This paper is published as part of a PCCP Themed Issue on:

Explicit-r_{12} Correlation Methods and Local Correlation Methods

Guest Editors: Hans-Joachim Werner and Peter Gill

Second-order Møller–Plesset calculations on the water molecule using Gaussian-type orbital and Gaussian-type geminal theory

Pål Dahle,[ab] Trygve Helgaker,*[c] Dan Jonsson[d] and Peter R. Taylor[e]

The Gaussian-type orbital and Gaussian-type geminal (GGn) model is applied to the water molecule, at the level of second-order Møller–Plesset (MP2) theory. In GGn theory, correlation factors are attached to all doubly-occupied orbital pairs (GG0), to all doubly-occupied and singly-excited pairs (GG1), or to all orbital pairs (GG2). Optimizing the GG2 model using a weak-orthogonality functional, we obtain the current best estimate of the all-electron MP2 correlation energy of water, -361.95 mE_h. In agreement with previous observations, the GG1 model performs almost as well as the GG2 model (-361.26 mE_h), whereas the GG0 model is poorer (-351.36 mE_h). For the barrier to linearity of water, we obtain an MP2 correlation contribution of -463 ± 5 cm^{-1}.

I. Introduction

Since the early work of Hylleraas, it has been known that the correlation energy converges very slowly with respect to expansion of the orbital basis.[1] In particular, if the orbitals of the expansion are chosen in an optimal fashion, the error in the correlation energy is proportional to N^{-1}, where N is the number of orbitals in the calculation.[2,3] Exploiting the smoothness of the convergence, it is possible to improve on this convergence by extrapolation. A more fundamental solution, however, is to improve upon the underlying description of the electrons by including the interelectronic distances explicitly in the wave function.[4,5]

Over the years, a number of such explicitly correlated techniques have been proposed. Of particular relevance to our work is the Gaussian-type geminal (GTG) method, introduced in 1982 by Szalewicz and coworkers.[6–9] With this model, a number of accurate second-order Møller–Plesset (MP2) calculations have been carried out on small systems, but applications to larger systems are difficult because of a nonlinear optimization of variational parameters (geminal centers and exponents) and the explicit evaluation of three-electron integrals. An alternative technique is the R12 method, introduced a few years later by Kutzelnigg and Klopper.[10,11] Using a linear r_{12} correlation factor and avoiding many-electron integrals through the resolution of the identity, R12 theory is applicable to large systems and has recently been generalized to F12 theory, with correlation factors $f(r_{12})$ different from r_{12}.[12]

We here discuss an alternative model, which uses a mixed Gaussian-type orbital (GTO) and GTG expansion,[13] avoiding the nonlinear optimization of the GTG method but otherwise closely following the approach of Szalewicz and coworkers.[6–9] In particular, we optimize the MP2 pair functions using their weak-orthogonality (WO) functional, with an explicit evaluation of three-electron integrals.[14]

As in F12 theory, GTO–GTG (GG) theory uses pair functions that combine a traditional, orbital-based pair function with an explicitly correlated part, consisting of orbital products multiplied by a correlation factor. However, whereas the correlation factors in F12 theory are only multiplied on products of two occupied orbitals (doubly-occupied pairs), there are no such restrictions in GG theory. Instead, we have a hierarchy of GGn models. In the simplest GG0 model, the correlation factor is only introduced in doubly occupied pairs; in the more general GG1 model, such factors are introduced also in all singly-excited orbital pairs; finally, in the GG2 model, we attach correlation factors to all possible pairs, even those that are doubly excited relative to the Hartree–Fock description. In ref. 15, we applied these models to atoms and diatomics, comparing their performance with orbital-based MP2 theory and different explicitly correlated methods. For an implementation of the GG0 and GG1 models in the context of local MP2 theory, see ref. 16. In the present paper, we present applications of MP2–GGn theory to the water molecule.

II. Theory

In Møller–Plesset theory, the second-order energy $E^{(2)}$ may be expressed in terms of the pair energies ε_{ij}^s

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

[a] *Norwegian Computing Center, Gaustadalléen 23, NO-0314 Oslo, Norway*
[b] *Department of Chemistry, University of Oslo, Box 1033, Blindern, NO-0315 Oslo, Norway*
[c] *Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Box 1033, Blindern, NO-0315 Oslo, Norway. E-mail: trygve.helgaker@kjemi.uio.no; Tel: +47 22855428*
[d] *Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, NO-9037 Tromsø, Norway*
[e] *Department of Chemistry and Centre for Scientific Computing, University of Warwick, Coventry, United Kingdom CV4 7AL*

where the ϕ_{ij}^s are singlet ($s = 1$) and triplet ($s = 3$) products of occupied molecular orbitals (MOs)

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

and where the Qu_{ij}^s are pair functions u_{ij}^s made strongly orthogonal to the occupied space $\{\varphi_k\}$ by the projection operator

$$Q(1,2) = [1 - O(1)][1 - O(2)], \quad O = \sum_i |\varphi_i\rangle\langle\varphi_i| \qquad (3)$$

The pair functions u_{ij}^s are symmetric and antisymmetric spatial functions, multiplied by singlet and triplet spin functions respectively. In the following, we concentrate on the spatial part and assume the spin part to be given.

Following our previous work,[15] the GGn pair functions are constructed as traditional orbital-based pair functions supplemented with three different geminal expansions:

$$u_{ij}^s = \sum_{a \geq b} \phi_{ab}^s c_{ij,s}^{ab} + \sum_{x \geq y}\sum_v g_{xy,v}^s c_{ij,s}^{xy,v},$$
$$\text{with } xy \in \{kl, kq, pq\} \qquad (4)$$

The first term is the traditional pair-function virtual orbital expansion (VOE) and consists of products of virtual orbitals ϕ_{ab}^s defined as in eqn (2). The second term is the explicitly correlated part, which is a linear combination of GTGs $g_{xy,v}^s$ each taken as a product of ϕ_{xy}^s and a Gaussian correlation factor (GCF) $\exp(-\gamma_v r_{12}^2)$ with a fixed exponent γ_v:

$$g_{xy,v}^s = \exp(-\gamma_v r_{12}^2)\phi_{xy}^s \qquad (5)$$

The GGn models differ in which GTGs are included in the pair functions: in the simplest GG0 model, only GTGs with both MOs occupied $g_{kl,v}^s$ are included; in the more flexible GG1 model, we also include GTGs with one virtual MO $g_{kq,v}^s$; finally, in the GG2 model, no restrictions are placed on the MOs in the GTGs. Thus, in the notation GGn, n gives the highest excitation level included in the GTG part of the pair function.

The linear expansion coefficients of eqn (4) can be variationally optimized by minimizing the strong-orthogonality (SO) functional

$$^{SO}F_{ij}^s[u_{ij}^s] = \frac{s}{2(1+\delta_{ij})}[\langle Qu_{ij}^s|f(1) + f(2) - \varepsilon_i - \varepsilon_j|Qu_{ij}^s\rangle + 2\langle Qu_{ij}^s|r_{12}^{-1}|\phi_{ij}^s\rangle], \qquad (6)$$

where the $f(1)$ and $f(2)$ are the Fock operators of electrons one and two, respectively, and the ε_i are orbital energies. To avoid the four-electron integrals that arise in the SO functional, we replace it by the weak-orthogonality (WO) functional developed by Szalewicz and coworkers:[6–9]

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

Here the removal of the strong-orthogonality operator in the first term is compensated for by the addition of a penalty term.

The factor Δ_{ij} of the penalty term is a level shift defined by $\Delta_{ij} = 1/2(\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta$ with $\varepsilon_1 \leq \varepsilon_i$ and $\eta \geq 0$. Clearly, this function penalizes valence pair functions more strongly than core and core–valence pair functions, potentially yielding pair energies which are too high. A modified WO penalty function, designed to remedy this situation, was proposed by Wenzel et al.[8] We have not observed a poorer valence convergence and have used the original WO in all calculations reported here.

If the Hartree–Fock equations have been solved exactly (that is, the orbitals are eigenfunctions of the operators $f(i)$), then the WO functional gives an upper bound to the SO functional, which, in turn, gives an upper bound to the exact pair energy:

$$^{WO}F_{ij}^s[u] \geq {}^{SO}F_{ij}^s[u] \geq \varepsilon_{ij} \qquad (8)$$

In contrast to the SO functional, strong orthogonality is not ensured when the pair function is optimized using the WO functional: instead, orthogonality is introduced in the course of the minimization of the WO functional provided that the pair function u_{ij}^s is sufficiently flexible. If the pair function lacks this flexibility, then the correlation energy becomes too high, in agreement with eqn (8). This was observed for the GGn models when we tried to replace the linear combination of GTGs in eqn (4) with a linear combination of ϕ_{xy}^s and a *fixed* linear combination of GCFs.[14] Recently, it has been demonstrated that the GG0 model may indeed give poor energies when optimized with the WO functional.[17] The GG1 and GG2 energies on the other hand converge very rapidly to the basis-set limit, as shown in ref. 15.

III. Computational considerations

A. One-electron basis sets

In our calculations we use the standard correlation-consistent basis sets cc-pVXZ of Dunning,[18] with and without the addition of diffuse and high-exponent functions. In addition, we also use truncations of these basis sets, omitting orbitals of high angular momentum. In such cases the orbital types retained in the basis are given in parentheses after the basis-set name. For example, in the basis cc-pVTZ(spd,sp) we have omitted the f shell on oxygen and the d shell on hydrogen.

B. Two-electron basis sets

The GCF expansions of eqn (4) may be changed by adjusting the exponents in each correlation factor $\exp(-\gamma_v r_{12}^2)$ and by changing the number of correlation factors included in the expansion. Following our previous work,[15] we use the set of nine GCFs in which the exponents γ_v are taken from the even-tempered sequence $\{1/9, 1/3, \ldots, 729\}$.

To examine the contributions from the different GCFs to the energy, we have carried out water calculations in the cc-pVDZ and aug-cc-pVTZ(spd,sp) basis sets using GCF expansions with up to nine terms. A level shift $\eta = 0.1$ was used in all calculations. The results are presented in Table 1.

As expected, the successive inclusion of more and more GCFs lowers the energy monotonically. Since the GTGs are primarily introduced to model the cusp region, we are

Table 1 All-electron MP2-GGn correlation energies ($-E/mE_h$) for water[a] calculated using GCF exponents γ_v taken from the sequence 1/9, 1/3, ..., 729

		cc-pVDZ			aug-cc-pCVTZ(spd,sp)[b]		
N_{GCF}	γ_{max}	GG0	GG1	GG2	GG0	GG1	GG2
0	—	203.96	203.96	203.96	300.22	300.22	300.22
1	1/9	204.11	204.34	229.85	300.22	300.32	306.82
2	1/3	214.38	258.21	283.43	300.90	326.68	339.98
3	1	256.60	300.18	311.03	315.81	344.66	350.89
4	3	282.17	318.25	328.14	328.49	352.24	356.55
5	9	291.24	328.60	337.29	332.67	356.03	358.71
6	27	295.72	332.12	340.94	335.50	358.09	359.52
7	81	297.41	333.66	342.41	337.09	359.21	359.92
8	243	297.94	334.17	342.84	337.64	359.56	360.12
9	749	298.07	334.28	342.97	337.75	359.65	360.14

[a] Structure: $\angle$(HOH) = 104.52° and r(O–H) = 95.720 pm. [b] In the GG2 calculations, we used d functions from the cc-pVDZ basis.

particularly concerned with the convergence with respect to the addition of high-exponent functions, noting that diffuse GTGs are essentially orbital products whose contribution to the correlation energy may be effectively recovered by the traditional orbital expansion. From an inspection of Table 1, we conclude that, with all nine GCFs included in the pair function, the description of the Coulomb hole is converged to within 0.1 mE_h. The conclusions drawn here for water are similar to those for neon in ref. 15.

C. The level-shift parameter

The dependence of the calculated energies and the strong orthogonality on the level-shift parameter η was discussed in ref. 15. A high value of η stabilizes the equations and improves strong orthogonality but incurs a penalty on the solution, raising the correlation energy. In a given WO calculation, the degree of strong orthogonality may be monitored by calculating

$$\chi_{ij}^{SO} = \langle u_{ij}^s|O(1)+O(2)|u_{ij}^s\rangle/\langle u_{ij}^s|u_{ij}^s\rangle, \qquad (9)$$

which, if small, indicates a more strongly orthogonal pair function u_{ij}^s. In Table 2, we have listed the total correlation energy E and pSO $= -\log_{10}\chi_{1s^2}^{SO}$, in water, for the three GGn models in the cc-pVDZ and aug-cc-pCVTZ(spd,sp) basis sets, using different level shifts. The pSO measure is based on the $1s^2$ pair function, which is the only pair function that is sensitive to small values of η.

In general, the energy changes little for level shifts in the range $0.001 < \eta < 1$. Moreover, the sensitivity to η is strongest for the GG0 model in the small basis and weakest for the GG2 model in the large basis. As expected, strong orthogonality increases with η. A comparison of the pSO value and the energy for different η indicates that a good compromise is achieved with $\eta = 0.1$, which is therefore used in all calculations discussed below. Again, similar conclusions were reached for neon in ref. 15.

D. Linear dependencies and numerical stability

From Table 1 we see that the GGn performance improves with increasing geminal excitation level n. At the same time, the WO optimization becomes more difficult—not only because the dimension of the linear equations increases with increasing n but also because these equations become more prone to linear dependencies and to numerical instabilities. To quantify the linear dependency problem of the GGn pair functions, we have listed in Table 3 the number of eigenvalues of the geminal–geminal overlap matrix in different ranges. For a given AO basis, the number of small eigenvalues increases with n as more and more GTGs are introduced into the GGn pair function. For the GG1 and GG2 pair functions, the number of small eigenvalues increases also with increasing dimension of the AO basis, since the number of GTGs for these models depends on the number of virtual orbitals. For instance, in the aug-cc-pCVTZ(spd,sp) basis there are 1053 eigenvalues less than or equal to 10^{-15}, making the solution of the linear equations more difficult. In Table 2 we see that, in the same basis set, the energy varies by as much as 0.04 mE_h for small η. These variations originate from numerical instabilities in the optimization of the $1s^2$ pair function. These problems are only observed with the GG2 model in the large basis set. For more details on the solution of the linear equations, see ref. 15.

IV. Results

A. The MP2 correlation energy of water

In Table 4 we present our MP2–GGn correlation energies for the water molecule. As observed for atoms and diatomics in ref. 15, the GG0 energy converges slowly with increasing basis set. Indeed, our best GG0 energy of -351.36 mE_h, obtained with the aug-cc-pCVTZ basis set, recovers only 97.1% of the

Table 2 Water[a] all-electron MP2-GGn correlation energies ($-E/mE_h$) and SO measures for different values of the level-shift parameter η

	cc-pVDZ						aug-pCVTZ(spd,sp)[b]					
	GG0		GG1		GG2		GG0		GG1		GG2	
$\log_{10}\eta$	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO	$-E$	pSO
+3	254.52	2.1	310.84	2.9	332.85	3.3	319.07	3.9	357.43	5.2	359.49	12.6
+2	279.41	1.5	325.49	2.3	338.88	2.5	329.20	3.1	358.94	4.8	359.82	11.2
+1	294.25	1.3	332.71	2.0	342.17	2.2	335.91	2.9	359.52	4.5	360.10	12.6
0	297.65	1.2	334.12	2.0	342.88	2.2	337.55	2.9	359.64	4.5	360.17	11.0
−1	298.07	1.2	334.28	2.0	342.97	2.2	337.75	2.9	359.65	4.5	360.14	9.8
−2	298.11	1.2	334.30	1.7	342.98	1.9	337.78	2.8	359.65	3.7	360.18	9.7
−3	298.13	0.4	334.30	0.3	342.98	0.4	337.78	1.7	359.65	1.8	360.18	8.1

[a] Structure: $\angle$(HOH) = 104.52° and r(O–H) = 95.720 pm. [b] In the GG2 calculations, we used d functions from the cc-pVDZ basis.

Table 3 Distribution of eigenvalues for some geminal–geminal overlap matrices for the water molecule.[a] Geminals are constructed from the full set of nine GCFs. Eigenvalues λ are reported as $\Delta(\lambda) = \max(0, \min(15, -\text{int}(\log_{10}\lambda)))$

Δ	cc-pVDZ			aug-cc-pCVTZ(spd,sp)[b]		
	GG0	GG1	GG2	GG0	GG1	GG2
0	17	262	245	17	281	709
1	21	233	227	21	267	681
2	23	305	298	23	340	938
3	29	363	339	29	409	1161
4	20	333	335	20	346	1232
5	17	309	301	17	323	1200
6	6	236	234	6	251	1131
7	2	188	208	2	229	1051
8		164	178		187	986
9		121	138		144	932
10		92	95		122	863
11		55	61		88	762
12		28	30		53	668
13		10	9		35	536
14		1	1		19	461
15			1		11	1053

[a] Structure: $\angle(\text{HOH}) = 104.52°$ and $r(\text{O–H}) = 95.720$ pm. [b] In the GG2 calculations, we used d functions from the cc-pVDZ basis.

current best MP2 correlation energy of 361.95 mE_h (see Table 5). The GG1 model, by contrast, converges rapidly: in the aug-cc-pCVDZ and aug-cc-pCVTZ basis sets, respectively, 97.7 and 99.8% of the correlation energy are recovered. Moreover, the good correlation energy obtained with the aug-cc-pCVTZ(spd,sp) basis set indicates that, with only s, p and d orbitals on oxygen and s and p orbitals on hydrogen, the GG1 model accurately recovers the correlation energy of water. However, as we shall see later, this basis set is nevertheless not sufficiently flexible for the calculation of the barrier to linearity of water. Finally, concerning the more flexible GG2 model, we note that it recovers as much as 99.4% of the correlation energy in the small aug-cc-pCVDZ basis set.

In Table 5, we compare our best MP2 correlation energies for water with literature values. The best literature values have been obtained using a combination of high-quality basis sets and the MP2–R12/B method—in particular, we note the correlation energy of -361.92 mE_h, obtained by Klopper in a large AO basis. The MP2–R12/A values in Table 5 are lower but less trustworthy, as this approximation is known to give energies that are too low by error cancellation. The MP2–GTG value of -356.43 mE_h obtained by Bukowski et al.[9] is less accurate. We note that in the WO optimization of this energy the GTGs were

Table 4 Water[a] all-electron MP2-GGn correlation energies ($-E/\text{m}E_\text{h}$)

Basis	VOE	GG0	GG1	GG2
cc-pVDZ	203.96	298.07	334.28	342.97
cc-pCVDZ	241.33	307.05	339.13	346.65
aug-cc-pVDZ	221.83	315.79	349.94	357.71
aug-cc-pCVDZ	259.24	324.72	353.48	359.66
aug-cc-pCVTZ (spd,sp)	300.21	337.75	359.65	361.74
aug-cc-pCVTZ (spd,spd)	307.86	342.83	360.35	361.86
aug-cc-pCVTZ (spdf,sp)	321.10	349.44	361.13	361.95
aug-cc-pCVTZ	324.14	351.36	361.26	—
aug-cc-pCVQZ (spd,sp)	309.62	341.34	360.49	—

[a] Structure: $\angle(\text{HOH}) = 104.52°$ and $r(\text{O–H}) = 95.720$ pm.

Table 5 Water[a] all-electron MP2 correlation energies ($-E/\text{m}E_\text{h}$). Comparison with literature data. Entries are listed in reverse chronological order

Authors	$E^{(2)}$
This work	
MP2–GG0 (aug-cc-pCVTZ)[a]	351.36
MP2–GG1 (aug-cc-pCVTZ)[a]	361.26
MP2–GG2 (aug-cc-pCVTZ(spdf,sp))[a]	361.95
Klopper[20]	
MP2–R12/B ($19s14p8d6f4g3h$, $9s6p4d3f$)[b]	361.92
Müller et al.[21]	
MP2–R12/A ($17s11p9d7f5g$, $10s7p5d$)[a]	362.32
MP2–R12/B ($17s11p9d7f5g$, $10s7p5d$)[a]	361.52
Klopper[22]	
MP2–R12/A ($15s9p7d5f3g1h$, $9s7p5d3f1g$)[a]	362.01
Bukowski et al.[9]	
Nonlinearly optimized GTGs[a]	356.43

[a] Structure: $\angle(\text{HOH}) = 104.52°$ and $r(\text{O–H}) = 95.720$ pm. [b] Structure: $\angle(\text{HOH}) = 104.225°$ and $r(\text{O–H}) = 95.7119$ pm.

fixed on the nuclei, rather than variationally optimized as is the normal procedure in GTG theory. By fixing the positions of the GTGs, the flexibility needed to create strong orthogonality is lost and the energy becomes too high.

In Table 6, our best MP2–GGn pair energies are compared with literature values. From the GG2 values in this table, we obtain a valence MP2 correlation energy of -300.426 mE_h, in agreement with $-300.4(3)$ mE_h recently obtained by Yamaki et al.[19]

B. The MP2 correction to the barrier to linearity of water

In the mid-1990s, rovibrational states characteristic of the water molecule were identified in the sunspot spectrum of the sun.[23,24]

Table 6 Water[a] MP2 pair correlation energies ($-E/\text{m}E_\text{h}$)

Spin	Pair	R12/A[b]	GTG[c]	GG0[d]	GG1[d]	GG2[e]
Singlet	$1a_1^2$	40.86	40.76	40.36	40.842	40.862
	$1a_1 2a_1$	3.21	3.20	3.12	3.228	3.232
	$2a_1^2$	13.31	13.17	12.98	13.290	13.309
	$1a_1 3a_1$	2.16	2.14	1.92	2.155	2.162
	$2a_1 3a_1$	17.67	17.21	16.95	17.627	17.663
	$3a_1^2$	25.81	25.09	25.05	25.751	25.794
	$1b_1^2$	26.31	25.98	25.46	26.253	26.318
	$1b_2^2$	25.65	25.10	25.15	25.597	25.637
	$1a_1 1b_1$	2.26	2.26	1.98	2.254	2.264
	$2a_1 1b_1$	18.93	18.72	18.05	18.883	18.936
	$3a_1 1b_1$	16.95	16.49	16.05	16.859	16.932
	$1a_1 1b_2$	1.53	1.53	1.34	1.535	1.539
	$2a_1 1b_2$	21.28	20.94	20.58	21.225	21.264
	$3a_1 1b_2$	17.78	17.35	17.24	17.725	17.776
	$1b_1 1b_2$	14.60	14.32	13.88	14.524	14.574
Triplet	$1a_1 2a_1$	1.54	1.53	1.41	1.544	1.547
	$1a_1 3a_1$	3.30	3.28	3.05	3.287	3.297
	$2a_1 3a_1$	8.49	8.25	8.28	8.474	8.491
	$1a_1 1b_1$	3.93	3.93	3.63	3.916	3.931
	$2a_1 1b_1$	9.40	9.19	9.12	9.376	9.401
	$3a_1 1b_1$	26.69	26.37	26.33	26.651	26.687
	$1a_1 1b_2$	2.69	2.69	2.50	2.687	2.694
	$2a_1 1b_2$	8.13	8.01	7.97	8.116	8.129
	$3a_1 1b_2$	23.84	23.40	23.57	23.803	23.821
	$1b_1 1b_2$	25.70	25.45	25.38	25.662	25.690
	$E^{(2)}$	362.01	356.43	351.36	361.264	361.954

[a] Structure: $\angle(\text{HOH}) = 104.52°$ and $r(\text{O–H}) = 95.720$ pm. [b] MP2–R12/A from ref. 22. [c] Nonlinearly optimized GTGs from ref. 9. [d] Using basis aug-cc-pCVTZ. [e] Using basis aug-cc-pCVTZ(spdf,sp).

Table 7 All-electron MP2 correlation-energy corrections to the barrier to linearity for the water molecule. Energies are given in mE_h. The water geometries[a] are taken from ref. 34

Basis	VOE	GG0	GG1	GG2
cc-pVDZ	+1.541	+0.397	−0.789	−1.631
cc-pVTZ	+0.014	−0.560	−1.176	−1.500
cc-pCVDZ	+1.666	+0.810	−0.620	−1.077
cc-pCVTZ	+0.028	−0.399	−1.151	−1.423
aug-cc-pVDZ	−0.399	−1.691	−2.245	−2.539
aug-cc-pVTZ	−1.092	−1.628	−2.095	—
aug-cc-pCVDZ	−0.311	−1.319	−2.053	−2.207
aug-cc-pCVDZ + ICP	−0.665	−1.664	−2.053	—
aug-cc-pCVTZ (spdf,sp)	+0.347	−1.611	−2.104	−2.127
aug-cc-pCVTZ	−1.086	−1.475	−2.088	—

[a] Bent molecule: $\angle$(HOH) = 104.343° and r(O–H) = 95.885 pm. Linear molecule: $\angle$(HOH) = 180° and r(O–H) = 93.411 pm.

In combination with an increased spectroscopic capability to detect higher-lying bending states,[25,26] this discovery triggered a renewed interest in the barrier to linearity of the water molecule.[27–34] Even though the barrier is relatively large, about 11 100 cm^{-1}, its accurate determination has become an important issue as it not only affects the prediction of high-lying vibrational bending states, but also low-lying bending states and the rotational states supported by these.[27–31]

The barrier to linearity of water is dominated by a large Hartree–Fock contribution (arising from orbital rehybridization), with a small negative correlation contribution of less than 2%. Moreover, the MP2 model overestimates the correlation correction by about a factor of two, while the CCSD barrier is in good agreement with the CCSD(T) and CCSDT barriers, indicating that the contributions from higher virtual excitations are negligible. For previous work on the barrier to linearity of water, see ref. 3 and 32–34.

The main difficulty in the calculation of the barrier to linearity in water is to establish the basis-set limit of the small correlation correction. In their large K4^{3i} basis, for instance, Valeev et al.[34] obtained an MP2 valence contribution of −325 cm^{-1}, as much as 9% above their extrapolated limit of −357 cm^{-1}. The accurate calculation of the basis-set limit of the correlation correction to this barrier is therefore a stringent test for explicitly correlated methods[33,34] and, in particular, for the MP2–GGn method.

Our calculated MP2–GGn corrections to the barrier to linearity of water are given in Table 7. Whereas the MP2 correction is negative in the basis-set limit, conventional orbital-based MP2 theory is seen to give a positive correction in all calculations without diffuse orbitals. The GG0 model performs slightly better, predicting a negative correction in the triple-zeta basis sets. By contrast, the GG1 and GG2 models give the correct sign in all cases although the magnitude is too small.

Proceeding to the aug-cc-pVXZ and aug-cc-pCVXZ basis sets, we see that conventional MP2 still does not consistently predict a lowering of the barrier even with diffuse functions added. The GG0 model, on the other hand, now correctly predicts a lowering of the barrier in all cases. Also, the different basis sets produce similar barriers. The best GG0 estimate is probably that obtained with an internal counterpoise correction (ICP) in the aug-cc-pCVDZ basis, where nearly 80% of the full barrier correction of −2.1 mE_h is recovered. In the ICP calculations, exactly the same basis is used for both the linear and bent molecules, meaning that we have hydrogen basis functions at both the linear and bent positions for both geometries.

While even the best GG0 barrier is only moderately accurate, the GG1 model performs well in all basis sets. In fact, even in the smallest augmented basis aug-cc-pVDZ, the GG1 energy differs by less than 10% from the estimated basis-set limit. Moreover, application of ICP does not change the GG1 barrier, suggesting that the two-electron basis set is saturated. Finally, the GG2 model does not perform better than the GG1 model in the augmented basis sets. In the largest common basis, the GG1 and GG2 models differ by only 0.02 mE_h. The best barrier estimates are the GG1/aug-cc-pCVTZ estimate of −2.088 mE_h and the GG2/aug-cc-pCVTZ(spdf,sp) estimate of −2.127 mE_h. These two levels of theory also give the lowest total correlation energies at the two water geometries.

In Table 8 we have decomposed these best GG1 and GG2 barrier corrections into core (core–core and core–valence) and valence contributions, and given these energies in cm^{-1} using an energy conversion factor of 1 mE_h = 219.47463 cm^{-1}. While the core contributions are similar, the GG2 valence contribution is lower than the GG1 contribution. From a comparison of the GG0 and GG1 corrections in the aug-cc-pCVTZ and aug-cc-pCVTZ(spdf,sp) basis sets, however, we expect the GG2 contribution to be slightly higher in the larger aug-cc-pCVTZ basis set. From the GG1/aug-cc-pCVTZ and GG2/aug-cc-pCVTZ(spdf,sp) calculations, we estimate that the core and valence correlation corrections to the barrier to linearity of water are −111.0 ± 0.5 cm^{-1} and −352 ± 5 cm^{-1}, respectively, giving a total correlation correction of −463 ± 5 cm^{-1}.

In Table 8 we have also given the best previous literature estimates of the water barrier. These values have been obtained using MP2–R12 theory in the large basis sets K2

Table 8 Core and valence contributions to the MP2 correlation-energy correction (E/cm^{-1}) to the barrier to linearity for the water molecule: a comparison with literature data.[a] Basis sets are specified in the text

Authors	ΔE[core]
This work	
MP2–GG1 with basis aug-cc-pCVTZ	−110.6
MP2–GG2 with basis aug-cc-pCVTZ(spdf,sp)	−110.9
Valeev et al.[34]	
MP2–R12/A with basis K2^{1h}	−110
Tarczay et al.[33]	
MP2–R12/A with basis K2	−109
MP2 with basis K2	−106

	ΔE[valence]
This work	
MP2–GG1 with basis aug-cc-pCVTZ	−347.6
MP2–GG2 with basis aug-cc-pCVTZ(spdf,sp)	−355.8
Valeev et al.[34]	
MP2–R12/A with basis K4^{3i}	−357
MP2 with basis K4^{3i}	−325
CBS limit	−353
Tarczay et al.[33]	
MP2–R12/B with basis K2 + ICP	−344

[a] Bent molecule: $\angle$(HOH) = 104.343° and r(O–H) = 95.885 pm. Linear molecule: $\angle$(HOH) = 180° and r(O–H) = 93.411 pm.

[(15s9p7d5f,9s7p5d)], K2^{1h}[(15s9p7d5f3g1h, 9s7p5d3f1g)], and K4^{3i} [(19s13p11d9f7g5h3i, 13s11p9d7f5g3h)].

For the core correction to the barrier, the MP2–GGn and MP2–R12/A approaches give similar results—indeed, in the K2^{1h} basis the R12/A result differs from ours by only 1 cm^{−1}. Incidentally, in this basis the difference between the MP2 and MP2–R12/A barriers is only 3 cm^{−1}, probably due to an error cancellation between the energies at the bent and linear geometries in the conventional calculations.

For the valence correction to the barrier in water, the different approaches produce quite different results. For instance, Valeev et al.[34] obtained a barrier of only −325 cm^{−1} using conventional MP2 in the large K4^{3i} basis, more than 30 cm^{−1} from their suggested limit. Our best valence results of 348 cm^{−1} (GG1) and 356 cm^{−1} (GG2) are close to the value of 357 cm^{−1} obtained by Valeev et al.[34] in their largest basis set. From a convergence analysis of our results, we believe the true valence MP2 value is −352 ± 5 cm^{−1}, slightly smaller in magnitude than the value of −357 ± 5 cm^{−1} proposed by Valeev et al.[34] The total correlation correction to the barrier to linearity is then −463 ± 5 cm^{−1} or −2.11 ± 0.02 mE_{h}.

V. Conclusions

In this work we have presented MP2–GGn correlation energies for the water molecule, using pair functions of the form shown in eqn (4) optimized using the WO functional eqn (7) as described in ref. 15. Our previous work on atoms and diatomics showed that the GG1 and GG2 models can give correlation energies close to the basis-set limit, even for small GCF expansions.[15] Applying the GG2 model, we then obtained the current best estimates of the MP2 correlation energies of the neon atom (−388.19 mE_{h}), the hydrogen molecule (−34.252 mE_{h}), and the hydrogen fluoride molecule (−384.41 mE_{h}).

In the present paper, we have presented the current best estimate of the all-electron MP2 correlation energy of the water molecule, −361.95 mE_{h}, obtained at the GG2/aug-cc-pCVTZ(spdf,sp) level of theory. The best GG1 and GG0 values are −361.26 and −351.36 mE_{h} respectively, calculated with the aug-cc-pCVTZ basis set. As observed for smaller systems in ref. 15, the GG1 performance is comparable to that of the GG2 model, whereas the performance of the GG0 model is poorer. We note, however, that the performance of the GG0 model is significantly improved by using the intermediate orthogonality (IO) functional in place of the WO functional used in our present implementation.[17]

We have also calculated the MP2 correlation correction to the barrier to linearity of water. Based on our own estimates of this correction and the value given by Valeev,[34] we suggest the value −463 ± 5 cm^{−1} for this correction.

Acknowledgements

References

1 E. A. Hylleraas, Z. Phys., 1928, 48, 469.
2 W. Klopper, M. Schütz, H. P. Lüthi and S. Leutwyler, J. Chem. Phys., 1995, 103, 1085.
3 T. Helgaker, P. Jørgensen and J. Olsen, Molecular Electronic-Structure Theory, John Wiley & Sons, Chichester, 2000.
4 E. A. Hylleraas, Z. Phys., 1929, 54, 347.
5 E. A. Hylleraas, Z. Phys., 1930, 65, 209.
6 K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitzky, Chem. Phys. Lett., 1982, 91, 169.
7 K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitzky, J. Chem. Phys., 1983, 78, 1420.
8 K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski and H. J. Monkhorst, J. Chem. Phys., 1986, 85, 3964.
9 R. Bukowski, B. Jeziorski, S. Rybak and K. Szalewicz, J. Chem. Phys., 1995, 102, 888.
10 W. Kutzelnigg, Theor. Chim. Acta, 1985, 68, 445.
11 W. Klopper and W. Kutzelnigg, Chem. Phys. Lett., 1986, 134, 17.
12 W. Klopper, F. R. Manby, S. Ten-no and E. F. Valeev, Int. Rev. Phys. Chem., 2006, 25, 427.
13 B. J. Persson and P. R. Taylor, J. Chem. Phys., 1996, 105, 5915.
14 P. Dahle, Accurate calculations using explicitly correlated wave functions, PhD thesis, University of Oslo, 2004.
15 P. Dahle, T. Helgaker, D. Jonsson and P. R. Taylor, Phys. Chem. Chem. Phys., 2007, 9, 3112.
16 R. Polly, H.-J. Werner, P. Dahle and P. R. Taylor, J. Chem. Phys., 2006, 124, 1.
17 D. P. Tew, W. Klopper and F. R. Manby, J. Chem. Phys., 2007, 127, 174105.
18 T. H. Dunning, Jr, J. Chem. Phys., 1989, 90, 1007.
19 D. Yamaki, H. Koch and S. Ten-no, J. Chem. Phys., 2007, 127, 144104.
20 W. Klopper, Mol. Phys., 2001, 99, 481.
21 H. Müller, W. Kutzelnigg and J. Noga, Mol. Phys., 1997, 92, 535.
22 W. Klopper, J. Chem. Phys., 1995, 102, 6168.
23 L. Wallace, P. Bernath, W. Livingstone, K. Hinkle, J. Busler, B. Gou and K. Zhang, Science, 1995, 268, 1155.
24 T. Oka, Science, 1997, 277, 328.
25 O. L. Polyansky, N. F. Zobov, J. Tennyson, J. A. Lotoski and P. F. Bernath, J. Mol. Spectrosc., 1997, 184, 35.
26 O. N. Ulenikov and G. A. Ushakova, J. Mol. Spectrosc., 1986, 117, 195.
27 N. F. Zobov, O. L. Polyansky, C. R. Le Sueur and J. Tennyson, Chem. Phys. Lett., 1996, 260, 381.
28 H. Partridge and D. W. Schwenke, J. Chem. Phys., 1997, 106, 4618.
29 A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov and J. Tennyson, Chem. Phys. Lett., 1998, 293, 317.
30 A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov and J. Tennyson, Chem. Phys. Lett., 1999, 312, 613.
31 J. S. Kain, O. L. Polyansky and J. Tennyson, Chem. Phys. Lett., 2000, 317, 365.
32 A. G. Császár, W. D. Allen and H. F. Schaefer III, J. Chem. Phys., 1998, 108, 9751.
33 J. Tarczay, A. G. Császár, W. Klopper, V. Szalay, W. D. Allen and H. F. Schaefer III, J. Chem. Phys., 1999, 110, 11971.
34 E. Valeev, W. D. Allen, H. F. Schaefer III and A. G. Császár, J. Chem. Phys., 2001, 114, 2875.