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An SCF Partitioning Scheme for the Hydrogen Bond*

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The total energy of hydrogen bonding is divided into electrostatic and delocalization contributions.

Introduction

In the history of hydrogen bonding, the work of Coulson and Danielson [1] and Tsubomura [2] has played a key role. Their work attempts to understand the successes and failures of the simple electrostatic model of the hydrogen bond by semiempirically estimating the various contributions to the hydrogen-bond energy. More recently, Duijneveldt and Murrell [3] have calculated the coulomb, exchange, induction, dispersion and charge transfer terms by using perturbation theory on a three-center, four-electron model.

In view of recent progress in a molecular orbital theory of hydrogen bonding [4], it is of interest to develop a descriptive model of the hydrogen bond within the molecular orbital framework. Especially significant in this context is the work of Grahn [5a, 5b]. In 1958 Grahn used the best available molecular orbital wavefunctions for H_2O, HF, H_2S and HCl and divided the "polarization"[1] energy of the hydrogen bond into two parts: (1) the interaction of a partially positive hydrogen with the electron donor fragment, and (2) the interaction of the lone-pair electrons with an X–H bond.

Procedure

In the method presented here we break up the total hydrogen-bonding energy into three main contributions: (1) is the electrostatic energy, defined as the difference in energy of two undistorted[2] water monomers at a finite separation from the energy at infinite separation. This is done computationally by using starting vectors in the SCF procedure from the two monomer fragments. These vectors are appropriately Schmidt orthogonalized. This energy corresponds to the electrostatic and charge cloud repulsion energies of the old valence-bond theories. (2) The second contribution is the delocalization energy[1], defined as

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[1] Grahn has used the term "polarization" energy to refer to the charge redistribution in the monomer fragments upon H-bond formation; we use "delocalization" energy to refer to the same effect, and it is to be noted that this does not include correlation energy.

[2] The molecular geometry is the same as the isolated monomers. The wavefunction is an antisymmetrized product of the isolated monomer wavefunctions.

the difference between the energy of the converged SCF solution for the dimer and the first iteration (electrostatic) energy. This corresponds to the "polarization"[1] and charge transfer energies of the valence-bond model, and this is the quantity obtained by Grahn. (3) A conservative estimate of the correlation energy (which corresponds to the dispersion energy of the old valance-bond theory) estimate is obtained by considering only that change which occurs due to the change in the *atomic* charge distribution and is computed from the strictly LCAO population change on the heavy atom weighted by the known difference between the free ion and free atom correlation energies.

Results and Discussion

The results of calculations on $(HF)_2$ and $(H_2O)_2$ are presented in Table 1[3]. The actual hydrogen bond energy appears to be overestimated in this scheme, but the calculated ΔE for hydrogen bonds has been shown to be quite basis set dependent[4]. The purpose of our decomposition, however, is not to get the exact number, but to separate out the principle contributing factors.

The total H-bond energy in both dimers contains important contributions from both electrostatic and delocalization (charge redistribution) effects but

Table 1. *Energies and Population Analysis*

$HF(R=1.73$ a. u.$)$ $E=-100.01463$ Atomic population on F 9.50208 H 0.49792				$H_2O(R=1.808$ a. u., $\theta=105°)$ $E=-76.00291$ Atomic population on O 8.79492 H 0.60254		
system	R(Å)	θ(°)	E_1(a. u.)	E_f(a. u.)	$O_1{}^a(F_1)$	$O_2(F_2)$
$(HF)_2$	2.3	0	−200.01800	−200.02997	9.542	9.573
$(HF)_2$	2.6	0	−200.03539	−200.03952	9.535	9.555
$(HF)_2$	2.8	0	−200.03763	−200.04000	9.530	9.544
$(HF)_2$	2.8	60	−200.03636	−200.03901	9.509	9.543
$(HF)_2$	3.0	0	−200.03756	−200.03907	9.525	9.535
$(HF)_2$	4.0	0	−200.03345	−200.03369	9.512	9.512
$(H_2O)_2$	2.8	0	−152.01300	−152.01787	8.860	8.854
$(H_2O)_2$	3.0	0	−152.01456	−152.01732	8.844	8.846
$(H_2O)_2$	3.0	50	−152.01446	−152.01734	8.829	8.849
$(H_2O)_2$	3.2	0	−152.01425	−152.01597	8.832	8.838

[a] See Ref. in footnote 3 for figures of linear $(HF)_2$ and $(H_2O)_2$. θ is the HFH angle in $(HF)_2$. In $(H_2O)_2$, it is the angle between the HOH bisector of the electron donor and the O···HO line. $O_1(F_1)$ is the oxygen (fluorine) on the electron donor; $O_2(F_2)$ is the oxygen (fluorine) on the electron acceptor.

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[3] See: Kollman, P. A., Allen, L. C.: J. chem. Physics **51**, 3286 (1969); J. chem. Physics **52**, 5085 (1970) for computational details. The basis set used here employs double zeta gaussian atomic orbitals in the LCAO procedure. Whitten's *s* functions [Whitten, J. L.: J. chem. Physics **44**, 359 (1966)] and Huzinaga's 5*p* set [Huzinaga, S.: J. chem. Physics **43**, 1201 (1965)] were used with a (4,2,2) contraction. For figures describing the geometries of linear $(HF)_2$ and $(H_2O)_2$, see: Kollman, P. A., Allen, L. C.: J. Amer. chem. Soc. **92**, 753 (1970).

[4] Kollman, P. A., Allen, L. C.: J. chem. Physics **52**, 5085 (1970). Compare also the *ab initio* dimerization energies of Morakuma and Pederson (−12 kcal/mole), J. chem. Physics **48**, 3275 (1968), with those of Diercksen (−4.8 kcal/mole): Chem. Physics Letters, **4**, 373 (1969).

Table 2. *Contributions to* H *bond energy (kcal/mole)*

system	R(Å)	θ	ΔE (electrostatic)	ΔE (delocalization)	ΔE (correlation)
$(HF)_2$	2.6	0	3.84	2.59	
$(HF)_2$	2.8	0	5.25	1.49	1.53
$(HF)_2$	2.8	60	4.45	1.66	
$(HF)_2$	3.0	0	5.20	0.95	
$(H_2O)_2$	2.8	0	4.50	3.05	
$(H_2O)_2$	3.0	0	5.48	1.73	1.54
$(H_2O)_2$	3.0	50	5.42	1.81	
$(H_2O)_2$	3.2	0	5.29	1.08	

Comparison with Grahn [5a]

	$(HF)_2$		$(H_2O)_2$	
	elect.	deloc.	elect.	deloc.
Grahn	7.5	1.9	5.1	1.4
This work	5.25	1.49	4.50	3.05

correlation energy difference[a] between:

O^- and O = 46.0 kcal/mole

F^- and F = 49.5 kcal/mole

	Energy Component Changes (a. u.)			
	ΔV_{nn}	ΔV_{ee}	ΔV_{ne}	ΔT
$(HF)_2$ $R = 2.8$ Å	19.30726	19.04697	−38.25379	−0.11115
$(H_2O)_2$ $R = 2.8$ Å	18.85704	18.74021	−37.43321	−0.17664

[a] See second article of Ref. in footnote 5 for more details on this procedure and how the correlation energy differences were found.

there is a significantly greater delocalization energy contribution in the water dimer than in the hydrogen fluoride dimer. Our finding that the delocalization energy plays a greater role in the water dimer than in the hydrogen fluoride dimer is in disagreement with Grahn's [5a] (results found in this study near the minimum energy X···Y separation are also compared with Grahn's (Table 2)). Dimers with a non-zero θ show, as expected, a lower electrostatic energy (less favorable dipoles), but a greater delocalization energy. In infinite linear chains and cyclic systems, the delocalization contribution is greater than in dimers (non-linear effect)[5] and that is why, in HF crystal, the F–F–F angle is 140° not 180°. It is also worthy of note that the electrostatic (first iteration) energy predicts a minimum energy X–Y distance for the dimers quite close (although as expected, slightly larger) than the minimum energy X–Y distance found from the total energy (converged SCF). This can be understood in the following way: the positive character of the hydrogen in the X—H···Y bond allows the electron acceptor (proton donor) X–H to approach to a certain distance (closer than the sum of Van der Waals radii) from the electron donor Y. Then charge redistribution,

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[5] See: Kollman, P. A., Allen, L. C.: J. Amer. chem. Soc. **92**, 753, 4108 (1970) for detailed calculations on HF polymers.

Table 3. CNDO *results (distances in Å and energies in a. u.)*

H_2O *monomer* ($R = 1.03$ Å, $\theta = 105°$) $E = -19.8911$				HF *monomer* ($R = 1.0$ Å) $E = -28.4367$	
Dimers[a]					
system	R	θ	E_1	E_f	ΔE
$(HF)_2$	2.2	0	−56.7738	−56.8726	+.0008
$(HF)_2$	2.4	0	−56.8348	−56.8877	−.0143
$(HF)_2$	2.6	0	−56.8594	−56.8860	−.0126
$(HF)_2$	2.4	60	−56.8336	−56.8878	−.0144
$(H_2O)_2$	2.3	0	−39.7019	−39.7837	−.0015
$(H_2O)_2$	2.5	0	−39.7495	−39.7956	−.0134
$(H_2O)_2$	2.7	0	−39.7695	−39.7939	−.0117
$(H_2O)_2$	2.6	50	−39.7612	−39.7950	−.0128

[a] See Ref. in footnote 3 for more details.

a much smaller effect which makes the hydrogen still more positive[3], allows a slightly closer approach.

Since CNDO/2 has been shown to give qualitatively reasonable results for energies of dimerization for H_2O and HF[5], we have attempted a similar energy decomposition for $(H_2O)_2$ and $(HF)_2$. The results (in Table 3) clearly show that the separate physical effects contributing to hydrogen bonding are not represented correctly by the CNDO/2 procedure. The CNDO/2 method gives reasonable dimerization energies by greatly overestimating the delocalization energy part of the hydrogen bond. This is partially due to the fact that CNDO/2 underestimates the minimum energy X···Y separation. However, the use of smaller *ab initio* bases [6] should allow this decomposition scheme to be applied to many larger hydrogen bonded systems.

A good feature of this decomposition scheme is that, unlike earlier methods, it is applicable to all relatively weak intermolecular complexes, not just hydrogen bonding. These include "charge transfer" and "dipole-dipole" complexes[6]. A further decomposition of the delocalization energy into: (a) delocalization in fragment A, (b) delocalization in fragment B, and (c) charge transfer terms, is now under development. It involves "freezing" the M. O. coefficients for one fragment while allowing the charge on the other to redistribute.

Since a total energy component analysis (separating the total energy into nuclear-nuclear, nuclear-electron, and electron-electron potential energies and the electron kinetic energy) has been of great utility in understanding the rotational barrier [7], a similar analysis was attempted with these hydrogen bonded systems (see Table 2 for results). It is interesting to observe that, unlike component changes during internal rotation, component changes during hydrogen-bond formation are many orders of magnitude greater than the strength of the hydrogen bond. From a physical model standpoint, the concept of component analysis is useful in understanding rotational barriers because: (a) The size of the system stays the same during the rotation process, and (b) Charges in the components can

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[6] See: Johnston, M. D., Gasparro, F. P., Kuntz, I. D.: J. Amer. chem. Soc. **91**, 5715 (1969) for an NMR study of various types of weak intermolecular complexes.

be of either a repulsive or attractive dominant nature. During hydrogen-bond formation, one has: (a) a change from two small systems to one large system, and (b). The physical effect (donor-acceptor complex formation) does not have a suggestive mathematical representation in terms of any one or combination of energy components. Thus total energy components (V_{nn}, V_{ee}, V_{ne} and T) are not appropriate in dealing with hydrogen bonding.

Finally, the donor-acceptor decomposition scheme, which has been the subject of this paper is not applicable to extremely strong interactions (e. g., $HF + F^- \rightarrow HF_2^-$), but the earlier methods [1, 2] and perturbation theory [3] cannot treat these cases either. Results on the application of this decomposition method to many different systems as well as further division of the delocalization term will be published separately.

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