Memoirs of the Faculty of Engineering, Okayama University, Vol.28, No. 1, pp.39-50, November 1993

A Simple Model for Hydrogen-Bonding Ferroelectrics

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(Received Semtember 30 , 1993)

SYNOPSIS

There are some substances in which their hydrogen bonds are considered to play quite important roles in their ferroelectric or antiferroelectric phase transition. These ferroelectrics usually have large isotope effects in phase transition temperatures and we expect the physics of hydrogen bonds is closely related to the effects. We propose a simple model describing the isolated hydrogen bond. Based on quantum-mechanical analyses of this model, we study the difference between the behavior of a proton and a deuteron in hydrogen bonds.

I. INTRODUCTION

Tripotassium hydrogendisulfate, $K_3H(SO_4)_2$, has hydrogen bonds between two SO_4 radicals which do not form networks and these isolated hydrogen bonds are often referred to as 0-dimensional. The ferroelectrics and antiferroelectrics which have hydrogen bonds are known to have large isotope effects in the critical temperature of phase transitions. While we have no phase transition in $K_3H(SO_4)_2$ down to very low temperature of the order of Kelvins, $K_3D(SO_4)_2$ undergoes the antiferroelectric phase transition at about 84K[1)]. The analysis of these 0-dimensional hydrogen bonds, especially of their isotope effects, on the basis of the electronic theory is not only important but also useful to clarify the nature of ferroelectric or antiferroelectric phase transition.

We propose a very simple model which, we expect, contains essential physics of hydrogen bonds. Our model is composed of two cations, A and B, a proton (or deuteron) P and an electron as shown in Fig. 1. Hereafter we denote the proton or the deuteron in our system simply as proton when

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not specified otherwise. We fix the distance between A and B at R_0 and solve the Schrödinger equation for the proton and the electron.

The total Hamiltonian in atomic units is

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_p + \mathcal{H}_{ep}, \tag{1}$$

where

$$\mathcal{H}_e = -\frac{1}{2}\nabla^2 - \frac{Z_A}{r_a} - \frac{Z_B}{r_b}, \tag{2}$$

$$\mathcal{H}_p = -\frac{1}{2M}\nabla^2 + \frac{Z_A Z_P}{R_1} + \frac{Z_B Z_P}{R_2} + \frac{Z_A Z_B}{R_0}, \tag{3}$$

and

$$\mathcal{H}_{ep} = -\frac{Z_P}{r_p}. \tag{4}$$

Here, r_a, r_b or r_p denotes the distance between the electron and A, B, or P, and R_1 or R_2 denotes the distance between P and A or B. Z_A, Z_B, and Z_P are electric charges of cations A, B, and the proton, respectively. The mass ratio of the proton and the electron is denoted by M. We assume that the proton always sits on the line connecting A and B.

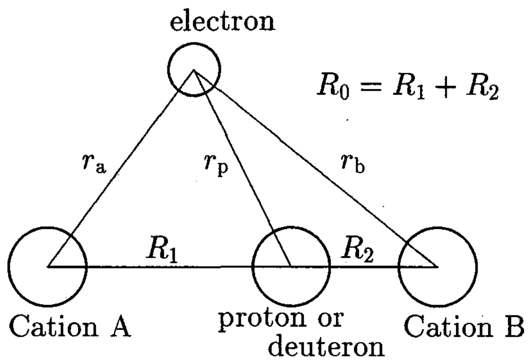

Fig.1 Model for hydrogen bond.

We apply the adiabatic approximation to our system. We first calculate electronic state $\varphi(\boldsymbol{r}, R)$ of the Hamiltonian $\mathcal{H}_e + \mathcal{H}_{ep}$ with the position of the proton R as a parameter:

$$(\mathcal{H}_e + \mathcal{H}_{ep})\varphi(\boldsymbol{r}, R) = E(R_0, R)\varphi(\boldsymbol{r}, R). \tag{5}$$

We then determine the wave function of the proton in the adiabatic potential $E(R_0, R)$ determined by $\varphi(\boldsymbol{r}, R)$ as

$$\mathcal{H}^A\psi(R) = E_{\text{total}}(R_0)\psi(R), \tag{6}$$

$$\mathcal{H}^{\mathrm{A}} = \mathcal{H}_{\mathrm{p}} + E(R_0, R). \tag{7}$$

The total energy of our system is given by $E_{\mathrm{total}}(R_0)$ as a function of R_0.

In this article, we present the formulation of this model in detail and some preliminary results.

II. CALCULATION

Our solution of the electronic wave function is based on the variational method[2]. The electronic state $\varphi(\boldsymbol{r}, R)$ and the adiabatic potential are obtained by minimizing the expectation of $\mathcal{H}_{\mathrm{e}} + \mathcal{H}_{\mathrm{ep}}$ as

$$E(R_0, R) = \min. \left\{ \frac{\int \varphi(\boldsymbol{r}, R)^* (\mathcal{H}_{\mathrm{e}} + \mathcal{H}_{\mathrm{ep}}) \varphi(\boldsymbol{r}, R) \mathrm{d}\boldsymbol{r}}{\int \varphi(\boldsymbol{r}, R)^* \varphi(\boldsymbol{r}, R) \mathrm{d}\boldsymbol{r}} \right\}. \tag{8}$$

We adopt the linear combination of three 1s electronic wave functions with variational parameters α_1, α_2, and α_3 as our trial function:

$$\varphi(\boldsymbol{r}, R) = \alpha_1 \chi_1 + \alpha_2 \chi_2 + \alpha_3 \chi_3, \tag{9}$$

$$\chi_1 = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r_{\mathrm{a}}}, \quad \chi_2 = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r_{\mathrm{b}}}, \quad \chi_3 = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r_{\mathrm{p}}}.$$

We rewrite the right-hand side of (8) into

$$E(R_0, R) = \min. \left\{ \frac{\sum_n \sum_{n'} \alpha_n \alpha_{n'} H_{nn'}}{\sum_n \sum_{n'} \alpha_n \alpha_{n'} \Delta_{nn'}} \right\}, \tag{10}$$

where

$$H_{nn'} = \int \chi_n (\mathcal{H}_{\mathrm{e}} + \mathcal{H}_{\mathrm{ep}}) \chi_{n'} \mathrm{d}\boldsymbol{r}, \qquad n,\ n' = 1,\ 2,\ 3, \tag{11}$$

and

$$\Delta_{nn'} = \int \chi_n \chi_{n'} \mathrm{d}\boldsymbol{r}, \qquad n,\ n' = 1,\ 2,\ 3. \tag{12}$$

The values of α_1, α_2 and α_3 which minimize $E(R_0, R)$ are determined by the conditions,

$$\frac{\partial E(R_0, R)}{\partial \alpha_k} = 0, \qquad k = 1,\ 2,\ \text{and } 3,$$

or

$$\sum_n \alpha_n \{ H_{nk} - \Delta_{nk} E(R_0, R) \} = 0, \quad k = 1,\ 2,\ \text{and } 3. \tag{13}$$

Solving this set of equations, we obtain $E(R_0, R)$ and $\alpha_i \, (i = 1,\ 2,\ 3)$. We now need to evaluate the values of $H_{nn'}$ and $\Delta_{nn'}$.

Since χ's are normalized, the diagonal elements of $\Delta_{nn'}$ reduce to unity;

$$\Delta_{11} = \Delta_{22} = \Delta_{33} = \frac{1}{\pi}\int e^{-2r}d\boldsymbol{r} = 1. \tag{14}$$

Using spheroidal coordinates (see Appendix I), we obtain the off-diagonal elements of $\Delta_{nn'}$ as

$$\Delta_{12} = \Delta_{21} = \frac{1}{\pi}\int e^{-(r_a+r_b)}d\boldsymbol{r} = e^{-R_0}\left(\frac{1}{3}R_0^2 + R_0 + 1\right), \tag{15}$$

$$\Delta_{23} = \Delta_{32} = \frac{1}{\pi}\int e^{-(r_b+r_p)}d\boldsymbol{r} = e^{-R_2}\left(\frac{1}{3}R_2^2 + R_2 + 1\right), \tag{16}$$

and

$$\Delta_{31} = \Delta_{13} = \frac{1}{\pi}\int e^{-(r_p+r_a)}d\boldsymbol{r} = e^{-R_1}\left(\frac{1}{3}R_1^2 + R_1 + 1\right). \tag{17}$$

An example of the diagonal elements of $H_{nn'}$ is

$$\begin{aligned} H_{11} &= \frac{1}{\pi}\int e^{-r_a}\left(-\frac{1}{2}\nabla^2 - \frac{Z_A}{r_a} - \frac{Z_B}{r_b} - \frac{Z_P}{r_p}\right)e^{-r_a}d\boldsymbol{r} \\ &= \frac{1}{\pi}\int e^{-2r_a}\left(-\frac{1}{2} + \frac{1}{r_a} - \frac{Z_A}{r_a}\right)d\boldsymbol{r} - \frac{Z_B}{\pi}\int \frac{e^{-2r_a}}{r_b}d\boldsymbol{r} - \frac{Z_P}{\pi}\int \frac{e^{-2r_a}}{r_p}d\boldsymbol{r}. \end{aligned}$$

Expressing the integrals $\int \exp(-2r_a)/r_b d\boldsymbol{r}$ and $\int \exp(-2r_a)/r_p d\boldsymbol{r}$ in spheroidal coordinates, we obtain

$$\begin{aligned} \frac{1}{\pi}\int \frac{e^{-2r_a}}{r_b}d\boldsymbol{r} &= \frac{1}{\pi}\int_{-1}^{1}d\mu\int_{1}^{\infty} e^{-R_0(\lambda+\mu)}\frac{2}{R_0(\lambda-\mu)}(\lambda^2-\mu^2)d\lambda\frac{\pi R_0^3}{4} \\ &= \frac{1}{R_0}[1 - e^{-2R_0}(1+R_0)]. \end{aligned} \tag{18}$$

We thus have

$$H_{11} = \frac{1}{2} - Z_A - \frac{Z_B}{R_0}[1 - e^{-2R_0}(1+R_0)] - \frac{Z_P}{R_1}[1 - e^{-2R_1}(1+R_1)]. \tag{19}$$

Other diagonal elements H_{nn} are similarly calculated as

$$H_{22} = \frac{1}{2} - Z_B - \frac{Z_A}{R_0}[1 - e^{-2R_0}(1+R_0)] - \frac{Z_P}{R_1}[1 - e^{-2R_1}(1+R_1)], \tag{20}$$

$$H_{33} = \frac{1}{2} - Z_P - \frac{Z_A}{R_1}[1 - e^{-2R_1}(1+R_1)] - \frac{Z_B}{R_2}[1 - e^{-2R_2}(1+R_2)]. \tag{21}$$

The off-diagonal elements need some more elaborate integrations. For example,

$$\begin{aligned} H_{12} &= H_{21} \\ &= \frac{1}{\pi}\int e^{-r_a}\left(-\frac{1}{2}\nabla^2 - \frac{Z_A}{r_a} - \frac{Z_B}{r_b} - \frac{Z_P}{r_p}\right)e^{-r_b}d\boldsymbol{r} \end{aligned}$$

or

$$\begin{aligned} H_{12} &= H_{21} \\ &= -\frac{1}{2}\Delta_{12} - \frac{1}{\pi}\int e^{-r_a}\frac{Z_A}{r_a}e^{-r_b}d\boldsymbol{r} - \frac{1}{\pi}\int e^{-r_a}\left(-\frac{1}{r_a} + \frac{Z_B}{r_b}\right)e^{-r_b}d\boldsymbol{r} \\ &\quad -\frac{1}{\pi}\int e^{-r_a}\frac{Z_P}{r_p}e^{-r_b}d\boldsymbol{r}. \end{aligned} \tag{22}$$

The second and the third terms on the right hand side of (22) can be calculated in the same way as (18);

$$\begin{aligned}\frac{1}{\pi}\int\frac{\mathrm{e}^{-(r_\mathrm{a}+r_\mathrm{b})}}{r_\mathrm{a}}\mathrm{d}\boldsymbol{r} &= \frac{1}{\pi}\int_{-1}^{1}\mathrm{d}\mu\int_{1}^{\infty}\mathrm{e}^{-R_0\lambda}\frac{2}{R_0(\lambda+\mu)}(\lambda^2-\mu^2)\mathrm{d}\lambda\frac{\pi R_0^3}{4}\\ &= \mathrm{e}^{-R_0}(1+R_0)\\ &= \frac{1}{\pi}\int\frac{\mathrm{e}^{-(r_\mathrm{a}+r_\mathrm{b})}}{r_\mathrm{b}}\mathrm{d}\boldsymbol{r}.\end{aligned}$$

The last term on the right hand side of (22) includes another type of integration but can be calculated similarly (see Appendix II). Finally $H_{12}=H_{21}$ reduces to

$$\begin{aligned}H_{12} &= H_{21}\\ &= -\frac{1}{2}\Delta_{12}+\mathrm{e}^{-R_0}(1-Z_\mathrm{A}-Z_\mathrm{B})(R_0+1)\\ &\quad -Z_\mathrm{P}\left[\frac{2R_1R_2}{R_0^3}\left\{\mathrm{e}^{-R_0}(3+3R_0+R_0^2)(\log 2R_0+\gamma)-3R_0\mathrm{e}^{-R_0}\right.\right.\\ &\quad \left.\left.+\mathrm{e}^{R_0}(3-3R_0+R_0^2)\mathrm{Ei}(-2R_0)\right\}+\frac{6R_1R_2-R_0^2}{R_0^3}\mathrm{e}^{-R_0}(R_0+R_0^2)\right]. \qquad (23)\end{aligned}$$

Here, $\gamma=0.5772\ldots$ is Euler's constant and

$$\mathrm{Ei}(-x)=-\int_x^\infty\frac{\mathrm{e}^{-t}}{t}\mathrm{d}t$$

is the exponential integral function.

For other off-diagonal elements, H_{13} and H_{23}, another kind of integrations like $\int\mathrm{e}^{-r_\mathrm{a}}\frac{1}{r_\mathrm{b}}\mathrm{e}^{-r_\mathrm{P}}\mathrm{d}\boldsymbol{r}$ are necessary (see Appendix III). The final results are

$$\begin{aligned}H_{13} &= H_{31}\\ &= -\frac{1}{2}\Delta_{13}+\mathrm{e}^{-R_1}(1-Z_\mathrm{A}-Z_\mathrm{P})(R_1+1)\\ &\quad -Z_\mathrm{B}\left[R_1^2\mathrm{e}^{-R_1}\left(\frac{2R_0R_2}{R_1^2}\log\frac{R_0}{R_2}-\frac{R_0+R_2}{R_1}\right)\right.\\ &\quad \times\left\{\mathrm{e}^{-2R_2}\left(\frac{6R_2^2}{R_1^3}+\frac{6R_2}{R_1^3}+\frac{3}{R_1^3}+\frac{6R_2}{R_1^2}+\frac{3}{R_1^2}+\frac{1}{R_1}\right)+\left(\frac{3}{R_1^3}+\frac{3}{R_1^2}+\frac{1}{R_1}\right)\right\}\\ &\quad -R_0R_2\mathrm{e}^{R_1}\left[-\mathrm{e}^{-2R_0}\left\{\left(-\frac{12R_0^2}{R_1^3}-\frac{12R_0}{R_1^3}-\frac{6}{R_1^3}+\frac{12R_0}{R_1^2}+\frac{6}{R_1^2}-\frac{2}{R_1}\right)\log\frac{2R_0}{R_1}\right.\right.\\ &\quad \left.\left.+\left(-\frac{6R_0}{R_1^3}-\frac{9}{R_1^3}+\frac{6}{R_1^2}\right)\right\}+\left(\frac{6}{R_1^3}-\frac{6}{R_1^2}+\frac{2}{R_1}\right)\mathrm{Ei}(-2R_0)\right]\\ &\quad +R_0R_2\mathrm{e}^{-R_1}\left[-\mathrm{e}^{-2R_2}\left\{\left(-\frac{12R_2^2}{R_1^3}-\frac{12R_2}{R_1^3}-\frac{6}{R_1^3}-\frac{12R_2}{R_1^2}-\frac{6}{R_1^2}-\frac{2}{R_1}\right)\log\frac{2R_2}{R_1}\right.\right.\\ &\quad \left.\left.+\left(-\frac{6R_2}{R_1^3}-\frac{9}{R_1^3}-\frac{6}{R_1^2}\right)\right\}+\left(\frac{6}{R_1^3}+\frac{6}{R_1^2}+\frac{2}{R_1}\right)\mathrm{Ei}(-2R_2)\right]\\ &\quad \left.+R_1^2\mathrm{e}^{-R_1}\mathrm{e}^{-2R_2}\left(\frac{1}{R_1}+\frac{2R_2}{R_1^2}+\frac{1}{R_1^2}\right)\left(1+\frac{6R_0R_2}{R_1^2}\right)\right]. \qquad (24)\end{aligned}$$

$$H_{23} = H_{32} = H_{13}(R_1 \to R_2,\ R_2 \to R_1,\ Z_A \to Z_B,\ Z_B \to Z_A). \tag{25}$$

Substituting Eqs.(14) through (25) into Eq.(13), we obtain the electronic potential $E(R_0, R)$. We calculate the total energy $E_{\text{total}}(R_0)$ again by the variational method or by minimizing

$$E_{\text{total}}(R_0) = \min. \left\{ \frac{\int \psi(R)^* \mathcal{H}^A \psi(R) \mathrm{d}R}{\int \psi(R)^* \psi(R) \mathrm{d}R} \right\}. \tag{26}$$

As the variational wave function for proton, we take a linear combination of two Gaussian functions

$$\psi(R) = \beta_1 \mathrm{e}^{-\lambda(R-z_0)^2} + \beta_2 \mathrm{e}^{-\lambda(R+z_0)^2}, \tag{27}$$

with variational parameters λ, z_0, β_1, and β_2. The variational procedures with respect to β_1, and β_2 are performed in the same way as determining α_1, α_2 and α_3, but those related to λ and z_0 require numerical treatment.

III. RESULTS

Some examples of adiabatic potential including the constant terms, $Z_A Z_P/R_1 + Z_B Z_P/R_2 + Z_A Z_B/R_0$, are shown in Fig.2. Although our computation may be performed for arbitrary set of Z_A, Z_B and Z_P, here we assume for the sake of later convenience $Z_A + Z_B + Z_P = 1$ and $Z_A = Z_B$. The widths of the figures are taken to bo proportional to the hydrogen bond length R_0.

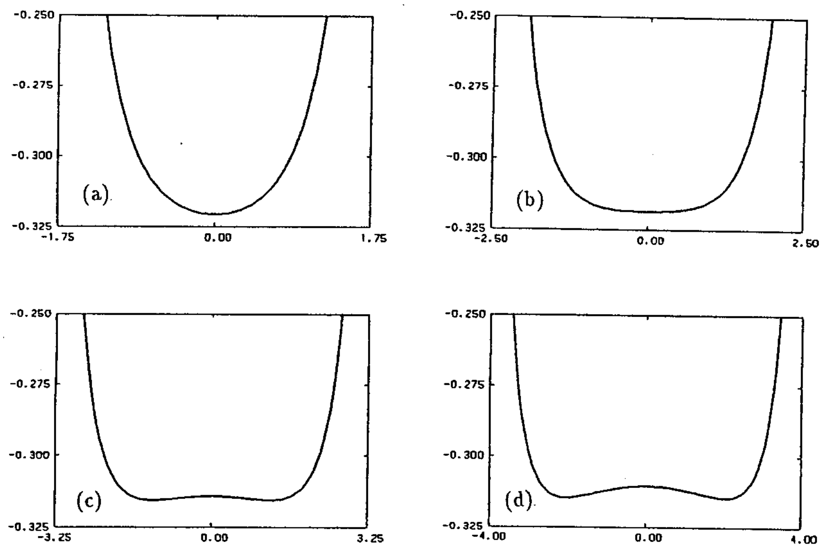

Fig.2 Adiabatic potentials for $Z_A = Z_B = 0.1$ and $Z_P = 0.8$:
(a)$R_0 = 3.5$, (b)$R_0 = 5.0$, (c)$R_0 = 6.5$, and (d)$R_0 = 8.0$ (in atomic units).

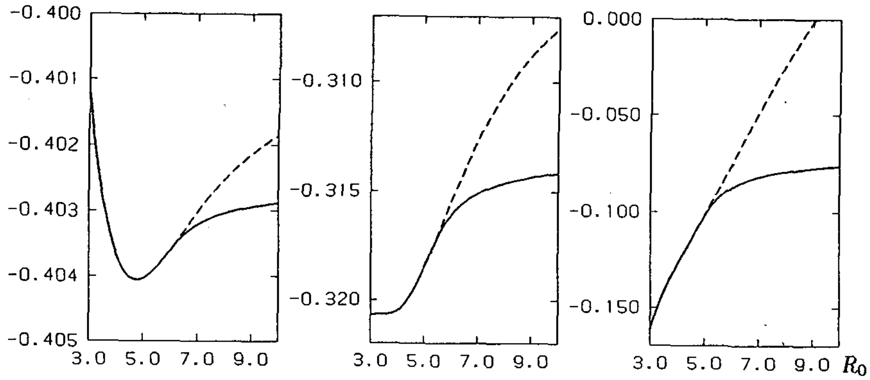

Fig.3 Minimum value of the adiabatic potential vs. R_0: (a)$Z_A = Z_B = 0.05$, $Z_P = 0.9$, (b)$Z_A = Z_B = 0.1$, $Z_P = 0.8$, and (c)$Z_A = Z_B = 0.3$, $Z_P = 0.4$. Solid lines denote the minimum of potential, and broken lines the potential at the center of A and B.

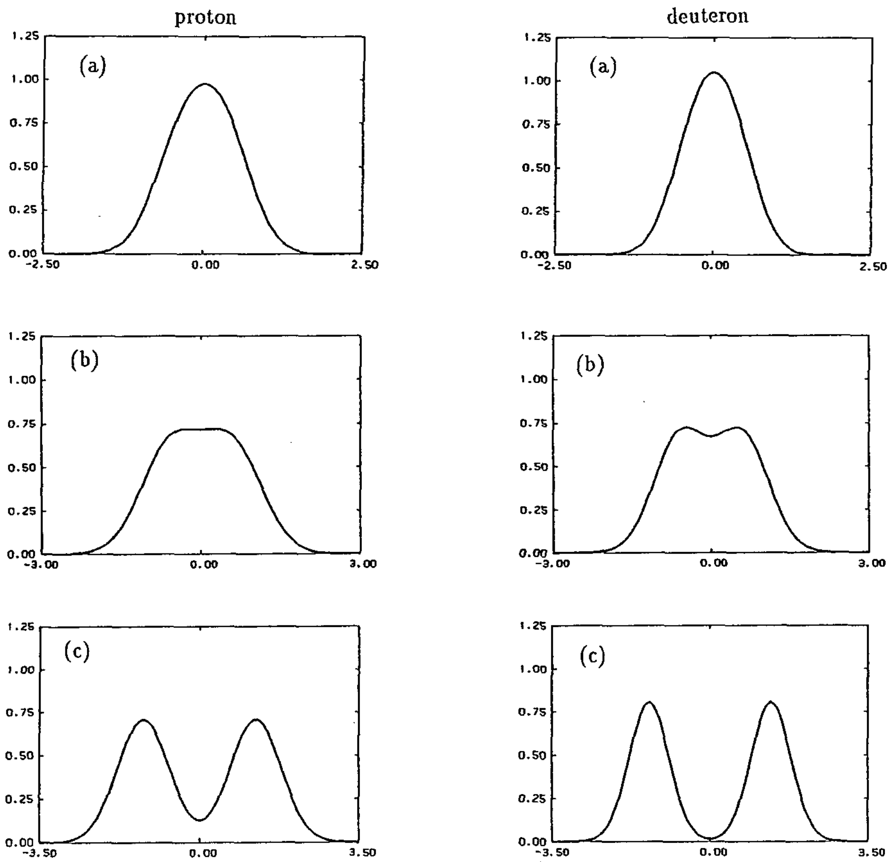

Fig.4 Wave functions of proton and deuteron ($Z_A = Z_B = 0.1$, $Z_P = 0.8$): (a)$R_0 = 5.0$, (b)$R_0 = 6.0$, and (c)$R_0 = 7.0$.

In Fig.3, we show the minimum of the potential as the function of R_0. Solid lines denote the minimum of potential, and broken lines the potential at the center of two cations. In the case of $R_0 \lesssim 3.0$, no minima are found in the potential and there is only a potential barrier at the center. We show the distributions of a proton and a deuteron in the hydrogen bond in Fig.4 for various values of R_0. The three figures on the left-hand side are wave functions of a proton, and those on the right-hand side are of a deuteron.

We also obtain the distribution of electron, $\rho(\boldsymbol{r})$, in the hydrogen bond as

$$\rho(\boldsymbol{r}) = \int |\varphi(\boldsymbol{r}, R)|^2 |\psi(R)|^2 \mathrm{d}R. \tag{28}$$

In Fig.5, we show an example which shows the difference in the electron distribution in the cases of the proton and the deuteron in the same adiabatic potential.

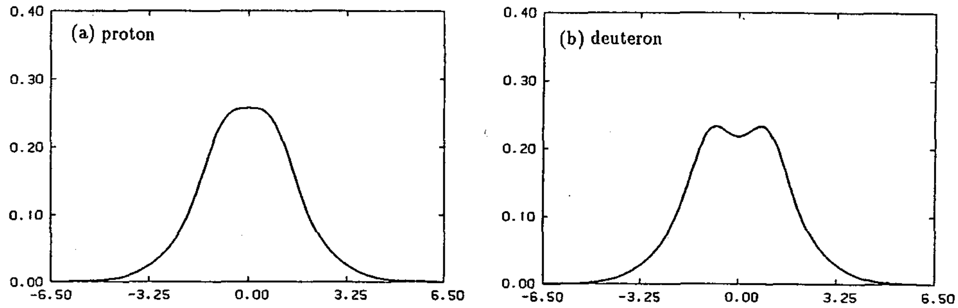

Fig.5 Distribution of electron ($Z_A = Z_B = 0.1$, $Z_P = 0.8$, and $R_0 = 6.5$): Cation A is at -3.25 and cation B at 3.25. (a) proton, and (b) deuteron.

These results are preliminary and more extensive investigation may be necessary to apply our model to real hydrogen-bonding materials. The analysis of the interactions between two dimers composed of two hydrogen bonds described above is now in progress and the results will be reported elsewhere.

REFERENCES

1) K. Gesi: J. Phys. Soc. Jpn., **48** (1980) 886.

2) for example, L. Pauling and E. B. Wilson: *Introduction to Quantum Physics*, McGraw-Hill Book Company.

APPENDIX I. INTEGRATION OF $\int \exp[-(r_a + r_b)]d\boldsymbol{r}$

We express the volume integral into the spheroidal coordinates

$$\lambda = \frac{r_1 + r_2}{R}, \quad \mu = \frac{r_1 - r_2}{R},$$

and,

$$\int d\boldsymbol{r} = \int_0^{2\pi} d\varphi \int_{-1}^{1} d\mu \int_1^{\infty} d\lambda \frac{R^3}{8}(\lambda^2 - \mu^2),$$

and evaluate the integral

$$\begin{aligned} \frac{1}{\pi}\int e^{-(r_a+r_b)} d\boldsymbol{r} &= \frac{1}{\pi} 2\pi \frac{R_0^3}{4} \int_{-1}^{1} d\mu \int_1^{\infty} e^{-R_0\lambda}(\lambda^2 - \mu^2) d\lambda \\ &= R_0^3 e^{-R_0}\left(\frac{1}{3R_0} + \frac{1}{R_0^2} + \frac{1}{R_0^3}\right). \end{aligned}$$

APPENDIX II. INTEGRATION OF $\int \exp[-(r_a + r_b)]/r_p d\boldsymbol{r}$

Taking spheroidal coordinates, we rewrite $1/r_p$ as

$$\begin{aligned} \frac{1}{r_p} &= \sqrt{\frac{R_0}{R_2 r_a^2 + R_1 r_b^2 - R_0 R_1 R_2}} \\ &= \frac{2}{\sqrt{R_0^2(\lambda^2 + \mu^2) + 2\lambda\mu R_0(R_2 - R_1) - 4R_1R_2}}. \end{aligned}$$

We then have

$$\begin{aligned} I_1 &= \frac{1}{\pi}\int e^{-r_a}\frac{1}{r_p}e^{-r_b} d\boldsymbol{r} \\ &= \frac{R_0^3}{4}\int_{-1}^{1}\int_1^{\infty} \frac{e^{-R_0\lambda}(\lambda^2 - \mu^2) d\lambda d\mu}{\sqrt{R_0^2(\lambda^2 + \mu^2) + 2\lambda\mu R_0(R_2 - R_1) - 4R_1R_2}} \\ &= \frac{R_0^2}{2}\int_1^{\infty} e^{-R_0\lambda}\left\{\lambda^2 \int_{-1}^{1} \frac{d\mu}{\sqrt{R_0^2(\lambda^2 + \mu^2) + 2\lambda\mu R_0(R_2 - R_1) - 4R_1R_2}}\right. \\ &\qquad \left. - \int_{-1}^{1} \frac{\mu^2 d\mu}{\sqrt{R_0^2(\lambda^2 + \mu^2) + 2\lambda\mu R_0(R_2 - R_1) - 4R_1R_2}}\right\} d\lambda \\ &= \frac{R_0^2}{2}\int_1^{\infty} e^{-R_0\lambda}\left\{\frac{2R_1R_2}{R_0^2}(3\lambda^2 - 1)\log\left|\frac{\lambda+1}{\lambda-1}\right| - 2\lambda\left(\frac{6R_1R_2}{R_0^2} - 1\right)\right\} d\lambda. \end{aligned}$$

The first term in { } of the right hand side is integrated as

$$\begin{aligned}
&\int_1^\infty e^{-\beta x}(3x^2-1)(\log|x+1|-\log|x-1|)dx \\
=\;& \int_2^\infty e^{-\beta(t-1)}(3t^2-6t+2)\log t dt - \int_0^\infty e^{-\beta(t+1)}(3t^2+6t+2)\log t dt \\
=\;& e^\beta\left[e^{-2\beta}\left\{\frac{9}{\beta^3}+\left(\frac{6}{\beta^3}+\frac{6}{\beta^2}+\frac{2}{\beta}\right)\log 2\right\}+\left(\frac{6}{\beta^3}-\frac{6}{\beta^2}+\frac{2}{\beta}\right)\int_2^\infty e^{-\beta t}\frac{1}{t}dt\right] \\
&-e^{-\beta}\left\{\frac{9}{\beta^3}+\frac{6}{\beta^2}-\left(\frac{6}{\beta^3}+\frac{6}{\beta^2}+\frac{2}{\beta}\right)(\gamma+\log\beta)\right\} \\
=\;& e^{-\beta}\left\{\left(\frac{6}{\beta^3}+\frac{6}{\beta^2}+\frac{2}{\beta}\right)(\log 2\beta+\gamma)-\frac{6}{\beta^2}\right\}-e^\beta\left(\frac{6}{\beta^3}-\frac{6}{\beta^2}+\frac{2}{\beta}\right)\mathrm{Ei}(-2\beta).
\end{aligned}$$

Here, we have used

$$\int_0^\infty e^{-\beta t}\log t dt = -(\gamma+\log\beta)/\beta.$$

The final result of I_1 is

$$\begin{aligned}
I_1 \;=\;& -\frac{2R_1R_2}{R_0^3}\left\{e^{-R_0}(3+3R_0+R_0^2)(\log 2R_0+\gamma)-3R_0e^{-R_0}\right. \\
&\left.+e^{R_0}(3-3R_0+R_0^2)\mathrm{Ei}(-2R_0)\right\}+\frac{6R_1R_2-R_0^2}{R_0^3}e^{-R_0}(R_0+R_0^2).
\end{aligned}$$

APPENDIX III. INTEGRATION OF $\int \exp[-(r_a+r_p)]/r_b d\boldsymbol{r}$

In spheroidal coordinates, $1/r_b$ is written as,

$$\frac{1}{r_b}=\frac{1}{R_1}\frac{2}{\sqrt{(\lambda^2+\mu^2)-2\lambda\mu\dfrac{R_0+R_2}{R_1}+\dfrac{4R_0R_2}{R_1^2}}}.$$

Substituting $r_1=-\dfrac{R_0+R_2}{R_1}$ and $r_2=-\dfrac{4R_0R_2}{R_1^2}$, we obtain

$$\frac{1}{r_b}=\frac{2}{R_1}\frac{2}{\sqrt{(\lambda^2+\mu^2)+2\lambda\mu r_1-r_2}}.$$

The integral we need becomes

$$\begin{aligned}
I_2 \;=\;& \frac{1}{\pi}\int e^{-r_a}\frac{1}{r_b}e^{-r_p}d\boldsymbol{r} \\
=\;& \frac{R_1^2}{2}\int_1^\infty e^{-R_1\lambda}\left\{\lambda^2\int_{-1}^1\frac{d\mu}{\sqrt{\mu^2+2\mu\lambda r_1+\lambda^2-r_2}}-\int_{-1}^1\frac{\mu^2 d\mu}{\sqrt{\mu^2+2\mu\lambda r_1+\lambda^2-r_2}}\right\}d\lambda \\
=\;& \frac{R_1^2}{2}\int_1^\infty e^{-R_1\lambda}\left\{\left(\lambda^2-\frac{3\lambda^2r_1^2-\lambda^2+r_2}{2}\right)\log\left|\frac{1+\lambda r_1+\sqrt{1+2\lambda r_1+\lambda^2-r_2}}{-1+\lambda r_1+\sqrt{1-2\lambda r_1+\lambda^2-r_2}}\right|\right. \\
&\left.-\frac{1-3\lambda r_1}{2}\sqrt{1+2\lambda r_1+\lambda^2-r_2}-\frac{1+3\lambda r_1}{2}\sqrt{1-2\lambda r_1+\lambda^2-r_2}\right\}d\lambda.
\end{aligned}$$

Here, we have to examine the range of variable λ before performing integration.

$$\sqrt{1-2\lambda r_2+\lambda^2-r_2}=\lambda-r_1, \qquad 1\le\lambda\le\infty,$$

$$\begin{cases} \sqrt{1+2\lambda r_2+\lambda^2-r_2}=-\lambda-r_1, & 1\le\lambda\le 1+\dfrac{2R_2}{R_1},\\ \sqrt{1+2\lambda r_2+\lambda^2-r_2}=\lambda+r_1, & 1+\dfrac{2R_2}{R_1}\le\lambda\le\infty. \end{cases}$$

The integral is thus divided into two parts:

$$\begin{aligned} I_2 &= \frac{R_1^2}{2}\left[\int_1^{1+2R_2/R_1} \mathrm{e}^{-R_1\lambda}\left\{-\frac{2R_0R_2}{R_1^2}(3\lambda^2-1)\log\frac{R_0}{R_2}+\frac{R_0+R_2}{R_1}(3\lambda^2-1)\right\}\mathrm{d}\lambda\right.\\ &\quad \left.+\int_{1+2R_2/R_1}^{\infty}\left\{-\frac{2R_0R_2}{R_1^2}(3\lambda^2-1)\log\left|\frac{\lambda+1}{\lambda-1}\right|+2\lambda\left(1+\frac{6R_0R_2}{R_1^2}\right)\right\}\mathrm{d}\lambda\right]. \end{aligned}$$

We can easily perform the first integral as

$$\begin{aligned} &\int_1^{1+2R_2/R_1}\mathrm{e}^{-R_1\lambda}\left\{-\frac{2R_0R_2}{R_1^2}(3\lambda^2-1)\log\frac{R_0}{R_2}+\frac{R_0+R_2}{R_1}(3\lambda^2-1)\right\}\mathrm{d}\lambda\\ &= \mathrm{e}^{-R_1}\left(\frac{2R_0R_2}{R_1^2}\log\frac{R_0}{R_2}-\frac{R_0+R_2}{R_1}\right)\\ &\quad\times\left\{\mathrm{e}^{2R_2}\left(\frac{12R_2^2}{R_1^3}+\frac{12R_2}{R_1^3}+\frac{6}{R_1^3}+\frac{12R_2}{R_1^2}+\frac{6}{R_1^2}+\frac{2}{R_1}\right)+2\left(\frac{1}{R_1}+\frac{3}{R_1^2}+\frac{3}{R_1^3}\right)\right\}. \end{aligned}$$

The first term of the second integral turns out to be

$$\begin{aligned} &\int_{1+2R_2/R_1}^{\infty}\mathrm{e}^{-R_1\lambda}(3\lambda^2-1)\log\left|\frac{\lambda+1}{\lambda-1}\right|\mathrm{d}\lambda\\ &= \int_{1+2R_2/R_1}^{\infty}\mathrm{e}^{-R_1\lambda}(3\lambda^2-1)\{\log|\lambda+1|-\log|\lambda-1|\}\mathrm{d}\lambda\\ &= \int_{2R_0/R_1}^{\infty}\mathrm{e}^{-R_1(t-1)}\{3(t-1)^2-1\}\log t\mathrm{d}t-\int_{2R_2/R_1}^{\infty}\mathrm{e}^{-R_1(t+1)}\{3(t+1)^2-1\}\log t\mathrm{d}t\\ &= \mathrm{e}^{R_1}\left[-\mathrm{e}^{-2R_0}\left\{\left(-\frac{12R_0^2}{R_1^3}-\frac{12R_0^2}{R_1^3}-\frac{6}{R_1^3}+\frac{12R_0}{R_1^2}+\frac{6}{R_1^2}-\frac{2}{R_1}\right)\log\frac{2R_0}{R_1}\right.\right.\\ &\quad\left.\left.+\left(-\frac{6R_0}{R_1^3}-\frac{9}{R_1^3}+\frac{6}{R_1^2}\right)\right\}+\left(\frac{6}{R_1^3}-\frac{6}{R_1^2}+\frac{2}{R_1}\right)\mathrm{Ei}\left(-\frac{2R_0}{R_1}\cdot R_1\right)\right]\\ &\quad-\mathrm{e}^{-R_1}\left[-\mathrm{e}^{-2R_2}\left\{\left(-\frac{12R_2^2}{R_1^3}-\frac{12R_2^2}{R_1^3}-\frac{6}{R_1^3}+\frac{12R_2}{R_1^2}+\frac{6}{R_1^2}-\frac{2}{R_1}\right)\log\frac{2R_2}{R_1}\right.\right.\\ &\quad\left.\left.+\left(-\frac{6R_2}{R_1^3}-\frac{9}{R_1^3}+\frac{6}{R_1^2}\right)\right\}+\left(\frac{6}{R_1^3}-\frac{6}{R_1^2}+\frac{2}{R_1}\right)\mathrm{Ei}\left(-\frac{2R_2}{R_1}\cdot R_1\right)\right]. \end{aligned}$$

The second term of the second integral becomes

$$\int_{1+2R_2/R_1}^{\infty}\mathrm{e}^{-R_1\lambda}\cdot 2\lambda\left(1+\frac{6R_0R_2}{R_1^2}\right)\mathrm{d}\lambda = 2\mathrm{e}^{-R_1}\mathrm{e}^{-2R_2}\left(\frac{1}{R_1}+\frac{2R_2}{R_1^2}+\frac{1}{R_1^2}\right)\left(1+\frac{6R_0R_2}{R_1^2}\right).$$

Finally we obtain

$$I_2 = R_1^2\mathrm{e}^{-R_1}\left(\frac{2R_0R_2}{R_1^2}\log\frac{R_0}{R_2}-\frac{R_0+R_2}{R_1}\right)$$

$$
\begin{aligned}
&\times \left\{ \mathrm{e}^{-2R_2} \left(\frac{6R_2^2}{R_1^3} + \frac{6R_2}{R_1^3} + \frac{3}{R_1^3} + \frac{6R_2}{R_1^2} + \frac{3}{R_1^2} + \frac{1}{R_1} \right) + \left(\frac{3}{R_1^3} + \frac{3}{R_1^2} + \frac{1}{R_1} \right) \right\} \\
&-R_0 R_2 \mathrm{e}^{R_1} \left[-\mathrm{e}^{-2R_0} \left\{ \left(-\frac{12R_0^2}{R_1^3} - \frac{12R_0}{R_1^3} - \frac{6}{R_1^3} + \frac{12R_0}{R_1^2} + \frac{6}{R_1^2} - \frac{2}{R_1} \right) \log \frac{2R_0}{R_1} \right.\right. \\
&\qquad \left.\left. + \left(-\frac{6R_0}{R_1^3} - \frac{9}{R_1^3} + \frac{6}{R_1^2} \right) \right\} + \left(\frac{6}{R_1^3} - \frac{6}{R_1^2} + \frac{2}{R_1} \right) \mathrm{Ei}(-2R_0) \right] \\
&+R_0 R_2 \mathrm{e}^{-R_1} \left[-\mathrm{e}^{-2R_2} \left\{ \left(-\frac{12R_2^2}{R_1^3} - \frac{12R_2}{R_1^3} - \frac{6}{R_1^3} - \frac{12R_2}{R_1^2} - \frac{6}{R_1^2} - \frac{2}{R_1} \right) \log \frac{2R_2}{R_1} \right.\right. \\
&\qquad \left.\left. + \left(-\frac{6R_2}{R_1^3} - \frac{9}{R_1^3} - \frac{6}{R_1^2} \right) \right\} + \left(\frac{6}{R_1^3} + \frac{6}{R_1^2} + \frac{2}{R_1} \right) \mathrm{Ei}(-2R_2) \right] \\
&+R_1^2 \mathrm{e}^{-R_1} \mathrm{e}^{-2R_2} \left(\frac{1}{R_1} + \frac{2R_2}{R_1^2} + \frac{1}{R_1^2} \right) \left(1 + \frac{6R_0 R_2}{R_1^2} \right).
\end{aligned}
$$

To calculate another integral $\frac{1}{\pi} \int \mathrm{e}^{-r_\mathrm{b}} \frac{1}{r_\mathrm{a}} \mathrm{e}^{-r_\mathrm{p}} \mathrm{d}\boldsymbol{r}$, we only need to replace R_1 by R_2 and R_2 by R_1 in the above result.