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NOTE

Comparison of Phase-Shift Calculations by Asymptotic Fit and Quadrature in Ultra-Low Temperature Scattering

Elastic scattering of atoms at ultra-low temperatures is dominated by s-wave or zero angular momentum scattering. Furthermore, at a low energy, E, of relative motion the phase-shift is $N_{bd}\pi + \eta$, where N_{bd} is the number of bound states and η is approximately $-ka$, where k is the wave number (given by $(1/\hbar)\sqrt{2\mu E}$, where μ is the reduced mass and $\hbar$ is the rationalized Planck's constant) and a is the scattering length; η is very small at an ultra-low energy. We shall refer to η *itself* as the phase-shift throughout this paper. We demonstrate below that some small phase-shifts are more accurately calculated by quadrature than by fitting numerical solutions of the Schrödinger equation to their asymptotic forms.

The radial part of the Schrödinger equation in terms of the radial coordinate or internuclear separation R is

$$y''(R) + \frac{2\mu}{\hbar^2}[E - V(R)]y(R) \equiv y''(R) + Q(R)y(R) \equiv y''(R) + K^2(R)y(R) = 0, \tag{1}$$

where $y(R)$ is R times the radial s-wave function, $V(R)$ is the interaction potential (vanishing asymptotically at large R), and Eq. (1) also defines the function $Q(R)$ and the *local* wave number $K(R)$; $K(R)$ coincides with k asymptotically and is imaginary in the non-classical region. The boundary conditions are

$$y(0) = 0 \tag{2}$$

and for large R

$$y(R) \to A\sin(kR + \eta). \tag{3}$$

In atomic scattering the potential is often taken as a hard core at small internuclear separation inside which the wave-function vanishes; we replace the origin in Eq. (2) by R_0, the starting point for numerical integration.

Equation (1) can be solved numerically by Numerov's method [1] in which the solution is generated as a table of values Y_i, approximating y_i, by the propagator

$$\left(1 + \frac{h^2}{12}Q_{i+1}\right)Y_{i+1} - 2\left(1 - \frac{5h^2}{12}Q_i\right)Y_i + \left(1 + \frac{h^2}{12}Q_{i-1}\right)Y_{i-1} = 0, \tag{4}$$

the subscripts indicating functions evaluated at $R_i = R_0 + ih$, where h is the step-length. Subtraction of h^2 times Eq. (1), $h^4/12$ times its second derivative, and $h^6/144$ times its fourth derivative from Eq. (4), all at R_i, leaves a *local* truncation error $-h^6 y_i^{(vi)}/240$ on the left-hand side. We may write

$$Y_i = y_i + \delta y_i, \tag{5}$$

where δy_i is the *global* truncation error. We can consider δy_i to be the value at R_i of a continuous error $\delta y(R)$ [2] introduced by addition of the perturbation $(\hbar^2/2\mu)(h^4/240)(d^6/dR^6)$ to the potential operator when Eq. (1) is solved by Numerov's method [3]; its leading term is $\mathcal{O}(h^4)$ satisfying the differential equation, derived from Eqs. (1) and (4) [2],

$$\delta y''(R) + Q(R)\delta y(R) = \frac{h^4}{240}y^{(vi)}(R). \tag{6}$$

The step-length should be chosen to keep the *local relative* truncation error, approximately $h^6K_i^6/240$ at R_i, where K_i is the local wave number, acceptably small [4].

The phase shift can be calculated by fitting the solution $y(R)$ to $\sin(kR)$ and $\cos(kR)$, the asymptotic solutions of Eq. (1). Let S_i and C_i denote $\sin(kR_i)$ and $\cos(kR_i)$, respectively. Fitting at R_i and R_j we find, for a small phase shift,

$$\eta \approx \tan(\eta) = -\frac{S_i y_j - S_j y_i}{C_i y_j - C_j y_i}. \tag{7}$$

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From Eqs. (5) and (7) we find that the relative error, $\delta\eta/\eta$, in the phase shift caused by use of the numerical wave functions Y_i and Y_j in Eq. (7) is, to $\mathcal{O}(h^4)$,

$$\frac{\delta\eta}{\eta} = -\frac{S_i\delta y_j - S_j\delta y_i}{(C_i y_j - C_j y_i)\eta} - \frac{C_i\delta y_j - C_j\delta y_i}{C_i y_j - C_j y_i}. \tag{8}$$

The relative error introduced into a small phase shift by the first term on the right-hand side of Eq. (8) can be large, as a consequence of cancellation, making the evaluation of expression (7) ill-conditioned. Both terms are proportional to the relative errors in the wave function. However, even if they are kept small by making the local truncation errors acceptably small (say $|hK(R)|^6/240 < 10^{-8}$ or $|hK(R)| < 0.1$), it is still possible for the phase shift to have an unexpectedly large relative error; a small step length might be needed to yield acceptable accuracy. In the special case where $\delta y_i/y_i = \delta y_j/y_j$ the error given by Eq. (8) vanishes as expected because the relative error, being the same at R_i and R_j, is absorbed into the normalization factor A.

The phase shift is also given by the quadrature [5]

$$\eta \approx \sin(\eta) = -\frac{2\mu}{k\hbar^2 A}\int_0^\infty \sin(kR)V(R)y(R)dR. \tag{9}$$

The normalization constant, A, obtained by fitting to the asymptotic expression (3) is

$$A^2 = \frac{y_i^2 + y_j^2 - 2y_i y_j \cos[k(R_i - R_j)]}{\sin^2[k(R_i - R_j)]}. \tag{10}$$

However, its relative error, $\delta A/A$, caused by use of the numerical wave-function and given by

$$\frac{\delta A}{A} = \frac{y_i\delta y_i + y_j\delta y_j - (y_j\delta y_i + y_i\delta y_j)\cos[k(R_i - R_j)]}{y_i^2 + y_j^2 - 2y_i y_j\cos[k(R_i - R_j)]}, \tag{11}$$

is well conditioned with respect to the errors in the wave function. The relative error, $\delta\eta/\eta$, in the phase-shift is

$$\frac{\delta\eta}{\eta} = -\frac{\delta A}{A} - \frac{2\mu}{k\hbar^2 A\eta}\int_0^\infty \sin(kR)V(R)\delta y(R)dR, \tag{12}$$

where $\delta y(R)$ satisfies Eq. (6). In the numerical example described below quadrature yields more accurate phase-shifts than asymptotic fitting. Unfortunately we cannot *predict* this accuracy because while the first term of expression (12) introduces no excessive errors the necessary analysis of the second (integral) term requires knowledge of the solution of the differential equation (6). The potential in our numerical example has the form of a steep repulsive core matched to a well, which in turn is matched to a slowly varying asymptotic tail. The wave-function has many oscillations in the well and the subsequent cancellation makes meaningful estimation of the contribution to the integral from the well impossible without a good analytic approximation to $\delta y(R)$. Furthermore, although we know a *particular asymptotic* solution to Eq. (6), as $-(h^4k^4/480)kR\cos(kR + \eta)$, we have insufficient knowledge of $\delta y(R)$ to match the *auxiliary* solution near the well and we cannot estimate the significant contribution of the tail to the integral. The only possible comment is that in the quadrature the error in the numerical wave-function is spread over the range of integration, whereas the fitting procedure is sensitive to the errors in the wave-function calculated at two points only.

To ensure validity of the asymptotic solutions in a calculation of scattering data at an ultra-low energy, Eq. (1) must be integrated out to a large internuclear separation where the asymptotic potential is small compared to $\hbar^2k^2/2\mu$. In atomic scattering the reduced mass is large, causing the value of the step-length necessary for accurate integration at small interatomic distances to be very much smaller than that needed in the asymptotic region for small wave numbers. Typically we should ensure that $|hK(R)|^2 \approx 0.01$ for a local relative truncation error of about 10^{-8}. Ideally the algorithm should incorporate an automatic interval adjustment which increases, say doubles, h if $|hK(R)|^2$ becomes much less than 0.01 and decreases, say halves, h if $|hK(R)|^2$ becomes a little greater than 0.01; in halving an extra intermediate point is needed and the solution at that point can be found by solving Eq. (4) once for Y_i instead of Y_{i+1} [4]. The effect of doubling or halving is to introduce discontinuities into the error. These are unimportant if the error is small but provide a useful diagnostic to check if small phase-shifts calculated by asymptotic fitting are sufficiently accurate. If the step is too large the calculated phase-shift exhibits discontinuities in both the internuclear separation and the energy of relative motion.

We compared asymptotic fitting with quadrature evaluation in a calculation of low energy scattering of two lithium atoms in a potential corresponding to the $X^1\Sigma_g^+$ state of Li_2. The potential was constructed from *ab initio* values fitted to an exponential short-range core and a long-range dispersion form [6]; we have presented the details elsewhere [7] in a more extensive study of lithium scattering at low energies. We incorporated step adjustment. We made separate calculations at various energies E of relative motion, in which the step was doubled when $|hK(R)|^2/12$ became smaller than 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-6} (division by 12 was included for computational convenience). With the 10^{-6} criterion greater accuracy was obtained but many steps were required and we took the asymptotically fitted phase-shifts to represent the accurate values for comparison. With the 10^{-2} criterion a relative local truncation error of about 10^{-4} might be expected from fitting but, as seen in Fig. 1, this was not achieved; furthermore, the fitted phase-shifts are discontinuous for both the step doubling criteria shown. The quadrature results are more accurate and have no discontinuities; for the 10^{-4} criterion they have negligible errors. More results of fitting and quadrature are compared on a larger scale in Fig. 2. The fitted results again exhibit discontinuities. In both figures they occur at intervals of $\log_{10}(4) \approx 0.6$ apart in log energy. This happens because as the energy is increased the number of step doublings performed in the long asymptotic tail is decreased; at very small energy the step doubling procedure is energy-dependent only in the tail. The error changes discontinuously as a function of R whenever the step is doubled. The doubling criterion depends asymptotically on h^2k^2 or h^2E which changes by a factor of 4 at each doubling. If we increase the energy by a factor of 4 we expect one step doubling fewer to be performed, leading to a discontinuity in the calculated phase-shift, as a function of E. The intervals between the discontinuities correspond to changes by factors of 4 in energy or changes of $\log_{10}(4)$ in log energy. The quadrature is much less sensitive to the number of step doublings because the error is spread over the range of integration.

The Schwinger integral formula [8],

$$\cot(\eta) = -\frac{(\hbar^2k/2\mu)\int_0^\infty V(R)y^2(R)dR + \int_0^\infty\int_0^\infty V(R')y(R')G(k,R,R')V(R)y(R)dR'dR}{[\int_0^\infty V(R)\sin(kR)y(R)dR]^2}, \tag{13}$$

where

$$G(k, R, R') \equiv \sin(kR_<)\cos(kR_>) \tag{14}$$

with $R_<$ and $R_>$ indicating the smaller and larger of R and R', yields a phase-shift correct to second order in the error of any approximation which may be substituted for the wave-function $y(R)$. It is usually used in variational methods, where analytic trial wave-functions are constructed. It should provide a very accurate phase-shift when the *numerical* wave-function, described above, is substituted. However, we found that its use is impractical in our example because the oscillation of the wave-function in the potential well introduces severe cancellation in the double integral; an extremely small step is required, not by the method used to solve Eq. (1) but by the method used to evaluate the double integral. The time needed for this integration increases as the square of the total number of steps, although symmetry does allow a cut by 2. We made one calculation at a log energy of -10.2, obtaining a phase shift of 1.076×10^{-4}. Substitution of a numerical wave-function in the Schwinger formula is likely to be unsatisfactory in any low energy atom–atom collision problem because the large reduced mass can introduce many oscillations in any well other than the shallowest; it is probably worse at medium to high energies and better for low energy electron–atom collisions.

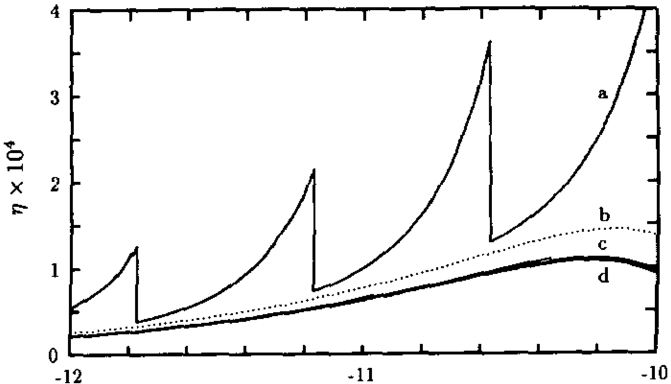

FIG. 1. Phase shifts, η, for different step-length doubling criteria: a. asymptotic fit doubling h when $|hK(R)|^2/12 < 10^{-2}$; b. quadrature doubling h when $|hK(R)|^2/12 < 10^{-2}$; c. asymptotic fit doubling h when $|hK(R)|^2/12 < 10^{-4}$; d. quadrature doubling h when $|hK(R)|^2/12 < 10^{-4}$.

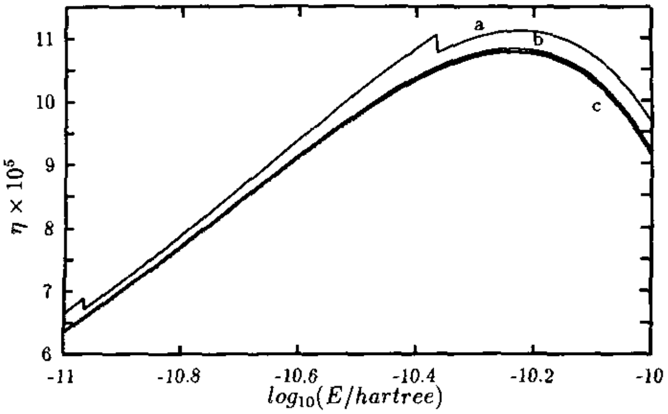

FIG. 2. Phase shifts, η, for different step-length doubling criteria: a. *asymptotic fit doubling* h when $|hK(R)|^2/12 < 10^{-4}$; b. *quadrature doubling* h when $|hK(R)|^2/12 < 10^{-4}$; c. quadrature doubling h when $|hK(R)|^2/12 < 10^{-6}$.

In conclusion, we recommend that the algorithm used to solve the Schrödinger equation in calculations of ultra-low energy scattering should incorporate automatic adjustment of the step-length [4] and that the results of asymptotic fitting and of quadrature should be made and compared for various step-doubling criteria to enable reliable phase-shifts to be determined.

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