Numerical Analysis of a Model for Isolated Hydrogen Bond

Chieko TOTSUJI* and Takeo MATSUBARA†

Large isotope effects have been observed in various kinds of hydrogen bonded ferro/antiferroelectrics. In clarifying their origin, thermodynamic properties of the hydrogen bond are of essential importance. Two numerical methods are applied to analyze the model for isolated hydrogen bond at finite temperatures and the results of excited energy levels of proton or deuteron are examined. It is found that the second excited state is not far enough from the first excited state to be neglected discussing the thermodynamic properties of hydrogen bond especially in their ordered states.

1. INTRODUCTION

The hydrogen bond may be one of the most important agents constructing structures of large molecules related to life including DNA. The nature of the hydrogen bond, however, is still not completely clear and is the subject of both theoretical and experimental studies. Large isotope effects observed in hydrogen bonded ferro/antiferroelectrics are expected to provide us with a key to understand the physics of the hydrogen bond.

We have proposed a simple dimer model for isolated hydrogen bond[1-3], analyzed numerically its isotope effect, and compared the results with experiments. This model dimer consists of an electron and a proton or a deuteron sitting on the line connecting two heavy ions with positive charges. The total charge of a dimer is assumed to be neutral.

Constructing a simple cubic lattice composed of many model dimers, we have investigated the difference in the ground state between hydrogen bonds with proton and those with deuteron. The adiabatic approximation and variational method are applied and the dipole approximation is adopted for the interaction between dimers. Molecular field approximation is used to determine the magnitude of dipole moment in the lattice. There are three characteristic parameters in this model lattice: The mass of the proton (or deuteron) in a dimer, the hydrogen bond length or the distance between two large ions in a dimer, and the lattice constant of this model cubic lattice.

The phase diagrams with respect to hydrogen bond length and lattice constant have been calculated at 0 K[4,5]. Upon deuteration of hydrogen bonds, remarkable isotope effects have

---

* Department of Electrical and Electronic Engineering
† Institute for Condensed Matter Theory

been found in the transition temperature from the paraelectric to the antiferroelectric phase in agreement with reported experimental results[6-11].

To investigate the behavior of this model lattice at finite temperatures we have to compute the energies of excited states. In this paper, we compare the results of two methods of numerical computation of the excited states, the variational method and the finite element method, and determine the phase transition temperatures using four higher energy levels obtained by latter.

2. NUMERICAL ANALYSIS AND RESULTS

2.1 Variational Method

The Schrödinger equation to be solved is

$$(\mathcal{H}_e + \mathcal{H}_{p/d} + \mathcal{H}_{dipole})\Psi = E\Psi. \tag{1}$$

The first term on the left hand side is the Hamiltonian for electron and the second and third terms are the Hamiltonian for proton or deuteron, where we describe the interactions with other dimers as the dipole-dipole interaction.

We first adopt the adiabatic approximation to obtain the electronic potential in the hydrogen bond. The wave function is then written as

$$\Psi = \phi_e \psi_{p/d}, \tag{2}$$

where ϕ_e is the wave function for electron and $\psi_{p/d}$ is the wave function for proton or deuteron. The energy states of the electron as the function of the position of proton (or deuteron) work as the adiabatic potential on the hydrogen bond. The values of the bottom and central barrier of these potentials with respect to hydrogen bond length R_0 are listed in Appendix 1. We assume the charge of a proton to be $0.5e$ ($-e$ is the electronic charge) throughout this work.

We next solve the Schödinger equation for proton or deuteron in this electronic potential. We put the hydrogen bond parallel to the z-direction, and assume that the proton (or deuteron) moves one-dimensionally. In our variational method, we take the superposition of two Gaussians $\psi_0(z)$ as a trial function of the ground state. There are four variational parameters, A_1, A_2, λ_0 and z_0:

$$\psi_0(z) = A_1 e^{-\lambda_0(z-z_0)^2} + A_2 e^{-\lambda_0(z+z_0)^2}. \tag{3}$$

Another two functions, $\psi_1(z)$ and $\psi_2(z)$, are used as the trial functions for the first excited state with four variational parameters

$$\psi_1(z) = B_1 e^{-\lambda_1(z-z_1)^2} + B_2 e^{\lambda_1(z+z_1)^2}, \tag{4}$$

and the second excited states with five variational parameters

$$\psi_2(z) = C_1 e^{-\lambda_2(z-z_2)^2} + C_2 e^{-\lambda_2 z^2} + C_3 e^{-\lambda_2(z+z_2)^2}. \tag{5}$$

To calculate higher excited states with high accuracy, however, we need much more variational parameters; for example, we may take one more new parameter λ_2' for the second excited states and write the wave function as

$$\psi_2(z) = C_1 e^{-\lambda_2(z-z_2)^2} + C_2 e^{-\lambda_2' z^2} + C_3 e^{-\lambda_2(z+z_2)^2} \tag{6}$$

instead of (5). Higher excited states naturally require more variational parameters and accordingly more complicated procedures to normalize and diagonalize wave functions. Therefore it may be impossible to obtain higher-than-third excited states. Some examples of parameters for wave functions of the forms (3), (4) and (5) are listed in Appendices 2 and 3.

2.2 Finite Element Method

In order to obtain higher excited states for proton or deuteron, the finite element method (FEM) may be one of useful methods. Since the wave function for proton or deuteron is one-dimensional, the formulation of FEM is quite straightforward. The one dimensional FEM provides us with as many eigen values and the eigen functions as the number of the elements. We divide the hydrogen bond length into 100 elements and adopt the linear basis functions.

The lowest three energy levels obtained are listed in Table I and II in comparison with the results of the variational method. In the latter, the trial function (5) is used to obtain the second excited energy. As can be seen in Appendix 1, the adiabatic potential has a profile of single minimum when the hydrogen bond length is less than about 4.8 a.u. (2.540 Å) in this model. The proton (or deuteron) therefore has no other place to sit than the center of the bond. The variational calculation with two or more Gaussian functions then encounters with some difficulties to minimize the energy especially in higher excited states. In also the region of large hydrogen bond lengths, our variational method can not find the minimum of energy.

We show the lowest five energy levels for proton and deuteron in the hydrogen bond with and without interactions with other dimers in Figs.1 and 2, respectively. The lattice constant is assumed to be $2R_0$. Some examples of wave functions are illustrated in Fig.3.

We have a good agreement between the results obtained by different methods for small R_0 and for lower energy levels. The variational method, however, can be used to discuss the properties of hydrogen bond only at very low temperatures.

Table I. Lowest three energy levels (in Ryd.) of isolated hydrogen bond with proton obtained by variational method and FEM.

| R_0(a.u.)	variational ε_0	FEM ε_0	variational ε_1	FEM ε_1	variational ε_2	FEM ε_2
4.8	-0.138389	-0.138389	-0.136107	-0.136105	-0.129958	-0.133198
4.9	-0.136639	-0.136640	-0.134686	-0.134686	-0.129350	-0.132018
5.0	-0.134897	-0.134898	-0.133279	-0.133479	-0.128569	-0.130831
5.1	-0.133172	-0.133176	-0.131892	-0.131895	-0.127659	-0.129633
5.2	-0.131483	-0.131492	-0.130538	-0.130545	-0.126705	-0.128417
5.3	-0.129858	-0.129877	-0.129230	-0.129240	-0.125657	-0.127166
5.4	-0.128335	-0.128373	-0.127981	-0.127997	-0.124432	-0.125857
5.5	-0.126958	-0.127020	-0.126807	-0.126829	-0.122982	-0.124471
5.6	-0.125762	-0.126830	-0.125718	-0.125745	-0.121432	-0.123026
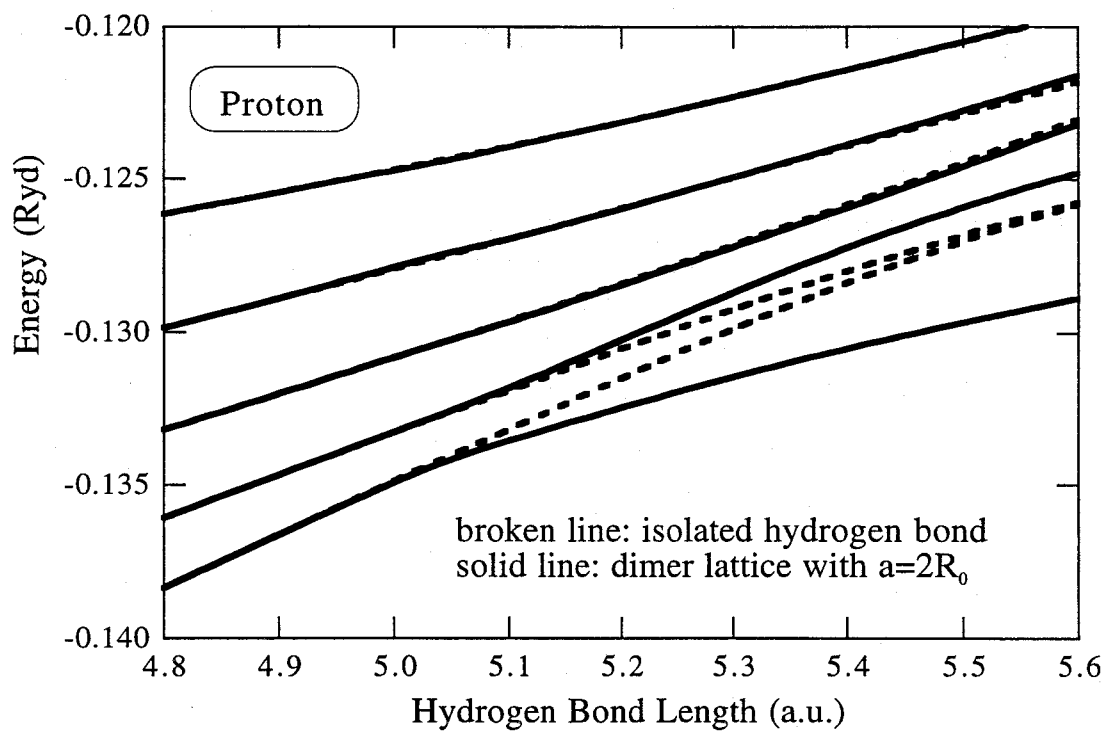
Fig.1 Lowest five energy levels of proton dimer obtained by FEM.
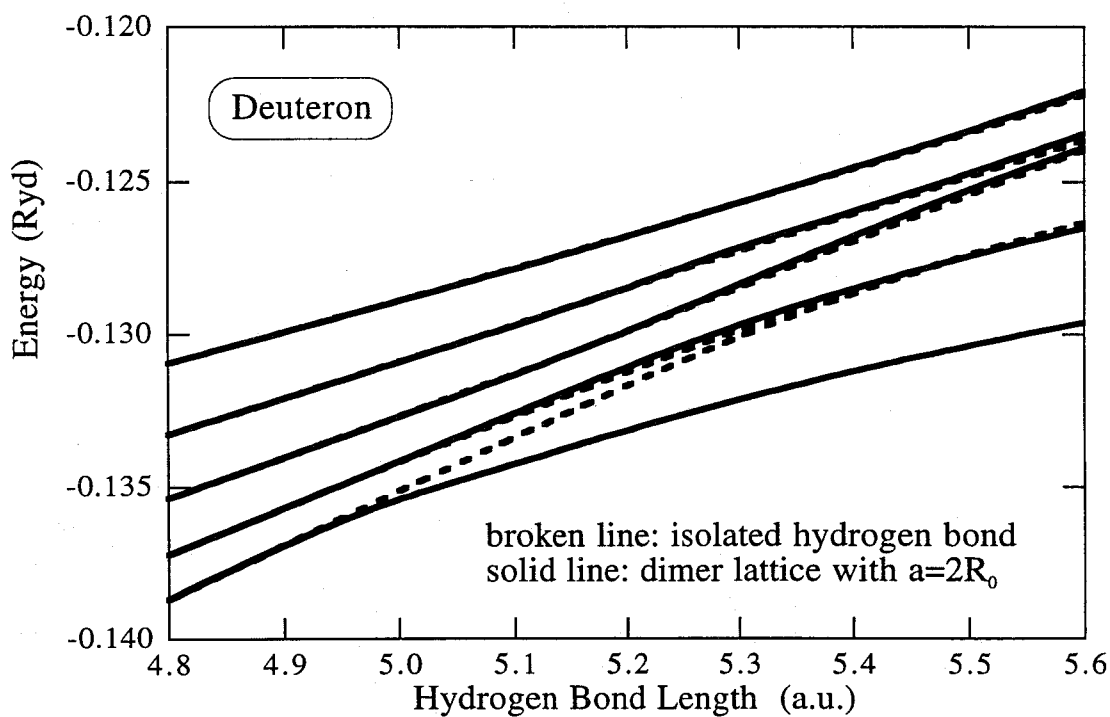

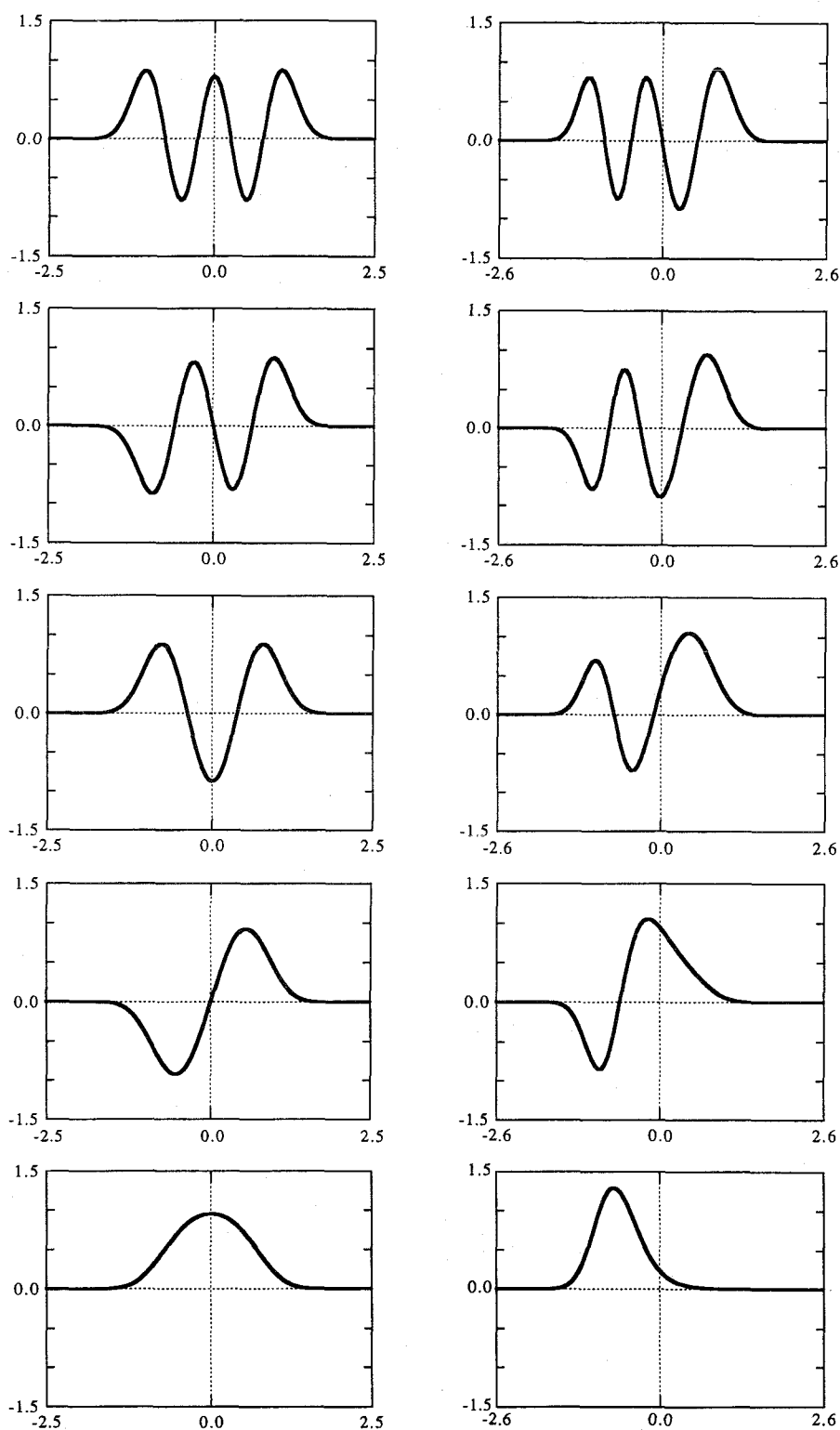Fig.2 Lowest five energy levels of deuteron dimer obtained by FEM.

Fig.3 Wave functions of proton and deuteron in hydrogen bond by FEM.
Left column: Proton with $R_0 = 5.0$ a.u. and $a = 2R_0$.
Right column: Deuteron with $R_0 = 5.2$ a.u. and $a = 2R_0$.
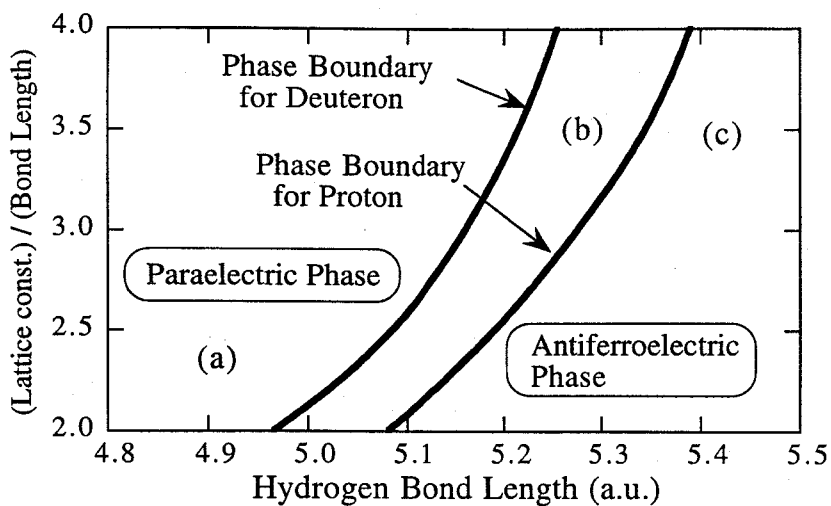(With increasing order in energy from bottom.)

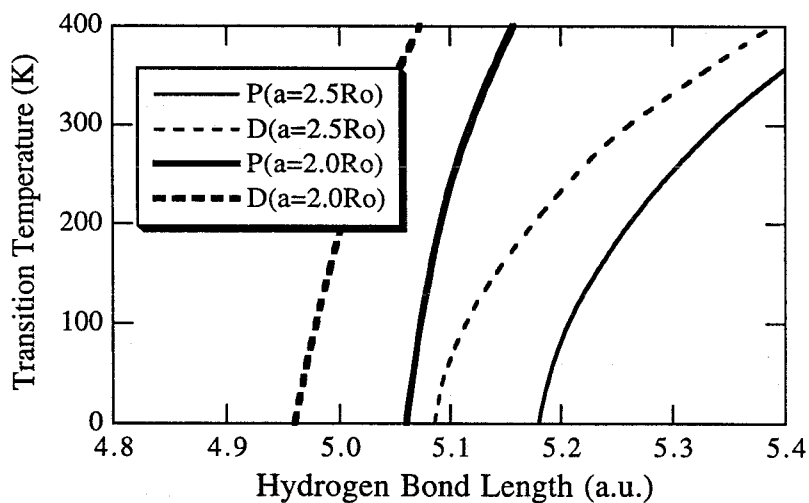**Fig.4 Phase diagram for hydrogen bonded dimer lattice at 0 K.**

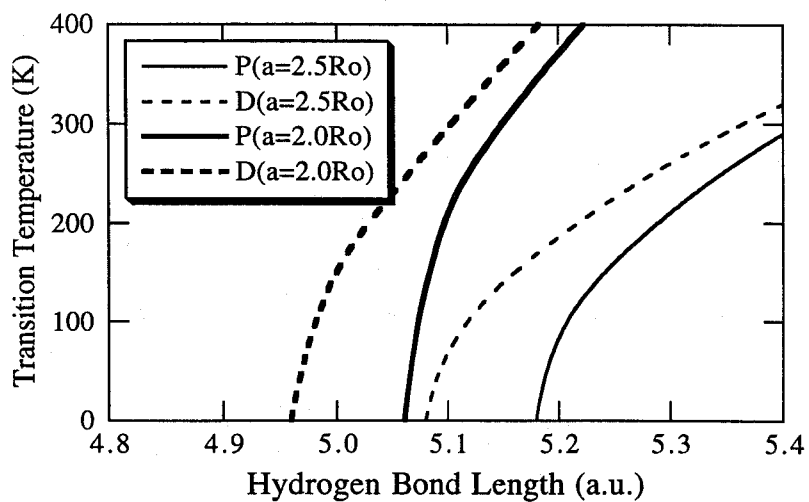**Fig.5 Transition temperature obtained from lowest two energy levels.**

Fig.6 Transition temperature obtained from lowest five energy levels.

Table II. Lowest three energy levels (in Ryd.) of isolated hydrogen bond with deuteron obtained by variational method and FEM.

R_0(a.u.)	variational ε_0	FEM ε_0	variational ε_1	FEM ε_1	variational ε_2	FEM ε_2
4.8	-0.138715	-0.138715	-0.137243	-0.137240	-0.133367	-0.135390
4.9	-0.136920	-0.136920	-0.135702	-0.135700	-0.132258	-0.134033
5.0	-0.135134	-0.135135	-0.134179	-0.134179	-0.131148	-0.132675
5.1	-0.133374	-0.133377	-0.132687	-0.132690	-0.130023	-0.131312
5.2	-0.131669	-0.131680	-0.131243	-0.131248	-0.128836	-0.129929
5.3	-0.130070	-0.130095	-0.129866	-0.129875	-0.127484	-0.128496
5.4	-0.128636	-0.128678	-0.128576	-0.128591	-0.125913	-0.126988
5.5	-0.127401	-0.127437	-0.127391	-0.127409	-0.124287	-0.125447
5.6	-0.126317	-0.126341	-0.126315	-0.126334	-0.122572	-0.123973

2.3 Thermodynamical Analysis

The electric dipole moment of a dimer is calculated from charge distributions of electron and proton (or deuteron) using their wave functions. We calculate expectation values of dipole moment at 0 K self-consistently and obtain the phase diagrams with respect to hydrogen bond length and lattice constant as shown in Fig.4. The phase boundaries are determined by the condition whether the dipole moment is finite or not.

In the area (a) in Fig.4, $\langle \mu \rangle_0 = 0$ for the hydrogen bond both with proton and with deuteron at 0 K. The lattice in this area is in the paraelectric state. When R_0 increases and/or a decreases and the lattice is in the area (b) in Fig.4, the expectation value of $\langle \mu \rangle_0^D$ (dipole moment of hydrogen bond with deuteron) becomes finite but we still have $\langle \mu \rangle_0^P$ (dipole moment of the hydrogen bond with proton) $= 0$: Thus only the lattice with deuteron dimers is in the antiferroelectric state. In the area (c), the lattice both with proton dimers and with deuteron dimers have finite values of $\langle \mu \rangle_0$. The existence of a wide area (b) indicates the large isotope effects in phase transition of hydrogen bond.

We calculate the magnitude of average dipole moment at finite temperatures $\langle \mu \rangle_T$ from the thermal average of positions of electron and proton (or deuteron) on the hydrogen bond by using five lowest energy states. The thermal average of dipole moment vanishes at the transition temperature.

The transition temperature is plotted as a function of R_0 for various values of lattice constant in Figs.5 and 6. The transition temperatures in Fig.5 are calculated from the lowest two energy levels obtained by variational method and those in Fig.6 are derived from five levels by FEM. A large difference between two results indicates the inaccuracy of the treatment based on the variation with two levels for this hydrogen bond model. Some examples of the magnitude of dipole moment at 0 K are listed and illustrated in Appendix 4.

3. CONCLUDING REMARKS

We have examined two numerical processes to analyze the nature of hydrogen bond. It is found that the second excited state is not far enough from the first excited state to be neglected when we discuss the thermodynamic properties of hydrogen bond, especially in their ordered states. More thermodynamical analyses such as entropies and heat capacities are now going on and will appear elsewhere.

ACKNOWLEDGEMENTS

REFERENCES

1. C. Totsuji and T. Matsubara, Memoirs of Fac. Eng. Okayama Univ. **28** 39 (1993).

2. C. Totsuji and T. Matsubara, Solid State Commun. **89** 677 (1994).

3. C. Totsuji and T. Matsubara, J. Phys. Soc. Jpn. **63** 2760 (1994).

4. C. Totsuji and T. Matsubara, J. Kor. Phys. Soc. Supp. (Proceedings of 9th Meeting on Ferroelectricity, Seoul, Korea, Aug. 1997) (in press).

5. C. Totsuji and T. Matsubara, Solid State Commun. **105** 731 (1998).

6. K. Geshi, J. Phys. Soc Jpn. **48** 886 (1980).

7. K. Geshi, J. Phys. Soc Jpn. **50** 3185 (1981).

8. Y. Noda, S. Uchiyama, K. Kafuku, H. Kasatani, and H. Terauchi, J. Phys. Soc Jpn. **59** 2804 (1990).

9. Y. Noda, and H. Kasatani, Y. Watanabe, and K. Geshi, J. Phys. Soc Jpn. **59** 3249 (1990).

10. M. Ichikawa, T. Gustafsson, and I. Olovsson, Acta Cryst. **C48** 603 (1992).

11. Y. Noda, I. Tamura, Y. Kuroiwa, T. Mochida, and T. Sugawara, J. Phys. Soc Jpn. **63** 4286 (1994).

Appendix 1. Adiabatic Potential

Table A1. Adiabatic potential (in Ryd) produced by an electron and two ions.

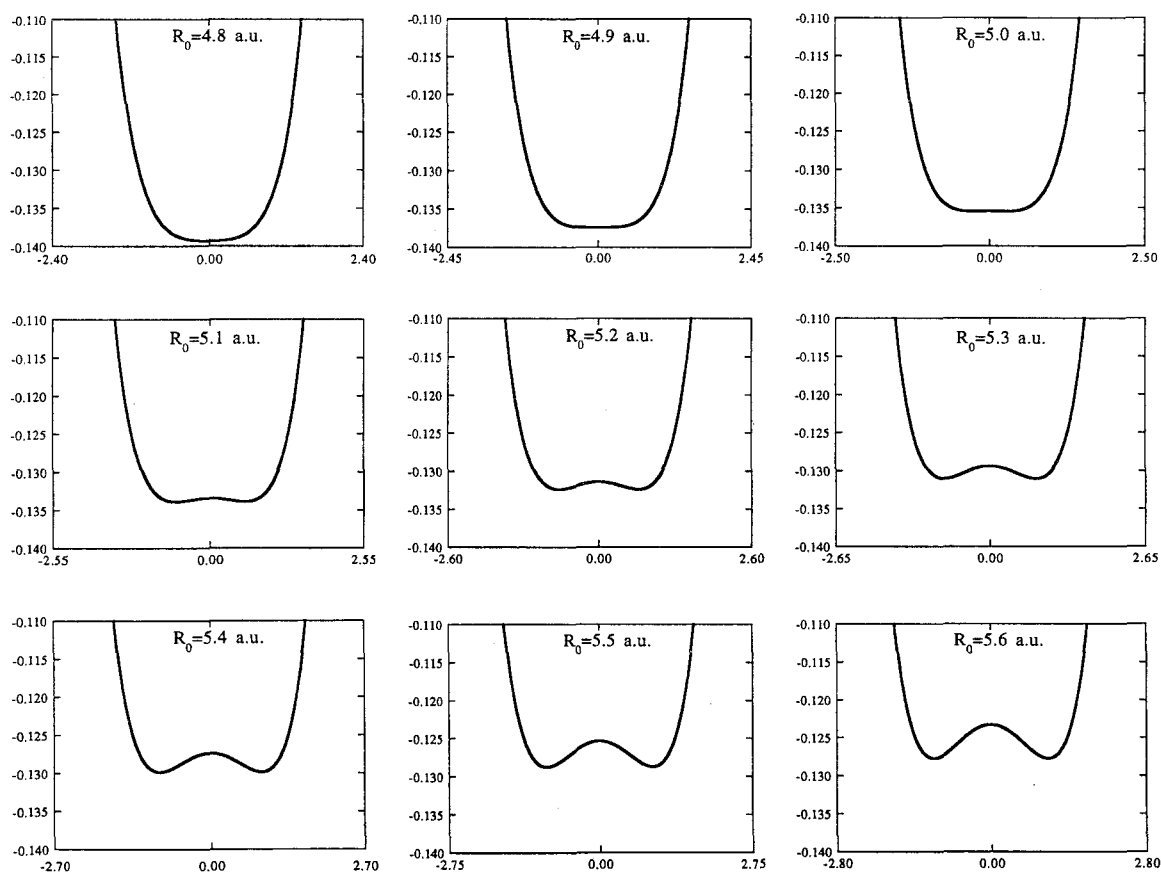| R_0(a.u.)	R_0(Å)	Minimum value at the bottom	Barrier height from the bottom
4.8	2.540	-0.13933500	0.0
4.9	2.593	-0.13738188	0.0000030
5.0	2.646	-0.13555032	0.0001433
5.1	2.699	-0.13390034	0.0004804
5.2	2.752	-0.13241242	0.0009939
5.3	2.805	-0.13106955	0.0016655
5.4	2.858	-0.12986028	0.0024823
5.5	2.910	-0.12876275	0.0034208
5.6	2.963	-0.12777210	0.0044742

Fig. A1. Profiles of adiabatic potential.

Appendix 2. Wave Function Parameters for Proton

Table A2-1. Parameters for proton wave function in the ground state.

R_0(a.u.)	λ_0	z_0	A_1	A_2
4.8	3.579	0.2770	0.563008	0.563008
4.9	3.348	0.3101	0.572553	0.572553
5.0	3.133	0.3516	0.585030	0.585030
5.1	2.941	0.4042	0.601382	0.601382
5.2	2.788	0.4709	0.622474	0.622474
5.3	2.694	0.5541	0.647868	0.647868
5.4	2.697	0.6547	0.674488	0.674488
5.5	2.867	0.7718	0.695769	0.695769
5.6	3.320	0.8988	0.705457	0.705457

Table A2-2. Parameters for proton wave function in the first excited state.

R_0(a.u.)	λ_1	z_1	B_1	B_2
4.8	4.359	0.4540	0.774198	-0.774198
4.9	4.138	0.4911	0.760672	-0.760672
5.0	3.993	0.5356	0.745842	-0.745842
5.1	3.831	0.5852	0.734230	-0.734230
5.2	3.678	0.6409	0.724991	-0.724991
5.3	3.654	0.7061	0.716540	-0.716540
5.4	3.587	0.7757	0.711872	-0.711872
5.5	3.657	0.8518	0.708866	-0.708866
5.6	3.710	0.9298	0.707686	-0.707686

Table A2-3. Parameters for proton wave function in the second excited state.

R_0(a.u.)	λ_2	z_2	C_1	C_2	C_3
4.8	14.79	0.890	-0.675004	0.301773	-0.675004
4.9	15.29	0.890	-0.675075	0.301243	-0.675075
5.0	15.68	0.890	-0.639289	0.429916	-0.639289
5.1	14.68	0.930	-0.620371	0.482049	-0.620371
5.2	13.39	0.985	-0.593493	0.545425	-0.593493
5.3	12.01	1.051	-0.549455	0.630891	-0.549455
5.4	10.44	1.133	-0.479131	0.736616	-0.479131
5.5	8.65	1.235	-0.373915	0.849771	-0.373915
5.6	6.79	1.357	-0.247248	0.937829	-0.247248

Appendix 3. Wave Function Parameters for Deuteron

Table A3-1. Parameters for deuteron wave function in the ground state.

R_0(a.u.)	λ_0	z_0	A_1	A_2
4.8	4.530	0.2416	0.560897	0.560897
4.9	4.182	0.2778	0.572708	0.572708
5.0	3.862	0.3263	0.589382	0.589382
5.1	3.594	0.3921	0.612868	0.612868
5.2	3.426	0.4806	0.644042	0.644042
5.3	3.446	0.5941	0.677966	0.677966
5.4	3.867	0.7310	0.701504	0.701504
5.5	4.688	0.8606	0.706766	0.706766
5.6	5.196	0.9561	0.707083	0.707078

Table A3-2. Parameters for deuteron wave function in the first excited state.

R_0(a.u.)	λ_1	z_1	B_1	B_2
4.8	5.420	0.3966	0.781711	-0.781711
4.9	5.172	0.4398	0.760387	-0.760387
5.0	4.942	0.4893	0.742810	-0.742810
5.1	4.684	0.5471	0.729545	-0.729545
5.2	4.616	0.6176	0.717795	-0.717795
5.3	4.616	0.6971	0.711123	-0.711123
5.4	4.657	0.7820	0.708298	-0.708298
5.5	4.878	0.8706	0.707324	-0.707324
5.6	5.186	0.9571	0.707136	-0.707136

Table A3-3. Parameters for deuteron wave function in the second excited state.

R_0(a.u.)	λ_2	z_2	C_1	C_2	C_3
4.8	24.50	0.723	-0.659382	0.363343	-0.659382
4.9	22.55	0.761	-0.650551	0.393779	-0.650551
5.0	20.64	0.805	-0.635429	0.440288	-0.635429
5.1	18.60	0.860	-0.609119	0.509141	-0.609119
5.2	16.38	0.929	-0.559915	0.611702	-0.559915
5.3	13.75	1.021	-0.468118	0.750210	-0.468118
5.4	10.64	1.145	-0.318984	0.893065	-0.318984
5.5	7.89	1.285	-0.185724	0.965441	-0.185724
5.6	6.25	1.401	-0.128948	0.983791	-0.128948

Appendix 4. Dipole Moment at Low Temperatures

Table A4-1. Dipole moment (in debye) of proton at 0 K.

R_0(a.u.)	$a = 2R_0$	$a = 2.5R_0$	$a = 3R_0$
4.8	0.0	0.0	0.0
4.9	0.0	0.0	0.0
5.0	0.0	0.0	0.0
5.1	0.169525	0.0	0.0
5.2	0.263214	0.108045	0.0
5.3	0.322448	0.266510	0.163086
5.4	0.368239	0.335955	0.306339
5.5	0.406819	0.383959	0.369603
5.6	0.440813	0.422812	0.413203

Table A4-2. Dipole moment (in debye) of deuteron at 0 K.

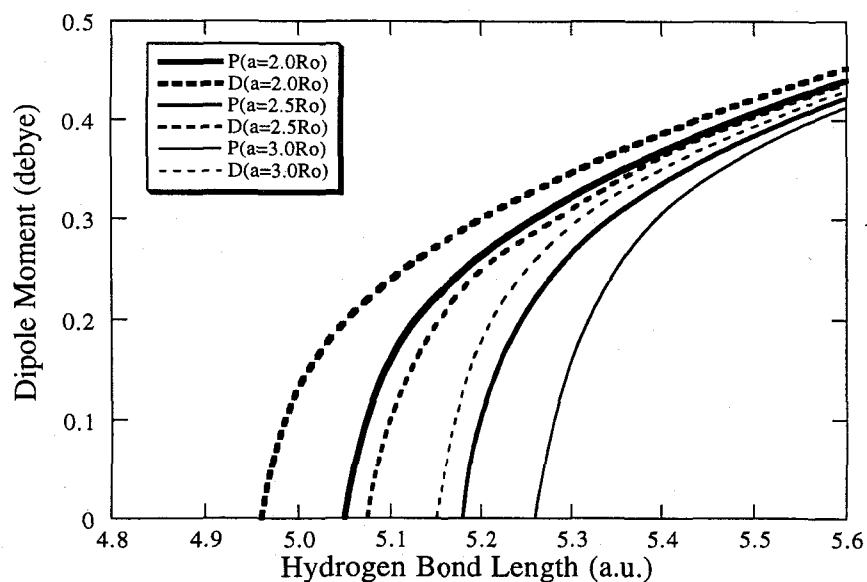| R_0(a.u.)	$a = 2R_0$	$a = 2.5R_0$	$a = 3R_0$
4.8	0.0	0.0	0.0
4.9	0.0	0.0	0.0
5.0	0.141761	0.0	0.0
5.1	0.239911	0.107050	0.0
5.2	0.300106	0.250347	0.183675
5.3	0.346833	0.309741	0.294183
5.4	0.386391	0.363520	0.350836
5.5	0.421346	0.402928	0.393491
5.6	0.452965	0.437531	0.429863

Fig A4. Dipole moment of proton and deuteron at 0 K.