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Eigenvalues of the anharmonic oscillator

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Abstract. A method of approximation for solving secular equations proposed by one of the authors is applied to the problem of finding the first few eigenvalues of the quantum mechanical anharmonic oscillator. Numerical results obtained compare favourably with those obtained by other methods.

1. Introduction

A method for finding the solutions of secular equations was proposed by one of the authors (Chan 1966, 1970). In this method, each eigenvalue satisfies an implicit equation, thus making it possible to find any one particular eigenvalue without finding the rest. We give a brief description.

Consider the secular equation of a Hermitian matrix $\mathbf{H}$:

$$\det (H_{ij} - E\delta_{ij}) = 0. \tag{1}$$

In what follows, the following notation will be used:

$$(i, j) = H_{ij} \qquad i \neq j$$

and

$$(i) = H_{ii} - E.$$

Define the cyclic product by

$$(ijkl \dots st) = (i, j)(j, k)(k, l) \dots (s,t)(t, i) \tag{2}$$

where all indices are different (alternatively one may consider the cyclic product to have the value zero if any two of the indices are equal). Furthermore, let

$$\textstyle\sum_{\mathrm{P}} (ijkl \dots st) \tag{3}$$

denote a summation of cyclic products over all possible non-equivalent cyclic permutations of the indices. It can then be shown that (Chan 1966)

$$(i) = H_{ii} - E = N_i/M_i \tag{4}$$

where

$$N_i = \sum_{\mathrm{P}\,\neq i}^{n-1} \left(\frac{(ij)}{(j)} - \frac{(ijk)}{(j)(k)} + \frac{(ijkl) - (ij)(kl)}{(j)(k)(l)} - \dots\right) \tag{5}$$

$$M_i = \sum_{\mathrm{P}\,\neq i}^{n-1} \left(1 - \frac{(jk)}{(j)(k)} + \frac{(jkl)}{(j)(k)(l)} - \frac{(jklm) - (jk)(lm)}{(j)(k)(l)(m)} + \dots\right). \tag{6}$$

Equations (4)–(6) define an implicit equation satisfied by the ith eigenvalue.

Certain special applications of the implicit equation may be mentioned. If we have a secular equation of the Mathieu type obtained from a matrix **H** with elements given by

$$(i, j) = H_{ij}(\delta_{ij} + \delta_{i,j+h} + \delta_{i,j-h}), \tag{7}$$

then the right-hand side of equation (4) can be reduced to a continued fraction (Chan 1966, 1970). This reduction facilitates considerably the solution of the equation.

The secular equation for the anharmonic oscillator, however, does not satisfy condition (7). For this problem, direct application of equation (4) is made.

2. The anharmonic oscillator

The Hamiltonian for an anharmonic oscillator is

$$\mathbf{H} = \frac{p^2}{2\mu} + \tfrac{1}{2}\mu\omega^2 x^2 + a x^4. \tag{8}$$

Using the harmonic oscillator eigenfunctions as a basis for expansion, the following matrix elements of **H** are obtained:

$$\begin{aligned} H_{n,n} &= 3\rho(2n^2 + 2n + 1) + (2n + 1)t \\ H_{n,n-2} = H_{n-2,n} &= 2\rho(2n - 1)[n(n-1)]^{1/2} \\ H_{n,n-4} = H_{n-4,n} &= \rho[n(n-1)(n-2)(n-3)]^{1/2}. \end{aligned} \tag{9}$$

All other matrix elements vanish and in (9)

$$\rho = a\left(\frac{\hbar}{2\mu\omega}\right)^2 \qquad t = \tfrac{1}{2}\hbar\omega. \tag{10}$$

In order to compare results with other calculations, we introduce the notation of Chan *et al* (1964) who used the following Hamiltonian:

$$\mathbf{H} = [(\mu\omega^2\hbar^2/16\mu) + (a\hbar^2/64\mu^2)^{2/3}]^{1/2}[P_\alpha^2 + (1-\alpha)X_\alpha^2 + \alpha^{3/2}X_\alpha^4]. \tag{11}$$

In equation (11),

$$\begin{aligned} X_\alpha &= (4\mu k'/\hbar^2)^{1/4} x \\ P_\alpha &= (4/\mu\hbar^2 k')^{1/4} p \\ \alpha &= \frac{(a^2\hbar^2/\mu)^{1/3}}{k'} \end{aligned} \tag{12}$$

where

$$k' = \mu\omega^2 + (a^2\hbar^2/\mu)^{1/3}.$$

In accordance with their work, we set

$$[(\mu\omega^2\hbar^2/16\mu) + (a\hbar^2/64\mu^2)^{2/3}]^{1/2} = 1. \tag{13}$$

In terms of ρ and t, this gives

$$\frac{t^2}{4} - \left(\frac{\rho t^2}{4}\right)^{2/3} = 1. \tag{14}$$

Furthermore, from the definition of α, we have

$$\frac{\alpha}{1-\alpha}=\left(\frac{2\rho}{t}\right)^{2/3}. \tag{15}$$

Thus for a given anharmonicity α, equations (14) and (15) can be used to determine the corresponding values of the parameters ρ and t.

We shall present calculations for $\alpha = 0{\cdot}2$. Such an anharmonicity is appropriate for triethylene oxide. The corresponding values for ρ and t are

$$\rho = 0{\cdot}1117894 \qquad t = 1{\cdot}7886318. \tag{16}$$

3. Procedure of calculation

In equations (5) and (6), we note that the terms are grouped according to the number of products of one-cycles (i.e. cyclic products with only a single index). These one-cycles contain the eigenvalue E and the way they are grouped offer a convenient way of truncating the sums in (5) and (6). It is of course possible to truncate (5) and (6) in different manners. For example, one might truncate (5) by dropping terms which contain the product of more than three one-cycles while in (6), terms with products of four one-cycles may be kept. There is no hard and fast rule here but we believe that a reasonable approach would be to truncate both equations in the same way. We shall call the maximum number of factors in the products of one-cycles which are kept the order of the approximation.

The calculation begins with choosing a suitable finite sub-matrix and determining the order of approximation desired. The sub-matrix should include the eigenvalue to be calculated.

We now give an example of the calculation for the anharmonic oscillator with matrix elements defined by (9) and values of the parameters ρ and t given by (16). An 8×8 sub-matrix is used and the calculation is for the second eigenvalue (i.e. the first excited state). Equation (4) with $i = 1$ then gives (to third order)

$$(1)=\frac{\dfrac{(13)}{(3)}+\dfrac{(15)}{(5)}-\dfrac{2(135)}{(3)(5)}+\dfrac{2(1375)-(13)(75)-(15)(37)}{(3)(5)(7)}}{1-\dfrac{(35)}{(3)(5)}-\dfrac{(37)}{(3)(7)}-\dfrac{(57)}{(5)(7)}-\dfrac{2(357)}{(3)(5)(7)}} \tag{17}$$

$$=\frac{N_1}{M_1}.$$

The numerical values are

$$N_1=\frac{7{\cdot}49812}{(3)}+\frac{1{\cdot}49963}{(5)}-\frac{60{\cdot}35117}{(3)(5)}-\frac{2266{\cdot}8645}{(3)(5)(7)}$$

$$M_1=1-\frac{80{\cdot}97972}{(3)(5)}-\frac{10{\cdot}49738}{(3)(7)}-\frac{354{\cdot}81113}{(5)(7)}+\frac{1098{\cdot}3913}{(3)(5)(7)}$$

$$(1)=7{\cdot}04274-E_1$$

$$(3)=20{\cdot}90463-E_1$$

$$(5) = 40{\cdot}13241 - E_1$$

$$(7) = 60{\cdot}72608 - E_1.$$

The eigenvalue E_1 is then obtained by solving (17) numerically.

The equation is first truncated to second order. Then using the first perturbation result as an initial approximation, one root of the second-order equation is found. This root in turn is used as the initial approximation in solving the third-order equation. The solution thus found is accepted as the best evaluation of the desired eigenvalue. In this and all subsequent calculations, the second- and third-order evaluations differ by less than five per cent. Also, the other roots of the second- and third-order equations are unrelated. This indicates that the procedure is quite reliable in locating the eigenvalue and that the method converges quite rapidly.

4. Results and discussion

The first five eigenvalues of the anharmonic oscillator were obtained by the method described in the previous section using a third-order approximation. Except for the fifth eigenvalue, the sub-matrices used were 8×8. For the fifth eigenvalue, a 9×9 sub-matrix was used so that the term $H_{44}-E$ would be centred in the sub-matrix. The results, together with those obtained by the other methods, are presented in table 1.

Table 1. The first five eigenvalues of the anharmonic oscillator ($\alpha = 0{\cdot}2$) according to various approximations.

Energy state	Variational method†	First-order perturbation	Second-order perturbation	Exact†	Our approximation
0	2·04810	2·124	1·977	2·04270	2·04261
1	6·52795	7·043	5·890	6·51051	6·51111
2	11·62670	13·300	9·007	11·62920	11·65268
3	17·20250	20·900	9·901	17·2332	17·25803
4	23·17400	29·850	7·148	23·2391	23·41999

† These results are taken from Chan *et al* (1964).

The perturbation results are rather poor. This is to be expected. The sheer size of the anharmonicity ($\alpha = 0{\cdot}2$) would make one suspect the accuracy of low-order perturbation results.

Using a fairly small sub-matrix, we have obtained results comparable in accuracy to those obtained from variational calculations and numerical inversion of a 20×20 sub-matrix. Our method thus offers a viable alternative.

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