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Computer Physics Communications 161 (2004) 109–118

Computer Physics Communications

www.elsevier.com/locate/cpc

On the use of higher-order formula for numerical derivatives in scientific computing

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Received 17 November 2003; accepted 15 February 2004

Abstract

In many situations, the numerical derivative of a function at a point x must be calculated since the function is not defined by a closed-form expression, but rather by values of the function at grid points at and around x. This typically arises when enforcing the boundary conditions while solving a differential equation. Usually, one employs a 2- or 3-point formula to approximate the derivative. On the other hand, the use of a higher-order formula, such as a 7- or even a 10-point approximation, based on the method of undetermined coefficients, can sometimes lead to better accuracy and enhanced computational efficiency. We show that significant improvements arise from using higher-order formulas for the first derivative in two important problems: the calculation of quantum mechanical reaction rates using the Miller–Schwartz–Tromp correlation function, and the calculation of the radioactivity migration in a porous medium.

PACS: 02.60.Jh

Keywords: Numerical differentiation; Method of undetermined coefficients; Radioactivity migration in Porous medium and MST formula

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1. Introduction

The need to evaluate the derivative of a function by numerical means arises when a closed-form expression for the function is not available. An example is the particle current **J** which under Fick's diffusion approximation is given by $-D\nabla n$, where D is the diffusion constant and n is the number density, whose value may be available at selected equidistant points. Another instance involves the derivatives needed to enforce the boundary conditions while solving differential equations.

Usually, one employs a 2- or 3-point formula to approximate the boundary derivative. On the other hand, the use of a higher-order formula, such as a 7- or even a 10-point approximation, based on the method of undetermined coefficients, can sometimes lead to better accuracy and enhanced computational efficiency. We show below that

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doi:10.1016/j.cpc.2004.02.014

significant improvements arise from using higher-order formulas for the first derivative in two important problems: the calculation of the radioactivity migration in a porous medium and the calculation of quantum mechanical reaction rates using the Miller–Schwartz–Tromp correlation function. For the radioactivity migration, a partial differential equation has to be solved numerically and here one of the boundary conditions needs the evaluation of the first order derivative. It is for the implementation of this crucial boundary condition we resort to higher-order approximation. The concentration of radioactivity in the porous medium depends on the particle current from the source (waste matrix) into the medium. The expression for the current involves the first derivative. Hence, the overall accuracy of the whole computation depends on the precision of this derivative approximation. We emphasise that we are not concerned about approximating the derivatives that occur in the differential equation. They are usually approximated by standard difference schemes, whose choice is governed by convergence, stability and accuracy requirements. Obviously, a higher-order discretisation scheme will result in better accuracy. In the case of the quantum mechanical reaction rate expression, there is no differential equation involved. We just need the first-order derivative of a flux vector whose numerical values are known. In both the cases, we use as high an order of approximation as possible till numerical saturation is reached.

2. The method of undetermined coefficients

The first derivative of $f(x)$ at the point x can be expressed by the method of undetermined coefficients [1] as

$$\begin{aligned} f'(x) = (1/h)\big[&a_m f(x-mh) + a_{m-1} f\big(x-(m-1)h\big) + a_{m-2} f\big(x-(m-2)h\big) + \cdots \\ &+ a_1 f(x-h) + a_0 f(x) + b_1 f(x+h) + b_2 f(x+2h) + \cdots + b_n f(x+nh)\big]. \end{aligned} \tag{1}$$

The above formula involves $(m+n+1)$ constants, $a_m, a_{m-1}, \ldots, a_0, b_1, b_2, \ldots, b_n$ which need to be fixed. For convenience, x is set to zero. Then choosing $f(x)$ as $1, x, x^2, x^3, \ldots, x^{m+n}$ successively and then equating the exact $f'(x)$ to the value of $f'(x)$ as determined by the above formula, we get $(m+n+1)$ linear equations which fix the $(m+n+1)$ constants. If $m = n$, then this amounts to symmetric differencing which in general gives better accuracy provided the function has the even symmetry. If $a_m, a_{m-1}, \ldots, a_1$ are all zero, then this implies forward differencing. If $b_1, b_2, \ldots, b_n$ are all zero, then this corresponds to the backward differencing situation. For example, the symmetric 4-point approximation for the first derivative can be written as

$$f'(x) \simeq \frac{f(x-2h) - 8f(x-h) + 8f(x+h) - f(x+2h)}{12h}. \tag{2}$$

The error in the above approximation is given by $\frac{h^4}{30} f^5(\xi)$. It must be noted that this symmetric differencing involves 5 points, namely $f(x-2h)$, $f(x-h)$, $f(x)$, $f(x+h)$ and $f(x+2h)$ but the coefficient of $f(x)$ happens to be zero by symmetry. One can obtain expression for higher-order derivatives too. For example the second derivative at x can be approximated as

$$f''(x) \simeq \frac{-f(x-2h) + 16f(x-h) - 30f(x) + 16f(x+h) - f(x+2h)}{12h^2} \tag{3}$$

with an error term, $\frac{h^6}{90} f^6(\xi)$. Alternatively, we can obtain these derivative approximants by differentiating the standard Lagrange interpolation formula which also yields the errors associated with these approximations. These coefficients for the first, second, third and derivatives of various orders for the forward and backward difference cases are tabulated in [2].

The usual tendency in approximating derivatives in boundary conditions and in similar scenarios is to use a 2- or 3-term derivative approximation formula. Typically, for a symmetric case, one tends to approximates the derivative as

$$f'(x) = \big[f(x+h) - f(x-h)\big]/2h. \tag{4}$$

However, there are occasions, when a 7- or even a 9-point derivative approximations can be used instead of just a 2- or 3-point approximation. In the following two examples, we show that the computational gain is substantial if we use a higher-order formula for the first derivative. In the first example, we consider the transport of radioactivity in a porous medium which is rock. Here the boundary conditions of the two coupled partial differential equations involve expressions involving the first derivative. The second example chosen is the evaluation of the quantum mechanical expression for the rate constant k, for a bimolecular chemical reaction with an Eckart barrier, using the Miller–Schwartz–Tromp formula. Here the evaluation of k needs the derivative of the wavefunction with respect to the reaction coordinate at the transition state, to calculate the reactive flux.

3. Radioactivity migration in a porous medium

The problem of storing radioactive wastes in underground sites is of utmost importance from radiological and environmental considerations. The long lived high level wastes from the nuclear industry are concentrated and then embedded in a glass matrix and subsequently stored at depths of around 600 m in containers. The containers are surrounded by rock. It is of interest to know how an accidental leakage of the radioactive material from the container will propagate in the rock as a function of time. For modelling this [3], the rock medium is considered as porous blocks separated by multiple fractures. The fractures are assumed to be planar, identical, parallel and equally spaced (Fig. 1). The fracture has a width $(2b)$ and the fractures are spaced at a distance of $(2B)$. b and B are of the order of 10^{-3} m and 10^3 m respectively. $z = 0^-$ and $z = 0^+$ correspond to the waste matrix and fracture sides respectively at the waste matrix-fracture interface. Similarly, $x = 0$ and $x = b$ respectively correspond to the centre of fracture and the fracture wall. The radioactive waste matrix is assumed to send a constant flux which propagates along the fracture and also diffuses across the fractures. Water flow is assumed to take place only in the fracture since the hydraulic conductivity of the porous rock matrix is low. However the rock permits molecular diffusion along the fracture (z direction) and also across the porous matrix (x direction). To cast this model into a one-dimensional problem, the following assumptions are made:

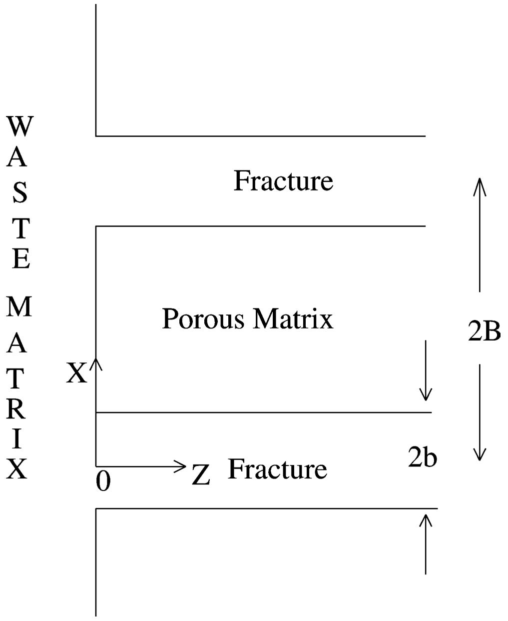

Fig. 1. Fracture waste–matrix system.

(1) The width of each fracture is much smaller than its length.
(2) Complete mixing is enabled by transverse diffusion and dispersion across each fracture. Hence concentration is uniform across each fracture.
(3) Flow of water is laminar in each fracture which allows the use of Darcy's law.
(4) Molecular diffusion is the only mechanism along the x direction (i.e., from the fracture into the porous matrix and across the porous matrix) which is much slower than the transport in z direction along the fracture.

By assuming that the velocity of water is constant, an analytical solution for this model is derived by Chen and Li [3]. But such an assumption is not necessary for the numerical solution of the governing partial differential equations. The model also considers the radioactive decay and the adsorption onto the fracture walls and within the porous matrix. More details can be found in Chen and Li [3]. Let D_p, R_p and C_p denote the diffusion coefficient, the matrix retardation factor and the concentration of radionuclide in the porous matrix. Then the partial differential equation (PDE) for C_p, describing the diffusive transport of radionuclide in the porous matrix is given by

$$\frac{\partial C_p}{\partial t} - \frac{D_p}{R_p}\frac{\partial^2 C_p}{\partial x^2} + \lambda C_p = 0, \quad b \leqslant x \leqslant B,\ t \geqslant 0. \tag{5}$$

Here λ is the decay constant of the radioactive substance. The PDE for the concentration C, describing the transport of radionuclide along the fracture is given by

$$\frac{\partial C}{\partial t} + \frac{\nu}{R}\frac{\partial C}{\partial z} - \frac{D}{R}\frac{\partial^2 C}{\partial z^2} + \lambda C + \frac{q}{Rb} = 0, \quad z \geqslant 0,\ t \geqslant 0. \tag{6}$$

Here R is the fracture retardation factor. D and ν are the dispersion coefficient and the ground water velocity in the fracture respectively. The second, third and the fourth terms of above equation account for advection, diffusion and decay respectively. q represents the molecular diffusive flux crossing the fracture-matrix boundary and is given by

$$q(z,t) = -\theta D_p \left\{\frac{\partial C_p}{\partial x}\right\}_{x=b}, \quad z \geqslant 0,\ t \geqslant 0. \tag{7}$$

Here θ denotes the matrix porosity. We need to prescribe the initial and boundary conditions for solving these two coupled PDEs. Initial concentrations in both the fracture and the porous matrix are zero which are given by Eqs. (8) and (9). We look for solutions that die down at infinity which is expressed by Eq. (10). The flux is continuous across the waste-fracture interface, which is given by Eq. (11). Eq. (12) expresses the fact that the concentration is continuous at the fracture-matrix interface. Eq. (13) implies that the concentration in the porous matrix takes a minimum value at the centreline which is a consequence of symmetry in the x direction.

$$C(z,0) = 0, \quad z \geqslant 0, \tag{8}$$

$$C_p(x,z,0) = 0, \quad b \leqslant x \leqslant B,\ z \geqslant 0, \tag{9}$$

$$C(\infty,t) = 0, \quad t \geqslant 0, \tag{10}$$

$$-D\left\{\frac{\partial C}{\partial z}\right\}_{z=0} + \nu C(0,t) = \nu C_0, \quad t \geqslant 0, \tag{11}$$

$$C_p(b,z,t) = C(z,t), \quad z \geqslant 0,\ t \geqslant 0, \tag{12}$$

$$\frac{\partial C_p}{\partial x}(B,z,t) = 0, \quad z \geqslant 0,\ t \geqslant 0. \tag{13}$$

We define a series of terms below.

$$G = (R_p/D_p)^{1/2}; \quad \sigma = G(B-b); \quad \alpha = \frac{\nu}{2D}; \quad \beta = \frac{(4RD)^{1/2}}{\nu}, \tag{14}$$

$$\varepsilon_R = -\frac{\xi\varepsilon}{2A}\frac{\sinh(\sigma\varepsilon) - \sin(\sigma\varepsilon)}{\cosh(\sigma\varepsilon) + \cos(\sigma\varepsilon)}, \tag{15}$$

$$\Omega = \frac{\xi\varepsilon}{2A}\frac{\sinh(\sigma\varepsilon) + \sin(\sigma\varepsilon)}{\cosh(\sigma\varepsilon) + \cos(\sigma\varepsilon)}, \tag{16}$$

$$F_1(z,\alpha,\beta,\xi,\lambda) = \frac{1}{\beta\sqrt{\pi\xi}}\exp\left(-\frac{(z\alpha\beta)^2}{4\xi} - \xi\left(\beta^{-2}+\lambda\right) + z\alpha\right), \tag{17}$$

$$F_2(z,\alpha,\beta,\xi,\lambda) = \frac{1}{\beta^2}\exp(2z\alpha - \lambda\xi)\operatorname{erfc}\left(\frac{z\alpha\beta}{2\sqrt{\xi}} + \frac{\sqrt{\xi}}{\beta}\right), \tag{18}$$

$$F_3(\varepsilon,\varepsilon_R,\lambda) = \frac{\varepsilon\exp(\varepsilon_R)}{\lambda^2 + (\varepsilon^4/4)}; \qquad F_4(\varepsilon,\Omega,\lambda) = \varepsilon^2/2 + \lambda\cos(\Omega), \tag{19}$$

$$F_5(\lambda,t,\xi) = \exp\left[-\lambda(t-\xi)\right]; \qquad F_6(\varepsilon,\varepsilon_I,\lambda) = \left(\varepsilon^2/2\right)\sin(\varepsilon_I)|_{t=t-\xi} - \lambda\cos(\varepsilon_I)|_{t=t-\xi}. \tag{20}$$

Let C_0 denote the concentration of the waste matrix. Then in terms of the above terms, the analytical solution can be written as

$$C(z,t) = \frac{2C_0}{\pi}\int_0^t \mathrm{d}\xi\,(F_1 - F_2)\int_0^\infty F_3[F_4 + F_5F_6]\,\mathrm{d}\varepsilon. \tag{21}$$

This is an elegant solution, obtained by Laplace transform technique [3]. The above two-dimensional integral can be evaluated for distances up to about 100 m easily. Beyond 100 m, the integrand is highly oscillatory and also the exponential terms reach high values which together preclude the possibility of numerical evaluation. For radiological assessment, one needs $C(z,t)$ for z values around 500 m and hence we resort to finite differencing the PDEs.

Let the time and space indices be denoted by j and i respectively. That is C_i^j denotes the concentration at $z = i(\Delta z)$ and at the time $= j(\Delta t)$. Using a forward differencing for the time derivative we get,

$$\frac{\partial C_i^j}{\partial t} \simeq \frac{C_i^{j+1} - C_i^j}{\Delta t}. \tag{22}$$

This implies a discretisation error of the order of (Δt). For the space variable we employ symmetric differencing and the first derivative is given by

$$\frac{\partial C_i^j}{\partial z} \simeq \frac{C_{i+1}^j - C_{i-1}^j}{2\Delta z} \tag{23}$$

which has an error of the order of $(\Delta z)^2$. The second derivative is given by

$$\frac{\partial^2 C_i^j}{\partial z^2} \simeq \frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{2(\Delta z)^2}. \tag{24}$$

The second derivative approximation has an error which is of the order of $(\Delta z)^2$ again. Choosing a maximum distance $z_{\max}$, we divide this distance into a number of equispaced grid points $\{z_i\}$ and at each z_i, we discretise the porous matrix in the x direction too. Let ${C_p}_i^j$ denote the concentration at $x = i(\Delta x)$ and at the time $= j(\Delta t)$ for a given z_k. Subjecting both the PDEs to the discretisation scheme indicated above, we end up with linear algebraic equations for the unknowns $\{C_i^j\}$ and $\{{C_p}_i^j\}$. If the variables C_i^j and ${C_p}_i^j$ are known for a given j and for all i, then C_i^{j+1} and ${C_p}_i^{j+1}$ can be evaluated for all i using the discretised version of the PDEs and the boundary conditions.

Crucially, for the derivatives appearing in Eqs. (3) and (7), we apply the same n-term derivative approximation formula given by

$$\left\{\frac{\partial C_p}{\partial x}\right\}_{x=b} \simeq (1/\Delta x)\big(a_1 C_p(b) + a_2 C_p(b+\Delta x) + a_3 C_p(b+2\Delta x) + \cdots + a_n C_p\big(b + \overline{n-1}\Delta x\big)\big), \tag{25}$$

$$\left\{\frac{\partial C}{\partial z}\right\}_{z=0} \simeq (1/\Delta z)\big(a_1 C(0) + a_2 C(\Delta z) + a_3 C(2\Delta z) + \cdots + a_n C\big(\overline{n-1}\Delta z\big)\big). \tag{26}$$

The various parameters for the solution of the PDEs are given below.

$$D = 1.0\ (\mathrm{m}^2/\mathrm{yr}); \qquad D_p = 0.01\ (\mathrm{m}^2/\mathrm{yr}); \qquad R = 1.0; \qquad R_p = 1.0;$$

$$v = 1.0\ (\mathrm{m}/\mathrm{yr}); \qquad T_{1/2} = 2.14\times 10^6\ (\mathrm{yr}); \qquad \lambda = \frac{\log(2)}{T_{1/2}}; \qquad b = 0.0005; \qquad \theta = 0.01.$$

With this choice of parameters, the calculations are carried out with double precision accuracy in FORTRAN which guarantees a 14 digit accuracy.

Table 1 gives the results of the numerical solution. These values correspond to a step size of 0.2 m in both x and z directions. $z_{\max}$ is chosen as 500 m. The number of grid points in the z and x directions are 2500 and 5000 respectively. The time step is 0.018 yr and the computation is carried out for a 1000 yr period. The second column gives the exact values computed by the 2-D analytical solution for distances up to 100 m. The values obtained by the finite difference scheme for various orders of derivative approximation are given in the remaining columns. We observe about 3 digit accuracy for the calculated values for distances up to 50 meters. Also it is noticed that even a 4-point derivative formula does not give better accuracy compared to a 5- or 6- or 7-point derivative formula. Beyond 7-point expansion, due to numerical saturation, the improvements become less. As z increases, we see that the use of 7-point formula gives better results than a 5- or a 6-point formula. This is illustrated by the values corresponding to $z = 200$ m. For this z value, there are no reported reference values. As we have discussed earlier, the analytical solution cannot be evaluated since the solution integral is highly oscillatory and also the values of integrand exceed the bound set by commonly used FORTRAN compilers for double precision computation. The value reported here, namely 2.9E−14 is the converged value. The 2-point derivative scheme yields a value 4.3E−12 which has a discrepancy of two units in the exponent when compared with the converged value. Also, the 2 digit convergence is observed only for the 7-point derivative. The superiority of the higher-order derivative scheme is thus clear for large z. In fact, but for the higher-order derivative, the estimation at distances beyond 200 m will be beset with uncertainties due to lack of convergence. This is understandable since the concentration at any distance z is governed by the diffusion that takes place in the z direction. In addition, it is dependent on the diffusion that takes place in the x direction and hence an accurate calculation of C for large z needs a precise evaluation of the diffusion in both z and x directions which call for a careful evaluation of the derivatives of the concentrations. We have employed a scheme which is only first order accurate in time with an error of the order of Δt and second order accurate in space having an error of the order of $(\Delta x)^2$. Hence the overall accuracy will improve significantly with higher-order finite difference schemes.

Table 1
Concentration C along z direction after 1000 years for various values of n, the order of derivative approximation. z is in meters

Z	Exact	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
10	0.62931	0.633338	0.629071	0.629192	0.629203	0.629203	0.629203
30	0.18410	0.195723	0.184272	0.184020	0.184029	0.184030	0.184030
50	3.2303E−2	3.9363E−2	3.2639E−2	3.2323E−2	3.2311E−2	3.2311E−2	3.2311E−2
70	3.4266E−2	5.3032E−3	3.5505E−3	3.4442E−3	3.4369E−3	3.4364E−3	3.4364E−3
100	4.7879E−5	1.3231E−04	5.3970E−5	4.9065E−5	4.8567E−5	4.8515E−5	4.8501E−5
200		4.30E−12	7.54E−14	3.58E−14	3.07E−14	2.99E−14	2.98E−14

In a series of papers Smith and his coworkers [4,5] have worked out solution methodology for very general advection–diffusion equations in one and more dimensions. The starting point of their approach can be viewed as modifications of the Crank–Nicholson method. The terms of the partial differential equation other than the time derivative term and the inhomogeneous terms are given optimal weights. For example the term λC during discretisation is chosen as $\lambda\{\theta_1 C(t) + (1-\theta_1)C(t+\Delta t)\}$. Similarly, the first and second partial derivative terms involving the space variable are weighted with parameters θ_2 and θ_3. Finally, the weights $\theta_i,\ i = 1, 2, 3, \ldots,$ are chosen optimally to improve accuracy. In the Crank–Nicholson like scheme, θ is chosen as $1/2$, giving equal weight to quantities at successive time steps. The spirit of the above approach is to improve the overall accuracy by giving optimal weights to quantities at consecutive time steps whereas in the present work, we improve the accuracy just by using a higher-order approximation for a crucial boundary derivative. The possibility of a judicious mix of the optimal weighting and higher-order boundary derivative approximation is to be explored in future.

4. Application to quantum rate theory

Here one considers a bimolecular chemical reaction of the type

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C}.$$

The rate of formation of the molecule AB is governed by the following equation,

$$\frac{\mathrm{d[AB]}}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}], \tag{27}$$

k is the reaction rate constant which is a function of T, the temperature. Given the potential energy surface, it is desirable to calculate k from first principles. For gas phase reactions, the reaction can be considered as a scattering event and in principle k can be calculated quantum mechanically from the scattering matrix S. However, the computational complexities are prohibitive for realistic cases. These complications can be minimised to a large extent by considering the reaction dynamics in the vicinity of the reaction barrier. Using this approach, Miller, Schwartz and Tromp [6] (MST) gave a quantum mechanically exact expression for the rate constant in terms of time correlation functions. In terms of the flux–flux autocorrelation function $C_f(t)$, the MST formula can be written as

$$kQ = \int_0^\infty \mathrm{d}t\, C_f(t) \tag{28}$$

where Q is the partition function for reactants. $C_f(t)$ is given in terms of the Hamiltonian H and the symmetrised flux operator $\overline{F}$ by

$$C_f(t) = \mathrm{tr}\big[\overline{F}\exp(\mathrm{i}Ht_\mathrm{c}^*/\hbar)\overline{F}\exp(-\mathrm{i}Ht_\mathrm{c}^*/\hbar)\big]. \tag{29}$$

Here trace denotes the quantum mechanical trace and k_B is the Boltzmann constant. The symmetrised flux operator $\overline{F}$ and the complex time t_c are given by

$$\overline{F} = (1/2)\big[\delta(s)(p/m) + (p/m)\delta(s)\big], \tag{30}$$

$$t_\mathrm{c} = t - \mathrm{i}\hbar\beta/2; \quad \beta = 1/(k_\mathrm{B}T). \tag{31}$$

Here s is the reaction coordinate and p is its conjugate momentum operator. m is the mass of the particle. We assume for simplicity that the total reactive system is one-dimensional. If $\{\phi_n(s)\}$ is a finite set of square integrable basis functions, diagonalising the matrix of H in this basis functions produces the eigenvalues $\{E_i\}$ and eigenfunctions $\{\psi_i(s)\}$. In this matrix representation the correlation function $C_f(t)$ is given by

$$C_f(t) = \sum_{i,j} \exp\bigl[-\beta(E_i + E_j)/2\bigr] \cos\bigl[(E_i - E_j)t/\hbar\bigr] \bigl|\langle i|\overline{F}|j\rangle\bigr|^2 \tag{32}$$

where

$$\bigl|\langle i|\overline{F}|j\rangle\bigr|^2 = (\hbar/2m)^2 \bigl|\psi_i'(0)\psi_j(0) - \psi_i(0)\psi_j'(0)\bigr|^2. \tag{33}$$

Numerical integration of $C_f(t)$ over a set of values of time t yields the quantity (kQ).

We have chosen the problem of one-dimensional Eckart barrier with the parameter values indicated in Park and Light [7]. The potential barrier is given by $V(s) = V_0\,\mathrm{Sech}^2(s)$ where V_0 has a value of 0.0114 and we use atomic units throughout. To construct the Hamiltonian matrix, We use the Discrete Variable Representation (DVR) basis (Colbert and Miller [8]). For a one-dimensional problem, with s restricted to the interval (a, b), the grid points $\{s_i\}$ and the basis functions $\{\phi_j(s)\}$ are given by

$$s_i = a + (b-a)\frac{i}{N}, \quad i = 1, \ldots, (N-1), \tag{34}$$

$$\phi_j(s) = \bigl[2/(b-a)\bigr]^{1/2} \sin\left(\frac{j\pi(s-a)}{b-a}\right), \quad j = 1, \ldots, (N-1). \tag{35}$$

In this representation, the potential energy operator is diagonal. That is

$$V_{ij} = V(s_i)\delta_{ij}. \tag{36}$$

The grid points are distributed over $(-5, 5)$. The kinetic energy matrix is given by

$$T_{ij} = \frac{\hbar^2}{2m}\frac{(-1)^{i-j}}{(b-a)^2}\frac{\pi^2}{2}\left(\frac{1}{\sin^2[\pi(i-j)/(2N)]} - \frac{1}{\sin^2[\pi(i+j)/(2N)]}\right), \quad i \neq j, \tag{37}$$

$$T_{ii} = \frac{\hbar^2}{2m}\frac{(-1)^{i-j}}{(b-a)^2}\frac{\pi^2}{2}\left((2N^2+1)/3 - \frac{1}{\sin^2(\pi i/N)}\right). \tag{38}$$

Diagonalising the Hamiltonian in this basis gives the eigenfunctions $\{\psi_i(s)\}$ and the eigenvalues $\{E_i\}$ from which $C_f(t)$ is evaluated as given by Eq. (32). To calculate the derivatives in Eq. (33), we use the higher-order derivative formula. Here we use symmetric derivative formulae up to 10th order.

There are two quantities of interest. First is the value of k, the quantum mechanical rate constant. kQ is given by the area under the curve, the time t versus flux auto correlation function $C_f(t)$ plot. The second quantity is $C_f(0)$. For $T = 500$, the correct values of kQ and $C_f(0)$ are 9.8 and 1.51 respectively (Wyatt [9]). Table 2 gives the values of both these quantities for various values of the order of the Hamiltonian N. These calculations are done with just a 2-point derivative. Each value is followed by its absolute relative percentage error, indicated within the

Table 2
Values of (kQ) and $C_f(0)$ for various values of N, the order of the Hamiltonian using a 2-point derivative

N	kQ	$C_f(0)$	CPU time
60	9.5168 (2.89%)	1.3641 (9.66%)	1.203
80	9.6530 (1.50%)	1.4207 (5.91%)	2.203
100	9.7147 (0.87%)	1.4486 (4.06%)	3.531
120	9.7478 (0.53%)	1.4643 (3.03%)	5.141
140	9.7676 (0.33%)	1.4739 (2.39%)	7.062
160	9.7804 (0.20%)	1.4802 (1.97%)	9.297
180	9.7892 (0.11%)	1.4846 (1.68%)	11.891
200	9.7954 (0.05%)	1.4877 (1.48%)	14.797

bracket. For $N = 60$, we get a value of 9.5168 for kQ which is having an error of 2.89%. As N increases, the error decreases and for $N = 200$, we get a value of 9.7954 which has an error of just 0.05%. This is to be contrasted with the values calculated by a 10-point derivative approximation using a Hamiltonian of order not exceeding 44. For $N = 38$, 40, 42 and 44 with 10-point derivative evaluation, (kQ) value has errors 0.16%, 0.11%, 0.10% and 0.12% as indicated in the last column of Table 3. To achieve a relative percentage error of 0.11% with a 2-point derivative, we need to have a Hamiltonian of order 180 whereas with a 10-point derivative, a Hamiltonian of order 40 suffices. For $N = 38$, 40 and 42, the (kQ) values are 9.816, 9.8106 and 9.8101, indicating a converged value of 9.81.

A similar trend is indicated for $C_f(0)$. Using a 2-point derivative we get the values 1.3641 and 1.4877 for $N = 60$ and $N = 200$ respectively, with corresponding errors 9.66% and 1.48% (Table 2). Using a 10-point derivative, the corresponding errors for $N = 32$, 34 and 36 are 0.43%, 0.14% and 0.06% which are indicated in the last column of Table 4. The advantage of the higher-order derivative scheme is once again demonstrated. Compared to the porous flow considered earlier, the computational gain is more impressive, which is partly due to the symmetry of the potential. Finally, Fig. 2 gives a plot of the flux–flux auto correlation function as a function of time for a 36 by 36 Hamiltonian for the Eckart barrier. data1, data2, data3 and data4 of legend of Fig. 2 correspond to derivative approximation orders 2, 4, 6 and 10 respectively.

We also give a comparison of the CPU times for generating the $C_f(t)$ values for a time interval of 35 fs. These CPU times are indicated in the last column of Table 2 where we use a 2-point derivative. For a Hamiltonian of order 180 with a 2-point derivative, a kQ value 9.7892 with a relative absolve error of 0.11% is obtained. This evaluation needs a CPU time of 11.891 units. This to be contrasted with the corresponding values using a Hamiltonian of order 40 employing a 10-point derivative scheme. For this Hamiltonian, the relative absolute error is 0.11% and the CPU time is just 0.516 units indicating a reduction by a factor of 23. The CPU times for a Hamiltonian of order 40 alone are indicated in Table 3 for different orders of derivative approximation. We also note that with N fixed, the increase in CPU time is marginal as the order of the derivative increases from 2 to 10. These calculations were performed under MATLAB.

Table 3
Values of (kQ) for various orders of the Hamiltonian N and for various orders of the derivative approximation n. For $N = 40$, the third row of entries give the CPU time

N	$n = 2$	$n = 4$	$n = 6$	$n = 8$	$n = 10$
32	8.6646 (11.59%)	10.5974 (8.14%)	10.5358 (7.51%)	10.2205 (4.29%)	9.9625 (1.66%)
34	8.8076 (10.13%)	10.4665 (6.80%)	10.3397 (5.51%)	10.0645 (2.70%)	9.8734 (0.75%)
36	8.9254 (8.92%)	10.3589 (5.70%)	10.2007 (4.09%)	9.9699 (1.73%)	9.8325 (0.33%)
38	9.0238 (7.92%)	10.2712 (4.81%)	10.1021 3.08%	9.9129 1.15%	9.8160 (0.16%)
40	9.1068 (7.07%)	10.1996 (4.08%)	10.0314 (2.36%)	9.8783 (0.80%)	9.8106 (0.11%)
	0.484	0.500	0.500	0.515	0.516
42	9.1774 (6.35%)	10.1411 (3.48%)	9.9802 (1.84%)	9.8571 (0.58%)	9.8101 (0.10%)
44	9.2380 (5.73%)	10.0930 (2.99%)	9.9428 (1.46%)	9.8440 (0.45%)	9.8114 (0.12%)

Table 4
Values of $C_f(0)$ for various orders of the Hamiltonian N and for various orders of the derivative approximation n

N	$n = 2$	$n = 4$	$n = 6$	$n = 8$	$n = 10$
32	1.1198 (25.84%)	1.4087 (6.71%)	1.4845 (1.6874%)	1.5084 (0.10%)	1.5165 (0.43%)
34	1.1511 (23.77%)	1.4239 (5.70%)	1.4888 (1.40%)	1.5070 (0.20%)	1.5122 (0.14%)
36	1.1793 (21.90%)	1.4365 (4.87%)	1.4920 (1.19%)	1.5058 (0.28%)	1.5091 (0.06%)
38	1.2047 (20.22%)	1.4468 (4.18%)	1.4943 (1.04%)	1.5049 (0.34%)	1.5069 (0.21%)
40	1.2275 (18.71%)	1.4553 (3.62%)	1.4961 (0.92%)	1.5042 (0.39%)	1.5053 (0.31%)
42	1.2480 (17.35%)	1.4624 (3.15%)	1.4974 (0.83%)	1.5036 (0.43%)	1.5041 (0.39%)
44	1.2666 (16.12%)	1.4682 (2.77%)	1.4984 (0.77%)	1.5031 (0.46%)	1.5033 (0.44%)

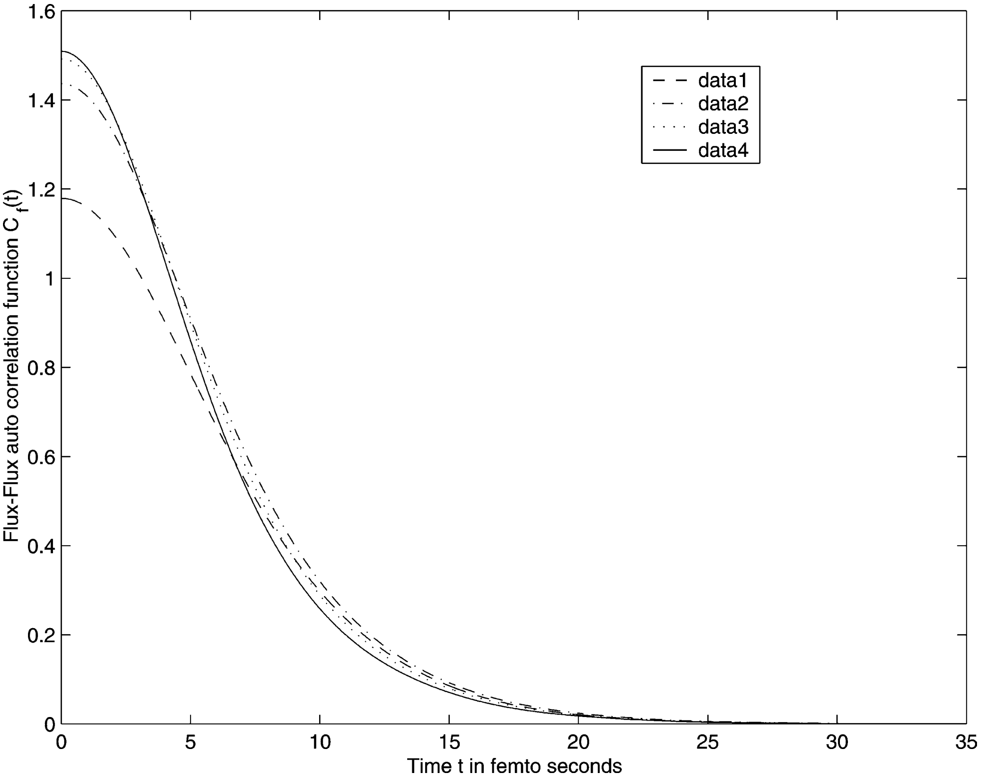

Fig. 2. Time versus flux–flux auto correlation function plot for a 36 by 36 Hamiltonian.

5. Conclusion

The two examples illustrate the point that one need not stop with a 2-point derivative approximation. One can use a higher-order derivative approximation for implementing boundary conditions of differential equations and in similar situations which will result in significant computational economy.

Acknowledgement

NMK acknowledges the very helpful discussions with Dr. Justin Fermann. We also thank one of the referees for bringing some interesting and recent references to our attention.

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