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Natural Energy Decomposition Analysis: Extension to Density Functional Methods and Analysis of Cooperative Effects in Water Clusters

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Natural energy decomposition analysis (NEDA) is a method for partitioning molecular interaction energies into physically meaningful components, including electrical interaction, charge transfer, and core repulsions. The method is a numerically stable procedure that was originally developed for analyzing Hartree−Fock (HF) wave functions based on the localized orbital description of natural bond orbital analysis. In this work, we extend NEDA to treat charge densities from density functional theory (DFT) calculations, replacing the intermolecular exchange (EX) component of the HF analysis with an exchange-correlation (XC) component. DFT/NEDA is applied to hydrogen bonding interactions and cooperative effects in water clusters. Electrical interactions and charge transfer contribute importantly to hydrogen bonding. Comparison of HF and DFT results reveals that the exchange and correlation effects of DFT slightly enhance the extent of charge transfer and core repulsions in the water clusters. Cooperative stabilization of the cyclic water trimer and tetramer is considered by performing a many-body expansion of the interaction energy. Natural energy decomposition analysis of this expansion suggests that charge transfer is the leading source of cooperative stabilization. Polarization effects have only marginal influence on cooperativity.

I. Introduction

Chemists who study intermolecular forces naturally seek to understand the factors that influence the varying structure and stability of clusters formed by molecules and ions. One of the tools available to chemists is energy decomposition analysis in which cluster binding energies from electronic structure calculations are partitioned into physically meaningful components. A number of decomposition schemes have been proposed, of which the method of Kitaura and Morokuma (KM)[1] is arguably the most widely used. This method partitions the Hartree−Fock (HF) binding energy into electrostatic interaction, polarization, exchange, charge transfer, and higher-order terms. Though still applied in recent work,[2] it has been recognized[3] for some time that the polarization and charge transfer components of this method are numerically unstable, their values depending significantly on the extent of the atomic orbital basis sets employed. This instability stems from the variational optimization of an intermediate wave function that is not fully antisymmetrized and thereby violates the Pauli exclusion principle. Several alternative decomposition schemes have been proposed that avoid this problem. Some of these methods include the restricted variational space (RVS) analysis,[4] the constrained space orbital variations (CSOV) method,[5] and the divide and conquer decomposition analysis.[6]

Several years ago we introduced natural energy decomposition analysis (NEDA),[7−9] a procedure for partitioning HF interaction energies into electrical interactions (EL), charge transfer (CT), and core repulsions (CORE). NEDA is based on the natural bond orbital (NBO) method of Weinhold and co-workers,[10] yielding a description of molecular interactions that, like NBO, tends to stress the role of charge transfer in molecular interactions.[11,12] NEDA is a numerically stable procedure that is straightforward to apply and is implemented in the most recent version of the NBO program.[13] The EL component, which describes both static and induced interactions between monomer charge densities, generally compares favorably with estimates from classical point multipole/polarizability approximations. CORE accounts for the quantum mechanical effects (Pauli repulsions and exchange) of filled orbital ($\sigma-\sigma$) interactions that arise from the required antisymmetry of the wave function for the interacting monomers. CT describes delocalizing, donor−acceptor ($\sigma-\sigma^*$) interactions between monomers. Like most other decomposition schemes, NEDA has only been applied to HF wave functions. Here, we extend NEDA to treat molecular interactions in density functional theory (DFT) calculations. After describing its extension to DFT, we use NEDA to investigate the origin of hydrogen bonding interactions and cooperativity in water clusters.

II. Natural Energy Decomposition Analysis

Extension of NEDA to treat DFT charge densities largely follows the original development of the method for HF wave functions.[9] Consider a system of interacting monomers A with nuclei of charge Z_α located at coordinates $\mathbf{R}_\alpha$. The total charge density for this system is given by

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_\alpha Z_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha) - 2\sum_a |\psi_a(\mathbf{r})|^2 \tag{1}$$

where the doubly occupied molecular orbitals ψ_a are the eigenvectors of the Kohn−Sham matrix. The interaction energy of this system is given by

$$\Delta E = E[\rho_{\text{tot}}(\mathbf{r})] - \sum_A E[\rho_A^0(\mathbf{r})] \tag{2}$$

where $E[\rho]$ represents an energy functional of the charge density and the relaxed charge densities $\rho_A^0(\mathbf{r})$ are those of the isolated monomers. For convenience, we neglect geometry relaxation

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effects so that the densities $\rho^0_A(\mathbf{r})$ only account for electronic relaxation as the interacting monomers are separated. That is, the relative coordinates of the nuclei in the separated monomers are identical to those of the interacting system.

The NEDA partitioning of ΔE into physically intuitive components relies on NBO analysis[11,13] of $\rho_{tot}(\mathbf{r})$ and subsequent construction of perturbed monomer densities $\rho_A(\mathbf{r})$. The NBO method searches $\rho_{tot}(\mathbf{r})$ for Lewis structures (sets of one- and two-center localized, orthogonal orbitals) that best describe the monomers of the interacting system. For example, analysis of the water dimer yields two Lewis structures, each consisting of an O 1s core, two OH bonds, and two O lone pairs. These Lewis structures typically account for over 99% of the total electron density, with most of the remaining density residing in antibonding orbitals, the result of delocalizing orbital interactions. Transforming the Kohn−Sham matrix to the localized NBO basis allows one to identify blocks of elements along the diagonal associated with each of the interacting monomers. Perturbed monomer densities are then constructed as follows

$$\rho_A(\mathbf{r}) = \sum_{\alpha}^{\text{on A}} Z_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha) - 2\sum_{a}^{\text{on A}} |\varphi_a(\mathbf{r})|^2 \tag{3}$$

where the summations are respectively over only the nuclei and occupied orbitals that comprise monomer A and the orbitals $\varphi_a(\mathbf{r})$ are eigenvectors of the monomer A block of the NBO Kohn−Sham matrix. Orbitals $\varphi(\mathbf{r})$ on different monomers are mutually orthogonal.

The localized charge density for the full interacting system is given by

$$\rho(\mathbf{r}) = \sum_A \rho_A(\mathbf{r}) \tag{4}$$

We note that $\rho(\mathbf{r})$ differs from the total charge density $\rho_{tot}(\mathbf{r})$ because the NBO Kohn−Sham matrix is not block diagonal but usually exhibits off-diagonal elements coupling monomer blocks that account for delocalizing (charge transfer) interactions between monomer units.

Charge transfer and deformation components of DFT/NEDA are evaluated exactly as in the HF analysis. Charge transfer is the difference between the energies of the total and localized charge densities

$$\text{CT} = E[\rho_{tot}(\mathbf{r})] - E[\rho(\mathbf{r})] \tag{5}$$

and deformation is the difference between the energies of the perturbed and relaxed monomer densities

$$\text{DEF}_A = E[\rho_A(\mathbf{r})] - E[\rho^0_A(\mathbf{r})] \tag{6a}$$

$$\text{DEF} = \sum_A \text{DEF}_A \tag{6b}$$

However, DFT/NEDA and HF/NEDA differ somewhat in their interpretation of the remaining contribution to ΔE,

$$\Delta E - \text{CT} - \text{DEF} = E[\rho(\mathbf{r})] - \sum_A E[\rho_A(\mathbf{r})] \tag{7}$$

It is convenient to consider here how the components of the energy functional contribute to eq 7. The energy can be expressed as a sum of three functionals

$$E = T + VJ + XC \tag{8}$$

where T describes the kinetic energy of the electrons, VJ gives the total potential energy due to Coulomb interactions of all particles (nuclei and electrons), and XC accounts for electron exchange and correlation effects. The kinetic energy contribution to the right-hand side of eq 7 vanishes

$$T[\rho(\mathbf{r})] - \sum_A T[\rho_A(\mathbf{r})] = 0 \tag{9}$$

in the independent electron model because $\rho(\mathbf{r})$ is simply a sum of the densities $\rho_A(\mathbf{r})$. The potential energy contribution

$$\begin{aligned} VJ[\rho(\mathbf{r})] - \sum_A VJ[\rho_A(\mathbf{r})] &= \frac{1}{2}\sum_{\substack{A,B\\A\neq B}} \int d\mathbf{r}\, d\mathbf{r}' \frac{\rho_A(\mathbf{r})\,\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &= \text{ES} + \text{POL} \end{aligned} \tag{10}$$

describes the classical Coulomb interactions of the perturbed monomer densities, which was previously defined as the sum of the electrostatic (ES) and polarization (POL) components. The remaining contribution to eq 7,

$$XC[\rho(\mathbf{r})] - \sum_A XC[\rho_A(\mathbf{r})] = \text{XC} \tag{11}$$

accounts for intermolecular electron exchange and correlation, which we will refer to as XC, the exchange-correlation component of DFT/NEDA. (When electron correlation is neglected, as in HF theory, this term reduces to the exchange component EX.) Thus, for DFT/NEDA, eq 7 can be re-expressed as a sum of three components,

$$\Delta E - \text{CT} - \text{DEF} = \text{ES} + \text{POL} + \text{XC} \tag{12}$$

electrostatic interaction, polarization, and exchange-correlation.

As was previously demonstrated,[9] a portion of the DEF component arises from the self-polarization energies of the monomers, that is, an energy penalty for each of the monomers to undergo polarization. A linear response treatment of this effect yields an estimate of the self-energy

$$\text{SE}_A = -\frac{1}{2}\sum_{\substack{B\\B\neq A}} \int d\mathbf{r}\, d\mathbf{r}' \frac{\Delta\rho_A(\mathbf{r})\,\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{13a}$$

$$\text{SE} = \sum_A \text{SE}_A \tag{13b}$$

where $\Delta\rho_A(\mathbf{r})$ is the induced monomer charge density,

$$\Delta\rho_A(\mathbf{r}) = \rho_A(\mathbf{r}) - \rho^0_A(\mathbf{r}) \tag{14}$$

Collecting terms, the components of DFT/NEDA include electrical interaction, charge transfer, and core repulsions

$$\Delta E = \text{EL} + \text{CT} + \text{CORE} \tag{15}$$

where the treatment of electrical interactions

$$\text{EL} = \text{ES} + \text{POL} + \text{SE} = \frac{1}{2}\sum_{\substack{A,B\\A\neq B}} \int d\mathbf{r}\, d\mathbf{r}' \frac{\rho^0_A(\mathbf{r})\,\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{16}$$

is consistent with that traditionally used in molecular dynamics simulations that employ instantaneous polarization response, and the core repulsion component

$$\mathrm{CORE} = \mathrm{DEF} + \mathrm{XC} - \mathrm{SE} \tag{17}$$

includes intermolecular Pauli repulsion, electron exchange, and correlation effects. We previously demonstrated[9] that the long-range character of the interaction potential is principally determined by EL and that the CT and CORE components only contribute importantly at short-range where monomer charge densities overlap considerably.

DFT/NEDA has been implemented in the GAMESS[14] version of the NBO 5.0 program.[13] The procedure can treat restricted closed-shell and unrestricted open-shell densities in all-electron or pseudopotential calculations using either conventional disk-based or direct two-electron integral techniques. NEDA employs the function counterpoise method,[15] evaluating all charge densities in the full atomic orbital basis set of the interacting system, to correct the calculated interaction energy and its components for basis set superposition error. All calculations reported here were performed with GAMESS.

III. NEDA of Water Clusters

As a representative application of DFT/NEDA, we examine the hydrogen bonding interactions in water clusters composed of two, three, and four monomers. The clusters were calculated using the B3LYP hybrid functional,[16] as implemented in GAMESS, with correlation-consistent, triple-ζ (aug-cc-pVTZ) basis sets.[17] We only consider the cyclic forms of the trimer (C_1) and tetramer (S_4) that correspond to the global minima of their respective interaction potentials. Figure 1 shows the equilibrium structures, and Table 1 compares the HF and B3LYP NEDA results.

NEDA suggests that electrical and charge transfer interactions both contribute importantly to hydrogen bonding forces in water clusters. Consider the B3LYP analysis of the dimer. Electrical interaction stabilizes the dimer by −9.85 kcal/mol, principally the result of a significant dipole−dipole interaction as reflected by the large electrostatic component (ES = −8.13 kcal/mol). Polarization effects are modest, contributing only −1.72 kcal/mol (POL + SE = EL − ES) of the total interaction energy. The perturbed monomer densities (eq 3) yield dipole moments of 2.04 and 2.09 D for the electron donor and acceptor units, respectively. Thus, the monomers are only slightly more polar than the isolated water molecule, which has a B3LYP dipole moment of 1.85 D. The dimer is also significantly stabilized by charge transfer (−8.91 kcal/mol), arising from the transfer of 0.015 electrons from an O lone pair of the donor monomer into the proximal OH antibond of the acceptor. Perturbative analysis of the NBO Kohn−Sham matrix reveals that this single $n_O \rightarrow \sigma_{OH}^*$ interaction is responsible for about 80% (7.3 kcal/mol) of the CT component.

NEDA of the trimer and tetramer reveals similarly important electrical and charge-transfer interactions. Polarization effects are enhanced somewhat in these larger clusters, as evidenced by the increasing monomer dipole moments, from about 2.1 D in the dimer to 2.2 and 2.3 D in the trimer and tetramer, respectively. POL + SE strengthens from −1.72 kcal/mol to −6.17 and −8.42 kcal/mol. Charge transfer effects are similarly enhanced with increasing cluster size as each of the three $n_O \rightarrow \sigma_{OH}^*$ interactions transfers an average 0.021 electrons in the trimer, and each of four interactions transfers 0.038 electrons in the tetramer. Perturbative estimates of these orbital interactions strengthen from −7.3 kcal/mol in the dimer to −8.7 and −17.1 kcal/mol in the trimer and tetramer, respectively.

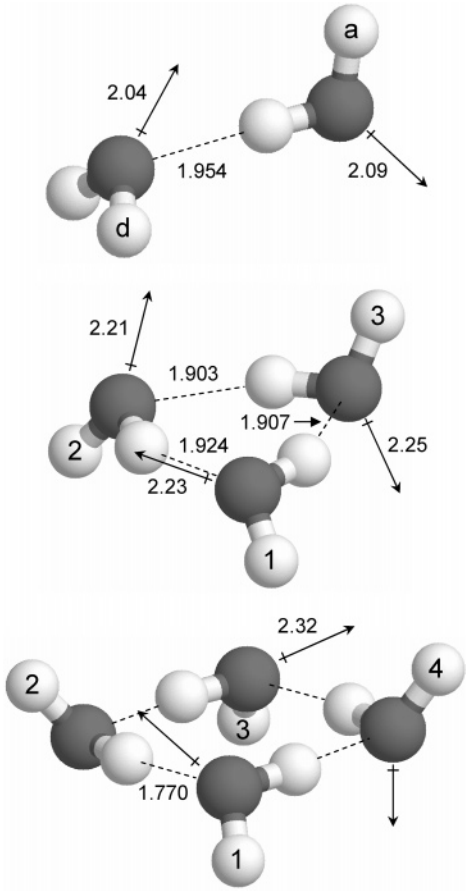

Figure 1. B3LYP/aug-cc-pVTZ optimized structures of the water dimer (C_s) and cyclic water trimer (C_1) and tetramer (S_4). Distances are given in Å, and monomer dipole moments in Debye.

TABLE 1: Comparison of HF and B3LYP NEDA for the Water Clusters[a]

	dimer		trimer		tetramer	
	HF	B3LYP	HF	B3LYP	HF	B3LYP
ΔE	−3.67	−4.52	−11.18	−14.53	−20.70	−26.92
EL	−9.76	−9.85	−32.97	−33.32	−58.69	−58.81
CT	−7.67	−8.91	−27.41	−32.91	−69.86	−79.58
CORE	13.75	14.24	49.20	51.69	107.85	111.47
ES	−8.22	−8.13	−27.14	−27.14	−50.47	−50.40
POL	−3.17	−3.56	−12.18	−12.94	−17.68	−18.34
SE	1.63	1.84	6.34	6.77	9.44	9.92
XC		−2.72		−9.28		−15.42
EX	−1.48		−5.31		−8.41	
DEF	16.87	18.81	60.86	67.74	125.72	136.84
$\mu(H_2O)$	2.14(d) 2.20(a)	2.04(d) 2.09(a)	2.33(1) 2.31(2) 2.34(3)	2.23(1) 2.21(2) 2.25(3)	2.43	2.32

[a] Energies in kcal/mol and dipole moments in Debye for the B3LYP/aug-cc-pVTZ optimized water clusters. Geometry relaxation of the separated monomers is neglected.

The principal differences in the HF and B3LYP analyses appear in the quantum mechanical components, CT and CORE, whereas the classical EL component is nearly unchanged. For example, the dimer is bound by −4.52 kcal/mol at the B3LYP level, 0.85 kcal/mol stronger than at the HF level. The enhanced B3LYP interaction results predominantly from increased charge transfer, which, at −8.91 kcal/mol, is 1.24 kcal/mol stronger than at the HF level. Strengthened charge transfer is consistent with a charge density that is more strongly delocalized than at the HF level. Indeed, NBO analysis of the HF dimer reveals a

$n_O \rightarrow \sigma_{OH}{}^*$ interaction that transfers only 0.010 electrons whereas the interaction transfers 0.015 electrons at the B3LYP level. We additionally find that the CORE component is somewhat more repulsive at the B3LYP level than at HF. Repulsions in the B3LYP dimer are 14.24 kcal/mol, 0.49 kcal/mol stronger than in the HF dimer. Although exchange-correlation favors weakened CORE repulsions (i.e., XC is −2.72 kcal/mol whereas EX is −1.48 kcal/mol), the deformation (DEF) term strengthens from 16.87 to 18.81 kcal/mol as it is apparently more costly at the B3LYP level to form a perturbed monomer density in the cluster environment.

IV. NEDA of Cooperative Effects in Water Clusters

Hankins, Moskowitz, and Stillinger[18] were the first to report a computational study of cooperative (nonpairwise additive) effects in water clusters. Their HF calculations revealed that three-body interactions were large and could either stabilize or destabilize a cluster depending on the arrangement of the interacting monomers. Cooperativity in water clusters has also been associated with contraction of nearest-neighbor O−O distances with increasing cluster size and with the concomitant red-shift of the hydrogen-bonded OH stretching frequencies. Several computational studies employing higher levels of theory have been reported recently.[19−21] We use NEDA here to determine the origin of nonpairwise additivity in the cyclic water trimer and tetramer.

The influence of cooperativity on the total interaction energy for a cluster of N monomers can be determined by expanding the total interaction energy, ΔE_N, as a sum of many-body contributions[18]

$$\begin{aligned}\Delta E_N = {} & \sum_{A} \Delta^1 E(\mathrm{A}) \qquad \text{(one-body)} \\ & + \sum_{A} \sum_{B<A} \Delta^2 E(\mathrm{AB}) \qquad \text{(two-body)} \\ & + \sum_{A} \sum_{B<A} \sum_{C<B} \Delta^3 E(\mathrm{ABC}) \qquad \text{(three-body)} \\ & + \ldots + \Delta^N E(\mathrm{ABC}\ldots N) \qquad (N\text{-body}) \end{aligned} \tag{18}$$

One-body terms correspond to the geometry relaxation of the monomers

$$\Delta^1 E(\mathrm{A}) = E(\mathrm{A}) - E^0(\mathrm{A}) \tag{19}$$

where E(A) and E^0(A), respectively, represent the energy of monomer A in the geometry of the cluster and the energy of the isolated monomer A at its equilibrium geometry. These terms typically contribute several tenths of a kcal/mol to the total interaction energy of the water clusters[20] and will be neglected here. Two-body and three-body terms are given by

$$\Delta^2 E(\mathrm{AB}) = E(\mathrm{AB}) - E(\mathrm{A}) - E(\mathrm{B}) \tag{20}$$

$$\Delta^3 E(\mathrm{ABC}) = E(\mathrm{ABC}) - [E(\mathrm{A}) + E(\mathrm{B}) + E(\mathrm{C})] - [\Delta^2 E(\mathrm{AB}) + \Delta^2 E(\mathrm{AC}) + \Delta^2 E(\mathrm{BC})] \tag{21}$$

where E(AB) and E(ABC) are, respectively, the energies of pairs and triples of monomers. We evaluate all energies in the full basis set of the complex so that the interaction energy and its many-body terms are counterpoise corrected. The NEDA components can be similarly expressed as a many-body expansion. Thus, for example, two-body and three-body CT terms are evaluated as

$$\Delta^2 \mathrm{CT}(\mathrm{AB}) = \mathrm{CT}(\mathrm{AB}) \tag{22}$$

$$\Delta^3 \mathrm{CT}(\mathrm{ABC}) = \mathrm{CT}(\mathrm{ABC}) - [\Delta^2 \mathrm{CT}(\mathrm{AB}) + \Delta^2 \mathrm{CT}(\mathrm{BC}) + \Delta^2 \mathrm{CT}(\mathrm{AC})] \tag{23}$$

where CT(AB) is the charge transfer in the AB monomer pair and CT(ABC) is the total charge transfer in the ABC monomer triple.

TABLE 2: NEDA of the Many-Body Terms for the Cyclic Water Trimer[a]

		two-body			three-body
	total	1,2	2,3	1,3	1,2,3
Δ*E*	−14.54	−3.73	−4.11	−4.14	−2.56
EL	−33.32	−10.79	−11.59	−11.55	0.61
CT	−32.91	−9.46	−10.52	−10.57	−2.36
CORE	51.69	16.52	18.00	17.98	−0.81
ES	−27.14	−8.47	−9.32	−9.36	0.00
POL	−12.94	−4.73	−4.67	−4.50	0.97
SE	6.76	2.41	2.40	2.31	−0.36
XC	−9.28	−3.40	−3.50	−3.48	1.10
DEF	67.73	22.33	23.90	23.77	−2.27

[a] B3LYP/aug-cc-pVTZ values in kcal/mol.

TABLE 3: NEDA of the Many-Body Terms for the Cyclic Water Tetramer[a]

		two-body		three-body	four-body
	total	1,2	1,3	1,2,3	1,2,3,4
Δ*E*	−26.92	−4.17	−1.34	−1.73	−0.64
EL	−58.81	−13.88	−1.75	−0.01	0.25
CT	−79.58	−17.77	−0.52	−1.92	0.22
CORE	111.47	27.48	0.93	0.20	−1.11
ES	−50.40	−11.89	−1.42	0.00	0.00
POL	−18.34	−4.13	−0.68	−0.25	0.54
SE	9.93	2.14	0.35	0.24	−0.29
XC	−15.42	−4.21	−0.18	0.42	0.10
DEF	136.82	33.83	1.46	0.02	−1.50

[a] B3LYP/aug-cc-pVTZ values in kcal/mol. Note that the total interaction is composed of six two-body interactions (four 1,2-type and two 1,3-type), four three-body interactions, and one four-body interaction.

As noted previously,[20] two-body terms dominate hydrogen bond forces in the water trimer and tetramer, accounting for 70−80% of the calculated binding energies. Tables 2 and 3 give the many-body analyses for the clusters. The individual two-body terms involving adjacent monomer pairs are comparable to the interaction of the water dimer. For instance, in the tetramer, the interaction of adjacent monomers is −4.17 kcal/mol, nearly as strong as the −4.52 kcal/mol binding energy of the dimer. In contrast, the interaction of monomers across the tetramer ring is relatively weak, −1.34 kcal/mol. NEDA reveals that the two-body terms arise, as in the water dimer, from a combination of electrical and charge-transfer interaction. For adjacent monomers in the tetramer, the two-body term (−4.17 kcal/mol) has significant electrical (−13.88 kcal/mol) and charge transfer (−17.77 kcal/mol) components. For monomers across the ring, the two-body term (−1.34 kcal/mol) arises principally from electrical interaction (−1.75 kcal/mol) because charge transfer (−0.52 kcal/mol) remains weak for weakly overlapping monomers.

Three-body terms are of particular interest because they are principally responsible for the cooperative (nonpairwise additive) stabilization of the water clusters. Three-body interactions collectively account for 18% and 26% of the total interaction energies for the trimer and tetramer, respectively. Xantheas[20] reported similar contributions based on MP2/aug-cc-pVDZ calculations of the cyclic trimer and tetramer. The four-body term is weaker, contributing only 2% of tetramer interaction.

NEDA suggests that charge transfer is the principal origin of the cooperative effect in the water clusters. For example, the results of Table 2 reveal a three-body term that stabilizes the trimer by −2.56 kcal/mol. Charge transfer, at −2.36 kcal/mol, is the dominant component of this term. Similarly, we find in Table 3 that charge transfer (−1.92 kcal/mol) is principally responsible for the three-body terms (−1.73 kcal/mol) of the tetramer. Interestingly, NEDA suggests that electrical interactions of the monomers contribute marginally to cooperative stabilization. In fact, in the trimer, three-body EL is *destabilizing* by 0.61 kcal/mol, an effect that arises entirely from polarization (POL + SE) because electrostatic interaction is strictly pairwise additive (ES = 0.00).

The suggestion that electrical interactions do not contribute importantly to cooperativity is at odds with conventional intuition regarding polarization effects on monomer interactions. Polarization is frequently used to treat nonpairwise additivity in potentials for molecular simulation.[22,23] However, we note that two factors contribute importantly to polarization in NEDA. For long-range interactions, polarization arises entirely from the response of the monomer charge densities to the electric field of the interacting cluster. For these large separations, EL is, in fact, reasonably well approximated by classical point dipole/polarizability expressions.[9] However, for short-range interactions, where monomer charge densities begin to overlap, polarization is additionally influenced by the requirement that the orbitals ($\varphi_a(\mathbf{r})$ of eq 3) of adjacent monomers remain mutually orthogonal. This orthogonality requirement is a consequence of the quantum mechanical constraint that the charge densities satisfy the Pauli exclusion principle for all monomer separations. Although the monomer dipole moments of the trimer and tetramer (see Figure 1) are larger than those of the dimer, perhaps suggesting an important classical polarization contribution to cooperativity, it appears more likely that these enhanced dipoles largely result from quantum mechanical perturbations as the charge densities adjust to avoid significant overlap in the crowded environment of the larger clusters. The enhanced dipole moments are apparently not optimally oriented to strengthen electrical interactions.

The important contribution of charge transfer to cooperativity in water clusters has been reported previously. Chen and Gordon[19] performed KM and RVS analyses of many-body expansions at the HF level, finding that the three-body terms had strong polarization and charge transfer components. They also considered the geometry dependence of cooperative effects in the trimer and tetramer, observing that three-body terms are only significant for small monomer separations. This result is consistent with cooperative interactions arising from short-range charge-transfer effects rather than from electrical interactions, which remain strong even at long-range.

V. Summary

We have extended natural energy decomposition analysis to treat charge densities from DFT calculations. DFT/NEDA retains all of the favorable qualities of the HF-based analysis, including its straightforward application, the numerical stability of the energy components, and the direct relationship between the EL term and classical electrical approximations used in molecular dynamics simulations. The principal difference between the HF- and DFT-based methods is the replacement of the intermolecular exchange component (EX) by exchange-correlation (XC). Analysis of water clusters reveals that hydrogen bond forces exhibit important electrical (electrostatic and polarization) interactions and charge transfer. However, cooperative stabilization of the cyclic water trimer and tetramer results principally from charge transfer with only weak contributions from polarization.

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References and Notes

(1) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325. (c) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294. (d) Morokuma, K.; Kitaura, K. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; p 215.

(2) See, for example: (a) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem. A* **2003**, *107*, 7062. (b) Liu, T.; Zhu, W.; Gu, J.; Shen, J.; Luo, X.; Chen, G.; Puah, C. M.; Silman, I.; Chen, K.; Sussman, J. L.; Jiang, H. *J. Phys. Chem. A* **2004**, *108*, 9400. (c) Pavelka, M.; Burda, J. V. *Chem. Phys.* **2005**, *312*, 193.

(3) (a) Frey, R.; Davidson, E. R. *J. Chem. Phys.* **1989**, *90*, 5555. (b) Cybulski, S. M.; Scheiner, S. *Chem. Phys. Lett.* **1990**, *166*, 57.

(4) Stevens, W. J.; Fink, W. H. *Chem. Phys. Lett.* **1987**, *139*, 15.

(5) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1984**, *80*, 4378.

(6) van der Vaart, A.; Merz, K. M., Jr. *J. Phys. Chem. A* **1999**, *103*, 3321.

(7) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900.

(8) Glendening, E. D. *J. Am. Chem. Soc.* **1996**, *118*, 2473.

(9) Schenter, G. K.; Glendening, E. D. *J. Phys. Chem.* **1996**, *100*, 17152.

(10) Weinhold, F. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; p 1792.

(11) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(12) Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*, 181.

(13) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute: Madison, WI, 2001 (http://www.chem.wisc.edu/~nbo5).

(14) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(15) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(16) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (c) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345.

(17) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(18) Hankins, D.; Moskowitz, J. W.; Stillinger, F. H. *J. Chem. Phys.* **1970**, *53*, 4544.

(19) Chen, W.; Gordon, M. S. *J. Phys. Chem.* **1996**, *100*, 14316.

(20) Xantheas, S. S. *Chem. Phys.* **2000**, *258*, 255.

(21) Mo, O.; Yanez, M.; Elguero, J. *J. Chem. Phys.* **1992**, *97*, 6628

(22) Caldwell, J.; Dang, L. X.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 9144.

(23) Sremaniak, L. S.; Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1996**, *105*, 3715.