Finite Element Approach for Schrödinger Equation

with Lennard–Jones Potential

Hideyuki Arai[*], Isao Kanesaka[**] and Yukio Kagawa

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Finite element approach is successfully applied to the vibrational Schrödinger equation with Lennard-Jones potential. Ar_2 atom molecules are considered for diatomic problem, for which the eigen values, the corresponding eigen functions and the vibrational level spacings are calculated. The calculated values agree with those experimentally obtained. This verifies the validity of the present approach, which paves the way to the application to the problems of this kind.

I. Introduction

Finite Element Method was originally developed for the analysis of structures and have now widely been applied to various classes of problem in engineering science because of its versatility.

Among others the method is successfully applied to the analysis of the field problems, of Laplace, Poisson and Helmholtz equation.[1,2] The Finite Element Method is a variant of Rayleigh-Ritz procedure and a process to discretize the continuum field with the best possible approximation by means of the variational calculus which minimizes the functional corresponding to the governing differential equation. Therefore the present procedure can be said to be an extended approach of the variational calculus which has intensively been utilized in wave mechanics.[3]

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

$$\frac{d^2 \psi}{d Q^2} + \frac{2\mu}{h^2}(E - V)\psi = 0 \tag{1}$$

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

If V is expressed by

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

[*] Computer Center　　　[**] Dept. of Science

where K is a force constant. Equation (1) is known as the Schrödinger equation of harmonic oscillator and can be solved precisely.

In case of Lennard-Jones potential,[4] V is expressed as:

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

where ε is a potential energy in equilibrium distance r, 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 are numerically calculated by means of flement element approach.

The results are compared with those obtained analitically and experimentally.

II. Functional and Finite Element Formulation

According to the variational calculus the solution of equation (6) is equivalent to finding the function ψ which minimizes the following functional:[3]

$$x = \int_Q \left\{ \frac{1}{2} \left(\frac{\partial \psi^2}{\partial Q} \right) - \frac{1}{2} \frac{2\mu}{h^2} (E - V) \psi^2 \right\} dQ \tag{4}$$

which physically corresponds to the expectation value in quantum theory. The integration is taken over the whole region under consideration.

The region in which the problem is to be solved is divided into small elements as shown in Figure 1, for which the trial function is assumed to be

$$\psi = \sum_{k=1}^{i} Q^{k-1} \alpha_k = \mathbf{N} \{\alpha\} \tag{5}$$

where the components of $\mathbf{N}$ are spatial function 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 specified within the element by the nodal values $\psi_1, \psi_2, \psi_3, \ldots, \psi_i$ and their associated coordinates as

$$\{\psi^{(e)}\} = \begin{Bmatrix} \mathbf{N}_1 \\ \mathbf{N}_2 \\ \vdots \\ \mathbf{N}_i \end{Bmatrix} \{\alpha\} = \mathbf{C}^{(e)} \{\alpha\} \tag{6}$$

where $(\ )^{(e)}$ refers to the element. $\{\psi^{(e)}\}$ indicates the values of ψ at the element nodes, which is

$$\{\psi^{(e)}\} = \{\psi_1 \quad \psi_2 \quad \psi_3 \cdots \psi_i\}^T$$

where T denotes the transpose, and $\mathbf{N}_i$ consists of the coordinate values corresponding to node i, which is

$$\mathbf{N}_i = \{1 \quad Q_i \quad Q_i^2 \quad Q_i^3 \cdots Q_i^{i-1}\}$$

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

$$\psi = \mathbf{N} \mathbf{C}^{(e)^{-1}} \{\psi^{(e)}\} \tag{7}$$

Substituting equation (7) into equation (4) the functional for the element is given by

where

$$x^{(e)} = \frac{1}{2} \{\psi^{(e)}\}^T [\mathbf{C}^{(e)^{-1}}]^T [\mathbf{A}^{(e)} - E\mathbf{B}^{(e)}] \mathbf{C}^{(e)^{-1}} \{\psi^{(e)}\} \tag{8}$$

$$\mathbf{A}^{(e)} = \int_e \frac{\partial}{\partial Q} \mathbf{N}^T \frac{\partial}{\partial Q} \mathbf{N} dQ + \frac{2\mu}{h^2} \int_e V\mathbf{N}^T\mathbf{N} dQ \tag{9}$$

$$\mathbf{B}^{(e)} = \frac{2\mu}{h^2} \int_e \mathbf{N}^T\mathbf{N} dQ \tag{10}$$

where the integration is taken over the element.

To minimize the functional x, we take the partial derivative with respect to $\{\psi^{(e)}\}$ and to give

$$\frac{\partial x^{(e)}}{\partial \{\psi^{(e)}\}} = [\mathbf{C}^{(e)^{-1}}]^T \mathbf{A}^{(e)} \mathbf{C}^{(e)^{-1}} \{\psi^{(e)}\} - E [\mathbf{C}^{(e)^{-1}}]^T \mathbf{B}^{(e)} \mathbf{C}^{(e)^{-1}} \{\psi^{(e)}\} = 0 \tag{11}$$

Equation (11) holds for all the elements that divide the space.

The values of ψ_i at the interconnecting nodes between abjoining elements must be the same. With this compatibility imposed, we obtain linear algebraic equation of the form

$$(A - E\mathbf{B})\{\psi\} = 0 \tag{12}$$

The eigen values and the wave functions are calculated from equation (12).

III. Numerical Examples

The functional of equation (4) is defined in unbounded space, for which the integration must be carried out. This can not be achieved in numerical analysis. Since the lower eigen values are generally of our interest, the potential distribution is first calculated for which the region where the potential forms the well are divided into the elements.

The first examples of the calculation are the harmonic oscillators of hydrogen and oxygen. That is, equation (1) is to be solved under equation (2), which can analytically be solved.

The sixth order polinomial is used as the trial function of the element, Six elements divide the region to be integrated which is chosen so as to cover the lowest some eigen values. Two schemes are considered for the way of division:

Case 1. Equal space division.

Case 2. Finer division are employed in the vicinity of the potential well.

The calculated lowest eight eigen values are shown in Table 1. The values obtained by the finite element approach reasonably agree with the analytical ones. The results are not free from the way of division. The number of the elements are not yet enough, which is limited because of the capacity

of the computer used.　The present approach is, however, promissing if proper way of division is cho-
sen (Case 2). Figure 2 shows the potential distribution and the eigen functions(which are not normalize
in the figure) corresponding to the lowest six eigen values.

　　The next examples of calculation are for the case of Lennard-Jones potential. lt is to solve equa-
tion (1) under equation (3).　Argon molecules are considered, for which the　experimental　values　of
the vibrational level spacings are already given.[5]　Lennard-Jones parameters are given in Table 2,
from which the potential of equation (3) is calculated.　The region where .the potential is negative
is chosen for integration.　The order of the polinomial of the trial function and the number of the
division are the same as above.　Finer division is used in the vicinity of the potential well(Case 2).

　　The calculated vibrational level spacings and their experimental counterparts are shown in Table 3.
　　Reasonable agreement is again obtained.

　　ln Figure 3, the potential distribution and the eigen functions for　argon　molecules in the Len-
nard-Jones potential are also shown.　The dotted lines for the eigen functions are hypothetically drawn,
as they are out of the region of integration.

IV. Final Remarks

　　Finite element approach is successfully applied to the vibrational Schrödinser equation.

　　ln the present paper, some simple examples of diatomic molesule problems are considered for the
verification of the approach.

　　The Finite Element Method is promissing and paves the way to the application to the wide range
of the problems of this kind.

　　The numerical calculation was performed at Toyama University Computer Center.

References

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Table 1. The eigen values for the harmonic oscillator of the diatomic molecules

v	Hydrogen			Oxygen		
	Analytical	Finite Element Approach Case 1	Case 2	Analytical	Finite Element Approach Case 1	Case 2
0	2205.7	2210.2	2205.6	791.3	794.0	791.2
1	6617.2	6725.3	6618.6	2374.0	2458.6	2373.9
2	11028.7	11172.2	11035.7	3956.7	4220.3	3959.0
3	15440.1	16585.7	15449.4	5539.4	5984.7	5545.5
4	19851.6	22291.7	19838.0	7122.0	9444.3	7169.9
5	24263.0	39015.9	24276.8	8704.7	10996.2	8751.4
6	28674.5	42265.1	28925.0	10287.4	16649.0	10434.2
7	33086.0	58842.3	33440.2	11870.0	19385.0	12074.3
8	37497.4	62265.5	37946.8	13452.7	22713.8	13731.9

(cm^{-1})

Table 2. The Lennard-Jones parameters for Ar_2

	ε (cm^{-1})	σ $(\overset{\circ}{A})$
Ar_2	115.1	3.35

Table 3. The eigen values for Ar_2 in the Lennard-Jones pottential

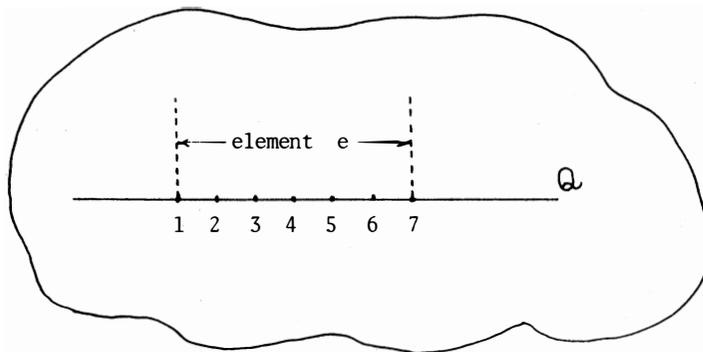| v	vibrational level spacings	
	Experimental	Finite Element Approach
0	25.0 - 26.7	23.74
1	18.6 - 20.8	18.97
2	14.8 - 16.2	14.55
3	9.2 - 11.3	9.81
4	5.9 - 8.0	8.47

(cm^{-1})
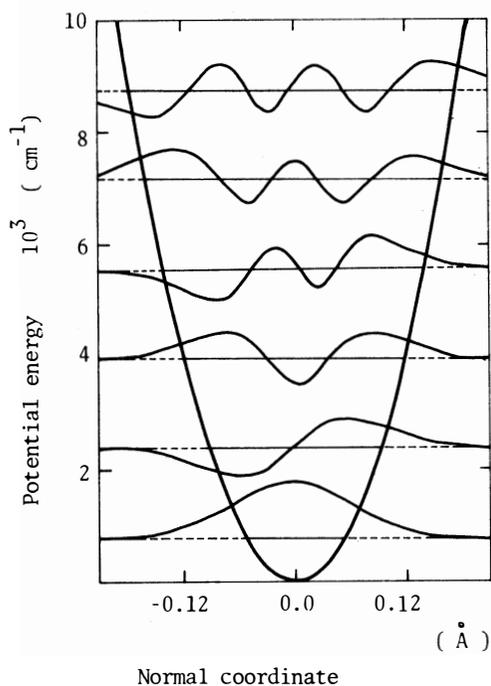
Figure.1 Division of a region into elements.

Figure 2.

The potential function and the calculated eigen functions for the harmonic oscillator of oxygen molecule.   The solid horizontal lines show the level of the eigen values.
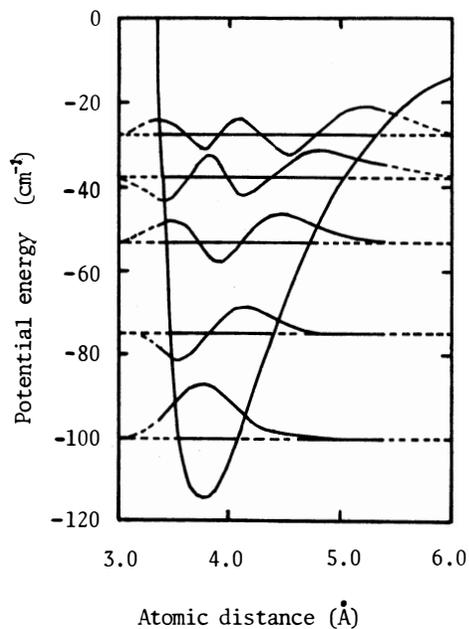
Figure 3. The potential function and the calculated eigen functions (arbitrary unit) of the Ar_2 molecule.

The solid horizontal lines show the level of the eigen values.   The dotted lines are hypothetically drawn.