A Quantitative View of Charge Transfer in the Hydrogen Bond: The Water Dimer Case

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The hydrogen bond represents a fundamental intermolecular interaction that binds molecules in vapor and liquid water. A crucial and debated aspect of its electronic structure and chemistry is the charge transfer (CT) accompanying it. Much effort has been devoted, in particular, to the study of the smallest prototype system, the water dimer, but even here results and interpretations differ widely. In this paper, we reassess CT in the water dimer by using charge-displacement analysis. Besides a reliable estimate of the amount of CT (14.6 me) that characterizes the system, our study provides an unambiguous context, and very useful bounds, within which CT effects may be evaluated, crucially including the associated energy stabilization.

There appears to be nowadays a general consensus that hydrogen bonding (HB)[1–4] possesses some non-negligible covalent character, conferred at least in part by a charge-transfer (CT) component from a HB acceptor (electron donor) to a HB donor (electron acceptor) species.[5,6] From the theoretical point of view, this observation needs qualification, for there are multiple, even conflicting, aspects to it. On the one hand, CT is quantum mechanically an ill-defined quantity and, therefore, does not appear at all in rigorous ab initio approaches for the accurate calculation and decomposition of intermolecular interaction energies, such as the symmetry-adapted perturbation theory[7] (but see refs. [8–10]). On the other hand, CT is, with good reason, an everlasting, omnipresent staple of chemical reasoning. A reliable estimate of CT effects, in terms of both electron density and energy contribution, appears to be indispensable to design useful potential models for intermolecular interactions that might, for example, simulate the physics and chemistry of bulk water or the role of HB in biomaterials.[11–13] Substantial evidence is also emerging that a CT energy contribution to weak water interactions may actually be precisely measured through scattering experiments and comparison with reliable interaction models. Accurate ab initio calculations and charge displacement analysis (see below) support this unequivocally.[14–17] Recently Wan et al. demonstrated

that charge fluctuations cause still unassigned bands to be present in the experimental Raman spectrum of water, which further justifies the urgency in the formulation of innovative strategies able to characterize these phenomena.[18]

Therefore, a CT term is explicitly included in many useful energy decomposition analysis (EDA) schemes,[19–29] and some models, often related to EDA, have also been devised, beyond the classic population analyses, to define and calculate an actual amount of charge transferred in intermolecular interactions.[28,30,31] The trouble with these models, as useful as they are to bring insight and stimulate further study, is that, starting from different assumptions and definitions, they often deliver quite different, even conflicting results, especially in weak interactions. Although it is sometimes possible to analyze these differences and understand the different meanings of different CT definitions, the situation is indeed "somewhat disconcerting"[32] and hardly helpful to spread confidence in the power of these calculations.

As a reference system, take for example the water dimer, which may rightly be regarded as the king prototype of HB systems.[33–35] Countless calculations have been performed on it, but a clear characterization of CT processes for this system is still far to be reached. Some results, published over a span of several years up to recent ones, obtained by using the most well-established energy decomposition methods are shown in Table 1. This clearly reveals the lack of a uniform view and points to the difficulties of a stable and reliable assessment of the various theoretical approaches used to describe the extent and consequences of electron transfer.

The aim of the present Communication is therefore not so much to add yet another row of results, however justified, to Table 1, as it is to provide a useful, arguably more "objective" context in which to evaluate CT estimates. We shall mainly discuss the CT extent itself in the water dimer and, at the end,

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Table 1. CT values and corresponding stabilization energies for the water dimer obtained by using well-established EDA models and reported in the literature.

Method	CT [me]	E_{CT} [kJ mol^{-1}]
Morokuma EDA[55]		7.53
ALMO-EDA(B3LYP)[51,54]	2.3	5.44–6.69
ALMO-EDA(CCSD)[32]		3.51
BLW-NPA[23]	5	
NOCV[31]	80	3.72
NBO[28,52]	8.1	38.6
SAPT[9]		2.95
IMPT[8,53]		3.4
Wu EDA[27]		2.68

briefly address the question of its contribution to the interaction energy.

We start from the following definition of a one-dimensional (1D) charge displacement (CD) function,[36] defined as [Eq. (1)]:

$$\Delta q(z) = \int_{-\infty}^{z} dz' \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Delta\rho(x,y,z')\,dx\,dy \qquad (1)$$

in which z is any chosen axis of interest, typically one joining the interacting species (in our case joining the oxygen atoms of the water molecules) and $\Delta\rho$ is the change in the electron density taking place upon formation of the intermolecular complex, that is, the density difference between the complex and the isolated noninteracting partners placed at the same positions they occupy in the complex. Δq measures, at each point along the z axis, the electron charge that, upon formation of the adduct, has crossed from the right to the left, the plane through z, perpendicular to the axis. If the Δq function never crosses zero in the region dividing the fragments, a net CT between the interacting species is clearly occurring. If a plane can reasonably be taken as separating the fragments, it is possible to obtain an estimate of the amount of charge that has been transferred from one system to the other. As the position of such a plane is of course arbitrary, the relevance and accuracy of the CT estimate depends critically on the Δq slope, on the strength of the interaction, on the distance between the interacting species, and on other factors. However, the CD function provides nevertheless an extremely useful context for study. When thus meaningful, we usually chose to separate the fragments at the so-called isodensity boundary, which is the point along z at which the electron densities of the noninteracting fragments become equal. This separation is usually comparable to that obtained by taking the minimum of the total molecular density between the fragments, or by taking the position of the bond-critical point.[37] This strategy was already successfully applied in recent work for studying weakly bound water adducts,[14,16,17] organometallic complexes,[38,39] Au–noble gases interactions,[36] and dye–TiO$_2$ adsorbates in dye-sensitized solar cells.[40,41] Recently, this approach was extended also to the investigation of the charge displacement accompanying electron excitation in molecules.[42] Note that $\Delta\rho$ as defined above is the total density change, including that due to the antisymmetrization of the noninteracting wavefunction.

Knowing that the interaction between the two water molecules leaves their internal geometry essentially unaffected, and that the changes in the interaction due to H$_2$O relaxation are negligible, we consider each water molecule as a rigid rotor with a nuclear geometry fixed at its free equilibrium configuration (O—H distance of 0.957 Å and H—O—H angle of 104.52°).[43] The geometry optimization of the intermolecular coordinates (shown in Figure 1) were performed at the MP2/aug-cc-pVQZ[44–46] level of theory. In this set of coordinates, the origin is centered on the oxygen atom of the first water molecule (left), and the z axis is fixed as that joining the two oxygen atoms. The O—O distance along this axis is denoted by r. The β and α angles are those between the C_2 axis of the first and
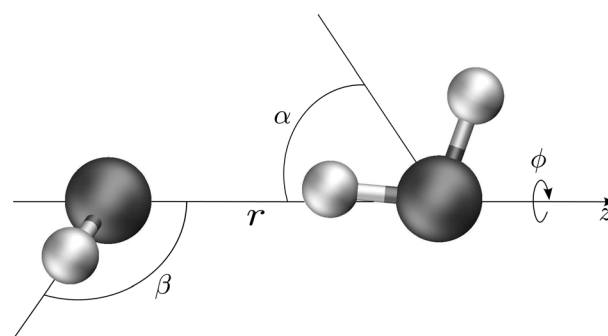

Figure 1. Intermolecular coordinates set as variables during the geometry optimization.

second (right) molecule, respectively, and the z axis. ϕ is defined as the dihedral angle describing the rotation of the second water molecule around the axis joining the oxygen atoms. Convergence tests for these structural parameters with respect to the method and the basis set are reported together with the corresponding dissociation energies in the Supporting Information. The program MOLPRO was used throughout.[47]

The electron densities used to perform the CD analysis were evaluated at the coupled-cluster level of theory,[48–50] with single and double excitations (CCSD) by using the aug-cc-pVTZ basis set[44] including the entire basis of the dimer also during the calculations on fragments (to estimate the basis-set superposition error, BSSE). More details about the method used to evaluate the CD curves and several tests made to verify their convergence with respect to the basis set dimension, the level of theory, and the effects due to the antisymmetrization of the fragments wavefunction can be found in the Supporting Information.

Our analysis of the water dimer interaction begins at the geometry of the two lowest minima of the potential energy surface. In Figure 2, we show the contour plots of the electron-density difference, the corresponding CD curves, and a 3D view of the density difference isosurfaces for the absolute and secondary minimum. The two arrangements are qualitatively quite similar. The density difference contour plot shows significant charge redistribution both in the intermolecular bonding area and inside the water molecules. These effects are mainly due to the polarization of the electron cloud in each molecule caused by the presence of the other. It is interesting that the molecule placed at the coordinate origin (left) displays some charge fluctuation around the oxygen site, with an evident density increase towards the intermolecular area. This is accompanied by charge depletion at the hydrogen atoms. The other molecule shows instead a considerable density decrease on the internal hydrogen atom, a reaccumulation in the OH binding area, and a sharp charge increase at the opposite side of the oxygen atom. The 3D plots reveal, moreover, that this last charge accumulation extends also to the external hydrogen atom.

The first and most evident feature of the CD curves is that they are negative everywhere, which indicates that in both nuclear configurations electrons move everywhere in the direc-
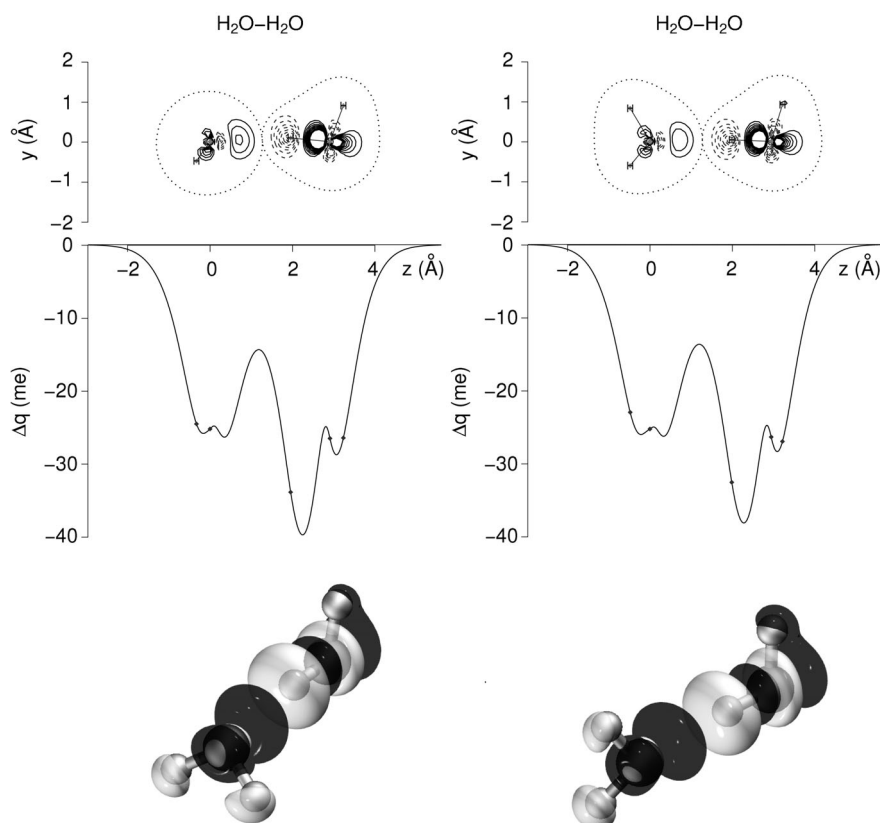
Figure 2. Contour plots of the electron density changes (top) and CD curves (bottom) for the $(H_2O)_2$ complex in the absolute (left) and secondary (right) minima configurations. In the contour plots, the dashed lines denote negative values (density depletion), and the solid line are positive contours. The dotted contours mark the isodensity boundary between the fragments (as defined in the text). The circles on the Δq curves mark the projection of the nuclear positions on the interfragment z axis (joining the oxygen atoms of the water molecules). The axis origin is at the oxygen atom of the first water. At the bottom, 3D representations of the electron density differences are shown, with isodensity surfaces corresponding to 0.001 e bohr^{-3} (black) and -0.001 e bohr^{-3} (white).

mum of about 14 me, and by considering a fairly large segment of the intermolecular zone, an upper limit of about 18–20 me appears reasonable. In this context, several previously reported estimates (ALMO-CTA→2.3 me,[51] NBO analysis→8.1 me,[28,52] BLW-NPA→5 me,[23] NOCV→80 me)[31] all correspond to points on the CD curve well outside the entire intermolecular region and appear therefore unrealistic (ALMO-CTA = absolutely localized molecular orbital charge-transfer analysis, NBO = natural bond orbital, BLW-NPA = block-localized wavefunction natural population analysis, NOCV = natural orbitals for chemical valence). The secondary minimum situation (right side of the figure) is also characterized as hydrogen bonded and, therefore, differs from the above only in quantitative details. Not unexpectedly, CT is here somewhat smaller (13.9 me at the isodensity boundary).

The two energy minima locations discussed above are evident HB arrangements. It seems at this point very interesting to perform the same analysis at other configurations and, more in general, examine CT as a function of the relative orientation of the molecules. The first simple but insightful orientation pathway appears to be that obtained by varying the β angle (which is 128.4° at the absolute minimum) and keeping all other geometrical parameters fixed at their minimum configuration value. The computed CT value (at the isodensity boundary) along this path is shown in the left panel of Figure 3. The most interesting global observation emerging from the plot is that the whole path is contained in a CT interval of only 2 me, which implies that the amount of transferred charge is relatively insensitive to the orientation of the HB-acceptor molecule as long as one OH bond of the HB donor points towards it. Thus, variations in the β angle never break the HB. Remarkably, notice further how the shape of the CT pattern along this pathway closely matches that of the associated energy stabilization calculated by Khaliullin et al.[51]

A second interesting orientation variable to be explored, defining a pronouncedly anisotropic section of the potential energy surface, is the α angle. Changes in this coordinate can break the hydrogen bond to produce significant changes in the interaction energy. Upon varying α, two particular values of β appear of special interest, namely, 0 and 180°, which cor-
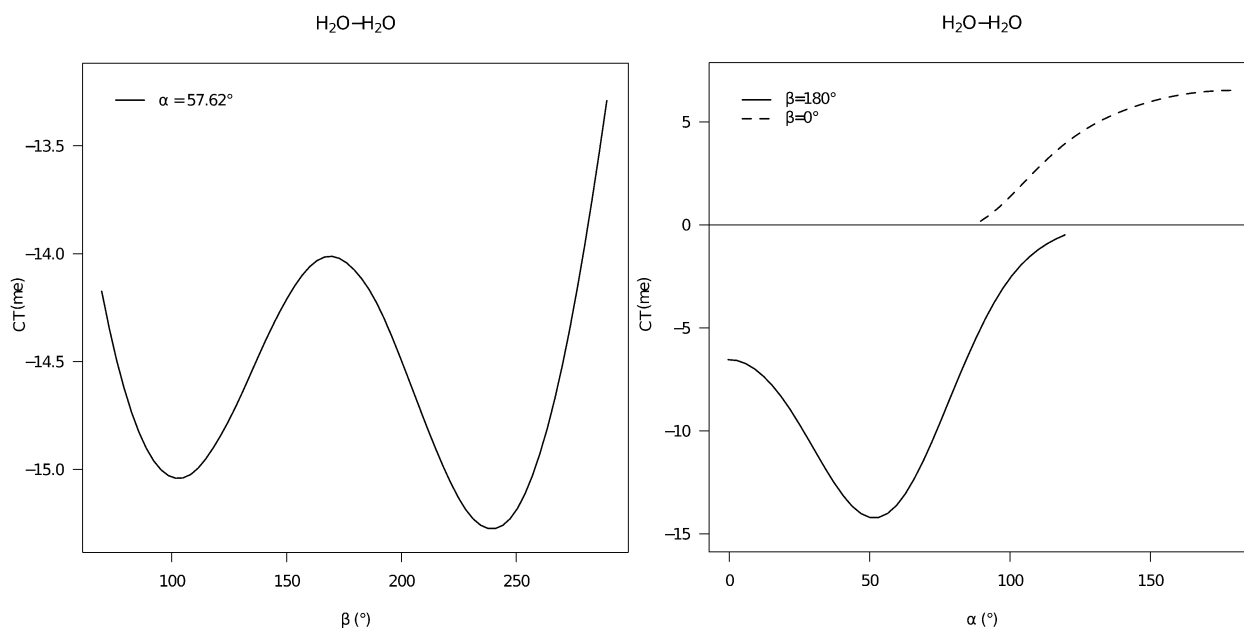
tion from the donor (left) to the acceptor (right) molecule. The strong polarization of the two molecules noted above is accurately pictured and quantified by the curves: the curve shows negative slope around the hydrogen atoms of the donor molecule, and this is indicative of charge depletion; it remains almost stationary in the oxygen area and increases significantly in the interfragments region. The function goes through a maximum (minimum CD) between the molecules and decreases sharply around the internal hydrogen atom of the acceptor (HB donor) molecule. Density then reaccumulates on the internal OH bond and to the right of the oxygen atom, across which there is instead a small charge decrease. A crucial finding is that, in the intermolecular region, the curve value remains always well below zero, which unequivocally describes a net CT from the donor to the acceptor molecule. At the isodensity boundary between the fragments (≈ 2.40 Å from the axes origin), the amount of CT is 14.6 me at the absolute minimum configuration. As pointed out above, the exact location of a boundary between the molecules—and therefore an exact CT amount—is a matter of convention, but the CD curve is nonetheless quite helpful in establishing unequivocal boundaries on CT. It seems evident that, in the absolute minimum nuclear arrangement, CT cannot be smaller than the curve maxi-

H₂O–H₂O

H₂O–H₂O

Figure 3. CT evaluated at the isodensity boundary of the CD curves for different values of the β (left) and α (right) angles. Negative CT is from the water molecule placed at the axes origin (left in Figures 1 and 2) to the other, positive CT is in the opposite direction. In the right panel two curves are shown for $\beta = 0$ and 180°.

respond to the hydrogen and oxygen atoms, respectively, of the left molecule pointing towards the interaction region (see Figure 1). These two pathways are shown in the right panel of Figure 3. The corresponding CD curves are reported in the Supporting Information. In this case, the coordinate r was re-optimized for each α value. Notice thus that both CT curves only cover limited α ranges: values outside these correspond to repulsive arrangements and CT is negligible. Let us consider first the CT curve for $\beta = 180°$ (Figure 3, ——), which corresponds to the oxygen atom of the HB acceptor pointing towards the HB donor. We can see that the curve, starting from the bifurcated configuration ($\alpha = 0°$), characterized by a CT of about 6.5 me, drops to a minimum (maximum CT of ≈ 14 me) at approximately 50° (one OH bond pointing towards the HB acceptor) and then increases (CT decreases) towards zero at larger α values. In the curve for $\beta = 0°$ (Figure 3, -----), α is shown to vary from 90 to 180°. Thus, the role of the two molecules is exchanged (CT is positive): the right molecule acts as an electron donor. CT is seen to increase slowly from zero for $\alpha = 90°$ to 6.5 me for the bifurcated configuration ($\alpha = 180°$).

As is well known, CT should fall off exponentially with increasing distance between the interacting molecules, as a consequence of its dependence on electron-cloud overlap. We show this for our CT estimate (CD value taken at the isodensity boundary) in the water dimer in Figure 4. The calculations performed refer to the bifurcated configuration. The linear fit of the CT logarithm versus distance is very accurate ($R^2 = 0.997$), which unequivocally proves the exponential decay. The exponent is equal to 1.99 Å^{-1}. A similar result was found in ref. [15] and represents an additional proof of the reliability of CD analysis for estimating CT effects.

One last crucial aspect of CT in the water dimer that we would like to briefly address is its effect on the dimer interaction energy. We adopted the simple model that the energy lowering associated with charge delocalization varies linearly with CT itself: $V_{CT} = k$CT.[28,51] This approach appears reasonable for systems in which the transferred charge is small, and indeed, it was successfully adopted by us in the investigation of other weakly bound water adducts such as water–Xe[15] and water–H₂.[14] By comparison with the intermolecular potential
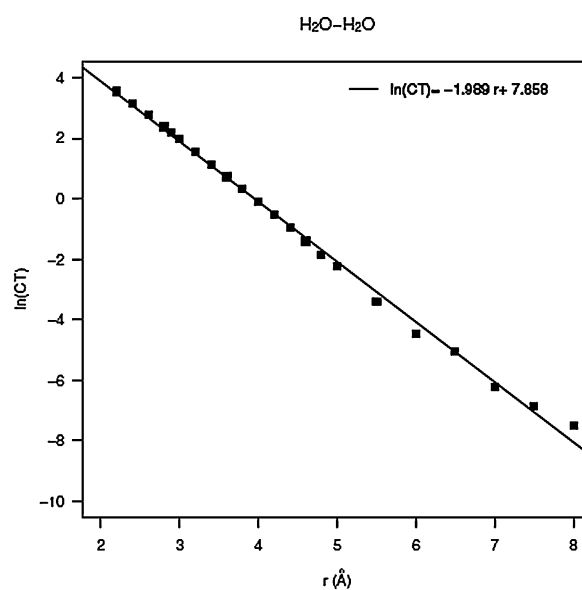
H₂O–H₂O

Figure 4. Logarithmic plot of the computed CT in the water dimer as a function of the distance between the oxygen atoms of the two water molecules in the bifurcated configuration.

extracted from state-of-the-art molecular-beam scattering experiments, we observed that the energy stabilization associated with the transfer of one electron (k) is rather constant in systems characterized by comparable dimensions, and in particular for water complexes, it assumes a value of about 2.5–2.6 eVe^{-1}. This order of magnitude for k can in fact be explained by a simple model for electron delocalization.[15] Applying this result, without any further elaboration, to the present case leads to an estimate of CT-induced stabilization in the water dimer at its equilibrium configuration (CT = 14.64 me) of 3.5–3.7 kJ mol^{-1}. This is remarkably similar to other estimates obtained by well-established EDA schemes, such as ALMO-EDA (CCSD) (3.51 kJ mol^{-1}),[32] symmetry-adapted perturbation theory (SAPT; 2.95 kJ mol^{-1}),[8] and intermolecular perturbation theory (IMPT; 3-4 kJ mol^{-1}).[8, 53] Notably, such agreement appears to be fairly stable with respect to the level of theory used to compute the electron densities, even if the absolute energy figures vary somewhat. For example, at the DFT/B3LYP level we obtain a CT energy contribution of 4.75 kJ mol^{-1} (the corresponding CD analysis is reported in the Supporting Information), whereas the corresponding ALMO-EDA calculation yields 5.44–6.69 kJ mol^{-1} (see refs. [51] and [54]). It seems truly remarkable and comforting to us that the CT energy constant obtained by us by using CD analysis and experimental scattering measurements leads to CT energy stabilization estimates so similar to those obtained by entirely different theoretical strategies, especially in view of the inaccurate values obtained by the latter for the absolute CT amounts themselves.

Concluding, in this paper we investigated the charge-transfer phenomena occurring in the water dimer by means of charge-displacement analysis. This reliable approach allowed us to estimate CT values at the equilibrium configurations and to describe for the first time the CT dependence on the relative orientation and distance of the two molecules. The CT estimate at the minimum is 14.6 me, and our study revealed the details of CT anisotropy with respect to hydrogen-bond breaking coordinates. One satisfactory aspect of CD analysis is its ability to put reliable boundaries on the calculated CT by providing a picture of charge displacement over the whole molecular complex and, therefore, a context for evaluating other methods. This has shown that previous wide-ranging estimates of CT must be considered unrealistic. By applying a simple model that we previously successfully proposed, we further estimated the energy contribution associated with CT in the water dimer. This turns out to be in good agreement with values obtained by well-established EDA schemes, even if the latter methods lead to grossly underestimated CT figures. We believe the present results cast new light on the role played by CT in hydrogen bonding and provide the basis to investigate its effect on experimental observables such as O—H stretching frequencies or NMR chemical shifts. Furthermore, the approach used herein may be easily transferrable to other kinds of intermolecular interactions, which may provide solid ground for further theoretical investigations.

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