The second-order Møller–Plesset limit for the barrier to linearity of water

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A series of high-quality conventional and explicitly correlated second-order Møller–Plesset energies, denoted as MP2 and MP2-R12/A, respectively, was computed in a state-of-the-art attempt to arrive at the *ab initio* limit for the barrier to linearity of water. [O/H]-centered Gaussian basis sets as large as $[19s13p11d9f7g5h3i/13s11p9d7f5g3h]$ were employed in the study. We find that basis functions with high orbital angular momentum quantum number (h and i) are important for highly accurate predictions of the electronic energy, even when explicitly correlated approaches are utilized. This observation is at variance with previous claims that explicitly correlated methods require basis sets saturated only to the level of f functions for spectroscopic accuracy. Our best explicitly computed value for the MP2 contribution to the barrier is -357 cm^{-1}. The resulting final *ab initio* estimate for the classical barrier to linearity of water is $11\,119 \pm 15$ cm^{-1}, in good agreement with the most recently obtained empirical value of $11\,105 \pm 5$ cm^{-1}. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1346576]

Based on an efficient algorithm[1] for the evaluation of molecular integrals appearing when explicitly correlated wave functions with linear r_{12} terms are employed, we recently extended the capability of our electronic structure code[2] PSI 3 to calculate second-order Møller–Plesset perturbation energies traditionally designated as MP2-R12/A.[3–6] This work is one of the few successful implementations[7–9] of linear R12 methods for closed-shell molecular systems. A particular feature of our implementation is that it works very well for Gaussian functions with orbital angular momentum numbers beyond those normally used in MP2-R12 computations. Here, we report our first application of the code, the computation of the barrier to linearity of water, with the aim of elucidating the intricacies of new methodologies for reaching *ab initio* limits for molecular systems.

The barrier to linearity of water has recently been investigated in considerable detail,[10–16] due partially to the discovery of water on the sun[17,18] and subsequent interest in the highly excited rovibrational states of water.[19] The height of the barrier has become an important issue, not because it is particularly low (its magnitude is about $11\,100$ cm^{-1}), but because it does affect the variational prediction of even low-lying bending vibrational states and, consequently, the rotational states they support.[12–16] Using the focal-point approach,[10,20] three of us deduced[10] a high-quality *ab initio* estimate of $11\,046 \pm 70$ cm^{-1} for the barrier, while later extensions[11] determined an improved value of $11\,127 \pm 35$ cm^{-1}. In work to reproduce available empirical rovibrational levels supported by the ground electronic state of water, Kain *et al.*[16] modified existing high-quality potential energy hypersurfaces (PESs)[12–15] and arrived at a value of $11\,105 \pm 5$ cm^{-1} for the barrier, which is bracketed by the

previous, well-converged *ab initio* predictions.[10,11] For a compilation of earlier predicted barriers, see Table II of Ref. 19.

Estimation of the complete basis set (CBS) limit at various levels of electronic structure theory is fundamental to the success of the focal-point scheme. Previous *ab initio* investigations[10,11] proved that for the barrier to linearity of water, it is easiest, as usual, to estimate the Hartree–Fock (HF) limit, the well-established HF value being $11\,247$ cm^{-1}, while it is hardest to arrive at the MP2 limit. Corrections beyond MP2 seem to be less dependent on the quality of the basis set; therefore, to arrive at an improved *ab initio* estimate of the barrier it is critical to arrive at the MP2 limit. The chosen estimate of Tarczay *et al.*[11] for the MP2 correlation contribution to the barrier, δ[MP2], at the CBS limit is -348 cm^{-1}, derived from extrapolation of conventional aug-cc-pV{Q,5}Z+intramolecular counterpoise results, whereas even using the aug-cc-pV6Z basis of Dunning (443 functions),[21,22] δ[MP2] is explicitly computed to be only -330 cm^{-1}. Furthermore, the MP2-R12/B numbers reported by Tarczay *et al.*[11] were not definitive in establishing the CBS MP2 limit. In fact, with the basis sets used for the R12 computations (K1 and K2, *vide infra*), it proved to be absolutely necessary to employ an intramolecular counterpoise (ICP) correction to arrive at a balanced description of the approximate resolution of the identity (RI) for the bent and linear reference structures of water. The RI approximation[5] is a simplification necessary in linear R12 theory in order to compute molecular integrals with 3 electrons or more. Tarczay and co-workers[11] observed that ''MP2 calculations are particularly vulnerable to unbalanced RI approximations.''

Here, we extend the theoretical armamentarium previously used for the computation of the barrier to linearity of water[10,11] by computing MP2-R12/A electronic energies for

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TABLE I. Description of primitive Gaussian basis sets used in this study and the corresponding MP2 and MP2-R12/A correlation energies (in E_h) of water.

Basis set	Number of functions	O/H primitives	E_{corr}(MP2)		E_{corr}(MP2-R12/A)	
			C_{2v}	$D_{\infty h}$	C_{2v}	$D_{\infty h}$
K1	186	$13s8p6d5f/7s5p4d$	−0.281 686	−0.282 107	−0.301 264	−0.303 154
K1+ICP	270	$13s8p6d5f/7s5p4d$	−0.284 176	−0.285 325	−0.301 037	−0.302 661
K2	222	$15s9p7d5f/9s7p5d$	−0.282 629	−0.282 828	−0.301 451	−0.303 319
K2+ICP	332	$15s9p7d5f/9s7p5d$	−0.285 058	−0.286 203	−0.301 178	−0.302 788
K2^{1h}	320	$15s9p7d5f3g1h/9s7p5d3f1g$	−0.293 432	−0.294 732	−0.300 650	−0.302 261
K2^{1h}+ICP	490	$15s9p7d5f3g1h/9s7p5d3f1g$	−0.294 347	−0.295 800	−0.300 682	−0.302 303
K3^{3h}	492	$17s11p9d7f5g3h/11s9p7d5f3g$	−0.295 046	−0.296 408	−0.300 589	−0.302 233
K4^{5h}	664	$19s13p11d9f7g5h/13s11p9d7f5g$	−0.295 304	−0.296 664	−0.300 585	−0.302 237
V1^{5h}	673	$21s13p11d10f7g5h/13s11p9d7f5g$	−0.296 036	−0.297 378	−0.300 680	−0.302 340
K3^{1i}	527	$17s11p9d7f5g3h1i/11s9p7d5f3g1h$	−0.296 050	−0.297 462	−0.300 545	−0.302 152
V1^{2i}	721	$21s13p11d10f7g5h2i/13s11p9d7f5g1h$	−0.297 253	−0.298 713	−0.300 623	−0.302 247
K4^{3i}	769	$19s13p11d9f7g5h3i/13s11p9d7f5g3h$	−0.296 929	−0.298 409	−0.300 562	−0.302 189

the two reference structures using basis sets of unprecedented quality. Most notably, the basis sets employed include angular momentum functions not through f, as before, but through i functions. Furthermore, following an earlier formula,[8,23] we report basis-set completeness (BSC) diagnostics for the singlet and triplet pairs (BSC/S and BSC/T, respectively) for each of the basis sets. We have also performed calculations employing the ICP approach. The goals of this study can be summarized as follows: (a) of general interest for calculations with explicitly correlated methods, investigation of the influence of basis functions beyond f on MP2-R12/A energies and, consequently, on the barrier; (b) unequivocal establishment of the valence-only CBS MP2 limit; (c) comparison of traditional MP2 energetics with MP2-R12/A predictions; (d) investigation, through BSC diagnostics, of the correspondence of basis-set incompleteness with deviation from the CBS MP2 limit; and (e) determination of the possible merits or demerits of the ICP correction.

The reference geometries employed for the H_2O calculations were taken from Ref. 10, and they are r(O–H) = 0.958 85(0.934 11) Å and $\angle$(H–O–H)= 104.343° (180°) in the C_{2v} ($D_{\infty h}$) cases. The 12 Gaussian basis sets employed in the present study are described in Table I. The unprecedented size of the basis sets required proper measures

to be taken to ensure numerical validity of the results. The effects of numerical instabilities within the horizontal recurrence relations of Head-Gordon and Pople[24] used in our integrals evaluation procedure were studied by comparing for the K3^{1i} basis set the MP2-R12/A energy of the linear conformer computed with integrals evaluated with 64-bit versus 128-bit precision. We found that both energy values were identical to 15 significant digits. We also found no evidence of numerical instabilities speculated to affect the orbital-invariant version of the MP2-R12/A method when the basis set is almost complete.[25]

Our results, along with the MP2-R12/B predictions for the barrier from Tarczay *et al.*,[11] are summarized in Table II. Disturbing discrepancies between the regular and ICP-corrected MP2-R12/A predictions obtained with the smaller basis sets (K1 and K2) hint at the inadequacy of these sets for the proper description of the barrier. Significantly smaller ICP corrections at the MP2-R12/B level of theory suggest that the K2 results at this level might already be very close to the CBS MP2 limit. However, our computations with basis sets including higher angular momentum Gaussians indicate otherwise. The majority of the MP2-R12/A energy increments was obtained with basis sets explicitly including up to h functions (namely, K2^{1h}, K3^{3h}, K4^{5h}, and V1^{5h}) and do

TABLE II. Basis set convergence of the MP2 contribution to the barrier to linearity of water. The δ[MP2] increments are reported in cm^{-1}. BSC/S and BSC/T denote the dimensionless basis set completeness diagnostics for singlet and triplet pairs, respectively, and are reported for the bent(linear) structure.

Basis set	ΔE_e (RHF)	δ[MP2]	δ[MP2-R12/A]	δ[MP2-R12/B]	BSC/S	BSC/T
K1	11 236	13	−429	−354	0.445(0.442)	0.203(0.202)
K1+ICP	11 239	−252	−356	−340	0.450	0.204
K2	11 241	−44	−410	−336	0.449(0.445)	0.210(0.207)
K2+ICP	11 243	−251	−353	−344	0.454	0.212
K2^{1h}	11 249	−285	−354	⋯	0.482(0.480)	0.229(0.221)
K2^{1h}+ICP	11 249	−319	−356	⋯	0.484(0.483)	0.230(0.229)
K3^{3h}	11 249	−299	−361	⋯	0.486(0.484)	0.238(0.235)
K4^{5h}	11 249	−299	−363	⋯	0.486(0.484)	0.238(0.236)
V1^{5h}	11 248	−296	−373	⋯	0.483(0.481)	0.235(0.233)
K3^{1i}	11 249	−310	−353	⋯	0.490(0.489)	0.241(0.238)
V1^{2i}	11 248	−320	−356	⋯	0.488(0.487)	0.239(0.236)
K4^{3i}	11 248	−325	−357	⋯	0.492(0.491)	0.243(0.241)
CBS	11 247	(−371 −370, −353)^a	−357		0.500	0.250

^{a}These three successive entries are obtained by two-point extrapolations, according to formula (Refs. 11, 32) $E_{CBS}=E_X+aX^{-3}$, of cc-pV{5,6}Z, aug-cc-pV{5,6}Z, and aug-cc-pV{5,6}Z+ICP data, respectively.

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not offer a conclusive limit. The sequence of $\delta[\text{MP2}]$ values computed with the K2^{1h}, K3^{3h}, and K4^{5h} bases, all constructed from the uncontracted cc-pV5Z basis set by appending extra primitive functions,[26,27] does seem to converge smoothly from above to the vicinity of -363 cm^{-1}. As an independent check of the accuracy of the explicitly correlated K4^{5h} MP2 increment, we constructed a basis set of similar quality from Feller and Peterson's pV7Z basis set (V1^{5h}).[28] Disappointingly, the explicitly correlated $\delta[\text{MP2}]$ increment computed with the V1^{5h} basis is 10 cm^{-1} lower than the K4^{5h} MP2-R12/A value. Note, however, that the conventional MP2 contributions computed with the K3^{3h}, K4^{5h}, and V1^{5h} basis sets are in excellent agreement with each other. Combining our (K3^{3h}, K4^{5h}, V1^{5h}) findings with those of Tarczay *et al.*[11] reveals that the conventional non-ICP-corrected MP2 contribution to the barrier computed with Gaussian basis sets nearly saturated to the level of h functions is around -300 cm^{-1}, barely 80% of the apparent one-particle limit! The addition of i functions to the K3^{3h}, K4^{5h}, and V1^{5h} bases drops the conventional MP2 increments by as much as 26 cm^{-1}, with detriment to the mutual agreement of the values. In contrast, and more importantly, the addition of i functions vastly improves the agreement among the explicitly correlated MP2 increments. Specifically, the MP2-R12/A increments computed with the K3^{1i}, K4^{3i}, and V1^{2i} sets are -353, -357, -356 cm^{-1}, in order, within a mere 4 cm^{-1} of each other. These data provide the basis for our final predictions below.

Overall, basis-set convergence of MP2-R12/A contributions to the barrier seems to be erratic due to the dual requirements of the one-particle basis set in an MP2-R12 energy computation. First, the one-particle basis is used to construct an n-particle basis for the expansion of the first-order wave function. The conventional part of the n-particle basis is comprised of doubly substituted Slater determinants which appear in the expansion of the first-order wave function in the MP2 method. The other, explicitly correlated part of the n-particle basis includes the reference determinant multiplied by factors of r_{ij}, and thus serves the purpose of correcting the analytic behavior of the conventional part of the wave function at small r_{ij}. Second, the one-particle basis is also used for evaluating certain many-electron integrals as products of two-electron integrals via an approximate RI. Hence, the accuracy of the MP2-R12 energy computed using present implementations of the method is affected by the suitability of the one-particle basis for diverse uses. Traditionally, accuracy of the MP2-R12 energy is indicated by BSC diagnostics.[8,23] The BSC diagnostics correspond to the mean coefficients of the r_{ij}-dependent terms, and thus should reach 1/2 and 1/4 for singlet and triplet pairs, respectively, as governed by the cusp conditions.[29] Deviation from the ideal values indicates that the r_{ij}-dependent terms provide modulations at large r_{ij} distances in response to inadequacies of the conventional part of the n-particle basis in that region. One could argue that the quality of the conventional part of the n-particle basis is indicated by the absolute MP2 correlation energies. Examination of Tables I and II reveals that addition of basis functions of g type and higher improves both the conventional MP2 energies and the BSC diagnostics

dramatically. However, as the basis sets are successively saturated with higher angular momentum functions, the two measures do not necessarily mirror each other, e.g., the V1^{2i} basis set yields the lowest MP2 energies but its BSC diagnostics are less satisfactory than those of the K3^{1i} and K4^{3i} bases. Also, the ICP correction seems to affect the conventional MP2 energy strongly, but its effect on the BSC diagnostics is very modest. These discrepancies between the two ways of evaluating the quality of a one-particle basis set may be a consequence of the current implementation of the MP2-R12 method and its standard approximations. It is likely that a one-particle basis well suited for use in the resolution of the identity may be less suitable for use in the wave function expansion, and vice versa. To analyze further the basis-set effects on the explicitly correlated energies, one needs to use different basis sets for the RI and for constructing the n-particle space.

In conclusion, the MP2-R12/A computations with our most extended basis sets suggest a CBS MP2 increment to the barrier of -357 ± 5 cm^{-1}. This result is significantly lower than either the ICP-corrected K2 MP2-R12/B value of -344 cm^{-1} or the extrapolated aug-cc-pV{Q,5}Z+ICP value of -348 cm^{-1} obtained by Tarczay *et al.*[11] Note that, out of the three conventional extrapolated CBS limits for the MP2 contribution to the barrier in Table II, our $\delta[\text{MP2-R12/A}]$ increment is closest to the aug-cc-pV{5,6}Z+ICP CBS estimate, -353 cm^{-1}, the value in substantial disagreement with the cc-pV{5,6}Z and aug-cc-pV{5,6}Z estimates of the CBS limit. We use our limiting value for the valence $\delta[\text{MP2}]$ contribution to arrive at a more reliable prediction for the classical barrier as follows. The electronic {HF, $\delta[\text{MP2}]$, $\delta[\text{CCSD(T)}]$} contributions to the limiting barrier are {11247, -357, $+266$} cm^{-1} obtained from the aug-cc-pV{5,6}Z HF extrapolation,[11] our explicit MP2-R12/A computations (Table II), and a CBS extrapolation of the MP2 and CCSD(T) ICP-corrected aug-cc-pV{Q,5}Z data,[11] respectively. Combined with a $+22$ cm^{-1} CCSD(T)$\rightarrow$BD(TQ) correction for connected quadruple excitations,[11] these predictions yield a valence-only classical barrier of 11 178 cm^{-1}. The core correlation correction to the water barrier can be estimated in the spirit of this study as follows: an explicitly computed correction at the K2^{1h} MP2-R12/A level of -110 cm^{-1} is combined with the value of $+12$ cm^{-1} for the MP2$\rightarrow$CCSD(T) core correlation increment extrapolated from cc-pCV{T,Q}Z energies (see Table II in Ref. 11). First-order effects of special relativity account for $+56$ cm^{-1} at the cc-pCVQZ CCSD(T) level (Table III of Ref. 11). Nonadiabatic effects are approximated by the diagonal Born–Oppenheimer correction (DBOC) at the DZP RHF level to be -17 cm^{-1}.[11] Thus, the final estimate for the barrier is $11\,178 - 98 + 56 - 17 = 11\,119 \pm 15$ cm^{-1}, in good agreement with the empirically fitted value of $11\,105 \pm 5$ cm^{-1} from Kain *et al.*[16] Note that relativistic corrections beyond the Dirac–Coulomb approximation, namely the low-frequency Breit correction and the Lamb shift of quantum electrodynamics, do not seem to change the barrier more than a few cm^{-1}.[30,31]

To summarize our findings:

(i)   Basis functions of orbital quantum number $l > 3$ (past f) contribute significantly to the completeness of the basis, as indicated by the BSC diagnostics. Accordingly, h-type and higher functions appear necessary for spectroscopic accuracy descriptions of the MP2 contribution to the barrier, even when explicitly correlated linear R12 methods are employed.

(ii) The most extensive explicit MP2-R12/A computations with basis sets including up to i functions on the oxygen atom suggest the limiting valence-only MP2 correlation contribution to the water barrier to be $-357 \pm 5 \text{ cm}^{-1}$. Thus, our revised value for the vibrationless barrier is $11\,119 \pm 15 \text{ cm}^{-1}$, in good agreement with the latest empirically fitted result[16] of $11\,105 \pm 5 \text{ cm}^{-1}$.

(iii) Explicit conventional MP2 computations with [O/H] basis sets as large as $[19s13p11d9f7g5h3i/13s11p9d7f5g3h]$ (769 Gaussian functions) still fail to recover more than 8% (or 30 cm^{-1}) of the second-order correlation contribution to the barrier to linearity of water. Various extrapolations of conventional (aug)-cc-pV{5,6}Z(+ICP) MP2 data scatter about the inferred CBS limit, and comparison with the best MP2-R12/A predictions reveal extrapolation errors as large as 15 cm^{-1}.

(iv) The basis-set completeness diagnostics[8,23] employed previously in conjunction with linear R12 methods are useful, but not directly correspondent with conventional energy-lowering measures for gauging the accuracy of an MP2 computation near the basis-set limit.

(v)   The intramolecular counterpoise (ICP) correction affects the absolute conventional MP2 energies dramatically, but its effect on the explicitly correlated MP2-R12/A energies evaluated with basis sets including g and h functions is very small. The effect of the ICP correction on the BSC diagnostics is rather insignificant.

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