Density fitting for three-electron integrals in explicitly correlated electronic structure theory

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The principal challenge in using explicitly correlated wavefunctions for molecules is the evaluation of nonfactorizable integrals over the coordinates of three or more electrons. Immense progress was made in tackling this problem through the introduction of a single-particle resolution of the identity. Decompositions of sufficient accuracy can be achieved, but only with large auxiliary basis sets. Density fitting is an alternative integral approximation scheme, which has proven to be very reliable for two-electron integrals. Here we extend density fitting to the treatment of all three-electron integrals that appear at the MP2-F12/3*A level of theory. We demonstrate that the convergence of energies with respect to auxiliary basis size is much more rapid with density fitting than with the traditional resolution-of-the-identity approach.

I. INTRODUCTION

Slow convergence of the error in the electron correlation energy with respect to orbital basis set, and consequent computational expense [1, 2], limits the accuracy of conventional quantum chemical methods.

Explicitly correlated methods overcome this slow convergence by introducing terms into the wavefunction that depend explicitly on the interelectronic distance, r_{12}, improving the description of the two-electron cusp [3, 4], and more importantly, the Coulomb hole [5, 6].

This amounts to the inclusion of two-electron basis functions in the wavefunction and results in the need to evaluate many-electron integrals (i.e. integrals over more than two electron coordinates). The number and complexity of these integrals is prohibitive—approximations are necessary for explicitly correlated methods to be applied to chemical problems.

A number of approaches to efficient evaluation of many-electron integrals have been developed. In the 1960s, Boys [7] and Singer [8] showed that all of the many-electron integrals arising from the use of Gaussian-type geminal basis functions could be evaluated in closed form. This approach was later adopted by Szalewicz *et al.* who introduced the weak orthogonality functional to avoid the evaluation of four-electron integrals [9, 10]. A combination of analytic integral evaluation and quadrature was used by Boys and Handy to evaluate three-electron integrals in the transcorrelated method [11], and Ten-no later applied the same technique in explicitly correlated MP2 [12]. Obara-Saika [13] type recurrence relations for efficient evaluation of three-electron integrals over Cartesian Gaussian functions have been derived by Ten-no [14], for use in the transcorrelated method, and May [15], in the context of R12 and F12 methods. In addition, an alternative numerical integration scheme for three-electron integrals has very recently been published

by Mehine *et al.*, where Coulomb operators are approximated to give factorizable forms for the integrals [16].

The resolution-of-the-identity (RI) method of integral approximation, introduced by Kutzelnigg in 1985 [17], is used in the successful R12 and F12 methods developed initially by Kutzelnigg and Klopper [18]. By inserting an approximate RI, many-electron integrals can be approximated as sums of products of two-electron integrals, e.g.

$$\langle ijm|r_{12}^{-1}f_{23}|mlk\rangle \approx \langle ijm|r_{12}^{-1}\hat{X}_2 f_{23}|mlk\rangle$$
$$= \langle ij|r_{12}^{-1}|mx\rangle\langle mx|f_{12}|kl\rangle \quad (1)$$

where $\hat{X} = |x\rangle\langle x| \approx \hat{1}$ is the identity operator approximated in an orthonormal basis, $\{|x\rangle\}$. Here and throughout summation over repeated dummy indices on the right of the equation is implied.

The R12 and F12 methods are currently the only explicitly correlated methods that can be applied to study systems larger than a few atoms. The success of these methods is perhaps largely a result of the effectiveness of the RI approximation in dealing with many-electron integrals. Early implementations of R12 methods used the orbital basis to represent the approximate identity operator [18] and a good approximation required a very large orbital basis set. The introduction of an auxiliary basis set (ABS) to perform the RI [19] removed the need for very large orbital basis sets, and allowed the error from the RI to be decreased systematically by increasing the ABS size. Valeev [20] discovered that the use of a complementary ABS (CABS), spanning the orthogonal complement of the orbital basis, led to faster RI convergence and simplifications in the derivation of the theory.

Aside from improvements in the approximation of the many-electron integrals, significant innovations have been introduced to the R12 and F12 methods in the past two decades, including: increased efficiency through density fitting two-electron, four-index integrals (DF-MP2-R12/F12) [21, 22]; enormously improved accuracy using non-linear correlation factors (F12 methods) [22–27]; reduced computational expense through local methods [28–33]; perturbative correction of the Hartree-Fock reference energy using the CABS singles correction

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[34–36]; and, the development of a variety of coupled-cluster F12 methods (see Refs. 37, 38 and 39 for details). Refs. 37 and 40 also offer detailed reviews of the background and theory of modern R12 and F12 methods. In this paper, we use the general orbital-invariant MP2-F12 formalism described in Ref. 41.

Though the use of RIs to approximate integrals in R12 and F12 methods has been very successful, the angular momentum requirements of the RI basis can be problematic. Approximation of the three-electron integral in Eq. (1) for an atom requires an RI basis containing functions up to $3\ell_{occ}$ units of angular momentum, where ℓ_{occ} is the maximum angular momentum of the occupied orbitals. This can be understood because RI is equivalent to a fitting procedure in which the basis $\{|x\rangle\}$ is used to fit objects with three occupied-orbital indices [21]. For other integral types the angular momentum required in the RI basis set can be greater (see Table 1 in Ref. 19).

To alleviate the angular momentum constraint on the RI basis, Ten-no and Manby developed a method of combining RI with density fitting (RI+DF), reducing the angular momentum requirement in the RI basis to $2\ell_{occ}$ for an atomic system [42] and also improving the accuracy of the approximation compared to standard RI. The RI+DF method and DF-MP2-F12 theory in general require multiple auxiliary basis sets, increasing the complexity of implementation and of reporting the results of calculations. This complexity could be reduced if many-electron integrals were approximated solely by density fitting of orbital pairs, avoiding any need for an RI basis. This would also address the angular momentum requirement of standard RI, since accurate fitting of occupied orbital pairs requires a basis set saturated only to $2\ell_{occ}$.

Performing RI-free R12 and F12 calculations by approximating many-electron integrals using density fitting has been suggested previously, but not implemented [21, 43]; in this paper we describe a proof-of-concept implementation of RI-free MP2-F12 theory, with many-electron integrals approximated using density fitting.

II. THEORY

In the following, we refer to a number of basis sets, which we label with the following indices: occupied orbitals, $ijklmn$; virtual orbitals, $abcdef$; general (occupied or virtual) molecular orbitals, $pqrstu$; atomic orbital basis functions, $\alpha\beta\gamma\delta\epsilon\zeta$; density fitting basis functions, $ABCDEF$; and primitive Cartesian Gaussian functions, **abcdef**.

A. MP2-F12/3*A(D) ansatz

For this simple implementation, the MP2-F12/3*A(D) ansatz [41] was used. This approximation uses the ansatz-3 strong-orthogonality projector

$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1\hat{v}_2), \quad (2)$$

where $\hat{o} = |i\rangle\langle i|$ and $\hat{v} = |a\rangle\langle a|$. The diagonal approximation is also assumed, where the summation in the explicitly correlated part of the MP2-F12 pair function

$$|u_{ij}\rangle = T_{ab}^{ij}|ab\rangle + \hat{Q}_{12}T_{kl}^{ij}f_{12}|kl\rangle, \quad (3)$$

is restricted to the diagonal orbital pairs $kl = ij$ or ji; here T_{ab}^{ij} and T_{kl}^{ij} are usual MP2 and explicitly correlated amplitudes, respectively, and f_{12} is the correlation factor.

In addition, the general and extended Brillouin conditions (GBC and EBC) are assumed [18]. The scheme also neglects exchange commutators $[f_{12}, \hat{k}_1 + \hat{k}_2]$.

With these simplifications the MP2-F12 pair energy becomes separable into a standard MP2 contribution, $\epsilon_{ij}^{(\text{MP2})}$, and a correction [22]

$$\epsilon_{ij}^{(\text{F12})} = T_{kl}^{ij}B_{kl,mn}T_{mn}^{ij} - (\varepsilon_i + \varepsilon_j)T_{kl}^{ij}X_{kl,mn}T_{mn}^{ij} \\ + 2T_{kl}^{ij}V_{kl}^{ij} \quad (4)$$

with

$$B_{kl,mn} = \langle kl|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2)\hat{Q}_{12}f_{12}|mn\rangle, \quad (5)$$

$$X_{kl,mn} = \langle kl|f_{12}\hat{Q}_{12}f_{12}|mn\rangle, \quad (6)$$

$$V_{kl}^{ij} = \langle ij|r_{12}^{-1}\hat{Q}_{12}f_{12}|kl\rangle, \quad (7)$$

where ε_i, ε_j are canonical orbital energies and $\hat{f}$ is a closed-shell Fock operator.

Under the 3*A(D) scheme, we can also neglect the **X** matrix. When the EBC is assumed and **B** has been symmetrized we have

$$B_{kl,mn} = \frac{1}{2}(A_{kl,mn} + A_{mn,kl}) + \frac{1}{2}(\varepsilon_k + \varepsilon_l + \varepsilon_m + \varepsilon_n)X_{kl,mn} \quad (8)$$

where

$$A_{kl,mn} = \langle kl|[f_{12}, \hat{f}_1 + \hat{f}_2]\hat{Q}_{12}f_{12}|mn\rangle \quad (9)$$

and when the diagonal approximation is applied, the F12 contribution to the pair energy becomes

$$\epsilon_{ij}^{(\text{F12})} = T_{kl}^{ij}A_{kl,mn}T_{mn}^{ij} + 2T_{kl}^{ij}V_{kl}^{ij} \quad (10)$$

where kl and mn are restricted to the diagonal orbital pairs ij and ji. The contributions to the MP2-F12 energy involving the **X** matrix (Eq. (6)) therefore vanish [41].

In determining the F12 contribution to the MP2-F12/3*A(D) pair energy we must evaluate the diagonal elements of the **V** and **A** matrices, both of which give integrals over three electron coordinates. When the projector (Eq. (2)) is expanded,

$$\hat{Q}_{12} = 1 + \hat{o}_1\hat{o}_2 - \hat{o}_1 - \hat{o}_2 - \hat{v}_1\hat{v}_2, \quad (11)$$

the **V** matrix elements take the form

$$V_{kl}^{ij} = K_{ij,kl}^F + K_{mn}^{ij}F_{kl}^{mn} - K_{ab}^{ij}F_{kl}^{ab} \\ - \langle ij|r_{12}^{-1}\hat{o}_1f_{12}|kl\rangle - \langle ij|r_{12}^{-1}\hat{o}_2f_{12}|kl\rangle \quad (12)$$

where

$$K_{rs}^{ij} = \langle ij|r_{12}^{-1}|rs\rangle, \quad (13)$$

$$K_{ij,kl}^{F} = \langle ij|r_{12}^{-1}f_{12}|kl\rangle, \quad (14)$$

$$F_{kl}^{rs} = \langle rs|f_{12}|kl\rangle. \quad (15)$$

The remaining terms are each instances of the general three-electron integral

$$v_{ij,kl} = \langle ijm|r_{12}^{-1}f_{23}|mlk\rangle. \quad (16)$$

Under approximation 3*A(D), the $A_{kl,mn}$ matrix elements are further simplified by the neglect of contributions from the exchange commutator, $[f_{12}, \hat{k}_1 + \hat{k}_2]$, such that

$$[f_{12}, \hat{f}_1 + \hat{f}_2] = [f_{12}, \hat{t}_1] + [f_{12}, \hat{t}_2] \quad (17)$$

where $\hat{t}_1$ and $\hat{t}_2$ are kinetic energy operators, $\hat{t}_1 = -\nabla_1^2/2$. Thus,

$$\begin{aligned} A_{kl,mn} &= \langle kl|[f_{12}, \hat{t}_1 + \hat{t}_2]\hat{Q}_{12}f_{12}|mn\rangle \\ &= U_{kl,mn}^F + U_{ij}^{kl}F_{mn}^{ij} - U_{ab}^{kl}F_{kl}^{ab} \\ &\quad - \langle kl|[f_{12}, \hat{t}_1 + \hat{t}_2]\hat{o}_1 f_{12}|mn\rangle \\ &\quad - \langle kl|[f_{12}, \hat{t}_1 + \hat{t}_2]\hat{o}_2 f_{12}|mn\rangle \end{aligned} \quad (18)$$

where

$$U_{kl,mn}^F = \langle kl|[f_{12}, \hat{t}_1 + \hat{t}_2]f_{12}|mn\rangle, \quad (19)$$

$$U_{rs}^{kl} = \langle kl|[f_{12}, \hat{t}_1 + \hat{t}_2]|rs\rangle, \quad (20)$$

and the last two terms can be expressed as the distinct three-electron integral classes

$$a_{kl,mn}^{(1)} = \langle kli|[f_{12}, \hat{t}_1]f_{23}|inm\rangle, \quad (21)$$

$$a_{kl,mn}^{(2)} = \langle kli|[f_{12}, \hat{t}_2]f_{23}|inm\rangle. \quad (22)$$

B. Robust density fitting

Density fitting of products of orbitals in an auxiliary basis,

$$|pq) \approx |\widetilde{pq}) = D_A^{pq}|A), \quad (23)$$

is now a very well established method for approximating electron repulsion integrals (ERIs)

$$(pq|r_{12}^{-1}|rs) = \int d\mathbf{r}_1 d\mathbf{r}_2 \, \phi_p^*(1)\phi_q(1)\frac{1}{r_{12}}\phi_r^*(2)\phi_s(2). \quad (24)$$

The coefficients are obtained by minimizing the Coulomb energy of the orbital-product fitting residuals

$$\Delta_{pq} = (pq - \widetilde{pq}|r_{12}^{-1}|pq - \widetilde{pq}), \quad (25)$$

giving

$$D_A^{pq} = [\mathbf{J}^{-1}]_{AB}J_{pq}^B \quad (26)$$

where $J_{AB} = (A|r_{12}^{-1}|B)$ and $J_{pq}^B = (B|r_{12}^{-1}|pq)$.

The ERIs can be approximated as

$$(\widetilde{pq}|r_{12}^{-1}|\widetilde{rs}) = D_A^{pq}J_{AB}D_B^{rs} = J_{pq}^A[\mathbf{J}^{-1}]_{AB}J_{rs}^B, \quad (27)$$

and the error in this fitted integral is

$$(pq|r_{12}^{-1}|rs) - (\widetilde{pq}|r_{12}^{-1}|\widetilde{rs}) = (pq - \widetilde{pq}|r_{12}^{-1}|rs - \widetilde{rs}), \quad (28)$$

which is quadratic in the error in the fitted densities. This is a "robust" fit, characterized by avoiding errors linear in the error in the fitted densities [44]. Robust fits offer a significant improvement in accuracy with respect to the size of the fitting basis compared to non-robust fits (see Ref. 45 and the results reported herein).

In DF-MP2-F12 theory it is necessary to use formulas for the fitted integrals that are explicitly robust [21], because the same density fitting coefficients are used for multiple target integral types. For example, a robust fit for an integral over the correlation factor can be written in the form

$$(pq|f_{12}|rs)_{\text{robust}} = (pq|f_{12}|\widetilde{rs}) + (\widetilde{pq}|f_{12}|rs) - (\widetilde{pq}|f_{12}|\widetilde{rs}). \quad (29)$$

The standard implementation of the DF-MP2-F12 method [21, 22] uses RIs to approximate many-electron integrals. In implementing MP2-F12/3*A(D) theory with density-fitted many-electron integrals, it was necessary to obtain robustly fitted forms for the three-electron integrals that arise (Eqs. (16), (21) and (22)).

For a general three-electron integral $(pq|rs|tu)$, the fitted form

$$\begin{aligned} (pq|rs|tu)_{\text{robust}} &= (pq|\widetilde{rs}|\widetilde{tu}) + (\widetilde{pq}|rs|\widetilde{tu}) \\ &\quad + (\widetilde{pq}|\widetilde{rs}|tu) - 2(\widetilde{pq}|\widetilde{rs}|\widetilde{tu}) \end{aligned} \quad (30)$$

leads to an integral error

$$\begin{aligned} &(pq|rs|tu) - (pq|rs|tu)_{\text{robust}} \\ &= (pq - \widetilde{pq}|rs - \widetilde{rs}|tu - \widetilde{tu}) + (pq - \widetilde{pq}|rs - \widetilde{rs}|\widetilde{tu}) \\ &\quad + (\widetilde{pq}|rs - \widetilde{rs}|tu - \widetilde{tu}) + (pq - \widetilde{pq}|\widetilde{rs}|tu - \widetilde{tu}) \end{aligned} \quad (31)$$

that has no terms linear in the fitting error, and thus represents a robust fit [43]. Since each orbital pair is fitted independently of the others, the density fitting coefficients are the same as for the two-electron case (Eq. (26)).

III. INTEGRALS

A. Density fitted three-electron integrals

We require density-fitted forms of the diagonal integrals v_{ij}^{ij}, $a_{ij,ij}^{(1)}$ and $a_{ij,ij}^{(2)}$ and their exchange counterparts. For this initial implementation we also considered the non-diagonal forms of these integrals (see Eqs. (16), (21) and (22)), in anticipation of potential non-diagonal implementations.

The robustly fitted form of the three-electron integral arising from V_{kl}^{ij} (Eq. (16)) is just a special case of Eq. (30):

$$
\begin{aligned}
v_{ij,kl}^{\text{robust}} &= (im|r_{12}^{-1}|jl|f_{23}|mk)_{\text{robust}} \\
&= D_B^{jl} D_C^{mk} (im|r_{12}^{-1}|B|f_{23}|C) \\
&\quad + D_A^{im} D_C^{mk} (A|r_{12}^{-1}|jl|f_{23}|C) \\
&\quad + D_A^{im} D_B^{jl} (A|r_{12}^{-1}|B|f_{23}|mk) \\
&\quad - 2 D_A^{im} D_B^{jl} D_C^{mk} (A|r_{12}^{-1}|B|f_{23}|C).
\end{aligned}
\tag{32}
$$

Deriving the robustly fitted forms of the three-electron integrals arising from $A_{kl,mn}$ (Eqs. (21) and (22)) is more involved because the kinetic energy operators do not commute with the orbitals.

In earlier work it was pointed out that

$$
|\{\hat{t}_1 p\} q \,-\, p\{\hat{t}_1 q\}) \;\equiv\; |[pq])
\tag{33}
$$

is a type of orbital-product density, and as such it can be fitted [21]. Writing the target quantity in terms of such orbital products, we have

$$
\begin{aligned}
a_{kl,mn}^{(1)} &= \langle kli|[f_{12}, \hat{t}_1] f_{23}|inm\rangle \\
&= \langle kli|f_{12} f_{23}|\{\hat{t}_1 i\} nm\rangle - \langle\{\hat{t}_1 k\} li|f_{12} f_{23}|inm\rangle \\
&= -(\{\hat{t}_1 k\} i - k\{\hat{t}_1 i\}|f_{12}|ln|f_{23}|im) \\
&= -([ki]|f_{12}|ln|f_{23}|im)
\end{aligned}
\tag{34}
$$

leading to the robust fit

$$
\begin{aligned}
a_{kl,mn}^{(1),\text{robust}} &= -([ki]|f_{12}|ln|f_{23}|im)_{\text{robust}} \\
&= -D_B^{ln} D_C^{im} ([ki]|f_{12}|B|f_{23}|C) \\
&\quad - D_A^{[ki]} D_C^{im} (A|f_{12}|ln|f_{23}|C) \\
&\quad - D_A^{[ki]} D_B^{ln} (A|f_{12}|B|f_{23}|im) \\
&\quad + 2 D_A^{[ki]} D_B^{ln} D_C^{im} (A|f_{12}|B|f_{23}|C) .
\end{aligned}
\tag{35}
$$

Here we have defined a new density fitting coefficient type, $D_A^{[pq]}$. This is determined by minimizing the Coulomb criterion, but with the density $|[pq])$,

$$
\Delta_{[pq]} = ([pq] - \widetilde{[pq]}|r_{12}^{-1}|[pq] - \widetilde{[pq]}),
\tag{36}
$$

where

$$
|\widetilde{[pq]}) = D_A^{[pq]}|A).
\tag{37}
$$

Minimizing this expression, we obtain

$$
D_A^{[pq]} = [\mathbf{J}^{-1}]_{AB} Y_{pq}^B
\tag{38}
$$

where $J_{AB} = (A|r_{12}^{-1}|B)$ and $Y_{pq}^B = (B|r_{12}^{-1}|[pq])$ [21].

The kinetic energy operator in $a_{kl,mn}^{(2)}$ is "trapped" between the two correlation factors:

$$
\begin{aligned}
\langle kli|[f_{12}, \hat{t}_2] f_{23}|inm\rangle \\
= \langle kli|f_{12} \hat{t}_2 f_{23}|inm\rangle - \langle kli|\hat{t}_2 f_{12} f_{23}|inm\rangle.
\end{aligned}
\tag{39}
$$

Further manipulation is required, since we cannot directly convert the integral into a form amenable to robust fitting (as in Eq. (34)). We start by recognizing that

$$
\begin{aligned}
\hat{t}_2 f_{23} \phi_n(2) &= -\frac{1}{2} \nabla_2 \cdot \nabla_2 f_{23} \phi_n(2) \\
&= -\frac{1}{2} \big(f_{23}\{\nabla_2^2 \phi_n(2)\} + 2(\nabla_2 f_{23}) \cdot (\nabla_2 \phi_n(2)) \\
&\quad + \phi_n(2)\{\nabla_2^2 f_{23}\} \big) .
\end{aligned}
\tag{40}
$$

Substituting this into Eq. (39), we obtain

$$
\begin{aligned}
&\langle kli|[f_{12}, \hat{t}_2] f_{23}|inm\rangle \\
&= -\frac{1}{2} \big[\langle kli|f_{12} f_{23}|i\{\nabla_2^2 n\} m\rangle - \langle k\{\nabla_2^2 l\} i|f_{12} f_{23}|inm\rangle \big] \\
&\quad - \langle kli|f_{12}(\nabla_2 f_{23})|i(\nabla_2 n) m\rangle - \frac{1}{2} \langle kli|f_{12}\{\nabla_2^2 f_{23}\}|inm\rangle \\
&= -(ki|f_{12}|[ln]|f_{23}|im) - (ki|f_{12}|l(\nabla_2 n)|(\nabla_2 f_{23})|im) \\
&\quad - \frac{1}{2}(ki|f_{12}|ln|\{\nabla_2^2 f_{23}\}|im),
\end{aligned}
\tag{41}
$$

each term of which can be robustly fitted. In the above, we have used the following notation:

$$
\begin{aligned}
&\langle kli|f_{12}(\nabla_2 f_{23})|i(\nabla_2 n) m\rangle \equiv (ki|f_{12}|l(\nabla_2 n)|(\nabla_2 f_{23})|im) \\
&= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \; \{\phi_k^*(1)\phi_l^*(2)\phi_i^*(3) \\
&\quad \times f_{12}(\nabla_2 f_{23}) \cdot (\nabla_2 \phi_n(2))\phi_i(1)\phi_m(3)\} .
\end{aligned}
\tag{42}
$$

The first term, $(ki|f_{12}|[ln]|f_{23}|im)$, can be robustly fitted as in Eq. (35),

$$
\begin{aligned}
&(ki|f_{12}|[ln]|f_{23}|im)_{\text{robust}} \\
&= D_B^{[ln]} D_C^{im} (ki|f_{12}|B|f_{23}|C) \\
&\quad + D_A^{ki} D_C^{im} (A|f_{12}|[ln]|f_{23}|C) \\
&\quad + D_A^{ki} D_B^{[ln]} (A|f_{12}|B|f_{23}|im) \\
&\quad - 2 D_A^{ki} D_B^{[ln]} D_C^{im} (A|f_{12}|B|f_{23}|C),
\end{aligned}
\tag{43}
$$

where the new density fitting coefficients $D_A^{[pq]}$ (Eq. (38)) have been employed.

Each Cartesian component ($\lambda = x, y, z$) of the second term in Eq. (41) can be robustly fitted,

$$
\begin{aligned}
&(ki|f_{12}|ln_\lambda|f_{2\lambda 3}|im)_{\text{robust}} \\
&= D_B^{ln_\lambda} D_C^{im} (ki|f_{12}|B|f_{2\lambda 3}|C) \\
&\quad + D_A^{ki} D_C^{im} (A|f_{12}|ln_\lambda|f_{2\lambda 3}|C) \\
&\quad + D_A^{ki} D_B^{ln_\lambda} (A|f_{12}|B|f_{2\lambda 3}|im) \\
&\quad - 2 D_A^{ki} D_B^{ln_\lambda} D_C^{im} (A|f_{12}|B|f_{2\lambda 3}|C),
\end{aligned}
\tag{44}
$$

where we have introduced a compact notation for partial derivatives such that for example

$$
(ki|f_{12}|ln_\lambda|f_{2\lambda 3}|im) \equiv (ki|f_{12}|l(\nabla_{2\lambda} n)|(\nabla_{2\lambda} f_{23})|im)
\tag{45}
$$

and $\nabla_{2\lambda} \equiv \partial/\partial r_{2\lambda}$. We now introduce another new density fitting coefficient, $D_A^{pq_\lambda}$. These coefficients are determined by minimizing the Coulomb energy of the fitting residual $|pq_\lambda - \widetilde{pq_\lambda})$, where

$$|\widetilde{pq_\lambda}) = D_A^{pq_\lambda}|A) \tag{46}$$

and

$$D_A^{pq_\lambda} = [\mathbf{J}^{-1}]_{AB} J_{pq_\lambda}^B \tag{47}$$

where $J_{pq_\lambda}^B = (B|r_{12}^{-1}|pq_\lambda)$ and $\lambda = x, y, z$.

The last term in Eq. (41) can be robustly fitted using

$$\begin{aligned}
&(ki|f_{12}|ln|\{\nabla_2^2 f_{23}\}|im)_{\text{robust}} \\
&= D_B^{ln} D_C^{im}(ki|f_{12}|B|\{\nabla_2^2 f_{23}\}|C) \\
&+ D_A^{ki} D_C^{im}(A|f_{12}|ln|\{\nabla_2^2 f_{23}\}|C) \\
&+ D_A^{ki} D_B^{ln}(A|f_{12}|B|\{\nabla_2^2 f_{23}\}|im) \\
&- 2D_A^{ki} D_B^{ln} D_C^{im}(A|f_{12}|B|\{\nabla_2^2 f_{23}\}|C),
\end{aligned} \tag{48}$$

and only the standard density fitting coefficients D_A^{pq} (Eq. (26)) are needed.

A saturated density fitting basis set requires functions with up to $2\ell_{\text{occ}}$ units of angular momentum when only products of occupied orbitals are fitted, $|ij) \approx |\widetilde{ij})$. Fitting densities which contain the derivative or kinetic energy operator, such as $|ij_\lambda) \approx |\widetilde{ij_\lambda})$ and $|[ij]) \approx |\widetilde{[ij]})$, may increase the amount of angular momentum required in the density fitting basis. This is considered in Section IV.

Under the diagonal approximation it is clear that some of the three-electron integrals in the robust fitting expressions are zero. For example, in the diagonal approximation, the $(ki|f_{12}|[ln]|f_{23}|im)$ integral becomes

$$(im|f_{12}|[jj]|f_{23}|im) = 0$$

in $a_{ij,ij}^{(2)}$ (Eq. (41)), since $|[jj]) = 0$. An optimized implementation could certainly benefit from these cancellations.

B. Primitive integrals

Implementation of the density-fitted approximations for $v_{ij,kl}$, $a_{kl,mn}^{(1)}$ and $a_{kl,mn}^{(2)}$ in Molpro [46, 47] required the implementation of some new classes of integrals.

All of the three-electron integrals over molecular orbitals (MOs) and DF functions present in the robust fitting expressions are generated by contraction of three-electron integrals over primitive Cartesian Gaussian functions with the relevant atomic orbital (AO), MO and DF coefficients. For example,

$$\begin{aligned}
&(\widetilde{im}|r_{12}^{-1}|\widetilde{jl}|f_{23}|mk) \\
&= D_A^{im} D_B^{jl} c_\gamma^m c_\delta^k (A|r_{12}^{-1}|B|f_{23}|\gamma\delta) \tag{49} \\
&= d_{\mathbf{a}}^A d_{\mathbf{b}}^B d_{\mathbf{c}}^\gamma d_{\mathbf{d}}^\delta D_A^{im} D_B^{jl} c_\gamma^m c_\delta^k (\mathbf{a}|r_{12}^{-1}|\mathbf{b}|f_{23}|\mathbf{cd}).
\end{aligned}$$

label	definition
J-F	$(\mathbf{a}\|r_{12}^{-1}\|\mathbf{b}\|f_{23}\|\mathbf{c})$
	$(\mathbf{ab}\|r_{12}^{-1}\|\mathbf{c}\|f_{23}\|\mathbf{d})$
	$(\mathbf{a}\|r_{12}^{-1}\|\mathbf{bc}\|f_{23}\|\mathbf{d})$
	$(\mathbf{a}\|r_{12}^{-1}\|\mathbf{b}\|f_{23}\|\mathbf{cd})$
F-F	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|f_{23}\|\mathbf{c})$
	$(\mathbf{ab}\|f_{12}\|\mathbf{c}\|f_{23}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{bc}\|f_{23}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|f_{23}\|\mathbf{cd})$
F-FX	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|\{\nabla_2^2 f_{23}\}\|\mathbf{c})$
	$(\mathbf{ab}\|f_{12}\|\mathbf{c}\|\{\nabla_2^2 f_{23}\}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{bc}\|\{\nabla_2^2 f_{23}\}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|\{\nabla_2^2 f_{23}\}\|\mathbf{cd})$
F-FD	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|f_{2_\lambda 3}\|\mathbf{c})$
	$(\mathbf{ab}\|f_{12}\|\mathbf{c}\|f_{2_\lambda 3}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{bc}\|f_{2_\lambda 3}\|\mathbf{d})$
	$(\mathbf{a}\|f_{12}\|\mathbf{b}\|f_{2_\lambda 3}\|\mathbf{cd})$
FT1-F	$(\mathbf{ab}\|[\hat{t}_1, f_{12}]\|\mathbf{c}\|f_{23}\|\mathbf{d})$
FT2-F	$(\mathbf{a}\|[\hat{t}_2, f_{12}]\|\mathbf{bc}\|f_{23}\|\mathbf{d})$

TABLE I. Integrals over primitive Cartesian Gaussian functions required to evaluate $v_{ij,kl}^{\text{robust}}$, $a_{kl,mn}^{(1),\text{robust}}$ and the robustly fitted components of $a_{kl,mn}^{(2)}$, where $\lambda = x, y, z$.

where c_γ^m, c_δ^k are MO coefficients, and $d_{\mathbf{a}}^A$ are coefficients describing basis-set contractions (and possibly spherical transformations). The primitive Cartesian Gaussian function

$$\begin{aligned}
|\mathbf{a}) &\equiv g(\mathbf{r}; \zeta_a, \mathbf{A}, \mathbf{a}) \\
&= (r_x - A_x)^{a_x}(r_y - A_y)^{a_y}(r_z - A_z)^{a_z} \exp(-\zeta_a|\mathbf{r} - \mathbf{A}|^2)
\end{aligned} \tag{50}$$

has exponent ζ_a, center $\mathbf{A} = (A_x, A_y, A_z)$ and angular momentum index $\mathbf{a} = (a_x, a_y, a_z)$.

The three-electron integrals over primitive Cartesian Gaussians required to evaluate $v_{ij,kl}^{\text{robust}}$ (Eq. (32)), $a_{kl,mn}^{(1),\text{robust}}$ (Eq. (35)) and the robustly fitted components of $a_{kl,mn}^{(2)}$ (Eqs. (43), (44) and (48)) are given in Table I.

Efficient evaluation of integrals over primitive Gaussians of arbitrary angular momentum can be achieved through the use of recurrence relations [13, 48]. For this initial implementation, however, we used an alternative method to generate the primitive three-electron integral classes required, avoiding the need to implement new recurrence relations and instead transforming two-electron integral classes that were already available in Molpro [46, 47]. The procedure for generating three-electron integrals of the form

$$(\mathbf{a}|\hat{u}_{12}|\mathbf{b}|f_{23}|\mathbf{c}) = c_i(\mathbf{a}|\hat{u}_{12}|\mathbf{b}|g_{23}^{\mu_i}|\mathbf{c}), \tag{51}$$

where $\hat{u}_{12}$ is a general two-electron operator and f_{23} is a linear combination of Gaussian geminals, $g_{23}^{\mu_i} = g(\mathbf{r}_2; \mu_i, \mathbf{r}_3, \mathbf{0})$, started with the generation of the two-electron integrals $(\mathbf{a}|\hat{u}_{12}|\mathbf{r})$ using existing, well-tested subroutines. These two-electron, two-index integrals were then transformed to two-electron, three-index in-

tegrals,

$$(\mathbf{a}|\hat{u}_{12}|\mathbf{bc}') = T_{\mathbf{r}}^{\mathbf{bc}'}(\mathbf{a}|\hat{u}_{12}|\mathbf{r}), \quad (52)$$

using the Gaussian product theorem [15, 49]:

$$|\mathbf{ab}) \equiv g(\mathbf{r};\zeta_a,\mathbf{A},\mathbf{a})g(\mathbf{r};\zeta_b,\mathbf{B},\mathbf{b}) = T_{\mathbf{p}}^{\mathbf{ab}}g(\mathbf{r};\zeta,\mathbf{P},\mathbf{p}), \quad (53)$$

where $\zeta = \zeta_a + \zeta_b$, $\mathbf{P} = (\zeta_a\mathbf{A} + \zeta_b\mathbf{B})/\zeta$, $\mathbf{p}$ runs from $(0,0,0)$ to $(a_x+b_x, a_y+b_y, a_z+b_z)$ and the transformation coefficients $T_{\mathbf{p}}^{\mathbf{ab}}$ can be precomputed.

The two-electron, three-index integrals are then transformed into three-electron, three-index integrals using a Gaussian transform of a Cartesian Gaussian function [50]. The Gaussian transform is written

$$\int d\mathbf{r}_2\, g_{12}^{\mu} g(\mathbf{r}_2;\zeta_a,\mathbf{A},\mathbf{a}) \equiv \langle\mathbf{0}_{\mathbf{r}_1}|\mathbf{a}\rangle$$
$$= C_{\mathbf{aa}'}^{\mu} g\left(\mathbf{r}_1; \frac{\zeta_a\mu}{\zeta_a+\mu}, \mathbf{A}, \mathbf{a}'\right) \quad (54)$$

where $\mathbf{a}'$ runs from $(0,0,0)$ to (a_x, a_y, a_z) and

$$C_{\mathbf{aa}'}^{\mu} = \binom{a_x}{a'_x}\binom{a_y}{a'_y}\binom{a_z}{a'_z}\left(\frac{\mu}{\zeta_a+\mu}\right)^{a'_x+a'_y+a'_z}$$
$$\times \int d\mathbf{r}\, r_x^{a_x-a'_x} r_y^{a_y-a'_y} r_z^{a_z-a'_z} \exp(-(\zeta_a+\mu)|\mathbf{r}|^2). \quad (55)$$

We can therefore transform our two-electron, three-index integrals, into three-electron, three-index integrals, e.g.

$$(\mathbf{a}|\hat{u}_{12}|\mathbf{b}g_{23}^{\mu}|\mathbf{c}) = C_{\mathbf{cc}'}^{\mu}(\mathbf{a}|\hat{u}_{12}|\mathbf{bc}'). \quad (56)$$

where $\mathbf{c}'$ runs from $(0,0,0)$ to (c_x, c_y, c_z). Summation over Gaussian geminals $g_{23}^{\mu_i}$ gives the three-electron, three-index integral in Eq. (51). A further application of the Gaussian product theorem results in three-electron, four-index integrals, e.g.

$$(\mathbf{ab}|\hat{u}_{12}|\mathbf{c}|f_{23}|\mathbf{d}) = T_{\mathbf{p}}^{\mathbf{ab}}(\mathbf{p}|\hat{u}_{12}|\mathbf{c}|f_{23}|\mathbf{d}). \quad (57)$$

This method of generating three-electron integrals can be used to generate the J-F, F-F, F-FX and F-FD integrals in Table I requiring the two-electron integrals $(\mathbf{a}|r_{12}^{-1}|\mathbf{b})$, $(\mathbf{a}|f_{12}|\mathbf{b})$, $(\mathbf{a}|\{\nabla_2^2 f_{12}\}|\mathbf{b})$, and $(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b})$, respectively. Of these, only the last had not previously been implemented in Molpro (see Ref. 22 for details regarding the implementation of f_{12} and $\{\nabla_2^2 f_{12}\}$ integrals).

In the following, the additional steps required to implement the new FT1-F, FT2-F and FD integrals are described.

1. Integrals FT1-F and FT2-F

We define the FT1-F type primitive integrals,

$$(\mathbf{ab}|[\hat{t}_1, f_{12}]|\mathbf{c}|f_{23}|\mathbf{d}) \equiv ([\mathbf{ab}]|f_{12}|\mathbf{c}|f_{23}|\mathbf{d})$$
$$= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_a(1)[\hat{t}_1, f_{12}]g_b(1)g_c(2)f_{23}g_d(3) \quad (58)$$

where $g_a(1) \equiv g(\mathbf{r}_1;\zeta_a,\mathbf{A},\mathbf{a})$. It has previously been shown for two-electron FT type integrals that [22, 51]

$$(\mathbf{ab}|[\hat{t}_1, f_{12}]|\mathbf{c}) = -\frac{1}{2}\frac{\zeta_a - \zeta_b}{\zeta_a + \zeta_b}(\mathbf{ab}|\{\nabla^2 f_{12}\}|\mathbf{c})$$
$$- \nabla_P \cdot \nabla_R(\mathbf{ab}|f_{12}|\mathbf{c}), \quad (59)$$

where

$$\mathbf{P} = \frac{\zeta_a}{\zeta}\mathbf{A} + \frac{\zeta_b}{\zeta}\mathbf{B}, \quad (60)$$

$$\mathbf{R} = \mathbf{A} - \mathbf{B}, \quad (61)$$

and $\zeta = \zeta_a + \zeta_b$. The same analysis can be used to show that the FT1-F three-electron integral type can be constructed from F-FX and F-F type integrals:

$$(\mathbf{ab}|[\hat{t}_1, f_{12}]|\mathbf{c}|f_{23}|\mathbf{d}) = -\frac{1}{2}\frac{\zeta_a - \zeta_b}{\zeta_a + \zeta_b}(\mathbf{ab}|\{\nabla_1^2 f_{12}\}|\mathbf{c}|f_{23}|\mathbf{d})$$
$$- \nabla_P \cdot \nabla_R(\mathbf{ab}|f_{12}|\mathbf{c}|f_{23}|\mathbf{d}). \quad (62)$$

The expression for the coefficients describing the gradient orbital product,

$$\nabla_P \cdot \nabla_R|\mathbf{ab}) = Q_{\mathbf{p}}^{\mathbf{ab}}|\mathbf{p}), \quad (63)$$

where the summation runs from $0 \le |\mathbf{p}| \le |\mathbf{a}| + |\mathbf{b}| + 1$ [21], does not appear to have been published elsewhere, though it has been implemented in Molpro [46, 47]. In terms of the product coefficients, $T_{\mathbf{p}}^{\mathbf{ab}}$ (Eq. (53)),

$$Q_{\mathbf{p}}^{\mathbf{ab}} = -2\zeta_b(2\xi R_\lambda^2 + a_\lambda)T_{\mathbf{p}}^{\mathbf{ab}} - 4\zeta_a\zeta_b R_\lambda T_{\mathbf{p}}^{\mathbf{a+1}_\lambda,\mathbf{b}}$$
$$+ 2\zeta_a b_\lambda T_{\mathbf{p}}^{\mathbf{a+1}_\lambda,\mathbf{b-1}_\lambda} + 2\zeta_b \eta a_\lambda R_\lambda T_{\mathbf{p}}^{\mathbf{a-1}_\lambda,\mathbf{b}}$$
$$+ 4\xi b_\lambda R_\lambda T_{\mathbf{p}}^{\mathbf{a},\mathbf{b-1}_\lambda} - \eta a_\lambda b_\lambda T_{\mathbf{p}}^{\mathbf{a-1}_\lambda,\mathbf{b-1}_\lambda}$$
$$+ \frac{\zeta_b}{\zeta}a_\lambda(a_\lambda - 1)T_{\mathbf{p}}^{\mathbf{a-2}_\lambda,\mathbf{b}} - \frac{\zeta_a}{\zeta}b_\lambda(b_\lambda - 1)T_{\mathbf{p}}^{\mathbf{a},\mathbf{b-2}_\lambda} \quad (64)$$

where the summation runs over $\lambda = x, y, z$, and

$$\xi = \frac{\zeta_a\zeta_b}{\zeta}, \quad (65)$$

$$\eta = \frac{\zeta_a - \zeta_b}{\zeta}. \quad (66)$$

The FT2-F integrals,

$$(\mathbf{a}|[\hat{t}_2, f_{12}]|\mathbf{bc}|f_{23}|\mathbf{d})$$
$$= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_a(1)g_b(2)[\hat{t}_2, f_{12}]g_c(2)f_{23}g_d(3) \quad (67)$$

arise in constructing $(ki|f_{12}|[ln]|f_{23}|im)_{\text{robust}}$ (Eq. (43)), since

$$(\mathbf{a}|f_{12}|[\mathbf{bc}]|f_{23}|\mathbf{d}) = (\mathbf{a}|[\hat{t}_2, f_{12}]|\mathbf{bc}|f_{23}|\mathbf{d})$$
$$- (\mathbf{a}|f_{12}|\mathbf{b}(\nabla_2\mathbf{c})|(\nabla_2 f_{23})|\mathbf{d})$$
$$- \frac{1}{2}(\mathbf{a}|f_{12}|\mathbf{bc}|\{\nabla_2^2 f_{23}\}|\mathbf{d}). \quad (68)$$

The FT2-F integrals cannot be decomposed using the same method used for the FT1-F integrals, because this relies upon the relationship

$$\nabla_P(\mathbf{ab}|M_{12}|\mathbf{c}) = (\mathbf{ab}|\{\nabla_1 M_{12}\}|\mathbf{c}), \qquad (69)$$

where $M_{12} = f_{12}$ or $(\nabla_1 f_{12})$. Klopper and Röhse [51] demonstrated that Eq. (69) was satisfied for $M_{12} = r_{12}$ or $\mathbf{r}_{12}/r_{12}$ using

$$\nabla_P|\mathbf{ab}) = -\nabla_1|\mathbf{ab}) \qquad (70)$$

to obtain

$$\nabla_P(\mathbf{ab}|M_{12}|\mathbf{c}) = \int d\mathbf{r_1}d\mathbf{r_2}g_a(1)g_b(1)\{\nabla_1 M_{12}\}g_c(2)$$
$$- \int d\mathbf{r_1}d\mathbf{r_2}(\nabla_1 g_a(1)g_b(1)M_{12})g_c(2) \qquad (71)$$

and integrating by parts to show that the second term is zero. This is also true for $M_{12} = f_{12}$ or $(\nabla_1 f_{12})$. It can therefore be shown that

$$\nabla_P(\mathbf{ab}|(\nabla_1 f_{12})|\mathbf{c}|f_{23}|\mathbf{d}) = (\mathbf{ab}|\{\nabla_1^2 f_{12}\}|\mathbf{c}|f_{23}|\mathbf{d}), \quad (72)$$

and

$$\nabla_P \cdot \nabla_R(\mathbf{ab}|f_{12}|\mathbf{c}|f_{23}|\mathbf{d}) = \nabla_R(\mathbf{ab}|(\nabla_1 f_{12})|\mathbf{c}|f_{23}|\mathbf{d}), \qquad (73)$$

which are key relationships in deriving Eq. (62). The equivalent relationship for the FT2-F integrals does not hold. Instead, we use

$$(\mathbf{a}|[\hat{t}_2, f_{12}]|\mathbf{bc}|f_{23}|\mathbf{d}) = \frac{1}{2}(\mathbf{a}|\{\nabla_2^2 f_{12}\}|\mathbf{bc}|f_{23}|\mathbf{d})$$
$$+ (\mathbf{a}|(\nabla_2 f_{12})|(\nabla_2 \mathbf{b})\mathbf{c}|f_{23}|\mathbf{d}) \qquad (74)$$

where

$$(\mathbf{a}|f_{12_\lambda}|\mathbf{b}_\lambda \mathbf{c}|f_{23}|\mathbf{d})$$
$$= -2(\mathbf{a}|f_{12_\lambda}|(\mathbf{b}+\mathbf{1}_\lambda)\mathbf{c}|f_{23}|\mathbf{d}) \qquad (75)$$
$$+ b_\lambda(\mathbf{a}|f_{12_\lambda}|(\mathbf{b}-\mathbf{1}_\lambda)\mathbf{c}|f_{23}|\mathbf{d}).$$

2. Integral FD

We define the FD-type two-electron primitive integrals,

$$(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b}) = -(\mathbf{a}|f_{12_\lambda}|\mathbf{b})$$
$$= \int d\mathbf{r_1}d\mathbf{r_2}\, g_a(1)(\nabla_{1\lambda} f_{12})g_b(2), \qquad (76)$$

where $\lambda = x, y, z$. The FD integrals are necessary in the construction of the F-FD type three-electron integrals, which themselves are required to generate the FT2-F integrals (Table I). When the correlation factor, f_{12}, is

a linear combination of Gaussian geminals, the $\nabla_{1\lambda} f_{12}$ operator ($\equiv f_{1_\lambda 2}$) may be simplified to

$$\nabla_{1\lambda} f_{12} = \frac{\partial}{\partial r_{1\lambda}} \sum_j c_j \exp(-\mu_j|\mathbf{r}_1 - \mathbf{r}_2|^2)$$
$$= (r_{1\lambda} - r_{2\lambda})G_{12} \qquad (77)$$

where we define a new correlation factor,

$$G_{12} = \sum_j c_j' g_{12}^{\mu_j}, \qquad (78)$$

with $c_j' = -2c_j\mu_j$ (for $\nabla_{2\lambda} f_{12}$, $c_j' = 2c_j\mu_j$). Recognizing that

$$(r_{1\lambda} - r_{2\lambda}) = (r_{1\lambda} - A_\lambda) - (r_{2\lambda} - B_\lambda) + (A_\lambda - B_\lambda) \quad (79)$$

we can expand $(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b})$ in terms of increased angular momentum in the primitives centered on $\mathbf{A}$ and $\mathbf{B}$:

$$(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b}) = (\mathbf{a}+\mathbf{1}_\lambda|G_{12}|\mathbf{b}) - (\mathbf{a}|G_{12}|\mathbf{b}+\mathbf{1}_\lambda)$$
$$+ (A_\lambda - B_\lambda)(\mathbf{a}|G_{12}|\mathbf{b}). \qquad (80)$$

To avoid needing to increase angular momentum in both indices, we can use the transfer equation described in Ref. 22,

$$(\mathbf{a}|g_{12}^\mu|\mathbf{b}+\mathbf{1}_\lambda) = \frac{a_\lambda}{2\zeta_b}(\mathbf{a}-\mathbf{1}_\lambda|g_{12}^\mu|\mathbf{b}) + \frac{b_\lambda}{2\zeta_b}(\mathbf{a}|g_{12}^\mu|\mathbf{b}-\mathbf{1}_\lambda)$$
$$- \frac{\zeta_a}{\zeta_b}(\mathbf{a}+\mathbf{1}_\lambda|g_{12}^\mu|\mathbf{b}), \qquad (81)$$

to obtain

$$(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b}) = \left(1 + \frac{\zeta_a}{\zeta_b}\right)(\mathbf{a}+\mathbf{1}_\lambda|G_{12}|\mathbf{b})$$
$$- \frac{b_\lambda}{2\zeta_b}(\mathbf{a}|G_{12}|\mathbf{b}-\mathbf{1}_\lambda) - \frac{a_\lambda}{2\zeta_b}(\mathbf{a}-\mathbf{1}_\lambda|G_{12}|\mathbf{b}) \qquad (82)$$
$$+ (A_\lambda - B_\lambda)(\mathbf{a}|G_{12}|\mathbf{b})$$

where $(\mathbf{a}|G_{12}|\mathbf{b})$ is an F-type integral, described in Ref. 22. Using Eq. (82), $(\mathbf{a}|f_{1_\lambda 2}|\mathbf{b})$ integrals can be generated from F-type integrals with angular momentum incremented in only one of the two primitive indices.

C. Contractions

To obtain integrals over molecular orbitals, the primitive three-electron integrals in Table I must be contracted with AO, DF and MO coefficients. The contraction of integrals over primitive Gaussians with AO coefficients is straightforward, but the subsequent contraction with DF and MO coefficients is complicated by the existence of multiple routes to the final, fully-contracted object. For example, there is more than one possible sequence

of contractions of the three-index components of $v_{ij,kl}^{\text{robust}}$ (Eq. (32)) with the relevant DF coefficients,

$$D_A^{im} D_B^{jl} D_C^{mk} (A|r_{12}^{-1}|B|f_{23}|C) \equiv (\widetilde{im}|r_{12}^{-1}|\widetilde{jl}|f_{23}|\widetilde{mk}) . \tag{83}$$

We could start by contracting two DF coefficients with a common index to obtain

$$X_{AC}^{ik} = D_A^{im} D_C^{mk}, \tag{84}$$

which has a computational scaling of $\mathcal{O}(o^3 D^2)$, where o is the number of occupied orbitals and D is the number of DF basis functions. Alternatively, we could start by contracting one of the three DF coefficients with the three-electron, three-index integral to obtain a different four-index object,

$$X_{BC}^{im} = D_A^{im} (A|\hat{u}_{12}|B|f_{23}|C) \tag{85}$$

which has a scaling of $\mathcal{O}(o^2 D^3)$. Each starting point leads to a different set of possible subsequent contractions, and these must be considered together to judge which sequence of contractions is the most efficient. In implementing the schemes for contracting three- and four-index AO integrals with the necessary MO and DF coefficients to obtain the robustly fitted three-electron integrals we selected sequences of operations with the lowest maximum computational scaling. Where there were multiple routes to the final, fully-contracted, object with the same maximum scaling step, our selection was guided by other considerations, such as the scaling of the other operations in the sequence or the storage requirements of intermediate, partially-contracted objects.

The implementation of the general robustly fitted three-electron integrals,

$$
\begin{aligned}
u_{ij,kl} &= (im|\hat{u}_{12}|jl|f_{23}|mk)_{\text{robust}} \\
&= u_{ij,kl}^{(4,1)} + u_{ij,kl}^{(4,2)} + u_{ij,kl}^{(4,3)} - 2u_{ij,kl}^{(3)}
\end{aligned}
\tag{86}
$$

where

$$
\begin{aligned}
u_{ij,kl}^{(3)} &= D_A^{im} D_B^{jl} D_C^{mk} (A|\hat{u}_{12}|B|f_{23}|C), \\
u_{ij,kl}^{(4,1)} &= D_B^{jl} D_C^{mk} c_\alpha^i c_\beta^m (\alpha\beta|\hat{u}_{12}|B|f_{23}|C), \\
u_{ij,kl}^{(4,2)} &= D_A^{im} D_C^{mk} c_\gamma^j c_\delta^l (A|\hat{u}_{12}|\gamma\delta|f_{23}|C), \\
u_{ij,kl}^{(4,3)} &= D_A^{im} D_B^{jl} c_\epsilon^m c_\zeta^k (A|\hat{u}_{12}|B|f_{23}|\epsilon\zeta)
\end{aligned}
\tag{87}
$$

required three contraction schemes, one for each of $u_{ij,kl}^{(3)}$ and $u_{ij,kl}^{(4,2)}$ and one for both $u_{ij,kl}^{(4,1)}$ and $u_{ij,kl}^{(4,3)}$.

For contracting three-index integrals with DF coefficients, we used the following three-step scheme, with a maximum scaling of $\mathcal{O}(N^5)$ (N is a measure of system size):

$$
\begin{aligned}
X_{BC}^{im} &= D_A^{im} (A|\hat{u}_{12}|B|f_{23}|C) &\quad \mathcal{O}(o^2 D^3) \\
Y_B^{ik} &= X_{BC}^{im} D_C^{mk} &\quad \mathcal{O}(o^3 D^2) \\
u_{ij,kl}^{(3)} &= D_B^{jl} Y_B^{ik} &\quad \mathcal{O}(o^4 D),
\end{aligned}
\tag{88}
$$

where the formal computational scaling is shown next to each step.

The contraction scheme implemented for the $u_{ij,kl}^{(4,1)}$ and $u_{ij,kl}^{(4,3)}$ terms is

$$
\begin{aligned}
(i\beta|\hat{u}_{12}|B|f_{23}|C) &= c_\alpha^i (\alpha\beta|\hat{u}_{12}|B|f_{23}|C) &\quad \mathcal{O}(a^2 o D^2) \\
(im|\hat{u}_{12}|B|f_{23}|C) &= c_\beta^m (i\beta|\hat{u}_{12}|B|f_{23}|C) &\quad \mathcal{O}(a o^2 D^2) \\
X_B^{ik} &= D_C^{mk} (im|\hat{u}_{12}|B|f_{23}|C) &\quad \mathcal{O}(o^3 D^2) \\
u_{ij,kl}^{(4,1)} &= X_B^{ik} D_B^{jl} &\quad \mathcal{O}(o^4 D)
\end{aligned}
\tag{89}
$$

where the most costly step has a scaling of $\mathcal{O}(N^5)$ and the a in the scaling expressions represents the size of the AO basis set.

The contraction scheme used to generate $u_{ij,kl}^{(4,2)}$ is

$$
\begin{aligned}
(A|\hat{u}_{12}|j\delta|f_{23}|C) &= c_\gamma^j (A|\hat{u}_{12}|\gamma\delta|f_{23}|C) &\quad \mathcal{O}(a^2 o D^2) \\
(A|\hat{u}_{12}|jl|f_{23}|C) &= c_\delta^l (A|\hat{u}_{12}|j\delta|f_{23}|C) &\quad \mathcal{O}(a o^2 D^2) \\
X_{AC}^{ik} &= D_A^{im} D_C^{mk} &\quad \mathcal{O}(o^3 D^2) \\
u_{ij,kl}^{(4,2)} &= X_{AC}^{ik} (A|\hat{u}_{12}|jl|f_{23}|C) &\quad \mathcal{O}(o^4 D^2).
\end{aligned}
\tag{90}
$$

There is an unavoidable $\mathcal{O}(N^6)$ step in the contraction of $u_{ij,kl}^{(4,2)}$ and the computational scaling of the entire robust fitting procedure for integrals of the general form $u_{ij,kl}$ is therefore $\mathcal{O}(N^6)$, the same scaling as the contractions and transformations involved in approximating an integral of the form $u_{ij,kl}$ using a standard RI.

A non-robust fitting procedure (where $u_{ij,kl} = u_{ij,kl}^{(3)}$) using the contraction scheme described would have the advantage of a lower $\mathcal{O}(N^5)$ scaling. For this reason, we include non-robustly fitted results type alongside the robustly fitted results in the next section.

The $\mathcal{O}(N^6)$ steps for a standard RI (Eq. 1) and the robust fitting procedure for $u_{ij,kl}$ (Eq. 90) are both matrix multiplications and thus the relative expense of each step can be estimated based on the difference in the number of operations involved. A standard RI (Eq. 1) has a scaling of $o^5 x \equiv (x/o)o^6$, where x represents the size of the RI basis, while the most costly step in the robust fitting procedure scales as $o^4 D^2 \equiv (D/o)^2 o^6$. The number of auxiliary basis functions (D and x) is typically much larger than the number of occupied orbitals, o, and assuming $x \approx D$, the $(D/o)^2$ prefactor before the common o^6 term for the robust fitting procedure would be larger than the prefactor for RI. However, further improvements and approximations may be possible.

It is notable that if only the diagonal terms are considered (i.e. $kl = ij$ and ji in Eq. 86), the formal scaling of the contractions involved in both robust fitting and applying a standard RI to $u_{ij,kl}$ is $\mathcal{O}(N^5)$, though the contraction schemes outlined here may not be optimal in this case.
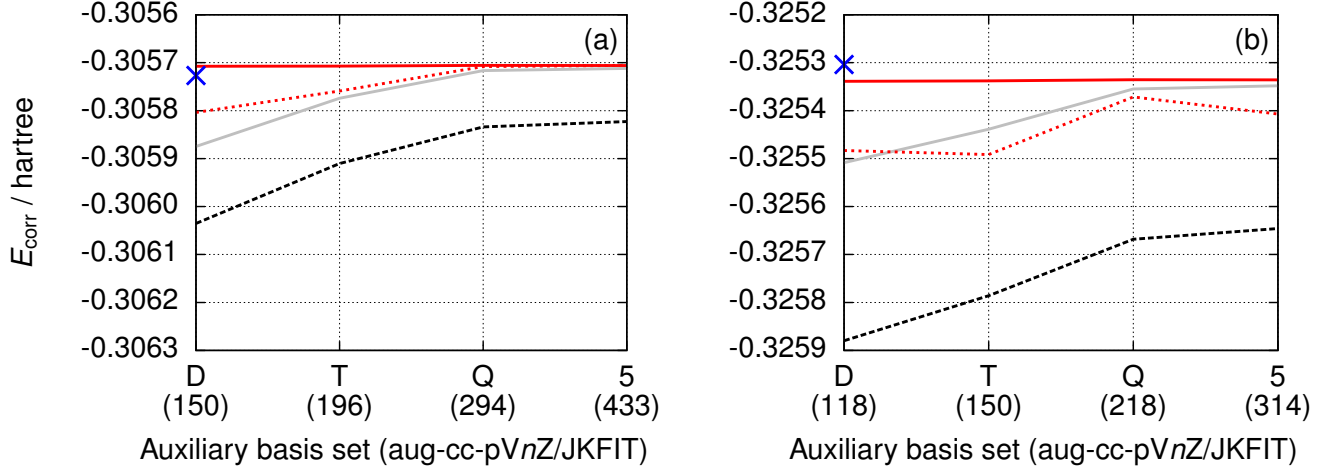
FIG. 1. DF-MP2-F12/3*A(FIX) correlation energy of (a) H_2O and (b) HF for increasing auxiliary basis set size, using ABS RI (black dashed line), CABS RI (gray solid line), robust DF3 (red solid line) and non-robust DF3 (red dotted line) to approximate the three-electron integrals. The AO basis set for all atoms was aug-cc-pVDZ [52, 53]. The auxiliary basis sets used for ABS RI, CABS RI and robust and non-robust DF integral approximations were of aug-cc-pVnZ/JKFIT type, where the cc-pVnZ/JKFIT basis sets of Ref. 54 were augmented by a single even-tempered function at each angular momentum level and the DZ set was constructed by removal of the highest angular momentum functions from the TZ set. The numbers in parentheses are the total numbers of basis functions in the auxiliary basis sets. A single OPTRI calculation (blue cross) was performed with the aug-cc-pVDZ/OPTRI basis set corresponding to the AO basis [55].

IV. RESULTS

The proof-of-concept implementation of the robustly fitted integrals required in MP2-F12/3*A(D) theory was carried out in Molpro [46, 47]. This involved inserting the robustly fitted $v_{ij,kl}$, $a_{kl,mn}^{(1)}$ and $a_{kl,mn}^{(2)}$ integrals into the pre-existing DF-MP2-F12 code [21, 22, 41].

In this section, we refer to the density fitting of the three-electron integrals in MP2-F12/3*A(D) theory as DF3, in contrast to the prefix DF- in DF-MP2-F12, which refers to the density fitting of four-index, two-electron integrals in MP2-F12 theory [21]. Robust DF3 refers to the density fitting of three-electron integrals using Eqs. (32), (35), (43), (44) and (48) while non-robust DF3 refers to density fitting of the same integral types, but using a single term in which all orbital pairs are fitted, i.e.

$$(im|r_{12}^{-1}|jl|f_{23}|mk) \approx v_{ij,kl}^{(3)} = (\widetilde{im}|r_{12}^{-1}|\widetilde{jl}|f_{23}|\widetilde{mk}). \quad (91)$$

To assess the effectiveness of the robust DF3 approximation in the context of full MP2-F12/3*A(D) calculations, we calculated correlation energies for H_2O, HF, the Zn atom and the Zn^{2+} cation. The DF-MP2-F12/3*A(FIX) method was used, where "FIX" refers to the fixed-amplitude ansatz in which the explicitly correlated amplitudes T_{ij}^{ij} are determined by the electronic cusp conditions [12, 56] and the diagonal approximation is applied. Calculations were performed with integrals approximated using ABS RI [19], CABS RI [20], non-robust DF3 and robust DF3, for increasingly large auxiliary basis sets.

The convergence of MP2-F12/3*A(FIX) correlation energies calculated using the RI and DF3 approximations with respect to the size of the auxiliary basis set is shown in Fig. 1 for the H_2O and HF molecules. The CABS RI correlation energies converge more rapidly with respect to auxiliary basis set than do the ABS RI energies and the robust DF3 energies converge more rapidly than the non-robust. It is clear that the robust DF3 energies converge much more rapidly than energies calculated using any of the other approximation schemes.

For both HF and H_2O, the robust DF3 correlation energy using a double-ζ (DZ) auxiliary basis set is converged to within $\sim 10^{-6}$ hartree of the value using a quintuple-ζ (5Z) set, while the difference between CABS RI using DZ and 5Z fitting sets is around two orders of magnitude larger. This suggests that it may be possible to use the robust DF3 method to obtain correlation energies converged to submillihartree accuracy using auxiliary basis sets even smaller than aug-cc-pVDZ/JKFIT.

For each molecule, we include a correlation energy calculated using CABS RI using the aug-cc-pVDZ/OPTRI auxiliary basis set [55, 57]. The correlation energies using CABS RI with an OPTRI basis set are converged to within $\sim 10^{-5}$ hartree of the 5Z result (with either robust DF3 or CABS RI)—a considerable reduction in the error compared to the aug-cc-pVDZ/JKFIT auxiliary basis.

The Zn atom has occupied d-orbitals ($\ell_{occ} = 2$) and accurate approximation of the $\mathbf{V}$ matrix elements requires a RI basis with functions up to at least $3\ell_{occ} = 6$ units of angular momentum; the DF3 basis formally requires functions with up to $2\ell_{occ} = 4$ to fit the same integrals. The convergence of the correlation energy
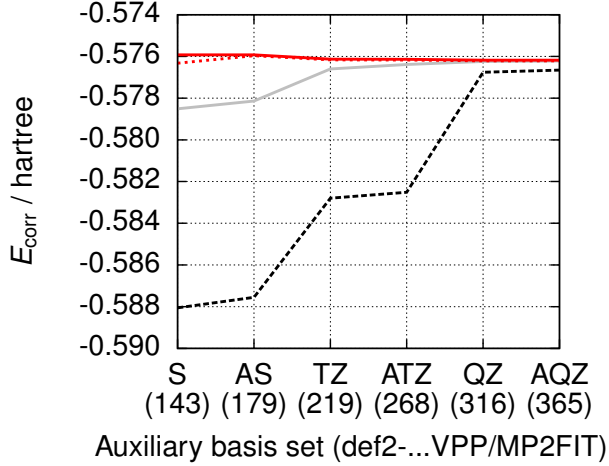
FIG. 2. DF-MP2-F12/3*A(FIX) valence correlation energy of the Zn atom $(4s^2 3d^{10})$, calculated using ABS RI (black dashed line), CABS RI (gray solid line), robust DF3 (red solid line) and non-robust DF3 (red dotted line) to approximate three-electron integrals for increasing auxiliary basis set size. The auxiliary basis sets were MP2FIT basis sets optimized for the def2 family of AO basis sets, where the ASVP, ATZVPP, and AQZVPP sets are formed by adding a set of even-tempered diffuse functions to the SVP, TZVPP and QZVPP MP2FIT sets from Refs. 58 and 59. The numbers in parentheses are the total numbers of basis functions in the auxiliary basis sets. The AO basis set was def2-TZVPP for all calculations [60].

FIG. 3. DF-MP2-F12/3*A(FIX) valence correlation energy of the Zn atom $(4s^2 3d^{10})$, calculated using ABS RI (black dashed line), CABS RI (gray solid line), robust DF3 (red solid line) to approximate three-electron integrals for increasing auxiliary basis set size. The auxiliary basis set was composed of functions with angular momentum up to and including the maximum angular momentum value, taken from the def2-QZVPP/JKFIT auxiliary basis set (the "Contracted, standard" basis set from Ref. 61). The AO basis set was def2-TZVPP for all calculations [60].

of the Zn atom $(4s^2 3d^{10})$ with respect to auxiliary basis set size is plotted in Fig. 2. The results demonstrate a similar trend to that seen in Fig. 1, though the range of energies is greater, largely due to the incompleteness of the SVP and ASVP basis sets, which include only up to h-functions ($l = 5$). On moving to def2-TZVPP/MP2FIT, i-functions ($l = 6$) are included in the auxiliary basis set and the accuracy of the correlation energies, particularly those calculated using RI, increases. Using the smallest def2-SVP/MP2FIT auxiliary basis set, the robust and non-robust DF3 energies are already within $\sim 10^{-4}$ hartree of the correlation energy calculated with the largest def2-AQZVPP/MP2FIT auxiliary basis set. The difference between the CABS RI correlation energy calculated using a def2-SVP/MP2FIT and a def2-AQZVPP/MP2FIT auxiliary basis set is, by comparison, of the order of a millihartree.

The relative insensitivity of the DF3 fitting to a formally unsaturated auxiliary basis set can be seen in Fig. 3, where the correlation energy of the Zn atom is plotted against increasing angular momentum available in the auxiliary basis set. The robust DF3 correlation energy is converged to within $\sim 10^{-6}$ hartree of the correlation energy calculated with the full def2-QZVPP/JKFIT auxiliary basis set (i.e. containing i-functions) with an auxiliary basis set containing only up to g-functions ($l = 4$). When the g-functions are removed from the auxiliary basis, the robust DF3 correlation energy rapidly di-
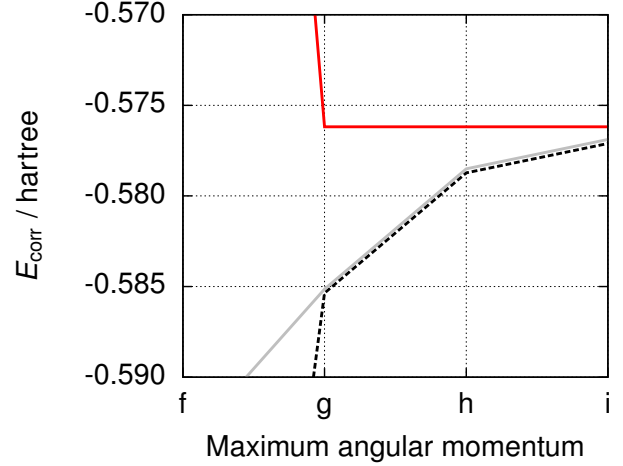
verges from the converged value—for an auxiliary basis containing up to f-functions, the difference is nearly 100 millihartree. This suggests that robust DF3 requires an auxiliary basis with functions up to $2\ell_{occ}$ units of angular momentum (for an atom) to obtain MP2-F12/3*A(D) correlation energies converged to submillihartree accuracy. This is particularly interesting considering that densities involving the derivative and kinetic energy operators, $|[ij])$ and $|ij_\lambda)$, are fitted by the DF3 basis and one might to expect a good fit of these densities to require functions with greater than $2\ell_{occ}$ units of angular momentum in the DF3 basis.

It is notable that the non-robust DF3 correlation energies do not converge to submillihartree accuracy until h-functions are added (non-robust DF3 correlation energies are omitted from Fig. 3 for clarity). This suggests that the robust fitting procedure is important in reducing the error in the fitted integrals where the auxiliary basis set may not be formally saturated in terms of angular momentum.

The same convergence behavior of the DF3 MP2-F12/3*A(FIX) correlation energies with respect to the maximum angular momentum available in the auxiliary basis set is evident in the Zn double ionization energies (Zn, $4s^2 3d^{10} \rightarrow Zn^{2+}$, $3d^{10}$) presented in Table II. When g-functions ($\ell_{max} = 4$) are included, the double ionization energies for both RI and DF3 are converged to submillihartree accuracy with respect to the double ionization energies calculated using the full def2-QZVPP/JKFIT auxiliary basis set ($\ell_{max} = 6$). The

robust DF3 double ionization energy with $\ell_{max} = 4$ is within $\sim 10^{-5}$ hartree of the value when the full def2-QZVPP/JKFIT auxiliary basis set is used—an order of magnitude smaller than the differences seen for the RI and non-robust DF3 energies.

Villani and Klopper's [62] very large (near the basis set limit) basis MP2-R12 valence correlation energy calculations predict a Zn double ionization energy of 981.13 millihartree, which is within a few millihartree of the converged double ionization energies in Table II (approximation diag-A, calculated using data in Tables 6 and 7 of Ref. 62). The converged double ionization energies in Table II, which are calculated using a def2-TZVPP orbital basis, are also close to the values calculated using TZVPP (970.77 millihartree) and QZVPP (977.07 millihartree) orbital basis sets (with very large auxiliary basis set) reported in Ref. 62. The error incurred by approximating integrals using robust DF3, where functions with more than $\ell_{max} = 2\ell_{occ} = 4$ units of angular momentum are omitted from the auxiliary basis is therefore ~ 1000 times smaller than the orbital basis set incompleteness error seen in Villani and Klopper's MP2-R12 calculations.

V. CONCLUSION

We have presented a proof-of-concept implementation of MP2-F12/3*A(D) theory with all three-electron integrals approximated using robust fitting, rather than by approximate RIs. The lower angular-momentum requirement of the DF3 basis, compared to the RI basis, is evident in the rapid convergence of correlation and double ionization energies with increasing size (Figs. 1 and 2) and maximum angular momentum (Fig. 3 and Table II) of the auxiliary basis set.

Our results suggest that the error from robust fitting the three-electron integrals can be significantly smaller than the typical basis-set incompleteness error in an MP2-F12 calculation using relatively small aug-cc-pVDZ/JKFIT and def2-SVP/MP2FIT auxiliary basis sets. The level of accuracy obtained with these small auxiliary basis sets suggests that even smaller sets may be sufficient to obtain submillihartree errors using

ℓ_{max}	ABS RI	CABS RI	Non-robust DF3	Robust DF3
3	974.483160	976.135720	978.263309	977.759893
4	974.778962	974.774913	974.718356	974.969957
5	974.917008	974.912959	974.966144	974.970005
6	974.963739	974.959690	974.966144	974.970005

TABLE II. Zn atom double ionization energies (Zn, $4s^2 3d^{10} \rightarrow Zn^{2+}$, $3d^{10}$) in millihartree, calculated with DF-MP2-F12/3*A(FIX) using RI or DF3 to approximate three-electron integrals for increasing auxiliary basis set size. The auxiliary basis set was composed of functions with angular momentum up to and including ℓ_{max}, as in Fig. 3. The AO basis set was def2-TZVPP for all calculations [60].

the robust DF3 procedure. It is clear, however, that accurate approximation of the three-electron integrals requires that the DF3 basis set contains functions with up to and including $2\ell_{occ}$ units of angular momentum (Fig. 3).

The robust DF3 MP2-F12/3*A(D) correlation energies we have reported appear to be relatively insensitive to the auxiliary basis set used. This is a useful property, since it means that the DF basis used to fit two-electron integrals in the DF-MP2-F12 method [21, 22] would likely also be sufficient for the DF3 fitting procedure, avoiding the introduction of an additional auxiliary basis set. Nevertheless, it may be worth investigating optimizing auxiliary basis sets specifically for DF3 fitting in future work. In this work we have used the JKFIT and MP2FIT families of fitting basis sets, which are optimized by minimizing the errors in fitted exchange integrals [54] and the DF-MP2 energy [63], respectively. It seems likely that JKFIT basis sets would be more appropriate, since these are optimized for fitting products of occupied orbitals, while MP2FIT basis sets are optimized for fitting occupied-virtual products [54, 63, 64]. A suitable method of optimizing auxiliary basis sets specifically for use in DF3 might utilize the same functional used in optimizing the OPTRI auxiliary basis sets [57] for CABS RI, which involves the diagonal elements of the $\mathbf{V}$ and $\mathbf{B}$ matrices.

Our proof-of-concept implementation is currently unsuitable for benchmarking the computational performance of the robust DF3-based MP2-F12 method against other MP2-F12 implementations. The formal scaling of the contractions involved in robust DF3 fitting is the same as that for conventional RIs, and we have observed very stable and rapid convergence of energies with respect to the density fitting basis used in DF3. The most costly $\mathcal{O}(N^6)$ contraction step in the robust fitting procedure scales quadratically with the size of the DF3 basis set (Eq. 90). Where the sizes of the DF3 and RI basis sets are similar, this step is likely to be more costly than the $\mathcal{O}(N^6)$ step in a standard RI (Eq. 1), which scales linearly with the size of the RI basis. The relative insensitivity of the robust DF3 procedure to the auxiliary basis set, and the lower formal angular momentum requirement, may mitigate this disadvantage in by allowing the use of smaller DF3 auxiliary basis sets. Alternatively, it may prove worth investigating whether non-robust DF3 (for which the scaling is lower than RI) is sufficient for computing typical energy differences.

In this work, we have used the MP2-F12/3*A(D) method as a framework in which to implement the robust DF3 procedure, primarily because the 3*A(D) approximation scheme avoids any integrals over more than three electron coordinates. Other MP2-F12 approximation schemes introduce additional matrix elements (see Table II in Ref. 41), some of which result in four-electron integrals containing the exchange operator, which would be complicated and expensive to fit robustly. To apply the robust DF3 scheme to these methods, techniques already developed for RI-based MP2-F12 could be adopted.

Intermediate orbitals [19] could be used to transform four-electron integrals involving the exchange operator to three-electron integrals, which could then be robustly fitted. Exchange terms where intermediate orbitals cannot be used might simply be neglected, in the spirit of the hybrid approximations [41, 65]. CCSD-F12 theory introduces further matrix-elements from which many-electron integrals arise [37, 38]. A first step toward implementing the robust DF3 scheme in explicitly correlated coupled cluster methods might involve the simplified CCSD-F12a and CCSD-F12b methods, which require only a single additional intermediate, V_{pq}^{kl}, not present in MP2-F12 theory [34, 36]. As with MP2-F12 methods, intermediate orbitals and hybrid-like approximations could potentially be applied to deal with problematic exchange terms.

Ultimately, many of the approximations used in the existing F12 approaches were developed assuming use of the RI approximation. It may therefore be worthwhile investigating new approximations specific to robust DF3, rather than simply adapting existing approximations.

It is clear that robust fitting is a potentially useful alternative to resolution of the identity for the approximation of many-electron integrals. The lower maximum angular momentum required in the auxiliary basis and rapid convergence with auxiliary basis set size demonstrated by this method are attractive features for explicitly correlated calculations on systems with high angular momentum occupied orbitals, such as transition metal complexes. Additionally, the apparent ability of this method to use a single auxiliary basis for density fitting both the two-electron and three-electron integrals should simplify implementation of the method. We suggest that these significant advantages make robust density fitting worthy of further development as an alternative to RIs in explicitly correlated methods, despite the potentially greater cost of the contractions involved in our current DF3-based MP2-F12 implementation.

ACKNOWLEDGMENTS

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