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ACCURATE EVALUATION OF QUANTUM INTEGRALS

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Abstract—Combining an appropriate finite difference method with Richardson's extrapolation results in a simple, highly accurate numerical method for solving a Schrödinger's equation. Important results are that error estimates are provided, and that one can extrapolate expectation values rather than the wavefunctions to obtain highly accurate expectation values. We discuss the eigenvalues, the error growth in repeated Richardson's extrapolation, and show that the expectation values calculated on a crude mesh can be extrapolated to obtain expectation values of high accuracy.

1. INTRODUCTION

Accurate eigenvalues are seldom needed in spectroscopy because they are directly observable. The eigenvalues are usually used to construct the potential function which is used in Schrödinger's equation to obtain the eigenfunctions, i.e., wavefunctions. The only need for the wavefunctions is for the evaluation of expectation values of operators, such as the dipole moment function to obtain intensities, or the overlap integrals to obtain Franck–Condon factors. Thus what we really need is a relatively quick, accurate numerical method to evaluate integrals involving wavefunctions. Preferrably, the method should have a reasonably good *a posteriori* error estimate. Such a method is found in combining the method of calculating wavefunctions as the eigenvectors of a symmetric matrix with the trapezoidal rule for numerical quadrature. This is not as accidental as we shall see. Letting $h = (b - a)/N$

$$\int_a^b f(x)\,\mathrm{d}x = h\left\{\frac{1}{2}[f(a)+f(b)] + \sum_{n=1}^{N-1} f(a+nh)\right\} + E_N(f,a,b) \tag{1}$$

where

$$E_N(f,a,b) = \sum_{j=1}^{m} c_j h^{2j} + o(h^{2m+1}) \tag{2}$$

when f has $(2m+2)$ continuous derivatives. The expansion (2) allows trapezoid rule values to be improved by Richardson's extrapolation. If the function $f(x)$ is approximated by another function which differs from it by an expansion like the error in the trapezoid rule, then the result retains the form of the error expansion in Eq. (1) and Richardson's extrapolation can still be used to obtain refined estimates for the value of the integral. Generating the extrapolation table by lines and using the approximations for the error, we have an estimate of the error in the value of the integral.

2. ALGORITHM (REPEATED RICHARDSON'S EXTRAPOLATION)[1]

Fundamental to the method of solution is the use of extrapolation to refine approximate answers. When the error can be expanded in powers of h^m, and we have a sequence of approximations for $h_0 > h_1 > \cdots > h_k > \cdots$, we can construct a table whose elements are called Richardson's extrapolations. These entries are arranged so that they are increasingly more accurate as one goes down

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columns (because of decreasing step sizes), and are of increasing order as one proceeds to the right (because of the elimination of more terms in the error expansion). For the case $m = 2$

$$T(h) = T(0) + \sum_{j=1}^{n} a_j h^{2j} + O(h^{2n+2}) \tag{3}$$

where $a_1, a_2, \ldots, a_n$ are unknown constants. Assume that $T(h_i)$, $i = 0(1)n$ have been numerically determined. We assume that $h_0 > h_1 > \cdots h_n > 0$, but are otherwise arbitrary.

Let

$$T_0^{(k)} = T(h_k), \tag{4}$$

$$H_k = h_k^2, \tag{5}$$

and

$$T_m^{(k)} = T_{m-1}^{(k+1)} + \frac{T_{m-1}^{(k+1)} - T_{m-1}^{(k)}}{H_k/H_{k+m} - 1} \tag{6}$$

where $m = 1, 2, \ldots, n$ and $k = 0, 1, \ldots, n - m$. The elements defined above may be arranged in a lower triangular table given in Table 1 and can be computed line by line. Above, $T_m^{(k)}$ is the polynomial of degree m in h^2 which interpolates the points $(H_{k+j}, T_0^{(k+j)})$, $j = 0, 1, \ldots, m$. Writing the elements of Table 1 as

$$T_m^{(k)} = T(0) + R_m^{(k)} \tag{7}$$

we have

$$R_m^{(k)} \sim (-1)^m [a_m + o(1)](h_k h_{k+1} \cdots h_{k+m})^2. \tag{8}$$

This expression follows from the error term for the interpolation polynomial expressed in divided differences. From Eqs. (7) and (8)

$$R_m^{(k+1)}/R_m^{(k)} = H_{k+m+1}/H_k \tag{9}$$

and

$$\Delta T_m^{(k)} = T_m^{(k+1)} - T_m^{(k)} = R_m^{(k+1)} - R_m^{(k)} \tag{10}$$

which may be combined to give the asymptotic error estimate

$$R_m^{(k+1)} \sim -\Delta T_m^{(k)}/(H_k/H_{k+m+1} - 1). \tag{11}$$

This error estimate can either be used to control when to stop the process, or we can use it to estimate the error obtained at the end of a predetermined amount of work. Clearly most of the work in using repeated Richardson's extrapolation involves calculating the first column. Calculating the remainder of the table is trivial.

Necessary and sufficient conditions for $T_m^{(k)}$ to converge to $T(0)$ is $\sup_{k\to\infty} h_{k+1}/h_k = \alpha < 1$. The two extreme cases are geometric increase, $h_k/h_{k+1} = 2$, and arithmetic, $h_k = h_0/(k+1)$. Note that the mesh size sequence is not absolute, but relative to some initial mesh size chosen by means appropriate to the actual problem. Of more importance is the effect of round-off errors in the first column elements on the accuracy of the later columns, and thus on the accuracy of the results of the algorithm. For a unit error in the elements of the first column, the geometric case amplifies initial errors by a factor of two; the arithmetic case amplifies error by considerably more as the number of extrapolations increases. Table 2 gives the amplification for an arithmetical sequence as a function of table position when assuming the initial column elements have unit error.

Table 1. Terms T_m^k for an n order extrapolation.

$k \backslash m$	0	1	$\cdots$	n
0	$T_0^{(0)}$			
1	$T_0^{(1)}$	$T_1^{(0)}$		
2	$T_0^{(2)}$	$T_1^{(1)}$		
$\vdots$	$\vdots$	$\vdots$		
n	$T_0^{(n)}$	$T_1^{(n-1)}$	$\cdots$	$T_n^{(0)}$

Table 2. Roundoff error amplification for arithmetic sequence.

$k\backslash m$	0	1	2	3	4	5	6	7	8	9
0	1									
1	1	2								
2	1	3	3							
3	1	4	6	6						
4	1	5	9	12	13					
5	1	6	14	21	25	26				
6	1	7	19	35	48	54	56			
7	1	8	26	54	84	106	116	119		
8	1	9	33	80	140	195	233	251	256	
9	1	10	42	113	222	343	446	513	545	553

Another, frequently suggested sequence of mesh sizes is $\{1, 2, 3, 4, 6, 8, 12, 16, 24, \ldots\}$. This sequence increases more slowly than the geometric series, but has almost as benign an amplification of initial error. The error amplification is given in Table 3. For practical purposes, say five extrapolations, there is no real difference among the error amplifications. Thus, any monotonically decreasing behavior in step size is practical.

3. DEVELOPMENT OF THE METHOD FOR ONE EQUATION

The numerical method that we use for solving a one dimensional Schrödinger's equation:[2] (a) requires only knowledge of the potential; (b) is based on the application of several simple ideas; (c) uses well established, accurate, and stable numerical methods; (d) has *a posteriori* error estimates; (e) achieves high accuracy with very little work and needs only "small" computers. The basic ideas behind the numerical method are very simple. We replace the differential equation with a set of difference equations based on a mesh. The initial problem is: Find (approximately) the eigenvalues and eigenfunctions of the second order differential equation

$$\frac{d^2y(r)}{dr^2} + [V(r) - E]y(r) = 0 \tag{12}$$

and $y(a) = y(b) = 0, 0 < a < b < \infty$, $V(r) > 0$. The finite difference method selects a mesh of points

$$r_j = a + (b - a)\frac{j}{n} \tag{13}$$

$j = 0, 1, \ldots, n$ and replaces the derivative using the centered difference method. The jth difference equation is

$$\frac{y_{j+1} - 2y_j + y_{j-1}}{h^2} + [V_j - E]y_j = 0 \tag{14}$$

where $h = (b - a)/n$ and $V_j = V(r_j)$. Simplifying and gathering terms, this becomes

$$-y_{j+1} + (2 - V_j h^2)y_j - y_{j-1} = Eh^2 y_j. \tag{15}$$

Table 3. Roundoff error amplification for intermediate sequence.

$k\backslash m$	0	1	2	3	4	5	6	7	8	9
0	1									
1	1	3								
2	1	4	6							
3	1	3	5	6						
4	1	4	6	7	8					
5	1	3	5	6	7	7				
6	1	4	6	7	8	9	9			
7	1	3	5	6	7	7	8	8		
8	1	4	6	7	8	9	9	9	9	
9	1	3	5	6	7	7	8	8	8	8

Writing the equations for $j = 1, 2, \ldots, n$ and remembering that $y_0 = y_{n+1} = 0$, gives

$$\mathbf{A}\mathbf{y} = h^2 E\mathbf{y} \tag{16}$$

where

$$\mathbf{A} = \begin{bmatrix} D_1 & 0 & & & \\ 0 & D_2 & 0 & & \\ & 0 & D_3 & \ddots & \\ & & \ddots & \ddots & 0 \\ & & & 0 & D_{n-1} \end{bmatrix}, \tag{17}$$

$$D_j = \begin{bmatrix} 2 - h^2 V_j & -1 \\ -1 & 2 - h^2 V_{j+1} \end{bmatrix}, \tag{18}$$

and

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_n \end{bmatrix}. \tag{19}$$

The corresponding discrete problem solution is: (a) find the eigenvalues and eigenvectors of **A**; (b) estimate the error between the eigensolutions of **A** and Eq. (12). The eigenvalues and the elements of the eigenvectors of the matrix **A** differ from the eigenvalues and wavefunction values on the finite difference mesh of the differential equation by errors that have expansions on h^2. The proof of this follows directly from theorems 1 and 2 of Ref. 3. Thus, the error in the approximate values of the wavefunctions at the mesh points is identical in form to the error expansion of the trapezoid rule.

4. DEVELOPMENT FOR THE METHOD FOR COUPLED EQUATIONS

The above result can easily be extended to the coupled differential equations arising in bound-state problems of quantum mechanics.[4,5] Here, the equations are assumed to be of the general form

$$[-\mathrm{d}^2/\mathrm{d}x^2 + V_{11}(x) - E]\Psi_1(x) = U(x)\Psi_2(x) \tag{20}$$

$$[-\mathrm{d}^2/\mathrm{d}x^2 + V_{22}(x) - E]\Psi_2(x) = U(x)\Psi_1(x) \tag{21}$$

When the differentials are replaced with the symmetric finite difference

$$\frac{\mathrm{d}^2\Psi_i(x)}{\mathrm{d}x^2} \approx \frac{\Psi_i(x+h) - 2\Psi_i(x) + \Psi_i(x-h)}{h^2} \tag{22}$$

and we interlace the resulting finite difference equations at each node, we get the symmetric pentadiagonal matrix equation

$$(\mathbf{C} - \lambda\mathbf{I})\boldsymbol{\Psi} = 0 \tag{23}$$

$$\mathbf{C} = \begin{bmatrix} C_1 & Q & & & \\ Q & C_2 & Q & & \\ & Q & C_3 & \ddots & \\ & & \ddots & \ddots & Q \\ & & & Q & C_N \end{bmatrix}, \tag{24}$$

$$C_j = \begin{bmatrix} 2 + h^2 V_{11}(x_j) & h^2 U(x_j) \\ h^2 U(x_j) & 2 + h^2 V_{22}(x_j) \end{bmatrix}, \tag{25}$$

$$Q = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \tag{26}$$

and all the other elements of **C** are zero. **I** is the identity matrix, N is the number of intervals of division of the internuclear distance, and $hN = 1$. The difference between the eigenvalues and eigenvectors and the corresponding eigenvalues and (intertwined) wavefunction values of the coupled differential equations (20) and (21) again have expansions in h^2. Here, the problem is to find the eigensolutions of a symmetric pentadiagonal matrix, but this is easily done by rotating the matrix to tridiagonal form and then applying the same standard methods used in the single equation method.

5. AN EXAMPLE

In a series of papers[2,5,6] we presented the results of applying Richardson's extrapolation to zero mesh to finite difference approximations of the eigenvalues and corresponding wavefunctions of Schrödinger's equation for some problems that have been difficult to solve by traditional methods. The method is limited to computing bound–bound transitions for the potential.

As an example of extrapolating integrals we have calculated the expectation value of x^2 for the harmonic oscillator. As is well known[7] the expectation value of x^2 is given by

$$\int_{-\infty}^{\infty} \Psi_n(x) x^2 \Psi_m(x)\, dx = (n + \tfrac{1}{2})\delta_{nm} \tag{27}$$

where n and m are the vibrational quantum numbers, $\delta_{n,m}$ is the Kronecker delta and the wavefunctions $\Psi_n(x)$ are given in terms of the Hermite polynomials by

$$\Psi_n(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} \exp(-x^2/2) H_n(x). \tag{28}$$

The wavefunctions $\Psi_n(x)$ are normalized to unity and Schrödinger's equation has been expressed in dimensionless units. In Table 4 we present the calculated expectation values obtained using wavefunctions resulting from solving Eq. (16) with 201 mesh points (G_1), 401 mesh points (G_2), and 801 mesh points (G_3). These expectation values are extrapolated to first order (G_{21} and G_{32}) and second order (G) using

Table 4. Second order extrapolation of the expectation value of x^2 for the harmonic oscillator.

n	G_1	G_2	G_3	G_{21}	G_{32}	G	$1 - G/(n + 1/2)$
0	0.497761	0.499442	0.499860	0.500002	0.500000	0.500000	2.4(−09)
1	1.488772	1.479206	1.499302	1.500017	1.500001	1.500000	1.1(−08)
2	2.470718	2.492730	2.498186	2.500067	2.500004	2.500000	3.6(−08)
3	3.443502	3.486008	3.496510	3.500176	3.500011	3.500000	8.9(−08)
4	4.407027	4.477034	4.494275	4.500369	4.500022	4.499999	1.8(−07)
5	5.361192	5.465802	5.491481	5.500673	5.500040	5.499998	3.3(−07)
6	6.305890	6.452307	6.488127	6.501113	6.500066	6.499996	5.4(−07)
7	7.241014	7.436543	7.484212	7.501720	7.500102	7.499994	8.3(−07)
8	8.166453	8.418504	8.479737	8.502521	8.500148	8.499990	1.2(−06)
9	9.082090	9.398184	9.474701	9.503548	9.500206	9.499984	1.7(−06)
10	9.987806	10.375576	10.469103	10.504833	10.500279	10.499975	2.3(−06)
11	10.883476	11.350675	11.462944	11.506409	11.500367	11.499964	3.1(−06)
12	11.768971	12.323475	12.456223	12.508310	12.500472	12.499950	4.0(−06)
13	12.644160	13.293970	13.448939	13.510573	13.500596	13.499931	5.1(−06)
14	13.508902	14.262153	14.441093	14.513237	14.500739	14.499906	6.5(−06)
15	14.363054	15.228018	15.432683	15.516340	15.500905	15.499876	8.0(−06)
16	15.206467	16.191559	16.423710	16.519923	16.501094	16.499839	9.8(−06)
17	16.038985	17.152770	17.414173	17.524032	17.501308	17.499793	1.2(−05)
18	16.860446	18.111644	18.404072	18.528710	18.501549	18.499738	1.4(−05)
19	17.670681	19.068174	19.393407	19.534005	19.501818	19.499672	1.7(−05)
20	18.469515	20.022355	20.382176	20.539968	20.502117	20.499593	2.0(−05)
21	19.256763	20.974179	21.370380	21.546652	21.502447	21.499500	2.3(−05)
22	20.032233	21.923641	22.358019	22.554110	22.502811	22.499391	2.7(−05)

$$G_{21} = G_2 + (G_2 - G_1)/3$$
$$G_{32} = G_3 + (G_3 - G_2)/3$$
$$G = G_{32} + (G_{32} - G_{21})/15. \tag{29}$$

The columns from the left are the vibrational quantum number, the calculated expectation values of x^2 at 201, 401 and 801 mesh points, the first order extrapolations, G_{21} and G_{32}, the second order extrapolation, G, and the fractional difference between the extrapolated expectation values and the exact result $n + 1/2$. We see that the final extrapolated values agree to better than 3 parts in 10^5 with the exact result. Note that for the lowest number of mesh points, the expectation value of x^2 at high vibrational number is quite far from the exact value.

6. CONCLUSION

We have shown that the expectation values calculated on a crude mesh can be extrapolated to obtain expectation values of high accuracy. Thus neither the intermediate wavefunctions nor the final extrapolated wavefunctions are needed to calculate accurate expectation values saving computer storage and time and simplifying the algorithm. As an example we have calculated the expectation values of x^2 of a harmonic oscillator. We have also shown how the error estimates can be obtained.

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