The weak orthogonality functional in explicitly correlated pair theories

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Recent advances have seen the convergence of the R12 and Gaussian geminal explicitly correlated methods, such that the principal remaining distinction is the way in which the many-electron integrals are handled. Here we examine the weak orthogonality functional and the resolution of the identity and find that the first, although exact in the limit of infinite basis, introduces a conflict between the physical description of the electronic cusp and the satisfaction of the strong orthogonality constraint. This leads us to propose an improved weak orthogonality functional where the explicitly correlated pair functions are almost orthogonal to the occupied orbitals by construction. For applications where 95%-98% accuracy in the total correlation energy is sufficient, we recommend use of the strong orthogonality functional in combination with the resolution of the identity for three- and four-electron integral evaluations. © *2007 American Institute of Physics.*
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I. INTRODUCTION

The importance of including the interelectronic distance r_{12} explicitly in the wave function form has been appreciated ever since the pioneering work of Hylleraas in 1929.[1] Not only is short-range electron correlation most naturally described by the coordinate r_{12}, but the exact wave function also exhibits derivative discontinuities at points of electron coalescence.[2,3] These discontinuities are completely absent in orbital based expansions and large basis sets containing functions of high angular momentum are required for accurate calculations. Both the Coulomb hole and the electron cusp can be efficiently represented by basis functions with explicit r_{12} dependence, leading to high accuracy with relatively few variational parameters. However, in contrast to orbital based methods, the n-electron integration required for the evaluation of Hamiltonian matrix elements does not in general simplify to two-electron integrals. Even for the explicitly correlated Gaussian method,[4,5] where the integrals are analytic, the sheer number of integrals that arise has prevented applications to systems with more than six electrons.[6] Consequently, with the exception of variational quantum Monte Carlo,[7] the development of explicitly correlated methods for general applications has concentrated on Hartree-Fock (HF) based pair theories, which rely on the rapid convergence of the coupled-cluster hierarchy to the full configuration interaction limit. The essential features of these methods are manifest at the second-order Møller-Plesset (MP2) level of theory.

The two prominent explicitly correlated pair methods in the current literature are the Gaussian-type geminal (GTG) and R12 theories, which arose from two alternative strategies

for incorporating explicitly correlated geminal basis functions in the representation of the first-order pair functions $\tilde{u}_{ij}(1,2)$. Although the original MP2-GTG (Refs. 8 and 9) and MP2-R12 (Ref. 10) theories differed significantly, subsequent developments in both methods have blurred the distinctions. In particular, the MP2-GTG method of Persson and Taylor[11–13] and the recent F12 variants of the MP2-R12 method[14–18] employ the same choice of explicitly correlated GTG basis functions:

$$|\tilde{u}_{ij}\rangle = \hat{Q}_{12}|u_{ij}\rangle, \tag{1}$$

$$|u_{ij}\rangle = \sum_{ab} t_{ij}^{ab}|ab\rangle + \sum_{pq,\nu} c_{ij}^{pq,\nu} e^{-\gamma_\nu r_{12}^2}|pq\rangle. \tag{2}$$

Here and throughout we use the notation $i,j,\dots$ for occupied and $a,b,\dots$ for virtual canonical HF orbitals. Arbitrary HF orbital (spanned by the finite HF basis) sets are denoted using $p,q,\dots$. The projector $\hat{Q}_{12}$ enforces strong orthogonality (SO) between the pair functions $\tilde{u}_{ij}(1,2)$ and the set of occupied orbitals, which is necessary to retain the separability of the MP2 expressions into decoupled pair equations:

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2), \quad \hat{O} = \sum_i |i\rangle\langle i|. \tag{3}$$

We consider the GTG basis functions of Eq. (2) to be superior to the linear-r_{12} geminal functions of the original MP2-R12 method, being damped at long range and containing sufficient flexibility to adapt to the shape of the Coulomb hole for intermediate values of r_{12}. Furthermore, the above GTGs yield high accuracy without the need for optimizing the nonlinear parameters and are therefore also preferable to the floating GTGs of the original MP2-GTG method.

Only two primary distinctions remain between MP2-F12 and Persson and Taylor's MP2-GTG. In the MP2-GTG

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method, matrix elements involving three-electron integrals are evaluated analytically and four-electron integration is avoided through the use of the weak orthogonality (WO) functional.[9] In the MP2-F12 method, the usual SO Hylleraas functional is employed and three- and four-electron integrals are approximated by inserting an approximate resolution of the identity (RI) and assuming the generalized Brillouin condition (GBC).[10,19] Further differences, related to the extent of the sum over pq in Eq. (2) or whether contracted or decontracted GTG sets are used, may be regarded as secondary.

Recent calculations by Dahle *et al.* have revealed that the MP2-GTG method appears to perform surprisingly poorly.[13] For example, using an aug-cc-pCVDZ basis and a decontracted set of nine GTGs in combination with occupied orbital products [restricting the sum over pq in Eq. (2) to kl only] yields a value of -333.1 mE_h for the correlation energy of Ne. The corresponding MP2-F12 value, using a single contraction of the same nine GTGs, is -380.6 mE_h and the basis set limit is -388.1 mE_h.[20] Furthermore, Valeev has demonstrated that the MP2-F12 values lower upon decontraction, as one would expect.[21] Due to the remarkable discrepancies identified by Dahle *et al.* we were motivated to reexamine the approximations in the MP2-GTG and MP2-F12 methods. Our investigations show that the discrepancies result from the poor performance of the MP2-GTG method, rather than from the deceptively good performance of the MP2-F12 method. The deficiency can be traced to the inability of the kl GTGs of Eq. (2) to form strongly orthogonal pairs, a property that is implicitly assumed when the WO functional is used. In this article we propose an improved WO functional, based on the concept of almost orthogonal geminals.[22] MP2-GTG calculations using this new functional yield results of similar quality to the MP2-F12 method while retaining the same computational requirements as the original WO functional.

In Sec. II we discuss the SO and WO MP2 functionals and present our improved WO functional. In Sec. III we give the details of our implementation of the WO functionals within the framework of the RI approximation. The discrepancy between the MP2-GTG method of Persson and Taylor and the MP2-F12 method occurs even for He and H_2 and in Sec. V we present illustrative calculations on these systems. We show that the RI error in the MP2-F12 method is completely negligible when aiming for an accuracy of 95%-98% in the total correlation energy and we present our analysis of the poor performance of Persson and Taylor's MP2-GTG method. We further demonstrate that the MP2-GTG method is greatly improved when our new WO functional is used and present results for the Ne atom.

II. WEAK ORTHOGONALITY FUNCTIONALS

A geminal function $u_I(1,2)$ is said to be strongly orthogonal to geminal $u_J(1,2)$ if, for any permutation of electron coordinates, they are one-electron orthogonal:

$$\langle u_I(1,2)|u_J(1,3)\rangle_1 = 0. \tag{4}$$

The geminal functions are said to be almost orthogonal if they are two-electron orthogonal:[22]

$$\langle u_I(1,2)|u_J(1,2)\rangle = 0. \tag{5}$$

Note that if Eq. (4) is satisfied, then Eq. (5) is also true, but not vice versa. Use of the SO condition in pair theories greatly simplifies the working equations in a manner similar to the Slater-Condon rules.[23] In MP2 methods SO is imposed between the first-order pair functions and the set of occupied pairs. Equation (5) is then simply the requirement for intermediate normalization of the first-order wave function. Following Arai[24] and expanding an arbitrary geminal function in terms of a complete set of orthogonal one-particle functions (spin orbitals) φ_κ:

$$u_I(1,2) = \sum_{\kappa\lambda} c^I_{\kappa\lambda} \varphi_\kappa(1)\varphi_\lambda(2), \tag{6}$$

it is obvious that intermediate normalization is equivalent to requiring that the coefficients for the occupied pairs vanish. The fulfillment of the SO condition in Eq. (4) additionally requires that the first-order pair functions do not contain any contributions from singly excited pairs (which we define here as pairs with one occupied HF spin orbital). The SO projector of Eq. (3) projects out exactly these components of the explicitly correlated geminal basis functions. Use of the SO projector in the MP2 Hylleraas functional permits the direct optimization of the unprojected first-order pair functions $u_{ij}(1,2)$ to obtain the associated MP2 pair energies:

$$^{SO}F[u_{ij}] = \langle u_{ij}|\hat{Q}_{12}(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)\hat{Q}_{12}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12}r_{12}^{-1}|ij\rangle, \tag{7}$$

where $\hat{f}_{12} = \hat{f}_1 + \hat{f}_2$. In the MP2-GTG method, the direct computation of the numerous four-electron integrals that arise presented a serious obstacle to molecular applications. The WO functional was proposed to circumvent this problem:[9]

$$^{WO}F[u_{ij}] = \langle u_{ij}|\hat{f}_{12} - \varepsilon_i - \varepsilon_j|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12}r_{12}^{-1}|ij\rangle$$
$$+ [\tfrac{1}{2}(\varepsilon_i + \varepsilon_j - 2\varepsilon_1) + \eta]\langle u_{ij}|\hat{O}_1 + \hat{O}_2|u_{ij}\rangle, \tag{8}$$

where ε_1 is the lowest occupied orbital eigenvalue. In this work we propose a new WO functional: The SO projector may be partitioned as

$$\hat{Q}_{12} = \hat{P}_{12} - \hat{O}_1(1 - \hat{P}_2) - (1 - \hat{P}_1)\hat{O}_2, \tag{9}$$

with

$$\hat{P}_{12} = 1 - \hat{O}_1\hat{O}_2 - \hat{O}_1\hat{V}_2 - \hat{V}_1\hat{O}_2, \quad \hat{P} = \sum_p |p\rangle\langle p|,$$

$$\hat{V} = \sum_a |a\rangle\langle a|. \tag{10}$$

Insertion into Eq. (7) and replacing $\hat{f}_\tau\hat{O}_\tau$ with $(\varepsilon_1 - \eta)\hat{O}_\tau$ and $\hat{f}_\tau(1 - \hat{P}_\tau)$ with $\frac{1}{2}(\varepsilon_i + \varepsilon_j)(1 - \hat{P}_\tau)$ for $\tau = 1,2$ yields

$$^{IO}F[u_{ij}] = \langle u_{ij}|\hat{P}_{12}(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)\hat{P}_{12}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12}r_{12}^{-1}|ij\rangle$$
$$+ [\tfrac{1}{2}(\varepsilon_i + \varepsilon_j - 2\varepsilon_1) + \eta]\langle u_{ij}|\hat{O}_1(1 - \hat{P}_2)$$
$$+ \hat{O}_2(1 - \hat{P}_1)|u_{ij}\rangle. \tag{11}$$

This is equivalent to replacing u_{ij} with $\hat{P}_{12}u_{ij}$ in the WO

functional in Eq. (8). No four-electron integrals arise and the nonstrongly orthogonal components of the geminal pair function that enter the Fock matrix are only partially cancelled by the penalty function. For any positive η, both functionals provide a strict upper bound to the MP2 correlation energy when given exact HF orbitals. The tightness of the bound depends on the ability of the chosen geminal basis to form strongly orthogonal pairs and in the limit of a complete geminal basis, the pair function satisfies the SO condition and the correct MP2 limit is obtained. In our new functional, however, the condition for almost orthogonality (AO) is explicitly satisfied and the SO-violating singles within the (finite) HF orbital basis are also projected out. The only SO-violating components of the explicitly correlated geminals that enter the Fock matrix are those that correspond to single replacements outside the space of the HF basis. The geminal basis need only be flexible enough to zero these terms. Furthermore, the corresponding SO-violating contributions to the Fock matrix are expected to be small and are in fact zero within the GBC approximation (under the GBC approximation $\langle \phi_i|\hat{f}|\phi_\alpha\rangle = 0$, where $\langle \phi_p|\phi_\alpha\rangle = 0$). We will refer to this functional as the intermediate orthogonality (IO) functional.

For a given GTG basis the computational expense of using the IO functional is very similar to that of using the WO functional since the same number of three-electron integrals is required for the two functionals. One might also consider an AO functional as an alternative to the IO functional, where u_{ij} is replaced with $\hat{O}_{12}u_{ij}$ in Eq. (8):

$$^{AO}F[u_{ij}] = \langle u_{ij}|\hat{O}_{12}(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)\hat{O}_{12}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12}r_{12}^{-1}|ij\rangle$$
$$+ [\tfrac{1}{2}(\varepsilon_i + \varepsilon_j - 2\varepsilon_1) + \eta]\langle u_{ij}|\hat{O}_1 + \hat{O}_2$$
$$- 2\hat{O}_1\hat{O}_2|u_{ij}\rangle, \tag{12}$$

with $\hat{O}_{12} = 1 - \hat{O}_1\hat{O}_2$. AO is explicitly enforced and the principal SO-violating terms that enter the Fock matrix correspond to terms that are neglected if the extended Brillouin condition (EBC) is assumed ($\langle \phi_a|\hat{f}|\phi_\alpha\rangle = 0$), which are somewhat larger than the GBC terms that enter the IO Fock matrix. The performance of this functional is therefore expected to be worse than the IO functional, but nonetheless a significant improvement over the WO method. The AO functional is slightly cheaper than the IO functional since only occupied orbitals enter the projection operators, which would be advantageous in the effort to combine explicitly correlated wave functions with local methods.[12,25,26] We have not pursued the AO functional in this work.

III. COMPUTER IMPLEMENTATION

We have implemented the WO and IO functionals within the R12 framework using the RI approximation to evaluate the three-electron integrals. In this work we use the geminal functions of Eq. (2) and restrict the sum over pq to kl. We write the unprojected first-order pair function as

$$|u_{ij}\rangle = |v_{ij}\rangle + |w_{ij}\rangle, \tag{13}$$

$$|v_{ij}\rangle = \sum_{ab} t_{ij}^{ab}|ab\rangle, \tag{14}$$

$$|w_{ij}\rangle = (1 - \hat{V}_1\hat{V}_2)\sum_{kl}\sum_{\nu} c_{ij}^{kl,\nu}f_\nu(r_{12})|kl\rangle. \tag{15}$$

An additional projector has been inserted to enforce almost orthogonality between v_{ij} and w_{ij}, which minimizes the coupling in the MP2 equations but does not affect the result. The MP2 energy may be evaluated using the method described in Ref. 19. All that is needed are the spin free matrix elements

$$V_{kl\nu}^{ij} = \langle \phi_k\phi_l|f_\nu(1 - \hat{V}_1\hat{V}_2)(1 - \hat{O}_1)(1 - \hat{O}_2)r_{12}^{-1}|\phi_i\phi_j\rangle, \tag{16}$$

$$C_{kl\nu,ab}^{ij} = \langle \phi_k\phi_l|f_\nu(1 - \hat{V}_1\hat{V}_2)(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)|\phi_a\phi_b\rangle, \tag{17}$$

$$^{WO}B_{kl\nu,mn\mu}^{ij} = \langle \phi_k\phi_l|f_\nu(1 - \hat{V}_1\hat{V}_2)(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)$$
$$\times (1 - \hat{V}_1\hat{V}_2)f_\mu|\phi_m\phi_n\rangle + \Delta_{ij}\langle \phi_k\phi_l|f_\nu$$
$$\times (\hat{O}_1 + \hat{O}_2)f_\mu|\phi_m\phi_n\rangle, \tag{18}$$

$$^{IO}B_{kl\nu,mn\mu}^{ij} = \langle \phi_k\phi_l|f_\nu(1 - \hat{P}_1\hat{P}_2)(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)$$
$$\times (1 - \hat{P}_1\hat{P}_2)f_\mu|\phi_m\phi_n\rangle + \Delta_{ij}\langle \phi_k\phi_l|f_\nu$$
$$\times (\hat{O}_1(1 - \hat{P}_2) + \hat{O}_2(1 - \hat{P}_1))f_\mu|\phi_m\phi_n\rangle, \tag{19}$$

where $\Delta_{ij} = \tfrac{1}{2}(\varepsilon_i + \varepsilon_j - 2\varepsilon_1) + \eta$. The **V** matrix is identical to that of *Ansatz* 3 for the MP2-F12 method:[27,28]

$$V_{kl\nu}^{ij} = s_{kl\nu}^{ij} - \sum_{pq} r_{kl\nu}^{pq} g_{pq}^{ij} - \sum_{p'q} r_{kl\nu}^{p'q} g_{p'q}^{ij} - \sum_{pq'} r_{kl\nu}^{pq'} g_{pq'}^{ij}. \tag{20}$$

We use the complementary auxiliary basis set (CABS) method for the RI approximation,[27] and have introduced the indices $p', q', \ldots$ to denote the orthonormal orbitals in the auxiliary basis set, which are also orthogonal to the orbital basis. Introducing the indices $p'', q'', \ldots$ to denote orbitals contained in the union of the finite and complementary auxiliary basis sets, the two-electron integrals have the usual definitions:

$$s_{p''q''\nu}^{r''s''} = \langle \phi_{p''}\phi_{q''}|f_\nu r_{12}^{-1}|\phi_{r''}\phi_{s''}\rangle, \tag{21}$$

$$r_{p''q''\nu}^{r''s''} = \langle \phi_{p''}\phi_{q''}|f_\nu|\phi_{r''}\phi_{s''}\rangle, \tag{22}$$

$$g_{p''q''}^{r''s''} = \langle \phi_{p''}\phi_{q''}|r_{12}^{-1}|\phi_{r''}\phi_{s''}\rangle. \tag{23}$$

The **C** matrix is also identical to that of *Ansatz* 3 and we use approximation B, where we do not neglect the exchange commutator integrals:

$$C_{kl\nu,ab}^{ij} = t_{kl\nu}^{\dagger ab} - (\varepsilon_a + \varepsilon_b - \varepsilon_k - \varepsilon_l)r_{kl\nu}^{ab} + K_k^{p''}r_{p''l\nu}^{ab} - r_{kl\nu}^{p''b}K_{p''}^a$$
$$+ K_l^{q''}r_{kq''\nu}^{ab} - r_{kl\nu}^{aq''}K_{q''}^b. \tag{24}$$

When computed in this way, C is the same for all pairs ij. We have used the definitions

$$t_{p''q''}^{r''s''\mu} = \langle \phi_{p''}\phi_{q''}|[\hat{T}_1 + \hat{T}_2, f_\mu]|\phi_{r''}\phi_{s''}\rangle, \tag{25}$$

$$K^{q''}_{p''} = \langle \phi_{p''} | \hat{K} | \phi_{q''} \rangle. \tag{26}$$

For the WO functional, the **B** matrix is easily computed via the usual techniques of the MP2-F12 method. Using similar notation to Ref. 19, we have

$$
\begin{aligned}
{}^{\mathrm{WO}}B^{ij}_{kl\nu,mn\mu} &= \tfrac{1}{2}(T_{kl\nu,mn\mu} + T_{mn\mu,kl\nu}) - \tfrac{1}{2}(Y_{kl\nu,mn\mu} \\
&\quad + Y_{mn\mu,kl\nu}) + \tfrac{1}{2}(\varepsilon_k + \varepsilon_l + \varepsilon_m + \varepsilon_n - 2\varepsilon_i \\
&\quad - 2\varepsilon_j)X_{kl\nu,mn\mu} + \tfrac{1}{2}(Q_{kl\nu,mn\mu} + Q_{mn\mu,kl\nu}) \\
&\quad - \tfrac{1}{2}(P_{kl\nu,mn\mu} + P_{mn\mu,kl\nu}) + \Delta_{ij}O_{kl\nu,mn\mu}, \tag{27}
\end{aligned}
$$

with

$$T_{kl\nu,mn\mu} = z^{mn\mu}_{kl\nu} - r^{ab}_{kl\nu} t^{mn\mu}_{ab}, \tag{28}$$

$$X_{kl\nu,mn\mu} = x^{mn\mu}_{kl\nu} - r^{ab}_{kl\nu} r^{mn\mu}_{ab}, \tag{29}$$

$$Y_{kl\nu,mn\mu} = c^{ab}_{kl\nu} r^{mn\mu}_{ab}, \tag{30}$$

$$Q_{kl\nu,mn\mu} = X_{kl\nu,p''n\mu} K^{m}_{p''} + X_{kl\nu,mq''\nu} K^{n}_{q''}, \tag{31}$$

$$P_{kl\nu,mn\mu} = r^{p''q''}_{kl\nu} p^{mn\mu}_{p''q''} - r^{ab}_{kl\nu} p^{mn\mu}_{ab}, \tag{32}$$

$$O_{kl\nu,mn\mu} = r^{p''o}_{kl\nu} r^{mn\mu}_{p''o} + r^{oq''}_{kl\nu} r^{mn\mu}_{oq''}, \tag{33}$$

and

$$z^{mn\mu}_{kl\nu} = \tfrac{1}{2}\langle \phi_k \phi_l | [f_\nu,[\hat{T}_1 + \hat{T}_2, f_\mu]] | \phi_m \phi_n \rangle, \tag{34}$$

$$x^{mn\mu}_{kl\nu} = \langle \phi_k \phi_l | f_\nu f_\mu | \phi_m \phi_n \rangle, \tag{35}$$

$$c^{ab}_{kl\nu} = C^{ij}_{kl\nu,ab}, \tag{36}$$

$$p^{mn\mu}_{p''q''} = K^{r''}_{p''} r^{mn\mu}_{r''q''} + K^{s''}_{q''} r^{mn\mu}_{p''s''}. \tag{37}$$

In the derivation of the above expressions we have assumed the GBC, but not the EBC. The analogous definitions of the components of $^{\mathrm{IO}}$**B** are

$$T_{kl\nu,mn\mu} = z^{mn\mu}_{kl\nu} - r^{pq}_{kl\nu} t^{mn\mu}_{pq}, \tag{38}$$

$$X_{kl\nu,mn\mu} = x^{mn\mu}_{kl\nu} - r^{pq}_{kl\nu} r^{mn\mu}_{pq}, \tag{39}$$

$$Y_{kl\nu,mn\mu} = c^{pq}_{kl\nu} r^{mn\mu}_{pq}, \tag{40}$$

$$Q_{kl\nu,mn\mu} = X_{kl\nu,p''n\mu} K^{m}_{p''} + X_{kl\nu,mq''\nu} K^{n}_{q''}, \tag{41}$$

$$P_{kl\nu,mn\mu} = r^{p''q''}_{kl\nu} p^{mn\mu}_{p''q''} - r^{pq}_{kl\nu} p^{mn\mu}_{pq}, \tag{42}$$

$$O_{kl\nu,mn\mu} = r^{p'o}_{kl\nu} r^{mn\mu}_{p'o} + r^{oq'}_{kl\nu} r^{mn\mu}_{oq'}. \tag{43}$$

We note in passing that, in the absence of a complementary auxiliary basis ($\{p'\} = \varnothing$), the IO penalty function contribution disappears and $(1 - \hat{V}_1 \hat{V}_2)(1 - \hat{O}_1)(1 - \hat{O}_2)$ becomes $(1 - \hat{P}_1 \hat{P}_2)$. If we also assume the EBC, the Y terms vanish and the IO equations reduce to those of the original MP2-R12 method. We have implemented the WO and IO equations

TABLE I. The acronyms and their meanings (see Sec. IV).

Method	$F[u_{ij}]$	$f(r_{12})$	$|pq\rangle$	RI
MP2-R12	SO	r_{12}	kl	Yes
SO-MP2-F12-kl	SO	GTG	kl	Yes
IO-MP2-F12-kl	IO	GTG	kl	Yes
WO-MP2-F12-kl	WO	GTG	kl	Yes
WO-MP2-GTG-kl	WO	GTG	kl	No
WO-MP2-GTG-kq	WO	GTG	kq	No
WO-MP2-GTG-pq	WO	GTG	pq	No

within the CC2-R12 module[29,30] of the TURBOMOLE program package, which utilizes the resolution of the identity to approximate four-center integrals as sums of products of three-center integrals. For the GTG integrals, the density fitting formulas of Refs. 31 and 32 are used. The t commutator integrals are not computed exactly but are approximated by insertion of the RI.[33] Our current program is limited to the case where the same contracted set of GTGs is used for all occupied orbital pairs: $c^{kl,\nu}_{ij} = c^{kl}_{ij} c^{\nu}$. We optimize the set of coefficients c^{ν} numerically, which, for two-electron systems, is equivalent to using a fully decontracted set.

IV. COMPUTATIONAL DETAILS AND NOMENCLATURE

In this work we report MP2 correlation energies computed using the cc-pVXZ and aug-cc-pVXZ basis sets for X=D, T, Q and 5.[34,35] Unless otherwise stated, we use a level shift parameter $\eta = 0.1$ for the penalty function. In all calculations we use an uncontracted, even tempered set of nine GTGs with exponents ranging from 3^{-2} to 3^{6}. These specifications are identical to those used by Dahle *et al.* in Ref. 13. For our calculations on He and H_2 we use an uncontracted aug-cc-pV6Z basis as the CABS for the RI approximation for the evaluation of the three- and four-electron integrals. For the RI approximation used to evaluate the four-center integrals as linear combinations of three-center integrals, we use the aug-cc-pV6Z auxiliary basis of Hättig.[36] For our calculations on Ne, we use the spd functions of the aug-cc-pCVTZ orbital basis,[37] an uncontracted aug-cc-pCV5Z CABS basis set, and an $18s15p13d11f9g7h5i3k$ basis for the density fitting. The CABS and density fitting basis sets are sufficiently complete for an accuracy of 0.01 mE_{h} in our correlation energies.

To distinguish between our new mixed methods and the MP2-F12 and MP2-GTG methods, we introduce the prefix SO, IO, or WO to denote the functional used to evaluate the pair functions [Eqs. (7), (11), and (8), respectively] and use F12 or GTG to indicate the method of evaluating the many-electron integrals (RI or exact). The method definition is completed by the specification of the extent of the sum over pq in Eq. (2) defining the geminal basis functions, which we add as a postfix. The resulting plethora of acronyms is summarized in Table I.

V. ILLUSTRATIVE CALCULATIONS

By comparing the results of our SO-MP2-F12-kl and WO-MP2-F12-kl with the WO-MP2-GTG-kl results of Dahle *et al.*, we are able to directly and separately evaluate

TABLE II. Helium MP2 correlation energies (in $-mE_\text{h}$, exact value is -37.38 mE_h, Ref. 38). The same nine GTGs are used in every explicitly correlated method.

Basis	F12 (RI)			GTG (exact)		
	SO-kl	IO-kl	WO-kl	WO-kl	WO-kq	WO-pq
cc-pVDZ	36.86	36.53	33.75	33.75	36.71	36.95
cc-pVTZ	37.18	37.03	35.87	35.87	37.18	37.30
cc-pVQZ	37.32	37.29	36.77	36.77	37.33	37.36
cc-pV5Z	37.36	37.35	37.09	37.09	37.36	37.37
aug-cc-pVDZ	36.99	36.84	35.23	35.23	37.17	37.29
aug-cc-pVTZ	37.22	37.12	36.52	36.52	37.26	37.36
aug-cc-pVQZ	37.34	37.31	37.06	37.06	37.35	37.38
aug-cc-pV5Z	37.36	37.36	37.23	37.23	37.37	⋯

the consequences of using the RI approximation and of using the WO functional. The MP2 correlation energies for these methods, with full optimization of the nine coefficients $c_{ij}^{kl,\nu}$, are presented in Table II for helium and Table III for molecular hydrogen. The combined error of the RI and GBC approximations is given by the difference between the WO-MP2-F12-kl and WO-MP2-GTG-kl values and is at most 0.05 mE_h, which, in every case, is completely negligible with respect to the remaining deviation from the basis set limit. The effect of using the WO functional in place of the SO functional is seen by comparing the WO-MP2-F12-kl and SO-MP2-F12-kl values and is orders of magnitude larger. For helium, with the cc-pVDZ basis, the percentage of the correlation energy recovered reduces from 99% for the SO functional to 90% for the WO functional. The source of the under performance of the MP2-GTG-kl method of Persson and Taylor is therefore connected to the WO functional.

Indeed, the size of the RI error in MP2-F12 calculations can always be reduced by increasing the CABS to saturate orbital space. Even for modest CABS, the RI error is typically less than 1% of the correlation energy for general molecular systems.[39] The magnitude of the GBC error has also been computed for a number of molecular systems and is typically less than a fraction of a percent of the total correlation energy for double-ζ or larger orbital basis sets.[16,28,40] For most practical applications, where an accuracy in the total correlation energy of 98% is sufficient, it is not neces-

TABLE III. Molecular hydrogen MP2 correlation energies (in $-mE_\text{h}$, exact value is -34.25 mE_h, Ref. 13). The same nine GTGs are used in every explicitly correlated method.

Basis	F12 (RI)			GTG (exact)		
	SO-kl	IO-kl	WO-kl	WO-kl	WO-kq	WO-pq
cc-pVDZ	33.93	33.45	31.58	31.63	33.58	33.80
cc-pVTZ	34.19	34.03	33.47	33.48	34.15	34.23
cc-pVQZ	34.23	34.21	33.99	34.00	34.23	34.24
cc-pV5Z	34.24	34.24	34.14	⋯	⋯	⋯
aug-cc-pVDZ	34.00	33.53	32.71	32.74	33.88	34.05
aug-cc-pVTZ	34.21	34.14	33.82	33.82	34.21	34.25
aug-cc-pVQZ	34.24	34.23	34.14	34.14	34.24	⋯
aug-cc-pV5Z	34.24	34.24	34.21	⋯	⋯	⋯

sary to evaluate the three-electron integrals exactly. The enormous additional computational expense involved is thus only warranted for benchmark calculations.

We have proceeded to investigate the reasons for the poor performance of the WO functional. When using the WO functional, one implicitly assumes that the geminal basis contains sufficient flexibility to form pair functions that are strongly orthogonal to the occupied orbitals. For the GTGs employed by Persson and Taylor, SO requires that

$$\langle \phi_m(1)\phi_{r''}(3)|\sum_{pq\nu} c_{ij}^{pq,\nu}e^{-\gamma_\nu r_{12}^2}|\phi_p(1)\phi_q(2)\rangle_1 = 0 \qquad (44)$$

for all occupied orbitals ϕ_m and arbitrary $\phi_{r''}$. Individually, none of the GTG basis functions satisfies this condition (since $\gamma_\nu \neq 0$). For a given GTG to contribute to u_{ij} without violating SO, it must always be accompanied by terms that remove the nonstrongly orthogonal components

$$e^{-\gamma_\nu r_{12}^2}|\phi_p(1)\phi_q(2)\rangle - \sum_m |\phi_m(1)\rangle$$
$$\times \langle \phi_m(1)|e^{-\gamma_\nu r_{12}^2}|\phi_p(1)\phi_q(2)\rangle_1, \qquad (45)$$

which may be written as

$$e^{-\gamma_\nu r_{12}^2}|\phi_p(1)\phi_q(2)\rangle - \sum_m |\phi_m(1)\tilde{\phi}_q(2)\rangle. \qquad (46)$$

This is possible if each component of the second term, which are all separable, can be represented exactly by the coupled GTG basis functions:

$$|\phi_m(1)\tilde{\phi}_q(2)\rangle = \sum_{rs\nu} d_{ij}^{rs,\nu}e^{-\gamma_\nu r_{12}^2}|\phi_r(1)\phi_s(2)\rangle. \qquad (47)$$

The equality is only true in the limit that rs span the complete basis [the functions $\exp(-\gamma_\nu r_{12}^2)$ do not even form a complete set of pair functions of S symmetry]. The convergence with orbital basis can be expected to be as slow as the representation of coupled functions in a basis of separable functions. Although the geminal basis functions in Eq. (2) are well chosen from the point of view of describing electron correlation, they are clearly incapable of satisfying the SO constraint. Moreover, similar arguments show that they are even incapable of satisfying AO. The resulting SO violation is particularly large when the sum over pq is restricted to kl. The SO-violating components of the geminal functions result in too large B matrix elements, primarily through the terms that violate AO, which leads to too small correlation energies.

The cusp conditions suggest that the most efficient way to describe the Coulomb hole is through the diagonal excitations $|ij\rangle \rightarrow f(r_{12})|ij\rangle$. In Fig. 1 we compare the correlation factors $f(r_{12}) = \sum_\nu c^\nu f_\nu(r_{12})$ from SO-, IO-, and WO-MP2-F12-kl calculations on helium using an aug-cc-pVTZ orbital basis. The functions have been normalized such that $\int r^2 f(r)^2 dr = 1$. The shape of the SO correlation factor follows the average short-range r_{12} dependence of the Coulomb hole $\Psi - \Psi_\text{HF}$.[17] In fact, it is closely fitted by $\exp(-0.8r_{12})$ over the range $0 \rightarrow 2a_0$ and is in good accord with the optimum CCSD-F12 correlation factor for helium computed in Ref. 17. The WO correlation factor, on the other hand, contains
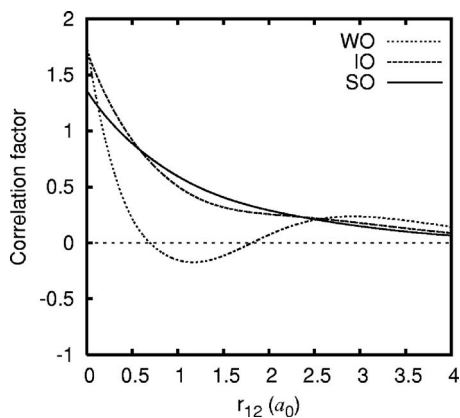
FIG. 1. The normalized correlation factor for He computed using the SO, IO, and WO functionals ($\eta = 0.1$) and an aug-cc-pVTZ orbital basis set.
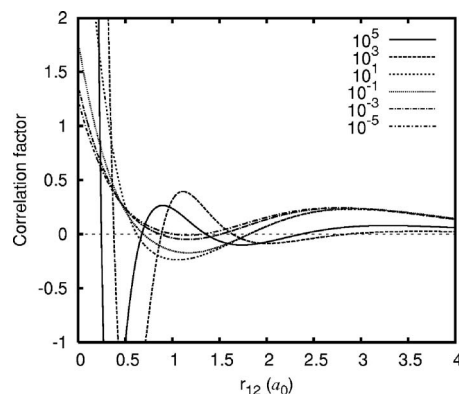

FIG. 2. Normalized WO-MP2-F12-*kl*/aug-cc-pVTZ correlation factors for He computed with $\eta = 10^{-5}, 10^{-3}, \dots, 10^{5}$.

nodes that have nothing to do with the physics of electron correlation in helium. The unprojected basis functions $f(r_{12})|ij\rangle$ violate SO. For two-electron systems, the only available flexibility to reduce the SO violation is in the coordinate r_{12} and nodes appear to reduce the one-electron expectation value. In Table IV we present WO-MP2-F12-*kl* and IO-MP2-F12-*kl* He correlation energies for several values of the level shift parameter $\eta = 10^{-5}, 10^{-4}, \dots, 10^{5}$ using an aug-cc-pVTZ orbital basis. We also tabulate the values of the penalty function $\Delta_{ij}\langle u_{ij}|\hat{O}_1 + \hat{O}_2|u_{ij}\rangle$ and pSO values, which are a measure of the non-SO character of the pair functions,

$$ \text{pSO} = -\log_{10}(\langle w_{ij}|(\hat{O}_1 + \hat{O}_2 - \hat{O}_1\hat{O}_2)|w_{ij}\rangle / \langle w_{ij}|w_{ij}\rangle). \tag{48} $$

The corresponding normalized correlation factors for the WO calculations are plotted in Fig. 2. The low pSO values in Table IV reflect the inability of the geminal basis to form pair functions SO to the occupied space. As η increases, the number of nodes in the WO correlation factor increases and the pSO values correspondingly increase. However, even for $\eta \rightarrow 0$ (and thus $\Delta_{ij} \rightarrow 0$ for the helium ground state), the WO functional gives a poor prediction of the correlation energy

TABLE IV. WO- and IO-MP2-F12-*kl* correlation energies, energy penalties, and pSO values of He computed using an aug-cc-pVTZ orbital basis and various vales of η. Energies are in $-mE_{\text{h}}$.

$\log_{10}\eta$	WO functional			IO functional		
	E	Penalty	pSO	E	Penalty	pSO
−5	36.53	0.00	−0.86	37.12	0.00	2.98
−4	36.53	0.00	−0.82	37.12	0.00	3.00
−3	36.52	0.00	−0.69	37.12	0.00	3.01
−2	36.52	0.00	−0.20	37.12	0.00	3.02
−1	36.52	0.01	0.06	37.12	0.00	3.02
0	36.47	0.05	0.14	37.12	0.00	3.04
1	36.24	0.15	0.73	37.10	0.02	3.57
2	35.88	0.15	2.60	37.04	0.04	4.94
3	35.48	0.21	4.06	36.86	0.14	5.70
4	34.80	0.36	4.75	36.45	0.19	7.27
5	34.09	0.20	6.03	35.83	0.32	8.43

and the shape of the correlation factor differs significantly from that of the SO functional.

For many-electron systems, the number of *kl* GTG basis functions increases quadratically with the number of electrons, while the number of SO constraints per pair function grows only linearly. However, the aforementioned results indicate that this additional flexibility is still insufficient for Ne with ten electrons. Dahle *et al.* reported calculations using the *kq* and *pq* Ansätze and their results for He and H_2 are presented in Tables II and III. The inclusion of GTGs with additional nodal structure in r_1 and r_2 independently has a large effect on the correlation energy since these functions are better suited for the expansion in Eq. (47), leaving the dominant diagonal excitations free to adopt a more physical form. WO-MP2-GTG-*kq* correlation energies are typically of equivalent quality to SO-MP2-F12-*kl* values.

In this work we propose an alternative solution that does not require extended geminal basis sets and also avoids the four-electron integrals present in the SO functional, namely the IO functional. From Tables II and III it can be seen that the IO-MP2-F12-*kl* correlation energies are of similar quality to those of the SO functional. For helium with the cc-pVDZ basis, 98% of the basis set limit correlation energy is recovered, compared to 99% and 90% for the SO and WO functionals, respectively. The presence of the projection operator $\hat{P}_{12}$ in the IO geminal basis ensures that the pair functions satisfy AO to the occupied space, and also removes the SO-violating components that correspond to single excitations within the orbital basis. Indeed, the pSO values in Table IV show that the SO-violating terms are three orders of magnitude smaller in the IO functional than in the WO functional. More importantly, the contribution of the nonstrongly orthogonal components to the IO Fock matrix is very small and consequently there is only a slight adverse effect on the computed correlation energies. As a result the IO correlation energies are much more stable with respect to η and the correlation factor in Fig. 1 is similar to that of the SO functional. We also report that the shape of the WO correlation factor is rather sensitive to the orbital basis set, but the IO correlation factor converges to that of the SO functional.

We have performed SO-, IO-, and WO-MP2-F12-*kl* calculations on Ne using the aug-cc-pCVTZ(*spd*) orbital basis and the set of nine GTGs used by Dahle *et al.* and $\eta = 0.1$. In

TABLE V. SO-, IO-, and WO-MP2-F12-*kl*/aug-cc-pCVTZ(*spd*) correlation energies of Ne using different geminal contraction schemes. The basis set limit is -388.1 mE_h.

Functional	Geminal contraction		
	$c_{ij}^{kl}c^{\nu}$	$c_{ij}^{kl}c_{ij}^{\nu}$	$c_{ij}^{kl,\nu}$
SO	-384.45	-385.31	-385.54[a]
IO	-369.72	-373.30	⋯
WO	-345.33	-351.17	-353.91[b]

[a]Reference 41.
[b]Reference 13.

Table V we present results from three geminal contraction schemes: $c_{ij}^{kl}c^{\nu}$, $c_{ij}^{kl}c_{ij}^{\nu}$, and $c_{ij}^{kl,\nu}$. The WO and SO values using a fully decontracted geminal basis, $c_{ij}^{kl,\nu}$, are from the WO-MP2-GTG-*kl* value in Ref. 13 and the SO-MP2-F12-*kl* value of Ref. 41 based on the work of Ref. 21. For the SO functional we see that the energy gain upon decontraction is relatively small, in agreement with the work of Valeev.[21] Indeed, 99% of the correlation energy has been obtained using the c^{ν} contraction, which corresponds to a single correlation factor. For the IO functional, with a different correlation factor for each occupied pair, c_{ij}^{ν}, 96% of the correlation energy of Ne is recovered, compared to 90% for the WO functional.

As a final comment on the application of the WO and IO functionals to many-electron systems, we address the role of the penalty function. For the ground states of two-electron systems, $\Delta_{ij} = \eta$ and the values of the penalty function presented in Sec. V are small. For many-electron systems, the eigenvalue difference $\varepsilon_i + \varepsilon_j - 2\varepsilon_1$ is nonzero and, when η is small, this is the dominant contribution to Δ_{ij} for all but the innermost electron pair. Dahle *et al.* have investigated the sensitivity of the MP2-GTG values to the level shift parameter η and shown that a value of 0.1 appears to be stable. We simply interpret this as the regime where η is a negligible contribution to Δ_{ij}. The presence of ε_1 in the penalty function is concerning for the general applicability of the WO and IO methods. The penalty function not only breaks size consistency but also leads to an unbalanced treatment of core and valence electron pairs such that the penalty for the SO-violating terms in valence pairs is much larger than it is for that of core electron pairs. For heavy elements it will become very large indeed, which will greatly decrease the efficiency with which the valence-shell electron correlation is described, even in calculations where core correlation is neglected. This imbalance was realized shortly after the WO functional was proposed and the modified WO functional addresses this issue, but it does fix the problem of size inconsistency.[42] The improved penalty function of the modified WO functional may be straightforwardly applied to the IO and AO functionals.

VI. CONCLUSION

In this work we set out to investigate the source of the poor performance of the MP2-GTG method of Persson and Taylor compared to the MP2-F12 method. Our investigations conclusively demonstrate that when the WO is used, the efficient description of electron correlation is frustrated by the additional requirement that the unprojected pair functions are strongly orthogonal to the occupied orbitals. Although the floating GTG basis used in the original MP2-GTG method has sufficient flexibility to satisfy this requirement, the basis used by Persson and Taylor does not. We have introduced a modified WO functional, which we call the IO functional, that greatly relaxes this constraint without requiring the evaluation of four-electron integrals present in the SO functional. For a given GTG basis, the computational expense of the IO method is very similar to that of the WO method, but much less flexibility is required in the geminal basis for a given accuracy in the correlation energy. In particular, we avoid the complexity involved in optimizing the large number of nonlinear parameters and the associated numerical difficulty of near linear dependencies, which are major obstacles to the application of the original MP2-GTG method to larger systems.[43] We therefore recommend that the IO functional replace the WO functional in GTG calculations where three-electron integrals are evaluated exactly. Furthermore, we recommend that the GTG methods should only be used for benchmark calculations, aiming at more than 99% of the correlation energy. Use of the RI to approximately evaluate the three- and four-electron integrals that arise in the SO functional is much more efficient and the resulting accuracy is more than sufficient for general chemical applications.

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