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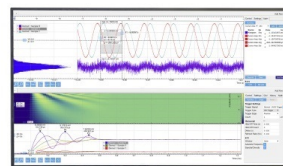
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Approximated electron repulsion integrals: Cholesky decomposition versus resolution of the identity methods

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We compare two procedures to gain efficiency by approximating two-electron integrals in molecular electronic structure calculations. The first one is based on a Cholesky decomposition (CD) of two-electron integrals, the second one on the use of preoptimized auxiliary or fitting basis sets employed in a “resolution of the identity” (RI) technique. We present and test auxiliary bases for approximating the Coulomb term, which further improves accuracy over previously proposed fitting bases. It is shown that RI methods lead to insignificant errors only, which are partly comparable to or even better than that of CD treatments; but RI procedures are superior in speed. CD methods have certain advantages, however, particularly for extended basis sets. © 2009 American Institute of Physics. [DOI: 10.1063/1.3116103]

I. INTRODUCTION

The evaluation of two-electron four-center electron repulsion integrals (ERIs) constitutes a major part of HF, MP2, and DFT molecular electronic structure calculations. This motivated the development of methods for an approximate treatment of ERI with the aim to reach a balance between accuracy and efficiency. An attractive and proven procedure is based on the use of auxiliary or fitting basis functions (ABFs) introduced in addition to the MO basis functions (MOBFs). A convenient shorthand characterization for using ABF is an approximate resolution of the identity (RI), which should hold with sufficient accuracy in the space spanned by products of MOBF,

$$\sum_{PQ} |P\rangle M_{PQ}^{-1} \langle Q| \approx 1, \quad (1)$$

where P and Q label ABF and M_{PQ}^{-1} denotes the inverse matrix specified below. The relationship (1) is then inserted where appropriate; the ERIs are approximated as

$$(\nu\mu|\kappa\lambda) \approx (\nu\mu|\kappa\lambda)_{\text{RI}} = \sum_{PQ} (\nu\mu|P) M_{PQ}^{-1} (Q|\kappa\lambda), \quad (2)$$

where $\nu, \mu, \kappa, \lambda$ label MOBF; ERI are in Mulliken notation. Almlöf and co-workers¹ demonstrated that RI works best if the scalar products in Eqs. (1) and (2) are evaluated in the sense of the Coulomb metric, e.g.,

$$M_{PQ} = (P|Q) = \int \frac{P(\vec{r}_1)Q(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \quad (3)$$

which was a finding of great importance. All subsequent discussions are based on Eqs. (1)–(3).

The advantage of Eq. (2) is that it decomposes a four-index ERI into two- and three-index integrals. Gains in efficiency resulting from the usage of Eq. (2) is expected to be the largest for Coulomb terms (the RI-J procedure), since the RI approximation leads to a factorization

$$J_{\nu\mu} \approx J_{\nu\mu}^{\text{RI}} = \sum_{PQ} (\nu\mu|P) M_{PQ}^{-1} \sum_{\kappa\lambda} (Q|\kappa\lambda) D_{\kappa\lambda} \quad (4)$$

for the Coulomb matrix. $D_{\kappa\lambda}$ denotes the density matrix

$$D_{\kappa\lambda} = \sum_i c_{\kappa i} n_i c_{i\lambda}, \quad (5)$$

where the sum over i includes molecular orbitals (MOs) that are occupied with n_i electrons and $c_{\nu i}$ are the MOBF-MO expansion coefficients. The evaluation of Eq. (4) is a formal $\mathcal{O}(N^3)$ step, whereas the conventional procedure is $\mathcal{O}(N^4)$.

Matters are quite different for the exchange matrix, which does not factorize

$$K_{\nu\mu}^{\text{RI}} = \sum_i \sum_P \sum_{QR} \sum_{\kappa\lambda} n_i c_{i\kappa} (\nu\kappa|Q) \times (Q|P)^{-1/2} (P|R)^{-1/2} (R|\lambda\mu) c_{\lambda i} \quad (6)$$

and remains $\mathcal{O}(N^4)$. Gains in efficiency here result from the skillfully chosen sequence of transformations indicated by the (inverse) sequence of summations: at first one MOBF index is transformed to the basis of occupied MOs, the number of which is usually much smaller than that of the MOBF. The subsequent operations then are accelerated by the ratio of number of MOBF and occupied MOs, as discussed in Ref. 2.

A similar situation is found if RI is used for integrals required for MP2 and related treatments,

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$$(ia|jb)_{\text{RI}} = \sum_P \sum_{QR} \sum_{\mu\lambda} \sum_{\nu\kappa} c_{a\mu} c_{i\nu} (\nu\mu|Q) \times (Q|P)^{-1/2} (P|R)^{-1/2} (R|\kappa\lambda) c_{\kappa j} c_{\lambda b}, \quad (7)$$

where a and b denote virtual MOs.³

We consider in this work the philosophies to determine ABF. The first one employs a Cholesky decomposition (CD) of ERI (or related quantities) and the second one is based on predefined or preoptimized ABF, which will be denoted as the RI approach (as proposed in Ref. 1). CD procedures very recently found much attention, which resulted in remarkable progress.^{4–6} It is the aim of the present work to compare these CD methods with RI approaches to discuss their strengths and weaknesses, which arise from differences in design. CD has the advantage that a single input parameter, the decomposition threshold δ , controls accuracy, although δ is not strictly related to the error in the energy. For RI calculations the user has to choose among existing preoptimized ABF. The question then is whether this incurs a tolerable loss in accuracy and is connected with a sufficient reduction in computational effort. In other words, we are concerned with the balance between accuracy and efficiency.

The paper is organized as follows. In the next section we characterize the ways of inserting the (approximate) resolution of the identity, i.e., CD and RI. This description will be very brief since the methods and their relationship are well described in the literature.^{1,4–6} We further show how the accuracy of RI-J can be further improved and document errors for a test set of more than 300 molecules. In Sec. III we compare accuracy and efficiency of both methods for the examples given in Refs. 4–6. The present calculations have been carried out with a development version of TURBOMOLE.⁷ Concluding remarks are given in Sec. IV.

II. SKETCH OF APPROXIMATE ERI TREATMENTS

A. Cholesky decomposition procedures

These go back to Beebe and Linderberg⁸ who proposed a CD of ERI leading to an ABF consisting of products of MOBF, the CD basis functions, CDBF

$$(\nu\mu|\kappa\lambda) \approx \sum_J L_{\nu\mu}^J L_{\kappa\lambda}^J. \quad (8)$$

This is a well defined and generally applicable method, which controls accuracy by an input parameter, the decomposition threshold δ . For an explicit representation one uses Eq. (2), where P and Q run over the pairs $\nu\mu$ kept in the CDBF. Aquilante, Lindh, and Pedersen [ALP1 (Ref. 4) and ALP2 (Ref. 5)] have recently shown that the CDBF can be constrained to include only products of MOBF centered at the same atom, the 1C-CD method. The 1C-CD then leads to molecule specific CDBF to be determined on the fly for each case. In a variant, denoted as aCD, one precomputes the (1C-CD) CDBF in treatments of isolated atoms; this approach is closely related to a proposal of Ten-no and Iwata.^{9,10} ALP1 demonstrated that 1C-CD and aCD are very close to the CD and there are only insignificant losses in accuracy.

Boman, Koch, and Sanches de Meras [BKSdM (Ref. 6)] very recently proposed and tested a “method specific CD” (MSCD). This variant of a CD is based on the decomposition of the term to be evaluated, which is most easily demonstrated for the Coulomb energy E_J ,

$$E_J = \frac{1}{2} \sum_{\mu\nu\kappa\lambda} M_{\mu\nu,\kappa\lambda}^J, \quad (9)$$

$$M_{\mu\nu,\kappa\lambda}^J = D_{\mu\nu}(\nu\mu|\kappa\lambda) D_{\kappa\lambda} = \sum_Q (L_{\mu\nu}^Q L_{\kappa\lambda}^Q). \quad (10)$$

In this way one obtains the most compact CD representation of E_J and similarly for other terms, which is an attractive procedure.

B. RI-X procedures and optimized auxiliary basis sets

There is no compelling reason to employ products of MOBF as a basis for ABF, any type of basis that is efficient and accurate is acceptable as first proposed by Billingsley and Bloor,¹¹ Whitten,¹² as well as by Baerends *et al.*¹³ In RI-X one employs predefined ABF optimized for representative cases, an approach followed, for example, by the Karlsruhe group for atoms across the periodic table. These developments were driven by the requirement of a reasonable balance between efficiency and accuracy. This leads to ABF optimized for specific purposes and we will briefly sketch history and present state of affairs.

RI-J1.¹⁴ We use this label to designate ABF optimized to approximate E_J , the electronic Coulomb energy for a given type of MOBF, e.g. split valence polarization¹⁵ (SVP) or triple zeta valence polarization (TZVP).¹⁶ According to Eq. (4), E_J is given as

$$E_J = \frac{1}{2} \sum_{i,j} (ii|jj) = \frac{1}{2} M_{\rho\rho}, \quad (11)$$

where ρ denotes the electron density. With RI-J1 one approximates E_J with typical errors of 0.1 mE_h per atom, at least an order of magnitude smaller than basis set errors of SVP or TZVP. RI-J1 was clearly meant to approximate just E_J in nonhybrid DFT calculations for specific types of MOBF providing a reasonable balance of MOBF and DFT errors.

RI-J2.¹⁷ This is the second generation of ABF to approximate E_J yielding errors that are significantly smaller (typically 0.03 mE_h/atom) and show a much smaller standard deviation than RI-J1. There is only a single universal ABF for each atom.

RI-JK.^{2,18} In HF and hybrid DFT one has to approximate E_J together with the exchange term E_K present in the energy expressions

$$E_K = \frac{1}{2} \sum_{i,j} (ij|ij). \quad (12)$$

RI-JK is designed for this purpose. Errors are around 0.03 mE_h per atom independent of MOBF (as for RI-J2).

RI-C.^{3,19} These ABFs are designed for MP2 and related treatments on top of conventional HF or HF/RI-JK calculations. The requirements for an optimal MP2 approximation

differ from those encountered in HF, which justifies a separate ABF. Since core MOs are usually frozen in MP2, there is no need to represent exchange integrals involving these MOs, but one has to achieve a better approximation for integrals involving (active) occupied and virtual MOs than necessary for HF.

Accuracy and efficiency of RI-X have been carefully tested in benchmark calculations for test sets^{3,17,18} with more than 300 molecules involving all atoms (except lanthanides) in all common oxidation states. This provides the necessary basis for the assessment of accuracies to be expected. The state of affairs is similar to those for CD approaches; although these are constructed with the use of a decomposition threshold δ , accuracy can only be established by benchmark studies, as pointed out in Ref. 6.

We continue with some general remarks concerning the dependence of the ABF size on the MOBF size and on the element to be described. From Eq. (11) it is evident that for the Coulomb energy only charge densities have to be fitted, i.e., only (sums of) products of type “ $\text{MO}_i \cdot \text{MO}_j$.” The size of the RI-J ABF will (roughly) increase linearly with the number of occupied MOs, i.e., linearly from the light to the heavier elements in the periodic table, just as for the MOBF. The ratio of RI-J ABF and MOBF thus is expected to be approximately constant. Further, occupied MOs are almost exactly described by triple zeta valence MOBF, changes in shape (and energy) from triple zeta to quadruple zeta valence MOBF are very small, and changes from quadruple zeta to larger sets are negligible. Thus, RI-J ABF optimized for one type of MOBF (preferably an extended basis) can be used for all other types of MOBF with similar accuracy. This was the idea behind RI-J2.

Matters are different for the exchange energy E_K , Eq. (12). This requires to approximate products $\text{MO}_i \cdot \text{MO}_j$, which leads to a quadratic increase in the size of RI-K ABF with atomic number, thus a linear increase in the ratio of RI-K ABF to MOBF. Like for RI-J only occupied MOs are involved, so RI-K ABF optimized for one type of MOBF can be used for any MOBF.

For RI-C the construction of an ABF to be used for all types of MOBF is not possible, at least, if the focus is set on efficiency. Here one has to describe products of occupied and virtual orbitals and the number of the latter very much depends on the type of the MOBF. Fortunately integrals of type $(ia|jb)$ usually occur in connection with a denominator of energy differences between occupied and virtual MOs, so the fit quality for the energetically high lying virtual orbitals is less critical. This was the reason for choosing the error functional for the optimization of RI-C described in Ref. 3.

For a good balance of efficiency and accuracy it appears reasonable to choose specific ABF for different purposes (E_J , E_K , E_C , the correlation energy), or even for different MOBF as in RI-C. Further, as products to be fitted for E_J are a subset of products to be fitted for E_K , it is obvious that ABF optimized for E_K can also be used for approximating E_J , which is done in fact in the RI-JK-HF procedure. Fitting E_J (e.g., in DFT treatments) with these ABF is of course less efficient than with RI-J1 or RI-J2 ABF, but more accurate, as will be demonstrated now.

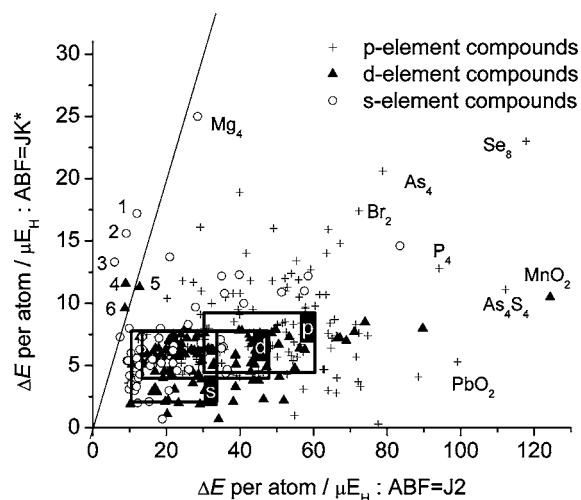


FIG. 1. Comparison of errors ΔE_J per atom obtained with RI-J2 vs RI-JK*, in connection with def2-QZVPP. The rectangles indicate the mean value \pm standard deviation for both ABF types separately for compounds containing only *p*-elements (plus hydrogen), *p*, compounds also containing *s*-elements, *s*, or *d*-elements, *d*. The test set was taken from Ref. 18. Explicitly listed are molecules with striking errors: 1–3 denote Be_2H_4 , MgH_2 , and BeH_2 , and 4–6 denote Au_2 , Au_3^- , and Ag_2 , respectively.

C. Improved accuracy in RI-J treatments with the ABF RI-JK*

The usage of RI-JK ABF promises an error reduction versus RI-J2 in RI-J treatments, simply because RI-JK is more extended and more flexible than RI-J2. Such an improvement is desirable if one aims for high accuracy (extended MOBF) and if HF exchange is not required, as in nonhybrid DFT treatments. After some test calculations for small molecules it turned out that decontracting the steep *s*-type RI-JK ABF further improves accuracy at low costs. The resulting ABFs are termed RI-JK*. As a thorough check we used the above-mentioned set of more than 300 molecules¹⁸ to compare RI-J errors for converged DFT(BP86) wave functions for RI-J2 ABF and RI-JK* ABF. RI-J2 versus RI-JK* errors are plotted in Fig. 1.²⁰ Errors for RI-JK* ABF typically amount to less than 0.01 mE_h per atom (mean deviation plus standard deviation), which would be sufficient for the use in connection with pentuple zeta MOBF in the sense of the energy criterion formulated above. This improvement in accuracy by roughly a factor of 4 is paid for by higher costs, in particular, for the heavier elements (see above); for the $2p$ elements the RI-JK ABF is 1.6 times as large as the RI-J2 ABF, for the $4p$ elements the factor amounts to 4.6.

Maximum errors for RI-J2 ABF are reduced from 0.125 mE_h (MnO_2) to 0.025 mE_h for RI-JK* ABF (Mg_4). For both ABF we find smallest average errors for *s*-element compounds (MgO , MgH_2 , Mg_4 , etc.), followed by transition metal compounds, and largest errors for *p*-block molecules. Although errors are reduced in going from RI-J2 ABF to RI-JK* ABF, this is not or hardly the case for Mg_4 and compounds labeled 1–6 in Fig. 1.

Of course, accuracy could be improved by adding further functions, but we do not recommend this. In cases where the documented accuracy appears to be insufficient (which is

TABLE I. Errors (in mE_h) resulting from integral approximations in HF (J and K approximated, JK-HF), DFT/BP86 (only J approximated, J-DFT), and MP2 calculations for benzene with MOBF SVP, TZVPP, and QZVPP. aCD n^* results from Ref. 4, where aCD n^* denotes an aCD with $\delta=10^{-n}$. RI results for different auxiliary bases (J2, JK, JK*) from the present work as described in text. C-MP2@JK-HF and C-MP2@HF denote MP2 treatments on top of JK-HF and conventional HF. The number of basis functions is given in parentheses.

	JK-HF	J-DFT	C-MP2@JK-HF	C-MP2@HF
MOBF: SVP(114)				
aCD3*	3.059	3.857	2.652	...
aCD4*	0.151	0.014	0.208	...
aCD5*	0.117	0.013	0.168	...
aCD8*	0.107	0.012	0.156	...
J2(360)	...	0.251
JK(558)	0.117	0.087
JK*(594)	0.111	0.081
C-SVP(372)	0.538	0.460
MOBF: TZVPP(270)				
J2(360)	...	0.285
JK(558)	0.137	0.107
JK*(594)	0.139	0.080
C-TZVPP(636)	0.274	0.153
MOBF: QZVPP(522)				
J2(360)	...	0.323
JK(558)	0.155	0.117
JK*(594)	0.159	0.011
C-QZVPP(1182)	0.292	0.074

hardly relevant in practice), it is rather recommendable to use RI-J (or RI-JK) for a preoptimization of the orbitals. A subsequent conventional procedure will usually converge within three or less SCF steps leading to nonapproximated energy. For optimization of structure parameters an analogous procedure may be carried out.

We finally note that even for 4p elements with comparably large ABF, the RI technique dramatically reduces computation (CPU) times; for Se_8/QZVPP (quadruple zeta valence polarization, Ref. 21) the conventional calculation of E_J takes 1364 s but only 33 s with RI-J using RI-JK* ABF.

III. COMPARISON OF CD AND RI APPROACHES

In ALP1 (Ref. 4) it was convincingly demonstrated that 1C-CD and aCD lead to ABF that simultaneously provide consistent accuracy for HF, MP2, and DFT (hybrid and non-hybrid) treatments. This is an important result, which is of

particular relevance for CASSCF and CASPT2 treatments.^{22,23} ALP1 has not properly documented the accuracy achievable with RI methods and has not considered efficiency in great detail. We will do this now.

A. Accuracy

ALP1 employed auxiliary basis sets RI-J1 (Ref. 14) and RI-C (Ref. 3) for cases for which they were not designed, e.g., HF calculations, with very poor results as expected. They also did not consider the more recent RI-J2 (Ref. 17) and RI-JK.^{2,18} Besides benchmark studies they documented detailed results for benzene. In Table I we compared CD and RI treatments for this molecule. MOBF employed were of type SVP (Ref. 21) like in Ref. 4, additional RI treatments were carried out with TZVPP (Ref. 21) and QZVPP.²⁴ The following conclusions are obvious. (i) RI-JK leads to errors of 0.1 mE_h –0.15 mE_h in HF energies for different MOBF, comparable to aCD-4* (in the nomenclature of ALP1, this is just an aCD with $\delta=10^{-4}$). aCD-5* and aCD-8* do not yield more accurate results, which indicates limits of accuracies that can be reached with aCD. (ii) MP2 treatments on top of conventional (exact) HF or HF/RI-JK are in error by about 0.5 mE_h for the small SVP basis with RI-C, which is poorer than aCD-4* (0.2 mE_h). For the larger MOBF the RI-C errors are smaller (down to 0.07 mE_h), since the corresponding ABFs are designed to balance RI-C and basis set errors. Again, an increase to aCD-5* and aCD-8* does not lead to significantly better results with errors around 0.16 mE_h . (iii) The following picture emerges for nonhybrid DFT, such as BLYP (Ref. 25) or BP86,^{26,27} which requires an approximation of E_J only. Errors in total energies for RI calculations are around 0.3 mE_h for RI-J2 and 0.1 mE_h for RI-JK or RI-JK*. This is much better than aCD-3* (error of 3.9 mE_h), but the best results are obtained for aCD-4* (error of 0.01 mE_h); an increase to aCD-8* does not lead to an improvement as for HF and MP2. We note for comparison that basis set errors, taken as a difference to the large QZVPP, range from 10 mE_h (TZVPP) to 261 mE_h (SVP) and are thus one to three orders of magnitude larger than RI errors. This comparison concerns only one example and one may wonder if general conclusions can be drawn from a single case. All features shown by the benzene treatments are perfectly in line with the picture revealed by the benchmarks for CD

TABLE II. Comparison of errors in total DFT(BLYP/cc-pVTZ) energies, ΔE in mE_h , and maximum error in bond distances, Δr in pm, for 1C-CD4 ($\delta=10^{-4}$) (Ref. 4). RI-J2 and RI-JK* (this work). n_{MOBF} and n_{ABF} denote the numbers of MOBF and ABF, respectively.

	1C-CD4			RI-J2			RI-JK*		
	n_{MOBF}	ΔE	Δr	n_{ABF}	ΔE	Δr	n_{ABF}	ΔE	Δr
N ₂	60	0.02	0.0002	96	0.04	0.0042	162	0.014	0.0006
C ₂ H ₂	88	0.06	0.0078	120	0.06	0.0106	198	0.028	0.0029
C ₂ H ₆	144	0.29	0.0072	164	0.20	0.0092	278	0.056	0.0023
Pyrrole	220	0.29	0.0081	300	0.30	0.0225	497	0.077	0.0023
Benzaldehyde	324	0.20	0.0022	458	0.33	0.0128	754	0.111	0.0022
Furan	206	0.16	0.0073	289	0.22	0.0125	477	0.074	0.0022

TABLE III. Comparison of CD and RI results of BLYP/cc-pVTZ calculations for linear Gly₁₀. t_{SCF} denotes the time per SCF iteration, t_{GRAD} the time for a gradient, in seconds, and ΔE errors of the total energy in mE_h. Auxiliary basis sets of type RI-J1, RI-J2, and RI-JK*, as described in text.

1C-CD calculations ^a				
	direct	$\delta=10^{-2}$	$\delta=10^{-4}$	
ΔE_{SCF}	0.0	n.d. ^b	n.d. ^b	
t_{SCF}	4970	871	993	
t_{GRAD}	15 757	2700	6007	
RI-X calculations, this work				
	Direct	RI-J1	RI-J2	RI-JK*
ΔE_{SCF}	0.0	5.0	2.3	0.58
$t_{\text{J}}^{(1)\text{c,d}}$	2618	43	70	88
$t_{\text{GRAD}}^{\text{e}}$	3466	366	404	506
$t_{\text{GRAD,MARIJ}}^{\text{e}}$		266	277	346

^apartial timings since “one electron and DFT grid calculations were excluded” (Ref. 5).

^bNot documented.

^cOne Coulomb matrix build with converged MOs.

^dDFT contribution to the Fock matrix requires between 47 s for grid 2 and 136 s for grid 4.

^eIncluding 150 s required for the DFT gradient contributions.

approaches collected in Ref. 4, by the benchmarks published for RI procedures,^{3,17,18} and by results discussed below in Table II.

ALP2 (Ref. 5) noted that the “very limited spreading (of the CD approach)... can to a large extent be ascribed to the lack of analytical derivatives within the CD formulation.” They filled the gap and documented the accuracy in the energy and maximum deviation Δr in bond distances with respect to conventional treatments. Basis sets of type cc-pVDZ and cc-pVTZ were used in DFT/BLYP calculations within the 1C-CD approximation. Finally we compare the results of ALP2 in Table II with RI calculations. The comparison is easy: 1C-CD4* is comparable to RI-J2 in the accuracy of the energy (ΔE) but leads to smaller Δr . The largest deviations of bond distances obtained with RI-J2 are still smaller than 0.0225 p.m. (for pyrrole), which is of no concern for most applications since experiments hardly reach this accuracy.²⁸ The most accurate results are obtained with RI-JK* for all molecules in Table II.

B. Efficiency

RI or density fitting procedures have been developed to increase efficiency. Lindh and co-workers,⁵ ALP2, documented the savings in CPU times for 1C-CD with cc-pVDZ and cc-pVTZ MOBF in BLYP calculations for linear glycine chains. In Table III we collected their results for Gly₁₀ with the cc-pVTZ (Ref. 29) in comparison to RI treatments. The calculations have been carried out on the same type of workstation, an AMD Opteron 2.4 GHz processor. We consider mainly timings for gradient calculations, which are clear-cut. SCF timings depend on many details such as convergence thresholds, integral-direct versus semidirect algorithms, and an assessment is more difficult.

The reduction in CPU time resulting from a new procedure is a convenient way to assess its merits, since this is

relatively independent of other algorithmic features. The 1C-CD with a decomposition threshold $\delta=10^{-4}$ reduces the partial gradient times (“one electron and DFT grid differentiation were excluded” in Ref. 5) by 62%, for other cases the reduction is less pronounced (between 57% and 30%), see Table VI in Ref. 5. Savings are larger for $\delta=10^{-2}$, but this leads to hardly acceptable errors, see Table I for benzene. A much different picture emerges for RI approaches: total timings for the gradient evaluation go down by at least a factor of 6.9, for RI-JK* versus direct. If we take out the timings for the DFT part and switch on the multipole assisted RI-J (MARIJ) feature,³⁰ the factors increase up to 29, for RI-J1 versus direct. We further note a surprising detail: the total gradient evaluation with TURBOMOLE is a factor 4.5 faster than the partial time reported for MOLCAS, we have no explanation for this large difference. As a consequence, the CD for $\delta=10^{-4}$ is even slower than the conventional gradient for TURBOMOLE and RI timings are an order of magnitude smaller than for 1C-CD4. A similar picture emerges for HF-SCF timings: ALP2 reports a reduction by a factor of 5 between a conventional and a 1C-CD calculation with $\delta=10^{-4}$; the reduction for the Coulomb matrix build in RI-X amounts to a factor of 30–60 depending on the ABF used.

Since the RI approximation for E_K is much less advantageous than for E_J , as indicated by Eqs. (4) and (6), we expect from our experience, Refs. 2 and 18, that savings of 1C-CD and aCD procedures in HF and/or hybrid DFT are even smaller than those shown in Table III for the nonhybrid BLYP functional. The rather moderate improvements in efficiency achieved with 1C-CD can at least partly be rationalized by consideration of the size of the ABF, the contraction depth of the ABF, and differences in algorithms. As for the size of auxiliary basis sets ALP1 stated that “on the average, the 1C-CD ($\delta=10^{-4}$) requires only 30% more functions than the RI-C basis set,” and ca. twice as much as RI-J1, Figs. 1 and 4 of Ref. 4, 1C-CD and aCD have no advantage concerning the ABF size in comparison to RI-X procedures.

With a contraction depth of 8 and 3 for atomic *s*- and *p*-basis functions in cc-pVTZ, one gets products, which serve as CDBF, including 36 (for 1*s*-2*s*) and 24 (1*s*-2*p*) primitives. The RI ABFs are only mildly contracted for RI-J and RI-JK. Integral evaluation times clearly depend on the number of ABF and the contraction depth, and CD is at a disadvantage here. Integral evaluation also differs for RI and CD procedures. All RI ABFs are chosen as proper eigenfunctions of L^2 , which considerably simplifies integral evaluations since the required three-center two-electron integrals then obey a two-term recursion relation instead of the four-term in the general case.³¹ This advantage is lost in CD procedures since products of basis functions are not eigenfunctions of L^2 in general.

Since CD and RI-X procedures are otherwise very similar in realization, the just mentioned aspects constitute the main differences, which explain at least in part the pronounced discrepancy in efficiency.

C. Comparison with method specific Cholesky decomposition

BKSdM (Ref. 6) tested the MSCD for the molecules water and benzene, a cluster of He atoms at large interatomic distances (4.2 Å) and for polyglycine chains in an alpha-helix conformation. Since we already considered polyglycine chains, we will compare results as far as possible. BKSdM used the geometry obtained from MOLDEN,³² which is the zwitterion form. This choice deserves some comments. The zwitterion is stabilized in polar solvents, the normal form $n\text{Gly}_n$ (with $-\text{COOH}$ and $-\text{NH}_2$ end groups) is the more stable of the two conformers in the gas phase. The high energy of the zwitterion is also reflected by poor SCF convergence of a closed shell calculation and the fact that the ground state is a triplet (for HF and DFT/BP). ΔE between the closed shell $n\text{Gly}_{10}$ and the triplet zwitterion amounts to about 280 kJ/mole. BKSdM provides only a single timing for E_K ; they probably assumed a closed shell state. The latter is actually found for $n\text{Gly}_{10}$, which also shows normal convergence within 14 iterations with an EHT guess. We will therefore compare timings given by BKSdM with those obtained in the present work for closed shell calculations of $n\text{Gly}_n$.

The calculations of BKSdM were done with an aug-cc-pVDZ basis (1231 basis functions), a decomposition threshold $\delta=10^{-8}$, and a local version of DALTON. For a Xeon 2.66 GHz quad-core processor, the following timings were reported for the construction of the Fock (t_F), the Coulomb (t_J), and exchange (t_K) matrices (in seconds) of Gly_{10} :

$$\text{direct SCF, } t_F = 60\,302, \quad (13a)$$

$$\text{standard CD, } t_F = 7750(43\,487), \quad (13b)$$

$$\text{MSCD, } t_J = 1889(442), \quad (13c)$$

$$\text{MSCD, } t_K = 1799(644). \quad (13d)$$

The first entry is for integral evaluation. The timings in parentheses are for the CD, which has to be done only once for the standard CD but in each iteration for MSCD, since the decomposition depends on the current density matrix. t_K is for the fastest of the three algorithms developed by BKSdM. The timings for MSCD clearly demonstrate the advantage in comparison to a conventional or a standard CD treatment.

TURBOMOLE timings were obtained with the same type of processor (a dual quad-core Xeon) but with 3.2 GHz, which should be at most 20% faster than a CPU with 2.66 GHz. We employed the same basis set as BKSdM and the auxiliary basis sets described above, the MARIJ option was switched off and no RI integrals were stored in memory. HF calculations without approximations (direct HF-SCF) and with the ABF RI-JK to approximate both Coulomb and exchange terms (RI-JK) required the following timings for one iteration with converged HF MOs:

$$\text{direct HF-SCF, } t_F = 5083, \quad (14a)$$

$$\text{RI-JK, } t_F = 2760. \quad (14b)$$

The following timings result if only the Coulomb term is approximated by RI-J with ABF RI-JK* and ABF RI-J2 for one iteration with converged DFT/BP86 MOs.

$$\text{RI-JK*}, t_J = 88, \quad (15a)$$

$$\text{RI-J2, } t_J = 65. \quad (15b)$$

The overhead for the CD of the auxiliary basis metric was 14 s for RI-JK*. We observed quite some scatter in the timings depending on current machine load. A comparison of DALTON and TURBOMOLE timings for a direct SCF confirms the observation of BKSdM that “the direct SCF of DALTON is perhaps not the fastest available code”; nevertheless a factor larger than 10 in execution times is surprising. As a consequence of the poor performance of DALTON, it is difficult to assess the efficiency of the MSCD procedure, but we note that the direct SCF of TURBOMOLE is competitive with MSCD in an SCF treatment since Coulomb and exchange have to be treated. Under these circumstances the present authors would prefer the conventional calculation. We further note that savings for RI-JK are moderate for the comparably small MOBF (aug-cc-pVDZ); more pronounced gains in efficiency are expected for larger MOBF.^{2,18} For instance, with the aug-cc-pVTZ basis, a single Fock matrix build with converged HF-SCF MOs needs 70 914 s for the direct HF-SCF calculation and 9351 s for the RI-JK procedure. The energy difference between the two procedures amounts to 1.14 mE_h for MOs converged within the respective treatment. In connection with timings we mention that BKSdM claims linear scaling (with system size) for their CD exchange algorithm, whereas RI-K includes an $\mathcal{O}(N^4)$ step (with a small prefactor) as discussed for Eq. (6) and in Ref. 2.

A comparison between the t_J is also not easy, MSCD is again more than ten times slower than RI-JK*, but MSCD is probably more accurate. Unfortunately, BKSdM did not report the accuracy for the glycine chains but we can give the error in the converged energy (for BP86 or HF, indicated as a subscript on ΔE) of RI-J procedures for the two auxiliary basis sets employed,

$$\Delta E_{\text{BP86}}(\text{RI-JK}^*) = 0.61 \text{ } mE_h, \quad (16a)$$

$$\Delta E_{\text{BP86}}(\text{RI-J2}) = 1.8 \text{ } mE_h \quad (16b)$$

$$\Delta E_{\text{HF}}(\text{RI-JK}) = 1.3 \text{ } mE_h. \quad (16c)$$

These errors are close to those obtained for the linear Gly_{10} employing a cc-pVTZ MOBF, Table III, which indicates robustness of the RI-J procedure. Better accuracy is of course an advantage although it is hard to imagine circumstances where the accuracy obtained with RI-JK* or even RI-J2 is insufficient for a system of this size. Errors of RI-J treatments have always the same sign and there is partial

cancellation for computed energy differences. We further point out that timings and errors are virtually identical for the normal and the zwitterion of Gly₁₀.

We finally report timings for $n\text{Gly}_n$ for $n=10, 20, 30$ to get an idea of the scaling behavior. For a DFT/BP86/aug-cc-pVDZ calculation with RI-J2 and grid $m4$ for the quadrature, the following timings have been measured on a 3.2 GHz Xeon quad-core (in a sequential run) for $n=10/20/30$:

$$\text{total run time: } 1893 \text{ s}/5435 \text{ s}/10\,958 \text{ s} \quad (17a)$$

$$\text{RI-J/iteration: } 42 \text{ s}/137 \text{ s}/253 \text{ s}. \quad (17b)$$

The total time is for a complete run with an EHT guess as start, convergence was reached in 14 iterations, 4 GB memory was used to store (three-center) integrals, and MARIJ was switched on. The above timings scale roughly as $N^{1.7}$ in agreement with conclusions reached in Ref. 30. The timings BKSdM report for Coulomb with MSCD and Gly₃₀ are 18 834 s for integral evaluation and 24 615 s for the decomposition per iteration.

Concerning reasons for differences in required CPU times for RI and CD procedures, we first note that MSCD and RI-X need a similar number of ABF. For a CD treatment of Gly₁₀ as specified in Table III of Ref. 6 2264 ABFs were used for Coulomb and 3361 or 6262 for HF exchange, depending on the actual procedure. This should be compared to 2361 ABFs for Coulomb with RI-J2 and 3693 for HF exchange with RI-JK. However, MSCD is expected to be more accurate for a given size of ABF. This comes with the disadvantage that a CD has to be carried out in each iteration, which is an expensive procedure, at least presently. MSCD also suffers from a relatively large contraction depth, like the above-mentioned 1C-CD and aCD procedures.

IV. CONCLUSIONS

We compared and discussed two methods that aim for increased efficiency by approximating ERI as sketched in Eqs. (1)–(3). The approaches differ in the way auxiliary or fitting basis sets $\{P\}$ are constructed. CD procedures are based on the underlying basis to represent MOs and use products of those functions for $\{P\}$. RI employs bases $\{P\}$ constructed for efficiency and accuracy without necessarily resorting to the MO basis; they are usually constrained to be atom-centered and of proper angular momentum. Stated differently, CD is tied to the MO basis whereas RI allows for a free optimization, which is a principle advantage. The question is then if predefined RI basis sets, optimized for well chosen model compounds, lead to significant losses in accuracy as compared to CD procedures.

ALP1 (Ref. 4) and ALP2 (Ref. 5), as well as BKSdM,⁶ expressed concern about the accuracy of RI procedures and claimed “loss of error control.” This opinion is neither supported by extensive benchmark studies^{3,17,18} nor by results presented in this work. Results for the RI-J approximation with RI-JK* ABF given in Table II are even more accurate than for 1C-CD. We stress that errors resulting from RI approximations are not only smaller than basis set errors or errors of DFT functionals, they are also much smaller than

uncertainties in experimental results, except for very small molecules.²⁸ Errors ΔE or Δr resulting from RI-J using RI-J2 ABF or RI-JK* ABF in Table II (with possible exception of smaller molecules) and Eq. (15) are certainly out of reach for presently available experimental procedures. On the other hand, RI does not reach the accuracy required for benchmark studies using basis sets up to aug-cc-pV7Z for water.⁶

Integral approximations discussed in this work certainly work best for the interelectronic Coulomb energy E_J , as expressed in Eq. (4). RI-J procedures have no problems with accuracy here and are much more efficient than available CD methods, Table III and Eqs. (13)–(15). We argued in Sec. III that this is partly inherent to CD (large contraction depth and more expensive integral evaluation), but it is also a result of inefficient algorithms employed. The situation is not so clear if E_J and E_K are approximated, since the gain in speed (conventional versus RI-JK) is much less pronounced for RI, and CD methods could become attractive. An alternative would be to use different techniques to approximate E_J and E_K as recently reported by Neese *et al.*³³ While RI-J is employed for the Coulomb part a pseudospectral technique is used for the HF exchange.

For better assessment of CD procedures it would help to have more extended tests, which include transition metal compounds and heavier p -block elements such as As. For RI procedures previous benchmark investigations^{3,17,18} demonstrated advantages and limitations, which paved the way for treatments of large clusters of As, up to As₁₄₄,³⁴ helped to determine the structure of transition metal compounds,³⁵ modeled silver mobility in a cluster with 666 atoms,³⁶ and clarified bonding in lanthanides.³⁷ These applications were done to determine properties of corresponding compounds in DFT and MP2 calculations with basis sets up to TZVPP. The RI technique is here very efficient and errors are of no concern. Matters are different if errors much smaller than achievable with RI are desired, which is necessary for benchmark studies including very extended basis sets; CD procedures certainly hold promise in this field.

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¹O. Vahtras, J. Almlöf, and M. Feyereisen, *Chem. Phys. Lett.* **213**, 514 (1993).

²F. Weigend, *Phys. Chem. Chem. Phys.* **4**, 4285 (2002).

³F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, *Chem. Phys. Lett.* **294**, 143 (1998).

⁴F. Aquilante, R. Lindh, and T. B. Pedersen, *J. Chem. Phys.* **127**, 114107 (2007).

⁵F. Aquilante, R. Lindh, and T. B. Pedersen, *J. Chem. Phys.* **129**, 034106 (2008).

⁶L. Boman, H. Koch, and A. S. de Meras, *J. Chem. Phys.* **129**, 134107 (2008).

⁷TURBOMOLE, version 5.10, TURBOMOLE GmbH Karlsruhe, 2008, www.turbomole.com.

⁸N. H. F. Beebe and J. Linderberg, *Int. J. Quantum Chem.* **12**, 683 (1977).

⁹S. Ten-no and S. Iwata, *Chem. Phys. Lett.* **240**, 578 (1995).

¹⁰S. Ten-no and S. Iwata, *J. Chem. Phys.* **105**, 3604 (1996).

¹¹F. P. Billingsley and J. E. Bloor, *J. Chem. Phys.* **55**, 5178 (1971).

- ¹² J. L. Whitten, *J. Chem. Phys.* **58**, 4496 (1973).
- ¹³ E. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.* **2**, 41 (1973).
- ¹⁴ K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, *Theor. Chem. Acc.* **97**, 119 (1997).
- ¹⁵ A. Schäfer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
- ¹⁶ A. Schäfer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.* **100**, 5829 (1994).
- ¹⁷ F. Weigend, *Phys. Chem. Chem. Phys.* **8**, 1057 (2006).
- ¹⁸ F. Weigend, *J. Comput. Chem.* **29**, 167 (2008).
- ¹⁹ F. Weigend, A. Köhn, and C. Hättig, *J. Chem. Phys.* **116**, 3175 (2002).
- ²⁰ See EPAPS Document No. E-JCPSA6-130-004916 for primary data for Fig. 1 (molecules and energies). For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- ²¹ F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ²² F. Aquilante, T. B. Pedersen, R. Lindh, B. O. Roos, A. S. de Merás, and H. Koch, *J. Chem. Phys.* **129**, 024113 (2008).
- ²³ F. Aquilante, P.-A. Malmqvist, T. B. Pedersen, A. Ghosh, and B. O. Roos, *J. Chem. Theory Comput.* **4**, 694 (2008).
- ²⁴ F. Weigend, F. Furche, and R. Ahlrichs, *J. Chem. Phys.* **119**, 12753 (2003).
- ²⁵ C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ²⁶ A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ²⁷ J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
- ²⁸ X-ray diffraction investigations of single-crystals have typical uncertainties of a few pm in bond distances, errors smaller than 1 pm can only be achieved in very fortunate cases.
- ²⁹ T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ³⁰ M. Sierka, A. Hogeckamp, and R. Ahlrichs, *J. Chem. Phys.* **118**, 9136 (2003).
- ³¹ R. Ahlrichs, *Phys. Chem. Chem. Phys.* **6**, 5119 (2004).
- ³² G. Schaftenaar and J. Noordik, *J. Comput.-Aided Mol. Des.* **14**, 123 (2000).
- ³³ F. Neese, F. Wenmohs, A. Hansen, and U. Becker, *Chem. Phys.* **356**, 98 (2009).
- ³⁴ P. Nava and R. Ahlrichs, *Chem.-Eur. J.* **14**, 4039 (2008).
- ³⁵ R. Ahlrichs, D. Fenske, M. McPartlin, A. Rothenberger, C. Schrod, and S. Wieber, *Angew. Chem., Int. Ed.* **44**, 3932 (2005).
- ³⁶ N. R. M. Crawford, C. Schrod, A. Rothenberger, W. Shi, and R. Ahlrichs, *Chem. Eur. J.* **14**, 319 (2008).
- ³⁷ M. T. Gamer, P. W. Roesky, S. N. Konchenko, P. Nava, and R. Ahlrichs, *Angew. Chem., Int. Ed.* **45**, 4447 (2006).