Accurate quantum-chemical calculations using Gaussian-type geminal and Gaussian-type orbital basis sets: applications to atoms and diatomics

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We have implemented the use of mixed basis sets of Gaussian one- and two-electron (geminal) functions for the calculation of second-order Møller–Plesset (MP2) correlation energies. In this paper, we describe some aspects of this implementation, including different forms chosen for the pair functions. Computational results are presented for some closed-shell atoms and diatomics. Our calculations indicate that the method presented is capable of yielding highly accurate second-order correlation energies with rather modest Gaussian orbital basis sets, providing an alternative route to highly accurate wave functions. For the neon atom, the hydrogen molecule, and the hydrogen fluoride molecule, our calculations yield the most accurate MP2 energies published so far. A critical comparison is made with established MP2-R12 methods, revealing an erratic behaviour of some of these methods, even in large basis sets.

1. Introduction

An important limitation in most current treatments of electron correlation in molecules arises from the expansion of the wave function in products of one-electron basis functions. The convergence of such an expansion of the exact wave function and the associated correlation energy is very slow: even very large basis sets, comprising hundreds of functions of angular momentum up to $l = 6$, cannot recover more than 95–98% of the exact correlation energy. The practical consequence is that the best orbital-based many-particle treatments can predict thermochemical quantities even for small molecules to an accuracy of only 2 kcal mol^{-1} or worse, unless extrapolation schemes are used.

The difficulty with using products of one-electron functions to describe many-electron wave functions is the poor description of the latter when two electrons approach one another, say, to within less than 1 bohr and, in particular, of the two-electron cusp for coinciding electrons. A good illustration of the inadequacies of products of one-electron functions is a comparison of various basis-set calculations with the exact wave function for He, discussed, for instance, by Helgaker *et al.*[1] It must be emphasized that these inadequacies are independent both of the particular many-electron approach chosen for the parameterization of the orbital-product expansion and of the type of orbital functions used for this expansion. For example, the inadequacies are not a limitation of Gaussian-type orbitals (GTOs) compared with Slater-type orbitals (STOs) nor a limitation of particular types of GTO basis sets, although the details differ, depending on what particular wave-function model and one-electron basis set are used.

From a mathematical perspective, the most attractive alternative to orbital expansions is to employ functions that provide a better description of the wave function as electrons approach one another, which naturally leads to a basis of two-electron functions. The earliest example of such an explicitly correlated approach was that of Hylleraas, whose calculations on He represent the first accurate quantum-chemical calculations on a many-electron system. In his work, Hylleraas augmented the basis of one-electron functions with terms that contain the interelectronic distance r_{12} to any desired order.[2–4] The terms linear in r_{12}, in particular, are extremely effective in improving the convergence of an approximate wave function at very short interelectronic distances, since the cusp in the exact wave function behaves as r_{12} as the interelectronic distance tends to zero. Unfortunately, although such terms dramatically accelerate convergence, they are difficult to use in practical calculations because of the complicated many-electron integrals that arise over the basis. To solve this problem, Kutzelnigg and Klopper retained only terms linear in r_{12} and avoided the explicit integration over more than two electrons by invoking the resolution of identity (RI), thereby reducing the computational work to a tractable level.[5–7] These approximations become exact as the one-electron basis approaches completeness and the convergence of the energy contributions with the two-electron basis is much better than that of methods employing only one-electron functions—namely, $\left(l+\frac{1}{2}\right)^{-6}$ rather than $\left(l+\frac{1}{2}\right)^{-4}$. Their R12 approach has since been successfully used not only in second-order Møller–Plesset (MP2) perturbation theory but also in coupled-cluster and multireference averaged coupled-pair functional theories. For a recent review on R12 theory, see ref. 8.

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A different explicitly correlated approach has been developed by Szalewicz, Jeziorski and their coworkers.[9–13] Rather than augmenting the orbital-product basis with terms linear in r_{12}, they expand the two-electron pair functions directly in Gaussian-type geminals (GTGs), optimizing all nonlinear parameters. In MP2 theory, the need for integrals involving more than three electrons is avoided by the use of the weak-orthogonality (WO) functional in place of the rigorous strong-orthogonality (SO) functional. Nevertheless, certain three-electron integrals must be computed and so the resulting GTG method is more expensive than the method of Klopper and Kutzelnigg. An advantage, however, is that the computed pair energies are upper bounds to the true pair energies. Moreover, although GTGs do not describe the inner part of the Coulomb hole as well as linear r_{12} does, they are better suited to describing its overall shape.

Here we investigate, within the framework of MP2 theory, the GTO–GTG (GG) model, where the WO pair functions are expanded in both GTO products and GTGs. These GTGs may be given in alternative forms as shown below. A paper has already been published that describes some aspects of our MP2-GG approach within the context of local MP2 theory, containing some sample calculations on medium-sized molecules.[14] Our purpose here is different in that we focus on high accuracy in closed-shell atoms and diatomics.

2. Theory and implementation

In this section, we discuss first the calculation of the MP2 energy using modified Hylleraas functionals. Next, we present the wave-function ansatz employed in these functionals and discuss its optimization. Finally, we consider some aspects related to the implementation of the method.

2.1. The MP2 energy functional

In general, the first-order wave function $\Psi^{(1)}$ can be determined by minimization of the Hylleraas functional

$$F[\Psi] = \langle\Psi|H^{(0)} - E^{(0)}|\Psi\rangle + 2\langle\Psi|V - E^{(1)}|\Psi^{(0)}\rangle \qquad (1)$$

which is bounded from below by the second-order energy

$$F[\Psi] \geq E^{(2)}, \quad F[\Psi^{(1)}] = E^{(2)} = \langle\Psi^{(1)}|V|\Psi^{(0)}\rangle \qquad (2)$$

In the Møller–Plesset theory where $\Psi^{(0)}$ is the Hartree–Fock wave function, the second-order energy $E^{(2)}$ may be expressed in terms of the pair energies ε_{ij}^s

$$E^{(2)} = \sum_{i\geq j}\varepsilon_{ij}^1 + \sum_{i>j}\varepsilon_{ij}^3, \quad \varepsilon_{ij}^s = \frac{s}{1+\delta_{ij}}\langle Qu_{ij}^s|r_{12}^{-1}|\phi_{ij}^s\rangle \qquad (3)$$

where the associated pair functions u_{ij}^s are obtained by minimizing the functional

$$F_{ij}^s[u_{ij}^s] = \frac{s}{2(1+\delta_{ij})}[\langle Qu_{ij}^s|f(1)+f(2)-\varepsilon_i-\varepsilon_j|Qu_{ij}^s\rangle + 2\langle Qu_{ij}^s|r_{12}^{-1}|\phi_{ij}^s\rangle] \qquad (4)$$

In these expressions, $f(1)$ and $f(2)$ are the Fock operators of the two electrons, the ε_i are orbital energies, the ϕ_{ij}^s are singlet ($s = 1$) and triplet ($s = 3$) products of occupied molecular orbitals (MOs)

$$\phi_{ij}^s = \frac{1}{\sqrt{2}}[\varphi_i(1)\varphi_j(2) + (2-s)\varphi_j(1)\varphi_i(2)], \qquad (5)$$

and strong orthogonality is enforced by the projection operator

$$Q(1,2) = [1-p(1)][1-p(2)], \quad p = \sum_k |\varphi_k\rangle\langle\varphi_k| \qquad (6)$$

where the summation is over all occupied MOs φ_k. The evaluation of matrix elements over QfQ gives rise to three- and four-electron integrals, the latter of which can be avoided if the SO functional $F_{ij}^s[u_{ij}^s]$ is replaced by one of the WO functionals developed by Szalewicz and coworkers.[9–12] The simplest such functional takes the form

$$J_{ij}^s[u_{ij}^s] = \frac{s}{2(1+\delta_{ij})}[\langle u_{ij}^s|\tilde{f}_{ij}(1)+\tilde{f}_{ij}(2)-\varepsilon_i-\varepsilon_j|u_{ij}^s\rangle + 2\langle Qu_{ij}^s|r_{12}^{-1}|\phi_{ij}^s\rangle] \qquad (7)$$

We have introduced here the modified Fock operator $\tilde{f}_{ij} = f + \Delta_{ij}p$ where p is the projector onto the occupied MO space and Δ_{ij} is defined by $\Delta_{ij} = \frac{1}{2}(\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta$ with $\varepsilon_1 \leq \varepsilon_i$ and $\eta \geq 0$. The purpose of $\Delta_{ij}p$ is to shift the expectation value of $\tilde{f}_{ij}(1) + \tilde{f}_{ij}(2)$ by an amount proportional to the level-shift parameter η, thereby ensuring that the matrix element between the pair functions in eqn (7) is positive definite and that the minimum principle applies. The level-shift parameter η introduces a penalty that is large if the pair function overlaps with the occupied space. We monitor the degree of strong orthogonality by calculating

$$\chi_{ij}^{\mathrm{SO}} = \frac{\left\langle u_{ij}^s\middle|p(1)+p(2)\middle|u_{ij}^s\right\rangle}{\left\langle u_{ij}^s|u_{ij}^s\right\rangle}, \qquad (8)$$

which, if small, indicates a more strongly orthogonal pair function u_{ij}. In general, $J_{ij}^s[u] \geq F_{ij}^s[u]$ for $\eta > 0$, provided the Hartree–Fock equations have been solved exactly. Although the optimized energy depends on the arbitrary parameter η, this dependence is weak as shown in section 3.1.3.

2.2. Choice of pair functions

The pair functions used in our calculations are symmetric and antisymmetric spatial functions, multiplied by singlet and triplet spin functions, respectively. For a given pair of occupied MOs i and j, a traditional pair function may thus be written as

$$u_{ij}^s = \sum_{a\geq b}\phi_{ab}^s c_{ij,s}^{ab} \qquad (9)$$

where ϕ_{ab}^s is defined as in eqn (5) and the summation is over all pairs of unoccupied MOs (denoted by indices a and b). The symmetric form $s = 1$ and the antisymmetric form $s = 3$ of u_{ij}^s are to be combined with normalized two-electron singlet and triplet spin functions, respectively. To include a linear r_{12} term, Kutzelnigg and Klopper[5–7] proposed the ansatz

$$u_{ij}^s = \sum_{a\geq b}\phi_{ab}^s c_{ij,s}^{ab} + Q_0 r_{12}\phi_{ij}^s c_{ij,s}, \qquad (10)$$

later generalized by Klopper[15] to

$$u_{ij}^s = \sum_{a\geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{k\geq l} Q_0 r_{12} \phi_{kl}^s c_{ij,s}^{kl}, \qquad (11)$$

to ensure invariance to rotations among the occupied MOs. The projection operator

$$Q_0 = [1 - p_0(1)][1 - p_0(2)], \; p_0 = \sum_p |\varphi_p\rangle\langle\varphi_p| \qquad (12)$$

ensures an orthogonality even "stronger" than the strong orthogonality enforced by Q in eqn (12)—that is, not just to the occupied MOs but all MOs.

Persson and Taylor[16] suggested replacing the linear r_{12} term in eqn (10) by a linear combination of GTGs $g_{ij,v}^s$, each taken as a product of ϕ_{ij}^s and a Gaussian correlation factor (GCF) $\exp(-\gamma_v r_{12}^2)$ with a fixed exponent γ_v:

$$g_{ij,v}^s = \exp(-\gamma_v r_{12}^2)\phi_{ij}^s \qquad (13)$$

With such geminals, our pair-function ansatz becomes

$$u_{ij}^s = \sum_{a\geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_v g_{ij,v}^s c_{ij,s}^v. \qquad (14)$$

where the linear coefficients $c_{ij,s}^v$ are variationally optimized in the course of the MP2 calculation. In the present work, we consider the following three generalizations of this pair function: the GG0 pair-function ansatz, with a summation over all pairs of occupied MOs in the geminal part in analogy with eqn (11):

$$u_{ij}^s = \sum_{a\geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{k\geq l}\sum_v g_{kl,v}^s c_{ij,s}^{kl,v} \qquad (15)$$

the GG1 pair-function ansatz, where at least one of the MOs in the summation in the geminal part is an occupied MO:

$$u_{ij}^s = \sum_{a\geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{k,q}\sum_v g_{kq,v}^s c_{ij,s}^{kq,v} \qquad (16)$$

and the GG2 pair-function ansatz, where we sum over all pairs of MOs in the geminal part:

$$u_{ij}^s = \sum_{a\geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{p\geq q}\sum_v g_{pq,v}^s c_{ij,s}^{pq,v} \qquad (17)$$

In general, therefore, the GGn ansatz contains geminals $g_{pq,v}^s$ with up to n virtual MOs, (with n denoting the highest excitation level). To distinguish the orbital-variant ansatz eqn (14) from the orbital-invariant GG0 ansatz eqn (16), we shall refer to eqn (14) as the GG0′ ansatz. In section 3, we shall compare the performance of the different GGn pair functions.

In the GGn pair functions, it is possible to use dual basis sets, one for the virtual-orbital expansion and one for the geminal expansion, thereby introducing more flexibility into the calculations.[16] In the present implementation, we always use the same basis for the two parts of the pair functions.

2.3. Optimization of MP2-GGn pair functions

With the GGn pair functions expanded in orbital products and geminals as in eqns (15)–(17), the WO functional may be parameterized as

$$J_{ij}^s[u_{ij}^s] = J_{ij}^s(\boldsymbol{C}_o, \boldsymbol{C}_g) \qquad (18)$$

where the matrices $\boldsymbol{C}_o$ and $\boldsymbol{C}_g$ contain the orbital and geminal expansion coefficients $c_{ij,s}^{ab}$ and $c_{ij,s}^{mn,v}$, respectively, arranged with ab and (mn, v) as composite row indices and with (ij, s) as a composite column index. The superscript mn is used here generically for kl, kq, pq, depending on which of the three ansätze eqns (15)–(17) is used.

Applying the minimum principle to the WO functional for each pair of electrons and collecting the resulting equations into a single matrix equation, we get

$$\begin{pmatrix} \boldsymbol{H}_{oo} & \boldsymbol{H}_{og} \\ \boldsymbol{H}_{go} & \tilde{\boldsymbol{H}}_{gg} \end{pmatrix} \begin{pmatrix} \boldsymbol{C}_o \\ \boldsymbol{C}_g \end{pmatrix} = -\begin{pmatrix} \boldsymbol{R}_o \\ \boldsymbol{R}_g \end{pmatrix} \qquad (19)$$

In the canonical MO basis, the elements of the orbital–orbital block $\boldsymbol{H}_{oo} = \boldsymbol{H}_{oo}^T$, the geminal–orbital block $\boldsymbol{H}_{go} = \boldsymbol{H}_{og}^T$, and the geminal–geminal block $\tilde{\boldsymbol{H}}_{gg} = \tilde{\boldsymbol{H}}_{gg}^T$ are given by

$$[\boldsymbol{H}_{oo}]_{ab,cd} = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\delta_{ac}\delta_{bd}, \qquad (20)$$

$$[\boldsymbol{H}_{go}]_{mnv,cd}^s = \langle g_{mn,v}^s | f(1) + f(2) - \varepsilon_i - \varepsilon_j | \phi_{cd}^s \rangle, \qquad (21)$$

$$[\tilde{\boldsymbol{H}}_{gg}]_{mnv,m'n'v'}^s = \langle g_{mn,v}^s | \tilde{f}_{ij}(1) + \tilde{f}_{ij}(2) - \varepsilon_i - \varepsilon_j | g_{m'n',v'}^s \rangle, \qquad (22)$$

while the elements of the orbital and geminal blocks $\boldsymbol{R}_o$ and $\boldsymbol{R}_g$, respectively, of the right-hand side are given by

$$[\boldsymbol{R}_o]_{ab}^s = \langle \phi_{ab}^s | r_{12}^{-1} | \phi_{ij}^s \rangle, \qquad (23)$$

$$[\boldsymbol{R}_g]_{mnv}^s = \langle g_{mn,v}^s | Q r_{12}^{-1} | \phi_{ij}^s \rangle. \qquad (24)$$

Note that, since the projector p gives zero when operating on ϕ_{ab}^s, the modified Fock operator $\tilde{f}$ only appears in the geminal–geminal block $\boldsymbol{H}_{gg}$.

If the pair functions are expanded in virtual orbitals only, then eqn (19) reduces to

$$\boldsymbol{C}_o = -\boldsymbol{H}_{oo}^{-1}\boldsymbol{R}_o \qquad (25)$$

where $\boldsymbol{H}_{oo}$ is diagonal, and the amplitudes $\boldsymbol{C}_o$ are then obtained trivially, as in the standard MP2 theory. By contrast, when the pair functions are expanded in GTGs, eqn (19) must be solved by some iterative process. Noting that $\boldsymbol{H}_{oo}$ is positive definite, we introduce the decomposition

$$\begin{pmatrix} \boldsymbol{H}_{oo} & \boldsymbol{H}_{og} \\ \boldsymbol{H}_{go} & \tilde{\boldsymbol{H}}_{gg} \end{pmatrix} = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{Z} & \boldsymbol{I} \end{pmatrix} \begin{pmatrix} \boldsymbol{H}_{oo} & \boldsymbol{0} \\ \boldsymbol{0} & \tilde{\boldsymbol{G}}_{gg} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{Z}^T \\ \boldsymbol{0} & \boldsymbol{I} \end{pmatrix} \qquad (26)$$

where

$$\boldsymbol{Z} = \boldsymbol{H}_{go}\boldsymbol{H}_{oo}^{-1}, \qquad (27)$$

$$\tilde{\boldsymbol{G}}_{gg} = \tilde{\boldsymbol{H}}_{gg} - \boldsymbol{H}_{go}\boldsymbol{H}_{oo}^{-1}\boldsymbol{H}_{og} \qquad (28)$$

are easily formed since $\boldsymbol{H}_{oo}$ is diagonal. Inserting this decomposition into eqn (19) and rearranging, we obtain

$$\begin{pmatrix} \boldsymbol{H}_{oo} & \boldsymbol{H}_{og} \\ \boldsymbol{0} & \tilde{\boldsymbol{G}}_{gg} \end{pmatrix} \begin{pmatrix} \boldsymbol{C}_o \\ \boldsymbol{C}_g \end{pmatrix} = -\begin{pmatrix} \boldsymbol{R}_o \\ \boldsymbol{S}_g \end{pmatrix} \qquad (29)$$

with

$$\boldsymbol{S}_g = \boldsymbol{R}_g - \boldsymbol{Z}\boldsymbol{R}_o \qquad (30)$$

The coefficients $\boldsymbol{C}_g$ are now found by solving the equation

$$\tilde{\boldsymbol{G}}_{gg}\,\boldsymbol{C}_g = -\boldsymbol{S}_g \qquad (31)$$

using some iterative method. Inserting the resulting amplitudes into eqn (29), $\boldsymbol{C}_o$ are obtained explicitly from

$$\boldsymbol{C}_o = -\boldsymbol{H}_{oo}^{-1}\boldsymbol{R}_o - \boldsymbol{Z}^T\boldsymbol{C}_g \tag{32}$$

Whereas the first part in eqn (32) is identical to the usual amplitudes of orbital-based MP2 theory eqn (25), the second part is a correction arising from the presence of geminals. Through the decomposition eqn (26), we have reduced the dimension of the linear equations to be solved iteratively from $N_o + N_g$ to N_g, where N_o is the number of functions in the virtual orbital expansion and N_g is the number of geminals. A similar decomposition is used in ref. 17.

2.4. Calculation of the MP2-GG*n* energy

From the converged amplitudes, the second-order MP2-GG*n* energy of eqn (3) is given as the sum over all pair energies and may be calculated from the expression

$$E^{(2)} = \mathrm{tr}(\boldsymbol{C}_o^T\overline{\boldsymbol{R}}_o) + \mathrm{tr}(\boldsymbol{C}_g^T\overline{\boldsymbol{R}}_g) \tag{33}$$

where we have introduced parity-weighed versions of the matrices $\boldsymbol{R}_o$ and $\boldsymbol{R}_g$ defined as

$$[\overline{\boldsymbol{R}}]_{ij}^s = \frac{s}{1+\delta_{ij}}[\boldsymbol{R}]_{ij}^s. \tag{34}$$

The relative magnitudes of the orbital and geminal contributions to the MP2-GG*n* energy may vary considerably, depending on the relative sizes of the orbital and geminal expansions. In Table 1, we have listed the percentage of the correlation energy contributed by the virtual-orbital and GTG expansions when they are used on their own, relative to the correlation energy recovered when both expansions are used simultaneously. Except for the GG0 ansatz, most energy is recovered by the geminal expansion. We also note that, whereas the proportion of the correlation energy recovered by the GTG expansion decreases with basis-set expansion with the GG0 ansatz, it increases with the GG1 and GG2 ansätze. In the GG0 ansatz eqn (15), basis-set expansion increases the size of the virtual-orbital expansion (by including more virtual orbitals), while the size of the GTG expansion is constant. With increasing basis set, therefore, more and more correlation energy is recovered by the virtual-orbital expansion, while the energy recovered by the GTG expansions remains essentially constant. By contrast, for the GG1 and GG2 ansätze eqns (16) and (17), basis-set expansion increases the size of both the virtual-orbital and GTG expansions; consequently, both expansions are able to recover more of the total correlation energy with increasing basis set.

Table 1 The percentage of the all-electron MP2-GG*n* correlation energy recovered for the neon atom by only the virtual-orbital expansion (VOE) part or only the geminal (GTG) part of the pair function, relative to the amount of energy recovered when both are used simultaneously

	GG0		GG1		GG2	
Basis	VOE	GTG	VOE	GTG	VOE	GTG
cc-pVDZ	62	54	54	83	53	99.2
cc-pVTZ	79	47	73	93	72	99.4
cc-pVQZ	88	44	85	95	84	99.6

The decomposition eqn (26) also allows us to rewrite the MP2-GG*n* energy as

$$E^{(2)} = -\mathrm{tr}(\boldsymbol{R}_o^T\boldsymbol{H}_{oo}^{-1}\overline{\boldsymbol{R}}_o) + \mathrm{tr}(\boldsymbol{C}_g^T\overline{\boldsymbol{S}}_g), \tag{35}$$

which is a conventional MP2 energy expression with a correction from the geminal expansion. In the limit of a complete one-electron basis, the orbitals become exact eigenfunctions of the Fock operator and $\Sigma_p|\varphi_p\rangle\langle\varphi_p| \to 1$. From a consideration of the detailed form of the matrix elements in eqns (20)–(24), we note that, in this limit, $\boldsymbol{S}_g \to \boldsymbol{0}$ in eqn (30). We conclude that, in the limit of a complete one-electron basis, the solution to eqn (29) becomes $\boldsymbol{C}_o \to -\boldsymbol{H}_{oo}^{-1}\boldsymbol{R}_o$ and $\boldsymbol{C}_g \to \boldsymbol{0}$. Thus, in this limit, all of the correlation energy in eqn (35) is recovered by the virtual-orbital expansion.

2.5. Notes on the implementation

The integrals needed for the theory presented here have been implemented in the GREMLIN[18] program, as an extension to an experimental version of DALTON,[19] in which the optimization of the pair functions has been implemented. The details of the implementation have been presented in ref. 20.

By far the most time-consuming step in our MP2 calculations is the calculation of three-electron integrals over GTGs. In calculations that require an hour of computer time, more than 59 min is typically spent computing these integrals and accumulating their contributions into various matrix elements, and for longer calculations the proportion of the time required for this step increases.

In traditional applications of GTGs, with nonlinear optimization of the geminal parameters, the emphasis has been on evaluating integrals over GTGs with low angular quantum numbers very rapidly. This is less appropriate for our mixed GTO/GTG basis sets, where higher angular-momentum functions are employed. We have developed a scheme for calculating GTG integrals efficiently by extending the Hermite-expansion approach suggested by McMurchie and Davidson[21] and combining it with the technique suggested originally by Boys[22] by which many-electron integrals over GTGs can be reduced to (more complicated) one- and two-electron integrals.[1] A full description of this formulation can be found in ref. 23. One way of reducing the number of integrals that must be calculated is to use molecular symmetry. We have implemented a scheme for evaluating integrals over symmetry-adapted functions from symmetry-distinct integrals, using a double-coset decomposition technique. Full details have been given in ref. 24.

3. Applications

3.1. Computational details and considerations

3.1.1. One-electron basis sets. The correlation-consistent basis sets cc-pV*XZ* of Dunning[25] constitute a principal expansion, belonging to the orbital spaces (2s1p), (3s2p1d), (4s3p2d1f), and so on.[1] They are widely used in traditional orbital-based correlated calculations, giving a smooth convergence of the correlation energy with increasing cardinal number X. In our work, we also consider the partial-wave expansion, where the expansion is instead truncated at a given

angular momentum. We generate these expansions by omitting high angular-momentum functions from the correlation-consistent basis sets. The orbital types retained in the basis are then given in parentheses after the basis-set name. For example, for the first-row elements hydrogen and helium, cc-pVTZ(sp) is a cc-pVTZ basis with the d shell omitted; for the second-row elements, it denotes a basis with the 2d1f part omitted. For systems containing both first- and second-row atoms, both expansions are given in parentheses, with that of the heavier atom first—for instance, in a calculation on hydrogen fluoride using the cc-pVTZ(spd,sp) basis, we have omitted the f shell on fluorine and the d shell on hydrogen.

Although cc-pV*X*Z basis sets are available for both lithium and beryllium[25,26] and cc-pCV*X*Z basis sets exist for lithium,[25] it is not clear how to augment these sets with diffuse functions. We have instead used an atomic natural-orbital basis of Roos and co-workers,[27] based on sets originally developed by van Duijneveldt.[28] This basis set is referred to as ANO-2.

3.1.2. Two-electron basis sets. The GTG expansions of eqns (15)–(17) may be modified both by adjusting the exponents γ_v in $\exp(-\gamma r_{12}^2)$ and by varying the number of such GCFs in the expansion. Following Persson and Taylor,[16] we use the fixed even-tempered exponents $\gamma_v = 3^{v-1}a$ with $a = 1/9$ and $1 \leq v \leq N_{\mathrm{GCF}}$. In our standard GTG basis set, we use $N_{\mathrm{GCF}} = 9$.

To examine the relative importance of the different GCFs, we have carried out a series of calculations on the neon atom where the GTGs have been constructed from the AO basis sets cc-pVDZ and aug-cc-pCVTZ(spd) and from GCFs with even-tempered exponents $\gamma_1 = 1/9$ and $0 \leq N_{\mathrm{GCF}} \leq 9$, see Table 2. For each AO set, the first entry ($N_{\mathrm{GCF}} = 0$) represents the conventional MP2 energy. When one (diffuse) GCF is included, the energy barely changes for the GG0 and GG1 ansätze but makes a significant jump for the GG2 ansatz. This happens since GTGs constructed from diffuse GCFs are essentially orbital products ($\exp(-\gamma r_{12}^2) \rightarrow 1$ when $\gamma_v \rightarrow 0$); according to the Brillouin theorem, only products of virtual orbitals contribute to the energy. Only the GG2 ansatz contains such products.

With more GCFs included, also the MP2-GG0 and MP2-GG1 energies improve, although the MP2-GG0 energy changes little from $N_{\mathrm{GCF}} = 1$ to $N_{\mathrm{GCF}} = 2$ in the aug-cc-pCVTZ(spd) basis. In the larger AO basis, therefore, GCFs with exponents smaller than one do not improve significantly upon the standard virtual-orbital expansion. By contrast, geminals with exponents equal to one and three make significant energy contributions for all three ansätze. For $N_{\mathrm{GCF}} = 9$, all MP2-GG*n* energies are converged to within 0.1 mE_{h}, the last three GCFs improving mainly the $1s^2$ singlet energy.

Table 2 Neon all-electron MP2-GG*n* correlation energies ($-E$/mE_{h}) calculated using geminal exponents from the sequence 1/9, 1/3, 1,. . .,729

	cc-pVDZ			aug-cc-pCVTZ(spd)		
N_{GCF}	GG0	GG1	GG2	GG0	GG1	GG2
0	187.567	187.567	187.567	309.078	309.078	309.078
1	187.655	187.758	206.325	309.078	309.126	335.423
2	196.870	240.497	280.170	309.368	337.466	364.538
3	229.085	294.675	307.021	319.221	362.224	376.800
4	274.410	320.640	331.566	337.957	374.004	382.839
5	290.017	335.968	345.550	346.125	380.437	385.912
6	296.844	343.290	352.874	350.167	383.779	387.156
7	299.810	345.784	355.252	352.651	385.416	387.591
8	300.708	346.621	356.144	353.695	386.062	387.905
9	300.976	346.932	356.372	353.914	386.232	388.008

3.1.3. The level-shift parameter. All calculations presented in the previous sections were carried out with the level-shift parameter $\eta = 0.1$. In the present section, we examine how the MP2-GG*n* energy and the strong orthogonality depend on the level shift, carrying out calculations with different η. In Table 3, we have, for each selected value of η, listed the energy and $p\mathrm{SO} = -\log_{10}\bar{\chi}^{\mathrm{SO}}$, where $\bar{\chi}^{\mathrm{SO}}$ is the average of χ_{ij}^{SO} in eqn (8) over all 15 singlet and 10 triplet pair functions in neon. The *p*SO value increases as the pair functions become more strongly orthogonal to the occupied orbitals. Since we have used the operator $p(1) + p(2)$ as an approximation to $1 - Q(1, 2) = p(1) + p(2) - p(1)p(2)$ in χ_{ij}^{SO}, the orthogonality will appear less than it really is, punishing the GG0 and GG1 ansätze the most.

From Table 3, we see that the MP2-GG*n* energy barely changes for $0.001 < \eta < 1$. Moreover, the sensitivity to η is strongest in the small AO basis and for the GG0 ansatz. Likewise, the most flexible pair functions also appear to be most strongly orthogonal to the occupied MOs, the largest *p*SO values occurring in the large AO basis with the GG2 ansatz. Whereas orthogonality increases only marginally from the GG0 ansatz to the GG2 ansatz in the small AO basis, it increases significantly (by many factors) in the large AO basis. The slightly nonmonotonic behaviour observed in the GG2/aug-cc-pCVTZ(spd) calculations is caused by numerical noise, which becomes apparent for very small χ_{ij}^{SO} of eqn (8).

As expected, strong orthogonality increases with η. A comparison of the *p*SO value and the energy for different η indicates that a good compromise is achieved with $\eta = 0.1$, which is therefore used in all calculations discussed below. Similar conclusions are reached for water in ref. 29.

3.1.4. Linear dependencies and numerical stability. From Table 2, we see that the GG*n* performance improves with increasing geminal excitation level *n*. However, these improvements come at a cost. Using LDL factorization to solve eqn (31), the complexity of the solution is, for each distinct MO pair *ij*, equal to $\mathcal{O}(N^3)$, where N is the number of GTGs. Denoting the total number of MOs by N_{tot} and the number of occupied MOs by N_{occ}, the cost of the solution, for each of the N_{occ}^2 pair functions u_{ij}^s, is thus $\mathcal{O}(N_{\mathrm{occ}}^6 N_{\mathrm{GCF}}^3)$ for the GG0 ansatz, $\mathcal{O}(N_{\mathrm{occ}}^3 N_{\mathrm{tot}}^3 N_{\mathrm{GCF}}^3)$ for the GG1 ansatz, and $\mathcal{O}(N_{\mathrm{tot}}^6 N_{\mathrm{GCF}}^3)$ for the GG2 ansatz. Since N_{tot} is usually several times larger than N_{occ}, the solution of the linear equations can be an order of magnitude more expensive for the GG2 ansatz than for the GG0 ansatz. Besides, the increased dimensionality of the GG2 ansatz makes it more prone to linear dependencies and to numerical instabilities than the GG0 ansatz.

To quantify the linear-dependency problem for the different pair-function ansätze, we have diagonalized the geminal–geminal overlap matrix using the standard GTG expansion

Table 3 Neon all-electron MP2-GG*n* correlation energies ($-E$/mE_h) and *p*SO values for different values of the level-shift parameter η

	cc-pVDZ						aug-cc-pCVTZ(spd)					
	GG0		GG1		GG2		GG0		GG1		GG2	
$\text{Log}_{10}\,\eta$	$-E$	*p*SO	$-E$	*p*SO	$-E$	*p*SO	$-E$	*p*SO	$-E$	*p*SO	$-E$	*p*SO
+3	252.462	1.9	315.307	2.6	336.135	2.6	334.630	4.1	384.519	4.9	387.811	11.6
+2	282.105	1.5	335.286	2.1	348.959	2.1	345.706	3.1	385.761	4.2	387.926	10.8
+1	297.655	1.2	344.908	1.8	355.068	1.8	352.384	2.6	386.162	3.9	387.996	10.3
0	300.625	1.2	346.721	1.7	356.235	1.8	353.749	2.5	386.225	3.9	388.008	10.2
−1	300.976	1.2	346.932	1.7	356.372	1.8	353.914	2.5	386.232	3.9	388.008	10.4
−2	301.014	1.1	346.954	1.7	356.386	1.7	353.932	2.4	386.232	3.8	388.009	10.2
−3	301.048	0.8	346.960	1.2	356.390	1.3	353.940	1.5	386.232	2.5	388.009	9.7

(N_{GCF} = 9) and the cc-pVDZ and aug-cc-pCVTZ(spd) orbital basis sets—see Table 4, where we have listed the number of eigenvalues λ transformed to a given integer by $\Delta(\lambda) = \max(0, \min(15, -\text{int}(\log_{10}\lambda)))$. For a given AO basis, the number of eigenvalues—in particular, the number of small eigen values—increases dramatically with *n*, as more and more GTGs are introduced into the GG*n* pair function. Except for the GG0 ansatz, the number of small eigenvalues also increases with increasing AO basis—in particular, for the GG2 ansatz. For instance, in the aug-cc-pCVTZ(spd) basis, there are 446 eigenvalues smaller than or equal to 10^{-15}, making the solution of the linear equations difficult.

The equation solver employed in this work uses the LDL approach of the LINPACK library,[30] with the pivoting strategy of Bunch and Kaufman[31] for general symmetric matrices. Higham has shown that this approach gives a stable factorization,[32] and linear dependencies are not expected to create severe numerical instabilities in the equation solver.

3.2. Results

3.2.1. Helium. The helium results in Table 5 show that the GG1 and GG2 pair functions perform excellently, while the GG0 performance is only fair. Thus, whereas the lowest MP2-GG0 energy is reached in the aug-cc-pV6Z basis, lower energies are obtained with the GG1 ansatz with only s and p orbitals. In fact, good MP2-GG1 and MP2-GG2 energies are already obtained with only s orbitals, the p orbitals contributing −0.2 mE_h or less to the correlation energy. Moreover, the GG1 and GG2 ansätze perform better in the aug-cc-pV5Z(sp) basis than in the cc-pV5Z basis, indicating that saturation with diffuse functions is more important for the energy than the inclusion of functions of high angular momentum. We shall later see that this is a typical feature of geminal calculations, valid also for the other systems.

In Table 6, we compare our MP2-GG*n* helium correlation energies with literature data. Our best energy of −37.3773 mE_h, obtained with the GG2 ansatz in the aug-cc-pV6Z(spd) basis containing only 50 orbitals, is close to the value of −37.37744 mE_h, obtained by Bukowski *et al.*[33] using GTGs of the form

$$g_i(1,2) = \exp[-\alpha_i(\boldsymbol{r}_1 - \boldsymbol{P}_i)^2 - \beta_i(\boldsymbol{r}_2 - \boldsymbol{Q}_i)^2 - \gamma_i r_{12}^2] \quad (36)$$

with the exponents α_i, β_i and γ_i and the centers $\boldsymbol{P}_i$ and $\boldsymbol{Q}_i$ (constrained to lie on the internuclear axis in diatomics and on the nucleus in atoms) variationally optimized using the WO functional. Each such GTG may be regarded as a pair of *s* orbitals multiplied by a GCF; higher angular-momentum functions are not used. For pair functions of Σ^+ symmetry, such geminals constitute a complete basis.[41–43] To obtain their helium MP2 energy, Bukowski *et al.* used 150 GTGs. For comparison, we used 2349, 153, and 9 GTGs, respectively, to obtain our best GG2, GG1, and GG0 energies. Moreover, Bukowski *et al.* obtained their limit with a pure GTG expansion, while we supplemented the GTGs with a conventional virtual-orbital expansion.

Table 4 Distribution of eigenvalues for some geminal–geminal overlap matrices for the neon atom. Geminals are constructed from the full standard set of nine GCFs. Eigenvalues λ are reported as $\Delta(\lambda) = \max(0, \min(15, -\text{int}(\log_{10}\lambda)))$

	cc-pVDZ			aug-cc-pCVTZ(spd)		
Δ	GG0	GG1	GG2	GG0	GG1	GG2
0	19	67	115	19	309	750
1	25	70	108	25	266	609
2	22	77	124	22	337	791
3	28	100	162	28	415	931
4	23	83	155	23	323	1018
5	13	60	104	13	220	865
6	3	36	71	3	197	727
7	1	20	35	2	130	671
8	1	12	32		125	567
9		7	27		93	438
10		5	4		57	416
11		3	8		48	373
12					18	317
13					15	225
14					12	171
15						446

Table 5 Helium MP2 correlation energies ($-E$/mE_h), calculated using a virtual-orbital expansion (VOE) and the GG0, GG1, and GG2 pair-function expansions

Orbital basis	VOE	GG0	GG1	GG2
cc-pVDZ	25.83	33.75	36.713	36.9501
cc-pVTZ	33.14	35.87	37.183	37.2998
cc-pVQZ	35.48	36.77	37.326	37.3628
cc-pV5Z	36.41	37.09	37.363	37.3738
aug-cc-pVDZ	26.96	35.23	37.169	37.2926
aug-cc-pVTZ	33.62	36.52	37.255	37.3610
aug-cc-pVQZ	35.72	37.06	37.354	37.3758
aug-cc-pV5Z	36.53	37.23	37.373	—
aug-cc-pV6Z	36.88	37.31	—	—
aug-cc-pV5Z(s)	13.44	29.59	37.235	37.3613
aug-cc-pV5Z(sp)	32.35	36.02	37.369	37.3769
aug-cc-pV5Z(spd)	35.46	36.98	37.371	37.3772
aug-cc-pV5Z(spdf)	36.29	37.19	37.372	37.3772

Table 6 Helium MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$), listed chronologically. For helium, the total correlation energy is $-42.044\ \mathrm{m}E_\mathrm{h}$[33]

Authors	Method	Energy
This work	MP2-GG0 (aug-cc-pV6Z)	37.305
	MP2-GG1 (aug-cc-pV6Z(spdf))	37.375
	MP2-GG2 (aug-cc-pV6Z(spd))	37.3773
Patkowski *et al.*[34]	600 nonlinearly optimized GTGs	37.37747452
Lee and Park[35]	extrapolation	37.4052
Bukowski *et al.*[33]	150 nonlinearly optimized GTGs	37.37744
Flores[36]	FEM-MP2 with $l \leq 12$ and angular extrapolation	37.376
Termath *et al.*[37]	MP2-R12/A with STO basis (12s11p11d9f9g)	37.375
	MP2-R12/B with STO basis (12s11p11d9f9g)	37.362
Petersson *et al.*[38]	CBS (complete basis-set) model	37.59
Malinowski *et al.*[39]	Partial-wave expansion with radial and angular extrapolation	37.359
Winter *et al.*[40]	First-order equation solved numerically	37.355

Table 7 Beryllium all-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$). All basis sets are based on ANO-2 and used in uncontracted form

Orbital basis	VOE	GG0	GG1	GG2
14s	15.91	55.76	66.239	68.217
14s9p	64.05	74.18	75.939	76.349
14s9p4d	68.28	75.39	76.318	76.355
14s9p4d3f	69.40	75.62	76.345	—

Very recently, Patkowski *et al.* have improved on this GTG result, obtaining an MP2 energy of $-37.37747452\ \mathrm{m}E_\mathrm{h}$, using 600 GTGs.[34] Presently, this energy is the best MP2 energy correction of helium. Although not the lowest overall, it does constitute the lowest upper bound to the true MP2 energy, and has been converged to within $1.0 \times 10^{-10}\ E_\mathrm{h}$.

3.2.2. Beryllium. Our beryllium MP2 correlation energies are presented in Table 7. Unlike for helium, an sp basis is needed for a good description of beryllium. Thus, taking the MP2 limit to be $-76.358\ \mathrm{m}E_\mathrm{h}$ (see Table 8), we find that the GG2 ansatz recovers only 89% of the correlation energy in an s basis but 99.99% in an sp basis. As for helium, the GG0 and GG1 ansätze are more reliant than the GG2 ansatz on high angular-momentum functions, the best MP2-GG0 and MP2-GG1 sp calculations recovering 97.1% and 99.5%, respectively, of the correlation energy. Comparing the 14s4p and 14s9p energies, we see that the addition of more p orbitals does not improve the MP2-GG1 energy substantially—in fact, the GG1 ansatz needs an spdf basis to match the performance of the GG2 ansatz in an sp basis. Although it probably needs g orbitals for convergence, the GG0 ansatz performs far better than the virtual orbital expansion, which recovers only 90% of the MP2 correlation energy in our largest basis.

The best beryllium MP2 correlation energy in the literature is $-76.358\ \mathrm{m}E_\mathrm{h}$, obtained independently by Bukowski *et al.*[45] and by Salomonsen and Öster[47] using different methods, see Table 8. Our lowest MP2-GG2 energy of $-76.355\ \mathrm{m}E_\mathrm{h}$, obtained in the 14s9p3d basis, is thus only $3\ \mu E_\mathrm{h}$ higher than their value; this is remarkably good, considering the size of the orbital basis and the fact that our GCF exponents were not optimized. With the GG1 ansatz, we obtain a slightly poorer MP2 correlation energy, $13\ \mu E_\mathrm{h}$ higher than the reference value of Bukowski *et al.* and Salomonsen and Öster.

The MP2-R12 energies of Termath *et al.*,[37] which have been obtained using the expansion eqn (11), are considerably lower than our lowest MP2-GG0 energy, demonstrating that good results can be achieved by including correlation factors only in occupied MO pairs, provided very large basis sets are used. However, since the GTGs do not contribute to the correlation energy beyond s orbitals, most of the energy is recovered by the virtual orbital expansion. Extrapolating their MP2-R12/B results, Termath *et al.* obtained $-76.316\ \mathrm{m}E_\mathrm{h}$ as the basis-set limit, $42\ \mu E_\mathrm{h}$ higher than the result of Bukowski *et al.* and of Salomonsen and Öster.

In Table 9 we have listed our best MP2-GG*n* pair energies for beryllium, along with pair energies from the literature. We first note that the GG2 ansatz performs better than the GG1 ansatz mainly for the $2s^2$ pair. Next, we note that the R12/A performance is inconsistent. While it performs well for the 1s2s pairs, being only one or two μE_h above our MP2-GG2 energies, it is smaller in magnitude than our $1s^2$ result by $9\ \mu E_\mathrm{h}$ but larger in magnitude than our $2s^2$ result by $30\ \mu E_\mathrm{h}$.

Table 8 Beryllium all-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$), listed chronologically. The total correlation energy is $-94.332\ \mathrm{m}E_\mathrm{h}$[44]

Authors	Method	Energy
This work	MP2-GG0 (14s9p4d3f)	75.62
	MP2-GG1 (14s9p4d3f)	76.345
	MP2-GG2 (14s9p3d)	76.355
Bukowski *et al.*[45]	350 nonlinearly optimized GTGs for each pair	76.358
Noga *et al.*[46]	MBPT-R12 (16s10p6d5f4g)	76.248
Termath *et al.*[37]	MP2-R12/A (STO basis 15s12p11d11f10g)	76.373
	MP2-R12/B (STO basis 15s12p11d11f10g)	76.311
Salomonsen and Öster[47]	Extrap. partial-wave expansion ($l \leq 10$) with num. orbitals	76.358
Petersson *et al.*[38]	CBS (complete basis-set) model	77.27
Alexander *et al.*[48]	Nonlinearly optimized even-tempered GTGs	76.350
Jankowski *et al.*[49]	Partial-wave expansion with $l \leq 9$	75.98
Malinowski *et al.*[39]	Partial-wave expansion with radial and angular extrapolation	76.29

Table 9 Beryllium MP2 pair correlation energies ($-E/\mathrm{m}E_\mathrm{h}$)

Pair	R12/A[a]	R12/B[a]	GTG[b]	GG0[c]	GG1[c]	GG2[d]
$1s^2$	40.334	40.325	40.340	39.883	40.341	40.343
1s2s, ^1S	3.252	3.249	3.251	3.211	3.253	3.253
1s2s, ^3S	2.217	2.217	2.219	2.165	2.219	2.219
$2s^2$	30.570	30.520	30.540	30.363	30.532	30.540
$E^{(2)}$	76.373	76.311	76.350	75.622	76.345	76.355

[a] MP2-R12/A(STO) and MP2-R12/B(STO) from ref. 37. [b] Non-linearly optimized even-tempered GTGs from ref. 48. [c] Using basis set 14s9p4d3f. [d] Using basis set 14s9p3d.

Table 10 Neon all-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$). A dagger (†) indicates calculations that failed to converge

Orbital basis	VOE	GG0	GG1	GG2
cc-pVDZ	187.57	300.98	346.93	356.37
cc-pVTZ	277.29	350.32	380.61	383.99
cc-pVQZ	326.26	371.77	386.19	387.30
cc-pCVDZ	228.30	310.43	356.40	364.16
cc-pCVTZ	329.10	362.47	383.67	385.49
cc-pCVQZ	361.51	378.51	†	—
aug-cc-pVDZ	209.06	323.58	369.27	380.66
aug-cc-pVTZ	285.91	358.89	384.86	387.55
aug-cc-pVQZ	330.01	375.51	387.21	—
aug-cc-pCVDZ	249.90	333.13	375.05	384.56
aug-cc-pCVTZ	337.29	370.72	387.14	388.19
aug-cc-pCVQZ	365.16	382.12	—	—
aug-cc-pCV5Z	375.93	385.54	—	—
aug-cc-pCVQZ (sp)	190.94	275.73	358.59	365.74
aug-cc-pCVQZ (spd)	319.34	358.23	387.14	388.10
aug-cc-pCVQZ (spdf)	354.18	377.17	†	—

Since a large orbital basis is used, it is difficult to see why the MP2-R12/A method should perform so differently for the different electron pairs. By contrast, the MP2-R12/B method does not show any inconsistency.

3.2.3. Neon. The all-electron MP2 correlation energies obtained for neon are listed in Table 10. Since the correlation-consistent polarized-valence basis sets cc-pV*XZ* are not sufficiently flexible for recovering core and core-valence correlation energies, we have also carried out calculations in the correlation-consistent polarized core-valence basis sets cc-pCV*XZ*.[50]

As for helium, the energy convergence is relatively fast for the GG1 and GG2 ansätze but only moderate for the GG0 ansatz, which still converges much faster than the conventional virtual-orbital expansion. We note a significant improvement when core orbitals are included in the cc-pCV*XZ* basis sets—in particular, for the nongeminal calculations. In the geminal calculations, the core orbitals are less important, reflecting the reduced role of the orbital expansion in these calculations. In fact, these calculations benefit more from the addition of diffuse functions in the aug-cc-pV*XZ* basis sets[51] than from the addition of core functions—in particular, for the GG1 and GG2 ansätze.

The aug-cc-pCV*XZ* basis sets, which contain both core and diffuse functions, perform very well for neon. In fact, our best estimate of the neon MP2 correlation energy in Table 11 (-388.19 mE_h) is obtained with the GG2 ansatz in the aug-cc-pCVTZ basis. The GG1 ansatz, the GG0 ansatz, and the virtual-orbital expansion recover 99.7%, 95.5%, and 86.9%, respectively, of this energy in the same basis. Clearly, for the latter two approaches, the lack of high angular-momentum functions in this triple-zeta basis becomes apparent. In the much larger aug-cc-pCV5Z basis, the GG0 ansatz recovers 99.3% of the MP2 correlation energy.

Since the augmented core-valence basis sets give excellent results, we have explored the partial-wave expansion with the aug-cc-pCVQZ basis—see Table 10. Lacking high angular-momentum functions, the first term in the partial-wave expansion sp gives poor correlation energies, as also observed for beryllium. In the larger spd basis, we recover 99.97%, 99.7%, and 92.6% of the MP2 correlation energy for the GG2, GG1, and GG0 ansätze, respectively. As we shall see below, the high angular-momentum functions are needed mainly for the ^1D pair, which cannot be properly described without d functions.

Accurate neon MP2 correlation energies have been given by several authors—see Table 11, which also contains our best (*i.e.*, variationally lowest) neon energies. Among the energies in this table, our MP2-GG2 result of -388.19 mE_h is the best variationally bounded energy, although not the lowest overall.

Table 11 Neon all-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$), listed chronologically. The total correlation energy is -390.47 mE_h[52]

Authors	Method	Energy
This work	MP2-GG0 (aug-cc-pCV5Z)	385.54
	MP2-GG1 (aug-cc-pVQZ)	387.21
	MP2-GG2 (aug-cc-pCVTZ)	388.19
Ten-no[53,54]	MP2-geminal (aug-cc-pV5Z, without h functions)	387.64
	MP2-geminal (aug-cc-pV5Z, without h functions)	387.55
Klopper and Samson[17]	MP2-R12/1A′ (20s14p11d9f7g5h3i)	387.69
	MP2-R12/1B (20s14p11d9f7g5h3i)	387.56
	MP2-R12/2A′ (20s14p11d9f7g5h3i)	388.24
	MP2-R12/2B (20s14p11d9f7g5h3i)	388.09
Wind *et al.*[55]	MP2-R12-SO (20s14p11d9f7g5h/exact 3-el. int.)	388.06
	MP2-R12/A (20s14p11d9f7g5h)	388.29
	MP2-R12/B (20s14p11d9f7g5h)	388.00
Flores[36]	FEM-MP2 with $l \leq 12$ and angular extrapolation	388.10
Petersson *et al.*[38]	CBS (complete basis-set) model	386.38
Wenzel *et al.*[11]	Nonlinearly optimized GTGs	385.26
Lindgren and Salomonsen[56,57]	Numerical integration of the coupled-cluster equations	388.31
Janowski and Malinowski[58]	Calculated	384.98
	Extrapolated	387.92

Table 12 Neon MP2 pair energies ($-E/\mathrm{m}E_\mathrm{h}$)

Pair	Symmetry	GTG[a]	R12-SO[b]	R12/2B[c]	GG0[d]	GG1[e]	GG2[f]	GG2[g]
$1s^2$		40.22	40.252	40.252	40.150	39.965	40.224	40.229
1s2s	^1S	3.95	3.974	3.974	3.960	3.929	3.974	3.975
1s2s	^3S	1.58	1.582	1.582	1.567	1.566	1.585	1.585
$2s^2$		12.00	12.038	12.039	11.984	12.033	12.044	12.046
1s2p	^1P	8.10	8.176	8.177	8.055	8.103	8.139	8.161
1s2p	^3P	13.86	13.911	13.910	13.846	13.763	13.825	13.880
2s2p	^1P	59.85	60.472	60.482	59.765	60.438	59.702	60.532
2s2p	^3P	26.55	26.708	26.708	26.633	26.679	26.439	26.757
$2p^2$	^1S	45.24	45.565	45.573	45.450	45.553	45.544	45.574
$2p^2$	^1D	87.06	88.042	88.057	86.907	87.891	65.957	88.031
$2p^2$	^3P	86.85	87.341	87.340	87.224	87.296	87.110	87.417
Sum		385.26	388.061	388.09	385.541	387.215	364.543	388.189

[a] Nonlinearly optimized GTGs from ref. 11. [b] MP2-R12-SO from ref. 55. [c] MP2-R12/2B from ref. 17. [d] Orbital basis aug-cc-pCV5Z. [e] Orbital basis aug-cc-pVQZ. [f] Orbital basis aug-cc-pCVTZ (sp). [g] Orbital basis aug-cc-pCVTZ.

Given that g orbitals were used in this calculation, we may reasonably assume that the true limit is somewhat lower than -388.19 mE_h, probably also lower than the lowest energy in Table 11—namely, -388.31 mE_h, obtained by Lindgren and Salomonsen.[56,57]

Somewhat surprisingly, in view of the good results of Bukowski *et al.* for helium and beryllium,[45] the neon correlation energy of -385.26 mE_h obtained by Wenzel *et al.* using nonlinearly optimized GTGs is rather poor.[11] For neon, these authors used GTGs of the form

$$g_i(1,2) = x_{1P}^{l_1} y_{1P}^{m_1} z_{1P}^{n_1} x_{2Q}^{l_2} y_{2Q}^{m_2} z_{2Q}^{n_2} \exp[-\alpha_i(\boldsymbol{r}_1 - \boldsymbol{P}_i)^2 - \beta_i(\boldsymbol{r}_2 - \boldsymbol{Q}_i)^2 - \gamma_i r_{12}^2], \quad (37)$$

which is identical to eqn (36) except for the angular factors. As for helium, all GTGs were centered on the nucleus, while the exponents were optimized under the restrictions

$$\alpha_i\beta_i + \alpha_i\gamma_i + \beta_i\gamma_i > 0 \text{ and } \alpha_i + \beta_i + \gamma_i > 0 \quad (38)$$

using the modified weak orthogonality (MWO) functional.[11] For each neon pair function, Wenzel *et al.* used a 40-term GTG expansion, compared with the 150 and 350 terms, respectively, used by Bukowski *et al.* to obtain their excellent helium and beryllium energies.[45] One reason for the relatively poor MP2-GTG result for neon was that the orbital pairs were not adapted to spherical symmetry, affecting the quality of the p^2 pairs.[13]

In Table 12, we give pair energies obtained by some selected methods, including the GTG approach by Wenzel *et al.*[11] The energies in the two rightmost columns are both obtained with the GG2 ansatz, with and without d orbitals. (The aug-cc-pCVTZ basis also contains f orbitals, but from Table 10 we see that these contribute less than 0.1 mE_h to the total energy.) Whereas seven of the eleven pair energies differ by less than 0.1 mE_h and three by less than 1 mE_h, the $^1D(2p^2)$ energies differ by more than 22 mE_h. Clearly, for this particular pair, d orbitals are essential. In MP2-R12 theory, Klopper and coworkers have also observed this slow convergence of the $^1D(2p^2)$ pair[37,59] and it was also discussed in the context of GTO/GTG basis sets by Persson and Taylor.[16]

We should note that the GG1 calculations of Table 12 were carried out in a GTO basis without core-correlating orbitals, which is why this ansatz yields poorer pair-correlation energies for pairs involving the 1s orbital than for instance the GG0 ansatz here (where core-correlating GTOs were included).

3.2.4. Comparison with various MP2-R12 approaches for neon. In Table 13, we compare our MP2-GG*n* results with those obtained by a selection of MP2-R12 methods. Before discussing energies, we shall briefly review the different ansätze.

The R12-SO results in Table 13 have been obtained with the MP2-R12-SO code of Wind *et al.*,[55] where all three-electron integrals are calculated explicitly and the RI approximation is needed only to approximate four-electron integrals. The pair functions are expanded using the orbital-variant approach of eqn (10) but with the projector Q_0 (with summation over all orbitals) replaced by Q (with summation over only occupied orbitals). With this code, the authors demonstrated that the error introduced by approximating three-electron integrals using an auxiliary 32s24p18d15f12g9h6i basis is less than 0.01 mE_h. Next, the MP2-R12/1A′ and MP2-R12/1B results of Klopper and Samson[17] have been obtained using the orbital-invariant pair function eqn (11) with the Q_0 projector and the same large auxiliary basis as in the R12-SO calculations. The MP2-R12/2A′ and MP2-R12/2B calculations differ from these calculations in the use of the Q projector rather than the Q_0 projector. Finally, the MP2-geminal results of Ten-no[53] have been obtained using numerical quadrature for two- and three-electron integrals, neglecting the exchange operator in commutators, and assuming the validity of the extended Brillouin condition. The pair function is similar to that of the GG0 ansatz eqn (15) but with fixed linear combinations of ten GCFs, with $0.5 \leq \gamma_v \leq 1000.0$.

Since the MP2-R12-SO calculations in Table 13 use an orbital-variant ansatz eqn (10) rather than the orbital-invariant ansatz eqn (11) used by all the other MP2-R12 calculations in the table, we have carried out additional neon calculations using the orbital-variant GG0′ ansatz. Since the GG0 model has a larger variational space than does the GG0′ model, with contributions from all $g_{kl,v}^s$ rather than from just $g_{ij,v}^s$, its correlation energy is lower. In the small aug-cc-pCVDZ basis, for example, the difference is 6 mE_h; however, it decreases with increasing X and is only 0.6 mE_h in the large

Table 13 Neon all-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$). All calculations have been carried out using the orbital-invariant GG0 ansatz with the Q projector except GG0′ and R12-SO (which use the orbital-variant ansätze eqns (14) and (10), respectively) and R12/1A′ and R12/1B (which use the stronger Q_0 projector)

Orbital basis	VOE	GG0	GG0′	R12-SO[a]	R12/1A′[b]	R12/1B[b]	R12/2A′[b]	R12/2B[b]	geminal[c]
cc-pVDZ	187.57	300.98	290.49	306.6	—	—	—	—	—
cc-pVTZ	277.29	350.32	343.19	343.1	—	—	—	—	—
cc-pVQZ	326.26	371.77	367.63	365.9	—	—	—	—	—
cc-pCVDZ	228.30	310.43	303.98	318.7	302.89	288.45	233.73	343.67	361.18
cc-pCVTZ	329.10	362.47	360.37	362.4	357.46	355.56	368.48	374.48	379.25
cc-pCVQZ	361.51	378.51	377.40	377.1	375.21	373.26	381.17	377.23	385.00
cc-pCV5Z	374.21	383.99	383.32	382.7	380.30	382.57	386.37	384.14	387.01[d]
aug-cc-pVDZ	209.06	323.58	313.00	322.7	—	—	—	—	—
aug-cc-pVTZ	285.91	358.89	351.85	356.1	—	—	—	—	—
aug-cc-pVQZ	330.01	375.51	371.42	373.2	—	—	—	—	—
aug-cc-pCVDZ	249.90	333.13	326.54	—	312.28	302.91	367.65	342.47	376.02
aug-cc-pCVTZ	337.29	370.72	368.78	—	362.35	360.07	383.94	378.00	383.79
aug-cc-pCVQZ	365.16	382.12	381.14	—	377.35	375.88	386.87	386.16	386.72
aug-cc-pCV5Z	375.93	385.54	384.97	—	384.46	383.92	388.44	387.25	387.55[d]

[a] MP2-R12-SO calculations by Wind *et al.*[55] [b] MP2-R12 calculations by Klopper and Samson.[17] [c] MP2-geminal calculations by Ten-no.[53] [d] h functions removed from the cc-pCV5Z and aug-cc-pCV5Z MP2-geminal calculations.[53]

aug-cc-pCV5Z basis. We expect these differences to be typical of all pair functions that differ from each other in the use of orbital-variant and orbital-invariant expansions.

Apart from differences in optimization, the main difference between the MP2-R12-SO and MP2-GG0′ models in Table 13 is the use of a single r_{12} correlation factor in the R12 ansatz and a combination of nine GCFs in the GG0′ ansatz. From Table 13, we see that, in comparison with the other ansätze in the table, these two ansätze behave in a strikingly similar manner—the difference decreases from 10–16 mE_h at the double-zeta level to 1–2 mE_h at the quadruple-zeta level and 0.6 mE_h at the quintuple-zeta level. Also, at the quadruple- and quintuple-zeta levels, the differences between the MP2-R12-SO and MP2-GG0′ energies are smaller than the differences between the MP2-GG0′ and MP2-GG0 energies. In view of the conclusions of May and coworkers[60] regarding the importance of using a local (Gaussian) correlation function rather than a non-local (linear) correlation function, this observation is surprising. Either the use of a local correlation function is unimportant for the neon atom, or the error incurred by the WO functional in the MP2-GG0′ calculation is similar to the error incurred by the nonlocal correlation function in the MP2-R12-SO calculation, for all cardinal numbers. Although we cannot exclude the latter possibility, we believe that the WO penalty is small for triple-zeta and larger basis sets, leading us to the conclusion that linear and Gaussian correlation factors perform in a similar manner for the neon atom.

Turning our attention to the MP2-R12/1A′ and MP2-R12/1B methods, we first note that these differ from the previous methods in the use of the Q_0 projector rather than the Q projector. Since Q_0 is stronger than Q, the resulting energies should be higher. Indeed, from Table 13, we see that the MP2-R12/1A′ and MP2-R12/1B energies are consistently higher than the MP2-GG0, MP2-GG0′ and MP2-R12-SO energies discussed above, for all basis sets. This is particularly true for the more rigorous MP2-R12/1B model; in the MP2-R12/1A′ model, an additional approximation (neglect of a commutator involving the exchange operator) reduces the energy somewhat, making it fortuitously similar to the MP2-GG0′ energy in the cc-pCVXZ basis sets but significantly higher than the MP2-GG0 energy. Finally, comparing the more rigorous MP2-R12/1B model with the MP2-GG0 model, we note that, apart from the difference in projectors, they differ in the correlation factors and in the optimization. Since the combined effect of different correlation factors and different optimizations was found to be small in our comparison of the MP2-GG0, MP2-GG0′, and MP2-R12-SO energies, we may assume that the energy difference between the GG0 and R12/1B ansätze arises mainly from the different projectors.

From the results in Table 13, we thus conclude in accordance with Klopper and Samson[17] that the use of the Q_0 projector carries a rather large penalty, lifting the MP2-R12/1A′ and MP2-R12/1B correlation energies by more than 20 mE_h at the double-zeta level, by about 10 mE_h at the triple-zeta level, and by 5 mE_h at the quadruple-zeta level. Otherwise, these models converge smoothly, closely following the MP2-GG0, MP2-GG0′ and MP2-R12-SO convergence patterns.

Since the MP2-R12/2A′ and MP2-R12/2B calculations differ from the MP2-R12/1A′ and MP2-R12/1B calculations only in the use of Q rather than Q_0, the resulting energies should be lower than the MP2-R12/1A′ and MP2-R12/1B energies. In fact, we would expect the MP2-R12/2A′ and MP2-R12/2B energies to be similar to the MP2-R12-SO energies or somewhat lower, since these methods use an orbital-invariant rather than orbital-variant ansatz, perhaps leading to energies similar to those of our GG0 ansatz.

However, an inspection of Table 13 reveals that this is not the case. Mostly, the MP2-R12/2A′ and MP2-R12/2B energies are considerably lower than the MP2-GG0 energies and closer to the basis-set limit. However, the performance is erratic. For example, whereas the MP2-R12/2A′ energy is the second highest energy in the cc-pCVDZ basis (after the conventional MP2 energy), it is the second lowest in the aug-cc-pCVDZ basis (after the MP2-geminal energy of Ten-no). Moreover, comparing the MP2-R12/2B and MP2-R12-SO methods in the cc-pCVXZ basis sets, we find that the former gives energies

that are lower by 35, 12, 0.1, and 1.4 mE_h, respectively, for $2 \leq X \leq 5$. Thus, the difference between the energies is much larger than we would expect at the double-zeta level and has an unexpected minimum at the quadruple-zeta level. It appears that the good behaviour of the MP2-R12/2B method may arise from an error cancellation that, for small basis sets, yields correlation energies closer to the basis-set limit than we would expect from the pair-function ansatz itself. The irregular behaviour for small basis sets has been identified by Fliegl *et al.*[61] as arising from negative eigenvalues in the ***B*** matrix in R12 theory.

Except in the cc-pCVQZ basis, the MP2-R12/2B method gives considerably lower correlation energies than the MP2-GG0 method, in spite of the more flexible pair function of the latter. Moreover, as diffuse functions are added to the cc-pCVQZ basis, the MP2-GG0 correlation energy decreases by 3.6 mE_h, comparable to 3.7 mE_h for conventional MP2 and 2.1 and 2.6 mE_h for MP2-R12/1A′ and MP2-R12/2B, respectively—by contrast, the MP2-R12/2A′ and MP2-R12/2B energies change by as much as 5.7 and 8.9 mE_h, respectively. Since the augmentation with diffuse functions should, in such large basis sets, only affect the virtual-orbital treatment (as observed for the MP2-GG0 model), we conclude that the MP2-R12/2A′ and MP2-R12/2B models have basis-set errors of about 2 and 5 mE_h, respectively, not related to the cusp treatment. When diffuse functions are added to the larger cc-pCV5Z basis, the basis-set errors of the two models reduce to 0.4 mE_h and 1.4 mE_h, respectively.

Finally, a comparison of the MP2-R12/2A′ and MP2-R12/2B energies further highlights their erratic behaviour. In the cc-pCV*X*Z basis sets with $2 \leq X \leq 5$, the MP2-R12/2B and MP2-R12/2A′ energies differ by −110, −6, 4, and 2 mE_h, respectively; with diffuse functions added, the differences become 25, 6, 0.7, and 1.2 mE_h, respectively. In short, the convergence of the new MP2-R12 methods seems unpredictable, noting in particular the strange behaviour at the quadruple-zeta level.

From Table 13, we see that the difference between the MP2-R12/2A′ energy and the MP2-geminal energy of Ten-no[53] in the large cc-pCVQZ basis is 4 mE_h, while the corresponding difference between the MP2-R12-SO and MP2-GG0′ energies is only 0.3 mE_h. This discrepancy cannot easily be explained by different cusp treatments, noting that the difference in the cusp treatment is the same in the two cases: the MP2-R12 energies have been obtained with r_{12} correlation factors, while the other energies have been obtained with GCFs. Moreover, the discrepancy disappears when the cc-pCVQZ basis is extended with diffuse functions, which might suggest that one or more of the approximations made in the MP2-R12/2A′ and MP2-geminal models is poor in the absence of diffuse functions. We note, however, that the discrepancy between the two models increases again in the larger aug-cc-pCV5Z basis, suggesting that other factors also contribute.

3.2.5 The hydrogen molecule. In Table 14, we give our MP2 correlation energies for the H_2 molecule with a bond length of $1.4a_0$ = 74.0848 pm. From our experience with helium, we might expect large pair-function expansions in s orbitals to give good MP2-GG1 and MP2-GG2 energies also for the hydrogen molecule. From a study of the s-orbital energies, this also appears to be the case. However, comparing with the aug-cc-pVTZ energy, we note that the MP2-GG2 energies obtained with the two s expansions are in fact below the true MP2 correlation energy, indicating that the Fock operator is poorly described. Because of polarization, the $1\sigma_g$ orbital contains a small p contribution and even smaller d and f contributions. Clearly, then, the Fock operator will be poorly described in basis sets without polarization functions, leading to incorrect (*i.e.*, too low) MP2 energies.

Table 14 MP2 correlation energies ($-E$/mE_h) of H_2 at an internuclear distance of 74.0848 pm. Energies marked with a double-dagger (‡) are larger in magnitude than the true energy, probably due to a non-positive-definite Fock operator

Orbital basis	VOE	GG0	GG1	GG2
aug-cc-pVDZ	27.29	32.74	33.879	34.0464
aug-cc-pVTZ	31.99	33.82	34.209	34.2525
aug-cc-pVQZ	33.25	34.14	34.241	—
aug-cc-pVQZ (s)	18.36	30.11	33.934	34.3232‡
aug-cc-pVQZ (sp)	30.45	33.50	34.220	34.2460
aug-cc-pVQZ (spd)	32.74	34.06	34.240	—
aug-cc-pV5Z (s)	18.43	30.13	33.943	34.3680‡
aug-cc-pV5Z (sp)	30.65	33.53	34.229	34.2491
aug-cc-pV5Z (spd)	32.98	34.11	34.247	—

By contrast, the H_2 energies obtained with sp basis sets are all above the MP2 limit. With the largest such sets, the MP2-GG*n* models with increasing *n* recover 97.9%, 99.93%, and 99.99% of the estimated limit—see Table 15. When the partial-wave expansion is extended to include d orbitals, the GG2 model gives our current best estimate of the MP2 correlation energy (−34.25 mE_h), while the GG1 and GG0 models recover 99.98% and 99.6%, respectively, of this energy. The best MP2-GG0 correlation energy (99.7%) is obtained in the aug-cc-pVQZ basis, which also includes f orbitals.

In Table 15, we compare our H_2 correlation energies with literature data. Less data exist for molecules than for atoms since accurate methods are often either restricted to atoms[36,56,58] or only implemented for atoms.[55] The best energies are our GG2 and GG1 values, obtained using 1710 and 171 GTGs, respectively. The energy of Bukowski *et al.*,[33] obtained with 120 nonlinearly optimized s-type GTGs located on the molecular axis, is only a few μE_h higher, however. The MP2-R12 energies of Klopper and Kutzelnigg[63] are also good, bearing in mind the relatively small basis set used.

3.2.6. Lithium hydride. In Table 16, we present all-electron MP2 correlation energies for LiH at a bond length of $3.015a_0$

Table 15 MP2 correlation energies ($-E$/mE_h) of H_2 at an internuclear distance of 74.0848 pm, listed chronologically. The total correlation energy is −40.8461 mE_h[62]

Authors	Method	Energy
This work	MP2-GG0 (aug-cc-pVQZ)	34.14
	MP2-GG1 (aug-cc-pV5Z (spd))	34.247
	MP2-GG2 (aug-cc-pVTZ)	34.252
Bukowski *et al.*[33]	120 nonlinearly optimized GTGs	34.244
Klopper and Kutzelnigg[63]	MP2-R12/A (9s8p4d1f)	34.23
	MP2-R12/B (9s8p4d1f)	34.17
Jeziorski *et al.*[64]	40 nonlinearly optimized GTGs	34.20

Table 16 All-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) of LiH at an internuclear distance of 159.547 pm. All basis sets are ANO-2 in uncontracted form

Basis	VOE	GG0	GG1
(14s9p, 8s)	49.99	63.81	70.900
(14s9p4d, 8s)	54.41	66.72	71.808
(14s9p, 8s4p)	61.78	69.52	72.678
(14s9p4d, 8s4p)	63.06	70.38	72.809
(14s9p4d3f, 8s4p)	63.68	70.79	72.850
(14s9p4d, 8s4p3d)	65.24	71.20	72.864
(14s9p4d3f, 8s4p3d)	65.40	71.33	72.877

(159.547 pm). No MP2-GG2 energies are listed, as singularities in the solver prevented us from using this ansatz. In its absence, good correlation energies are recovered with the GG1 ansatz, in agreement with our observations for H_2. In the (14s9p4d3f, 8s4p3d) basis, this ansatz yields our best correlation energy of -72.877 mE_h, which according to Table 17 (see below) constitutes 99.98% of the estimated limit. Reasonably good energies are also obtained without f orbitals on lithium. The best MP2-GG0 energy is -71.20 mE_h, which represents only 97.9% of the limit. We recall that, with this ansatz, far better correlation energies were obtained for H_2.

In Table 17, we compare our best LiH correlation energies with literature data. The best correlation energy is that of Bukowski *et al.*[45] Using 350 GTGs of the form of eqn (36), with five of the nonlinear parameters for each GTG optimized variationally, these authors obtained -72.890 mE_h. Their result is almost matched by Noga *et al.*,[46] who obtained -72.869 mE_h with the MBPT-R12/B method. This method is not variational, however, making it difficult to evaluate the quality of the result. The extrapolated complete basis-set (CBS) value of Petersson *et al.*[38] is far off the limit.

Compared with the literature data, the GG1 ansatz performs very well. In Table 18, we have decomposed the best correlation energies obtained with the GG1 and GG0 ansätze into pair energies, comparing with the results of Alexander *et al.*[66] and of Klopper and Kutzelnigg[63] (no pair energies were published by Bukowski *et al.* and by Noga *et al.*). Except for the $1\sigma2\sigma$ triplet energy, the GG1 ansatz gives the lowest pair energies.

3.2.7. Hydrogen fluoride. In Table 19, we present our MP2 correlation energies for HF at a bond length of $1.73280a_0$ (91.6958 pm), calculated in the augmented core-valence aug-cc-pCVDZ and aug-cc-pCVTZ basis sets. If we compare energies obtained from subsets of the aug-cc-pCVTZ basis set, the importance of d orbitals (as previously observed for neon) becomes evident. For the GG1 ansatz, for instance, merely 92.9% of the correlation energy limit of -384.41 mE_h (see Table 20 below) is recovered by the aug-cc-pCVTZ(sp,sp) basis, which is well saturated in the sp space. However, once d orbitals have been added to fluorine, as much as 99.5% of the correlation energy is recovered. The GG2 ansatz behaves similarly, recovering 95.4% in the aug-cc-pCVTZ(sp,sp) basis, and 99.98% in the aug-cc-pCVTZ(spd,sp) basis. Therefore, good HF correlation energies are obtained with spd- and sp-saturated basis sets on fluorine and hydrogen, respectively, in agreement with our results for Ne and H_2.

Table 17 MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) of LiH at an internuclear distance of 159.547 pm, listed chronologically. The total correlation energy is -83.2 mE_h[65]

Authors	Method	Energy/ mE_h
This work	MP2-GG0 (14s9p4d3f, 8s4p3d)	71.33
	MP2-GG1 (14s9p4d3f8s4p3d)	72.877
Bukowski *et al.*[45]	350 nonlinearly optimized GTGs	72.890
Noga *et al.*[46]	MBPT-R12/A (11s8p6d5f, 9s8p6d5f)	72.973
	MBPT-R12/B (11s8p6d5f, 9s8p6d5f)	72.869
Klopper and Kutzelnigg[63]	MP2-R12/A (11s7p4d1f, 9s6p3d1f)	72.76
	MP2-R12/B (11s7p4d1f, 9s6p3d1f)	72.16
Petersson *et al.*[38]	CBS (complete basis-set) model	73.54
Alexander *et al.*[66]	700 nonlinearly optimized, randomly tempered GTGs	72.781

Table 18 MP2 pair correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) of LiH at an internuclear distance of 159.547 pm

Pair		R12/A[a]	R12/B[a]	GTG[b]	GG0[c]	GG1[c]
$1\sigma^2$	$^1\Sigma^+$	39.51	39.45	39.590	38.527	39.609
$1\sigma2\sigma$	$^1\Sigma^+$	1.48	1.41	1.471	1.409	1.490
	$^3\Sigma^+$	1.37	1.30	1.324	1.284	1.340
$2\sigma^2$	$^1\Sigma^+$	30.41	30.00	30.396	30.106	30.437
$E^{(2)}$		72.76	72.16	72.781	71.326	72.877

[a] Basis (11s8p6d5f, 9s8p6d5f).[63] [b] Nonlinearly optimized GTGs.[66] [c] Basis (14s9p4d3f, 8s4p3d).

In Table 20, we compare our best correlation energies for the HF molecule with literature data. The current best MP2 correlation energy of -384.41 mE_h has been obtained with the GG2 ansatz in the aug-cc-pCVTZ(spd,sp) basis. The best energy obtained with the GG1 ansatz was in the aug-cc-pCVTZ basis, in which 99.81% of the estimated limit was recovered. From our experience with neon, we expect the true MP2 correlation energy to be 0.2 to 0.3 mE_h lower than our aug-cc-pCVTZ(spd,spd) value.

A good estimate of the limit has also been obtained by Klopper,[68] who recovered -384.38 mE_h with the MP2-R12/B method, using a 19s14p8d6f4g3h basis for fluorine and a 9s6p4d3f basis for hydrogen. All other highly accurate correlation energies reported in the literature have also been

Table 19 All-electron MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) of HF at an internuclear distance of 91.6958 pm

Basis	VOE	GG0	GG1	GG2
aug-cc-pCVDZ	263.71	337.79	374.03	382.01
aug-cc-pCVTZ (sp,s)	197.21	276.21	350.87	360.05
aug-cc-pCVTZ (sp,sp)	207.60	285.11	357.05	366.66
aug-cc-pCVTZ (spd,s)	309.14	351.26	381.36	383.69
aug-cc-pCVTZ (spd,sp)	313.51	354.70	382.35	384.34
aug-cc-pCVTZ (spd,spd)	317.00	357.35	382.64	384.41
aug-cc-pCVTZ	339.89	370.41	383.69	—

Table 20 The MP2 correlation energy ($-E/\mathrm{m}E_\mathrm{h}$) of HF at an internuclear distance of 91.6958 pm, listed chronologically. The total correlation energy is -388 mE_h[67]

Authors	Method	Energy
This work	MP2-GG0 (aug-cc-pCVTZ)	370.41
	MP2-GG1 (aug-cc-pCVTZ)	383.69
	MP2-GG2 (aug-cc-pCVTZ(spd,spd))	384.41
Ten-no[53]	MP2-geminal (aug-cc-pV5Z, without h functions)	384.16
Klopper and Samson[17]	MP2-R12/1A′ (aug-cc-pV5Z)	381.61
	MP2-R12/1B (aug-cc-pV5Z)	381.09
	MP2-R12/2A′ (aug-cc-pV5Z)	384.67
	MP2-R12/2B (aug-cc-pV5Z)	383.57
Klopper[68]	MP2-R12/B (19s14p8d6f4g3h, 9s6p4d3f)	384.38
Muller *et al.*[67]	MP2-R12/A (18s12p10d8f6g, 10s7p5d)	384.36
	MP2-R12/B (18s12p10d8f6g, 10s7p5d)	384.17
Klopper[59]	MP2-R12/A (15s9p7d5f3g1h, 9s7p5d3f1g)	384.47
	MP2 (15s9p7d5f3g1h, 9s7p5d3f1g)	371.68
Petersson *et al.*[38]	CBS (complete basis-set) model	378.80

obtained using different MP2-R12 approaches with one-electron basis sets of high quality. As seen from Table 20, these estimates are in good agreement with one another. In two cases, Klopper and coworkers have obtained an energy lower than our variationally bounded MP2 correlation energy of -384.41 mE_h, but this has been achieved with the MP2-R12/A model rather than with the more complete MP2-R12/B model. A CBS estimate of the correlation energy has been reported by Petersson *et al.*[38] Although better than conventional orbital-based MP2 theory, their CBS result is clearly inferior to that of MP2-R12 theory. Three totally symmetric pair energies have been published in a discussion of a then-new optimization technique by Wenzel and Zabolitzky,[69] but the complete correlation energy of HF has not yet been calculated using the GTG method with nonlinear optimization.

Table 21 The MP2 pair energies ($-E/\mathrm{m}E_\mathrm{h}$) of HF at an internuclear distance of 91.6958 pm

Spin	Pair	R12/A[a]	GG0[b]	GG1[b]	GG2[c]	GG2[d]	GTG
Singlet	$1\sigma^2$	40.57	40.038	40.546	40.561	40.568	40.2
	$1\sigma2\sigma$	3.60	3.493	3.614	3.608	3.618	
	$2\sigma^2$	13.06	12.643	13.057	13.279	13.078	12.4
	$1\sigma3\sigma$	2.07	1.859	2.076	2.083	2.084	
	$2\sigma3\sigma$	20.16	19.230	20.116	19.623	20.166	
	$3\sigma^2$	29.30	28.574	29.243	28.968	29.229	27.2
	$1\sigma1\pi$	4.99	4.422	4.981	4.986	5.000	
	$2\sigma1\pi$	39.97	37.670	39.884	39.217	39.956	
	$3\sigma1\pi$	33.15	31.201	32.998	27.797	33.097	
	$1\pi^2$	71.30	68.057	71.067	61.614	71.273	
Triplet	$1\sigma2\sigma$	1.59	1.455	1.596	1.608	1.599	
	$1\sigma3\sigma$	3.31	3.082	3.300	3.276	3.311	
	$2\sigma3\sigma$	8.81	8.590	8.802	8.840	8.811	
	$1\sigma1\pi$	8.56	7.957	8.532	8.521	8.556	
	$2\sigma1\pi$	18.79	18.143	18.764	18.635	18.822	
	$3\sigma1\pi$	56.49	55.711	56.416	55.441	56.494	
	$1\pi^2$	28.74	28.287	28.699	28.599	28.751	
Sum		384.47	381.412	383.691	366.656	384.411	

[a] MP2-R12/A from ref. 59. [b] Using basis aug-cc-pCVTZ. [c] Using basis aug-cc-pCVTZ (sp, sp). [d] Using basis aug-cc-pCVTZ (spd, spd).

Table 22 MP2 correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) obtained in this work compared with current best estimates

System	This work	Current best	Energy recovered
He	37.37729	37.37747[a]	99.9995%
Be	76.355	76.358[b]	99.996%
Ne	388.19	388.19	100%
H_2	34.252	34.252	100%
LiH	72.877	72.890[b]	99.98%
HF	384.41	384.41	100%

[a] Patkowski *et al.*[34] [b] Bukowski *et al.*[45]

In Table 21, we compare pair energies of HF for some selected methods. As for the neon atom in Table 12, we have carried out two sets of calculations with the GG2 ansatz, with and without d orbitals on fluorine. The calculations also differ in the d orbitals on hydrogen, but these orbitals change the total MP2 energy by less than 0.1 mE_h (see Table 19) and are therefore unimportant. Whereas the d orbitals on neon are crucial for the $2p^2$ singlet pair function, they are needed in HF not only for the $1\pi^2$ singlet but also for the $3\sigma1\pi$ singlet, which follows from the large d contribution to the 3σ orbital in this molecule.

4. Conclusions

We have presented the MP2-GG*n* method for calculating highly accurate MP2 energies for atomic and molecular closed-shell systems. Our method may be regarded as a hybrid of the MP2-R12 method developed by Klopper and Kutzelnigg[5-7] and of the GTG method developed by Szalewicz, Jeziorski, and others.[9–12] The pair energies are obtained by minimizing the WO functional of Szalewicz and coworkers,[9–12] explicitly evaluating all three-electron integrals. Since only linear parameters are optimized, the pair energies are obtained by solving a set of linear equations.

We have demonstrated that GG*n* pair functions of the form eqns (15)–(17) give accurate energies for both atoms and molecules when these functions are optimized with the WO functional, expanding the GTGs in nine GCFs with even-tempered exponents 1/9, 1/3, 1, … 729. In Table 22, we compare our best MP2-GG*n* correlation energies with the best estimates in the literature. For the three systems Ne, H_2, and HF, the MP2-GG*n* correlation energies constitute an improvement on all previous results; for He, Be, and LiH, the MP2-GG*n* energies are within 0.02% of the best literature data.

Most of these values have been obtained with the GG2 ansatz, which has a limited applicability because of high memory requirements. The GG1 ansatz also performs well, however, and can be used for a wider range of systems. From a memory perspective, the most widely applicable ansatz is the GG0 ansatz. Although the performance of this ansatz is far better than that of the orbital approximation, it is perhaps not as good as hoped for. Since the occupied orbitals are reasonably well described even in small basis sets, the only way to improve such correlation energies is to enlarge the virtual-orbital expansion. To avoid computing redundant geminal integrals, separate basis sets should then be introduced for the orbital and geminal parts of the pair functions. The

introduction of such dual basis sets would enable calculations on larger molecules, although the calculation of three-electron integrals would still limit the size of systems that can be treated. For instance, the aug-cc-pCVTZ calculations on neon and the aug-cc-pCVTZ(spd,sp) calculations on HF presented here required 8 and 54 hours, respectively, on a modern Linux PC, for all three ansätze.

However, the purpose of this paper has not been to present an efficient method for molecular studies but rather to provide benchmark values for the pair functions eqns (15)–(17), optimised with a WO functional. As discussed in ref. 20, the explicit calculation of three-electron integrals in MP2-GG*n* theory can be avoided by invoking the RI approximation, making the cost of the methods presented here similar to that of the MP2-R12 methods. Such a development would also allow us to study in great detail the effects of the RI approximation, since we would then be able to run calculations that would be identical except for the use of this approximation. In the present paper, we have made careful comparisons with related RI-based methods, providing useful information about the effects of the RI approximation.

For neon, the MP2-GG0 method performs better than the MP2-R12-SO method and the MP2-R12/1A′ and MP2-R12/1B methods—partly because a more restricted projector is used and partly because the nine GCFs are more flexible than a single r_{12} and therefore better suited to describe the Coulomb hole except for very small inter-electronic distances. Comparing with the newer MP2-R12/2A′ and MP2-R12/2B methods, our approach appears to be more robust, noting that the R12 methods show some erratic behaviour even at the quadruple- and quintuple-zeta levels, suggestive of error cancellation. Although the errors in MP2-R12 theory have already been thoroughly studied by May and coworkers,[60] their conclusion that the error incurred by the various approximations in the MP2-R12 theory is at most 0.4 mE_h at the cc-pVQZ level (for a set of small molecules) is not in accordance with the larger errors we have identified. A closer examination of the errors and their partial cancellations in this important method may be warranted.

Assuming that the WO penalty is small in triple-zeta and larger basis sets, we do not find that the Gaussian correlation factors perform significantly better than linear correlation factors for the systems studied here, the replacement of linear r_{12} by a set of variationally optimised GCFs improving the convergence only marginally, contradicting the conclusion of May and coworkers[60] regarding the relative performance of local and nonlocal correlations functions. However, until we can quantify the WO penalty more precisely, a definite conclusion regarding the relative performance of local (Gaussian) and nonlocal (linear) correlation factors in small systems cannot be drawn.

For the MP2-GG*n* method presented here, the major defect in the pair-function ansatz lies not in the form of the correlation factor but rather in the set of orbitals with which the correlation factors are combined to form geminals. When correlation factors are introduced in singly- and doubly-excited MO pairs, a significant improvement in the energy is observed. It would be interesting to investigate whether a similar energy improvement is also observed for the MP2-R12 methods.

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