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Energy decomposition analysis of intermolecular interactions using a block-localized wave function approach

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An energy decomposition scheme based on the block-localized wave function (BLW) method is proposed. The key of this scheme is the definition and the full optimization of the diabatic state wave function, where the charge transfer among interacting molecules is deactivated. The present energy decomposition (ED), BLW-ED, method is similar to the Morokuma decomposition scheme in definition of the energy terms, but differs in implementation and the computational algorithm. In addition, in the BLW-ED approach, the basis set superposition error is fully taken into account. The application of this scheme to the water dimer and the lithium cation–water clusters reveals that there is minimal charge transfer effect in hydrogen-bonded complexes. At the HF/aug-cc-PVTZ level, the electrostatic, polarization, and charge-transfer effects contribute 65%, 24%, and 11%, respectively, to the total bonding energy (-3.84 kcal/mol) in the water dimer. On the other hand, charge transfer effects are shown to be significant in Lewis acid–base complexes such as H_3NSO_3 and H_3NBH_3 . In this work, the effect of basis sets used on the energy decomposition analysis is addressed and the results manifest that the present energy decomposition scheme is stable with a modest size of basis functions. © 2000 American Institute of Physics. [S0021-9606(00)30313-0]

I. INTRODUCTION

It is of interest to decompose the total intermolecular interaction energy into specific energy components.¹ This can lead to deeper understanding of intermolecular interactions, and the quantitative results may be used to guide development of empirical, yet computationally fast force fields for biomolecular simulation and modeling.² For example, state-of-the-art molecular mechanics force fields for liquid and biopolymer simulations make use of pairwise potentials and fixed partial charges on atoms.³ There is need to improve these force fields by incorporating explicit many-body polarization terms into the potential energy function.⁴ Furthermore, recent studies⁵ using semiempirical divide-and-conquer quantum mechanical methods⁶ suggest that charge transfer interactions could be significant in aqueous solvation of biological systems such as proteins.⁷ Since these findings have important implications in force field development, an accurate estimate of the polarization and charge transfer interaction as well as the electrostatic component is warranted. In this article, we present an interaction energy decomposition method to analyze these effects using a block-localized wave function (BLW) technique that was developed recently for the study of electronic resonance energies.⁸

There are a number of algorithms in the literature for energy decomposition analyses.^{5,9–15} However, the energy components defined by various methods are not necessarily

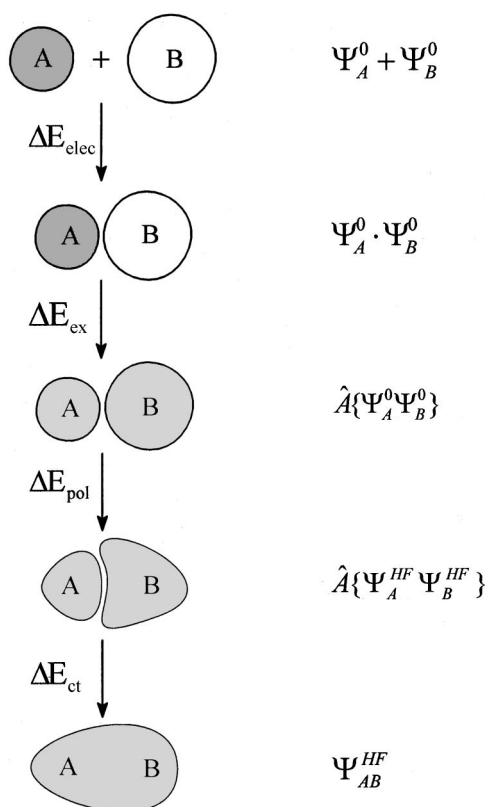
unique, resulting in numerical differences in the computational results. In general, energy decomposition schemes fall into two categories. The first is based on perturbation theory, where the interaction energy is partitioned into a series of energy terms according to the nature of the perturbation energy expression.^{10–13} An excellent summary of this approach is available in the textbook by Stone.¹² The perturbation theory has been used to construct effective fragment potentials in hybrid quantum mechanical and molecular mechanical (QM/MM) calculations.¹³ A scheme has also been proposed at the correlated level of theory (MPn).^{11d,e}

The second approach includes methods that formulate individual energy terms based on physical processes.^{5,14,15} Here, the energy decomposition is typically carried out at the Hartree–Fock (HF) level, and the total interaction energy is partitioned into electrostatic, exchange-repulsion, polarization, and charge transfer terms. Energy decomposition analysis involves the following steps (Scheme 1). First, the Coulombic interaction energy is determined using the Hartree product wave function of the isolated monomers in the complex configuration. The exchange repulsion energy arising from the Pauli exclusion principle is then obtained by antisymmetrizing the wave functions of monomer **A** and **B**. The perturbation of electron distribution of each monomer in the presence of the second monomer leads to charge redistribution within the same monomer species, and the energy accompanying this charge relaxation is the induction or polarization energy. Expansion of the charge density of each monomer into the virtual orbital space of the other monomer gives rise to the charge transfer term.

The Kitaura–Morokuma scheme perhaps is the best

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Scheme 1



known algorithm in this category.¹⁴ In this method, energy terms are obtained by solving a series of model HF equations, consisting of certain carefully defined elements in the Fock-type interaction matrix. Because of its simplicity and connection to intuitive concepts, the Kitaura–Morokuma scheme has been widely used.^{7,16} Similarly, Glendening and Streitwieser, using natural bond orbitals, proposed a natural energy decomposition analysis (NEDA) scheme¹⁵ to evaluate the electrostatic, polarization, and charge transfer energies. Recently, Vaart and Merz⁵ reported a decomposition algorithm, making use of “buffer densities” in the divide-and-conquer method at the semiempirical AM1 and PM3 level,⁶ and have applied it to proteins and liquid water calculations. In the latter study, the charge transfer component was found to be even greater than the total intermolecular interaction energy, while polarization effects make only minor contributions. Clearly, an important ingredient in determining the charge transfer energy is the need to construct a localized diabatic state that restricts the electron density of individual monomers within its own physical space. This of course cannot be strictly done, and consequently, depending on the actual procedure used to define the charge localized state, significant uncertainty may exist in the charge transfer term since it must disappear at the limit of a complete basis set.

In this article, we present an energy decomposition (ED) procedure, based on a block-localized wave function (BLW) method that was designed for describing charge localized valence bond configurations. Here, we extend the BLW method to studying charge-transfer effects in intermolecular interactions. Our decomposition scheme is analogous to

the Morokuma method (Scheme 1), but differs in implementation and computational algorithm. In addition, we include the basis set superposition error (BSSE) correction in the charge transfer term. In comparison with the NEDA method,¹⁵ the advantage of the present BLW-ED method lies in the fact that the diabatic state wave function is fully optimized under the condition that the orbitals of individual monomers are nonorthogonal.^{8,17} In the following, we first present the theoretical background for the BLW energy decomposition scheme (BLW-ED). Then, the method is illustrated by studies of the water dimer, the Li^+ –water clusters, $\text{Li}(\text{H}_2\text{O})_n^+$ ($n=1-4$), and Lewis acid–base complexes. In each case, the effect of basis set used in the computation is carefully addressed. To establish the relationship between the amount of charge transfer and the corresponding stabilization energy, Weinhold’s natural population analysis (NPA) has been used to determine atomic partial charges.¹⁸ The article concludes with a summary of the main findings from this study.

II. METHODOLOGY

A. The Block-localized wave function (BLW) method

Recently, we described a block-localized wave function (BLW) method,⁸ which is designed to localize electrons in specific regions of a molecular system. The method allows us to determine resonance energies due to electronic delocalization, and has been applied to organic compounds to estimate the resonance effects in allylic ions^{8a} and trisilylamine.^{8b} The BLW method can also be formulated to provide energy-decomposition analysis of intermolecular interactions, which is described in this article. In the BLW method, we partition all electrons and basis orbitals of a system into k subgroups. For example, the electrons and primitive basis orbitals of a molecular complex can be divided into subgroups of individual monomers. Each molecular orbital (MO) in a subgroup is written as a linear combination of the primitive basis functions in that particular subspace. The block-localized wave function for a specific valence bond configuration is expressed by a Slater determinant as follows:

$$\Psi^{\text{BLW}} = \hat{A}\{\Phi_1 \Phi_2 \dots \Phi_k\}, \quad (1)$$

where \hat{A} is an antisymmetrizing operator, and Φ_i is a successive product of the occupied molecular orbitals in subgroup i . In the BLW method, Ψ^{BLW} can be optimized iteratively by the Jacobi-rotation method,^{8a} or by a reorthogonalization algorithm of Gianinetti and Raimondi *et al.*¹⁹

It should be noted that the wave function defined in Eq. (1) has the restriction that the MOs in the same subgroup must be orthogonal (similar to the normal HF method). However, molecular orbitals in different subgroups are nonorthogonal (a feature of the valence bond approach). The restriction on the length of each MO expansion corresponds to the hypothesis that each electron is confined to a physical region defined by the subgroup. The BLW MOs avoid both orthogonalization and delocalization tails, which are always

present in orbitals localized from unitary transformation of canonical orbitals. Consequently, the BLW method can be used to estimate the conventional conjugation and hyperconjugation effect as well as charge-transfer effect between groups and molecules.⁸ Note that once we remove the restriction on the length of expansion of the MOs in Eq. (1), the BLW method returns to the familiar HF theory.

B. Energy decomposition analysis

A number of energy decomposition schemes have been proposed and are available in most quantum chemistry software. The primary difference of these methods stems from the implementation of the computational procedure. In the present study, we make use of the BLW approach, which allows a convenient separation of contributing energy terms. With the inclusion of the correction for basis set superposition error (BSSE),²⁰ the interaction energy for a bimolecular complex **AB** is defined as follows:

$$\Delta E_{\text{int}} = E(\Psi_{\text{AB}}) - E(\Psi_{\text{A}}^0) - E(\Psi_{\text{B}}^0) + \Delta E(\text{BSSE}), \quad (2)$$

where Ψ_{AB} is the optimized wave function for the complex **AB**, and Ψ_{A}^0 and Ψ_{B}^0 are, respectively, the wave functions for monomers **A** and **B**. $\Delta E(\text{BSSE})$ is the correction for BSSE, estimated using the Boyd and Bernardi counterpoise method.²⁰

At the HF level, most energy decomposition schemes eventually lead to separation of the total interaction energy of a molecular complex into four specific contributing terms, including electrostatic ΔE_{elec} , exchange repulsion, ΔE_{ex} , polarization ΔE_{pol} , and charge transfer (ct) ΔE_{ct} :

$$\Delta E_{\text{int}} = \Delta E_{\text{elec}} + \Delta E_{\text{ex}} + \Delta E_{\text{pol}} + \Delta E_{\text{ct}}. \quad (3)$$

We adopt the decomposition scheme outlined in Scheme 1 using the BLW wave function. We first define a BLW wave function for the molecular complex **AB** by partitioning the system into two blocks, one corresponding to monomer **A** and the other monomer **B**,

$$\Psi_{\text{AB}}^{\text{BLW}} = \hat{A} \{ \Psi_{\text{A}}^{\text{HF}} \Psi_{\text{B}}^{\text{HF}} \}, \quad (4)$$

where the superscript HF is to emphasize that Hartree–Fock wave functions are used for monomers **A** and **B**. The antisymmetrizing operator in Eq. (4) is to account for exchanging electrons between monomer **A** and monomer **B** in the complex. Note that the wave function $\Psi_{\text{A}}^{\text{HF}}$ and $\Psi_{\text{B}}^{\text{HF}}$ are different from Ψ_{A}^0 and Ψ_{B}^0 for the isolated monomers [Eq. (2)] since the former include polarization and exchange interactions for the monomers in the complex (Scheme 1).

The BLW wave function of Eq. (4) restricts the charge distribution of each monomer within its own primitive atomic orbital space, i.e., the charge densities of individual monomers are localized. Extending the orbital expansion space over the entire complex **AB**, leading to the standard Hartree–Fock wave function, represents charge delocalization or charge transfer (CT) between the constituent monomers. The energy change accompanying this process is defined as the charge transfer energy (Scheme 1)

$$\Delta E_{\text{ct}} = E(\Psi_{\text{AB}}^{\text{HF}}) - E(\Psi_{\text{AB}}^{\text{BLW}}) + \Delta E(\text{BSSE}). \quad (5)$$

Here, we have included the BSSE correction in the CT term because only this step in the energy decomposition analysis involves expansion of the basis set space, leading to charge delocalization. The difficulty, however, is to enumerate the $\Delta E(\text{BSSE})$ term accurately. The traditional counterpoise correction tends to overestimate the BSSE.²¹ Consequently, the CT energy will be underestimated if $\Delta E(\text{BSSE})$ is included in this fashion. We propose to consider the CT energy determined with and without the $\Delta E(\text{BSSE})$ term as the lower and upper bound for this energy term. Interestingly, Eq. (5) is also used to define the electronic delocalization (resonance) energy of organic compounds.^{8b}

Equation (5) is formally identical to the definition of CT energy in the NEDA method,¹⁵ although the actual computational algorithms are different. In the NEDA method, the localized wave function is constructed using natural bond orbitals (NBO)¹⁸ for fragments **A** and **B**, derived from $\Psi_{\text{AB}}^{\text{HF}}$. These NBOs are used in energy calculations without SCF optimization, as opposed to full SCF calculation in the BLW method. As a result, the energy of the localized state in the NEDA method is higher than the relaxed one, and thus, the CT energy is overestimated. In contrast to the Morokuma scheme,¹⁴ we explicitly construct and optimize the localized diabatic BLW wave function, whereas Kitaura and Morokuma employ an elaborate scheme to zero the corresponding Fock matrix elements. Thus, a residual mixing term ΔE_{mix} is left in this scheme, which cannot be attributed to charge transfer nor polarization. In addition, our BLW scheme can easily be extended to systems consisting of any number of monomers, and many-body interaction terms can be conveniently defined.²² The BSSE correction term is not specifically considered in the Morokuma algorithm.

The electrostatic energy ΔE_{elec} corresponds to the interaction energy for the process of bringing monomers **A** and **B** into the final configuration of the **AB** complex, but keeping constant the wave functions of the isolated species **A** and **B**,

$$\Delta E_{\text{elec}} = \langle \Psi_{\text{A}}^0 \Psi_{\text{B}}^0 | \hat{H} | \Psi_{\text{A}}^0 \Psi_{\text{B}}^0 \rangle - E(\Psi_{\text{A}}^0) - E(\Psi_{\text{B}}^0), \quad (6)$$

where $\Psi_{\text{A}}^0 \Psi_{\text{B}}^0$ indicates a Hartree product wave function of two Slater determinants. The exchange–repulsion term ΔE_{ex} in Eq. (3) is a quantum-mechanical phenomenon that the electronic wave function must be antisymmetric due to the Pauli exclusion principle, which is given as follows:

$$\Delta E_{\text{ex}} = E(\Psi_{\text{AB}}^0) - \langle \Psi_{\text{A}}^0 \Psi_{\text{B}}^0 | \hat{H} | \Psi_{\text{A}}^0 \Psi_{\text{B}}^0 \rangle. \quad (7)$$

Note that the exchange–repulsion term in Eq. (7) is always positive. The wave function Ψ_{AB}^0 for this “computational complex” is defined as follows (Scheme 1):

$$\Psi_{\text{AB}}^0 = \hat{A} \{ \Psi_{\text{A}}^0 \Psi_{\text{B}}^0 \}. \quad (8)$$

The interaction between monomers in the complex will result in distortion of their respective electron densities. The induction of the change in the monomer wave function gives rise to the polarization stabilization of the system, which is defined by Eq. (9),

$$\Delta E_{\text{pol}} = E(\Psi_{\text{AB}}^{\text{BLW}}) - E(\Psi_{\text{AB}}^0). \quad (9)$$

The polarization and CT terms [Eqs. (5) and (9)] are intimately related in that both terms account for the charge re-

TABLE I. Computed energy components for the water dimer (kcal/mol) and results with selected basis sets from the Morokuma analysis.^{a,b}

Basis set	ΔE_{elec}	ΔE_{ex}	$\Delta E_{\text{elec+ex}}$	ΔE_{pol}	ΔE_{ct}	$\Delta E(\text{BSSE})^c$	$\Delta E_{\text{int}}^{\text{HF}}$
STO-3G	-3.8	2.9	-0.9	-0.2	-0.9	2.7	-2.0
4-31G	-8.3	3.1	-5.2	-0.7	-0.6	1.1	-6.5
6-31G(<i>d</i>)	-6.8	3.1	-3.7	-0.6	-0.5	0.7	-4.8
6-31G(<i>d,p</i>)	-6.7	3.2	-3.5	-0.6	-0.6	0.7	-4.7
6-311G(<i>d,p</i>)	-6.7	3.2	-3.5	-0.6	-0.3	1.2	-4.4
6-31++G(<i>d,p</i>)	-7.8	4.2	-3.6	-0.7	-0.2	0.6	-4.5
6-31++G(2 <i>d</i> ,1 <i>p</i>)	-6.9	4.1	-2.8	-0.7	-0.4	0.3	-3.9
6-31++G(2 <i>d</i> ,2 <i>p</i>)	-6.9	4.1	-2.8	-0.7	-0.5	0.3	-3.9
6-311++G(<i>d,p</i>)	-7.5	4.1	-3.4	-0.7	-0.3	0.5	-4.3
6-311++G(2 <i>d</i> ,2 <i>p</i>)	-6.8	4.0	-2.8	-0.7	-0.4	0.3	-3.8
aug-cc-pVTZ	-6.4	4.0	-2.4	-0.9	-0.4	0.1	-3.7
Morokuma analysis							
6-31G(<i>d</i>)	-6.8	3.2	-3.6	-0.5	-1.3	-0.1	-5.5
6-311++G(2 <i>d</i> ,2 <i>p</i>)	-6.8	4.0	-2.8	-0.8	-0.9	0.4	-4.1
aug-cc-pVTZ	-6.4	4.0	-2.4	-1.3	-1.2	1.1	-3.8

^aThe geometry is optimized at the HF/6-311++G(2*d*,2*p*) level.^bThe estimated complete basis set limit is -3.55 kcal/mol for the RHF method (Ref. 26).^cCoupling energies are listed for the Morokuma analysis since BSSE is not included.

organization due to intermolecular interactions. The polarization energy as defined in Eq. (9) describes the energy change due to intramolecular charge delocalization, whereas the charge transfer term [Eq. (5)] results from intermolecular electronic delocalization. Both energy terms provide stabilization of the molecular system and thus are always negative. The reason that it is possible to separate electronic polarization of individual monomers and intermolecular charge transfer in these calculations is because we have defined the charge-localized diabatic state using the BLW method. At the limit of a complete basis set, the CT term must vanish. Alternatively, as is done in the Morokuma decomposition, the charge transfer term can be determined by formulating a Fock interaction matrix that includes interactions between the occupied orbitals with virtual orbitals of the other monomer. The charge transfer interaction energy can also be determined via a perturbation approach, making use of the non-orthogonal occupied and virtual molecular orbitals from the BLW calculation.

The BLW calculations described in this article are performed using a program developed in our laboratory, while HF SCF calculations are carried out using GAUSSIAN94.²³

III. RESULTS AND DISCUSSION

We apply the present BLW-ED scheme to a number of small systems that have been extensively studied previously for comparison to illustrate its applicability. This includes the water dimer, $\text{Li}(\text{H}_2\text{O})_n$ where $n = 1-4$, and Lewis acid-base complexes. Additional applications of the method to the solvation of molecules of biological interest will be presented in the future to analyze the importance of polarization and CT effect between solute and solvent molecules.

A. Water dimer

The water dimer has been thoroughly investigated including energy decomposition analysis.²⁴⁻²⁷ The present calculation is to illustrate that the BLW-ED analysis can yield reasonable results for estimating components of hydrogen

bonding interactions. Furthermore, recent studies employing the divide-and-conquer technique suggest that there is significant CT energy in hydrogen bonding interactions between water molecules, both as a dimer and in the liquid state.⁵ Surprisingly, the electrostatic interaction energy was predicted to be repulsive (positive) for liquid water, whereas polarization only plays a minor role in the overall interaction energy. However, the divide-and-conquer calculations were carried out using a minimal basis set at the semiempirical AM1 and PM3 levels. Since these findings have important implications in the development of next-generation molecular mechanics force fields that include explicit polarization terms and perhaps charge transfer components, it seems desirable to revisit the same system at the *ab initio* level using extended basis functions.

We used the linear hydrogen bonding geometry for the water dimer with a C_s symmetry, which is obtained by optimizing the hydrogen bond distance (2.089 Å) at the HF/6-311++G(2*d*,2*p*) level using fixed monomer geometry at the experimental values [$R(\text{OH})=0.9572$ Å and $\angle\text{HOH}=104.52^\circ$].^{27b} Table I lists the total and individual energy terms using various basis sets ranging from STO-3G to aug-cc-pVTZ, along with results from Morokuma decomposition calculations.

It is obvious in Table I that the predicted interaction energies for the water dimer readily converges to values close to the estimated HF limit of -3.55 kcal/mol.²⁶ The only exceptions are the STO-3G and 4-31G basis sets, which are not adequate for computing hydrogen bonding energies as noted repeatedly in the literature.^{24a} In exact agreement with the Morokuma analysis,^{14a} the leading term in the predicted $\Delta E_{\text{int}}^{\text{HF}}$ is the electrostatic energy. Interestingly, the polarization energy computed using the BLW-ED method is almost independent of basis set except STO-3G, while the CT term shows only small variations beyond the 6-31G(*d,p*) basis set. Polarization and CT energies tend to be somewhat overestimated by the Morokuma analysis due to the presence of a relatively large coupling (mixing) term.

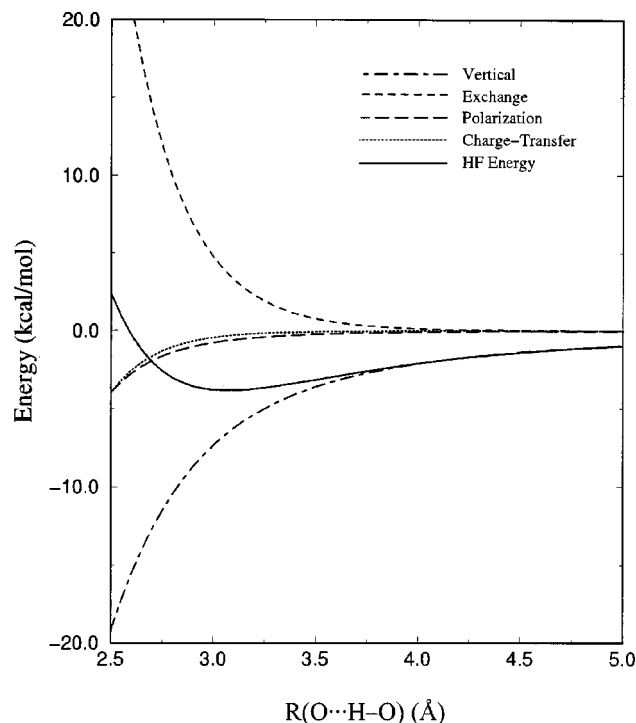


FIG. 1. Interaction energy profiles for the water dimer at the HF/6-311G++G(2d,2p) level.

Based on our BLW-ED scheme using the aug-cc-pVTZ basis set, the electrostatic, polarization, and CT interactions contribute, respectively, 65%, 24%, and 11% to the total HF interaction energy. We find that the CT effect contributes the least among all energy terms, while polarization energy is significant, consistent with early combined QM/MM simulation studies.²⁸ For comparison, Morokuma analyses yield the following relative contributions from the electrostatic, polarization, CT, and polarization-CT mixing term: 63%, 34%, 32%, and -29%.²⁹ The large mixing term, which is opposite in sign, significantly increases polarization and CT energies in the Morokuma analysis.

Figure 1 examines the dependence of individual energy terms as a function of the hydrogen bond distance at the HF/6-311++G(2d,2p) level. Clearly, the polarization energy and CT effects are important only at short distances, whereas the electrostatic interaction extends to longer ranges. In fact, beyond the van der Waals regime the hydrogen bonding energy is almost exclusively due to the electrostatic interaction and the Pauli exchange repulsion. At short range, the exchange repulsion term increases more rapidly than all other terms.

The amount of charge transfer in the water dimer is determined by the natural population analysis (NPA) using the 6-311++G(2d,2p).¹⁸ The change of partial charges from the isolated molecule to that computed using the BLW wave function Ψ_{AB}^{BLW} represents the mutual polarization effect, while relaxation from Ψ_{AB}^{BLW} to the HF wave function Ψ_{AB}^{HF} yields the amount of intermolecular charge transfer for the water dimer at the hydrogen bonding distance. The net intermolecular charge transfer in the water dimer is only 0.005e going from the hydrogen bond acceptor into the donor mono-

mer (Table A1). The charge relaxation between Ψ_{AB}^{BLW} and Ψ_{AB}^{HF} is even smaller, with only 0.003e charge transfer. In contrast, polarization effects, which correspond to the change in charge density from $\hat{A}\{\Psi_A^0\Psi_B^0\}$ to Ψ_{AB}^{BLW} , lead to significant charge reorganization within each monomer. The donor hydrogen atom loses 0.032e in electron density, corresponding an increase in partial charge from +0.464 to +0.496e, and the donor oxygen gains 0.028 electrons in density. Concomitantly, the partial charge on the acceptor oxygen changes from -0.929 to -0.946e, and the partial charge on the hydrogen atoms increases from 0.464 to 0.474e. The NPA analysis suggests that intramolecular polarization effects have much greater impact on the charge redistribution within each monomer than intermolecular charge transfer. Since the difference between these two effects is nearly by an order-of-magnitude in the present analysis, it appears that efforts in improving molecular mechanics force fields to model hydrogen bonding interactions involving water should be focused on intramolecular charge polarization rather than intermolecular charge transfer.

B. $\text{Li}(\text{H}_2\text{O})_n^+$ clusters

The $\text{Li}(\text{H}_2\text{O})_n^+$ ($n=1,\dots,4$) complexes involve strong hydrogen bonding interactions with significant covalent character.³⁰⁻³⁵ Experimental studies have established that the hydration number of lithium in aqueous solution is about four.³⁵ In the present work, the geometries for the four clusters are optimized at the HF/6-311++G(2d,2p) level, again, with the geometry for water molecules fixed at its experimental values. The Li-O distance in $\text{Li}(\text{H}_2\text{O})_4^+$ is predicted to be 1.960 Å, in good agreement with the value of 1.96 ± 0.02 Å in aqueous solution determined by the neutron diffraction experiment.³⁶

Selected results from BLW-ED and Morokuma analysis are listed in Table II for the $\text{Li}(\text{H}_2\text{O})^+$ complex. The computed binding energies generally fall in the range of -35.1 to -37.5 kcal/mol. The HF limit for the $\text{Li}^+\cdots\text{OH}_2$ complex has been estimated to be -35.8 kcal/mol.^{15c} It is found that diffuse functions are important to reduce the BSSE correction. Without the diffuse functions the BSSE correction is about 2 kcal/mol, whereas with inclusion of diffuse functions, the errors are lowered to zero using the aug-cc-pVTZ basis set. For the $\text{Li}(\text{H}_2\text{O})^+$ complex, 64% of the total interaction energy are due to electrostatic contributions, 31% are from polarization, and 5% originate from charge transfer effects. Surprisingly, the Morokuma analysis failed to converge for the $\text{Li}(\text{H}_2\text{O})^+$ complex because the mixing term becomes unreasonably large as the basis function increases.

The small charge transfer contribution to the $\text{Li}(\text{H}_2\text{O})^+$ binding energy is echoed by the NPA charge population (Table A2). Intramolecular charge polarization results in an increase of the oxygen partial charge by 0.114e, from -0.929 to -1.043e. This remarkable polarization effect enhances the dipole moment of water, leading to significant polarization energy in the complex. On the other hand, the charge transfer effect from water to the lithium ion is estimated to be only 0.003e.

The binding energy computed at the HF/6-311+

TABLE II. Estimated energy components for the $\text{Li}^+\cdots\text{H}_2\text{O}$ complex (kcal/mol) and results with selected basis sets from the Morokuma analysis.^a

Basis set	ΔE_{elec}	ΔE_{ex}	$\Delta E_{\text{elec+ex}}$	ΔE_{pol}	ΔE_{ct}	$\Delta E(\text{BSSE})^b$	$\Delta E_{\text{int}}^{\text{HF}}$
STO-3G	-31.6	3.5	-28.1	-3.3	-15.8	30.7	-47.2
4-31G	-49.3	10.5	-38.8	-5.4	-1.0	2.7	-45.2
6-31G(<i>d</i>)	-40.5	11.1	-29.4	-7.3	-0.8	2.1	-37.5
6-31G(<i>d,p</i>)	-39.9	10.9	-29.0	-7.4	-1.2	2.2	-37.5
6-311G(<i>d,p</i>)	-39.9	10.9	-29.0	-7.1	-1.2	2.3	-37.3
6-31++G(<i>d,p</i>)	-41.3	14.1	-27.2	-7.7	-0.8	0.8	-35.6
6-31++G(2 <i>d</i> ,1 <i>p</i>)	-36.9	13.2	-23.7	-9.8	-1.4	0.3	-34.9
6-31++G(2 <i>d</i> ,2 <i>p</i>)	-36.7	13.1	-23.5	-9.8	-1.6	0.3	-34.9
6-311++G(<i>d,p</i>)	-40.7	13.8	-26.9	-7.5	-1.3	0.9	-35.7
6-311++G(2 <i>d</i> ,2 <i>p</i>)	-36.6	13.0	-23.6	-9.3	-2.2	0.3	-35.1
aug-cc-pVTZ	-35.2	12.3	-22.9	-10.9	-1.9	0.0	-35.7
Morokuma Analysis							
6-31G(<i>d</i>)	-40.5	11.1	-29.4	-9.6	-3.0	2.4	-39.6
6-311++G(2 <i>d</i> ,2 <i>p</i>)	-36.6	13.0	-23.6	-15.2	-5.4	8.8	-35.4
aug-cc-pVTZ	-35.2	12.3	-22.9	-24.5	-8.1	19.8	-35.7

^aThe geometry is optimized at the HF/6-311++G(2*d*,2*p*) level.^bCoupling energies between ΔE_{pol} and ΔE_{ct} are listed in Morokuma analysis.

+G(2*d*,2*p*) level for the following processes with *n* up to 4 water molecules are listed in Table III,



Although the total binding energy increases as the number of water molecules increases, the incremental contribution from subsequent water molecules decreases due to increase electrostatic repulsion from other water molecules. The energy decomposition analyses for these cluster complexes reveal the same energetic trends. Remarkably, while both the total electrostatic and polarization energies increase as more water molecules are added, the CT term remains roughly unchanged. For $\text{Li}(\text{H}_2\text{O})_4^+$, the relative contributions from electrostatic, polarization, and CT terms are, respectively, 73%, 25%, and 2%. NPA population analyses also indicate minimal charge transfer from water to the cation. In $\text{Li}(\text{H}_2\text{O})_n^+$ complexes, inclusion of the BSSE term has minimal effects on the overall CT energy.

Before closing this section, we consider the nonadditive water–water interactions in the $\text{Li}(\text{H}_2\text{O})_n^+$ complexes. The interaction energies among the water molecules in the configuration of the complex are predicted to be 1.9, 6.8, and 14.1 kcal/mol for *n*=2, 3, and 4, respectively, at the HF/6-311++G(2*d*,2*p*) level. These positive energy terms are largely responsible for the successively less contribution from Li–water interactions.

C. Lewis acid–base complexes

Lewis acid–base or donor–acceptor complexes such as H_3NSO_3 and $\text{H}_3\text{N–BH}_3$ have been extensively studied both experimentally and theoretically because of their important role in structural chemistry.³⁷ Of special interest is the bonding character of the dative bonds, which exhibit significant variations up on a change in the medium. For example, the N–S bond in sulfamic acid is 1.957 Å in the gas phase,³⁸ which is considerably longer than a value of 1.7714 Å from x-ray crystal structure determination.³⁹ Furthermore, analysis of the nitrogen quadrupole hyperfine structure from a micro-

wave spectroscopic investigation suggests that there is significant electron transfer (about 0.36 electrons) upon formation of the complex.³⁸ Although the structure, energy, and medium effects on sulfamic acid have been investigated,⁴⁰ a detailed characterization of the intermolecular interaction in terms of energy components has not been performed.

Computed total interaction energy and energy components obtained from the present BLW-ED method and from Morokuma analysis are listed in Table IV. In both Lewis acid–base complexes, there is strong electrostatic attraction, which is offset by the exchange repulsion term, leading to overall positive electrostatic energies of 68.2 and 33.0 kcal/mol for H_3NSO_3 and H_3NBH_3 , respectively. The agreement in electrostatic term between the BLW-ED and Morokuma results is excellent. However, the mixing term in the Morokuma analysis is basis set dependent, which becomes very large as the size of basis set increases. This was recognized a long time ago because the polarization and CT terms in the Morokuma analysis contain the same interaction terms between occupied and vacant orbitals, and are identical at the limit of infinite basis set. Thus, the mixing term has to compensate for these negative energies to yield a large positive energy. Fortunately, the present BLW-ED method is reasonably stable in computed polarization and CT energies on going from 6-31+G(*d*) to cc-pVTZ. This is because we have specifically constructed localized, diabatic wave functions, corresponding to polarization and charge transfer

TABLE III. Computed energy components for the reaction of $\text{Li}^+ + (\text{H}_2\text{O})_n \rightarrow \text{Li}(\text{H}_2\text{O})_n^+$ (*n*=1–4) using the 6-311++G(2*d*,2*p*) basis set (kcal/mol).

System	ΔE_{vert}	ΔE_{ex}	ΔE_{elec}	ΔE_{pol}	ΔE_{ct}	$\Delta E(\text{BSSE})$	$\Delta E_{\text{int}}^{\text{HF}}$
$\text{Li}(\text{H}_2\text{O})^+$	-36.6	13.0	-23.6	-9.3	-2.2	0.3	-35.1
$\text{Li}(\text{H}_2\text{O})_2^+$	-68.3	21.9	-46.3	-17.8	-2.7	1.0	-66.8
$\text{Li}(\text{H}_2\text{O})_3^+$	-92.1	25.2	-66.9	-24.8	-2.8	1.3	-94.5
$\text{Li}(\text{H}_2\text{O})_4^+$	-109.2	23.8	-85.4	-29.5	-2.0	1.7	-117.0

TABLE IV. Computed interaction energies and energy components for $\text{H}_3\text{N}-\text{SO}_3$ and $\text{H}_3\text{N}-\text{BH}_3$ (kcal/mol).

	BLW-ED			Morokuma		
	6-31G(d)	6-311+G(d,p)	cc-pVTZ	6-31G(d)	6-311+G(d,p)	cc-pVTZ
$\text{H}_3\text{N}-\text{SO}_3$						
ΔE_{es}	-116.8	-126.3	-109.4	-116.8	-125.8	-110.7
ΔE_{ex}	161.6	180.7	163.5	161.6	180.0	165.8
$\Delta E_{\text{es}} + \Delta E_{\text{ex}}$	44.8	54.4	54.1	44.8	54.2	55.1
ΔE_{pol}	-25.0	-29.1	-34.6	-45.7	-270.4	-253.6
$\Delta E_{\text{ct}}^{\text{a}}$	-53.6	-53.1	-49.6	-62.2	-389.3	-85.8
ΔE_{mix}				29.3	574.0	253.0
$\Delta E_{\text{tot}}^{\text{a}}$	-28.8	-27.8	-30.1	-33.7	-31.5	-31.4
$\text{H}_3\text{N}-\text{BH}_3$						
ΔE_{es}	-90.5	-87.8	-80.4	-90.5	-87.8	-80.6
ΔE_{ex}	101.7	111.6	102.4	101.7	111.6	103.4
$\Delta E_{\text{es}} + \Delta E_{\text{ex}}$	11.2	23.8	22.0	11.2	23.8	22.8
ΔE_{pol}	-19.4	-26.8	-30.4	-28.8	-49.1	-151.2
$\Delta E_{\text{ct}}^{\text{a}}$	-27.0	-30.6	-27.6	-33.1	-61.0	-62.8
ΔE_{mix}				13.0	51.6	155.3
$\Delta E_{\text{tot}}^{\text{a}}$	-35.2	-33.5	34.9	-37.7	-31.5	-35.9

^aCorrections for the basis set superposition error have been included in the charge transfer term and in the total interaction energy. BSSE are 4.9, 3.7, and 1.3 kcal/mol for $\text{H}_3\text{N}-\text{SO}_3$; and 2.5, -2.0, and 1.0 kcal/mol for $\text{H}_3\text{N}-\text{BH}_3$ using the 6-31G(d), 6-311+G(d,p), and cc-pVTZ basis sets, respectively.

states. Using the cc-pVTZ basis set, the computed polarization and CT energies are -34.6 and -49.6 kcal/mol for H_3NSO_3 , and -30.4 and -27.6 kcal/mol for H_3NBH_3 . In an alternative formulation, Morokuma proposed to use a Dewar-Chat-Duncanson scheme involving "donation" and "back-donation" mechanisms. This gives relatively basis set insensitive results, though the coupling term is still 17 kcal/mol for H_3NBH_3 .^{14b} The computed total interaction energies of -16.0 and -23.9 kcal/mol, which are computed by including a geometry deformation term to account for the energy change associated with geometry variation from isolated monomers to that in the complex, for sulfamic acid and H_3NBH_3 are in accord with previous theoretical studies.⁴⁰

The charge migration, both in terms of intramolecular polarization and intermolecular charge transfer, can be illustrated by the change in electron density between the localized and delocalized wave functions corresponding to the respective polarization and CT states. This is illustrated in Fig. 2 for $\text{H}_3\text{N}-\text{SO}_3$. Both polarization and CT show electron flow from N to S along the N-S bond. Natural bond orbital population analysis using the 6-311++G(2d,2p) basis set yields a net charge transfer of $0.23e$, which may be compared with Leopold's experimental estimate of $0.36e$.³⁸

IV. CONCLUSIONS

Based on the BLW method, we have presented an energy decomposition scheme for analysis of specific electrostatic, exchange-repulsion, polarization, and charge transfer

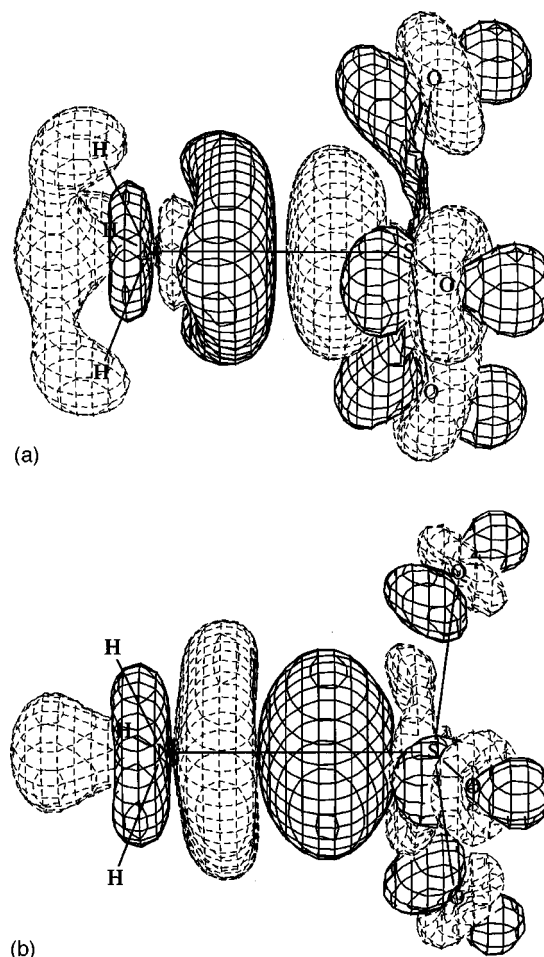


FIG. 2. Electron density difference plot for sulfamic acid ($\text{H}_3\text{N}-\text{SO}_3$). Electron density changes due to intramolecular charge polarization are shown in (A), and charge transfer between the two monomers are given in (B). Contour levels are $0.015 e/\text{au}^3$. Solid curves indicate an increase in electron density, and dashed curves represent a depletion in charge density.

energy contributions to the overall interaction energy of molecular clusters. An essential component in the presentscheme is the definition of diabatic reference states, where polarization and charge transfer interactions are deactivated. Comparison of the electron density obtained from the diabatic state wave function (Ψ^{BLW}) and from the adiabatic state wave function (Ψ^{HF}) can uniquely manifest the charge flow between interacting monomers and its accompanying energies. The present BLW-ED method is similar to the Morokuma decomposition scheme in definition of the energy terms, but differ in practical implementation and the computational algorithm.

In this study, we demonstrate the applicability of the BLW-ED method for energy decomposition analysis by examining hydrogen bonding interactions in the $\text{H}_2\text{O} \cdots \text{HOH}$, $\text{Li}(\text{H}_2\text{O})_n^+$, and H_3NSO_3 and $\text{H}_3\text{N}-\text{BH}_3$ Lewis acid–base complexes. In the first two cases, charge transfer effects play a minimal role in intermolecular interactions, both in terms of the absolute amount of charge transfer and charge transfer energy. The charge-transfer interaction in the water dimer is less pronounced than the polarization effect, while the dominant energy term is due to the electrostatic interaction, which consists of an attractive interaction term and a repulsive Pauli exchange contribution. At the HF aug-cc-pVTZ level, the electrostatic energy, polarization energy, and charge-transfer effects contribute, respectively, 65%, 24%, and 11% of the total interaction energy in the water dimer. For the Li^+ –water complexes, charge transfer effects play a negligible role, making contributions of only 2%–6% to the total interaction energy. On the other hand, electronic polarization of the water molecules is important, which provides up to 25% of the interaction energy. Significant charge transfer effects and electronic polarization are found in the Lewis acid–base complexes. In comparison with results from Morokuma analyses, the present BLW-ED method yields stable results for polarization and charge transfer energies as the size of basis sets increases. On the other hand, Morokuma analysis contains a large, unphysical coupling term for strong bimolecular interactions, leading to divergent polarization and charge transfer energies. The present BLW-ED method provides a complement to the Morokuma analysis for studying strong intermolecular interactions.

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APPENDIX

Weinhold natural atomic charges determined from natural bond orbital analyses are given for each system considered. All computations are carried out at the HF/6-311++G(2d,2p) level (see Tables A1–A3).

Table A1. Weinhold natural atomic charges (e) for the monomer, and the delocalized and localized water dimer at the HF/6-311++G(2d,2p) level.

Atom	$\Psi_A^0(\Psi_B^0)$	Ψ_{AB}^{HF}	Ψ_{AB}^{Loc}
O ₁	−0.929	−0.945	−0.946
H ₂ (H ₃)	0.464	0.475	0.474
H ₄	0.464	0.493	0.496
O ₅	−0.929	−0.956	−0.957
H ₆	0.464	0.458	0.459

Table A2. Weinhold natural atomic charges (e) for the monomers, and the delocalized and localized $\text{Li}^+ \cdots \text{H}_2\text{O}$ complex.

Atom	$\Psi_A^0(\Psi_B^0)$	Ψ_{AB}^{HF}	Ψ_{AB}^{Loc}
Li	1.000	0.994	0.997
O	−0.929	−1.043	−1.043
H	0.464	0.525	0.523

Table A3. Weinhold natural atomic charges (e) for the monomers, and the delocalized and localized $\text{Li}(\text{H}_2\text{O})_n^+$ complex.^a

System	Atom	$\Psi_A^0(\Psi_B^0)$	Ψ_{AB}^{HF}	Ψ_{AB}^{Loc}
$\text{Li}(\text{H}_2\text{O})_2^+$	Li	1.000	0.975	0.980
	O	−0.929	−1.023	−1.025
	H	0.464	0.518	0.517
$\text{Li}(\text{H}_2\text{O})_3^+$	Li	1.000	0.949	0.954
	O	−0.929	−1.001	−1.002
	H	0.464	0.509	0.509
$\text{Li}(\text{H}_2\text{O})_4^+$	Li	1.000	0.922	0.927
	O	−0.929	−0.982	−0.983
	H	0.464	0.500	0.500

^aMonomers refer to Li^+ and $(\text{H}_2\text{O})_n$.

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