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Application of the Electrostatically Embedded Many-Body Expansion to Microsolvation of Ammonia in Water Clusters

Anastassia Sorokin, Erin E. Dahlke, and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute,
University of Minnesota,
Minneapolis, Minnesota 55403-0431

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Abstract: The electrostatically embedded many-body expansion (EE-MB), at both the second and third order, that is, the electrostatically embedded pairwise additive (EE-PA) approximation and the electrostatically embedded three-body (EE-3B) approximation, are tested for mixed ammonia–water clusters. We examine tetramers, pentamers, and hexamers for three different density functionals and two levels of wave function theory. We compare the many-body results to the results of full calculations performed without many-body expansions. Because of the differing charge distributions in the two kinds of monomers, this provides a different kind of test of the usefulness of the EE-MB method than was provided by previous tests on pure water clusters. We find only small errors due to the truncation of the many-body expansion for the mixed clusters. In particular, for tests on tetramers and pentamers, the mean absolute deviations for truncation at second order are 0.36–0.98 kcal/mol (average: 0.66 kcal/mol), and the mean absolute deviations for truncation at third order are 0.04–0.28 kcal/mol (average: 0.16 kcal/mol). These may be compared to a spread of energies as large as 4.24 kcal/mol in the relative energies of various structures of pentamers and to deviations of up to 8.57 kcal/mol of the full calculations of relative energies from the best estimates of the relative energies. When the methods are tested on hexamers, the mean unsigned deviation per monomer remains below 0.10 kcal/mol for EE-PA and below 0.03 kcal/mol for EE-3B. Thus the additional error due to the truncation of the expansion is small compared to the accuracy needed or the other approximations involved

in practical calculations. This means that the EE-MB expansion in combination with density functional theory or wave function theory for the oligomers provides a useful practical model chemistry for making electronic structure calculations and simulations more affordable by improving the scaling with respect to system size.

1. Introduction

The accurate calculation of energies and other characteristics of large systems is a challenging physical and chemical problem. Molecular mechanics is able to treat large systems but does not provide sufficient accuracy for many problems. On the other hand, more accurate post Hartree–Fock methods (such as MP2, CCSD, or CCSD(T)) and density functional theory (DFT) are very expensive (relative to molecular mechanics) and their computational cost increases quickly with the system size (for example CCSD(T) scales as N^7 , where N is the number of atoms in this system), which make applications of these methods to very large systems impractical.

Recently, the electrostatically embedded many-body (EE-MB) method was developed.¹ This method is similar to methods developed by Kitaura and Fedorov^{2,3} and Hirata et al.⁴ but is easier to apply; in particular the method was formulated in such a way that it is very easy to calculate energy gradients. In the EE-MB method, the system is divided into fragments (typically dimers or trimers), and each fragment is treated in a field of point charges representing the electrostatic potential of the other fragments. The locations of the point charges depend on the geometry of the other fragments, but the magnitudes do not. (Generalizations to more complicated prescriptions for the point charges are possible but will not be considered in the present work.) It was shown in previous work^{1,5} that the three-body version (EE-3B) of EE-MB with this simple prescription for the electrostatics, when applied to water clusters containing 5–21 water molecules, yields a mean error less than 0.4 kcal/mol for all levels of theory examined.

Small $\text{NH}_3(\text{H}_2\text{O})_n$ clusters play an important role in atmospheric aerosol formation.^{6,7} $\text{NH}_3(\text{H}_2\text{O})_n$ and similar complexes have been extensively studied both experimentally^{8–11} and theoretically,^{12–16} and in the present article we have applied the EE-MB method to calculate total energies of such clusters with $n = 3–5$. The calculations were done with three density functionals (PBE, B3LYP, and M06-2X) and two wave function methods (MP2 and CCSD(T)) with various basis sets. The accuracies of the EE-PA (two-body) and EE-3B (three-body)

* Corresponding author e-mail: truhlar@umn.edu.

Table 1. Sets of Charges Used in the Present Calculations

	ammonia		water	
	q_N	q_H	q_O	q_H
M1	-0.867	0.289	-0.690	0.345
M2	-0.908	0.303	-0.716	0.358
M3	-0.953	0.318	-0.749	0.374
CM4	-0.906	-0.302	-0.648	0.324

Table 2. Relative Energies (kcal/mol) Predicted by Full Calculations of Tetramers: $\text{NH}_3(\text{H}_2\text{O})_3^c$

	B	C	D	E
PBE/DZ	5.01	6.27	14.31	9.11
PBE/TZ	3.77	5.28	12.07	7.77
B3LYP/DZ	4.29	5.75	7.42	7.91
B3LYP/6-311+G(d,p) ^a	3.97	5.75	6.91	7.36
B3LYP/TZ	3.30	4.80	6.23	6.78
M06-2X/DZ	3.80	3.72	6.92	7.28
M06-2X/TZ	2.60	2.90	5.64	6.10
MP2/DZ	4.15	4.75	6.83	7.19
MP2/6-311+G(d,p) ^a	4.03	4.70	6.60	7.00
MP2/TZ	3.32	3.91	6.02	6.53
CCSD(T)/DZ	3.87	4.58	6.45	6.85
QCISD(T)/6-311+G(d,p) ^a	3.79	4.52	6.32	6.74
extrapolated ^b	3.08	3.73	5.74	6.27

^a Reference 16. ^b Best estimate obtained by eq 1. ^c All energies are relative to the isomer A.

Table 3. Relative Energies (kcal/mol) Predicted by Full Calculations of Pentamers: $\text{NH}_3(\text{H}_2\text{O})_4^c$

	B	C	D	E
PBE/DZ	2.06	0.95	2.62	4.24
PBE/TZ	1.15	0.65	2.12	3.43
B3LYP/DZ	2.09	0.92	2.40	4.18
B3LYP/6-311+G(d,p) ^a	1.94	0.77	2.25	4.12
B3LYP/TZ	1.12	0.003	2.01	3.36
M06-2X/DZ	1.71	0.79	1.17	3.41
M06-2X/TZ	1.50	0.94	1.85	3.37
MP2/DZ	0.80	0.66	1.52	3.29
MP2/6-311+G(d,p) ^a	0.75	0.85	1.59	3.33
MP2/TZ	-0.09	0.14	0.97	2.34
CCSD(T)/DZ	0.84	0.68	1.52	3.46
QCISD(T)/6-311+G(d,p) ^a	0.42	0.69	1.37	3.18
extrapolated ^b	-0.42	-0.02	0.75	2.19

^a Reference 13. ^b Best estimate obtained by eq 1. ^c All energies are relative to the isomer A.

versions of EE-MB were ascertained by comparison to full calculations, i.e., calculations that do not employ a many-body expansion.

2. Computational Details

All calculations in this paper were carried out using the *MN-GFM* module version 3.0 for incorporation of new DFT models into *Gaussian03*.¹⁷

The starting geometries of ammonia–water clusters $\text{NH}_3(\text{H}_2\text{O})_n$ with $n = 3, 4$ were taken from Bacelo,¹⁶ who optimized them at the MP2/6-311+G** level. We reoptimized these structures with the PBE,¹⁸ B3LYP,^{19–22} and M06-2X²³ functionals and the MP2²⁴ post Hartree–Fock method with the 6-311++G(2d,2p) basis set. (The M06-2X functional was recently found to be very accurate for main-group thermochemistry and kinetics and for noncovalent interactions.²³) EE-PA and EE-3B calculations were carried out with each of the methods with geometries optimized by the full

Table 4. Mean Unsigned Deviations (kcal/mol) from Full Calculations for Four Models of Point Charges for Five Tetramers $\text{NH}_3(\text{H}_2\text{O})_3$ and Five Pentamers $\text{NH}_3(\text{H}_2\text{O})_4^a$

	M1	M2	M3	CM4
	EE-PA			
PBE/DZ	0.85	0.75	0.63	0.98
PBE/TZ	0.72	0.61	0.50	0.45
B3LYP/DZ	0.81	0.69	0.58	0.93
B3LYP/TZ	0.64	0.54	0.47	0.77
M06-2X/DZ	0.71	0.62	0.52	0.83
M06-2X/TZ	0.54	0.48	0.36	0.71
MP2/DZ	0.76	0.66	0.60	0.85
MP2/TZ	0.71	0.62	0.51	0.83
	EE-3B			
PBE/DZ	0.21	0.20	0.18	0.22
PBE/TZ	0.23	0.22	0.20	0.24
B3LYP/DZ	0.12	0.12	0.11	0.12
B3LYP/TZ	0.18	0.19	0.19	0.17
M06-2X/DZ	0.27	0.26	0.26	0.28
M06-2X/TZ	0.16	0.15	0.14	0.17
MP2/DZ	0.08	0.07	0.06	0.08
MP2/TZ	0.06	0.05	0.04	0.06

^a Deviations in absolute electronic energies averaged over ten structures.

Table 5. Mean Unsigned Errors (in kcal/mol) from Full Calculations of the Relative Energies for Four Models of Point Charges for Tetramers $\text{NH}_3(\text{H}_2\text{O})_3^a$

	M1	M2	M3	CM4
	EE-PA			
PBE/DZ	0.85	0.79	0.72	0.92
PBE/TZ	0.86	0.79	0.73	0.92
B3LYP/DZ	0.42	0.39	0.35	0.47
B3LYP/TZ	0.39	0.35	0.31	0.43
M06-2X/DZ	0.31	0.28	0.24	0.34
M06-2X/TZ	0.24	0.21	0.17	0.28
MP2/DZ	0.25	0.18	0.26	0.29
MP2/TZ	0.25	0.22	0.18	0.28
CCSD(T)/DZ	0.28	0.25	0.24	0.32
	EE-3B			
PBE/DZ	0.13	0.12	0.11	0.13
PBE/TZ	0.12	0.12	0.11	0.13
B3LYP/DZ	0.05	0.04	0.04	0.05
B3LYP/TZ	0.05	0.05	0.04	0.06
M06-2X/DZ	0.09	0.09	0.08	0.09
M06-2X/TZ	0.08	0.07	0.07	0.08
MP2/DZ	0.03	0.03	0.04	0.04
MP2/TZ	0.02	0.02	0.01	0.02
CCSD(T)/DZ	0.04	0.04	0.04	0.05

^a Averaged over ten pairs of structures.

calculations with the corresponding method. The calculations, including new geometry optimizations, were then repeated with the 6-31+G(d,p) basis set. EE-PA and EE-3B calculations with the CCSD(T)/6-31+G(d,p)²⁵ calculations were performed with the geometries optimized with B3LYP/6-311++G(2d, 2p) method.

Bacelo¹⁶ noted that the geometry of $\text{NH}_3(\text{H}_2\text{O})_n$ clusters with small n are similar to the geometries of stable water clusters. Therefore two starting geometries of $\text{NH}_3(\text{H}_2\text{O})_5$ were generated from the geometries of water hexamers (cage and ring), taken from the *The Cambridge Cluster Database*,²⁶ and one water molecule in each hexamer was replaced by an ammonia molecule. The resulting structures were optimized with the PBE, B3LYP, and M06-2X functionals and the MP2 method, all with

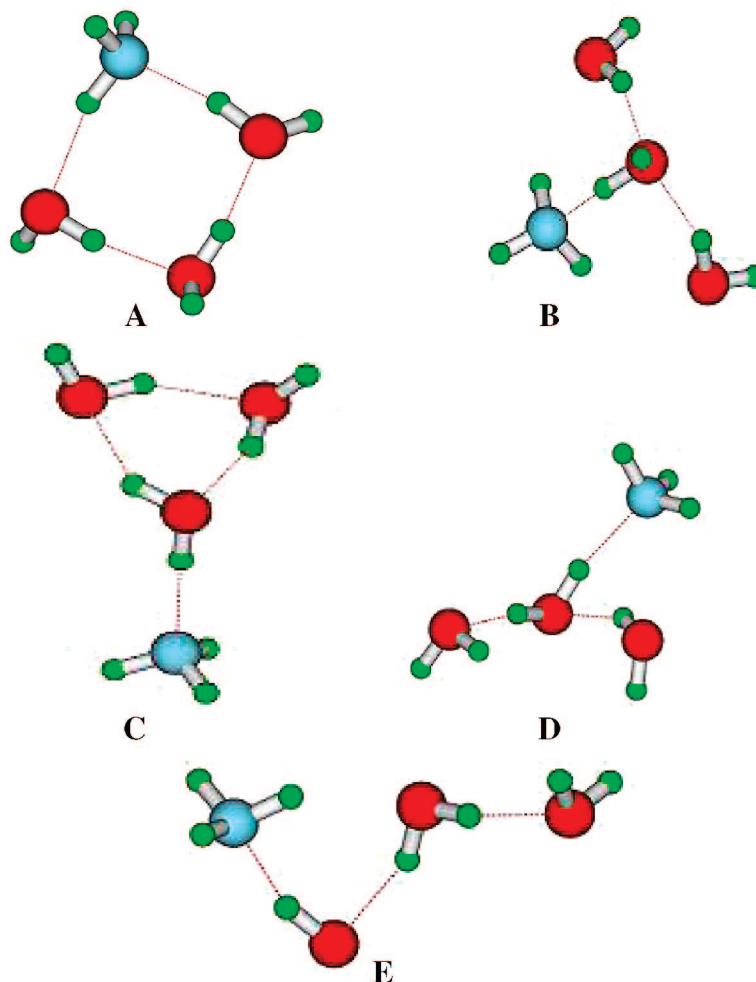


Figure 1. Structural isomers of $\text{NH}_3(\text{H}_2\text{O})_3$ (tetramers) used in this work.

Table 6. Mean Unsigned Errors (kcal/mol) from Full Calculations of the Relative Energies for Four Models of Point Charges in Pentamers $\text{NH}_3(\text{H}_2\text{O})_4$ ^a

	M1	M2	M3	CM4
EE-PA				
PBE/DZ	0.69	0.67	0.64	0.68
PBE/TZ	0.79	0.78	0.76	0.81
B3LYP/DZ	0.63	0.64	0.65	0.62
B3LYP/TZ	0.41	0.36	0.60	0.44
M06-2X/DZ	0.30	0.30	0.30	0.28
M06-2X/TZ	0.28	0.28	0.27	0.29
MP2/DZ	0.30	0.29	0.27	0.32
MP2/TZ	0.18	0.17	0.16	0.21
EE-3B				
PBE/DZ	0.21	0.20	0.18	0.22
PBE/TZ	0.23	0.21	0.22	0.23
B3LYP/DZ	0.31	0.32	0.31	0.32
B3LYP/TZ	0.16	0.16	0.16	0.16
M06-2X/DZ	0.11	0.10	0.10	0.11
M06-2X/TZ	0.10	0.10	0.09	0.11
MP2/DZ	0.09	0.08	0.08	0.08
MP2/TZ	0.05	0.04	0.04	0.05

^a Averaged over ten pairs of structures.

the 6-311++G(2d,2p) basis set. EE-PA and EE-3B calculations were also carried out for these hexamers.

The EE-PA and EE-3B calculations were tested with 4 sets of charges listed in Table 1. The three sets of charges M1, M2, and M3 were calculated respectively with PBE, B3LYP, and

Table 7. Mean Unsigned Deviations (kcal/mol) for Hexamers $\text{NH}_3(\text{H}_2\text{O})_5$ for Four Models of Point Charges in the EE-3B Approximation Calculated with the TZ Basis Set^a

	M1	M2	M3	CM4
EE-PA				
PBE	0.66	0.58	0.53	0.70
B3LYP	0.75	0.73	0.61	0.86
M06-2X	0.55	0.50	0.39	0.63
MP2	0.62	0.59	0.49	0.69
EE-3B				
PBE	0.35	0.34	0.33	0.37
B3LYP	0.09	0.09	0.06	0.10
M06-2X	0.35	0.34	0.34	0.36
MP2	0.09	0.09	0.08	0.10

^a Deviations in absolute electronic energies averaged over two structures.

MP2, in each case using the ChelpG scheme²⁷ on the monomers and the 6-311++G(2d,2p) basis set. The last set of charges, CM4, was calculated with the CM4 charge model²⁸ using B3LYP/6-31+G(d,p) on monomers. In our original test² (for pure water clusters), we found that the best results were obtained with $q_{\text{O}} = -0.778$ and $q_{\text{H}} = -0.834$. Of the four sets of charges in Table 1, the M3 set has the value of q_{O} that is closest to these values. Thus we shall consider the M3 set to be our primary test set, and the results for the other three sets of charges

should be considered just as a way to show the sensitivity or insensitivity to choice of charge set.

In the rest of this article and in all tables, the 6-31+G(d,p) basis will be abbreviated DZ, and the 6-311++G(2d,2p) basis will be abbreviated TZ. In the rest of the article the combination of a density functional and a basis set or of a wave function method and a basis set will be called a level.

We obtain our best estimates of the energy E by a standard type of extrapolation procedure, namely

$$E(\text{extrap}) = \text{QCISD(T)}/6\text{-}311\text{+G(d,p)} + \text{MP2}/\text{TZ} - \text{MP2}/6\text{-}311\text{+G(d,p)} \quad (1)$$

3. Results and Discussion

3.1. Full Calculations of Tetramers and Pentamers. Tables 2 and 3 show the energies (relative to the ring configuration) of the structures of the tetramers and pentamers used in this paper as calculated at various levels of theory.

The results calculated with DFT are very sensitive to the basis set. In the case of tetramers the energies calculated with the small DZ and 6-311+G(d,p) basis sets are closer to the CCSD(T)/DZ values calculated here and to the QCISD(T)²⁹/6-311+G(d,p) results taken from ref 16 than are the energies calculated with the larger TZ basis set.

As was found previously for small water clusters,¹ the results obtained by MP2 and CCSD(T) are in semiquantitative agreement with each other in our calculations. The differences, with the DZ and 6-311+G(d,p) basis sets, do not exceed 0.38 kcal/mol in either Table 2 or Table 3. The energy ordering of tetramers agrees for all the methods except PBE and M06-2X; PBE is the only method that finds structure E to be more favorable than D, and M06-2X predicts structure C to be lower in energy than D, and M06-2X predicts structure C to be lower in energy than D. The results of the B3LYP and M06-2X methods with the DZ basis set are close to MP2, CCSD(T)/DZ, and QCISD(T)/6-311+G(d,p) for the B and D structures, but for the C structure the results differ by more than 1 kcal/mol.

In the case of pentamers the extrapolated calculation predicts that structure B is the lowest-energy structure, but most nonextrapolated calculations predict that the energy of the ring configuration A is lower. The reason why density functional theory and wave function theory give different trends is unknown. However the main focus of the present study is how well the EE-MB for a given level reproduces a full calculation for a given level, not the accuracies of the individual levels. The EE-MB is considered useful if it can reproduce a full calculation at a given level with a mean deviation smaller than a reasonable expectation of the error in the full calculation.

3.2. EE-MB Results for Absolute Energies of Tetramers and Pentamers. In order to evaluate the usefulness of the electrostatically embedded many-body method in the case of ammonia–water clusters, we compare their predicted energies to the results of the full calculations at each level of theory. Table 4 shows the mean unsigned deviations (MUDs) between the electrostatically embedded two- and three-body calculations for tetramers and pentamers and the full calculations. As was anticipated from studies of pure water clusters¹ the errors of the EE-PA calculations are 5–10 times larger than the errors of EE-3B calculations. Additional tables given in the Supporting

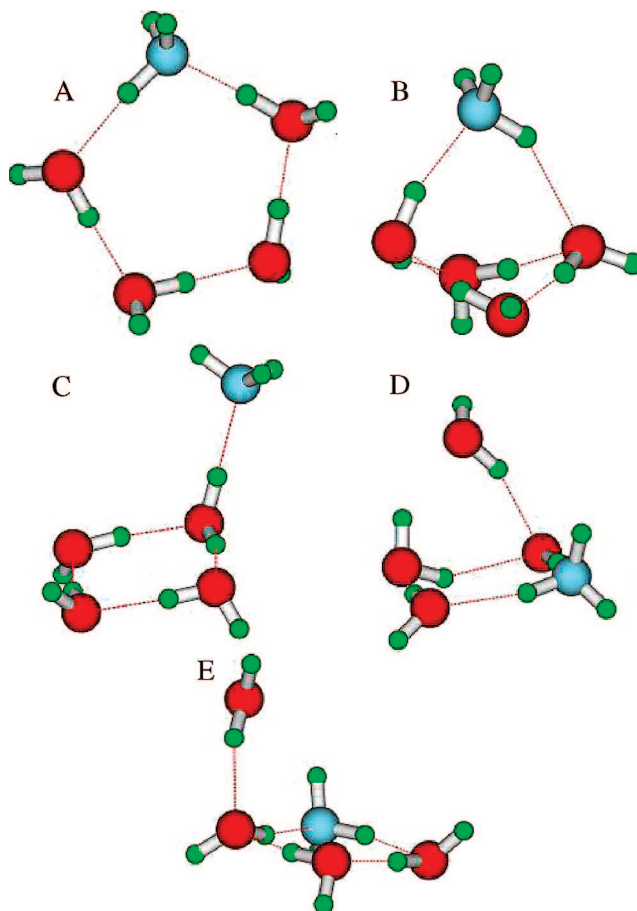


Figure 2. Structural isomers of $\text{NH}_3(\text{H}_2\text{O})_4$ (pentamers) used in this work.

Information show that the errors in the pentamer energies are larger than the errors of the tetramers; for tetramers the MUDs with the M3 charge set do not exceed 0.10 kcal/mol per monomer for EE-PA and 0.023 kcal/mol per monomer for EE-3B; for pentamers these MUEs rise to 0.17 kcal/mol per monomer and 0.084 kcal/mol per monomer for EE-PA and EE-3B, respectively.

Almost all results show that the errors of calculations with M1 and CM4 charges are largest, while the calculations with M3 charges are the most accurate. That means that the electrostatically embedded many-body calculations of these mixed clusters are more accurate with larger charges on either kind of monomer. The EE many-body calculations for water clusters show the same trends.¹ It is, however, important to keep the comparison of charge models in context; that is, none of the charge models yields unacceptably large errors. In particular, the largest deviation in the MUD for any two sets of charges (at a given level of theory) never exceeds 0.35 kcal/mol at the EE-PA level of theory or 0.04 kcal/mol at the EE-3B level of theory.

3.3. EE-MB Results for Relative Energies of Tetramers and Pentamers. With five structures, there are ten pairs of structures, and it is interesting to test how well EE-MB can predict these relative energies. Table 5 shows the results for tetramers, and Table 6 shows them for pentamers. Both tables show the mean unsigned deviation of the electrostatically embedded pairwise and three-body calculations of relative energies as compared to full calculations at the same level. The

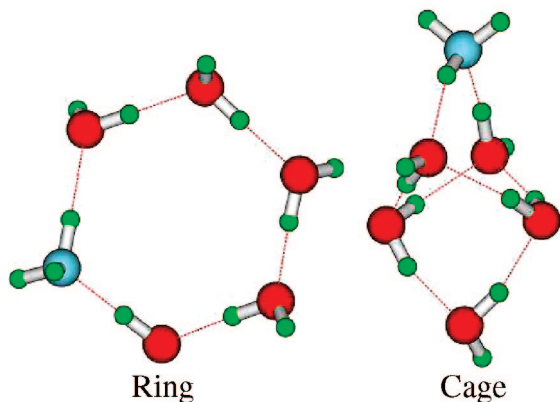


Figure 3. Structural isomers of $\text{NH}_3(\text{H}_2\text{O})_5$ (hexamers) used in this work.

M06-2X, MP2, and CCSD(T) methods show the best agreement. The magnitudes of the mean unsigned deviations are encouragingly small; with the M3 model charges the mean unsigned deviations are 0.16–0.76 kcal/mol (average: 0.41 kcal/mol) for EE-PA (top halves of Tables 5 and 6) and 0.01–0.31 kcal/mol (average: 0.10 kcal/mol) for EE-3B (lower halves of Tables 5 and 6).

Note that the deviations from the full result due to truncating the expansions at second order (top halves of Tables 5 and 6) are smaller than the typical deviation of the full calculations from the extrapolated ones in Tables 2 and 3, and the deviations due to truncating at third order (lower halves of Tables 5 and 6) are even smaller. Thus the combination of the truncated many-body expansions with DFT and/or MP2 calculations provides economical “model chemistries”^{30–33} that should be as useful as the untruncated DFT and MP2 calculations for many applications but at considerably reduced cost for large systems.

3.4. Full Calculations and EE-MB Results for Hexamers. The hexamer is the hardest test of the usefulness of EE-MB because the PA and 3B approximations omit the most interactions for these largest clusters. Our full calculations of the $\text{NH}_3(\text{H}_2\text{O})_5$ clusters show that the cage structure is more favorable than the ring one. The energies (in kcal/mol) of the cage geometry of the $\text{NH}_3(\text{H}_2\text{O})_5$ hexamer relative to the ring geometry as predicted by full calculations are -2.02 for PBE/TZ, -1.28 for B3LYP/TZ, -5.69 for M06-2X/TZ, and -2.96 for MP2/TZ. This shows that, of four full calculations, the M06-2X/TZ method predicts the largest energy gap between these two structures.

Table 7 shows that the EE-MB method agrees well with full calculations for the hexamer configurations. For the M3 charges, the MUD per monomer for hexamers does not exceed 0.10 kcal/mol per monomer for the EE-PA method and 0.055 kcal/mol per monomer for the EE-3B method. The results for hexamers show the same charge trend as was observed in tetramers and pentamers, namely that the deviation between the full and EE-MB calculation is smaller when the charges of all atoms in the water and ammonia molecules are larger, as in the M3 model charges. The EE-PA calculations with the M06-2X and MP2 methods show the best agreement with full calculations, while

for EE-3B calculations the B3LYP and MP2 show the smallest truncation errors.

4. Conclusions

The present test of the electrostatically embedded many-body method is an important step in its validation because we consider mixed clusters with the same kinds of choices for the charge models that were previously successful for pure water clusters. Furthermore, the polarization of ammonia has new aspects because it is nonplanar. Therefore, it is encouraging that our calculations show that the electrostatically embedded three-body approximation is very accurate for calculations of small ammonia–water clusters (tetramers, pentamers, and hexamers), and the electrostatically embedded pairwise additive approximation also provides useful accuracy. The success for clusters with mixed electrostatics, the good scaling properties of the pairwise and three-body approximations, the fact that the error per monomer does not increase when the size of the cluster increases, and our recent demonstration³⁴ that the truncated expansions can yield accurate and convenient gradients are all promising features for future applications to large systems.

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Supporting Information Available: Coordinates of the clusters and additional error tables (22 tables). This material is available free of charge via the Internet at <http://pubs.acs.org/floyd.lib.umn.edu>.

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