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Electrostatic Interactions Based upon Floating Basis ab Initio Calculations. The Water Pentamer

J. J. Dannenberg*,†

Department of Chemistry, City University of New York—Hunter College and The Graduate School, 695 Park Avenue, New York, New York 10021, and Departament de Química, Unitat de Química Fisica, Universtitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Sílvia Simon and Miquel Duran*

Institute of Computational Chemistry and Department of Chemistry, University of Girona, 17071 Girona, Catalonia, Spain

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Electrostatic interactions derived from floating basis HF/D95** ab initio calculations are presented for a tetrahedral water pentamer. Since floating basis ab initio calculations approximately satisfy the Hellmann−Feynman theorem, indicating that the forces on the nuclei can be calculated classically; and, since the wave function of the pentamer includes all polarization and mutual polarization effects, the intermolecular interactions can be calculated classically by using molecular properties extracted from the wave function of the aggregate. We compare classical interactions based upon floating basis functions, as well as analogous interactions based upon normal (nonfloating) Hartree−Fock calculations with supermolecular interaction energies and pairwise interactions. We also compare classical electrostatic calculations based upon interacting point charges with those based upon interactions of charges one molecule with the electric field of the others. We show that the latter method (which is free of penetration effects) coupled with the floating basis wave functions gives the supermolecular energy to 0.2 kcal/mol. The electrostatic interactions derived from the "normal" wave functions are significantly too strong. Point charge interactions for the "normal" wave functions are closer to the supermolecular interaction due to fortuitous approximate cancelation of the effects of penetration and the overestimation of the electrostatic interaction. We also show that the dipole moments of the possible dimers cannot be derived additively from the monomers, nor those of the pentamer from those of either the monomers or the dimers.

The Hellmann−Feynman theorem states that the forces on the nuclei can be calculated classically from the exact wave function.[1] Extension of this principle indicates that intermolecular interactions can be obtained classically from the exact wave functions of the monomeric units of an aggregate. The classical interactions will be entirely electrostatic[2] if the wave functions of the monomeric units reflect their electronic and nuclear distortions upon transformation from free monomers to the aggregate. Thus, electrostatic calculations based upon the exact wave function for the *aggregate* should correctly define the aggregation energy. Such calculations should be entirely pairwise additive. Most classical treatments are based upon properties derived from the monomeric unit. These are not properly pairwise additive as they do not account for polarization and mutual polarizations which are three-body and many-body effects, respectively.[3] However, molecular properties derived from the wave function of the aggregate will already include the effects of both kinds of polarization.

Unfortunately, most available approximate wave functions are not accurate enough for the Hellmann−Feynman theorem to be practically useful. However, several groups[4] have shown that floating bases provide calculations that satisfy this theorem reasonably well. Floating basis calculations allow the foci of the various shells of atomic basis functions to be different from the nucleus with which they are usually associated.

In this paper, we employ wave functions that reasonably satisfy the Hellmann−Feynman theorem to calculate a pentamer of water molecules. We accomplish this by using floating bases at the Hartree−Fock level.[5] In addition, we investigate the relaxation due to polarization in the aggregate and the various possible pairs. From the many water cluster calculations in the literature, we have chosen the tetrahedral pentamer considered by Hermansson[6] for ready comparison with the *n*-body interactions previously reported.

Methods

Using the Gaussian 92 program,[7] we performed ab initio calculations at the Hartree−Fock level using the D95** basis set. The "massage" and "bq" options allow one to obtain bare nuclei and shells of basis functions focused on a "nucleus" of zero charge. In some cases we constrained the entire atomic basis of an atom to float together, in others we allowed each spherically symmetrical shell[8] to individually float.

We performed three classes of calculations:

(A) Normal single-point Hartree-Fock (HF) calculations, without floating bases, designated no-float (**NF**).

(B) The water pentamer nuclei were frozen in the geometry previously reported. However, the bases could freely move. In this type of calculation, each monomeric water is polarized differently, except for W_4 and W_5, which are the same by symmetry. Three different levels of freedom were considered: (1) all basis functions move together, designated 1-center (**1C**); (2) all basis functions corresponding to the same valence orbital move together, designated valence-shell (**VS**); (3) each spherically symmetrical shell moves independently, designated all

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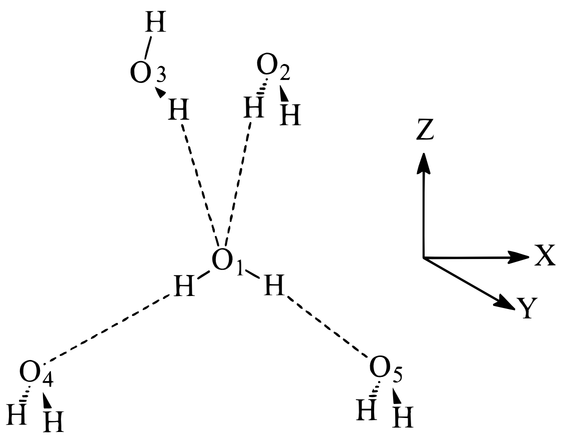

Figure 1. Geometry and Cartesian axes for the water pentamer. The numbers on the oxygens identify the specific monomers.

TABLE 1: Interaction Energies (kcal/mol) for Water Pentamer Calculated Using Different Methods[a]

	two-body	**qV**	**PC**	supermolecule
		NF		
W1	−13.77	−21.07	−15.56	
W2	−3.55	−5.69	−4.82	
W3	−5.39	−7.36	−6.61	
W4	−3.64	−4.25	−3.39	
W5	−3.64	−4.25	−3.39	
total/2	−14.99	−21.31	−16.88	−16.00
		1C		
W1	−13.80	−21.55	−16.34	
W2	−3.56	−5.90	−4.34	
W3	−5.40	−7.57	−6.14	
W4	−3.64	−4.31	−3.58	
W5	−3.65	−4.30	−3.58	
total/2	−15.03	−21.82	−16.99	−16.04
		VS		
W1	−13.76	−20.98	−15.29	
W2	−3.00	−5.70	−4.06	
W3	−4.85	−7.26	−5.69	
W4	−4.19	−4.13	−3.34	
W5	−4.19	−4.13	−3.34	
total/2	−14.99	−21.10	−15.86	−15.99
		AF		
W1	−12.36	−15.72	−6.06	
W2	−3.11	−2.31	−0.95	
W3	−4.50	−3.70	−2.42	
W4	−3.40	−3.73	−1.45	
W5	−3.40	−3.72	−1.45	
total/2	−13.39	−14.59	−6.16	−14.42

[a] The value for each water (W1−5) represents the sum of its interactions with the others. The supermolecular value represents the supermolecule less the sum of the 5 waters corrected for BSSE. See text for description of methods used.

floating (**AF**). For **1C**, one point per atom must be optimized (the nuclei are fixed); for **VS** two centers per hydrogen (s, p) and three per oxygen (s, p, d) must be optimized; while for **AF**, three centers per hydrogen (s-inner, s-outer, 2p) and seven per oxygen (1s-inner, 1s-outer, 2s-inner, 2s-outer, 2p-inner, 2p-outer, 3d). Thus the three different approaches require consideration of 30, 50, and 80 centers, respectively (including the 15 nuclei which are not optimized in this work).

(C) All possible pairs of monomers are calculated (i.e., 1−2, 1−3, 1−4, and 1−5 interactions) using floating bases fixed in the positions of the pentamer. In these calculations the polarizations will be different for the monomers in each pair.

In all three sets of calculations (A, B, and C, above), we corrected for basis set superposition error (BSSE) using the counterpoise correction[9,10] (CP). In order not to bias the correction, all CPs were calculated with ghosts for the full pentamer.

Electrostatic calculations were performed in two different ways. In the first (**PC**), we approximated the electronic density of each shell as a point charge at its focus and the nuclei as point charges at their positions. The electronic charges were considered to have the values of the Mulliken populations for each orbital shell.

In the second method (**qV**), we calculate the energy of each molecule in the electric field generated by the others. To do this, we used the pentamer with appropriately optimized foci (**NF**, **1C**, **VS**, or **AF**), with the nuclei removed for the molecule in question (the bases for this molecule remain as "ghost" orbitals as in a counterpoise calculation). The electric field was calculated at each point that represented a nuclear position or the focus of a basis shell for the missing molecule. The missing molecule is calculated using the same level of floating bases. The sum of interactions of the field at each defined point with the nuclear charge or Mulliken populations at the corresponding point give the interaction energy between the field generated by the four remaining members of the aggregate with the molecule that has been removed. Summing over the interactions of each molecule with the field of the other four gives twice the supermolecular interaction energy. The Mulliken populations of the individual "missing" molecules are calculated without ghost orbitals to ensure that the full electron density on the molecule is taken into account.

Results and Discussion

We took the pentamer geometry ref 6 (Figure 1). All five waters have equivalent internal geometries with O−H distances of 0.957 Å and H−O−H angles of 104.4°. The O···O distances are all 2.90 Å, while the angle between the H−bonds of waters 2 and 3 is 109.5°. All the H-bonds were constrained to be linear. Table 1 provides the data for the interaction energy calculated in several different ways. The supermolecular energy is calculated by taking the energy of the pentamer and subtracting the energy of each of the five monomers with its orbital positions frozen as in the pentamer. Each monomeric energy is slightly different due to the differing positions of the floating functions and the different orientations of the ghost orbitals with each (except for waters 4 and 5, which are equivalent by symmetry). These energies do not include the geometric or electronic distortion energies from the completely optimized isolated monomer. As each water is geometrically fixed in this study, there is no geometric distortion energy. However, the basis functions are in different positions for the optimized monomers from those for the optimized pentamer. The difference between the sum of the energies of the monomeric waters frozen as in the pentamer and five times the monomer with optimized orbital positions is 0.50 kcal/mol for the **AF** calculations.

Pairwise (2-body) interactions are calculated for each possible pair with ghost orbitals on the other three molecules. The floating functions were fixed at their positions in the pentamer. Classical interactions were performed in the two ways previously indicated: interaction of the point charges (**PC**) and interaction of the charges of each molecule with the electric field generated by the other four (**qV**).

For the supermolecular calculations, the total **NF** interaction energies as well as the sum of the 2-body **NF** interactions agree very well with those reported by Hermansson, despite the differences in basis sets. The total interaction energies decrease when the orbitals are allowed to float. The greatest difference is for the **AF** calculation. This observation reflects the fact that allowing the orbitals to float lowers the energies of the individual water molecules more than that of the pentamer. Interestingly, the sum of the two-body interactions remains about 1 kcal/mol less than the supermolecular interaction energy for each level of float. Thus, the effects of polarization (including mutual polarization) are similar for the floating and nonfloating bases when they are in fixed positions.

The **PC** calculations are instructive. For both the **NF** and **1C** cases, they predict an interaction that is stronger than the supermolecular interaction. As the freedom to float is increased, the **PC** method predicts progressively weaker interactions. At the **VS** level, the **PC** interaction energy matches the supermolecular energy very well. However, at the **AF** level, the interaction is predicted to be about 8 kcal/mol too weak by this method.

The **qV** method gives results that are somewhat different. For the **NF**, **1C**, and **VS** methods, the interactions are much (about 6 kcal/mol) stronger than the supermolecule prediction. However, using **qV** with the **AF** method gives a value within 0.2 kcal/mol of the supermolecular interaction energy.

The reasons for these discrepancies have roots in three approximations that are necessary to calculate the classical interactions between the molecules: (a) the definition of each individual molecule within the pentamer; (b) the manner in which the electron densities of the molecules/aggregate are defined; (c) the manner in which the interaction of the electron densities of the molecules/aggregates interact with the nuclei and each other is calculated. Let us consider each in turn.

Just as the definition of an atom in a molecule poses certain problems, so does the definition of a molecule in a supermolecular aggregate. In particular, one must decide which electron density belongs to which atom. While there have been numerous definitions suggested in the literature, there is clearly no “correct” manner to do this, as the Schrödinger equation for a molecule (or supermolecule) does not distinguish which electrons belong to which atoms. We have used the Mulliken populations to define the point charges. This is, perhaps, the simplest approach, but probably not the best. Nevertheless, it illustrates the point. Since the charge density of one molecule will necessarily overlap that of the others, the interaction energies calculated using the **PC** method should underestimate the strength of real electrostatic interactions. The fact that these interaction are sometimes stronger than those calculated by the supermolecular method (for **NF** and **1C**) only underscores the fact that the wave functions used in these cases do not satisfy the Hellmann−Feynman theorem.

The definition of which electron density belongs to which molecule suffers from the same problems outlined above. If one uses the Mulliken populations summed over all the atoms of a particular molecule to define its density, one invites the same errors in the **PC** calculations since the densities of each molecule penetrate the others.

The way the electrostatic interactions are calculated can magnify or diminish the effects of the first two problems. We have seen that the **PC** method is quite adversely affected by these problems. This is particularly evident for the **AF** calculations, where the interaction is underestimated by about 8 kcal/mol. The reason for this becomes apparent when one considers that certain basis functions (particularly the 1s-outer functions on the H’s) move quite far (up to about 0.5 Å) from their respective nuclei in the directions of the H-bonds. Furthermore, these functions are more diffuse than the 1s-inner bases, causing even greater penetration.

We considered several other approaches to calculating the electrostatic interactions that circumvent the problems noted. One approach is to use the electronic integrals that are calculated during the HF calculation. This approach does not eliminate the penetration problem. Nevertheless, it showed some promise during test calculations. However, due to the necessity to either store or recalculate large tables of integrals, it is much too impractical to use extensively for large systems. Multipolar expansions were also considered. However, interactions between multipoles at short separations will not relieve the penetration problems.

We eventually chose the **qV** method. We calculate the electric field directly from the molecular wave function. Clearly, one obtains a much more accurate determination of the electric field than with point charges, multipoles, etc., which are extracted from the same wave function. Since all classical electrostatic approximations essentially estimate the interactions of the electric fields generated by various molecules with the charge densities of the others, the **qV** method provides most direct approach of those methods considered. Since the molecules of the aggregate are defined as the nuclei and electron densities assigned to the atomic basis functions belonging to these nuclei, the molecular definition becomes unambiguous, if still arbitrary.[12] Since the molecule that interacts with the field is removed in the **qV** calculation, one is not faced with the problems related to the overlap populations between basis functions on different molecules. This approximation will, likewise, be free of the penetration problems, as the elecron density of the molecule interacting with the field is entirely removed when the field is calculated. The remaining discussion will refer to **qV** interactions unless specified otherwise.

The fact that the **AF** calculations clearly better approximate the interaction energies provokes several observations:

(1) Use of wave functions that do not satisfy the Hellmann−Feynman theory to fit electrostatic potentials for dynamics calculations can lead to large errors. The **NF** wave functions yielded interactions that were 33% higher than the supermolecular interaction and 42% stronger than the two-body interaction energy calculated with the same method. The observation that the **PC** calculations are only 6% stronger than the supermolecular interaction energy is misleading. The **PC** calculations are more properly compared with the sum of the two-body interactions. In this case they are 12% stronger. We shall see (below) that the two-body interactions already include some polarization. Thus they overestimate the electrostatic two-body interactions, so the error in the **PC** calculation is even greater. The **PC** calculations match the interaction energy almost exactly for the **VS** calculations, but the **qV** interaction energies are still substantially in error. At the **AF** level, the **qV** calculation is accurate, but the **PC** calculation is flawed due to the substantial increase in the penetration, as discussed above. These results strongly suggest that the **PC** model can appear to give good results due to accidental cancellation of errors (this point has been made previously).[10d] The **NF** wave function does not satisfy the Hellmann−Feynman theorem causing overestimation of the electrostatic interactions. At the same time, the penetration errors lead to underestimation of the same interactions. In certain situations, the two errors almost cancel, leading to the inaccurate conclusion that the electrostatic interaction are reasonably approximated.

Clearly, the Hellmann−Feynman theorem must be satisfied for the electrostatic interactions to be accurately approximated from MO wave functions. However, wave functions which could not be expected to satisfy this theorem have often been used to parameterize electrostatic models based upon point charges or multipole expansions with moderate success.[12] We

TABLE 2: Dipole Moments (debye) for Water Monomers, Dimers, and Pentamer Calculated by the Different Methods[a]

	X	*Y*	*Z*	total	*X*	*Y*	*Z*	total	differ
NF									
	monomers								
W1	0.00	0.00	2.23	2.23					
W2	0.00	0.09	2.22	2.22					
W3	0.00	−2.12	−0.65	2.22					
W4	−0.01	0.00	2.24	2.24					
W5	0.01	0.00	2.24	2.24					
	dimers				from monomers				
D12	0.00	0.55	4.69	4.73	0.00	0.09	4.45	4.45	−0.27
D13	0.00	−2.50	1.93	3.16	0.00	−2.12	1.57	2.64	−0.51
D14	−0.44	0.00	4.75	4.77	−0.01	0.00	4.46	4.46	−0.31
D15	0.44	0.00	4.75	4.77	0.01	0.00	4.46	4.46	−0.31
D23	0.00	−2.06	1.53	2.56	0.00	−2.03	1.57	2.57	0.00
D24	−0.04	0.14	4.49	4.49	−0.01	0.09	4.46	4.46	−0.03
D25	0.04	0.14	4.49	4.49	0.01	0.09	4.46	4.46	−0.03
D24	−0.03	−2.14	1.62	2.69	−0.01	−2.12	1.58	2.65	−0.04
D35	0.03	−2.14	1.62	2.69	0.01	−2.12	1.58	2.65	−0.04
D45	0.00	0.00	4.43	4.43	0.00	0.00	4.47	4.47	0.05
	pentamer								
monomers	0.00	−2.03	8.27	8.51					−1.17
dimers	0.00	−2.00	8.57	8.80					−0.88
supermol.	0.00	−1.91	−9.50	9.68					
1C									
	monomers								
W1	0.00	0.00	2.23	2.23					
W2	0.00	0.09	2.22	2.22					
W3	0.00	−2.12	−0.65	2.22					
W4	0.01	0.00	2.24	2.24					
W5	−0.01	0.00	2.24	2.24					
	dimers				from monomers				
D12	0.00	0.55	4.69	4.73	0.00	0.09	4.45	4.45	−0.27
D13	0.00	−2.50	1.93	3.15	0.00	−2.12	1.57	2.64	−0.51
D14	−0.44	0.00	4.75	4.77	0.01	0.00	4.47	4.47	−0.31
D15	0.44	0.00	4.75	4.77	−0.01	0.00	4.47	4.47	−0.31
D23	0.00	−2.06	1.53	2.56	0.00	−2.03	1.57	2.57	0.00
D24	−0.04	0.14	4.49	4.49	0.01	0.09	4.46	4.46	−0.03
D25	0.04	0.14	4.49	4.49	−0.01	0.09	4.46	4.46	−0.03
D24	−0.04	−2.14	1.62	2.69	0.01	−2.12	1.58	2.65	−0.04
D35	0.04	−2.14	1.62	2.69	−0.01	−2.12	1.58	2.65	−0.04
D45	0.00	0.00	4.43	4.43	0.00	0.00	4.47	4.47	0.05
	pentamer								
monomers	0.00	−2.03	8.27	8.52					−1.17
dimers	0.00	−2.00	8.57	8.80					−0.88
supermol.	0.00	−1.91	9.50	9.69					
VS									
	monomers								
W1	0.00	0.00	2.23	2.23					
W2	0.00	0.09	2.21	2.21					
W3	0.00	−2.11	−0.65	2.21					
W4	−0.02	0.00	2.23	2.23					
W5	0.02	0.00	2.23	2.23					
	dimers				from monomers				
D12	0.00	0.54	4.68	4.71	0.00	0.09	4.43	4.44	−0.27
D13	0.00	−2.48	1.92	3.14	0.00	−2.11	1.57	2.63	−0.51
D14	−0.45	0.00	4.74	4.76	−0.02	0.00	4.45	4.45	−0.30
D15	0.45	0.00	4.74	4.76	0.02	0.00	4.45	4.45	−0.30
D23	0.00	−2.05	1.52	2.55	0.00	−2.02	1.56	2.55	0.00
D24	−0.05	0.14	4.47	4.47	−0.02	0.09	4.44	4.44	−0.03
D25	0.05	0.14	4.47	4.47	0.02	0.09	4.44	4.44	−0.03
D24	−0.05	−2.13	1.62	2.68	−0.02	−2.11	1.58	2.64	−0.04
D35	0.05	−2.13	1.62	2.68	0.02	−2.11	1.58	2.64	−0.04
D45	0.00	0.00	4.41	4.41	0.00	0.00	4.46	4.46	0.05
	pentamer								
monomers	0.00	−2.02	8.24	8.49					−1.35
dimers	0.00	−1.99	8.55	8.77					−1.06
supermol.	0.00	−1.90	9.65	9.83					

TABLE 2: (Continued)

	X	Y	Z	total	X	Y	Z	total	differ
AF									
	monomers								
W1	0.00	0.00	2.05	2.05					
W2	0.00	0.10	1.96	1.96					
W3	0.00	−1.90	−0.58	1.99					
W4	−0.10	0.00	1.99	2.00					
W5	0.10	0.00	1.99	2.00					
	dimers				from monomers				
D12	0.00	0.54	4.25	4.29	0.00	0.10	4.01	4.01	−0.27
D13	0.00	−2.26	1.82	2.90	0.00	−1.90	1.48	2.41	−0.50
D14	−0.51	0.00	4.34	4.37	−0.10	0.00	4.05	4.05	−0.32
D15	0.51	0.00	4.34	4.37	0.10	0.00	4.05	4.05	−0.32
D23	0.00	−1.82	1.34	2.26	0.00	−1.80	1.38	2.27	0.00
D24	−0.13	0.14	3.98	3.98	−0.10	0.10	3.95	3.95	−0.03
D25	0.13	0.14	3.98	3.98	0.10	0.10	3.95	3.95	−0.03
D24	−0.12	−1.92	1.45	2.41	−0.10	−1.90	1.42	2.37	−0.04
D35	0.12	−1.92	1.45	2.41	0.10	−1.90	1.42	2.37	−0.04
D45	0.00	0.00	3.94	3.94	0.00	0.00	3.99	3.99	0.04
	pentamer								
monomers	0.00	−1.80	7.42	7.63					−1.18
dimers	0.00	−1.77	7.72	7.92					−0.89
supermol.	0.00	−1.68	8.65	8.81					

[a] The dimer dipoles are compared with the vector sums of the monomers. The pentamer dipole is compared with the vector sums of the monomers and one-fourth the vector sums of the dimers.

now see that the results of these models are sometimes usable due to fortuitous cancellation of errors.

Table 2 presents the dipole moments of the individual water molecules in the various different MO treatments. The **NF**, **1C**, and **VS** calculations all predict larger dipoles than do the **AF** calculations. Furthermore, the directions of the dipoles change when the Gaussians are allowed to float. For example, waters 4 and 5 have a dipole *X* component of 0.01 for the **NF** calculation with the pentamer basis set. These values change to 0.10 for the **AF** calculation. At the same time, the total dipole moments for these same waters decrease from 2.24 to 2.00. If there be no change in electron densities of the monomers upon aggregation, the dipole moment of the pentamer should be determinable from vector addition of the dipoles of the individual waters. Similarly, the dipoles of each of the pairs that were calculated should be determinable from the vector addition of the dipoles of its two components. One should also be able to obtain the dipole moment of the pentamer by taking one-fourth of the vector sum of the dimer dipole moments.

From Table 2, we see that one cannot accurately obtain the dipole moment of the pentamer from those of the monomers or the dimers. Nor can one accurately obtain the dipole moment of the various dimers from those of the monomers. The dipole of each pair is larger than the vector sum of its components. That of the pentamer is larger than the vector sum of both the monomeric dipoles and one-fourth the vector sum of the dimer dipoles. If one examines the dipole components along the *Y* and *Z* axes (the *X* component in the pentamer is 0 by symmetry), one sees that the *Y* component decreases and the *Z* component increases as one calculates the pentamer dipole from those of the monomers or dimers or from the supermolecule directly. These data provide evidence that the waters are polarized differently in the monomers, dimers, and pentamer. Thus, the electrostatic interactions of two monomeric waters might be expected to underestimate the collective interaction energies of the dimers, while the electrostatic interaction energies of waters taken either from the monomers or dimers might be expected to underestimate the interaction in the pentamer. The discrepancy between the two-body interactions and the supermolecular interaction energy of the aggregate gives rise to the nonadditive cooperativity. However, the failure of the monomer dipoles to accurately predict the dimer dipoles indicate that the two-body interactions, themselves, are not properly described by simple electrostatic interactions but are stronger than expected (see above).[2]

We have already seen from the **qV** interactions (Table 1) that the **NF** calculations overestimate the electrostatic interactions. Yet, the dipole moments increase upon formation of dimers and of the pentamer. This can be due to increased polarization, as noted above. It can also be due to the inadequate definition of dipole−dipole interactions at short separations. If there be significant penetration between the entities, the dipole moment of the dimer (or aggregate) will not be properly described by the vector sum. Nevertheless, the facts that the dipoles of the monomeric units are insufficient to describe the dimers or the pentamer suggest that the electrostactic interactions are probably still understated.

The **AF** dipoles also increase by roughly the same amounts as do the **NF** dipoles upon formation of dimers and pentamer. The **AF** calculations freeze the electron densities of the individual waters by immobilizing the floating bases in the positions they take in the pentamer. Some electronic reorganization is inevitable; however, as after HF convergence, the density matrix for the water will be different from that in the pentamer. The nonadditivity of the **AF** dipoles is not inconsistent with the good agreement of the **qV** and supermolecular interaction energies. For the **qV** calculations, the charges are taken from the Mulliken populations based on the *pentamer density matrix.*

Conclusions

Intermolecular interactions for the tetrahedral water pentamer can be calculated by classical electrostatic interactions from charge densities based upon molecular wave functions if (1) the wave functions are obtained from floating basis set calculations and (2) the wave function is calculated for the aggregate (not the monomeric units). The Hellmann−Feynman theorem should be satisfied for classical electrostatic interactions to be accurate. Using floating basis functions satisfies this criterion. The wave function used must include the effects of polarization and mutual polarization of the monomers. Using the wave function for the aggregate satisfies this criterion, as the individual monomeric components are already appropriately polarized.

Classical electrostatic interactions calculated using the electric fields calculated without a monomeric component interacting with the charges on that component, the **qV** method, are preferable to interactions between point charges. The reasonable interactions sometimes calculated using point charges are likely due to fortuitous cancellations of errors.

The nonadditive cooperativity for the water pentamer is underestimated by the summation over two-body interactions. The monomeric units in the two-body calculations are already significantly polarized. They become more (and differently) polarized in the pentamer.

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