

An explicitly correlated second order Møller-Plesset theory using a frozen Gaussian geminal

Andrew J. May and Frederick R. Manby

Citation: *J. Chem. Phys.* **121**, 4479 (2004); doi: 10.1063/1.1780891

View online: <http://dx.doi.org/10.1063/1.1780891>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v121/i10>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics



- plasma source characterization
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue 

An explicitly correlated second order Møller-Plesset theory using a frozen Gaussian geminal

Andrew J. May and Frederick R. Manby^{a)}

School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, United Kingdom

(Received 7 June 2004; accepted 17 June 2004)

A variant of the MP2-R12 class of theories is introduced using an arbitrary geminal function in the place of r_{12} . Integrals are derived for the case where the geminal is expanded in a basis of Gaussian functions in the interelectronic distance. Recurrence relations are derived that do not depend on the exponents of the Gaussian geminals, allowing much of the integration work to be performed after summations over the geminal expansion. Sample calculations at various levels of explicitly correlated MP2 theory are presented for He, Ne, and water. © 2004 American Institute of Physics. [DOI: 10.1063/1.1780891]

I. INTRODUCTION

Accurate quantum chemical calculations are limited to small molecules partly owing to the poor convergence of orbital based methods. One solution to this problem is to use explicitly correlated electronic structure theories.¹ These methods give very accurate energies for small molecules, but become computationally difficult for larger systems. The problem arises from the need to compute three- and four-electron integrals, which are both complicated and extremely numerous.

Since the bottleneck in explicitly correlated calculations lies in the computation of the many-electron integrals, most work in the field has concentrated on finding ways either to approximate these integrals, or to eliminate them altogether. In practice only the R12 methods of Kutzelnigg and Klopper²⁻⁴ can be applied to nontrivial problems.

These methods lead to greatly improved convergence of correlation energies, but have two disadvantages: First, some of the many-electron integrals involving linear r_{12} cannot be solved in closed form; second, the inclusion of r_{12} in the wave function leads to integrals that become increasingly large as basis functions become further apart. This does not present physical problems: the ratio of the exact wave function to the Hartree-Fock wave function diverges even more quickly in r_{12} . Nevertheless these large integrals ultimately contribute very little to the total energy, and may lead to numerical errors.

This problem can be avoided by using a correlation factor that decays to zero at long range. One such possibility is to use a linear combination of Gaussian type geminals.⁵⁻⁷ These functions cannot exactly reproduce the interelectronic cusps in the wave function owing to their vanishing gradient at $r_{12}=0$. However the volume element, $4\pi r_{12}^2$, ensures that the contribution to the correlation energy at very short r_{12} is negligible. An alternative is to use a damped r_{12} term, such as $r_{12} \exp(-\gamma r_{12}^2)$.⁸ As we will show, the extra work implied

by using n Gaussian geminals in place of a single damped r_{12} term is minimal.

In this work we develop a version of MP2-R12 theory for an arbitrary correlation factor and derive recurrence relations for the integrals needed when the correlation factor is a frozen Gaussian geminal.

It will be possible in the current framework to vary the geminal function to obtain more accurate results; furthermore it is possible to compute the three-electron integrals directly when the correlation factor has the form of a Gaussian geminal. These aspects are not discussed further here, but will be the subject of future investigations.

II. THEORY

A. The MP2-F12/2**A' Ansatz

In MP2-R12 theories various approximations are applied to make the matrix elements that appear in the Hylleraas functional more tractable, and this leads to a variety of *Ansätze*. To illustrate our frozen geminal implementation we develop an *Ansatz* referred to as 2**A', mentioned in the work of Klopper and Samson (KS) (Ref. 9) and referred to as R12-SO* elsewhere.¹⁰ The theory will be developed with resolutions of the identity (RIs) in an auxiliary basis. The derivation follows closely that of Ref. 10, but with the linear r_{12} factor replaced by an arbitrary function f_{12} of the interelectronic distance. Throughout, we employ the following notation for the labeling of orbitals: $ijklmn$ for occupied molecular orbitals (MOs); $abcd$ for virtual MOs; $pqrs$ for any MOs; and $p'q'r's'$ for the orthonormal RI basis. We use $ABCD$ for density fitting basis functions. Summation over repeated dummy indices is assumed throughout.

We minimize the Hylleraas pair functional^{11,12}

$$\epsilon_{ij}^{(2)} = \langle u_{ij} | \hat{f}_1 + \hat{f}_2 - \epsilon_i - \epsilon_j | u_{ij} \rangle + 2 \langle u_{ij} | r_{12}^{-1} | ij \rangle, \quad (1)$$

where in the MP2-F12 *Ansatz* the standard MP2 basis of doubly excited determinants is augmented by explicitly correlated terms

$$|u_{ij}\rangle = t_{ab}^{ij} |ab\rangle + t_{kl}^{ij} \hat{Q}_{12} f_{12} |kl\rangle, \quad (2)$$

^{a)}Author to whom correspondence should be addressed. Electronic mail: fred.manby@bris.ac.uk

where f_{12} is a function of r_{12} .

Expanding the Hylleraas functional gives

$$\epsilon_{ij}^{(2)} = \epsilon_{ij}^{\text{MP2}} + \epsilon_{ij}^{\text{F12}} + 2t_{ab}^{ij}t_{kl}^{ij}\langle kl|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \epsilon_i - \epsilon_j)|ab\rangle, \quad (3)$$

where $\epsilon_{ij}^{\text{MP2}}$ is the conventional MP2 pair energy expression and

$$\epsilon_{ij}^{\text{F12}} = t_{kl}^{ij}B_{kl,mn}^{ij}t_{mn}^{ij} + 2t_{kl}^{ij}V_{kl}^{ij}, \quad (4)$$

where

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

and

$$V_{kl}^{ij} = \langle kl|f_{12}\hat{Q}_{12}r_{12}^{-1}|ij\rangle. \quad (6)$$

The remaining term in Eq. (3) couples the standard MP2 and F12 parts, but the inconvenience of this coupling can be avoided by choosing an appropriate form for the projection operator. In this work we have

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2), \quad (7)$$

where $\hat{O} = |i\rangle\langle i|$ projects onto the one-particle occupied space, and $\hat{V} = |a\rangle\langle a|$ onto the virtual space in the atomic orbital (AO) basis. Other choices for this operator are available, the only essential feature being that it ensures strong orthogonality to the occupied space; alternatives discussed elsewhere⁹ include $\hat{Q}_{12}^O = (1 - \hat{O}_1)(1 - \hat{O}_2)$ and $\hat{Q}_{12}^P = (1 - \hat{P}_1)(1 - \hat{P}_2)$, where $\hat{P} = |p\rangle\langle p|$ projects onto the entire MO space. In the absence of further approximations it makes no difference whether one uses \hat{Q}_{12} or \hat{Q}_{12}^O , but the commonly used approximations in R12 theories may make one choice more accurate than the other. \hat{Q}_{12}^P is distinct owing to the presence of additional terms that are singly exterior to the given AO basis.

Even with the projection operator of Eq. (7), the coupling between $|ab\rangle$ and $\hat{Q}_{12}f_{12}|kl\rangle$ does not exactly vanish; it can however be seen to be small by assuming the validity of the so-called generalized and extended Brillouin conditions (GBC and EBC, respectively).⁴ In the GBC it is assumed that the Fock equations are solved exactly for the occupied orbitals ($\hat{f}|i\rangle = \epsilon_i|i\rangle$); this is clearly not the case in a finite basis set, but becomes more valid as the basis set is extended. In the EBC it is further assumed that the Fock equations are exactly satisfied by the virtual orbitals ($\hat{f}|a\rangle = \epsilon_a|a\rangle$). Assuming the EBC to hold, we have $[\hat{Q}_{12}, \hat{f}_1] = 0$. Since $\hat{Q}_{12}|ab\rangle = 0$ the coupling terms of Eq. (3) can then be seen to vanish, and the MP2 and F12 pair energies can be evaluated in isolation.

Spin adaptation and minimization of the pair energies in Eq. (4) is dealt with straightforwardly through Eqs. (7)–(10) of KS;⁹ all that remains here is to derive expressions for the Fock-like \mathbf{B}^{ij} and exchange-like \mathbf{V}^{ij} matrices.

We first consider the evaluation of the simpler V_{kl}^{ij} matrix elements. Inserting the definition of \hat{Q}_{12} into Eq. (6) gives

$$V_{kl}^{ij} = \langle kl|f_{12}[1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{O}_2 - \hat{V}_1\hat{V}_2]r_{12}^{-1}|ij\rangle. \quad (8)$$

The terms containing two projection operators factorize, so that, for example,

$$\langle kl|f_{12}\hat{O}_1\hat{O}_2r_{12}^{-1}|ij\rangle = \langle kl|f_{12}|mn\rangle\langle mn|r_{23}^{-1}|ij\rangle; \quad (9)$$

those that contain a single projector, however, take the form of unfactorizable three-electron integrals,

$$\langle kl|f_{12}\hat{O}_1r_{12}^{-1}|ij\rangle = \langle klm|f_{12}r_{23}^{-1}|mji\rangle. \quad (10)$$

Using the notation $\langle F \rangle_{pq}^{rs} = \langle pq|f_{12}|rs\rangle$, $\langle J \rangle_{pq}^{rs} = \langle pq|r_{12}^{-1}|rs\rangle$, and $\langle FJ \rangle_{pq}^{rs} = \langle pq|f_{12}r_{12}^{-1}|rs\rangle$, we have

$$V_{kl}^{ij} = \langle FJ \rangle_{kl}^{ij} - \langle kl|f_{12}(\hat{O}_1 + \hat{O}_2)r_{12}^{-1}|ij\rangle + \langle F \rangle_{kl}^{mn}\langle J \rangle_{mn}^{ij} - \langle F \rangle_{kl}^{ab}\langle J \rangle_{ab}^{ij}. \quad (11)$$

The three-electron integrals are avoided in the standard R12 way, namely, by the introduction of an approximate resolution of the identity. Let $\hat{P}' = |p'\rangle\langle p'|$ be such an approximate identity operator; then $\hat{O}_1 \approx \hat{O}_1\hat{P}'_2$ and

$$\langle kl|f_{12}\hat{O}_1r_{12}^{-1}|ij\rangle \approx \langle F \rangle_{kl}^{mp'}\langle J \rangle_{mp'}^{ij}. \quad (12)$$

Then we have

$$V_{kl}^{ij} = \langle FJ \rangle_{kl}^{ij} - \langle F \rangle_{kl}^{mp'}\langle J \rangle_{mp'}^{ij} - \langle F \rangle_{kl}^{p'm}\langle J \rangle_{p'm}^{ij} + \langle F \rangle_{kl}^{mn}\langle J \rangle_{mn}^{ij} - \langle F \rangle_{kl}^{ab}\langle J \rangle_{ab}^{ij}, \quad (13)$$

and this expression straightforwardly reflects the structure of the projection operator after the insertion of RIs,

$$\hat{Q}_{12} \approx 1 - \hat{O}_1\hat{P}'_2 - \hat{P}'_1\hat{O}_2 + \hat{O}_1\hat{O}_2 - \hat{V}_1\hat{V}_2. \quad (14)$$

The exact form of $B_{kl,mn}^{ij}$ is given in Eq. (5), but several distinct approximations are made to arrive at an expression that can be evaluated efficiently. It is first assumed that the EBC holds, because then $[\hat{Q}_{12}, \hat{f}_1 + \hat{f}_2] = 0$, and

$$B_{kl,mn}^{ij} = \langle mn|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \epsilon_i - \epsilon_j)f_{12}|kl\rangle. \quad (15)$$

The relationship in Eq. (15) is only approximate in a finite basis, and care has to be taken to symmetrize the final, approximate \mathbf{B}^{ij} to restore Hermiticity.

The second step is to observe the identity

$$B_{kl,mn}^{ij} = \langle mn|f_{12}\hat{Q}_{12}\{[\hat{f}_1 + \hat{f}_2, f_{12}] + f_{12}(\hat{f}_1 + \hat{f}_2 - \epsilon_i - \epsilon_j)\}|kl\rangle. \quad (16)$$

Relying on the GBC and symmetrizing we have

$$B_{kl,mn}^{ij} = \frac{1}{2}\{B_{kl,mn} + B_{mn,kl}\} + \frac{1}{2}(\epsilon_k + \epsilon_l + \epsilon_m + \epsilon_n - 2\epsilon_i - 2\epsilon_j)X_{kl,mn}, \quad (17)$$

where

$$B_{kl,mn} = \langle mn|f_{12}\hat{Q}_{12}[\hat{f}_1 + \hat{f}_2, f_{12}]|kl\rangle \quad (18)$$

and

$$X_{kl,mn} = \langle mn|f_{12}\hat{Q}_{12}f_{12}|kl\rangle. \quad (19)$$

The ‘‘overlap’’ matrix \mathbf{X} is computed exactly like \mathbf{V} : using the RI approximation one has

$$X_{kl,mn} = \langle F^2 \rangle_{mn}^{kl} - \langle F \rangle_{mn}^{ip'} \langle F \rangle_{ip'}^{kl} - \langle F \rangle_{mn}^{p'i} \langle F \rangle_{p'i}^{kl} \\ + \langle F \rangle_{mn}^{ij} \langle F \rangle_{ij}^{kl} - \langle F \rangle_{mn}^{ab} \langle F \rangle_{ab}^{kl}, \quad (20)$$

where $\langle F^2 \rangle_{mn}^{kl} = \langle mn | f_{12}^2 | kl \rangle$.

A further approximation is made in the evaluation of the $B_{kl,mn}$: the local parts of the Fock operator naturally commute with the projection operator \hat{Q}_{12} , and here we further assume that $[\hat{Q}_{12}, \hat{K}_1] \approx 0$. This in the language of Klopper and Kutzelnigg⁴ renders the current work an approximation of type A. We are therefore left only with kinetic energy, so that

$$B_{kl,mn} = \langle mn | f_{12} \hat{Q}_{12} [\hat{t}_1 + \hat{t}_2, f_{12}] | kl \rangle. \quad (21)$$

This can immediately be treated in the same way as before to obtain (in the RI approximation)

$$B_{kl,mn} = \langle FTF \rangle_{mn}^{kl} - \langle F \rangle_{mn}^{ip'} \langle TF \rangle_{ip'}^{kl} - \langle F \rangle_{mn}^{p'i} \langle TF \rangle_{p'i}^{kl} \\ + \langle F \rangle_{mn}^{ij} \langle TF \rangle_{ij}^{kl} - \langle F \rangle_{mn}^{ab} \langle TF \rangle_{ab}^{kl}, \quad (22)$$

where $\langle FTF \rangle_{mn}^{kl} = \langle mn | f_{12} [\hat{t}_1 + \hat{t}_2, f_{12}] | kl \rangle$ and $\langle TF \rangle_{mn}^{kl} = \langle mn | [\hat{t}_1 + \hat{t}_2, f_{12}] | kl \rangle$.

To summarize, the MP2-F12 method implemented here uses Eqs. (13), (20), and (22) to form all of the necessary matrix elements. The four-index two-electron integrals are generated by density fitting, as described in the following section.

B. Density fitting

Following previous work¹³ we compute the integrals over r_{12}^{-1} , f_{12} , $f_{12} r_{12}^{-1}$, $[\hat{t}_1, f_{12}]$, and $f_{12} [\hat{t}_1, f_{12}]$ using robust density fitting formulas. We treat in detail only those cases that do not form a trivial extension of our previous work. We consider the expansion of a general orbital product density $|pq\rangle$ in an auxiliary basis

$$|pq\rangle \approx |\widetilde{pq}\rangle = (\bar{J})_{pq}^A |A\rangle, \quad (23)$$

where $(\bar{J})_{pq}^A = [\mathbf{J}^{-1}]_{AB} (J)_{pq}^A$ and where $J_{AB} = (J)_B^A = (A|B)$ and $(J)_{pq}^A = (A|pq)$, the two- and three-index Coulomb integrals, respectively. The coefficients $(\bar{J})_{pq}^A$ are used to compute all classes of four-index integrals.

The normal exchange integrals are given by

$$\langle J \rangle_{pr}^{qs} \equiv (J)_{pq}^{rs} \approx (\bar{J})_{pq}^A (J)_{rs}^A \quad (24)$$

but integrals over other kernels must be computed using explicitly robust equations^{14,15} as discussed previously.¹³ Thus, for example, the integrals over f_{12} are given by

$$(F)_{pq}^{rs} \approx (F)_{pq}^A (\bar{J})_{rs}^A + (\bar{J})_{pq}^A (F)_{rs}^A - (\bar{J})_{pq}^A (F)_B^A (\bar{J})_{rs}^B, \quad (25)$$

where $(F)_B^A$ and $(F)_{pq}^A$ are two- and three-index integrals over f_{12} .

In r_{12} methods, the $(FJ)_{rs}^{pq}$ integrals are trivial (because $r_{12} r_{12}^{-1} = 1$) and the integrals $(F^2)_{pq}^{rs}$ factorize; with a general correlation factor f_{12} neither of these simplifications take place, and one needs to compute expressions analogous to Eq. (25) using two- and three-index integrals $(FJ)_B^A$, $(FJ)_{pq}^A$, $(F^2)_B^A$, and $(F^2)_{pq}^A$.

The kinetic energy integrals $(TF)_{rs}^{pq}$ are treated by noting that

$$\langle pr | [\hat{t}_1, f_{12}] | qs \rangle = ([pq] | f_{12} | rs), \quad (26)$$

where $[[pq]] = |\{\hat{t}_1 p\} q - p \hat{t}_1 q\rangle$, and that $[[pq]]$ is a density that can also be subjected to fitting. Then (as before¹³) one has

$$([pq] | f_{12} | rs) \approx (\bar{TJ})_{pq}^A (F)_{rs}^A + (TF)_{pq}^A (\bar{J})_{rs}^A \\ - (\bar{TJ})_{pq}^A (F)_B^A (\bar{J})_{rs}^B \quad (27)$$

and

$$(TF)_{rs}^{pq} = ([pq] | f_{12} | rs) + (pq | f_{12} | [rs]). \quad (28)$$

In Eq. (27) one requires the integrals $(TJ)_{pq}^A = (A | [\hat{t}_1, r_{12}^{-1}] | pq)$ the evaluation of which has been described before.¹³

C. Integrals

1. Cartesian Gaussian functions

We consider two-index two-electron integrals over unnormalized Cartesian Gaussian functions¹⁶

$$|\mathbf{a}\rangle \equiv g(r; \alpha, \mathbf{a}, \mathbf{A}) = (x - A_x)^{\alpha_x} (y - A_y)^{\alpha_y} (z - A_z)^{\alpha_z} \\ \times \exp[-\alpha |\mathbf{r} - \mathbf{A}|^2]. \quad (29)$$

It is important to note that a single Gaussian geminal function can be represented as

$$e^{-\gamma r_{12}^2} \equiv g_{12}^\gamma = g(\mathbf{r}_1; \gamma, \mathbf{0}, \mathbf{r}_2). \quad (30)$$

As detailed above several types of integral are required for the MP2-F12/2**A' method. Here we will present the derivation of all integral classes using a frozen Gaussian geminal of the form

$$f_{12} = c_\mu g_{12}^{\gamma\mu}. \quad (31)$$

The analysis closely follows the work of Obara and Saika.¹⁶

Since both two- and three-index integrals are needed we compute two-index integrals as the basic quantities and use precomputed Gaussian product tensors to build three-index integrals, as described previously.¹³ This also makes any future development of a four-index program comparatively straightforward.

2. Integral type $(\mathbf{a} | g_{12}^\gamma | \mathbf{b})$

This integral forms the basis for the computation of the other integral classes so we present its derivation in some detail. The two-electron, six-dimensional integral is defined explicitly as

$$(\mathbf{a} | g_{12}^\gamma | \mathbf{b}) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 g(\mathbf{r}_1, \alpha, \mathbf{a}, \mathbf{A}) g_{12}^\gamma g(\mathbf{r}_2, \beta, \mathbf{b}, \mathbf{B}). \quad (32)$$

For convenience we define a number of constants related to the Gaussian exponents,

$$\zeta = \alpha + \beta, \quad \xi = \frac{\alpha\beta}{\zeta}, \quad \eta = \alpha\beta + \beta\gamma + \gamma\alpha.$$

We begin by rewriting Eq. (32) in the form

$$\langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} \rangle = \int d\mathbf{r}_2 \langle \mathbf{a} | g_{12}^\gamma \rangle g(\mathbf{r}_2; \beta, \mathbf{b}, \mathbf{B}). \quad (33)$$

The overlap integrals $\langle \mathbf{a} | g_{12}^\gamma \rangle$ obey the well known recurrence relation¹⁶

$$\begin{aligned} \langle \mathbf{a} + \mathbf{1}_i | g_{12}^\gamma \rangle &= \left(\frac{\alpha A_i + \gamma r_{2i} - A_i}{\alpha + \gamma} - A_i \right) \langle \mathbf{a} | g_{12}^\gamma \rangle \\ &+ \frac{a_i}{2(\alpha + \gamma)} \langle \mathbf{a} - \mathbf{1}_i | g_{12}^\gamma \rangle. \end{aligned} \quad (34)$$

Now performing the integral of Eq. (33) we obtain

$$\begin{aligned} \langle \mathbf{a} + \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle &= \int d\mathbf{r}_2 \left[\left(\frac{\gamma(r_{2i} - A_i)}{\alpha + \gamma} \right) \langle \mathbf{a} | g_{12}^\gamma \rangle \right. \\ &+ \left. \frac{a_i}{2(\alpha + \gamma)} \langle \mathbf{a} - \mathbf{1}_i | g_{12}^\gamma \rangle \right] g(\mathbf{r}_2; \beta, \mathbf{b}, \mathbf{B}), \end{aligned} \quad (35)$$

which, using $r_{2i} - A_i = r_{2i} - B_i - AB_i$, $AB_i = \mathbf{A}_i - \mathbf{B}_i$ and Eq. (33), can be rewritten as

$$\begin{aligned} \langle \mathbf{a} + \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle &= \frac{\gamma AB_i}{\alpha + \gamma} \langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} \rangle + \frac{\gamma}{\alpha + \gamma} b_i \langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} + \mathbf{1}_i \rangle \\ &+ \frac{a_i}{2(\alpha + \gamma)} \langle \mathbf{a} - \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle. \end{aligned} \quad (36)$$

An analogous expression can be derived for $\langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} + \mathbf{1}_i \rangle$ and these two equations can be used to obtain a recurrence relation for $\langle \mathbf{a} + \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle$ that involves only integrals with lower angular momentum,

$$\begin{aligned} \langle \mathbf{a} + \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle &= -\frac{\beta \gamma AB_i}{\eta} \langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} \rangle + \frac{\gamma}{2\eta} b_i \langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} - \mathbf{1}_i \rangle \\ &+ \frac{\beta + \gamma}{2\eta} a_i \langle \mathbf{a} - \mathbf{1}_i | g_{12}^\gamma | \mathbf{b} \rangle. \end{aligned} \quad (37)$$

The recurrence relation requires the initial case

$$\langle \mathbf{0} | g_{12}^\gamma | \mathbf{0} \rangle = \frac{\pi^3}{\eta^{3/2}} \exp \left\{ \frac{-|\mathbf{A} - \mathbf{B}|^2 \alpha \beta \gamma}{\eta} \right\}. \quad (38)$$

Integrals of types F and F^2 are linear combinations of these basic integrals over Gaussians, so that, for example,

$$\langle \mathbf{a} | f_{12} | \mathbf{b} \rangle = c_\mu \langle \mathbf{a} | g_{12}^{\gamma_\mu} | \mathbf{b} \rangle. \quad (39)$$

The recurrence relation of Eq. (37) appears to be quite generally useful. For example, by using the Gaussian representation of the Dirac δ function it is possible to see that

$$\lim_{\gamma \rightarrow \infty} \left(\frac{\gamma}{\pi} \right)^{1/2} \langle \mathbf{a} | g_{12}^\gamma | \mathbf{b} \rangle = \langle \mathbf{a} | \mathbf{b} \rangle; \quad (40)$$

applying this limit to the recurrence relation yields the recurrence relation for the overlap integrals.¹⁶ Similarly, integration of Eq. (37) yields the recurrence relation for two-index Coulomb integrals owing to the well known Gaussian transform¹⁷

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int_0^\infty du e^{-u^2 r_{12}^2}. \quad (41)$$

In the following section recurrence relations for the FJ integrals are derived using this transform.

3. Integral type FJ

The target integral can be represented as

$$\langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty du \langle \mathbf{a} | e^{-(\gamma+u^2)r_{12}^2} | \mathbf{b} \rangle. \quad (42)$$

Substituting $\gamma \rightarrow \gamma + u^2$ into Eq. (37) and integrating with respect to u gives

$$\begin{aligned} \frac{2}{\sqrt{\pi}} \int_0^\infty du \langle \mathbf{a} + \mathbf{1}_i | e^{-(\gamma+u^2)r_{12}^2} | \mathbf{b} \rangle &= \frac{2}{\sqrt{\pi}} \int_0^\infty du \left\{ -\frac{\beta(\gamma+u^2)AB_i}{\eta + \zeta u^2} \langle \mathbf{a} | e^{-(\gamma+u^2)r_{12}^2} | \mathbf{b} \rangle \right. \\ &+ \frac{\gamma+u^2}{2(\eta + \zeta u^2)} b_i \langle \mathbf{a} | e^{-(\gamma+u^2)r_{12}^2} | \mathbf{b} - \mathbf{1}_i \rangle \\ &+ \left. \frac{\beta + \gamma + u^2}{2(\eta + \zeta u^2)} a_i \langle \mathbf{a} - \mathbf{1}_i | e^{-(\gamma+u^2)r_{12}^2} | \mathbf{b} \rangle \right\}. \end{aligned} \quad (43)$$

By making use of an auxiliary integral

$$\langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m)} = \frac{2}{\sqrt{\pi}} \int_0^\infty du \left(\frac{u^2}{\kappa + u^2} \right)^m \langle \mathbf{a} | e^{-r_{12}^2(u^2 + \gamma)} | \mathbf{b} \rangle \quad (44)$$

(where $\kappa = \eta/\zeta$) and the formula

$$\frac{1}{\kappa + u^2} = \frac{1}{\kappa} \left\{ 1 - \frac{u^2}{\kappa + u^2} \right\}, \quad (45)$$

it is possible to complete the integration,

$$\begin{aligned} \langle \mathbf{a} + \mathbf{1}_i | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m)} &= -\frac{\beta AB_i}{\eta} [\gamma \langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m)} + \xi \langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m+1)}] \\ &+ \frac{b_i}{2\eta} [\gamma \langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} - \mathbf{1}_i \rangle^{(m)} \\ &+ \xi \langle \mathbf{a} | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} - \mathbf{1}_i \rangle^{(m+1)}] \\ &+ \frac{a_i}{2\eta} \left[(\gamma + \beta) \langle \mathbf{a} - \mathbf{1}_i | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m)} \right. \\ &- \left. \frac{\beta^2}{\zeta} \langle \mathbf{a} - \mathbf{1}_i | r_{12}^{-1} g_{12}^\gamma | \mathbf{b} \rangle^{(m+1)} \right]. \end{aligned} \quad (46)$$

The starting case for the recurrence relation is

$$\langle \mathbf{0} | r_{12}^{-1} g_{12}^\gamma | \mathbf{0} \rangle^{(m)} = \frac{2\pi^{5/2}}{\eta\zeta^{1/2}} \exp \left\{ \frac{-|\mathbf{A} - \mathbf{B}|^2 \alpha \beta \gamma}{\eta} \right\} F_m(T), \quad (47)$$

where $F_m(T)$ is the Boys function¹⁷

$$F_m(T) = \int_0^1 dt t^{2m} \exp\{-Tt^2\} \quad (48)$$

and

$$T = |\mathbf{A} - \mathbf{B}|^2 \alpha \beta \xi / \eta. \quad (49)$$

4. The transfer equation

Integral types F , F^2 , and FJ involve a summation over exponents defining the Gaussian geminal. This increases the time for the integrals significantly so it is desirable to perform this summation as early as possible in the integral evaluation. This is not possible using Eq. (37) directly because γ , the geminal exponent, appears in the coefficients of the recursion. By taking Eq. (37) and the equivalent expression for $(\mathbf{a}|g_{12}^\gamma|\mathbf{b} + \mathbf{1}_i)$ it is possible to derive a transfer equation in which the coefficients do not have this dependence,

$$2\alpha(\mathbf{a} + \mathbf{1}_i|g_{12}^\gamma|\mathbf{b}) + 2\beta(\mathbf{a}|g_{12}^\gamma|\mathbf{b} + \mathbf{1}_i) \\ = a_i(\mathbf{a} - \mathbf{1}_i|g_{12}^\gamma|\mathbf{b}) + b_i(\mathbf{a}|g_{12}^\gamma|\mathbf{b} - \mathbf{1}_i). \quad (50)$$

This transfer equation can be used directly for any linear combination of Gaussian, or indeed for any two-electron integrals having a kernel that can be expressed as a Gaussian transform. Suppose ϕ_{12} is a two-electron operator that can be written in the form

$$\phi_{12} = \int_0^\infty du \tilde{\phi}(u) e^{-u^2 r_{12}^2}; \quad (51)$$

then the integrals over ϕ_{12} satisfy the recurrence relation

$$2\alpha(\mathbf{a} + \mathbf{1}_i|\phi_{12}|\mathbf{b}) + 2\beta(\mathbf{a}|\phi_{12}|\mathbf{b} + \mathbf{1}_i) \\ = a_i(\mathbf{a} - \mathbf{1}_i|\phi_{12}|\mathbf{b}) + b_i(\mathbf{a}|\phi_{12}|\mathbf{b} - \mathbf{1}_i). \quad (52)$$

Angular momentum is built up say in $|\mathbf{a}\rangle$ by the normal recurrence relations (37) to the total angular momentum of the target integral. The $(\mathbf{a}|g_{12}^\gamma|\mathbf{0})$ integrals are then summed over the geminal coefficients, and only then the transfer equation is used to build the target integrals. Since only a small proportion of the time is spent building the $(\mathbf{a}|g_{12}^\gamma|\mathbf{0})$ integrals, the overhead for having n Gaussian geminals is minimal. If the geminal is varied it will not be possible to perform this summation in advance. However, two points should be considered: (1) the increased accuracy from varying the geminal may be worth the extra effort; (2) the $O(n^2)$ computation of the $\langle F^2 \rangle$ integrals can be avoided by using a direct solver to minimize the Hylleraas functional. In this case one of the two summations can be performed early, leading to a linear dependence on the length of the geminal expansion.

5. Integral type FT

These integrals are computed directly in three-index form. Following our own previous work¹³ and the earlier work of Klopper and Röhse¹⁸ we write

$$(\mathbf{ab}|\hat{t}_1, f_{12}|\mathbf{c}) = \frac{1}{2} \frac{\alpha - \beta}{\alpha + \beta} (\mathbf{ab}|\{\nabla_{12}^2 f_{12}\}|\mathbf{c}) \\ + \nabla_P \cdot \nabla_R (\mathbf{ab}|f_{12}|\mathbf{c}), \quad (53)$$

where $\mathbf{R} = \mathbf{A} - \mathbf{B}$ and $\mathbf{P} = (\alpha\mathbf{A} + \beta\mathbf{B})/\zeta$. The integrals over $\nabla_{12}^2 f_{12}$ are computed using the relation

$$\nabla_{12}^2 f_{12} = 4r_{12}^2 f_{12}^{(2)} - 6f_{12}^{(1)}, \quad (54)$$

where

$$f_{12}^{(n)} = c_\mu \gamma_\mu^n g_{12}^{\gamma_\mu}. \quad (55)$$

The integrals over r_{12}^2 multiplied by a geminal expansion are discussed in the following section. The evaluation of integrals analogous to the second term on the right-hand side of Eq. (53) is discussed elsewhere.¹³

6. Integral type FTF

When r_{12} is used, the kinetic energy integrals over $r_{12}[\hat{t}_1 + \hat{t}_2, r_{12}]$ become trivial,⁴ but in the general case they have to be computed explicitly. Some manipulation reveals that the matrix elements of twice the symmetrized operator $[f_{12}, [\hat{t}_1, f_{12}]]/2$ have the form

$$(\mathbf{a}|[f_{12}, [\hat{t}_1, f_{12}]]|\mathbf{b}) = (\mathbf{a}|\nabla_{12} f_{12}|\mathbf{b}) \quad (56)$$

[cf. Eqs. (6) and (12) of Ref. 8]. The kernel of this integral can readily be shown to be

$$|\nabla_{12} f_{12}|^2 = 4c_\mu c_\nu \gamma_\mu \gamma_\nu r_{12}^2 e^{-(\gamma_\mu + \gamma_\nu)r_{12}^2} = 4r_{12}^2 \{f_{12}^{(1)}\}^2. \quad (57)$$

Combining Eqs. (56) and (57) we have

$$\frac{1}{2} (\mathbf{a}|[f_{12}, [\hat{t}_1, f_{12}]]|\mathbf{b}) = 2(\mathbf{a}|r_{12}^2 \{f_{12}^{(1)}\}^2|\mathbf{b}). \quad (58)$$

The integral on the right-hand side of Eq. (58) can be expressed in terms of integrals over the geminal with higher angular momenta,

$$(\mathbf{a}|r_{12}^2 f_{12}'|\mathbf{b}) = \sum_{i=x,y,z} \{(\mathbf{a} + \mathbf{2}_i|f_{12}'|\mathbf{b}) - 2(\mathbf{a} + \mathbf{1}_i|f_{12}'|\mathbf{b} + \mathbf{1}_i) \\ + 2AB_i(\mathbf{a} + \mathbf{1}_i|f_{12}'|\mathbf{b}) + (\mathbf{a}|f_{12}'|\mathbf{b} + \mathbf{2}_i) \\ - 2AB_i(\mathbf{a}|f_{12}'|\mathbf{b} + \mathbf{1}_i) + AB_i^2(\mathbf{a}|f_{12}'|\mathbf{b})\}. \quad (59)$$

By applying the transfer equation [Eq. (52)] to Eq. (59) it is possible to obtain expressions for the FTF (and TF) integrals that have increased angular momentum only in the bra.

III. EXAMPLES

To illustrate the behavior of the MP2-F12 method, and to check for code correctness, we have performed some preliminary calculations on helium, neon, and the water molecule. Explicitly correlated calculations using various MP2 *Ansätze* were performed using the cc-pVQZ AO basis.^{19,20} When used, the auxiliary RI basis was the uncontracted cc-pVQZ basis, and the cc-pVQZ fitting basis of Weigend *et al.*²¹ was used for density fitting. The Gaussian geminal consisted of 21 even tempered Gaussians with exponents centered on 15 and with a ratio of 2. The coefficients were determined by a least squares fit to r_{12} using a Gaussian weight function with exponent 0.2. The geometry of H₂O was taken from Ref. 22. The results are shown in Table I. It

TABLE I. Correlation energies [$-E_{\text{corr}}$ (millihartree)] for He, Ne, and water using a variety of MP2 methods. Details of the calculations are in the text. Basis sets of the form cc-pVnZ are abbreviated as VnZ. Footnotes refer to sources for the MP2 methods, rather than to the data presented.

Method	Basis	He	Ne	H ₂ O
MP2	VQZ ^a	35.478	293.573	282.816
	V5Z ^b	36.407	306.164	291.522
	V6Z ^c	36.807	311.791	295.218
	V[5,6]Z ^d	37.358	319.519	300.295
MP2-R12/A ^e	VQZ	36.371	309.567	293.633
DF-MP2-R12/A ^f	VQZ	36.340	309.571	293.643
DF-MP2-R12/A ^g	VQZ	36.340	309.913	294.062
DF-MP2-R12/2**A ^h	VQZ	36.317	311.162	294.915
DF-MP2-F12/2**A ⁱ	VQZ	36.319	311.137	294.893

^aReferences 19 and 20.

^bReferences 19 and 20.

^cReference 29.

^dExtrapolation based on V5Z and V6Z results (Refs. 30 and 31).

^eReference 4.

^fReference 13.

^gDensity fitted version of Ref. 32.

^hDensity fitted version of Ref. 9.

can be seen that DF-MP2-F12/2**Aⁱ achieves approximately cc-pV6Z accuracy using only the cc-pVQZ basis. The deviation between the R12 and F12 results is on the order of 20 microhartree.

IV. CONCLUSIONS

We have developed an explicitly correlated MP2 theory that uses a frozen geminal function in place of the more usual linear r_{12} . The three-electron integrals are calculated using RI approximations⁴ in an auxiliary basis.⁹ All of the resulting two-electron integrals are computed using density fitting. This has a very small effect on the computed correlation energies, consistent with previous work.¹³

Much of the extra work associated with using a geminal expansion of n Gaussians arises from the need to compute $O(n^2)$ more integrals than in linear r_{12} methods. This extra load has been mitigated in the current work by the introduction of a transfer equation [Eq. (52)] that allows most of the integration work to be performed after the summation over Gaussian geminals. The transfer equation is analogous to the horizontal recursion relation of Head-Gordon and Pople, which allows the contraction loops to be performed before the transfer of angular momenta in the construction of standard Gaussian electron repulsion integrals.²³

This work forms the basis of a number of future projects. We are in the first instance interested in relaxing the coefficients of the Gaussian geminal to provide an MP2 method with greater variational flexibility. Second, we also are investigating the use of density fitting directly on the three-electron integrals, without the use of the RI approximation. This is relatively straightforward in an F12 theory, because all of the three-electron integrals required can be computed analytically.^{24–26} Third, we are examining the status of the various approximations used in MP2-R12 (or-F12) theories. In particular, it will be interesting to compare the current work with geminals methods that rely on the weak orthogonality

functional^{27,28} as this may shed light on the errors introduced by the GBC and other approximations.

Finally we have begun to investigate an alternative form for the strong orthogonality projection operator \hat{Q} . Using Eq. (7), the identity $\hat{P} = \hat{O} + \hat{V}$ and the definition $\hat{P}^\perp = \hat{P}' - \hat{P}$, it is possible to show that in the RI approximation

$$\hat{Q} \approx 1 - \hat{P}_1 \hat{P}_2 - \hat{O}_1 \hat{P}_2^\perp - \hat{P}_1^\perp \hat{O}_2. \quad (60)$$

This is interesting for two reasons: first because it reveals that the 2** Ansatz has the projection operator of the original MP2-R12 Ansatz⁴ plus a correction term $-\hat{O}_1 \hat{P}_2^\perp - \hat{P}_1^\perp \hat{O}_2$ that takes account of the incompleteness of the AO basis set.

But secondly it reveals that the RI need only be performed in the orthogonal complement of the AO basis. Thus, for example, in a calculation on the neon atom, it is possible to use the s , p , and d functions of cc-pVQZ for the AO basis and *only* the f functions for the orthogonal RI basis that is used to form P^\perp . This yields exactly the same energy as a conventional MP2-R12/2**Aⁱ calculation using the full cc-pVQZ basis for the resolution of the identity. Of course for molecules, the construction of such an orthogonal RI basis is less trivial, and requires further investigation.

ACKNOWLEDGMENTS

The authors are grateful to the EPSRC for funding this research (Grant No. GR/R93704/01) and F.R.M. thanks the Royal Society for funding his Research Fellowship. F.R.M. acknowledges helpful discussions with E. Valeev, and we record that Dr. Valeev has independently devised the orthogonal RI method discussed in the Conclusion.

¹E. A. Hylleraas, Z. Phys. **54**, 347 (1929).

²W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).

³W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987).

⁴W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).

⁵B. J. Persson and P. R. Taylor, J. Chem. Phys. **105**, 5915 (1996).

⁶S. Ten-no, Chem. Phys. Lett. **330**, 169 (2000).

⁷S. Ten-no and F. R. Manby, J. Chem. Phys. **119**, 5358 (2003).

⁸C. C. M. Samson, W. Klopper, and T. Helgaker, Comp. Phys. Commun. **149**, 1 (2002).

⁹W. Klopper and C. C. M. Samson, J. Chem. Phys. **116**, 6397 (2002).

¹⁰P. Wind, W. Klopper, and T. Helgaker, Theor. Chem. Acc. **107**, 173 (2002).

¹¹E. A. Hylleraas, Z. Phys. **65**, 209 (1930).

¹²O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962).

¹³F. R. Manby, J. Chem. Phys. **119**, 4607 (2003).

¹⁴B. I. Dunlap, Int. J. Quantum Chem. **64**, 193 (1997).

¹⁵B. I. Dunlap, Phys. Chem. Chem. Phys. **2**, 2113 (2000).

¹⁶S. Obara and A. Saika, J. Chem. Phys. **84**, 3963 (1986).

¹⁷S. F. Boys, Proc. R. Soc. London, Ser. A **200**, 542 (1950).

¹⁸W. Klopper and R. Röhse, Theor. Chim. Acta **83**, 441 (1992).

¹⁹T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

²⁰D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).

²¹F. Weigend, A. Köhn, and C. Hättig, J. Chem. Phys. **116**, 3175 (2002).

²²W. Klopper, Mol. Phys. **99**, 481 (2001).

²³M. Head-Gordon and J. A. Pople, J. Chem. Phys. **89**, 5777 (1988).

²⁴S. F. Boys, Proc. R. Soc. London, Ser. A **258**, 402 (1960).

- ²⁵K. Singer, Proc. R. Soc. London, Ser. A **258**, 412 (1960).
- ²⁶B. J. Persson and P. R. Taylor, Theor. Chem. Acc. **97**, 240 (1997).
- ²⁷K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, Chem. Phys. Lett. **91**, 169 (1982).
- ²⁸K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).
- ²⁹A. K. Wilson, T. van Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).
- ³⁰K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, J. Chem. Phys. **112**, 9229 (2000).
- ³¹A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).
- ³²W. Klopper, Chem. Phys. Lett. **186**, 583 (1991).