

Scaling reduction of the perturbative triples correction (T) to coupled cluster theory via Laplace transform formalism

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A reformulation of the perturbative triples correction to coupled cluster singles and doubles (CCSD) based on the numerical Laplace transform of the energy denominator is presented. Rearranged equations reduce the $\mathcal{O}(N^7)$ canonical scaling to $\mathcal{O}(N^6)$, where N is a size measure of the electronic system. Two to three quadrature points is adequate for chemical predictions. The Laplace ansatz permits simple, noniterative expressions in noncanonical orbital representations. Furthermore, substituting canonical by *generalized* CCSD natural orbitals, the Laplace ansatz exhibits scaling close to $\mathcal{O}(N^5)$, while retaining accuracy and providing crossover with respect to canonical triples for small size systems. A developing atomic orbital formulation is also introduced.

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I. INTRODUCTION

Accurate prediction of molecular properties requires an explicit and precise treatment of electron correlation.^{1,2} Current *ab initio* methods treat electron correlation by a hierarchical truncation of the complete, n -electron Fock space. Higher than doubles excitations are regarded as necessary electronic contributions in accurate treatments.¹ The peculiar truncations arising from the *exponential ansatz* expansions in coupled cluster (CC) theory³ has produced several—among the most reliable—approaches to electron correlation.^{1–4} The CCSD(T) method,^{5,6} a coupled cluster approach including all single and double excitations plus a perturbational correction due to connected triple excitations, provides so far the best balance between efficiency and accuracy.⁴ As the system size increases, the computational cost of singles and doubles scales as $\mathcal{O}(N^6)$, where N is a measure of size, typically related to the number of basis functions. Computational scaling when full triples are also included is $\mathcal{O}(N^8)$, in an iterative CCSDT formalism.^{7,8} On the other hand, computing a perturbative triples correction through converged singles and doubles amplitudes scales as $\mathcal{O}(N^7)$. The particular choice of perturbative triples (T),⁶ besides its efficiency, yields results close to the complete CCSDT treatment; hence such a choice is a good compromise between speed and accuracy.

In addition to high-order excitations, large basis sets are important. Orbital product expansions poorly reproduce interelectronic cusps in correlated wave functions; hence, convergence to the complete basis set limit is extremely slow.⁹ Extrapolation schemes to complete basis sets limits had been developed to reduce the actual size of the atomic orbital (AO) basis sets.^{10,11} Complete basis set (CBS) model chemistries¹² are a well-established methodology that uses reduced expansions and yet provides reliable predictions for molecular properties. Interestingly, it has also been shown that triples contribution converges faster to the complete basis set limit than single and double excitations, suggesting that a dual basis set scheme would speed up CCSD(T) computations.¹³ Similarly, Gaussian-3 theory considers mul-

tipole basis sets on the different stages of a molecular modeling procedure.¹⁴ Although such techniques enhance the applicability of CCSD(T) methodology, the steep scaling of the perturbative triple correction (T) still restricts its use to small size systems.

The steep scaling in *ab initio* electron correlation treatments, usually referred as the *exponential scaling wall*, is an artifact stemming from the delocalized nature of the usual molecular orbital (MO) formalisms.¹⁵ Local formalisms reveal that excitation amplitudes and correlation integrals (defined as the product between two-electron integrals and density matrix elements¹⁵) present a power law decay with distance between local centers. In large systems, most localized amplitudes and integrals become numerically negligible. Efficient and accurate screening protocols yield low-order scaling methods, proving that scaling steepness is not necessarily related to the physics of the electron interaction. Within CC theory, several advances in this area of scaling have been done so far. The Pulay and Saebo¹⁶ local correlation method has been successfully applied to the CCSD level of theory.¹⁷ Rewriting CC equations in the local, AO basis, Scuseria and Ayala¹⁵ have argued that the whole hierarchy of equations scales linearly in CPU time with molecular size in the large system asymptote. Maslen *et al.*¹⁸ presented evidence that triple excitations are accurately described using physical models that restrict substitutions among atomic, occupied and virtual orbitals to only a given set of atoms. In addition, the Schütz and Werner¹⁹ local triples method achieves linear scaling albeit recovering 80%–90% of the conventional energy. It should be noted that this approach is not exact in the limit of zero thresholds.

Although localized or atomic formulations for treating electron correlation are nowadays generally recognized, perturbative methods were historically formulated in the canonical, delocalized orbital basis. The canonical representation, i.e., the one that diagonalizes the Fock operator, produces simpler, closed expressions, with lower computational prefactors. Thus, canonical representations are perfectly suited to

small or spatially reduced systems. Perturbative expressions appear divided by differences among Fock matrix eigenvalues, i.e., the MO energies in the canonical basis. These denominators impede simple rederivations in a noncanonical or in a nonorthogonal basis, as localized and atomic formulations require. In pioneering work,²⁰ Almlöf replaced the energy denominators by its Laplace transform, the exponential function. Accordingly, the orbital energy differences appear as exponents. Splitting the exponential function in single exponent products, results in exponential factors that are identifiable as weights defining *attenuated* integrals or amplitudes. The resulting perturbative expressions in terms of the attenuated integrals and amplitudes keep the simple, closed form of the canonical formulation. Interestingly, the correlation energy remains invariant under unitary transforms that do not mix occupied with virtual orbitals. As a consequence, localized orbital treatments are simpler within the Laplace transform formalism.^{21–23}

Besides lifting the canonical orbital constraint, the Laplace ansatz permits decoupling of nested summations in higher-order perturbation theory thus producing lower scaling equations.²⁴ Such a reduction in scaling properties does not hinge on the assumption of large molecule asymptote, but on a numerical approach to an integral transform. Therefore, accurate energies for medium sized systems, as for example organometallics, are attainable at a considerably reduced cost.

In the present article, we apply the Laplace transform to the perturbative CCSD(T) triples correction as a means to reduce its canonical, $\mathcal{O}(N^7)$ scaling. Rather than explicitly formulate all resulting terms and their lower $\mathcal{O}(N^6)$ contractions, the general procedure is illustrated on a specific subset of terms. Apart from exemplifying the whole formulation process such a subset evidences both the need for noncanonical representations and the suitability of the Laplace ansatz to lift the canonical constraint. It is shown that few, two to three, quadrature points suffice for adequate accuracy. Cross-over with respect to the conventional formulation already occurs in small systems if a *generalized* CCSD natural orbital (NO) derivation and screening protocols are considered. Moreover, the NO derivation proves particularly useful when using large basis sets, where the MO Laplace ansatz nearly scales as $\mathcal{O}(N^5)$.

The article is organized as follows. In the Theory section, the perturbative triples equations are introduced, and properly rearranged to illustrate the Laplace transform procedure. An efficient integration scheme is also described. The section concludes illustrating an AO *rewriting* of the Laplace ansatz. In the Results and Discussion section, some test computations are presented, discussing accuracy and timings for the NO Laplace ansatz.

II. THEORY

A. Perturbative triples correction (T)

The standard triples correction $E_{(T)}$ is split into a fourth and fifth order component, $E_T^{[4]}$ and $E_{ST}^{[5]}$, respectively, being^{4,6,25–27}

$$E_{(T)} = E_T^{[4]} + E_{ST}^{[5]}. \quad (1)$$

In the closed-shell canonical derivation, these terms are^{28–30}

$$E_T^{[4]} = 1/3 \sum_{ijk} \sum_{abc} W_{ijk}^{abc} R[W]_{ijk}^{abc} / D_{ijk}^{abc}, \quad (2)$$

and

$$E_{ST}^{[5]} = -1/3 \sum_{ijk} \sum_{abc} V_{ijk}^{abc} R[W]_{ijk}^{abc} / D_{ijk}^{abc}, \quad (3)$$

respectively. As usual, indices i, j, k, \dots , (a, b, c, \dots) refer to occupied (unoccupied) MOs in the Hartree–Fock reference configuration. Intermediates $R[W]_{ijk}^{abc}$, W_{ijk}^{abc} , and V_{ijk}^{abc} are given by

$$R[W]_{ijk}^{abc} = 4W_{ijk}^{abc} + W_{kij}^{abc} + W_{jki}^{abc} - 2W_{kji}^{abc} - 2W_{ikj}^{abc} - 2W_{jik}^{abc}, \quad (4)$$

$$W_{ijk}^{abc} = \mathcal{P}_{ijk}^{abc} \left[\sum_f v_{af}^{ib} t_{kj}^{cf} - \sum_m v_{am}^{ij} t_{mk}^{bc} \right], \quad (5)$$

and

$$V_{ijk}^{abc} = 1/2 \mathcal{P}_{ijk}^{abc} v_{ab}^{ij} t_k^c, \quad (6)$$

respectively. The permutation operator \mathcal{P}_{ijk}^{abc} is defined as

$$\mathcal{P}_{ijk}^{abc}(\cdot) = \cdot_{ijk}^{abc} + \cdot_{jki}^{bca} + \cdot_{kij}^{cab} + \cdot_{ikj}^{acb} + \cdot_{kji}^{cba} + \cdot_{jik}^{bac}. \quad (7)$$

The energy denominator D_{ijk}^{abc} contains differences among closed-shell Fock matrix eigenvalues, i.e., the canonical MO energies,

$$D_{ijk}^{abc} \equiv f_{aa} + f_{bb} + f_{cc} - f_{ii} - f_{jj} - f_{kk}. \quad (8)$$

Quantities v_{rs}^{pq} , with indices p, q, r, s, \dots referring to unspecified molecular orbitals, are two-electron integrals,

$$v_{rs}^{pq} = \int p(1)q(2) \frac{1}{r_{12}} r(1)s(2) dr_1 dr_2, \quad (9)$$

while t_i^a and t_{ij}^{ab} are singles and doubles excitation amplitudes, respectively.

The number of occupied (unoccupied) MOs will be denoted as O and V , respectively. Number N will refer to the number of correlated orbitals, thus representing a simple measure of size of the electronic system. According to the above formulas, the computational scaling for the triples correction term is $\mathcal{O}(O^3V^4 + O^4V^3)$, or roughly $\mathcal{O}(N^7)$, due to the construction of W_{ijk}^{abc} . In the Laplace transform approach, W_{ijk}^{abc} does not need to be assembled and the scaling for both the $E_T^{[4]}$ and $E_{ST}^{[5]}$ terms can be reduced. The $E_T^{[4]}$ term is the most important contribution in terms of magnitude and computational cost. The focus of the present article is set on this term. Scaling reduction for the $E_{ST}^{[5]}$ term is achieved by applying the same principles as the ones discussed here for $E_T^{[4]}$.

B. The MO- $E_T^{[4]}$ ansatz

The Laplace transform applied to the denominator of Eq. (2) gives the fourth order triples contribution $E_T^{[4]}$ as the integral,

$$E_T^{[4]} = 1/3 \int_0^\infty \sum_{ijk} \sum_{abc} W_{ijk}^{abc} R[W]_{ijk}^{abc} e^{-D_{ijk}^{abc} s} ds. \quad (10)$$

Expanding the integral in a series, Eq. (10) yields the ansatz

$$E_T^{[4]} = 1/3 \sum_l w_l \sum_{ijk} \sum_{abc} W_{ijk}^{abc} R[W]_{ijk}^{abc} e^{-D_{ijk}^{abc} s_l}, \quad (11)$$

where w_l are appropriate quadrature weights. Since the Laplace transformed weight $e^{-D_{ijk}^{abc} s_l}$ factorizes, the six indices $i, j, k, a, b,$ and c are not coupled by denominator D_{ijk}^{abc} . At this point, ansatz (11) permits lower, $\mathcal{O}(N^6)$ scaling contractions for the triples energy. Much more advantageous contractions are apparent after a complete expansion of Eq. (11) in terms of 2-integral-2-amplitude products. Expanded terms can be classified into three groups, regarding the innermost f and m indices in intermediate W_{ijk}^{abc} defined in Eq. (5). Denoting by o any of the occupied indices i, j, k , by v any of the a, b, c virtuals, and g and n the innermost indices in $R[W]_{ijk}^{abc}$, the three groups are characterized by templates $v_{vf}^{ov} v_{vg}^{ov} t_{oo}^{vf} t_{oo}^{vg}$, $v_{ov}^{mo} v_{ov}^{no} t_{oo}^{mv} t_{oo}^{nv}$, and $v_{vf}^{ov} v_{ov}^{mo} t_{oo}^{vf} t_{oo}^{mv}$. After expanding, there are a total of 216 terms in each of these three groups. Some of those terms are equivalent once completely summed up. Subsequent to collecting terms, the number of nonredundant ones is 26, 26, and 36, for each of the above groups, respectively. From the total 88 nonredundant 2-integral-2-amplitude products contributing to energy $E_T^{[4]}$, 76 can be contracted to formally scale as $\mathcal{O}(N^6)$, while the remaining 12 terms allow a contraction scaling as $\mathcal{O}(N^5)$. We note in passing that the reduction in a factor slightly higher than 6 leading to the 88 nonredundant terms is similar to introducing the constraint $a \geq b \geq c$ in Eq. (2), as it appears in Ref. 30. This constraint is initially removed in the above presentation to permit different orderings on these indices, hence making possible the sought $\mathcal{O}(N^6)$ contractions.

A detailed analysis on the steepest scaling parts regarding basis set limit, i.e., $V \gg O$, indicates the following performance. A six term subset in the $v_{vf}^{ov} v_{vg}^{ov} t_{oo}^{vf} t_{oo}^{vg}$ group scales as $\mathcal{O}(OV^5)$, while another sixteen term subset scales as $\mathcal{O}(O^2V^4)$, and the remaining four terms scale as $\mathcal{O}(OV^4)$. The steepest parts in the $v_{vf}^{ov} v_{ov}^{mo} t_{oo}^{mv} t_{oo}^{nv}$ group are eight terms scaling as $\mathcal{O}(O^2V^4)$. Scaling costs in the $v_{ov}^{mo} v_{ov}^{no} t_{oo}^{mv} t_{oo}^{nv}$ group are not severe, since the most expensive part scales as $\mathcal{O}(O^3V^3)$. Therefore, for large basis sets, the steepest scaling would occur when evaluating the $\mathcal{O}(OV^5)$ terms. The OV^5 terms will merit special attention and will be taken as a representative example below.

The six-term, OV^5 contribution to the $E_T^{[4]}$ energy is

$$E^{OV^5} = -8 \Theta_{fg}^{ab} T_{fg}^{ab} + 4 \Theta_{fg}^{ab} \bar{T}_{fg}^{ab} + 2 \bar{\Theta}_{fg}^{ab} T_{fg}^{ab} - 4 \bar{\Theta}_{fg}^{ab} \bar{T}_{fg}^{ab} + 8 \Theta_{fg}^{ab} T_{fg}^{ab} - 4 \Theta_{fg}^{ab} \bar{T}_{fg}^{ab}, \quad (12)$$

assuming implicit summation over repeated indices. The intermediate contractions Θ , $\bar{\Theta}$, Θ , T , and \bar{T} are given by the expressions

$$\Theta_{fg}^{ab} = \bar{v}_{af}^{ic} \bar{v}_{cg}^{ib}, \quad (13)$$

$$\bar{\Theta}_{fg}^{ab} = \bar{v}_{af}^{ic} \bar{v}_{bg}^{ic}, \quad (14)$$

$$\Theta_{fg}^{ab} = \bar{v}_{cf}^{ia} \bar{v}_{cg}^{ib}, \quad (15)$$

$$T_{fg}^{ab} = \bar{t}_{kj}^{bf} \bar{t}_{jk}^{ag}, \quad (16)$$

$$\bar{T}_{fg}^{ab} = \bar{t}_{kj}^{bf} \bar{t}_{kj}^{ag}. \quad (17)$$

Barred integrals and amplitudes in contractions include the Laplace transformed denominator in the convenient way

$$\bar{v}_{af}^{ic} = e^{-1/2f_{aa}s_l} e^{-1/2f_{cc}s_l} e^{1/2f_{ii}s_l} v_{af}^{ic}, \quad (18)$$

$$\bar{t}_{kj}^{bf} = e^{-1/2f_{bb}s_l} e^{1/2f_{jj}s_l} e^{1/2f_{kk}s_l} t_{kj}^{bf}. \quad (19)$$

Consequently, these attenuated integrals and amplitudes depend on the transformed variable s , and one needs to construct them at each quadrature point l .

For the sake of computational efficiency, the OV^5 terms can be rewritten defining the intermediate

$$\bar{\Theta}_{fg}^{ab} = (2\bar{v}_{cf}^{ia} - \bar{v}_{af}^{ic})(2\bar{v}_{cg}^{ib} - \bar{v}_{bg}^{ic}), \quad (20)$$

to determine the off-diagonal terms of an \mathbf{E}^{OV^5} matrix constructed after a and b summations. In this way, each fg element is given by

$$E_{f>g}^{OV^5} = 4 \bar{\Theta}_{fg}^{ab} T_{fg}^{ab} - 2 \bar{\Theta}_{fg}^{ab} \bar{T}_{fg}^{ab} - 6 \bar{\Theta}_{fg}^{ab} \bar{T}_{fg}^{ab}. \quad (21)$$

Matrix \mathbf{E}^{OV^5} is symmetric, as well as negative definite. Accordingly, the OV^5 contribution is simply

$$E^{OV^5} = \sum_{f \geq g} E_{fg}^{OV^5}. \quad (22)$$

The Laplace ansatz is invariant under unitary transformations of the attenuated virtual (occupied) orbitals. Therefore, *generalized* CCSD NOs, defined here as the orbital representation that diagonalize the *attenuated*, two-particle matrix

$$D_{ab}^{(2)} = \bar{t}_{ij}^{ac} \bar{t}_{ij}^{bc}, \quad (23)$$

can be used to substitute without further rearrangement of the canonical virtuals in Eq. (11). Such NO representations have proven advantageous over canonical orbitals when seeking convenient space truncations.¹³ We show here that NOs also enhance an effective screening protocol for the off-diagonal elements $E_{fg}^{OV^5}$.

The magnitude distribution for the $E_{fg}^{OV^5}$ pair contributions, as displayed in Fig. 1, indicates that the largest fg contributions are in slightly larger number in the NO case than in the canonical one. Furthermore, the NO representation definitely presents the greatest number of numerically negligible pair contributions, thus clearly favoring an fg pair screening. Since matrix \mathbf{E}^{OV^5} is definite, an off-diagonal screening based on the Schwarz inequality

$$|E_{fg}^{OV^5}| \leq |E_{ff}^{OV^5} E_{gg}^{OV^5}|^{1/2}, \quad (24)$$

is rigorous, and yet effective. As shown in Fig. 2, considering a threshold $|E_{fg}^{OV^5}| \leq 10^{-5}$ the number of significant fg pairs grows linearly as basis set size increases, without significant loss in accuracy. Figure 2 considers the case of the

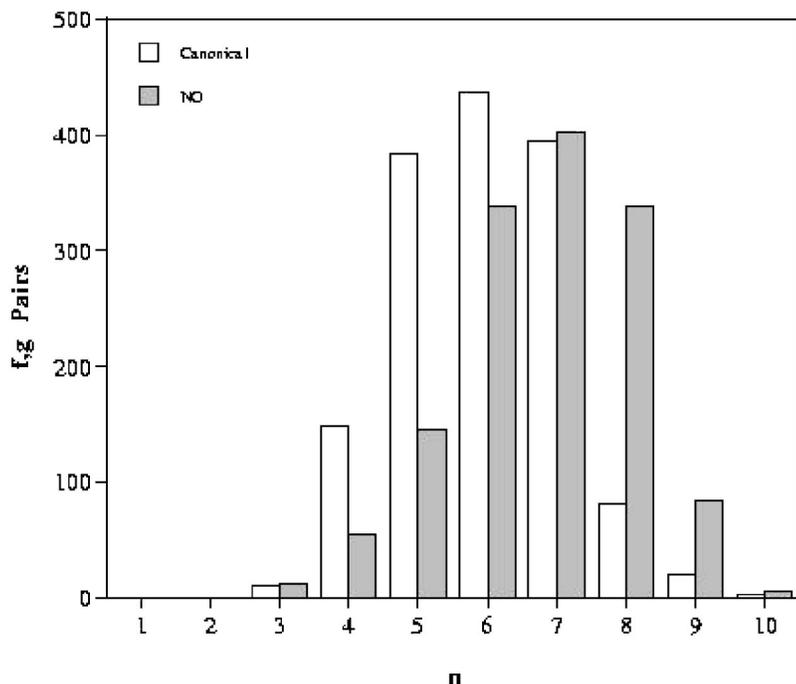


FIG. 1. Magnitude distribution (10^{-n}) for the E_{fg}^{OV5} pair contributions using the canonical virtual basis (clear bars) and the CCSD virtual NO basis (shaded bars). Carbon monoxide molecule [CCSD(T)=fc/cc-pVTZ; $r_{CO}=1.12 \text{ \AA}$; $s_l=0.32$].

CO molecule at the Laplace quadrature points $s_1 \cong 0.005$. As it is apparent from Eqs. (18) and (19), the above truncation becomes still more effective when other, higher s_l points in numerical integration are considered.

The above treatment is extensible to all terms in the $v_{vf}^{ov} v_{vg}^{ov} t_{oo}^{vf} t_{oo}^{vg}$ set, simplifying the most expensive part in practical Laplace ansatz computations. One can generalize the E^{OV5} matrix by summing up all indices but f and g , and including the complete set of fg terms. The matrix considering the sum of all $v_{vf}^{ov} v_{vg}^{ov} t_{oo}^{vf} t_{oo}^{vg}$ terms will be denoted by E^{fg} . Matrix E^{fg} is also symmetric and definite. Each element fg will be denoted, accordingly, as E_{fg}^{fg} , and its definition is analogous to the E_{fg}^{OV5} element definition in Eq. (21), but, as indicated, including all 26 energy terms in the $v_{vf}^{ov} v_{vg}^{ov} t_{oo}^{vf} t_{oo}^{vg}$ set. The screening of the off-diagonal elements E_{fg}^{fg} produces a $\mathcal{O}(N^5)$ algorithm, while keeping truncation

errors below the ones introduced by numerical integration. Similar screenings are applicable to the remaining terms in the other two groups, $v_{ov}^{mo} v_{ov}^{no} t_{mo}^{vv} t_{no}^{vv}$ and $v_{vf}^{ov} v_{ov}^{mo} t_{oo}^{vf} t_{mo}^{vv}$. This would practically lead to a complete $\mathcal{O}(N^5)$ algorithm. However, since evaluating these two sets of terms is comparative faster in moderate basis sets, this avenue has not been further explored.

Concerning the fifth-order correction term $E_{ST}^{[5]}$, the Laplace transform approach produces 2×9 nonredundant terms classified according to the templates $v_{oo}^{vv} t_{oo}^{vo} v_{oo}^{vg} t_{oo}^{vg}$ or $v_{oo}^{vv} t_{oo}^{vm} v_{oo}^{vv} t_{oo}^{om}$. Ten of these terms, the most expensive ones, specifically scale as $\mathcal{O}(O^3 V^3)$. The remaining eight terms scale only $\mathcal{O}(N^5)$. We note that the ten $\mathcal{O}(O^3 V^3)$ terms can be further grouped into 4 terms and that thanks to a Schwarz screening protocol the whole $E_{ST}^{[5]}$ term can be evaluated at a cost scaling as $\mathcal{O}(N^5)$.

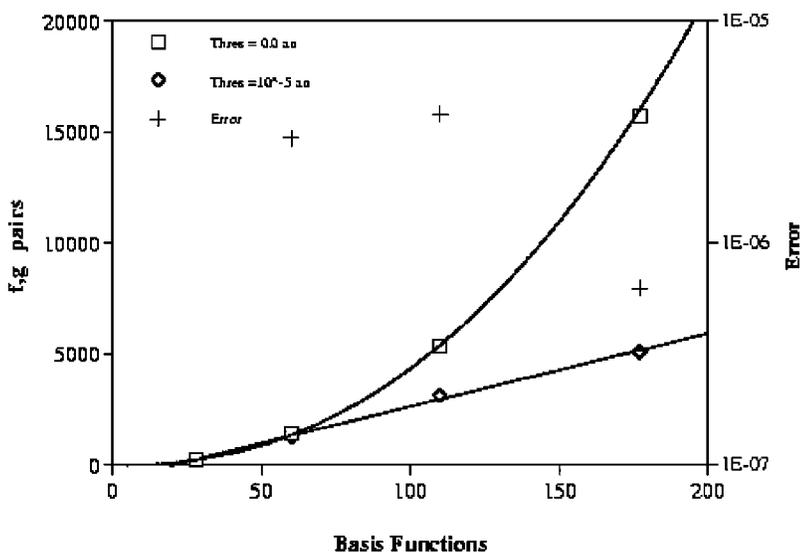


FIG. 2. Number of virtual NO, E_{fg}^{OV5} pair contributions using cc-pVnZ basis sets for carbon monoxide molecule [CCSD(T)=fc/cc-pVnZ, $n=2, 5$; $r_{CO}=1.12 \text{ \AA}$], at the Laplace quadrature point $s_l=0.0054 \pm 0.0003$, depending on the basis set. Truncation errors on the right-hand axis are in hartrees.

C. Numerical Laplace transform

Numerical integration of the Laplace transform in Eq. (10) is simple, yet accurate. Formally, the integration is over a series of exponential functions,

$$E_{\Gamma}^{[4]} = - \int_0^{\infty} \sum_v z_v e^{-D_v s} ds, \quad (25)$$

with coefficients z_v and exponents D_v . The integrand is a well-behaved function, monotonically decreasing and positive everywhere. To highlight these properties, a direct correspondence of z_v coefficients with the variable, positive and negative $W_{ijk}^{abc} R[W]_{ijk}^{abc}$ products in Eq. (10) is avoided here. Logarithm transformations have proven valuable on numerical integration of exponential type functions.³¹ Radial quadratures in density-functional,³² and effective core potential³³ calculations constitute successful examples of their application. Accordingly, substituting variable s by

$$s = -1/\alpha \ln x, \quad (26)$$

the integral in Eq. (25) becomes a power expansion,

$$E_{\Gamma}^{[4]} = -1/\alpha \int_0^1 \sum_v z_v x^{(D_v/\alpha)-1} dx, \quad (27)$$

mapped on the integration interval 0 to 1. Choosing the parameter α smaller or equal to the minimum exponent in the series, D_{\min} , the integrand is bounded everywhere. Therefore integral (27) is proper and suited for a simple, numerical integration. The minimum exponent D_{\min} is readily identifiable as being the minimum denominator in energy equation (2) or *triples gap*. The change of variable in Eq. (26), if $\alpha \leq D_{\min}$, also preserves the well behaved nature of the integrand. Consequently, since errors in Gauss quadratures for a function $f(x)$ are estimated to be proportional to its $2n$ -derivative $f^{(2n)}(\xi)$, with n being the number of quadrature points and $0 < \xi < 1$,³¹ optimal parameter values will lay close to the triples gap value. In other words, $\alpha = D_{\min}$ minimizes the slope of the integrand thus shortening error bounds. After the logarithm transformation, the quadrature is straightforward by conventional techniques. Gauss–Legendre integration is a particularly useful choice. As an open rule, it eludes numerical computations at the point $x = 0$, corresponding to $s = \infty$. In addition, no other rule of the type $\sum_l w_l f(x_l)$, with w_l being quadrature weights and x_l abscissas, can integrate exactly any function f belonging to the polynomial, \mathcal{P}_{2n} class just using n points. In practice, the optimality of this integration scheme will be affected by the closeness of \mathcal{P}_{2n} polynomials to the power expansion.²⁷

D. The AO- $E_{\Gamma}^{[4]}$ ansatz

Once the perturbative energy denominator is replaced by its Laplace transform, the constraint of using canonical orbitals is removed. In addition, rewriting a nonorthogonal, AO algorithm just requires slight modifications of the Laplace $E_{\Gamma}^{[4]}$ ansatz. AO formulations can be written in a different number of ways. Identifying optimal local magnitudes, in the sense of rapid decay and powerful screening availability, constitutes a task that is beyond the scope of this work. Instead, the following AO reformulation intends to illustrate

the potentiality of the Laplace ansatz toward local, triple substitution treatments. Among potentialities, besides cutoff-based techniques, rearranged Laplace equations offer a unique and simple perspective toward devising and testing local, physical models. Some possible models had been recently proposed,^{18,34} its approximate translation into Laplace ansatz is quite immediate.

In order to rewrite the $E_{\Gamma}^{[4]}$ correction in the AO basis, one needs to expand MO integrals and amplitudes in terms of localized, atomic magnitudes. Then, such expressions are plugged into the $E_{\Gamma}^{[4]}$ equation, and the equation appropriately rearranged, in a way that all integrals and excitation amplitudes are written with AO indices. This AO *rewriting* can be illustrated by taking a representative term, e.g., the first 2-integral-2-amplitude product from Eq. (12),

$$\Theta_{fg}^{ab} T_{fg}^{ab} = \bar{v}_{af}^{ic} \bar{v}_{cg}^{ib} \bar{t}_{kj}^{bf} \bar{t}_{jk}^{ag}. \quad (28)$$

Defining the attenuated atomic integrals according to the change of basis transformation

$$\bar{v}_{af}^{ic} = c_{\mu i} c_{\alpha a} c_{\sigma c} c_{\delta f} \bar{v}_{\alpha \delta}^{\mu \sigma}, \quad (29)$$

and conveniently, defining the atomic, attenuated amplitudes as

$$\bar{t}_{\kappa \nu}^{\beta \delta} = c_{\nu j} c_{\kappa k} c_{\beta b} c_{\delta f} \bar{t}_{kj}^{bf}, \quad (30)$$

the term $\Theta_{fg}^{ab} T_{fg}^{ab}$ in atomic indices is

$$\Theta_{\delta \gamma}^{\alpha \beta} T_{\delta \gamma}^{\alpha \beta} = Q_{\pi \bar{\nu}}^{\sigma} \bar{v}_{\alpha \delta}^{\mu \pi} P_{\lambda}^{\mu} \bar{v}_{\sigma \gamma}^{\lambda \beta} R_{\nu}^{\epsilon} \bar{t}_{\kappa \epsilon}^{\beta \delta} R_{\kappa}^{\nu} \bar{t}_{\nu \gamma}^{\alpha \gamma}. \quad (31)$$

Coefficients c are the ones that define the molecular orbitals as linear combinations of the atomic basis functions or orbitals. Greek letters denote the AOs. Projector P is the AO one-particle density matrix of the reference state,

$$P_{\mu}^{\nu} = c_{\mu i} c_{\nu i}, \quad (32)$$

and Q its complementary projector,

$$Q_{\mu}^{\nu} = c_{\mu a} c_{\nu a}. \quad (33)$$

Since the attenuated MO \bar{t}_{kj}^{bf} amplitudes can be recovered from the $\bar{t}_{\kappa \nu}^{\beta \delta}$ amplitudes using the inverse transformation of Eq. (30),

$$\bar{t}_{kj}^{bf} = \bar{c}_{\nu j} \bar{c}_{\kappa k} \bar{c}_{\beta b} \bar{c}_{\delta f} \bar{t}_{\kappa \nu}^{\beta \delta}, \quad (34)$$

with the \bar{c} coefficients being

$$\bar{c}_{\mu p} = S_{\mu}^{\alpha} c_{\alpha p}, \quad (35)$$

and S the AO overlap matrix, projector R is then defined as

$$R_{\mu}^{\nu} = \bar{c}_{\mu i} \bar{c}_{\nu i}. \quad (36)$$

Omitting further details, the intermediate contractions Θ , $\bar{\Theta}$, Θ , T , and \bar{T} , in Eqs. (13)–(17), are given in AO indices by

$$\Theta_{\delta \gamma}^{\alpha \beta} = (Q_{\pi}^{\sigma} \bar{v}_{\alpha \delta}^{\mu \pi}) (P_{\rho}^{\mu} \bar{v}_{\sigma \gamma}^{\rho \beta}), \quad (37)$$

$$\bar{\Theta}_{\delta \gamma}^{\alpha \beta} = (Q_{\pi}^{\sigma} \bar{v}_{\alpha \delta}^{\mu \pi}) (P_{\rho}^{\mu} \bar{v}_{\beta \gamma}^{\rho \sigma}), \quad (38)$$

$$\Theta_{\delta \gamma}^{\alpha \beta} = (Q_{\sigma}^{\pi} \bar{v}_{\pi \delta}^{\mu \alpha}) (P_{\rho}^{\mu} \bar{v}_{\sigma \gamma}^{\rho \beta}), \quad (39)$$

$$T_{\delta \gamma}^{\alpha \beta} = (R_{\nu}^{\pi} \bar{t}_{\kappa \pi}^{\beta \delta}) (R_{\kappa}^{\rho} \bar{t}_{\nu \rho}^{\alpha \gamma}), \quad (40)$$

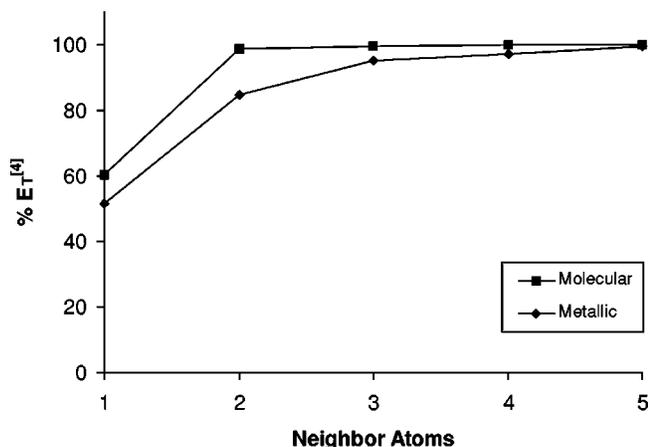


FIG. 3. Effect of AO integral truncation on triples contribution $E_T^{[4]}$ in hydrogen chains containing sixteen atoms, using minimal basis set STO-3G. Integrals are truncated according to the given radius of neighbor atoms, and according to the same-electron indices. In the *molecular* chain, intramolecular distances are 1.4 a.u., while shorter intermolecular distances are 3.0 a.u. In the *metallic* chain, all interatomic separations are 2.0 a.u.

$$\bar{T}_{\delta\gamma}^{\alpha\beta} = (R_v^\pi \bar{t}_{\kappa\pi}^{\beta\delta})(R_\kappa^\rho \bar{t}_{\rho\nu}^{\alpha\gamma}). \quad (41)$$

Parentheses indicate the contractions defining projected integrals and amplitudes. Finally, using the above intermediates, the E^{OV^5} contribution to the $E_T^{[4]}$ energy is

$$E^{OV^5} = -8\Theta_{\delta\gamma}^{\alpha\beta} T_{\delta\gamma}^{\alpha\beta} + 4\Theta_{\delta\gamma}^{\alpha\beta} \bar{T}_{\delta\gamma}^{\alpha\beta} + 2\bar{\Theta}_{\delta\gamma}^{\alpha\beta} T_{\delta\gamma}^{\alpha\beta} - 4\bar{\Theta}_{\delta\gamma}^{\alpha\beta} \bar{T}_{\delta\gamma}^{\alpha\beta} + 8\Theta_{\delta\gamma}^{\alpha\beta} T_{\delta\gamma}^{\alpha\beta} - 4\Theta_{\delta\gamma}^{\alpha\beta} \bar{T}_{\delta\gamma}^{\alpha\beta}, \quad (42)$$

clearly analogous to its MO formulation in Eq. (12).

The degree of locality of triple substitutions is neatly illustrated in minimal basis set hydrogen chains. In these systems, since there is just one electron and one basis function per atom, decay properties might be physically interpreted in terms of atomic neighbor contributions. Besides, by just rearranging interatomic distances, one can move from a pure ensemble of noninteracting molecules—alternating *short* and *long* interatomic distances—to a completely delocalized or metallic system—approximately equal interatomic distances. Two specific hydrogen chains are considered in Fig. 3. The figure visualizes the impact of atomic truncations on the recovered triples energy. Atomic truncations are restricted to the simplest possible ones. Only integral cutoffs involved in the exponential decay are considered. Accordingly, just integrals $v_{\lambda\sigma}^{\mu\nu}$ with μ and λ , and ν and σ , in a given radius of atomic neighbors are used. Besides, the projected integrals are cut in an analogous manner. This proves that projections within Eqs. (37)–(41) do not destroy decay properties. In the molecular chain case, a radius of two neighboring atoms recovers nearly the 100% of the $E_T^{[4]}$ energy. The delocalized, metallic chain exhibits a slightly slower convergence, but locality in terms of integral, exponential decay is noteworthy. As a final remark, in the asymptote and omitting the cost for evaluating $T_{\alpha\beta}^{\alpha\beta}$ and $\bar{T}_{\alpha\beta}^{\alpha\beta}$ intermediates, the above integral truncation leads to a quadratic-scaling algorithm.

TABLE I. Minimum, maximum, and mean absolute deviations $|\Delta_e|$ regarding conventional vs Laplace ansatz $E_T^{[4]}$, for the G2-1 test set of molecules n is the number of quadrature points. Deviations are in mH.

Basis	n	Min $ \Delta_e $	Max $ \Delta_e $	Mean $ \Delta_e $
6-31G**	1	0.044	3.499	1.219
	2	0.001	0.060	0.014
	3	0.000	0.029	0.005
	4	0.000	0.015	0.003
6-311G**	1	0.128	8.843	2.690
	2	0.001	0.800	0.170
	3	0.002	0.106	0.021
	4	0.000	0.021	0.006
6-311+G**	1	0.242	10.002	3.372
	2	0.005	1.083	0.253
	3	0.000	0.115	0.028
	4	0.001	0.024	0.008
cc-pVDZ ^a	1	0.019	4.115	1.145
	2	0.001	0.063	0.015
	3	0.000	0.031	0.006
	4	0.000	0.016	0.003
cc-pVTZ ^a	1	0.238	13.798	4.826
	2	0.004	1.872	0.399
	3	0.000	0.109	0.020
	4	0.000	0.015	0.003

^aThe Li_2 and LiF molecules are excluded.

III. RESULTS AND DISCUSSION

The main differences between the conventional CCSD(T) method in the canonical MO, and the approach presented here are the numerical Laplace transform and the off-diagonal screening in evaluating matrix $\mathbf{E}^{[fg]}$. They are discussed separately below.

A. Quadrature accuracy

Quadrature performance is assessed on the 34 closed-shell molecules in the G2-1 test set.³⁵ The basis sets considered are 6-31G**, 6-311G**, and 6-311+G** of Pople and co-workers, together with the correlation consistent basis sets of Dunning, cc-pVDZ, and cc-pVTZ.³⁶ Correlation consistent basis sets are not reported for lithium, thus molecules Li_2 and LiF are excluded in these two basis set cases. The numerical Laplace transform is performed according to the integration scheme described in previous section, exploring the use of one to four quadrature points. Occupied, core orbitals are frozen, while all virtual orbitals are correlated in our computations, which have been carried out on a Gaussian development version.³⁷

Minimal, maximal, and mean absolute deviations $|\Delta_e|$ from the canonical $E_T^{[4]}$ frozen core energies are reported in Table I. One quadrature point, as might be expected, only gives a crude estimate of triples contributions, although in the smaller basis sets relative errors are moderately reduced. The largest deviations 3.499 and 4.115 mH also correspond to the largest $E_T^{[4]}$ energies, 25.831 and 26.028 mH, for the basis sets 6-31G** and cc-pVDZ, respectively. Also, as expected, increasing the number of quadrature points increases accuracy. Two quadrature points provide, in average, energies completely within mH accuracy. Maximal differences,

TABLE II. Deviations Δ_e in mH, in Roman, and timing ratios (conventional/Laplace ansatz), in italics, for the cyclic water trimer, at the CCSD(T)=fc/cc-pVDZ level of theory. n is the number of quadrature points and τ is the screening threshold for $E_{fg}^{\{fg\}}$ terms.

n	$\tau=0$		$\tau=10^{-7}$		$\tau=10^{-6}$		$\tau=10^{-5}$	
1	-3.244	<i>1.77</i>	-3.244	<i>1.65</i>	-3.244	<i>1.67</i>	-3.242	<i>1.90</i>
2	-0.045	<i>0.88</i>	-0.045	<i>0.83</i>	-0.046	<i>0.90</i>	-0.112	<i>1.05</i>
3	0.001	<i>0.59</i>	0.001	<i>0.57</i>	-0.004	<i>0.60</i>	-0.051	<i>0.70</i>
4	0.001	<i>0.44</i>	0.001	<i>0.44</i>	0.000	<i>0.47</i>	-0.072	<i>0.52</i>

slightly above mH, 1.083 and 1.872 mH for 6-311+G** and cc-pVTZ, respectively, also coincide with the largest $E_T^{[4]}$ energies, 32.365 and 39.429 mH. Average deviations when using three quadrature points are within μ H accuracy for the 6-31G** and cc-pVDZ basis sets, and around 0.02–0.03 mH in the other basis sets. Maximum deviation for this quadrature corresponds to LiF molecule, when using 6-311+G** basis set. Four points provide average deviations within μ H accuracy in all basis sets. Microhartree accuracy is clearly more than adequate for most practical purposes. We note in passing, that no correlation deviations versus triples gap is found on the above test computations.

B. Accuracy and timings for MO Laplace transform

Both the number of required quadrature points and Schwarz screening impact on the performance of the Laplace ansatz. Accuracy and timing performance is analyzed considering increases in the number of correlated electrons as well increases on the basis set size. For clarity, thresholds in Schwarz screening are kept fix, although an optimal accuracy and timing performance should consider different thresholds at each quadrature point.

Water trimer and hexamer using a moderate basis set are considered in order to highlight the scaling reduction achieved by the Laplace ansatz. The specific trimer and hexamer structures are the cyclic ones, as appearing in Figs. 31 and 64 in Ref. 38, respectively. Geometries are optimized at the MP2(full)/6-31g(d) level of theory, while $E_T^{[4]}$ energies are computed at the CCSD(T)=fc/cc-pVDZ level. Conventional $E_T^{[4]}$ energies are -11.3216 and -23.0488 mH for the trimer and hexamer, respectively. Deviations Δ_e for conventional versus Laplace ansatz energies are reported in Tables II and III, respectively, for the trimer and hexamer, exploring, as before, the one to four-point quadratures. Timing ratios for conventional over Laplace ansatz appear in italics. Each column corresponds to different screening thresholds

TABLE III. Deviations Δ_e in mH, in Roman, and timing ratios (conventional/Laplace ansatz), in italics, for the cyclic water hexamer, at the CCSD(T)=fc/cc-pVDZ level of theory. n is the number of quadrature points and τ is the screening threshold for $E_{fg}^{\{fg\}}$ terms.

n	$\tau=0$		$\tau=10^{-7}$		$\tau=10^{-6}$		$\tau=10^{-5}$	
1	-6.898	<i>3.42</i>	-6.898	<i>3.22</i>	-6.898	<i>3.30</i>	-6.894	<i>3.85</i>
2	-0.109	<i>1.72</i>	-0.109	<i>1.62</i>	-0.111	<i>1.80</i>	-0.249	<i>2.20</i>
3	0.002	<i>1.14</i>	0.002	<i>1.10</i>	-0.008	<i>1.26</i>	-0.118	<i>1.45</i>
4	0.001	<i>0.86</i>	0.001	<i>0.87</i>	-0.002	<i>0.93</i>	-0.261	<i>1.11</i>

TABLE IV. Conventional $E_T^{[4]}$ energies, Laplace ansatz deviations Δ_e in mH, and timing ratios R (conventional/Laplace ansatz), in italics, for the chlorine molecule [CCSD(T)/cc-pVnZ, $n=2,5$; $r_{\text{ClCl}}=2.02$ Å; $E_{fg}^{\{fg\}}$ screening threshold $\tau=5.10^{-6}$], considering a two-point quadrature. The number of virtuals is denoted by V . Timing ratios R_{CO} consider canonical orbital Laplace ansatz, while R_{NO} consider NOs plus Schwarz screening. Timing ratio $R_{\text{CO/NO}}^{\{fg\}}$ only reflects $v_{vf}^{ov}v_{vg}^{ov}v_{oo}^{fg}v_{og}^{vg}$ term computations for canonical respect screened NO ansatz.

Basis	V	$E_T^{[4]}$	R_{CO}	Δ_e	R_{NO}	$R_{\text{CO/NO}}^{\{fg\}}$
cc-pVDZ	19	-6.874	<i>0.60</i>	-0.104	<i>0.59</i>	<i>0.91</i>
cc-pVTZ	51	-19.145	<i>1.19</i>	-0.836	<i>1.29</i>	<i>1.20</i>
cc-pVQZ	99	-23.927	<i>0.95</i>	-1.779	<i>1.32</i>	<i>1.79</i>
cc-pV5Z	171	-27.097	<i>0.71</i>	-3.873	<i>1.47</i>	<i>3.09</i>

for the off-diagonal elements in matrix $\mathbf{E}^{\{fg\}}$. The $\tau=0$ columns illustrate the performance of the canonical orbital Laplace ansatz. Accuracy follows a similar pattern as the one seen in the G2-1 set analysis. Crossover with respect to conventional triples, i.e., timing ratios greater than one, is attained in the hexamer cluster for an accuracy within mH and μ H. Columns with an actual threshold τ correspond to the Schwarz screened NO Laplace ansatz. A threshold of $\tau=10^{-7}$ does not affect accuracy, as the comparison with $\tau=0$ columns indicates. Only few $E_{fg}^{\{fg\}}$ pairs fall below this threshold, however. In the trimer case for instance, and when a two-point quadrature was used, just 38 upon 2×1596 off-diagonal terms were omitted in the screening process. The slight increase in timing ratios reflects the costs to transform required integrals and amplitudes to the NO representation. Thresholds τ equal to 10^{-6} and 10^{-5} introduce noticeable advantages in these computations. The former value slightly increases efficiency while keeping quadrature accuracy. The latter, coarser value, produces crossover within mH accuracy even for the trimer system, when using a two-point quadrature. It should be stressed here, that efficient thresholds do depend on the specific quadrature point, and that such an optimal value for a target accuracy can be inferred from the diagonal elements of matrix $\mathbf{E}^{\{fg\}}$ and from the corresponding quadrature weight. Most importantly, however, data in Tables II and III reflect the scaling reduction from the conventional $\mathcal{O}(N^7)$ to the Laplace ansatz $\mathcal{O}(N^6)$. Such a reduction indicates that when the size of the system is doubled, the Laplace ansatz is twice faster than conventional computations. The comparison of timing ratios for the trimer and hexamer cases neatly indicates this achievement.

Schwarz screening becomes especially effective on large basis sets. This fact was already illustrated in the example in Fig. 2. Some numerical insight is provided by considering the Cl_2 molecule. As in all previous cases, the geometry used is optimized at the MP2(full)/6-31g(d) level of theory. For demonstrative purposes, only the two innermost occupied orbitals, as well the two outermost virtuals are frozen in the CCSD(T) computation. In this way, the effectiveness of Schwarz screening is already evident on relatively moderate size computations. Results for chlorine $E_T^{[4]}$ energies are presented in Table IV, for the cc-pVnZ basis sets, from double to quintuple zeta. A two-point quadrature and a fixed threshold value $\tau=5 \times 10^{-6}$ is considered. The threshold value τ

$=5 \times 10^{-6}$ keeps truncation error confined within the quadrature accuracy. However, it produces an essentially better performance in terms of timing ratios. To compare the two performances, Table IV includes the canonical Laplace ansatz timing ratios, R_{CO} , in addition to the Schwarz screened NO ones, R_{NO} . The former ansatz suffers from the existence of the previously mentioned OV^5 terms, which increases the *effective prefactor* in large basis sets cases. The R_{NO} ratios, nonetheless, monotonically increase with the basis set size. The ratios $R_{\text{CO/NO}}^{\{fg\}}$, which compare canonical vs NO timings on only the $v_{ov}^{ov} v_{vg}^{ov} v_{oo}^{vf} v_{oo}^{vg}$ set of terms, show a reduction from an $\mathcal{O}(N^6)$ to an $\mathcal{O}(N^3)$ scaling in that part of the computation. Accordingly, the approximately 1.7 increase in the size of the system when going from pVQZ basis set to pV5Z produces the same increase in the corresponding ratios. The overall performance, however, is not close to such $\mathcal{O}(N^5)$ scaling. As mentioned in the Theory, there are eight terms in the $v_{ov}^{ov} v_{oo}^{mo} v_{ov}^{vf} v_{oo}^{vv}$ group scaling as $\mathcal{O}(O^2V^4)$, where Schwarz screening has not yet been exploited in our present code.

We finally note that Schwarz screening on the NO Laplace ansatz efficiently exploits the integral and amplitude attenuation. For instance, the two-point quadrature for Cl_2 molecule when using cc-pV5Z basis sets is evaluated at the abscissas $s_1=0.145$ and $s_2=0.948$. The latter evaluation, which contains the most attenuated integrals and amplitudes, is ~ 11 times faster than the former. The reported ratios throughout this work are obtained on an IBM RS/6000 7043 260/200 MHz workstation. We have found that timing ratios are machine-dependent. Preliminary tests under Linux platforms, for instance, produce more advantageous ratios for the Laplace ansatz, by a factor greater than 2 in some instances.

IV. CONCLUDING REMARKS

The present work enhances and expands the applicability of accurate, electron-correlated methodologies. The developed Laplace ansatz to the CCSD(T) method appears especially useful in the framework of complete basis sets techniques and in Gaussian-3 theories. Large basis sets computations benefit the most from the introduced NO treatment. An even greater efficiency can be expected once the NO Laplace ansatz is implemented for all terms in the fourth and fifth order triples components, $E_{\text{T}}^{[4]}$ and $E_{\text{ST}}^{[5]}$. As pointed out above, the achieved scaling reduction does not hinge on the assumption of large molecule asymptotes. Hence, the MO Laplace ansatz fills the region of high-accurate computations of middle sized molecules.

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