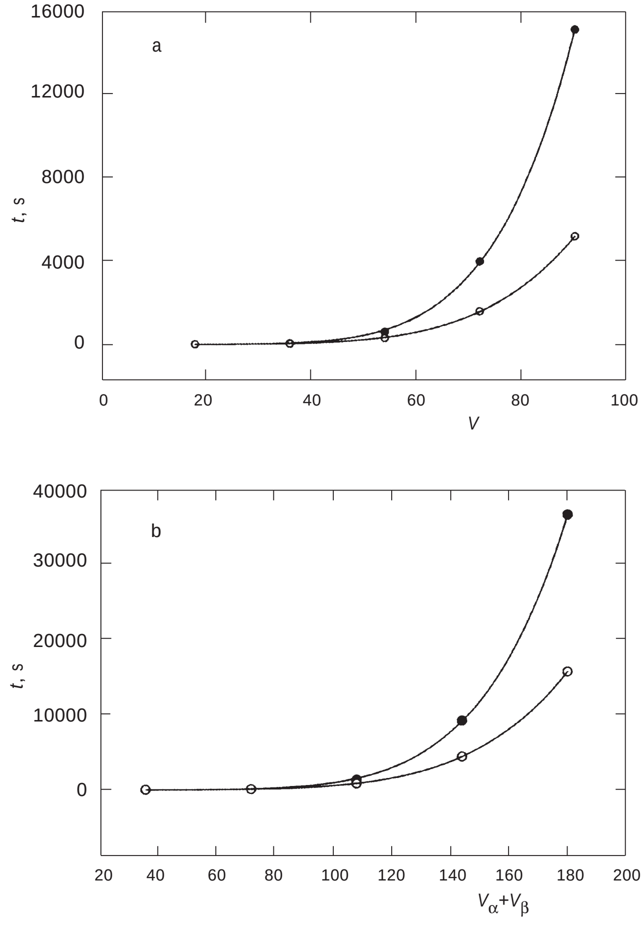

FIG. 4

Triples timing *versus* number of virtuals V (O = *const.*) for neon chains of 2, 4, 6, 8 and 10 atoms, at CCSD(T) = fc/cc-pVDZ, using a two-point quadrature and a threshold $\tau = 10^{-6}$. a closed-shell, b open-shell codes. Open marks indicate the timings for the Laplace computations while solid marks correspond to canonical computations. The fitted parameter b – see text – is 5.5 for the Laplace curves and 6.7 for the canonical ones the Laplace quadrature. In total, 288 molecules are considered, with 131 open-shell and 157 closed-shell computations.

The fourth-order triples correction $E_T^{[4]}$ is computed for CCSD(T), BD(T), QCISD(T) and MP4(T). Although all four methods share the same triples equations, amplitude values may differ significantly. A separate analysis of accuracy is therefore desirable for each of them. Table I reports the mean absolute deviation $|\Delta_e|$, the minimal and maximal deviations, Δ_{min} and Δ_{max}, respectively, and the percentiles 10 and 90, p_{10} and p_{90}, for the four methods.

The two- and three-point quadratures provide energies completely within mE_h accuracy in all molecules and methods. Maximal negative differences include the small species CN^+, CF_4 and N_2O in all methods, though on a slightly different ranking. At the other end, maximal positive differences correspond to the atoms $^3B^-$, ^4C and $^1N^+$. Except for some outlayers, as shown by the percentile values, the accuracy using a three-point quadrature is close to μE_h accuracy for the 230 molecules within p_{10} and p_{90}.

Naphthalene, an Illustrative Computation

A practical example on the accuracy and computational gains of the Laplace ansatz is presented here. Accuracy is analyzed in terms of thermochemical and absorption data. Computational speedups are reported as ra-

TABLE I
Mean absolute deviation, minimum and maximum deviations and percentiles 10 and 90 of Laplace *versus* canonical $E_T^{[4]}$ energies, for the G2/97 test set of molecules and for the number n of quadrature points. Deviations Δ in mE_h

Method	n	$\lvert\overline{\Delta}\rvert$	Δ_{min}	Δ_{max}	p_{10}	p_{90}
CCSD(T)	2	0.049	–0.086	1.077	–0.013	0.114
	3	0.019	–0.048	0.848	–0.014	0.003
BD(T)	2	0.053	–0.084	1.084	–0.012	0.119
	3	0.018	–0.038	0.830	–0.013	0.003
QCISD(T)	2	0.049	–0.092	1.079	–0.015	0.113
	3	0.019	–0.056	0.848	–0.015	0.003
MP4(T)	2	0.039	–0.095	0.504	–0.011	0.115
	3	0.012	–0.046	0.466	–0.014	0.005

tios over the canonical triples. The selected benchmark is the singlet and triplet states of naphthalene. Their planar geometries are optimized at the MP2(full)/6-31g(d) level of theory and the triples $E_{\mathrm{T}}^{[4]}$ energies are computed at the CCSD(T) = fc/cc-pVDZ and CCSD(T) = full/cc-pVDZ level. The Laplace ansatz, as in the previous section, considers two- and three-point quadratures.

Table II reports the values of the canonical $E_{\mathrm{T}}^{[4]}$ energies, heats of formation $\Delta_f H_0$, and the singlet-triplet gap $\Delta E_{\mathrm{T}\leftarrow\mathrm{S}}$. Laplace values are the corresponding deviations, expressed as mE_{h}, kcal/mol and eV, respectively. Timing ratios $t_{\mathrm{C}}/t_{\mathrm{L}}$ refear to canonical over Laplace, and t_{pp} are averaged times per quadrature point, on the time-scale given by the extent of the canonical computation.

Accuracy follows a similar pattern as the one seen in the G2/97 set analysis. Core-correlated energies exhibit a sensibly lower accuracy due to the larger range of energy denominators appearing in the transform quadrature. In all cases, however, heats $\Delta_f H_0$ deviate less than 1 kcal/mol if two in-

TABLE II
Canonical *versus* Laplace singlet and triplet CCSD(T)/cc-pVDZ energies for naphthalene. The number of quadrature points is n. Timings $t_{\mathrm{C/L}}$ are canonical with respect to Laplace ratios and t_{pp} are per quadrature point with respect to the canonical time

Parameter	Singlet			Triplet		
	canonical	n = 2	n = 3	canonical	n = 2	n = 3
$E_{\mathrm{T}}^{[4]a}$	–64.718	–0.784	–0.052	–64.367	–1.017	–0.022
$\Delta_{\mathrm{f}}H_0{}^b$	–2004.84	–0.49	–0.03	–1938.85	–0.64	–0.01
$\Delta E_{\mathrm{T}\leftarrow\mathrm{S}}{}^c$				2.86	–0.03	0.00
$t_{\mathrm{C}}/t_{\mathrm{L}}$		1.57	1.20		1.25	0.96
t_{pp}		0.32	0.28		0.40	0.35
			full			
$E_{\mathrm{T}}^{[4]a}$	–65.209	–1.239	–0.193	–64.866	–1.500	–0.189
$\Delta_{\mathrm{f}}H_0{}^b$	–2012.56	–0.78	–0.12	–1946.50	–0.94	–0.12
$\Delta E_{\mathrm{T}\leftarrow\mathrm{S}}{}^c$				2.86	–0.04	–0.01
$t_{\mathrm{C}}/t_{\mathrm{L}}$		2.90	2.23		2.25	1.71
t_{pp}		0.17	0.15		0.22	0.19

[a] In mE_{h}. [b] In kcal/mol. [c] In eV.

tegration points are used, and around a tenth of kcal/mol for a three-point quadrature. Singlet-triplet gaps $\Delta E_{T \leftarrow S}$ appear in all cases within hundredth eV accuracy.

The crossover with respect canonical implementations is sensitive to the number of occupied orbitals involved in the computation. Systems rich in hydrogen atoms or frozen-core computations on light atoms exhibit crossover at relatively large sizes. There is a strong contrast between the naphthalene t_C/t_L ratios in Table II and the attained crossover at the Ne[4] chain for those equivalent, CCSD(T) = fc calculations. The higher prefactors effecting Laplace implementations need to be absorbed by their scaling advantages. As seen before, both Laplace and canonical implementations exhibit an effective $\mathcal{O}(V^4)$ scaling. On the other hand, the prefactor-scaling tradeoff easily favors Laplace transform if the number of involved occupied orbitals O is large. The effective scalings are then $\mathcal{O}(O^{2.4})$ and $\mathcal{O}(O^{3.5})$ for the Laplace and canonical implementations, respectively. As a rule of thumb, on naphthalene-like systems fully correlated Laplace computations within mE_h accuracy are approximately as expensive as the canonical, frozen-core ones. Both, the full-correlation Laplace and the frozen-core canonical computations require approximately five CPU hours, while the fully correlated canonical one requires about fifteen hours.

Regarding a comparison of the two, closed- and open-shell implementations, the time per point ratios t_{pp} relative to the canonical computation indicate that the closed-shell one is slightly more efficient.

CONCLUSIONS

This article has dealt on the general, spin-unrestricted implementation of the Laplace fourth-order perturbative triples. The Laplace factorization of the energy denominators permits a lower scaling arrangement of the triples equations. The scaling is reduced from $\mathcal{O}(N^7)$ to $\mathcal{O}(N^6)$ without hinging on large molecule assumptions. The required numerical integration of the Laplace transform readily produces results within chemical accuracy.

The large-basis-sets disadvantage intrinsic to the Laplace triples is obviated through a convenient application of the orbital invariance properties of the Laplace energies. The relative efficiency of the Laplace closed- and open-shell codes with respect to the canonical implementations has to be analyzed in terms of the number of correlated electrons rather than in terms of the number of basis functions. The applicability of the Laplace triples appears best suited in a context of a sufficiently large number of correlated electrons.

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