A MODEL FOR THE STUDY OF ELECTROSTATIC BINDING BETWEEN A PAIR OF MOLECULES AT LARGE DISTANCES

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ABSTRACT

A model for electrostatic interaction that leads to a stable equilibrium or binding at large distances between a pair of molecules is presented. The approach assumes one of the pair of molecules to be perceived by the other, at long-range, as made up of point-multipoles. An electrostatic potential energy of interaction between the pair of molecules derived from a single theory has both attractive and (shorter-range) repulsive energy terms for each multipole moment of the multipolar molecule. For $(H_2O)_2$ dimer, which has been shown to be primarily stable due to electrostatic interaction between the water monomers [Acc. Chem. Res., 10, 294, (1977)], the model predicts a binding energy of -6.1882 kcal mol^{-1} and 2.727Å equilibrium O·····O distance in good agreement with the experimental values.

INTRODUCTION

The electrostatic energy of interaction between the undistorted charge distributions of molecules *a* and *b* is given[1-4] by

$$E_{es} = \sum_i \sum_j \frac{q_{ai} q_{bj}}{\left| R_{ab} - r_{ai} + r_{bj} \right|} \qquad \text{..........(1)}$$

where R_{ab} points from the centre of the charge distribution of molecule *a* to the centre of charge distribution of molecule *b* and the r_{ai} and r_{bj} go from thr centres to arbitrary points of the respective charge distributions i and j. in terms of the multipole moments of the two charge distributions, E_{es} is expanded either in Taylor series

$$E_{es} = \iint \sum_i \sum_j q_{ai} q_{bj} \exp[-(r_{ai} - r_{bj}).\nabla]\left(\frac{1}{R_{ab}} \right) dr_{ai} dr_{bj} \qquad \text{................................(2)}$$

where ∇ operates only on R_{ab}, or in Legendre functions

$$E_{es} = \sum_{n_a=0}^{\infty} \sum_{n_b=0}^{\infty} \sum_{m=-n<}^{m=+n<} \sum_i \sum_j \frac{(-1)^{n_b+|m|}(n_a + n_b)!}{(n_a + |m|)!(n_b + |m|)!} \frac{r_{ai}^{n_a} r_{bj}^{n_b}}{R_{ab}^{n_a+n_b+1}} q_{ai} q_{bj} P_{n_a}^{m}(\cos\theta_a)$$

$$\times P_{n_b}^{m}(\cos\theta_{ba}) e^{im(\phi_{bj} - \phi_{ai})}$$

$$= \sum_{n_a=0}^{\infty} \sum_{n_b=0}^{\infty} \sum_{m=-n<}^{m=+n<} \frac{(-1)^{n_b+|m|}(n_a + n_b)!}{(n_a + |m|)!(n_b + |m|)!} \frac{Q_{n_a}^{m*} Q_{n_b}^{m}}{R_{ab}^{n_a+n_b+1}} \qquad \text{........................(3)}$$

which leads to the so-called multipole expansion[1-20], where

$$Q_{n_a}^{m} = \sum_i q_{ai} r_{ai}^{n_a} P_{n_a}^{m}(\cos\theta_{ai}) e^{im\phi_{ai}} \quad \textit{and}$$

$$Q_{n_b}^{m} = \sum_i q_{bj} r_{bj}^{n_a} P_{n_b}^{m}(\cos\theta_{bj}) e^{im\phi_{bj}} \qquad \text{.....(4)}$$

respectively. In general, (3) is evaluated by using experimental values of the permanent multipole

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moments of molecules a and b for various orientations and R_{ab}[4,10-12,20] or by calculating the permanent multipole moments quantum mechanically from first principles[6-9,13-19]. In calculating the permanent multipole moments, Mullken's population analysis and its extensions, which includes the *distributed multipole analysis* (DMA)[18], *multipole-fitted point charge* (MFPC) *model*[16,17] and the *multicentre multipole expansion* (MME)[2,13,14] etc., are used. Alternatively, E_{es} is calculated quantum mechanically[21] from

$$E_{es} = < \Phi_a^0 \Phi_b^0 | H_{ab} | \Phi_a^0 \Phi_b^0 > - \sum_{a,b} < \Phi_l^0 | H_l | \Phi_l^0 > \quad ...(5)$$

where H_{ab} is the Hamiltonian of the $a.b$ complex that is expressed as a sum of single-molecule (H_l) and bi-molecule (H_{ll}) contributions. Φ_a^0 and Φ_b^0 are the zeroth order wavefunctions of molecules a and b.

However, it has been amply demonstrated that the multipole pair electrostatic energy (3) or (5) is either attractive or repulsive and *cannot give a potential minimum* or electrostatic binding[3,10,13,14,21-33]. As a result, it has always been found necessary to make further assumptions for some steric hindrance (i.e. repulsion) between molecules a and b at short distances so as to maintain their separation and integrity[21-33]. A total energy of the form

$$W = E_{es} + E_{rep} \quad ....(6)$$

was assumed[24-26], where E_{rep} is the invoked short-range repulsion term and is treated separately and differently, purely empirically[24-28,34-40] and quantum mechanically[21,23,25,29,30], from E_{es} in the literature. Quantum theoretically, E_{rep} is said to arise from *overlap or electronic exchange repulsion* as a result of inter-penetration of the charge clouds of molecules a and b at short-range[21]

$$E_{rep} = < a''\Phi_a^0 \Phi_b^0 | H_{ab} | a''\Phi_a^0 \Phi_b^0 > - \sum_{a,b} < \Phi_l^0 | H_l | \Phi_l^0 > \quad ...(7)$$

where a'' is an antisymmetrizer. Equation (6) has been the basis of numerous calculations of the interaction energy between pairs of undistorted molecules[1-40].

A question of great importance is whether the electronic interaction between a pair of molecules could actually lead to a stable equilibrium, that is intermolecular binding without the invocation of the overlap or electronic exchange repulsion energy term (7). However, we have previously reported a model for electrostatic interaction that leads to a stable equilibrium or binding at large distances between two molecules a and b[41]. The model assumes the electrons of molecule a to perceive b as point-dipole at long-range. Although the electrostatic potential energy of interaction derived leads to a stable equilibrium between the two molecules it contains dipole and odd higher multipole terms only. In the present work, the interaction is effectively generalized by assuming the electrons of a to perceive b as made of point-dipole and point-quadrupole. As we shall show in the following sections, the electrostatic potential energy of interaction derived also leads to a stable equilibrium at large distances and *contains all multipole terms.*

A MODEL FOR ELECTROSTATIC INTERACTION BETWEEN A PAIR OF MOLECULES AT LONG-RANGE DISTANCES

For identical pair of molecules a and b, the electrons of a may be taken to perceive b as consisting of point-multipoles, when molecule a is very far away from molecule b and vice versa. Then the coulombic or electrostatic energy of interaction between the electrons of a and the point-multipoles of b is taken as the pair electrostatic energy of interaction. Also, a body fixed coordinate is chosen for the derivation of the interaction potential energy between the electrons of molecule a and the point-dipole and -quadrupole of molecule b as shown in Figs. 1 and 2. To avoid the overlap of the charge distributions of the two molecules, the length of the ideal multiples and the size of molecule a are taken to be very much smaller than the intermolecular distance in the analysis which implies that

$$(i) \quad r_j << TP_j \quad ....(8a)$$

$$(ii) \quad l << TP_j \quad ....(8b)$$

in both Figs. 1 and 2.

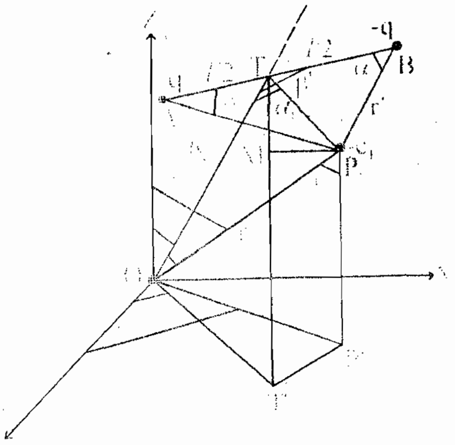

Fig. 1. A model for electrostatic interaction between the electrons of molecule *a* and a point-dipole of molecule *b*.

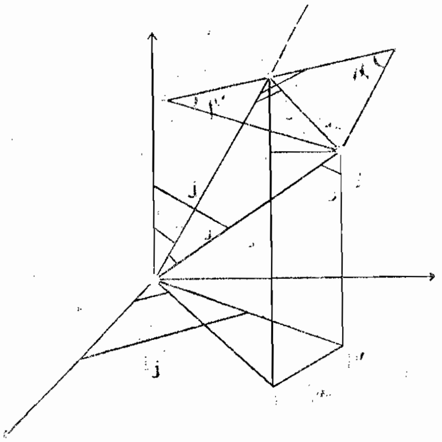

Fig. 2. A model for electrostatic interaction between the electrons of molecule *a* and a point-quadrupole of molecule *b*.

A. The dipolar interaction potential energy

The basic expression for the interaction potential energy U_{1j} between a point-dipole, μ, centred on molecule *b* and an electron $-e_j$ of molecule *a* may be seen from Fig. 1 to be given by

$$U_{1j} = e_j q\left(\frac{1}{r'} - \frac{1}{AP_j}\right) \quad \text{....................(9)}$$

From the geometry of Fig. 1 equation (9) may be shown to become

$$U_{1j} = \frac{e_j q}{TP_j \sin(\beta - a_j)}(\sin\alpha - \sin\beta') \text{.......(10)}$$

where it can be shown that

$$\sin\alpha = \frac{[TP_j^2 \sin^2(\beta - a_j)]^{1/2}}{[TP_j \sin^2(\beta - a_j) + (l/2 - TP_j\cos(\beta - a_j))^2]^{1/2}} \quad \text{..................................(11)}$$

$$\sin\beta' = \frac{[TP_j^2 \sin^2(\beta - a_j)]^{1/2}}{[TP_j \sin^2(\beta - a_j) + (l/2 + TP_j\cos(\beta - a_j))^2]^{1/2}} \quad \text{..................................(12)}$$

Inserting equations (11) and (12) in (10) we have

$$U_{1j} = \frac{\pm e_j q}{TP_j}\left\{\frac{1}{(1 + K_1)^{1/2}} - \frac{1}{(1 + K_2)^{1/2}}\right\} \text{..(13)}$$

where we put

$$K_1 = \frac{l^2}{4TP_j^2} - \frac{l\cos(\beta - a_j)}{TP_j} \quad \textit{and}$$

$$K_2 = \frac{l^2}{4TP_j^2} + \frac{l\cos(\beta - a_j)}{TP_j} \quad \text{.......(14)}$$

From equation (8b) and (14), it follows that $K_1, K_2 << 1$ so that (13) can be expanded. By choosing the -ve sign in (13) and summing over all the electrons of molecule *a*, the result of the expansion is given by

$$U_1 = \sum_j U_{1j}$$

$$= -\mu \sum_j \frac{e_j}{TP_j^2}\cos(\beta - a_j)$$

+ terms for odd higher multipoles ....(15)

where μ is the dipole moment of molecule *b* defined as

$$\mu = ql \quad \text{......................................(16)}$$

B. The quadrupolar interaction potential energy

Similarly, the basic expression for the interaction potential energy U_{2j} between an electron $-e_j$ of molecule *a* and a poit-quadrupole centred on molecule *b* may be seen from Fig. 2 to be given by

$$U_{2j} = e_j q\left(\frac{1}{r'} + \frac{1}{AP}\right) - \frac{2e_j q}{TP_j}$$

$$= \frac{e_j q}{TP_j \sin(\beta - a_j)}(\sin a + \sin\beta') - \frac{2e_j q}{TP_j} \quad .....(17)$$

Following the procedure for eliminating $\sin\alpha$ and $\sin\beta'$ from the steps of (11) to (13), using Fig. 2, we obtain

$$U_{2j} = \frac{\pm e_j q}{TP_j}\left\{\frac{1}{(1+K_3)^{1/2}} + \frac{1}{(1+K_4)^{1/2}}\right\} - \frac{2e_j q}{TP_j} \quad ...(18)$$

where we put

$$K_3 = \frac{l^2}{TP_j^2} - \frac{l\cos(\beta - a_j)}{TP_j} \quad and$$

$$K_4 = \frac{l^2}{TP_j^2} + \frac{2l\cos(\beta - a_j)}{TP_j} \quad ....(19)$$

From (8b) and (19) also, $K_3, K_4 << 1$ so that (18) can be expanded. Again by choosing the -ve sign in (18) and summing over all the electrons of molecule *a*, the result of the expansion is also given by

$$U_2 = \sum_j U_{2j}$$

$$= -C\sum_j \frac{4e_j}{TP_j} - Q\sum_j \frac{e_j}{TP_j^3}[3\cos^2(\beta - a_j) - 1]$$

+ terms for even higher multipoles ...(20)

where *C* and *Q* are the monopole (i.e. net charge) and quadrupole moments centred on molecule *b* defined as

$$C = q \quad and \quad Q = ql^2 \quad ....(21)$$

C. The total pair electrostatic interaction potential energy

The total pair electrostatic potential energy, *U*, of interaction is a sum over the individual interaction energies between the electrons of molecule *a* and the monopole, dipole, quadrupole, ..., Nth multipole moments centred on molecule *b*. Luckily, this is given by the sum of equations (15) and (20), viz

$$U = U_1 + U_2$$

$$= -C\sum_j \frac{4e_j}{TP_j} - \mu\sum_j \frac{e_j}{TP_j^2}\cos(\beta - a_j)$$

$$- Q\sum_j \frac{e_j}{TP_j^3}[\cos^2(\beta - a_j) - 1]$$

+ terms for higher multipoles ....(22)

where *C*, μ, *Q*, etc. are permanent multipole moments centred on molecule *b*.

It is no doubt better to have the angular dependence on the right hand side of (22) in terms of β only, the orientation of the point-multipoles with respect to the intermolecular axis, R_{ab}, in Figs. 1 and 2 (which can be fixed classically). This allows the elimination of a_j, which is the inclination of the vectorial distance between electron j of molecule *a* and the centre of the charge distribution of molecule *b* with respect to the intermolecular axis (which is difficult to handle). Now, from ΔTOP_j of both Figs. 1 and 2

$$\sin a_j = \frac{r_j \sin\gamma_j}{TP_j} \quad ....(23)$$

so that

$$\cos(\beta - a_j) = \cos\beta\left(1 - \frac{r_j^2 \sin^2\gamma_j}{TP_j^2}\right)^{1/2} + \frac{r_j \sin\gamma_j}{TP_j}\sin\beta$$

..............................(24)

By equation (24), the angle a_j has been eliminated but the right hand side of (24) for $cos(\beta - a_j)$ in (22) leads to very complicated expressions for the higher multipole terms. However, the simplest cases, as can be seen from Figs. 1 and 2, are those for which the point-dipole and -quadrupole [illegible] along the intermolecular axis, R_{ab}, [illegible] bonded systems and the binding of [illegible] by metal ions fall into this category, for instance. For such a special case (i.e. $\beta = 0^o$), the potential energy U in (22) reduces to

$$U = -C\sum_j \frac{4e_j}{TP_j} - \mu\sum_j \frac{e_j}{TP_j^2}\left(1 - \frac{r_j^2 \sin^2\gamma_j}{TP_j^2}\right)^{1/2}$$

$$-Q\sum_j \frac{e_j}{TP_j^3}\left(2 - \frac{3r_j^2 \sin^2\gamma_j}{TP_j^2}\right)$$

+ terms for higher multipoles ....(25)

Employing the large intermolecular distance approximation of equation (8*a*) allows us to expand $\left(1 - r_j^2 \sin^2\gamma_j / TP_j^2\right)$ to obtain an infinite series but which converges immediately since, for large distances, $r_j << TP_j$. Hence from (8*a*), all terms in $\left(r_j \sin\gamma_j / TP_j\right)$ higher than quadratic may be neglected. The Expression for U resulting from this is thus

$$U = -C\sum_j \frac{4e_j}{TP_j} - \mu\sum_j \left(\frac{e_j}{TP_j^2} - \frac{1}{2}\frac{e_j r_j^2 \sin^2\gamma_j}{TP_j^4}\right)$$

$$-Q\sum_j \left(\frac{2e_j}{TP_j^3} - \frac{3e_j r_j^2 \sin^2\gamma_j}{TP_j^5}\right)$$

+ terms for higher multipoles ....(26)

Except for the monopole, *each multipole has two terms*: the first, as can be seen from (26), is attractive while the second is repulsive (of shorter-range than the attractive term) so that *each multipole term leads to a stable equilibrium or binding*. Neutral molecules, however, have zero monopole, i.e. no net charges, hence the monopole term vanishes for them. Lastly, we have seen that the elimination of the angle a_j in (22) leads to the extraction of attractive and repulsive components for each multipole term for neutral molecules.

Up till now, we have not arrived at the final form for the electrostatic potential energy U because the TP_j^{-n} factors in equation (26) above may be expanded in terms of Gegenbauer polynomials. From both Figs. 1 and 2, we see that

$$TP_j^{-1} = \left(r_j^2 + R_{ab}^2 - 2r_j R_{ab}\cos\gamma_j\right)^{-1/2};$$

$$TP_j^{-n} = \left(r_j^2 + R_{ab}^2 - 2r_j R_{ab}\cos\gamma_j\right)^{-n/2} \quad ..(27)$$

The expansion of TP_j^{-n} is written as

$$TP_j^{-n} = \frac{1}{R_{ab}^n}\sum_{k=0}^{\infty}\left(\frac{r_j}{R_{ab}}\right)^k C_k^{(n/2)}(\cos\gamma_j) \quad ...(28)$$

where $cos\gamma_j$ can be shown to be given by

$$\cos\gamma_j = \cos\theta_N \cos\theta_j + \sin\theta_N \sin\theta_j \cos(\phi_j - \phi_N)$$

....................................(29)

where also the subscript N stands for μ or Q as can be seen from the Figs. 1 and 2.

Putting the values of the TP_j^{-n} from equation (28) in (26) U becomes

$$U = -C\sum_j \sum_{k=0}^{\infty} \frac{4e_j r_j^k C_k^{(1/2)}(\cos\gamma_j)}{R_{ab}^{k+1}}$$

$$-\mu\sum_j \sum_{k=0}^{\infty}\left(\frac{e_j r_j^k C_k^{(1)}(\cos\gamma_j)}{R_{ab}^{k+2}} - \frac{1}{2}\frac{e_j r_j^{k+2}\sin^2\gamma_j C_k^{(2)}(\cos\gamma_j)}{R_{ab}^{k+4}}\right)$$

$$-Q\sum_j \sum_{k=0}^{\infty}\left(\frac{2e_j r_j^k C_k^{(3/2)}(\cos\gamma_j)}{R_{ab}^{k+3}} - \frac{3e_j r_j^{k+2}\sin^2\gamma_j C_k^{(5/2)}(\cos\gamma_j)}{R_{ab}^{k+5}}\right)$$

+ terms for higher multipoles ....(30)

where the $C_k^{(s)}$ polynomials are expressed in terms of spherical harmonics as

$$C_k^{(s)}(\cos\gamma_j) = \sum_{t=0}^{k/2}\sum_{m=-k+2t}^{m=+k-2t}\frac{s(s-1/2)(k-t)(1+2k-t)}{(3/2)t!}$$

$$\times \frac{4\pi}{2(k-2t)+1} Y_{k-2t}^{m*}(\theta_N, \phi_N) Y_{k-2t}^{m}(\theta_j, \phi_j) \quad ...(31)$$

Thus from (31), the total electrostatic potential energy, U of (30), is a function of both $(R_{ab}, \theta_N, \phi_N)$, point-dipole and quadrupole coordinates - which can be fixed classically, and

(r_j, θ_j, ϕ_j), the coordinates of the electrons of molecule a - which must be dealt with quantum mechanically. In other words the potential energy, U, must be averaged over the ground electronic state of molecule a, Φ_a^0 say, using first order perturbation theory in order to obtain the electrostatic potential energy surface, viz

$$\Delta U = < \Phi_a^0 | U | \Phi_a^0 >$$

$$= \Delta U_{attrac.,monop.} + \sum_{N=\mu}^{all\, multipole} \left[\Delta U_{attrac,N} + \Delta U_{repul.N} \right] \quad \ldots\ldots\ldots\ldots(32)$$

where $\Delta U_{attrac.N}$ *and* $\Delta U_{repul,N}$ are the quantum mechanically averaged attractive and repulsive interaction energy components of the dipole, quadrupole, etc. terms in (30) and the $(R_{ab}, \theta_\mu, \phi_\mu)$ and $(R_{ab}, \theta_Q, \phi_Q)$ coordinates are to be fixed classically. Also, $\Delta U_{attrac,monop}$ is the quantum mechanically averaged monopole (attractive) term in (30) which vanishes for neutral molecules.

D. The calculation of electrostatic binding energy of water dimer - $(H_2O)_2$

The hydrogen bond was extensively studied by Morokuma and his colleagues[42-44] using the energy decomposition

$$E = E_{es} + E_{rep} + E_{PL} + E_{EX-PL} \quad \ldots\ldots(33)$$

and charge distribution analysis. On the right hand side of (33) are electrostatic energy (E_{es}), overlap or electronic-exchange repulsive energy (E_{rep}), polarization and exchange-polarization energy (E_{PL} and E_{EX-PL}, respectively) contributions to the total energy E of the hydrogen bond. The hydrogen bonded bimolecular complexes they considered include $(H_2O)_2$, $(NH_3)_2$ etc. and the results of their study showed that, at equilibrium geometry, the repulsion energy term E_{rep} is nearly compensated by the E_{PL} and E_{EX-PL} attractive terms. Thus Morokuma described the hydrogen bonds in these dimers as strongly electrostatic in nature and appears to justify the assumption that the stability of hydrogen bonded complexes is essentially governed by electrostatic interaction.

As a test of our model, the electrostatic binding energy of the water dimer $(H_2O)_2$ is calculated. A linear acceptor-donor $(H_2O)_2$ geometry (Fig. 3) was assumed. The donor water molecule is perceived by the acceptor water molecule as made up of point-multipoles - specifically dipole and quadrupole since these are experimentally known for this molecule. The intermolecular axis was taken to coincide with the z-axis and the perturbation matrix element (32) was computed over a (2,1/1) minimal basis[45] of the acceptor water molecule that yields -75.655a.u. H_2O binding energy at 105° H-O-H angle. A potential energy curve with a single minimum was obtained from the calculations.

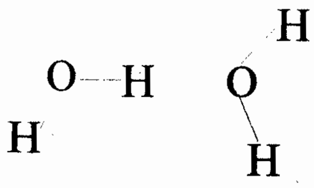

Fig. 3. A linear acceptor-donor geometry for the $(H_2O)_2$ dimer: the z-axis is chosen to coincide with the O······O direction.

RESULTS AND DISCUSSIONS

The calculated electrostatic binding energy and the O······O distance, together with some experimental and theoretical results of other authors for this dimer, are presented in Table 1. An

Table 1. Summary of $(H_2O)_2$ results

	This model	Experimental	Others
Binding energy (kcal mol^{-1})	-6.1886	-6.2±1.5[46]	-3.71[49] -5.27[50] -4.73[51] -4.84[52] -3.67[53] -2.0[54]
Equilibrium $R_{O \cdots\cdots O}$ distance (Å)	2.727	2.97[47,48]	3.0[50,52] 3.1[54]

electrostatic binding energy of -6.1886 kcal mol^{-1} and 2.727Å O······O equilibrium distance were obtained. The electrostatic energy, according to the study of Morokuma and his colleagues[42-44], is the net hydrogen bond energy and, therefore, the observed binding energy of the $(H_2O)_2$ dimer. The experimental binding energy and O······O distance of water dimer are -6.2±1.5 kcal/mol[46] and 2.97Å[47,48] respectively. The corresponding values obtained from our model for these quantities agree very well with the experimental values. Several quantum theoretical calculations exist on the binding energy and O······O distance of water dimer. The most widely employed quantum mechanical method is the *ab initio* SCF MO approach and these quantities are either calculated by the *supermolecule* or Morokuma's energy decomposition schemes. In spite of its sophistication and the enormous computational effort involved in the calculations, the *ab initio* SCF MO method predicts hydrogen bond energy in the range of 2- to -5 kcal/mol[49-54] for the $(H_2O)_2$ dimer. These values are worse than the one obtained by our simple electrostatic model. The O······O distance predicted by the *ab initio* SCF MO are also worse, these being in the range of 3 - 3.1Å for some calculations[50,52,54]. The consistency of this electrostatic model with experiment supports its validity and the work has shown that electrostatic interaction between a pair of molecules actually *leads to a stable equilibrium or binding* without contribution from overlap or electronic-exchange interactions which was previously thought to be necessary for intermolecular binding.

CONCLUSION

A model for electrostatic interaction between a pair of molecules that leads to a stable equilibrium or binding at large intermolecular distances without overlap or electronic-exchange repulsion invocation has been presented in this article. The model has worked very well for the water dimer and showed that the binding in the $(H_2O)_2$ complex is due primarily to attractive and repulsive physical forces emanating from electrostatic interaction but not chemical forces resulting from the overlap of their wavefunctions.

ACKNOWLEDGEMENT

This work was financially supported by Ahmadu Bello University, Zaria, Nigeria.

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accepted 02/10/2000
received 14/09/2000