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A Finite Element Approach to the Two-dimensional Vibrational Schrödinger Equation and Its Application to the Hydrogen Bond

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The finite element method was examined in relation to the two-dimensional vibrational Schrödinger equation. Some boundary conditions were used because of the symmetry of the potential, resulting in a higher precision in the case of the symmetrical potential, where the harmonic oscillators and the symmetrical hydrogen bond without anharmonicity were examined satisfactorily. An application was made to the symmetrical hydrogen bond with anharmonicity, where the precision was less for the higher levels. By a comparison of the calculated with the observed infrared spectra, the anharmonic potential constants for the assumed potential function were estimated.

A finite element approach has been successfully applied to a one-dimensional vibrational Schrödinger equation[1] with a harmonic or Lennard-Jones potential. Our purpose in this study is to examine the adaptability of the method to a two-dimensional vibrational Schrödinger equation, which is given by:

$$\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial S_1^2}+\frac{\hbar^2}{2M}\frac{\partial^2\Psi}{\partial S_2^2}+(E-V)\Psi=0, \tag{1}$$

where S_1 and S_2 are the symmetry coordinates of the vibrations with the effective masses of m and M respectively; Ψ, a wave function; E, an energy, and V, a potential with a potential surface expressed by a rectangular coordinate system due to S_1 and S_2, as is shown in Figs. 1—3.

In the harmonic oscillators, V is given by:

$$V=\frac{1}{2}kS_1^2+\frac{1}{2}KS_2^2, \tag{2}$$

where k or K is a force constant. In the symmetric hydrogen bond, which is of interest to us, V is assumed to be:[2,3]

$$V=\frac{1}{2}(FS_1^4-fS_1^2)+\frac{1}{2}KS_2^2+V', \tag{3}$$

where V' is assumed to be:

$$V'=\frac{1}{2}(F'S_1^4-f'S_1^2)S_2. \tag{4}$$

The potential constants in Eqs. 3 and 4 may be estimated reliably for the system of the $[X-H-X]^+$ ion, where X is a pyridine derivative.

Finite Element Formulation and Boundary Conditions

The functional of Eq. 1 is found to be:

$$\chi=\frac{1}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left\{\frac{\hbar^2}{2m}\left(\frac{\partial\Psi}{\partial S_1}\right)^2+\frac{\hbar^2}{2M}\left(\frac{\partial\Psi}{\partial S_2}\right)^2-(E-V)\Psi^2\right\}\mathrm{d}S_1\mathrm{d}S_2, \tag{5}$$

where the integration is limited in a numerical calculation over the region considered. A trial function is assumed to be:

$$\Psi=\alpha_1+\alpha_2S_1+\alpha_3S_2+\alpha_4S_1^2+\alpha_5S_1S_2+\alpha_6S_2^2=\boldsymbol{N\alpha}. \tag{6}$$

That is, six nodes are used for a triangular element; they are shown in Figs. 1—3. By using the same nota-

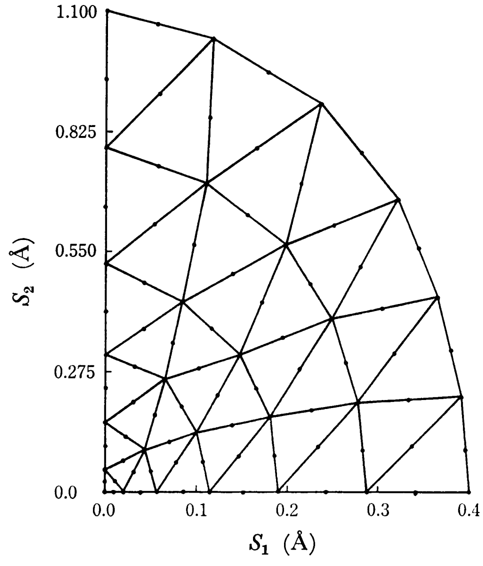

Fig. 1. The triangular elements and the nodes (·) used for harmonic oscillators.

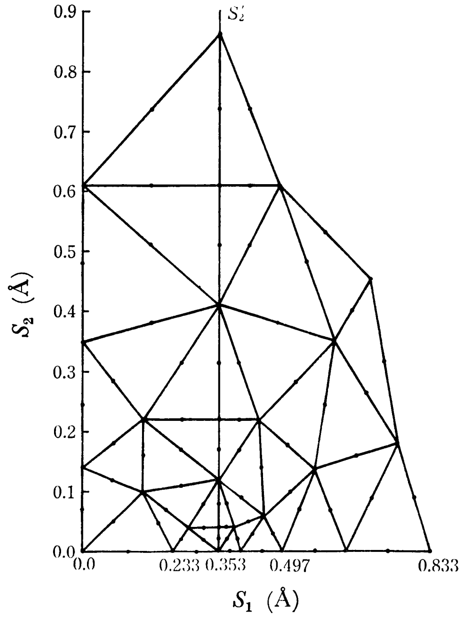

Fig. 2. The triangular elements and the nodes (·) used for the hydrogen bond with $V'=0$.

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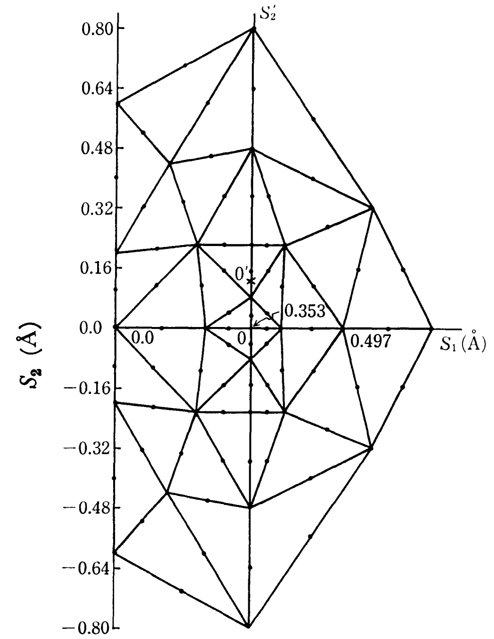

Fig. 3. The triangular elements and the nodes (·) used for the hydrogen bond (H) with $V' \neq 0$. This figure is symmetrical.

as the previous paper,[1] the functional for an element is expressed by:

$$\chi^{(e)} = \frac{1}{2}\boldsymbol{\Psi}^{(e)\mathrm{T}}(\boldsymbol{C}^{(e)-1})^{\mathrm{T}}(\boldsymbol{P}^{(e)} - \boldsymbol{E}\boldsymbol{R}^{(e)})\boldsymbol{C}^{(e)-1}\boldsymbol{\Psi}^{(e)}, \tag{7}$$

where $\boldsymbol{E}$ is the eigenvalue diagonal matrix and where

$$\begin{aligned}\boldsymbol{P}^{(e)} &= \frac{\hbar^2}{2m}\iint\frac{\partial \boldsymbol{N}^{\mathrm{T}}}{\partial S_1}\frac{\partial \boldsymbol{N}}{\partial S_1}\mathrm{d}S_1\mathrm{d}S_2 \\ &\quad + \frac{\hbar^2}{2M}\iint\frac{\partial \boldsymbol{N}^{\mathrm{T}}}{\partial S_2}\frac{\partial \boldsymbol{N}}{\partial S_2}\mathrm{d}S_1\mathrm{d}S_2 + \iint V\boldsymbol{N}^{\mathrm{T}}\boldsymbol{N}\mathrm{d}S_1\mathrm{d}S_2,\end{aligned} \tag{8}$$

$$\boldsymbol{R}^{(e)} = \iint \boldsymbol{N}^{\mathrm{T}}\boldsymbol{N}\mathrm{d}S_1\mathrm{d}S_2, \tag{9}$$

where the integration is taken over the element. From the procedure given in Appendix I, we obtain:

$$\begin{aligned}\frac{\mathrm{d}\chi^{(e)}}{\mathrm{d}\boldsymbol{\Psi}^{(e)}} &= (\boldsymbol{C}^{(e)-1})^{\mathrm{T}}\boldsymbol{P}^{(e)}\boldsymbol{C}^{(e)-1}\boldsymbol{\Psi}^{(e)} \\ &\quad - \boldsymbol{E}(\boldsymbol{C}^{(e)-1})\boldsymbol{R}^{\mathrm{T}(e)}\boldsymbol{C}^{(e)-1}\boldsymbol{\Psi}^{(e)} = 0\end{aligned} \tag{10}$$

The eigenvalues and the eigenfunctions are calculated by interconnecting Eq. 10 over all the elements.

The boundary condition[4] additional to the normal one, which is omitted here, is applied because of the symmetry property of the potential function. In the harmonic oscillators, where the vibrational quantum number for S_1 or S_2 is denoted by v or v' respectively, there are four cases orthogonal to each other;

v, v': even	Non-boundary condition
v: even; v': odd	Zero on the S_1 axis
v: odd; v': even	Zero on the S_2 axis
v, v': odd	Zero on the S_1 and S_2 axes.

They are calculated separately under the boundary conditions, which reduce the matrix of the eigenvalue problem, by using a quarter of the whole region, as is shown in Figs. 1 and 2. If the potential function is symmetric for only one axis, a half of the whole region is necessary, as is shown in Fig. 3. It is clear from Eq. 5 that these treatments give precision to the numerical calculation.

Symmetrical Potential

Harmonic Oscillators. A computational precision of the finite element approach will be examined here by a comparison of the eigenvalues calculated by this method with those obtained analytically.

Since the area of an element greatly affects the calculated eigenvalues, one has to set the elements out carefully in the region considered. We set out the 36 elements with 91 nodes in the elliptical region required by the normal boundary condition, as is shown in Fig. 1. This condition is equal to setting out 144 elements with 337 nodes in the whole region. The i-th element from the origin has the length of id along the coordinate axis, where d is the size of the first element, as has been

TABLE 1. THE EIGENVALUES (cm^{-1}) OF THE HARMONIC OSCILLATORS WITH 3000 AND 300 cm^{-1} FREQUENCIES AND THE HYDROGEN BOND WITH $V'=0$

	Harmonic oscillators		Hydrogen bond			
			H		D	
v v'	Anal.	Calcd	Anal.	Calcd	Anal.	Calcd
0—0	1650	1650.0	-2300.0	-2290.2	-2662.0	-2646.7
0—1	1950	1953.8	-2142.8	-2128.8	-2504.8	-2481.5
0—2	2250	2262.9	-1985.6	-1971.9	-2347.6	-2321.6
1—0	4650	4653.6	-2283.1	-2273.4	-2661.0	-2645.7
1—1	4950	4964.8	-2125.9	-2112.2	-2503.8	-2480.5
1—2	5250	5285.4	-1968.7	-1956.6	-2346.6	-2320.6
2—0	7650	7661.2	-224.4	-217.8	-921.9	-894.3
2—1	7950	7986.6	-67.2	-53.4	-764.7	-720.5
2—2	8250	8271.1	90.0	119.5	-607.5	-604.5
3—0	10650	10651	226.6	233.4	-863.0	-832.5
3—1	10950	10949	383.8	408.2	-705.8	-655.3
3—2	11250	11211	541.0	608.9	—548.6	-602.6

established previously for the one-dimensional problem.[1]

As we will treat later a problem involving two modes separated extremely in the ir frequencies, ν_1 and ν_2, the higher one is set at 3000 cm^{-1}, and the lower one, at 300 cm^{-1}. Under the conditions shown in Fig. 1, the calculated eigenvalues for small numbers of v and v' are given in Table 1; they are compared with the values obtained analytically.

As is shown in Table 1, the agreement between the calculated and the analytical values is regarded to be satisfactory as an approach made computationally. The manners of variation of the eigenvectors are the same as expected.

Hydrogen Bond with $V'=0$. In the case of a double-minimum potential, it is not easy to divide the region into the elements. By means of a trial-and-error method we set out the elements and nodes as is shown in Fig. 2, where the axis of S_2' is drawn through a bottom of the potential minimas. The S_1 coordinate is defined here by the displacement coordinate of the H atom from the center of the X···X bond as the one-dimensional expression.[5] The potential constants for the vibration of S_1 are set as $F=9.5$[6] (mdyn/Å^3) and $f=2.37$[6] (mdyn/Å); they give the potential minimum of -3721 cm^{-1} at ±0.353 Å. The value of m of H(D) is assumed to be 0.984 (1.938) amu. The normal frequency of the S_2 mode, which is the X···X stretching vibration, is assumed to be 157 cm^{-1}.

The calculated eigenvalues for the small numbers of v and v' under the conditions shown in Fig. 2 are given in Table 1, along with those obtained *analytically* by the method shown in Appendix II. The agreement between the calculated and the *analytical* values may be satisfactory by making allowance for the fact that there is a certain limit in the way of dividing the region into the elements, as is shown in Fig. 2.

From Table 1 we can find the difference between the precisions for the H and the D systems. The result for the D system is less satisfactory than that for the H system, but may be improved by the adjustment of the nodal values, as will be shown later.

Application

In most hydrogen-bond systems, the anharmonicity is particularly large; thus, it is hard to use an ordinary method of vibrational analysis. The finite element method described here is, then, useful in examining the vibration of those systems. We make an application of this method to a problem for the symmetrical hydrogen bond. In this sort of system, however, it is inevitable that, because the boundary condition for one axis can not be used, the precision of calculation is more or less lowered, and so is the convergence of the eigenvectors.

The elements and nodes are set out in the symmetrical potential with $V'=0$, as is shown in Fig. 3. The calculated eigenvalues for the H system under these conditions are given in Table 2 ($F'=0.0$). The calculated eigenvalues for the D system under these conditions are less satisfactory than those for the H system, but they can be improved by adjusting the area of elements to make it somewhat smaller. The results for the D system are given in Table 3 ($F'=0.0$). The agreement between the calculated values given in Table 2 or 3 with the analytical ones for the H or the D system in Table 1 is, as the whole, less than that between them in Table 1. However, the results given in Tables 2 and 3 can be useful in the estimation of the anharmonic potential constants or in the assignment of the observed spectra.

TABLE 2. THE EIGENVALUES (cm^{-1}) OF THE H SYSTEM WITH $V'\neq 0$

v v'	$F'=0.0$	$F'=1.0$	$F'=2.0$	$F'=4.0$
0—0	−2292.6	−2300.2	−2324.1	−2420.8
0—1	−2118.2	−2123.9	−2146.6	−2241.7
0—2	−1970.0	−1970.7	−1988.8	−2074.8
1—0	−2275.7	−2283.6	−2308.0	−2407.0
1—1	−2101.3	−2107.0	−2130.3	−2227.5
1—2	−1956.1	−1956.5	−1974.5	−2061.2
2—0	−214.5	−215.2	−218.4	−238.4
2—1	−22.6	−27.0	−44.4	−85.0
2—2	121.0	126.9	128.0	113.4
3—0	241.3	238.8	230.5	194.3
3—1	441.8	437.7	413.0	353.6
3—2	561.5	574.5	587.4	(628.2)

TABLE 3. THE EIGENVALUES (cm^{-1}) OF THE D SYSTEM WITH $V'\neq 0$

v v'	$F'=0.0$	$F'=1.0$	$F'=2.0$	$F'=4.0$
0—0	−2650.0	−2651.9	−2686.1	−2797.9
0—1	−2482.0	−2483.7	−2513.8	−2622.3
0—2	−2327.4	−2324.8	−2342.1	−2443.7
1—0	−2649.0	−2650.9	−2685.2	−2797.2
1—1	−2481.1	−2482.8	−2513.0	−2621.7
1—2	−2326.7	−2324.0	−2341.3	−2442.9
2—0	−890.9	−887.6	−904.3	−939.9
2—1	−729.4	−727.9	−680.1	−748.9
2—2	−560.9	−555.4	−555.1	−601.3
3—0	−830.4	−826.8	−846.1	−892.9
3—1	−669.5	−668.9	(−624.2)	−690.4
3—2	−500.8	−520.2	(−486.9)	−533.6

The intensity is calculated by means of this expression:[7]

$$I_{ij} = \nu_{ij}[\exp\{-(\nu_i-\nu_0)/kT\} - \exp\{-(\nu_j-\nu_0)/kT\}]M_{ij}^2, \tag{11}$$

where ν_{ij} is the transition frequency from the i to the j level; ν_i, ν_j, and ν_0 are the eigenvalues of the i, j, and ground levels respectively, k and T have their usual meanings, and M_{ij} is given by:

$$M_{ij} = \iint \Psi_i S_1 \Psi_j \mathrm{d}S_1 \mathrm{d}S_2, \tag{12}$$

where the integration is carried out in the region considered[3] by using the normalized function.

The relative intensities, I_{ij}, calculated under the conditions described above for the H and the D systems are shown schematically in Fig. 4-a, in which the observed spectra[8,9] for the pyridine–H(D)–pyridine system are also given to make a comparison. As is shown in Fig. 4-a, the ν_{ij} values calculated for the H system are

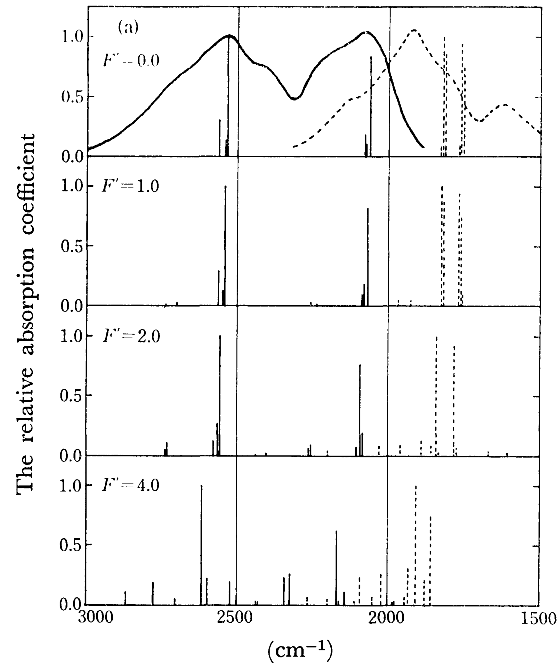

Fig. 4. Variation of the spectra with F'.

in accordance with the observed ones, but those for the D system are not. This disagreement may be attributed mainly to the inadaptability of the potential function assumed for those systems. An other type of potential function, such as the Lippincott-Schroeder potential,[5,10] may be appropriate, though others were not examined here.

In the case with $V' \neq 0$, the force constant, f', in Eq. 4 is assumed to be:

$$f' = 2F'S_e^2, \tag{13}$$

where S_e is the distance between the origin and the potential minimum with $V'=0$ on the S_1 axis. Under the assumption of Eq. 13, the potential minimum is displaced to the point, 0′, on the S_2' axis in Fig. 3; the potential is now asymmetric with respect to the abscissa through 0′. Since the more the elements are put on the vicinity of the potential well, the more the result is refined, all elements are transferred parallel with the S_2' axis by a distance between two points, 0 and 0′. Further, the elements above the abscissa are so adjusted that their areas are smaller than those taken under the condition with $V'=0$. On the other hand, the elements below the abscissa remain as they were taken in a good condition with $V'=0$.

The variation in the eigenvalues with F', whose value is set as 1.0, 2.0, or 4.0 (mdyn/Å^3), is given in Tables 2 and 3 for the H and D systems respectively. One notices from those tables that the eigenvalues with a lower quantum number, v, are lowered greatly with an increase in the value of F', while those with a higher v number are lowered only slightly. The eigenvalues in brackets are abnormal and are regarded as being perturbed by a Fermi resonance, since other levels, which are not assigned and which are omitted from the discussion here, appear near those eigenvalues.

The variation in the spectra with the F' is shown schematically in Fig. 4. The spectral feature observed for the H system can be interpreted approximately by I_{ij} calculated with $F'=4.0$; that is, some of the shoulders observed can be assigned satisfactorily to the combination bands. Two places where the observed intensity is higher than the calculated one are seen at about 2100 cm^{-1} in the H system and 1650 cm^{-1} in the D system. This may result from the overlap with the other bands, which may be assigned to a combination band not considered here. When $F=9.0$ and $F'=4.0$ (mdyn/Å^3), the I_{ij} calculated for the H system accords quite well with the observed spectra, but the values, ν_{ij}, calculated for the D system are dislocated much as may be seen in Fig. 4-a.

In the H system, the overtone of the S_1 mode has been observed at 5218 cm^{-1} [8] with a shoulder at 5050 cm^{-1}; it is evaluated *analytically* to be 5211.6 cm^{-1}. When $F'=4.0$ (mdyne/Å^3), it is given as 5178.8 cm^{-1} with the intensity of 0.23 of the maximum given in Fig. 4; this intensity seems to be a little higher than that expected, taking into account the fact that the eigenvectors of the 5-0 level do not converge completely. The transition to the 4-0 level is omitted because of the less convergence of the eigenvectors. On the other hand, in the D system, the eigenvectors of these levels with $F'=4.0$ (mdyn/Å^3) converge well and the calculated intensities are quite weak, in good accordance with the observation.

A very weak band has been observed near 140 cm^{-1} in both systems; it has been assigned to an overlap of such transitions as 0-0→1-1.[3] The calculated intensities in both systems are about 1/1000 of the maximum given in Fig. 4 and nearly half of the observed values.[3,8] This shows that the quadratic term of the transition moment may be quite important, as has been discussed by Singh and Wood.[3] The region near 550 cm^{-1} could not be examined here because of the less convergence of the eigenvectors of the higher v' levels.

Conclusion

The finite element method was examined for the two-dimensional vibrational Schrödinger equation with a high precision in the case of the symmetrical potentials. Thus, even further precision might be obtained if this method were applied to such a symmetrical system as a three-fold potential. On the other hand, though the method is obviously useful for a system with anharmonicity, it would only be adaptable for a system with a large anharmonicity, such as has been examined here, if the eigenvalues of the higher levels are necessary.

The numerical calculation was carried out by using the computer, FACOM 230-45S, of Toyama University.

Appendix

I. Stationary Value in Eq. 5 and the Finite Element Method. We will justify here Eq. 10 by a procedure employing a calculus of variation.[11-13] First, we assume a functional as follows:

$$\chi = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f(\Psi, p, q, S_1, S_2)\,\mathrm{d}S_1\mathrm{d}S_2, \tag{A-1}$$

where $p=\partial\Psi/\partial S_1$ and $q=\partial\Psi/\partial S_2$. According to Euler's condition, a characteristic equation is as follows:

$$\frac{\partial}{\partial S_1}\left(\frac{\partial f}{\partial p}\right)+\frac{\partial}{\partial S_2}\left(\frac{\partial f}{\partial q}\right)-\frac{\partial f}{\partial \Psi}=0. \tag{A-2}$$

If we take f as follows:

$$f=\frac{1}{2}\left\{\frac{\hbar^2}{2m}\left(\frac{\partial\Psi}{\partial S_1}\right)^2+\frac{\hbar^2}{2M}\left(\frac{\partial\Psi}{\partial S_2}\right)^2-(E-V)\Psi^2\right\}, \tag{A-3}$$

we find that Eq. A-2 is equal to Eq. 1. Thus, χ, which is called the associated variational functional with Eq. 1, has a stationary value.

Second, we resolve Eq. 5 directly by using a Rayleigh-Ritz approximation, where Ψ is assumed by:

$$\Psi=\sum_i \alpha_i S_1{}^{m_i} S_2{}^{n_i}=\boldsymbol{N\alpha}, \tag{A-4}$$

where the summation should be done generally for a very large number of terms. On the other hand, in a finite element method, Eq. A-4 is assumed for an element. To justify this assumption, we introduce a square matrix, $\underline{\boldsymbol{C}}^{(e)}$, which is defined by:

$$\boldsymbol{\Psi}^{(e)}=\underline{\boldsymbol{C}}^{(e)}\boldsymbol{\alpha}, \tag{A-5}$$

and which is determined by the coordinate values. From Eqs. A-4 and A-5, we obtain:

$$\Psi^{(e)}=\boldsymbol{NC}^{(e)-1}\boldsymbol{\Psi}^{(e)}, \tag{A-6}$$

where it should be noticed that $\Psi^{(e)}$ is defined at any point in the element through the matrix $\boldsymbol{N}$ and $\boldsymbol{\Psi}^{(e)}$ for six nodal points.

Finally, since χ in Eq. A-1 is expressed by the integration of the whole region, this is expressed by the summation of the integration of each element:

$$\chi=\sum_i^{\text{all}}\chi_i{}^{(e)}, \tag{A-7}$$

where $\chi_i{}^{(e)}$ is obtained by using Eq. A-6 and is given by Eq. 7. Now, χ is expressed by the nodal value Ψ_k. From the first condition, we obtain:

$$\frac{\mathrm{d}\chi}{\mathrm{d}\Psi_k}=0 \qquad (k=1, 2,\cdots \text{ all nodes}), \tag{A-8a}$$

or:

$$\frac{\mathrm{d}\chi^{(e)}}{\mathrm{d}\boldsymbol{\Psi}_i{}^{(e)}}=0 \qquad (i=1, 2,\cdots \text{ all elements}), \tag{A-8b}$$

or:

$$\frac{\mathrm{d}\chi}{\mathrm{d}\boldsymbol{\Psi}}=0, \tag{A-8c}$$

where $\boldsymbol{\Psi}$ is a column vector consisting of all nodal values. The resultant total equation has a form:

$$(\boldsymbol{A}-\boldsymbol{EB})\boldsymbol{\Psi}=0. \tag{A-9}$$

The eigenvalues and the eigenvectors are calculated from Eq. A-9.

II. Eigenvalues for a One-dimensional Hydrogen Bond.

There is no analytical method to obtain the eigenvalues for the double-minimum potential. Thus, to estimate them we used a finite element method previously reported,[1] because it is clear that the one-dimensional approach is more precise than the two-dimensional one, as may be found from Eq. 5. If the second term in Eq. 1 is neglected and m is replaced by μ, Eq. 1 is equal to Eq. 1 in Ref. 1. The eigenvalues are calculated by using the same potential as used here. The *analytical* values in Table 1 are obtained by the sum of these values and the eigenvalues of the S_2 mode.

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