

ELECTROSTATIC POTENTIAL FUNCTIONS APPLIED TO HYDROGEN BONDING

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ABSTRACT

The application of electrostatic potential functions derived from the H...multipole model to study van der Waals electrostatic interaction in the H...OH₂, H...NH₃, H...⁺OH₃, H...OH, H...OCO, H...O₂ and H...Cl₂ systems as model for hydrogen bonding has been presented. The model potentials yield hydrogen bond energies and bond lengths in agreement with experiment, and suggest that the bonding is non-overlap or non-electronic exchange type.

INTRODUCTION

Obtaining both the repulsive and attractive components of the van der Waals intermolecular electrostatic potential function from a single theory was the major problem in the development of intermolecular potentials¹⁻¹⁵. It has been presumed that the classical multipole expansions of the intermolecular electrostatic potential do not yield the two components from a single theory. So it has been the practice to treat the attractive and repulsive components of the intermolecular potential differently and separately^{1-15,16}.

However, the ad hoc or *ab initio* treatment of the intermolecular interaction potential corresponds to a physical model for intermolecular forces involving valence and non-valence binding. Since valence binding is included, the resultant theory leaves open the theoretical question of whether purely non-valence (or non-electronic exchange) intermolecular binding exists. Although it should always be borne in mind that overlap or electronic exchange interactions between two molecules are possible, we do not believe that these overlap or electronic exchange forces are *essential* for van der Waals bonding so long as the two interacting molecules retain their identity in the combined state. They may, however, *augment, orchestrate or modify* the

overall intermolecular binding. Viewing both the two interacting molecules, as is done in the classical regime, rather excludes some detail. This may be the reason for the concealment of the repulsive part of the intermolecular electrostatic potential energy function. We think therefore that the electrons of one of the molecules actually 'view' the other molecule, at long distances, as a body with a definite charge distribution such as a point dipole or quadrupole, etc. and vice versa. The interaction of the point dipole or quadrupole (molecule) with the electrons of the other molecule (or atom) would then be the van der Waals electrostatic interaction between the two molecules. We believe this to be a more realistic physical picture of van der Waals electrostatic interaction between the two molecules that opens up more electrostatic interaction than the classical model but not up to the level of overlap or electronic exchange (i.e. chemical) interaction. Proceeding this way, we derived^{16,17} complete intermolecular potential energy functions for the electrostatic interaction between two molecules (or a molecule and an atom) that contain a non-overlap (or non-electronic exchange) short range repulsion energy component in addition to the long range attractive part from a unified treatment.

In this paper, we present the result of the application of this electrostatic model to the study of van der Waals electrostatic interaction

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in the H...OH₂, H...NH₃, H...⁺OH₃, H...OH, H...OCO, H...O₂ and H...Cl₂ systems as model for hydrogen bonding.

EXPERIMENTAL

The interaction of a point dipole or quadrupole with the electron of hydrogen atom as a model for hydrogen bonding

If the potential energy of interaction between the electron of hydrogen atom and the point dipole is denoted by U_μ , then we begin by writing the total electronic Hamiltonian for the electron of the hydrogen atom in the presence of the dipole as

$$H = H_0 + U_\mu \dots\dots\dots(1)$$

In the same fashion if U_Q represents the potential energy of interaction between a point quadrupole and the electron of H atom, then, as in (1), we can write the total electronic Hamiltonian for the electron of the H atom in the presence of the quadrupole as

$$H = H_0 + U_Q \dots\dots\dots(2)$$

where H_0 is the total non-relativistic electronic Hamiltonian of the isolated H atom. The solution Ψ to the Schrodinger equation, $H_0\Psi = E_0\Psi$, for the H atom is known so that both U_μ and U_Q could be taken as first order perturbations. Now, the potential energy functions U_μ and U_Q are given by¹⁶⁻¹⁷ equations (3) and (4)

$$U_\mu(X, r, \theta, \phi) = \sum_{k=0}^{\infty} \sum_{m=-k}^{m=+k}$$

$$\frac{\mu A_k^m(\theta_\mu, \phi_\mu) \sum (j) C_k^m(r_j, \theta_j, \phi_j)}{R_\mu^{2k+2}}$$

$$+ \frac{1}{2} \frac{\mu B_k^m(\theta_\mu, \phi_\mu) \sum (j) Q_k^m}{R_\mu^{2k+2}}$$

$$\frac{(r_j, \theta_j, \phi_j)}{R_\mu^{4k+4}} \dots\dots\dots(3)$$

$$U_Q(X', r, \theta, \phi) = \sum_{k=0}^{\infty} \sum_{m=-k}^{m=+k}$$

$$-2 \frac{QD_k^m(\theta_\mu, \phi_\mu) \sum (j) G_k^m}{R_Q^{3k+3}}$$

$$(r_j, \theta_j, \phi_j)$$

$$+3 \frac{QW_k^m(\theta_\mu, \phi_\mu) \sum (j) H_k^m}{R_Q^{5k+5}}$$

$$(r_j, \theta_j, \phi_j) \dots\dots\dots(4)$$

where

$$A_k^m(\theta_\mu, \phi_\mu) = \left[\frac{4\pi}{2k+1} Y_k^{m*}(\theta_\mu, \phi_\mu) \right]^2;$$

$$B_k^m(\theta_\mu, \phi_\mu) = \left[\frac{4\pi}{2k+1} Y_k^{m*}(\theta_\mu, \phi_\mu) \right]^4; \dots\dots\dots(5)$$

$$D_k^m(\theta_Q, \phi_Q) = \left[\frac{4\pi}{2k+1} Y_k^{m*}(\theta_Q, \phi_Q) \right]^3;$$

$$W_k^m(\theta_Q, \phi_Q) = \left[\frac{4\pi}{2k+1} Y_k^{m*}(\theta_Q, \phi_Q) \right]^5 \dots\dots\dots(6)$$

and depend on the dipole and quadrupole coordinates only which can be viewed classically, whereas,

$$C_k^m(\theta_j, \phi_j) = \left[\frac{4\pi}{2k+1} Y_k^m(\theta_j, \phi_j) \right]^2 r_j^{2k};$$

$$Q_k^m(\theta_j, \phi_j) = \left[\frac{4\pi}{2k+1} Y_k^m(\theta_j, \phi_j) \right]^4$$

$$\sin^2 \theta_j r_j^{4k+2} \dots \dots \dots (7)$$

$$G_k^m(\theta_j, \phi_j) = \left[\frac{4\pi}{2k+1} Y_k^m(\theta_j, \phi_j) \right]^3 r_j^{3k};$$

$$H_k^m(\theta_j, \phi_j) = \left[\frac{4\pi}{2k+1} Y_k^m(\theta_j, \phi_j) \right]^5.$$

$$\sin^2 \theta_j r_j^{5k+2} \dots \dots \dots (8)$$

depend on electronic coordinates. X and X' in (3) and (4) denote the coordinates (R_μ, q_μ, f_μ) and (R_Q, θ_Q, ϕ_Q) of the dipole and quadrupole respectively. The R_μ and R_Q are the intermolecular distances between the centre of mass of the H atom and the centre of the charge separation of the point dipole and quadrupole respectively.

The potential energy functions in (3) and (4) are complete and the second terms in both equations are *non-overlap or non-electronic exchange repulsion component* of the perturbation terms U_μ and U_Q . The first order matrix elements of these perturbation terms are to be calculated over the appropriate electronic state of the H atom for various (R_μ, q_μ, f_μ) and (R_Q, θ_Q, ϕ_Q) . When this is done, non-overlap (or non-electronic exchange) equilibrium binding energies and bond lengths would be obtained from the potential energy curves. The potential (3) and (4) have shown that overlap or electronic exchange interactions are not essential for van der Waals bonding after all. It should be noted, however, that the terms

with $k = 0$ in both (3) and (4) already span the totally symmetric representation. To find the appropriate expression for U_μ and U_Q , that remains invariant, the symmetry of the van der Waals molecule must be taken into consideration.

The multipole molecules considered in this work are H_2O , NH_3 , H_3O^+ , OH^- , CO_2 , O_2 and Cl_2 . Thus, we calculated the H...dipole and H...quadrupole interaction energies separately, and then together (for those molecules that possess both permanent-dipole and -quadrupole moments) for the ground electronic state of the H-atom using an STO *1s orbital*. All the calculations were done for $(R_\mu, 0^\circ, 0^\circ)$ and $(R_Q, 0^\circ, 0^\circ)$ only (i.e. the dipole or quadrupole lies along the z-axis). For this case, all terms for which $m = 0$ vanish in the expansions (3) and (4). The calculation soon converges at $k=3$ for the dipole and $k=2$ for the quadrupole.

RESULTS AND DISCUSSION

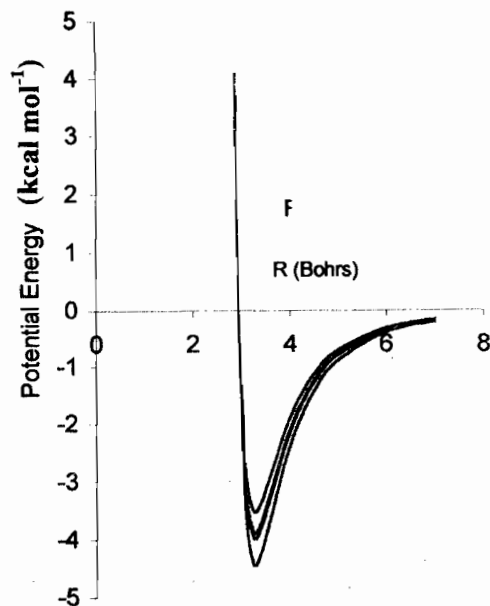


Figure 1. Potential energy curves for the (H.....dipole; dipole = H_2O , NH_3 , H_3O^+ and OH^-) hydrogen bonds. The curves are for $H \dots OH_2$, $H \dots OH^-$, $H \dots ^+OH_3$ and $H \dots NH_3$ respectively in order of decreasing potential well depth.

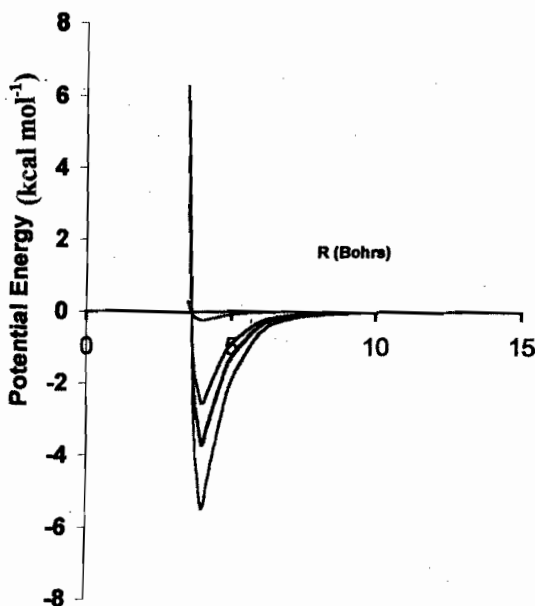


Figure 2. Potential energy curves for the (H.....quadrupole; quadrupole = H₂O, NH₃, CO₂, O₂ and Cl₂) hydrogen bonds. The curves are for H...NH₃, H...Cl₂, H...OH₂, H...OCO and H...O₂ respectively in order of decreasing potential well depth.

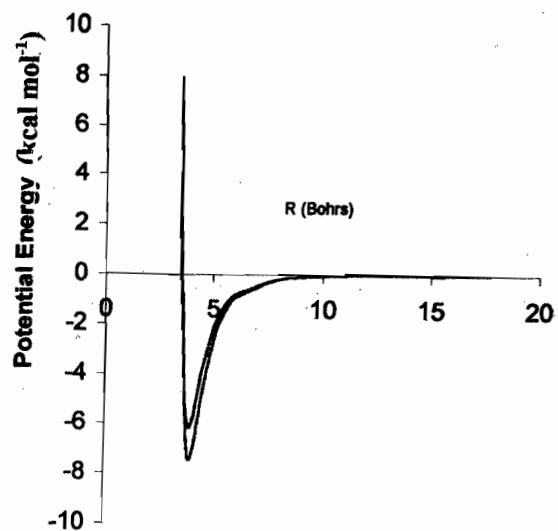


Figure 3. Potential energy curves for the [H.....(dipole + quadrupole); dipole + quadrupole = H₂O, NH₃] hydrogen bonds. The curves are for H...NH₃ and H...OH₂ respectively in order of decreasing potential well depth.

Table 1. Hydrogen bond energy and equilibrium bond length of some van der Waals systems (kcal/mol)

Multipolar molecule	Calculated H- bond energy			Observed energy
	H..Dipole	H..Quadrupole	H..(Dipole + Quadrupole)	
H ₂ O	-4.4610	-3.6553	-6.1886 [2.063Å]	-6.2 ± 1.5
NH ₃	-3.5467	-5.5047	-7.4337 [2.084Å]	-7.66 ^a
H ₃ O ⁺	-3.9095			
OH ⁻	-4.0069			
CO ₂	-	-2.5798		
O ₂	-	-0.2457		
Cl ₂	-	-3.7468		
R(Å)	[1.735Å]	[2.111Å]		[1.7 - 2.2Å]

^a Ref. [19]

Table 2. Hydrogen bond energy and equilibrium bond length of some van der Waals systems (kcal/mol)

Multipolar Molecule	H....Dipole	H....Quadrupole	H....(Dipole + Quadrupole)	Observed
H ₂ O	-4.4610	-3.6553	-6.1886	-6.2 ± 1.5
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H ₃ O ⁺	-3.9095			
OH ⁻	-4.0069			
CO ₂	-	-2.5798		
O ₂	-	-0.2457		
Cl ₂	-	-3.7468		
R(Å)	1.735	2.111	2.063	1.7 to 2.2

The potential energy (P. E.) curves obtained from the calculations are given in Figures 1, 2 and 3 respectively, and the equilibrium binding energies and bond lengths obtained from the P. E. curves are found in Table 1.

The H....dipole model yields good binding energy values, although, the value for H....OH₂ is higher than the experimental H-bond energy of H₂O.... H₂O dimer by about 28%. The equilibrium bond length of the H....dipole system agrees well with the observed value for the OH...O hydrogen bond¹⁸. Since no electronic exchange is allowed between H atom and the molecules, the constancy of bond length is to be expected because the dipole moment of the molecules is just a multiplier in (3); it only determines the magnitude of the binding energy.

The same could be said about the H....quadrupole results except that the H....quadrupole interaction is, surprisingly, not weak for all the molecules except for oxygen. The H.... NH₃ quadrupole binding

energy is higher since the latter is multipole determined. However, the equilibrium bond length comes much closer to the generality of observed hydrogen bond lengths - 1.9Å for OH....N, 2.2Å for NH....N and 2.0Å for NH....O¹⁸.

For molecules that possess both permanent-dipole and -quadrupole moments, the total hydrogen bond interaction is better represented as H....(dipole + quadrupole). This has been calculated for the H.... OH₂ and H....NH₃ systems. Our H-bond energy for H....OH₂ system agrees excellently with the observed H-bond energy of H₂O....H₂O dimer - with less than 0.18% error. The observed H-bond energy for the NH₃ group is not readily available; but the -7.4337 kcal/mol we got agrees very well with *ab initio* ones reported in the literature. For example, Meunier et al.¹⁹, using *STO basis*, obtained -7.66 kcal/mol H-bond energy for the H₃N...H₂O dimer. Also, Kollman and Allen²⁰ reported -7.4 kcal/mol as -H₂N....H₂O H-bond energy. However, we find that the total H....NH₃ bond energy is considerably stronger than all the

others. The NH_3 group appears to be a -1.25 kcal/mol better proton acceptor than H_2O . Also in comparing $\text{H}\dots\text{OH}_2$ bond strength with that of either $\text{H}\dots^+\text{OH}_3$ or $\text{H}\dots\text{OH}^-$, the results indicate $\text{H}\dots\text{OH}_2 > \text{H}\dots\text{OH}^- > \text{H}\dots^+\text{OH}_3$, as the order of proton acceptance. For the case of the other multipoles, the order of H-bond energy is in the order $\text{CO}_2 > \text{Cl}_2 > \text{O}_2$ and only the magnitude of $\text{H}\dots\text{O}_2$ H-bond energy is less than RT_{ROOM} .

As for the $\text{H}\dots(\text{dipole} + \text{quadrupole})$ bond length, the values we got completely agree with the experimental hydrogen bond lengths for H_2O and NH_3 groups. The 2.063\AA and 2.084\AA bond lengths for $\text{H}\dots\text{NH}_3$ and $\text{H}\dots\text{OH}_2$, respectively calculated fall in the 2.0 to 2.2\AA observed range for H_2O and NH_3 groups¹⁸.

One might ask why we have to compare our results with that obtained from the ad hoc or *ab initio* calculations even though they portrayed van der Waals interaction as electronic exchange or chemical interaction. Well, their H-bond energy has 'some credibility' in some cases as far as the number is concerned for the following reason: in the *ab initio* methods, extensive geometry search for the dimers are done until they found a geometry whose H-bond energy agrees with experiment. However, the agreement is achieved with respect to the H-bond energy only, and because this geometry may not necessarily be realistic, the corresponding H-bond length is always in total disagreement with experimental values. Their H-bond length values lie between 2.7 and 3.5\AA which is completely outside the $2.0 - 2.2\text{\AA}$ observed range for H_2O and NH_3 groups¹⁸. Now, the difference between our scheme and the *ab initio* or *valence methods* is that we have achieved agreement in both H-bond energies and bond lengths even for the most difficult H_2O and NH_3 groups by adopting a simple but linear structure without recourse to the invocation of electronic exchange or overlap forces to account for the repulsive part of the potential energy in our model

CONCLUSION

The theory has worked very well for the hydrogen bonded van der Waals system. It has also distinguished, as mirrored in the treatment, the van der Waals bond, represented by the H-bond, from a chemical bond. Lastly, the potential energy functions yielded hydrogen bond energies and bond lengths in agreement with experimental data.

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