17. Relation of Scattering Parameters to Potential

A. Summary of Semiclassical Analysis
B. Reduced Variable for Angular Distribution
C. Relation of Glory Undulations to Supernumerary Rainbows
D. Inversion Methods
Table I. Semiclessical analysis of angular distribution

<table>
<thead>
<tr>
<th>Deflection Function</th>
<th>Reduced Polar Cross Section</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Attractive branch:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta = -(15\pi/8)K\beta^6 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Rainbow branch:</strong></td>
<td>( H_R(B,K)\alpha^2(x) )</td>
<td></td>
</tr>
<tr>
<td>( \theta = \theta_R + a_R(\beta - \beta_R)^2 )</td>
<td></td>
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<tr>
<td>( \Delta\theta_R = B^{-1/3}K^{-1/3}a_R^{1/3} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_R = 3.60B^{1/6}K^{5/6}a_R^{2/3} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Orbiting branch:</strong></td>
<td>( H_o(K)\exp(-\theta/\Delta\theta_o) )</td>
<td></td>
</tr>
<tr>
<td>( \theta = \theta_o + a_o\ln</td>
<td>\beta - \beta_o</td>
<td>/\beta_o</td>
</tr>
<tr>
<td>( \Delta\theta_o = a_o )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_o = (2\beta_o^2/a_o)\exp(-\theta_o/a_o) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Glory branch:</strong></td>
<td>( H_g(K)G(y) )</td>
<td></td>
</tr>
<tr>
<td>( \theta = \theta_g + a_g(\beta - \beta_g) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta\theta_g = B^{-1/2}K^{-1/2}a_g^{1/2} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_g = 4\beta_g/a_g )</td>
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</table>
Table II. Notation, units, and handy numerical formulas

\[ E = \text{relative kinetic energy} = \frac{1}{2} \mu v^2, \text{ kcal/mole} \]
\[ L = \text{orbital angular momentum} = \mu vb = (l + \frac{1}{2})h \]
\[ v = \text{relative velocity}, 10^4 \text{ cm/sec} \]
\[ b = \text{impact parameter} = (l + \frac{1}{2})\lambda, \AA \]
\[ \mu = \text{reduced mass} = m_1m_2/(m_1 + m_2), \text{ gm/mole} \]
\[ \epsilon = \text{potential well depth, kcal/mole} \]
\[ r_m = \text{radius of potential minimum, } \AA \]

\[ a = 1.2897 \left( \frac{T}{M} \right)^{1/2}, \text{ most probable velocity in oven} \]
\[ v = 28.95 \left( \frac{E}{\mu} \right)^{1/2} \]
\[ E = 1.185 \times 10^{-3} \mu v^2 \]
\[ \lambda = 6.3522/\mu v = 0.2196 (\mu E)^{-1/2} \]
\[ \epsilon + \frac{1}{2} = 0.15743 \mu vb = 4.558 (\mu E)^{1/2}b \]

\[ r_m = 2^{1/6} = 1.225\sigma \text{ for Lennard-Jones potential} \]
\[ \theta (\text{radians}) = 57.2958 \theta (\text{degrees}), \text{ scattering angle} \]

\[ A = r_m/\lambda = (3\lambda)^{1/2} = DK \]
\[ B = 2\mu cr_m^2/h = AD = D^2/k \]
\[ D = 2\epsilon r_m/\hbar = B/A = \frac{\lambda}{\lambda} = (B/K)^{1/2} \]
\[ K = E/\epsilon = A/D = \frac{\lambda^2}{B} = D/B^2 \]
\[ \delta = b/r_m = (l + \frac{1}{2})/A \]
\[ L^2 = L/h\hbar^{1/2} = \lambda^{1/2} \delta \]

\[ A = 0.15743 \mu vr_m = 4.558 (\mu E)^{1/2} r_m \]
\[ B = 21.3 \mu cr_m^2 \]
\[ D = 135.5 \epsilon r_m/v \]
Table III. Form factors for the rainbow and glory contributions.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A_i^2(x)^a$</th>
<th>$y$</th>
<th>$G(y)^b$</th>
</tr>
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<tbody>
<tr>
<td>0.50</td>
<td>0.195</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>0.00</td>
<td>0.433</td>
<td>0.1</td>
<td>0.308</td>
</tr>
<tr>
<td>-1.02</td>
<td>1.000</td>
<td>0.2</td>
<td>0.630</td>
</tr>
<tr>
<td>-1.75</td>
<td>0.433</td>
<td>0.3</td>
<td>0.918</td>
</tr>
<tr>
<td>-2.34</td>
<td>0.000</td>
<td>0.4</td>
<td>1.155</td>
</tr>
<tr>
<td>-3.25</td>
<td>0.612</td>
<td>0.5</td>
<td>1.493</td>
</tr>
<tr>
<td>-4.09</td>
<td>0.000</td>
<td>0.6</td>
<td>1.585</td>
</tr>
<tr>
<td>-4.82</td>
<td>0.505</td>
<td>0.7</td>
<td>1.710</td>
</tr>
<tr>
<td>-5.52</td>
<td>0.000</td>
<td>0.8</td>
<td>1.806</td>
</tr>
<tr>
<td>-6.16</td>
<td>0.446</td>
<td>0.9</td>
<td>1.849</td>
</tr>
<tr>
<td>-6.79</td>
<td>0.000</td>
<td>0.92</td>
<td>1.855</td>
</tr>
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<td></td>
<td></td>
<td>1.0</td>
<td>1.835</td>
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<tr>
<td></td>
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<td>1.1</td>
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<td>1.582</td>
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<td></td>
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<td>1.4</td>
<td>1.350</td>
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<td>1.8</td>
<td>1.050</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>1.000</td>
</tr>
</tbody>
</table>

$^a$Square of the Airy integral, normalized to unity at its maximum.

$^b$Square of the zero order Bessel function multiplied by $y^2$ and smoothly joined to unity in the region $1.5 < y < 2$. 
Table IV. Small angle scattering approximation for the Lennard-Jones (6,12) potential.

\[ V(r) = \epsilon \left[ \left( \frac{r_m}{r} \right)^{12} - 2 \left( \frac{r_m}{r} \right)^{6} \right] \]

\[ \eta = \frac{3\pi}{16} \frac{D}{\beta^5} \left\{ 1 - \frac{21}{64} \frac{1}{\beta^6} \right\} \]

\[ \Theta = -\frac{15\pi}{8} \frac{1}{K\beta^6} \left\{ 1 - \frac{231}{320} \frac{1}{\beta^6} \right\} \]

\[ \frac{\partial \Theta}{\partial \beta} = \frac{45\pi}{4} \frac{1}{K\beta^7} \left\{ 1 - \frac{231}{160} \frac{1}{\beta^6} \right\} \]

\[ \frac{\partial^2 \Theta}{\partial \beta^2} = -\frac{315\pi}{4} \frac{1}{K\beta^8} \left\{ 1 - \frac{429}{160} \frac{1}{\beta^6} \right\} \]

\[ \beta_L = 0.947 \quad \beta_R = 1.056 \]

\[ \eta_L = 0.422 \quad \eta_R = 0.306 \]

\[ a_L = -52.0/K \quad a_R = 63.5/K \]
17B. Reduced Variables for Angular Distribution

By carrying out an expansion about the high energy or small-angle limit, one can obtain expressions of the form:

$$E\chi(E,b) = \sum_{n=0}^{\infty} a_n(b)/E^n$$

and

$$\chi_{\text{sin} \chi I}(\chi,E) = \sum_{n=0}^{\infty} \alpha_n(E\chi)/E^n$$

Thus, to lowest order

$$E\chi(E,b) = a_0(b)$$

is solely a function of impact parameter and not energy and

$$\chi_{\text{sin} \chi I}(\chi,E) = \alpha_0(E\chi)$$

is solely a function of the product of energy times angle. Furthermore, calculations for a variety of potentials show that the higher order terms in the expansion of $\chi_{\text{sin} \chi I}(\chi)$ decrease rapidly as $E\chi \to 0$. Thus, a plot of $\chi_{\text{sin} \chi I}(\chi)$ versus $E\chi$ for various values of the collision energy $E$ gives a set of curves that all coalesce to the asymptote $\alpha_0(E\chi)$ for small values of $E\chi$ and then fan out for larger values of $E\chi$. Each of these curves of course terminates at $\chi = \pi$ for a realistic potential with a repulsive core. On this kind of plot features such as rainbow structure appear at nearly the same value of $E\chi$ regardless of the collision energy. This holds because such features occur at approximately the same impact parameter as long as the collision energy is substantially above the well depth. (E.g., recall the rainbow angle result, $\chi_{\text{r}} = -2.06/E$, for a $L = J 6,12$ potential). Plots versus $E\chi$ thus provide a very useful means to correlate the experimental data.

Several expansion techniques have been developed. We outline one for $E\chi(E,b)$ given by F. T. Smith, R. P. Marchi, and K. G. Dedrick, Phys. Rev. 150, 79 (1966). This proceeds by use of a Lagrange expansion, which is the natural inverse of a Taylor expansion. The Lagrange expansion enables a function $f(y)$ to be expressed in terms of a new variable $x$. This in turn is defined by $x = 1 - g(y)$. Lagrange showed that, when $y$ is sufficiently close to $x$,

$$f(y) = h(y)/(dg(y)/dy) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n}{dx^n} [g^n(x)h(x)].$$

We want to apply this to $\chi(E,b)$, starting with the formula obtained in Sec. 5,
\[ \chi(E, b) = -2b \int_{r_c}^{\infty} \left[ 1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right]^{1/2} \frac{dr}{r^2} + 2b \int_{b}^{\infty} \left[ 1 - \frac{b^2}{r^2} \right]^{1/2} \frac{dr}{r^2} \]

Introduce new variables,
\[ y = r^2, \quad 2dr/r = dy/y, \quad y_c = r_c^2 \]

and
\[ x = y[1 - V(y^2)/E], \quad x_c = b^2. \]

Then we may rewrite \( \chi(E, b) \) as
\[ \chi(E, b) = -b \int_{b}^{\infty} \left[ \frac{1}{y} \frac{dy}{dx} - \frac{1}{x} \right] \frac{dx}{(x-b^2)^{1/2}} \]

If we now identify \( x \) and \( y \) with the variables of Lagrange, we see that
\[ g(y) = yV(y^2)/E \]

and \( dx/dy = -dg/dy \). Now if we let \( h(y) = y^{-1} \), the theorem of Lagrange gives
\[ f(y) = \frac{1}{y} \frac{dy}{dx} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n}{dx^n} \left\{ \frac{1}{E} \frac{1}{y^n(y^2)} \frac{1}{y} \right\} \]
\[ = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{1}{E^n} \frac{d^n}{dx^n} \left\{ \frac{1}{y^{n-1}y^n(y^2)} \right\} + \frac{1}{x} \]
\[ = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \frac{1}{E^{n+1}} \frac{d^{n+1}}{dx^{n+1}} \left\{ \frac{1}{y^{n+1}y^n(y^2)} \right\} + \frac{1}{x} \]

Hence we obtain for \( E\chi(E, b) \) the result quoted above
\[ E\chi(E, b) = \sum_{n=0}^{\infty} \frac{a_n(b)}{E^n} \]

where
\[
an_n(b) = \frac{-b}{(n+1)!} \int_b^\infty \frac{d^{n+1}}{dx^{n+1}} \left[ x^n V^{n+1}(x^2) \right] \frac{dx}{(x-b^2)^{\frac{3}{2}}}\]

From the relation \( x = y[1 - V(y')/E] \) and the requirement of Lagrange that \( x \) and \( y \) be similar in magnitude, we expect this expansion to be valid when

\[
\left| \frac{x-y}{y} \right| = \left| \frac{V(r)/E}{1-V(r)/E} \right| = \left| \frac{V(r)}{E} \right| \ll 1
\]

along the entire trajectory. Thus we expect the expansion will converge for relatively small deflection angles, i.e. either large impact parameters or high collision energy.

By employing a different choice for \( x \) and \( y \) with this same technique, Smith, Marchi, and Dedrick obtain the analogous expansion for \( x \sin x I(x) \) cited above. They also derive other expansions valid for large deflection angles near \( x = \pi \). Another treatment of the wide-angle case, which provides a means to extract the well depth \( \varepsilon \) from the shape of \( I(x) \) in that region, is given by R. J. Cross, J. Chem. Phys. 48, 1480 (1968).

For reference purposes, we recast the first two terms in the \( E x(E,b) \) expansion,

\[
E x(E,b) = a_0(b) + a_1(b)/E,
\]

where

\[
a_0(b) = \int_b^\infty \frac{d}{dx} \frac{1}{x^2} \frac{dx}{(x-b^2)^{\frac{3}{2}}} = \int_b^\infty \frac{1}{x^2} \frac{dx}{(x-b^2)^{\frac{3}{2}}}\]

\[
a_1(b) = -\frac{b}{2} \int_b^\infty \frac{d^2}{dx^2} \left[ x^n V^{n+1}(x^2) \right] \frac{dx}{(x-b^2)^{\frac{3}{2}}}\]

\[
= -\frac{b}{2} \left\{ \frac{3V''}{4} + \frac{V'^2}{4} + \frac{3V''}{4} \right\} \frac{dx}{(x-b^2)^{\frac{3}{2}}}\]

where \( V'(z) = dV(z)/dz, \) etc. On changing variables to \( x^2 = r, \ dx/2x = dr, \) we obtain

\[
\frac{1}{2} \left( \frac{r V''}{4} + \frac{r V'^2}{4} + \frac{r V''}{4} \right) = \frac{1}{2} \frac{dx}{(x-b^2)^{\frac{3}{2}}}
\]
\[ a_0(b) = -b \int_{b}^{\infty} V'(r) \frac{dr}{(r^2-b^2)^{1/2}} \]

\[ a_1(b) = - \frac{b^2}{2} \int_{b}^{\infty} \{3V(r)V'(r) + rV''(r) + rV(r)V''(r)\} \frac{dr}{(r^2-b^2)^{1/2}} \]

Note that the first order result,

\[ \chi(E,b) = a_0(b)/E \]

is identical to the Kennard approximation for small-angle scattering.
17C. Relation of Glory Undulations to Supernumerary Rainbows

The glory undulations in the total cross section provide phase information that at first appears to be independent of the information obtained from the rainbow structure, and these features have often been analyzed independently. Actually, it can be shown that the determination of $N_0$, the maximum phase shift, from the glory undulations yields no information on which cannot be determined from the supernumerary oscillations in the angular distribution. As illustrated in Fig. 17C-1, the number of supernumerary rainbow oscillations that appear at a particular collision energy equals the number of glory maxima which appear above that energy.

\[ i_1(x) = \left| f_1(x) + f_2(x) + f_3(x) \right|^2 \]

Fig. 17C-1. Total cross section $Q(\nu)$ versus $\nu$ (log-log plot, upper abscissa scale) and differential cross section $I(\theta)$ versus $\theta$ (semilog plot, lower abscissa scale). The $I(\theta)$ distribution is calculated for the same potential as $Q(\nu)$ and shown for three velocities which correspond to successive glory maxima.

This relation was first pointed out by U. Buck and H. Pauly, Z. Physik 208, 390 (1968), and Fig. 17C-1 is taken from their paper. The relation is readily derived from the semiclassical approximation for the scattering amplitude. In the domain of interest, the angular distribution contains contributions from three branches of the deflection function:

\[ f_n(\chi) = \left[ I_n(\chi) \right]^{1/2} e^{\frac{i\pi}{2} \chi_n} \]
with
\[ I_n(\chi) = \frac{\chi(\ell + \frac{1}{2})}{|\sin \chi(\partial \chi/\partial \ell)|} \]

\[ \beta_n = 2n - 2(\ell + \frac{1}{2})n' - \left( 2 - \frac{n'}{|n'|} - \frac{n''}{|n''|} \right) \pi \frac{\ell}{4} \]

The signs of the various terms in \( \beta_n \) for the three branches may be read from Fig. 17C-2, which shows the form of \( \eta(\ell) \) and \( \chi(\ell) \) corresponding to the usual form of potential function:

Branch  \[ \ell_1 < \ell_2 < \ell_3 \]

Sign of \( n' \) and \( \chi \):  
+  -  -

Sign of \( n'' \) and \( \chi' \):  
-  -  +

Since the observed scattering angle \( \theta \) is related to \( 2n' = \chi \) by
\[
2n' = \theta \quad \text{if} \quad n' > 0 \\
= -\theta \quad \text{if} \quad n' < 0,
\]

we find
\[
\beta_1 = 2n_1 - (\ell_1 + \frac{1}{2})\theta - \frac{\pi}{2} \\
\beta_2 = 2n_2 + (\ell_2 + \frac{1}{2})\theta - \pi \\
\beta_3 = 2n_3 + (\ell_3 + \frac{1}{2})\theta - \frac{\pi}{2}
\]

The interference terms in \( I(\chi) \) contain the phase differences:
\[
\beta_1 - \beta_2 = 2(n_1 - n_2) - (\ell_1 + \ell_2)\theta + \frac{\pi}{2} \\
\beta_2 - \beta_3 = 2(n_2 - n_3) + (\ell_2 - \ell_3)\theta - \frac{\pi}{2} \\
\beta_3 - \beta_1 = 2(n_3 - n_1) + (\ell_3 + \ell_1)\theta
\]

where for simplicity we write \( \ell + \frac{1}{2} = \ell \). The glory structure involves \( \beta_1 - \beta_2 \), the supernumerary rainbow structure \( \beta_2 - \beta_3 \), and the "fast oscillations" \( \beta_3 - \beta_1 \). Thus, we have
\[
I(\chi) = I_{cl}(\chi) + I_{int}(\chi)
\]
Fig. 17C-2. Phase shift and deflection functions, showing contributions from three collisional angular momenta at same scattering angle $\theta$. 
\[ I_{c1} = I_1(\chi) + I_2(\chi) + I_3(\chi) \]
\[ I_{\text{int}} = 2(I_1I_2)^{1/2}\cos(\beta_1 - \beta_2) + 2(I_2I_3)^{1/2}\cos(\beta_2 - \beta_3) \]
\[ + 2(I_3I_1)^{1/2}\cos(\beta_3 - \beta_1) \]

The interference of branches 1 and 2 may be evaluated using
\[ \chi(\ell) = a_g(\ell - \beta_1) \text{ and } \eta(\ell) = \eta_g + \frac{1}{4}a_g(\ell - \bar{\ell}_g)^2 \]

Thus,
\[ \bar{\ell}_g - \bar{\ell}_1 = \bar{\ell}_2 - \bar{\ell}_g = \chi/a_g = 2[[(\eta_g - \eta)/a_g]^{1/2} \]
and
\[ \bar{\ell}_1 + \bar{\ell}_2 = 2\bar{\ell}_g \]
\[ \chi_1 = -\chi_2, \quad \eta_1 = \eta_2 \]
Hence,
\[ \beta_1 - \beta_2 = -2\bar{\ell}_g \theta + \frac{\pi}{2} \]

The interference of branches 2 and 3 is evaluated assuming the collision energy is high enough to make \( \theta_r \) small. Then, especially for \( \theta < \theta_r' \),
\[ \bar{\ell}_2 \sim \bar{\ell}_g \text{ and } \eta_2 \sim \eta_g \text{ whereas } \ell_3 \text{ is far enough out on the attractive branch to make } \eta_3 \sim 0. \] Also, since
\[ \chi(\ell) = \chi_r + a_r(\ell - \bar{\ell}_r)^2 \]
we have
\[ \ell_3 - \ell_r = \ell_r - \ell_2 = \left( \frac{\chi - \chi_r}{a_r} \right)^{1/2} = \left( \frac{1}{\theta_r} \right)^{1/2} \left( 1 - \frac{\theta}{\theta_r} \right)^{1/2} \]
\[ = (\ell_r - \ell_g) \left( 1 - \frac{\theta}{\theta_r} \right)^{1/2} \]
Hence,
\[ \beta_2 - \beta_3 = 2\eta_g + 2(\ell_r - \ell_g)\theta \left( 1 - \frac{\theta}{\theta_r} \right)^{1/2} - \frac{\pi}{2} \]

The interference of branches 3 and 1 is likewise evaluated from the above results. Thus we take \( \eta_3 \sim 0 \) and \( \eta_1 \sim \eta_2 \sim \eta_g \) and
\[ \ell_1 + \ell_2 = 2 \ell_g \]
\[ \ell_3 - \ell_2 = 2(\ell_r - \ell_g) \left( 1 - \frac{\theta}{\theta_r} \right)^{1/2} \approx 2(\ell_r - \ell_g) \]

or
\[ \ell_3 + \ell_2 \approx 2 \ell_r \]

Hence
\[ \beta_3 - \beta_1 \approx -2 \eta_g + 2 \theta_r \theta \]

Now we consider \( I(\chi) \) for \( \theta = 0 \), which corresponds to \( \ell_1 = \ell_2 = \ell_g \) so \( I_1(0) = I_2(0) = I_0 \).

Then
\[
I(0) = I_1 + I_2 + I_3 + 2(I_1 I_2)^{1/2} \cos \frac{\pi}{2} + 2(I_2 I_3)^{1/2} \cos \left( \frac{2 \eta_g - \pi}{2} \right) + 2(I_3 I_1)^{1/2} \cos 2 \eta_g
\]

\[ = 2I_0 + I_3 + 2(I_0 I_3)^{1/2} \left[ \cos \left( \frac{2 \eta_g - \pi}{2} \right) + \cos 2 \eta_g \right] \]

Using
\[ \cos \alpha + \cos \beta = 2 \cos \frac{1}{2} (\alpha + \beta) \cos \frac{1}{2} (\alpha - \beta) \]

we have
\[ \cos \left( \frac{2 \eta_g - \pi}{2} \right) + \cos 2 \eta_g = 2^{1/2} \cos \left( \frac{2 \eta_g - \pi}{4} \right) \]

and finally
\[ I(0) = 2I_0 + I_3 + 2^{3/2} (I_0 I_3)^{1/2} \cos \left( \frac{2 \eta_g - \pi}{4} \right) \]

This shows that the differential cross section at \( \theta = 0 \) has the same undulatory velocity dependence as the glory structure in the total cross section. At a velocity corresponding to a glory maximum in \( Q(\chi) \), there likewise occurs a rainbow maximum in \( I(\theta) \). When the velocity is decreased, this rainbow maximum moves off to angles \( \theta > 0 \). The principal rainbow maximum will first become observable when the corresponding angle \( \theta_r \) becomes larger than the angle \( \theta_0 \), which occurs in the treatment of small-angle scattering and represents the "uncertainty-principle cut-off". The velocity corresponding to \( \theta_r = \theta_0 \) is that at which the first glory maximum occurs in the total cross section. As the velocity is decreased, successive supernumerary rainbows emerge at velocities corresponding to additional glory maxima. This continues down through the orbiting realm until the full spectrum of oscillations corresponding to the bound states has been swept out when the velocity reaches zero.
The problem of determining the potential function $V(r)$ from experimental scattering data was, until a few years ago, treated by the "cut-and-try" method. A convenient functional form containing adjustable parameters was chosen for $V(r)$, the scattering was calculated and compared with the data to obtain "best fit" values of the parameters. As the data improved, this procedure became more and more cumbersome and unsatisfactory. In particular, it was found that the rainbow structure could not be fitted well in this way. For some time it was assumed that direct inversion of the data to obtain $V(r)$ would not be feasible. The existing theory had solved this problem only for the case of a monotonic potential, of limited interest in chemical physics. It turned out that the semiclassical method led to a straightforward and numerically convenient inversion procedure, applicable to nonmonotonic potentials. Appropriately, the rainbow structure turned out to provide the key information. An extensive review of these developments is given by U. Buck, Rev. Mod. Phys. 46, 369 (1974).

In quantum (rather than semiclassical) theory, study of the inversion problem led to discouraging results. There are two steps:

$I(\theta) \text{ or } Q(\nu) \xrightarrow{I} \eta_\ell(E) \xrightarrow{I} V(r)$

Most attention has been devoted to step II; reviews are given in the books by Newton and by Wu and Omhura. The main results pertain to the question of uniqueness of $V(r)$. It has been shown that knowledge of $\eta_\ell(E)$ for fixed $\ell$ and all energies will yield an ambiguous result, an $n$-parameter family of potentials, where $n$ is the number of bound states. Likewise, knowledge of $\eta_\ell(E)$ for fixed $E$ and all $\ell$ will also not uniquely determine the potential unless additional constraints are imposed.

For semiclassical scattering, the appropriate inversion route is

$I(\theta) \text{ or } Q(r) \xrightarrow{I} \chi(b) \xrightarrow{I} V(r)$

We consider step II first, the determination of the potential from the classical deflection function. Several treatments have been given; see,
The Firsov Method starts with the classical deflection function:

\[ \chi(b) = \pi \int_{r_C}^{\infty} \frac{2b \, dr}{r[r^2(1 - V(r)/E) - b^2]^{1/2}} \]  \hspace{1cm} (1)

We suppose that \( \chi(b) \) is known at one energy.

Define \( u(r) = r \left[ 1 - \frac{V(r)}{E} \right]^{1/2} \) \hspace{1cm} (2)

If \( V(r) = 0 \), \( u(r) = r \) and if \( r = r_C \), \( u(r_C) = b \). It is easy to show that \( du/dr > 0 \) if \( E > V(r) + \frac{1}{2} rV'(r) \) for all \( r \) for which \( E > V(r) \). This will hold if \( E \) exceeds the largest energy at which classical orbiting can occur. In that case the inverse function of \( u(r) \) exists; it is denoted by \( r(u) \). If the integration variable is changed from \( r \) to \( u \), we have

\[ \chi(b) = 2b \int_{b}^{\infty} \frac{du}{u(u^2 - b^2)^{1/2}} - 2b \int_{b}^{\infty} \frac{dr}{r} \frac{du}{u(u^2 - b^2)^{1/2}} \]

\[ = 2b \int_{b}^{\infty} \left[ \frac{1}{u} - \frac{dr}{r} \right] \frac{du}{(u^2 - b^2)^{1/2}} \]  \hspace{1cm} (3)

Define \( T(u) = 2\ln \frac{r(u)}{u} \) \hspace{1cm} (4)

Then we have

\[ \chi(b) = -2b \int_{b}^{\infty} \frac{dT}{du} \frac{du}{(u^2 - b^2)^{1/2}} \]  \hspace{1cm} (5)

Hence we recognize that \( T(u) \) is related to \( \chi(b) \) by an Euler transformation and
\[ T(u) = \frac{1}{\pi} \int_{u}^{\infty} \frac{x(b)db}{(b^2 - u^2)^{1/2}} \]  

Now if \( T(u) \) is derived from \( x(b) \) via (6), then (4) and (2) provide

\[
\begin{cases}
  r = u e^{T(u)} \\
  V(r) = E[1 - e^{-2T(u)}]
\end{cases}
\]  

This gives a parametric representation of \( V(r) \): as \( u \) varies from 0 to \( \infty \), (7) generates points \((r, V)\). Since \( T(u = 0) = \infty \), \( u = 0 \) generates the point \( r = r_C \), \( V = E \), where \( V(r_C) = E \) (and \( b = 0 \)). Also, since \( du/dr > 0 \), \( u > 0 \) implies \( r > r_C \) and \( V(r) < E \); thus, from \( x(b) \) at energy \( E \) we can construct \( V(r) \) at all \( r \) for which \( V(r) < E \).

The integration in (6) can be carried out analytically for a large variety of functions; a tabulation is given by G. Vollmer, Z. Phys. 226, 423 (1969). When numerical integration of (6) is employed, the singularity at \( b = u \) creates some difficulties. Some alternative forms which avoid this problem are given by U. Buck, J. Chem. Phys. 54, 1923 (1971).

Now we consider step I, the determination of the deflection function from scattering data. In practice, the most straightforward procedure is to adopt a parameterized form for \( x(b) \) for which \( I(\theta) \) can be explicitly computed and to determine the parameters from the data. If the potential and hence \( x(b) \) is monotonic or if we deal with the region \( \theta > \theta_r \), where \( b(\chi) \) is monotonic, the relation between \( I(\theta) \) and \( x(\chi) \) is given by

\[ b^2(x) = \int_{\chi}^{\pi} I(\theta) \sin \theta d\theta \]  

However, in the region \( \theta < \theta_r \), the \( b(\chi) \) function is multiple-valued since three impact parameters correspond to the same deflection angle. The interference between these three impact parameters results in oscillatory structure in \( I(\theta) \). There are two kinds of oscillations: "supernumery rainbows" and "fast oscillations", which are readily distinguished because they have
different angular separations and amplitudes. The rainbow gives the main oscillatory structure with the fast oscillations superimposed on it.

The procedure used in the region $\theta < \theta_r$ consists of two steps:
(i) The deflection function $\chi(b)$ is written as the sum of several convenient component functions, $\chi(b) = \sum x_i(b)$, where each $x_i$ function is monotonic and contains appropriate adjustable parameters.

(ii) The cross section $I(\theta)$ is calculated and compared with the experimental $I_{\text{exp}}(\theta)$ at a number of angles $\theta_j$. The optimum parameters are determined by minimizing

$$\sum [I_{\text{exp}}(\theta_j) - I(\theta_j)]^2.$$  

As exemplified in the work of Buck and Pauly, this procedure is efficient and yields an accurate determination of the potential if the data provide several rainbow extrema.

In the region $\theta < \theta_r$, the cross section $I(\theta)$ can be evaluated using the uniform approximation which holds throughout the region. Thus,

$$I(\theta) = \pi [I_2^{1/2} + I_3^{1/2}] |z|^{1/3} \text{Ai}^2(-|z|) + \pi [I_3^{1/2} - I_2^{1/2}] |z|^{-1/3} \text{Ai'}^2(-|z|)$$  

(9)

where $I_2(\theta)$ and $I_3(\theta)$ are the classical cross sections for branches 2 and 3 of the deflection function, $\text{Ai}$ and $\text{Ai'}$ are the Airy function and its first derivative, and

$$4/3 z^{3/2} = \beta_2 - \beta_3 + \frac{\pi}{2}$$  

(10)

with

$$\beta_2 - \beta_3 + \frac{\pi}{2} = 2(n_2 - n_3) + \lambda(b_2 - b_3)$$  

(11)
This uniform approximation was derived by M. V. Berry, Proc. Phys. Soc. (London) 89, 479 (1966). It omits the fast oscillations and assumes $\theta_\rho < \pi$ but these conditions are appropriate in practice. For both large and small $z$, Berry's formula reduces to the results of Ford and Wheeler.
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