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Finite Difference Boundary Value Method for Solving One-Dimensional Eigenvalue Equations

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The finite difference boundary value method for obtaining eigenvalues and eigenfunctions of the one-dimensional Schroedinger equation is discussed. The method is noniterative and may be applied to one-dimensional problems on $(-\infty, \infty)$ or to the radial equation on $(0, \infty)$. A computer program which computes the eigenvalues and any desired matrix elements involving the eigenfunctions is available from Quantum Chemistry Program Exchange.

INTRODUCTION

For a few potential energy functions the one-dimensional Schroedinger equation can be solved analytically [1–6]; however, in most cases a numerical method must be used or one must make rough approximations. The numerical methods may generally be classified as expansion in a basis-set [7–9, 10, 11] and numerical integration. The relative advantages and disadvantages of the basis-set and numerical-integration types of solution are well known. The numerical integration method is generally applied by treating the eigenvalue equation as an initial value problem. The method of inward and outward integrations with matching and an iterative procedure to find the eigenvalue is commonly used. The program of Cooley [12] as modified by Zare and Cashion [13–16] is such a program which is in wide use for applications to diatomic molecule vibrational problems. Usually on the order of 1000 points are used in the integration grid. The same numerical integration method is also in very wide use for solving the radial equation in the Hartree–Fock problem for atoms [17–21]. Below we discuss a noniterative technique for solving the one-dimensional eigenvalue problem. This is based on treating the problems as a boundary-value problem. In addition to the advantage of being noniterative, it has the advantage that it can easily be applied to multidimensional problems. In fact, the method has been applied successfully to many multidimensional eigenvalue problems [22–28]. However, the method also has advantages in some cases for one-dimensional problems. Some applications of the

boundary-value method to one-dimensional problems have been made previously [29–32]. The version of the boundary-value method described below for one-dimensional problems is based on the careful applications of the method to multi-dimensional problems by Winter, McKoy, and coworkers [25, 27, 28]. This version has already been applied to some practical problems [33]. A program which performs calculations by this method has been submitted to Quantum Chemistry Program Exchange [34].

METHOD

The Schroedinger equation is

$$H(R)\,\phi_k(R) = [T(R) + V(R)]\,\phi_k(R) = \epsilon_k\phi_k(R), \tag{1}$$

where (letting $\hbar = 1$)

$$T(R) = -(1/2\mu)(d^2/dR^2), \tag{2}$$

$V(R)$ is the potential energy (including the centrifugal potential for a radial equation problem), and μ is the mass or reduced mass. Equation (1) must be solved with the boundary conditions

$$\phi_k(R_0) = 0, \tag{3}$$

$$\phi_k(R) \xrightarrow[R\to\infty]{} 0, \tag{4}$$

where $R_0 = -\infty$ for a real one-dimensional problem and $R_0 = 0$ for a radial equation. The system of Eqs. (2)–(4) is treated as a boundary-value problem. For R_s small enough and R_r large enough a good approximation to the boundary conditions is that $\phi_k(R_s) = \phi_k(R_r) = 0$. The equation is then solved by making the finite difference approximation. Although we could use high order difference formulas we will consider the 3-point difference formula [35]. We find that sufficiently accurate eigenfunctions could be obtained by using the 3-point difference formula and a large number of grid points or extrapolation to a small step size or both. Further, the higher order difference formulas can be used without extra assumptions only in the interior of the grid point region for a boundary value problem and extra testing is required to find out the effects of the special approximations which must be used near the boundary. Consider a set of N mesh points (or grid points) R_i^h (with $i = 1, 2, \ldots, N$) evenly spaced with $R_1^h = R_s + h$ and $R_N^h = R_r - h$. Then the step size h between mesh points is $(R_r^h - R_s^h)/(N + 1)$. Let

$$\phi_{ik} = \phi_k(R_i) \tag{5}$$

and let ϕ_{ik}^h be the approximation to ϕ_{ik} obtained by making the finite difference approximation [35]

$$\left.\frac{\delta^2\phi_k}{\delta R^2}\right|_{R=R_i} \simeq \frac{1}{h^2}(\phi_{i-1,k} - 2\phi_{i,k} + \phi_{i+1,k}). \tag{6}$$

In this approximation the differential equation and its boundary conditions reduce to a set of linear equations for the values of the eigenfunction at the mesh points. These equations can be written in matrix form as

$$\sum_j F_{ij}^h \phi_{jk}^h = \lambda_k{}^h \phi_{ik}^h, \tag{7}$$

where

$$F_{ij}^h = \delta_{ij}[-(2/\mu) + U_{ii}^h] + 1/\mu[\delta_{i,j-1}(1 - \delta_{i1}) + \delta_{i,j+1}(1 - \delta_{iN})], \tag{8}$$

$$U_{ii} = -2h^2V(R_i{}^h), \tag{9}$$

and

$$\epsilon_k = -\lim_{h\to 0}(\lambda_k{}^h/2h^2), \tag{10}$$

$$\phi_k(R) = \lim_{h\to 0}\phi_{jk}^h(R_j{}^h). \tag{11}$$

The limit in (11) must be taken including only grids which have a grid point $R_j{}^h$ at R. Further, each member of the sequence whose limit is $\phi_k(R)$ has a different j such that $R_j{}^h = R$. The eigenvalue Eq. (7) can be solved by a standard subroutine for eigenvalues of real, symmetric matrices. Here the Givens–Householder method is used [36]. The extrapolation in (10) and (11) can be carried out using Richardson's h^2-extrapolation [37]. The various extrapolants are arranged in a Neville table [38] and the last element in the table is the most accurate approximation to ϵ_k. The other elements of the table are useful in giving an estimate of the accuracy. The Richardson extrapolation procedure is well known to many numerical analysts but for completeness is reviewed, along with the method of display of the results in a Neville table, in Appendix 1.

To be consistent with $O(h^2)$ error in the 3-point approximation to the second derivative in the differential equation, integrals over the approximate wavefunctions should be computed using the quadrature formula with the same order of accuracy, namely, the trapiezoidal rule [39]. Thus the normalization condition is

$$h\sum_{j=1}^{N} |\phi_{jk}|^2 = 1. \tag{12}$$

The matrix element

$$f_{kl} = \int dR\ \phi_k^*(R) f(R)\ \phi_l(R) \tag{13}$$

is determined as

$$f_{kl} = \lim_{h \to 0} f_{kl}^h, \tag{14}$$

where

$$f_{kl}^h = h \sum_{j=1}^{N} \phi_{jk}^{h*} \phi_{jl}^h f(R_j^h). \tag{15}$$

The limit in (14) is accomplished by Richardson extrapolation.

Examples and Discussion

The following example is intended to show that the method can be used accurately and conveniently. The example is in Hartree atomic units [40] except that Tables I–III are in cm^{-1}. The potential is the Levine potential [41] for the $X^1\Sigma^+$ state of CO.

$$V(R) = D_e[s(R)]^2 - D_e$$
$$s(R) = 1.0 - (R_e/R) \exp[-a(R^p - R_e^p)],$$

where $D_e = 0.41321$, $R_e = 2.13207$, $a = 0.2069074$, and $p = 1.869$. D_e is the diatomic potential energy well depth, R_e is the position of the minimum in the potential energy well, and a is Levine's parameter β. These parameters are obtained from the data in Ref. [42]. The reduced mass is taken as 12510.63. The vibrational wavefunctions are numbered $v = 1, 2,...$, instead of the usual 0, 1,... . By performing trial calculations with very small R_s and very large R_r we estimated that to have $\phi_9(R_s) < 10^{-10}$ and $\phi_9(R_r) < 10^{-10}$ would require $R_s = 1.5$ and $R_r = 3.2$. We will consider two different choices of boundary conditions: (A) $R_s = 1.15$, $R_r = 4.0$; (B) $R_s = 1.05$, $R_r = 3.7$. Neville tables for the eigenfunctions with v equals 1, 3, and 9 for these examples are given in Tables I–III. The tables show the following expected significant features: (a) the final extrapolated eigenvalue is independent of the exact choice A or B of where the boundary condition is imposed; (b) each succeeding column converges faster than the previous one; (c) high accuracy can be achieved either by a high order extrapolation of several runs with small n or a low order extrapolation of a few runs with large n; (d) the accuracy of a given number is about equal to its difference from the number just above it in the Neville table.

The finite difference boundary value method is most accurate for $v = 1$. In

TABLE I

Neville tables for the $v = 1$ (ground state) eigenvalue of the CO example problem with boundary conditions imposed according to plans A and B[a]

(A)	50	0.05588	1054.826									
				1081.539								
	70	0.04014	1067.910		1081.437							
				1081.468		1081.475						
	90	0.03132	1073.266		1081.467		1081.484					
				1081.468		1081.483		1081.488				
	110	0.02568	1075.978		1081.479		1081.488		1081.490			
				1081.473		1081.487		1081.490		1081.491		
	130	0.02176	1077.539		1081.484		1081.490		1081.491		1081.491	
				1081.478		1081.490		1081.491		1081.491		1081.491
	150	0.01887	1078.519		1081.489		1081.491		1081.491		1081.491	
				1081.488		1081.491		1081.491		1081.491		
	350	0.00812	1080.943		1081.491		1081.491		1081.491			
				1081.491		1081.491		1081.491				
	600	0.00474	1081.304		1081.491		1081.491					
				1081.491		1081.491						
	800	0.00356	1081.386		1081.491							
				1081.491								
	1000	0.00285	1081.424									
(B)	500	0.00529	1081.259									
				1081.491								
	725	0.00365	1081.381		1081.491							
				1081.491								
	950	0.00287	1081.427									

[a] The eigenvalues are in cm^{-1}.

TABLE II

Neville tables for the $v = 3$ eigenvalue of the example problem with boundary conditions imposed according to plans A and B[a]

	N	h									
(A)	50	0.05588	4998.692								
				5361.619							
	70	0.04014	5176.452		5349.429						
				5353.191		5350.682					
	90	0.03132	5246.275		5350.423		5350.747				
				5351.544		5350.738		5350.792			
	110	0.02568	5281.075		5350.646		5350.787		5350.823		
				5351.077		5350.776		5350.822		5350.832	
	130	0.02176	5300.957		5350.729		5350.821		5350.832		5350.834
				5350.916		5350.818		5350.832		5350.834	
	150	0.01887	5313.391		5350.809		5350.832		5350.834		5350.835
				5350.824		5350.831		5350.834		5350.835	
	350	0.00812	5343.948		5350.830		5350.834		5350.835		
				5350.830		5350.834		5350.835			
	600	0.00474	5350.488		5350.834		5350.835				
				5350.833		5350.835					
	800	0.00356	5349.514		5350.834						
				5350.834							
	1000	0.00285	5349.989								
(B)	500	0.00529	5347.915								
				5350.832							
	725	0.00365	5349.445		5350.834						
				5350.834							
	950	0.00287	5350.025								

[a] The eigenvalues are in cm^{-1}.

TABLE III

Neville tables for the $v = 9$ eigenvalue of the example problem with boundary conditions imposed according to plans A and B[a]

	N	h									
(A)	50	0.05588	13135.44								
				18302.88							
	70	0.04014	15666.43		17569.97						
				17796.18		17586.15					
	90	0.03132	16507.81		17582.80		17622.23				
				17669.21		17616.89		17611.97			
	110	0.02568	16891.74		17607.01		17613.11		17613.93		
				17636.82		17613.93		17613.89		17613.98	
	130	0.02176	17103.36		17611.44		17613.86		17613.98		17614.00
				17625.09		17613.86		17613.97		17614.00	
	150	0.01887	17233.22		17613.62		17613.97		17614.00		17614.00
				17615.21		17613.97		17614.00		17614.00	
	350	0.00812	17545.04		17613.95		17614.00		17614.00		
				17614.03		17613.99		17614.00			
	600	0.00474	17590.56		17613.99		17614.00				
				17614.00		17614.00					
	800	0.00356	17600.81		17614.00						
				17614.00							
	1000	0.00285	17605.56								
(B)	500	0.00529	17584.82								
				17614.00							
	725	0.00365	17600.12		17614.00						
				17614.00							
	950	0.00287	17605.92								

[a] The eigenvalue are in cm^{-1}.

this case accuracy of much better than 0.002 cm^{-1} can be achieved by making calculations with 110, 130, and 150 points and then making a h^4-extrapolation. Accuracy of much better than 0.02 cm^{-1} for the same problem can be achieved by making calculations with 50 and 70 points and then making an h^2-extrapolation. Such calculations are very easy and fast. For the higher v good accuracy can be achieved by using finer grids.

Two sample Neville tables for the matrix element $\langle v = 6 \mid R \mid v = 3 \rangle$ are given in Table IV. This is a typical example, again showing the high accuracy. High accuracy can also easily be obtained for even more difficult matrix elements involving higher Δv.

TABLE IV

Neville tables for the matrix element $\langle v = 6 \mid 10^4(R - R_e) \mid v = 3 \rangle$ computed with boundary conditions imposed according to plans A and B[a]

	N	h			
(A)	600	0.00474	9.435972		
				9.106346	
	800	0.00356	9.291761		9.106459
				9.106418	
	1000	0.00285	9.225038		
(B)	500	0.00529	9.516660		
				9.106329	
	725	0.00365	9.301492		9.106469
				9.106430	
	950	0.00287	9.220036		

[a] The matrix element is in bohrs.

Conclusion

The finite difference boundary value method is a rapid, convenient method for obtaining the eigenvalues of and matrix elements involving the eigenfunctions of the radial Schroedinger equation.

APPENDIX 1: Richardson extrapolation procedure and use of the Neville Table

Let $A(h_i)$ be a numerically computed quantity corresponding to step size h_i and let A_0 be the exact result (corresponding to the solution of the differential

equation rather than the difference equations). The extrapolation procedure consists in obtaining solutions at n different stepsizes and approximating $A(h_i)$

$$A(h_i) = \sum_{i=0}^{n-1} A_i h^{2i}. \tag{A1}$$

The fact that only even terms appear in (A1) is a consequence of the application of central differences [Eq. (6)] to this boundary value problem [37]. We then solve the n simultaneous linear Eqs. (A1) for the set of n values of A_i. This is exactly equivalent to performing Aitken inverse interpolation [43] on the sequence of $A(h_i)$ and interpolating to the point $h = 0$. Note that since $h = 0$ is outside the range of h_i for which $A(h_i)$ is available, this is technically an extrapolation. It is most convenient to arrange the Aitken inverse interpolation calculation according to the suggestion of Neville [38]. This yields a "Neville Table" in which each element has an obvious and useful interpretation. For example, in part A of Table II, 5176.452 is the result of the calculation with 70 points, 5353.191 is from an h^2-extrapolation using the 70- and 90-point calculations, 5350.423 is the result of an h^4-extrapolation using the 70-, 90-, and 110-point calculations. Finally, the furthest right number in the table is the result of an h^{18}-extrapolation using all the calculations.

This extrapolation process, with a given value of n, is called Richardson's $h^{2(n-1)}$-extrapolation.

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