Ab Initio Localized Charge Distributions: Theory and a Detailed Analysis of the Water Dimer-Hydrogen Bond

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The method of localized charge distributions, originally implemented for semiempirical molecular orbital (MO) theory, is reintroduced and implemented for ab initio self-consistent field MO theory. This theory is then used in conjunction with localized second-order Möller–Plesset (MP2) pair energies to analyze the hydrogen bond in the water dimer. It is found that this hydrogen bond can be explained as the competition between the intrawater electronic kinetic energy pressure and the interwater potential energy suction.

I. Introduction

"Current progress towards better quantum chemical calculations is leading to increasingly complex wavefunctions, making it more and more difficult to relate them to qualitative ideas about chemical binding. Thus a need arises for conceptual interpretations which are appropriate for such wavefunctions and at the same time allow for the development of a corresponding physical and chemical intuition." 1

While this was written nearly a quarter of a century ago, it is certainly no less true today. The method of localized charge distributions2 addresses this need for conceptual interpretations by decomposing wave functions and properties of the wave functions into components on which most chemical intuition is fundamentally based: inner shells, bonds, and lone pairs. Although these components were originally devised as conceptual tools for the interpretation of molecular structure, they have a strong theoretical footing in quantum mechanics through the theory of equivalent orbitals3 and subsequently localized molecular orbitals (LMOs).4 However, a similar partitioning of the molecular energy and one-electron properties into contributions from such components proves difficult since the terms involving the nuclei are not easily assigned. The central idea behind the concept of localized charge distributions (LCDs) is to assign part of a nuclear charge to a particular LMO that is predominantly associated with that nucleus. This "local" nuclear charge (or charges) and the LMO respectively constitute the nuclear and electronic part of an electrically neutral LCD. This idea appears to date back at least as far as 1951, when Lennard-Jones and Pople5 considered hydrogen bonding in water. In 1958 Parks and Parr made use of the concept in their theory of separated electron pairs.6 Pritchard and Kern7 used the LCD approach to define bond dipole and quadrupole moments about a decade later. The implementation of the theory of LCDs presented in this paper was originally formulated in 1971 by England and Gordon8 and implemented for semiempirical INDO theory. Numerous applications and extensions followed in later years, and some are listed in ref 8. For example, Amos and Crispin9 used LCDs to derive parameters for classical intermolecular interaction formulas, and Tomasi and co-workers8b partitioned molecular electrostatic potentials into LCD components.

In this paper we present the implementation of this method for ab initio SCF MO theory (RHF and high-spin ROHF). First, the underlying theory will be introduced, and cases for which the nuclear partitioning is not obvious will be discussed. Second, a compatible representation of the correlation energy is presented. Finally, these two methods are used to analyze the hydrogen bond in the water dimer. In addition to being a most important chemical phenomenon, hydrogen-bond formation is easily analyzed using LCDs since no covalent bonds are broken or formed. Many energy decomposition schemes9 have been applied to hydrogen-bonded systems. Virtually all decompose the total energy into components such as Coulomb interaction, polarization, exchange repulsion, charge transfer, and electron density deformation. The approach taken in this paper is rather different in that it highlights the interplay between the electronic kinetic energy and the potential energy.

II. Theory

A. Theory of Localized Charge Distributions. 1. Nuclear Charge Partitioning. A localized charge distribution (LCD) consists of a localized molecular orbital (LMO,ψi) plus its assigned local nuclear charge distribution [Zi(A) for all atoms A]. A charge distribution of a neutral molecule consisting of 2N electrons in N orbitals and M nuclei can be partitioned into N neutral LCDs by setting

\[ Z_i(A) = \begin{cases} 2 & \text{if } \psi_i \text{ is an inner-shell or a lone-pair} \\ & \text{LMO predominantly localized on atom A} \\ 1 & \text{if } \psi_i \text{ is a bond LMO predominantly localized} \\ & \text{on atom A and its bonded partner} \\ 0 & \text{otherwise} \end{cases} \]  

(1)

The total nuclear charge on a given atom (A) must be preserved:

\[ \sum_{i=1}^{N} Z_i(A) = Z_A \]  

(2)

where Za is the nuclear charge on atom A. Consider the BH molecule as an example. Localizing the electronic wave function yields three doubly occupied LMOs: an inner shell, a lone pair, and a bond orbital. The first two are predominantly localized on one atom (B), whereas the bond orbital is localized on both atoms (B and H). These three orbitals can now be used to define their corresponding localized nuclear charge distributions: inner-shell and lone-pair LMOs are assigned +2 charges positioned at the one atom on which they are localized,
whereas the bond LMOs are assigned +1 charges on each of the two atoms on which they are localized:

These three types of localized charge distributions can be used to describe most, but not all, molecules. What follows are five examples of molecules with other types of LMOs and some suggestions about how to assign nuclear charges to them to form LCDs. In all cases, the LMOs are those obtained using the energy localization scheme of Edmiston and Ruedenberg. In general it is important to note that the partitioning of the nuclear charge is completely arbitrary as long as eq 2 is satisfied, and we rely on chemical intuition to make sensible choices.

(a) BF: Back Bonding. If the hydrogen in BH is replaced with a fluorine to form BF, the new wave function gives five valence LMOs. One LMO is predominantly localized on B while four LMOs are predominantly localized on the F. However, only one of the latter is a nearly pure lone-pair orbital on F. The other three are bent toward B and may be thought of as highly polarized BF bonds. Since assigning one +2 charge to B and four +2 charges to F violates eq 2 (when the inner shells are included), the chemically sensible way to partition the nuclear charges is to assign +1/3 and +5/3 to B and F, respectively for these three LMOs:

(b) B2H6: Three-Center/Two-Electron Bonds. Nonstandard partitionings are required when LMOs extend over more than two centers, as the assignment of nuclear charges becomes less obvious. A classic example is B2H6. An LMO analysis of the electronic charge distribution reveals two doubly occupied bonding LMOs that extend over three centers: both B atoms and one of the H atoms. Equal partitioning of the +2 charge in this LCD among the three centers leads to only a +5/3 charge on the bridging hydrogens. Since no other LMOs are associated with these centers, a more sensible partitioning of the nuclear charges in the three-center bond is a +1/2 charge on both B atoms and a +1 charge on the hydrogen:

In many, if not most, cases there is an even number of such bridging bonds, and eq 2 will then be satisfied for the two bridged atoms. Other molecules must be treated on an individual basis.

(c) NH2+ and OH−: Ions. The scheme outlined in eq 1 will produce only neutral LCDs. For charged species at least one LCD must possess a net charge. In NH2+, for example, a +1 formal charge resides on the N. The least arbitrary assignment of this charge is to partition it among the four NH bond LCDs:

For OH−, where a −1 formal charge resides on the O, a total valence charge of +6 must be assigned to one bond and three lone-pair LMOs. One option is to assign +1/2 to each valence LMO, but it seems more chemically sensible to consider the bond and lone pairs separately (keeping the net charge in each LCD to a minimum) and assign a +1 charge to the O in the bond LCD and divide the remaining +5 charge among the lone pair LMOs:

(d) NH3 + H2O → NH4+ + OH−: Proton Transfer. Analyzing chemical reactions using the LCD method can be complicated since the nature of an individual LCD may change during the course of the reaction. One solution is presented here using proton-transfer reactions as an example. To get a continuous description of intermediate structures along the reaction path, reactants and products must be described by identical sets of LCDs. This may be accomplished by considering an intermediate structure along the reaction path, and viewing reactants and products as extreme representations of this intermediate structure. For example, consider the reaction

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- 
\]

While the two neutral reactants are easily described with standard inner-shell, bond, and lone pair LCDs, this LCD description will differ significantly from those discussed in the previous section for the two products. On the other hand, both [NH3 + H2O] and [NH4+ + OH−] and hence all structures along the connecting reaction path can be described as [NH3 + H+ + OH−]. To facilitate this, an additional “LCD”, consisting only of a +1 charge at the position of the proton being transferred (i.e., no LMO is associated with this LCD), may be defined:

This method has been used successfully for a variety of proton transfer reactions involving the amino acid glycine and will be discussed in a forthcoming paper.10

(e) Triplet H2O. Electronic excitations pose the same basic problem to the LCD method as that encountered for chemical
reactions. For example, the wave functions for singlet and triplet water give rise to very different LMOs:

To maintain energy invariance, only orbitals with like occupancy can be mixed during the MO localization. The two singly occupied MOs on triplet water do not mix and so they remain canonical: one is essentially a pure p orbital on O, and the other is a +I/-I combination of the H/O/H's orbitals. It may be tempting to describe the latter as a three-center/two-electron LCD discussed previously. However, this LCD description would have very little in common with that of singlet water and does not easily facilitate an understanding of the singlet–triplet splitting. An alternative approach is to consider one of the lone pairs in singlet water as two identical singly occupied LMOs and assign a +I charge from the O to each.11 Their triplet LMO counterparts then may give rise to similar LCDs, and a +I charge from the O are assigned to both as well:

Using this approach the singlet–triplet energy difference then simply arises from an orbital deformation, plus an extra electron exchange term arising from the change in spin.

2. SCF Energy Decomposition. As noted previously,2 once the \( \{Z_i(A)\} \) are defined, it is possible to partition any molecular expectation value of interest into localized contributions. Of prime interest, of course, is the total molecular SCF energy, \( E_{SCF} \). For a system of \( N \) localized orbitals (each containing two electrons for RHF wave functions and \( N \) electrons in general) and \( M \) atoms:

\[
E_{SCF} = \sum_{i=1}^{N} e_i
\]  

where

\[
e_i = T_i + \sum_{j=1}^{N} v_{ij}
\]  

is the total energy of localized charge distribution \( i \).

The first term is the total kinetic energy of the electrons in LMO \( i \):

\[
T_i = N_i \int \psi_i^*(1) \left( -\frac{1}{2} \nabla_i^2 \right) \psi_i(1)
\]  

Each term has three Cartesian contributions:

\[
T_i = T_i^x + T_i^y + T_i^z
\]  

where

\[
T_i^x = N_i \int \psi_i^*(1) \left( -\frac{1}{2} \frac{\partial^2}{\partial x^2} \right) \psi_i(1)
\]

The subdivision is useful since, for example, for a bond LMO the two KE components perpendicular to the bond axis (\( T_{L} \)) can behave very differently from the parallel component (\( T_{I} \)). The most important example is the crucial role of \( T_{I} \) in the formation of covalent bonds.1

The second term in eq 4 is the total potential energy of interaction of localized charge distribution \( i \) with itself, and all other localized charge distributions. The potential energy term

\[
v_{ij} = V_{ij} + G_{ij} + g_{ij}
\]

is comprised of contributions due to electron–nuclear attraction:

\[
V_{ij} = V_{Z_i} + V_{Z_j}
\]

\[
= \sum_{A=1}^{M} V_{Z_i(A)} + \sum_{A=1}^{M} Z_{j(A)}
\]

\[
= -\frac{1}{2} \int d \psi_i^{*}(1) \left[ \sum_{A=1}^{M} \frac{Z_i(A)}{R_{1A}} \right] \psi_i(1)
\]

\[
-\frac{1}{2} \int d \psi_j^{*}(1) \left[ \sum_{A=1}^{M} \frac{Z_j(A)}{R_{1A}} \right] \psi_j(1)
\]

electron–electron repulsion:

\[
G_{ij} = \frac{1}{2} \int \psi_i^*(1) \psi_j^*(1) \psi_i(1) \psi_j(2)
\]

\[
-\frac{1}{2} \int \psi_i^*(1) \psi_j^*(2) \psi_i(1) \psi_j(2)
\]

and nuclear–nuclear repulsion:

\[
g_{ij} = \frac{1}{2} \sum_{A=1}^{M} \sum_{B=1}^{M} Z_i(A) Z_j(B) R_{AB}
\]

Here \( R_{AB} \) is the distance between electron 1 and atom \( A \), \( r_{12} \) is the distance between electrons 1 and 2, and \( R_{AB} \) is the distance between atoms \( A \) and \( B \). It is immediately apparent that

\[
v_{ij} = v_{ji}
\]

3. LCD Dipoles and Quadrupoles. The localized electrostatic potential due to a LCD can be expanded in terms of LCD multipoles. A LCD dipole is comprised of a nuclear and electronic component:

\[
\mu_i = \sum_{A=1}^{M} Z_i(A) R_A - N_i \int d \psi_i^*(1) r \psi_i(1)
\]

where \( R_A \) and \( r \) denote the nuclear position vector and electronic position operator, respectively. The dipole is not affected by the choice of origin if the overall charge of the LCD is zero,
and so the dipole of a molecule comprised of neutral LCDs can be written as the sum of the LCD dipoles:

$$\mathbf{\mu} = \sum_{i=1}^{N} \mathbf{\mu}_i$$  \hspace{1cm} (15)

A LCD quadrupole

$$\Theta_i = \frac{1}{2} \sum_{A=1}^{M} Z_i(A)[3R_A R_i - R_i^3] - \frac{1}{2} R_i^2 \int \text{d}r \int \psi^*_{i}(1) [3\mathbf{r} - \mathbf{r}_i^2] \psi_{j}(1)$$  \hspace{1cm} (16)

will depend on the choice of origin unless the LCD dipole is zero. One can either choose a common origin for all LCDs to get LCD contributions to the molecular quadrupole at that origin or choose different origins for each LCD to best describe its local electrostatic potential.

B. Second-Order Møller–Plesset Energy Decomposition

The error in the energy introduced by the molecular orbital approximation is partially recovered by second order Møller–Plesset perturbation theory.\textsuperscript{13} The MP2 energy correction ($E^{(2)}$) to the RHF energy can be written as the sum of pair correlation energies of doubly occupied spatial orbitals:

$$E^{(2)} = \sum_{i,j=1}^{N} \sum_{P} e^{(2)}_{ij}$$  \hspace{1cm} (17)

where each $e^{(2)}_{ij}$ is the correlation energy associated with a pair of electrons in orbitals $i$ and $j$. Each pair energy is given by a linear combination of two-electron integrals connecting occupied orbitals $i$ and $j$ with all virtual orbitals ($P$ is the total number of virtuals):

$$e^{(2)}_{ij} = \sum_{P=1}^{P} \sum_{i,j=1}^{N} C^P_{ij} K^{ij}_P$$  \hspace{1cm} (18)

$$K^{ij}_P = \int \int \text{d}r \int \text{dr}_2 \psi^*_{i}(1) \psi_{i}(1) (1/r_{12}) \psi^*_{j}(2) \psi_{j}(2)$$  \hspace{1cm} (19)

For an arbitrary set of occupied orbitals (e.g., localized orbitals), the $C^P_{ij}$ coefficients must be determined iteratively.\textsuperscript{14} However, if canonical MOs are used, the underlying equations simplify greatly (due to the fact that the Fock matrix is diagonal), and it is possible to derive an analytical expression:

$$C^P_{ij} = \frac{2K^{ij}_P - K^{ij}_P}{\varepsilon_i + \varepsilon_j - \varepsilon_i}$$  \hspace{1cm} (20)

where the $\varepsilon$'s are the canonical MO energies. Once the $K^{ij}_P$'s and $C^P_{ij}$'s are calculated in the canonical MO basis, they can be transformed to a LMO basis by the same unitary transformation that transforms the canonical MOs to the LMO basis.\textsuperscript{15}

C. Physical Interpretation of the Electronic Kinetic Energy

The role of the electronic kinetic energy in chemical phenomena has not received the prominence it deserves. In most physical interpretations of quantum chemical results, the virial theorem is invoked (implicitly or explicitly) and the kinetic energy is then considered merely as a function of the potential energy. As a result, potential energy considerations dominate most interpretations.\textsuperscript{17} Feinberg and Ruedenberg\textsuperscript{18} have pointed out numerous drawbacks to this approach. In this study we consider LCD energy components, for which the virial theorem does not apply and so the kinetic and potential energies must be given equal consideration.

Ruedenberg and co-workers\textsuperscript{1} have noted that an alternative expression to eq 5

$$T_i = \frac{1}{2} N_i \int \text{d}r \int (\nabla \psi_i(1))^2$$  \hspace{1cm} (21)

facilitates physical interpretations, since it is easier to discuss the gradient of a wave function than the curvature and since all volume elements make a positive contribution to the kinetic energy. For example, it is then easy to see that a localized function will have a higher kinetic energy than a more delocalized one:

This geometrical argument has its fundamental underpinning in the expression of the uncertainty principle that relates position and momentum:

$$\Delta x \Delta p_x \geq \frac{1}{2}$$  \hspace{1cm} (22)

Ruedenberg has introduced the terminology “kinetic energy pressure” to describe this driving force for wave function expansion. The opposing force is then the “potential energy suction”, a term that describes the increase in the attractive potential energy associated with the contraction of a wave function.

Thus, in this study a kinetic energy decrease for a particular LMO is invariably ascribed to a spatial expansion of the LMO, an assertion that is corroborated by density difference plots of the individual LMOs, to be described later.

III. A Detailed Analysis of the Water Dimer Hydrogen Bond

A. Computational Details. The reference water dimer geometry used in this work, shown in Figure 1a, is that used by Feller.\textsuperscript{19} The internal geometries of the two water molecules are the MP2/6–311++G(2d,2p) optimized structure of isolated water ($r_{OH} = 0.9571$ Å, HOH angle = 104.34°). The remaining degrees of freedom of the water dimer are those of the fully optimized water dimer structure at the same level of theory.\textsuperscript{20} 

Using this geometry as a reference, the $O$–$O$ distance (hereafter referred to as $R$) was then varied and the energy recomputed at
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The localized molecular orbitals were obtained by using the MP2/aug-cc-pVDZ\textsuperscript{21} level of theory, without reoptimization. This level of theory was shown by Feller\textsuperscript{19} to give an interaction energy that is essentially converged with respect to basis set (see Figure 6 in ref 19), and well within experimental accuracy. Keeping the internal monomer geometries fixed at the gas-phase values as \( R \) is decreased separates the primary electronic effects from the secondary effects due to the slight change in other internal coordinates. At the equilibrium distance the energy of the fully optimized system is only 0.11 kcal/mol lower in energy. Since geometry optimization can change individual energy components dramatically,\textsuperscript{20} this is addressed in section G.

The localized molecular orbitals were obtained by using the energy localization method of Edmiston and Ruedenberg.\textsuperscript{8} This localization method is computationally more expensive than others since two-electron integrals in the MO basis are required. However, many of these integrals are required in the LCD energy expression as well and have to be calculated anyway. In addition the Edmiston–Ruedenberg scheme uses the localization criterion that is theoretically most sound. The LMOs used in the SCF energy decomposition differ very slightly from the ones used in the decomposition of the MP2 energy correction, since the canonical core MOs are included in the localization that produces the former LMOs but not in the latter. This is due to the fact the core MOs are not included in the MP2 energy evaluation.

All calculations were performed with the quantum chemistry code GAMESS,\textsuperscript{22} except that the constrained MP2 optimizations discussed in section G which were done with GAUSSIAN92.\textsuperscript{23}

B. Total Energy Partitioning. The energy localization of the water dimer SCF wave function yields 10 localized molecular orbitals (LMOs), which in turn give rise to 10 LCDs (depicted and numbered in Figure 1b). Five of these LCDs have nuclear components exclusively from nuclei in either the hydrogen acceptor or donor (labeled A and D, respectively, in Figure 1b). For interpretative purposes, the LMO part of these five LCDs are considered to belong exclusively to either A or D, though all orbitals in reality extend over all space. Thus, the total energy of the system can be partitioned into three components:

\[
E = E(A) + E(D) + E(A|D) \tag{23}
\]

The first two terms have similar expressions. The first is given by

\[
E(A) = KE(A) + PE(A) + E^{(2)}(A)
\]

\[= \sum_{i \in A} [T_i + PE(i) + E^{(2)}(i)]\]

\[= \sum_{i \in A} [T_i + \sum_{j \in A} v_{ij} + \sum_{j \in A} v_{ij}^{(2)}] \tag{24}
\]

and is the internal energy of \( A \), comprised of electronic kinetic energy (KE), potential energy (PE), and MP2 correlation energy components. The SCF energy component is the energy expectation value due to the Hamiltonian of a free water molecule acting on the part of the water dimer wave function assigned to \( A \). Since the corresponding wave function of free water represents the variational energy minimum, \( E^{SCF}(A) > E^{MC}(H_2O) \) for all \( R \) except infinity.\textsuperscript{24} The same argument cannot be made for the MP2 correction for two reasons: one is that Möller–Plesset perturbation theory is not variational; the other is that the sum in eq 18 extends over all virtual orbitals, which have doubled in number on going to the water dimer.

Figure 2 shows how the three energy components in eq 23 vary with \( R \), relative to their value in free water. First note the small energy scale of the total energy (left y axis) and its internal and interaction components (remaining curves, right y axis), both relative to their respective values in free water and as a function of the OO separation. In this, and all following plots, the bold curve represents the sum of all other curves.

The remaining term in eq 23 is the interaction energy of \( A \) and \( D \):

\[
E(A|D) = PE(A|D) + E^{(2)}(A|D) = \sum_{i \in A} \left[ PE(i|D) + E^{(2)}(i|D) \right] \]

\[= \sum_{i \in A} \left( \sum_{j \in D} v_{ij} + \sum_{j \in D} v_{ij}^{(2)} \right) \tag{25}\]

where

\[
v_{ij} = v_{ij} + v_{ji} \tag{26}\]

and similarly for \( \epsilon_{ij}^{(2)} \). Note that there is no kinetic energy contribution to the interaction energy, only to the energies of the monomers. Given these definitions, the total binding energy can be written as

\[
\Delta E = E(A) + E(D) + E(A|D) - 2E(H_2O) = [E(A) - E(H_2O)] + [E(D) - E(H_2O)] + E(A|D) = \Delta E(A) + \Delta E(D) + E(A|D) \tag{27}\]

where \( E(H_2O) \) is the energy of an isolated water molecule. Similarly, differences in individual LCD energy components are defined as the difference of the water dimer value and that of the corresponding component in free water.

Figure 2 shows how the three energy components in eq 23 vary with \( R \), relative to their value in free water. First note the small energy scale of the total energy (left y axis) compared to that of the energy components (right y axis). The total energy decreases to a minimum value of -5.1 kcal/mol relative to two isolated water molecules as \( R \) is decreased to 2.91 Å (\( R_{eq} \)) whereupon it rises sharply and at \( R = 2.38 \) Å the relative total energy is +3.9 kcal/mol. As pointed out previously, the internal monomer energies must increase as the wave function of one monomer deviates from that of isolated water, because of the presence of the other monomer. The interaction energy is always decreasing in the \( R \) range considered in this study. So the decrease in total energy as \( R \) decreases from \( \infty \) to \( R_{eq} \) arises from a decrease in the \( A|D \) interaction energy. Conversely the increase in total energy as \( R \) is decreased past \( R_{eq} \) arises solely from the internal energies of the monomers. In fact, the characteristic shape of the total-energy curve can be viewed as a competition between the internal and interaction energy as \( R \) is decreased.

C. Donor/Acceptor Interaction Energy. While the two monomer SCF energies must increase as their separation is
reverses true for the SCF section.

explanation for why these pairs of LCDs have negative although there is a small net repulsive contribution from the energy of A and components, e.g., kinetic energy, e-n attraction, etc. The competition between e-n attraction and e-e of individual LCDs of A with all of its A-LCD components relative to their values in free water as a function of the OO separation.

decreased because of the shift away from the variational energy minimum of the isolated monomer, no a priori determination can be made about the behavior of the individual energy components, e.g., kinetic energy, e-n attraction, etc. The reverse is true for the SCF interaction energy; the absolute value of all three potential energy components (eq 8) must increase relative to their value at infinite separation (=0); however, no a priori determination can be made about whether they will add up to a net positive or negative potential energy of interaction. It follows that it is the interaction energy—ultimately the competition between e-n attraction and e-e plus n-n repulsion—that determines whether the overall SCF energy will decrease. The data presented in Figure 2 show that for the relative orientations chosen for this study the interaction energy always decreases. The reasons are discussed in this section.

The MP2 electron correlation contribution to the interaction energy of A and D (eq 24) is at most 9% over the range of R considered. Thus, this contribution has only a minor effect on the overall behavior and will be discussed in section F. The SCF contribution is decomposed further into interaction energies of individual LCDs of A with all of D in Figure 3a. The interaction energy is essentially the energy of the hydrogen bonded lone pair LCD on A (lp') interacting with D, although there is a small net repulsive contribution from the other lone pair (LCD 8) that increases PE(A|D), especially at small R. Further analysis (Figure 3b) reveals that the decrease other lone pair LCDs on D with \( V_{lp'沃尔'} \) becoming dominant as \( R \) is decreased past \( R_{eq} \). At \( R = R_{eq} \), these three terms constitute 116% of the total interaction energy, with the bond and each lone pair contributing 51% and 33%, respectively. Thus an explanation for why these pairs of LCDs have negative interaction energies explains the vast majority of the total interaction energy. From the discussion in the previous paragraph it is obvious that the interaction energy decreases because the e-n attraction term is larger than the e-e and n-n repulsion terms combined. The reason the e-n attraction dominates is best explained by considering the orientation of the LMOs. Consider the SCF/aug-cc-pVVDZ wave function of the following water dimer orientation (the internal water geometry is that shown in Figure 1) in which the oxygens are directly facing each other:

A LCD analysis reveals a LCD pair with an interaction energy \( V_{lp'沃尔'} \) of +6.5 kcal/mol which provides a point of comparison for \( V_{lp'沃尔'} \) and \( V_{lp'沃尔'} \).

Clearly, the lone-pair LCDs on D make important contributions to the interaction energy. The reason the e-n attraction dominates \( V_{lp'沃尔'} \) is that the lone pair LMOs \( lp' \) are pointing away from LMO \( lp' \) giving rise to a relatively small e-e repulsion. Evidence for this assertion is found when the components of \( V_{lp'沃尔'} \) are compared to the components of \( V_{lp'沃尔'} \):

The e-e repulsion is increased more than the e-n attraction energy is decreased (the n-n repulsion of course stays the same) on going from left to right, leading to an overall positive energy of interaction.

The e-n attraction dominates \( V_{lp'沃尔'} \) in comparison to \( V_{lp'沃尔'} \) due to the +1 charge at the hydrogen position. If the +1 charge at the H_2 position is moved to the O_1 position in bo' without letting the two LMOs adjust, the e-e repulsion is unchanged, the n-n repulsion decreases, but the e-n interaction energy increases even more. This results in an overall positive \( V_{lp'沃尔'} \):

The difference between +26.2 and +13.0 kcal/mol for \( V_{lp'沃尔'} \) is then an estimate of the energy change introduced when the MOs are allowed to relax. However, the interaction energy for these two LCDs is still repulsive. Similarly, if a +1 charge is removed from the oxygen and placed at the position of the hydrogen in one of the lone-pair LCDs in the lplp pair considered above, one finds a \( V_{lp'沃尔'} \) of -22.8 kcal/mol.

The LCD method can also be used to obtain a more qualitative description of the interaction energy through the use of LCD multipoles (described in section A.3). In the spirit of Leonard-Jones and Pople, the electrostatic potentials of lone pair and bond LCDs are described as dipoles and quadrupoles, respectively. The interaction energy \( V_{lp'沃尔'} \) is then approximated by the interaction energy of the dipole of LCD \( lp' \) and \( lp', \) and \( V_{lp'沃尔'} \) by the dipole of \( lp' \) interacting with the quadrupole of
The results, shown in Figure 4, show that this description gives semiquantitative interaction energies even at small values of $R$ where the multipolar expansion of the interaction energy breaks down. If the exchange contribution (described in the Appendix) is subtracted from the total interaction energy, the dipole–dipole and dipole–quadrupole interaction energies account for 71% of $\psi_{D}(2,3)$, respectively, at $R_{eq}$.

In summary, the interaction energy between $A$ and $D$ is essentially that of the two LCDs directly involved in the hydrogen bond ($lp'$ and $bo'$, respectively) and the interaction of $lp'$ with the two lone-pair LCDs on $D$ ($lp$). The former can be qualitatively described as a dipole–quadrupole interaction and the latter as a dipole–dipole interaction.

**D. Hydrogen Donor Energy.** The individual LCD components of the change in internal energy of $D$ is shown in Figure 5. It is apparent that the increase of $\Delta E(D)$ is due to an increase in both potential energy (PE) and kinetic energy (KE). At large $R$, $\Delta KE(D)$ dominates, while at small $R$, $\Delta KE(D)$ increases sharply as the potential energy component levels off. The two curves cross around $R_{eq}$ with values of 4.4 and 3.8 kcal/mol, respectively, for $\Delta KE$ and $\Delta PE$. So the rise in internal energy of $D$ as $R$ is decreased past $R_{eq}$ is largely due to a rise in the kinetic energy pressure. The MP2 correction has a relatively small effect at all values of $R$ and will be discussed in section F.

1. **Kinetic Energy.** The individual LCD contributions to the $\Delta KE$ of $D$ are shown in Figure 6a. Clearly the increase in the internal kinetic energy of $D$ is due entirely to an increase in the kinetic energy of the OH bond LMO directly involved in the hydrogen bond (LMO 4 = $bo'$). At $R > 4$ Å this increase is canceled by a concomitant kinetic energy decrease for the remaining LMOs, but for shorter distances this decrease is insufficient for a complete cancelation. The changes in LMO kinetic energy can be explained by the contraction and expansion of the LMOs. Figure 7 shows the three symmetry-unique valence LMOs of $D$ at $R = R_{eq}$, together with their difference in density relative to the corresponding LMOs in free water. The difference density may be written as

$$\Delta \psi_{R_{eq}}^{2} = \psi_{R_{eq}}^{2} - \psi_{LMO}^{2}$$

As expected, the largest change occurs in $bo'$ (Figure 7e) where the electron density is pushed toward $O_1$, presumably by the hydrogen-bonded lone pair on $A$ (LMO 7). This leads to orbital contraction and an increase in the orbital kinetic energy. The remaining valence MOs are pushed away from $O_1$ by $bo'$:

leading to MO expansion and thus a drop in orbital kinetic energy, in the order $|\Delta KE| > |\Delta T_{bo'}|$.  

2. **Potential Energy.** Figure 6b shows the individual LCD components of the $\Delta PE$ of $D$. Again, the largest single change is the decrease in $\Delta PE(bo')$. However, the remaining LCD
components, especially the two lone-pair LCDs, more than counteract this change, leading, overall, to only a slight increase in potential energy. The potential energy changes are mainly a result of the changes in the electron–nuclear (e–n) attraction between the valence LMOs and the D-oxygen nucleus (see Appendix). This term dominates the change in all other e–n terms as well as electron–electron repulsion terms (the nuclear–nuclear repulsion terms do not change since the internal monomer geometry is frozen). So the e–n attraction energy decrease due to the contraction of $b'$ is nearly canceled by the e–n attraction energy increase due to the expansion of the remaining LMOs.

E. Hydrogen Acceptor Energy. Comparing Figure 8, which shows the kinetic energy, potential energy, and MP2 energy components of $E(A)$, with Figure 5 it is apparent that the internal electronic structure of $A$ becomes quite different...
from that of D as R is varied. For $R > \sim 3.5 \text{ Å}$ all contributions are essentially zero, but at smaller R the change in kinetic energy increases sharply while the change in potential energy decreases less sharply, leading to an overall increase in the internal energy of A. So the rise in internal energy of A as R is decreased past $R_{eq}$ is due entirely to a rise in the kinetic energy pressure. These changes are rationalized by considering the change in the density of each valence LMO at $R_{eq}$ shown in Figure 9. The MP2 correction again has a very small effect for all values of R and is discussed in Section F.

1. Kinetic Energy. The individual LCD components of the kinetic energy of A are displayed in Figure 10a. The kinetic energy of the two OH LMOs (9 and 10 = ho; cf. Figure 1b) as well as the lone pair not directly involved in the hydrogen bond (LMO 8 = lp) all increase relative to the free water molecule. The kinetic energy of the other lone pair (LMO 7 = lp') exhibits more complicated behavior: it decreases initially but once the two water molecules approach past $R_{eq}$, the kinetic energy increases sharply. Figure 9d shows that at $R_{eq}$, electron density is transferred away from $O_1$ (and toward the hydrogen-bonded OH LCD on D). This lowers the kinetic energy by 11.5 kcal/mol due to expansion of the orbital. A breakdown of $T_{lp}$ into Cartesian components (Figure 11a) shows that most (74% or 8.5 kcal/mol at $R_{eq}$) of this drop comes from LMO expansion parallel to the OO axis ($T_{lp}^{x}$; cf. Figure 1a). Further decrease in R reverses this expansion and all three Cartesian components increase dramatically. A density-difference plot at the smallest value of $R (2.38 \text{ Å})$ for $lp'$, shown in Figure 11b, reveals that charge density is still shifted away from the oxygen relative to $R = \infty$ but that a strong tail is building up on D to satisfy the orthogonality condition. Furthermore, electron density is accumulating on the hydrogen-bond axis, presumably due to the increasing net positive charge on $H_2$. As a result, $T_{lp}$ increases by 16.4 kcal/mol relative to its $R_{eq}$ value (+7.9 relative to $R_{eq}$) and $\Delta T_{lp}$ has increased to $+34.2 \text{ kcal/mol}$. Thus, the two perpendicular components of $\Delta T_{lp}$ are the major (77%, 26.3 kcal/mol) contributors at $R = 2.38 \text{ Å}$. So, as A and D are brought together, $lp'$ initially expands as it is drawn away from $O_2$ but then contracts again due to (1) the condition that it must remain orthogonal to the other LMO in the hydrogen bond (LMO 4) and (2) the concentration of charge on the hydrogen-bond axis by $H_2$:

$$lp' \text{ at } R=\infty, \quad lp' \text{ at } R=2.91\text{Å}, \quad lp' \text{ at } R=2.38\text{Å}$$

Therefore, the increase in the orbital kinetic energy of LMOs $bo$ and $lp$ is explained by the concentration of electron density near $O_4$ (see Figure 9e–f) and resulting orbital contraction, in response to the electron density depletion in $lp'$:

$$lp(8), \quad lp'(7), \quad bo(9,10)$$

2. Potential Energy. The density rearrangement exemplified in Figure 9 effects little change in the internal potential energy of A at large $R (>3.2 \text{ Å})$. A look at the individual LCD components of $\Delta P E(A)$ (Figure 10b) shows that this is due to near perfect cancelation of the increase in the potential energy of $lp'$ and decrease in the potential energy of the remaining valence LCDs. As $R$ is decreased further, the former increase levels off first, resulting in an overall decrease in $\Delta P E(A)$, and then decreases as well which accelerates the potential energy drop. Evidence presented in the Appendix shows that the overall decrease of $\Delta P E(A)$ is due to the increased electron–nuclear attraction terms resulting from the MO contractions.

F. Correlation Energy. The neglect of electron correlation in SCF theory results in a wave function in which the electron distribution on average is too compact and in a molecular energy that is too high. As mentioned previously, in this study the energy lowering due to electron correlation is estimated using second order Møller–Plesset (MP2) perturbation theory. Components of this correlation energy are rigorously ascribed to particular parts of the wave function, i.e., particular LMOs. While these LMO correlation pair energies will sum to a negative total correlation energy, their individual values are not necessarily less than zero because individual SCF energy components do not necessarily represent an upper bound. In the case of water dimer formation, electron correlation effects are important if SCF theory fails to properly describe (a) the interaction energy of the two water monomers or (b) the change in the internal monomer energies, both as $R$ is decreased.

Figure 12a shows the SCF and MP2 contribution to the total energy as a function of $R$. The MP2 contribution grows larger with decreasing $R$ and as a result the optimum O–O separation is shortened by about 0.1 Å relative to the SCF value. At $R_{eq}$, the relative MP2 correlation energy is $-1.4 \text{ kcal/mol}$. Figure 12b shows that the energy lowering by MP2 is entirely due to the MP2 interaction energy and the internal MP2 energies of the two water molecules actually increase slightly. Thus the effect of correlation increases with decreasing $R$ because SCF theory increasingly overestimates the energy of interaction. Part of this error is compensated for by the fact that SCF theory underestimates the change in the internal energy of the two monomers. The components of these errors are discussed in the Appendix.

G. Role of Complete Geometry Relaxation. As mentioned in section A, using frozen monomer geometries raises the total energy by only 0.11 kcal/mol, however, it is well-known that full geometry optimization can change individual energy components dramatically, and this concern is addressed as follows: The water dimer geometries used above are used as initial guesses for MP2/6–311+ +G(2d,2p) optimizations in which all parameters except $R$ are optimized. For $R = 2.38 \text{ Å}$, geometry optimization changes the two intermolecular angles, $\theta_1$ and $\theta_2$ (cf. Figure 1a), to 61.1° and 50.1°, respectively. This effectively reverses the donor and acceptor functions of the monomers, and so this structure is not included in the energy analysis. For the remaining values of $R$, the geometry optimizations leads to much smaller changes: for $R = 2.65 \text{ Å}$, $\Delta \theta_1 = -7.4^\circ$, and $\Delta \theta_2 = 5.9^\circ$, and these discrepancies grow smaller.
Figure 9. Plots of the symmetry-unique valence LMOs of A at $R = R_{eq}$ (a–c), and the density difference relative to LMOs in free water (d–f). The plotting plane is the $\sigma_c$ plane with the exception of (c) and (f) where the plane is that defined by H$_5$, O$_4$, and O$_1$. The relative water dimer orientation is depicted schematically in the lower left-hand corner of (a) where the water molecule in question is boxed. The largest magnitude contour and contour increment is 1.0 and 0.05 bohr$^{-3}$, and 0.025 and 0.001 bohr$^{-3}$ for a–c and d–f, respectively.

The energy components of $\Delta E(D)$ based on both optimized and unoptimized structures are shown in Figure 13a (the energy components based on optimized structures are marked with an asterisk). For $R > 3.17$ Å the potential energy rises much faster; however, the shapes of the curves are unchanged. At smaller $R$ the rate of change in these two energy components is essentially identical for the optimized and unoptimized case, and so the previously discussed sharp increase in $\Delta E(D)$ for $R < 3$ Å remains a function of the kinetic energy. This correlates well with the change in $r_0$ which has increased to 0.964 at $R = 3.17$ whereafter it remains essentially constant as $R$ is decreased further. As expected, the vast majority (91% and 95% for the
Ab Initio Localized Charge Distributions

Figure 10. Plot of the change in the internal (a) kinetic energy and (b) potential energy of A and their LCD components relative to their values in free water and as a function of the OO separation.

Figure 11. (a) Plot of the change in the kinetic energy of LMO 7 and its three Cartesian components relative to their values in free water and as a function of the OO separation. (b, c) Plots of LMO 7 at $R = 2.38$ Å (b) and the density difference relative to the LMO in free water (c). The plotting plane is the $\alpha$ plane. The relative water dimer orientation is depicted schematically in the lower left hand corner of (b) where the water molecule in question is boxed. The largest magnitude contour and contour increment is 1.0 and 0.05 bohr$^{-3/2}$ and 0.025 and 0.001 bohr$^{-3}$ for b and c, respectively.

kinetic and potential energy, respectively, at $R_{eq}$ of the differences between the optimized and unoptimized values are due to the hydrogen bonded OH bond LCD ($b'$). The differences in the kinetic and potential energy very nearly cancel and so $\Delta E(D)$ and $\Delta E(D)^*$ are within 0.45 kcal/mol over the range of $R$ considered.

The energy components of $\Delta E(A)$, shown in Figure 13b, are much less sensitive to geometry optimizations. Again the kinetic and potential energies are decreased and increased, respectively, though much less than for $D$. More importantly, the rate of change is essentially unchanged, and the overall effect on $\Delta E(A)$ is always less than 0.32 kcal/mol. The same is true for the interaction energy, where the largest discrepancy between energies based on optimized and unoptimized structures are at most 0.69 kcal/mol.

In summary, the increase in the total energy is $\leq 0.20$ kcal/mol for all $R$ considered, while the absolute value of the changes in the monomer and interaction energies upon geometry optimization are up to 0.70 kcal/mol. However, underlying these modest changes are larger, opposing, changes in the kinetic and potential energy components that mostly cancel.

IV. Summary

The hydrogen-bond energy curve of the water dimer (Figure 2) has been analyzed in terms of a partitioning of the total SCF energy (using the theory of localized charge distributions) into internal energies of the hydrogen donor ($D$) and hydrogen acceptor ($A$), and an interaction energy between the two monomers. The MP2 energy correction does not alter the qualitative behavior of the energy curve as $R$ is varied (Figure 12a). Two points concerning the SCF energies are known a priori: (1) The two internal energies must increase as the
monomers are brought together, so the initial energy lowering must be due to the interaction energy. (2) This energy lowering must be due to the fact that the electron–nuclear (e–n) attraction terms dominate the potential energy of interaction. So two questions were posed: (I) Why does the e–n attraction term dominate the potential energy of interaction? (II) What is the source of the sharp increase in energy for \( R < R_{eq} \)? On the basis of the LCD analysis, the following are concluded:

I. The interaction energy between \( A \) and \( D \) is that of the two LCDs directly involved in the hydrogen bond (\( lp' \) and \( bo' \), respectively) and the interaction of \( lp' \) with the two lone-pair LCDs on \( D \) (Figures 3b).

IIa. The rise in the internal energy of \( D \) is largely due to the rise in the kinetic energy of \( bo' \) due to its contraction (Figure 5 and 6a). The associated change in the overall internal potential energy of \( D \) (Figure 6b) is nearly zero.

IIb. The rise in the internal energy of \( A \) is solely due to the rise in the kinetic energy associated with the contraction of all the valence LMOs except \( lp' \) (Figures 8 and 10a). The internal potential energy of \( A \) decreases due to orbital contraction (Figure 10b), but this decrease is not competitive with the kinetic energy increase.

Thus, the initial decrease and subsequent energy increase with decreasing \( R \) is a result of the competition between the interwater potential energy suction and intrawater kinetic energy pressure.

The lack of correlation leads SCF theory to underestimate both the magnitude of the interaction energy and the increase in the internal energies of the monomers. The former is larger in magnitude, so the MP2 energy correction lowers the relative energy of the water dimer at all \( R \) (Figure 12b).

We expect the LCD method to be of equal value in understanding other chemical systems.

V. Appendix: Further Details

A1. Hydrogen-Donor Potential Energy. In section D.2 it was shown that the modest change in the internal potential energy of \( D \) (Figure 6b) is due to a near cancellation of the increase in the potential energy of the hydrogen bonded OH bond LCD (\( bo' = 4 \)) with the decrease in the potential energy of the remaining valence LCDs. It is shown below that the source of this near cancellation is the decrease and increase in the electron–nuclear (e–n) attraction energy due to the contraction of \( bo' \) and the remaining valence LMOs, respectively.

The largest of the LCD components of \( \Delta PE(bo') \) shown in Figure 14a is not the internal potential energy of \( bo' \) (\( \Delta \nu_{bo'/bo} \)) but rather the PE due to \( bo' \) interacting with the two equivalent lone pairs (\( lp' = 2.3; \Delta \nu_{bo'lp'} = \Delta \nu_{bo'lp} \)). In fact \( \Delta \nu_{bo'lp} \) makes the smallest contribution to \( \Delta PE(bo') \) of all the valence LCDs. The reason is the balance or imbalance of the electron–electron (e–e) repulsion with the electron–nuclear (e–n) attraction (nuclear–nuclear repulsions do not contribute since the monomer geometries are frozen). Notice, for example that \( \Delta \nu_{bo'/lp} \) has one of the smallest changes in e–e repulsion (Figure 14b) and the second-largest change in e–n attraction (Figure 14c). This can be rationalized by considering the individual components of \( \Delta \nu_{bo'/lp} \) (up and down arrows signify an energy increase and decrease, respectively):

\[
\begin{align*}
\Delta V_{bo'/lp} &= +1 \\
\Delta V_{lp'/bo} &= +2 \\
\Delta G_{bo'/lp} &= +3.9 \text{kcal/mol at } R_{eq}
\end{align*}
\]

The concentration of electronic charge near the oxygen will decrease the interaction energy of \( bo' \) with the +2 charges in \( lp \) (\( \Delta V_{bo'/lp} \)), while the expansion of the \( lp \) LMOs will increase \( \Delta V_{lp'/bo} \). The former term dominates \( \Delta V_{bo'/lp} \) (e.g., \( \Delta V_{bo'/lp} = -19.3 \text{kcal/mol and } \Delta V_{lp'/bo} = +3.9 \text{kcal/mol at } R_{eq} \)) since the orbital change is much larger for \( bo' \) and since \( Z_{eq}(O) = 2Z_{eq}(O) \). The concomitant increase in e–e repulsions (\( \Delta G_{bo'/lp} \)) is smaller in comparison because the two LMOs are pointing in different directions and the concentration of electronic charge in \( lp \) near the oxygen is decreased.

The rise in the concentration of electronic charge near the oxygen will decrease the interaction energy of \( bo' \) with the +2 charges in \( lp \) (\( \Delta V_{bo'/lp} \)), while the expansion of the \( lp \) LMOs will increase \( \Delta V_{lp'/bo} \). The former term dominates \( \Delta V_{bo'/lp} \) (e.g., \( \Delta V_{bo'/lp} = -19.3 \text{kcal/mol and } \Delta V_{lp'/bo} = +3.9 \text{kcal/mol at } R_{eq} \)) since the orbital change is much larger for \( bo' \) and since \( Z_{eq}(O) = 2Z_{eq}(O) \). The concomitant increase in e–e repulsions (\( \Delta G_{bo'/lp} \)) is smaller in comparison because the two LMOs are pointing in different directions and the concentration of electronic charge in \( lp \) near the oxygen is decreased.
Figure 14. (a) Plot of the change in the internal potential energy of LCD 4 and its LCD components, relative to their values in free water and as a function of the OO separation. (b) Plot of the change in the components of the electron-electron repulsion part of the internal potential energy of LCD 4, relative to their values in free water and as a function of the OO separation. (c) Plot of the change in the components of the electron-nuclear attraction part of the internal potential energy of LCD 4, relative to their values in free water and as a function of the OO separation.

Similar reasoning can be used to explain the increase in $\Delta PE(lp)$. Figure 15a shows the individual LCD contributions to $\Delta PE(lp)$, while Figure 15b,c shows the e–e repulsion and e–n attraction contributions, respectively. The dominant negative component is $\Delta v_{ppbo}$ discussed in the previous paragraph, while the dominant positive component is the change in internal potential energy of one lp (e.g., LCD 2), and the interaction energy with the other lp (LCD 3). The two latter changes are both due to the expansion of lp which causes an increase in the e–n interaction energy, and a relatively smaller decrease in intra- and interorbital repulsions. It is interesting to note that while $G_{22}$ and $G_{23}$ differ by around 0.4 hartree, $\Delta G_{22}$ and $\Delta G_{23}$ differ by at most 0.3 kcal/mol. Also, since $\Delta V_{22} = \Delta V_{23}$, $\Delta v_{22} \approx \Delta v_{23}$.

The remaining valence LCD component, $\Delta v_{ppbo}$ [bo (=5) is the other OH bond LCD in D] is also increasing. The same reasoning used for $\Delta v_{ppbo}$ holds here: the $\Delta V_{2ppbo}$ term dominates the change in potential energy, leading to an overall increase in energy, due to the increased e–n attraction energy.

Figure 15. Same as for Figure 14 but for LCD 2.

Figure 16. Plot of the change in the internal potential energy of LCD 5 and its LCD components, relative to their values in free water and as a function of the OO separation.

The remaining valence term in Figure 6a is $\Delta PE(bo)$, the secondary contributor to $\Delta PE(D)$. A breakdown of $\Delta PE(bo)$ into individual LCD components is shown in Figure 16. All but one valence term, $\Delta v_{ppbo}$, has been discussed previously and this term, like $\Delta v_{ppbo}$, makes a relatively modest contribution. This is due to the fact that this LMO is the least perturbed of the valence LCDs, as evidenced by the relatively small change in kinetic energy, and the fact that $Z_{bo}(O1) = +1$. 
To summarize, the decrease in $\Delta P E(bo')$ and the increase in the potential energy of the remaining valence LCDs are mainly due to a respective increase and decrease in the e–n attraction energy between the LMOs and the two +2 charges in the $bp$s. These two opposing energy trends lead to a very small overall change in $\Delta P E(D)$ with $R$.

**A2. Hydrogen Acceptor Potential Energy.** In section E.2 it was shown that the modest change in the internal potential energy of $A$ (Figure 10b) at $R > 3.2$ Å is due to a near cancelation of the increase in the potential energy of the hydrogen-bonded lone pair ($lp' = 7$) and the decrease in potential energy of the remaining valence LCDs. For $R < 3.2$ Å, $\Delta P E(lp')$ levels off first, resulting in an overall decrease in the potential energy of $A$, and then decreases as well. This accelerates the potential energy drop. It is shown below that the potential energy is dominated by the effect of LMO contraction and expansion on the electron–nuclear (e–n) attraction term.

Figure 17a shows the individual LCD contributions to $\Delta P E(lp')$. Clearly, the change in potential energy associated with $lp'$ itself is dominant and reflects the expansion and contraction of the LMO. A further breakdown reveals that this is much more strongly reflected in the e–n interaction term than in the self-repulsion term ($\Delta V_{lp'lp'}$ and $\Delta G_{lp'lp'}$ in Figure 17c,b, respectively) for all but the smallest value of $R$. Hence, the behavior of $\Delta P E(lp')$ is largely governed by $\Delta V_{lp'lp'}$.

It is evident from Figure 10b that $\Delta P E(A)$ is negative for $R \leq 3.2$ Å because of the drop in potential energy of the other lone pair ($lp = 8$), and the two equivalent OH bond LCDs ($bo = 9,10$) relative to free water. Further decomposition of $\Delta P E(lp)$ (Figure 18a) shows that this is primarily a result of a decrease in the e–n interaction energy in $\Delta V_{lpbo}$ and $\Delta V_{lpbo}$ due to the orbital contraction discussed in section E.1. In the case of $\Delta V_{lpbo}$ ($=\Delta V_{lpz(l,O_{2})}$) this is obviously due to an increased attraction of $lp$ to $O_{2}$. This is also true, albeit less obvious, for $\Delta V_{pho}$ whose respective components (up and down arrows signify an energy increase and decrease, respectively)

\[
\begin{align*}
\Delta V_{lpbo} &= +1.2, -0.006, \text{ and } -4.3 \text{ kcal/mol at } R_{eq}; \\
\Delta V_{lpz(l,O_{2})} &= \Delta V_{lpz(l,H_{2}O)}, \Delta V_{lpz(H_{2}O)}, \Delta V_{lpz(H_{2}O)}.
\end{align*}
\]

Similarly for $\Delta P E(bo)$ [$=\Delta P E(9)$ and $\Delta P E(10)$] (Figure 18b) where the two largest terms are $\Delta V_{9s}$ and $\Delta V_{9s}$. Again, the change in potential energy is dominated by the e–n interaction energy. Since LCD 9 and 10 are equivalent by symmetry

\[
\begin{align*}
\Delta V_{10} &= 2\left(\Delta V_{z(l,O_{2})} + \Delta V_{z(l,H_{2}O)}\right) \\
\Delta V_{9s} &= 2\left(\Delta V_{z(l,O_{2})} + \Delta V_{z(l,H_{2}O)}\right)
\end{align*}
\]

at $R_{eq}$ the two latter components equal $-4.4$ and $-0.4$ kcal/mol, respectively. The reason $\Delta V_{9s}$, which also includes a term $2\Delta V_{z(l,H_{2}O)}$, is exactly equal to the first of the two components, is that the second component $2\Delta V_{z(l,O_{2})}$ increases with decreasing $R$ ($+1.0$ at $R_{eq}$).
To summarize, the initial \( R > 3.2 \) Å increase and subsequent \( R < 3.2 \) Å decrease in \( \Delta PE(lp') \) is predominantly a reflection of similar changes in the internal e–n attraction energy of \( lp' \).

To summarize, the initial \( R > 3.2 \) Å increase and subsequent \( R < 3.2 \) Å decrease in \( \Delta PE(lp') \) is predominantly a reflection of similar changes in the internal e–n attraction energy of \( lp' \).
correlation energy is equally divided among the remaining LMOs. Figure 21b shows that the major contribution (56% at $R_{eq}$) to $E^{(2)}(p|D)$ is the interaction energy with $b_{o'}$. So overall, SCF theory underestimates the interaction energy, especially the interaction energy between $l_{p'}$ and $b_{o'}$. The latter not only makes the single largest contribution but also is almost solely responsible for the large rate of increase in $E^{(2)}(A|D)$ as the two monomers are brought together.

**A4. Role of Electron Exchange.** In this section the electron–exchange component of the electron–electron (e–e) repulsion term (eq 10) is given special attention. This term is important, for example, in density functional theory and the theory of intermolecular forces, so it is useful to study this term within an ab initio framework.

This study employs LMOs, for which the interorbital e–e repulsions have been minimized. As a result, the energy due to electron exchange

$$EX = \sum_{i<j} \sum_{m<n} G^k_{ij}$$

(29)

where

$$G^k_{ij} = \int \frac{1}{4\pi N_i N_j} \int dr_1 dr_2 \psi_i^*(1) \psi_j^*(2) \psi_i(1) \psi_j(2)$$

(30)

is minimized. Hence, the energetic interpretation presented in this paper is the one for which the role of exchange is as small as possible.

Figure 22a presents a breakdown of the total change in the exchange energy with decreasing $R$ in terms of intra- and intermonomer energies. Even when minimized, the electron-exchange energy cannot be ignored for $R < 4 \, \text{Å}$. At $R_{eq}$, $\Delta EX$
= −6.2 kcal/mol is mostly due to an increase in electron exchange in D (40%) and exchange interactions between A and D (56%). The small change in \( \text{EX}(A) \) is due to a cancellation of an increase in \( \Delta \text{EX}(b') \) by the remaining LMO contributions (Figure 22b). Increase in electron exchange of \( b' \) (LMO 4) with the other LMOs in D (Figure 23b) is largely responsible for the relatively large contribution made by \( \text{EX}(D) \) (Figure 23a).

The increase of electron exchange between the two fragments is very localized: at \( R_\text{eq}, G_{b'(b')} \) alone constitutes 62% of \( \text{EX}(A/D) \) and is almost solely responsible for the rate of decrease of \( \Delta \text{EX} \) with decreasing \( R \) (Figure 24).

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References and Notes


10. This is mainly a conceptual exercise as no new LCDs are defined and the occupation number and nuclear charge are simply reduced by one half in the energy formula for the appropriate LCD.


21. (c) references do not occur. (d) The polarization function is described by six Cartesian components rather than the five spherically averaged components used by Dunnings et al.


24. Rigorously, this statement is true only in the limit of a complete basis set where basis set superposition error (BSSE) does not occur. However, it is shown in ref 18 that the basis set used here is essentially complete with respect to BSSE.

25. The centroid of charge of each LMO is used as the local origin of a LCD.


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