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Finite Element Approach to the Vibrational Schrödinger Equation of Diatomic Species

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The finite element approach was successfully applied to the vibrational Schrödinger equation of diatomic species. An O_2 molecule with a harmonic potential and an Ar_2 molecule with a Lennard-Jones potential were examined and their eigen values and the associated eigen function were obtained. The calculated eigen values of the O_2 molecule agree with those expected. In the case of the Ar_2 molecule the calculated eigen values agree with those experimentally obtained when Lennard-Jones parameters are $\varepsilon = 115.1$ (cm^{-1}) and $\sigma = 3.35$ (Å). This verifies the validity of the present approach.

The finite element method was originally developed for the analysis of structures and has been widely applied to various problems in engineering science because of its versatility.

The method has been successfully applied to the analysis of the field problems, Laplace, Poisson and Helmholts equations.[1,2] It is a variant of the Rayleigh-Ritz procedure, turning a continuum field discrete with the best possible approximation by means of variational calculus which minimizes the functional corresponding to the governing differential equation. The present procedure might be an extended approach of the variational calculus widely used in wave mechanics.[3]

The purpose of this paper is to present the finite element method for the vibrational Schrödinger equation with two body potential V which is expressed as follows:

$$\frac{d^2\Psi}{dQ^2} + \frac{2\mu}{\hbar^2}(E-V)\Psi = 0 \tag{1}$$

where Ψ is a wave function, Q a normal coordinate, μ a reduced mass, and E an eigen value.

If V is given by

$$V(Q) = \frac{1}{2}kQ^2 \tag{2}$$

where k is a force constant, Eq. 1 is the Schrödinger equation of harmonic oscillator.

In the case of the Lennard-Jones potential, which is of interest to us, V is given by

$$V(Q) = 4\varepsilon\left\{\left(\frac{\sigma}{r_e+Q}\right)^{12} - \left(\frac{\sigma}{r_e+Q}\right)^6 + 0.25\right\} \tag{3}$$

where ε is a potential energy in equilibrium distance r_e and σ a distance of two bodies at $V=\varepsilon$.

The eigen values and their associated wave functions for harmonic oscillators as well as those under the Lennard-Jones potential were numerically calculated by means of the finite element approach. The results are compared with those obtained analytically and experimentally.

Functional and Finite Element Formulation

According to variational calculus the solution of Eq. 1 is equivalent to finding the function Ψ which minimizes the following functional:[3]

$$\chi = \int_Q \left\{\frac{1}{2}\left(\frac{d\Psi}{dQ}\right)^2 - \frac{1}{2}\frac{2\mu}{\hbar^2}(E-V)\Psi^2\right\}dQ \tag{4}$$

where the integration is taken over the whole region under consideration.

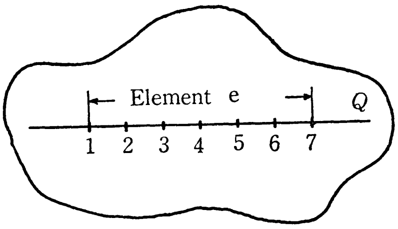

Fig. 1. The division of the region into the elements.

The region is divided into small elements (Fig. 1) for which the trial function was assumed to be:

$$\Psi = \sum_k^7 \alpha_k Q^{k-1} = \mathbf{N}\alpha \tag{5}$$

where the components of $\mathbf{N}$ are spatial functions and the α_s are seven unknown constants to be chosen so as to satisfy the nodal values at the element nodes.

Thus the function Ψ is uniquely specific within the element by the nodal values $\Psi_1, \Psi_2, \Psi_3, \cdots\cdots, \Psi_7$, their associated coordinates being

$$\Psi^{(e)} = [\mathbf{N}_1\mathbf{N}_2 \cdots \mathbf{N}_7]^T\alpha = \mathbf{C}^{(e)}\alpha \tag{6}$$

where (e) refers to the element and $\Psi^{(e)}$ indicates the values of Ψ at the nodes and is given by

$$\Psi^{(e)} = [\Psi_1\Psi_2 \cdots \Psi_7]^T \tag{7}$$

T denotes transposition, and $\mathbf{N}_i$ consists of the coordinate value corresponding to node i, and is given by

$$\mathbf{N}_i = [1 Q_i Q_i^2 \cdots Q_i^6] \tag{8}$$

Premultiplying each side of Eq. 6 by $\mathbf{C}^{(e)-1}$ (inverse of $\mathbf{C}^{(e)}$ matrix) and substituting $\boldsymbol{\alpha}$ into Eq. 5, we obtain the trial function

$$\Psi = \mathbf{N}\mathbf{C}^{(e)-1}\Psi^{(e)} \tag{9}$$

Substituting Eq. 9 into Eq. 4, we get the functional for the element

$$\chi^{(e)} = \frac{1}{2}\Psi^{(e)T}(\mathbf{C}^{(e)-1})^T(\mathbf{P}^{(e)} - E\mathbf{R}^{(e)})\mathbf{C}^{(e)-1}\Psi^{(e)} \tag{10}$$

where

$$\mathbf{P}^{(e)} = \int_e \frac{d}{dQ}\mathbf{N}^T\frac{d}{dQ}\mathbf{N}dQ + \frac{2\mu}{\hbar^2}\int_e V\mathbf{N}^T\mathbf{N}dQ \tag{11}$$

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$$\mathbf{R}^{(\mathrm{e})}=\frac{2\mu}{\hbar^2}\int_{\mathrm{e}}\mathbf{N}^{\mathrm{T}}\mathbf{N}\mathrm{d}Q \tag{12}$$

where the integration is taken over the element.

In order to minimize the functional $\chi^{(\mathrm{e})}$, we take the partial derivative with respect to $\boldsymbol{\Psi}^{(\mathrm{e})}$ and obtain

$$\begin{aligned}\frac{\mathrm{d}\chi^{(\mathrm{e})}}{\mathrm{d}\boldsymbol{\Psi}^{(\mathrm{e})}}&=(\mathbf{C}^{(\mathrm{e})^{-1}})^{\mathrm{T}}\mathbf{P}^{(\mathrm{e})}\mathbf{C}^{(\mathrm{e})^{-1}}\boldsymbol{\Psi}^{(\mathrm{e})}\\&\quad-\mathbf{E}(\mathbf{C}^{(\mathrm{e})^{-1}})^{\mathrm{T}}\mathbf{R}^{(\mathrm{e})}\mathbf{C}^{(\mathrm{e})^{-1}}\boldsymbol{\Psi}^{(\mathrm{e})}\\&=0\end{aligned} \tag{13}$$

The equation holds for all the elements which divide the space.

The values of $\boldsymbol{\Psi}_1$ at the interconnecting nodes between adjoining elements should be the same. Under these condition we obtain a linear algebraic equation of the form

$$(\mathbf{A}-\mathbf{E}\mathbf{B})\boldsymbol{\Psi}=0 \tag{14}$$

The eigen values and the wave functions are calculated from Eq. 14.

Numerical Examples

The functional of Eq. 4 is defined in unbounded space where the integration should be carried out. This can not be achieved by numerical analysis. Since the lower eigen values are of interest, the potential is calculated for the lower well region, which is divided into elements.

The first example for calculation is of the O_2 molecule with harmonic potential. That is, Eq. 1 is to be solved under the conditions of Eq. 2. The eigen values and their eigen functions are resolved analytically.

Six elements divided the integrated region which was chosen so as to cover lower eigen values. Two schemes were considered for the method of division: Case 1, equal space division; Case 2, finer division employed for the vicinity of the potential well.

TABLE 1. THE OBSERVED AND CALCULATED EIGEN VALUES (cm^{-1}) OF THE O_2 AND Ar_2 MOLECULES

	O_2			Ar_2		
v	Anal[a]	Calcd		Obsd[b]	Calcd	
		Case 1	Case 2		[I]	[II]
0	791.3	794.0	791.2	15.1	13.9	14.7
1	2374.0	2458.6	2373.9	40.6	37.6	40.1
2	3956.7	4220.3	3959.0	60.7	56.4	60.7
3	5539.4	5984.7	5545.5	75.8	68.6	76.8
4	7122.0	9444.3	7169.9	86.4	79.3	87.3

a) Obtained from $k=11.8$ (mdyn/Å). b) From Refs. 4 and 6.

The calculated lower six eigen values are given in Table 1. The values obtained by the finite element approach agree reasonably with the analytical ones obtained on the basis of $\kappa=11.8$ (mdyn/Å). The results are not independent of the division method. Elements are not enough because of the limitation of the capacity of the computer. However, the present approach is promising if the division is proper by chosen (Case 2); the spacing of the i-th element from the origin is as follows: $\Delta Q^{(\mathrm{e}_i)}=0.025|i|$, $i=\pm1$, ±2, ±3. The potential function used is shown in Fig. 2 with the eigen functions (not normalized) corresponding to the six lower eigen values.

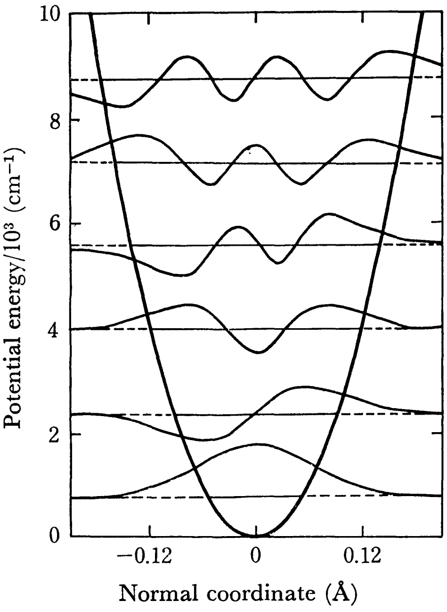

Fig. 2. The potential function and the calculated eigen functions (arbitrary unit) of the O_2 molecule. The solid horizontal lines show the level of the eigen values.

The next example of calculation is for the case with Lennard-Jones potential; it is to solve Eq. 1 under the conditions of Eq. 3. In this case the Ar_2 molecule is taken as an example. The experimental eigen values obtained by spectroscopic[4] and molecular beam[5] methods are given in Table 1. From the results we obtain: ε in Eq. 3 is 98.7 cm^{-1} and r_e 3.85 Å which gives the value of σ, 3.35 Å.

The region where the potential is negative in the

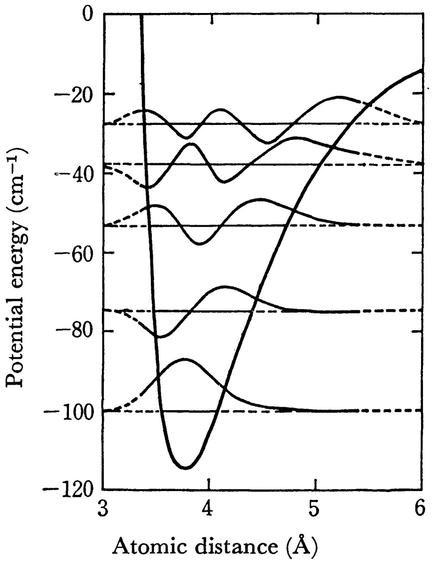

Fig. 3. The potential function and the calculated eigen functions (arbitrary unit) of the Ar_2 molecule. The solid horizontal lines show the level of the eigen values. The dotted lines are hypothetically drawn.

ordinary Lennard-Jones potential form was chosen for integration. Finer division was used for the vicinity of the potential well (Case 2); the spacing of the *i*-th element from the potential minimum is as follows: $\Delta Q^{(e_i)}=2^{|i|-1}\{(2)^{1/6}\sigma-\sigma\}/3$, $i=\pm1$, ±2, 3, 4. The calculated eigen values (Calcd I) are also given in Table 1. The agreement between the observed and calculated values is not satisfactory, *the calculated ones* being as a whole lower than the observed ones. We thus varied the value of ε. When ε is 115.1 cm^{-1}, the values of Calcd II are obtained, agreeing with those observed. This shows that since the Lennard-Jones potential explained the spectroscopic result,[4] this potential is proper for the bound state, though it has been unfavorable for the collision data.[5,6]

The potential function and the eigen functions for the Ar_2 molecule in the case of Calcd II are given in Fig. 3. The dotted lines for the eigen functions out of the region of integration are hypothetical.

Conclusion

The finite element approach is successfully applied to the vibrational Schrödinger equation. Simple examples of diatomic species are considered for verification of the approach. The method is promissing and seems to deserve further application.

The numerical calculations were performed at the Computer Center of Toyama University.

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References

1) O. C. Zienkiewicz, "The Finite Element Method in Engineering Science," McGraw-Hill, London (1971).

2) H. N. Douglas and G. Vries, "The Finite Element Method," Academic Press, New York and London (1973).

3) L. I. Schiff, "Quantum Mechanics," McGraw-Hill, London (1968), p. 255.

4) Y. Tanaka and K. Yoshino, *J. Chem. Phys.*, **53**, 2012 (1970).

5) J. M. Parson, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, **56**, 1511 (1972).

6) K. K. Docken and T. P. Schafer, *J. Mol. Spectry.*, **46**, 454 (1973).