Water Cluster Anions Studied by the Long-Range Corrected Density Functional Theory

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Long-range corrected density functional theory (LC-DFT) is applied to a series of small water cluster anions ($n = 2-6$) to compute their vertical detachment energies (VDEs). The LC scheme is shown to eliminate an unphysical overestimation of the electron−water attraction in the hybrid functional by properly accounting for the long-range exchange repulsions. It is shown that a correct correlation energy behavior for a rapidly varying density is also important for describing a spatially extent, excess electron. The one-parameter progressive (OP) correlation functional, which satisfies this condition, leads to a remarkable improvement in the calculated VDE over the conventional one. The LC-BOP method produces highly accurate VDEs with a mean absolute deviation of 13.8 meV from the reference CCSD(T) results, reducing the error of B3LYP by more than 15 times. LC-BOP is found to be more accurate than MP2 which yields an excess electron underbound by 43.6 meV. The effect of basis sets on the calculated VDE is also examined. The aug-cc-pVDZ basis set with an extra diffuse function is found to be more accurate and reliable than the extended Pople-type basis sets used in the previous works. The extrapolation of the calculated VDE of different electron binding motifs is compared with the VDEs of experimentally observed three isomers (Verlet, J. R. R.; Bragg, A. E.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. *Science* 2005, *307*, 93).

I. Introduction

The water cluster anion, since its first observation,[1] has been extensively studied as a useful model to understand the hydrated electron in bulk water.[2−4] The hydrated electron plays a crucial role in charge transfer and electron transport in the condensed phase and biomolecular systems. A series of photoelectron experiments[5−12] on size-selected water cluster anions has compiled data of vertical detachment energies (VDEs), i.e., the energy to remove an excess electron from anions. Interestingly, the early experiments have witnessed a "magic number" in the produced cluster sizes, where only those of $n = 2$, 6, 7, and $n \geq 11$ were predominantly observed (n being the number of water molecules).[5,10,39] Johnson and co-workers later succeeded in producing the missing clusters ($n = 3$, 5, 8, and 9)[10] and ($n = 4$)[11] and reported the vibrational predissociation spectrum[13−20] to unravel their structures. The infrared spectra have revealed that the excess electron is most likely attached to a specific water molecule, the so-called "AA-water", which accepts two hydrogen bonds without donating any OH bond to the hydrogen-bonding network.[15] The AA-water has two OH bonds that are highly polarized and thus strongly capture the excess electron at the surface of the cluster (e.g., Figure 2).

For larger clusters, Coe et al.[5] have found that the observed VDEs in the range of $11 \leq n \leq 69$ correlate to the photoelectric threshold of bulk water in the extrapolated limit. This finding strongly suggests that the observed cluster was a bulklike isomer wherein the electron is internally solvated. However, mixed quantum/classical simulations based on one-electron pseudopotentials[21,22] have concluded that the observed cluster was a surface state based on the prediction that the crossover from the surface to the internally solvated state occurs at a much larger size ($n > 60$). Such a discrepancy in the experiment and theory has stimulated recent measurements in an extended range up to $n = 200$.[12] Surprisingly, the new series of VDEs was found to linearly extend the previous data without showing an indication of crossover. Furthermore, the measurement has detected two other isomers with smaller VDEs than the original ones. The new isomers were deemed surface-bound states based on the fact that they were generated from a colder neutral cluster which may lack sufficient energy to reorient the hydrogen-bonding network and solvate the attached electron. These findings have stimulated a renewed mixed quantum/classical simulation based on a newly determined pseudopotentials.[23−25] However, it was again concluded that there are no cavity states for $n < 200$ except at very low temperatures ($T < 50$ K). Recent theoretical works by Jordan and co-workers[26−31] have also indicated that the surface-bound state was more stable than the interior in the intermediate size ($n = 12-24$). These theoretical models rely on a rather drastic one-electron approximation and suffer from the uncertainty in the quality of the pseudopotential representing the electron−water interaction and the parametrized classical water molecules. Therefore, a more accurate and reliable electronic structure theory is required to address this long-standing issue.

So far, many ab initio electronic structure calculations have been carried out on small water cluster anions.[14,17,32−43] These studies have revealed that an additional diffuse basis function is indispensable, because Gaussian basis sets are designed for valence or core molecular orbitals but not for a spatially extent,

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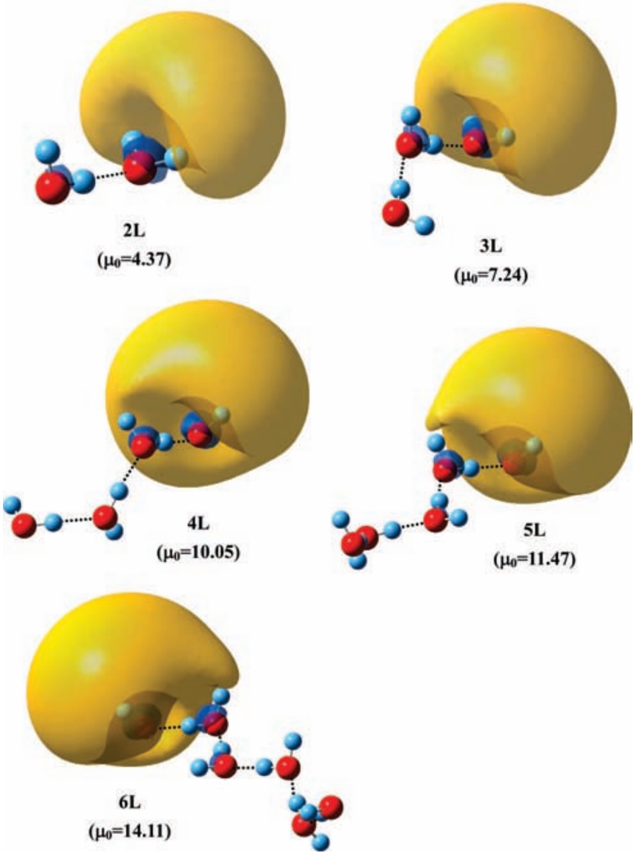


Figure 1. Isomer (L) with an excess electron trapped to a linear water cluster. For each isomer, the dipole moment of the neutral cluster (μ_0) and the singly occupied molecular orbital (SOMO) obtained at the LC-BOP/adz+diff level of theory are indicated. The SOMO is depicted with an isovalue of 0.015. Broken lines denote hydrogen bonds.

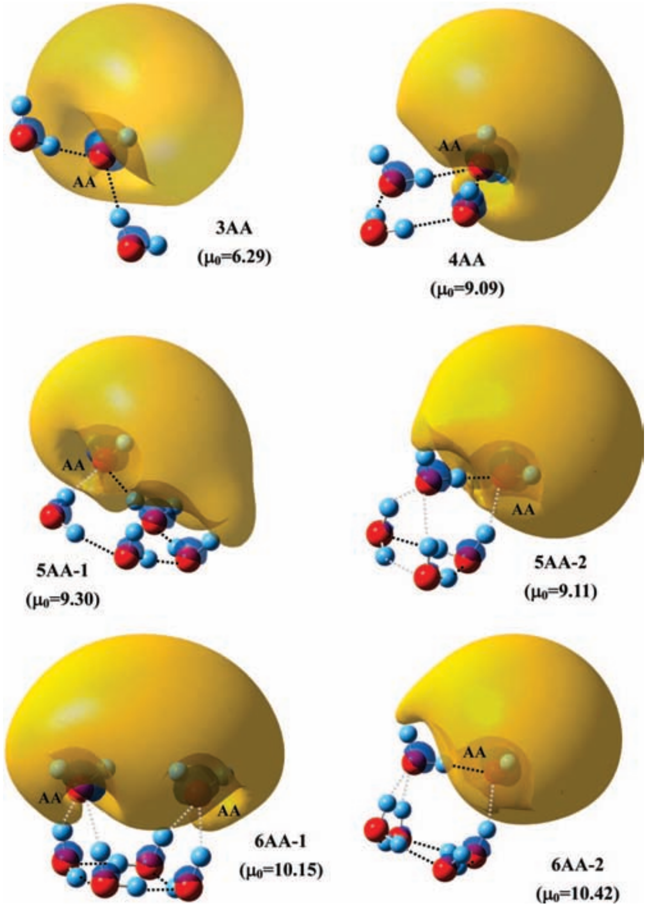
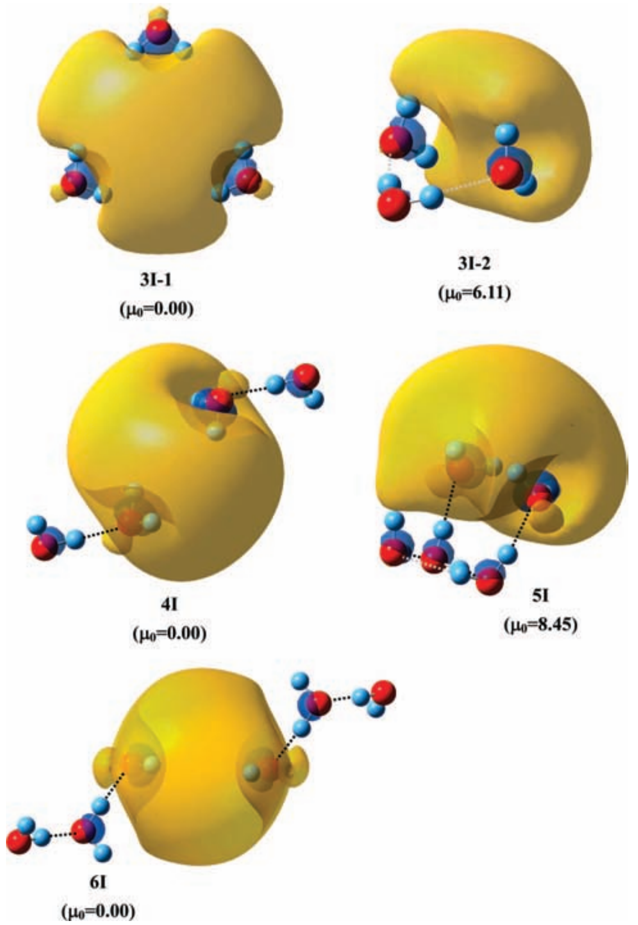


Figure 2. Isomer (AA) with an excess electron trapped to an AA-water (labeled "AA"). Gray broken lines denote weak hydrogen bonds with a OH···O distance larger than 2.0 Å. 3AA, 4AA, and 5AA-1 are taken from ref 36 (denoted $3L_{aa}$, $4R_{dd2}$, and $5R_{dd1}$ therein), 5AA-2 is from ref 38 (denoted 5W3f therein), and 6AA-1 and 6AA-2 are from ref 34 (denoted 6W-b and 6W-c therein). Notes are also given in the caption of Figure 1.

excess electron. Herbert and Head-Gordon[40] have investigated the effect of basis sets on the calculated VDE by systematically increasing the size of the basis sets and showed that the use of standard augmented basis sets results in an excessive error of more than 0.2 eV. It is also well-known that a treatment of electron correlation is essential in such systems. Although one might anticipate a simple electrostatic picture where an electron is trapped by the dipole moment of the neutral water cluster, nonclassical interactions such as dispersions and exchange repulsions are not negligible even for qualitative analyses. It is well established that the second-order Møller−Plesset perturbation (MP2) theory is a minimal requirement. The contribution of the higher-order correlation beyond MP2 is rather constant, which may be sizable for the anions having small VDE,[26,44−47] but decays to a small fraction for water cluster anions having VDEs larger than 0.4 eV.[41] Lee et al.[39] has recently employed MP2 and some higher-order correlation theories together with their tailored basis sets to investigate the structures, energetics, and vibrational spectra of various low-lying isomers of the water cluster anions up to $n = 6$. However, electron correlation calculations coupled with a high-quality basis set are computationally impractical for larger clusters. As the midsize clusters are a subject of intense debate, it is desirable to have a useful, low-scaling method in place of them.

Despite of its feasibility, density functional theory (DFT) has been met with a deep skepticism in the calculations of water cluster anions (and dipole-bound anions in general).[26] The hybrid B3LYP[48] functional, which is overwhelmingly used for many chemical systems, is inadequate for exploring the water cluster anions since it gives an overly bound excess electron.[14,26,40,41] One of the shortcoming of the hybrid functionals lies in the incorrect asymptotic behavior of the exchange-correlation potential. Since the dynamic correlation falls off rapidly as $1/R^6$ (R being the electron−electron distance), the Hartree−Fock (HF) exchange becomes dominant in the long-range region having an asymptotic decay of $1/R$.[49,50] Hybrid functionals do not incorporate this feature and thus underestimate the long-range exchange repulsions. In other words, they overly attract the electrons that are far departed.

The long-range correction (LC) scheme to alleviate this problem has been developed by two of the authors.[51] This scheme divides the Coulomb operator into short- and long-range portions using the standard error function and combines the short-range part of an exchange functional with the long-range part of the HF exchange integral.[51−53] In this way, the exact asymptote of the exchange potential is retained. The method has been shown to lead to a remarkable improvement upon conventional functionals in predicting the polarizabilities of π-conjugated polyenes,[51,57] charge-transfer and Rydberg excitations,[54,55] nonlinear optical properties,[56] and chemical reactions.[58] Scuseria and co-workers[59,60] have recently shown that the LC scheme combined with the Perdew−Burke−Ernzerhof functional is accurate in predicting various chemical properties. The LC scheme is a powerful approach to solve a wide variety of problems in existing density functionals.



3I-1 (μ_0=0.00)

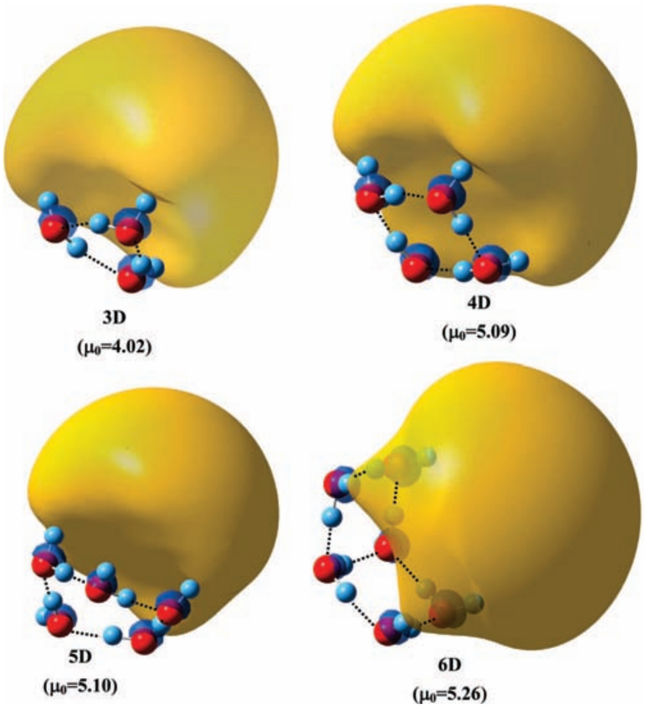
3I-2 (μ_0=6.11)

4I (μ_0=0.00)

5I (μ_0=8.45)

6I (μ_0=0.00)

Figure 3. Isomer (I) with an excess electron trapped internally. Gray broken lines denote weak hydrogen bonds with a OH···O distance larger than 2.0 Å. 3I-1, 3I-2, and 5I are taken from ref 36 (denoted 3Ic3h, 3Ldd, and 5Y32 therein), and 4I and 6I are from ref 34 (denoted 4W-a and 6W-a therein). Notes are also given in the caption of Figure 1.



3D (μ_0=4.02)

4D (μ_0=5.09)

5D (μ_0=5.10)

6D (μ_0=5.26)

Figure 4. Isomer (D) with an excess electron attached to aligned dangling OH bonds. The SOMO is depicted with an isovalue of 0.010. 3D, 4D, and 5D are taken from ref 36 (denoted 3Rda, 4Rda, and 5Rda therein), and 6D is from ref 38 (denoted 6Bd). Notes are also given in the caption of Figure 1.

In this study, we apply the LC scheme to a series of small water cluster anions and calibrate its accuracy in predicting the VDE and other properties. It is shown that the LC scheme eliminates the unphysical overbinding of the excess electron in the standard hybrid functional, producing a highly accurate VDE comparable to ab initio predictions.

II. Computational Details

We studied 20 types of isomers for water cluster anions in a range of $2 \leq n \leq 6$ as illustrated in Figures 1−4. Various types of electron binding motifs are selected for a comprehensive assessment of the electronic structure methods employed: (1) linear clusters forming dipole-bound anions [Figure 1; denoted isomer (L)], (2) surface states involving the AA-water [Figure 2; denoted isomer (AA)], (3) internally solvated states [Figure 3; denoted isomer (I)], and (4) the clusters having an electron bound to aligned, dangling OH bonds [Figure 4; denoted isomer (D)]. These clusters have already been identified by the previous authors as indicated in the captions of Figures 1−4. Note that some of the isomers studied here lie high in energy which may not be detected in experiments. However, this fact does not concern our purpose to survey a theoretical method that renders an appropriate description of the water cluster anion.

We carried out DFT calculations based on long-range corrected[51] BLYP[61,62] and BOP[61,63] (LC-BLYP and LC-BOP, respectively), and B3LYP.[48] The numerical integrations in DFT calculations were carried out using a fine grid of 99 590 having 99 radial shells and 590 angular points per shell for benchmarking the LC scheme. We note, however, that the standard grid of 75 302 induces a small error less than 1 meV in VDE and is probably accurate enough. The SCF convergence criterion for the density was set to 10^{-6} au, which lead to a convergence in both energy and gradient with sufficient accuracy. The parameter in the LC scheme was set to $\mu = 0.33$ au, which has been shown to be valid for the calculations of the excited states.[54] We note that the μ value larger than 0.33 au has been recently reported to be more suitable for predicting the reaction barriers and heat of formations.[58−60] However, we found in the preliminary calculations that this is not the case for predicting the VDE and hence used the original value of μ in this work. Ab initio calculations were also carried out at the MP2 and CCSD(T) levels of theory for reference. All the calculations were performed by a locally modified version of Gaussian03,[64] into which the long-range correction scheme and one-parameter progressive (OP) correlation functional were implemented.

We employed Dunning's aug-cc-pVDZ basis set[65,66] with additional diffuse functions for both oxygen and hydrogen atoms having exponents of 9.87×10^{-3} au [O(s)], 8.57×10^{-3} au [O(p)], and 3.72×10^{-3} au [H(s)] which were obtained by reducing the exponents of the "aug-" basis by a factor of one-eighth (denoted adz+diff). This basis set gives virtually equivalent results to those of Kim and co-workers,[36−39] who included two shells of diffuse functions, namely, (2s2p/2s), with exponents decremented by the same factor.

The equilibrium geometries of all the isomers were computed by each method except for CCSD(T). In CCSD(T) calculations, geometry optimization was carried out only for the dimer anion. For larger clusters ($n \geq 3$), the electronic energies of CCSD(T) were calculated at the geometry of either LC-BOP or MP2. We used the modified GDIIS algorithm[67,68] for geometry optimiza-

TABLE 1: Number of Hydrogen Bonds (N_{HB}) and the Relative Energies of the Water Cluster Anions with Respect to 3D, 4D, 5D, and 6D (ΔE) Calculated by the Long-Range Corrected DFT (LC-BLYP, LC-BOP), B3LYP, MP2, and CCSD(T) Methods Using adz+diff Basis Functions

		ΔE^a				
isomer	N_{HB}	B3LYP	LC-BLYP	LC-BOP	MP2	CCSD(T)[b]
3D	3	0.0	0.0	0.0	0.0	0.0
3L	2	0.2	2.3	1.8	1.8	1.6
3AA	2	2.0	5.2	4.5	4.0	3.4
3I-2	0 + 2[c]	2.6	6.0	5.5	4.7	4.1
3I-1	0	7.9	15.7	13.7	12.7	12.3
4D	4	0.0	0.0	0.0	0.0	0.0
4AA	4	2.8	5.2	5.2	4.1	3.1
4L	3	3.1	6.0	5.0	4.8	4.4
4I	2	7.1	13.0	11.5	10.4	9.8
5D	5	0.0	0.0	0.0	0.0	0.0
5AA-2	3 + 4[c]	1.0	0.3	2.0	0.7	−0.7
5AA-1	4 + 1[c]	3.1	5.7	5.7	4.3	3.2
5I	4 + 1[c]	3.2	5.2	5.9	4.8	3.5
5L	4	3.4	6.3	5.3	5.2	4.7
6AA-2	5 + 3[c]	−0.2	−0.7	0.4	−0.3	−1.3
6D	7	0.0	0.0	0.0	0.0	0.0
6AA-1	4 + 4[c]	2.9	4.1	5.2	4.2	2.7
6L	5	5.8	10.2	7.8	8.2	8.1
6I	4	8.8	16.3	13.4	12.3	11.9
MaxD[d]		4.4	4.4	2.7	1.5	
MAD[e]		1.6	2.0	1.5	0.7	

[a] Units in kcal/mol. [b] CCSD(T) energies are calculated at the MP2 geometry. [c] The number of strong hydrogen bonds + weak ones. [d] Maximum deviations from the CCSD(T) results. [e] Mean absolute deviations from the CCSD(T) results.

tion which is suitable for obtaining the geometry of a floppy system. The geometries obtained by LC-BOP and MP2 are available in the Supporting Information.

III. Results and Discussion

III.1. Geometries and Relative Energies. Table 1 summarizes the number of hydrogen bonds and the relative energies of the isomers by their sizes. It is obvious from Table 1 that the formation of hydrogen bonds makes the cluster more stable. The isomers with highly structured hydrogen-bonding network (e.g., 6AA-2) are more favored than the linear or internal isomers having a fewer number of hydrogen bonds. The strength of the hydrogen bond is an important factor as well. 6AA-1 is less stable than 6AA-2 and 6D even though it has eight hydrogen bonds, because four of these hydrogen bonds (gray broken lines in Figure 2) are relatively weak compared to the others which are longer than 2.0 Å in length. Table 2 shows that the average OH···O distance correlates with the relative stability of the isomer. For example, that of 5D is obtained as 1.77 Å from MP2 which is considerably shorter than that of the others. Therefore, the stability of the cluster is primary determined by the number and strength of the hydrogen bonds.

It is found from Table 1 that MP2 gives accurate relative energies in comparison to the CCSD(T) values with a mean absolute deviation (MAD) of 0.7 kcal/mol. MP2 also provides 1.93 Å for the OH···O distance of 2L in excellent agreement with the CCSD(T) result (1.94 Å). Note that MP2 gives an accurate description of the hydrogen-bonded complexes in general.[72] Thus, the CCSD(T) energies at the MP2 geometry are the reliable ones to be compared with the DFT results in the following.

TABLE 2: Average OH···O Distance of the Water Cluster Anions for Each Cluster Size Calculated by the Long-Range Corrected DFT (LC-BLYP, LC-BOP), B3LYP, and MP2 Methods Using adz+diff Basis Functions[a]

isomer	B3LYP	LC-BLYP	LC-BOP	MP2
2L[b]	1.91	1.78	1.84	1.93
3D	1.94	1.78	1.82	1.92
3L	1.84	1.71	1.76	1.85
3AA	1.98	1.85	1.91	1.99
3I-2	2.06	1.92	1.97	2.03
4D	1.80	1.66	1.70	1.80
4AA	1.98	1.84	1.90	1.97
4L	1.80	1.67	1.72	1.82
4I	1.89	1.76	1.81	1.89
5D	1.77	1.63	1.67	1.77
5AA-2	1.92	1.78	1.83	1.91
5AA-1	1.95	1.81	1.86	1.94
5I	1.95	1.81	1.86	1.94
5L	1.77	1.65	1.69	1.79
6AA-2	1.95	1.81	1.86	1.94
6D	1.82	1.68	1.72	1.81
6AA-1	2.03	1.88	1.94	2.02
6L	1.76	1.63	1.68	1.78
6I	1.82	1.74	1.74	1.83

[a] Units in angstroms. [b] The optimized OH···O distance is obtained as 1.94 Å by the CCSD(T)/adz+diff method.

As shown in Table 1, the relative energies are found accurate in the B3LYP, LC-BLYP, and LC-BOP calculations with a MAD of 1.6, 2.0, and 1.5 kcal/mol, respectively. Note that the B3LYP results show relatively large deviations as much as 4.4 kcal/mol, whereas LC-BOP gives an improved result with the largest deviation of 2.7 kcal/mol. In the LC-BOP results, the isomers with three-dimensional structures such as 5AA-2 are found to have slightly larger deviations. These deviations may be due to a short OH···O distance predicted by the LC-DFT method as indicated in Table 2. The hydrogen-bond lengths are underestimated by 0.087 and 0.135 Å in average by LC-BOP and LC-BLYP, respectively. On the other hand, the relative energies of isomer (L), which are free from the structural effects, are accurately obtained with small deviations less than 1 kcal/mol. Thus, the *strength* of the hydrogen bond is well described by LC-BOP without causing sizable errors in the relative energies. Among the tested DFT functionals, LC-BOP shows

TABLE 3: Vertical Detachment Energies of the Water Cluster Anions Calculated by the Long-Range Corrected DFT (LC-BLYP, LC-BOP), B3LYP, MP2, and CCSD(T) Methods Using adz+diff Basis Functions[a]

isomer	B3LYP	LC-BLYP	LC-BOP	MP2	CCSD(T)
2L	193.9	77.1	27.5	8.7	28.6
3L	345.6	245.1	160.6	114.6	146.2,[b] 160.8[c]
4L	478.0	394.0	283.1	213.5	254.9,[b] 280.5[c]
5L	527.2	460.9	337.8	249.6	294.0,[b] 333.2[c]
6L	642.6	564.8	425.8	331.0	380.6,[b] 420.4[c]
3AA	399.2	301.6	202.0	146.1	186.7,[b] 200.1[c]
4AA	561.1	502.2	373.1	283.4	336.1,[b] 362.9[c]
5AA-1	600.4	520.0	365.9	312.7	369.5,[b] 369.9[c]
5AA-2	592.3	540.0	408.3	318.1	376.3,[b] 401.8[c]
6AA-1	846.6	840.9	634.0	481.8	553.3,[b] 603.8[c]
6AA-2	705.6	658.7	507.0	413.7	477.1,[b] 501.3[c]
3I-1	526.0	423.2	227.4	155.2	190.4,[b] 220.5[c]
3I-2	426.6	338.6	197.5	138.0	174.6,[b] 199.2[c]
4I	713.0	683.5	488.7	394.1	438.5,[b] 465.5[c]
5I	757.4	718.9	516.4	405.9	468.9,[b] 503.9[c]
6I	1119.9	1160.0	922.1	793.4	838.9,[b] 872.7[c]
3D	184.1	32.3	−8.6	−13.8	5.7,[b] 9.3[c]
4D	239.4	74.6	21.2	22.4	48.5,[b] 46.2[c]
5D	285.0	82.3	18.2	30.7	61.1,[b] 47.6[c]
6D	346.7	152.9	58.0	62.7	104.2,[b] 95.0[c]
MaxD[d]	336.1	321.1	83.2, 49.4[e]	63.4	
MAD[f]	238.3	151.9	35.2, 13.8[e]	43.6	

[a] Units in meV. [b] CCSD(T) values at the MP2 geometry. [c] CCSD(T) values at the LC-BOP geometry. [d] Maximum deviations from CCSD(T) values. [e] Deviations from CCSD(T) values at the LC-BOP geometries. [f] Mean absolute deviations from CCSD(T) values.

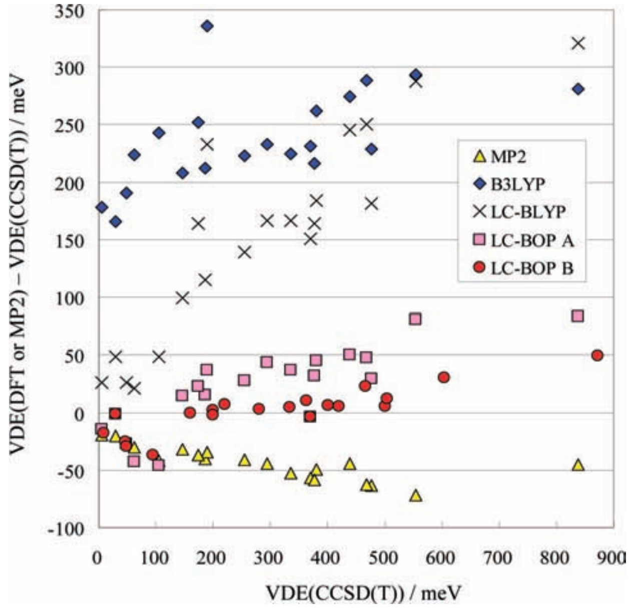


Figure 5. Plots of the vertical detachment energy (VDE) obtained by the CCSD(T) method vs the deviations in the MP2 (yellow triangles), B3LYP (blue diamonds), LC-BLYP (crosses), and LC-BOP results from the CCSD(T) values obtained at the MP2 geometry ("LC-BOP A", pink squares), and the deviations in the LC-BOP results from the CCSD(T) values obtained at the LC-BOP geometry ("LC-BOP B", red circles).

the best performance with the smallest MAD and maximum deviation (2.7 kcal/mol).

III.2. Vertical Detachment Energies. Table 3 summarizes the VDE of each isomer calculated by B3LYP, LC-BLYP, LC-BOP, MP2, and CCSD(T). The deviations are estimated from the reference CCSD(T) values and plotted in Figure 5. As reported in the previous studies,[26,40] B3LYP yields an overly bound excess electron and results in an excessively large MAD, 238.3 meV. Figure 5 shows that B3LYP overestimates the VDE of all types of isomer, though the errors are relatively larger than the others for the internal states. Since B3LYP mixes only a constant fraction of the HF exchange irrespective of the electron−electron distance, it underestimates the exchange repulsions in the long-range region. The lack of exchange repulsions leads to an excess electron bound too strongly in the B3LYP calculations.

The most notable feature in Figure 5 is that the long-range correction leads to a substantial improvement over B3LYP in predicting the VDE for all types of isomers. The LC-BOP results are in excellent agreement with the CCSD(T) values at the MP2 geometries: the MAD is 35.2 meV ("LC-BOP A" in Figure 5). The deviations are further reduced when the results are compared to the CCSD(T) values at the LC-BOP geometries: the MAD is 13.8 meV ("LC-BOP B" in Figure 5). This result indicates that the deviations in LC-BOP A are mainly due to the structural differences between MP2 and LC-BOP. Note that LC-BOP yields slightly longer OH···O distance than MP2 does as discussed in the previous subsection. Figure 5 shows that the LC-BOP B results are superior to the MP2 results, indicating that LC-BOP is capable of predicting an accurate VDE for a given geometry. The surprisingly accurate prediction of LC-BOP is highly satisfactory in view of its low computational cost.

Figure 5 shows that the deviations of the LC-BLYP results are rapidly ever-increasing in terms of the VDE values. Although LC-BLYP yields good results for the isomers having weakly bound electron such as isomer (D), the results for the others having large VDE are found with larger deviations. In particular, LC-BLYP recovers only a small fraction of the B3LYP errors for 4I (12%) and 5I (15%) isomers. Furthermore, LC-BLYP gives a worse result for 6I than B3LYP. The drawback of LC-BLYP may be attributed to the LYP correlation functional. It has been proven that the LYP functional violates several fundamental conditions for the correlation energy. The most serious one above all is the condition for rapidly varying limit of the density, which may be of particular importance in describing a spatially extent, excess electron. In contrast, the OP functional satisfies all the fundamental conditions including the one for the rapidly varying density.[63] The present result

TABLE 4: Vertical Detachment Energies of the Water Cluster Anions Calculated by the LC-BOP Method Using Various Types of Basis Sets[a]

	adz+diff	atz+diff2	6-31(1+3+)G*[b]	6-31(2+3+)G*[b]	6-311(2+3+)G(d,p)[b]	6-311(2+3+)G(2df,2pd)[b]	6-311(2+3+)G(3df,3pd)[b]
N_{bf}[c]	47	100	28	32	44	72	83
2L	27.7	30.0	47.8	56.3	48.6	31.3	28.3
3L	160.6	159.7	188.9	201.0	188.2	162.7	159.0
4L	283.1	281.3	322.1	333.7	317.4	286.1	281.9
5L	337.8	335.9	368.7	382.0	366.8	339.2	336.6
6L	425.8	423.5	463.1	477.4	459.7	427.9	424.7
MAD[d]	1.8		32.0	44.0	30.1	3.4	1.0
3AA	202.0	201.1	262.8	272.6	254.8	210.9	202.2
4AA	373.1	370.1	446.2	446.8	423.8	379.2	372.7
5AA-1	365.9	364.0	435.5	443.2	420.5	373.6	365.9
5AA-2	408.3	406.3	475.7	478.9	458.8	414.6	408.7
6AA-1	634.0	634.1	739.3	742.5	714.3	648.9	638.6
6AA-2	507.0	503.9	589.4	588.4	563.8	513.9	506.8
MAD[d]	1.8		78.2	82.1	59.4	10.3	2.6
3I-1	227.3	235.3	331.1	363.3	334.0	258.4	244.5
3I-2	197.5	200.2	233.1	276.4	268.4	215.2	196.8
4I	488.7	489.1	596.2	609.7	575.2	504.0	494.4
5I	516.4	520.7	622.9	641.3	604.7	534.9	524.4
6I	922.1	919.7	1052.5	1061.2	1016.8	934.1	925.3
MAD[d]	3.6		94.2	117.4	86.8	16.3	5.4
3D	−8.6	−6.4	6.6	14.1	8.0	−6.7	−9.9
4D	21.2	23.3	32.3	43.3	35.7	19.0	15.6
5D	18.2	21.0	37.6	42.9	35.3	19.4	16.1
6D	58.0	58.9	85.4	92.6	82.9	62.1	58.1
MAD[d]	2.0		16.3	24.0	16.3	2.4	4.2

[a] The geometry obtained at the LC-BOP/adz+diff level is employed. Units in meV. [b] See ref 40 for more details about these basis sets. [c] The number of basis functions for water molecule. [d] Mean absolute deviations from the LC-BOP/atz+diff2 results.

clearly demonstrates that an appropriate correlation functional should be used for studying water cluster anions.

Although LC-BOP produces remarkable improvements in VDE calculations, it is found that the VDEs of isomer (D) are systematically underestimated by 20−30 meV. This error, though small in magnitude, may cause a qualitatively different result since these isomers typically have small VDEs. For example, LC-BOP gives the VDE of 3D as −8.6 meV, whereas CCSD(T) estimates 5.7 meV. In these isomers, the excess electron weakly trapped to the cluster extends farther away from the water molecules compared to other types of cluster (see Figure 4). Thus, the discrepancy may be attributed to the near-sightedness of the correlation functional which relies on the generalized gradient approximation (GGA). Note that the weak intermolecular interaction between dispersion complexes is not reproduced by current GGA-based functionals and requires an additional van der Waals type of functional for its correct description.[69−72] Nonetheless, the discrepancy is not prominent in other isomers having larger VDE, where the relevant interactions are more local. We, therefore, conclude that LC-BOP is sufficiently accurate to predict the VDE of water cluster anions.

It is interesting that MP2 and LC-BOP (and all DFTs) give the error in an opposite direction. This feature has been previously investigated by Herbert and Head-Gordon.[40,41] They reported that the MP2 results based on HF and DFT (BHLYP functional) orbitals brackets the CCSD(T) value, providing the lower and upper bound to the VDE, respectively. Furthermore, they found that increasing the portion of the HF exchange integrals of the BHLYP functional leads to a decrease in the calculated VDE, which, at some point, turns the sign of the error from plus to minus. We observed a similar tendency by varying the parameter μ of the error function which controls the amount of the HF exchange in the middle-range: for example, the use of $\mu = 0.47$ led to an underestimation of VDE by 74 meV in average. Thus, the present LC-BOP results with $\mu = 0.33$ may be fortuitous to some extent given that the calculated VDE is sensitive to the value of μ. A subtle balance between the HF integrals and the DFT functionals is crucial for an accurate prediction of VDE. We will investigate this point in our future work using a more elaborate scheme of the long-range correction.[76]

III.3. Calibration of the Basis Sets. Herbert and Head-Gordon[40] have previously calculated the VDE of water cluster anions using various types of extended Pople-type bases sets.[73−75] As a result they concluded that 6-31(1+,3+)G* was the most cost-effective one based on their finding that higher angular momentum basis functions were relatively unimportant for calculating the VDE. Note that adz+diff allocates 47 functions on a water molecule, whereas 6-31(1+3+)G* allocates only 28. Thus, the latter is computationally more feasible than the former. However, we show in the following that 6-31(1+3+)G* gives a large error in predicting the VDE of isomers (AA) and (I).

A series of extended Pople-type basis sets was derived using a factor of 3.32[41] to decrement the "+" basis sets; (2+3+) allocated two s-functions on hydrogen with exponents of 1.08×10^{-2} au and 3.27×10^{-3} au and one sp-function on oxygen with 2.55×10^{-2} au, whereas (1+3+) allocated the extra diffuse functions only on hydrogen. The aug-cc-pVTZ basis set was also employed with extra diffuse functions (denoted atz+diff2), having one s-function for hydrogen with an exponent of 7.44×10^{-3} au in addition to the "diff" set in adz+diff. The VDEs were estimated at a geometry optimized at the LC-BOP/adz+diff level. We have preliminary checked the structural effect by comparing the VDE results obtained from the LC-BOP/6-31(1+3+)G* geometries and found that it was not essential. The calculated VDEs using the basis sets mentioned above are listed in Table 4. The atz+diff2 result is employed as a reference value in the following.

TABLE 5: Calculated and Experimental VDE of the Water Cluster Anions ($n = 2-6$) in meV

n	isomer	LC-BOP/ adz+diff	CCSD(T)/ adz+diff	exptl
2	2L	27.7	28.6	50 ± 30,[a] 45 ± 6[b]
3	3L	160.6	146.2	130 ± 30,[a] 142 ± 7[c]
4	4AA	373.1	336.1	350 ± 20[d]
				250[d,e]
	4D	21.2	48.5	60[d]
5	5AA-2	408.3	376.3	410 ± 30[a]
6	6AA-2	507.0	477.1	480 ± 30[a]
	6D[f]	58.0	104.2	210 ± 30[a]

[a] Ref 10. [b] Ref 5. [c] Ref 7. [d] Ref 11. [e] Not calculated in this study. It is assigned to a ring isomer with an AA-water. See ref 11 for more details. [f] Assigned to 6D by the infrared spectrum (ref 17).

As shown in Table 4, the 6-31(1+3+)G* basis sets produce reasonably accurate VDEs for isomers (L) and (D) with MADs of 32.0 and 16.3 meV, respectively. This result is consistent with the findings in the previous study, where an error of ~50 meV is admitted.[40] However, the VDEs of isomers (AA) and (I) are found with larger deviations of 78.2 and 94.2 meV in the MAD, respectively. In particular, excessively large errors of more than 100 meV are detected for most of the isomers in isomer (I). This result indicates that the 6-31(1+3+)G* basis set is unable to hold a consistent accuracy between different types of isomer due to imbalances in the basis set. 6-31(2+3)G*, which allocates an extra diffuse basis function also on an oxygen atom, makes the result even worse. We have tested the addition of more diffuse functions decremented by the factor of 3.32, but the resulting VDEs were not essentially improved: the change in the VDE was less than 10 meV. Only with the use of split valence functions of triple-ζ quality as well as higher angular momentum polarization functions does the resulting VDE converge to the atz+diff2 values. The largest basis set, 6-311(2+3+)G(3df,3pd), induces small deviations with a maximum of merely 9.2 meV for 3I-1.

In contrast, the use of the adz+diff basis set renders a nearly convergent result for all types of isomers. The calculated VDEs of adz+diff are in excellent agreement with the atz+diff2 values with minuscule deviations of less than 5 meV. The accuracy of the adz+diff basis is comparable to that of the 6-311(2+3+)G(3df,3pd) basis, even though the number of basis functions is much smaller (47 vs 83 per water molecule). Thus, the adz+diff basis set, which was first proposed by Kim et al.,[36] is reliable for computing the VDE of water cluster anions.

III.4. Comparison with Experiment. In this section, we present some brief remarks on the related experimental data. The VDEs of water cluster anions in the range of $n = 2-6$ have been measured by Johnson and co-workers,[10,11] and others.[5,7] In Table 5, the observed VDEs are compared with the present theoretical results. It is found that both LC-BOP and CCSD(T) results accurately reproduce the observed VDEs within the experimental error bar, attesting to the validity of the present theoretical scheme. The only exception is found for 6D: the VDE calculated by CCSD(T) as 104.2 meV deviates significantly from the experimental value of 210 meV. The small VDE seems plausible since 6D should weakly capture the electron through aligned, dangling OH bonds. Note that isomer (D) gives a VDE of less than 100 meV. Furthermore, LC-BOP underestimates the VDE of CCSD(T) by 46 meV: this tendency is also found in the other isomers of this type. Therefore, we suspect that the second hexamer may have been incorrectly assigned to 6D. This isomer has been recently assigned to 6D based on the fact that the experimental and computed vibrational spectra agree very well.[17] A possible candidate would be another book-shape isomer having an AA-water that renders a similar IR band and a VDE as large as 210 meV. However, we have not been successful in identifying such an isomer so far. Recent theoretical work by Sommerfeld et al.[30] based on a Drude model has predicted that cagelike isomers are more stable than 6AA-2 possessing a VDE around 200 meV. These isomers may also be a strong candidate. We leave the assignment of the second hexamer an open question.

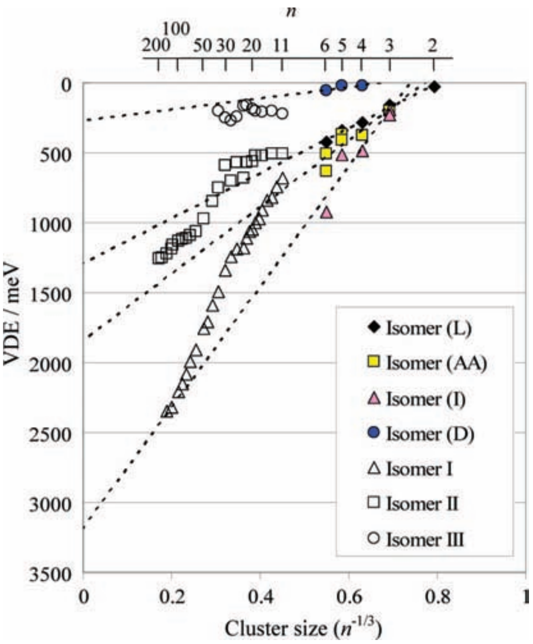


Figure 6. Plots of the vertical detachment energy (VDE) with respect to the cluster size ($n^{-1/3}$). The VDEs of isomers (L) (black diamonds), (AA) (yellow squares), (I) (pink triangles), and (D) (blue circles) obtained by the LC-BOP method in the range of $n = 2-6$ are extrapolated to the limit in the bulk indicated by the broken lines. The experimental VDEs of isomers I (open triangles), II (open squares), and III (open circles) in the range of $n = 11-200$ taken from ref 12 are also plotted.

It is interesting to note that the observed isomer is not always the most stable one. In the trimer, for example, 3D is not observed even though it is more stable than 3L by ~2 kcal/mol. In the tetramer, the most stable isomer 4D does appear in the spectrum, but the main large peak is 4AA which is less stable than 4D by as much as 3−4 kcal/mol. The type of the produced cluster is not necessarily determined by its stability but sensitively depends on the condition in which the clusters are formed. In a recent experimental study[12] it has been verified that the temperature of the cluster is an important factor that leads to the production of different anionic isomers controlled by a different source backing pressure. Recent theoretical works[29,30,43] have also indicated that the nonequilibrium nature of the cluster is essentially important to identify the isomers sampled by the experiment and that dynamics must be explicitly taken into account.

We may thus take the liberty to plot the VDE of all the isomers studied in this work with respect to the size of the cluster ($n^{-1/3}$) and examine the behavior of each electron binding motif in the limit of the bulk, as shown in Figure 6. It is notable that the VDE of isomer (I) is extrapolated in the limit to 3.19 eV, which is surprisingly close to the photoelectric threshold of water, 3.2 eV. In Figure 6, the VDEs of three types of isomers (I, II, and III) in the range of $n = 11-200$ found in the photoelectron experiment[12] are also plotted. It is clearly seen that the VDEs of the isomer III are extrapolated from those of the isomer (D), indicating that the isomer III may be a cluster having an excess electron trapped by dangling OH bonds. It seems that the isomer II is a linear cluster in the range of $n = 11-30$ and suddenly transits to a different type of cluster having an excess electron trapped by the AA-water. The VDE of isomer I initially follows the line of isomer (AA) but gradually grows closer to the line of isomer (I). This result may indicate that the transition from surface to internally solvated state occurs in the range of $n = 30-100$. Of course, an extrapolation of only a small portion of data to the limit of bulk size would not lead to an ultimate conclusion and further investigation is needed in the midsize regime. This will be the scope of our future work.

IV. Conclusions

The LC-DFT is applied to a series of water cluster anions ($n = 2-6$), and its capability to predict the VDE is examined. The calculated VDEs are compared with that of hybrid DFT (B3LYP) and ab initio electron correlation theories (MP2 and CCSD(T)). It is found that the long-range exchange repulsions are crucial for a quantitative prediction of the VDE. B3LYP, which does not sufficiently incorporate them, gives an overly bound excess electron significantly overestimating the VDE. The LC scheme combined with the BOP functional is shown to clearly solve this problem, providing substantially improved results. The VDEs predicted by the LC-BOP method are in excellent agreement with the CCSD(T) values with a MAD of 13.7 meV. For clusters with large VDEs, LC-BLYP results are found to be less accurate due to the deficiency in the correlation functional. The LYP correlation functional violates the condition of the correlation energy in the rapidly varying limit of the density. The OP functional, on the other hand, satisfies all the fundamental conditions and, thus, is one of the best candidates for correlation functional. We conclude that LC-BOP provides an accurate description of water cluster anions by properly accounting for electron correlation as well as long-range exchange interactions that are of critical importance to describe the spatially extent, excess electron.

The accuracy of the extended Pople-type basis sets [6-31(1+3+)G*][40] in predicting the VDE is also investigated. The 6-31(1+3+)G* basis set is found to yield reasonably accurate results for isomers (L) and (D), as indicated in the previous study. However, a large error is observed for isomers (AA) and (I) with MADs of 78.2 and 94.2 meV, respectively. It is found that a high-quality basis set is needed to recover the accuracy, i.e., 6-311(1+3+)G(3df,3pd). On the other hand, the aug-cc-pVDZ basis set with extra diffuse functions (adz+diff) renders a compact and reliable representation for all types of electron binding motifs studied in this work.

The VDEs computed by LC-BOP and CCSD(T) are found to be in good agreement with the corresponding experimental values except for 6D, indicating that the second hexamer may have been misassigned. The variation of VDE with respect to the cluster size is also examined for each electron binding motif, which is found to resemble that of isomers I, II, and III detected experimentally.[12] In order for a clear assignment of the observed isomers, further work in the midsize regime is now in progress.

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Supporting Information Available: Structure of the water cluster anions studied in this work obtained by the MP2 and LC-BOP method with the use of adz+diff basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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