ON CALCULATING PHASE SHIFTS AND PERFORMING FITS
TO SCATTERING CROSS SECTIONS OR TRANSPORT PROPERTIES[*]

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Improved methods of calculating quantum mechanical phase shifts and for performing least-squares fits to scattering cross sections or transport properties, are described. Their use in a five-parameter fit to experimental differential cross sections reduces the computer time by a factor of 4—7.

1. Introduction

Differential and integral scattering cross sections measured by molecular beam scattering techniques are an important source of information about intermolecular potential energy functions [1—3]. In general, potentials may be obtained from data of this type either by use of formal inversion procedures, or by using least squares fits to determine the values of the potential parameters which yield the best agreement between calculated and experimental cross sections [4]. For the inversion method to be used, the experimental data must be both of very high quality and relatively extensive. These requirements are difficult to satisfy, and hence most results obtained to date have used the fitting approach. The present communication examines two questions associated with this second procedure. The first of these concerns the efficient quantum mechanical calculation of the phase shifts for a given spherical potential, while the second examines the least squares fitting procedures for determining potential parameters from cross section data. The discussion in section 2 is complementary to that in a recent paper by Cohen [5] which supplanted an earlier critical study [6] by presenting an improved method for calculating phase shifts in the first-order JWKB (or classical [7]) approximation.

2. Quantum mechanical calculation of scattering phase shifts

The radial Schrödinger equation for partial wave l at collision energy E on the potential $V(r)$ may be written as [8]

$$d^2\psi/dr^2 + \{(2\mu/\hbar^2)[E - V(r)] - l(l + 1)/r^2\}\psi = 0,\tag{1}$$

where the zero of energy is chosen such that $\lim_{r\to\infty}[V(r)] = 0$, and the radial wavefunction is asymptotically normalized as

$$\psi(r) = \simeq \psi_\infty(r) = \sin(kr + \eta_l - l\pi/2).\tag{2}$$

As usual, μ is the reduced mass, $k^2 \equiv 2\mu E/\hbar^2$, and $\eta_l = \eta_l(E)$ is the phase shift. At sufficiently large r that the non-centrifugal part of the potential [i.e., $V(r)$] is effectively negligible, the wavefunction becomes

$$\psi_l(r) = kr[j_l(kr)\cos(\eta_l) - y_l(kr)\sin(\eta_l)], \tag{3}$$

where $j_l(z)$ and $y_l(z)$ are spherical Bessel functions, and $\lim_{r \to \infty} \psi_l(r) = \psi_\infty(r)$.

Determination of $\eta_l(E)$ requires one to numerically integrate the radial Schrödinger equation outward from $r = 0$ while using repeated comparisons of the exact solution with $\psi_l(r)$ of eq. (3) to determine a converged value of $\eta_l(E)$. A convenient procedure for doing this [9,10] stops the integration each time the wavefunction $\psi(r)$ changes sign and interpolates to determine the position, r_n, of the wavefunction node. If the non-centrifugal part of the potential were identically zero for all $r \geq r_n$, then the exact wavefunction on this interval would be given by eq. (3). An apparent quantal phase shift associated with the nth node may therefore be defined as

$$\eta_l^n = \arctan[j_l(kr_n)/y_l(kr_n)]. \tag{4}$$

Repetition of this procedure at successive wavefunction nodes until $|\eta_l^n - \eta_l^{n-1}|$ and $|\eta_l^{n-1} - \eta_l^{n-2}|$ are both smaller than some chosen convergence criterion, was the procedure for determining $\eta_l(E)$ recommended by Bernstein [9] in 1960.

The above approach implicitly assumes that the non-centrifugal part of the potential is negligible beyond r_n, and uses comparisons of the ensuing η_l^n values to determine when this is true. Unfortunately, this usually requires the numerical integration of eq. (1) to be carried out to fairly large values of r. In addition to the computational expense, the large range of integration magnifies problems due to cumulative errors in the numerical integration procedure. In order to minimize these difficulties, Munn et al. [10] proposed that each quantal "nodal" phase shift η_l^n be corrected by adding to it the contribution to the corresponding JWKB phase shift [1,5–8] due to non-zero $V(r)$ in the region $r \geq r_n$:

$$\Delta\eta_l^n = \int_{r_n}^{\infty} \{[k^2 - U(r) - l(l+1)/r^2]^{1/2} - [k^2 - l(l+1)/r^2]^{1/2}\} \, dr, \tag{5}$$

where $U(r) \equiv (2\mu/\hbar^2)V(r)$. If this integral were evaluated exactly, the only error in the resulting corrected apparent phase shift would be that arising from the inadequacy of the first-order JWKB approximation for the wavefunction on the interval $[r_n, \infty)$. As r_n increases, such errors decrease very rapidly and this corrected local phase shift rapidly converges to the true value, even for r_n values fairly close to the turning points where $\Delta\eta_l^n$ is quite large.

Rather than use eq. (5) directly, Munn et al. [10] introduced two additional approximations which allowed them to obtain an analytic expression for $\Delta\eta_l^n$. First, making use of the known inverse-power form of long-range potentials, $V(r) \simeq C_m/r^m$, they replaced $U(r)$ in eq. (5) by $(2\mu/\hbar^2)C_m/r^m$. Truncating binomial expansions of the resulting integrand then yielded [10]:

$$\Delta\eta_l^n(\text{MMS}) = (\mu C_m/\hbar^2 k)[1/(m-1)(r_n)^{m-1} + l(l+1)/2k^2(m+1)(r_n)^{m+1}]. \tag{6}$$

The resulting analytically-corrected local phase shifts are certainly more accurate and converge more rapidly than do the nodal phase shifts η_l^n. However, we wish to examine whether use of eq. (5) without any additional approximations is significantly more efficient.

The present approach is to evaluate the quadrature in eq. (5) directly. Defining $x = 2r_n/r - 1$, eq. (5) becomes

$$\Delta\eta_l^n(\text{quad.}) = 2r_n \int_{-1}^{1} (x+1)^{-2} \{[k^2 - U(r) - l(l+1)/r^2]^{1/2} - [k^2 - l(l+1)/r^2]^{1/2}\} \, dx. \tag{7}$$

In the region of interest, the integrand of eq. (7) is quite well-behaved, so a simple low-order quadrature procedure should prove adequate. In the present work, a 4-point Gauss–Legendre quadrature formula was used [11]. Use of higher order or more sophisticated quadrature procedures made small improvements to $\Delta\eta_l^n(\text{quad.})$ values at the nodes nearest the outermost classical turning point, *but had no effect* on the convergence of the resulting

quadrature-corrected phase shifts η_l^Q,

$$\eta_l^Q \equiv \eta_l^n + \Delta\eta_l^n(\text{quad.}),\qquad(8)$$

since most of the error in $\Delta\eta_l^n$ is due to use of the JWKB approximation.

The procedure described above has been tested extensively, and its convergence rate quantitatively compared to that for the analytically-corrected Munn et al. [10] phase shift,

$$\eta_l^{MMS} \equiv \eta_l^n + \Delta\eta_l^n(\text{MMS})\qquad(9)$$

and to that for the nodal phase shift itself. The range of numerical integration, $\mathcal{R}$, out to the node at which the desired degree of convergence is achieved, provides a good measure of the quality of the three procedures, since both the computational expense and the cumulative numerical error in a phase shift calculation increase linearly with $\mathcal{R}$. Using Stwalley's [12] potential for HgH as a model problem, comparisons for a convergence criterion ranging from 10^{-3} to 10^{-7} radians at various l and E values showed that typically,

$$\mathcal{R}(\eta_l^Q) \lesssim 0.7\,\mathcal{R}(\eta_l^{MMS}) \lesssim 0.5\,\mathcal{R}(\eta_l^n),\qquad(10)$$

where the relative savings are most dramatic when high accuracy is desired.

Note that the definition of the JWKB phase shift [1,5–8] implies that the correction functions $\Delta\eta_l^n$ of eqs. (5)–(7) should not be calculated until $r_n \geq r_x(l)$, where $r_x(l) \equiv [l(l+1)]^{1/2}/k$ is the classical turning point on the pure centrifugal potential for partial wave l. Thus, to minimize computational expense the nodal phase shifts η_l^n should not be computed for $r_n < r_x(l)$. A listing of our computer program [13] for calculating η_l^Q may be obtained from the authors on request.

3. Least square fits to scattering or transport cross sections to determine potential parameters

3.1. General method

For the sake of clarity, the following discussion explicitly considers the analysis of atom–atom elastic differential scattering cross section data. However, a precisely analogous presentation may be made for integral (total) scattering cross sections or virial or transport property coefficients, or indeed for any other property which may be calculated from a knowledge of the scattering phase shifts for the system [14–16].

The differential cross section for scattering at an angle θ, in centre of mass coordinates, of particles with a relative velocity g and relative collision energy $E = \frac{1}{2}\mu g^2$, is [8]:

$$\frac{d\sigma(\theta)}{d\omega} = \frac{1}{4k^2}\left\{\left[\sum_l (2l+1)P_l(\cos\theta)\sin(2\eta_l)\right]^2 + \left[\sum_l(2l+1)P_l(\cos\theta)[\cos(2\eta_l)-1]\right]^2\right\},\qquad(11)$$

where k, l and η_l are as defined above, and $P_l(z)$ is the (unnormalized) Legendre polynomial of order l. Unfortunately, molecular beam sources yield beams with finite angular and velocity spread, the detector subtends a finite scattering angle, and the measurements are made in laboratory, not centre of mass coordinates. As a result, the observed scattering intensity at angle Θ in laboratory coordinates is proportional to (see, e.g. ref. [17]):

$$I(\Theta) = \iiint dA\, dg\, d\theta\, f(A,g,\theta)\, d\sigma(\theta)/d\omega.\qquad(12)$$

Here, A represents the various apparatus parameters, while the (known) function $f(A,g,\theta)$ is completely defined by the properties of the experimental apparatus. All dependence of the observed intensity $I(\Theta)$ on the potential energy function comes from the phase shifts $\eta_l(E)$ from which $d\sigma(\theta)/d\omega$ is calculated.

Determination of potential parameters from differential cross section data is best done [17,18] using an (iterative) non-linear least squares fitting procedure which finds the minimum of the function,

$$\chi^2(\{p_\alpha\}) = \sum_i [I_0(\Theta_i) - I_c(\Theta_i; \{p_\alpha\})]^2 / [\Delta I_0(\Theta_i)]^2, \tag{13}$$

where $I_0(\Theta_i)$ are the observed scattering intensities, $\Delta I_0(\Theta_i)$ their experimental uncertainties, and $I_c(\Theta_i; \{p_\alpha\})$ are the intensities calculated from eqs. (11) and (12) using a trial potential defined by the parameter $\{p_\alpha; \alpha = 1, 2, 3, ...\}$. This approach requires one to compute both χ^2 and its partial derivative with respect to each of the trial potential parameters (i.e., to calculate both $I_c(\Theta)$ and $\partial I_c(\Theta)/\partial p_\alpha$), in each cycle of iteration. In previous work, these partial derivatives were always (to our knowledge) calculated by differences. If N potential parameters are being varied, this means that for each cycle of iteration a complete set of predicted scattering intensities must be computed for either $(2N + 1)$ or $(N + 1)$ different sets of potential parameters (depending on whether or not the partial derivatives are computed from symmetric [18] or asymmetric [17] differences)*.

The purpose of the present section is to demonstrate that it is computationally *much* less expensive (as well as more accurate) to evaluate the partial derivatives $\partial I_c/\partial p_\alpha$ exactly, rather than by differences. Clearly,

$$\frac{\partial I_c(\Theta_i)}{\partial p_\alpha} = \iiint dA \, dg \, d\theta \, f(A, g, \theta) \frac{\partial}{\partial p_\alpha} \left(\frac{d\sigma}{d\omega}\right), \tag{14}$$

where

$$\frac{\partial}{\partial p_\alpha}\left(\frac{d\sigma}{d\omega}\right) = \frac{1}{k^2}\left\{\left[\sum_l (2l+1)P_l(\cos\theta)\sin(2\eta_l)\right]\left[\sum_l (2l+1)P_l(\cos\theta)\cos(2\eta_l)\frac{\partial\eta_l}{\partial p_\alpha}\right]\right.$$

$$\left. - \left[\sum_l (2l+1)P_l(\cos\theta)[\cos(2\eta_l) - 1]\right]\left[\sum_l (2l+1)P_l(\cos\theta)\sin(2\eta_l)\frac{\partial\eta_l}{\partial p_\alpha}\right]\right\}. \tag{15}$$

Comparison of eqs. (11) and (12) with eqs. (14) and (15) shows that the only additional quantities appearing in the latter are the phase shift derivatives, $\partial\eta_l/\partial p_\alpha$. If they were available, the partial derivatives $\partial I_c(\Theta)/\partial p_\alpha$ could be computed at the same time as $I_c(\Theta)$ itself, at *very little additional computational expense*. The following section describes quantal and semiclassical ways of computing these phase shift derivatives, while tests of the present approach versus the derivative-by-differences approach are presented in section 3.3.

3.2. Partial derivative of η_l with respect to potential parameter p_α

Within the JWKB approximation [1,5–8], the phase shift derivative referred to above is given by:

$$\partial\eta_l/\partial p_\alpha = -(\mu/\hbar^2)\int_{r_0}^{\infty} [\partial V(r)/\partial p_\alpha][k^2 - U(r) - l(l+1)/r^2]^{-1/2} \, dr. \tag{16}$$

The (integrable) singularity in the integrand of eq. (16) at the classical turning point $r = r_0$ shows that the phase shift is most sensitive to the potential near that point. This provides a quantitative justification for the observation by Olson and Mueller [19] that the main contribution to the phase shift comes from the region near the classical turning point. The change of variables $x = r_0/r$ transforms eq. (16) into

$$\partial\eta_l/\partial p_\alpha = -(\mu r_0/\hbar^2)\int_0^1 [1 - x]^{-1/2} f(x) \, dx,$$

where

$$f(x) = x^{-2}[\partial V(r)/\partial p_\alpha][1 - x]^{1/2}[k^2 - U(r) - l(l+1)/r^2]^{-1/2}$$

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* A "symmetric" partial derivative by differences is defined as $\partial I_c/\partial p_\alpha \approx [I_c(p_\alpha + \Delta p_\alpha) - I_c(p_\alpha - \Delta p_\alpha)]/2\Delta p_\alpha$, while the "asymmetric" partial derivative is $\partial I_c/\partial p_\alpha \approx [I_c(p_\alpha + \Delta p_\alpha) - I_c(p_\alpha)]/\Delta p_\alpha$.

is a well-behaved function with no singularities. Use of the appropriate Gauss—Mehler type quadrature procedure (see eq. (25.4.36) in ref. [11]) allows integrals of this type to be evaluated with high accuracy using relatively few function evaluations. Moreover, if the JWKB phase shifts are evaluated in the manner suggested by Cohen [5], no additional function evaluations would be required.

As shown by Dickinson and Shizgal [20], the quantum mechanical analogue of eq. (16) is:

$$\partial \eta_l / \partial p_\alpha = -(k/E) \int_0^\infty [\partial V(r)/\partial p_\alpha] |\psi(r)|^2 \, dr, \tag{17}$$

where E and $V(r)$ have the same energy units. Since the exact wavefunction $\psi(r)$ must be calculated for the quantal phase shift calculation, little additional work is involved in concurrently accumulating the integral appearing in eq. (17), for the various p_α's. However, as in the phase shift calculation, to minimize computational expense and cumulative numerical error, it is desirable to achieve an appropriate marriage of the semiclassical and quantal methods described above. This is readily done, yielding as the analog of eqs. (7) and (8):

$$\partial \eta_l / \partial p_\alpha = -(k/E) \int_0^{r_n} [\partial V(r)/\partial p_\alpha] |\psi(r)|^2 \, dr - (\mu/\hbar^2) \int_{r_n}^\infty [\partial V(r)/\partial p_\alpha] [k^2 - U(r) - l(l+1)/r^2]^{-1/2} \, dr. \tag{18}$$

The first integral appearing in eq. (18) is readily evaluated by applying a simple quadrature formula such as trapezoidal or Simpson's rule [11] to the values of $\psi(r)$, as they are generated in the phase shift calculation. Since $r_n > r_0$, the integrand of the second integral in eq. (18) is well behaved with no singularities; the substitution $x = 2r_n/r - 1$ therefore transforms it into a form precisely analogous to eq. (7) so that it may be evaluated using the same 4-point Gauss—Legendre quadrature formula used in computing $\Delta \eta_l$(quad). Thus, the quadrature-corrected quantum mechanical phase shift η_l^Q and its various partial derivatives $\partial \eta_l / \partial p_\alpha$ may be computed simultaneously, with the latter requiring very little additional computational effort.

One additional problem associated with the use of eq. (18) is the fact that the numerical integration procedure provides an unnormalized $\psi(r)$ function, while the wavefunction appearing in eq. (18) must have the asymptotic normalization of eq. (2). It is therefore necessary to determine a normalization factor $F = F(r_n')$ for $\psi(r)$ on the interval $[0, r_n]$ by matching it to eq. (3) at a mesh point r_n' near the node at r_n:

$$F(r_n') = k r_n' [j_l(k r_n') \cos(\eta_l') - y_l(k r_n') \sin(\eta_l')] / \psi(r_n'). \tag{19}$$

Note that the apparent phase shift η_l' appearing in eq. (19) differs from η_l'' by an amount calculable from eq. (5) with the lower and upper bounds on the integral replaced by r_n and r_n', respectively[+]. A residual (JWKB) amplitude correction, which takes account of the fact that the non-centrifugal potential $V_n(r)$ is not zero for all $r \geq r_n'$, may be included by multiplying $F(r_n')$ by the factor:

$$[k^2 - l(l+1)/(r_n')^2]^{1/4} / [k^2 - U(r_n') - l(l+1)/(r_n')^2]^{1/4}.$$

3.3. Test of the new method

For the above procedure to be most efficient, arrays of $\partial V(r)/\partial p_\alpha$ would have to be created and stored, and computer core storage would also be required for quantities such as $\partial \eta_l / \partial p_\alpha$ and $(\partial/\partial p_\alpha)(d\sigma/d\omega)$. However, the partial derivatives $\partial \eta_l / \partial p_\alpha$ may be computed at the same time as η_l itself, for very little additional effort. Similarly, the averaging [see eq. (12)] over θ, g and the apparatus parameters A can be performed simultaneously for $d\sigma(\theta)/d\omega$ and its partial derivatives with respect to the various p_α's. Thus, while it does require some additional computer memory, the present approach should involve only slightly more execution time (per cycle of iteration) than a single calculation of $I(\Theta)$ alone, and this "CPU" time should increase very slowly with N, the number of parameters being varied.

[+] Since r_n and r_n' are close together, a two-point trapezoidal rule should suffice for this quadrature.

Table 1
Comparison of CPU time (on an IBM 360-75) per iteration cycle required by fits to experimental differential cross sections [21] for H_2—Ar. N is the number of potential parameters being varied

N	Potential form	Computation time per cycle (s)		
		new method [a]	old method [b]	old method [c]
1	LJ(12,6)	82	104	156
2	LJ(12,6)	88	154	260
5	BC	116	312	572
N [d]	general	$72 + 9N$	$52(N + 1)$	$52(2N + 1)$

[a] Exact partial derivatives from eqs. (14), (15) and (18).   [b] Partial derivatives by asymmetric differences.
[c] Partial derivatives by symmetric differences.   [d] Extrapolation.

To test the above procedure, fits to the experimental differential cross sections of Rulis et al. [21] for the system H_2 + Ar have been performed. Their 41 $I_0(\Theta_i)$ values for collision energy 207 K were used as data in fits which used LJ(12,6) and Buckingham—Corner (BC) potential forms. The computing times per cycle of iteration required by the new and old methods are compared in table 1.

In his review article on the inversion of molecular scattering data, Buck [4] indicated that the computation time required by a χ^2 minimization fitting procedure is typically 5 to 10 times larger than an inversion procedure of the same precision. Since the inversion procedures require experimental data of relatively high quality, a good fit to data of this quality would likely require use of a fairly flexible potential form (i.e., one with many variable parameters). The results in eq. (10) and table 1 show that introduction of the techniques presented above would reduce the computation time of fits to a 5-parameter potential by a factor of between 4 and 7, and the savings would be even more dramatic for potentials with $N > 5$. Thus, use of the present methods essentially removes the computation time advantage of inversion techniques for determining potentials from scattering cross sections.

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References

[1] H. Pauly and J.P. Toennies, Advan. At. Mol. Phys. 1 (1965) 195.
[2] R.B. Bernstein and J.T. Muckerman, Advan. Chem. Phys. 12 (1967) 389.
[3] J.P. Toennies, in: Physical chemistry. an advanced treatise, Vol. 4. Kinetics of gas reactions. ed. D. Henderson (Academic Press, New York, 1973) ch. 6.
[4] U. Buck, Rev. Mod. Phys. 46 (1974) 369.
[5] J.S. Cohen, J. Chem. Phys. 68 (1978) 1841.
[6] M. Kennedy and F.J. Smith, Mol. Phys. 13 (1967) 443.
[7] F.T. Smith, J. Chem. Phys. 42 (1965) 2419.
[8] R.B. Bernstein, Advan. Chem. Phys. 10 (1966) 75.
[9] R.B. Bernstein, J. Chem. Phys. 33 (1960) 795.
[10] R.J. Munn, E.A. Mason and F.J. Smith, J. Chem. Phys. 41 (1964) 3978.
[11] M.W. Abramowitz and I.A. Stegun, Handbook of mathematical functions (Dover, New York, 1965) section 25.4.
[12] W.C. Stwalley, J. Chem. Phys. 63 (1975) 3062.
[13] R.J. le Roy, University of Waterloo, Chemical Physics Research Report CP-107 (1978).

[14] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids (Wiley, New York, 1954) 2nd printing 1964.

[15] S. Imam-Rahajoe, C.F. Curtiss and R.B. Bernstein, J. Chem. Phys. 42 (1965) 530.

[16] R.J. Munn, F.J. Smith, E.A. Mason and L. Monchick, J. Chem. Phys. 42 (1965) 537.

[17] R.W. Bickes Jr., G. Scoles and K.M. Smith, Can. J. Phys. 53 (1975) 435.

[18] P.E. Siska, J.M. Parson, T.P. Schafer and Y.T. Lee, J. Chem. Phys. 55 (1971) 5762.

[19] R.E. Olson and C.R. Mueller, J. Chem. Phys. 45 (1966) 2519.

[20] A.S. Dickinson and B. Shizgal, Mol. Phys. 30 (1975) 1221.

[21] A.M. Rulis, K.M. Smith and G. Scoles, Can. J. Phys. 56 (1978), to be published.