# Density fitting in second-order linear-r12 Møller–Plesset perturbation theory

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# ARTICLES

# Density fitting in second-order linear-$r_{12}$ Møller–Plesset perturbation theory

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Density fitting is used to approximate all of the 4-index 2-electron integrals in the explicitly correlated MP2-R12 theory of Kutzelnigg and Klopper. The resulting method—DF-MP2-R12—requires only 2- and 3-index integrals over various 2-electron operators, and is extremely efficient. The errors arising from the fitting process can be made small by using robust fitting formulas throughout, such that the error in each fitted integral is quadratic in the error of the fitted orbital product densities. Sample calculations on glycine reveal that for large basis sets DF-MP2-R12 is faster than a standard MP2 calculation and takes only a small fraction of the time for the Hartree–Fock calculation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1594713]

## I. INTRODUCTION

One of the major barriers to accurate electronic structure calculations on systems of chemical interest is the $\mathcal{O}(l^{-3})$ convergence of orbital-based CI expansions with maximum orbital angular momentum $l$ in the atomic orbital (AO) basis. This slow convergence can be attributed to the difficulty of describing the 2-electron cusp[1] in terms of sums of products of 1-electron functions.[2–4] It was understood many decades ago that highly accurate correlation energies could be obtained by incorporating into the wave function terms depending explicitly on the interelectronic distances.[5,6]

Such explicitly correlated methods are capable of delivering highly accurate energies and properties for light atoms and small molecules, but are fraught with difficulties for larger systems. These difficulties arise from the need to compute integrals over 3- and 4-electron operators, which are not only individually complicated to evaluate, but are extremely numerous. In a calculation with $m$ basis functions there are $\mathcal{O}(m^6)$ 3-electron integrals, and for the kind of molecules to which such methods are presently applicable, there is no hope of reaching the asymptotic region where integral screening and local methods might reduce this to $\mathcal{O}(m^3)$ or less.

All advances concerning the application of explicitly correlated wave functions to larger molecules have therefore concentrated on avoiding or simplifying the many-electron integrals. For instance, the 4-electron integrals in explicitly correlated MP2 theory can be avoided by the use of the weak-orthogonality functional.[7] The transcorrelated approach[8–11] uses a non-Hermitian, transformed Hamiltonian which has eigenfunctions lacking the usual correlation cusp. Orbital-based CI expansions therefore converge much quicker in the transcorrelated method, and only 3-electron integrals ever arise. There has been a recent revival of interest in this type of theory.[12–15]

The early studies by Hylleraas on the helium atom[5,6] (see Ref. 16 for a modern perspective and Ref. 17 for English translations) revealed that inclusion of the linear term $r_{12}$ lead to a great increase in accuracy in the treatment of correlation. This observation is of course closely related to the linear form of the correlation cusp at the point of coalescence.[1] There are two problems with linear $r_{12}$ terms in a molecular context: first, the integrals are extremely difficult;[18] and second, integrals over $r_{12}$ become ever-larger as the charge distributions describing the two electrons get further apart. The contribution to the correlation energy from such distant charge distributions is small, because, in insulators at least, correlation effects die away like $R^{-6}$. Nonetheless these spuriously large integrals may present numerical and computational problems.

A popular alternative to linear $r_{12}$ is an expansion in Gaussian geminals of the form $\exp(-\gamma r_{12}^2)$.[19–22] These functions are not capable of delivering the exact cusp shape at the point of coalescence, but the volume element $4\pi r_{12}^2$ makes the contribution to the correlation energy from short $r_{12}$ very small. Numerical experiments have shown that $r_{12}$ can be fitted accurately in the relevant range with even modest sets of 6–15 Gaussian geminals.[22] The two advantages of Gaussian geminals are that they are short-ranged $r_{12}$ and that they lead to much simpler integrals which can be treated in essentially the same way as standard Coulomb integrals.[23,24]

Notwithstanding the progress in these directions there is still really only one explicitly correlated approach which has escaped the restriction to tiny molecules. The R12 ansatz of Kutzelnigg and Klopper offers enormous savings in the work involved in linear-$r_{12}$ theories by using resolutions of the identity (RIs) to reduce all 3- and 4-electron integrals to sums of products of various 2-electron integrals.[25,26] Thus for example the integrals $\langle pqr|r_{12}r_{23}^{-1}|stu\rangle$ are simplified by inserting an RI in the coordinates of the electron that couples the two 2-electron operators,

$$\langle pqr|r_{12}r_{23}^{-1}|stu\rangle \approx \langle pq|r_{12}|sx\rangle\langle xr|r_{12}^{-1}|tu\rangle. \tag{1}$$

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Here and throughout the paper, summation over repeated dummy indices is implied. In a similar way all many-electron integrals can be approximated as sums of products of 2-electron integrals.

In the simplest such theory, denoted MP2-R12,[25–28] the usual first-order expansion in doubly excited determinants,

$$|1\rangle = t_{ab}^{ij}|\Phi_{ij}^{ab}\rangle \tag{2}$$

is augmented with double excitations into explicitly correlated 2-electron terms of the form,

$$|u_{ij}\rangle = \hat{Q}_{12} r_{12}|ij\rangle. \tag{3}$$

Here $\hat{Q}_{12}$ is the strong orthogonality projector

$$\hat{Q}_{12} = [1 - \hat{P}(1)][1 - \hat{P}(2)], \tag{4}$$

where

$$\hat{P}(\mu) = |i(\mu)\rangle\langle i(\mu)| \tag{5}$$

with the summation restricted to occupied orbitals. One proceeds by minimizing the Hylleraas functional [see Eq. (7a) of Ref. 6 and the text that precedes it]

$$\langle 1|H_0 - E_0|1\rangle + 2\langle 1|H_1 - E_1|0\rangle \geqslant E_2 \tag{6}$$

to obtain the MP2 energy. Extensive details are given elsewhere and will not be repeated here.[26,29]

The minimization of the Hylleraas functional and the evaluation of the MP2-R12 energy involves the normal 2-electron repulsion integrals,

$$(pq|rs) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_p^*(\mathbf{r}_1)\psi_q(\mathbf{r}_1) r_{12}^{-1} \psi_r^*(\mathbf{r}_2)\psi_s(\mathbf{r}_2), \tag{7}$$

and the new 2-electron integrals,

$$(pq|r_{12}|rs) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_p^*(\mathbf{r}_1)\psi_q(\mathbf{r}_1) \\ \times r_{12}\psi_r^*(\mathbf{r}_2)\psi_s(\mathbf{r}_2) \tag{8}$$

and

$$(pq|[\hat{t}_1, r_{12}]|rs) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_p^*(\mathbf{r}_1)\psi_q(\mathbf{r}_1) \\ \times [\hat{t}_1, r_{12}]\psi_r^*(\mathbf{r}_2)\psi_s(\mathbf{r}_2), \tag{9}$$

where $\hat{t}_1 = -1/2\nabla_1^2$. No 3- or 4-electron integrals are required. The cost of the method largely resides in the evaluation and transformation of these three classes of 2-electron integrals, and MP2-R12 should cost only around 4–5 as much as conventional MP2.[30]

Modern applications of MP2 to larger systems, however, are only possible because the ''conventional'' approach is seldom used. There are many ingenious formulations of MP2 theory that are efficient enough to allow calculations on large systems and/or with large basis sets. The local methods introduced by Pulay and Saebø[31–34] capitalize on the short-range nature of the correlation (which decays in insulators like $R^{-6}$) and programs can be written for which all resources (CPU time, disk, memory) have asymptotic linear scaling with respect to system size.[35,36] The Laplace trans-

form approach of Almlöf[37–39] allows the MP2 energy to be evaluated in the AO basis, and here again it is possible to take advantage of the short-ranged behavior of correlation effects.[40]

Alternatively dual basis sets can be used[41] in which a larger basis set is used to span the virtual space than the occupied; this has the added advantage of reducing the time needed for the SCF calculation, a bottleneck in large-scale MP2 calculations. Yet another approach is to eliminate the need for 4-index integrals by using density fitting. This approach does not reduce the asymptotic scaling of MP2 theory with respect to system size, but does substantially reduce the prefactor and reduces the scaling with respect to the number of basis functions per atom[42,43] from quartic to cubic. Unfortunately such methods have tended to be denoted by the prefix RI-; here, to avoid confusion with the RIs that form the basis of MP2-R12 theory, such methods are described as ''density fitted'' so that DF-MP2 refers to the fitted MP2 theory. Combined methods such as DF-LMP2 (Ref. 44) and DF-LCCSD (Ref. 45) appear to have great potential in the effort to perform calculations with realistically large basis sets on extended molecules.

## II. THEORY

### A. Density fitting

Density fitting has a long and varied history in *ab initio* correlation methods, and was probably first used by Boys and Shavitt in a calculation of the potential energy surface of $H_3$.[46] They avoided the 3-center Coulomb integrals in their Slater basis set by least-squares fitting 2-center products of Slater functions in a small auxiliary basis. A similar idea was used to avoid such integrals in DFT,[47] but in the *ab initio* context the next important paper is by Whitten[48] in which two crucial conclusions are drawn. The integral $(pq|rs)$ is approximated by fitting $|pq)$ and $|rs)$ in an auxiliary basis set,

$$|pq) \approx |\widetilde{pq}) = C_{pq}^A|A) \tag{10}$$

and computing the approximate integral $(\widetilde{pq}|\widetilde{rs})$.

The first important conclusion of Whitten is that the coefficients that best describe $|pq)$ for the purpose of approximating $(pq|rs)$ are independent of $|rs)$. If this were not the case, the number of equations to solve would be prohibitive. The second important conclusion is that the coefficients should be obtained not by least squares but by minimizing

$$\Delta_{pq} = (pq - \widetilde{pq}|pq - \widetilde{pq}), \tag{11}$$

the Coulomb energy of the fitting residual $|pq - \widetilde{pq})$. This observation was made, apparently independently, by Dunlap *et al.* who used the Coulomb criterion to fit the whole electronic density in DFT;[49] these authors also point out that minimizing the error in Eq. (11) minimizes the least-squares error in the electric fields because

$$(pq - \widetilde{pq}|pq - \widetilde{pq}) = \frac{1}{4\pi} \int d\mathbf{r}|\mathbf{E}_{pq}(\mathbf{r}) - \mathbf{E}_{\widetilde{pq}}(\mathbf{r})|^2, \tag{12}$$

where $\mathbf{E}_{pq}$ and $\mathbf{E}_{\widetilde{pq}}$ are the electric fields arising from the exact and fitted orbital product densities.

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So, the procedure is to minimize $\Delta_{pq}$ to obtain the coefficients that appear in the expansion of Eq. (10) by setting $\partial\Delta_{pq}/\partial C_{pq}^A = 0$. This yields the linear equations

$$J_{AB}C_{pq}^B - J_{pq}^A = 0, \tag{13}$$

where $J_{AB}\equiv(A|B)$ and $J_{pq}^A\equiv(A|pq)$. The approximate matrix element can then be computed by

$$(pq|rs)\approx(\widetilde{pq}|\widetilde{rs}) = C_{pq}^A J_{AB} C_{rs}^B = J_{pq}^A[\mathbf{J}^{-1}]_{AB}J_{rs}^B. \tag{14}$$

Writing $\bar{J}_{rs}^A = [\mathbf{J}^{-1}]_{AB}J_{rs}^B \equiv C_{pq}^A$ we arrive at the condensed expression

$$(\widetilde{pq}|\widetilde{rs}) = J_{pq}^A \bar{J}_{rs}^A \tag{15}$$

for the approximate integral.

The significance of the approximation in Eq. (15) is exposed when one considers the error

$$(pq|rs) - (\widetilde{pq}|\widetilde{rs}) = (pq-\widetilde{pq}|rs-\widetilde{rs}) + (\widetilde{pq}|rs-\widetilde{rs})$$
$$+ (pq-\widetilde{pq}|\widetilde{rs}) \tag{16}$$

between the exact and the fitted integral. The last two terms of Eq. (16) can be seen [through Eq. (13)] to be zero and so

$$(pq|rs) - (\widetilde{pq}|\widetilde{rs}) = (pq-\widetilde{pq}|rs-\widetilde{rs}) \tag{17}$$

and the error in the fitted integral is quadratic in the errors in the fitted densities. This analysis is due to Dunlap and fitting expressions of this kind are called *robust*; see Refs. 50 and 51 for recent accounts of robust fitting in DFT and other contexts, respectively.

For evaluating standard 2-electron integrals one can ignore the issue of robustness because the simple approximation $(\widetilde{pq}|\widetilde{rs})$ happens to be robust; but in MP2-R12 there are other 2-electron integrals, and care has to be taken to use explicitly robust formulas. Such formulas play an important role in the current work, and may well be useful elsewhere, so they are described below.

Suppose we wish to approximate integrals over a 2-electron operator $\hat{v}_{12}$ using a fitting criterion $\hat{w}_{12}$. Then we obtain the coefficients by minimizing

$$\Delta_{pq}^w = (pq-\widetilde{pq}|\hat{w}_{12}|pq-\widetilde{pq}). \tag{18}$$

However the error in the simple, approximate integral $(\widetilde{pq}|\hat{v}_{12}|\widetilde{rs})$

$$(pq|\hat{v}_{12}|rs) - (\widetilde{pq}|\hat{v}_{12}|\widetilde{rs})$$
$$= (pq-\widetilde{pq}|\hat{v}_{12}|rs-\widetilde{rs}) + (\widetilde{pq}|\hat{v}_{12}|rs-\widetilde{rs})$$
$$+ (pq-\widetilde{pq}|\hat{v}_{12}|\widetilde{rs}) \tag{19}$$

contains terms linear in the error in the fitted densities which—unlike those in Eq. (16)—do not vanish. The form of Eq. (19) suggests the alternative approximation,

$$(pq|\hat{v}_{12}|rs)_{\text{robust}} = (\widetilde{pq}|\hat{v}_{12}|rs) + (pq|\hat{v}_{12}|\widetilde{rs})$$
$$- (\widetilde{pq}|\hat{v}_{12}|\widetilde{rs}) \tag{20}$$

which does satisfy the requirement that $(pq|\hat{v}_{12}|rs) - (pq|\hat{v}_{12}|rs)_{\text{robust}}$ is quadratic in the fitting error.[51]

The need for robust formulas for the $r_{12}$ integrals could in principle be lifted by choosing $\hat{w}_{12} = r_{12}$. This is inconvenient, though, because the integral operator with kernel $r_{12}$ is

indefinite, and although a fitting scheme can be made with this criterion,[52] charge constraints have to imposed. Constraining the linear equations leads to terms in $(pq|r_{12}|rs) - (\widetilde{pq}|r_{12}|\widetilde{rs})$ linear in the fitting error, and robust formulas are therefore necessary anyway. Since the work can be reduced by using the Coulomb $(\hat{w}_{12}=r_{12}^{-1})$ criterion throughout, the $r_{12}$ criterion will not be considered further here.

## B. MP2-R12 viewed in terms of orbital fitting

It is interesting from the point of view the current work to note that the RI of R12 theories can also be cast in terms of a fitting procedure. To see this it is convenient to use a generalized Mulliken notation for the 3-electron integral we will consider so that

$$\langle prt|r_{12}r_{23}^{-1}|qsu\rangle \equiv (pq|r_{12}|rs|r_{23}^{-1}|tu). \tag{21}$$

The integral $(pq|r_{12}|rs|r_{23}^{-1}|tu)$ can be viewed as an overlap integral between a pair of one electron functions,

$$\phi_{pq}^r(\mathbf{r}_2) = \int d\mathbf{r}_1[\psi_p\psi_q](\mathbf{r}_1)\psi_r(\mathbf{r}_2)r_{12} \tag{22}$$

and

$$\psi_{tu}^s(\mathbf{r}_2) = \int d\mathbf{r}_3[\psi_t\psi_u](\mathbf{r}_3)\psi_s(\mathbf{r}_2)r_{23}^{-1}, \tag{23}$$

where real orbitals have been assumed. Overlap integrals between one of these objects and an orbital are the 2-electron integrals,

$$\langle\phi_{pq}^r|y\rangle = (pq|r_{12}|ry) \tag{24}$$

and

$$\langle y|\psi_{tu}^s\rangle = (ys|tu) \tag{25}$$

and the overlap of these two objects together is the 3-electron integral,

$$\langle\phi_{pq}^r|\psi_{tu}^s\rangle = (pq|r_{12}|rs|r_{23}^{-1}|tu). \tag{26}$$

The RI procedure for this integral turns out to be equivalent to fitting $|\phi_{pq}^r\rangle$ and $|\psi_{tu}^s\rangle$ in a basis—in the original Kutzelnigg and Klopper formulation in the MO basis[25,26] but more recently using a different fitting basis.[29] To see the equivalence, we denote the fitted objects $|\tilde{\phi}_{pq}^r\rangle$ and $|\tilde{\psi}_{tu}^s\rangle$ and introduce a measure of the fitting error,

$$\Delta_\phi = \langle\phi_{pq}^r - \tilde{\phi}_{pq}^r|\phi_{pq}^r - \tilde{\phi}_{pq}^r\rangle \tag{27}$$

with a similar expression for $\psi_{tu}^s$. Representing the fitted object in an orthonormal basis

$$|\phi_{pq}^r\rangle \approx |\tilde{\phi}_{pq}^r\rangle = C_{pq}^{r;y}|y\rangle \tag{28}$$

and minimizing $\Delta_\phi$ with respect to the $C_{pq}^{r;y}$ we obtain

$$C_{pq}^{r;y} = (pq|r_{12}|ry). \tag{29}$$

The coefficients for $|\tilde{\psi}_{tu}^s\rangle$ can be found in a similar way, and one has

$$|\tilde{\psi}_{tu}^s\rangle = (tu|sx)|x\rangle. \tag{30}$$

Taking Eq. (26) and using the approximations above we can compute

$$(pq|r_{12}|rs|r_{23}^{-1}|tu) \approx \langle \tilde{\phi}_{pq}^r | \tilde{\psi}_{tu}^s \rangle = (pq|r_{12}|ry)(ys|tu) \quad (31)$$

which, after translation to Dirac notation, can be seen to be equivalent to the RI expression in Eq. (1). It is perhaps interesting to note that the fit implicit in MP2-R12 theory is robust because

$$(pq|r_{12}|rs|r_{23}^{-1}|tu) - (pq|r_{12}|ry)(ys|tu)$$
$$= \langle \phi_{pq}^r - \tilde{\phi}_{pq}^r | \psi_{tu}^s - \tilde{\psi}_{tu}^s \rangle. \quad (32)$$

## C. Density fitting in MP-R12 theory

As we have discussed one needs in MP2-R12 theory standard 2-electron integrals and also integrals of the form $(pq|r_{12}|rs)$ and $(pq|[\hat{t}_1,r_{12}]|rs)$. Using the robust formula of Eq. (20) we are ready to treat the first of these,

$$(pq|r_{12}|rs) \approx (pq|r_{12}|rs)_{robust}$$
$$= (\widetilde{pq}|r_{12}|rs) + (pq|r_{12}|\widetilde{rs}) - (\widetilde{pq}|r_{12}|\widetilde{rs}). \quad (33)$$

Inserting the expansion [Eq. (10)] and the definition of the coefficients [Eq. (13)] we obtain

$$(pq|r_{12}|rs)_{robust} = \bar{J}_{pq}^A R_{rs}^A + R_{pq}^A \bar{J}_{rs}^A - \bar{J}_{pq}^A R_{AB} \bar{J}_{rs}^B, \quad (34)$$

where $R_{AB} \equiv (A|r_{12}|B)$ and $R_{pq}^A \equiv (pq|r_{12}|A)$.

Fitting the commutator integrals $(pq|[\hat{t}_1,r_{12}]|rs)$ is a little more complicated. The presence of the kinetic energy operator eliminates the possibility of fitting $|pq)$ directly because the $\hat{t}_1$ acts on $|q\rangle$ and not on $|pq)$ as a whole. One can still fit $|rs)$ to obtain the nonrobust approximation

$$(pq|[\hat{t}_1,r_{12}]|rs) \approx (pq|[\hat{t}_1,r_{12}]|\widetilde{rs}) = X_{pq}^A \bar{J}_{rs}^A, \quad (35)$$

where $X_{pq}^A \equiv (pq|[\hat{t}_1,r_{12}]|A)$ but this leads to serious errors in the final energies.

A robust formula can be derived by rearranging the target integral,

$$(pq|[\hat{t}_1,r_{12}]|rs) = (\{\hat{t}_1 p\}q - p\{\hat{t}_1 q\}|r_{12}|rs)$$
$$= ([pq]|r_{12}|rs), \quad (36)$$

where the last equality defines the notation $|[pq])$. Since $|[pq])$ is essentially just an orbital product density it can be fitted, although the adequacy of available fitting basis sets remains to be seen. Using Eqs. (20) and (36), the robust fitting formula

$$(pq|[\hat{t}_1,r_{12}]|rs)_{robust} = ([\widetilde{pq}]|r_{12}|rs) + ([pq]|r_{12}|\widetilde{rs})$$
$$- ([\widetilde{pq}]|r_{12}|\widetilde{rs}) \quad (37)$$

can be derived. Expanding each term we obtain

$$(pq|[\hat{t}_1,r_{12}]|rs)_{robust} = \bar{Y}_{pq}^A R_{rs}^A + X_{pq}^A \bar{J}_{rs}^A - \bar{Y}_{pq}^A R_{AB} \bar{J}_{rs}^B, \quad (38)$$

where $\bar{Y}_{pq}^A \equiv [\mathbf{J}^{-1}]_{AB} Y_{pq}^B$ and $Y_{pq}^A \equiv (pq|[\hat{t}_1,r_{12}^{-1}]|A)$.

The DF-MP2-R12 method can be summarized as MP2-R12 theory with the three classes of 2-electron integrals approximated according to Eqs. (15), (34), and (38).

## D. Implementation of integrals

DF-MP2-R12 requires no 4-index integrals, but requires four kinds of 3-index integrals $(\alpha\beta|A)$, $(\alpha\beta|r_{12}|A)$, $(\alpha\beta|[\hat{t}_1,r_{12}]|A)$, and $(\alpha\beta|[\hat{t}_1,r_{12}^{-1}]|A)$, and two types of 2-index integrals $(A|B)$ and $(A|r_{12}|B)$.

The 2-index integral evaluation is based on the recursive approach of Obara and Saika (OS),[53] and we use (almost) their notation. The basic objects are unnormalized Cartesian Gaussians

$$|\mathbf{a}) \equiv g(\mathbf{r};\alpha,\mathbf{A},\mathbf{a}) = x_A^{a_x} y_A^{a_y} z_A^{a_z} e^{-\alpha r_A^2} \quad (39)$$

with exponent $\alpha$, center $\mathbf{A}$, and angular momentum vector $\mathbf{a}$. Here $x_A = x - A_x$, with similar expressions for $y_A$ and $z_A$, and $r_A = |\mathbf{r} - \mathbf{A}|$. We also use the notation $\mathbf{1}_x = (1,0,0)$, etc.

The recurrence relation for the 2-index Coulomb integrals is simple specialization of the 4-index formula of OS,

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{b})^{(m)} = PA_i(\mathbf{a}|\mathbf{b})^{(m+1)} + \frac{a_i}{2\alpha}\left[(\mathbf{a}-\mathbf{1}_i|\mathbf{b})^{(m)}\right.$$
$$\left. - \frac{\xi}{\alpha}(\mathbf{a}-\mathbf{1}_i|\mathbf{b})^{(m+1)}\right] + \frac{b_i}{2\zeta}(\mathbf{a}|\mathbf{b}-\mathbf{1}_i)^{(m+1)}, \quad (40)$$

where $\zeta = \alpha + \beta$, $\mathbf{P} = (\alpha\mathbf{A} + \beta\mathbf{B})/\zeta$, $PA_i = P_i - A_i$, and $\xi = \alpha\beta/\zeta$. The required integrals are obtained as $(\mathbf{a}|\mathbf{b}) = (\mathbf{a}|\mathbf{b})^{(0)}$. The recurrence starts from the $s$-only integrals $(\mathbf{0}_A|\mathbf{0}_B)^{(m)}$ which are a special case of Eqs. (44)–(47) in OS.

The 2-index $r_{12}$ integrals are obtained as a specialization of Eq. (17) of Ref. 54,

$$(\mathbf{a}+\mathbf{1}_i|r_{12}|\mathbf{b}) = \frac{a_i}{2\alpha}(\mathbf{a}-\mathbf{1}_i|r_{12}|\mathbf{b}) + \frac{1}{2\xi}(\mathbf{a}+\mathbf{1}_i|\mathbf{b})$$
$$+ \frac{AB_i}{2\alpha}(\mathbf{a}|\mathbf{b}) - \frac{1}{4\alpha\beta}[a_i(\mathbf{a}-\mathbf{1}_i|\mathbf{b})$$
$$+ b_i(\mathbf{a}|\mathbf{b}-\mathbf{1}_i)]; \quad (41)$$

this recurrence and that of Eq. (40) are executed simultaneously.

All four classes of 3-index integrals are obtained by by summing the $(\mathbf{a}|\mathbf{b})$ and $(\mathbf{a}|r_{12}|\mathbf{b})$ with precomputed coefficients that describe a product of two Cartesian Gaussians as a sum of Cartesian Gaussians. Thus,

$$|\mathbf{ab}) = T_p^{ab}|\mathbf{p}) \quad (42)$$

and so, for example,

$$(\mathbf{ab}|\mathbf{c}) = T_p^{ab}(\mathbf{p}|\mathbf{c}). \quad (43)$$

The implicit summation in Eq. (43) runs over all components $\mathbf{p}$ with $0 \leq |\mathbf{p}| \leq |\mathbf{a}| + |\mathbf{b}|$.

The commutator integrals are treated in a similar manner. Following the analysis of Klopper and Röhse[30] we have

$$(\mathbf{ab}|[\hat{t}_1,r_{12}]|\mathbf{c}) = \frac{\alpha-\beta}{\alpha+\beta}(\mathbf{ab}|\mathbf{c}) + \nabla_P \cdot \nabla_R(\mathbf{ab}|r_{12}|\mathbf{c}), \quad (44)$$

where $\mathbf{R} = \mathbf{A} - \mathbf{B}$. It is possible to precompute the coefficients $Q_p^{ab}$ which define the gradient orbital product $\nabla_P \cdot \nabla_R|\mathbf{ab})$, then

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TABLE I. MP2 and MP2-R12/A correlation energies (in hartree) for water in various basis sets. Fitting errors relative to unfitted methods are given in microhartree: $\delta_J$ is the error when only Coulomb integrals are fitted; $\delta_{JR}$ is the error with Coulomb and $r_{12}$ integrals fitted; and $\delta_{DF}$ is the error in the fully fitted method. Basis sets are labeled V$n$Z meaning cc-pV$n$Z for the AO basis; V$n$Z in the auxiliary basis column refers to the cc-pV$n$Z/MP2-fit basis set optimized for the corresponding AO set.

| Basis | | MP2 | | MP2-R12 | | | |
|---|---|---|---|---|---|---|---|
| AO | Aux | Energy | $\delta_{DF}$ | Energy | $\delta_J$ | $\delta_{JR}$ | $\delta_{DF}$ |
| VDZ | VDZ | −0.219 749 | −87 | −0.300 108 | −5 | 51 | 81 |
| | VTZ | | −38 | | 8 | 29 | 18 |
| | VQZ | | −21 | | −10 | −5 | −2 |
| VTZ | VTZ | −0.266 692 | −57 | −0.291 200 | −3 | 51 | 86 |
| | VQZ | | −18 | | 7 | −5 | 2 |

$$\nabla_P \cdot \nabla_R(\mathbf{ab}|\mathbf{c}) = Q_p^{ab}(\mathbf{p}|\mathbf{c}), \tag{45}$$

where the summation runs over components up to the total angular momentum plus one: $0 \leqslant |\mathbf{p}| \leqslant |\mathbf{a}| + |\mathbf{b}| + 1$.

For the second class of commutator integrals we can use the identities

$$[\hat{t}_1, r_{12}^{-1}] = 2\pi\delta(r_{12}) - (\nabla_1 r_{12}^{-1}) \cdot \nabla_1 \tag{46}$$

and $(\mathbf{ab}|\delta(r_{12})|\mathbf{c}) = \langle \mathbf{abc} \rangle$ to obtain

$$(\mathbf{ab}|[\hat{t}_1, r_{12}^{-1}]|\mathbf{c}) = 2\pi\frac{\alpha - \beta}{\alpha + \beta}\langle \mathbf{abc} \rangle + \nabla_P \cdot \nabla_R(\mathbf{ab}|\mathbf{c}), \tag{47}$$

where $\langle \mathbf{abc} \rangle$ are 3-index overlap integrals.

### E. Implementation of DF-MP2-R12

DF-MP2-R12 has been implemented in the quantum chemistry package MOLPRO.[55] The 3-index integrals described in the preceding section are computed, transformed on-the-fly and stored in core. Although this presents a bottleneck for large cases, the method can readily be applied to interesting problems using a standard PC. An integral direct version is currently in preparation. Only closed-shell DF-MP2-R12/A has been implemented[26] but the generalization to DF-MP2-R12/B requires no new 2-electron integrals. The most time consuming step is the assembly of the 4-index integrals, but these are implemented as $N(N+1)/2$ multiplications of $M \times m$ matrices for $N$ occupied MOs, $m$ AOs, and $M$ auxiliary functions. These matrix multiplications can therefore be parallelized using existing parallel routines.

### III. EXAMPLES

We first examine the accuracy of the approximations in DF-MP2-R12 for the water molecule. The errors arising from fitting the three types of integrals are analyzed in Table

I for uncontracted cc-pVDZ and cc-pVTZ basis sets,[56] using the fitting sets of Weigend *et al.*[57] The deviation between MP2-R12 and DF-MP2-R12 is of the same order of magnitude as that between MP2 and DF-MP2, but typically of the opposite sign. Furthermore, the errors in DF-MP2-R12 arising from the fitting of Coulomb, $r_{12}$ and commutator integrals tend to cancel, and particularly with larger fitting basis sets, this leads to extremely small fitting errors of just a few microhartree. It is worth noting that this cancellation should not be relied upon to apply to different geometries, systems or levels of correlation treatment, but in any case the errors arising from the fitting of each class of integrals remain acceptably small.

To assess the accuracy of the fitting process in more detail, calculations were performed on a test set of twenty small systems ($BH_3$, $CH_4$, $NH_3$, $H_2O$, HF, Ne, $SiH_4$, $PH_3$, $H_2S$, HCl, Ar, $F_2$, $N_2$, HCN, CO, $H_2CO$, $H_2O_2$, $N_2H_4$, $C_2H_2$, and $C_2H_4$) using the uncontracted cc-pVDZ basis and fitting basis sets optimized for DF-MP2, cc-pV$n$Z/MP2-fit with $n = D, T, Q$.[57] For each set of calculations the mean error $\bar{\delta}$ and standard deviation $\sigma$ were computed, and the normal distribution functions,

$$\rho(\delta) = \frac{1}{\sigma\sqrt{2\pi}} e^{-|\delta - \bar{\delta}|^2/(2\sigma)} \tag{48}$$

plotted. In Fig. 1 the normal distributions of fitting errors in DF-MP2-R12 are compared with those in DF-MP2, and also with the errors that arise in DF-MP2-R12 if the nonrobust formula for the fitted commutator integrals is used [Eq. (35)]. It should be noted that a spuriously large error was noted for the calculation on Ne using the cc-pVQZ/MP2-fit basis, and this error is the main contributor to the surprisingly large standard deviation of the errors in this case. This is probably due to a defect in the $s$-type functions of that fitting basis, since replacing them with the uncontracted $s$-type orbitals of the aug-cc-pV5Z basis reduces the error in DF-MP2-R12 by a factor of over 20.

It is clear that the robust expression for the commutator integrals in Eq. (38) performs much better than the standard expression, despite the need to fit the derivative AO products $[pq]$. It can be seen from Fig. 1 that the fitting errors one can expect in DF-MP2-R12 are similar in magnitude to those in DF-MP2. These errors will of course be reduced when fitting basis sets are optimized specifically for use in DF-MP2-R12. It would be convenient if there were some correlation between the fitting error in DF-MP2 and that in DF-MP2-R12, however no such correlation is found.

To assess the performance of the method for a slightly larger system, calculations were performed on the glycine

cc-pVDZ/MP2-fit          cc-pVTZ/MP2-fit          cc-pVQZ/MP2-fit
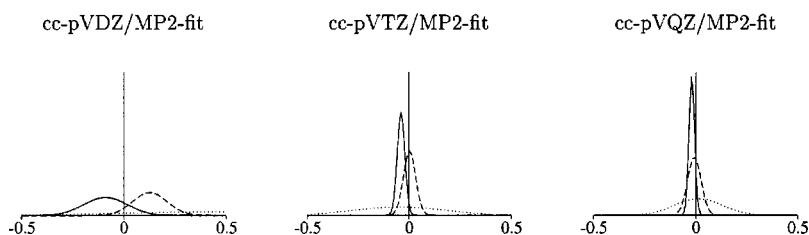


FIG. 1. Normal distribution functions for the errors between MP2 and DF-MP2 (solid line) and between MP2-R12 and DF-MP2-R12 (dashed line for robust method; dotted line with nonrobust commutator integrals). All calculations used the uncontracted cc-pVDZ AO basis and three increasingly large DF-MP2 fitting basis sets, optimized for cc-pV{D,T,Q}Z. In each case the horizontal axis is an error in millihartree.

TABLE II. MP2, DF-MP2, and DF-MP2-R12 valence correlation energies in hartree for the glycine molecule in three correlation consistent basis sets, both contracted and uncontracted. In each case the appropriate cc-pV$n$Z/MP2-fit fitting basis was used.

| | Contracted | | | Uncontracted | | |
|---|---|---|---|---|---|---|
| Basis | $-E_2^{MP2}$ | $-E_2^{DF-MP2}$ | $-E_2^{DF-MP2-R12}$ | $-E_2^{MP2}$ | $-E_2^{DF-MP2}$ | $-E_2^{DF-MP2-R12}$ |
| VDZ | 0.8019 | 0.8019 | 1.0511 | 0.8602 | 0.8601 | 1.1194 |
| VTZ | 1.0068 | 1.0067 | 1.0678 | 1.0217 | 1.0215 | 1.0991 |
| VQZ | 1.0806 | 1.0805 | 1.1079 | 1.0845 | 1.0844 | 1.1214 |

molecule using contracted and uncontracted correlation consistent basis sets up to quadruple zeta. MP2, DF-MP2, and DF-MP2-R12 correlation energies are shown in Table II. Particularly noteworthy is the speed of these calculations: the uncontracted cc-pVQZ calculation has 500 AOs and 935 fitting functions and the DF-MP2-R12 calculation takes around 30 min on a single 2 GHz Intel Xeon PC. This compares with almost 4 h for the HF calculation and 45 min for the conventional MP2; all calculations were performed direct and without symmetry.

## IV. CONCLUSIONS

It has been shown that all of the 4-index integrals required in the explicitly correlated MP2-R12 theory can be treated by robust density fitting. The resulting DF-MP2-R12 method is already significantly quicker than conventional MP2 calculations, but comparisons with an existing DF-MP2 code[44] suggest that there is substantial room for improvement. Nevertheless, the CPU times are not currently a bottleneck (DF-MP2-R12 calculation is invariably quicker than the preceding HF calculation). The current in-core implementation of DF-MP2-R12 is bound by the cubically scaling memory requirements, however a direct algorithm, which circumvents this bottleneck, is currently being developed. For extremely large problems the assembly step will become dominant, however it has recently been demonstrated that the assembly step in DF-MP2 is rendered completely negligible in a local formalism.[44] The local DF-LMP2-R12 method is an interesting possibility for the future, and will probably require the use of a damped correlation factor as described by Samson et al.[58]

There is much to be gained by considering a RI basis set distinct from the AO basis. This has been explored by Klopper and Samson[29] and will soon be implemented in the DF-MP2-R12 method. Then the 3-index integrals have at most one index from the large RI basis set, and considerable savings will be possible. It is also possible to consider alternative and novel combinations of density fitting and RIs in explicitly correlated theories, and it turns out that improvements on the convergence properties of MP2-R12 are possible.[59]

Finally it is of course tempting to ask whether, in a density fitted explicit correlation code, RIs are needed at all. Work is in progress towards a Gaussian geminals program that uses density fitting to simplify the 3-electron integrals, and developments in this direction will be reported elsewhere.

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