Inner projection techniques for the low-cost handling of two-electron integrals in quantum chemistry

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Abstract

The density fitting technique for approximating electron repulsion integrals relies on the quality of auxiliary basis sets. These are commonly obtained through data fitting, an approach that presents some shortcomings. On the other hand, it is possible to derive auxiliary basis sets by removing elements from the product

space of both contracted and primitive orbitals by means of a particular form of inner projection technique that has come to be known as Cholesky decomposition (CD). This procedure allows for on-the-fly construction of auxiliary basis sets that may be used in conjunction with any quantum chemical method, i.e., unbiased auxiliary basis sets. One key feature of these sets is that they represent the electron repulsion integral matrix in atomic orbital basis with an accuracy that can be systematically improved by lowering the threshold for approximate linear dependences – in the sense of a Coulomb metric ("$1/r_{12}$"). Another key feature is represented by the fact that locality of fitting coefficients is obtained even with the long-ranged Coulomb metric, as result of integral accuracy.

Here we report on recent advances in the development of the CD-based DF technology. In particular, the implementation of analytical gradients algorithms is reviewed and the present status of local formulations – potentially linear scaling – is analyzed in great details.

1 Introduction

Per-Olof Löwdin left a monumental legacy for the advance of understanding in quantum chemistry. Among its contributions, the study of inner projections of positive-definite operators spans over several of his publications and has lead to important results especially in the context of perturbation theory. At the same time, one possible use of inner projections in quantum chemistry that seems to have escaped Löwdin's attention[1] was instead brought to light by one of his former students. Jan Linderberg, in collaboration with Nelson H. F. Beebe, published in 1977 a paper[2] entitled "Simplifications in the Generation and Transformation of Two-Electron Integrals in Molecular Calculations" that would go almost unnoticed for the next two decades or more. The paper showed how inner projection of the Coulomb operator could be used in order to reduce the number of electron repulsion integral (ERIs) that need to be calculated. The idea exploits the presence of numerical linear dependencies among the columns of the ERI matrix and results in an algorithm that is in all respects a

form of incomplete Cholesky decomposition of the ERI matrix. Despite sporadic attempts[3–5] to further develop the idea of Beebe and Linderberg, what is now known as Cholesky decomposition (CD) approximation to the two-electron integrals seemed to be destined to stay a forgotten method at the bottom of the quantum chemistry toolbox. The breakthrough arrived in 2003 with a paper by Koch *et al.* presenting the first fully fledged implementation of the CD approximation within Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory (MP2).[6]

Since this first general implementation the CD approximation has been used in many computational chemistry studies,[7–24] and it is now available within several quantum chemistry packages for a wide range of electronic structure methods, including density-functional theory (DFT) and HF,[6,25,26] multiconfigurational second-order perturbation theory (CASSCF/CASPT2),[27–29] multireference configuration interaction,[30–33] Møller–Plesset perturbation theory,[6,34–36] Coupled Cluster (CC) theory,[37–40] electron propagator methods,[41] symmetry-adapted perturbation theory,[42] fragment molecular orbital theory,[43] and quantum Monte Carlo.[44]

The use of CD-based algorithms has made possible nowadays calculations at the correlated level with thousands of basis functions,[45] and for systems with up to hundreds of atoms through the use of the Local Exchange (LK) screening algorithm[25] and the localized Cholesky orbitals basis.[46] Moreover, the cost of correlation methods can be reduced even further by invoking the frozen natural orbital (FNO) approximation.[47–50] In the context of the FNO approximation we have employed CD of the molecular orbital (MO) ERIs to effectively compute a correlated density matrix from which a spectral decomposition is used to reduce the size of the secondary orbital space with no significant loss of accuracy.[51,52]

In this wave of revived interest for the pivotal idea of Beebe and Linderberg, a major shortcoming of the original formulation of the CD method has been eliminated that allows for the formulation of analytical gradients. For many years the CD approximation was in fact thought as a purely numerical technique to represent the integral matrix through a tensor product. When computing energy gradients, O'Neal

and Simons[4] attempted to perform a CD of the supermatrix that includes derivative integrals in addition to the ERIs, hence remaining in the framework of a numerical apporach to the problem. Fortunately, a truly analytical gradient formulation became possible after it was recognized that CD approximation is a particular type of density fitting (DF) approximation to the ERIs in which the auxiliary basis set is generated from the set of atomic orbital (AO) product densities.[53] Presently, analytical gradients are available for a variety of *ab initio* wave function and DFT methods, showing similar speed-ups as for the energy calculation, while hardly affecting the computed equilibrium structures. These latest developments have been of particular impact in photochemistry, where CD-based multiconfigurational wave function methods can now be used to optimize excited-state structures and photochemical reaction paths thanks to the availability of energy gradients and non-adiabatic coupling vectors.

The standard DF technique for approximating ERIs relies on the quality of auxiliary basis sets that are obtained through data fitting and are usually biased towards specific types of quantum chemistry methods and problems—thermodynamic energy differences, valence or core excited states, etc. With the proof of the equivalence between the DF and the CD paradigms for ERI approximation, not only became possible to complement the CD approximation with analytical properties, but at the same time the DF idea was freed from the need to use pre-optimized auxiliary basis sets. In fact, the removal of linear dependence in the product space of both contracted and primitive orbitals allows for on-the-fly construction of auxiliary basis sets that may be used in conjunction with any quantum chemical method, i.e., unbiased auxiliary basis sets. The use of such "Cholesky basis" effectively defines an *ab initio* DF approximation with nearly complete error control as well as intrisic locality that can be exploited towards the formulation of linear-scaling algorithms.

2 Inner projection of the Coulomb operator

Given a positive definite operator V and a projector P onto a subspace in the domain of V, the following mathematical properties hold

$$V = V^{1/2} V^{1/2} \succeq V^{1/2} P V^{1/2} \succeq 0 \,, \tag{1}$$

where $V^{1/2}$ denotes the positive square root of V and the inequalities are to be understood in the expectation value sense of Löwdin.[1] A new operator $\tilde{V} = V^{1/2} P V^{1/2}$ – the inner projection of V with respect to P – can then be defined that provides a lower bound to the initial operator V.

For the purpose of using the inner projection of eq. (1) in the context of ERIs approximation, we start by mapping the product densities $\chi_\mu \chi_\nu$, where χ are atomic basis functions, onto a set of one-index functions h_K. A new set of functions $\tilde{h}_J$ can be obtained by the following Gram–Schmidt orthogonalization:

$$\tilde{h}_J = h_J - \sum_{K=1}^{J-1} \tilde{h}_K \frac{\langle \tilde{h}_K | V | h_J \rangle}{\langle \tilde{h}_K | V | \tilde{h}_K \rangle^{1/2}} \qquad (J = 1, \ldots, M) \,. \tag{2}$$

The above set of functions constitutes a basis for a projector operator defined as

$$P = V^{1/2} |\tilde{\boldsymbol{h}}\rangle \langle \tilde{\boldsymbol{h}} | V | \tilde{\boldsymbol{h}} \rangle^{-1} \langle \tilde{\boldsymbol{h}}| \, V^{1/2} \,, \tag{3}$$

onto which to form the inner projection of V as follows:

$$\tilde{V} = V \, |\tilde{\boldsymbol{h}}\rangle \langle \tilde{\boldsymbol{h}} | V | \tilde{\boldsymbol{h}} \rangle^{-1} \langle \tilde{\boldsymbol{h}}| \, V \,. \tag{4}$$

The matrix elements of $\tilde{V}$ are then obtained from (4) as

$$\langle h_I | \tilde{V} | h_K \rangle = \sum_{J=1}^{M} \frac{\langle h_I | V | \tilde{h}_J \rangle}{\langle \tilde{h}_J | V | \tilde{h}_J \rangle^{1/2}} \frac{\langle \tilde{h}_J | V | h_K \rangle}{\langle \tilde{h}_J | V | \tilde{h}_J \rangle^{1/2}} = \sum_{J=1}^{M} L_I^J L_K^J \,. \tag{5}$$

The orthogonalization (2) is continued until the subtraction produces negligibly small

diagonal elements $\langle h_I|\tilde{V}|h_I\rangle$, which arises if the functions $\boldsymbol{h}$ are nearly linearly dependent, hence the number M of functions $\tilde{h}$ is always smaller than the total number $N(N+1)/2$ of unique product densities h in an AO basis composed of N functions. In typical cases, the resulting value for M is in the range $3N$ to $5N$ and scales linearly with the number of AO basis functions N, as shown in the example of fig. 1. Moreover, eq. (5) is equivalent to the corresponding Cholesky decomposition of the matrix V continued until M so-called Cholesky vectors $\boldsymbol{L}$ have been generated.[13,53] Finally, due to the inner product nature of the approximation, the matrix regenerated by the Cholesky vectors is actually the matrix representation of $\tilde{V}$, which means that expectation values computed from these two-electron integrals will be lower bounds to the results obtained using the original matrix elements.

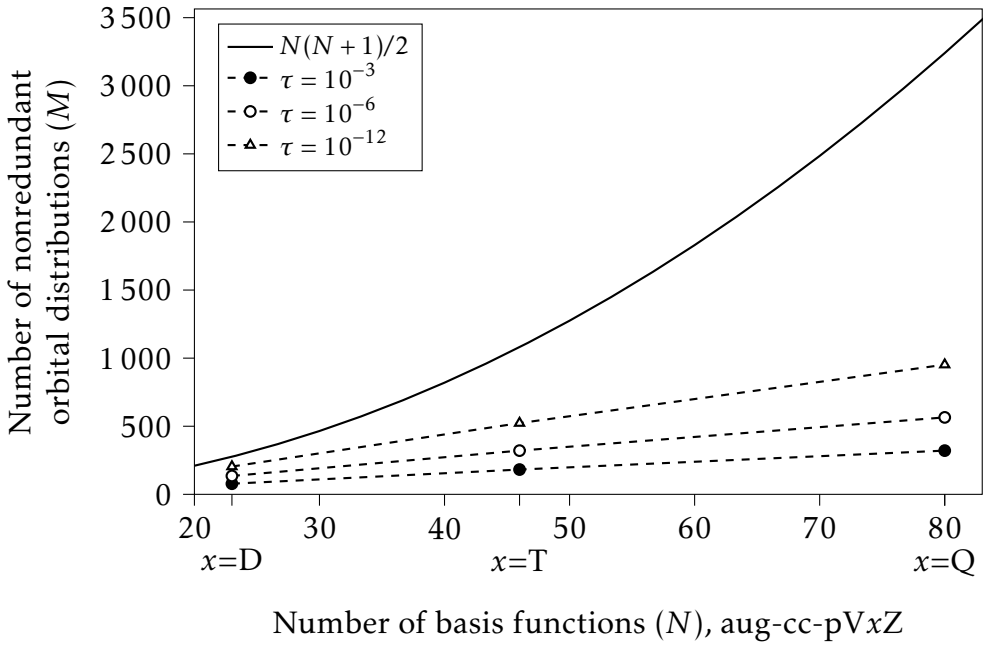

Figure 1: Carbon atom. Number of linearly-independent functions $\tilde{h}$ at different CD thresholds (τ). The total number of product densities $\boldsymbol{h}$ in each aug-cc-pVXZ basis is reported for comparison.

3 The "density fitting/resolution of identity" point of view

The idea behind DF is to approximate the AO product densities with a linear expansion on a set of auxiliary basis functions $\chi_K = |K\rangle$:

$$\chi_\mu \chi_\nu = |\mu\nu\rangle \approx |\widetilde{\mu\nu}\rangle = \sum_K |K\rangle\, C^K_{\mu\nu} \,. \tag{6}$$

To this aim, one starts by defining a suitable error function for the approximation, of the type

$$\Delta_{\mu\nu} = \left(\chi_\mu \chi_\nu - \sum_K C^K_{\mu\nu} \chi_K \middle| \hat{g} \middle| \chi_\mu \chi_\nu - \sum_K C^K_{\mu\nu} \chi_K \right) , \tag{7}$$

which is in fact a measure of the "distance" (in Hilbert space) between the fitted and the target product densities, defined through a given positive definite metric $\hat{g}$. Minimization of the above function leads to the set of linear equations for the expansion coefficients:

$$\sum_I G_{IK} C^I_{\mu\nu} = \langle \mu\nu | K \rangle_g \,, \tag{8}$$

where $G_{IK} = \langle I|K\rangle_g$ and $\langle \cdot|\cdot\rangle_g = (\cdot|\hat{g}|\cdot)$. The Coulomb metric, $\hat{g} = r_{12}^{-1}$, gives the most accurate representation of the ERIs[54,55] and it is therefore the most common choice for the metric. In this case, ERIs can be expressed in a form that is reminiscent of a resolution of the identity (RI), namely

$$(\mu\nu|\lambda\sigma) \approx \widetilde{(\mu\nu|\lambda\sigma)} = \sum_{IK} C^I_{\mu\nu} (I|K) C^K_{\lambda\sigma} = \sum_{IK} (\mu\nu|I)(I|K)^{-1}(K|\lambda\sigma) \,, \tag{9}$$

from which comes the name "RI approximation" often employed for the DF approximation to the ERIs. (Note that we have used the common but somewhat misleading short-hand notation $(I|K)^{-1}$ which is intended to mean $(\boldsymbol{W}^{-1})_{IK}$ with $W_{IK} = (I|K)$.) Still within the choice of the Coulomb metric, the solution of eq. (8) leads to a well-defined

measure of the error introduced by the DF/RI approximation:

$$\Delta_{\mu\nu}^{\min} = (\mu\nu|\mu\nu) - \sum_{IK} C_{\mu\nu}^{I}(I|K)C_{\mu\nu}^{K} \,. \tag{10}$$

The quantity $\Delta_{\mu\nu}^{\min}$ measures the error in representing the diagonal element of the ERI matrix, indicating that an externally defined auxiliary basis set will in general not lead to the global minimum for the DF variational condition, eq. (7). As $\Delta_{\mu\nu}$ is nonnegative, the global minimum is *zero* and is reached only when the auxiliary basis set spans the same space as the product densities $\chi_\mu\chi_\nu$. The ERI matrix is then represented exactly by the DF approach.

Standard auxiliary basis sets are chosen to be Gaussian functions centered on the nuclei. The number of auxiliary basis functions scales therefore linearly with system size and the computed electronic energy is a continuous function of the nuclear positions. These auxiliary basis sets have been optimized to reproduce, within an allowed error span, some specific quantities (e.g., Coulomb energy, MP2 correlation energy correction, etc.) for each valence basis set by minimization of the energy errors in a set of atomic calculations.[56–59] Since such optimization is performed without any direct constraint regarding the representation of the integral diagonals, as measured by eq. (10), the resulting basis set cannot be used to approximate the ERI matrix without major concerns. This is an important issue but is often overlooked as, for instance, is the problem of the intrinsic higher difficulty in fitting exchange or MP2 energy compared to the Coulomb energy. We can view this problem in terms of the matrices that need to be accurately represented when approximating the different energy contributions in a spin-compensated formulation. For MP2, it is the occupied-virtual block $(ia|jb)$ of the ERI matrix in MO basis. For Coulomb (E_C) and exhcange (E_X) energies we have, respectively :

$$E_C = 2\sum_{ij}(ii|jj) \qquad\qquad E_X = -\sum_{ij}(ij|ij)\,, \tag{11}$$

where the orbital indices belong to the occupied space only. It is immediate to rec-

ognize that the Coulomb matrix is exactly representable by at most O auxiliary functions (Cholesky vectors) in MO basis, where O is the number of occupied orbitals. Already for the K matrix, this limit is instead O^2 and becomes OV for the integrals needed in MP2, with V being the number of virtual orbitals. The success in reproducing Coulomb energies by externally optimized auxiliary basis does not imply a similar fate for these other quantities. In particular, there is a fundamental inconsistency in trying to fit directly the $(ij|kl)$ and $(ai|bj)$ quantities using atom-centered auxiliary functions: the number of significant product densities in (canonical) MO basis, $|ij\rangle$ or $|ai\rangle$, scales quadratically with the size of the molecule while the auxiliary basis by definition will scale only linearly! This inconsistency is not present in fitting the Coulomb energy since the number of $|ii\rangle$ scales linearly too. The only way to ensure a consistent fit of these quantities by atom-centered auxiliary functions is indeed by producing an accurate fit of the AO ERI matrix. Once this condition is fulfilled, any quantity in MO basis will be reproduced with the same accuracy since it is derived through algebraic manipulations from the corresponding one in AO basis. Since in AO basis the number of significant product densities $\chi_\mu\chi_\nu$ does scale linearly with the size of the system, the inconsistency disappears.

On the other hand, if we consider an isolated atom, the CD of its ERI matrix[2] provides an upper bound for the value of $\Delta^{\min}_{\mu\nu}$, eq. (10),

$$\Delta^{\min}_{\mu\nu} = (\mu\nu|\mu\nu) - \sum_J \left(L^J_{\mu\nu}\right)^2 \leq \tau \,, \tag{12}$$

where $L^J_{\mu\nu}$ are the Cholesky vectors and τ is the decomposition threshold. From eq. (2) we identify the "Cholesky basis" h_K's through atomic CDs (aCDs) for atom $A, B, \ldots$. Hence, we obtain an auxiliary basis set for DF approximation to the molecular ERI matrix, but one for which there is strict error control on the one-center and two-center "Coulomb" ERIs, namely the integrals of the type $(AA|AA)$ and $(AA|BB)$, respectively. This can be understood by considering the fact that the DF approximation is an inner

projection and therefore the following Cauchy–Schwarz inequality holds:

$$\left|\Delta^{\min}_{\mu\nu,\lambda\sigma}\right| = \left|(\mu\nu|\lambda\sigma) - \sum_{IK} C^{I}_{\mu\nu}(I|K)C^{K}_{\lambda\sigma}\right| \leq \Delta^{1/2}_{\mu\nu}\Delta^{1/2}_{\lambda\sigma} \,. \tag{13}$$

From eqs. (12) and (13), we can see that the errors in the DF approximation to the ERIs of the type $(AA|AA)$ and $(AA|BB)$ are bound by the aCD threshold τ, whereas those of the type $(AB|**)$ may be affected by larger errors. In fig. 2 it is clearly shown how these errors are nonetheless much smaller than those arising from standard auxiliary basis sets[56–59] tailored specifically for Coulomb contributions (RI-J)[60] and MP2 contributions (RI-C)[58] to the energy. The robustness of the aCD-based DF approximation has been further established in a number of benchmark studies.[61–63]

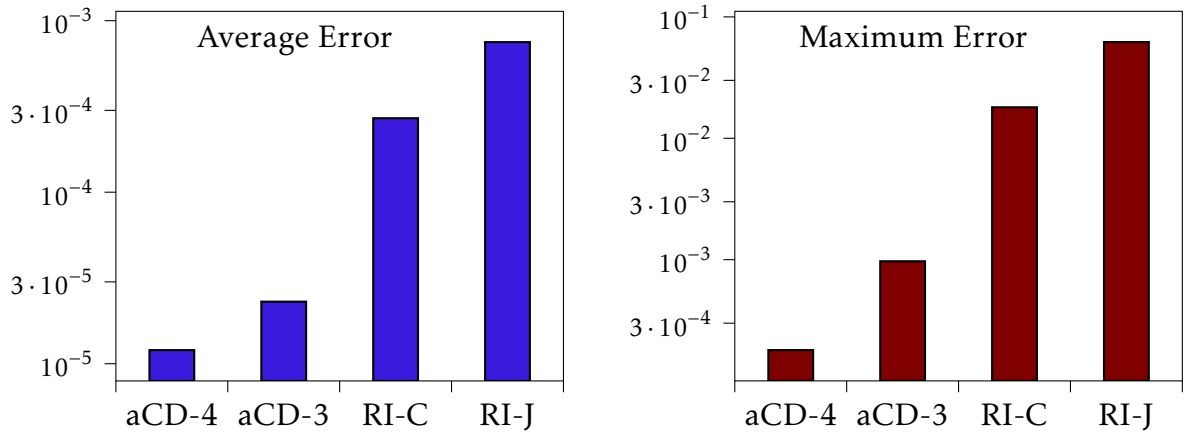

Figure 2: Benzene molecule, cc-pVTZ basis set: average and maximum error in the approximation of the AO diagonal ERIs with various types of DF approximations. The notation aCD-n is used to indicate an auxiliary basis set generated by CD of atomic ERIs with a threshold $\tau = 10^{-n}E_{\mathrm{h}}$. Auxiliary basis "RI-J" as in Eichkorn *et al.*[60] and "RI-C" as in Weigend *et al.*[58]

The quality of such aCD auxiliary basis set is controlled by the aCD threshold, thus defining a hierarchy of sets by varying the threshold. This also implies that contrary to standard auxiliary basis sets the aCD sets are generated on-the-fly rather than stored in a standard basis set library format. Consequently, aCDs are by way of construction available for any atom type and AO basis set. Finally, as they are derived *ab initio* by ensuring upper bounds on the DF error function of eq. (10), the unbiased nature of the resulting DF approximation is guaranteed.[28,63] From a practical point of view, a raw

aCD auxiliary basis set does not have the structure of complete shells and therefore they are not spherically balanced. This is somewhat incompatible with standard integral code implementations. This problem is circumvented by adding auxiliary functions to get a complete shell structure at the price of slightly increased computational costs associated with the subsequent use of the DF representation. Another drawback of the aCDs compared to standard auxiliary basis sets is the large number of primitive functions. This problem is eliminated by exploiting the linear dependence in an atomic ERI matrix constructed in the primitive basis. This is a natural extension of the principle underlying the aCD auxiliary basis sets, and defines the atomic compact CD (acCD) class of auxiliary basis sets.[64] The acCD sets achieve virtually the same level of accuracy as the corresponding aCD sets, but require only a fraction of the primitive space needed by the latter. This is particularly important for regular basis sets constructed as contractions of large primitive sets, such as the atomic natural orbitals (ANO) class of regular basis sets.

4 Local fitting with Cholesky decomposition

Solving the linear equations (8) requires an effort that scales cubically with system size. However, a very low prefactor is achieved by Cholesky decomposition rather than explicit inversion of the symmetric positive definite metric matrix $\boldsymbol{G}$ and other computational tasks dominate for all but the very largest systems. Among such tasks, one of the most challenging is the evaluation of the exact-exchange matrix in single- as well as multireference calculations. The exact-exchange matrix is given by

$$K_{\mu\nu} = \sum_{\lambda\sigma} (\mu\lambda|\nu\sigma) D_{\lambda\sigma} \,, \tag{14}$$

where $\boldsymbol{D}$ is a one-electron density matrix. With $\boldsymbol{D}$ dense, exact-exchange evaluation scales quadratically with system size. If the number of non-zero elements in $\boldsymbol{D}$ scales linearly, as is the case for wide-gap insulators, the exact-exchange matrix can be evaluated in linear time,[65,66] albeit with a computational prefactor and an onset to linear

scaling that both grow rapidly with basis set quality (i.e., basis set size per atom).

While the prefactor can be reduced with the RI technique,[59] it becomes impossible to achieve linear scaling with system size when the most accurate Coulomb metric is used. Even if density-matrix sparsity is exploited the best possible scaling is quadratic.[25] The reason for this behavior is the expansion of all *local* AO product densities in a *delocalized* auxiliary basis, making the expansion coefficients determined by the linear equations (8) decay slowly in general, even as slowly as the Coulomb operator itself.[55,67] Consequently, different approaches have been proposed to reduce the scaling. These approaches fall in two overall but not disjoint categories: local metric fitting and local domain fitting. Local metric fitting forces the expansion coefficients to decay more rapidly through the use of a short-ranged metric,[55,67,68] while local domain fitting achieves the same by restricting the expansion to auxiliary functions in a chosen vicinity of each local AO product density.[69–73] Combinations of local metric fitting and local domain fitting have been proposed, too.[74,75]

Since neither of the two categories of local fitting can be recast as a proper inner projection of the Coulomb operator, strict integral-error control is lost in general. It is possible to restore, at least partially, error control by using Dunlap's robust fitting formula in place of eq. (9),[76]

$$\widetilde{(\mu\nu|\lambda\sigma)} = (\widetilde{\mu\nu}|\lambda\sigma) + (\mu\nu|\widetilde{\lambda\sigma}) - (\widetilde{\mu\nu}|\widetilde{\lambda\sigma}) \,. \tag{15}$$

This ensures that the integral error is bilinear in the fitting error

$$(\mu\nu|\lambda\sigma) - \widetilde{(\mu\nu|\lambda\sigma)} = (\mu\nu - \widetilde{\mu\nu}|\lambda\sigma - \widetilde{\lambda\sigma}) \,, \tag{16}$$

and, in the Coulomb metric, provides us with an upper bound to the integral error

$$\left|(\mu\nu - \widetilde{\mu\nu}|\lambda\sigma - \widetilde{\lambda\sigma})\right| \leq \Delta_{\mu\nu}^{1/2}\Delta_{\lambda\sigma}^{1/2} \,, \tag{17}$$

since each "distance" $\Delta_{\mu\nu}$ is then minimized for a given auxiliary basis. Strict error

control is only guaranteed if the auxiliary functions spans the same space as the AO product densities to within a small tolerance $\tau \geq 0$ such that $\Delta_{\mu\nu} \leq \tau$ for all $\mu\nu$.

Robust fitting suffers from one major drawback: Eq. (15) is not unconditionally positive semidefinite, occasionally resulting in spurious attractive interactions among the electrons, which causes convergence problems in self-consistent field solvers or even convergence to an unphysical solution.[77] In actual calculations the lack of positive semidefiniteness reveals itself in much too low, often negative, two-electron energies. This can be understood in the following manner. With a given density matrix or, equivalently, a given space of occupied orbitals, the difference between the direct Coulomb energy calculated with exact and approximate integrals is strictly nonnegative,[78]

$$E_C - \tilde{E}_C = 2 \sum_{ij} (ii - \widetilde{ii}|jj - \widetilde{jj}) \geq 0 \,. \tag{18}$$

While $E_C = 2\sum_{ij}(ii|jj) \geq 0$, $\tilde{E}_C$ may be negative due to negative eigenvalues of the approximate integral matrix $\widetilde{(ii|jj)}$ without violating the inequality above. Variational calculations aim to minimize the energy and thus may lead to a formally valid density matrix with associated negative two-electron energy. The exchange energy behaves differently; the difference between the exchange energy calculated with exact and approximate integrals is strictly nonpositive,[79]

$$E_X - \tilde{E}_X = -\sum_{ij} (ij - \widetilde{ij}|ij - \widetilde{ij}) \leq 0 \,. \tag{19}$$

Hence, $\tilde{E}_X \geq E_X$ for any given density matrix, and variational instabilities do not occur due to this contribution. In conclusion, Dunlap's robust fitting should only be used with great care for Coulomb contributions but may be used with impunity for exchange contributions.

We now return to the problem of slow decay of the expansion coefficients obtained from eq. (8) in the Coulomb metric. To appreciate the underlying problem, we first study a generalized example. Suppose that we have expanded a set of functions $|\boldsymbol{f}\rangle$, known to be (near-) linearly dependent in a positive definite metric $\hat{g}$, in a linearly

independent set $|\boldsymbol{A}\rangle$, i.e.

$$|\boldsymbol{f}\rangle \approx |\tilde{\boldsymbol{f}}^{(0)}\rangle = |\boldsymbol{A}\rangle \boldsymbol{C}_{\boldsymbol{A}}^{(0)} \,, \tag{20}$$

where the coefficients are determined from eq. (8) as

$$\boldsymbol{C}_{\boldsymbol{A}}^{(0)} = \langle \boldsymbol{A}|\hat{g}|\boldsymbol{A}\rangle^{-1} \langle \boldsymbol{A}|\hat{g}|\boldsymbol{f}\rangle \,. \tag{21}$$

Next, suppose we extend the auxiliary basis to include another set $|\boldsymbol{B}\rangle$ such that

$$|\boldsymbol{f}\rangle \approx |\tilde{\boldsymbol{f}}\rangle = |\boldsymbol{A}\rangle \boldsymbol{C}_{\boldsymbol{A}} + |\boldsymbol{B}\rangle \boldsymbol{C}_{\boldsymbol{B}} \,. \tag{22}$$

In this case, the fitting equations (8) yield the coefficients

$$\boldsymbol{C}_{\boldsymbol{A}} = \boldsymbol{C}_{\boldsymbol{A}}^{(0)} - \langle \boldsymbol{A}|\hat{g}|\boldsymbol{A}\rangle^{-1} \langle \boldsymbol{A}|\hat{g}|\boldsymbol{B}\rangle \boldsymbol{C}_{\boldsymbol{B}} \,, \tag{23}$$

$$\boldsymbol{C}_{\boldsymbol{B}} = \left[\langle \boldsymbol{B}|\hat{g}|\boldsymbol{B}\rangle - \langle \boldsymbol{B}|\hat{g}|\boldsymbol{A}\rangle \langle \boldsymbol{A}|\hat{g}|\boldsymbol{A}\rangle^{-1} \langle \boldsymbol{A}|\hat{g}|\boldsymbol{B}\rangle\right]^{-1} \langle \boldsymbol{B}|\hat{g}|\boldsymbol{f} - \tilde{\boldsymbol{f}}^{0}\rangle \,. \tag{24}$$

Evidently, $\boldsymbol{C}_{\boldsymbol{B}} \neq \boldsymbol{0}$ in general. In the context of RI, this result implies that auxiliary basis functions far away from the AO product density will contribute significantly to the fit, even if the original local expansion (20) is sufficiently accurate for all practical purposes. The exact decay of the coefficients generally depends in a complicated manner both on the metric and on the dimensionality of the auxiliary basis and is hard to predict in real-life applications.[67] However, eq. (24) directly verifies the obvious solution: if the auxiliary set $|\boldsymbol{A}\rangle$ is *locally complete*, i.e. spans the same space as the target functions $|\boldsymbol{f}\rangle$, then $|\boldsymbol{f} - \tilde{\boldsymbol{f}}^{0}\rangle = \boldsymbol{0}$ so that no extension of the auxiliary basis will change the fit: $\boldsymbol{C}_{\boldsymbol{B}} = \boldsymbol{0}$ and $\boldsymbol{C}_{\boldsymbol{A}} = \boldsymbol{C}_{\boldsymbol{A}}^{(0)}$ regardless of distance. As discussed previously, Cholesky decomposition provides a route to locally complete auxiliary sets by removing linear dependence among the target functions in a given metric and may thus be viewed as inherently local.[13,64,77] In fig. 3, we see an example of such "*locality from completeness*" of the aCD auxiliary basis sets: at variance with standard RI-C and similar basis sets, contaminants in Cholesky-based approximations can be smoothly eliminated by lowering the decomposition threshold, independently of the geometry of the system and

the nature of the metric chosen.

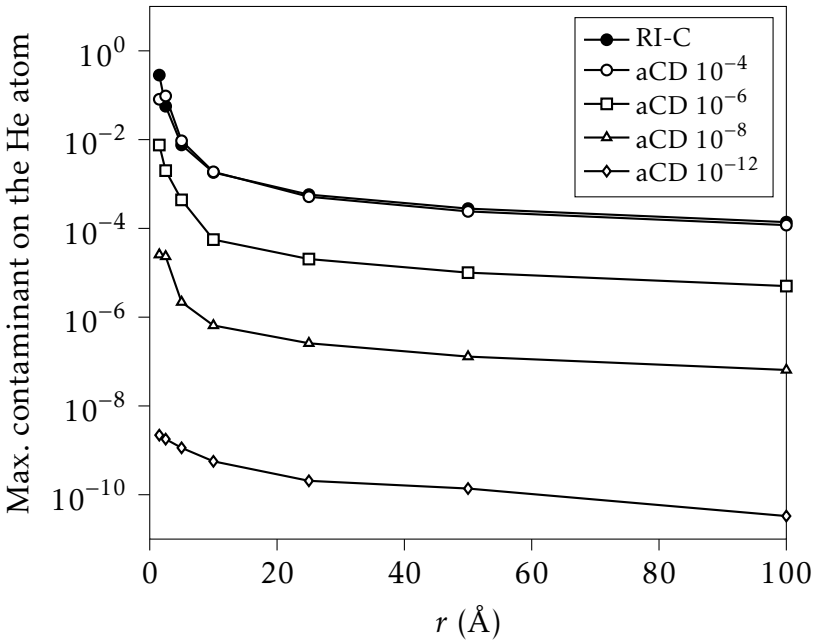

Figure 3: He$-$C$_6$H$_6$ system. Decay of the largest contaminant of the fitting coefficients on He atom as function of the point-plane distance r between He atom and benzene molecule. Logarithmic scale is employed for the vertical axis. The AO basis set used for He is cc-pVTZ whereas a cc-pVDZ basis set is used for the atoms of the benzene molecule. Auxiliary basis "RI-C" as in Weigend *et al.*[58]

We shall now examine the most local form of RI, known as the pair-atomic resolution-of-the-identity (PARI) method.[77] Let $\{\mu_A\nu_B\}$ denote the set of AO product densities where the AOs are centered on atoms A and B as indicated by the subscripts. The number of such sets scales linearly with system size, since $\mu_A\nu_B \to 0$ exponentially as the distance between atoms A and B increases. For each overlapping atom pair AB we can now fit the AO product densities in a Cholesky basis obtained by incomplete Cholesky decomposition of the ERI pair-atomic diagonal block $(AB|AB)$ with threshold τ,

$$|\mu_A\nu_B) \approx |\widetilde{\mu_A\nu_B}) = \sum_{I\in AB} |I) C^I_{\mu_A\nu_B} \,. \tag{25}$$

By construction of the auxiliary basis, the integral error is bounded from above according to

$$\left|(\mu_A\nu_B|\lambda_A\sigma_B) - (\widetilde{\mu_A\nu_B}|\widetilde{\lambda_A\sigma_B})\right| \leq \tau \,, \tag{26}$$

for each atom pair AB. Strict integral-error control is achieved through the robust

integral formula (15), i.e.

$$\left|(\mu_A \nu_B - \widetilde{\mu_A \nu_B}|\lambda_C \sigma_D - \widetilde{\lambda_C \sigma_D})\right| \leq \tau \,, \tag{27}$$

and the problems associated with negative eigenvalues disappear with small enough τ,[77] since

$$\tau \longrightarrow 0 \quad \Longrightarrow \quad (\widetilde{\mu_A \nu_B}|\lambda_C \sigma_D) + (\mu_A \nu_B|\widetilde{\lambda_C \sigma_D}) - (\widetilde{\mu_A \nu_B}|\widetilde{\lambda_C \sigma_D}) \longrightarrow (\widetilde{\mu_A \nu_B}|\widetilde{\lambda_C \sigma_D}) \,, \tag{28}$$

which is a positive semidefinite matrix by construction. The PARI method thus becomes exact with the Cholesky basis as $\tau \to 0$.

There are, however, substantial problems associated with this approach. The Cholesky basis is composed of products of AOs centered on different atoms and thus becomes a function of atomic positions. First of all, this feature may result in potential-energy-surface discontinuities, although these must become insignificant as the threshold is decreased (continuity is, of course, fully restored at $\tau = 0$). Second, using AO products as auxiliary functions implies that expensive four-center ERIs must be evaluated, thus annihilating one of the main computational advantages of the RI approach. For these reasons, the PARI approach is normally formulated as an expansion in atom-centered auxiliary functions[77]

$$|\mu_A \nu_B) \approx |\widetilde{\mu_A \nu_B}) = \sum_{I \in A \cup B} |I) C^I_{\mu_A \nu_B} \,, \tag{29}$$

where the summation restriction is meant to imply that $|I)$ is centered on either atom A or atom B. The atom-centered auxiliary functions may be chosen freely, although the choice decisively impacts both accuracy and precision of the results. Choosing the aCD or acCD auxiliary sets obtained with a given threshold τ, this formulation guarantees the accuracy of integral blocks of the types $(AA|AA)$ and, provided the robust integral formula (15) is used, $(AA|BB)$—all other integral blocks typically have errors significantly greater than τ and, more importantly, these errors can not be reduced by

decreasing τ. It is still possible to restore strict integral-error control by adding to the auxiliary basis, for each atom pair individually, those linearly independent AO products that are not spanned (to within a specified target accuracy) by the atom-centered auxiliary functions. Even this approach turns out to require too many four-center ERIs to be of general practical interest, however.

The accuracy and computational performance of the robust PARI method has been rather well tested over the past few years.[77,79–82] Although these investigations all employ standard auxiliary basis sets rather than aCD and acCD, we note that using the latter is unlikely to alter the conclusions dramatically. The tests include total and relative energy errors obtained within HF, hybrid DFT, and range-separated hybrid DFT methods. The earlier tests use the PARI approach for both the Coulomb and exchange contributions,[77,80] whereas the most recent tests use the PARI method only for the exchange contribution to circumvent convergence issues due to the loss of positive semidefiniteness.[79,81,82] Convergence issues are rare, occuring in about 1% of the cases where the PARI method is applied to the Coulomb contribution,[77,80] and occurrences can be further reduced, but not completely removed, using larger auxiliary basis sets in conjunction with the semi-exact PARI modification of Hollman *et al.*[80] in which all diagonal blocks of the ERI matrix are treated exactly. It is worth noting that the semi-exact PARI approach yield total energy errors well below those observed with the (full) RI approach. Although total-energy errors are somewhat greater and more spread with robust PARI than with RI and other well-established approximations, satisfactory results are obtained for energy differences such as atomization energies and reaction energies.

It is also clear, however, that while the robust PARI method is faster than the RI method, it does not accelerate the calculation of the exchange contribution sufficiently to be comparable with the Coulomb contribution computed using RI.[82] The main bottleneck is the calculation of terms involving the three-center ERIs of the robust formula. (15) Considering also the loss of positive semidefiniteness, it becomes attractive to use the nonrobust formula (9) within the PARI method. This, however, requires

auxiliary basis sets that are close to locally complete to be successful. The nonrobust PARI approximation, though not thoroughly investigated with Gaussian basis sets, has been proven useful with numerical basis set.[83] To achieve the flexibility required in the auxiliary basis set to make the nonrobust PARI method usable, whilst insisting on atom-centered functions, Ihrig *et al.*[83] employ a philosophy reminiscent of the aCD and acCD sets. For the sole purpose of generating an atom-centered auxiliary basis set, they first add an additional set of functions, including high angular momenta functions, to the regular basis set, followed by removal of linearly dependent functions in the set of AO products obtained from the extended regular basis on the atom in question. This maintains the accuracy of atomic integral blocks and significantly improves the accurary of atom pair blocks, which implies accuracy improvements in all ERI blocks. It should be possible to apply this idea to Gaussian basis sets too—work along these lines is in progress in our labs.

5 Analytical gradients in Cholesky decomposition-based quantum chemistry

The usefulness and appeal of any quantum chemistry technique increases significantly if a practical way to compute analytical derivatives with respect to nuclear displacements is available. This opens the door to using the tool for an efficient exploration of potential energy surfaces: geometry optimization of minima and transition states, molecular dynamics, etc.

The initial formulations of the Cholesky decomposition technique were a purely numerical approximation to the ERI matrix, which made defining analytical derivatives a difficult task. O'Neal and Simons[4] proposed applying the CD to an extended positive semidefinite matrix that includes undifferentiated and differentiated integrals. Since most of the first derivative atomic orbital product functions belong to the space spanned by the undifferentiated products, the number of Cholesky vectors is not much larger than in the standard undifferentiated decomposition. But when the

connection between CD and DF was identified, it became possible to directly calculate the exact analytical derivatives of the approximate integrals, instead of an approximation to the exact integral derivatives.

With the two-electron integrals approximated as in eq. (9), there are several dependences on the nuclear coordinates to consider. First there is an explicit dependence of the auxiliary basis functions, coming from the fact that the primitive functions they are built on are typically centered on the atomic nuclei. Second, the fitting coefficients $C^K_{\mu\nu}$ are also dependent on the geometry. And finally, the number and type of auxiliary functions included in the summation are subject to change with the molecular structure too.

The second dependence is only apparent, as the two-electron integrals can be expressed only in terms of two- and three-center integrals involving auxiliary functions (eq. (9)), and thus the derivatives of the fitting coefficients are not required. Moreover, when an externally defined auxiliary basis set is used, the third dependence disappears, since the auxiliary functions are fixed. But if an on-the-fly auxiliary basis set is generated through Cholesky decomposition, it is problematic to treat rigorously and can in fact lead to discontinuities in potential energy surfaces. Although the difficulty can be reduced by allowing only one-center product functions in the Cholesky basis and with a small enough decomposition threshold,[53] it can be strictly removed by using one of the atomic variants of the Cholesky decomposition, aCD or acCD. Indeed, in these variants the auxiliary basis functions are derived exclusively from the atomic blocks of the ERI matrix and are therefore independent of the molecular geometry, leaving only the explicit dependence of the integrals to take care of.

Thus, with fixed one-center auxiliary functions (external or CD), the first derivative of the density-fitted ERIs can be evaluated analytically:

$$\widetilde{(\mu\nu|\lambda\sigma)}^{(1)} = \sum_K C^K_{\mu\nu}(K|\lambda\sigma)^{(1)} + \sum_K C^K_{\lambda\sigma}(K|\mu\nu)^{(1)} - \sum_{KL} C^K_{\mu\nu}(K|L)^{(1)} C^L_{\lambda\sigma} \,, \tag{30}$$

involving only the derivatives of two- and three-center integrals and the fixed coef-

ficients $C^K_{\mu\nu}$. But simply using eq. (30) to evaluate two-electron integral derivatives would provide little gain, if any, over an integral-direct scheme where integral derivatives $(\mu\nu|\lambda\sigma)^{(1)}$ are computed on the fly as needed. The actual improvement is manifested when the expression is carried over to the two-electron contribution to the total molecular gradient. This contribution can in general be expressed as:

$$E_2^{(1)} = \sum_{\mu\nu\lambda\sigma} d^{\text{eff}}_{\mu\nu\lambda\sigma} (\mu\nu|\lambda\sigma)^{(1)} \,, \tag{31}$$

where $\boldsymbol{d}^{\text{eff}}$ is an effective two-particle density matrix whose exact definition depends on the method used to calculate the energy. Substituting eq. (30) into eq. (31) gives:

$$E_2^{(1)} = 2 \sum_{K\mu\nu} P^K_{\mu\nu} (K|\mu\nu)^{(1)} - \sum_{KL} P_{KL} (K|L)^{(1)} \,, \tag{32}$$

where P_{KL} and $P^K_{\mu\nu}$ are elements of the effective two- and three-index density matrices, respectively, given by:

$$P_{KL} = \sum_{\mu\nu\lambda\sigma} d^{\text{eff}}_{\mu\nu\lambda\sigma} C^K_{\mu\nu} C^L_{\lambda\sigma} \tag{33}$$

$$P^K_{\mu\nu} = \sum_{\lambda\sigma} d^{\text{eff}}_{\mu\nu\lambda\sigma} C^K_{\lambda\sigma} \,. \tag{34}$$

For a Hartree–Fock wave function, the two-particle density matrix can be defined in terms of the one-particle density matrix $\boldsymbol{D}$, readily giving Coulomb and exchange contributions:

$$d^{\text{eff}}_{\mu\nu\lambda\sigma} = d_{\mu\nu\lambda\sigma} = D_{\mu\nu} D_{\lambda\sigma} - \tfrac{1}{2} D_{\mu\sigma} D_{\nu\lambda} \,. \tag{35}$$

As is the case for the energy evaluation, computing the Coulomb contribution is straightforward, but for the exchange additional manipulations are needed to avoid four-index summations.[84] The resulting algorithm has a still unfavorable scaling, and a technique based on the LK (local exchange) screening devised for the exchange contribution to the Fock matrix[53] can be used to identify the pairs of orbitals that contribute

significantly to the energy gradient and skip all other (negligible) contributions. In this way, by taking advantage of the sparsity of the density matrix for sufficiently large systems, a quadratic scaling (instead of quartic) can be achieved.[84]

In the case of a state-average complete active space self-consistent field (SA-CASSCF) wave function, the calculation of analytic energy gradients is based on solving a set of linear equations to obtain the Lagrange multipliers, which are then used to compute the effective one- and two-particle density matrices, $\boldsymbol{D}^{\text{eff}}$ and $\boldsymbol{d}^{\text{eff}}$.[85,86] The two-particle density matrix cannot be expressed as compactly as eq. (35), but it can still be decomposed as:[87]

$$d_{\mu\nu\lambda\sigma} = d^{\text{A}}_{\mu\nu\lambda\sigma} + D^{\text{D}}_{\mu\nu}D^{\text{B}}_{\lambda\sigma} + D^{\text{B}}_{\mu\nu}D^{\text{D}}_{\lambda\sigma} - \tfrac{1}{2}\left(D^{\text{D}}_{\mu\sigma}D^{\text{B}}_{\nu\lambda} + D^{\text{B}}_{\mu\sigma}D^{\text{D}}_{\nu\lambda}\right), \tag{36}$$

where $\boldsymbol{d}^{\text{A}}$ is the two-particle density matrix involving only the active orbitals; $\boldsymbol{D}^{\text{D}}$ is a one-particle density matrix constructed, in MO basis, with 2 in the inactive diagonal and zero elsewhere; $\boldsymbol{D}^{\text{B}}$ is obtained subtracting half the inactive part ($\boldsymbol{D}^{\text{I}}$) from the total one-particle density matrix: ($\boldsymbol{D}^{\text{B}} = \boldsymbol{D} - \frac{1}{2}\boldsymbol{D}^{\text{I}}$). The distinction between $\boldsymbol{D}^{\text{D}}$ and $\boldsymbol{D}^{\text{I}}$ becomes important when computing nonadiabatic coupling vectors instead of gradients, since in this case the density matrices to use are transition density matrices, where the inactive part is zero, but the definition of $\boldsymbol{D}^{\text{D}}$ still holds. As for Hartree–Fock, Coulomb and exchange contributions can be identified, plus an active-only contribution. This latter contribution does not benefit from LK screening, but due to the usually small size of the active space it normally does not represent a significant overhead.[86,88]

In systems of medium-large size, the manipulation of the density matrices, especially for the exchange and active contributions, can become the most expensive part of computing molecular gradients, a situation any local fitting scheme would resolve. This is shown for a very simple test (series of linear alkanes C_nH_{2n+2} at random conformations, HF/ANO-RCC-VDZP energies and gradients) in fig. 4. For both conventional integrals and acCD integrals the figure shows the total CPU time spent on a full gradient calculation (including undifferentiated integrals, HF energy and gradient), as well as the two main tasks in the gradient proper: density matrix manipulation and inte-

gral derivatives. The total time is about one order of magnitude lower with acCD. The reduction of time spent in integral derivatives is even larger. Although the work on the density matrix manipulation increases substantially, the combined performance is still beneficial for the acCD calculations.

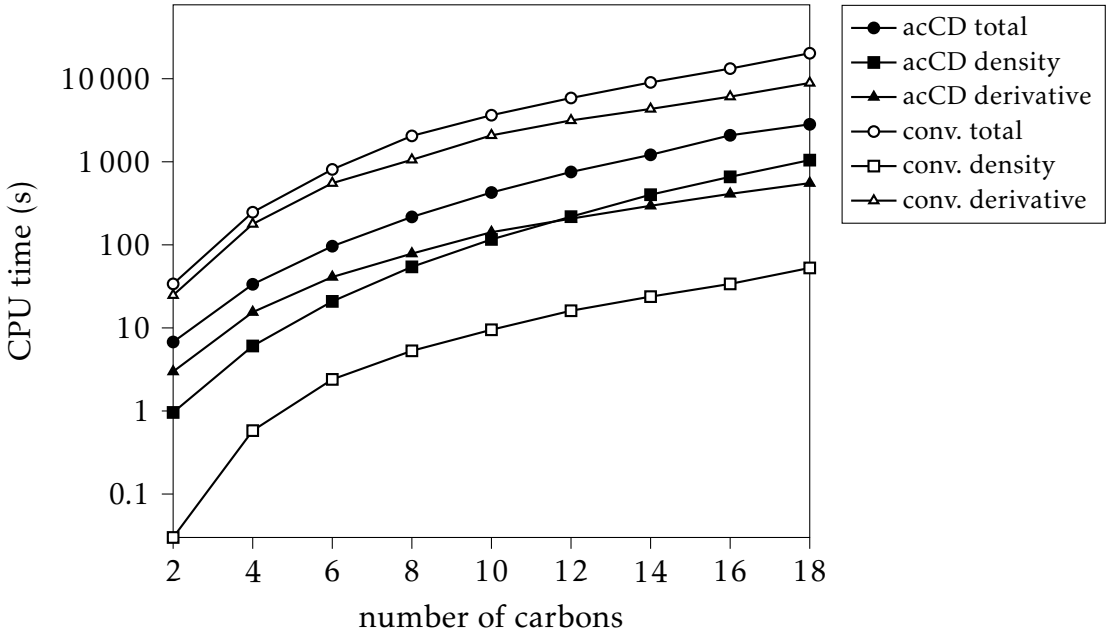

Figure 4: Timings for gradient calculations at HF/ANO-RCC-VDZP level of a linear alkane series, C_nH_{2n+2}. Calculations with acCD and conventional ("conv.") integrals. In the total CPU time, the energy evaluation and undifferentiated integrals generation are included. The other lines refer to the density matrix manipulation and the computation of the integral derivatives.

6 Conclusions and outlook

Cholesky decomposition (CD) of the ERIs is a form of inner projection *à la Löwdin* that seeks a tensor-decomposition of the ERIs by eliminating linear dependences in the atomic orbital product space. Here, we have reviewed some of the quantum chemistry technology that can arise from the development of the CD idea. In particular, we have pointed out the possibilities for state of the art applications due to recent advances in the implementation of CD-based analytical gradients as well as local formulations.

However, the generality of the method would suggest that the same technique applied to other contexts than the ERI matrix could provide comparable computa-

tional advantages, for instance as means to recognize and eliminate redundancies in the number of parameters used to describe the N-electron wave function. If this is the case, a consistent reduction in the computational costs of any correlated method could be achieved by simply recasting the working equations in a reduced space of parameters. Work in this direction is currently carried out by the present authors.

Finally, further development along the lines of local fitting has to be explored to utilize the full potential of the inner projection method on efficient handling of two-electron integrals.

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