

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

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## Abstract

We have implemented the use of mixed basis sets of Gaussian one- and two-electron functions, for the calculation of second-order perturbation corrections and correlation energies. In this paper we describe some aspects of this implementation, including different forms chosen for the first-order pair functions. Computational results are presented for some closed shell atoms and diatomics. Our tests indicate that our method is capable of yielding up to 99% of the correlation energy using rather modest Gaussian-type orbital basis sets, and in a calculation on Ne using up to  $g$  type functions we obtain more than 99.9% of the estimated MP2 limit. For the hydrogen molecule we present the currently best MP2 energy. We also show that the MP2-R12/2A' and MP2-R12/2B' methods...

## I. INTRODUCTION

One of the most important limitations 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 energy is very slow: even very large basis sets, comprising hundreds of functions and angular momenta 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 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  $1a_0$  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 emphasised that these inadequacies are independent both of the particular many-electron approach chosen for the parametrization 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 functions compared with Slater functions nor a limitation of particular types of Gaussian basis sets.

From a mathematical perspective, the most attractive alternative 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 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 inter-electronic distance  $r_{12}$  to arbitrary orders [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 inter-electronic distances, since the cusp in the exact wave function behaves as  $r_{12}$  as the inter-electronic 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, 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 one-electron basis is much better than methods employing only one-electron functions—namely,  $(l + \frac{1}{2})^{-6}$  rather than  $(l + \frac{1}{2})^{-4}$ . Their R12 approach has since been successively used not only in second-order Møller–Plesset (MP2) perturbation theory but also in coupled-cluster and multi-reference averaged coupled-pair functional theories.

A different explicitly correlated approach has been developed by Szalewicz, Jeziorski and their coworkers [8–11]. Rather than augmenting an orbital-product basis with terms linear in  $r_{12}$ , they expand the two-electron pair functions directly in Gaussian-type geminals (GTGs), optimising 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. The resulting GTG method is therefore 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 in R12 theory, they are better suited for describing its overall shape.

Here we investigate, within the framework of MP2 theory, the combined expansion of WO pair functions in orbital products and in fixed (contracted) linear combinations of GTGs. A paper has already been published that describes the main ideas of our approach within the context of local MP2 theory, containing some sample calculations on medium-sized molecules [12]. Our purpose is here different in that we focus on high accuracy in closed-shell atoms and diatoms.

## II. 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 calculation and manipulation of the necessary many-electron integrals.

### A. The MP2 energy functional

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

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

which is bounded from below by the second-order energy

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

In Møller–Plesset theory, where  $\Psi^{(0)}$  is the Hartree–Fock wave function, the  $\Psi^{(1)}$  and  $E^{(2)}$  can be expressed in terms of pair functions  $u_{ij}^s$  (whose form is discussed in Section II B) and the associated pair energies  $\epsilon_{ij}^s$

$$F_{ij}^s[u_{ij}^s] = \frac{s}{2(1 + \delta_{ij})} [\langle Q u_{ij}^s | f(1) + f(2) - \epsilon_i - \epsilon_j | Q u_{ij}^s \rangle + 2\langle Q u_{ij}^s | r_{12}^{-1} | \phi_{ij}^s \rangle] \quad (3)$$

$$E^{(2)} = \sum_{i \geq j} \epsilon_{ij}^1 + \sum_{i > j} \epsilon_{ij}^3 \quad (4)$$

$$\epsilon_{ij}^s = \frac{s}{1 + \delta_{ij}} \langle Q u_{ij}^s | r_{12}^{-1} | \phi_{ij}^s \rangle \quad (5)$$

Here  $f(i)$  is the Fock operator of electron  $i$ , orbital energies are denoted by  $\epsilon_i^s$ , the  $\phi_{ij}^s$  are singlet ( $s = 1$ ) and triplet ( $s = 3$ ) products of occupied molecular orbitals (MOs)

$$\phi_{ij}^s = \frac{1}{\sqrt{2}} [\varphi_i(1)\varphi_j(2) + (2 - s)\varphi_j(1)\varphi_i(2)] \quad (6)$$

and SO is enforced by the projection operator

$$Q(1, 2) = [1 - p(1)][1 - p(2)], \quad p = \sum_k |\varphi_k\rangle\langle\varphi_k| \quad (7)$$

where the summation is over all occupied MOs  $\varphi_k$ . 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 [8–11]. The simplest such functional takes the form

$$J_{ij}^s[u_{ij}^s] = \frac{s}{2(1 + \delta_{ij})} [\langle u_{ij}^s | \tilde{f}_{ij}(1) + \tilde{f}_{ij}(2) - \epsilon_i - \epsilon_j | u_{ij}^s \rangle + 2\langle Q u_{ij}^s | r_{12}^{-1} | \phi_{ij}^s \rangle] \quad (8)$$

We have here introduced the modified Fock operator  $\tilde{f}_{ij} = f + \Delta_{ij}p$  where  $p$  is the projector onto the occupied MO space and where  $\Delta_{ij} = \frac{1}{2}(\epsilon_i + \epsilon_j) - \epsilon_1 + \eta$  with  $\epsilon_1 \leq \epsilon_i$  and  $\eta \geq 0$ . The

presence of  $\Delta_{ij}p$  makes the expectation value of  $\tilde{f}(1) + \tilde{f}(2)$  greater than  $\epsilon_i + \epsilon_j$  for all  $u_{ij}$ , thereby ensuring that second-order term in Eq. (8) positive definite and that the minimum principle applies. The level-shift parameter  $\eta$  introduces a penalty that is large if the pair function overlaps with the occupied space. We monitor the degree of SO by calculating

$$\chi_{ij}^{\text{SO}} = \frac{\langle u_{ij}^s | p(1) + p(2) | u_{ij}^s \rangle}{\langle u_{ij}^s | u_{ij}^s \rangle}, \quad (9)$$

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  $\eta$ , this dependence is weak as shown in Section III A 3.

## B. Choice of pair functions

The pair functions used in our calculations are symmetric and anti-symmetric 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

$$u_{ij}^s = \sum_{a>b} \phi_{ab}^s c_{ij,s}^{ab} \quad (10)$$

where the summation is over all pairs of unoccupied MOs (denoted by indices  $a$  and  $b$ ) and where the symmetric form  $s = 1$  and the antisymmetric form  $s = 3$  are to be combined with normalized two-electron singlet and triplet spin functions, respectively. To include a linear  $r_{12}$  term, Kutzelnigg and Klopper proposed the ansatz

$$u_{ij}^s = \sum_{a>b} \phi_{ab}^s c_{ij,s}^{ab} + Q_0 r_{12} \phi_{ij}^s c_{ij,s}, \quad (11)$$

later generalised by Klopper to

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

to ensure invariance to rotations among the occupied MOs. The projection operator  $Q_0 = [1 - p_0(1)][1 - p_0(2)]$  used here, with  $p_0 = \sum_p |\varphi_p\rangle\langle\varphi_p|$ , ensures an orthogonality even “stronger” than the SO—that is, not just to the occupied MOs but all MOs. Previously,

we suggested replacing the linear  $r_{12}$  term in Eq. (11) with a combination of fixed-exponent Gaussian correlation factors (GCFs)

$$u_{ij}^s = \sum_{a>b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_v g_{ij,v}^s c_{ij,s}^v. \quad (13)$$

where we have introduced the short-hand notation

$$g_{pq,v}^s = \exp(-\gamma_v r_{12}^2) \phi_{pq}^s \quad (14)$$

and where the linear coefficients  $c_{ij,s}^v$  are variationally optimised in the course of the MP2 calculation. In the present work, we shall consider the following forms, which may be viewed as variations of Eq. (12) where the pair summation over occupied MOs is generalized: the  $kl$  pair-function ansatz, with a summation over all pairs of occupied MOs in the geminal part:

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

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

$$u_{ij}^s = \sum_{a>b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{p>q} \sum_v g_{pq,v}^s c_{ij,s}^{pq,v} \quad (16)$$

and the  $kq$  pair-function ansatz, where at least one MO is occupied in the geminal part:

$$u_{ij}^s = \sum_{a>b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{q>k,q} \sum_v g_{kq,v}^s c_{ij,s}^{kq,v} \quad (17)$$

In Section III, we shall compare the performance of the  $kl$ ,  $pq$ , and  $kq$  pair functions. When the summations are over all MOs (as in the two last pair functions), they may be carried out in the atomic-orbital (AO) basis, although linear dependencies may then sometimes arise with the  $kq$  expansion. In the pair functions, it is possible to use different basis sets for the virtual and GTG expansions but we have not explored this flexibility here.

### C. Optimisation of pair functions

When the pair functions are expanded in pairs of virtual MOs and geminals as in Eqs. (15)–(17), the WO functional may be parametrised as

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

where the matrices  $\mathbf{C}_o$  and  $\mathbf{C}_g$  contain the orbital and geminal expansion coefficients  $c_{ij,s}^{ab}$  and  $c_{ij,s}^{pq,v}$ , respectively, arranged with  $ab$  and  $(pq, v)$  as composite row indices and with  $ij$  as a composite column index. Note that the functional form of  $J_{ij}^s(\mathbf{C}_o, \mathbf{C}_g)$  is different for singlet and triplet pair functions  $u_{ij}^s$  and that, being a function for orbital pair  $ij$ ,  $J_{ij}^s$  depends only on the elements of column  $ij$  in  $\mathbf{C}_o$  and  $\mathbf{C}_g$ .

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

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

where, in the canonical MO basis, the elements of the Hermitian orbital–orbital block  $\mathbf{H}_{oo}$ , the geminal–orbital block  $\mathbf{H}_{go} = \mathbf{H}_{og}^\dagger$ , and the Hermitian geminal–geminal block  $\tilde{\mathbf{H}}_{gg}$  are given by

$$[\mathbf{H}_{oo}]_{ab,cd} = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) \delta_{ac} \delta_{bd}, \quad (20)$$

$$[\mathbf{H}_{go}]_{pqv,cd} = \langle g_{pq,v}^s | f(1) + f(2) - \epsilon_i - \epsilon_j | \phi_{cd}^s \rangle, \quad (21)$$

$$[\tilde{\mathbf{H}}_{gg}]_{pqv,p'q'v'} = \langle g_{pq,v}^s | \tilde{f}(1) + \tilde{f}(2) - \epsilon_i - \epsilon_j | g_{p'q',v'}^s \rangle, \quad (22)$$

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

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

$$[\mathbf{R}_g]_{pqv} = \langle g_{pq,v}^s | Q_{occ} r_{12}^{-1} | \phi_{ij}^s \rangle. \quad (24)$$

Note that, because of the presence of the projector  $p$ , the modified Fock operator  $\tilde{f}$  only appears in the geminal–geminal block  $\tilde{\mathbf{H}}_{gg}$ .

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

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

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

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

where

$$\mathbf{Z} = \mathbf{H}_{g\text{o}} \mathbf{H}_{\text{o}\text{o}}^{-1} \quad (27)$$

$$\tilde{\mathbf{G}}_{g\text{g}} = \tilde{\mathbf{H}}_{g\text{g}} - \mathbf{H}_{g\text{o}} \mathbf{H}_{\text{o}\text{o}}^{-1} \mathbf{H}_{\text{o}g} \quad (28)$$

are easily formed since  $\mathbf{H}_{\text{o}\text{o}}$  is diagonal. Inserting this decomposition into Eq. (19) and rearranging, we obtain

$$\begin{pmatrix} \mathbf{H}_{\text{o}\text{o}} & \mathbf{H}_{\text{o}g} \\ \mathbf{0} & \tilde{\mathbf{G}}_{g\text{g}} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{\text{o}} \\ \mathbf{C}_{g} \end{pmatrix} = - \begin{pmatrix} \mathbf{R}_{\text{o}} \\ \mathbf{S}_{g} \end{pmatrix} \quad (29)$$

with

$$\mathbf{S}_{g} = \mathbf{R}_{g} - \mathbf{Z}\mathbf{R}_{\text{o}} \quad (30)$$

The coefficients  $\mathbf{C}_{g}$  are now found by solving the equation

$$\tilde{\mathbf{G}}_{g\text{g}} \mathbf{C}_{g} = -\mathbf{S}_{g} \quad (31)$$

using some iterative method. Inserting the resulting amplitudes into Eq. (29),  $\mathbf{C}_{\text{o}}$  are obtained directly as

$$\mathbf{C}_{\text{o}} = -\mathbf{H}_{\text{o}\text{o}}^{-1} \mathbf{R}_{\text{o}} - \mathbf{Z}\mathbf{C}_{g} \quad (32)$$

Whereas the first contribution is identical to the usual amplitudes of orbital-based MP2 theory Eq. (25), the second contribution is a correction arising from the presence of the geminals. We note that, through the decomposition Eq. (26), we have reduced the dimension of the linear equations to be solved iteratively from  $N_{\text{o}} + N_{g}$  to  $N_{g}$ , where  $N_{\text{o}}$  is the number of functions in the virtual orbital expansion and  $N_{g}$  is the number of geminals.

In the limit of a complete one-electron basis, the orbitals becomes exact eigenfunctions of the Fock operator and  $\sum_p |\varphi_p\rangle\langle\varphi_p| \rightarrow 1$ . From a consideration of the detailed form of the matrix elements in Eqs. (20)–(24), we note that, in this limit,  $\mathbf{S}_{g} \rightarrow \mathbf{0}$  in Eq. (30). We conclude that, in the limit of a complete one-electron basis, the solution to Eq. (29) becomes  $\mathbf{C}_{\text{o}} \rightarrow -\mathbf{H}_{\text{o}\text{o}}^{-1} \mathbf{R}_{\text{o}}$  and  $\mathbf{C}_{g} \rightarrow \mathbf{0}$ . The geminal contribution to the solution therefore depends not only on the geminals but also on the size of the one-electron basis.

#### D. Calculation of the energy

From the converged amplitudes, the second-order MP2 energy Eq. (5) is given as the sum over all pair energies and may be calculated from the expression

$$E^{(2)} = \text{tr}(\mathbf{C}_o^\dagger \overline{\mathbf{R}}_o) + \text{tr}(\mathbf{C}_g^\dagger \overline{\mathbf{R}}_g), \quad (33)$$

where we have introduced a parity-weighted version of the matrices  $\mathbf{R}_o$  and  $\mathbf{R}_g$  defined as

$$[\overline{\mathbf{R}}]_{ij} = \frac{s}{1 + \delta_{ij}} [\mathbf{R}]_{ij}. \quad (34)$$

The decomposition Eq. (26) also allows us to rewrite the energy as

$$E^{(2)} = -\text{tr}(\mathbf{R}_o^\dagger \mathbf{H}_{oo}^{-1} \overline{\mathbf{R}}_o) + \text{tr}(\mathbf{C}_g^\dagger \overline{\mathbf{S}}_g), \quad (35)$$

where the two terms represent the contributions from the orbital and geminal expansions, respectively. The relative magnitudes of the orbital and geminal contributions to the second-order energy may vary considerably, depending on the relative sizes of the orbital and geminal expansions. As discussed above, the geminal contribution vanishes in the limit of a complete one-electron basis.

#### E. Many-electron integrals

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 minutes is typically spent computing these integrals and accumulating their contributions into various matrix elements, and for longer calculations the fraction of time required for this step only increases.

In traditional applications of GTGs, with nonlinear optimisation 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 and combining it with the technique suggested originally by Boys by which many-electron integrals over GTGs can be reduced to (more complicated) one-

and two-electron integrals. A full description of this formulation can be found in Ref. 13. One way of reducing the number of integrals that must be calculated is to use molecular symmetry. We have implemented a scheme for evaluating only symmetry-distinct integrals and using symmetry-adapted basis functions using a double coset decomposition technique. Full details have been given elsewhere [14].

Although the calculation of three-electron integrals is very expensive, the storage requirements are modest since the integrals are contracted with one-particle density matrices as soon as they are computed, so there are no major storage requirements. At present, we employ no integral pre-screening strategy other than the elimination of integral batches based on the “pre-exponential factor”. In particular, we do not use any density matrix-based screening in the times reported here.

These times could undoubtedly be reduced substantially using density matrix screening, and this will be implemented in future work. However, our previous experience, combined with the results of the next section, suggests that the most profitable strategy for reducing the computer time will result from the use of dual basis sets.

### III. APPLICATIONS

#### A. Computational details and considerations

##### 1. One-electron basis sets

The cc-pVXZ basis sets are composed as principal expansions [1], meaning that they belong to one of the following orbital spaces ( $2s1p$ ), ( $3s2p1f$ ), ( $4s3p2f1g$ ), and so on. To examine the convergence of the partial-wave expansion as well as that of the principal expansion, we shall often truncate the correlation-consistent basis sets at some angular-momentum level. The orbital types retained in the basis are then given in parentheses after the basis-set name. Thus, 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 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. Thus, in the cc-pVTZ(sp,d,sp) basis, we have omitted the  $f$  shell on oxygen and the  $d$  shell on hydrogen.

Although there are cc-pVXZ basis sets available for both lithium and beryllium [15, 16]

TABLE I: All-electron MP2 correlation energies ( $-E/mE_h$ ) of neon calculated using geminal exponents of the sequence  $1/9, 1/3, 1, \dots, 729$ .

$N_g$	cc-pVDZ			aug-cc-pCVTZ(sp)		
	$kl$	$kq$	$pq$	$kl$	$kq$	$pq$
0	<b>187.567</b>	<b>187.567</b>	<b>187.567</b>	<b>309.078</b>	<b>309.078</b>	<b>309.078</b>
1	<b>187.655</b>	<b>187.758</b>	206.325	<b>309.078</b>	<b>309.126</b>	335.423
2	196.870	240.497	280.170	<b>309.368</b>	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

and cc-pCVXZ basis sets for lithium [15], it is not clear how to augment these sets with diffuse functions. We have instead used the atomic natural-orbital (ANO) augmented triple-zeta and smaller basis sets of Roos and co-workers [17, 18]. These basis sets, which are extensions to basis sets originally made by van Duijneveldt [19] are referred to as ANO-1 and ANO-2 respectively.

## 2. Two-electron basis sets

The GCF expansions of Eqs. (15)–(17) may be modified both by adjusting the exponents in the correlation factors  $\exp(-\gamma_v r_{12}^2)$  and by varying the number of such correlation factors in the expansion. Following Persson and Taylor [20], we use even-tempered exponents  $\gamma_v = 3^v a$ , with  $a = 1/9$  and  $0 \leq v \leq N_g - 1$ . In the standard basis, we use  $N_g = 9$ .

Combining the cc-pVDZ and aug-cc-pCVTZ(sp) AO sets with standard GCFs basis sets with  $\gamma_0 = 1/9$  and  $0 \leq N_g \leq 9$ , we carried out a series of calculations on the neon atom, see Table I. For each AO set, the first entry ( $N_g = 0$ ) represents the conventional MP2 energy. When one (diffuse) GCF is added, the energy barely changes for the  $kl$  and  $kq$

TABLE II: Neon all-electron MP2 correlation energies ( $-E/mE_h$ ) and pSO values atom for different values of the level-shift parameter  $\eta$

$\log_{10} \eta$	cc-pVDZ						aug-cc-pCVTZ(sp)					
	<i>kl</i>		<i>kq</i>		<i>pq</i>		<i>kl</i>		<i>kq</i>		<i>pq</i>	
	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO
+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	2.6	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

ansätze but makes a significant jump for the  $pq$  ansatz. This happens since diffuse GTGs are essentially orbital products—according to the Brillouin theorem, only products of virtual orbitals contribute to the energy; only the  $pq$  ansatz contains such products.

With more GCFs included, also the  $kl$  and  $kq$  energies improve, although the  $kl$  energy changes very little from  $N_g = 1$  to  $N_g = 2$  in the aug-cc-pCVTZ(sp) basis, as indicated by bold face in Table I. In the larger AO basis, therefore, GCFs with exponents smaller than one do not improve significantly upon the standard virtual orbital description. By contrast, geminals with exponents equal to one and three make significant energy contributions for all three ansätze. For  $N_g = 9$ , all energies are converged to within  $0.1mE_h$ , the last three GCFs improving mainly the  $1s^2$  singlet energy.

### 3. The level-shift parameter

In Section III A 2, all calculations were carried out with level-shift parameter  $\eta = 0.1$ . To examine how the MP2 energy and the SO varies with  $\eta$ , we have repeated the calculations with  $N_g = 9$  using different values of  $\eta$ . In Table II, we have, for each value of  $\eta$ , listed the energy and  $\text{pSO} = -\log_{10} \bar{\chi}^{\text{SO}}$ , where  $\bar{\chi}^{\text{SO}}$  is the average of  $\chi_{ij}^{\text{SO}}$  in Eq. (9) over all 25 singlet and 15 triplet pair functions in neon. A high pSO value indicates that the pair functions

are strongly orthogonal, to a good approximation.

From Table II, we see that the energy hardly changes in the range  $0.001 < \eta < 1$ . Moreover, the sensitivity to  $\eta$  is strongest in the small AO basis and for the  $kl$  ansatz. Likewise, the most flexible pair functions appear to be most strongly orthogonal to the occupied MOs, the largest pSO values occurring in the large AO basis for the  $pq$  ansatz. Whereas the pSO value increases only marginally from the  $kl$  ansatz to the  $pq$  ansatz in the small AO basis, it increases significantly (by many factors) in the large AO basis.

As expected, the pSO value increases with  $\eta$ . A comparison of the pSO value and the energy for different  $\eta$  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. 21.

#### 4. Linear dependencies and numerical stability

From Table I, we see that the  $pq$  ansatz performs better than the  $kq$  ansatz, which in turn outperforms the  $kl$  ansatz. However, these improved energies do not come without a cost. Using LDL factorisation to solve Eq. (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  $g_{pq,v}^s$ . Denoting the total number of MOs by  $N_{\text{tot}}$  and the number of occupied MOs by  $N_{\text{occ}}$ , the cost of solution is thus  $\mathcal{O}(N_{\text{occ}}^4 N_{\text{g}})$  for the  $kl$  ansatz,  $\mathcal{O}(N_{\text{occ}}^3 N_{\text{tot}} N_{\text{g}})$  for the  $kq$  ansatz, and  $\mathcal{O}(N_{\text{occ}}^2 N_{\text{tot}}^2 N_{\text{g}})$  for the  $pq$  ansatz. Since  $N_{\text{tot}}$  is usually several times larger than  $N_{\text{occ}}$ , the solution of the linear equations can be an order of magnitude more expensive for the  $pq$  ansatz than for the  $kl$  ansatz. Besides, the increased dimensionality of the  $pq$  ansatz makes it more prone to linear dependencies and to numerical instabilities than the  $kl$  ansatz.

To quantify the linear-dependency problem for the different pair-function ansätze, we have diagonalised the geminal–geminal overlap matrix for the neon wave functions of Sections III A 2 and III A 3. In Table III, we have listed, for each calculation, the number of eigenvalues  $\lambda$  transformed to a given integer by  $\Delta(\lambda) = \max(0, \min(-\text{int}(\log_{10} \lambda), 15))$ . Four different GCF expansions were investigated: three of these consist of a single GCF with exponent 1/3, 9, or 243, while the fourth (denoted “Full” in the table) is the standard expansion of Section III A 2.

For a given AO basis, the number of eigenvalues—in particular, the number of small

TABLE III: Distribution of eigenvalues for some geminal-geminal overlap matrices for the neon atom. Geminals are constructed using either one GCF with exponent  $\frac{1}{3}$ , 9 or 243, or the full standard set of GCFs. Eigenvalues  $\lambda$  are reported as  $\Delta = -\text{int}(\log_{10} \lambda)$

	<i>kl</i>				<i>kq</i>				<i>pq</i>				
	$\Delta$	1/3	9	243	Full	1/3	9	243	Full	1/3	9	243	Full
cc-pVDZ	0	15	1		19	59	1		67	80	2		115
	1		13	1	25	1	20	1	70	24	34	1	108
	2				22	15			77	1	26	1	124
	3		1	9	28	17	20	100		21	31		162
	4			4	23	7	9	83		21	19		155
	5				13			9	60		1	13	104
	6			1	3			10	36			6	71
	7				1				20			14	35
	8				1			8	12			9	32
	9							3	7			11	27
	10								5				4
	11								3				8
aug-cc-pCVTZ(spd)	0	15	1		19	227	15		309	440	78	4	750
	1		13	1	25	42	82	5	266	298	118	22	609
	2				22	16	59	10	337	168	109	34	791
	3		1	9	28	39	49	415		107	127	57	931
	4			4	23	38	41	323		18	131	73	1018
	5				13	25	32	220		4	91	63	865
	6			1	3	12	29	197		104	87		727
	7				2	11	22	130		99	72		671
	8						1	27	125		86	66	567
	9							36	93		31	86	438
	10						3	16	57		28	95	416
	11							6	48		27	91	373
	12							8	18		3	64	317
	13							4	15		3	66	225
	14				14				12			36	171
	15											119	446

eigenvalues—increases dramatically from the  $kl$  ansatz to the  $kq$  ansatz and then from the  $kq$  ansatz to the  $pq$  ansatz, as more and more geminals  $g_{pq,v}^s$  are introduced in the pair function. Except for the  $kl$  ansatz, the number of small eigenvalues also increases with increasing AO basis—in particular, for the  $pq$  ansatz. Thus, in the large aug-cc-pCVTZ(sp) basis with a full  $pq$  geminal expansion, there are 446 eigenvalues smaller or equal to  $10^{-15}$ , making the solution of the linear equations difficult. (Examples of nonconvergence arising from linear dependencies among the geminals are found in Table X.) As expected, there are fewer small eigenvalues with a single geminal function. We also note that the overlap between different geminals  $g_{pq,v}^s$  increases with increasing exponent  $\gamma_v$ .

The equation solver employed in this work uses the LDL approach of the LINPACK [22] library, with the pivoting strategy of Bunch and Kaufman [23] for general symmetric matrices. Higham has shown that this approach gives a stable factorisation [24], and linear dependencies are not expected to create severe numerical instabilities in the equation solver.

### 5. Parallelisation

To obtain the GTG-MP2 energy, we must evaluate the matrix elements in Eqs. (21)–(24), consisting of integrals that are well-suited to parallelisation. We parallelise the loop over geminal exponents  $\gamma_v$  and  $\gamma_w$  and the outermost loop over overlap distributions  $\Omega_{\mu\sigma}$ , using the master/slave paradigm as described in Ref. [25]. In Table IV, we present timings for neon, obtained using from 1 to 256 processors of a cluster of 512 MIPS R14000 (600 MHz) processors. The speed-up is calculated as  $t_1/t_N$ , where  $t_1$  and  $t_N$  are the wall times needed for 1 and  $N$  processors, respectively. The efficiency (i.e., the percentage of processors that are efficiently used) is calculated as  $100N(t_N/t_1)$ . In Figure ??, we have plotted the speed-ups and efficiencies obtained in the two basis sets.

While speed-up increases with the number of processors, efficiency is best for 8–32 processors in the small basis and for 8–64 processors in the large basis. The lower efficiency for fewer processors arises since one processor (the master) is used only for task distribution. The drop in efficiency observed for more than 32 or 64 processors can be explained by the relatively small number of tasks available for parallelisation combined with the large granularity of some of these tasks. For the smaller basis, the tasks with the largest granularity are those involving three-electron integrals over  $d$  orbitals. When the calculation time reaches

TABLE IV: Parallelisation results for neon.  $t_N$  is the wall time (in minutes) for  $N$  processors

$N$	aug-cc-pVDZ			aug-cc-pVTZ		
	$t_N$	$\frac{t_1}{t_N}$	$\frac{100Nt_N}{t_1}$	$t_1$	$\frac{t_1}{t_N}$	$\frac{100Nt_N}{t_1}$
1	94.3	1.0	100.0	2912.3	1.0	100.0
4	31.6	3.0	74.5	1123.7	2.6	64.8
8	13.9	6.8	84.6	445.5	6.6	81.9
16	6.5	14.6	91.3	211.0	13.8	86.3
32	3.2	29.5	92.0	103.9	28.0	87.6
64	1.9	49.1	76.7	52.5	55.5	86.7
96	1.5	62.9	65.5	38.8	75.1	78.2
128	1.4	66.4	51.9	35.6	81.9	64.0
160	1.4	68.3	42.7	32.6	89.4	55.9
192	1.3	70.7	36.8	29.7	98.0	51.0
224	1.3	70.7	31.6	28.1	103.6	46.2
256	1.2	76.6	29.9	28.2	103.2	40.3

one and a half minute, we are probably getting close to the calculation time needed for one such task, further reducing performance. For the larger basis, which includes integrals over  $f$  orbitals, some tasks may require more than 20 minutes, reducing speed-up accordingly. For larger systems, better scaling properties than those reported for neon are expected.

## B. Results

### 1. Helium

The helium results in Table V show that the  $kq$  and  $pq$  pair functions perform excellently, while the  $kl$  performance is only fair. Thus, whereas the lowest  $kl$  energy is obtained in the aug-cc-pV6Z basis, even lower  $kq$  energies are obtained using only  $s$  and  $p$  orbitals. In fact, good  $kq$  and  $pq$  energies are already obtained using only  $s$  orbitals, the  $p$  orbitals contributing  $-0.2$  m $E_h$  or less to the correlation energy. Moreover, the  $kq$  and  $pq$  ansätze perform better with the aug-cc-pVXZ(sp) basis sets than with the corresponding cc-pVXZ

TABLE V: MP2 correlation energies ( $-E/mE_h$ ) of the helium atom, calculated using virtual-orbital expansion (VOE) and with the  $kl$ ,  $kq$ , and  $pq$  pair-function expansions. The entry marked † failed to converge.

Orbital basis	VOE	KL	KQ	PQ
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(s)	11.50	29.39	36.941	37.0913
aug-cc-pVTZ(s)	12.90	29.48	37.053	37.2166
aug-cc-pVQZ(s)	13.28	29.57	37.208	37.3353
aug-cc-pV5Z(s)	13.44	29.59	37.235	37.3613
aug-cc-pV6Z(s)	13.47	29.59	37.239	37.3689
aug-cc-pVDZ	26.96	35.23	37.169	37.2926
aug-cc-pVTZ(sp)	31.11	35.77	37.251	37.3460
aug-cc-pVQZ(sp)	32.06	35.97	37.350	37.3724
aug-cc-pV5Z(sp)	32.35	36.02	37.369	37.3769
aug-cc-pV6Z(sp)	32.42	36.04	37.372	37.3772
aug-cc-pVTZ	33.62	36.52	37.255	37.3610
aug-cc-pVQZ(sp)	35.03	36.88	37.352	37.3755
aug-cc-pV5Z(sp)	35.46	36.98	37.371	37.3772
aug-cc-pV6Z(sp)	35.58	37.00	37.375	37.3773
aug-cc-pVQZ	35.72	37.06	37.354	37.3758
aug-cc-pV5Z(sp)	36.29	37.19	37.372	n/a
aug-cc-pV6Z(sp)	36.47	37.22	37.376	n/a
aug-cc-pV5Z	36.53	37.23	37.373	n/a
aug-cc-pV6Z(sp)	36.78	37.26	†	n/a
aug-cc-pV6Z	36.88	37.305	n/a	n/a
d-aug-cc-pVDZ	27.01	35.29	37.190	37.3079
d-aug-cc-pVTZ(sp)	31.12	35.78	37.258	37.3547
d-aug-cc-pVQZ(sp)	32.06	35.98	37.351	37.3736
d-aug-cc-pV5Z(sp)	32.35	36.02	37.369	37.3770
d-aug-cc-pVTZ	33.63	36.53	37.263	37.3678
d-aug-cc-pVQZ(sp)	35.04	36.89	37.353	37.3762

TABLE VI: MP2 correlation energies ( $-E/mE_h$ ) for the helium atom. Entries are listed chronologically. For helium, the total correlation energy is  $-42.044 mE_h$  [26].

authors	method	energy
this work	<i>kl</i> ansatz (aug-cc-pV6Z)	37.305
	<i>kq</i> ansatz (aug-cc-pV6Z-spdf)	37.375
	<i>pq</i> ansatz (aug-cc-pV6Z-spd)	37.37729
Lee and Park [27]	extrapolation	37.4052
Bukowski <i>et al.</i> [26]	150 nonlinearly optimised GTGs	37.37744
Flores [28]	FEM-MP2 with $l \leq 12$ and angular extrapolation	37.376
Termath <i>et al.</i> [29]	MP2-R12/A with STO basis (12s11p11d9f9g)	37.375
	MP2-R12/B with STO basis (12s11p11d9f9g)	37.362
Petersson <i>et al.</i> [30]	CBS (complete basis-set) model	37.59
Malinowski <i>et al.</i> [31]	partial-wave expansion with radial and angular extrapolation	37.359
Winter <i>et al.</i> [32]	first-order equation solved numerically	37.355

sets, indicating that saturation with diffuse functions is more important for the pair energy than the inclusion of orbitals of high angular momentum. We shall later see that this is a typical feature of geminal calculations, valid also for the other systems.

The lowest helium energy is obtained with the *pq* pair function in the relatively small aug-cc-pV6Z(spd) basis, consisting of 50 orbitals (7s6p5d). Because of an internal-memory limit of 2 GB (the 32-bit architecture limit), we were unable to use the aug-cc-pV5Z(spdf) basis with the *pq* ansatz.

In Table VI, we compare our helium correlation energies with literature data. Our *pq* result of  $-37.37729 mE_h$  is very close to  $-37.37744 mE_h$ , obtained by Bukowski *et al.* using GTGs of the form

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

with the exponents  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  variationally optimized using the WO functional and the centres  $\mathbf{P}_i$  and  $\mathbf{Q}_i$  fixed on the nucleus. Such GTGs may be regarded as a pair of *s* orbitals multiplied by a GCF; higher angular-momentum functions are not used. For the totally symmetric helium atom, such geminals constitute a complete pair-function basis [33].

To obtain their helium MP2 energy, Bukowski and *et al.* used 150 GTGs. For comparison, we used 2349, 153, and 9 GTGs, respectively, to obtain our  $pq$ ,  $kq$ , and  $kl$  energy limits. However, whereas Bukowski *et al.* obtained their limit with a pure GTG expansion, we supplemented the GTGs with a conventional virtual-orbital expansion.

The energy of Bukowski and *et al.* should be considered the current best MP2 energy correction of helium. Although their correlation energy is not the lowest, it does constitute the lowest upper bound to the true MP2 energy. Together with our  $pq$  energy, it is the only correlation energy converged to within  $1\mu E_h$ . The importance of the variation principle is not always emphasized in literature [27, 34, 35].

## 2. Beryllium

Our beryllium MP2 correlation energies are presented in Table VII. In an  $s$  basis, our lowest correlation energy is  $-68.217mE_h$ . Assuming an MP2 limit of  $-76.358mE_h$  (see Table VIII), the  $s$  orbitals recover only 89% of the correlation energy, even with the  $pq$  ansatz. However, with  $p$  orbitals included, as much as 99.99% of the estimated limit is recovered by the  $pq$  ansatz. Both  $s$  and  $p$  orbitals are therefore essential for the correlation energy of beryllium atom.

As for the helium atom, the  $kq$  and  $kl$  ansätze are more reliant than the  $pq$  ansatz on the use of high angular-momentum functions, the best such  $sp$  calculations recovering 99.5% and 97.1% of the correlation energy of beryllium, respectively. Comparing the  $kq$  energies in the  $(14s4p)^*$  and  $(14s9p)^*$  basis sets, we see that the addition of more  $p$  orbitals does not improve the energy substantially—in fact, both  $d$  and  $f$  orbitals are needed for the  $kq$  ansatz to perform as well as the  $pq$  ansatz in the  $sp$  basis. For the  $kl$  ansatz, we must also include  $g$  orbitals for convergence of the MP2 correlation energy. Nevertheless, the  $kl$  ansatz performs far better than the virtual orbital expansion, which is far from the basis-set limit even in the largest basis used here, recovering only 90% of the MP2 correlation energy of beryllium.

The best beryllium MP2 correlation energy in the literature is  $-76.358 mE_h$ , obtained by Bukowski *et al.* [37] and by Salomonsen and Öster[39] using different methods, see Table VIII. Our best  $pq$  energy of  $-76.355 mE_h$ , obtained in a  $14s9p3d$  basis, is thus only  $3 \mu E_h$  higher than their value; this is remarkably good, considering the size of the orbital basis and the fact that GCF exponents were not optimised. With the  $kq$  ansatz, we obtain a slightly

TABLE VII: All-electron MP2 correlation energies ( $-E/mE_h$ ) for the beryllium atom. Basis sets marked with an asterisk (\*) are used uncontracted

Orbital basis	VOE	KL	KQ	PQ
ANO-1 (3s)	2.05	51.97	59.59	60.05
ANO-1 (4s)	3.75	52.58	61.10	62.20
ANO-1 (5s)	6.79	53.76	64.91	66.35
ANO-1 (6s)	14.84	55.61	65.94	67.04
ANO-1 (10s)*	15.68	55.67	66.04	67.42
ANO-1 (6s1p)	34.86	68.22	75.31	75.98
ANO-1 (6s2p)	36.40	68.44	75.42	76.18
ANO-1 (6s3p)	38.63	69.54	75.70	76.25
ANO-1 (6s4p)	42.00	70.21	75.74	76.26
ANO-1 (10s4p)*	42.84	70.28	75.81	76.28
ANO-1 (6s4p1d)	44.89	71.14	76.072	76.299
ANO-1 (6s4p2d)	45.49	71.29	76.097	76.304
ANO-1 (6s4p3d)	45.61	71.35	76.108	76.307
ANO-1 (10s4p3d)*	46.45	71.43	76.167	76.317
ANO-2 (14s)*	15.91	55.76	66.239	68.217
ANO-2 (14s4p)* <sup>a</sup>	43.10	70.33	75.866	76.333
ANO-2 (14s9p)*	64.05	74.18	75.939	76.349
ANO-2 (14s9p3d)* <sup>b</sup>	67.67	75.27	76.314	76.3555
ANO-2 (14s9p4d)*	68.28	75.39	76.318	n/a
ANO-2 (14s9p4d3f)*	69.40	75.62	76.345	n/a

<sup>a</sup> Using the four  $p$ -orbitals of the ANO-1 basis set.

<sup>b</sup> Using the three  $d$ -orbitals of the ANO-1 basis set.

poorer correlation energy,  $13 \mu E_h$  higher than this reference value.

The MP2-R12 energies obtained by Termath *et al.* [29] are considerably better than our best  $kl$  energy, demonstrating that good results can be achieved with the  $kl$  ansatz in sufficiently large basis sets. However, since the GTGs do not contribute to the correlation energy beyond  $s$  orbitals, the largest proportion of the energy must then be recovered by

TABLE VIII: All-electron MP2 correlation energies ( $-E/mE_h$ ) for the beryllium atom. Entries are listed chronologically. The total correlation energy is  $-94.332 mE_h$  [36].

authors	method	energy
this work	<i>kl</i> ansatz (ANO-2 14s9p4d3f*)	75.62
	<i>kq</i> ansatz (ANO-2 14s9p4d3f*)	76.345
	<i>pq</i> ansatz (ANO-2 14s9p3d*)	76.355
Bukowski <i>et al.</i> [37]	350 nonlinearly optimised GTGs for each pair	76.358
Noga <i>et al.</i> [38]	MBPT-R12 (16s10p6d5f4g)	76.248
Termath <i>et al.</i> [29]	MP2-R12/A (STO basis 15s12p11d11f10g)	76.373
	MP2-R12/B (STO basis 15s12p11d11f10g)	76.311
Salomonsen and Öster [39]	extrap. partial-wave expansion ( $l \leq 10$ ) with num. orbitals	76.358
Petersson <i>et al.</i> [30]	CBS (complete basis-set) model	77.27
Alexander <i>et al.</i> [40]	nonlinearly optimised GTGs	76.350
Janowski <i>et al.</i> [41]	partial-wave expansion with $l \leq 9$	75.98
Malinowski <i>et al.</i> [31]	partial-wave expansion with radial and angular extrapolation	76.29

the virtual orbital expansion. When the MP2-R12/B results were extrapolated, Termath *et al.* obtained  $-76.316 mE_h$  as the MP2 basis-set limit,  $42 \mu E_h$  higher than the result of Bukowski *et al.* and of Salomonsen and Öster [37, 39].

In Table IX, we have listed our pair energies of beryllium, comparing with literature data. First, we note that the *pq* ansatz performs better than the *kq* ansatz mainly for the  $2s^2$  pair. Next, we note that the performance of the MP2-R12/A method is somewhat inconsistent. For the  $1s2s$  singlet and triplet pairs, it performs well, being only a few  $\mu E_h$  above our *pq* energies. However, it overshoots our  $1s^2$  result by  $9 \mu E_h$  and undershoots our  $2s^2$  result by  $30 \mu E_h$ . Since a large orbital basis is used, it is hard to see why the R12/A method should perform so differently for the different electron pairs. The MP2-R12/B method is not afflicted by this inconsistency.

TABLE IX: Beryllium MP2 pair correlation energies ( $-E/mE_h$ )

Pair	R12/A <sup>a</sup>	R12/B <sup>a</sup>	GTG <sup>b</sup>	KL <sup>c</sup>	KQ <sup>c</sup>	PQ <sup>d</sup>
$1s^2$	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

<sup>a</sup> MP2-R12/A(STO) and MP2-R12/B(STO) from Ref. [29].

<sup>b</sup> Nonlinearly optimised GTGs from Ref. [40].

<sup>c</sup> Using basis set ANO-2 (14s9p4d3f)\*

<sup>d</sup> Using basis set ANO-2 (14s9p3d)\*

### 3. Neon

The all-electron MP2 correlation energies obtained for neon are listed in Table X. Since the polarized valence correlation-consistent basis sets cc-pVXZ are not sufficiently flexible for recovering core and core–valence correlation energies using standard virtual-orbital expansion techniques, we have also carried out calculations in the polarized core–valence correlation-consistent basis sets cc-pCVXZ.

As for helium, the energy convergence is relatively fast for the  $kq$  and  $pq$  ansätze but only moderate for the  $kl$  ansatz, which nevertheless converges much faster than the conventional virtual-orbital expansion. We note a significant improvement when core orbitals are included—in particular, for the geminal-free calculations. When geminals are included, the core orbitals become less important, reflecting the reduced role of the orbital expansion in these calculations.

Whereas the cc-pCVXZ basis sets contain additional core functions, the aug-cc-pVXZ basis sets are supplemented with diffuse functions so as to improve the description of the outer-valence region. We note that, while the virtual-orbital expansion and the  $kl$  ansatz benefit more from additional core functions, additional diffuse functions are more important for the  $kq$  and  $pq$  ansätze.

The aug-cc-pCVXZ basis sets, which contain core as well as diffuse functions, perform

TABLE X: Neon all-electron MP2 correlation energies ( $-E/mE_h$ ) A dagger ( $\dagger$ ) is given for calculations that failed to converge, and two daggers ( $\dagger\dagger$ ) is given for calculations too computationally demanding.

Orbital basis	VOE	KL	KQ	PQ
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	$\dagger$	n/a
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	n/a
aug-cc-pCVDZ (sp)	157.71	265.30	344.39	356.17
aug-cc-pCVTZ (sp)	187.48	273.91	357.11	364.54
aug-cc-pCVQZ (sp)	190.94	275.73	358.59	365.74
aug-cc-pCV5Z (sp)	191.74	276.26	359.24	366.36
aug-cc-pCVDZ	249.90	333.13	375.05	384.56
aug-cc-pCVTZ (spd)	309.08	353.91	386.23	388.008
aug-cc-pCVQZ (spd)	319.34	358.23	387.14	n/a
aug-cc-pCV5Z (spd)	321.57	359.37	$\dagger\dagger$	n/a
aug-cc-pCVTZ	337.29	370.72	387.14	388.189
aug-cc-pCVQZ (spdf)	354.18	377.17	$\dagger$	n/a
aug-cc-pCVQZ	365.16	382.12	$\dagger\dagger$	n/a
aug-cc-pCV5Z	375.93	385.54	$\dagger\dagger$	n/a

very well for neon. In fact, our best estimate of the neon MP2 correlation energy in Table XI is obtained with the  $pq$  ansatz in the aug-cc-pCVTZ basis. In this basis, the  $kq$  ansatz retrieves 99.7% of the estimated limit, while the  $kl$  ansatz and the virtual-orbital expansion retrieve 95.5% and 86.9%, respectively. For the latter two approaches, the lack of high-angular momentum functions becomes apparent. For the  $kl$  ansatz, the best estimate is

TABLE XI: The all-electron MP2 correlation energy ( $-E/mE_h$ ) of neon, listed chronologically

authors	method	energy
this work	<i>kl</i> ansatz (aug-cc-pCV5Z)	385.54
	<i>kq</i> ansatz (aug-cc-pVQZ)	387.21
	<i>pq</i> ansatz (aug-cc-pCVTZ)	388.19
Ten-no [42, 43]	MP2-GTG (aug-cc-pV5Z, without <i>h</i> -functions)	387.64
	MP2-GTG (aug-cc-pV5Z, without <i>h</i> -functions)	387.55
Klopper and Samson [44]	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 <i>et al.</i> [45]	MP2-R12-SO (20s14p11d9f7g5h/exact 3-el. int.)	388.06
	MP2-R12/A (20s14p11d9f7g5h)	388.29
	MP2-R12/B (20s14p11d9f7g5h)	388.00
Flores [28]	FEM-MP2 with $l \leq 12$ and angular extrapolation	388.10
Petersson <i>et al.</i> [30]	CBS (complete basis-set) model	386.38
Wenzel <i>et al.</i> [10]	bonlinearly optimised GTGs	385.26
Lindgren and Salomonsen [46, 47]	numerical integration of the coupled-cluster equations	388.31
Janowski and Malinowski [48]	calculated	384.98
	extrapolated	387.92

obtained with the aug-cc-pCV5Z basis, which recovers 99.3% of the MP2 correlation energy.

Since the aug-cc-pCVXZ basis sets give excellent results for the neon atom, we have used these to explore the partial-wave expansion. For neon, the smallest such expansion contains *s* and *p* orbitals. However, lacking high-angular momentum functions, such basis sets give poor correlation energies (see Table X), in accordance with our observations for beryllium. As we shall see below, high-angular momentum functions are for neon needed mainly for the  $^1D$  pair, which cannot be properly described without *d* functions. With *d* functions included, we recover 99.97%, 99.7%, and 92.6% of the MP2 correlation energy for the *pq*, *kq*, and *kl* ansätze, respectively.

Accurate estimates of the neon MP2 correlation energy have been given by several

authors—see Table XI, which also contains our best (i.e., variationally lowest) neon energies. Among the energies in this table, our  $pq$  result of  $-388.19 mE_h$  is the best variationally bounded energy, although not the lowest overall. However, comparing the energies obtained with this ansatz in aug-cc-pCVDZ, aug-cc-pCVTZ(sp), and aug-cc-pCVTZ basis sets, we may reasonably assume that the true limit is lower than  $-388.19 mE_h$ , probably also lower than the lowest energy in Table XI—namely,  $-388.31 mE_h$ , obtained by Lindgren and Salomonsen [46, 47].

Somewhat surprisingly, in view of the good results of Bukowski *et al.* for helium and beryllium [37], the neon correlation energy of  $-385.26 mE_h$  obtained by Wenzel *et al.* using nonlinearly optimised GTGs is rather poor [10]. For neon, these authors used GTGs of the form

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

which is identical to Eq. (36) except for the angular factors. As for helium, all GTGs are centred on the nucleus, while the exponents were optimised under the restrictions

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

using the modified weak orthogonality (MWO) functional [10]. The nonnegative monomial exponents are chosen according to the completeness criteria of King [33]. For each neon pair function, Wenzel *et al.* used a 40-term GTG expansion, compared with the 150- and 350-term expansions, respectively, used by Bukowski *et al.* to obtain their excellent helium and beryllium energies [37]. Although Bukowski *et al.* obtained good pair energies with only 30 terms, the 40 GTGs of Wenzel *et al.* must describe all symmetry components of the  $2p^2$  interactions, leaving less variationally flexibility for each—as discussed below, the poor results of Wenger *et al.* stem mainly from a poor  $2p^2$  description.

In Table XII, we give pair energies obtained by some selected methods, including the GTG approach by Wenzel *et al.* [10]. The pair energies in the two rightmost columns are both obtained with the  $pq$  ansatz, but with and without the use of  $d$  orbitals. Whereas seven of the eleven pair energies differ by less than  $0.1 mE_h$  and three by less than  $1 mE_h$ , the  $^1D(2p^2)$  energy differs by more than  $22 mE_h$ . Clearly, for this particular interaction,  $d$  orbitals are essential. Using MP2-R12 theory, Klopper and coworkers have also observed the slow convergence of the  $^1D(2p^2)$  interaction [29, 49].

TABLE XII: Neon MP2 pair energies ( $-E/mE_h$ )

pair	symmetry	GTG <sup>a</sup>	R12/SO <sup>b</sup>	R12/2B <sup>c</sup>	$kl^d$	$kq^e$	$pq^f$	$pq^g$
$1s^2$		40.22	40.252	40.252	40.150	39.965	40.224	40.229
$1s2s$	<sup>1</sup> S	3.95	3.974	3.974	3.960	3.929	3.974	3.975
$1s2s$	<sup>3</sup> S	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
$1s2p$	<sup>1</sup> P	8.10	8.176	8.177	8.055	8.103	8.139	8.161
$1s2p$	<sup>3</sup> P	13.86	13.911	13.910	13.846	13.763	13.825	13.880
$2s2p$	<sup>1</sup> P	59.85	60.472	60.482	59.765	60.438	59.702	60.532
$2s2p$	<sup>3</sup> P	26.55	26.708	26.708	26.633	26.679	26.439	26.757
$2p^2$	<sup>1</sup> S	45.24	45.565	45.573	45.450	45.553	45.544	45.574
$2p^2$	<sup>1</sup> D	87.06	88.042	88.057	86.907	87.891	65.957	88.031
$2p^2$	<sup>3</sup> P	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

<sup>a</sup> Nonlinearly optimised GTGs from Ref. [10].

<sup>b</sup> MP2-R12-SO from Ref. [45].

<sup>c</sup> MP2-R12/2B from Ref. [44].

<sup>d</sup> Orbital basis aug-cc-pCV5Z.

<sup>e</sup> Orbital basis aug-cc-pVQZ.

<sup>f</sup> Orbital basis aug-cc-pCVTZ (sp).

<sup>g</sup> Orbital basis aug-cc-pCVTZ (spd)

Considering that only  $s$  and  $p$  orbitals are used, Wenzel *et al.* [10] obtain a reasonably good estimate of the <sup>1</sup>D interaction with their nonlinearly optimised GTGs ( $-87.1 mE_h$ ), much better than the poor  $pq$  pair energy obtained by us without  $d$  functions ( $-66.0 mE_h$ ). This disagreement is surprising in view of the similarity between the two wave functions. The main difference between the calculations is that, in the optimisation of exponents carried out by Wenzel *et al.*, negative  $\alpha_i$ ,  $\beta_i$ , and  $\gamma_i$  are allowed subject to Eq. (38), whereas we only use positive exponents. From an inspection of Table III in Ref. [10], we note that some of the exponents are indeed negative for this particular pair function, explaining the large differences in energies.

TABLE XIII: Neon all-electron MP2 correlation energies ( $-E/mE_h$ ) compared with R12 results

Orbital basis	VOE	$kl$	IJ	R12/SO <sup>a</sup>	R12/1A <sup>b</sup>	R12/1B <sup>b</sup>	R12/2A <sup>b</sup>	R12/2B <sup>b</sup>	GTG <sup>c</sup>
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	370.93	—	—	382.7	380.30	382.57	386.37	384.14	387.01
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

<sup>a</sup> The MP2-R12/SO method described in Ref. [45]. This method uses a  $ij$ -ansatz.

<sup>b</sup> The approximations of MP2-R12 theory described in Ref. [44]. These methods use a  $kl$ -ansatz.

<sup>c</sup> The MP2-geminal approach of Ref. [42]. This method uses a variant of the  $kl$ -ansatz.

An inspection of Table XII also reveals that the  $kq$  ansatz performs poorly for all pairs that involve the  $1s$  orbital—in fact, even poorer than the  $kl$  ansatz except for  $^1P(1s2p)$ . The reason for the poor  $kq$  performance is that these calculations have been carried out without core-correlating orbitals, unlike the  $kl$  and  $pq$  calculations—see Table XII.

In Table XIII, we compare our  $kl$  results with the results obtained by a selection of related explicitly correlated MP2 methods. The method labelled IJ uses the rotational variant  $ij$ -ansatz which differs from the  $kl$ -ansatz in that only the  $ij$  pair is used in the GTGs. Since the  $kl$ -ansatz provides a larger variation space the correlation energy becomes better. For the basis set aug-cc-pCVDZ, for instance, the difference between the two ansätze is more than  $6mE_h$ . As the orbital basis increases, however, the difference in performance diminishes, and for the basis set aug-cc-pCV5Z, it is down to  $0.6mE_h$ .

The ansatz denoted R12/SO refers to the MP2-R12/SO implementation of Wind *et al.* [45] in which three-electron integrals can be calculated explicitly, and the resolution-of-the-identity (RI) approximation is only needed to approximate four-electron integrals. Wind and co-workers used this implementation to show that the effect of approximating three-electron integrals with an RI of quality *32s24p18d15f12g9h6i* is less than  $0.01mE_h$ . The energies given in Table XIII were calculated using this approximation and were therefore only given to the nearest  $0.1mE_h$ . Pair functions were expanded using the orbital *variant* approach of Equation (11), but the projection operator  $Q_0$  running over all orbitals were replaced by the operator  $Q$  running over occupied orbitals only. Energies obtained with this method may be compared with energies obtained with the *ij*-ansatz.

For the cc-pVXZ series of basis sets the MP2-R12/SO method gives a lower energy than the *ij*-ansatz for the DZ basis, in the TZ basis the energies are equal, and in the QZ basis the *ij*-ansatz gives the lower energy. Since the *ij*-ansatz has a more flexible pair function, the corresponding pair energies should be better. That the opposite is observed for the DZ basis can be an effect of the RI approximation, the assumption of exact Hartree-Fock orbitals, or deficiencies in the WO functional.

For the cc-pCVXZ series of basis set the MP2-R12/SO approach gives lower energies than the *ij*-ansatz for the DZ and TZ basis sets, while the *ij*-ansatz gives a lower energy for the QZ basis. Since the WO functional becomes a better approximation to the SO functional when the basis set increases, one would expect the *ij*-ansatz to perform better relative to the MP2-R12/SO method in the cc-pCVXZ basis than in the cc-pVXZ basis sets. This is not what we observe. The cc-pCVQZ results look plausible however. In this basis the orbital part of the MP2 energy is  $-361.51mE_h$ , and the geminal corrections for the *ij*-ansatz and MP2-R12/SO method are not more than  $15\text{--}16mE_h$ .

For the aug-cc-pVXZ basis sets the energies obtained with the MP2-R12/SO method are all lower than the energies obtained with the *ij*-ansatz; also for the aug-cc-pVQZ where the difference is  $1.8mE_h$ . This apparently better performance of the MP2-R12/SO method may be related to the poor description of core orbitals, and should not be given too much attention.

In Table XIII we have also listed correlation energies obtained with the conventional MP2-R12 methods—labelled 1A' and 1B—as well as the newer 2A' and 2B methods. While the conventional methods use the rotational invariant pair function of Equation (12) where

the projection operator runs over all orbitals, the newer methods have limited the projection operator to run over occupied orbitals only, like the MP2-R12/SO method. The auxiliary basis set was for all calculations the same as that used for the MP2-R12/SO calculations. In this basis set the RI-approximation can be assumed to hold, at least in the approximation of three-electron integrals, and this should allow us to do a direct comparison with the GTG-MP2 methods presented here.

The MP2-R12 methods 1A' and 1B behaves as expected: When the cardinal number is increased, both the cc-pCVXZ and aug-cc-pCVXZ basis sets converge smoothly against the basis set limit. Moreover, both methods give energies that are higher than the energies obtained with the *kl*-ansatz, consistent with the more flexible pair functions provided for the latter. The difference between the GTG method and MP2-R12 methods diminishes with increasing cardinality, however, and for the 1B method and basis sets aug-cc-pCVXZ it is  $30mE_h$ ,  $11mE_h$ ,  $6mE_h$ , and  $1.6mE_h$  for cardinal numbers D-5. The 1A' and 1B methods, in turn, have more flexible pair functions than the MP2-R12/SO method, and might therefore have been expected to have a performance in between the *kl*-ansatz and the MP2-R12/SO method. The latter performs better however, due to the different projection operator.

The new MP2-R12 methods—2A' and 2B—may be compared more directly with the MP2-R12/SO method, since they use the same projection operator. If we, for instance, compare the 2B method with the MP2-R12/SO method within the cc-pCVXZ basis sets, we see that the former gives energies that are lower by  $35mE_h$ ,  $12mE_h$ ,  $.1mE_h$ , and  $1.4mE_h$  for cardinal numbers D-5. First, we notice that the convergence pattern for the 2B method is strange. Next, based on results obtained with the *ij*- and *kl*-ansätze, we know that the difference between the orbital variant and orbital invariant is around  $6mE_h$ ,  $2mE_h$ ,  $1mE_h$ , and  $0.5mE_h$ . For the MP2-R12 approach it is actually less, since the difference in flexibility is greater between the GTG *ij*- and *kl*-ansätze than between their corresponding MP2-R12 counterparts. It therefore seems that the energies produced by the MP2-R12/2B method are incorrect. A comparison with the *kl*-ansatz supports this view. For all basis sets except cc-pCVQZ, the 2B method gives considerably lower energies than the *kl*-ansatz, even though the latter has the more flexible pair function.

It is also worthwhile to note how the energy difference between the 2A' and 2B methods converges. For the basis sets cc-pCVXZ and cardinal numbers D-5, the difference is  $-110mE_h$ ,  $-6mE_h$ ,  $4mE_h$ , and  $2mE_h$ , while it is  $25mE_h$ ,  $6mE_h$ ,  $.7mE_h$ , and  $1.2mE_h$  for the basis sets

aug-cc-pCVXZ. The convergence behaviour of the new MP2-R12 methods thus seems unpredictable. Note especially that the difference increases as we go from the aug-cc-pCVQZ to the aug-cc-pCV5Z basis.

The last column of numbers presented in Table XIII are the MP2-GTG numbers of Ten-no [42]. Ten-no used numerical quadratures for two- and three-electron integrals and neglected the exchange operator in commutators. He also assumed the extended Brillouin condition (EBC) to be valid, making his method comparable to the MP2-R12/2A' method. The pair function was similar to that of the  $kl$ -ansatz given in Equation (15), with the difference that the expansion coefficients of the Gaussian correlation factors were kept fixed. Ten-no used ten correlation factors with exponents ranging from 1000.0 and to 0.5. The result is correlation energies that are lower than those of the MP2-R12/2A' method for the cc-pCVXZ basis sets, but higher than those of the MP2-R12/2A' for the aug-cc-pCVTZ basis sets except for the aug-cc-pCVDZ basis.

#### 4. *The hydrogen molecule*

The hydrogen molecule is an important test system since it is the smallest possible molecule. Methods that do not describe the electron structure of hydrogen appropriately, are not reliable for larger molecules.

In Table XIV we give our second-order correlation energies for a hydrogen molecule with bond length  $1.4a_0 = 74.0848\text{pm}$ . We shall concentrate on the lower part of the table in which we use the aug-cc-pVXZ series of basis sets to explore partial-wave expansions in the  $s$ -,  $sp$ -, and  $spd$ -orbital spaces.

Expansion of the pair function in  $s$ -orbitals appears to give good energy estimates with the  $kq$ - and  $pq$ -ansätze, and may seem like a good idea. If we compare with energies obtained with the full aug-cc-pVTZ basis set, however, inconsistencies are seen. Clearly, the energies obtained with the  $pq$ -ansatz and the two largest  $s$ -expansions are undershooting the true MP2 correction energy. This may happen if the Fock operator is poorly described. A quick look at the Hartree–Fock orbitals obtained with the aug-cc-pVQZ basis set shows that the occupied  $1\sigma$  orbital contains small amounts of  $p$ -functions, as well as smaller amounts of  $d$ - and  $f$ -functions, so that an  $s$ -orbital based Fock operator will be deficient. Since the Fock operator is of equal or less quality for all  $s$ -expansions, the energies obtained with  $s$ -orbitals

TABLE XIV: MP2 correlation energies ( $-E/mE_h$ ) of the hydrogen molecule. An inter-nuclear distance of 74.08481 pm was used. Energies marked with a double-dagger ( $\ddagger$ ) undershoot the true energy, probably due to a non-positive-definite Fock operator

Orbital basis	VOE	KL	KQ	PQ
cc-pVDZ	26.38	31.63	33.580	33.8019
cc-pVTZ	31.68	33.48	34.151	34.2263
cc-pVQZ	33.11	34.00	34.226	n/a
aug-cc-pVDZ (s)	15.95	29.82	33.535	33.7943
aug-cc-pVTZ (s)	17.91	30.07	33.836	34.1317
aug-cc-pVQZ (s)	18.36	30.11	33.934	34.3232 $\ddagger$
aug-cc-pV5Z (s)	18.43	30.13	33.943	34.3680 $\ddagger$
aug-cc-pVDZ	27.29	32.74	33.879	34.0464
aug-cc-pVTZ (sp)	29.88	33.31	34.177	34.2434
aug-cc-pVQZ (sp)	30.45	33.50	34.220	34.2460
aug-cc-pV5Z (sp)	30.65	33.53	34.229	34.2491
aug-cc-pVTZ	31.99	33.82	34.209	34.2525
aug-cc-pVQZ (spd)	32.74	34.06	34.240	n/a
aug-cc-pV5Z (spd)	32.98	34.11	34.247	n/a
aug-cc-pVQZ	33.25	34.14	34.241	n/a

are all incorrect even though most of them are well above the MP2 correction limit.

The pair energies obtained with  $sp$ -expansions are all above the limit, and for the larger expansions we have reason to assume that the Fock operator is described accurately. For the largest expansion we also get good energy estimates, and the  $pq$ -,  $kq$ - and  $kl$ -ansätze recover some 99.99%, 99.93%, and 97.9% of the estimated limit, respectively (see Table XV). When  $d$ -orbitals are included in the partial-wave expansions, the  $pq$ -ansatz give the current best estimate of the MP2 correction energy, while the  $kq$ - and  $kl$ -ansätze recover some 99.98% and 99.6%, respectively, of this limit estimate. The best correlation energy using the  $kl$ -ansatz is obtained with the aug-cc-pVQZ basis set. In this case some 99.7% of the correlation energy is recovered.

In Table XV, we compare our best correlation energies with values obtained from the

TABLE XV: MP2 correlation energies ( $-E/mE_h$ ) of the  $H_2$  at an internuclear distance of 71.42857 pm, listed chronologically. The total correlation energy is  $-40.8461 mE_h$  [50].

authors	method	energy
this work	<i>kl</i> ansatz (aug-cc-pVQZ)	34.14
	<i>kq</i> ansatz (aug-cc-pVQZ)	34.247
	<i>pq</i> ansatz (aug-cc-pV5Z-spd)	34.252
Bukowski <i>et al.</i> [26]	120 nonlinearly optimised GTGs	34.244
Klopper and Kutzelnigg [51]	MP2-R12/A ( <i>9s8p4d1f</i> )	34.23
	MP2-R12/B ( <i>9s8p4d1f</i> )	34.17
Jeziorski <i>et al.</i> [52]	40 nonlinearly optimised GTGs	34.20

literature. Note, that there are fewer energy estimates available for molecules than for atoms, as several of the methods giving accurate correlation energies, are either specialised for atoms [28, 46, 48] or only implemented for atoms [45].

The best correlation energies given in Table XV are the energy estimates obtained with the *pq*- and *kq*-ansätze. These estimates were obtained using 1710 and 171 GTGs, respectively. The value obtained by Bukowski and co-workers [26] using 120 nonlinearly optimised GTGs is only a few  $\mu E_h$  behind, however. Bukowski defined the pair function as for the helium atom, but included the coordinates of the GTGs lying in the direction of the molecular axis in the optimisation. For linear molecules it has been shown [53, 54] that any two-electron pair function belonging to the totally symmetric representation can be represented by geminals with no angular components. If Bukowski and co-workers include more GTGs in their pair function expansion, therefore, they ought to be able to improve on the energy estimate presented here.

The energies obtained by Klopper and Kutzelnigg [51] using the two MP2-R12 approximations are also acceptable, considering the size of the basis set used.

### 5. Lithium hydride

In Table XVI we present all-electron second-order correlation energies for a lithium hydride molecule with bond length  $3.015a_0 = 159.6\text{pm}$ . We have not listed any energies for

TABLE XVI: All-electron MP2 correlation energies ( $-E/mE_h$ ) of the lithium hydride molecule at an internuclear distance of  $r(\text{Li-H})=159.5469$  pm. Due to problems with singular matrices the  $pq$ -ansatz could not be used. Basis sets marked with an asterisk (\*) are used uncontracted

Orbital basis (Li,H)	VOE	KL	KQ
ANO-1 (10s4p , 7s)*	28.97	58.13	70.549
ANO-1 (10s4p3d , 7s)*	32.83	60.76	71.419
ANO-1 (10s4p , 7s3p)*	40.80	63.79	72.373
ANO-1 (10s4p3d , 7s3p)*	41.80	64.50	72.511
ANO-2 (14s9p , 8s)*	49.99	63.81	70.900
ANO-2 (14s9p4d , 8s)*	54.41	66.72	71.808
ANO-2 (14s9p , 8s4p)*	61.78	69.52	72.678
ANO-2 (14s9p4d , 8s4p)*	63.06	70.38	72.809
ANO-2 (14s9p4d3f, 8s4p)*	63.68	70.79	72.850
ANO-2 (14s9p4d , 8s4p3d)*	65.24	71.20	72.864
ANO-2 (14s9p4d3f, 8s4p3d)*	65.40	71.33	72.877

the  $pq$ -ansatz, however, as singularities in the equation solver prevented us from using this ansatz. Since the systems studied above obtained their best energy estimates with the  $pq$ -ansatz, we will probably not be able to exploit the full potential of the GTG-MP2 method for the lithium hydride molecule.

As shown in Table XVI we manage to recover good correlation energies using the  $kq$ -ansatz. This is in agreement with observations made for the hydrogen molecule. When the  $kq$ -ansatz is combined with the basis set (14s9p4d3f, 8s4p3d)\* we get  $-72.877mE_h$ , which is our best correlation energy for the lithium hydride molecule. A comparison with Table XVII shows that we have recovered 99.98% of the estimated limit. Note also, that reasonably good correlation energies are obtained even when the  $f$ -orbitals on lithium are not used.

For the  $kl$ -ansatz the best correlation energy obtained is  $-71.20mE_h$  which is only 97.9% of the limit. With this ansatz, far better correlation energies were obtained for the hydrogen molecule.

In Table XVII we compare our best correlation energies with literature data. The best correlation energy for the lithium hydride molecule is given by Bukowski *et al.* [37]. Using 350

TABLE XVII: The MP2 correlation energy ( $-E/mE_h$ ) of LiH at an internuclear distance of  $r(\text{Li-H})=159.5469$  pm, listed chronologically. The total correlation energy is  $-83.2mE_h$  [55]

authors	method	energy
this work	<i>kl</i> ansatz [ANO-2 (14s9p4d3f, 8s4p3d)*]	71.33
	<i>kq</i> ansatz [ANO-2 (14s9p4d3f, 8s4p3d)*]	72.877
Bukowski <i>et al.</i> [37]	350 nonlinearly optimised GTGs	72.890
Noga <i>et al.</i> [38]	MBPT-R12/A (11s8p6d5f, 9s8p6d5f)	72.973
	MBPT-R12/B (11s8p6d5f, 9s8p6d5f)	72.869
Klopper and Kutzelnigg [51]	MP2-R12/A (11s7p4d1f, 9s6p3d1f)	72.76
	MP2-R12/B (11s7p4d1f, 9s6p3d1f)	72.16
Petersson <i>et al.</i> [30]	CBS (complete basis-set) model	73.54
Alexander <i>et al.</i> [56]	700 nonlinearly optimised, randomly tempered GTGs	72.781

TABLE XVIII: Second-order pair correlation energies ( $-E/mE_h$ ) for the lithium hydride molecule with an inter-nuclear distance of  $r(\text{Li-H})=159.5469$  pm.

Pair	R12/A <sup>a</sup>	R12/B <sup>a</sup>	GTG <sup>b</sup>	KL <sup>c</sup>	KQ <sup>c</sup>
$1\sigma^2 \quad ^1\Sigma^+$	39.51	39.45	39.590	38.527	39.609
$1\sigma 2\sigma \quad ^1\Sigma^+$	1.48	1.41	1.471	1.409	1.490
	$^3\Sigma^+$	1.37	1.30	1.324	1.284
$2\sigma^2 \quad ^1\Sigma^+$	30.41	30.00	30.396	30.106	30.437
$E^{(2)}$	72.76	72.16	72.781	71.326	72.877

<sup>a</sup> The MP2-R12/A and MP2-R12/B methods in a basis of quality (11s8p6d5f, 9s8p6d5f). From Ref. [51].

<sup>b</sup> Using nonlinearly optimised GTGs. From Ref. [56].

<sup>c</sup> Using basis set ANO-2 (14s9p4d3f, 8s4p3d)\*.

GTGs of the type given in Eq. (36) in which five of the nonlinear parameters were optimised variationally, they obtained  $-72.890mE_h$ . This excellent result is almost matched by Noga *et al.* [38] who obtained  $-72.869mE_h$  using the MBPT-R12/B method. This method is not variational, however, and this makes it difficult to evaluate the quality of the result. The complete-basis-set (CBS) value of Petersson [30] is far off the limit.

Compared with literature data, the  $kq$ -ansatz performs very well. In Table XVIII we have split the best correlation energy obtained with this ansatz and the  $kl$ -ansatz into pair energies, and compared these to pair energies from literature. Unfortunately, neither Bukowski nor Noga listed pair energies in their papers, and we can therefore only compare with the pair energies given by Alexander *et al.* [56] and Klopper and Kutzelnigg [51]. Except for the  $1\sigma 2\sigma$  triplet energy obtained with the MP2-R12/A method, we see that the  $kq$ -ansatz give slightly lower energies for all pairs.

### 6. Hydrogen fluoride

We have established that our GTGs perform well for the hydrogen and lithium hydride molecules, and turn to the larger hydrogen fluoride molecule. This molecule differs from  $H_2$  and LiH in that it has electron pairs that do not belong to the totally symmetric representation. Based on our experience with the neon atom, we expect  $d$ -orbitals centred at the fluorine atom to be important for such pairs.

In Table XIX we present our second-order correlation energies for a hydrogen fluoride molecule with a bond length of  $1.73280a_0 = 91.6958\text{pm}$ . For hydrogen fluoride we have mainly investigated the aug-cc-pCVXZ series of basis sets, but due to extensive memory requirements, the  $pq$ -ansatz could not be applied in all cases. We shall also see that some of the correlation energies obtained with the  $pq$ -ansatz cannot be fully trusted.

By comparing energies obtained from subsets of different aug-cc-pCVXZ basis sets, the importance of  $d$ -orbitals becomes evident. For the  $kq$ -ansatz, for instance, merely 93.3% of the correlation energy limit (cf. Table XX) is recovered by the aug-cc-pCVQZ(sp,sp) basis set, although the basis set is well saturated in the  $s$ - and  $p$ -orbital spaces. Once  $d$ -orbitals are added on the fluorine atom, however, the energy recovery increases to 99.5%. The same trend is observed for the  $pq$ -ansatz. With the basis set aug-cc-pCVTZ(sp,s), only 93.7% of the correlation energy is recovered, while for the basis set aug-cc-pCVTZ(sp,d,s), the recoverage is 99.8%. For the hydrogen fluoride molecule, therefore, good correlation energy estimates can be obtained if we use basis sets saturated in the  $s$ -,  $p$ - and  $d$ -orbital spaces for fluorine and the  $s$ - and  $p$ -orbital spaces for hydrogen. This agrees with results obtained for the neon atom and the hydrogen molecule.

For the  $kl$ -ansatz, however, much larger basis sets must be used. Based on our experience

TABLE XIX: All electron second-order correlation energies ( $-E/mE_h$ ) for the hydrogen fluoride molecule. For the structure we have used  $r(\text{H-F})=91.6958$  pm.

Orbital basis (F, H)	VOE	KL	KQ	PQ
cc-pVDZ	203.78	306.89	350.48	360.21
cc-pCVDZ	242.85	316.33	356.63	365.24
aug-cc-pVDZ	224.56	328.36	369.51	379.21
aug-cc-pCVDZ (sp, s)	173.76	270.15	342.20	353.93
aug-cc-pCVDZ (sp, sp)	181.81	277.41	347.24	359.99
aug-cc-pCVDZ (spd, s)	260.01	334.59	373.02	381.59
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	383.685
aug-cc-pCVTZ (spd, sp)	313.51	354.70	382.35	n/a
aug-cc-pCVTZ (spd, spd)	317.00	357.35	382.64	n/a
aug-cc-pCVTZ	339.89	370.41	383.690	n/a
aug-cc-pCVQZ (sp, s)	200.46	277.74	352.03	361.17
aug-cc-pCVQZ (sp, sp)	212.02	287.47	358.65	367.92
aug-cc-pCVQZ (spd, s)	318.47	354.94	382.25	n/a
aug-cc-pCVQZ (spd, sp)	323.31	358.65	383.221	n/a
aug-cc-pCVQZ (spd, spd)	327.53	361.68	383.529	n/a

with the neon atom, basis sets should be of aug-cc-pCV5Z quality or better if more than 99% of the correlation energy is to be recovered. For the hydrogen fluoride molecule, however, we were not able to use a better basis set than the aug-cc-pCVTZ basis, for which only 96.4%, of the second-order correlation energy was recovered.

In Table XX, we compare our best correlation energies for the hydrogen fluoride molecule with literature data. The current best estimate of the limit,  $-384.38mE_h$ , has been obtained by Klopper [58] using the MP2-R12/B method. Klopper obtained this estimate using a basis set of  $19s14p8d6f4g3h$  quality for fluorine and  $9s6p4d3f$  quality for hydrogen. Even though the MP2-R12/B method is not variational, experience shows that correlation energies

TABLE XX: The MP2 correlation energy ( $-E/mE_h$ ) of HF at an internuclear distance of 91.6958 pm, listed chronologically. The total correlation energy is  $-388 mE_h$  [57]

authors	method	energy
this work	<i>kl</i> ansatz (aug-cc-pCVTZ)	370.41
	<i>kq</i> ansatz (aug-cc-pCVTZ)	383.69
	<i>pq</i> ansatz (aug-cc-pCVTZ-spd-s)	383.69
Ten-no [42]	MP2-GTG (aug-cc-pV5Z, without <i>h</i> -functions)	384.16
Klopper and Samson [44]	MP2-1A' (aug-cc-pV5Z)	381.61
	MP2-1B (aug-cc-pV5Z)	381.09
	MP2-2A' (aug-cc-pV5Z)	384.67
	MP2-2B (aug-cc-pV5Z)	383.57
Klopper [58]	MP2-R12/B (19s14p8d6f4g3h, 9s6p4d3f)	384.38
Müller <i>et al.</i> [57]	MP2-R12/A (18s12p10d8f6g, 10s7p5d)	384.36
	MP2-R12/B (18s12p10d8f6g, 10s7p5d)	384.17
Klopper [49]	MP2-R12/A (15s9p7d5f3g1h, 9s7p5d3f1g)	384.47
	MP2 (15s9p7d5f3g1h, 9s7p5d3f1g)	371.68
Petersson <i>et al.</i> [30]	CBS (complete basis-set) model	378.80

obtained with this method converges to the limit from above. Since a rather large one-electron basis set was employed, the value obtained by Klopper ought to be considered the best.

The best correlation energy obtained for hydrogen fluoride in this work was obtained using the *kq*-ansatz and the aug-cc-pCVTZ basis set. A comparison with the value of Klopper, shows that 99.82% has been recovered. The true limit is probably lower than Klopper's value, however. If use the basis set observations made for the neon atom as a guideline for the hydrogen fluoride molecule, the true second-order correlation energy is slightly more than  $1mE_h$  lower in energy than our aug-cc-pCVTZ value, or approximately  $-384.8mE_h$ .

All highly accurate correlation energies reported in literature have been obtained using different MP2-R12 approaches with one-electron basis sets of high quality. As shown in Table XX, these estimates are in good agreement with each other.

An estimate of the correlation energy has also been reported by Petersson [30] using his

CBS theory. Although he obtains better energies than conventional MP2, the performance of the CBS theory is clearly inferior to that of the MP2-R12 methods.

Note also, that there are no correlation energies listed in Table XX for the GTG method where the nonlinear parameters are optimised. Although Wenzel and Zabolitzky [59] have reported pair energies for three totally symmetric pairs, there are no total correlation energies available. The pair energies given are those of the  $1\sigma^2$ ,  $2\sigma^2$ , and  $3\sigma^2$  pairs and are  $40.2mE_h$ ,  $12.4mE_h$ , and  $27.2mE_h$ , respectively. These pair energies were only computed to illustrate a new optimisation technique.

In Table XXI we compare pair energies for hydrogen fluoride for some selected methods. The two rightmost columns list pair energies obtained with the  $pq$ -ansatz but different one-electron basis sets. The two basis sets differ only in that one of them has four  $d$ -orbitals for the fluorine atom while the other has none. Differences observed in pair energies between the two columns illustrate the importance of  $d$ -orbitals. For electron pairs involving  $\sigma$ -orbitals only, there is little difference between the two columns. This is to be expected as  $\sigma$ -orbitals are symmetric around the bond axis, and the interaction between two such orbitals has little to gain from the angular flexibility provided by  $d$ -orbitals. For electron pairs involving  $\pi$ -orbitals, however, some large differences are observed between the two columns. Assuming that the molecular bond lies along the  $z$ -axis, a  $\pi$ -orbital consists of either  $p_x$ - or  $p_y$ -orbitals as well as small amounts of appropriate  $d$ -orbitals. For the major part, these  $p$ - and  $d$ -orbitals come from the fluorine atom, but if they are provided for hydrogen, small amounts of these orbitals also participate in the  $\pi$ -orbital. This is not the case here, however, and the  $\pi$ -orbitals therefore behave as fluorine  $p$ -orbitals. As expected, Table XXI shows that the largest basis set dependency is observed for the singlet interaction between two such  $\pi$ -orbitals. This is in full agreement with observations made for neon pair energies in Table XII. Note also, that the singlet interactions between the  $3\sigma$ -orbital and the two  $1\pi$ -orbitals also need  $d$ -functions in order to be properly described. This is easily explained by a high  $p_z$  content in the  $3\sigma$ -orbital.

The pair energy decomposition given in Table XXI also shows something else. For the  $^1(2\sigma^2)$ ,  $^1(1\sigma 1\pi)$ ,  $^3(1\sigma 2\sigma)$ , and  $^3(2\sigma 3\sigma)$  interactions, the pair energies obtained with the  $pq$ -ansatz in the small aug-cc-pCVTZ(sp,s) basis set are lower than the energies obtained in the aug-cc-pCVTZ(sp,d,s) basis. This is due to deficiencies in the Fock operator, similar to the problems observed for the hydrogen molecule

TABLE XXI: The MP2 pair energies ( $-E/mE_h$ ) of HF at an internuclear distance of 91.6958 pm

spin	pair	R12/A <sup>a</sup>	$kl^b$	$kq^b$	$pq^c$	$pq^d$
singlet	$1\sigma^2$	40.57	40.038	40.546	40.558	40.570
	$1\sigma 2\sigma$	3.60	3.493	3.614	3.598	3.616
	$2\sigma^2$	13.06	12.643	13.057	13.471	13.107
	$1\sigma 3\sigma$	2.07	1.859	2.076	2.064	2.075
	$2\sigma 3\sigma$	20.16	19.230	20.116	19.057	20.236
	$3\sigma^2$	29.30	28.574	29.243	28.878	29.271
	$1\sigma 1\pi$	4.99	4.422	4.981	5.010	5.006
	$2\sigma 1\pi$	39.97	37.670	39.884	38.653	39.818
	$3\sigma 1\pi$	33.15	31.201	32.998	25.370	32.517
	$1\pi^2$	71.30	68.057	71.067	60.887	71.531
triplet	$1\sigma 2\sigma$	1.59	1.455	1.596	1.614	1.598
	$1\sigma 3\sigma$	3.31	3.082	3.300	3.217	3.293
	$2\sigma 3\sigma$	8.81	8.590	8.802	8.826	8.783
	$1\sigma 1\pi$	8.56	7.957	8.532	8.558	8.570
	$2\sigma 1\pi$	18.79	18.143	18.764	18.586	18.836
	$3\sigma 1\pi$	56.49	55.711	56.416	53.246	56.143
	$1\pi^2$	28.74	28.287	28.699	28.457	28.717
sum	384.47	381.412	383.691	360.050	383.687	

<sup>a</sup> MP2-R12/A from Ref. [49].

<sup>b</sup> Using basis aug-cc-pCVTZ

<sup>c</sup> Using basis aug-cc-pCVTZ (sp, s)

<sup>d</sup> Using basis aug-cc-pCVTZ (spd, s)

We finally note that since our pair energies are supposedly variational, we may combine pair energies obtained with the  $kq$ - and  $pq$ -ansätze, depending of which gives the better energy, in pursuit of the second-order correlation energy limit. Assuming that the energies obtained with the  $pq$ -ansatz and the aug-cc-pCVTZ(sp,d,s) basis set may be trusted, this approach gives  $-384.53mE_h$  as an upper bound to the second-order correlation energy of the hydrogen fluoride molecule.

## IV. CONCLUSIONS

We have presented a new method for calculating highly accurate MP2 energies for atomic and molecular closed-shell systems. This GTG-MP2 methods may be regarded as an mixture/intermediate between the MP2-R12 method developed by Klopper and Kutzelnigg [5–7] and the Gaussian-type geminals (GTG) method developed by Szalewicz, Jeziorski, and others [8–11].

Pair energies are obtained by minimising the WO functional of Szalewicz and co-workers. We only optimise linear parameters, however, and pair energies are therefore easily obtained by solving a set of linear equations. To get efficient evaluation of three-electron integrals, the integral code has been parallelised.

==== burde dette inn i innledningen? Even though we have used our explicitly correlated pair functions for obtaining accurate MP2 energies only, they may also be used to obtain molecular properties; either using the Hellman–Feynman approximation as done by Bakken *et al.* [60] for molecular geometric properties, or using explicit formulas as done by Bukowski *et al.* [61] for multipole moments.

The use of explicitly correlated basis functions is not limited to MP2 theory, but may also be developed for the coupled-cluster and CASPT2 theories, for example. For the coupled-cluster singles and doubles theory Noga and co-workers [57, 62–65] have made an implementation in which the linear  $r_{12}$  terms are utilised (CCSD-R12), while Bukowski and co-workers [37] have made an implementation utilising Gaussian correlation factors (GTG-CCSD). Robert Polly has made an GTG-CASPT2 implementation, but no results are published yet... =====

We have shown that pair functions of the form (15)–(17) give high quality energies for both atoms and molecules when the functions are optimised with the WO functional. For simplicity we have restricted the GTGs to be made from nine GCFs with exponents  $\gamma_v \in \{1/9, 1/3, \dots, 729\}$ . No attempt has been made to optimise the non-linear exponents of either the GCFs or the one-electron basis sets, and the results merely show the potential of the pair functions and not the ultimate performance. In Table XXII we compare our best second-order correlation energies with the best estimates found in literature.

For almost all calculations presented in this work, the  $kl$ -ansatz performs poorly. From the neon results in Table XIII, however, we know that the GTG-MP2 method with the  $kl$ -

TABLE XXII: Second-order correlation energies ( $-E/mE_h$ ) obtained in this work compared with current best estimates.

System	this work	Current best	Recovery
He	37.37729	37.37744	99.9996%
Be	76.355	76.358	99.996%
Ne	388.19	388.19	100%
H <sub>2</sub>	34.252	34.252	100%
LiH	72.877	72.890	99.98%
HF	383.69	384.4	99.82%

ansatz perform better than the MP2-R12 methods in the same one-electron basis. Obtaining good energies with the  $kl$ -ansatz is therefore only a question of using a sufficiently large basis for the virtual orbital expansion. This can be done by introducing separate basis sets for the orbital part and the geminal part of the pair functions. The use of multiple basis sets will allow calculations on larger molecules, but the use of three-electron integrals will still limit the size of systems than can be treated. A remedy to this is to introduce the RI approximation in three-electron integrals as well as prescreening techniques. This has been discussed in Ref. [25].

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- [1] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Structure Theory* (John Wiley & Sons, Chichester, 2000).

- [2] E. Hylleraas, Z. Phys. **48**, 469 (1928).
- [3] E. Hylleraas, Z. Phys. **54**, 347 (1929).
- [4] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).
- [5] W. Kutzelnigg, Theoret. Chim. Acta **68**, 445 (1985).
- [6] W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1986).
- [7] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
- [8] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, Chem. Phys. Lett. **91**, 169 (1982).
- [9] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).
- [10] K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. J. Monkhorst, J. Chem. Phys. **85**, 3964 (1986).
- [11] R. Bukowski, B. Jeziorski, S. Rybak, and K. Szalewicz, J. Chem. Phys. **102**, 888 (1995).
- [12] R. Polly, H.-J. Werner, P. Dahle, and P. Taylor, J. Chem. Phys. **124**, 1 (2006).
- [13] B. J. Persson and P. Taylor, Theoret. Chim. Acta **97**, 240 (1997).
- [14] P. Dahle and P. R. Taylor, Theoret. Chem. Acc. **105**, 401 (2001).
- [15] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).
- [16] D. Feller, unpublished work.
- [17] P.-O. Widmark, P.-Å. Malmqvist, and B. O. Roos, Theoret. Chim. Acta **77**, 291 (1990).
- [18] K. Pierloot, B. Dumez, P.-O. Widmark, and B. O. Roos, Theoret. Chim. Acta **90**, 87 (1995).
- [19] F. van Duijneveldt, *IBM technical research report RJ945* (1970).
- [20] B. J. Persson and P. Taylor, J. Chem. Phys. **105**, 5915 (1996).
- [21] P. Dahle, T. Helgaker, D. Jonsson, and P. R. Taylor, in preparation.
- [22] *J.J Dongarra, J.R. Bunch, C.B. Moler, G.W. Stewart, LINPACK users' guide. Society for Industrial and Applied Mathematics, Philadelphia, PA, USA, ISBN 0-89871-172-X* (1979).
- [23] J. R. Bunch and L. Kaufman, Math. Comp. **37**, 163 (1977).
- [24] N. J. Higham, Linear Algebra App. **287**, 181 (1998).
- [25] P. Dahle, *Accurate calculations using explicitly correlated wave functions.*, dr.philos thesis (May 2004), university of Oslo.
- [26] R. Bukowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **104**, 3306 (1996).
- [27] J. S. Lee and S. Y. Park, J. Chem. Phys. **112**, 10746 (2000).

- [28] J. R. Flores, J. Chem. Phys. **98**, 5642 (1993).
- [29] V. Termath, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **94**, 2002 (1991).
- [30] G. A. Petersson, A. Bennet, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, and J. Mantzaris, J. Chem. Phys. **89**, 2193 (1988).
- [31] P. Malinowski, M. Polasik, and K. Janowski, J. Phys. B: At. Mol. Phys. **12**, 2965 (1979).
- [32] N. W. Winter, V. McKoy, and A. Laferriere, Chem. Phys. Lett. **6**, 175 (1970).
- [33] H. F. King, J. Chem. Phys. **46**, 705 (1967).
- [34] S. Y. Park and J. S. Lee, J. Chem. Phys. **116**, 5389 (2002).
- [35] S. B. Huh and J. S. Lee, J. Chem. Phys. **118**, 3035 (2003).
- [36] J. Komasa, W. Cencek, and J. Rychlewski, Phys. Rev. **A** **52**, 4500 (1995).
- [37] R. Bukowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **110**, 4165 (1999).
- [38] J. Noga, D. Tunega, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **103**, 309 (1995).
- [39] S. Salomonsen and P. Öster, Phys. Rev. **A** **41**, 4670 (1990).
- [40] S. S. Alexander, H. J. Monkhorst, and K. Szalewicz, J. Chem. Phys. **85**, 5821 (1986).
- [41] K. Janowski, D. Rutowska, and A. Rutowski, J. Phys. B: At. Mol. Phys. **15**, 4063 (1982).
- [42] S. Ten-no, J. Chem. Phys. **121**, 117 (2004).
- [43] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
- [44] W. Klopper and C. C. M. Samson, J. Chem. Phys. **116**, 6397 (2002).
- [45] P. Wind, W. Klopper, and T. Helgaker, Theoret. Chem. Acc. **107**, 173 (2002).
- [46] I. Lindgren and S. Salomonsen, Phys. Scr. **21**, 335 (1980).
- [47] I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer, New York, 1982).
- [48] K. Janowski and P. Malinowski, Phys. Rev. **A** **21**, 45 (1980).
- [49] W. Klopper, J. Chem. Phys. **102**, 6168 (1995).
- [50] W. Cencek and W. Kutzelnigg, Chem. Phys. Lett. **266**, 383 (1997).
- [51] W. Klopper and W. Kutzelnigg, J. Chem. Phys. **94**, 2020 (1991).
- [52] B. Jeziorski, K. Monkhorst, Hendrik J. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984).
- [53] B. Jeziorski, R. Bukowski, and K. Szalewicz, Int. J. Quantum Chem. **61**, 769 (1997).
- [54] R. N. Hill, Int. J. Quantum Chem. **68**, 357 (1998).
- [55] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **79**, 5543 (1983).

- [56] S. S. Alexander, H. J. Monkhorst, and K. Szalewicz, *J. Chem. Phys.* **87**, 3976 (1987).
- [57] H. Müller, W. Kutzelnigg, and J. Noga, *Mol. Phys.* **92**, 535 (1997).
- [58] W. Klopper, *Mol. Phys.* **99**, 481 (2001).
- [59] K. B. Wenzel and J. G. Zabolitzky, *J. Chim. Phys.* **84**, 691 (1987).
- [60] V. Bakken, T. Helgaker, W. Klopper, and K. Ruud, *Mol. Phys.* **96**, 653 (1999).
- [61] R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **108**, 7946 (1998).
- [62] J. Noga, W. Kutzelnigg, and W. Klopper, *Chem. Phys. Lett.* **199**, 497 (1992).
- [63] J. Noga and W. Kutzelnigg, *J. Chem. Phys.* **101**, 7738 (1994).
- [64] W. Klopper and J. Noga, *J. Chem. Phys.* **103**, 6127 (1995).
- [65] T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).