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The Electrostatic Model in the Theory of H-Bonds

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The perturbational treatment of H-bonded systems reduces the discussion of H-bond properties to that of proton donor and proton acceptor properties. Among the variety of interaction contributions within perturbation theory it is simply the electrostatic interaction which mainly seems to control H-bond strength and stereochemistry of H-bonds. The easy accessible classical and clear electrostatic potential of the proton acceptor is found to be a useful indicator for H-bond properties.

INTRODUCTION

For the calculation of intermolecular interactions between two molecules A and B there are mainly two methods of specific importance: Within the molecular orbital approximation (MO) the system A . . . B is treated as a super molecule, whereas from the view of perturbation theory (PT) the system A . . . B is constructed by means of the subsystems A and B. Because of its general structure the MO method is especially easy to handle and widely applicable — in principle. Perturbation theory, however, is restricted to the supposition that the system A . . . B can be subdivided uniquely in two subsystems A and B. Then the advantage of perturbation theory is a specific insight into the nature of intermolecular interactions.

Especially for one case of association of molecules, the H-bonded systems AH . . . B, there can be found numerous results in the literature which are based on MO calculations. These results are mainly concerned with the stereochemistry of H-bonds as well as with bond strength $\Delta E = E\,(\text{AH} \ldots \text{B}) - E\,(\text{AH}) - E\,(\text{B})$[1]. The range of application of the MO methods is strongly limited because of the huge numerical work. Therefore the general treatment of a super molecule should be specified considering the fact, that always a proton donor (don) interacts with a proton acceptor (acc). Every more or less polar AH bond (FH, OH, NH, ClH) is able to act as a proton donor. For example methane, being a proton donor, forms extremely weak associates with $\Delta E = -0.8$ kcal/mol[2]. A proton acceptor has at least one more or less directed lone electron pair (for example N_2 is not a proton acceptor). Occasionally π electrons in local double and triple bonds can act also as proton acceptors (C_2H_4, C_2H_2)[3]. Summarizing the electronic situation in H-bonds can be described qualitatively as follows: A proton, partially screened by an energetically low lying and highly localized orbital, dives into the range of

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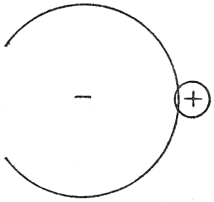
an energetically high lying and spread out orbital of a lone electron pair. The atomic radii of proton acceptors exceed the hydrogen radius by a factor 3—7. In the following this situation is used to be the starting point for the calculation of H-bond properties within the framework of perturbation theory.



PERTURBATION THEORY

For the calculation of intermolecular interaction perturbation theory distinguishes itself, besides numerical advantages, by the capability that the interaction energy can be subdivided into contributions which mostly have physical meanings.

$$\Delta E = \underbrace{\Delta E_{\mathrm{Coul}} + \Delta E_{\mathrm{Ex}}}_{\text{1 st order}} + \underbrace{\Delta E_{\mathrm{Pol}} + \Delta E_{\mathrm{ChT}} + \Delta E_{\mathrm{Dis}}}_{\text{2 nd order}}$$

Contributions of first order are the electrostatic Coulomb interaction and the electron exchange term. Contributions of second order are the mutually polarization of the molecules, the charge transfer term which sometimes is called the covalent contribution, and the energy of dispersion forces. The sum $\Delta E_{\mathrm{Pol}} + \Delta E_{\mathrm{ChT}}$ is called the delocalization energy. A detailed discussion for this energy partitioning is found for example in[4].

The energy partitioning described can also be performed in connection with a MO calculation of the super molecule AH . . . B. The only exception is ΔE_{Dis}. An energy partitioning in connection with a MO calculation is possible only if the orbitals can be subdivided unequivocally among the two subsystems[5]. The energy partitioning fails for strong symmetric H-bonds such as FHF^-, $H_5O_2^+$, etc. For H-bonds of intermediate strength the deformation energy of the subsystems must be taken into account.

As an example the energy partitioning for the system $(H_2O)_2$ in its equilibrium distance (O . . . O = 3Å) is presented[6] (kcal/mol).

ΔE	ΔE_{Coul}	ΔE_{Ex}	ΔE^1	ΔE_{Pol}	ΔE_{ChT}	ΔE^2
— 4.7	— 7.3	4.5	— 2.8	— 0.7	— 1.2	— 1.9

For weak H-bonds there are energy contributions of first and second order which are of comparable order of magnitude and which mutually compensate partially. Besides the energy contributions in the intermolecular equilibrium distance, the distance dependency of these terms is of particular interest. For polar neutral subsystems there exist well known relations such as $\Delta E_{\mathrm{Coul}} \sim R^{-3}$ and $\Delta E_{\mathrm{Pol}} \sim R^{-6}$. The terms ΔE_{Ex} and ΔE_{ChT} disappear exponentially and are therefore of short range. In the following section a concept for the description of stereochemistry and bond strength of H-bonds is delineated by means of the easy accessible classical and clear ΔE_{Coul}.

THE SEMICLASSICAL ELECTROSTATIC APPROACH

The electrostatic energy contribution for the intermolecular interaction has the form

$$\Delta E_{\mathrm{Coul}} = \sum_{k}\sum_{l} Z_k Z_l / |\vec{R}_k - \vec{R}_l| - \sum_{k} Z_k \int \varrho_B(\vec{r}_2)/|\vec{R}_k - \vec{r}_2| \, d\vec{r}_2$$

$$- \sum_{l} Z_l \int \varrho_A(\vec{r}_1)/|\vec{R}_l - \vec{r}_1| \, d\vec{r}_1 + \int\int \varrho_A(\vec{r}_1) \, \varrho_B(\vec{r}_2)/|\vec{r}_1 - \vec{r}_2| \, d\vec{r}_1 \, d\vec{r}_2$$

$$k \in A, \quad l \in B$$

This expression can be simplified if one of the two charge distributions — ϱ_A, ϱ_B — is approximated by point charges q_k (semiclassical approach). For H-bonds the bridging proton can be seen as a shielded point charge in the charge distribution of the proton acceptor. This situation is shown in the figure in section 1. Thus we arrive at

$$\Delta E_{\mathrm{Coul}} \sim \sum_{k}\sum_{l} q_k Z_l / |\vec{R}_k - \vec{R}_l| - \sum_{k} q_k \int \varrho_B(\vec{r})/|\vec{R}_k - \vec{r}| \, d\vec{r} = \sum_{k} q_k V_B(\vec{R}_k)$$

For the approximation of ΔE_{Coul} the calculation of only the electrostatic molecular potential of the proton acceptor B for the points $\vec{R}_k$ is necessary.

$$V_B(\vec{R}) = \sum_{l} Z_l / |\vec{R} - \vec{R}_l| - \int \varrho_B(\vec{r})/|\vec{R} - \vec{r}| \, d\vec{r}$$

An excellent survey about the use of the electrostatic molecular potential is given in ref.[7]. The crucial advantage for the use of V_B instead of ΔE_{Coul} can be seen in the fact that ΔE_{Coul} must be calculated for any donor-acceptor pair AH...B, whereas V_B is simply a property of an acceptor. The search for donor and acceptor properties for H-bonds was important at all times[8]. Some examples are presented in the following section.

PROTONDONOR AND PROTONACCEPTOR PROPERTIES

There are numerous attempts to explain H-bond properties by means of classical electrostatic properties. In Table I a few important properties of proton donors and proton acceptors are listed up. Extremely global properties such as the dipole moment of the donor show no correlation with the strengths of H-bonds. The electronic charge of the bridging proton, defined by Mulliken's population analysis, indicates the H-bond strength with respect to one acceptor, at least for proton donors with first row atoms. A similar statement is valid for a variety of proton acceptors with respect to one donor. The comparably strong H-bond with HCl as a donor cannot be explained electrostatically. Even the high polarizability and a probably high charge transfer contribution (low-lying LUMO) cannot explain this bond strength. Presumably deformation energy (proton transfer) plays an important role. After all in NH_4Cl the HCl distance is enlarged by 0.4 Å with respect to the free HCl molecule[8]. Finally the HOMO-LUMO differences indicate the reciprocal charge transfer energies.

TABLE I

Calculated H-bond Energies (kcal/mol)[8], q: *Atomic Charges (Mulliken)* μ: *Experimental Dipole Moment (D),* α: *Experimental Polarizability* (Å^3), *HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital (a. u.)*

Acc / Don	NH_3	H_2O	HF	q_H	LUMO	μ	α[9]
CH_4	1.1	0.9	0.5	0.769	0.036	0	2.600
NH_3	4.3	4.1	3.6	0.698	0.091	1.47	2.196
H_2O	8.9	8.1	5.4	0.635	0.162	1.82	1.455
HF	16.3	13.4	7.8	0.556	0.215	1.74	0.800
HCl	10.8	8.2	4.6	0.879	0.069	1.07	2.630
q_X	7.906	8.730	9.444				
HOMO	—0.373	—0.463	—0.602				

A further important property for the discussion of H-bond strengths are the proton affinities. These are listed for some systems in Table II. In Table III it is shown that the sum of the deprotonation energy of the donor and the proton affinity of the acceptor correlates with the H-bond strength. The amount PI + PA can be seen as an analogon to Pauling's electronegativity.

TABLE II

Experimental Proton Affinities (kcal/mol)[10]

CH_3^-	OH^-	NH_2^-	F^-	CN^-	Cl^-
—500	—411	—380	—366	—338	—324
NH_3	CH_3OH	H_2O	C_2H_4	CH_4	HF
—216	—180	—164	—157	—122	—121

STRUCTURES AND BOND STRENGHTS OF HALIDE ION — WATER COMPLEXES

The electrostatic potential of the halide anions F^-, Cl^-, and Br^-, calculated by the use of the gaussian basis sets (13s, 8p), (15s, 9p), and (17s, 10p, 2d), respectively, is shown in Figure 1. For comparison the experimental interatomic distances of the hydrides HF, HCl, and HBr as well as the proton affinities of the halide anions are marked by dots. It is shown that the semiclassical approach is capable for qualitative predictions in the range of chemical bond. Thus we have to expect predictions of at least similar accuracy if we extend the range of interatomic distances to that of H-bonds.

TABLE III

Sum of Deprotonation Energy PI and Proton Affinity PA, and H-bond Energy ΔE (kcal/mol)

Donor	Acceptor	$PI_{don}+PA_{acc}$	—ΔE[11]
FH	F^-	0	60.2
OH_3^+	OH_2	0	31.6
NH_4^+	NH_3	0	24.8
OH_2	F^-	45	23.3
OH_2	OH^-	0	22.5 (24.3)
OH_2	Cl^-	87	13.1
FH	NH_3	150	11.7
ClH	NH_3	108	10.8 (19.5)
FH	OH_2	202	9.4
ClH	OH_2	160	8.2
FH	FH	245	7.0
OH_2	CH_3OH	231	5.2
OH_2	OH_2	247	5.1
OH_2	FH	290	3.0
NH_3	FH	259	1.3
CH_4	NH_3	284	1.1
OH_2	C_2H_4	254	0.6
CH_4	CH_4	378	—

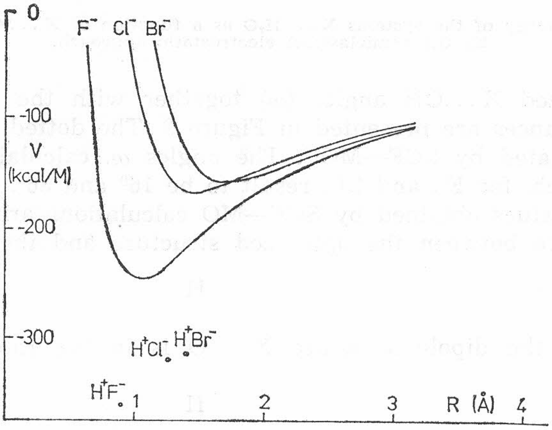
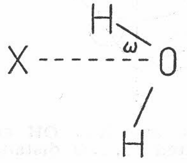


Figure 1. Electrostatic potential of halide anions. Experimental interatomic distances of the hydrides HF, HCl, HBr and proton affinities of the halide anions are marked by dots

In the following the bare proton is replaced by a set of point charges in order to describe a water molecule. The results of Mulliken's population analysis are used so that for oxygen and hydrogen the appropriate charges are —0.5868 and 0.2934, respectively. In Figure 2 the H-bond energy is drawn over the X...O distance where the angle ω is energetically optimized.



SCF — MO calculations[12] for X = F^-, Cl^- show, that the X . . . O distances, calculated by the semiclassical approach, result to be 0.4 Å shorter, whereas the H-bond energies result to be only 1—2 kcal/mol lower than those from SCF—MO calculations. For comparison, SCF—MO calculations at the STO—3G level give the X . . . O distances too short by 0.2—0.3 Å[13].

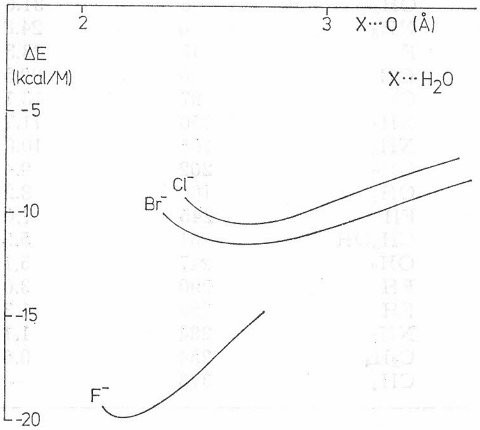


Figure 2. H-bond energy of the systems X . . . H_2O as a function of X . . . O distance calculated by the semiclassical electrostatic approach.

The optimized X . . .OH angles (ω) together with the ionic radii[14] and the X . . . O distances are presented in Figure 3. The dotted X . . . O distances are those calculated by SCF—MO[12]. The angles ω, calculated by the semiclassical approach, for F^-, and Cl^-, result to be 16° and 36°, respectively. The corresponding values obtained by SCF—MO calculations are 5° and 15°. The energy difference between the optimized structure and the linear structure X . . . H—O′, or the dipole structure $\mathrm{X}\ldots\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}}$ is in the range of only 1—2 kcal/mol for Cl^-, and Br^-. The lowest state of the »in plane« motion of the H_2O molecule has about the same height as this energy barrier. Thus the H_2O molecule associated with X = Cl^-, Br^- is almost free in motion[15].

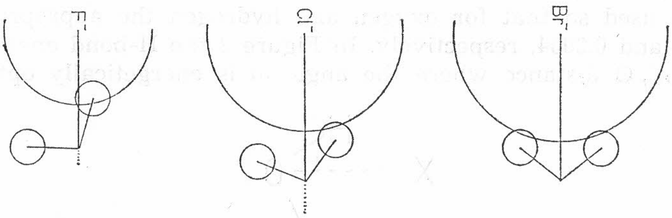
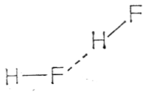


Figure 3. Ionic radii, X . . . O distances, and X . . . OH angles calculated by the semiclassical electrostatic approach. The dotted X . . . O distances indicate SCF-MO results.

The semiclassical approach can, in principle, also be performed by the calculation of the electrostatic potential of the water molecule and by the replacement of the anion by a negative point charge[16]. In Figure 9 of ref.[16] it is shown that for X...O distances larger than 6 a. u. (3.1 Å), as is the case for X = Cl^-, Br^-, the dipole structure is adopted. This reversed concept of the semiclassical approach has the disadvantage, however, that no equilibrium structures and H-bond energies can be obtained, since the interaction energy goes to minus infinity for decreasing X...H distance.

STEREOCHEMISTRY OF H-BONDS

The most simple and well examined H-bond system is $(HF)_2$. The steric arrangement is experimentally evident,



where the H—F...H angle is found to be 108°. One attempt to explain this angle was undertaken by Kollman[17], where the electrostatic plus polarization contribution which together should prefer energetically the linear arrangement (H—F...H = 180°), and the charge transfer contribution which is optimized for the perpendicular arrangement (H—F...H = 90°), are in competition.

It can be seen as a success of the electrostatic potential that it has overruled Kollman's assumption. An accurate calculation (F (13s, 8p, 1d), H (6s, 1p)) of the electrostatic potential of the HF molecule, shown in Figure 4, yields for F...H^+ = 1.9 Å a H—F...H^+ angle of 150° ($\Delta E_{\mathrm{H}}+$ in Table IV). Earlier calculations of the electrostatic potential are of too low quality as to predict sensitive quantities such as the H—F...H angle[8,18]. The more realistic presentation of the proton donor molecule by two point charges (Table I) yields a H—F...H angle of 120° and a dimerization energy of 6.3 kcal/mol (ΔE_{HF} in Table IV) in best agreement with experimental findings.

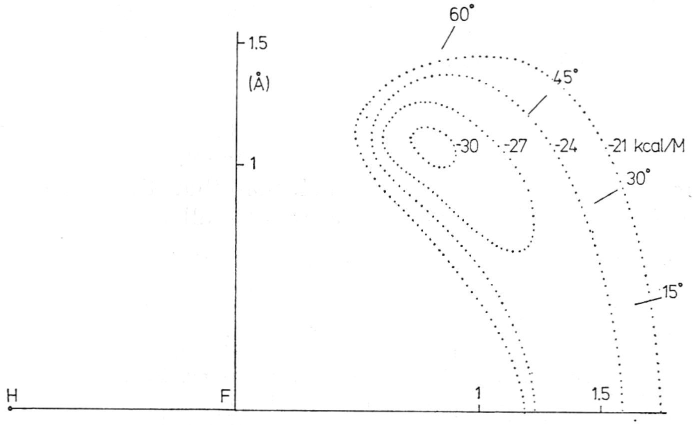


Figure 4. Electrostatic potential of the HF molecule.

In a perturbational treatment the charge transfer contribution results to be smaller than the electrostatic contribution by a factor 70[19], in contrast to Kollman's assumption.

Similar calculations were performed for the HCl molecule. The electrostatic potential yields a H—Cl...H$^+$ angle of 110° for a fixed distance Cl...H$^+$ = 2.54 Å (Table IV and Figure 5). The presentation of the proton donor by means of two point charges (Table I) yields an angle of 90° and a dimerization energy of somewhat more than 1 kcal/mol in agreement with experiment[20].

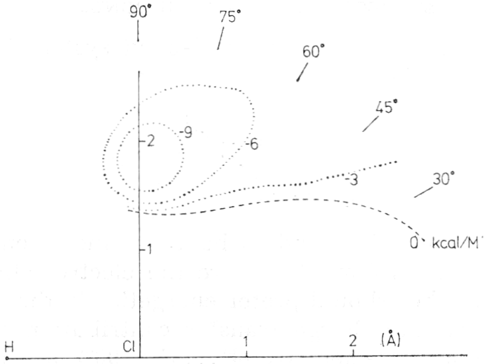


Figure 5. Electrostatic potential of the HCl molecule.

TABLE IV

Angular Dependency of H-bond Energy for $(HF)_2$ with F...H = 1.9 Å and for $(HCl)_2$ with Cl...H = 2.54 Å

ΔE_{H^+}: *Electrostatic Molecular Potential,*
ΔE_{HX}: *H-bond Energy for Point Charge Approximation of the Proton Donor (kcal/mol)*

H—F...H	120°	135°	150°	165°	180°	
ΔE_{H^+}	—19.1	—20.6	—21.0	—20.8	—20.7	
ΔE_{HF}	—6.3	—6.2	—5.7	—5.3	—5.1	
H—Cl...H	105°	120°	135°	150°	165°	180°
ΔE_{H^+}	—6.7	—6.3	—4.6	—2.4	—0.6	+0.1
ΔE_{HCl}	—1.0	—0.7	—0.2	+0.3	+0.8	+0.9

The water dimer was treated in a similar manner by the use of point charges located at the centres of localized orbitals[21].

Summarizing we can draw the conclusion that the steric arrangement of $(HF)_2$ and $(HCl)_2$ can be explained electrostatically.

REFERENCES

1. P. Schuster in *The Hydrogen Bond,* Eds. P. Schuster, G. Zundel, and C. Sandorfy, North Holland, Amsterdam 1976.
2. W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, in *Progress in Physical Organic Chemistry,* Eds. A. Streitwieser, R. W. Taft, Vol. **11**, J. Wiley 1974 and ref. [8].
3. J. E. Del Bene, *Chem. Phys. Letters* **24** (1974) 203
4. F. B. van Duijneveldt, J. N. Murrell, *J. Chem. Phys.* **46** (1967) 1759.

5. P. A. Kollman, L. C. Allen, *Theoret. Chim. Acta* **18** (1970) 399; M. Dreyfus, A. Pullman, *Theoret. Chim. Acta* **19** (1970) 20.
6. P. Schuster, H. Lischka, A. Beyer in *Progress in Theoretical Organic Chemistry*, Ed. I. G. Csizmadia, Vol. **2**, Elsevier.
7. E. Scrocco, J. Tomasi in *Topics in Current Chemistry*, Vol. **42**, Springer, 1973.
8. P. A. Kollman, J. McKelvey, A. Johansson, S. Rothenberg, *J. Amer. Chem. Soc.* **97** (1975) 955.
9. *D'Ans, Lax, Taschenbuch für Chemiker und Physiker*, Bd. III, Springer, 1970.
10. A. C. Hopkinson, N. K. Holbrook, K. Yates, I. G. Csizmadia, *J. Chem. Phys.* **49**, 3596 (1968); P. H. Owens, R. A. Wolf, A. Streitwieser, *Tetrahedron Lett.* 3385 (1970); V. Dyczmons, V. Staemmler, W. Kutzelnigg, *Chem. Phys. Let* **5** (1970) 361.
11. Ref. 1 and 8.
12. H. Kistenmacher, H. Popkie, E. Clementi, *J. Chem. Phys.* **58** (1973) 5627.
13. J. D. Dill, L. C. Allen, W. C. Topp, J. A. Pople, *J. Amer. Chem. Soc.* **97** (1975) 7220
14. H. R. Christen, *Grundlagen der allgemeinen und anorganischen Chemie*, Sauerländer-Salle, 1968.
15. R. Janoschek in *Proceedings III International Symposium on Specific Interactions between Molecules or Ions*, Wroclaw, 1976.
16. P. Schuster, W. Jakubetz, W. Marius in *Topics in Current Chemistry*, Vol **60**, Springer 1975.
17. P. A. Kollman, *J. Amer. Chem. Soc.* **94** (1972) 1837.
18. B. Howard, *J. Chem. Phys.* **39** (1963) 2524.
19. P. Otto, J. Ladik, *Chem. Phys.* **8** (1975) 192.
20. C. Girardet, D. Robert, *J. Chem. Phys.* **58** (1973) 4110
21. R. Bonaccorsi, C. Petrongolo, E. Scrocco, J. Tomasi, *Theort. Chim. Acta* **20** (1971) 331.

IZVLEČEK

Elektrostatski model v teoriji vodikove vezi

Rudolf Janoschek

Za računanje intermolekularne interakcije molekul A in B sta pomembni dve metodi. Pri metodi molekularnih orbital (MO) obravnavamo sistem A... B kot super molekulo, pri perturbacijski metodi pa si predstavljamo isti sistem, sestavljen iz dveh podsistemov A in B. Za poseben tip molekulskih asocijacij in vodikovo vezane sisteme AH... B, lahko najdemo v literaturi mnogo rezultatov, ki slonijo na MO metodi. Računi se v glavnem nanašajo na stereokemijo vodikovih vezi in na njihovo jakost.

$$\Delta E = E(AH \ldots B) - E(AH) - E(B)$$

MO metoda je glede na svojo strukturo široko uporabna in vsaj v principu preprosta. Obseg njene uporabnosti pa je ostro omejen, ker izredno hitro narašča obseg računov. Perturbacijska metoda pa sloni na domnevi, da je možno sistem A... B enolično razdeliti v dva podsistema A in B. Njena prednost je v tem, da omogoča specifičen vpogled v naravo intermolekularnih interakcij. Perturbacijska obravnava vodikovo vezanih sistemov omeji diskusijo na lastnosti protonskih donorjev in akceptorjev. Kaže, da je med vsemi možnimi interakcijskimi prispevki elektrostatska interakcija tista, ki odloča o moči in stereokemiji vodikove vezi. Pokazalo se je tudi, da je enostavno dosežen klasični elektrostatski potencial protonskega akceptorja uporaben indikator lastnosti vodikove vezi.

Dimer vode je v članku predstavljen z modelom točkastih nabojev tako, da so naboji nameščeni na centre lokaliziranih orbital. Prostorsko razmestitev dimerov $(HF)_2$ in $(HCl)_2$ je možno razložiti s pomočjo elektrostatskega modela.