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

Edward F. Valeev, Wesley D. Allen, and Henry F. Schaefer III

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2525

Attila G. Császár

Department of Theoretical Chemistry, Eötvös University, H-1518 Budapest 112, P.O. Box 32, Hungary

(Received 21 June 2000; accepted 15 December 2000)

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 $-357 \text{ cm}^{-1}$. The resulting final ab initio estimate for the classical barrier to linearity of water is 11 119±15 cm$^{-1}$, in good agreement with the most recently obtained empirical value of 11 105±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$^{16}$ a high-quality ab initio estimate of 11 046±70 cm$^{-1}$ for the barrier, while later extension$^{11}$ determined an improved value of 11 127±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±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, $\delta[\text{MP2}]$, at the CBS limit is $-348 \text{ cm}^{-1}$, 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),$^{21,22}$ $\delta[\text{MP2}]$ is explicitly computed to be only $-330 \text{ cm}^{-1}$.

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...
the two reference structures using basis sets of unprec-
emed quality. Most notably, the basis sets employed in-
clude angular momentum functions not through $f$, as before,
but through $i$ functions. Furthermore, following an earlier
formula, we report basis-set completeness (BSC) diag-
nostics for the singlet and triplet pairs (BSC/S and BSC/T,
respectively) for each of the basis sets. We have also per-
formed 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 di-
agnostics, of the correspondence of basis-set incompleteness
with deviation from the CBS MP2 limit; and (e) determina-
tion of the possible merits or demerits of the ICP correction.

The reference geometries employed for the $\text{H}_2\text{O}$ calcu-
lations were taken from Ref. 10, and they are $r(\text{O}--\text{H}) = 0.958\ \text{Å}$ and $\angle(\text{H}--\text{O}--\text{H}) = 104.34^\circ$
($180^\circ$) in the $C_{2v}$ ($D_{sh}$) cases. The 12 Gaussian basis sets
employed in the present study are described in Table I. The unpre-
cedented 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 recur-
rence relations of Head-Gordon and Pople used in our in-
tegrals evaluation procedure were studied by comparing for the
K3$^{11}$ basis set the MP2-R12/A energy of the linear con-
former 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-
variant version of the MP2-R12/A method when the basis
set is almost complete.

Our results, along with the MP2-R12/B predictions for the
barrier from Tarczay et al., are summarized in Table II. Disturbing
ourselves between the regular and ICP-corrected MP2-R12/A predic-
tions 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 includ-
ing higher angular momentum Gaussians indicate otherwise. The majority of the MP2-R12/A energy incre-
ments was obtained with basis sets explicitly including up to $h$
functions (namely, K$^{2,3,4}$, K$^{2,3,4}$, and V$^{1,2,3,4}$) and do

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Number of functions</th>
<th>O/H primitives</th>
<th>$E_{\text{cont}}$(MP2)</th>
<th>$E_{\text{cont}}$(MP2-R12/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>186</td>
<td>13s8p6d5f7s5p4d</td>
<td>$-0.281\ 686$</td>
<td>$-0.282\ 0177$</td>
</tr>
<tr>
<td>K1+ICP</td>
<td>270</td>
<td>13s8p6d5f7s5p4d</td>
<td>$-0.284\ 174$</td>
<td>$-0.285\ 3527$</td>
</tr>
<tr>
<td>K2</td>
<td>222</td>
<td>15s9p7d5f9s7p5d</td>
<td>$-0.282\ 629$</td>
<td>$-0.282\ 828$</td>
</tr>
<tr>
<td>K2+ICP</td>
<td>332</td>
<td>15s9p7d5f9s7p5d</td>
<td>$-0.285\ 058$</td>
<td>$-0.286\ 203$</td>
</tr>
<tr>
<td>K$^{2,3}$</td>
<td>320</td>
<td>15s9p7d5f3g1h8s7p5d3f1g</td>
<td>$-0.293\ 432$</td>
<td>$-0.294\ 732$</td>
</tr>
<tr>
<td>K$^{2,3}$ + ICP</td>
<td>490</td>
<td>15s9p7d5f3g1h8s7p5d3f1g</td>
<td>$-0.294\ 347$</td>
<td>$-0.295\ 800$</td>
</tr>
<tr>
<td>K3$^{11}$</td>
<td>492</td>
<td>17s11p9d7f5g3h11s11p9d5f3g1h8s7p5d3f1g</td>
<td>$-0.295\ 046$</td>
<td>$-0.296\ 408$</td>
</tr>
<tr>
<td>K$^{4,5}$</td>
<td>664</td>
<td>19s13l1d9f7g5h13s11p9d7f5g8s7p5d3f1g</td>
<td>$-0.295\ 304$</td>
<td>$-0.296\ 664$</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>673</td>
<td>21s13l1d9f7g5h13s11p9d7f5g8s7p5d3f1g</td>
<td>$-0.296\ 036$</td>
<td>$-0.297\ 378$</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>527</td>
<td>17s11p9d7f5g3h11s11p9d5f3g1h</td>
<td>$-0.296\ 050$</td>
<td>$-0.297\ 462$</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>721</td>
<td>21s13l1d9f7g5h13s11p9d7f5g8s7p5d3f1g</td>
<td>$-0.297\ 253$</td>
<td>$-0.298\ 713$</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>769</td>
<td>19s13l1d9f7g5h3i11s11p9d7f5g3h8s7p5d3f1g</td>
<td>$-0.296\ 929$</td>
<td>$-0.298\ 409$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$\Delta E_e$ (RHF)</th>
<th>$\delta$[MP2]</th>
<th>$\delta$[MP2-R12/A]</th>
<th>$\delta$[MP2-R12/B]</th>
<th>BSC/S</th>
<th>BSC/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>11 236</td>
<td>13</td>
<td>$-429$</td>
<td>$-354$</td>
<td>0.445(0.442)</td>
<td>0.203(0.202)</td>
</tr>
<tr>
<td>K1+ICP</td>
<td>11 239</td>
<td>$-252$</td>
<td>$-356$</td>
<td>$-340$</td>
<td>0.450</td>
<td>0.204</td>
</tr>
<tr>
<td>K2</td>
<td>11 241</td>
<td>$-44$</td>
<td>$-410$</td>
<td>$-336$</td>
<td>0.449(0.445)</td>
<td>0.210(0.207)</td>
</tr>
<tr>
<td>K2+ICP</td>
<td>11 243</td>
<td>$-251$</td>
<td>$-353$</td>
<td>$-344$</td>
<td>0.454</td>
<td>0.212</td>
</tr>
<tr>
<td>K$^{2,3}$</td>
<td>11 249</td>
<td>$-285$</td>
<td>$-354$</td>
<td>$...$</td>
<td>0.482(0.480)</td>
<td>0.229(0.221)</td>
</tr>
<tr>
<td>K$^{2,3}$ + ICP</td>
<td>11 249</td>
<td>$-319$</td>
<td>$-356$</td>
<td>$...$</td>
<td>0.484(0.483)</td>
<td>0.230(0.229)</td>
</tr>
<tr>
<td>K$^{3,4}$</td>
<td>11 249</td>
<td>$-299$</td>
<td>$-361$</td>
<td>$...$</td>
<td>0.486(0.484)</td>
<td>0.238(0.235)</td>
</tr>
<tr>
<td>K$^{4,5}$</td>
<td>11 249</td>
<td>$-299$</td>
<td>$-363$</td>
<td>$...$</td>
<td>0.486(0.484)</td>
<td>0.238(0.236)</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>11 248</td>
<td>$-296$</td>
<td>$-373$</td>
<td>$...$</td>
<td>0.483(0.481)</td>
<td>0.235(0.233)</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>11 249</td>
<td>$-310$</td>
<td>$-353$</td>
<td>$...$</td>
<td>0.490(0.489)</td>
<td>0.241(0.238)</td>
</tr>
<tr>
<td>K$^{4,5}$</td>
<td>11 246</td>
<td>$-325$</td>
<td>$-357$</td>
<td>$...$</td>
<td>0.482(0.487)</td>
<td>0.239(0.236)</td>
</tr>
<tr>
<td>V$^{1,2,3}$</td>
<td>11 247</td>
<td>$-371$</td>
<td>$-370$</td>
<td>$-353$</td>
<td>0.500</td>
<td>0.250</td>
</tr>
</tbody>
</table>

These three successive entries are obtained by two-point extrapolations, according to formula (Refs. 11, 32) $E_{\text{CBS}} = E_X + aX^{-3}$, of cc-pV(5,6)Z, aug-cc-
pV(5,6)Z, and aug-cc-pV(5,6)Z+ICP data, respectively.
not offer a conclusive limit. The sequence of $\delta \text{[MP2]}$ values computed with the $K_2$, $K_3$, and $K_4$ bases, all constructed from the uncontracted $cc$-$pV5Z$ basis set by appending extra primitive functions, does seem to converge smoothly from above to the vicinity of $-363 \text{ cm}^{-1}$. As an independent check of the accuracy of the explicitly correlated $K_4$ MP2 increment, we constructed a basis set of similar quality from Feller and Peterson's $pV7Z$ basis set (V1,26,27 Disappointingly, the explicitly correlated $\delta \text{[MP2]}$ increment computed with the V1 basis is $10 \text{ cm}^{-1}$ lower than the $K_4$ $\text{MP2-R12/A}$ value. Note, however, that the conventional $\text{MP2}$ contributions computed with the $K_3$, $K_4$, and V1 bases are in excellent agreement with each other. Combining our ($K_3$, $K_4$, V1) findings with those of Tarczay et al.11 reveals that the conventional non-ICP-corrected $\text{MP2}$ contribution to the barrier computed with Gaussian basis sets nearly saturated to the level of $a$ functions is around $-300 \text{ cm}^{-1}$, barely 80% of the apparent one-particle limit! The addition of $i$ functions to the $K_3$, $K_4$, and V1 bases drops the conventional $\text{MP2}$ increments by as much as $26 \text{ cm}^{-1}$, 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 $\text{MP2}$ increments. Specifically, the $\text{MP2-R12/A}$ increments computed with the $K_3$, $K_4$, and V1 bases are $-353$, $-357$, $-356 \text{ cm}^{-1}$, in order, within a mere $4 \text{ cm}^{-1}$ of each other. These data provide the basis for our final predictions below.

Overall, basis-set convergence of $\text{MP2-R12/A}$ contributions to the barrier seems to be erratic due to the dual requirements of the one-particle basis set in an $\text{MP2-R12}$ 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 $\text{MP2}$ 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 $\text{MP2-R12}$ 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 $\text{MP2-R12}$ energy is indicated by BSC diagnostics.25 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 $\text{MP2}$ correlation energies. Examination of Tables I and II reveals that addition of basis functions of $g$ type and higher improves both the conventional $\text{MP2}$ 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 $\text{basis set}$ yields the lowest $\text{MP2}$ energies but its BSC diagnostics are less satisfactory than those of the $K_3$ and $K_4$ bases. Also, the ICP correction seems to affect the conventional $\text{MP2}$ 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 $\text{MP2-R12}$ 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 $\text{MP2-R12/A}$ computations with our most extended basis sets suggest a CBS $\text{MP2}$ increment to the barrier of $-357\pm5 \text{ cm}^{-1}$. This result is significantly lower than either the ICP-corrected $K_2$ $\text{MP2-R12/B}$ value of $-344 \text{ cm}^{-1}$ or the extrapolated aug-$cc$-$pV(Q5)Z$ $\text{ICP}$ value of $-348 \text{ cm}^{-1}$ obtained by Tarczay et al.11 Note that, out of the three conventional extrapolated CBS limits for the $\text{MP2}$ 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, $-353 \text{ cm}^{-1}$, the value in substantial disagreement with the aug-$cc$-$pV(5,6)Z$ 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 $\{11247, -357, +266\} \text{ cm}^{-1}$ obtained from the aug-$cc$-$pV(5,6)Z$ HF extrapolation,11 our explicit $\text{MP2-R12/A}$ computations (Table II), and a CBS extrapolation of the MP2 and CCSD(T) ICP-corrected aug-$cc$-$pV(Q5)Z$ data,11 respectively. Combined with a $+22 \text{ cm}^{-1}$ CCSD(T)→BD(TQ) correction for connected quadruple excitations,11 these predictions yield a valence-only classical barrier of $11178 \text{ cm}^{-1}$. 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 $K_2$ $\text{MP2-R12/A}$ level of $-110 \text{ cm}^{-1}$ is combined with the value of $+12 \text{ cm}^{-1}$ for the $\text{MP2}→\text{CCSD(T)}$ 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 $+56 \text{ cm}^{-1}$ at the cc-pCVQZ CCSD(T) level (Table III of Ref. 11). Nondiabatic effects are approximated by the diagonal Born–Oppenheimer correction (DBOC) at the DZP RHF level to be $-17 \text{ cm}^{-1}$.11 Thus, the final estimate for the barrier is $11178-98+56-17=11195+15 \text{ cm}^{-1}$, in good agreement with the empirically fitted value of $11105\pm5 \text{ cm}^{-1}$ 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 \( -57 \pm 5 \text{ cm}^{-1} \). Thus, our revised value for the vibrationless barrier is \( 11.19 \pm 1 \text{ cm}^{-1} \), in good agreement with the latest empirically fitted result\(^{16} \) of \( 11.105 \pm 5 \text{ cm}^{-1} \).

(iii) Explicit conventional MP2 computations with \([\text{O/H}]\) basis sets as large as \([19s13p11d9f7g5h3i/13s11p9d7f5g3h3] \) (769 Gaussian functions) still fail to recover more than \( 8\% \) (or 30 \text{ cm}^{-1}) of the second-order correlation contribution to the barrier to linearity of water. Various extrapolations of conventional (aug)-cc-pV\( (5,6)Z + \text{ICP} \) MP2 data scatter about the inferred CBS limit, and comparison with the best MP2-R12/A predictions reveal extrapolation errors as large as 15 \text{ 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.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant No. DE-FG02-00ER14748. A.G.C. was supported in part by a NATO Linkage Grant No. CRG.LG 973 892. E.F.V. is a John C. Slater Graduate Fellow.

7W. Klopper, SORE program.
9J. Noga and W. Klopper, DRCR12 program.
25The K\(^3\) and K\(^4\) basis sets were obtained by augmenting the K\(^2\) basis with equal numbers of evenly tempered tight and diffuse primitive functions parametrized by the ratios of exponents of the two tightest and two most diffuse primitive Gaussians, respectively. The K\(^3\) basis set was obtained by appending the primitive \([1i1i1a]\) manifolds of the cc-pV6Z basis to the K\(^3\) set. The K\(^4\) set is the K\(^4\) basis set augmented by primitive manifolds on O and H with exponents \( \alpha_0(i)=5.101,2.03,0.9 \) and \( \alpha_0(O)=(4.953,2.253,1.02) \), respectively. These basis sets are available from the authors upon request.
26The V\(^1\) basis for O is the uncontracted version of the pV7Z basis set from D. Feller and K. A. Peterson, J. Chem. Phys. 110, 8384 (1999) augmented by tight and diffuse primitive functions with the following exponents: \( \alpha_0(i)=11.211,0.077,0.0644,0.0287 \), \( \alpha_0(O)=(5.696,0) \), \( \alpha_0(O)=(100,0,43.38,20.89,0.125,0.06) \), \( \alpha_0(O)=(100,0,40.0,17.0,0.205,0.08) \), \( \alpha_0(i)=(325,15.34,0.2) \), \( \alpha_0(O)=(127.1,0.524) \). The V\(^1\) basis for O is obtained by appending the primitive \( i \) functions from the pV7Z basis to the V\(^1\) set. The V\(^2\) basis for H is the uncontracted cc-pV6Z basis augmented by additional tight and diffuse functions parametrized by the ratios of exponents of the two tightest and two most diffuse functions in each angular momentum shell. Sets of functions with the following exponents were appended: \( \alpha_0(H)=(12.428,0.028,0.0126) \), \( \alpha_0(H)=(349.7,138.7,54.99,21.81,0.085,0.0337) \), \( \alpha_0(O)=(53.59,23.30,0.13,0.166,0.0729) \), \( \alpha_0(H)=(21.74,9.44,0.336,0.146) \), and \( \alpha_0(H)=(18.63,77.20,0.55) \). Further addition of the \( h \) function from the cc-pV6Z basis produces the V\(^1\) basis set for H. These basis sets are available from the authors upon request.