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

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It is shown that the convergence of R12-type explicitly correlated electronic structure theories can be improved by rearranging the three-electron integrals before using a resolution of the identity to decompose them into expressions involving only two-electron integrals. The new scheme is illustrated for some test systems within the explicitly correlated second order many-body perturbation theory. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1600431]

I. INTRODUCTION

In calculations of molecules with post-Hartree-Fock methods, it is laborious to handle the large basis sets that are required to obtain converged orbital-based configuration interaction (CI) calculations. The exact wave function at small r_{12} obeys the cusp condition,[1] and the description of this cusp converges slowly with respect to the maximum angular momentum in the one-electron basis. Various alternatives to pure orbital-based methods have been proposed, and it was proven long ago that the inclusion of two-electron basis functions in the CI expansion leads to greatly improved convergence.[2]

The penalty is the introduction of three- and four-electron integrals, which are so numerous that applications are restricted to light atoms and very small molecules. The key to any practical explicitly correlated method lies in the efficient handling of the many-electron integrals. Thus, for example, the weak orthogonality functional can be used to eliminate all four-electron integrals from explicitly correlated MP2 theory with Gaussian-type geminals (GTG).[3] Transcorrelated methods[4,5] (in which there has been recent interest in conjunction with multi-determinantal treatments[6,7]) introduce a three-particle operator into the Hamiltonian, but no higher-rank operators arise. Even calculations which require only three-electron integrals rapidly become impractical for large systems, and the only class of methods which have transcended the restriction to very small molecules are those which rely on the resolution of the identity (RI) to break up many-electron integrals into sums of products of two-electron integrals.[8]

Henceforward, we denote orthonormalized occupied, virtual, and general orbitals in a given basis set as $ij...$, $ab...$, and $pq...$, respectively. In MP2 methods with an explicitly correlated geminal, f_{12}, the construction of the Hylleraas functional requires the evaluation of three-electron integrals in the direct

$$\langle ij|X_{12}P_2 f_{12}|ij\rangle = \sum_k \langle ijk|X_{12}f_{13}|ikj\rangle \tag{1}$$

and exchange forms

$$\langle ij|X_{12}P_2 f_{12}|ji\rangle = \sum_k \langle ijk|X_{12}f_{13}|jki\rangle, \tag{2}$$

where P_n is a one-electron projector in the occupied space,

$$P_n = \sum_i |i(n)\rangle\langle i(n)|. \tag{3}$$

The two-body operator, X_{12}, can take the form of the single commutator, $K_{12}^{(L)} = [T_1 + T_2, f_{12}]$, or of the Coulomb repulsion, r_{12}^{-1}. In R12 methods one chooses $f_{12} = r_{12}$, but one can alternatively expand f_{12} as a linear combination of GTGs.[3,9] The use of the transcorrelated Hamiltonian[4-7] dispenses with the requirement of the integrals with the Coulomb operator because of the commutability between f_{12} and the local potential in the original Hamiltonian. The advantages of GTGs over linear r_{12} terms are firstly that the many-electron integrals have relatively simple forms,[10] and secondly that the short-ranged nature of Gaussians may confer numerical and computational advantages in larger systems. The three-electron integrals in R12 methods *can* be calculated explicitly for atoms,[11] but in either case it is disadvantageous to maintain the three-electron integrals in full as their number increases prohibitively with the size of the one-electron basis.

Klopper and Kutzelnigg avoided the explicit generation of three-electron integrals by the use of the resolution of the identity (RI) in their R12 method to give

$$\langle ijk|X_{12}f_{13}|ikj\rangle = \sum_p \langle X_{12}\rangle_{pk}^{ij}\langle f_{12}\rangle_{ij}^{pk}, \tag{4}$$

$$\langle ijk|X_{12}f_{13}|jki\rangle = \sum_p \langle X_{12}\rangle_{pk}^{ij}\langle f_{12}\rangle_{ji}^{pk}, \tag{5}$$

where we have used the abbreviated notation for the integrals, $\langle X_{12}\rangle_{rs}^{pq} = \langle pq|X_{12}|rs\rangle$. In Eqs. (4) and (5) the equalities hold only for an infinite set of orbitals p; nonetheless, useful approximations arise when the RI is carried out either with the original set of MOs or with an auxiliary RI basis.[12] Since the two-electron integrals in the RI expressions involve three occupied orbitals, the maximum angular momentum required in the RI basis becomes $3L_{occ}$ for the highest

occupied angular momentum, L_{occ}, in an atomic calculation. Thus s-, f-, and i-functions contribute for systems with s-, p-, and d-occupied shells, respectively. This is the main bottle-neck in RI methods, especially for the treatment of molecules with heavy atomic elements.

In this article, we propose a novel decomposition scheme for the three-electron integrals using density fitting. The method reduces the maximum angular momentum required in the RI expansion from $3L_{occ}$ to $2L_{occ}$. We present the formulation in the following section. Numerical results are shown in Sec. III for the calculations of some atoms and molecules.

II. COMBINING THE RI APPROACH WITH DENSITY FITTING

In the present work on improving the convergence of the RI, orbital products are approximately represented as

$$\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \cong \sum_A d_{ij}^A \Xi_A(\mathbf{r}), \tag{6}$$

where $\Xi_A(\mathbf{r})$ and d_{ij}^A are auxiliary basis functions and expansion coefficients, respectively, and we have assumed the orbitals to be real. To distinguish the expansion of the density with the RI in explicitly correlated methods, we refer to the former as density fitting. Since the basic idea of density fitting was first introduced by Boys and Shavitt,[13] such approximations have been used for improving the efficiency of the computation and manipulation of electron repulsion integrals in density functional theory,[14] MP2,[15] and other theories.[16] One of us (FRM) has recently introduced a density fitted MP2-R12 theory which has essentially the same numerical properties as the original MP2-R12 formulation, but at a fraction of the cost.[17]

There exist efficient ways to determine d_{ij}^A for specific purposes, but the simplest expression utilizes the three-center overlap integrals with orthonormalized auxiliary functions,

$$d_{ij}^A = \langle i|A|j\rangle = \int d\mathbf{r}\,\phi_i(\mathbf{r})\Xi_A(\mathbf{r})\phi_j(\mathbf{r}). \tag{7}$$

The key in the present improvement of the RI approach is to combine the orbitals in a coordinate shared by the pair of two-body operators. For a spatial operator, $X_{12}=r_{12}^{-1}$, one can move an orbital from the ket to the bra to give the integral identity

$$\langle ijk|r_{12}^{-1}f_{13}|ikj\rangle = \langle (ii)jk|r_{12}^{-1}f_{13}|1kj\rangle, \tag{8}$$

which can then be resolved using the RI to give

$$\langle ijk|r_{12}^{-1}f_{13}|ikj\rangle = \sum_p \langle (ii)j|r_{12}^{-1}|pk\rangle\langle pk|f_{12}|1j\rangle, \tag{9}$$

where the symbol, 1, as an orbital index means that the orbital is made unity.

Applying density fitting to avoid the five-index integral in Eq. (9), the three-electron integrals can be expressed as

$$\langle ijk|r_{12}^{-1}f_{13}|ikj\rangle = \sum_{pA} d_{ii}^A \langle r_{12}^{-1}\rangle_{pk}^{Aj}\langle f_{12}\rangle_{1j}^{pk}, \tag{10}$$

$$\langle ijk|r_{12}^{-1}f_{13}|jki\rangle = \sum_{pA} d_{ij}^A \langle r_{12}^{-1}\rangle_{pk}^{Aj}\langle f_{12}\rangle_{1i}^{pk}, \tag{11}$$

in the direct and exchange forms. Then the maximum angular momentum required for the RI in Eqs. (10) and (11) is reduced from $3L_{occ}$ to $2L_{occ}$ in the atomic limit; the integrals with the operator, f_{12}, involve just two occupied orbitals besides the auxiliary function, p. Thus for s-, p-, and d-occupied shells, we require s-, d-, and g-functions instead of s-, f-, and i-functions in the RI expansion.

For the integrals with the operator, $X_{12}=K_{12}^{(L)}$, using the fact that the operator includes at most one differential operator, the sum of integrals is rewritten as,

$$\langle pqr|K_{12}^{(L)}f_{13}|stu\rangle + \langle sqr|K_{12}^{(L)}f_{13}|ptu\rangle$$
$$= \langle 1qr|K_{12}^{(L)}f_{13}|(ps)tu\rangle + \langle (ps)qr|K_{12}^{(L)}f_{13}|1tu\rangle. \tag{12}$$

Then we obtain the desired expressions of direct and exchange components substituting the indices and using the completeness insertion,

$$\langle ijk|K_{12}^{(L)}f_{13}|ikj\rangle = \frac{1}{2}\sum_{pA} d_{ii}^A(\langle K_{12}^{(L)}\rangle_{pk}^{1j}\langle f_{12}\rangle_{Aj}^{pk}$$
$$+ \langle K_{12}^{(L)}\rangle_{pk}^{Aj}\langle f_{12}\rangle_{1j}^{pk}), \tag{13}$$

$$\langle ijk|K_{12}^{(L)}f_{13}|jki\rangle = -\sum_p \langle K_{12}^{(L)}\rangle_{pk}^{jj}\langle f_{12}\rangle_{ii}^{pk}$$
$$+ \sum_{pA} d_{ij}^A(\langle K_{12}^{(L)}\rangle_{pk}^{1j}\langle f_{12}\rangle_{Ai}^{pk}$$
$$+ \langle K_{12}^{(L)}\rangle_{pk}^{Aj}\langle f_{12}\rangle_{1i}^{pk}). \tag{14}$$

The first term of the exchange integral in Eq. (14) has the form of a standard RI decomposition. However, the maximum angular momentum is usually much less than $3L_{occ}$ since the integrals involve the same occupied indices. For atoms saturated in degenerate shells, the vector coupling coefficients survive just for $l=0$ in the total energy because of the independent summation over the coincident orbitals. As a result, only L_{occ} is required in the auxiliary basis for a saturated energy with RI. It should be noted that the transcorrelated Hamiltonian involves only three-electron integrals in the commutator form for which the migration of an orbital is more straightforward,

$$\langle pqr|[K_{12}^{(L)},f_{13}]|stu\rangle = \sum_A d_{ps}^A \langle Aqr|[K_{12}^{(L)},f_{13}]|1tu\rangle. \tag{15}$$

The reason why the term, which is unable to be dealt with the density fitting, appears in Eq. (14) is concerned with the fact that the single excitations due to the geminal are projected out in the explicitly correlated wavefunction. Such inclusion of singles will be discussed elsewhere.

III. RESULTS AND DISCUSSIONS

We apply the new decomposition with density fitting (DF) to the second order many-body perturbation theory with strongly orthogonal functions of frozen GTG in addi-
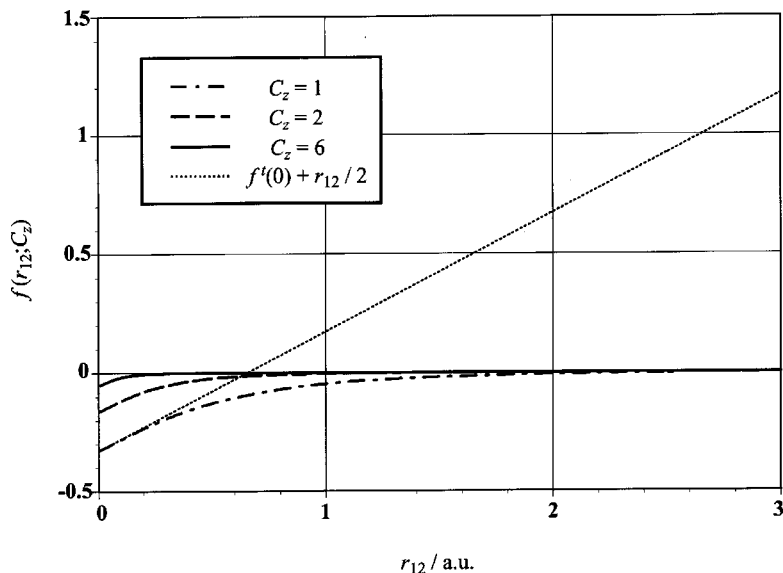
FIG. 1. Profiles of scaled geminal functions, f_{12}, for various values of the scaling parameter, c_Z.

tion to the usual orbital products. The second order correction in the Hylleraas energy functional is in the form,

$$\Delta E_V^{(2)} = -\Delta E_N^{(2)} + 2\Delta E_Z^{(2)}, \tag{16}$$

$$\Delta E_N^{(2)} = \sum_{SM} \sum_{i \geqslant j} (c_{ij}^{(S,M)})^2 \langle \{ij\}^{(S,M)} | K_{12}^{(L)} (Q_1^* Q_2^* $$
$$- Q_1 Q_2) f_{12} | \{ij\}^{(S,M)} \rangle, \tag{17}$$

$$\Delta E_Z^{(2)} = \sum_{SM} \sum_{i \geqslant j} c_{ij}^{(S,M)} \langle \{ij\}^{(S,M)} | r_{12}^{-1} (Q_1^* Q_2^* $$
$$- Q_1 Q_2) f_{12} | \{ij\}^{(S,M)} \rangle, \tag{18}$$

where Q_n^* and Q_n are one-electron projectors in the virtual spaces for the complete and given basis sets, respectively, $\{ij\}^{(S,M)}$ denotes the spin-adapted antisymmetrized pair functions, and $c_{ij}^{(S,M)}$ are variational parameters. The quantum numbers take the values, $(S,M)=(0,0)$, $(1,0)$, $(1,\pm 1)$ for $i \neq j$ and $(S,M)=(0,0)$ for $i=j$.[9] The commutator involving the exchange operator is neglected as in the MP2-R12-A approximation.[8] All three energy corrections become identical, $\Delta E_V^{(2)} = \Delta E_N^{(2)} = \Delta E_Z^{(2)}$, when the geminal is exact outside the Hilbert space spanned by the given basis set,

$$(Q_1^* Q_2^* - Q_1 Q_2)(c_{ij}^{(S,M)} K_{12}^{(L)} + r_{12}^{-1}) | \{ij\}^{(S,M)} \rangle$$
$$= 0, \quad \forall ijSM. \tag{19}$$

Thus the ratio,

$$\chi = \Delta E_Z^{(2)} / \Delta E_N^{(2)}, \tag{20}$$

which becomes unity in the above condition, is a good measure to indicate the appropriateness of geminals. According to the expansion,

$$Q_1^* Q_2^* = 1 - P_1 - P_2 + P_1 P_2, \tag{21}$$

the functionals are divided as

$$\Delta E_N^{(2)} = \Delta E_N^{(2)}[1] - \Delta E_N^{(2)}[P_1 + P_2] + \Delta E_N^{(2)}[P_1 P_2]$$
$$- \Delta E_N^{(2)}[Q_1 Q_2], \tag{23}$$

where

$$\Delta E_N^{(2)}[O] = \sum_{SM} \sum_{i \geqslant j} (c_{ij}^{(S,M)})^2$$
$$\times \langle \{ij\}^{(S,M)} | K_{12}^{(L)} O f_{12} | \{ij\}^{(S,M)} \rangle, \tag{24}$$

and a similar expression for $\Delta E_Z^{(2)}$. In Eq. (23), the specific terms which are approximated using the RI are those involving just one occupied projector, P_n. Hence, the quantity,

$$\tau = \Delta E_N^{(2)}[Q_1^* P_2 + P_1 Q_2^*] - 2\Delta E_Z^{(2)}[Q_1^* P_2 + P_1 Q_2^*]$$
$$= \Delta E_N^{(2)}[P_1 + P_2] - 2\Delta E_Z^{(2)}[P_1 + P_2] + 4\Delta E_Z^{(2)}[P_1 P_2], \tag{25}$$

which we refer to as the RI index, measures the contribution to the energy that arises directly from the RI. In Eq. (25), the term, $\Delta E_N^{(2)}[P_1 P_2]$, vanishes because $K^{(L)}$ is an anti-hermitian. Deviations in the RI index between the calculations in the given basis set and in an essentially complete basis set can therefore be used as a guide to the accuracy of the RI. The exact energy for a given basis and a given f_{12} can then be estimated as

$$\bar{E}_V^{(2)} = E_V^{(2)} - \Delta\tau, \tag{26}$$

using the deviation of the index, $\Delta\tau = \tau - \bar{\tau}$, from $\bar{\tau}$ computed using an augmented basis set.

Throughout this paper, we use a template geminal, f_{12}^t, expanded as a linear combination of 10 Gaussian-type functions. The coefficients are determined in such a way that the Coulomb repulsion multiplied by a short-range weight Gaussian is suppressed in the similarity transformed Hamiltonian.[6,7] For the exponents, we use an even-tempered sequence in the range between 10^6 and 0.5 and the weight Gaussian has the exponent, 5. The template geminal, f_{12}^t, is further transformed with a scaling parameter, c_Z, according to

$$f(r_{12}; c_Z) = \frac{f^t(c_Z r_{12})}{c_Z}. \tag{27}$$

TABLE I. Errors in the index, τ, the ratios, χ, and the second order energies (in mEh) of Ne.

Basis set	c_z	$\Delta\tau_{RI}$[a]	$\Delta\tau_{DF}$[a]	χ	$E_V^{(2)}$	$\bar{E}_V^{(2)}$	E_{MP2}
VDZ	1.0	-41.05	-12.64	0.79	-353.22	-340.6	-255.48
$(9s4p1d)$	2.0	-16.54	0.75	1.00	-333.81	-334.6	
	3.0	-7.89	-0.65	1.17	-314.75	-314.1	
VTZ	1.0	-6.98	-3.27	0.76	-373.61	-370.3	-321.93
$(10s5p2d1f)$	2.0	-3.58	-0.60	0.96	-372.13	-371.5	
	3.0	-2.14	-0.19	1.13	-362.31	-362.1	
VQZ	1.0	-1.52	-2.50	0.77	-382.23	-379.7	-351.22
$(12s6p3d2f1g)$	2.0	-0.87	0.00	0.88	-381.84	-381.8	
	3.0	-0.63	-0.05	1.05	-378.84	-378.8	
CVTZ	1.0	-5.40	-2.91	0.85	-379.50	-376.6	-333.49
$(12s7p3d1f)$	2.0	-1.79	-0.67	1.04	-373.16	-372.5	
	3.0	-0.91	-0.19	1.18	-363.80	-363.6	
AVDZ	1.0	-27.45	2.30	0.75	-365.27	-367.6	-278.21
$(10s5p2d)$	2.0	-15.32	0.51	1.00	-355.25	-355.8	
	3.0	-7.66	-0.34	1.16	-336.12	-335.8	
AVTZ	1.0	-3.20	-0.12	0.75	-378.70	-378.6	-330.17
$(11s6p3d2f)$	2.0	-3.24	-0.28	0.95	-378.68	-378.4	
	3.0	-2.06	-0.13	1.12	-369.65	-369.5	
ACVQZ[b]	1.0	-13.43	0.00	0.92	-386.35	-386.4	-320.08
$(16s10p6d)$	2.0	-5.60	0.00	1.25	-367.82	-367.8	
	3.0	-2.44	0.00	1.47	-352.00	-352.0	
ACVQZ[b]	1.0	0.00	0.00	0.89	-387.48	-387.5	-354.94
$(16s10p6d4f)$	2.0	0.00	0.00	1.11	-382.20	-382.2	
	3.0	0.00	0.00	1.29	-375.50	-375.5	
ACVQZ[b]	1.0	0.00	0.00	0.85	-387.07	-387.1	-365.91
$(16s10p6d4f2g)$	2.0	0.00	0.00	1.00	-385.93	-385.9	
	3.0	0.00	0.00	1.17	-382.62	-382.6	
Limit						-388.1	

[a]The subscripts, RI and DF, denote the original RI of Kutzelnigg and Klopper and the decomposition scheme with density fitting, respectively. The reference values of the index, $\bar\tau$, are based on the calculations with the aug-cc-pCVQZ (uncontracted) set; they are 1354.27, 447.03, and 200.98 mEh in RI, and 1354.34, 447.18, 201.04 mEh in DF for $c_z = 1.0$, 2.0, and 3.0, respectively.

[b]Angular subcomponents of the reference primitive set, aug-cc-pCVQZ (uncontracted).

Figure 1 shows some profiles of $f(r_{12};c_Z)$ with different scaling parameters. The effective radius of the explicitly correlated function varies with changing c_Z whereas the slope of $1/2$ at $r_{12}=0$ is maintained by the transformation. The energy functional can be minimized for individual pairs with respect to multiplied coefficients.[18] In this context, Klopper developed a unitary invariant formulation to pair functionals.[19] Such a convention is not employed in this particular work to keep the short-range behavior of f_{12}, and hence we use $c_{ij}^{(0,0)}=1$, for all singlet pairs. The triplet pairs, $S=1$, are antisymmetric in the spatial part to follow the p-wave cusp condition[20] and the parameters, $c_{ij}^{(1,M)}=1/2$, are used for the pairs. The latter condition is not crucial especially for the use of a short-range geminal since the triplet pairs have no amplitude at $r_{12}=0$.

In Table I, we show the calculated $\Delta\tau$, χ, and MBPT2 energies of Ne with the correlation consistent basis sets (uncontracted).[21,22] The error in the RI index, $\Delta\tau$, is also plotted in Fig. 2. The amplitude of τ and accordingly $\Delta\tau$ in the approximate treatments of three-electron integrals reduce significantly as c_z increases (i.e., more localized f_{12}). The overall results of the present decomposition with DF are more accurate than the original RI. Since the electron correlation is a short-range phenomenon, the choice of c_z hardly affects the result especially beyond the regular VTZ set. Taking the accuracy and scalability into account, it would be

advantageous to use geminals damped relatively quickly as the present application with $c_z=2$. According to the results with the angular components of the ACVQZ set, the absence of the f-shell ($L=3$) reduces the accuracy of RI by 13mEh for $c_z=1$. As a result, the second order energies in RI become -395.07 and -399.84 mEh with the AVDZ and AVQZ ($16s10p6d$) sets, respectively, which are lower than the MP2 limit artificially. It is the manifest advantage of the present decomposition with DF that enables us to bypass the requirement of f-functions.

The next application is the ground state Cu$^+$, in which the RI saturates at i-shell whereas DF requires up to g-functions. We used the $(21s15p12d8f4g)$ primitives of the atomic natural orbitals (ANOs)[23] augmented by tight $(2d2f)$ functions with the exponents, $14\,400.0\,(d)$, $3600.0\,(d)$, $250.0\,(f)$, and $50.0\,(f)$ along with the scaling parameter, $c_Z=2$. Table II shows the calculated pair correlation energies. The present implementation without minimizing pair functionals leads to a positive correction for the $1s3d$ pair though the amplitude is very small. This is because the deviations from the s- and p-wave cusp conditions are prominent for the pair, i.e., the component in $\Delta E_Z^{(2)}$ is much smaller than the corresponding one in $\Delta E_N^{(2)}$. All MBPT2 energies of the explicitly correlated methods including MP2-R12/A[24] are in a small range compared to the conventional MBPT2 energy. Most of the difference between RI
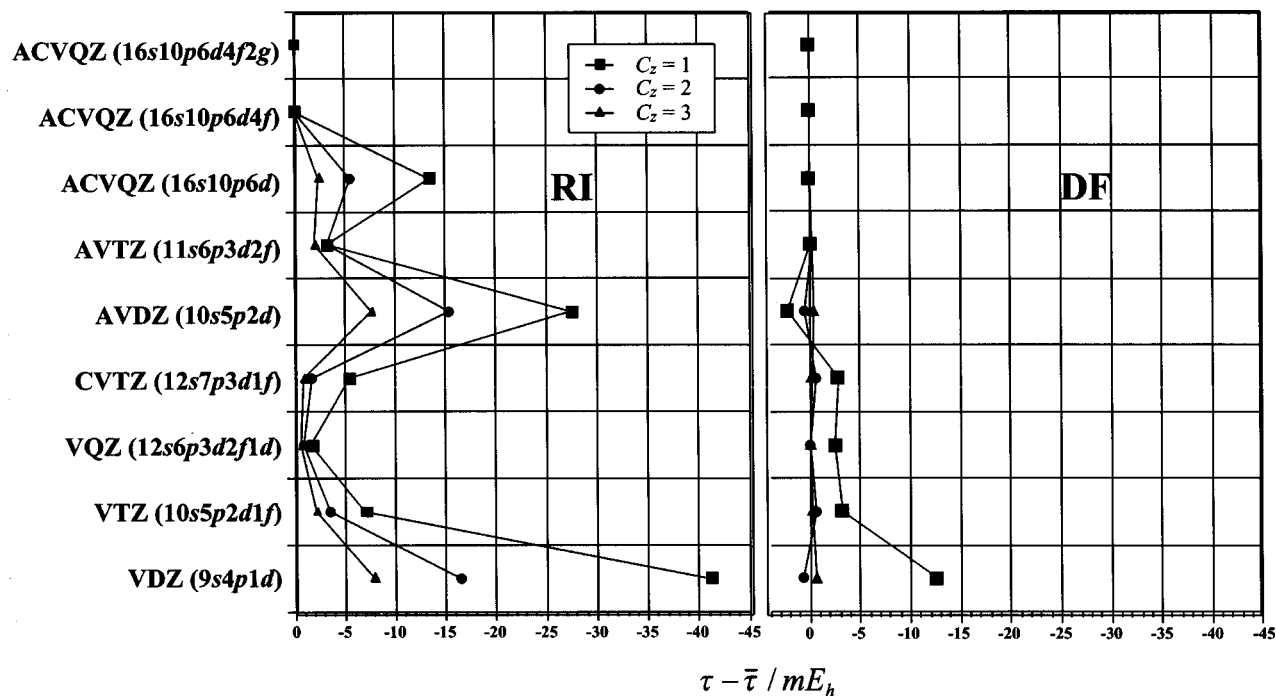
FIG. 2. Errors in the RI index in calculations on the neon atom with (aug)-cc-(C)VXZ basis sets.

and DF, ca. $14 mE_h$, is originating from the pairs, $2p3d$, $3p3d$, and $3d^2$. To repair this discrepancy, h- and i-functions must be included in the RI case.

We close this section by mentioning briefly the statistical errors in calculations of some small first-row molecules. We performed on calculations on CH_2, CH_4, NH_3, H_2O, HF, Ne, CO, N_2, and F_2 with cc-pVDZ and cc-pVTZ basis sets

(uncontracted). Figure 3 shows the relation between the RI index, τ, of the VTZ set for $c_Z = 2$ and the absolute deviation from it with VDZ set, $|\tau(\text{VDZ}) - \tau_{DF}(\text{VTZ})|$. There are approximately linear relations between them and the obtained slopes of the least square fittings are 3.00% and 0.23% in RI and DF, respectively. The present method with DF is thus on average more accurate by one order of magnitude than the original RI.

IV. CONCLUSION

We have proposed a novel decomposition for the three-electron integrals in explicitly correlated electronic structure theories. The normal completeness insertion is applied after a

TABLE II. MBPT2 pair energies (in mEh) of Cu^+:GTO $(21s15p12d8f4g)$ and $Cz=2$.

Pair	$E^{(2)}$	$E^{(2)}_{V,RI}$	$E^{(2)}_{V,DF}$	MP2-R12/A[a]
$1s^2$	−33.24	−36.11	−36.11	−36.60
$1s2s$	−6.58	−7.06	−7.05	−7.19
$1s3s$	−0.99	−1.05	−1.05	−1.08
$2s^2$	−9.33	−10.74	−10.74	−10.81
$2s3s$	−3.32	−3.66	−3.66	−3.69
$3s^2$	−5.50	−6.38	−6.38	−6.37
$1s2p$	−35.00	−37.30	−37.23	−38.04
$1s3p$	−4.07	−4.33	−4.33	−4.40
$2s2p$	−53.72	−65.32	−65.32	−66.10
$2s3p$	−12.15	−13.30	−13.29	−13.37
$3s2p$	−14.28	−15.51	−15.49	−15.70
$3s3p$	−37.39	−44.30	−44.30	−44.31
$1s3d$	−0.45	−0.23	−0.23	−0.51
$2s3d$	−14.47	−18.62	−18.44	−18.27
$3s3d$	−71.59	−84.53	−84.51	−84.20
$2p^2$	−172.00	−191.40	−190.94	−192.73
$2p3p$	−53.74	−57.35	−57.19	−57.92
$3p^2$	−70.74	−81.40	−79.67	−81.54
$2p3d$	−69.81	−79.68	−77.26	−77.98
$3p3d$	−298.26	−339.07	−334.22	−337.87
$3d^2$	−510.98	−544.40	−538.96	−538.07
Σ	−1477.60	−1641.74	−1628.05	−1636.8

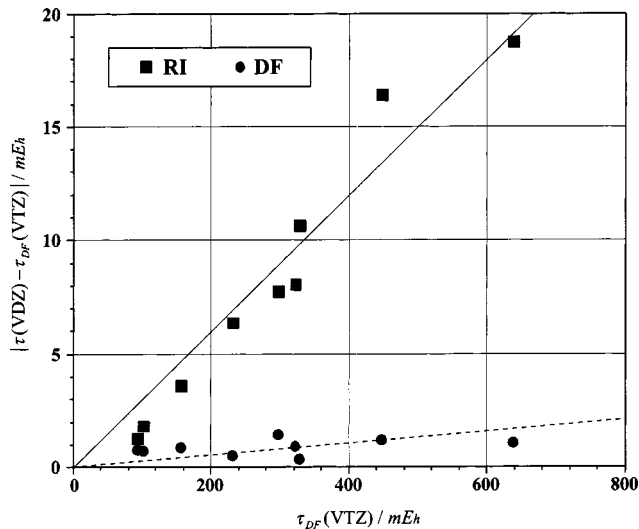[a]Reference 24. STO basis: $12s12p12d11f9g9h6i$.

FIG. 3. Distributions of the RI index deviations for a selection of small first-row molecules.

migration of an occupied orbital, and the five-index integrals this leads to are avoided through density fitting. At the same time, the migration of the orbital reduces the maximum angular momentum required for the completeness insertion from $3L_{occ}$ to $2L_{occ}$ in an atomic calculation. The scheme with DF turned out to be more accurate by one order of magnitude than the original RI method. It should be noted that there are two different sources which can cause error in DF. One is the truncation of the RI basis in the completeness insertion and the other is that of DF basis to represent orbital products. The RI basis is basically assumed to be complete with finite angular momentum. Contrarily, the auxiliary basis set for DF to reproduce orbital products can be designed systematically for a given orbital basis set. Such a development is quite important since all of the remaining four-center integrals can be replaced by DF expressions as already implemented in MP2-R12 theory with the standard RI.[17] Combining the results of this work with the DF-MP2-R12 method[17] will lead to a new explicitly correlated approach in which density fitting delivers increases in both accuracy and efficiency.

ACKNOWLEDGMENTS

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