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LETTER TO THE EDITOR

Numerical calculation of wavefunctions near a strongly repulsive potential

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Abstract. It is shown that inverse-power representations of the strongly repulsive potentials sometimes used in molecular eigenvalue and scattering calculations introduce extra errors into the wavefunctions, not normally expected from the finite difference integration formulae used.

In the numerical determination of bound state and scattering wavefunctions arising in molecular calculations the potentials and energies, being multiplied by the large reduced masses, become large themselves especially at short range. Although the potentials are the sums of Coulomb interactions between the constituent charged particles and therefore cannot be more singular than the Coulomb potential itself, they are often replaced by strongly repulsive potentials for computational convenience. This can cause difficulties in multichannel calculations where it is important to know the potentials accurately because reaction cross sections can be altered significantly by interference effects at short range, as shown by Cooper *et al* (1987). In single-channel calculations the lack of accurate short-range potentials is less important and is usually compensated for by a judicious choice of starting point for the integration (where the wavefunction is taken as zero) and use of sufficiently small step lengths in the finite difference integration formula. However, a useful test of the reliability of a numerical result found by finite difference methods is to recalculate it for different step lengths h, to check for correct h dependence (Fox and Mayers 1968). It is shown below that, in this context, an accurate short-range potential can be important even in a single-channel calculation because, for example, replacing it by an inverse power introduces unexpected h dependence. Coulomb potentials and centrifugal barriers induce errors which are simple powers of h (Jamieson 1988) but the extra h dependence is more dramatic for inverse powers exceeding two. Frank *et al* (1971) in an extensive review include the latter potentials amongst the singular. It is the singular inverse-power potentials which introduce errors with the more exotic h dependences. It is shown that such a singular potential introduces a solution of the differential equation violating the inner boundary condition into the wavefunction numerically determined by a finite difference integration formula. This unwanted solution alters any calculated phase shift or eigenfunction and eigenvalue. The analysis below generalises an earlier investigation (Jamieson 1983) of the effect of an inverse sixth-power potential on the eigenvalues of an harmonic oscillator.

At small internuclear distance r, the equation to be solved is

$$y''(r) = c^2 r^{-2q-2} y(r) \tag{1}$$

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with the inner boundary condition that $y(0)$ vanishes; here c^2 is a positive constant and $2q$ is a positive integer. In molecular calculations it is tempting to use such short-range potentials because they are large at small r, are continuous and with careful choice of c and q do not unduly upset the medium- and long-range potentials. This equation is obtained in Cayley's method for solving the Riccati equation (Watson 1944, with q replacing $-q$). The independent solutions of (1), $u(r)$ and $v(r)$, are given by $r^{1/2}K_{1/2q}(c/qr^q)$ and $r^{1/2}I_{1/2q}\ (c/qr^q)$ where I and K denote modified Bessel functions; the solution $u(r)$ vanishes at the origin while $v(r)$ does not. The correct solution is proportional to $u(r)$. We investigate the error when the simplest finite difference formula, that of Hartree, is used to solve the equation with starting conditions

$$\begin{aligned} y(0) &= 0 \\ y(h) &= 1. \end{aligned} \tag{2}$$

As in the earlier paper we use the error analysis of Mayers (1964) because of the singularity. The leading error (in h) $w(r)$ satisfies the differential equation

$$w''(r) = c^2 r^{-2q-2} w(r) + \tfrac{1}{12} h^2 u^{(iv)}(r)/u(h) \qquad r \geqslant h. \tag{3}$$

The value of $w(2h)$ must be constructed from the finite difference formula. The boundary conditions on the error are

$$\begin{aligned} w(h) &= 0 \\ w(2h) &= u(2h)/u(h) - 2 - c^2 h^{-2q}. \end{aligned} \tag{4}$$

The error may be written as the complete primitive

$$w(r) = A(h)u(r)/u(h) + B(h)v(r)/v(h) + p(r)u(r)/u(h) \tag{5}$$

where the last term is a particular solution of equation (3) and $A(h)$, $B(h)$ are to be determined from (4); the ratios are used for algebraic convenience because they remove constant multipliers. The first term and the particular solution vanish at the origin and merely alter the overall normalisation of the solution of equation (1) to be used in a scattering or eigenvalue calculation but the second term is an error. We find

$$B(h) = [p(2h) - p(h) - 1 + (2 + c^2 h^{-2q})u(h)/u(2h)]/[1 - \{v(h)/v(2h)\}/\{u(h)/u(2h)\}]. \tag{6}$$

For small values of r the arguments of the Bessel functions are large and we can use asymptotic expansions (Watson 1944)

$$\begin{aligned} u(r)/u(h) &\simeq (r/h)^{(q+1)/2} \exp(-c/qr^q + c/qh^q) \\ v(r)/v(h) &\simeq (r/h)^{(q+1)/2} \exp(c/qr^q - c/qh^q) \end{aligned} \tag{7}$$

and after some algebra we find the function $p(r)$ of the particular solution to be

$$p(r) \simeq -\{h^2 c^3/[24(3q+2)]\} r^{-3q-2} \tag{8}$$

so that

$$B(h) \simeq (\{c^3/[24(3q+2)]\} h^{-3q}(1 - 2^{-3q-2}) - 1 + (2 + c^2 h^{-2q}) 2^{-(q+1)/2} \times \exp[-c(1-2^{-q})/qh^q])(1 - \exp[-2c(1-2^{-q})/qh^q])^{-1}. \tag{9}$$

From (5), (7) and (9) we see that the error term has a complicated dependence on h and that it vanishes if h vanishes. However, we have the unexpected result, verified

numerically earlier (Jamieson 1983), that the smaller the value of c is the smaller is the value of h required to reduce the error. This seems contradictory since it suggests that the worse the singularity is, the easier it is to deal with numerically. It can be explained as follows. We have omitted the non-singular (in the terminology of Frank *et al* (1971)) potential. The Hartree formula can follow the solution for the non-singular potential but away from the origin it can also follow the solution for the singular potential reasonably well. Near the origin it attempts to follow the solution under the influence of the very rapidly changing singular potential. If c is small most of the effect of this potential occurs in the interval $(0, h]$. Because the finite difference formula effectively starts at $r = h$ (the wavefunction being set to zero at the origin) it misses much of the effect of the singular potential. The potential cuts off quite sharply at $r = c^{1/q}$, particularly if q is large. For larger values of c the cut-off does not occur until several steps of the finite difference integration have been completed and the formula makes a better attempt at following the solution away from the origin.

The error must vanish if c is allowed to vanish for a fixed step h. From equation (9) and the special case discussed earlier (Jamieson 1983) we see that this does not appear to be so. This is because in the derivation of equation (9) and the special case we have used asymptotic expansions for the Bessel functions which are not valid for small c. We must use instead series expansions in ascending powers of c (Watson 1944)

$$\begin{aligned} u(r)/u(h) &\simeq x/h + \mathrm{O}(c^{1/q}) \\ v(r)/v(h) &\simeq 1. \end{aligned} \tag{10}$$

If $q = \frac{1}{2}$ the Bessel functions are of integer order. Use of the appropriate series for $K_1(2c/r^{1/2})$ shows that there is an extra term of order $c^2 \ln(c)$ in the first of equations (10) which does not affect our subsequent discussion. We find

$$p(r) \simeq -\{(2q+1)(2q+2)h^2c^2/[12(2q+3)]\}r^{-2q-3}. \tag{11}$$

In the numerator of expression (6) for $B(h)$ we see that the first two terms and the last term are proportional to c^2 while the rest have some cancellation leaving a term in $c^{1/q}$ so that the whole expression vanishes if c vanishes, as required.

The complicated form of the error does not depend on the choice of Hartree's integration formula. It arises because the singularity is an essential one and similar behaviour is expected with any Lagrangian integration formula, including those designed for stiff differential equations. An example of the latter is, in obvious notation,

$$\mathbf{z}_{n+1} = \mathbf{F}_n \mathbf{z}_n + \mathbf{G}_{n+1} \mathbf{z}_{n+1} \tag{12}$$

where $\mathbf{z}$ denotes the two-element vector with components y and y', $\mathbf{F}$ is a two-by-two matrix with unit diagonal elements and upper right and lower left elements of zero and $\frac{1}{3}hc^2r^{-2q-2}$ respectively and $\mathbf{G}$ is a two-by-two matrix with diagonal elements of $-\frac{1}{2}h^2c^2r^{-2q-2}$ and zero, and upper right and lower left elements of h and $\frac{2}{3}hc^2r^{-2q-2}$ respectively. It is easy to show that the leading error satisfies equation (3) with the inhomogeneous term reversed in sign; the boundary conditions (4) are modified. The error is given by equation (5) differing only in the particular solution and subsequent analysis reveals the same kind of exotic behaviour as we have inferred above.

In conclusion we see that the representation of a strongly repulsive potential by a singular potential introduces an exotic-looking error which can be removed by use of a small enough step length. It vanishes, as it should, as the strength of the potential is reduced. The error must be taken into account when testing numerical software. It is best to start with a small enough step that only the other simple error terms remain.

It is worth noting that calculations which are made by starting the integration away from the origin at r_0, say, are subject to a different error induced by the boundary condition that the wavefunction vanishes at r_0, not at the origin. This error depends on the ratio $u(r_0)/v(r_0)$ which here is approximately $\exp(-2c/qr_0^q)$ provided r_0 is small enough to allow use of the asymptotic expansion (7).

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