A Molecular Orbital Study on the Effects of Excess Charges at the Donor and Acceptor Atoms on the Hydrogen Bond

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Effects of the excess charges at the donor and acceptor atoms on the properties of the hydrogen bond were studied in a simple three-center four-electron model for a hydrogen bond system using CNDO/2 type molecular orbital calculation. It was shown that three types of hydrogen bonds, normal, proton transferred and abnormal, are possible according to the value of the excess charges. The dependence of the hydrogen bond distance, proton equilibrium distance, frequency of proton stretching vibration and hydrogen bond energy on the excess charges were calculated for the normal type hydrogen bond. The correlations between these quantities obtained by changing the amounts of the excess charges are in good agreement with the experimental results, suggesting that the excess charges at the donor and acceptor atoms primarily determine the correlation. The potential of proton movement at the equilibrium hydrogen bond distance is shown not to have double minima for any value of the excess charges, indicating that the excess charges are not essential for producing a double well potential.

Many theoretical works have been carried out on the hydrogen bond (HB) which can be classified into two categories, those based on the simplified three-center four-electron model using the valence bond (VB)[1-3] or the molecular orbital (MO)[4,5] method and those on the calculations for total HB systems using the non-empirical[7-9] or the semi-empirical[6] MO method. The early works belong to the former category, but the main trend in recent works seems to be in the latter one. Morokuma and Pedersen[7] and Kollman and Allen,[8] from their non-empirical calculation for total HB systems, emphasized that electron reorganization within them is important, and the simple three-center model has nothing to do with the explanation of the properties of the HB. Their criticism is sound as far as the original simple three-center model is concerned. However, they seem to underestimate the usefulness of a suitably modified three-center model in explaining the properties of the HB. The three-center model can be modified to incorporate some effects of the residual part of the HB system into its parameters. Such modifications of the three-center model were studied for the HB in ice with positive and negative defect,[4] the HB coupled with π electron system[5] and the HB with donor and acceptor atoms of varying net charges.[3]

We have studied the effects of the excess charges at donor and acceptor atoms on the properties of the HB by means of the three-center model and semi-empirical MO calculation. Change in the net charges at the donor and acceptor atoms is considered to be one of the most important factors of the residual part of the HB system which would strongly affect the properties of the HB. The model was studied by Hasegawa *et al.*[3] with use of the VB method. However, their calculation was not extensive enough to confirm the importance of the change of the net charges at the donor and acceptor atoms. We have shown that this model can satisfactorily explain the empirical correlations between the HB distance, proton equilibrium position, frequency of proton stretching vibration and HB energy. A comparison of the calculations for this model and those for total HB systems provides a quantitative estimation of the dynamical effects of the residual part of HB system which cannot be renormalized into the effect of the net charges of the donor and acceptor atoms.

Model and Method of Calculation

We take the three-center four-electron model of the HB system (Fig. 1) and consider the case in which donor A, acceptor B and proton H are arranged linearly, both A and B being oxygen atoms. The HB MO is constructed from the three atomic orbitals (AO), the 1s AO of H and the two AO's, one from A and the other from B each extending toward H. The hybridization of the AO's of A and B is assumed and fixed to be sp^3. Four electrons, two from B and one from A and one from H, enter into the HB MO. The electrons in the other hybridized AO's of A and B are treated as the source of external charges, and they are not constrained to be the integers 5 and 4 respectively. The excess charges at A and B are denoted by $\delta_A e$ and $\delta_B e$ respectively. The 1s cores of A and B are treated as the points with charge of 6e. In the following, we use the term "the core of A or B" meaning that it represents the 1s core and the electrons in the hybridized AO's at A or B not involved in the HB MO.

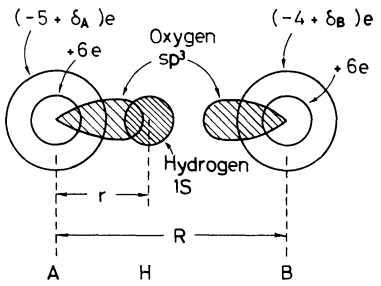


Fig. 1. Three-center four-electron model of hydrogen bond with excess charges.

The HB MO was calculated by CNDO/2 approximation.[10] To obtain consistency with CNDO/2 approximation, the core-core interaction between A and B should be estimated by

$$E_{cc} = \frac{(6e)^2}{R} + \gamma_{AB}\{(5-\delta_A)(4-\delta_B)-6(5-\delta_A)-6(4-\delta_B)\}, \quad (1)$$

and the electron-core interactions by

$$V_{iA} = (1+\delta_A)\gamma_{iA}$$
$$V_{iB} = (2+\delta_B)\gamma_{iB} \quad (2)$$

where i is either A, B, or H. The values of the ionization potential 24.39 eV and electron affinity 6.11 eV were used for the sp^3 AO's involved in HB MO after Hinze and Jaffé.[11]

Calculations were carried out for the mesh of R and r with a 0.1 Å interval and that of δ_A and δ_B in the range from -1.0 to 1.0 with a 0.2 interval. The equilibrium distance R_e of A–B and r_e of A–H, the potential energy E_{eq} and the stretching frequency ν_s of proton at the equilibrium position of proton were calculated by an interpolation of the four mesh points of R and r around the energy minimum. The HB energy ΔE_e at the equilibrium position of A, B, and H was calculated by

$$\Delta E_e = \left(E_{eq}+\frac{1}{2}h\nu_s\right)^{\delta_A,\,\delta_B}_{R=R_e} - \left(E_{eq}+\frac{1}{2}h\nu_s\right)^{\delta_A,\,\delta_B}_{R=\infty}, \quad (3)$$

taking into account the zero point energy of proton motion since the frequency shift due to it is not negligible when δ_A or δ_B is large.

Results

Three Types of Hydrogen Bonds in Relation to the Excess Charges at the Donor and Acceptor Atoms. The dependence of ΔE_e on δ_A and δ_B is shown in Table 1. We see that an attractive HB occurs in the region of δ_A and δ_B with opposite signs. The region may be divided into regions I, II, and III (Fig. 2). When δ_A and δ_B satisfy the relation

$$\delta_A = \delta_B + 1, \quad (4)$$

we see from Eqs. (1) and (2) that the cores of A and B are equivalent and the system becomes symmetric, *viz.*, the potential curve of proton is always symmetric for any value of R. For two points in regions I and II which are mirror images of each other with respect to the straight line (4), the potential curves of proton for the two systems are mirror images of each other for any value of R.

Table 1. Dependence of E_e (eV) on the excess charges δ_A and δ_B

Symbol + denotes the repulsive HB without equilibrium R.

δ_A \ δ_B	1.0	0.8	0.6	0.4	0.2	0.0	0.2	0.4	0.6	0.8	1.0
1.0	-17.41	-13.78	-10.39	-7.28	-4.44	-1.91	+	+	+	+	+
0.8	-14.31	-11.43	-8.46	-5.78	-3.41	-1.35	+	+	+	+	+
0.6	-11.95	-9.11	-6.59	-4.40	-2.51	-0.92	+	+	+	+	+
0.4	-9.20	-6.85	-4.84	-3.14	-1.74	-0.58	+	+	+	+	+
0.2	-6.54	-4.72	-3.23	-2.04	-1.09	-0.35	+	+	+	+	+
0.0	-4.28	-2.76	-1.79	-1.07	-0.56	-0.20	+	+	+	+	+
-0.2	-1.75	-1.00	-0.53	-0.26	-0.13	-0.10	-0.13	-0.20	-0.28	-0.37	-0.47
-0.4	+	+	+	+	+	-0.05	-0.32	-0.60	-0.90	-1.22	-1.55
-0.6	+	+	+	+	+	-0.02	-0.51	-1.02	-1.56	-2.12	-2.70
-0.8	+	+	+	+	+	+	-0.71	-1.45	-2.24	-3.06	-3.91
-1.0	+	+	+	+	+	+	-0.90	-1.89	-2.93	-4.01	-5.15

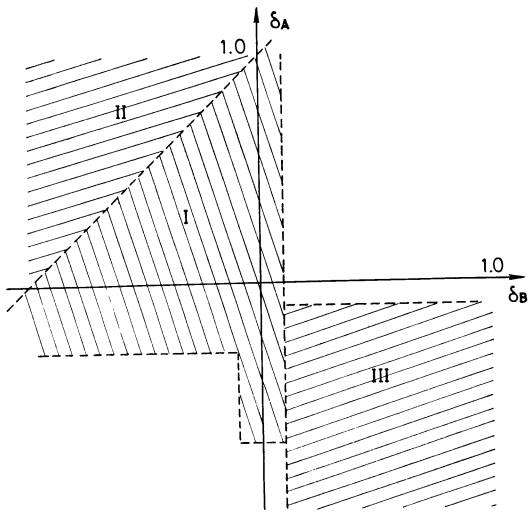


Fig. 2. Three regions of attractive HB.
I: normal HB, II: proton transferred HB, III: abnormal HB.

Region I corresponds to the normal HB in the form of $A^{\delta+}$–H---$B^{\delta'-}$ where the equilibrium position of H is on the side of A. Region II corresponds to the HB in

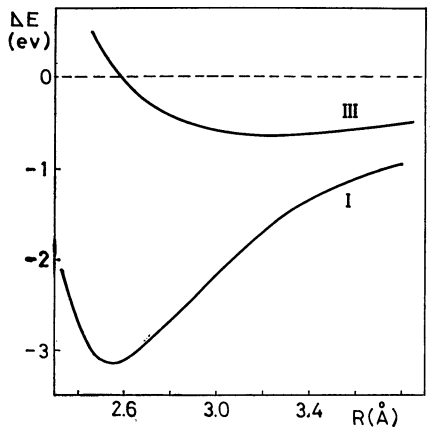


Fig. 3 (a).

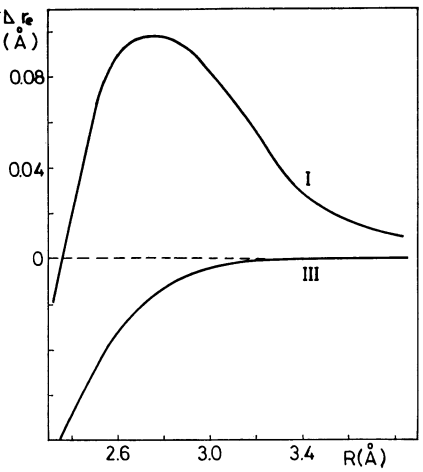


Fig. 3 (b).

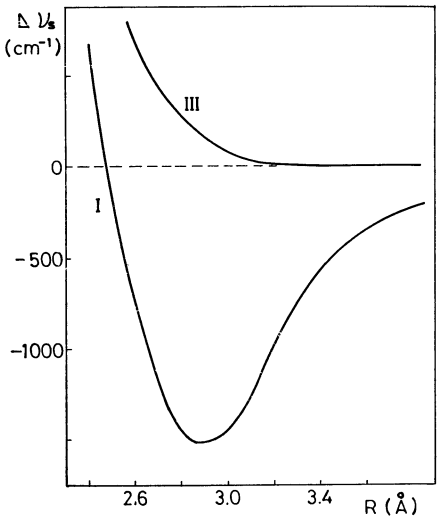


Fig. 3 (c).

Fig. 3. Dependences of the hydrogen bond energy ΔE(a), the shift of proton equilibrium distance Δr_e (b) and the shift of frequency of stretching vibration of proton $\Delta \nu_s$ (c) on the A–B distance R. Typical cases are represented;
I(δ_A=0.4, δ_B=−0.4) and III (δ_A=−0.4, δ_B=0.4).

the form of $A^{\delta+}$---H–$B^{\delta'-}$ in which the effect of the excess charge is so strong that the equilibrium position of H is shifted toward the side of B, namely, the HB of proton transferred state. The HB in the region III is of the form $A^{\delta-}$–H---$B^{\delta'+}$ and abnormal. The R dependence of ΔE, Δr_e and $\Delta \nu_s$ for typical systems in regions I and III is shown in Fig. 3, where ΔE, Δr_e and $\Delta \nu_s$ are respectively the HB energy and the shifts of r_e, ν_s being due to HB at A–B distance R. For the HB system in region I, $\Delta r_e > 0$ and $\Delta \nu_s < 0$ at $R = R_e$ exhibit the normal character of HB (Fig. 3). Distance R giving the maximal Δr_e and $\Delta \nu_s$ coincides with R_e in a weak HB with a small ΔE_e, while Δr_e and $\Delta \nu_s$ at R_e tend to be somewhat smaller than their maximal values in a strong HB with large ΔE_e. This seems to be the effect of compression of R_e in the strong HB.

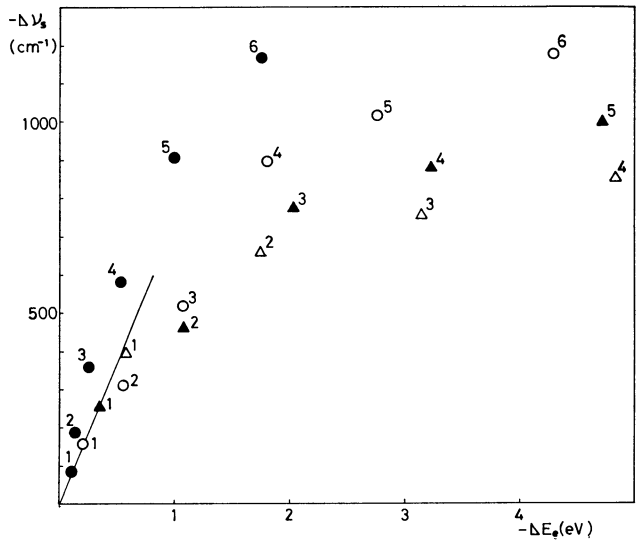


Fig. 4 (a).

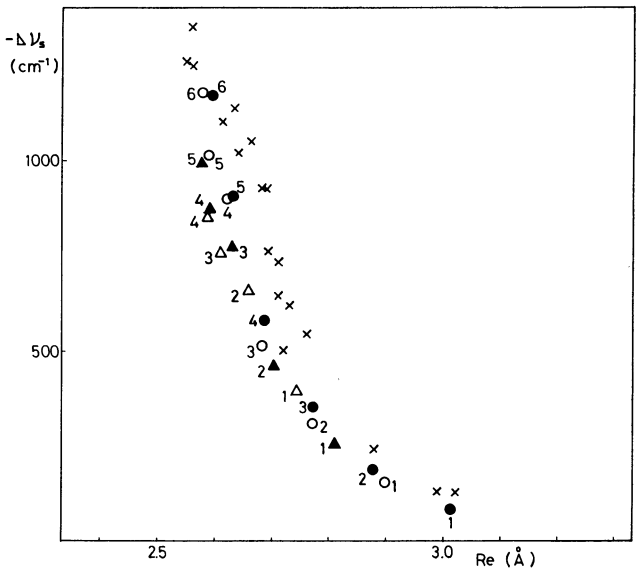
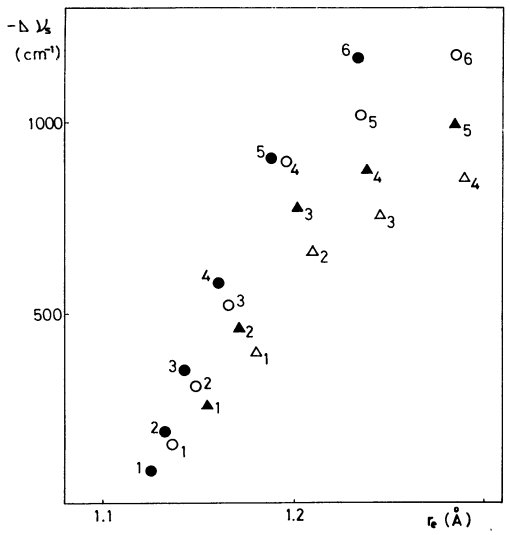


Fig. 4 (b).



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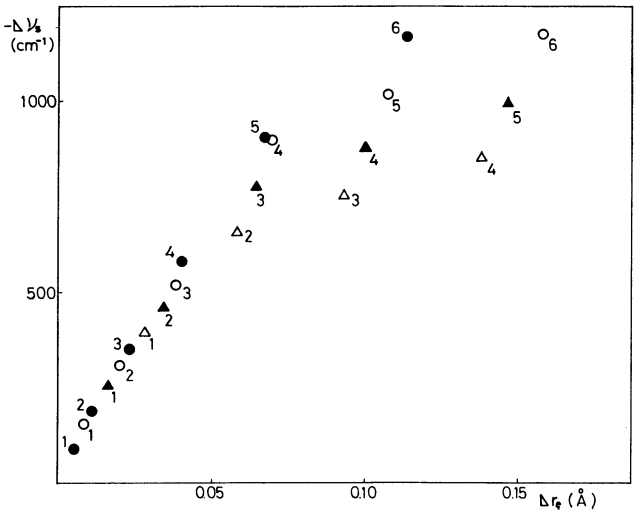

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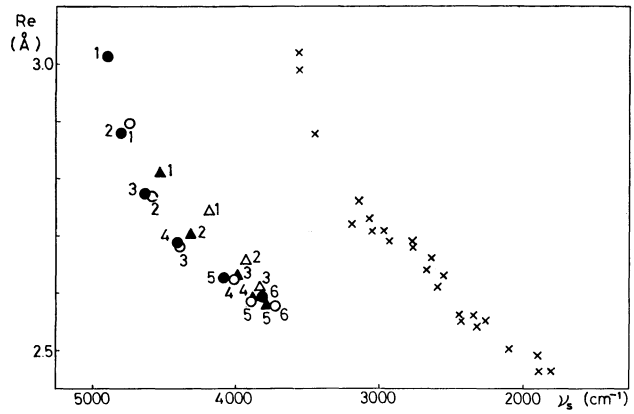

Fig. 4 (e).

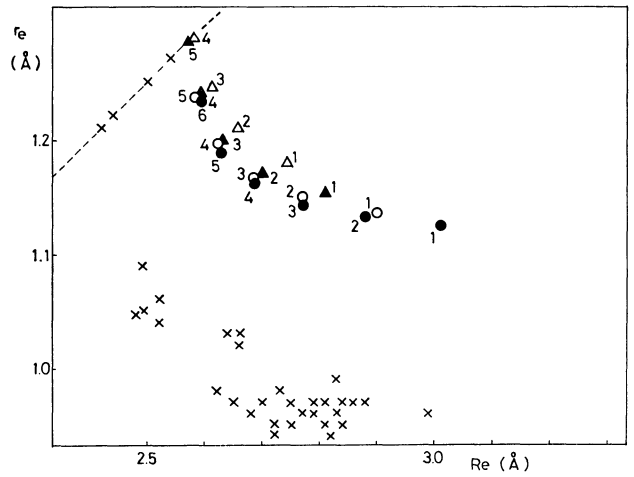

Fig. 4 (f).

Fig. 4. Correlations between the hydrogen bond distance R_e, the proton equilibrium position r_e, the shift Δr_e of r_e due to formation of HB, the frequency of proton stretching vibration ν_s, the shift $\Delta\nu_s$ of ν_s and hydrogen bond energy ΔE_e. The correlations shown are those between $-\Delta E_e$ and $-\Delta\nu_s$ (a), R_e and $-\Delta\nu_s$ (b), r_e and $-\Delta\nu_s$ (c), Δr_e and $-\Delta\nu_s$ (d), ν_s and R_e (e) and between R_e and r_e (f).

The values of the excess charges δ_A and δ_B are discriminated by the following symbols;
$\delta_A=-0.2(\bullet)$, $0(\circ)$, $0.2(\blacktriangle)$, $0.4(\triangle)$.
$\delta_B=0(1)$, $-0.2(2)$, $-0.4(3)$, $-0.6(4)$, $-0.8(5)$, $-1.(6)$.

The solid line in (a) is the experimental curve given by Badger and Bauer[13] for water and alcohol.

The points x in (b) and (e) are the experimental points compiled by Nakamoto *et al.*[14] for O–H---O bonds and those in (f) are the data compiled by Hamilton and Ibers[15] for O–H···O bonds in solid.

The dashed line in (f) represents the case of symmetric HB with $r_e=R_e/2$.

On the other hand, for the HB system in region III, we have $\Delta r_e<0$ and $\Delta\nu_s>0$ at $R=R_e$ exhibiting an abnormal character in contrast to the normal HB.

Correlation between the Hydrogen Bond Distance, Proton Equilibrium Position, Frequency of Proton Stretching Vibration and Hydrogen Bond Energy. We may obtain the theoretical correlation between R_e, r_e, Δr_e, ν_s, $\Delta\nu_s$ and ΔE_e for the normal HB by adjusting δ_A and δ_B within region I. The results are shown in Fig. 4. The theoretical correlation plots including r_e or ν_s are shifted toward larger values of r_e and ν_s (Figs. 4e and f). However, when we subtract the constant amounts of 0.2 Å and 1300 cm^{-1} from r_e and ν_s respectively, the theoretical correlation plots overlap the observed ones. Apart from these constant deviations of r_e and ν_s, agreement of the theoretical correlation plots with the observed ones is good. The deviation of theoretical values of r_e and ν_s in a larger direction than the observed ones is already present in the isolated A–H system and seems to be due to a failure of the CNDO/2 method to give a correct potential for the covalent bond.

In some of the observed correlation plots, the experimental points exhibit a considerable scattering (Figs. 4b, e, and f). However, if the experimental points are selected in such a way that either one of the acid or base is fixed and the other changed, then the correlation plot, which exhibits considerable scattering when both acid and base are arbitrarily changed, becomes a smooth one. This behavior is also reproduced in the present calculation. When either one of δ_A or δ_B is fixed and the other changed, then the theoretical correlation plot becomes a smooth one, but

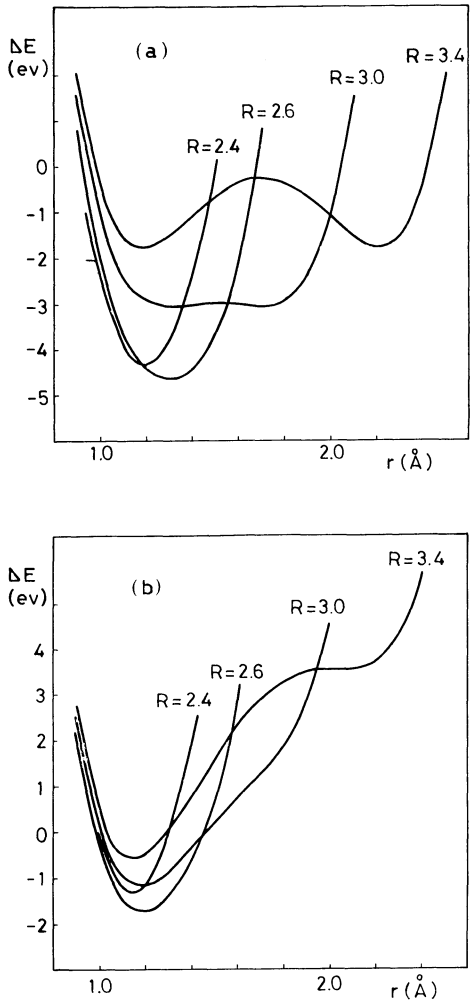

Fig. 5. The proton potential curves at various AB distances R.
(a) The symmetric system with $\delta_A=0.2$, $\delta_B=-0.8$
(b) The asymmetric system with $\delta_A=0.0$, $\delta_B=-0.6$

the correlation plots with different values of the fixed δ are not identical, and each of the theoretical correlation exhibits a spread (Fig. 4).

The good agreement between the theoretical correlation plots and the experimental ones strongly suggests that the correlation plots are primarily determined by the excess charges at the donor and acceptor atoms.

Potential Shape for Proton Movement. Many studies have been carried out concerning the potential shape for proton movement in the HB system, particularly the existence or non-existence of double minima. Hardly any MO calculations carried out so far on total systems with a single HB between oxygens led to a double well potential at theoretical R_e although it may be obtained at larger R. Clementi[9] emphasized in his non-empirical calculations that a coupling between more than two HB's would be a necessary requisite for the second minimum to occur. Nevertheless, the factors principally responsible for occurrence of double minima do not seem to have been determined.

The present model does not give a double well potential at R_e for all values of δ_A and δ_B. If δ_A and δ_B are close to the symmetric system satisfying Eq. (4), then a double well potential appears at slightly larger R than R_e (Fig. 5a). For the system in region I, the minimum of the potential well is on the side near A, but for that in region II it is on the side near B. If the asymmetry of the system becomes large, the R where the double well potential appears shifts toward much larger R than R_e (Fig. 5b). Thus, the excess charges at the donor and acceptor atoms are not the essential factor to produce a double well potential although the excess charges with the signs $\delta_A>0$ and $\delta_B<0$ stabilize the configuration A---H–B and facilitate occurrence of the second minimum.

Mechanism of the Effect of Excess Charges on the Hydrogen Bond and Proton Transfer. We now consider the mechanism of how the excess charges with the signs $\delta_A>0$ and $\delta_B<0$ enhance HB and proton transfer. As represented in the scheme $A–H+B\rightarrow A^{\delta-}–H\cdots B^{\delta+}$, formation of the HB leads to an increase in the electron density at A and a decrease at B. This change in the electron density is due to an increase of the lone pair electron density at A by transfer of the lone pair electrons at B to the antibonding orbital of A–H as seen from the HB MO (Fig. 6b). Let $E_l(z)$ and $E_s(z)$ respectively be the energies of the lone pair in A^- or

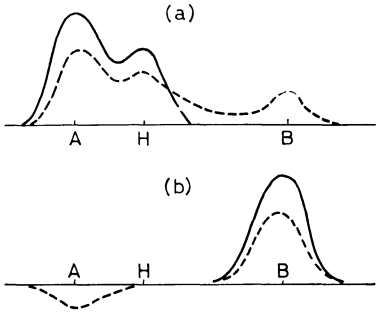

Fig. 6. A change in molecular orbitals induced by HB. Isolated state (——) and hydrogen bonding state (----). Bonding orbital (a) and lone pair orbital (b).

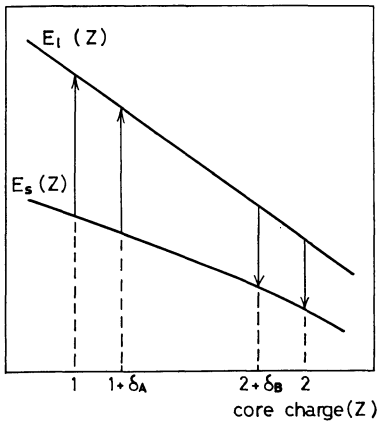

Fig. 7. Dependences of the lone pair energy E_l and the single bond energy E_s on the core charge.

B and the single bond A–H or $H–B^+$ regarded as the functions of the core charge z. We show their z dependence in Fig. 7. The energy loss by the process $A–H\rightarrow A^-$ may be related to $E_l(1+\delta_A)-E_s(1+\delta_A)$. Since the effect of the core charge is greater for the lone pair electrons than those in the single bond, a greater change is induced in $E_l(1+\delta_A)$ than in $E_s(1+\delta_A)$ by an increase in δ_A. Thus it follows that $E_l(1)-E_s(1)>E_l(1+\delta_A)-E_s(1+\delta_A)$ for $\delta_A>0$ (Fig. 7). This means that the energy loss accompanied by the process $A–H\rightarrow A^-$ is smaller for $\delta_A>0$ than for $\delta_A=0$, and the HB and proton transfer are made easier by the excess charge $\delta_A>0$.

As site B, HB formation leads to a decrease of the lone pair density and to an increase of electrons in the single bond $H–B^+$. The energy gain by the process $B\rightarrow H–B^+$ may be related to $E_l(2+\delta_B)-E_s(2+\delta_B)$. As seen in Fig. 7, $E_l(2+\delta_B)-E_s(2+\delta_B)>E_l(2)-E_s(2)$ for $\delta_B<0$. This means that the energy gain accompanied by the process $B\rightarrow H–B^+$ is greater for $\delta_B<0$ than $\delta_B=0$, and HB and proton transfer are enhanced by the excess charge $\delta_B<0$. As both processes occur in the HB, the quantity

$$\Delta(\delta_A,\delta_B)=\{E_l(1+\delta_A)-E_s(1+\delta_A)\}-\{E_l(2+\delta_B)-E_s(2+\delta_B)\}$$

may well be related to the power of the HB. Since there is an approximately linear correlation between ΔE_e and Δ (Fig. 8), a very simplified picture of the HB regarded as a combined process of $A–H\rightarrow A^-$ and $B\rightarrow H–B^+$ might explain the dependence of HB strength on the excess charges, though it might fail to explain more detailed properties of the HB. The functional dependence of $\Delta(\delta_A,\delta_B)$ on δ_A and δ_B is similar to ΔE_e when either one of δ_A or δ_B is changed, but it leads to a different ordering of HB energy from that of MO calculation when both δ_A and δ_B are changed. For instance, $\Delta(\delta_A=0,\ \delta_B=-0.2)>\Delta(\delta_A=0.2,\ \delta_B=0)$ although the MO calculation leads to $\Delta E_e(\delta_A=0,\ \delta_B=-0.2)<\Delta E_e(\delta_A=0.2,\ \delta_B=0)$. A similar correlation between ΔE_e and Δ is obtained for the calculation on the total HB systems.[12]

In the process of proton transfer, $A–H\rightarrow A^-$ and $B\rightarrow H–B^+$ occur to a greater extent than in the normal

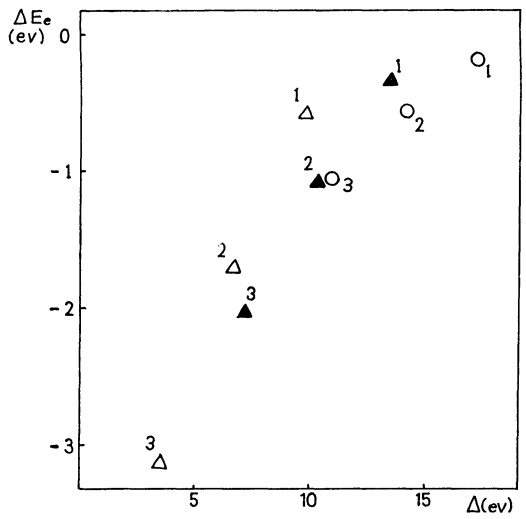

Fig. 8. Correlation between ΔE_e and Δ.
δ_A and δ_B for each point are discriminated by the same symbols as Fig. 4.

HB. Thus, the above interpretation for the effect of the excess charges is more applicable to the systems in region II.

Discussion

In contrast to our result, Hasegawa *et al.*[3] obtained a double well potential in their VB calculation with changing orbital exponents using a similar model to ours. They calculated the potential at an R near the experimental one without confirming whether it was close to the theoretical equilibrium distance or not. However, even if the R they chose was the one deviated from the theoretical R_e, the extent of the appearance of the double minima was more enhanced than that in the present result. Thus, either the electron correlation or the change of the orbital exponent, which are not taken into consideration in the present MO calculation, might be important for producing the double well potential.

In the present model the amounts of excess charges δ_A and δ_B are fixed parameters, but in a real hydrogen bond system they may be changed by the dynamic polarization of the molecules caused by HB formation. It seems possible that the dynamic polarization affects the HB dominantly through a change of the excess charges at the donor and acceptor atoms. The present model may be utilized as a reference system to evaluate validity of such mechanism. If the dynamic polarization affects the HB mainly through a change of the excess charges, the correlation plots between the quantities such as R_e, r_e *etc.* obtained for the system with the effect of dynamic polarization should be almost the same as those obtained for the present model. A good agreement of the theoretical correlation plots in the present model with the experimental ones offers indirect support for such a mechanism.

The shape of the proton potential, in contrast to the correlation curves, is affected by the change of the excess charges due to dynamic polarization. It is of interest to see how the proton potential is affected by dynamic polarization.

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