

Benchmark Calculations of the Energies for Binding Excess Electrons to Water Clusters

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S Supporting Information

ABSTRACT: State-of-the-art ADC(2), EOM-EA-CCSD, and EOM-EA-CCSD(2) many-body methods are used to calculate the energies for binding an excess electron to selected water clusters up to (H₂O)₂₄ in size. The systems chosen for study include several clusters for which the Hartree–Fock method either fails to bind the excess electron or binds it only very weakly. The three theoretical methods are found to give similar values of the electron binding energies. The reported electron binding energies are the most accurate to date for such systems, and these results should prove especially valuable as benchmarks for testing model potential approaches for describing the interactions of excess electrons with water clusters and bulk water.

1. INTRODUCTION

There has been a long-running debate concerning the nature of excess electrons attached to intermediate sized water clusters.^{1–7} At the forefront of this debate is whether experimental studies have indeed observed species with the excess electron localized in the interior of the cluster. Given the size of the clusters needed to be viable for supporting an interior bound electron and the need to account for finite temperature effects, most of the theoretical work in this area has been carried out with model Hamiltonian approaches.^{8–19} This obviously leads to the question of the sensitivity of the results of the theoretical studies to the details of the model potential employed.²⁰ This issue has recently received considerable attention in the context of the hydrated electron in bulk water (e_{aq}[−]), where a recent model potential study of this species questioned the validity of the long-accepted cavity model.²¹ However, the conclusions of this study have been challenged by two other theoretical groups.^{22,23} The recent debate about the nature of e_{aq}[−] has underscored the need for high-quality ab initio data for parametrizing and testing model Hamiltonian approaches.

The identities of the isomers responsible for the major peaks in the measured photodetachment spectra of (H₂O)_n[−] clusters are known only for $n \leq 6$, making accurate calculations of the electron binding energies (EBEs) of the larger clusters especially valuable. However, at the present time, accurate ab initio calculations of the EBEs—e.g., using the CCSD(T) method²⁴ together with large basis sets—have been reported only for clusters as large as (H₂O)₆[−].^{14,25} Comparable quality theoretical data are lacking for larger clusters that are candidates for interior-bound excess electron states. The most comprehensive set of ab initio results on the EBEs of larger water clusters is that of Herbert and Head-Gordon,^{26,27} who have reported MP2-level EBEs for a series of (H₂O)₂₀[−] and

(H₂O)₂₄[−] clusters. These results, obtained using a 6-31(1+,3+)-G basis set, formed by augmenting the 6-31+G(d) basis set²⁸ with diffuse s and p functions,^{26,27} have proven valuable in testing model potential approaches. However, they are limited by the truncation of correlation effects at the second order and by the use of a relatively small basis set. We note, in particular, that the success of the EBE calculations with the 6-31(1+,3+)G* basis set is due in part to a cancellation of errors, as this basis set is not sufficiently flexible to fully describe the electron correlation effects on the EBEs but also gives a dipole moment of the monomer too large by about 0.25 D (MP2 result), which, for most geometrical structures of interest, would act so as to artificially enhance the resulting EBEs. The most ambitious calculation of an EBE of a large water cluster appears to be that of Jungwirth who recently reported an EBE of a (H₂O)₃₂[−] cluster obtained at the RI-MP2 level using the aug-cc-pVDZ basis set^{29,30} augmented with s and p diffuse functions.³¹

For a subset of (H₂O)_n[−] clusters for which the excess electron binds in the interior, there is an additional challenging problem in that the Hartree–Fock approximation does not bind the excess electron or binds it only weakly.^{13,27} In such cases, neither the MP2 nor the CCSD(T) method can be trusted to give reliable electron binding energies (and, in general, they will fail to bind the excess electron). This problem was recognized by Herbert and Head-Gordon, who introduced a procedure that they designated MP2(BHLYP) for calculating the EBEs. This approach employs the DFT orbitals and orbital energies in the MP2 energy expressions of the neutral and anionic clusters and exploits the fact that the BHLYP density functional method^{32,33} generally binds the excess electron in

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those cases that the Hartree–Fock method does not. The final EBEs were obtained by scaling the MP2(BHLYP) values. The accuracy of the scaled MP2(BHLYP) approach for calculating the EBEs of $(\text{H}_2\text{O})_n^-$ clusters for which the Hartree–Fock method does not provide a suitable starting point remains to be demonstrated.

Clearly, there is a compelling need for accurate ab initio electron binding energies of $(\text{H}_2\text{O})_n^-$, $n \geq 20$, clusters for use in testing and parametrizing model potential approaches for the accommodation of excess electrons by water. In this work, we address this need by employing the second-order algebraic diagrammatic construction (ADC(2))³⁴ many-body Green's function method to calculate the EBEs of several water clusters, including three $(\text{H}_2\text{O})_{24}^-$ isomers (W24a, W24c, W24e) for which the Hartree–Fock method either fails to bind the excess electron or binds it only very weakly. In addition, for a symmetrized W24a cluster, denoted W24a*, for several smaller clusters derived from W24a*, and for two $(\text{H}_2\text{O})_6^-$ clusters, the EBEs were calculated using the equations-of-motion electron-affinity coupled-cluster-singles-doubles (EOM-EA-CCSD)³⁵ and EOM-EA-CCSD(2)³⁶ methods, as well as with the ADC(2) method. (In this manuscript, Wn refers to the $(\text{H}_2\text{O})_n^-$ cluster.)

Both the ADC(2) and EOM-EA methods are able to describe anion states for which the Hartree–Fock approximation is not a suitable starting point. However, they differ in terms of the electron correlation effects recovered. Specifically, the ADC(2) method retains only second-order terms in the expression of the self-energy of the Green's function, while EOM-EA-CCSD includes many higher-order contributions missing in the ADC(2) procedure. The ADC(2) method is inherently size-consistent³⁷ and has been found to predict accurate electron binding energies for many classes of anions.^{38–40} In addition, it has proven useful for calculating the energies and lifetimes of metastable anion states.^{41,42} However, given the fact that ADC(2) uses a second-order approximation to the self-energy, when applying it to a new class of anions, it is important to compare with theoretical methods that include correlation effects missing in the ADC(2) approach.

In the EOM-EA-CCSD method, one first does a CCSD calculation on the ground state of the neutral molecule and then uses the resulting amplitudes to construct an effective Hamiltonian $e^{-T}H_eT$, which is then used to carry out for the anion state a configuration interaction calculation, including all symmetry-allowed one-particle (1p) and two-particle-one-hole (2p1h) configurations. The EOM-EA-CCSD(2) method is similar except that the ground state is treated at the MP2 level, and the MP2 doubles amplitudes are used in carrying out the similarity transform of the Hamiltonian. An alternative direct equations-of-motion method for calculating electron affinities was pioneered by Simons and Smith.⁴³ Additional information on the EOM-EA-CCSD(2) calculations is provided in the Supporting Information.

2. COMPUTATIONAL DETAILS

The ADC(2), EOM-EA-CCSD(2), and EOM-EA-CCSD methods scale as N^5 , N^5 , and N^6 , respectively, where N is the number of water monomers in the cluster. As a result of its relatively low scaling with cluster size, the use of Cholesky decomposition,⁴⁴ and a high degree of parallelization,⁴⁵ the ADC(2) method is applicable to much larger clusters than is the EOM-EA-CCSD method. Thus, it is of interest to

determine if the ADC(2) method gives EBE values close to those obtained using the more computationally demanding EOM methods. For the smaller clusters for which the excess electron does bind in the Hartree–Fock approximation, EBEs were also calculated using the more computationally demanding CCSD(T) method (i.e., by taking the difference of the CCSD(T) energies of the anion and neutral).

The EOM-EA-CCSD and EOM-EA-CCSD(2) calculations were carried out with the CFOUR code,^{46,47} and the ADC(2) calculations were performed with the P-RICDΣ code,⁴⁵ which has been interfaced with MOLCAS v7.⁴⁸ The ADC(2) Dyson orbitals of the excess electron were generated with aug-cc-pVDZ+A basis set (see below for more details about basis sets used). The MP2, CCSD, and CCSD(T) calculations on the smaller clusters were performed with the MOLPRO code.⁴⁹

The clusters considered are shown in Figures 1–3. These include two isomers of $(\text{H}_2\text{O})_6^-$, designated W6a and W6f, for

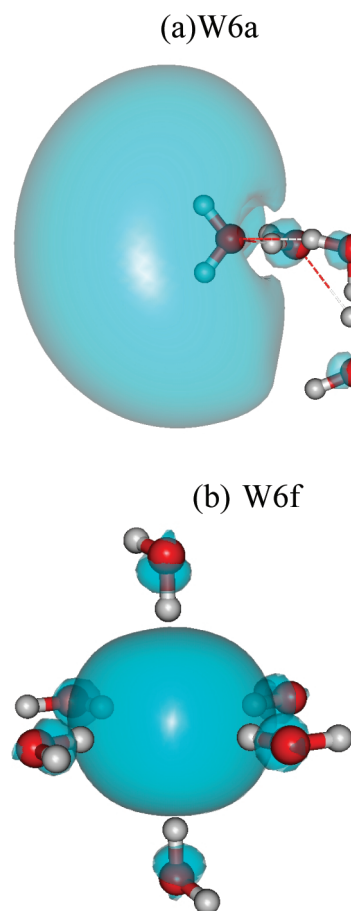


Figure 1. Structures of the W6 clusters studied in this work. (a) W6a, (b) W6f. The figures also display the electron density of the Dyson orbitals of the excess electron using surfaces enclosing 90% of the density.

which the Hartree–Fock method does bind the excess electron, two isomers of $(\text{H}_2\text{O})_{24}^-$ for which the Hartree–Fock method does not bind the excess electron (W24a, W24c), and one isomer of $(\text{H}_2\text{O})_{24}^-$ for which it binds the excess electron but only weakly (W24e). In labeling these W24 clusters, we have adopted the nomenclature of ref 13. In addition, we consider a series of $(\text{H}_2\text{O})_n^-$, $n = 4, 8, 12, 16$, and 20 clusters, derived from W24a, which are shown in Figure 2 and are described below.

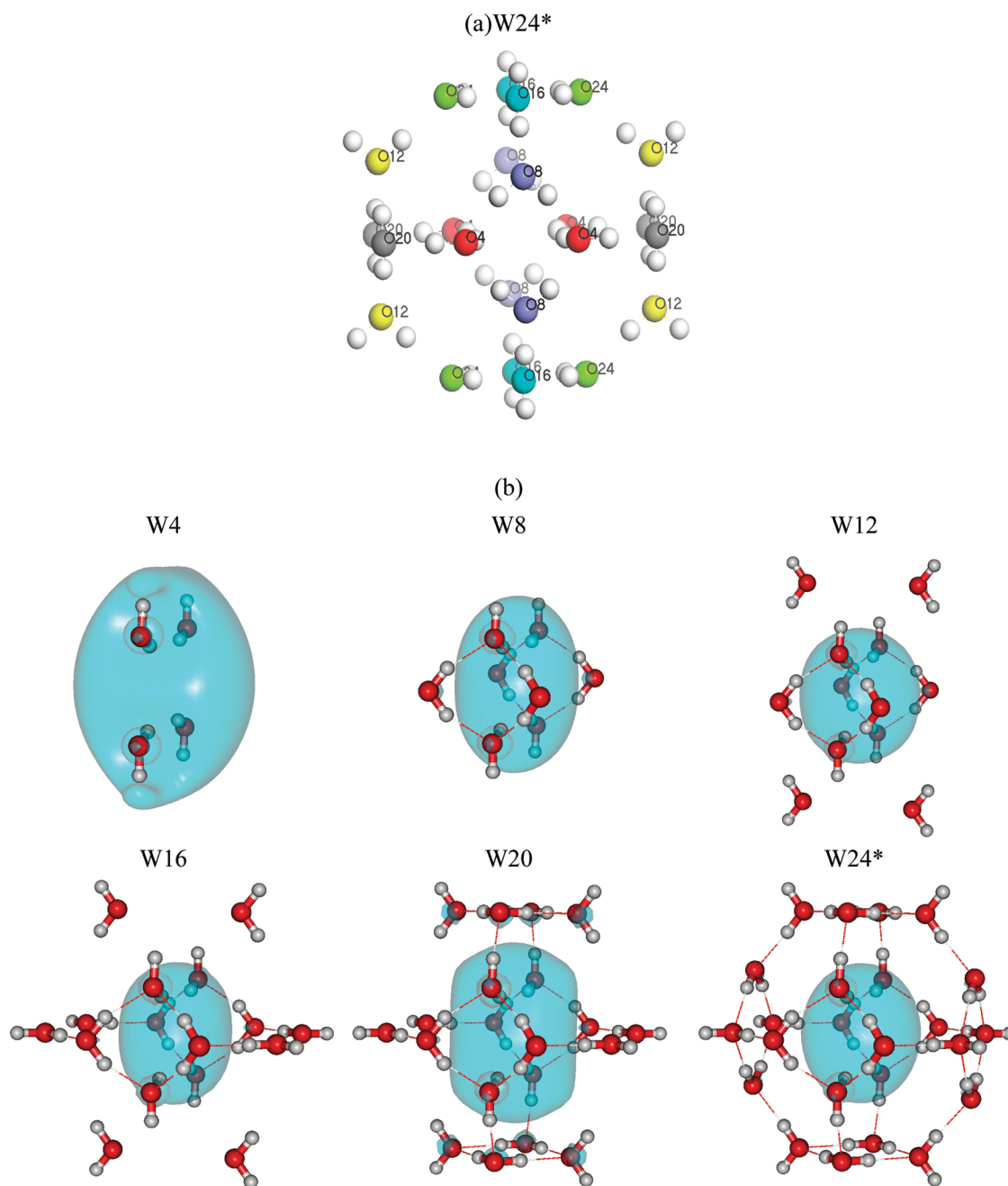


Figure 2. (a) W24a* and (b) the subclusters examined in the present work. The numbers in part a identify the monomers retained in the W4, W8, W12, W16, and W20 subclusters, where, for example, the W8 cluster includes all molecules labeled with either 4 or 8. Part b also displays the electron densities of the Dyson orbitals of the excess electron using surfaces that enclose 90% of the density.

W6a is of interest as it is the dominant isomer of $(\text{H}_2\text{O})_6^-$ observed experimentally.⁵⁰ It has a double acceptor (AA) monomer that points two free OH groups toward the charge distribution of the excess electron. W6f⁻ is not a local minimum on the potential energy surface of the hexamer anion but is of interest, as it has the so-called Kevan structure, which has been proposed for the first hydration shell of e_{aq}^- .⁵¹ Large basis set CCSD(T) EBEs are available for these two species.¹³ The three $(\text{H}_2\text{O})_{24}^-$ species selected for study were considered previously by Herbert and Head-Gordon²⁶ and by Sommerfeld et al.¹³ W24a and W24c are of interest as examples of clusters in which the excess electron has considerable charge density located in the cluster interior. It is not expected that any of these three isomers corresponds to the observed $(\text{H}_2\text{O})_{24}^-$ ion.

The calculations presented in this work, with the exception of those on W24a, W24b, and W24c, were carried out under the constraint of rigid monomers, i.e., with the monomer OH bond lengths and HOH angles constrained to the experimental values for the gas-phase monomer. This constraint was imposed to facilitate testing model Hamiltonian approaches employing rigid monomers. The geometry of W6a was optimized at the MP2 level under the constraint of rigid monomers, while the rigid-monomer geometries of the $(\text{H}_2\text{O})_{24}^-$ clusters were generated by adjusting the fully optimized geometries of ref 27. The structure of W6f was constructed by hand so as to have a cavity roughly comparable in size to that of e_{aq}^- .

Without the exploitation of symmetry, large basis set EOM-EA-CCSD, and even EOM-EA-CCSD(2), calculations of the

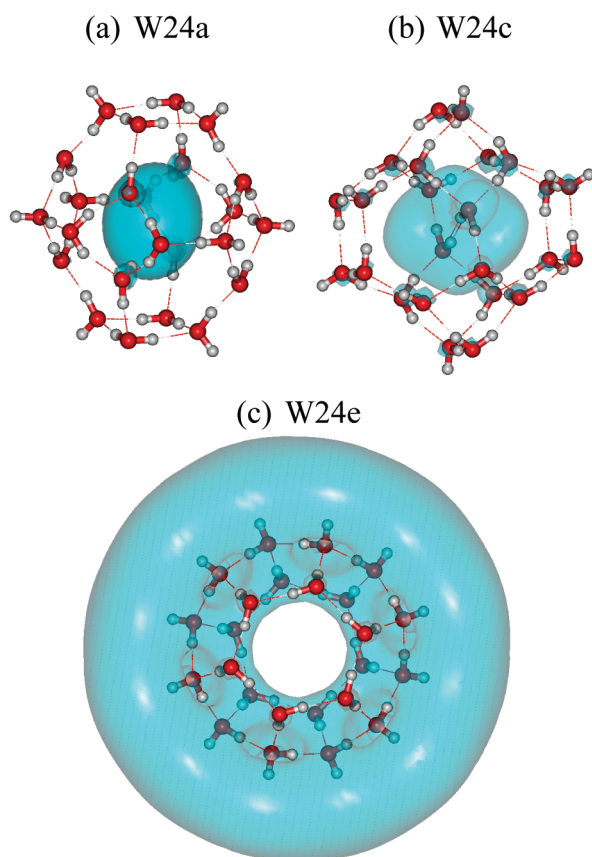


Figure 3. The structures of the three W24 clusters studied in this work. The surfaces indicate the electron densities of the Dyson orbitals of the excess electron using surfaces enclosing 90% of the density.

EBEs for clusters the size of $(\text{H}_2\text{O})_{24}^-$ would be computationally prohibitive with the CFOUR code and other codes in which this approach is implemented. We note however that with the use of Cholesky decomposition and more extensive parallelization of the algorithm, such calculations would be feasible even in the absence of symmetry. The optimized structure of the W24a anion is close to having D_{2h} symmetry, and to facilitate EOM-EA-CCSD calculations on this species,

we adjusted the geometry to give D_{2h} symmetry. Hereafter, this structure is designated as W24a*. The W4, W8, W12, W16, and W20 subclusters were extracted from W24a*, and all have a common W4 core and D_{2h} symmetry.

For each cluster depicted in Figures 1–3, the EBEs were calculated using the ADC(2) method. In addition, with the exception of W24a, W24b, and W24c, EOM-EA-CCSD and EOM-EA-CCSD(2) calculations of the EBEs were carried out. For the $(\text{H}_2\text{O})_4^-$ and $(\text{H}_2\text{O})_6^-$ clusters, EBEs are also calculated at the Koopmans' Theorem (KT), Hartree–Fock, MP2, and CCSD(T) levels of theory. The basis sets employed include aug-cc-pVDZ,^{21,22} aug-cc-pVTZ,^{29,30} aug-cc-pVDZ+A, aug-cc-pVDZ+B, aug-cc-pVTZ+A, and aug-cc-pVTZ+B, where the A and B denote, respectively, supplemental sets of 7s7p and 6s6p6d diffuse functions.⁵² The supplemental basis functions are located at the center-of-mass of the cluster with the exception of W6a, where they are centered on the O atom of the AA water. For the W4 and W8 clusters, EOM-EA-CCSD(2) calculations were also carried out using the aug-cc-pVQZ+A^{29,30} basis set, and for the W4 cluster it was also possible to carry out EOM-EA-CCSD calculations using the aug-cc-pVQZ+B basis set, allowing us to establish the convergence of the EBEs with basis set.

3. RESULTS

Table 1 summarizes the KT, EOM-EA-CCSD, EOM-EA-CCSD(2), and ADC(2) EBEs obtained for various water clusters. From the results reported in Table 1, it is also clear that different clusters and different electron binding motifs (e.g., surface vs interior) have very different requirements on the basis set in order to achieve convergence of the EBE. For example, for W6f, calculations with the aug-cc-pVDZ basis set give an EBE within 10% of the value obtained with the largest basis set considered (aug-cc-pVTZ+B), whereas for W6a, the EBE obtained with the aug-cc-pVDZ basis set is nearly a factor of 2 smaller than that obtained with the aug-cc-pVDZ+B basis set. (EOM-EA-CCSD(2) and EOM-EA-CCSD results are not reported for W6a with the larger basis sets as these calculations were not feasible with CFOUR due to the lack of symmetry.) It also appears that, with the exception of W4, near convergence in the EBEs is reached with the aug-cc-pVTZ+A basis set. In the case of W4, the inclusion of diffuse d functions at the

Table 1. Electron Binding Energies (meV) of Selected Water Clusters^a

basis	method	W24a* and its subclusters						W6 clusters	
		W4	W8	W12	W16	W20	W24	W6a	W6f
TZ+A	KT	<0	403	54	<0	<0	<0	231	39
DZ	ADC(2)	19	905	535	398	291	393	239	725
	EOM-EA-CCSD	37	907	551	420	298	366	250	728
DZ+A	ADC(2)	132	922	558	416	318	409	400	748
	EOM-EA-CCSD	150	920	568	432			415	744
	EOM-EA-CCSD(2)	147	922	554	403	301	366	418	744
DZ+B	EOM-EA-CCSD	181	934						
	EOM-EA-CCSD(2)	179	937	565	412	311		422	757
TZ+A	ADC(2)	163	971	611	478	376	474	424	823
	EOM-EA-CCSD	175	948						788
	EOM-EA-CCSD(2)	174	955	590					792
TZ+B	EOM-EA-CCSD(2)	192	956	593					794
QZ+A	EOMEA-CCSD(2)	183	965						
QZ+B	EOMEA-CCSD(2)	197							

^aXZ = aug-cc-pVXZ, where X = D, T, or Q.

center-of-mass (aug-cc-pVTZ+B basis set) also proves to be important, contributing 18 meV to the EBE. The adoption of the aug-cc-pVQZ rather than aug-cc-pVTZ as the core basis set contributes 10 meV or less to the EBEs of W4 and W8. Such an expansion of the basis set is likely to be even less important for the larger clusters.

Before discussing the results for the individual clusters, we observe that for all clusters considered, the ADC(2), EOM-EA-CCSD, and EOM-EA-CCSD(2) methods give similar values for the EBE when the same basis set is used in each case.

3.1. $(\text{H}_2\text{O})_6^-$. With the aug-cc-pVDZ+A basis set, the KT, HF, MP2, and CCSD(T) EBEs of W6a are 233, 259, 361, and 422 meV, respectively. The corresponding results for W6f are 45, 254, 750, and 777 meV. These results were obtained with the supplemental functions centered on the O atom of the AA water of W6a and at the center of mass of W6f. For W6a, these values of the EBEs differ somewhat from those published in ref 13, primarily due to the use of a structure with rigid monomers in the present study. Interestingly, although electron correlation effects are much more important for the EBE for W6f than for W6a, the change in the EBE going from the MP2 to the CCSD(T) method is more important for W6a. This is a consequence of the fact that the corrections due to triple excitations and to higher than second order double excitations enter with opposite signs for W6f but are of the same sign for W6a. Comparison of the results in Tables 1 and 2 reveals that

Table 2. Comparison of Electron Binding Energies (meV) of W4, W6a, and W6f, Obtained Using Various Theoretical Methods^a

method	W4 ^b	W6a ^c	W6f ^c
KT	2	233	45
HF	3	259	254
MP2	51	361	750
CCSD	166	399	717
CCSD(T)	191	422	777
EOM-CCSD	192	418	744
EOM-CCSD(2)	192	415	744
ADC(2)	192	400	748

^aCalculated for structures with rigid monomer geometries. ^bResults obtained using the aug-cc-pVTZ+B basis set. ^cResults obtained using the aug-cc-pVDZ+A basis set.

for W6a and W6f, essentially the same EBEs are obtained with the EOM-EA and ADC(2) methods as found in the CCSD(T) calculations. This is most encouraging, given the much lower computational cost of EOM-EA-CCSD(2) and ADC(2) calculations compared to CCSD(T) or EOM-EA-CCSD calculations.

3.2. W24a* and Its Subclusters. As noted above, EOM-EA-CCSD calculations are very computationally demanding for clusters the size of $(\text{H}_2\text{O})_{24}^-$. Indeed, for the W24 isomers, EOM-EA-CCSD calculations were carried out only in the case of W24a*, where we were able to exploit D_{2h} symmetry, and even then, we were restricted to the aug-cc-pVDZ basis set without supplemental diffuse basis functions. The resulting EBE is close to that obtained from the ADC(2) calculations employing the same basis set (393 vs. 366 meV), providing further evidence that the computationally less demanding ADC(2) method is adequate for calculating EBEs of water clusters, even in cases where the Hartree–Fock method fails to bind the excess electron. With the ADC(2) method and the

aug-cc-pVTZ+A basis set, the EBE of W24a* is calculated to be 474 meV. On the basis of the results for the smaller clusters where larger basis sets could be employed, we expect this result to be converged to within 3%.

We now consider the $(\text{H}_2\text{O})_n^-$, $n = 4, 8, 12, 16$, and 20, clusters derived from W24a*. In each case, the subcluster contains the same $(\text{H}_2\text{O})_4$ core (Figure 2), which retains D_{2h} symmetry. In the case of W4[−], the Hartree–Fock approximation either fails to bind or binds very weakly (by a few meV) the excess electron depending on the basis set employed, making questionable the application of methods such as MP2 and CCSD(T) for calculation of the EBE of this cluster.

Of the clusters considered, W4 binds the excess electron most weakly, with our best estimate of the EBE (described below) being 198 meV. Given the relatively small EBE value, use of a basis set with supplemental diffuse functions is especially important in this case. Moreover, this cluster experiences the greatest increase in the EBE (25%) in going from the aug-cc-pVDZ+A to the aug-cc-pVTZ+B basis set. With the aug-cc-pVTZ+B basis set, the ADC(2) and EOM-EA-CCSD(2) methods give an EBE of 192 meV for W4, whereas calculations at the KT, SCF, MP2, CCSD, and CCSD(T) levels of theory give EBEs of 2, 3, 51, 166, and 191 meV, respectively. It is remarkable that, given the very weak binding of the excess electron in the Hartree–Fock approximation, the CCSD(T) method gives an EBE essentially identical to that obtained using the EOM-EA-CCSD and ADC(2) methods. For the W4 cluster, the EBE was also calculated using the EOM-EA-CCSD method and the aug-cc-pVQZ+B basis set, giving a value of 198 meV, within 1 meV of the value obtained with the EOM-EA-CCSD(2) method. A detailed analysis of when the CCSD(T) method is able to accurately characterize $(\text{H}_2\text{O})_n^-$ ions will be reported in a subsequent paper.⁵³

Although the W8 cluster strongly binds the excess electron at the KT level, the W12 cluster binds the excess electron only weakly, and the W16, W20, and W24a* clusters fail to bind it at the KT level. Yet, all of these clusters have sizable EBEs when correlation effects are included. For example, the ADC(2) method with the aug-cc-pVTZ+A basis set gives EBEs of 971, 611, 478, 376, and 474 meV for W8, W12, W16, W20, and W24a*, respectively.

Interestingly, the EBE undergoes a sizable increase in going from W4 to W8; decreases along the sequence W8, W12, W16, and W20; and then increases at W24. This behavior is the consequence of the interplay of competing factors contributing to the binding of the excess electron. Specifically, the net EBE arises from a combination of electrostatics, exchange-repulsion (including the kinetic energy contribution), induction, and dispersion interactions between the excess electron and the electrons of the water molecules. The polarization terms included in many model potentials effectively account for both the induction and dispersion contributions to the EBE.¹³

For W24a* and its subclusters considered in this study, the electrostatic potential for the excess electron is highly attractive near the center of the cluster. In the case of the model tetramer, the electrostatics contribution is comparable to the exchange-repulsion contribution, with the result that the excess electron does not bind or binds only weakly in the KT approximation, depending on the basis set used. As water molecules are added to the tetramer, the electrostatic potential near the center of the cluster can either increase or decrease, depending on the orientations of the additional water molecules. The additional water molecules also act so as to further confine the excess

electron, which destabilizes it due to enhanced exchange-repulsion contributions. For the W16, W20, and W24a* clusters, the confinement effect wins out, and the excess electron does not bind in the KT approximation.

Thus far, the discussion has focused on the interactions present in the KT (or static exchange) approximation. Each additional water molecule also introduces attractive polarization interactions (which are dominated by dispersion-like correlation contributions). These correlation contributions are sufficiently large so as to result in stable anions, even in those cases where the anion is unbound in the Hartree–Fock approximation. It is this subtle interplay of the different contributions to the EBE that makes the development of quantitatively accurate model potential approaches for describing these species especially challenging.

For clusters for which the excess electron does not bind in the Hartree–Fock approximation but does bind in the ADC(2), EOM-EA-CCSD, and EOM-EA-CCSD(2) approaches, it is tempting to conclude that the anions are purely correlation bound. However, this is not the case since, if the attractive electrostatics contribution were eliminated, the excess electron would not bind or would bind only weakly. This was confirmed by model potential calculations with the electrostatic terms zeroed out. Of the W4, W8, W12, W16, W20, W24a* sequence of clusters, the excess electron is predicted to bind only to W24a* in the absence of electrostatic interactions, and then only by about 37 meV.

3.3. W24a, W24c, and W24e. Table 3 reports for W24a, W24c, and W24e the EBEs calculated using the ADC(2)

Table 3. Electron Binding Energies (meV) of Three $(\text{H}_2\text{O})_{24}^-$ Clusters Calculated Using the ADC(2), s-MP2, and s-MP2(BHLYP) Methods

cluster	ADC(2)		s-MP2 ^a	s-MP2(BHLYP) ^a
	DZ+A(DZ+B)	TZ'+A(TZ'+B)		
24a	626 (636)	687	601	632
24c	147 (162)	199	4	302
24e	132 (194)	170 (212)	192	316

^aResults from ref 27.

method. These results were obtained using the geometries of ref 27 (Figure 3), i.e., without the constraint of rigid monomers. With the aug-cc-pVDZ+A basis set, the ADC(2) calculations give EBEs of 626, 147, and 132 meV for W24a, W24c, and W24e, respectively. For the three W24 isomers considered, enlarging the basis set from aug-cc-pVDZ+A to aug-cc-pVDZ+B has a sizable impact only on W24e. Here, the basis set expansion causes an increase of the EBE from 132 to 194 meV. Further enlargement of the valence basis set from aug-cc-pVDZ to aug-cc-pVTZ' (where the prime indicates that the diffuse *f* functions on the O atoms and the diffuse *d* functions on the H atoms have been omitted) leads to a further increase in the EBE of W24c, with the EBE obtained with the aug-cc-pVTZ'+B basis set being 212 meV. The ADC(2) calculations with the aug-cc-pVTZ'+A (24a and 24c) and aug-cc-pVTZ'+B (24e) basis sets (1828 and 1854 contracted Gaussian basis functions) give the most accurate EBEs to date for these clusters. Table 3 also reports EBEs obtained using the scaled MP2 and MP2-(BHLYP) methods of Herbert and Head-Gordon.²⁷ Most significantly, it is found that the scaled MP2 (s-MP2) approach drastically underestimates the EBE of W24c, whereas the s-

MP2(BHLYP) method significantly overestimates the EBEs of W24c and W24e as compared with the results of the ADC(2) calculations. The failure of scaled MP2 approach for W24c is not surprising as that anion is not bound in the Hartree–Fock approximation.

4. CONCLUSIONS

The EBEs of a series of water clusters ranging from $(\text{H}_2\text{O})_4^-$ to $(\text{H}_2\text{O})_{24}^-$ in size were calculated using the EOM-EA-CCSD, EOM-EA-CCSD(2), and ADC(2) methods. The three theoretical methods were found to give similar values of the EBEs even in those cases where the Hartree–Fock approximation does not bind the excess electron. For clusters for which the Hartree–Fock method does bind the excess electron and for which CCSD(T) calculations are computationally feasible, it is found that the EBEs from CCSD(T) calculations are very close to the ADC(2) and EOM values. These results are most encouraging since the ADC(2) and EOM-EA-CCSD(2) methods are much less computationally demanding than EOM-EA-CCSD calculations. A major advantage of the ADC(2) method over EOM-EA-CCSD(2) is that there is a highly efficient, highly parallel implementation. This has made possible accurate calculations of the EBEs of water clusters up to $(\text{H}_2\text{O})_{24}^-$ in size.

This study also demonstrates the need to adopt large, flexible basis sets to obtain well converged EBEs of $(\text{H}_2\text{O})_n^-$ clusters. The most challenging systems are non-dipole-bound anions with a small EBE, e.g., W4 and W24e. In the former case, a basis set as large as aug-cc-pVQZ+B is needed to achieve a well converged value of the EBE. For W24e, it is anticipated that the converged BE could be as much as 5% larger than that obtained with the largest basis set employed for this species. For other clusters that bind the excess electron more strongly, the EBEs should be converged to within a few percent of their complete-basis-set limit values when using the aug-cc-pVTZ+A basis set. The EBEs reported in this study should prove to be especially valuable for testing model potential approaches designed for describing excess electrons interacting with water.

The major problem facing traditional wave function-type approaches such as MP2 or CCSD(T) in describing $(\text{H}_2\text{O})_n^-$ clusters for which Hartree–Fock method fails to give a binding or gives only weak binding of the excess electron is that none of the virtual orbitals including the LUMO has a charge distribution that even qualitatively resembles that of the bound excess electron. This problem is especially acute when large basis sets are employed, as then the low-lying virtual orbitals acquire considerable “continuum character”. The key to treating such problems within an *ab initio* framework is to optimize the singly occupied orbital, allowing for the correlation interactions with the electrons of the water monomers. The resulting “correlated” orbital, the so-called Dyson orbital in the ADC(2) procedure, is a linear combination of the Hartree–Fock orbitals of the appropriate symmetry. The success of the ADC(2), EOM-EA-CCSD(2), and EOM-EA-CCSD methods for treating this class of anions is that they account for both the long- and short-range correlation effects involving the excess electron and also allow for its relaxation in response to those correlation effects. As has been shown by Sommerfeld et al.¹³ and by Simons,⁵⁴ the dominant correlation effects between the excess electron and the valence electrons of the molecules can be viewed as generating an attractive polarization potential which when combined with the electrostatic and exchange-repulsion contributions results in a

bound excess electron. Indeed, the success of the one-electron Drude^{13,14,55} and polarization models^{9–13,21} for treating excess electron–water systems stems from their determining the excess electron orbital in the presence of a potential that effectively incorporates such correlation effects. This potential may be viewed as a simple representation of the self-energy in the ADC(2) approach.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional computational details on EOM-EA-CCSD(2) and geometry of W24*. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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