The Nature of the Hydrogen-Bond. I. The Delocalization Energy in the Hydrogen-Bond as Calculated by the Atomic-orbital Method

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Until quite recently it has been assumed that the energy of the hydrogen-bond is mainly electrostatic. Such an assumption seems to be very valid in regard to the experimental evidence that this bond is formed only between molecules which contain polar groups. Also the energies of the electrostatic interaction between hydrogen-bonded molecules calculated by some authors[1,2] agreed fairly well with experimental values of the bond energies and were taken as evidences for the above mentioned assumption.

We face to some difficulties, however, if we try to explain the strengths of hydrogen-bonds of various molecules only from the electrostatic point of view. Let us consider, for example, acetone and ethyl ether. Both act as proton-acceptors in the hydrogen-bond and according to the electrostatic theory we are forced to conclude that the proton-accepting strength of the former is greater than that of the latter since the carbonyl group of the former is much more polar than the C-O group of the latter. But it is known experimentally that the accepting strength of acetone is nearly equal to, or rather less than that of ethyl ether.[3] It is also known that nitriles are moderate proton-acceptors in spite of the strong polarity of their C≡N group.[3]

These phenomena strongly suggest that other sources of the interaction energy exist in the hydrogen-bond. Quite naturally what we can obtain experimentally as the energy of a hydrogen-bond may be, from a theoretical point of view, interpreted as the algebraic sum of the following terms: (1) Electrostatic energy, (2) Dispersion force, (3) Exchange repulsion, (4) Delocalization energy due to the electron-transfer from a proton-acceptor to a proton-donor. Hence, even if the calculated value of the electrostatic energy of a hydrogen-bond agrees with the experimental dissociation energy, we cannot say that the former is the dominant part of the latter. It only shows that the algebraic sum of (2), (3) and (4) is practically zero. Therefore, a complete clarification of the energy of the hydrogen-bond would not be attained until we were able to calculate or estimate these terms precisely.

Unfortunately it is extremely difficult to calculate non-empirically the energy of a hydrogen-bond as the sum of the above mentioned terms. For the energy of a hydrogen-bond is of the order of several kilocalories, that is 0.01 atomic unit, and, to calculate it exactly, we should calculate numerous energy integrals which appear in the course of calculation within the error of, at most, 0.001 atomic unit. Practically, it is almost impossible to carry out such accurate calculations. Nevertheless, it seems important for the discussion of the nature of the hydrogen-bond to calculate, even approximately, each of the above-mentioned terms. The author's aim in this paper is to clarify the nature and to estimate the magnitude of the fourth term, that is, the delocalization energy.

The importance of this term has been quite recently recognized. In 1951, C.A. Coulson[4]

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[1] N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

[2] J. A. Pople, *Proc. Roy. Soc.*, **A205**, 11 (1951).

[3] M. Tsuboi, *Kagaku-no-Ryôiki* (*J. Japanese Chem.*), **7**, 611 (1953).

[4] C. A. Coulson, "Valence", Oxford Univ. Press (1952). p. 305

described a study of the magnitude of the contribution of various resonance hybrids in the hydrogen-bonded water molecules, and stated that the contribution of the hybrids which is related to the charge delocalization is considerably great. Nukasawa, Tanaka and Nagakura[5] have also emphasized the importance of this term and have proposed that it may conveniently be estimated by use of a second order perturbation theory in terms of molecular orbitals and with some empirical values of the ionization potentials and the excitation energies. Though it seems that their method is very convenient and significant for the qualitative discussion of the problem, it may be also important to carry out an exact non-empirical calculation and to decide whether their qualitative conclusion is correct or not. In this paper the results of the calculations of the hydrogen-bonded water molecules by the atomic orbital method are given.

The Basis of the Calculation

The structure of the two hydrogen-bonded water molecules has been assumed to be that shown in Fig. 1; namely, the two water molecules lie in a common plane and the hydrogen atom of the proton-donating molecule is situated on the straight line which connects the two oxygen atoms and which, at the same time, coincides with the symmetry axis of the proton-accepting molecule. The individual atoms constituting these molecules have been designated in the way shown in this figure. The O-H and O-O' distances have been taken to be 0.96 Å and 2.70 Å, respectively.

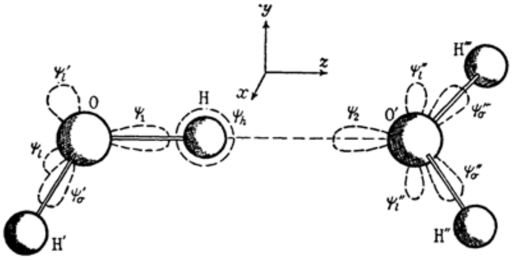

Fig. 1. The assumed structure of the hydrogen-bonded water molecules.

In the present calculation, it is assumed, as is usual, that each of the oxygen atoms has four s, p-hybridized AO's, two of which are directed to the two hydrogen atoms and form electron-pair bonds with the 1s-AO's of the hydrogen atoms, respectively, while each of the remaining two AO's directed toward the opposite side to the O-H bonds, is occupied by two spin-antiparallel electrons and has no influence upon the O-H bonds.

The coefficients of hybridization of $2s$ and $2p$ AO's in these AO's have a strong influence on the electronegativity of oxygen atoms, and therefore on the energy of the hydrogen-bond. The best way is, of course, to make the variation treatment with inclusion of these coefficients. But, since the hydrogen-bond is a week perturbation, one may expect a good result by use of orbitals with constant hybridizations, if the coefficients of the hybridization are properly chosen. The result of the equivalent molecular orbitals obtained by J.A.Pople[6] has shown that the two bonding AO's and the two lone-pair AO's of the oxygen atom in a water molecule can be described by orbitals nearly tetrahedral. Relying upon this result, tetrahedral orbitals have been adopted for the present work. In this case, however, the hydrogen atom of the proton donor finds itself in the middle of the directions of the two lone-pair AO's of the proton acceptor in our assumed configuration of the two water molecules. As the inclusion of the two lone-pair AO's in the calculation complicates the problem, they have been transformed into a $2p_y$ AO and a diagonally hybridized AO (ψ_2) directed to the H atom. Then, only the latter is to be included in the calculation since the $2p_y$ AO is owing to its anti-symmetric character, unable to interact with the 1s AO of the hydrogen atom. Consequently, the valence AO's of the oxygen atoms we assumed here are as shown in Fig. 1, and their explicit forms are given by the following formulas:[7]

$$\begin{aligned}
\psi_1 &= 1/2(s+\sqrt{3}\,z) \\
\psi_\sigma' &= s/2+\sqrt{2}/3x-z/2\sqrt{3} \\
\psi_l &= -s/2+x/\sqrt{6}+z/\sqrt{12}=y/\sqrt{2} \\
\psi_l' &= -s/2+x/\sqrt{6}+z/\sqrt{12}-y\sqrt{2}
\end{aligned}
\qquad
\begin{aligned}
\psi_2 &= (1/\sqrt{2})(s'-z') \\
\psi_\sigma'' &= (1/2)(s'+\sqrt{2}x'+z') \\
\psi_\sigma''' &= (1/2)(s'-\sqrt{2}x'+z') \\
\psi_l'' &= y.
\end{aligned}
\qquad (1)$$

where s, x, y, and z denote the $2s$, $2p_x$, $2p_y$, and $2p_z$, AO's of O, and s', x', y', and z', denote those of O', respectively.

Since the complete treatment of the problem is extremely tedious, and since the aim of the author is not to carry out a precise calculation for the particular case of water, but to discuss the magnitude and the nature of the delocalization energy for the hydrogen-bond in general, the problem was reduced to the variation treatment of the energy of four electrous over the three atomic orbitals, ψ_1, ψ_2 and ψ_h, in the potential field of the nuclea and of the remaining electrons which are distributed over the inner-shells and lone-pairs of oxygen atoms and other O-H bond.

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[5] K. Nukasawa, J. Tanaka and S. Nagakura, *J. Phys. Soc. Japan*, **8**, 792 (1953).

[6] J. A. Pople, *Proc. Roy. Soc.*, **A202**, 323 (1950).

[7] S. Maeda, *Busseiron-Kenkyu*, **70**, 101 (1954). In this paper, S. Maeda reports his results on the SCF LCAO MO calculation of the water molecule. By the transformation of his SCF MO, he obtained as the equivalent AO'S of the oxygen atom approximately tetrahedral ones. It seems that his result also supports the validity of employing the tetrahedral AO's in the present calculation.

orbitals. Such a treatment will give a fairly good result if the assumed distribution of these electrons agrees with the true one for the ground state of the system. According to Pople's result[5], the coefficients of the valence AO's of oxygen and hydrogen in the localized MO of the O-H bond of a water molecule are nearly the same. Hence, it is not so dangerous to replace the potentials of the bonding electrons for the OH′, OH″, and OH‴ bonds (See Fig. 1) by those of the six electrons which occupy, one by one, the valence AO's of the oxygen atoms, ψ_{σ}', ψ_{σ}'', ψ_{σ}''', and the 1s AO's of the three hydrogen atoms. Furthermore, the potentials induced by these hydrogen 1s-electrons may be assumed to cansel those of the atomic nuclea of hydrogen, in view of the large distances between these hydrogen atoms and the centres of the orbitals, ψ_1, ψ_2 and ψ_h. Thus, in the present calculation, we assume a core potential arising from the following nuclea charges and electronic clouds.

$$\begin{array}{ll} \text{for O,} & +8e,\ (\psi_{1sO})^2,\ (\psi_{\sigma}')^1,\ (\psi_{l})^2,\ (\psi_{l}')^2, \\ \text{for O}', & +8e,\ (\psi_{1sO'})^2,\ (\psi_{\sigma}'')^1,\ (\psi_{\sigma}''')^1,\ (\psi_{2p\pi O'})^2 \\ \text{for H,} & +e. \end{array} \qquad (2)$$

The Method of the Calculation

Based on these considerations, five resonance hybrids shown in the following formulas are assumed.

$$\begin{array}{llll} \text{(A)} & \mathrm{O{-}H\ldots\ldots O} & \text{(D)} & \mathrm{O^-\ \ H{-\!-}O^+} \\ \text{(B)} & \mathrm{O^-\ H^+\ldots.O} & \text{(E)} & \underbrace{\mathrm{O\quad H^-\quad O^+}} \\ \text{(C)} & \mathrm{O^+\ H^-\ldots.O} & & \end{array} \qquad (3)$$

Eigenfunctions for these can be written as follows:

$$\begin{array}{ll} \Psi_A=N_A(\phi_1-\phi_2) & \Psi_D=N_D(\phi_4-\phi_5) \\ \Psi_B=N_B\,\phi_3 & \Psi_E=N_E(\phi_7-\phi_8), \\ \Psi_C=N_C\,\phi_6 & \end{array} \qquad (4)$$

in which N_A, N_B, etc., are the normalizing factors and the ϕ's are the four-electron determinantal wave functions:

$$\begin{array}{ll} \phi_1=(1\alpha^1\cdot h\beta^2\cdot 2\alpha^3\cdot 2\beta^4) & \phi_5=(1\alpha^1\cdot 1\beta^2\cdot h\beta^3\cdot 2\alpha^4) \\ \phi_2=(1\beta^1\cdot h\alpha^2\cdot 2\alpha^3\cdot 2\beta^4) & \phi_6=(h\alpha^1\cdot h\beta^2\cdot 2\alpha^3\cdot 2\beta^4) \\ \phi_3=(1\alpha^1\cdot 1\beta^2\cdot 2\alpha^3\cdot 2\beta^4) & \phi_7=(1\alpha^1\cdot h\beta^2\cdot h\alpha^3\cdot 2\beta^4) \\ \phi_4=(1\alpha^1\cdot 1\beta^2\cdot h\alpha^3\cdot 2\beta^4) & \phi_8=(1\beta^1\cdot h\beta^2\cdot h\alpha^3\cdot 2\alpha^4), \end{array} \qquad (5)$$

where, for example,

$$(1\alpha^1\cdot h\beta^2\cdot 2\alpha^3\cdot 2\beta^4)=\begin{vmatrix} (1\alpha)^1 & (h\beta)^1 & (2\alpha)^1 & (2\beta)^1 \\ (1\alpha)^2 & (h\beta)^2 & (2\alpha)^2 & (2\beta)^2 \\ (1\alpha)^3 & (h\beta)^3 & (2\alpha)^3 & (2\beta)^3 \\ (1\alpha)^4 & (h\beta)^4 & (2\alpha)^4 & (2\beta)^4 \end{vmatrix},$$

and $1=\psi_1$, $2=\psi_2$, $h=\psi_h$, α, and β are the two spin functions.

By use of these functions, the matrix elements H_{AA}, H_{BB}, etc. were calculated and the lowest root of the secular determinant,

$$|H-S.E|=0$$

was determined. This gives the energy of the O-H...O system in the ground state.

The Hamiltonian is given by the kinetic energy operator plus the three bare-nuclea field potentials and potentials caused by the electrons whose configuration is shown in (2). For ψ_1 and ψ_h, however, the core potential of O′ was set equal to

$$(\text{potential of the neutral oxygen atom})-2\int\psi_2^*(\mu)(e^2/r_{\nu\mu})\psi_2(\mu)d\tau_{\mu},$$

and the former was ignored. The values of integrals were taken, if possible, from Kotani, Amemiya and Simose's table[8], and in other cases either directly calculated or estimated by the overlap approximation. Some of the directly culculated integrals were given in the Appendix. Slater-type atomic orbitals were used, and the effective nuclea charge of oxygen for the valence shells were taken to be 4.55. The coulombic integrals between AO's of O and O′ were calculated by the point-charge approximation.

In the calculation of $(\phi_i\mid H\mid\phi_j)$, the terms which arise by twice or more exchanges of electrons were ignored. Also, the exchange integral and overlap integral over ψ_1 and ψ_2 were neglected throughout the calculation. All the remaining terms were thoroughly included.

For comparison, the lowest energy of the O-H bond in a free water molecule was also determined. In this case, three resonance hybrids, A′, B′, and C′, similar to the types, A, B and C in (3) may be assumed. The bond eigenfunctions for them are:

$$\begin{array}{l} \Psi_A'=N_A'(\phi_1'-\phi_2') \\ \Psi_B'=N_B'(\phi_3') \\ \Psi_C'=N_C'(\phi_3') \end{array} \qquad (6)$$

in which the ϕ''s are of the following form, when one uses the same abbreviated formula as used before,

$$\begin{array}{ll} \phi_1'=(1\alpha^1\cdot h\beta^2) & \phi_6'=(h\alpha^1\cdot h\beta^2). \\ \phi_2'=(1\beta^1\cdot h\alpha^2) & \\ \phi_3'=(1\alpha^1\cdot 1\beta^2) & \end{array} \qquad (7)$$

$$\begin{array}{c|ccccc} & A & B & C & D & E \\ \hline A & -E & 0.43-0.70E & 0.56-0.70E & 0.37-0.26E & 0.21-0.32E \\ B & & -(1.28+E) & 0.75-0.32E & -(0.17+0.38E) & 0.31-0.23E \\ C & & & -(0.92+E) & 0.36-0.12E & 0.34-0.24E \\ D & & & & -(2.55+E) & -(0.53+0.56E) \\ E & & & & & -(2.25+E) \end{array} = 0 \qquad (8)$$

$$\begin{array}{c|ccc} & A' & B' & C' \\ \hline A' & -E & 0.42-0.69E & 0.58-0.69E \\ B' & & -(1.29+E) & 0.71-0.31E \\ C' & & & -(0.90+E) \end{array} = 0 \qquad (9)$$

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8) Kotani, Amemiya and Simose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra Number 1, **22**, Extra Number.

Results and Discussion

The calculated matrix elements for the O-H . . . O system and for the free molecule are given in (8) and (9), respectively.

As may be seen from these equations, the zero point of the energy was taken at the value of H_{AA} for (8) and at the value of H_{AA}' for (9). Since in absolute value $H_{AA} \neq H_{AA}'$, the zero points of these two equations are not the same. (The calculated values are, $H_{AA}=12.298$, $H_{AA}'=5.429$, in atomic unit.)

TABLE I

	Lowest eigenvalue	C_A^2	C_B^2	C_C^2	C_D^2	C_E^2
(1)	0.3015	0.705	0.088	0.194	0.007	0.008
(2)	0.2756	0.715	0.098	0.187	/	/
(3)	0.2787	0.721	0.088	0.190	/	/

In Table I, (1) shows the result of the solution of the secular equation (8), (2) shows that of the three-dimensional secular equation obtained by dropping the terms, H_{DX}'s and H_{EX}'s, and (3) shows that of the secular equation (9)$\cdot C_A^2$, C_B^2, etc. are the coefficients for the resonance hybrids, A, B, etc. for the lowest eigenvalue.

From this table, it can be seen that C_C^2 is always larger than C_B^2. This difference occurs mainly for the reason that in the secular determinant, (8) and (9), H_{CC} is larger than H_{BB}, and it means that the structure of O^+H^- contributes more to the ground state of the molecule than the structure of O^-H^+. This is contradictory to the usual chemical concept that the O-H bond is characterized, to a certain extent, by the O^-H^+ structure. Hence, in order to examine the validity of the results here obtained, the dipole moment of the water molecule was calculated. From the supposition of the AO's of the oxygen atom in a valence state, on which the present calculation is based‘ it is conceivable that the dipole moment of the water molecule consists of two bond dipoles and a lone-pair dipole[9] as shown in Fig. 2. By use of the coefficients for the lowest-energy-state bond eigenfunction listed in the third row of Table I, the O-H bond moment was calculated to be 1.79D (O^+H^-). The main part of this moment, however, does not arise from the fact that C_C^2 is larger than C_B^2, but it arises from the resonance hybrid indicating homopolar bond (type A). As the calculated lone-pair dipole moment is 3.23 D and directs in the opposite side to the O-H bonds, the total moment amounts to 1.17 D, a value somewhat smaller than the experimental one, 1.84 D. On the contrary, if one assumes, as Pople assumed, that C_B^2 is a little larger than C_C^2, the calculated dipole moment will approach to the experimental value. Therefore, it can be concluded that in the present calculation H_{BB} has been a little underestimated compared to H_{CC}. It seems difficult, however, to avoid errors of this degree in view of the approximation of the method employed in the present work. Further discussions on the validity of the present calculation will be made later in this paper.

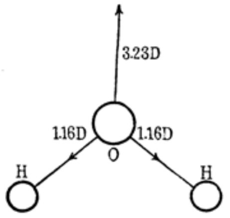

Fig. 2.

The energy of the delocalization due to the D- and E-structures may be given by the difference of the lowest eigen-values listed in the first and second rows of Table I, which amounts to 0.0259 AU., that is, 8.1 kcal./mol. On the other hand, the calculated electrostatic energy of the hydrogen-bond between two water molecules given by Pople[2], is 5.95 kcal./mol. A comparison of these two values allows us to conclude that the delocalization energy is of the same order of magnitude as, or rather larger than, the electrostatic energy.

From a survey of the features of the secular equations, (8) and (9), one can obtain some knowledge on the general character of the delocalization energy. First, we have seen that the inclusion of the D- and E-structures modifies the lowest energy of the system by only 0.0259 AU., a very small value compared to each matrix element. Therefore the problem can be, to some degree of exactness, treated by the second-order perturbation theory for the ground-state of the O-H group with inclusion of the higher energy states, D and E. The ground state of the O-H group may be given by a wave function

$$\Psi_O = c_A\Psi_A + c_B\Psi_B + c_C\Psi_C \qquad (10)$$

The second-order perturbation energy will then be,

$$(\Delta E)_{OD} = (H_{OD} - S_{OD}\cdot E)^2/(H_{OO} - H_{DD}),$$
$$(\Delta E)_{OE} = (H_{OE} - S_{OE}\cdot E)^2/(H_{OO} - H_{EE}). \qquad (11)$$

It will be interesting to calculate the perturbation energy by use of (11), and compare the results with the exact value. As a rough approximation H_{OO} in (11) may be replaced

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[9] J. A. Pople, ref. 6. C. A. Coulson, ref. 4.

by H_{AA} since the major part of Ψ_O consists of Ψ_A. Correspondingly, we get,

$$(\varDelta E)_{AD}=(H_{AD}-S_{AD}\cdot \mathrm{E})^2/(H_{AA}-H_{DD}),$$
$$(\varDelta E)_{AE}=(H_{AE}-S_{AE}\cdot E)^2/(H_{AA}-H_{EE}), \quad (12)$$

where, for the E, 0.28 may be used. (See (3) of Table I).

The numerical results are:

$$(\varDelta E)_{AD}=0.0346\mathrm{AU.}=11\,\mathrm{kcal./mol.},$$
$$(\varDelta E)_{AE}=0.0066\mathrm{AU.}=2\,\mathrm{kcal./mol.},$$

The sum of these two values, 13 kcal./mol., is considerably larger than the true one, 8.1 kcal./mol. This may result from the negative value of $(H_{BD}-S_{BD}\cdot E)$, and $(H_{DE}-S_{DE}\cdot E)$.

From the above equations we can see that the delocalization energy becomes the greater, as the differences between H_{DD} or H_{EE} and other diagonal matrix elements decrease, and it is clear that these differences become the smaller,the larger the electron affinity of O and the smaller the ionization potential of O'*.

We can also see that the energy depends on the resonance integrals, $(H_{DX}-S_{DX}\cdot E)$ and $(H_{EX}-S_{EX}\cdot E)$. (Here X designates the elements A, B and C.) From the survey of the explicit forms of these terms, it can be seen that all of these terms, except $(H_{CE}-S_{CE}\cdot E)$, are approximately proportional to the overlap integral between ψ_2 and ψ_h, denoted hereafter by S_{2h}. Therefore it may be concluded that the delocalization energy increases with increasing S_{2h}. In general, S_{2h} depends on the distance between H and O′, the formal charge of O′ and the hybridization factor of ψ_2. Concerning the last factor it can be easily shown that S_{2h} has a maximum at a certain hybridization factor α. $(1>\alpha>0)$

Therefore, if one confines his attention within the influence of the overlap integral, he can conclude that the delocalization energy for a proton-acceptor which has an s, p-hybridized lone-pair orbital is, if the hybridization factor is appropriate, larger than the delocalization energy for a proton-acceptor which has pure s- or p-lone-pair orbital. It is interesting to note that, from the electrostatic point of view, a conclusion similar to that mentioned above can also be drawn, concerning the relation between the strength of hydrogen-bonds and the hybridization of the lone-pair of the proton-acceptor[10].

Eqs. (11) also suggest the limit of the accuracy for the obtained value of the delocalization energy. Namely, its accuracy is approximately the same as the accuracy of such terms as $(H_{AA}-H_{DD})$, $(H_{AD}-S_{AD}\cdot E)$, etc. As for the validity of these values, of course, there are many points to be discussed. For example, it is a question whether or not Slater-type AO's give reasonable results for the energy of interaction between atoms which are so separated as in this case. S. Maeda, in private communication, has pointed out that, when we used SCF AO's, the overlap integral, S_{2h}, will become much larger than the value calculated by use of Slater AO's. Also, when we calculate such terms as $(H_{AA}-H_{DD})$, some error will enter into the result on account of the fact that the same screening constant is used for both neutral and ionized states[11]. The correction of this error will increase our value of the delocalization energy.

Influence of the Formal Cahrge at O'

Thus far, it has been assumed that the proton-accepting oxygen atom has no formal charge. This assumption may be valid in many cases where the accepting molecule has only single bonds, because it has been recently accepted that even for a bond, usually thought to be polar, the main part of its polarity arises from the atomic dipole and the bond itself is for many cases nearly homopolar. But when the molecule with which we are concerned is a conjugated double-bond system, such as, for example, phenol or benzoquinone, the oxygen atoms will definitely carry a considerable positive or negative charge. In such cases the formal charge will not only modify the electrostatic interaction energy between proton-donors and proton-acceptors but will also modify the contribution of the delocalization energy by its effect of reducing the ionization potential of the lone-pair of the proton-acceptor and by increasing the overlap integral between the hydrogen 1s AO and the lone-pair AO. The increase of this overlap integral is caused by the change of the screening constant of the oxygen atom due to the formal charge. For instance, the same calculations were made for the case when the oxygen atom, O′ has −0.2e formal charge. In this case the matrix elements corresponding to those given in (8) are a little modified and the following results are obtained.

$$H_{AA}-H_{DD}=2.33\mathrm{AU.},$$
$$H_{AD}-S_{AD}\cdot E=0.39\mathrm{AU.}\ -0.26E.$$

By use of these values and Eq. (12), the second-order perturbation energy arising only from the D-structure is calculated to be 13.5 kcal./mol., showing a 2.7 kcal. increase in comparison with the former result. On the other hand the increase of the electrostatic energy due to the same formal charge is about 1 kcal./mol.

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* This has been already pointed out by Nukasawa, Tanaka and Nagakura[5].

10) W. S. Fyfe, *J. Chem. Phys.*, **21**, 2 (1953).

11) W. Moffitt, *Proc. Roy. Soc.*, **A210**, 236 (1951).

Comparison with the Experimental Facts

From the present results of calculation, it has been concluded that the delocalization energy amounts to about 8 kcal./mol. for the hydrogen-bond between water molecules. On the other hand the calculated electrostatic energy for the bond is about 5 kcal./mol. The experimental value of the heat of sublimation for ice is 12.2 kcal./mol., and if one tentatively assumes that about one fourth of this value is attributed to the interaction of non-neighbors, the energy of the hydrogen-bonds may be estimated to be about 9 kcal./mol. Since two hydrogen-bonds exist per one water molecule, the energy of the single hydrogen-bond is estimated to be about 5 kcal./mol. Hence, in order to assume that the theoretical and experimental energy values are consistent, one should consider that a repulsive energy of the order of 8 kcal./mol. is present in the hydrogen-bond. It may be easily understood that this repulsive energy is provided by the difference between exchange repulsion and the dispersion force, since the O-O distance for the hydrogen-bonded molecules must be shortened by the attractive electrostatic and charge-transfer forces, compared to the equilibrium O-O distance which would be attained when only usual dispersion force and exchange repulsion are present.

From the present results, it seems that the disagreement between the order of the experimentally found proton-accepting strengths of some proton-acceptors and the electrostatically predicted ones may be explained by taking into account the delocalization energies. For example, as is described before, the proton-accepting strengths of diethyl ether, acetone and acetonitrile are known to be as follows:

diethyl ether $\fallingdotseq$ acetone $>$ acetonitrile.

In these compounds, it can be concluded that the delocalization energy for the hydrogen-bond grows stronger from right to left in the above formula, and thus compensates or overwhelms the increase of the electrostatic energy from left to right. For, as is concluded previously, the delocalization energy increases as the ionization potential of the lone-pair of the accepting molecule decreases, and the lowest ionization potentials of these molecules, which may be considered to correspond to those of the lone-pairs, are as follows:

diethyl ether[12] $>$ acetone[13] $>$ acetonitrile[12].

The delocalization energies depend, however, not only on the ionization potentials but also on various other terms, for example, the overlap integral between hydrogen and lone-pair AO's which have not yet been clarified for such complex molecules. Hence a precise argument on these points remains to be made in future.

Summary

The delocalization energy for the hydrogen-bonded water molecules has been calculated non-empirically by use of the atomic orbital method, with a simplified model. The delocalization energy thus calculated amounts to about 8 kcal./mol. which is rather greater than the calculated electrostatic energy that has been usually considered to be the most important source of the binding force. The proton-accepting strengths of ether, acetone and acetonitrile have been discussed by use of this result.

Appendix

Some of the integrals calculated by the author are listed below in atomic unit. The notations are the same as those used by J. F. Mulligan (*J. Chem. Phys.*, **19**, 347 (1951)). s, σ, and π are the 2s, $2p\sigma$, and $2p\pi$ AO's of the atom O, and s', σ', and π', are those of the atom O', respectively.

Overlap integrals	
$S(s,s')$	0.00594
$S(s,\sigma')$	0.00867
$S(\sigma,\sigma')$	0.01260
$S(\pi,\pi')$	0.00156

Exchange integrals (Approximate value)	
$(hs' : hs')$	0.0359
$(h\sigma' : h\sigma')$	0.0483

Bare nuclea-field-potential energy integrals		
$(H : s',s')$		0.6066
$(H : \sigma'\sigma')$		0.6208
$(H : \pi'\pi')$		0.5995
$(H : s'\sigma')$		0.1166
$(H : hs')$		0.1616
$(H : hs')$		0.1761
$(O' : hh)$	=	$(s's' : hh)$
$(O' : hs')$		0.2502
$(O' : h\sigma')$		0.1715

Coulomb integrals	
$(s's' : hh)$	0.6029
$(\sigma'\sigma' : hh$	0.6078
$(\pi'\pi' : hh)$	0.6011

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[12] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1221 (1952).

[13] T. M. Sugden and W. C. Price, *Trans. Farad. Soc.*, **44**, 116 (1948).