Linear Least-Squares Fitting of Molecular-Beam Differential Cross Section
Data Using Spline Functions*

by

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ABSTRACT

A method is presented for using spline functions to unfold center-of-mass differential elastic cross-sections from scattering data by a linear least squares technique. The role of various averaging processes in reducing structure in the scattered intensity is illustrated.

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I. Introduction.

Molecular beam scattering data have proved to be very useful for deriving information about interaction potentials between molecules. The most common interpretative approach has been to assume a potential form described by a set of parameters whose values are determined by a comparison of the calculated differential cross sections with the experimental data^{1,2}. However, the measured cross sections have recently been inverted directly to obtain the potentials^{3,4}. Both methods make use of structure in the differential cross section, particularly the "rainbow" structure. In purely elastic scattering, the degree to which this structure may be discerned depends largely on how well defined the beams are as to angular divergence, the narrowness of their velocity distributions, and the resolution of the detector. When inelastic scattering is possible, the availability of many different exit channels further complicates the interpretation. The present discussion will be confined to elastic scattering, though many of the conclusions are also applicable to scattering which is inelastic.

As Buck and Pauly⁴ have shown, if the position of many extrema can be located, it is possible to achieve a direct inversion, and the more extrema the greater the degree of certainty with the potential which is derived. If the amplitude of the oscillations could also be determined the inversion would be improved appreciably⁵. Although velocity- and angular-averaging may not significantly change the positions of the extrema⁶, the amplitudes are strongly affected (see Figure 5 of reference 6). In this paper we present a computational scheme for retrieving the

center of mass (CM) cross sections $\sigma(\theta, E_{12})$, θ is the CM scattering angle and E_{12} the relative translational energy, from laboratory (LAB) data. Ideally the LAB data should be related to the CM cross section through the Jacobian of transformation between the two coordinate systems. However in practice this relation is complicated by experimentally unavoidable averaging processes due to non-zero beam sizes, velocity distributions, finite detectors, etc. Thus in obtaining CM cross sections from LAB data these averaging processes should be accounted for and use made of an appropriate unfolding method. The method discussed here makes use of a least-squares comparison between experimental data and simulated data using a form of $\sigma(\theta, E_{12})$ defined by interpolation between values specified at certain angles and at a specific energy. The set of $\sigma(\theta, E_{12})$ values are thus the fitting parameters. Unfolding procedures employing functional forms that depend non-linearly on the parameters require non-linear fitting. This can be costly in computer time if many iterations are needed for convergence, and the attainment of convergence may depend on how closely the initially guessed parameters are to the "correct" ones. Expansions of σ as a linear combination of orthogonal polynomials or some other functions defined on the entire range of independent variables eliminate these problems but may produce their own difficulties such as non-physical oscillatory structure or a concealed bias as to the final form of the cross section. The method discussed here represents $\sigma(\theta, E_{12})$ as a third degree spline function⁷. This provides local fitting around each fixed point and permits sizeable excursions of the fitted function from any preconceived behavior, yet suppresses oscillatory structure that is not required for a good fit. More importantly, since the spline function

varies linearly with each of the coordinates defining it (see the appendix) there is the additional advantage with respect to computational economy of being able to use linear least squares fitting. Under favorable circumstances, both the positions and amplitudes of the oscillations in $\sigma(\theta, E_{12})$ can be recovered.

For testing, laboratory data are needed for which the "correct" CM cross section is known. We have used for this purpose simulated data derived by a careful CM to LAB transformation (with averaging over typical experimental conditions) of a semiclassicaly calculated cross section given by Harris and Wilson² for $K + CCl_4$ scattering. This cross section exhibits primary and supernumerary rainbow structure but no fine-spaced "quantum" oscillations. Data were generated for $K + CCl_4$ and for $CCl_4 + K$ (the convention is that the first number of the pair is the primary beam and the detected species). Although the process of data simulation used some of the same programs as the fitting, the functional form of $\sigma(\theta, E_{12})$ and the details of averaging in the two computations were sufficiently different to guarantee their independence.

II. Kinematic Considerations.

Our coordinate system, illustrated in Figure 1, is similar to that used by Warnock and Bernstein³. The laboratory (LAB) scattered velocity v_3 is defined by ϕ , $\odot$ and v_3 ($-\pi/2 < \phi < \pi/2$, $-\pi < \odot < \pi$); the corresponding center-of-mass (CM) velocity w_3 is specified by w_3 , θ , and ϕ ($0 \leq \theta \leq \pi$, $0 \leq \phi < 2\pi$). The angle between the primary and secondary beam velocities v_1 and v_2 is ζ . The scattered intensity into a detector at nominal LAB angles ϕ_1 and $\odot_1$

is described by

$$I(\phi, \theta) = n_1 \int d\ell \int dv_2 \int dv_1 \int d\Omega_{LAB} (\phi, \theta) \sigma(\phi, \theta, E_r) v_r f_\ell(n_2[\ell]) f_1(v_1) f_2(v_2) \quad (1)$$

where $\sigma(\phi, \theta, E_r)$ is the LAB cross section, $f_1(v_1)$ is the distribution of primary beam velocities and $f_2(v_2)$ that of the secondary beam velocities; $\Omega(\phi, \theta)$ is the solid angle subtended at the scattering center by the detector (here assumed to be flux sensitive), and n_1 is the number density of the primary beam.

In order to simulate scattering data that may be considered typical the following choices of apparatus parameters have been used. The primary beam has been assumed to be velocity selected by a conventional toothed wheel velocity filter having a resolution of 3%. Thus $f_1(v_1)$ is triangular in shape. The secondary beam has been assumed to effuse from a point source and thus its distribution of velocities $f_2(v_2)$ is Maxwellian. This point source is located a distance ℓ from the center line of the primary beam with the secondary beam particles travelling there from in straight lines until they intersect the primary beam. The angular divergence of the secondary beam therefore defines the scattering volume. In equation (1) the quantity $f(n_2[\ell])$ is associated with both the finite extent of the scattering volume and the variation within it of n_2 , the number density of the secondary beam. From a knowledge of the height of the primary beam and ℓ it is possible to calculate the extent of the scattering volume. For integration, this volume is subdivided into a number of component scattering volumes τ_i , each with its

own scattering center. Associated with each component volume is a weight $f_{\zeta}(n_2[\zeta_1])$, which represents the product of the component volume with the corresponding value of the number density. Relocation of the scattering center for each τ_1 also means that Φ and Θ as well as the other quantities on the right of equation (1) vary with the ζ_1 associated with the scattering center of τ_1 ; they also will take on different values when particles are recorded at different positions on the surface of the detector. Two distributions for $f(n_2[\zeta])$ have been used, one Gaussian in shape with a half width of ten degrees and the other a distribution that is constant over forty degrees and zero elsewhere. Both distributions are symmetrical about $\zeta = 90^\circ$.

Since the object of the program is to determine the CM cross section, the laboratory cross section $\sigma(\Phi, \Theta, E_r)$ in equation (1) must be replaced by its equivalent in the CM⁹:

$$\sigma(\Phi, \Theta, E_r) = \sum_1 \sigma(\theta, E_r) v_{31}^2 w_3^{-2} / \cos(\underline{w}_3, \underline{v}_{31}) \quad (2)$$

where $v_{31}^2 w_3^{-2} / \cos(\underline{w}_3, \underline{v}_{31})$ represents the Jacobian for this transformation. The sum in equation (2) indicates the possibility that there may be two values of the CM scattering angle corresponding to scattering into a given laboratory angle. All the functions in the integrand of equation (1) except for $\sigma(\theta, E_r)$ can be determined from the initial conditions as they are established by the apparatus. Thus $\sigma(\theta, E_r)$ as the only unknown, may be treated as a set of parameters to be determined from the measured intensities by least-squares fitting.

III. Description of the Fitting Program.

The program may be divided into two major parts. The first part approximates the integral in (1) for a selected set of laboratory angles, using some form for $\sigma(\theta, E_r)$ (here the spline function). In the simulation of scattering data only the first section of the program is used. Integration over each of the variables in equation (1) was performed by numerical quadrature. Equation (1) therefore becomes a weighted multiple summation over the many individual scattering events defined by the choices of $v_1, v_2, \tau, \phi, \mathbb{H}$ and the dimensions of the detector. Each of these events may be considered conveniently in terms of its associated velocity vector diagram of which Figure 1 is an example. Thus equation (1) may now be written

$$I_K = \sum_{\beta} O_{K\beta} \sigma(\theta_{K\beta}, E_{12}(S)) \quad K = 1 \cdots M \quad (3)$$

which is really a derived quadrature formula for scattering data simulation. In equation (3) $I_K = I(\phi_K, \mathbb{D}_K)$; the index β runs over all the velocity vector diagrams for each choice of laboratory angle (including double values of θ where they occur). The $O_{K\beta}$ values are products of weights from the various quadratures with Jacobians for the LAB to CM transformation. As the number of velocity vector diagrams is equal to the product of the numbers of points chosen for each numerical quadrature it follows that β can be quite large and likewise the range of $\theta_{K\beta}$. Thus for each I_K , β interpolations are needed to find values of $\sigma(\theta_{K\beta}, E_{12}(S))$ from the given fixed points. However the fixed points are for one specified energy so that a method of accounting for the energy dependence of the cross section as well as the angular dependence must

he sought. The fact that plotting cross sections for the same system at various energies versus the product θE_{12} causes the main rainbow maxima to line up¹⁰ is useful in this respect. In our examples it has been assumed that σ depends only on θE_{12} . Thus a set of values $\sigma(\theta_j)$ ($j = 1, N$) are chosen as fixed points along with a "nominal" kinetic energy E_{12}^0 . (In our examples E_{12}^0 is taken as the value resulting when the primary beam has its central velocity and v_2 is the average speed of a molecule in the Maxwellian secondary beam and $\zeta = 90^\circ$.) It is thus possible to construct a new interpolation variable x defined by,

$$x_K = \frac{\theta_{K\beta} E_{12}(\zeta)}{E_{12}^0} \quad (4)$$

The interpolations are accomplished with the spline function. A spline function through a given set of points is constructed by piecewise fitting with a different polynomial between each two adjacent points (a cubic for the third order spline used here), with the proviso that the pieces have the same value for the function and all its derivatives up to order one less than that of the polynomial at the joining points. In the interpolations there may occur values of $x_{K\beta}$ which lie outside the range of fixed points and thus outside the region of the spline function. For values of $x_{K\beta}$ less than the smallest specified θ value, $\sigma(x_{K\beta})$ is extrapolated linearly using the first derivative of the spline function at that point in our program, and beyond the largest specified value of θ , $\sigma(x_{K\beta})$ is extrapolated as perfectly flat (a not unreasonable assumption in the case of elastic scattering provided $x_{K\beta}$ is large enough). From equation (4) and A4, which illustrates just how the spline function

$S(x)$ is a linear function of the fixed points, equation (3) may be now written,

$$I_K = \int_B O_K S(x_{k\beta}) \quad (5)$$

$$= \int_B O_K \sum_{j=1}^N \gamma_j (x_{k\beta}) \sigma(\theta_j) \quad (6)$$

Least Squares.

Having established the scattering intensity as a linear function of the fixed points, one can compare the scattering data simulated by means of equation (3) with the measured values and minimize the difference between them in a least-square sense. Thus the unfolded set of parameters may be obtained using the conventional Gaussian linear least squares formula¹¹.

$$P = [B'WB]^{-1} B'WF \quad (7)$$

where P is an $N \times 1$ matrix consisting of the fitted values of the cross sections at energy E_{12}^0 . F is an $M \times 1$ matrix whose elements F_i are the measured values of the scattered intensity. W is the weight matrix, chosen in our examples to be diagonal and with $W_{ii} = \frac{1}{F_i^2}$ (equivalent to assuming an evenly distributed fractional mean statistical error in the data). Finally the matrix B is $N \times M$ with $B_{ij} = \frac{\partial I_i}{\partial p_j}$ which from equation (5) can be written

$$B_{ij} = \int_B O_{i\beta} \frac{\partial S(x_i)}{\partial p_j} \quad (8)$$

The evaluation of $\frac{\partial S(x_i)}{\partial p_j}$, the derivative of the spline function with respect to the fixed points defining it, is given in the appendix where it is noted to be independent of the cross section parameters P_j .

Although the least-squares adjustment to the initial values of the cross section is quite straightforward, some thought must be given to the number and location of the initial parameters. As a general rule in data fitting, the parameters being adjusted should be overdetermined. To conform to this, the program uses half as many parameters as data points ($N = 2M$). The question of where to specify the parameters (that is, at which particular values of x is σ to be fitted) is more difficult. The most satisfactory choice found in practice has been to use the values of θ_j corresponding to forward scattering obtained from the ideal velocity vector diagrams (i.e., those for which all the variables have their most probable value) at every other value of (ϕ_i, θ_i) .

IV. Example Applications.

The example computation proceeded in two distinct steps - first data simulation from an assumed C^1 cross-section, then inversion of the data to examine the reliability with which the original cross section can be retrieved. The simulation portion involves only a straightforward evaluation of the multiple integrations of (1). The form of $\sigma(\theta, E_{12})$ used here is that of figure (3) of Harris and Wilson², replotted as figure (2) of this paper.

Several intermediate sets of partially averaged data were produced to determine which variables distributions were most damaging in smearing

the laboratory data. The "nominal" transformation of the CM cross section into LAB, i.e., the one for which each distribution is a delta function at the most probable value of the variable, is the standard of the comparison since it represents the best experimental situation possible. These data were generated for both the kinematically "favorable" ($K + \text{CCl}_4$) and for the kinematically "unfavorable" ($\text{CCl}_4 + K$) cases. In all these cases some of the loss of definition of structure came from the L -distribution, but the main source of smearing was the v_2 -distribution. Distributions in the other variables had only very minor effects but were included in the complete averaging process. Convergence of the quadratures in the full averaging was tested by increasing the number of quadrature points until no further changes were noted.

The fully averaged results (figures 3b and 4b) were taken as typical data and the least-squares-spline function unfolding technique outlined in section III was used to fit an "experimental" $\sigma(\theta)$ which could be compared to the "true" one used in the simulation. Although the integrals of (1) are approximated in the same way in the simulation and the unfolding, the simulation was performed over a much larger range and higher density of laboratory angles. Five quadrature points were used to describe each variable in the two programs, except that ten points were used in the v_2 distribution in the case of CCl_4 and K in the simulation but only five in the unfolding. Also, the spline function used in the simulation was determined by specification at 40 points whereas the fitted curve in the unfolding procedure was determined only at

$N/2 = 30$ points whose positions were chosen by the unfolding program in the manner described in section III. Hence the second procedure is not simply an undoing of the first.

In figures 5 and 6 $\sin \theta \sigma(\theta)$ is shown for $K + CCl_4$ and $CCl_4 + K$ respectively. Figures 5a and 6a show the result of performing the unfolding with the crudest approximation to the integrals -- i.e., taking only one point in each of the quadratures. Although the fitted points reproduce the primary rainbow reasonably (the "true" cross section is the solid curve), the general agreement is quite poor, as expected. In particular the supernumerary structure is very poorly reproduced. Figures 5b and 6b show the results of the unfolding, taking into account only the v_2 -distribution (by five-point quadrature), and figures 5c and 6c show the results when all the distributions are taken into account. For both these cases the primary rainbow and the supernumerary structure are extremely well fitted in amplitude as well as position. The results for full consideration of averaging are not conspicuously better than when only the v_2 -distribution is done properly -- a not surprising result in view of the finding of the previous section that virtually all the smearing is due to v_2 .

In the two inversions that reproduce the rainbow structure well, the most serious departures from the correct $\sigma(\theta)$ occur at the largest values of θ . These errors are believed to result from the fact that the intensities computed by the unfolding program at the last few LAB angles are deficient in contributions from atypical velocity diagrams. These atypical diagrams arise from nominal C' angles well beyond the largest

θ , but which nevertheless contribute to scattering at smaller LAB angles through the averaging. The simulated scattering intensities used as input data are not lacking in these atypical velocity diagrams. As the range of the LAB data is increased these errors in the parameters move to higher values of CM angles.

In order to unfold the cross section reliably it is necessary to have a sufficient density of points in CM space for the cross section to be adequately described by the spline function. That is particularly pertinent for the structure of the rainbow region. In order to achieve the density of CM parameters in figure 5 for K and CCl_4 it was assumed that data were taken 0.3° intervals in the LAB region transforming to the region in CM space encompassing the supernumerary rainbow structure, 0.5° intervals for the rainbow maximum and 1° intervals thereafter. In figure 6 for CCl_4 and K the corresponding spacings were 0.2° , 0.5° and 1° .

V. Conclusions.

The results presented in figures 3 and 4 confirm the conclusions of Barwig et al.⁶ that velocity and angular averaging serve to reduce the amplitude of structure in the cross section but have much less effect on the position of the rainbow maxima. We also found that the experimental parameter contributing most to smearing the measured laboratory data is the velocity distribution of the secondary beam. Thus if the distribution of velocities of the secondary beam could be narrowed through the use of a nozzle or seeded beam less reduction in the amplitude of the structure could be anticipated.

With regard to the unfolding shown in figures 5 and 6, it may be stated that the linearization of the least-squares fit through use of the spline function to represent the fixed points makes it possible to recover the amplitude as well as the position of the rainbow structure provided a convergent method is used to account for the averaging.

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Appendix: Derivatives of the Spline Function with Respect to the Ordinates

The third order natural spline function $S(x)$ passing through the ordinates P_i ($i = 1, M$) at, respectively, abscissas x_i ($i = 1, M$) is given, for x in the interval between x_i and x_{i+1} , by [7]:

$$S(x) = P_i + (x-x_i) (P_{i+1} - P_i)/(x_{i+1} - x_i) + \frac{1}{6} (x - x_i) \times (x + x_{i+1}) [(2x_{i+1} - x - x_i)S''(x_i) + (x + x_{i+1} - 2x_i)S''(x_{i+1})]/(x_{i+1}-x_i) \quad (A1)$$

where $S''(x)$ is the second derivative of $S(x)$ with respect to x .

$S''(x)$ is zero at the two end points for the spline function, and it is evaluated at the intermediate abscissas by solution of the following matrix equation:

$$\underline{S''} = \underline{C}^{-1} \underline{E}$$

where $\underline{S''}$ is an $(M-2) \times 1$ vector of second derivative values at the intermediate points, and the elements of the square $(M-2) \times (M-2)$ matrix $\underline{C}$ are defined for $(i = 2, M-1)$, $(j = 2, M-1)$ by

$$C_{ij} = (x_i - x_j) (\delta_{i-1,j} - \delta_{i+j,j}) + 2(x_{i+1} - x_{i-1}) \delta_{ij} \quad (A2)$$

The $(M-2) \times 1$ matrix $\underline{E}$ is defined for $i = 2, M-1$ by

$$E_1 = 6 \left[(P_{i+1} - P_i)/(x_{i+1} - x_i) - (P_i - P_{i-1})/(x_i - x_{i-1}) \right] \quad (A3)$$

Since C depends on only the values of x at which the function is to be specified, $S''(x_i)$ varies linearly with each of the P_j , and therefore so does $S(x)$ itself at any value of x within the range between the smallest and largest abscissas. That is, we may write

$$S(x) = \sum_{\alpha} \gamma_{\alpha}(x) P_{\alpha} \quad (A4)$$

From equations (3) and (4) and using the spline function to represent $S(x)$ we may write

$$\begin{aligned} I_k &= \sum_{\beta} a_{k\beta} S(x_{\beta}) \\ &= \sum_{\beta} a_{k\beta} \sum_{\alpha} \gamma_{\alpha}(x_{\beta}) P_{\alpha} \end{aligned}$$

which shows I_k , the calculated value of the intensity, to be a linear function of each of the parameters defining the cross section at the specified points.

Continuing, we obtain the P -independent derivatives $\partial S(x)/\partial P_j$ from

$$\begin{aligned} \partial S(x)/\partial P_j &= [(x_{i+1} - x)\delta_{i,j} + (x - x_i)\delta_{i+1,j}]/(x_{i+1} - x_i) \\ &+ \frac{1}{6} (x - x_i)(x - x_{i+1})[(2x_{i+1} - x - x_i) \partial S''(x_i)/\partial P_j \\ &+ (x + x_{i+1} - 2x_i) \partial S''(x_{i+1})/\partial P_j]/(x_{i+1} - x_i) \quad (A5) \end{aligned}$$

The derivatives $\partial S''(x_i)/\partial p_j$ are given by

$$\begin{aligned} \partial S''(x_i)/\partial p_j = & -6C_{ij}^{-1} [(x_{i+1} - x_j)^{-1} + (x_j - x_{j-1})^{-1}] \\ & + 6C_{i,i-1}^{-1}/(x_i - x_{j-1}) + 6C_{i,j+1}^{-1}/(x_{i+1} - x_j) . \end{aligned} \quad (A6)$$

Footnotes

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FIGURE CAPTIONS

Figure 1. Velocity vector diagram showing the relation between LAB coordinates ϕ , $\textcircled{H}$, v_3 (origin O) and CM coordinates θ , ϕ , v_3 (origin C). The velocity of the center of mass is v_c .

Figure 2. The CM differential cross section for $K + CCl_4$ and $CCl_4 + K$ at $0.84 \text{ kcal mole}^{-1}$ taken from Figure 3 of Harris and Wilson [2]. For σ greater than 90° $\sigma(\sigma)$ is taken to be constant.

Figure 3. Results of averaging the cross-section of Figure 3 over various distributions for the system $K + CCl_4$. The graphs are arbitrarily displaced from each other.

(a) Direct transformation of CM cross-section to LAB system with all distributions single-valued. The angle ζ was taken to be 90° .

(b) Averaging due to the combination of f_ζ , $f_1(v_1)$, $f_2(v_2)$, and the height of the detector. Five point quadratures for all variables except v_2 for which ten point quadrature was used.

Figure 4. Results of averaging the cross-section of Figure 2 over various distributions for the system $CCl_4 + K$. The graphs are arbitrarily displaced from each other.

(a) Direct transformation of CM cross-section to LAB system with all distributions single-valued. The angle ζ was taken to be 90° .

(b) Averaging due to the combination of f , $f_1(v_1)$, $f_2(v_2)$, and the

height of the detector. Five point quadratures for all variables except v_2 , for which ten point quadrature was used.

Figure 5. Results of unfolding the C^1 cross-section from the fully averaged simulated data of figure 4e for the system $K + CCl_4$. The curve in full represents the correct solution. The points represent the cross sections adjusted by the least squares, and the dotted line adjoining them is the spline function they define. Each graph has been displaced vertically a decade from the adjacent ones.

- (a) Result of unfolding the cross-section using only a nominal transformation i.e., one with each variable taking only its average value.
- (b) Result of unfolding the cross-section using only the velocity distribution of the secondary beam, $f_2(v_2)$.
- (c) Result of unfolding the cross-section using full distributions in all the variables.

Figure 6. Results of unfolding the C^1 cross-section from the full averaged simulated data of figure 4e for the system $CCl_4 + K$. The curve in full represents the correct solution. The points represent the cross sections adjusted by the least squares, and the dotted line joining them is the spline function they define. Each graph has been displaced vertically a decade from the adjacent ones.

- (a) Result of unfolding the cross-section using only a nominal transformation, i.e., one with each variable taking only its average value.
- (b) Result of unfolding the cross-section using only the velocity distribution of the secondary beam, $f_2(v_2)$.
- (c) Result of unfolding the cross-section using full distributions in all the variables.

$\text{CCl}_4 + \text{K}$