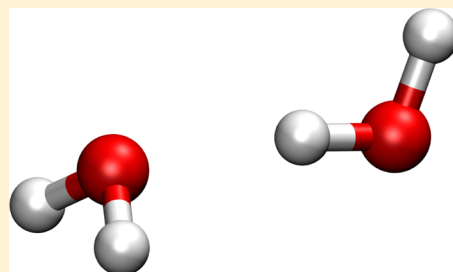


## CCSDTQ Optimized Geometry of Water Dimer

Joseph R. Lane<sup>\*,†</sup><sup>†</sup>Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

**ABSTRACT:** The equilibrium geometry of the lowest energy structure of water dimer  $[(\text{H}_2\text{O})_2]$  has been investigated using coupled cluster theory. A hierarchy of conventional coupled cluster methods is utilized up to singles doubles triples and quadruples excitations (CCSDTQ). The geometry of  $(\text{H}_2\text{O})_2$  is also optimized using the explicitly correlated coupled cluster singles doubles and perturbative triples [CCSD(T)-F12b] method. Overall, we find that the effect of including excitations beyond CCSD(T) is smaller than inclusion of core–valence correlation and comparable to scalar-relativistic and adiabatic effects.



## ■ INTRODUCTION

The coupled cluster singles doubles and perturbative triples [CCSD(T)] method has emerged as the so-called “gold standard” of modern electronic structure theory and is widely used for the accurate description of hydrogen bonding and other weak intermolecular interactions. In the past few years, significant progress has been made in the development of explicitly correlated CCSD(T)-F12 methods, which include a small number of terms at the CCSD level of theory that depend explicitly on the interelectronic distance  $r_{12}$ .<sup>1–6</sup> This greatly accelerates the otherwise painfully slow convergence of electron correlation energy with increasing basis set size, enabling larger systems to be investigated at or close to the CCSD(T) complete basis set (CBS) limit. See for example, refs 7–10. The one-electron error in these explicitly correlated calculations is comparatively small and hence approaches the inherent accuracy of the  $N$ -electron error.

With exception of the noble gas dimers, there have been only a few studies of weakly bound complexes beyond the CCSD(T) method. Pittner and Hobza considered how the interaction energies of the formamide  $[(\text{CHONH}_2)_2]$ , formamidine  $[(\text{CHOHNH}_2)_2]$ , ethylene  $[(\text{C}_2\text{H}_2)_2]$ , and formaldehyde  $[(\text{CH}_2\text{O})_2]$  dimers differ with the CCSD(T) and CCSDT methods.<sup>11</sup> Hopkins and Tschumper investigated differences in the CCSD(T) and CCSD(TQ) interaction energies for the helium nitrogen ( $\text{He}-\text{N}_2$ ) and argon acetylene ( $\text{Ar}-\text{C}_2\text{H}_2$ ) complexes and the nitrogen  $[(\text{N}_2)_2]$  and ethylene  $[(\text{C}_2\text{H}_2)_2]$  dimers.<sup>12</sup> Most recently, Pitonak et al. compared the CCSD(T) and CCSD(TQ) interaction energies of various benzene dimer  $[(\text{C}_6\text{H}_6)_2]$  structures.<sup>13</sup> To our knowledge there have been no geometry optimizations for weakly bound complexes beyond CCSD(T).

The objective of this investigation is to ascertain the importance of higher order excitations beyond CCSD(T) for describing hydrogen bonding interactions. Our target system is water dimer  $[(\text{H}_2\text{O})_2]$ , which has been the subject of numerous theoretical investigations. See for example, refs 14–19 and references within. This prototypical weakly bound complex is small enough to permit geometry optimization including full

quadruple excitations (CCSDTQ) and is important both in terms of its fundamental physical properties and for its role in applications such as atmospheric chemistry. Our work extends on earlier benchmarking studies with regard to the geometry and interaction energy of  $(\text{H}_2\text{O})_2$  by Halkier et al.,<sup>20</sup> Klopper et al.,<sup>15</sup> Tschumper et al.,<sup>16</sup> and Salmi et al.<sup>18</sup> It also extends on previous investigations for  $\text{H}_2\text{O}$  by Cortez et al. and Feller and Peterson within the twin hierarchy of coupled cluster methods and correlation consistent basis sets.<sup>21,22</sup>

We begin this investigation by first optimizing the geometry of  $(\text{H}_2\text{O})_2$  at the frozen core CCSD(T)-F12b/CBS limit. We then consider how inclusion of higher order excitations up to CCSDTQ affects the optimized geometry and interaction energy of  $(\text{H}_2\text{O})_2$ . We then put the importance of these higher order excitations into context by considering the effect of core–valence correlation, scalar-relativistic effects, and adiabatic effects. Where possible, we have tried to calculate the magnitude of each effect with more than one basis set or basis set combination to check for convergence.

## ■ THEORETICAL DETAILS

We have optimized the geometry of  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$  at the complete basis set (CBS) limit with the explicitly correlated coupled cluster singles doubles and perturbative triples [CCSD(T)-F12b] method as implemented in MOLPRO 2010.1.<sup>7,23</sup> Two different CBS extrapolation schemes are investigated, namely an inverse power-law as first proposed by Helgaker and co-workers<sup>24</sup>

$$E_{\text{CBS}}^{\text{corr}} = \frac{X^{\text{pow}} E_X^{\text{corr}} - Y^{\text{pow}} E_Y^{\text{corr}}}{X^{\text{pow}} - Y^{\text{pow}}} \quad (1)$$

and a more generalized two-point scheme as first proposed by Schwenke<sup>25</sup>

$$E_{\text{CBS}}^{\text{corr}} = (E_Y^{\text{corr}} - E_X^{\text{corr}}) F_{XY}^{\text{corr}} + E_X^{\text{corr}} \quad (2)$$

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where  $X$  is the cardinal number of the smaller basis set,  $Y$  is the cardinal number of the larger basis set, and  $E_X^{corr}$  and  $E_Y^{corr}$  are the corresponding correlation energies. For both schemes, we separately extrapolate the CCSD-F12b and (T) contributions to the correlation energy and add this to the reference Hartree–Fock (HF) energy. We use the optimized extrapolation coefficients from Tables X and XI of Hill et al.<sup>26</sup> We have written custom geometry optimization routines in MOLPRO 2010.1 that implement these two CBS extrapolation schemes. For  $(\text{H}_2\text{O})_2$ , we first correct the energies for basis set superposition error (BSSE) before inclusion in the CBS extrapolation schemes using the counterpoise correction

$$E_{(\text{H}_2\text{O})_2}^{CP} = E_{(\text{H}_2\text{O})_2}^{AD} - E_{(\text{H}_2\text{O})_a}^{AD} - E_{(\text{H}_2\text{O})_d}^{AD} + E_{(\text{H}_2\text{O})_a}^A + E_{(\text{H}_2\text{O})_d}^D \quad (3)$$

where the subscripts  $a$  and  $d$  denote the acceptor and donor  $\text{H}_2\text{O}$  molecules of  $(\text{H}_2\text{O})_2$ , and the superscripts  $A$ ,  $D$ , and  $AD$  denote that the energy was evaluated using the basis set of the acceptor molecule, donor molecule, or complex, respectively. The geometries of a few hydrogen bonded complexes, including  $(\text{H}_2\text{O})_2$ , have been recently optimized using a similar counterpoise corrected CBS extrapolated scheme at the MP2 level of theory.<sup>27</sup>

Density fitting approximations<sup>28,29</sup> and the resolution of the identity (RI) approximation were utilized in all explicitly correlated calculations with the default auxiliary basis sets.<sup>30–33</sup> The default CABS singles correction was applied,<sup>7</sup> which substantially improves the accuracy of the Hartree–Fock contributions particularly with smaller orbital basis sets.<sup>34</sup> The diagonal, fixed amplitude  $3\text{C}(\text{FIX})$  ansatz was used, which is orbital invariant, size consistent, and free of geminal basis set superposition error.<sup>3,39,35–39</sup> The values of the geminal Slater exponent  $\beta$  were 1.0 and 1.1 for the cc-pVTZ-F12 and cc-pVQZ-F12 orbital basis sets<sup>26,40</sup> and 1.4 for the aug-cc-pVQZ and aug-cc-pVSZ basis sets.<sup>26,41,42</sup>

To assess the importance of higher order excitations, we have optimized geometries of  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$  with a hierarchy of coupled cluster methods up to full quadruple excitations [CCSD, CCSD(T), CCSDT, CCSDT(Q), and CCSDTQ]. We utilize the MOLPRO interface to MRCC<sup>43</sup> and do not include counterpoise correction for these optimizations as the computational time required is prohibitive. Furthermore it has been previously shown that for  $(\text{H}_2\text{O})_2$ , counterpoise corrected optimized geometric parameters and interaction energies obtained with the CCSD(T) method and the aug-cc-pVDZ and aug-cc-pVTZ basis sets are actually in poorer agreement with the CCSD(T)/CBS limit than the non-counterpoise corrected results.<sup>19</sup> To reduce the computational cost, we use the partially augmented so-called “calendar” correlational consistent basis sets of Papajak and Truhlar.<sup>44</sup> For  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$ , the jul-cc-pVDZ and jul-cc-pVTZ basis sets correspond to the aug-cc-pVXZ basis sets for the oxygen atoms and the cc-pVXZ basis sets for the hydrogen atoms. For  $(\text{H}_2\text{O})_2$  at the CCSD(T) level of theory, these jul-cc-pVXZ basis sets have been previously shown to reduce the magnitude of basis set superposition error and improve convergence with respect to the CCSD(T)/CBS limit, as compared to results obtained with the full aug-cc-pVXZ basis sets.<sup>19</sup> The jun-cc-pVDZ and may-cc-pVTZ basis sets are slightly smaller again and exclude the  $d$  diffuse functions of the oxygen atoms as compared to the jul-cc-pVDZ and jul-cc-pVTZ basis sets, respectively.

Unless specified, all coupled cluster calculations utilize the frozen core approximation for the oxygen 1s electrons. To

assess the impact of freezing the core electrons, we have optimized the geometries of  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$  with all electrons correlated using the CCSD(T)-F12b method and the cc-pCVQZ-F12 orbital basis set with a geminal Slater exponent  $\beta$  of 1.5.<sup>45</sup> For comparison, we have also optimized these geometries with all electron conventional CCSD(T) and the aug-cc-pCVSZ basis set.

To assess the importance of scalar-relativistic effects, we have optimized geometries of  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$  with and without a fourth order Douglas-Kroll-Hess (DKH) Hamiltonian using the all electron conventional CCSD(T) method. For these calculations, we utilize the aug-cc-pCVSZ, aug-cc-pwCVSZ, and aug-cc-pCVSZ-DK basis sets.<sup>46–48</sup>

Very tight convergence criteria were used in all calculations to ensure that results are numerically stable to at least the number of significant figures shown. The optimization criteria for all MOLPRO calculations were set to the following: gradient =  $1 \times 10^{-6}$  a.u., stepsize =  $1 \times 10^{-6}$  a.u., energy =  $1 \times 10^{-8}$  a.u. with all single point energies converged to  $1 \times 10^{-9}$  a.u.

The geometries of  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$  were also optimized with and without a diagonal Born–Oppenheimer correction (DBOC) as implemented in CFOUR.<sup>49</sup> For these calculations the frozen core CCSD/aug-cc-pVTZ and all electron CCSD/aug-cc-pCVTZ methods were used. The CFOUR optimization and single point convergence threshold criteria were set to the following: GEO\_CONV =  $1 \times 10^{-9}$  a.u., SCF\_CONV =  $1 \times 10^{-9}$  a.u., CC\_CONV =  $1 \times 10^{-9}$  a.u., LINEQ\_CONV =  $1 \times 10^{-9}$  a.u.

## RESULTS AND DISCUSSION

In Figure 1 we show the lowest energy structure of  $(\text{H}_2\text{O})_2$  with labels to indicate the corresponding intramolecular and

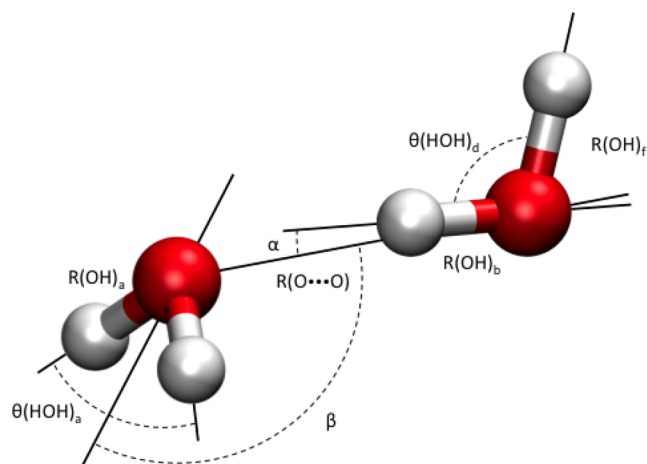


Figure 1. The equilibrium structure of  $(\text{H}_2\text{O})_2$ .

intermolecular geometric parameters that will be discussed in this investigation.

**CCSD(T)-F12b/CBS Limit.** In Table 1 we present optimized geometric parameters and the interaction energy for  $(\text{H}_2\text{O})_2$  obtained with a counterpoise corrected CCSD(T)-F12b/CBS limit optimization scheme. These results have been obtained using two different extrapolation schemes and with two different basis set pairs to investigate the sensitivity of the CBS extrapolation. We find that the Schwenke and Power extrapolation schemes yield essentially identical results for a

**Table 1.** Counterpoise Corrected Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in kJ mol<sup>-1</sup>) at the Frozen Core CCSD(T)-F12b/CBS Limit

|                                     | cc-pVTZ-F12/cc-pVQZ-F12 |               | aug-cc-pVQZ/aug-cc-pV5Z |               |
|-------------------------------------|-------------------------|---------------|-------------------------|---------------|
|                                     | Schwenke                | Power         | Schwenke                | Power         |
| R(OH) <sub>f</sub>                  | 0.95748                 | 0.95748       | 0.95744                 | 0.95744       |
| R(OH) <sub>b</sub>                  | 0.96469                 | 0.96469       | 0.96464                 | 0.96464       |
| R(OH) <sub>a</sub>                  | 0.95907                 | 0.95907       | 0.95902                 | 0.95902       |
| θ(HOH) <sub>d</sub>                 | 104.803                 | 104.803       | 104.801                 | 104.802       |
| θ(HOH) <sub>a</sub>                 | 104.890                 | 104.890       | 104.892                 | 104.891       |
| R(O...O)                            | 2.91228                 | 2.91228       | 2.91278                 | 2.91278       |
| α                                   | 5.720                   | 5.720         | 5.703                   | 5.704         |
| β                                   | 123.256                 | 123.256       | 123.379                 | 123.377       |
| E[(H <sub>2</sub> O) <sub>2</sub> ] | -152.75888362           | -152.75888360 | -152.75810567           | -152.75810491 |
| E[H <sub>2</sub> O]                 | -76.37546879            | -76.37546878  | -76.37508166            | -76.37508128  |
| D <sub>e</sub> <sup>a</sup>         | 20.862                  | 20.862        | 20.853                  | 20.853        |

$$^a(2 \times E[\text{H}_2\text{O}] - E[(\text{H}_2\text{O})_2]) \times 2625.5 \text{ kJ mol}^{-1}.$$

**Table 2.** Optimized Geometric Parameters (in Å and degrees) of H<sub>2</sub>O Obtained with the HF and CCSD-CCSDTQ Methods

|                  | jun-cc-pVDZ |         | may-cc-pVTZ |         | apr-cc-pVQZ |         |
|------------------|-------------|---------|-------------|---------|-------------|---------|
|                  | R(OH)       | θ(HOH)  | R(OH)       | θ(HOH)  | R(OH)       | θ(HOH)  |
| HF               | 0.94605     | 105.389 | 0.94092     | 106.271 | 0.93974     | 106.323 |
| CCSD             | 0.96563     | 103.049 | 0.95793     | 104.221 | 0.95567     | 104.534 |
| CCSD(T)          | 0.96727     | 102.800 | 0.96039     | 103.921 | 0.95837     | 104.259 |
| CCSDT            | 0.96735     | 102.799 | 0.96035     | 103.930 | 0.95833     | 104.268 |
| CCSDT(Q)         | 0.96775     | 102.770 | 0.96071     | 103.893 | 0.95869     | 104.230 |
| CCSDTQ           | 0.96769     | 102.776 | 0.96065     | 103.898 | 0.95864     | 104.235 |
| CCSDT-CCSD(T)    | 0.00008     | 0.000   | -0.00004    | 0.009   | -0.00004    | 0.009   |
| CCSDT(Q)-CCSD(T) | 0.00048     | -0.029  | 0.00032     | -0.028  | 0.00032     | -0.029  |
| CCSDTQ-CCSDT(Q)  | -0.00006    | 0.006   | -0.00005    | 0.005   | -0.00005    | 0.005   |

given basis set pair. This is in part expected, as the extrapolation coefficients for the two schemes were determined from the same training set of individual molecules,<sup>26</sup> but it is nevertheless reassuring that the coefficients are also applicable for a hydrogen bonded complex like (H<sub>2</sub>O)<sub>2</sub>. It also indicates that our convergence criteria are sufficiently tight to obtain numerically stable results. We find that the extrapolated results obtained with the cc-pVTZ-F12/cc-pVQZ-F12 and aug-cc-pVQZ/aug-cc-pV5Z basis set pairs are in excellent agreement with each other, with small but non-negligible differences. These differences are approximately an order of magnitude larger for the intermolecular parameters [R(O...O), α and β] than the intramolecular parameters [R(OH)<sub>f</sub>, R(OH)<sub>b</sub>, R(OH)<sub>a</sub>, θ(HOH)<sub>d</sub>, and θ(HOH)<sub>a</sub>]. We find that the cc-pVTZ-F12/cc-pVQZ-F12 interaction energy (ΔE) is approximately 0.01 kJ mol<sup>-1</sup> larger than the aug-cc-pVQZ/aug-cc-pV5Z result, and consequently the cc-pVTZ-F12/cc-pVQZ-F12 intermolecular distance is also 0.0005 Å shorter. The present frozen-core CCSD(T)-F12b/CBS optimized intermolecular distances are in good agreement with earlier frozen-core CCSD(T)/CBS estimates that were obtained with geometric constraints of 2.915<sup>15</sup> and 2.9125 Å.<sup>19</sup> The corresponding frozen-core CCSD(T)-F12b/CBS optimized interaction energies are also in good agreement with previous frozen-core CCSD(T)/CBS values of 21,<sup>20</sup> 20.83,<sup>15</sup> 20.84,<sup>16</sup> and 20.85 kJ mol<sup>-1</sup>.<sup>50</sup>

It is not clear whether extrapolation of results obtained with the cc-pVTZ-F12/cc-pVQZ-F12 or aug-cc-pVQZ/aug-cc-pV5Z basis set pair necessarily gives more accurate results. While the basis sets of the latter pair obviously have functions of higher angular momentum, the basis sets of the former pair are specifically optimized for explicitly correlated methods. Hill et

al. have previously shown that CCSD(T)-F12b correlation energies extrapolated to the CBS limit using the aug-cc-pVQZ/aug-cc-pV5Z basis sets yield statistical errors (with respect to the reference correlation energies) that are slightly smaller than the corresponding cc-pVTZ-F12/cc-pVQZ-F12 extrapolated results.<sup>26</sup> Nonetheless, it is important to note that the differences between our cc-pVTZ-F12/cc-pVQZ-F12 and aug-cc-pVQZ/aug-cc-pV5Z extrapolated results are comparable to the magnitude of some of the other corrections considered in the subsequent sections.

**Higher Order Excitations.** With our present computational resources, jun-cc-pVDZ is the largest practicable basis set that can be used with the CCSDTQ method to optimize the geometry of (H<sub>2</sub>O)<sub>2</sub>. The lower computational cost of the CCSDT(Q) method permits optimization of (H<sub>2</sub>O)<sub>2</sub> with the may-cc-pVTZ basis set. These two basis sets are relatively small and will obviously give results that are in an absolute sense far from the CBS limit. However, the difference between the CCSD(T) optimized geometry and CCSDT, CCSDT(Q), and CCSDTQ optimized geometries obtained with a given basis set is expected to be better converged.<sup>22</sup> To investigate this, in Table 2 we present the optimized geometric parameters of H<sub>2</sub>O obtained with the HF and CCSD-CCSDTQ methods using the jun-cc-pVDZ, may-cc-pVTZ, and apr-cc-pVQZ basis sets. The convergence of our optimized geometric parameters for H<sub>2</sub>O with the coupled cluster method is consistent with previous investigations using analytical gradients by Cortez et al. and using numerical gradients by Feller and Peterson.<sup>21,22</sup> In general, we find that R(OH) increases and θ(HOH) decreases as higher orders of excitation are included, although the convergence is not monotonic. This small oscillation is

**Table 3. Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in kJ mol<sup>-1</sup>) Obtained with the jun-cc-pVDZ Basis Set**

|                             | HF            | CCSD          | CCSD(T)       | CCSDT         | CCSDT(Q)      | CCSDTQ        | $\Delta Q^a$ |
|-----------------------------|---------------|---------------|---------------|---------------|---------------|---------------|--------------|
| R(OH) <sub>f</sub>          | 0.94536       | 0.96488       | 0.96656       | 0.96664       | 0.96704       | 0.96698       | -0.00006     |
| R(OH) <sub>b</sub>          | 0.95031       | 0.97006       | 0.97210       | 0.97216       | 0.97262       | 0.97255       | -0.00007     |
| R(OH) <sub>a</sub>          | 0.94686       | 0.96635       | 0.96806       | 0.96813       | 0.96853       | 0.96847       | -0.00006     |
| $\theta$ (HOH) <sub>d</sub> | 105.266       | 103.069       | 102.840       | 102.844       | 102.813       | 102.819       | 0.006        |
| $\theta$ (HOH) <sub>a</sub> | 105.733       | 103.588       | 103.363       | 103.363       | 103.336       | 103.341       | 0.005        |
| R(O...O)                    | 3.02816       | 2.97402       | 2.95779       | 2.95811       | 2.95796       | 2.95801       | 0.00005      |
| $\alpha$                    | 0.497         | 1.158         | 1.325         | 1.332         | 1.337         | 1.339         | 0.001        |
| $\beta$                     | 144.151       | 138.737       | 137.714       | 137.738       | 137.639       | 137.656       | 0.017        |
| $E[(H_2O)_2]$               | -152.08265700 | -152.51587900 | -152.52376417 | -152.52414515 | -152.52523825 | -152.52514172 | 0.0009653    |
| $E[H_2O]$                   | -76.03777894  | -76.25378232  | -76.25755996  | -76.25775123  | -76.25829015  | -76.25824340  | 0.00004675   |
| $D_e^b$                     | 18.639        | 21.829        | 22.695        | 22.691        | 22.731        | 22.723        | -0.008       |

<sup>a</sup>CCSDTQ-CCSDT(Q). <sup>b</sup>(2 ×  $E[H_2O]$  -  $E[(H_2O)_2]$ ) × 2625.5 kJ mol<sup>-1</sup>.

**Table 4. Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in kJ mol<sup>-1</sup>) Obtained with the may-cc-pVTZ Basis Set**

|                             | HF            | CCSD          | CCSD(T)       | CCSDT         | CCSDT(Q)      | $\Delta(Q)^a$ |
|-----------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| R(OH) <sub>f</sub>          | 0.94016       | 0.95707       | 0.95956       | 0.95952       | 0.95988       | 0.00032       |
| R(OH) <sub>b</sub>          | 0.94489       | 0.96314       | 0.96625       | 0.96618       | 0.96660       | 0.00035       |
| R(OH) <sub>a</sub>          | 0.94150       | 0.95858       | 0.96111       | 0.96105       | 0.96141       | 0.00031       |
| $\theta$ (HOH) <sub>d</sub> | 106.263       | 104.435       | 104.166       | 104.177       | 104.139       | -0.028        |
| $\theta$ (HOH) <sub>a</sub> | 106.569       | 104.730       | 104.476       | 104.485       | 104.450       | -0.026        |
| R(O...O)                    | 3.04271       | 2.94263       | 2.92295       | 2.92372       | 2.92304       | 0.00008       |
| $\alpha$                    | 2.671         | 3.958         | 4.088         | 4.082         | 4.093         | 0.005         |
| $\beta$                     | 137.652       | 129.679       | 128.272       | 128.311       | 128.130       | -0.142        |
| $E[(H_2O)_2]$               | -152.12762743 | -152.66565378 | -152.68206496 | -152.68220489 | -152.68299020 | -0.00092524   |
| $E[H_2O]$                   | -76.06074535  | -76.32900045  | -76.33700993  | -76.33708468  | -76.33746459  | -0.00045466   |
| $D_e^b$                     | 16.112        | 20.093        | 21.122        | 21.097        | 21.164        | 0.042         |

<sup>a</sup>CCSDT(Q)-CCSD(T). <sup>b</sup>(2 ×  $E[H_2O]$  -  $E[(H_2O)_2]$ ) × 2625.5 kJ mol<sup>-1</sup>.

primarily due to the overestimated magnitude of perturbative triples [CCSD(T)] and perturbative quadruples [CCSDT(Q)] excitations, with respect to the full CCSDT and CCSDTQ methods, respectively. Nonetheless, the very close agreement between the CCSD(T) and CCSDT results and between the CCSDT(Q) and CCSDTQ results demonstrates that perturbative treatment of excitations is a very effective way to reduce computational time with minimal loss of accuracy.<sup>21</sup>

We find that the difference between the optimized geometric parameters of H<sub>2</sub>O obtained with the CCSDT(Q) and CCSD(T) methods is well converged using the may-cc-pVTZ basis set and is in good agreement with the more computationally demanding apr-cc-pVQZ results. The smaller jun-cc-pVDZ basis set overestimates the difference between the CCSDT(Q) and CCSD(T) methods, particularly for R(OH). We find that the difference between the CCSDTQ and CCSDT(Q) optimized geometric parameters converges even more rapidly, with results obtained using the jun-cc-pVDZ basis set in good agreement with the larger may-cc-pVTZ and apr-cc-pVQZ basis sets. In summary, our results for H<sub>2</sub>O suggest that the may-cc-pVTZ basis set is adequate to describe the geometric effects of including perturbative quadruple excitations and the jun-cc-pVDZ basis set is adequate for estimating the geometric effects of including full quadruple excitations.

In Table 3 and Table 4 we present optimized geometric parameters and the interaction energy for (H<sub>2</sub>O)<sub>2</sub> obtained using a hierarchy of coupled cluster methods. In Table 3 results are presented for the HF and CCSD-CCSDTQ methods with the jun-cc-pVDZ basis set, and in Table 4 results are presented

for the HF and CCSD-CCSDT(Q) methods with the may-cc-pVTZ basis set. Consistent with the H<sub>2</sub>O results in Table 2, we find that the optimized geometric parameters and interaction energy for (H<sub>2</sub>O)<sub>2</sub> converge (although not monotonically) as higher orders of excitations are included from CCSD to CCSDTQ. The overall convergence of our geometric parameters for (H<sub>2</sub>O)<sub>2</sub> with coupled cluster method is similar to that for H<sub>2</sub>O.<sup>21,22</sup> We find that variation in the optimized intermolecular geometric parameters is generally larger than variation in the optimized intramolecular geometric parameters, particularly  $\alpha$  and  $\beta$ .

The increase in the interaction energy and decrease in the intermolecular distance from CCSD to CCSD(T) is already well documented for (H<sub>2</sub>O)<sub>2</sub>.<sup>15,20</sup> However, to our knowledge, there have been no investigations of (H<sub>2</sub>O)<sub>2</sub> with the CCSDT, CCSDT(Q), or CCSDTQ methods. We find that there are relatively small differences between the geometry of (H<sub>2</sub>O)<sub>2</sub> calculated using the CCSD(T) and CCSDT methods.<sup>14,21,22,51</sup> However, somewhat worryingly these differences are calculated to be of varying magnitudes and indeed different signs with the jun-cc-pVDZ and may-cc-pVTZ basis sets. For example with the jun-cc-pVDZ basis set, full triple excitations causes the intramolecular bond lengths to increase by ~0.00008 Å, whereas with the may-cc-pVTZ basis set the intramolecular bond lengths decrease by ~0.00005 Å. However, this basis set sensitivity for inclusion of full triples excitations can also be seen in Table 2 for H<sub>2</sub>O with the jun-cc-pVDZ and may-cc-pVTZ basis sets. To check the accuracy of our CCSDT-CCSD(T) corrections, we have also optimized the geometry of



**Table 5. All Electron and Frozen Core Counterpoise Corrected Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in  $\text{kJ mol}^{-1}$ ) Obtained with the CCSD(T) and CCSD(T)-F12b Methods**

|                             | CCSD(T)-F12b |              |             | CCSD(T)      |               |             |
|-----------------------------|--------------|--------------|-------------|--------------|---------------|-------------|
|                             | cc-pVQZ-F12  | cc-pCVQZ-F12 | $\Delta$    | aug-cc-pV5Z  | aug-cc-pwCV5Z | $\Delta$    |
| $R(\text{OH})_f$            | 0.95750      | 0.95657      | −0.00092    | 0.95762      | 0.95667       | −0.00094    |
| $R(\text{OH})_b$            | 0.96466      | 0.96379      | −0.00087    | 0.96471      | 0.96381       | −0.00089    |
| $R(\text{OH})_a$            | 0.95908      | 0.95816      | −0.00091    | 0.95917      | 0.95824       | −0.00094    |
| $\theta(\text{HOH})_d$      | 104.785      | 104.903      | 0.118       | 104.759      | 104.883       | 0.124       |
| $\theta(\text{HOH})_a$      | 104.875      | 104.998      | 0.124       | 104.850      | 104.980       | 0.129       |
| $R(\text{O}\cdots\text{O})$ | 2.91422      | 2.91094      | −0.00328    | 2.91683      | 2.91346       | −0.00337    |
| $\alpha$                    | 5.695        | 5.641        | −0.054      | 5.679        | 5.628         | −0.051      |
| $\beta$                     | 123.346      | 123.769      | 0.423       | 123.427      | 123.866       | 0.439       |
| $E[(\text{H}_2\text{O})_2]$ | −152.7560139 | −152.8811869 | −0.12517301 | −152.7484769 | −152.8725054  | −0.12402848 |
| $E[\text{H}_2\text{O}]$     | −76.37405163 | −76.43661713 | −0.0625655  | −76.37029827 | −76.43229082  | −0.06199255 |
| $D_e^a$                     | 20.769       | 20.880       | 0.110       | 20.690       | 20.804        | 0.114       |

$$^a(2 \times E[\text{H}_2\text{O}] - E[(\text{H}_2\text{O})_2]) \times 2625.5 \text{ kJ mol}^{-1}.$$

$\text{H}_2\text{O}$  with the CCSD(T) and CCSDT methods using analytical gradients in CFOUR. We obtain identical results for the CCSDT-CCSD(T) corrections if calculated with either numerical or analytical gradients. We find that the differences between the CCSD(T) and CCSDT optimized geometric parameters for  $\text{H}_2\text{O}$  obtained with the may-cc-pVTZ and apr-cc-pVQZ basis sets are in good agreement. Consequently, we assume that the difference between the CCSD(T) and CCSDT geometry of  $(\text{H}_2\text{O})_2$  is also reasonably well converged with the may-cc-pVTZ basis set.

We find that the effect of perturbative quadruple excitations is less sensitive to basis set than full triple excitations, with the CCSDT(Q)-CCSDT correction having the same sign and approximate magnitude if obtained using the jun-cc-pVDZ or may-cc-pVTZ basis sets. With the may-cc-pVTZ basis set, inclusion of perturbative quadruple excitations causes the intramolecular bond lengths to increase by  $\sim 0.0004$  Å and the intramolecular bond angles to decrease  $\sim 0.04^\circ$ , which is consistent with the changes to  $\text{H}_2\text{O}$  in Table 2. The intermolecular bond length is found to decrease by  $\sim 0.0007$  Å, while  $\alpha$  increases by  $0.011^\circ$  and  $\beta$  decreases more noticeably by  $0.181^\circ$ . Inclusion of perturbative quadruple excitations relative to CCSDT has a greater impact on the geometry of  $(\text{H}_2\text{O})_2$  than inclusion of full triple excitations does relative to CCSD(T). Consequently, the sign and magnitude of the CCSDT(Q)-CCSD(T) correction, which is denoted  $\Delta(Q)$  in Table 4, is also in broad agreement with both the jun-cc-pVDZ and may-cc-pVTZ basis sets. Our estimate of  $\Delta(Q)$  for  $(\text{H}_2\text{O})_2$  is further supported by the fact that the CCSDT(Q)-CCSD(T) difference for  $\text{H}_2\text{O}$  is also well converged with the may-cc-pVTZ basis set (Table 2).

Finally, we find that inclusion of full quadruple excitations has the smallest overall effect, with the CCSDT(Q) and CCSDTQ geometries in closest agreement of any two consecutive coupled cluster methods. This is consistent with the  $\text{H}_2\text{O}$  results in Table 2 and indicates, as first suggested by Bomble et al., that the CCSDT(Q) method has an accuracy comparable to CCSDTQ itself.<sup>52</sup>

The convergence of the optimized interaction energy for  $(\text{H}_2\text{O})_2$  with the coupled cluster method is comparable to the convergence of the geometric parameters. We find that inclusion of full triple excitations decreases the interaction energy by  $0.004 \text{ kJ mol}^{-1}$  with the jun-cc-pVDZ basis set and by  $0.025 \text{ kJ mol}^{-1}$  with the may-cc-pVTZ basis set. It is clear

that this difference between the CCSD(T) and CCSDT interaction energies is not converged to the CBS limit; however, a quadruple- $\zeta$  CCSDT optimization is not practicable with our present computational resources. The variation between the CCSD(T) and CCSDT optimized interaction energies for  $(\text{H}_2\text{O})_2$  is comparable to the differences previously calculated for the single point CCSD(T) and CCSDT interactions energies of formamide and formamide dimers obtained with the aug-cc-pVDZ basis set.<sup>11</sup> We find that inclusion of perturbative quadruple excitations [CCSDT(Q)] increases the interaction energy for  $(\text{H}_2\text{O})_2$  compared with CCSDT by  $0.040 \text{ kJ mol}^{-1}$  with the jun-cc-pVDZ basis set and by  $0.067 \text{ kJ mol}^{-1}$  with the may-cc-pVTZ basis set. As with the geometric parameters, inclusion of full quadruple excitation has a very small effect, causing the interaction energy to decrease by  $0.008 \text{ kJ mol}^{-1}$ .

In summary, we estimate the effect of including higher order excitations beyond CCSD(T) as the sum of the difference between CCSDT(Q) and CCSD(T) obtained with the may-cc-pVTZ basis set [ $\Delta(Q)$ ] and the difference between CCSDTQ and CCSDT(Q) obtained with the jun-cc-pVDZ basis set ( $\Delta Q$ ). It follows that the intramolecular bond lengths increase by  $0.00025$ – $0.00028$  Å, the intramolecular bond angles increase by  $\sim 0.02^\circ$ , the intermolecular bond length increases by  $0.00013$  Å,  $\alpha$  increases by  $0.004^\circ$ ,  $\beta$  decreases by  $0.126^\circ$ , and the interaction energy increases by  $0.034 \text{ kJ mol}^{-1}$ . Finally, we conclude that for the additional computational expense, there is no significant improvement in the accuracy of the optimized geometric parameters or interaction energy for  $(\text{H}_2\text{O})_2$  from CCSD(T) to CCSDT or from CCSDT(Q) to CCSDTQ. However, for very accurate investigations the CCSDT(Q) method may be considered an appropriate improvement over CCSD(T).

**Core–Valence Correlation.** In Table 5 we present counterpoise corrected optimized geometric parameters and the interaction energy for  $(\text{H}_2\text{O})_2$  obtained with both the frozen core approximation and with all electrons correlated. These results have been obtained using explicitly correlated CCSD(T)-F12b with the cc-pVQZ-F12 and cc-pCVQZ-F12 basis sets and using conventional CCSD(T) with the aug-cc-pV5Z and aug-cc-pwCV5Z basis sets. The optimized geometry and interaction energy obtained with the all electron explicitly correlated CCSD(T)-F12b/cc-pCVQZ-F12 method is expected to be closer to the all electron CCSD(T) CBS limit

**Table 6. Relativistic<sup>a</sup> and Nonrelativistic Counterpoise Corrected Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in kJ mol<sup>-1</sup>) Obtained with the All Electron CCSD(T) Method**

|                             | nonrelativistic | relativistic  | $\Delta$    | nonrelativistic | relativistic    | $\Delta$    |
|-----------------------------|-----------------|---------------|-------------|-----------------|-----------------|-------------|
|                             | aug-cc-pwCVSZ   | aug-cc-pwCVSZ |             | aug-cc-pCVSZ    | aug-cc-pCVSZ-DK |             |
| R(OH) <sub>f</sub>          | 0.95667         | 0.95671       | 0.00004     | 0.95670         | 0.95674         | 0.00005     |
| R(OH) <sub>b</sub>          | 0.96381         | 0.96383       | 0.00001     | 0.96384         | 0.96386         | 0.00002     |
| R(OH) <sub>a</sub>          | 0.95824         | 0.95827       | 0.00004     | 0.95826         | 0.95830         | 0.00004     |
| $\theta$ (HOH) <sub>d</sub> | 104.883         | 104.823       | -0.060      | 104.878         | 104.816         | -0.062      |
| $\theta$ (HOH) <sub>a</sub> | 104.980         | 104.916       | -0.064      | 104.974         | 104.909         | -0.066      |
| R(O...O)                    | 2.91346         | 2.91386       | 0.00040     | 2.91361         | 2.91387         | 0.00026     |
| $\alpha$                    | 5.628           | 5.665         | 0.037       | 5.629           | 5.665           | 0.036       |
| $\beta$                     | 123.866         | 123.627       | -0.239      | 123.851         | 123.612         | -0.239      |
| $E[(\text{H}_2\text{O})_2]$ | -152.87250540   | -152.97272714 | -0.10022174 | -152.87246067   | -152.97705578   | -0.10459511 |
| $E[\text{H}_2\text{O}]$     | -76.43229082    | -76.48241188  | -0.05012106 | -76.43226937    | -76.48457748    | -0.05230811 |
| $D_e^b$                     | 20.804          | 20.750        | -0.054      | 20.799          | 20.744          | -0.055      |

<sup>a</sup>Obtained using a fourth order Douglas-Kroll-Hess Hamiltonian. <sup>b</sup> $(2 \times E[\text{H}_2\text{O}] - E[(\text{H}_2\text{O})_2]) \times 2625.5$  kJ mol<sup>-1</sup>.

**Table 7. CCSD Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_e$  in kJ mol<sup>-1</sup>) Obtained with and without a Diagonal Born–Oppenheimer Correction**

|                             | aug-cc-pVTZ <sup>a</sup> |               |            | aug-cc-pCVTZ <sup>b</sup> |               |            |
|-----------------------------|--------------------------|---------------|------------|---------------------------|---------------|------------|
|                             | non-DBOC                 | DBOC          | $\Delta$   | non-DBOC                  | DBOC          | $\Delta$   |
| R(OH) <sub>f</sub>          | 0.95796                  | 0.95800       | 0.00004    | 0.95684                   | 0.95687       | 0.00003    |
| R(OH) <sub>b</sub>          | 0.96421                  | 0.96428       | 0.00007    | 0.96320                   | 0.96327       | 0.00007    |
| R(OH) <sub>a</sub>          | 0.95955                  | 0.95959       | 0.00004    | 0.95839                   | 0.95843       | 0.00004    |
| $\theta$ (HOH) <sub>d</sub> | 104.733                  | 104.748       | 0.015      | 104.831                   | 104.846       | 0.015      |
| $\theta$ (HOH) <sub>a</sub> | 104.811                  | 104.827       | 0.016      | 104.937                   | 104.952       | 0.015      |
| R(O...O)                    | 2.93248                  | 2.93160       | -0.00087   | 2.93064                   | 2.92977       | -0.00087   |
| $\alpha$                    | 5.329                    | 5.323         | -0.007     | 5.132                     | 5.127         | -0.005     |
| $\beta$                     | 124.067                  | 124.087       | 0.021      | 125.177                   | 125.197       | 0.021      |
| $E[(\text{H}_2\text{O})_2]$ | -152.67522216            | -152.66967793 | 0.00554423 | -152.78870036             | -152.78308946 | 0.00561090 |
| $E[\text{H}_2\text{O}]$     | -76.33366894             | -76.33088490  | 0.00278404 | -76.39043112              | -76.38761325  | 0.00281751 |
| $D_e^c$                     | 20.7002                  | 20.763        | 0.063      | 20.5790                   | 20.642        | 0.063      |

<sup>a</sup>Obtained with the frozen core CCSD method. <sup>b</sup>Obtained with the all electron CCSD method. <sup>c</sup> $(2 \times E[\text{H}_2\text{O}] - E[(\text{H}_2\text{O})_2]) \times 2625.5$  kJ mol<sup>-1</sup>.

and hence more accurate than the all electron conventional CCSD(T)/aug-cc-pwCVSZ results. However, as relativistic effects cannot yet be calculated using a DKH Hamiltonian with explicitly correlated CCSD(T)-F12b in MOLPRO 2010.1 (*vide infra*), it is important to check the accuracy of the conventional all electron CCSD(T) results. Pleasingly, we find that the differences between the frozen core and all electron results obtained with the CCSD(T) and CCSD(T)-F12b methods are very similar. Furthermore, the absolute agreement between the conventional and explicitly correlated geometric parameters is also very good. However, it should be noted that much larger variations between the two methods are observed if counterpoise correction is not included, indicating that BSSE is still appreciable with these large 5- $\zeta$  basis sets.

We find that inclusion of core–valence correlation reduces the intramolecular bond lengths by  $\sim 0.0009$  Å and increases the intramolecular bond angles by  $\sim 0.12^\circ$ . These changes are in agreement with the 0.0009 Å decrease in the OH bond length and 0.1189° increase in the HOH angle of H<sub>2</sub>O previously observed by Cortez et al. with the frozen core CCSD(T)/aug-cc-pV5Z and all electron CCSD(T)/aug-cc-pCVSZ methods.<sup>21</sup> We find that the intermolecular bond distance decreases more markedly by  $\sim 0.003$  Å, and for the intermolecular bond angles,  $\alpha$  decreases by  $\sim 0.05^\circ$  and  $\beta$  increases by  $\sim 0.4^\circ$ . The change in our fully optimized intermolecular distance with inclusion of core–valence correlation is in agreement with the 0.003 Å contraction previously calculated by Klopper et al. at the

CCSD(T) all electron and frozen core CBS limits using a constrained two-dimensional optimization.<sup>15</sup>

The optimized interaction energy of (H<sub>2</sub>O)<sub>2</sub> obtained with the all electron CCSD(T)-F12b and CCSD(T) methods is  $\sim 0.11$  kJ mol<sup>-1</sup> larger than the corresponding frozen core results. This difference is in agreement with Klopper et al. who calculate a single point energy difference at the CCSD(T) all electron and frozen core limits of 0.11 kJ mol<sup>-1</sup>.<sup>15</sup>

**Relativistic Effects.** In Table 6 we present counterpoise corrected optimized geometric parameters and the interaction energy for (H<sub>2</sub>O)<sub>2</sub> obtained with the all electron CCSD(T) method. We estimate the magnitude of scalar-relativistic effects by comparing results obtained with and without a fourth-order DKH Hamiltonian.<sup>53</sup> These results are obtained using variants of the aug-cc-pCVSZ correlation consistent basis set, optimized for core correlation (aug-cc-pwCVSZ) and for DKH Hamiltonians (aug-cc-pCVSZ-DK). Overall, we find that the impact of scalar-relativistic effects on our optimized geometric parameters is relatively small and calculated to be similar with the two basis set pairs considered.

We find that inclusion of scalar-relativistic effects increases the intramolecular bond lengths by 0.00001–0.00005 Å and decreases the intramolecular bond angles by  $\sim 0.06^\circ$ . These changes are comparable to the 0.000014 Å decrease in the OH bond length and 0.0584° increase in the HOH angle of H<sub>2</sub>O previously calculated by Cortez et al. with the frozen core CCSD(T)/cc-pV6Z method inclusive and exclusive of a

**Table 8. Best Estimate of Optimized Geometric Parameters (in Å and degrees), Electronic Energies (in a.u.), and Interaction Energies ( $D_o$  in  $\text{kJ mol}^{-1}$ ) Obtained at the Counterpoise Corrected CCSD(T)-F12b/CBS Limit with Corrections for Higher Order Excitations, Core Correlation, Relativistic Effects, and Diagonal Born–Oppenheimer Effects**

|                             | CCSD(T)-F12b/CBS <sup>a</sup> | higher order <sup>b</sup> | core <sup>c</sup> | relativistic <sup>d</sup> | DBOC <sup>e</sup> | total correction <sup>f</sup> | best estimate <sup>g</sup> |
|-----------------------------|-------------------------------|---------------------------|-------------------|---------------------------|-------------------|-------------------------------|----------------------------|
| R(OH) <sub>f</sub>          | 0.95744                       | 0.00026                   | −0.00092          | 0.00004                   | 0.00003           | −0.00059                      | 0.95685                    |
| R(OH) <sub>b</sub>          | 0.96464                       | 0.00028                   | −0.00087          | 0.00001                   | 0.00007           | −0.00050                      | 0.96414                    |
| R(OH) <sub>a</sub>          | 0.95902                       | 0.00025                   | −0.00091          | 0.00004                   | 0.00004           | −0.00059                      | 0.95843                    |
| $\theta(\text{HOH})_d$      | 104.801                       | −0.022                    | 0.118             | −0.060                    | 0.015             | 0.052                         | 104.854                    |
| $\theta(\text{HOH})_a$      | 104.892                       | −0.021                    | 0.124             | −0.064                    | 0.015             | 0.053                         | 104.945                    |
| R(O⋯O)                      | 2.91278                       | 0.00013                   | −0.00328          | 0.00040                   | −0.00087          | −0.00362                      | 2.90916                    |
| $\alpha$                    | 5.703                         | 0.004                     | −0.054            | 0.037                     | −0.005            | −0.017                        | 5.686                      |
| $\beta$                     | 123.379                       | −0.126                    | 0.423             | −0.239                    | 0.021             | 0.079                         | 123.458                    |
| $E[(\text{H}_2\text{O})_2]$ | −152.75810567                 | −0.00082871               | −0.12517301       | −0.10022174               | 0.00561090        | −0.22061256                   | −152.97871823              |
| $E[\text{H}_2\text{O}]$     | −76.37508166                  | −0.00040791               | −0.06256550       | −0.05012106               | 0.00281751        | −0.11027696                   | −76.48535862               |
| $D_e^h$                     | 20.853                        | 0.034                     | 0.110             | −0.054                    | 0.063             | 0.154                         | 21.007                     |

<sup>a</sup>CCSD(T)-F12b/CBS extrapolation scheme with the aug-cc-pVQZ/aug-cc-pVSZ basis sets from Table 1. <sup>b</sup>Sum of  $\Delta Q$  and  $\Delta(Q)$  from Table 3 and Table 4, respectively. <sup>c</sup>Difference between the frozen core cc-pVQZ-F12 and all electron cc-pCVQZ-F12 results from Table 5. <sup>d</sup>Difference between the nonrelativistic aug-cc-pCVSZ and relativistic aug-cc-pCVSZ-DK results from Table 6. <sup>e</sup>Difference between the non-DBOC aug-cc-pCVTZ and DBOC aug-cc-pCVTZ results from Table 7. <sup>f</sup>Sum of the higher order, core, relativistic, and DBO corrections. <sup>g</sup>Sum of the CCSD(T)-F12b/CBS results and total correction. <sup>h</sup> $(2 \times E[\text{H}_2\text{O}] - E[(\text{H}_2\text{O})_2]) \times 2625.5 \text{ kJ mol}^{-1}$ .

second-order DKH Hamiltonian.<sup>21</sup> We find that scalar-relativistic effects increase the intermolecular bond length more significantly than the intramolecular bond lengths, by 0.00026–0.00040 Å. For the intermolecular bond angles, scalar-relativistic effects increase  $\alpha$  increase by  $\sim 0.04^\circ$  and decrease  $\beta$  more markedly by  $\sim 0.24^\circ$ .

Our optimized CCSD(T) interaction energies corrected for scalar-relativistic effects are 0.054–0.055  $\text{kJ mol}^{-1}$  smaller than the noncorrected values. This destabilization of the complex is in agreement with the 0.05  $\text{kJ mol}^{-1}$  decrease in the interaction energy obtained by Klopper et al. from single point energies calculated with and without mass-velocity one- and two-electron Darwin terms using the frozen core CCSD(T)/aug-cc-pCVTZ method.<sup>15</sup>

**Diagonal Born–Oppenheimer Correction.** In Table 7 we present optimized geometric parameters and the interaction energy for  $(\text{H}_2\text{O})_2$  obtained with and without a DBOC. These results have been obtained with either the frozen core CCSD method and the aug-cc-pVTZ basis set or the all electron CCSD method and the aug-cc-pCVTZ basis set. We find that the impact of including a DBOC on the optimized geometric parameters and interaction energy is calculated to be essentially identical with the two methods. The absolute magnitude of the all electron and frozen core CCSD DBOCs (in terms of total energy) differ by  $\sim 2\%$ . Our calculated DBOCs for  $(\text{H}_2\text{O})_2$  are expected to be reasonably accurate as Gauss et al. have previously shown that for  $\text{H}_2\text{O}$  the HF method accounts for 97% of DBOC and the CCSD method recovers approximately 90% of the remaining 3% correlation effect.<sup>54</sup> They also find that CCSD DBOCs obtained with the aug-cc-pVTZ and aug-cc-pCVTZ basis sets are well converged with respect to the corresponding frozen core and all electron CBS limits.

We find that inclusion of the DBOC causes the intramolecular bond lengths to increase by 0.00003–0.00007 Å and the intermolecular bond length to decrease more markedly by  $\sim 0.0009$  Å. This appreciable contraction of the intermolecular distance is also reflected in the  $\sim 0.06 \text{ kJ mol}^{-1}$  increase in the interaction energy of  $(\text{H}_2\text{O})_2$ . We find that inclusion of the DBOC causes the intramolecular bond angles to increase by  $\sim 0.015^\circ$  with the intermolecular bond angles  $\alpha$  decreasing by  $\sim 0.01^\circ$  and  $\beta$  increasing by  $\sim 0.02^\circ$ .

**Summary.** In Table 8 we summarize the results from Table 1 and Table 3–Table 7 to produce our best estimate of the optimized geometric parameters and interaction energy for  $(\text{H}_2\text{O})_2$ . Our starting point is the counterpoise corrected frozen core CCSD(T)-F12b CBS extrapolated limit obtained with the aug-cc-pVQZ/aug-cc-pVSZ basis set pair. Of the various corrections/extensions beyond this level of theory, it is clear that inclusion of core–valence correlation has the largest impact on both the geometry and interaction energy of  $(\text{H}_2\text{O})_2$ . We find that the impact of core–valence correlation is generally larger for the intermolecular geometric parameters as compared to the intramolecular parameters, which is perhaps not surprising given the relatively large corresponding enhancement in the interaction energy (0.11  $\text{kJ mol}^{-1}$ ). Inclusion of higher order excitations has the next largest effect on the intramolecular geometric parameters but the smallest effect on the intermolecular geometric parameters. Again, the magnitude of the change in the intermolecular geometric parameters can be rationalized by the fact that inclusion of higher order excitations causes the smallest change in the interaction energy (0.034  $\text{kJ mol}^{-1}$ ). Scalar-relativistic effects and inclusion of the DBOC have a comparable impact on the intramolecular bond lengths; however, the intramolecular bond angles are more perturbed by scalar-relativistic effects than by the DBOC. The impact of these two corrections/extensions on the interaction energy is also comparable, although of opposite sign, with scalar-relativistic effects reducing the interaction energy by 0.054  $\text{kJ mol}^{-1}$  and adiabatic effects increasing the interaction energy by 0.063  $\text{kJ mol}^{-1}$ . Consequently, scalar-relativistic effects increase the intermolecular bond length by 0.00040 Å and adiabatic effects decrease the intermolecular bond length by  $-0.00087$  Å. Overall, we find that the CCSD(T)-F12b/CBS limit overestimates the intramolecular bond lengths by  $\sim 0.0005$  Å, underestimates the intramolecular bond angles by  $\sim 0.05^\circ$ , overestimates the intermolecular bond length by 0.0362 Å, overestimates  $\alpha$  by  $0.017^\circ$ , and underestimates  $\beta$  by  $0.079^\circ$ . Furthermore, we find that the CCSD(T)-F12b/CBS limit interaction energy is also underestimated by 0.154  $\text{kJ mol}^{-1}$ .

In summary, we conclude that inclusion of higher order excitations up to full quadruples makes a relatively small but non-negligible improvement in the optimized CCSD(T)



geometry and interaction energy for  $(\text{H}_2\text{O})_2$ . Overall, this impact is smaller than inclusion of core–valence correlation and comparable to scalar-relativistic and adiabatic effects. It follows that investigation of hydrogen-bonded complexes beyond CCSD(T) theory is only prudent if these other effects are also considered.

Our present “best estimate” of  $21.007 \text{ kJ mol}^{-1}$  for the interaction energy of  $(\text{H}_2\text{O})_2$  is in excellent agreement with the previous benchmark results of  $20.97 \text{ kJ mol}^{-1}$  and  $20.99 \text{ kJ mol}^{-1}$ ,<sup>15,16</sup> validating some of the approximations made in these earlier studies. This refined value for  $D_e$  should slightly improve the accuracy of potential energy surfaces for  $(\text{H}_2\text{O})_2$  scaled to a benchmark  $D_e$  value,<sup>55</sup> and ultimately lead to slightly improved theoretical estimates for experimentally observable properties such as the dissociation energy ( $D_0$ ). See for example, refs 56 and 57.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: jlane@waikato.ac.nz.

### Notes

The authors declare no competing financial interest.

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