# Inversion of molecular scattering data

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Solutions of the inverse problem of scattering are reviewed. Quantum mechanical, semiclassical, and classical methods in the high-energy limit are discussed for both the step from the cross section to the phase shifts or the deflection function and the step from these functions to the potential. The emphasis is on the practical applicability of such procedures in molecular physics rather than on the question of existence and uniqueness. The procedures which had been applied to the determination of spherically symmetric, interatomic potentials by the inversion of actual scattering data are critically surveyed and illustrated by approprite examples.

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## I. INTRODUCTION

The main purpose of elastic scattering experiments is to determine the forces of interaction between the colliding particles. Molecular beam experiments have proved to be the most powerful method for obtaining detailed information on the interaction potential of molecular systems, which do not form a stable compound under ordinary conditions. (See, for example, Pauly and Toennies, 1965; Bernstein and Muckermann, 1967; Toennies, 1973.) However, it is not a simple matter to analyze the observables, e.g., the differential or the integral cross section, in order to get quantitative information on the potentials. The most widely used method is to assume for the interaction a specific functional form and then to calculate the scattering phase shifts and the cross section. In practice potentials are derived by varying the parameters inserted in the potential by trial and error so as to obtain the best fit to the measured cross section. Such a procedure converges very slowly and the number of iterations increases rapidly with the number of trial parameters and thus requires a large amount of computing time. This is especially true for the high resolution measurements of differential and integral cross sections now available for molecular systems, which require for a good fit more and more flexible model potentials (Olson and Mueller, 1967; Buck and Pauly, 1968; Düren *et al.*, 1968; Mittmann *et al.*, 1971; Siska *et al.*, 1971; Cantini *et al.*, 1972; Gengenbach *et al.*, 1973).

These difficulties can be avoided if the so-called inverse problem of scattering is solved, that is, the construction of the potential directly from the measured data. A set of phase shifts is obtained from the observed angular and energy dependence of the cross section, and then the potential is deduced from these phase shifts. Any procedure which contains at least the second step, will be referred to as inversion.

It is quite obvious that the solution of this problem is of great interest for both intrinsic theoretical studies and practical purposes. An extensive mathematical theory dealing with the theoretical aspect of the problem has been developed. (See, e.g., Agranovich and Marchenko, 1963; De Alfaro and Regge, 1965; Newton, 1966.) The questions of the existence and uniqueness of the potential have been studied in detail. Since in most cases a unique solution has not been found, the problem of constructing all equivalent potentials for a given set of phase shifts has attracted great interest. These theoretical aspects are surveyed in an excellent and authoritative manner by Newton (1972) for the inverse problem, where the phase shifts are known for all energies, and by Sabatier (1972a) for the problem, where the phase shifts are given for all angular momenta.

The discussion of the second aspect of the problem, the practical application of such inverse methods, will be the main topic of this article. The exact quantum mechanical procedures have rarely been applied to the practical problem of finding potentials from actual data sets. Most of the applications, which can be found in the literature, are artificially simplified cases or simulated examples (Bargmann, 1949; Jost and Kohn, 1952; O'Brien and Bernstein, 1969; Sabatier and Quyen Van Phu, 1971).[1] This is even true for the scattering of two nucleons, where only a few phase shifts have to be determined. For molecular scattering the situation is more complicated since generally a large number of phase shifts are necessary to describe the scattering process. Therefore, a

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[1] For an exception see Benn and Scharf (1967).

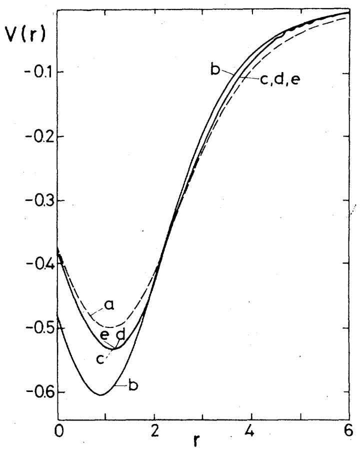

FIG. 1. Convergence of the Hylleraas solution. Curve a is the "unknown" potential. Curve b is the initial trial potential. Curves c, d, e are repeated iterations converging to a potential which is phase equivalent to the true potential a (O'Brien and Bernstein, 1969).

practical solution will largely depend upon the special features of the particles under study, e.g., the special form of the potential or certain approximations for the treatment of the scattering process, which will simplify the problem in one or the other way.

Since short wavelength approximations have been proved to be good approximations in the scattering of ions, atoms, and molecules, semiclassical or classical procedures will mainly be considered (Ford and Wheeler, 1959). Therefore the main scope of this article will be a critical review of inverse procedures with respect to their possible application in molecular physics and a comprehensive survey of the results obtained up until now in this field. The question of experimental accessibility of the input information, the feasibility of the mathematical procedure for numerical applications, and the stability of the method with respect to random perturbations, caused by experimental error, will be considered rather than uniqueness and existence problems. Procedures which have been applied to practical cases are treated in more detail than others which have only been suggested.

It should be pointed out that most of the results available up until now have been achieved for the elastic scattering with spherically symmetric potentials. Although some of the procedures can easily be extended to general cases such as complex potentials (absorption corresponding to inelastic channels or chemical reactions) and nonspherical potentials (occurring in molecular scattering), the contents of this article will be restricted to the spherically symmetric case. All extensions are mentioned, but not treated extensively. Literature will be covered up to June 1973 for all cases of molecular physics.

Although quantum mechanical solutions have rarely been applied to practical problems, they give deep insight into the mechanism of the inversion. This article starts therefore with a brief summary of quantum mechanical results in Section II, where methods for obtaining the potential from the phase shifts (Sec. II A) and the phase shifts from the cross section are treated (Sec. II B). A description of approximate solutions which are mainly obtained in the JWKB approximation (Sec. III A) and the high-energy approximation of classical mechanics (Sec. III B) is then given. These solutions require different input information ranging from the phase shifts and the deflection function to the integral cross section. How this input information (if it is not the cross section) is obtained in practical cases is treated in Sec. IV. Finally Sec. V gives some examples of results which are obtained by various procedures outlined in Secs. III and IV. The section concludes with remarks on the requirements of cross section data for an inversion procedure and with a comparison of the advantages of such a procedure over a method of trial and error.

## II. EXACT SOLUTIONS AND FORMAL METHODS

### A. Determination of the potential from the phase shifts

There have been numerous attempts to solve the inverse problem in the framework of quantum mechanics. The simplest case, the scattering of two spinless particles, is governed by a spherically symmetric potential and may be described by the partial wave analysis of the Schrödinger equation, which gives for the differential cross section

$$\sigma(\vartheta) = |f(\vartheta)|^2, \tag{2.1}$$

where the scattering amplitude $f(\vartheta)$ is given by

$$f(\vartheta) = (2ik)^{-1} \textstyle\sum_l (2l+1)[\exp(2i\eta_l) - 1]P_l(\cos\vartheta). \tag{2.2}$$

$\vartheta$ is the angle of deflection, $l$ the angular momentum, $P_l$ the Legendre polynomials, and $k$ the wavenumber corresponding to the collision energy $E$ and the reduced mass $\mu$: $k = (2\mu E)^{1/2}/\hbar$. The phase shifts $\eta_l$ may be obtained from the radial Schrödinger equation

$$-\psi''_l + l(l+1)r^{-2}\psi_l + W(r)\psi_l = k^2\psi_l, \tag{2.3}$$

with $W(r) = (2\mu/\hbar^2)V(r)$. The wavefunctions satisfy the boundary conditions

$$\lim_{r\to 0} r^{-l-1}\psi_l(r)(2l+1)! = 1 \quad \text{and} \quad \psi_l(r) \sim A_l(\sin kr - l\pi/2 + \eta_l). \tag{2.4}$$

Since the phase shifts are a function of the angular momentum and the energy, the inverse problem provides solutions for fixed angular momentum (IIA1) and fixed energy (IIA2). Section II.A3 summarizes the results, where several studies are included, which start with the scattering amplitude and use an integral equation formalism. The step from the differential cross section to the phase shifts is discussed in Sec. IIB.

#### *1. The fixed angular momentum problem*

Since this subject has been reviewed in an excellent manner (Newton, 1966, 1972), I shall outline only one particular way of solving this problem, which shows the requirements for a unique solution (Gelfand and Levitan, 1951). The inverse scattering problem is posed by asking for $V(r)$ in the radial Schrödinger equation under the assumption that the asymptotic phase shifts, $\eta_l(E)$, of the regular solution, $\varphi(E,r)$, are given for all positive $E$. The main tool for the solution is the fact that the functions $\varphi(E,r)$ form a complete set, which can be written symbolically as

$$\int_{-\infty}^{\infty} d\rho(E)\varphi(E,r)\varphi(E,x) = \delta(r-x). \tag{2.5}$$

$\rho(E)$ is the spectral function. For $E \leq 0$ the spectrum is discrete and corresponds to the bound states of the system. For $E > 0$ the spectrum is continuous. Now the problem is solved if we are able to relate the spectral function $\rho(E)$ to the phase shifts $\eta_l(E)$, and to calculate the potential $V(r)$ from the given spectral function. The last step is discussed first. For simplicity we shall restrict ourselves to the case $l = 0$, starting with a known solution $\varphi_1(E, r)$ of the radial Schrödinger equation for an arbitrary comparison potential $W_1$ with the spectral function $\rho_1(E)$. The key to the solution of Gelfand and Levitan (1951) is the function $K(r, x)$, referred to as the transformation kernel or generalized translation operator, which yields the potential

$$W(r) = 2d/drK(r,r) + W_1(r). \tag{2.6}$$

$K(r, x)$ is constructed with the help of an auxiliary function $g(r, x)$,

$$g(r,x) = \int [d\rho_1(E) - d\rho(E)]\varphi_1(E,r)\varphi_1(E,x), \tag{2.7}$$

by solving the Fredholm integral equation

$$K(r,x) = g(r,x) + \int_0^r dyK(r,y)g(y,x). \tag{2.8}$$

This equation can be shown to have a unique solution under very general conditions. By adopting an arbitrary comparison potential $W_1$, e.g., $W_1 = 0$, one can calculate $g(r, x)$ from the known function $\varphi_1$ and the spectral function $\rho(E)$. The spectral function is obtained by writing the completeness relation (2.5) explicitly. We find

$$\frac{2\mu}{\hbar^2}\frac{1}{\pi}\int_0^\infty dE \frac{k}{|f(E)|^2}\varphi(E,r)\varphi(E,x) + \sum_n \frac{\varphi_n(r)\varphi_n(x)}{N_n^2} = \delta(r - x), \tag{2.9}$$

where the first term is valid for $E > 0$ and the second for $E \leq 0$. The spectral function $\rho(E)$ is uniquely determined from a knowledge of the constants $N_n$ of the bound state normalization

$$N_n^2 = \int_0^\infty dr[\varphi_n(r)]^2 \tag{2.10}$$

and the Jost function $f(E)$ which can be calculated via a dispersion relation of phase shifts and bound state energies,

$$|f(k)| = \exp\left[\frac{1}{\pi}\int_{-\infty}^{\infty} dk' \frac{\hat{\eta}(k')}{k - k'}\right] \tag{2.11}$$

with

$$\hat{\eta}(k) = \eta(k) + 2\textstyle\sum_n \arctan(\zeta_n/k) \tag{2.12}$$

and

$$2\mu/\hbar^2 E_n = -\zeta_n^2.$$

The result may be summarized as follows: There exists a unique solution of the inverse scattering problem with fixed angular momentum if the completeness relation is fulfilled; that means that the constants of normalization, $N_n$, and the Jost function have to be known. The latter must be calculated from the phase shifts and all bound state energies. Hence, for a given set of phase shifts and bound state energies $E_n$, there is a family of associated potentials with $n$ free parameters called "phase equivalent" potentials, where $n$ is the number of the bound states. It should be mentioned that for potentials which satisfy the condition $\lim_{r\to\infty} e^{2\zeta}V(r) = 0$, where $\zeta$ corresponds to the binding energy of the lowest bound state, the constants $N_n$ can be determined in a unique manner removing the bound-state arbitrariness (Jost and Kohn, 1952).

In addition to the procedure of Gelfand and Levitan (1951) there are numerous papers in the literature dealing with other solutions (see for instance Newton, 1972). But there are only a few actual examples of potentials which are obtained by an inversion of real phase shifts. The procedure of Hylleraas (1948, 1963, 1964) has been used by O'Brien and Bernstein (1969) to construct potentials of the Bargmann (1949) class from simulated examples. The rapid convergence of the procedure is shown in Fig. 1 . Curve b is the initial trial potential, curves c, d, and e show the results of successive iterations. But the procedure converges to the phase equivalent potential, not to the potential a, from which the input phase shifts have been obtained. The procedure of Marchenko (Agranovich and Marchenko, 1963) has been applied by Benn and Scharf (1967) for the inversion of real scattering phase shifts of $\alpha$-$\alpha$-particle interactions. Due to the short-range behavior of the potentials, the ambiguity of the solution could be avoided. The problem of knowing the phase shifts from zero to infinity was overcome by an extrapolation of the experimental phase shifts according to the behavior of the hard-core phase shifts.

### 2. *The fixed energy problem*

It has taken a long time to solve this problem in a way which gives definite answers not only to the questions of existence and uniqueness but also to the explicit construction of the solution. The reason is that an important tool for the solution of the fixed angular momentum problem is the completeness of the radial wavefunctions for one angular momentum and all energies. The wavefunctions for one energy and all angular momenta do not have such a property. The general solution is based on an analogy with the Gelfand and Levitan equation introduced by Regge (1959) and applied by Newton (1962) for the solution of the inverse problem (see the excellent review of Sabatier, 1972a). In analogy to Eq. (2.7) the auxiliary function $f(r, x)$ can be written as

$$f(r,x) = \int_C dh(l)\varphi_1(l,r)\varphi_1(l,x), \tag{2.13}$$

where $h(l)$, in contrast to Eq. (2.5), is any piecewise differentiable function of $l$ including isolated points. The choice of the potential $W_1$ [and therefore of $\varphi_1(l, r)$] and the contour $C$ determine to a large extent the constraints on the potentials obtained by the inversion procedure (Sabatier, 1968; Coudray and Coz, 1970). According to the choice of the expansion of $f(r, x)$, two kinds of solutions are available in the literature, the Regge–Loeffel approach (Regge, 1959; Loeffel, 1968) and the Newton–Sabatier method (Newton, 1962; Sabatier, 1966a; 1966b; 1967a, 1967b; Newton, 1967; Sabatier, 1968). Loeffel was able to prove that $f(r, x)$ has a unique spectral expansion and that this expansion can be related to properties of dynamical interpolation of the Jost function. Though the question of uniqueness could be studied extensively by this method, no constructive method could be given for a practical application. Furthermore, Viano (1969) showed that the stability of the interpolation process in the complex angular momentum plane is highly questionable if real data with superimposed errors are used. These perturbations, no matter how small they are, prevent the use of theorems which guarantee the uniqueness of the interpolation in the complex plane of angular momentum. Newton (1962) replaced the integration over $C$ by a summation over integer $l$. In this case $C$ is reduced to discrete points on the real axis. This choice has the advantage that the inverse problem can be solved by an algebraic equation, but on the other hand the class of potentials considered is restricted. With $W_l = 0$ and therefore $\varphi_l(r,l) = u_l(r)$ (the regular spherical Ricatti–Bessel functions) one obtains

$$f(r,x) = \sum_{l'} c_l u_l(r) u_l(x). \tag{2.14}$$

The coefficients $c_l$ can be obtained from the phase shifts by solving the equation

$$\tan \eta_l = \sum_{l'} M_{ll'} a_{l'} (1 + \tan \eta_l \tan \eta_{l'}), \tag{2.15}$$

where $M_{ll'} = [(l' + \frac{1}{2})^2 - (l + \frac{1}{2})^2]^{-1}$ for odd $l' - l$ and zero for even $l' - l$, and by substituting $a_l$ in the formula

$$b_l = a_l / \cos \eta_l$$

to obtain

$$A_l = \cos \eta_l - \pi(4l + 2)^{-1} b_l - \sum_{l'} M_{ll'} b_{l'} \sin(\eta_{l'} - \eta_l)$$

and

$$c_l = b_l / A_l. \tag{2.16}$$

The key to the procedure is the inversion of the matrix $M_{ll'}$. Sabatier (1966a) was able to construct this matrix explicitly. Unfortunately the solution depends on the arbitrary parameter $\alpha$ so that the solution of the inverse problem is not unique and a family of potentials will correspond to a given set of phase shifts. It is interesting to note that this method yields a potential approaching zero like

$$V(r) \sim C(\alpha - \beta) r^{-3/2} \cos(2r - \pi/4) + \mathcal{O}(r^{-2+\epsilon}), \tag{2.17}$$

where $\alpha$ is an arbitrary parameter and $\beta$ a phase-dependent function (Sabatier 1966a). Among these phase equivalent potentials there is one and only one which tends to zero faster than $r^{-2+\epsilon}$. This is the case for the special choice $\alpha = \beta$ so that the uniqueness achieved corresponds to a very special property of the potential. The other equivalent potentials have an oscillating tail, damped by a factor $r^{-3/2}$. Furthermore the study of the analytic properties shows that this class of potentials is rather restricted (Sabatier, 1966b). The reason for this behavior is the restriction of the spectral measure $h(l)$ to integer values of $l$ on the real axis. An extension of the method allows $l$ to take any real value larger than $- 1/2$, including the integers. This yields a much larger class of potentials, which now depend on infinitely many independent parameters (Sabatier, 1967a).

This section then shows that the inversion problem at a fixed energy yields in general infinitely many equivalent solutions. The different methods establish different restrictions on selecting special classes of potentials for which detailed information can be obtained. Sabatier (1971, 1972a, 1972b) tried to give a complete solution to this problem by characterizing the classes of equivalent potentials by simple properties of the potential itself and giving appraisals for the deviations of the phase equivalent potentials from each other. The main tool used here has been the representation of $f(r,x)$ by a Fourier integral. The solutions which have been found belong to a very large class of potentials which include, for instance, potentials whose second derivative does not diverge more rapidly than $r^{-3}$ at the origin and goes faster to infinity than $r^{-5}$ as $r$ becomes infinite. Sabatier was able to characterize the deviations of the potentials from each other in terms of the Fourier spectrum. The Newton–Sabatier method for a specified $\alpha$ [see Eq. (2.17)] is one such example which shows a truncated Fourier spectrum from 0 to $k$, whereas the equivalent potentials of the class mentioned above have a spectrum ranging from 0 to $\infty$ (Sabatier and Quyen Van Phu, 1971). The deviations of these spectra from each other become smaller for smaller bounds to the derivative of the potential and larger energies. Thus the ambiguity disappears if all phase shifts are smaller than $\pi/2$, a condition which is fulfilled for high energies. Since the method is suited for a numerical study (it involves no analytic continuation and complex interpolation techniques), Sabatier and Quyen Van Phu (1971) performed calculations for checking the dependence of the phase equivalent potentials on several input parameters. Figure 2 shows the results. A set of 28 phase shifts was generated by solving the Schrödinger equation for a Gaussian shaped potential $V = -\alpha \exp(-br^2)$. This set of phase shifts was now inverted by the formulas given above with the $\alpha$ specification mentioned. The solid line is the input potential. The various dotted lines correspond to different energies. As expected, the input potential and the resulting "equivalent potentials" approach each other with increasing energy.

## 3. Discussion

We have seen that, within a certain large class of potentials, a single phase shift as a function of $E$ deter-

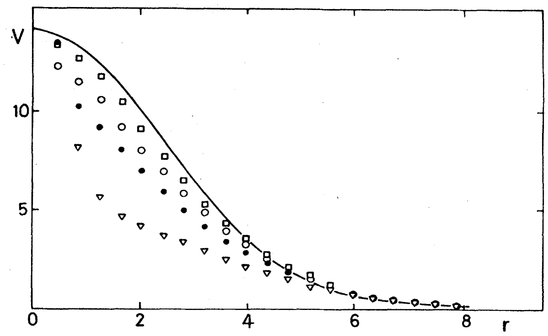

FIG. 2. Phase equivalent potentials of the Newton–Sabatier solution. The energy is measured in MeV, the internuclear separation in Fermi. The solid line represents the potential to which the solution should converge. The results of the inversion procedure at different energies are indicated by different symbols, ∇ 10 MeV, ● 50 MeV, ○ 150 MeV, and □ 1200 MeV (Sabatier and Quyen Van Phu, 1971).

mines an $n$-parameter family of potentials where $n$ is the number of bound states. The conditions and class of potentials are very well established, depending at most on the properties of the bound state wavefunction. Similar results hold for the problem where the phase shift is given as a function of the angular momentum. Depending on the choice of the interpolation, we get either a unique, a one-parameter, or an infinite parameter solution to the problem. All these methods are quite formal, since they provide detailed studies on the existence and uniqueness, but answers have not been given to the following questions: how does the lack of completeness in data influence the solution and does a solution exist for a set of phase shifts given as a function of $l$ and $E$?

The practical applicability of these quantum mechanical procedures is, in general, difficult for molecular scattering processes, though possible in principle. First there is the problem of getting the complete input information. This is especially true for the procedure of Sec. IIIA1, where the phase shifts at one $l$ have to be known for all energies. (For an exception see Sec. IVC.) Then a complicated integral equation of the Fredholm type has to be solved. The ambiguity of the equivalent potentials can only be removed by detailed information on the bound states in the fixed angular momentum problem. For the fixed energy problem all procedures requiring complex interpolation or analytic continuation from the physical region are unstable with respect to the perturbations generated by the noise of the experimental data. Arbitrarily small errors in the data can induce arbitrarily large errors in the solution. Therefore only the Newton–Sabatier method appears to be applicable from the numerical point of view. In order to achieve a unique solution, the phase shifts have to be restricted to small values.

Extensions of the above methods to noncentral or optical interaction potentials are available. Generalizations of the Gelfand and Levitan procedure to the scattering of spin $\frac{1}{2}$ particles with tensor forces and spin–orbit coupling were given by Newton (1955), Newton and Jost (1955), Fulton and Newton (1956), and Newton and Fulton (1957). Many-channel scattering for Bargmann potentials was treated by Cox (1962). Generalizations of the Newton–Sabatier method were done for Coulomb and complex potentials (Coudray and Coz, 1970) and for spin–orbit potentials (Sabatier, 1968; Coudray and Coz, 1970). These studies are either developed for the scattering of two nucleons or are still in a "formal" state so that a direct application to molecular physics is not obvious. A special attempt in this direction was made by Gerber (1973). For a particular class of nonspherical potentials (whose Fourier transform is a product of two functions depending only on the magnitude and the direction of the transform-space vector $k$) an iterative inversion procedure was established (Prosser, 1969) which converges in a unique way if the Born series converges for the $k$ chosen. The input data required are the backward scattering amplitudes for all directions of the incident momentum at fixed energy and the value of the spherically averaged potential.

## B. Determination of the phase shifts from the cross section

It is well known that the problem of determining the phase shifts from the cross section is equivalent to the problem of finding the scattering amplitude for all angles from the measured differential cross section (which is the square modulus of the scattering amplitude). The scattering amplitude can like any complex number, be written as a product of the modulus and the phase

$$f(\vartheta) = |f(\vartheta)|e^{i\varphi(\vartheta)} = G(\vartheta)e^{i\varphi(\vartheta)}. \tag{2.18}$$

Hence, the phase shifts are given in terms of $G(\vartheta)$ and $\varphi(\vartheta)$ by

$$2\sin^2\eta_l = k\int_0^\pi G(\vartheta)\sin\varphi(\vartheta)P_l(\cos\vartheta)\sin\vartheta\, d\vartheta. \tag{2.19}$$

Once the complex values of the scattering amplitude are known, the phase shifts are known too. Therefore the problem is reduced to the problem of finding the complex-values $f(\vartheta)$ from the cross section. One approach to this problem is to have a special experimental arrangement with three interacting beams (Hanbury Brown and Twiss, 1956; Goldberger *et al.*, 1963). The most general procedure used here is to apply the generalized unitarity theorem which follows from the conservation of flux

$$4\pi\,\mathrm{Im}\, f(\mathbf{p},\mathbf{k}) = k\int d\Omega_q f^*(\mathbf{q},\mathbf{p})f(\mathbf{q},\mathbf{k}), \tag{2.20}$$

where $\mathbf{k}$ denotes the initial and $\mathbf{p}$ the final state of relative momentum. The integration is over all directions of $\mathbf{q}$, where $k = |\mathbf{k}| = |\mathbf{p}| = |\mathbf{q}|$ is valid. For central potentials we have $f(\mathbf{p},\mathbf{k}) = f(k,\cos\vartheta) = f(\vartheta)$, $\vartheta$ being the angle between $\mathbf{p}$ and $\mathbf{k}$. Substituting (2.18) in (2.20) we obtain, suppressing the explicit $k$ dependence of $G$ and $\varphi$,

$$\begin{aligned} 4\pi G(\vartheta)\sin\varphi(\vartheta) &= k\int d\Omega_q G(\zeta)G(\chi)\cos[\varphi(\zeta)-\varphi(\chi)] \\ &= k\int_0^{2\pi} d\xi\int_0^\pi d\zeta\,\sin\zeta\, G(\zeta)G(\chi)\cos[\varphi(\zeta)-\varphi(\chi)], \end{aligned} \tag{2.21}$$

where $\zeta$ is the angle between $\mathbf{k}$ and $\mathbf{q}$ and $\chi$ the angle between $\mathbf{p}$ and $\mathbf{q}$. The azimuthal angles of the vectors $\mathbf{p}$ and $\mathbf{q}$ are denoted $\phi$ and $\xi$, respectively. Then $\chi$ is related to $\vartheta$ and $\zeta$ by $\cos\chi = \cos\zeta\cos\vartheta + \sin\zeta\sin\vartheta\cos(\phi - \xi)$. If the cross section, and therefore $G(\vartheta)$, is known as a function of the scattering angle $\vartheta$ for a fixed $k$ value, Eq. (2.21) constitutes a nonlinear integral equation for the phase function $\varphi(\vartheta)$. Now it is necessary to show that this equation has a unique solution besides the two trivial ambiguities that if $\varphi(\vartheta)$ is a solution then so are $2n\pi\varphi(\vartheta)$ and $\pi - \varphi(\vartheta)$. The latter can be traced back to Eq. (2.20) which is satisfied by $f(\vartheta)$ and $-f^*(\vartheta)$. Three different approaches have been made for solving this problem (Newton, 1968; Martin, 1969; Gerber and Karplus, 1970). Let us define the quantity

$$R(\vartheta) = 4\pi k^{-1}\int d\Omega_q G(\zeta)G(\chi)G(\vartheta)^{-1}. \tag{2.22}$$

Then a sufficient condition for the existence of a solution for Eq. (2.21) is that there exists a constant $M$ so that

$$R(\vartheta) \le M < 1 \tag{2.23}$$

holds. From this $2M(1-M^2)^{-1/2} < 1$ can be derived. If $R(\vartheta) < 2^{-1/2}$ is valid, then the solution is unique and can be obtained by iteration (Newton, 1968). Martin (1969) showed that the solution is unique for $R(\vartheta) < 0.79$. It is not known whether the gap between 0.79 and 1 is real or only a technical difficulty. Gerber and Karplus (1970) proved the existence and uniqueness under the stronger conditions $R(\vartheta) \leq M$ and $J = 2M[1 + M(1 - M^2)^{-1/2}] < 1$. Then the sequence of iteration

$$4\pi \sin \varphi_N(\vartheta) = k \int d\Omega_q G(\zeta) G(\chi) G(\vartheta)^{-1} \times \cos[\varphi_{N-1}(\zeta) - \varphi_{N-1}(\chi)], \quad \text{with } \varphi_0(\vartheta) = 0 \tag{2.24}$$

converges to a unique solution of Eq. (2.21). The error pertaining to the $N$th iterant is bounded by

$$|\sin \varphi(\vartheta) - \sin \varphi_N(\vartheta)| \leq MJ^N(1 - J)^{-1}. \tag{2.25}$$

Gerber and Karplus (1970) formulated a modified iteration scheme where the phase $\varphi(\vartheta)$ is approximated by an alternating sequence of upper and lower bounds.

To state the result in another way, the condition (2.23) means that the cross section must be small and smooth. It is easy to generalize all formulas to many channel problems since the optical theorem, which is the basis of this procedure, is not restricted to spherically symmetric one-channel problems. Gerber and Karplus (1970) introduced several approximations [small phases, $\cos \varphi(\vartheta) \approx 0$], which may be important in molecular physics.

## III. APPROXIMATE SOLUTIONS FOR THE POTENTIAL

In the last section we have seen that the quantum mechanical inversion procedures, though rigorous in concept, are very difficult to handle from the practical point of view. Therefore it is much more promising to turn to approximate solutions. Especially semiclassical and classical methods in the high-energy limit have proven to be very successful in describing atomic and molecular collision processes. These approximations are valid when the wavelength associated with the relative motion of the two particles remains small compared to a characteristic potential distance over which the potential varies appreciably.

In Sec. IIIA all procedures are summarized which make use of the JWKB approximation for the phase shifts with no restrictions on the potential. Using the semiclassical relationship $2d\eta/dl = \Theta(l)$ which combines the phase shifts with the classical deflection function, one obtains solutions for the classical inversion schemes. The needed input information are the phase shift or the deflection function. Sec. IIIB contains all methods valid within the framework of the eikonal or high-energy approximation which are mainly deduced for repulsive potentials. In these cases solutions are often available which start directly from the measured cross section. The common tool for all these inversion procedures is the Abelian integral equation

$$g(x) = \int_0^x dy f(y)(x - y)^{-1/2} \tag{3.1}$$

which can be solved uniquely with the result

$$f(y) = \frac{1}{\pi}\int_0^y \frac{dg}{dx}\frac{dx}{(y - x)^{1/2}}, \tag{3.2}$$

where $g(0) = 0$ and $f(0) = 0$ is assumed and $g(x)$ is a known differentiable function.

### A. Semiclassical methods

### 1. *The angular momenum dependence*

Starting with the expression of the JWKB phase shift,

$$\eta(E,\lambda) = k\left[\int_{r_0}^{\infty} dr\left(1 - \frac{V(r)}{E} - \frac{\lambda^2}{k^2r^2}\right)^{1/2} - \int_{\lambda/k}^{\infty} dr\left(1 - \frac{\lambda^2}{k^2r^2}\right)\right], \tag{3.3}$$

where $\lambda = l + \frac{1}{2}$, $k^2 = 2\mu E/\hbar^2$, $r_0$ the classical turning point, and using the transformation (Sabatier, 1965; Vollmer and Krüger, 1968; Vollmer, 1969)

$$s^2 = r^2(1 - V(r)/E), \tag{3.4}$$

and $\lambda/k = b$ one obtains

$$\eta(E,b) = \int_b^{\infty} ds(s^2 - b^2)^{1/2}\left[\frac{dr}{ds}\frac{1}{r} - \frac{1}{s}\right], \tag{3.5}$$

as long as this transformation may be uniquely reversed to $r(s)$ (the condition for this behavior will be given later). Integrating by parts gives

$$\eta(E,b) = -k\int_0^{\infty} \ln[r(s)/s)]s(s^2 - b^2)^{-1/2} ds, \tag{3.6}$$

where $\lim_{r\to\infty} rV(r) = 0$ is used. Now the phase function is of the simple form of a Born integral. It is linear in the expression

$$I(s,E) = \ln[r(s)/s] \tag{3.7}$$

which occurs instead of the potential and which of course is energy-dependent. Equation (3.6) has the form of an Abelian integral equation, which can be solved as follows. Let us multiply Eq. (3.6) with $2b(b^2 - t^2)^{-1/2}$ and integrate over $db$ from $t$ to infinity. After exchanging the two integrals we have

$$\begin{aligned} 2\int_t^{\infty} db \frac{\eta(E,b)b}{k(b^2 - t^2)^{1/2}} &= -\int_t^{\infty} dsI(s,E)s\int_t^s db\frac{2b}{[(b^2 - t^2)(s^2 - b^2)]^{1/2}} \\ &= -\pi\int_t^{\infty} dsI(s,E)s. \end{aligned} \tag{3.8}$$

Now we differentiate Eq. (3.8) with respect to $s$ and with $t = s$ it yields by use of partial integration and $\eta(\infty) = 0$

$$I(s,E) = \frac{2}{\pi}\int_s^{\infty} db\frac{d\eta(E,b)}{db}\frac{1}{k(b^2 - s^2)^{1/2}}. \tag{3.9}$$

Now it is easy to calculate $V(r)$. First $I(s,E)$ is determined by Eq. (3.9) and then, inverting (3.7) and (3.4), one gets

$$r(s) = s\exp[I(s,E)] \tag{3.10}$$

and

$$V(r) = E(1 - s^2/r^2) = E\{1 - \exp[-2I(s,E)]\}.$$

With the semiclassical relationship $2(d\eta/db) = k\Theta(b)$

one obtains at once

$$I(s,E) = \pi^{-1}\int_s^\infty db\Theta(b,E)(b^2 - s^2)^{-1/2}, \quad (3.11)$$

which is just the classical result (Firsov, 1953; Miller, 1969).[2] Now let us discuss the conditions under which this inversion procedure works.

(a) The energy has to be larger than or equal to the potential $V(r_0) = E$, otherwise $s(r)$ would be a complex function. That means that the potential can only be determined up to the classical turning point $r_0$. If $\Theta(b)$ is not known over the whole range of impact parameters from 0 to $\infty$ then it is possible to perform the procedure up to a certain value of $r$, as can be seen from the type of integration. For the integration to infinity $\Theta(b)$ has to be extrapolated. This can often be done, due to the known long-range forces (see Sec. IV).

(b) In order to determine the potential in a unique manner Eq. (3.6) must have a unique solution; this means $s(r)$ must be a monotonic function, otherwise the inverse function would not exist. This condition gives

$$\frac{ds}{dr} = \left(1 - \frac{V(r)}{E} - \frac{dV}{dr}\frac{r}{2E}\right)\left(1 - \frac{V(r)}{E}\right)^{-1/2} > 0. \quad (3.12)$$

With $2V(r) + rdV/dr = 2E_c$ we have $E > E_c$. It can be shown (Vollmer, 1969; Miller, 1969) that $E_c$ is the energy at which orbiting occurs.

(c) The phase shifts have to be interpolated from discrete values of $l$ so as to give a continuous function of $b$. Sabatier (1972a, b) in particular points out that the existence of infinitely many interpolations shows that the apparent uniqueness of such a procedure does not exist. Since this interpolation is known to be very critical in determining a unique potential, he has some doubts concerning these procedures. On the other hand, if the WKB approximation is valid, a smooth and continuous fit of the phase shifts should give the right results. For potentials with real values the WKB procedure should give an answer very near to the truth. For optical potentials the problem of interpolation is a severe objection (Sabatier, 1972a).

The integration of Eq. (3.9) can be performed numerically, but for a large number of functions the integration can be done explicitely. Vollmer (1969) gives a list of these functions. Special solutions are available for Gaussian shaped exponentials and negative power forms. Since $I(s,E)$ is linear, it can be constructed from a sum of single terms with great variety. Higher-order correction terms of the WKB phase shifts (Rosen and Yennie, 1964; Sabatier, 1965) can be treated in the same way as the usual WKB solution (Vollmer, 1969) so that $I(s,E)$ can be obtained by successive approximation steps.

## 2. The energy dependence

The WKB phase shift can be written as follows:

$$\eta(E,\lambda) = m\left\{\int_{r_0}^\infty dr[E - V - \lambda^2(mr)^{-2}]^{1/2} - \int_{r_1}^\infty dr[E - \lambda^2(mr)^{-2}]^{1/2}\right\} \quad (3.13)$$

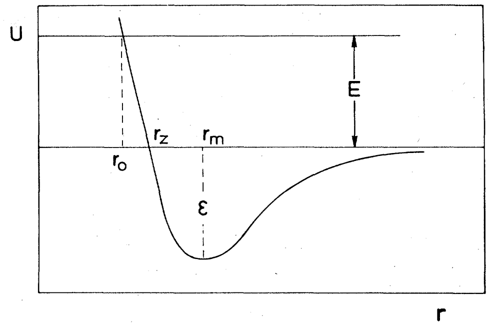

FIG. 3. Potential curve for atomic interactions.

with $m = (2\mu/\hbar^2)^{1/2}$ and $r_0$ and $r_1$ the zeros of the integrands. In order to apply the theory of Abelian integral equations we split the effective potential $U = V(r) + \lambda^2(mr)^{-2}$, which usually shows an attractive minimum in molecular physics [see Fig. 3], into two branches:

$$\begin{aligned} r &= r_1(U) \qquad r_0 \le r \le r_m \\ r &= r_2(U) \qquad r_m \le r \le \infty, \end{aligned} \quad (3.14)$$

where $r_1(U)$ and $r_2(U)$ are the corresponding inverse function. Here it is assumed that two branches are sufficient, which is fulfilled if either $l = 0$ or $l > l_{\text{orb}}$, with $2l_{\text{orb}}^2 = m \cdot \max[r^3V'(r)]$. Then differentiating Eq. (3.13) with respect to $E$ and introducing the quantities $y = U(r)$ and $z = Z(\rho) = \lambda^2(m\rho)^{-2}$ as new variables of integration we have[3]

$$\frac{d\eta}{dE} = \frac{m}{2}\left[\int_E^0 dy\frac{r_1'(y)}{(E-y)^{1/2}} + \int_0^{-\varepsilon} dy\frac{r_1'(y) - r_2'(y)}{(E-y)^{1/2}} - \int_E^0 dz\frac{\rho'(z)}{(E-z)^{1/2}}\right]. \quad (3.15)$$

Because of the transformation (3.14), the inverse functions $r_1(y)$ and $r_2(y)$ exist. Now multiplying (3.15) by $(\alpha - E)^{-1/2}$, integrating over $dE$ from 0 to $\alpha$, changing the order of integration, and using

$$\int_y^\alpha dE[(\alpha - E)(E - y)]^{-1/2} = \pi, \quad (3.16)$$

one arrives at

$$\frac{2}{\pi}\frac{1}{m}\int_0^\alpha \frac{d\eta}{dE}\frac{dE}{(\alpha - E)^{1/2}} = -r_1(\alpha) + r_1(0) + \frac{\lambda}{k} - \rho(0) + I. \quad (3.17)$$

The integral $I$ can now be calculated with the abbreviation $R(y) = r_1(y) - r_2(y)$ as

$$\begin{aligned} I &= \pi^{-1}\int_0^{-\epsilon} dyR'(y)\int_0^\alpha dE[(\alpha - E)(E - y)]^{-1/2} \\ &= R(-\varepsilon) - R(0) + \pi^{-1}\int_0^{-\varepsilon} dyR'(y) \\ &\quad \times \int_0^y dE[(\alpha - E)(E - y)]^{-1/2}. \end{aligned} \quad (3.18)$$

To solve the remaining integral we change the order of integration and find the result, keeping in mind that the

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[2] A form of this integral suitable for numerical application has been given by Buck (1971) and Klingbeil (1972a).

[3] The (′) denotes the derivative with respect to the variable in parentheses.

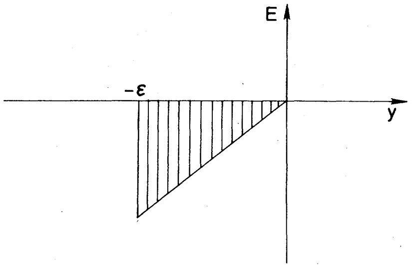

FIG. 4. The area of integration of the double integral of Eqs. (3.18) and (3.19).

areas of integration must be the same [see Fig. 4]

$$I = R(-\varepsilon) - R(0) + \frac{1}{\pi}\int_0^{-\varepsilon} \frac{dE}{(\alpha - E)^{1/2}} \int_{-E}^{-\varepsilon} dy \frac{R'(y)}{(E - y)^{1/2}}. \tag{3.19}$$

The second integral can be expressed by the number of bound states which are given by

$$(n + \tfrac{1}{2})\pi = m \int_{r_1}^{r_2} dr[E_n - U(r)]^{1/2}. \tag{3.20}$$

(See, for example, Mason and Monchick, 1967.) One obtains for the integral $I$

$$I = R(-\varepsilon) - R(0) + \frac{2}{m}\int_0^{-\varepsilon} \frac{dn}{dE}\frac{dE}{(\alpha - E)^{1/2}}. \tag{3.21}$$

Since we have $R(-\varepsilon) = r_1(-\varepsilon) - r_2(-\varepsilon) = 0$, $R(0) = r_1(0) - r_2(0)$, and $r_2(0) = \rho(0)$, insertion of Eq. (3.21) in Eq. (3.17) yields, by setting $\alpha = U$,

$$r_1(U) = \frac{2}{\pi}\frac{1}{m}\int_0^U \frac{d\eta}{dE}\frac{dE}{(U - E)^{1/2}} + \frac{2}{m} \times \int_0^{-\varepsilon} \frac{dn}{dE}\frac{dE}{(U - E)^{1/2}} + \frac{\lambda}{k}. \tag{3.22}$$

The value of the potential is obtained by

$$V(r) = U(r) - \lambda^2(mr)^{-2}. \tag{3.23}$$

A more convenient form is obtained by changing the integration variables in both integrals (Miller, 1969; Feltgen *et al.*, 1973):

$$r_1(U) = -2(\pi m)^{-1}\int_{\eta(0)}^{\eta(U)} d\eta[U - E(\eta)]^{-1/2} - 2/m \int_{-1/2}^{n(0)} dn[U - E(n)]^{-1/2} + (\lambda/k), \tag{3.24}$$

where $E(\eta)$ is the inverse function of the energy dependence of the phase shifts and $E(n)$ is the inverse function of the WKB bound state eigenvalue function. The potential for $U > 0$ is given by this expression if the phase shifts are known as a function of $E$ for $l$ = const. In addition some knowledge of the attractive part of the potential which can be expressed by the bound states of the system is necessary [see integral $I$, Eq. (3.18)], just as in the quantum mechanical case. The following restrictions have to be imposed on Eq. (3.24):

(a) The value of $l$ must be such that the effective potential $U(r)$ does not possess a local maximum.

(b) $\eta(E)$ has to be known as a smooth and differentiable function.

(c) $\eta(E)$ has to be known in the limit $E \to 0$. Suitable guesses can be obtained from a knowledge of the attractive part for $E < 0$ which has to be known in any case for such an inversion. A restriction of the data to large $E$ leads to a restricted range of the potential.

Some new inversion formulas can be found by differentiating Eq. (3.13) with respect to $\lambda$ and applying the same procedure

$$\frac{d\eta}{d\lambda} = -\frac{m}{2}\left[\int_{r_0}^{\infty} \frac{2\lambda\, dr}{r^2 m^2 (E - U)^{1/2}} - \int_{r_1}^{\infty} \frac{2\lambda\, dr}{r^2 m^2 (E - Z)^{1/2}}\right]. \tag{3.25}$$

One obtains in this case the same results as before, the only difference being that now

$$dr/d\lambda = g'(y) = r^{-2}$$

is valid. That means that instead of $r(U)$ we have $g(y) = r^{-1}(U)$ with the complete result

$$\frac{1}{r}(U) = \frac{k}{\lambda} - \frac{2}{\pi}\frac{m}{2\lambda}\int_0^U \frac{d\eta}{d\lambda}\frac{dE}{(U - E)^{1/2}} + \frac{m}{\lambda}\int_0^{-\varepsilon} \frac{dn}{d\lambda}\frac{dE}{(U - E)^{1/2}}. \tag{3.26}$$

If $2d\eta/d\lambda = \Theta(\lambda)$ is used, (3.26) is simplified to

$$\frac{1}{r}(U) = \frac{k}{\lambda} - \frac{m}{2\lambda\pi}\int_0^U \frac{\Theta(\lambda)\, dE}{(U - E)^{1/2}} + \frac{m}{\lambda}\int_0^{-\varepsilon} \frac{dn}{d\lambda}\frac{dE}{(U - E)^{1/2}}. \tag{3.27}$$

This expression has been derived by Miller (1971). It is Hoyt's (1939) result if we restrict the potential to a monotonic behavior so that the second term can be neglected. In general, the deflection function for a fixed $\lambda$ is required as a function of $E$ and the bound state eigenvalue function $n(E, \lambda)$ has to be known. The restrictions which must be imposed on this equation are the same as discussed above. For purely repulsive potentials with the backward scattering cross section, $\sigma(\pi, E)$, Eq. (3.27) gives (Miller, 1971)

$$r(U) = 2\pi / \int_0^U dE[\sigma(\pi, E) E (U - E)^{-1/2}]. \tag{3.28}$$

### B. High energy methods

In the previous section we have seen that the input information for solutions in the semiclassical limit of the inverse problem are the phase shift curve or the deflection function, both of which cannot usually be determined in a straightforward manner from the cross section. The high-energy approximation (Glauber, 1959), which is equivalent to the eikonal approximation for straight paths or the first-order momentum approximation (Lehmann and Leibfried, 1962; Smith *et al.*, 1966), provides solutions which often start directly from the measured cross section, especially for purely repulsive potentials. This introduces no significant restriction on the application of these methods since the approximation is only valid for $|V(r)| \ll E$ and thus the influence of an attractive well is, in any case, very small. The importance of this approximation for atomic scattering processes lies in the presentation and analysis of experimental data which was reported for the first time by F. T. Smith *et al.* (1966).

### 1. Starting from the differential cross section

Following Smith *et al.* (1966), an expansion in $E^{-1}$ is made of the classical deflection function

$$\Theta(E, b) = \pi - 2b \int_{r_0}^{\infty} dr[1 - V(r)/E - b^2 r^{-2}]^{-1/2} r^{-2}, \tag{3.29}$$

where $b$ is the impact parameter, $V(r)$ the potential, $E$ the kinetic energy, and $r_0$ the zero of the argument in the square root. The first-order approximation to this function is

$$\Theta(E, b) E = -b \int_{b}^{\infty} dr(r^2 - b^2)^{-1/2} dV/dr + E^{-1} \cdots. \tag{3.30}$$

This expression led F. T. Smith *et al.* (1966) to introduce a new variable

$$\tau(E, b) = \tau_0(b) + E^{-1}\tau_1(b) + \cdots, \tag{3.31}$$

where the first term $\tau_0(b) = \Theta(E, b)E$ is only dependent on the impact parameter $b$. Such an expansion also exists for the impact parameter $b$,

$$b(\tau, E) = b_0(\tau) + E^{-1} b_1(\tau) + \cdots \tag{3.32}$$

and the reduced cross section

$$\begin{aligned}\rho(\tau, E) &= \vartheta \sin \vartheta\sigma(\vartheta, E) = 0.5\tau|db^2/d\tau| \\ &= \rho_0(\tau) + E^{-1}\rho_1(\tau) \cdots = \rho_0(\tau) + \vartheta\tau^{-1}\rho_1(\tau) + \cdots.\end{aligned} \tag{3.33}$$

Thus the expansion is valid either for high energies at a fixed angle of scattering or at small angles for any energy (F. T. Smith, 1969; F. T. Smith *et al.*, 1966). Equation (3.30) is an Abelian integral equation which can be directly inverted to obtain the potential

$$V(r) = 2\pi^{-1} \int_{r_0}^{\infty} (b^2 - r^2)^{-1/2} \tau_0(b)\, db. \tag{3.34}$$

$\tau_0(b)$ is easily obtained by integrating Eq. (3.33)

$$b_0^2(\tau) = 2 \int_{\tau}^{\infty} \rho_0(\tau')/\tau'\, d\tau'. \tag{3.35}$$

The quantity $\rho_0(\tau)$ can be obtained from a plot of $\rho(E, \tau)$ versus $\tau = E\Theta$ for several energies $E$. All curves should be asymptotic to $\rho_0(\tau)$ at small $\tau$. Figure 5 shows this behavior. It is quite clear that this procedure combines all data from a wide range of energies into a single curve, a fact which is especially important if the data at one energy is incomplete. A similar expansion at small $b$ for backward scattering processes is also available (F. T. Smith *et al.*, 1966).

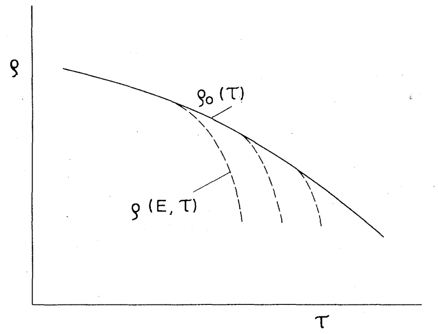

FIG. 5. Schematic reduced cross section $\rho(E, \tau) = \vartheta \sin \vartheta\sigma(E, \vartheta)$ as a function of the reduced angle $\tau = E \cdot \vartheta$ (F. T. Smith, 1969). $\rho_0(\tau)$ is the first member of an expansion in $E^{-1}$ which is only a function of $\tau$.

### 2. Starting from the integral cross section

The phase shift is given in the high-energy approximation by

$$\eta(b, k) = -\frac{\omega(b)}{2k} = \frac{2\mu}{\hbar^2} \int_{b}^{\infty} dr r V(r)(r^2 - b^2)^{-1/2}. \tag{3.36}$$

This equation may be inverted (Miller, 1969) to give

$$V(r) = -2\hbar^2/(\pi 2\mu) \int_{r}^{\infty} db \omega'(b)(b^2 - r^2)^{-1/2}. \tag{3.37}$$

Now the reduced phase shifts, $\omega(b)$, are related to the cross section by a Fourier sine transformation,

$$b^2(\omega) = \pi^{-2} \int_{0}^{\infty} dk k^{-1} Q(k) \sin(\omega/k) \equiv \overline{Q}(\omega) \tag{3.38}$$

which, by changing the integration variables in Eq. (3.37), leads to

$$V(r) = 2\hbar^2/(\pi 2\mu) \int_{0} d\omega[\overline{Q}(\omega) - r^2]^{-1/2}. \tag{3.39}$$

The upper limit of the above integral is the zero of the radicand. For another method of this kind see Henry *et al.* (1974). A similar procedure for incomplete integral cross sections has been proposed by Sigmund and Lillemark (1973). The incomplete cross section is given by

$$Q(E) = \int_{\vartheta > \vartheta_c} d\sigma(E, \vartheta)/d\vartheta\, d\vartheta = \pi b_c^2, \tag{3.40}$$

where $\vartheta_c$ is the limiting scattering angle defined by an aperture and $b_c$ is the corresponding impact parameter. From Eq. (3.30) one obtains, by use of Eq. (3.40),

$$\vartheta_c = \frac{1}{E}\sqrt{\frac{Q}{\pi}} \int_{(Q/\pi)^{1/2}}^{\infty} dr \frac{dV}{dr}\left(r^2 - \frac{Q}{\pi}\right)^{-1/2}. \tag{3.41}$$

This is an Abelian integral equation which gives the result

$$dV/dr = -2\vartheta_c(\pi r)^{-1} \int_{0}^{E_m(r)} dE(1 - \pi r^2/Q)^{-1/2}, \tag{3.42}$$

where $E_m(r)$ is a limiting energy defined by $Q(E_m) = \pi r^2$. Further integration yields

$$V(r) = 2\vartheta_c \pi^{-1} \int_{0}^{E_m} dE \cosh^{-1}(\sqrt{Q/\pi r^2}). \tag{3.43}$$

The main problem in the evaluation of Eq. (3.43) is the finite energy range covered by any given experimental set of data. The upper limit determines only the range of the potential whereas the lower limit influences the resulting potential. This is shown in Fig. 6 for the data of $K^+ - Ar$ (Amdur *et al.*, 1972) where two different guesses are used for the lack of data between $E_1 = 150$ eV and zero.

(a) $Q(E)$ continues down to $E = 0$ with that functional form which is valid near $E_1$.

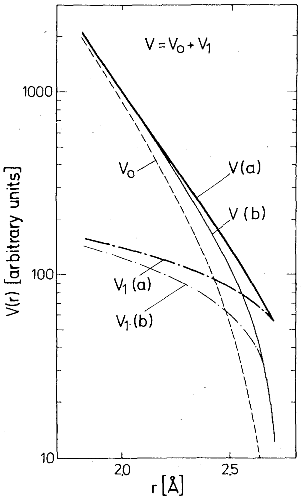

FIG. 6. The influence of different extrapolations on the potential curve obtained from the inversion of incomplete integral cross-section data (Sigmund and Lillemark, 1974). Dashed line: $V_0$ based on experimental data. Dashed-dotted lines: $V_1$ is the contribution of the extrapolated part of the cross section for two different extrapolations (a) and (b). Solid lines: The resulting potential $V = V_0 + V_1$. The curves correspond to real data for $K^+ - Ar$.

(b) $Q(E) = \text{const}$ .

The dashed line represents the potential $V_0$ derived from the data without extrapolation. The dashed dotted lines are the contributions of the extrapolation $V_1$ for the two guesses. $V = V_0 + V_1$ are the final results (solid lines). The difference between these curves should be a measure of the error. It should be pointed out that there is a wide region where $V_1$ is actually greater then $V_0$. In order to get reliable results, therefore, the energy range covered by experimental data should extend over at least an order of magnitude.

### C. Historical remarks

All the solutions discussed are closely related to the Rydberg–Klein–Rees method for obtaining $V(r)$ from diatomic molecular rotation-vibration spectra (see, e.g , Mason and Monchick, 1967). Klein himself suggested such a procedure for scattering states to Hoyt, who gave the first description of Eq. (3.27) in 1939. Equation (3.11) was first described by Firsov in 1953. Both authors assumed monotonic potentials and used classical mechanics. Independently Keller, Kay, and Shmoys (1956) got the same results as Firsov. An important step forward was obtained by the impact expansions of F. T. Smith *et al.* (1966) when a set of reduced variables which are easily obtained from experiment were related to the known inversion schemes. In 1955 Wheeler suggested that the problem could also be solved for nonmonotonic potentials in the WKB approximation. The first results of these problems were published, along with other results, by Sabatier (1965) and then very extensively by Vollmer (1969) and Miller (1969). They studied the conditions under which all these problems could be solved and made several practical suggestions for applying such a procedure for molecular physics. Equation (3.24) and a similar formula were given by Miller (1969, 1971). The procedure he uses is analogous to a method of inversion of term formulas of vibrational and rotational spectra (Miller, 1971; Vollmer and Flügge, 1971). At the same time the first nonmonotonic potential obtained by inversion of molecular beam scattering data was published (Buck and Pauly, 1969). An extension of the semiclassical method to optical potentials by use of a perturbation formalism has been done by Roberts and Ross (1970).

The structure of these methods shows that they are applicable whenever some information on phase integrals can be deduced from experiments. Besides the phase shifts of scattering processes and the bound states eigenvalues there are other possibilities for the occurance of such phase integrals. For instance certain processes in molecular physics which involve electronic transitions can be treated as a product of a slowly varying factor and a Franck–Condon factor. This Franck–Condon factor is intimately related to phase integrals containing information on the initial and final potential curves. Thus Child (1970) was able to utilize the energy dependence of such Franck–Condon factors obtained from predissociation data to get some information on the potential curves involved.

## IV. PRACTICAL METHODS

Most of the procedures given in the preceding section need as input information the energy or angular momentum dependence of the phase shifts or deflection function. Thus we are left with the problem of finding these quantities from experimental data. The rigorous approach to this problem given in Sec. IIB has not yet been applied to practical problems. But often much more of the general form of the potential or the phase shifts is known than the fact that these quantities exist. When this knowledge is taken into account, this step of the inversion problem can be solved by simpler methods. For the scattering of two atoms or one atom and an ion the essential features of the potential are assumed to be known. It consists of a short-range repulsive and a long-range attractive part forming a minimum in between. This leads to a special form for the phase shifts or the deflection function regarded as a function of angular momentum $l$. This fact can be used for a parameterization of the phase shift or the $S$ matrix. In addition, the form and the linear dimensions of the potential give rise to special characteristics of the cross sections which are suitably described by semiclassical methods. According to Ford and Wheeler (1959), the differential cross section can be written as (F. T. Smith, 1969)

$$\sigma(E,\vartheta) = |\sum_k f_k(E,\vartheta)|^2, \tag{4.1}$$

with

$$f_k(E,\vartheta) = \sigma_k^{1/2}(E,\vartheta)\exp[i(\hbar^{-1}A_k(E,\vartheta) + \gamma_k)] \tag{4.2}$$

and

$$\sigma_k = (b_k/\sin\vartheta)|db_k/d\vartheta|; \quad A_k\hbar^{-1} = 2\eta_k - l_k\vartheta, \tag{4.3}$$

$\sigma_k$ is the classical cross section, $A_k$ the action integral, and $\gamma_k$ some phase constant. The sum has to be taken over all points of stationary phase. If there is only one point, one gets the classical result. If there are two or more points of stationary phase, the cross section shows a characteristic oscillatory behavior. The maxima and minima of the oscillations will be located at the extrema of (assuming $\gamma_i - \gamma_k = 0$)

$$\cos[(A_i - A_k)\hbar^{-1}] = \cos(2\pi N) = \cos\alpha. \tag{4.4}$$

Therefore the spacings of the oscillations are roughly a measure of a sum or difference of impact parameters

$$2\pi\Delta N/\Delta\vartheta = l_i - l_k = k(b_i - b_k). \tag{4.5}$$

The amplitudes are a measure of the derivatives of the deflection function. For many problems one needs only a small number of terms, $f_k$, in order to express the cross section in a correct manner. Each component $f_k$ may correspond to a different classical trajectory arising from the same (rainbow scattering, symmetry oscillation) or a different potential (oscillation due to exchange). In practice three methods have been used to obtain $\Theta(b)$ or $\eta(b)$ from experimental data.

(a) Deriving the unknown coefficients of a parameterized phase shift or $S$ matrix through a minimisation procedure on measured and calculated data; the exact formulas are used for the calculation of the cross section (Sec. IVA1).

(b) Comparing the semiclassical features of the cross section with calculated values obtained via the parameterization of the deflection function (Sec. IVA2).

(c) Directly determining certain parts of $\Theta(b)$ or $\eta(E)$ by using semiclassical cross sections (Sec. IVA3, IVC, and IVE).

Parametric and direct methods are applied for the differential cross section (IVA). The possibilities of an inversion procedure for the integral cross section (IVB) and exchange cross section (IVD) are then discussed. Finally identical particle scattering (IVC) and potential crossing (IVE) are presented. In these cases direct methods have predominately been applied.

## A. Differential cross section

In general, the interaction potential shows an extremum as does the phase shift curve and the deflection function. Therefore there are three contributions to the scattering cross section with three different impact parameters which correspond to the same scattering angle. This behavior is displayed in Fig. 7. To discuss this problem quantitatively, the methods outlined at the beginning of this section have to be refined (Berry, 1966; Miller, 1968) by mathematical methods which take into account the problem of coincidence of stationary points (Chester *et al.*, 1957) at the rainbow angle $\vartheta_R$. As a result the cross section exhibits two groups of oscillations. The interference between the outer two branches $b_2$ and $b_3$ gives rise to the rainbow oscillations with large separation of angles. The interference of the innermost branch $b_1$ with the other two gives a set of high-frequency oscillations, the rapid oscillations. For angles greater than the rainbow angle $\vartheta_R$, the oscillations die out and there will be only one contribution to the cross section which can be expressed by Eq. (4.3).

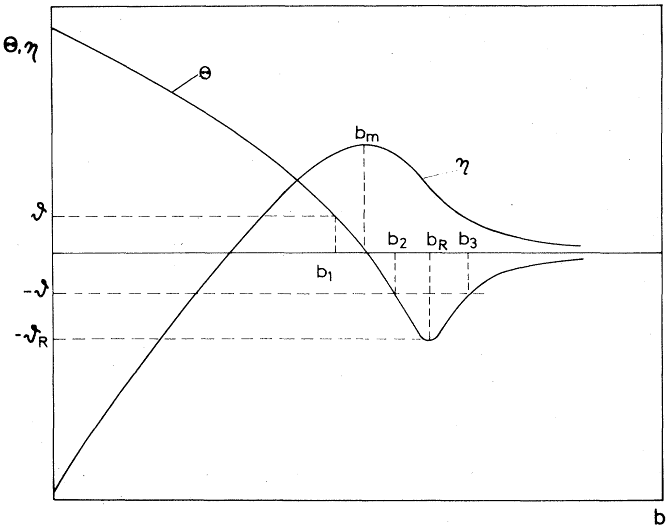

FIG. 7. The phase shifts $\eta$ and the angle of deflection $\Theta$ is a function of the impact parameter $b$ for a typical interaction potential valid in molecular physics. The three impact parameters $b_1$, $b_2$, and $b_3$ correspond to the same angle of deflection $\vartheta$. $\vartheta_R$ is the rainbow angle, $b_R$ is the rainbow impact parameter, and $b_m$ the glory impact parameter.

In the vicinity of the first rainbow maximum the cross section can be evaluated, with the parabola approximation for the deflection function

$$\Theta(b) = -\vartheta_R + q(b - b_R)^2, \tag{4.6}$$

$$\sigma(\vartheta) = 2\pi b_R(\sin\vartheta)^{-1}k^{1/3}q^{-2/3}\mathrm{Ai}^2(z), \tag{4.7}$$

with

$$z = k^{2/3}q^{-1/3}(\vartheta_R - \vartheta), \tag{4.8}$$

where $b_R$ is the rainbow impact parameter, and Ai the Airy function.

### 1. Parametric methods for phase shifts

The easiest way to determine the phase shifts from the cross section is to assume a specific functional form for the phase shifts which represents the behavior of the real phase function (see Fig. 7): negative phase shifts at small $b$, a maximum for positive values at larger $b$, and an asymptotic behavior of the phase shift at large $b$ of the form

$$\eta \propto Cb^{-(n-1)}, \tag{4.9}$$

if the potential has the asymptotic form $V(r) = -Cr^{-n}$ (Pauly and Toennies, 1965; Bernstein and Muckerman, 1967; Pauly, 1973). Then the unknown coefficients of the phase function are determined by a nonlinear least-squares algorithm which minimizes the expression $\sum_i[\sigma(\vartheta_i) - I(\vartheta_i)]^2$, where $\sigma(\vartheta_i)$ is the value of the differential cross section calculated via the partial wave sum (2.2) with use of the phase shifts generated from the ansatz. $I(\vartheta_i)$ are the corresponding measured values.

Several functional forms have been used. Brackett *et al.* (1963) employ a sum of exponentials, whereas Vollmer (1969) describes the phase shifts by a superposition of functions for which Eq. (3.9) can be solved analytically. Klingbeil (1972a) proposed a method where all phase shifts were treated as free parameters, except those for large $b$, where the expression (4.9) holds. The procedure does not seem well suited for atom–atom scattering processes, where more than hundreds of angular momenta $l$ are involved. However, if a good estimate of the starting parameters is available (about 10% deviation), a rapid convergence of the minimalization process is achieved (e.g., 20 iterations for 126 phase shifts). An advantage of this procedure is that it is not based on any assumption concerning the analytic form for the phase shifts.

Quite a different procedure has been proposed by Remler (1971). First the partial wave series is decomposed into a repulsive and an attractive part,

$$f(\vartheta) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\vartheta)[S_r S_a - 1] = f_a + f_r, \tag{4.10}$$

with

$$f_a(\vartheta) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\vartheta)[S_a - 1] \tag{4.11}$$

and

$$f_r(\vartheta) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\vartheta)[S_a(S_r - 1)], \tag{4.12}$$

where $S = \exp[2i(\eta_a + \eta_r)] = S_a S_r$ is the $S$ matrix. Then the $S$ matrix for the attractive part is parameterized by

$$S_a = \prod_{p=1}^{N} \left( \frac{\lambda^2 - \lambda_p^{*2}}{\lambda^2 - \lambda_p^2} \right), \tag{4.13}$$

where $\lambda$ is the angular momentum with $\mathrm{Re}\,\lambda = l + \frac{1}{2}$ and $\lambda_p$ is the position of the $p$th pole in the complex angular momentum plane. The scattering amplitude can now be computed using the Regge–Watson–Sommerfeld transformation (De Alfaro and Regge, 1965)[4]

$$f_a(\vartheta) = \frac{1}{2ik} \sum_{p=1}^{N} \frac{\pi}{\cos \pi\lambda} P_{\lambda-1/2}(-\cos\vartheta) \operatorname*{Res}_{p} [\lambda S_a(\lambda, k) - 1]$$

$$+ \oint_C d\lambda \frac{\lambda}{2k} \frac{S_a(\lambda, k) - 1}{\cos \pi\lambda} P_{\lambda-1/2}(-\cos\vartheta). \tag{4.14}$$

The integral has to be taken over the imaginary axis and the half-circle including the complex plane for $\lambda > 0$. Since the function $S$ is a quadratic function of $\lambda$, the integral over the imaginary axis vanishes and the remaining part is assumed to be zero. Therefore one gets

$$f_a(\vartheta) = \frac{1}{2ik} \sum_{p=1}^{N} \frac{\pi}{\cos \pi\lambda_p} P_{\lambda-1/2}(-\cos\vartheta)$$

$$(\lambda_p^2 - \lambda_p^{*2}) \prod_{\substack{i=1 \\ p \neq i}}^{N} \left( \frac{\lambda_p^2 - \lambda_i^{*2}}{\lambda_p^2 - \lambda_i^2} \right). \tag{4.15}$$

The partial wave sum is now reduced to a sum over a few pole contributions in the complex plane of $\lambda$.

The contribution of a single pole to the phase shift function and the deflection function can be obtained from the parameterization (4.13). The phase shift is then

$$\eta_p(l) = \arctan\left( \frac{\mathrm{Im}\,\lambda_p}{\lambda - \mathrm{Re}\,\lambda_p} \right) - \arctan\left( \frac{\mathrm{Im}\,\lambda_p}{\lambda + \mathrm{Re}\,\lambda_p} \right) \tag{4.16}$$

and the deflection function

$$\Theta_p(l) = 2\left[ \frac{\mathrm{Im}\,\lambda_p}{(\lambda + \mathrm{Re}\,\lambda_p)^2 + (\mathrm{Im}\,\lambda_p)^2} - \frac{\mathrm{Im}\,\lambda_p}{(\lambda - \mathrm{Re}\,\lambda_p)^2 + (\mathrm{Im}\,\lambda_p)^2} \right]. \tag{4.17}$$

Figure 8 illustrates these results. $\Theta_p(l)$ is essentially a pulse centered at $l = \mathrm{Re}(\lambda_p - \frac{1}{2})$ with the depth $2/\mathrm{Im}\,\lambda_p$ and the width $2\,\mathrm{Im}\,\lambda_p$. Now one proceeds as follows. Starting with a number of $N$ poles, which are placed on a small circle centered at $\lambda_p$ in the complex $\lambda$ plane, the number of these poles ($N$) and the real and imaginary part of the central pole ($\lambda_p$) are derived from semiclassical quantities. The rainbow angle is given by $\vartheta_R = 2N/\mathrm{Im}\,\lambda_p$, the rainbow angular momentum by $l_R = \mathrm{Re}\,\lambda_p$, and the width of the deflection function at $\vartheta = \vartheta_R/2$ by $\Gamma_{1/2} \approx 2\,\mathrm{Im}\,\lambda_p$.[5]

Equation (4.15) is then summed, the results compared with the experimental data, and the input information varied until a satisfactory agreement is achieved between the experimental and calculated cross sections. The number of poles which are sufficient for attaining good agreement with the experiment has been found to lie between 5 and 16 (Rich *et al.*, 1971). The repulsive part of the scattering amplitude $f_r$ cannot be treated in this way, since here the large number of repulsive poles contributing to the cross section is cumbersome. Although the results which have been obtained by this method are striking, a disadvantage should be mentioned. The chosen parameterization of the $S$ matrix leads to the wrong asymptotic behavior of the phase shift, which should be important for systems where weak but long-range forces are involved.

The methods described above have one common scheme. The phase shift function is obtained by varying several parameters (the phase shifts themselves, the poles of the $S$ matrix in the complex $\lambda$ plane, or some constants of assumed functions), the cross section is then calculated by using the exact formulas given by quantum mechanics.

## 2. Parametric methods for the deflection function

Several methods are now described which take advantage of the close relationship between the semiclassical cross section and the deflection function. There the main problem arises from most of the expressions for the semiclassical cross section containing $b(\vartheta)$ rather than $\Theta(b)$, and from $b(\vartheta)$ being in general a multivalued function. A procedure which uses nearly all measurable quantities has been proposed and applied by Buck

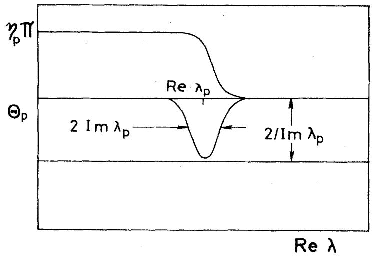

FIG. 8. Phase shift $\eta_p$ and deflection function $\Theta_p$ of a single pole $\lambda_p$ in the complex $\lambda$ plane (Remler, 1971).

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[4] This expression is obtained by evaluating the integral which gives both $f_a(\vartheta)$, which thus accounts for the poles due to $\cos \pi\lambda$, and the sum, which accounts for the poles of $S_a$.

[5] For a definition of these quantities see Fig. 7 and Fig. 8.

(1971). In order to unfold the multivalued character of $b(\vartheta)$, the deflection function is separated into monotonic functions $g_i(b)$ such that $\Theta(b) = \sum_i g_i(b)$ and $b = g_i^{-1}(\vartheta)$. The $g_i$ are represented by the usual functional approximations made in the semiclassical scattering theory; a parabola in the minimum, a straight line in the vicinity of the zero point, and an inverse power law for the asymptotic region [see Eq. (4.6)]. The measurable quantities are then calculated with help of these functions. The correct functional behavior is tested and the functions $g_i$ are then determined by a direct comparison with the measured cross sections. A measured quantity is, e.g., the angular position of the rainbow oscillations $z$ which is given by

$$z = 0.75\ \alpha^{2/3}, \tag{4.18}$$

with

$$\alpha = 2\eta b_2(\vartheta) - 2\eta b_3(\vartheta) + k\vartheta[b_2(\vartheta) - b_3(\vartheta)].$$

Often such a determination is easy to perform; for instance, the parabola approximation in the minimum [see Eq. (4.6)] gives for $z$ a linear dependence on $\vartheta$ [see Eq. (4.8)]. The rapid oscillations, the velocity positions of the glory oscillations of the integral cross section, the amplitude of the first rainbow maximum, and the scattering at large angles are treated in the same way. With some requirements of continuity, the deflection function can then be determined over the whole angular range. The rainbow oscillations determine certain areas bounded by the deflection function (Boyle, 1971), whereas the rapid oscillations are a direct measure of $b_m$ [the zero point of $\Theta(b)$] if the rainbow oscillations are known. If some additional information on the amplitudes, say the ratio of the first maximum to the monotonic scattering cross section at large angles, is known, the determination is unique. It should be pointed out that only data which are not severely influenced by the averaging processes is used.

Two other procedures similar to the one described have been proposed by Miller (1969) and Boyle (1971). To overcome the multivalued character of the inverse of the deflection function $b(\vartheta)$, Miller introduces monotonic functions $p(x)$ and their inverses $p^{-1}$ which are parameterized by suitable expansions of simple power series. Boyle calculates the deflection function first from an assumed potential. This $\Theta(b)$ is then adjusted in a way such that the special features of the cross section measured (say the rainbow and the rapid oscillations) are well represented. The potential is calculated by use of the inversion techniques of Sec. IIIA. The procedure is then repeated until there is agreement between measured and calculated quantities.

### *3. Direct methods and reduced energy variables*

A direct determination of the deflection function is possible if the cross section is monotonic. This is always the case for angles greater than the rainbow angle and for cross sections based on a monotonic potential. There exists then only one contribution to the semiclassical cross section of Eq. (4.1) and the inverse problem is solved completely. The deflection function is obtained by direct integration over the measured cross section:

$$b^2(\vartheta) = 2\int_{\vartheta}^{\pi} \sigma(\vartheta')\sin\vartheta'\,d\vartheta'. \tag{4.19}$$

The potential is determined by applying one of the procedures given in Sec. IIIA. It is possible to combine Eq. (4.19) and the results of Sec. IIIA with Eq. (3.11), for instance, into one formula (Keller *et al.* , 1956). The resulting integrals are then solvable for Coulomb and inverse square potentials in an analytic way. The question of how to obtain the absolute value of the cross section then arises. Since this quantity is very difficult to measure, the problem must be overcome by calibrating the cross section through values obtained from theoretical considerations or other inversion procedures which are based on an interference pattern and provide an absolute value of the impact parameter. This leads directly to the other possibility, namely obtaining direct information on the deflection function through the interference data (F. T. Smith *et al.*, 1965; Pritchard, 1972). By differentiating the phases of Eq. (4.4) one obtains directly the difference between impact parameters [Eq. (4.5)]. This method has the advantage of determining the deflection function without assuming a parameterized model. Pritchard proposes a method which starts from this equation with additional information similar to that mentioned above, the rainbow cross section, the classical cross section, and the envelopes of the amplitudes. He suggests in addition the usefulness of the reduced variables, introduced by F. T. Smith *et al.* (1966) for a small angle or high-energy approximation, for data taken at large angles and thermal energies. The advantage of such a procedure is obvious. Instead of Eq. (4.4) the reduced action difference becomes

$$\begin{aligned} a(E,\tau) &= (E/2\mu)^{1/2}\alpha(E,\tau) \\ &= 2\pi[N(\tau,E) - N_0](E/2\mu)^{1/2}, \end{aligned} \tag{4.20}$$

with

$$a(E,\tau) = a_0(\tau) + E^{-1}a_1(\tau) + \cdots. \tag{4.21}$$

The quantity $N_0$ describes a quantal contribution to the relative phase. Thus the data taken at different energies can be combined into a single curve with greater accuracy than would be possible for the single curves. In addition this method helps to clarify and extend the range of data. The limits of applicability of these reduced variables for scattering at thermal energies have not yet been studied by a rigorous approach. Numerical calculations show that this relation is fulfilled to within 2% if the energies do not differ by more than 25%. Such reduced variables are indispensable for studying and identifying unknown features of the cross section.

## B. Integral cross section

The information obtained from the differential cross section mainly covers the angular momentum dependence of the phase shift whereas the energy dependence is preferably provided by the energy dependence of the integral cross section. Indeed, the glory oscillations of the integral cross section are a direct measure of the maximum phase shift $\eta_m$ which occurs for potentials with a minimum. This oscillation is proportional to $\cos(2\eta_m - \pi/4)$. Thus it is easy to deduce $\eta_m$ from the measured extrema. Unfortunately these values cannot be used for an inversion procedure since $b_m$, the impact parameter where the maximum occurs, is energy-dependent. Therefore the integral cross section provides little information for inversion schemes, even in the semiclassical approximation. There are a few exceptions, however. One will be treated below together with the scattering of identical particles. Another exception has been treated by Vollmer (1971). By using parameterized phase shifts he was able to write down explicitly the integral cross section in terms of the free parameters. Two additional examples which are valid in the high-energy approximation are given in Sec. IIIA. A method where the orbiting resonances are used as input information has been proposed by Stwalley (1973).

### C. Identical particle scattering

Apart from the interferences described, the cross section for identical particles shows an additional feature which is due to the symmetry requirement under the exchange of the nuclei. Depending on the symmetry of the rest of the wavefunction, the partial wave summation runs over only even or odd values of $l$ and the scattering amplitude is either an even or an odd function of $\vartheta - \pi/2$ which can be expressed by

$$f(\vartheta) = \tfrac{1}{2}[f(\vartheta) \pm f(\pi - \vartheta)], \qquad (4.22)$$

where (+) is valid for $l$ even, and (−) for $l$ odd. The resulting oscillations in the differential cross section represent the interference between direct and recoil scattering. The cross section is now symmetric about $\pi/2$. Figure 9 shows the interfering impact parameters (Siska *et al.*, 1971). For systems with $E > E_c$ [see Eq. (3.12)] these oscillations are obviously very sensitive to the repulsive part of the potential. This is especially true for the same type of oscillations in the integral cross section, since then the region near the classical turning point ($l = 0$) is probed by a measurement. The analysis of these identical particle oscillations of the differential cross section can be done by one of the methods described in the previous section. The cross section oscillates with the phase

$$\alpha = 2\eta(b_1) - 2\eta(b_4) + kb_1\vartheta - kb_4(\pi - \vartheta). \qquad (4.23)$$

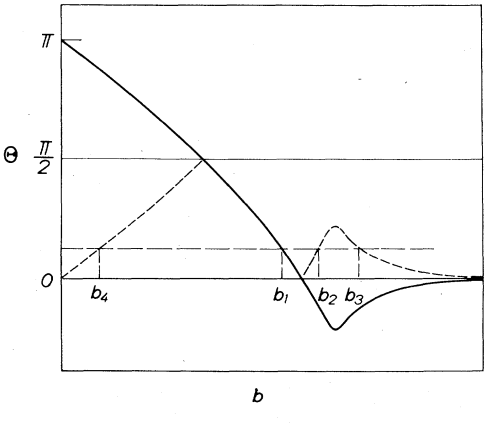

FIG. 9. Deflection function for identical particle scattering. Due to the indistinguishability of the particles, the scattering is symmetric about $\pi/2$ and an additional interference pattern arises between $b_4$ and $b_1$ (Siska *et al.*, 1971).

The spacings of the oscillations are a measure of the sum of the two impact parameters $b_1 + b_4$ (F. T. Smith, 1969). This result can be used to construct the whole $b(\vartheta)$ curve by an iterative procedure (Kennedy and F. J. Smith, 1969). The smoothness of the $b(\vartheta)$ curve and an approximate knowledge of the potentials help in calculating the $b(\vartheta)$ curve which then can be compared with the values obtained from experiment. The procedure of Buck (1971) can also be applied to this type of measurement. F. T. Smith (1969) has shown that it is possible to derive some information on the energy dependence of the impact parameter, for $\vartheta = \pi/2$, from this type of oscillation. He expands the cross section about $\vartheta = \pi/2$ and from the resulting power series one gets information on the impact parameters and their derivatives.

The integral cross section can be treated by similar considerations. We have already seen that the interference is mainly produced by head-on collision, for which $l = 0$ is valid. Expanding the phase shift near this point, one gets for small $l$

$$\eta(l) = \eta(0) + \tfrac{1}{2}\pi l - \kappa l^2. \qquad (4.24)$$

Because of the statistics—let us assume Bose statistics—only scattering phase shifts of even angular momentum contribute to the cross section. This means that the phase shifts have the separation $\pi$ for all following $l$ except for a small correction $\kappa l^2$. In other words, all phase shifts make the same contribution to the cross section as the $s$-wave phase shift. The integral cross section therefore oscillates (Helbing, 1969):

$$Q \propto \cos[2\eta(0) - \pi/2 + \varphi] \qquad (4.25)$$

with

$$\varphi = \arctan[1 + 2(\pi\kappa)^{-1/2}]^{-1}.$$

The $s$-wave phase shifts can then be obtained simply from the cross section via

$$\eta_E(0) = [N(E) - \tfrac{1}{4}]\pi - \varphi(E)/2, \qquad (4.26)$$

where $N$ is the index of the extremum measured as a function of energy.

### D. Exchange cross sections

The examples discussed so far are interferences which arise when two or more impact parameters corresponding to a single potential contribute to the scattering amplitude. As mentioned in the beginning, this is not a necessary condition for interference. Several cases are now studied where the interference structure arises due to contributions from different potentials. The most prominent examples where this type of interference occurs are in calculating the charge and spin exchange cross sections. In the first case two electronic states of different symmetry exist ($g$ and $u$) leading to two different potentials. The actual physical situation where the charge is definitely located on one particle or the other must be described by a combination of the $g$ and $u$ states; the cross section is given by

$$\sigma_\pm = \tfrac{1}{4}|f_g \pm f_u|^2, \qquad (4.27)$$

with (+) referring to the direct and (−) to the exchange cross section. An example for this type of analysis is given by Kennedy and F. J. Smith (1969) who explore the elastic differential cross section of $He^+ - He$. Nearly the same is valid for the spin exchange cross section where the two potentials arise from the different spins and produce, for spin 1/2 particles, deep minima for the singulet potential (because of the large exchange forces) and shallow van der Waals minima for the triplet case (Pritchard, 1972). In both cases an analysis of the interference data will provide some information on the difference of actions, from which the deflection function can be constructed if additional information on one of the two contributions is known.

### E. Potential crossings

In the semiclassical theory of electronic transitions a new type of interference arises from a crossing of two or more of the potential curves involved (F. T. Smith, 1969; Olson and Smith, 1971). The $S$-matrix elements can be written as

$$S_{kl}(E,b) = \sum_n q_n(E,b)\exp[2i\eta_n(E,b)], \tag{4.28}$$

where $n$ symbolizes a summation over all possible elements. The functions $q_n$ are slowly varying functions responsible for the transition probability. The scattering amplitude is then given by

$$f_{kl}(E,\vartheta) = \sum_n q_n \sigma_n^{1/2}\exp[i\hbar^{-1}A_n(E,\vartheta) + i\gamma_n], \tag{4.29}$$

where $\sigma_n$, $A_n$, and $\gamma_n$ are defined in Eq. (4.2) and (4.3).

Generally a transition between the two states occurs with significant probability only near the crossing point. Two possible trajectories then lead to the same final state. The scattering amplitude at a given angle, therefore, contains two components which will interfere to give an oscillating pattern. Figure 10 shows an example where $He^+ + Ne$ in the ground state is crossed by the potential of the excited $He^+ + Ne^*$ state. In the elastic channel there are two trajectories, one corresponding to the basic diabatic potential and the other arising from a transition to the excited state on the inward passage and a transition to the ground state on the outward passage. The interference pattern will be seen to be a perturbation on elastic scattering. Inelastic scattering can be treated in a similar manner. This type of interference pattern has been predicted by Stueckelberg (1932). The oscillations begin at a threshold angle $\tau_c$. Three significant types of information are available from these elastic perturbations and inelastic oscillations: the reduced angle of the starting point of the oscillations $\tau_c$, the oscillatory spacings, and the amplitudes of the oscillations. By using the reduced angle $\tau$ rather than the angle itself to describe the threshold behavior, it is easy to estimate the crossing distance from such $\tau_c$ values. Since $\tau$ is only a function of the impact parameter $b$, with some knowledge of the potential it can be related to the corresponding $r$ values (for details see F. T. Smith *et al.*, 1967; Coffey *et al.* 1969). The spacings are analyzed in terms of the reduced action difference [see Eq. (4.20) and (4.21)]. The quantity $N_0$ which describes a quantal contribution to the relative phase may be determined either theoretically or by adjusting the experimental data so that the results from different energies fall into a common pattern. A plot of $E^{1/2}(N - N_0)$ versus $\tau$ is used to determine the coefficients in

$$a_0(\tau) = B_1(\tau - \tau_0) + B_2(\tau - \tau_0)^2 + \cdots. \tag{4.30}$$

The slope of this curve is a direct measure of the difference in impact parameters involved, $\Delta b(\tau)$. The spacings of the oscillations are therefore directly connected to differences in impact parameter which can then be used for a determination of the potentials involved if one of the two potentials is known. One can check that the series of Eq. (4.21) are truncated after the first member by plotting $d(E^{1/2}N)/dt$ vs $E$. The amplitudes of the oscillations associated with crossings contain information about the energy associated with the coupling between the states $H_{12}(r_c)$. Assuming that the simple Landau–Zener model (Landau, 1932; Zener, 1933) is valid, this energy is related to a characteristic velocity which can be estimated from the energy dependence of the transition probability (Coffey *et al.*, 1969). This type of information can be obtained, in principle, for all processes in which curve crossing is involved, as in charge transfer problems (F. T. Smith *et al.*, 1970) or the crossing of ionic and covalent potentials of alkali halides (Delvigne and Los, 1973). All these interferences give information on the difference of the action, which can be used to construct the deflection function and (via the results of Sec. III) the potential.

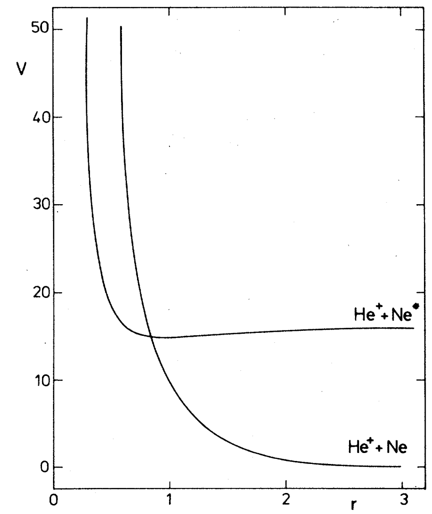

FIG. 10. Schematic potential curves for a two-state crossing. The curves correspond roughly to the scattering of $Ne^+ + Ne$ (Coffey *et al.*, 1969), when $V$ is measured in [eV] and $r$ in [A].

## V. RESULTS

The preceding sections show that inversion schemes are available which allow the determination of the potential directly from the measured cross section without assuming a parameterized potential model. These solutions are valid both in the exact quantum mechanical theory as well as in the semiclassical approximation. The quantum mechanical treatments are found to entail more difficult steps than the semiclassical treatments. Therefore such a procedure has not yet been applied to an actual set of data in molecular physics. In the semiclassi-

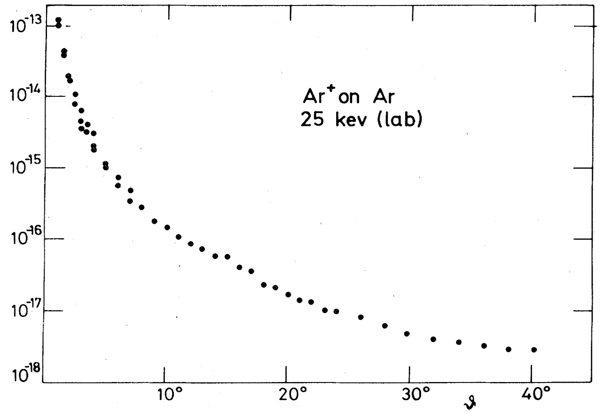

FIG. 11. Differential cross section data in laboratory coordinates for $Ar^+$ on Ar (Lane and Everhardt, 1960).

cal approximation there are now several practical applications available. They are a combination of one of the procedures of Sec. IV with the results of Sec. III. The classical inversion, though known for a long time, has rarely been used for the determination of potentials. This may be due to the fact that the first published work (Hoyt, 1939 and Firsov, 1953) was restricted to monotonic potentials. Most of the examples given below are measurements of differential cross sections which show a pronounced rainbow structure with superimposed rapid oscillations. This allows a precise determination of the potential without measuring the absolute value of the cross section. The renewed interest in the inversion procedures in the semiclassical limit is mainly due to molecular beam methods providing precise and accurate measurements of the cross section.

### A. Monotonic cross sections

If the cross section is measured over the whole angular range, $b(\vartheta)$ can be calculated by direct integration, using Eq. (4.19), and the potential is obtained via Eq. (3.10) and (3.11). Lane and Everhart (1960) applied this procedure to the differential cross section data of $Ar^+$ on Ar, $Ne^+$ on Ne, and $Ne^+$ on Ar for energies of 25, 50, and 100 keV in the laboratory system. The cross section is displayed in Fig. 11. Two difficulties arise in applying this procedure: the lack of data between 40° and 180° for the first integration and the lack of data between 0–1° for the inversion. Both problems have been overcome by a suitable extrapolation which can be shown to cause only small errors. The results are displayed in Fig. 12, along with a theoretical calculation and the screened Coulomb potential which is valid only at very small distances. The origin of the gap between the potentials obtained from different energies could not be clarified. The energy dependence of the potential, inelasticities, and experimental errors are possibly responsible for this effect.

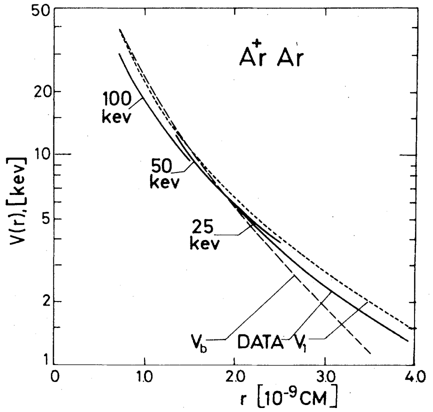

FIG. 12. The potential between $Ar^+$ and Ar obtained by the inversion of experimental data at three different energies (solid lines). The dotted line ($V_1$) refers to a potential based on the Thomas–Fermi statistical model, and the dashed line ($V_b$) is an exponentially screened Coulomb potential (Lane and Everhardt, 1960).

A very recent example has been given by Barwig *et al.* (1973) for the scattering of K on Hg in the energy range of 30 to 300 eV. At these energies the scattering is mainly determined by the repulsive part of the potential. The influence of the attractive portion of the potential is restricted to very small angles, not investigated in the experiment. Therefore the cross section is monotonic and can be directly inverted as described. The attractive part of the deflection function, which is necessary for the correct integration of Eq. (3.11) although it is very small compared to the repulsive part, was taken from the results obtained from scattering experiments at thermal energies (Buck *et al.*, 1972, see below). The potential derived from measurements at five different energies is illustrated in Fig. 13. The different symbols correspond to different energies. At small distances the potential shows an exponential increase with decreasing distance.

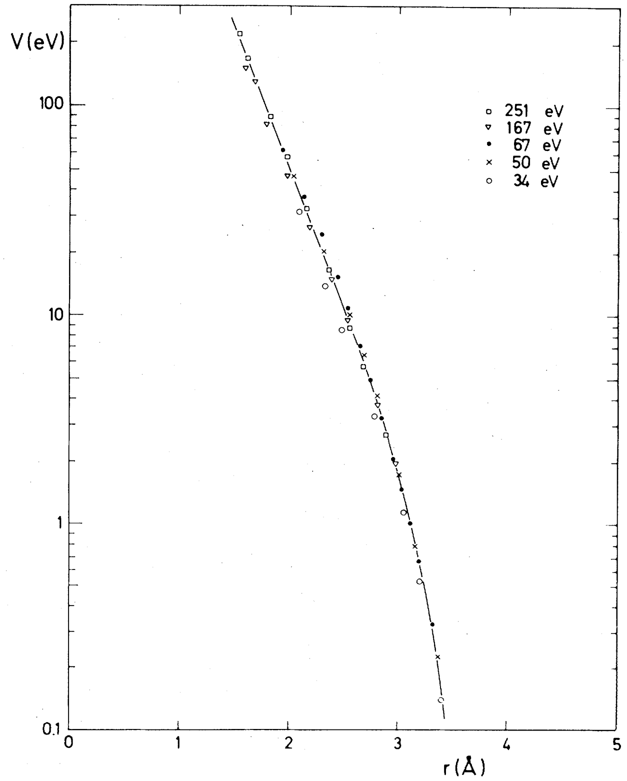

FIG. 13. Potential curve for KHg derived by the inversion of experimental differential cross section at five different energies from 30 to 300 eV (Barwig *et al.*, 1973).

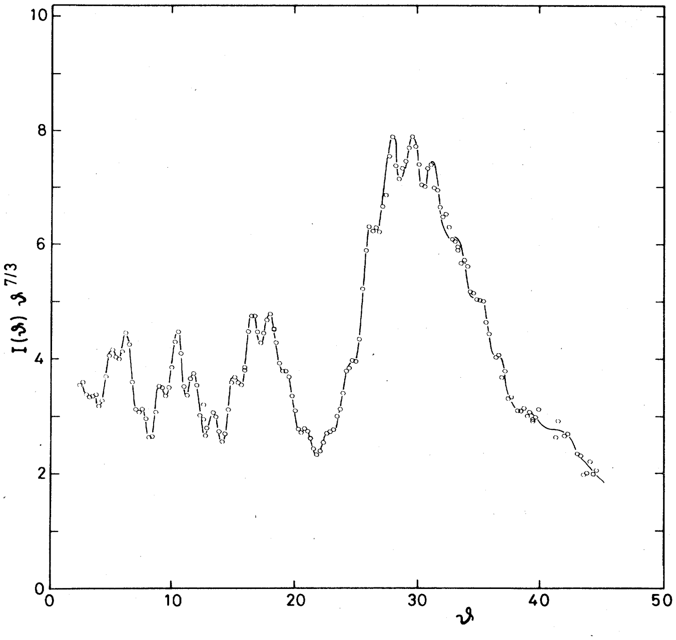

FIG. 14. Differential cross section data for LiHg at the relative energy $E = 0.305$ eV in the center of mass system (arbitrary units) as a function of the deflection angle (degrees). The cross section is multiplied by $\vartheta^{7/3}$ in order to remove the steep angular dependence at small angles. Rainbows as well as the superimposed rapid oscillations are well resolved (Buck *et al.*, 1973).

## B. Rainbow oscillations

Most of the examples of inverted cross sections show a well resolved rainbow structure as displayed in Fig. 14 for the scattering of Li on Hg (Buck *et al.*, 1973). The supernumerary rainbow oscillations, which end up with the classical rainbow, and the superimposed rapid oscillations are clearly resolved. This structure is very sensitive to the absolute scale and form of the potential. Therefore these cross sections provide an important tool for the determination of the phase shifts (or the deflection function). For the determination of the potential the procedures of Sec. IIIA1 are used.

(a) The procedure of Buck (1971) has been applied to the scattering of alkali atoms on mercury (Buck and Pauly, 1971; Buck *et al.*, 1972; Buck *et al.*, 1973) measured in the thermal energy range (about 0.2 eV). The following experimental data were used as input information for the inversion procedure.

(i) The positions of the rainbow oscillations.

(ii) The separation of the rapid oscillations.

(iii) The backward scattering of the differential cross section.

(iv) The position of the extrema of the glory oscillations in the velocity dependence of the integral cross section.

(v) The van der Waals constant from semiempirical calculations.

(vi) The ratio of the amplitude of the first rainbow oscillation to the backward scattering.

The measured positions of the two interference oscillations are the heart of the procedure. For high-resolution experiments they are not influenced by any averaging process and can easily be deduced from experimental data. From this information the deflection function for the attractive part is built up by minimizing the difference between calculated and measured positions. The repulsive part is obtained from the monotonic part of the backward cross section, in the same way as described above. The glory oscillations and the van der Waals constant are used as additional information for the small angle part of the deflection function, since this region is not probed exactly by differential cross section data. The disadvantage to taking only the position of the extrema is that they are only sensitive to certain areas of the deflection function (Boyle, 1971, see Sec. IVA; Pritchard, 1972) and do not determine $\Theta(b)$ uniquely. This can be overcome by certain conditions of continuity, say on the repulsive part of the deflection function, and by a final comparison to the amplitude of the cross section. In our opinion it is easier to start from well defined positions and to adjust the fine details afterwards rather than to start from the amplitudes which are severely affected by averaging processes, even with good experimental energy resolution. Figure 15 shows an example of the resulting potential derived from such an inversion procedure for CsHg (Buck *et al.*, 1972). The displayed points have been obtained from a measurement of the rainbow cross sections at five different energies with the backward scatter-

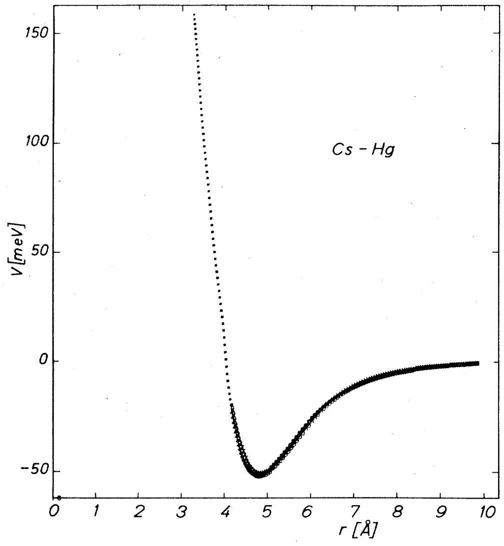

FIG. 15. The potential for CsHg obtained by the inversion of cross section data at five different energies which are denoted by different symbols (Buck *et al.*, 1972).

TABLE I. Potential well depth $\varepsilon$ and minimum separation $r_m$ for hydrogen–mercury and alkali–mercury systems.

| | $\varepsilon$[eV] | $r_m$[Å] |
|---|---|---|
| H–Hg[a] | 0.458 | 1.74 |
| Li–Hg[b] | 0.108 | 3.00 |
| Na–Hg[c] | 0.055 | 4.72 |
| K–Hg[d] | 0.052 | 4.91 |
| Cs–Hg[d] | 0.050 | 5.09 |

[a] Stwalley (1972). [b] Buck *et al.* (1973).
[c] Buck and Pauly (1971). [d] Buck *et al.* (1972).

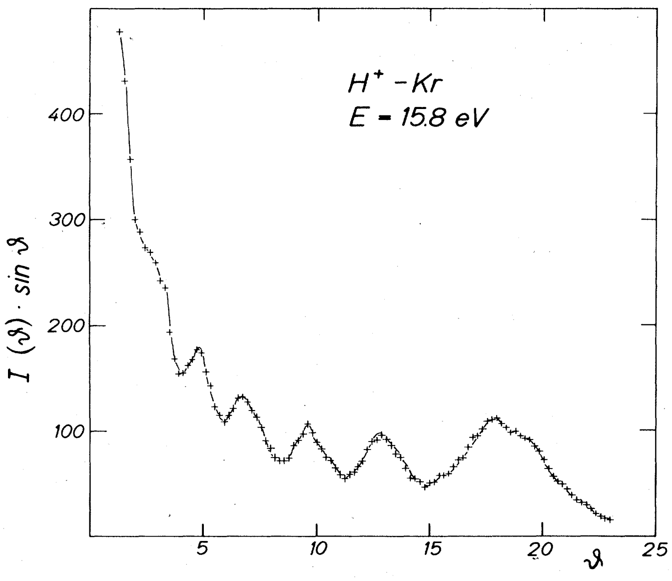

FIG. 16. Differential cross section data (arbitrary units) for $H^+Kr$ at 15.8 eV in center-of-mass coordinates as a function of the deflection angle (degrees). A well resolved rainbow structure is displayed (Weise *et al.*, 1971).

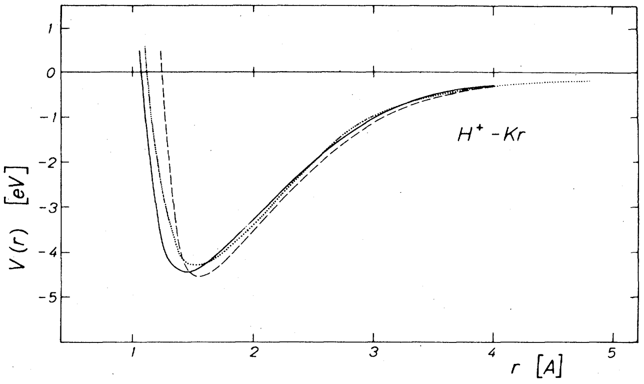

FIG. 17. Potential energy functions for $H^+ - Kr$. The dashed line is obtained by the inversion of the data of Rich *et al.* (1971) by the method of Remler (1971). The dotted line represents the results of the inversion procedure of Buck (1971) of the data measured by Weise *et al.* (1971). The same data set is used for a fit procedure displayed by the solid line (Weise *et al.*, 1971).

ing of one energy; each energy is indicated by a different symbol. One can see at a glance that the potentials, within the experimental error, are the same. Similar results have been obtained for LiHg (Buck *et al.*, 1973), NaHg (Buck and Pauly, 1971) and KHg (Buck *et al.*, 1972). The values of the size parameters for all these potentials, the well depth $\varepsilon$, and the minimum distance $r_m$ are given in Table I along with the results for HHg which have been obtained from spectroscopic data by the RKR method (Stwalley, 1972). These values indicate that the heavy systems behave like a van der Waals molecule, whereas HHg is governed by chemical exchange forces. The system LiHg can be regarded as a transition between these two types. The shape is quite different from the Lennard-Jones (L.-J.) (12-6) potential commonly used in molecular physics. The repulsive part is much softer. The minimum is wider and it approaches zero much more rapidly as $r$ approaches infinity. Another interesting point should be mentioned. Evidence has been found which shows that for the distances probed by the measurements the asymptotic behavior of the potential cannot be explained by a simple $C_6 r^{-6}$ term. The difference could be attributed to a $C_8 r^{-8}$ term.

(b) Results of similar precision are available for the scattering of protons on the rare gases in the energy range from 5 to 30 eV (Mittmann *et al.*, 1971; Rich *et al.*, 1971; Udseth *et al.*, 1971; Weise *et al.*, 1971). An example for $H^+Kr$ (Weise *et al.*, 1971) is shown in Fig. 16. Rich *et al.*, (1971) inverted their measurements by the method of Remler (1971) for $H^+$ on He, Ne, Ar, and Kr in the energy range of 4.0 to 6.0 eV. Here the measured cross section is directly compared with a calculated scattering amplitude of the Watson–Sommerfeld type. The pole contributions are varied until there is agreement between calculated and measured values. The initial choice of pole parameters is clearly motivated by semiclassical considerations. The rainbow angle $\vartheta_R$ and the width of the deflection function $\Gamma_{1/2} = (2\vartheta_R/q)^{1/2}$ may be quickly approximated by fitting the rainbow maximum [see Eq. (4.7)] to the experimental data. The rainbow oscillations at small scattering angles give a reasonable approximation to $b_m$, whereas the rainbow impact parameter $b_R$ can be determined from the rapid oscillations near the rainbow angle. The optimal parameters for $H^+Ar$ and $H^+Kr$ are shown in Table II. No more than 16 pole contributions placed in a unit circle around the complex $\lambda_p$ were necessary to generate the cross section. By applying this procedure one has to consider that only the attractive part of the potential can be treated in this way. The repulsive part has to be determined by other methods. Unaveraged data, though, is necessary for comparison. This problem has been solved, using a

TABLE II. Pole parameters used to fit the calculated cross section to the experimental cross section (Rich *et al.*, 1971)

| | $E$ | Re $\lambda_p$ | Im $\lambda_p$ | $N$ | $l_m$ |
|---|---|---|---|---|---|
| $H^+Ar$ | 5.0 eV | 100.2 | 25.78 | 13 | 67 |
| $H^+Kr$ | 6.0 eV | 138.2 | 33.6 | 16 | 91.2 |

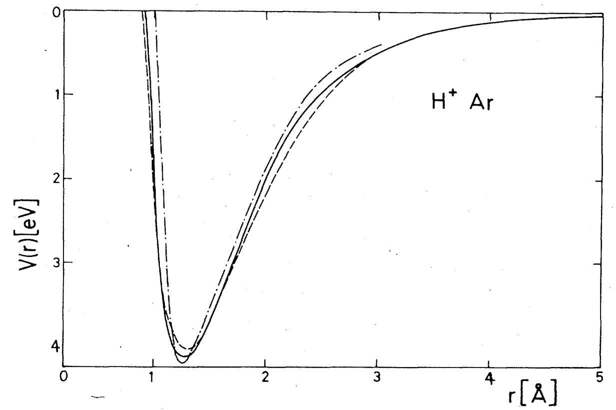

FIG. 18. The potential of $H^+Ar$ obtained by the inversion of the data measured by Rich *et al.* (1971) by the Remler method (1971) (dashed dotted line) and by the method of Klingbeil (1972b) (solid line). The dashed line is the result of the fit procedure of Mittmann *et al.* (1971) using their own data. This potential has been used as initial potential by Klingbeil for his inversion.

deconvolution procedure which can only be applied if the data shows a well resolved structure. Results for $H^+Kr$ are illustrated in Fig. 17 by the dashed line. The points display the results of an inversion of the data of Weise *et al.* (1971), using the procedure of Buck (1971) for the same system. The solid line indicates the fit procedure of Weise *et al.* (1971). Most of the discrepancies are due to the different sets of data. For instance, Rich *et al.* (1971) were unable to resolve the rapid oscillations and thus this data set is perhaps not so reliable. If one compares the potential at $r = 4.5$ Å with that of a $r^{-4}$ behavior (which should be valid for a charge-induced dipole interaction), the constant is more than a factor of two higher than the predicted one.

(c) The data of Rich *et al.* (1971) for $H^+Ar$ have also been inverted by Klingbeil (1972b). In this method all phase shifts are used as free parameters and adjusted by comparing calculated and measured cross sections. The phase shifts of the fitted potential of Mittmann *et al.* (1971) were used as starting values. The phase shifts in the limits $14 \leq l \leq 220$ were then varied in order to obtain an optimal set of data. The result is shown in Fig. 18 together with the initial potential and the potential obtained by the inversion of the same data by the Remler method (Rich *et al.*, 1971). The deviations are not very significant, but not negligibly small either. Problems with this method arise because of the requirements of deconvoluted data and a well behaved starting potential. However, since the procedure works without any assumptions, it is well suited for the inversion of differential cross section curves which display well resolved rapid oscillations without rainbow structure, and which are sensitive mainly to the repulsive part of the potential. Such a case can be solved neither by the method of (a) and (b) nor by the procedures of Sec. IVA3. An example of this is the differential cross section of LiAr measured by Detz (1970) and inverted by Klingbeil (1973).

(d) Another example for the determination of the potential from rainbow scattering is given by Boyle (1971). The deflection function is constructed by varying a calculated one (say from an L.-J. potential). The final form is then adjusted by comparing the experimental value to the calculated cross section. The potential is determined by the method of Sec. IIIA. This procedure has been applied to the system NaXe, for which differential cross sections of high-energy resolution have been measured (Barwig *et al.*, 1966). The results do not differ very much from carefully performed fit procedures (Buck and Pauly, 1968; Düren *et al.*, 1968).

### C. Identical particle oscillations

All methods described above are performed by applying the procedure of Sec. III.A1 in the second step of the whole procedure; this means the phase shift curve is known for one energy and as many $l$ as possible. This information is mainly obtained from the differential cross section. We shall conclude this chapter with an example where a procedure of Sec. III.A.2 is used. Here the phase shifts have to be known as a function of energy for one $l$. Usually such information cannot be obtained from cross section measurements in molecular physics. There is one exception, however, the integral cross section for two He atoms. Figure 19 shows this cross section as measured by Feltgen *et al.* (1973). The identical particle oscillations are clearly seen over the whole velocity range. Since the potential well is very small, most of the structure is sensitive to the repulsive part of the potential. Only the first shoulder is sensitive to the attractive part due to the special behavior of the $s$-wave phase shift (analogous to the Ramsauer effect in electron scattering). An analysis of this cross section shows (see Sec. IVC) that all phase shifts are coupled to the $s$-wave phase shift and therefore these phase shifts can be deduced from the measured extrema of the cross section. Obviously this procedure is not valid for small energies. Nevertheless the larger part of the phase shifts can be determined in this way. If the potential well is also known, the procedure of Sec. IIIA2 can be applied. The difficulties of this method arise from the necessity that a part of the potential has to be known *a priori*; this problem can only be solved by assuming several forms for the potential, performing the inversion, and comparing the results with measurements. It should be noted that this procedure is, in any case, better than the usual fit procedure, since a part of the cross section curve is correctly reproduced in any iteration step, regardless of any assumed potential well. The results of such an inversion (Feltgen *et al.*, 1973) are displayed in Fig. 20 along with other potentials derived from molecular beam experiments and gaseous properties. The inverted points agree well with *ab initio* calculations, not

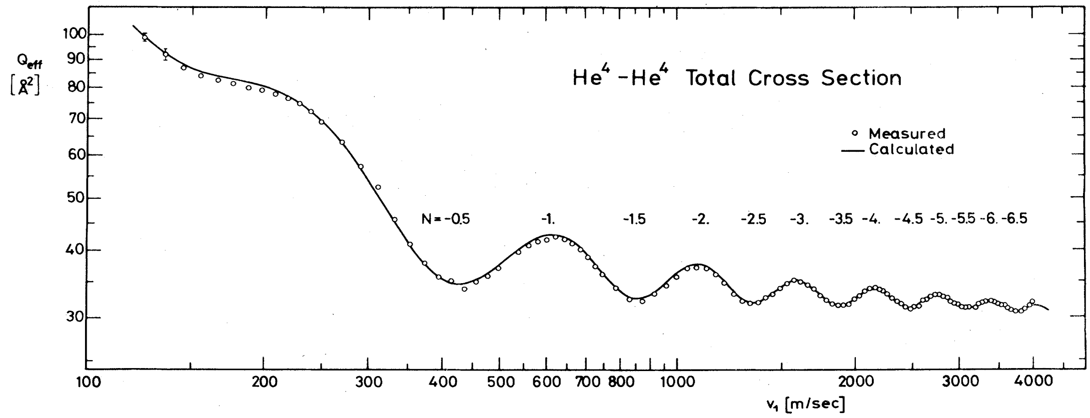

FIG. 19. Measured and calculated integral effective cross section for $He^4He^4$ as a function of the primary beam velocity. The solid curve calculated from the potential obtained by inversion. The oscillation are due to the indistinguishability of the particles (Feltgen *et al.*, 1973).

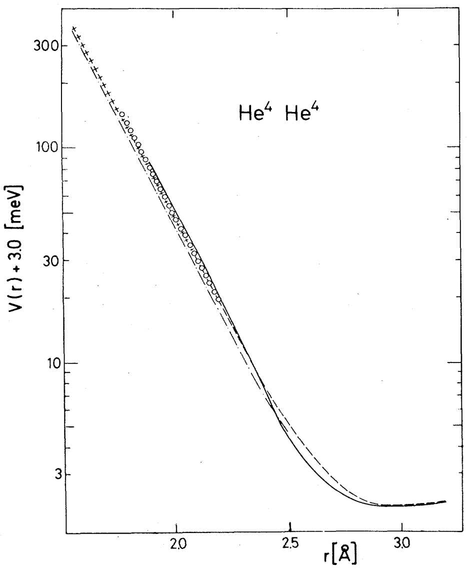

FIG. 20. The He$^4$ – He$^4$ potential. The circles denote the potential obtained by the inversion of the data of Fig. 19 (Feltgen *et al.*, 1973). The other potentials are determined by molecular beam scattering data: solid line (Farrar and Lee, 1972), dashed line (Bennewitz *et al.*, 1972), crosses (Gengenbach *et al.*, 1972); and by gaseous properties: dashed dotted line (Beck, 1968). Several other potentials derived for this system could not be displayed in this figure since they lie directly on the curves shown, e.g., Cantini *et al.* (1972), Gilbert and Wahl (1967).

shown in the figure (Gilbert and Wahl, 1967; Schaefer *et al.*, 1970).

## D. Discussion

Inverse procedures are indeed a powerful tool for deducing potentials from measured cross sections. Several of these advantages over the usual fitting procedures should be pointed out. The potential is automatically determined only for the region which is probed by the measurements. This point should not be overlooked. Most of the differences in the literature on molecular interaction potentials arise from many authors overestimating the range of the potential to which the measurement is sensitive. Computation time is also significantly reduced, being, in the average, 5 to 10 times smaller than that for a fit procedure of the same precision. These values are based on the experience of the author in comparing an inversion procedure of the type described in Sec. IVA and a trial and error procedure with $\chi^2$ techniques, where the differential cross section is used as input information. An additional point is that, due to the apparent structure of the different steps involved in any inverse problem, the question of errors and uniqueness can be solved in a straightforward manner. The following scheme summarizes the different steps in the semiclassical approximation:

$$\begin{Bmatrix}\sigma(E,\vartheta)\\ Q(E)\end{Bmatrix} \xrightarrow[(1)]{} \begin{Bmatrix}\eta(E,b)\\ \Theta(E,b)\end{Bmatrix} \xrightarrow[(2)]{} V(r).$$

The second step from the phase shifts or the deflection function to the potential is achieved by solving an Abelian integral equation. If the input information is known only as a function of energy, additional information about the potential well (bound states) is necessary for a unique solution; whereas for the angular momentum dependence of the input information, a unique solution is achieved if the interpolation from the angular momentum $l$ to the impact parameter $b$ is unique. The first step in the above scheme is easily achieved if the data, the differential and the integral cross section, is of absolute accuracy over the full range of the variable. In practice we are obliged to deal with a limited range of data with limited accuracy. The procedures of Sec. IV and the results given in Sec. V clearly show the requirements for experimental data which is to be inverted to potentials in a unique manner. The limited angular (energy) range can practically be overcome At small angles (or low energies) an appropriate interpolation must be found, while a lack of large-angle data (or high-energy data) limits the range of the deduced potential. Another possibility is to vary the complementary, fixed parameter, e.g., the energy (the angular momentum). The different sets of phase shifts should then give the same potential. A more elegant possibility is the reduced variable formalism originally derived by F. T. Smith (1969) as a small-angle or high-energy approximation. This procedure leads to an extension of the domain of available data. A severe restriction for all data is the finite resolution of energy and angles, which cannot be avoided in any real experiment. Since most of the procedures which have been applied need, as main input information, the positions and the amplitudes of the interference oscillations of the cross sections, they can always be performed if the resolution is good enough that these two quantities are not affected by a large amount of averaging. Uniqueness is achieved if the whole interference structure is known, together with some additional information from large-angle scattering, the amplitudes, or the averaged cross section. The examples treated in this article display a very simple structure from which the potential could be derived. More complicated cases such as atom-molecule scattering or interactions where several potential curves are involved will hopefully be attacked in the near future.

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## REFERENCES

Agranovich, Z. S., and V. A. Marchenko, 1963, *The Inverse Problem of Scattering Theory* (Gordon and Breach, New York).
Amdur, I., J. E. Jordan, K. -R. Chien, L. W. -M. Fung, R. L. Hance, E. Hulpke, and S. E. Johnson, 1972, J. Chem. Phys. **57**, 2117
Bargmann, V., 1949, Rev. Mod. Phys. **21**, 488.
Barwig, P., U. Buck, E. Hundhausen, and H. Pauly, 1966, Z. Phys. **196**, 343.
Barwig, P., U. Buck, and H. Pauly, 1973, Proceedings, IVth International Conference on Molecular Beams, Cannes (to be published).
Beck, D. E., 1968, Mol. Phys. **14**, 311.
Benn, J., and G. Scharf, 1967, Helv. Phys. Acta **40**, 271.

Bennewitz, H. G , H. Busse, H. D. Dohmann, D. E. Oates, and W. Schrader, 1972, Z. Phys. **253**, 435.

Bernstein, R. B. and J. T. Muckerman, 1967, Adv. Chem. Phys. **12**, 389.

Berry, M. V., 1966, Proc. Phys. Soc. Lond. **89**, 479.

Boyle, J. F., 1971, Mol. Phys. **22**, 993.

Brackett, J. W., C. R. Mueller, and W. A. Sanders, 1963, J. Chem. Phys. **39**, 2564.

Buck, U., 1971, J. Chem. Phys. **54**, 1923.

Buck, U. and H. Pauly, 1968, Z. Phys. **208**, 390.

Buck, U. and H Pauly, 1969, J. Chem. Phys. **51**, 1662.

Buck, U. and H. Pauly, 1971, J. Chem. Phys. **54**, 1929.

Buck, U., M. Kick, and H. Pauly, 1972, J. Chem. Phys. **56**, 3391.

Buck, U., H. O. Hoppe, F. Huisken, and H. Pauly, 1973, Discuss. Faraday Soc. **55**, 185.

Cantini, P., M. G. Dondi, G. Scoles, and F. Torello, 1972, J. Chem. Phys. **56**, 1946.

Chester, C., B. Friedmann, and F. Ursell, 1957, Proc. Camb. Philos. Soc. **53**, 599.

Child, M. S., 1970, J. Mol. Spectrosc. **33**, 487.

Coffey, D., D. C. Lorents, and F. T. Smith, 1969, Phys. Rev. **187**, 201.

Coudray, C. and M. Coz, 1970, Ann. Phys. (N.Y.) **61**, 488.

Cox. J. R., 1962, J. Math. Phys. **5**, 1065.

De Alfaro, V. and T. Regge, 1965, *Potential Scattering* (Wiley, New York).

Delvigne, G. A. L. and J. Los, 1973, Physica **67**, 166.

Detz, C., 1970, Ph.D. dissertation, University of Chicago (unpublished).

Düren, R., G. P. Raabe, and Ch. Schlier, 1968, Z. Phys. **214**, 410.

Farrar, J. M. and Y. T. Lee, 1972, J. Chem. Phys. **56**, 5801.

Feltgen, R., H. Pauly, F. Torello, and H. Vehmeyer, 1973, Phys. Rev. Lett. **30**, 820.

Firsov. O. B., 1953, Zh. Eksp. Teor. Fiz. **24**, 279.

Ford, K. W., and J. A. Wheeler, 1959, Ann. Phys. (N.Y.) **7**, 259.

Fulton, T., and R. G. Newton, 1956, Nuovo Cimento **3**, 677.

Gelfand, I. M., and B. M. Levitan, 1951, Isvest. Akad. Nauk SSSR, Ser. Math. **15**, 309 (Am. Math. Soc. Transl. **1**, 253).

Gengenbach, R., Ch. Hahn, and W. Welz, 1972 (private communication).

Gengenbach, R., Ch. Hahn, and J. P. Toennies, 1973, Phys. Rev. A**7**, 98.

Gerber, R. B., 1973, J. Phys. A **6**, 770.

Gerber, R. B., and M. Karplus, 1970, Phys. Rev. D**1**, 998.

Gilbert, T. L., and A. C. Wahl, 1967, J. Chem. Phys. **47**, 3425.

Glauber, R. J., 1959, in *Lectures in Theoretical Physics*, edited by V. E. Brittin and L. G. Dunham (Interscience, New York), Vol. 1, p. 315.

Goldberger, M. L., H. W. Lewis, and K. M. Watson, 1963, Phys. Rev. **132**, 2764.

Hanbury Brown, R., and R. Q. Twiss, 1956, Nature (Lond.) **168**, 1447

Helbing, R. K. B., 1969, J. Chem. Phys. **50**, 493.

Henry, J. H., I. J. Raju, Y. W. Wong, and R. P. Andres, 1973, *Abstracts of papers*, VIII ICPEAC, Beograd, p. 36.

Hoyt, F. C., 1939, Phys. Rev. **55**, 664.

Hylleraas, E., 1948, Phys. Rev. **74**, 48.

Hylleraas, E., 1963, Ann. Phys. (N.Y.) **25**, 309.

Hylleraas, E., 1964, Nucl. Phys. **57**, 208.

Jost, R., and W. Kohn, 1952, Phys. Rev. **88**, 382.

Keller, J. B., I. Kay, and J. Shmoys, 1956, Phys. Rev. **102**, 557.

Kennedy, M., and F. J. Smith, 1969, Mol. Phys. **16**, 131.

Klingbeil, R., 1972a, J. Chem. Phys. **56**, 132.

Klingbeil, R., 1972b, J. Chem. Phys. **57**, 1066.

Klingbeil, R., 1973, J. Chem. Phys. **59**, 797.

Landau, L., 1932, Phys. Z. Sowjet. **2**, 46.

Lane, G. H., and E. Everhardt, 1960, Phys. Rev. **120**. 2064.

Lehmann, C., and G. Leibfried, 1962, Z. Phys. **172**, 465.

Loeffel, J. J., 1968, Ann. Inst. Henri Poincaré **4**, 339.

Martin, A., 1969, Nuovo Cimento A **59**, 131.

Mason, E. A., and L. Monchick, 1967, Adv. Chem. Phys. **12**, 35.

Miller, W. H., 1968, J. Chem. Phys. **48**, 464.

Miller, W. H., 1969, J. Chem. Phys. **51**, 3631.

Miller, W. H., 1971, J. Chem. Phys. **54**, 4174.

Mittmann, H. U., H. P. Weise, A. Ding, and A Henglein, 1971, Z. Naturforsch. A **26**, 1112.

Newton, R. G., 1955, Phys. Rev. **100**, 412.

Newton, R. G., 1962, J. Math. Phys. **3**, 75.

Newton, R. G., 1966, *Scattering of Waves and Particles* (McGraw-Hill, New York), Chap. 20.

Newton, R. G., 1967, J. Math. Phys. **8**, 1566.

Newton, R. G., 1968, J. Math. Phys **9**, 2050.

Newton, R. G., 1972, in *Mathematics of Profile Inversion*, edited by Laurence Colin, NASA Technical Memorandum X-62.

Newton, R. G., and R. Jost, 1955, Nuovo Cimento **1**, 590.

Newton, R. G., and T. Fulton, 1957, Phys. Rev. **107**, 1103.

O'Brien, T. J. P., and R. B. Bernstein, 1969, J. Chem. Phys. **51**, 5112.

Olson, R. E., and C. R. Mueller, 1967, J. Chem. Phys. **46**, 3811

Olson, R. E., and F. T. Smith, 1971, Phys. Rev. A **3**, 1607.

Pauly, H., 1973, *Physical Chemistry an Advanced Treatise* (Academic, New York), Vol. IV, Chap. 4

Pauly, H., and J. P. Toennies, 1965, Adv. At. Mol. Phys. **1**, 195.

Pritchard, D E., 1972, J. Chem. Phys. **56**, 4206.

Prosser, R. T., 1969, J. Math. Phys. **10**, 1819.

Regge, T., 1959, Nuovo Cimento **14**, 951.

Remler, E. A., 1971, Phys. Rev. A **3**, 1949.

Rich, W. G., S. M. Bobbio, R. L. Champion, and L. Doverspike, 1971, Phys. Rev. A **4**, 2253.

Roberts, R. E., and J. Ross, 1970, J. Chem. Phys. **53**, 2126.

Rosen, M., and D. R. Yennie, 1964, J. Math. Phys. **5**, 1505.

Sabatier, P. C., 1965, Nuovo Cimento **37**, 1180.

Sabatier, P. C., 1966a, J. Math. Phys. **7**, 1515.

Sabatier, P. C., 1966b, J. Math. Phys. **7**, 2079.

Sabatier, P. C., 1967a, J Math. Phys. **8**, 905

Sabatier, P. C., 1967b, J. Math. Phys. **8**, 1957.

Sabatier, P. C., 1968, J. Math. Phys. **9**, 1241.

Sabatier, P. C., 1971, J. Math. Phys. **12**, 1393.

Sabatier, P. C., 1972a in *Mathematics of Profile Inversion*, edited by Laurence Colin, NASA Technical Memorandum X-62.

Sabatier, P. C., 1972b, J. Math. Phys. **13**, 675.

Sabatier, P. C., and F. Quyen Van Phu, 1971, Phys. Rev. D **4**, 127.

Schaefer III, H. F., D. R. McLaughlin, F. E. Harris, and B. J. Alder, 1970, Phys. Rev. Lett. **25**, 988.

Sigmund, P., and U. Lillemark, 1974, Physica (to be published).

Siska, P. E., J. M. Parson, T. P. Schafer, and Y. T. Lee, 1971, J. Chem. Phys. **55**, 5762.

Smith, F. T., 1969, in *Lectures in Theoretical Physics*: *Atomic Collision Processes*, edited by S. Geltman *et al.* (Gordon and Breach, New York) Vol. XIC, p. 95.

Smith, F. T., R. P. Marchi, and K. G. Dedrick, 1966, Phys. Rev. **150**, 79.

Smith, F T., R. P. Marchi, W. Aberth, D. C. Lorents, and O. Heinz, 1967, Phys. Rev. **161**, 31.

Stueckelberg, E. C. G., 1932, Helv. Phys Acta **5**, 369.

Stwalley, W. C., 1972 (private communication).

Stwalley, W. C., 1973, in *Abstracts of papers*, VIII ICPEAC, Beograd, p. 40.

Toennies, J. P., 1973, in *Physical Chemistry, an Advanced Treatise*, Vol. IV Kinetics of Gas Reactions, edited by D. Hinderson (Academic, New York), Chap. 6.

Udseth, H., C. F. Geise, and W. R. Gentry, 1971, in *Proceedings, International Conference on Electronic and Atomic Collisions*, 7th, Amsterdam, p. 264.

Viano, G. A., 1969, Nuovo Cimento A **63**, 581.

Vollmer, G., 1969, Z. Phys. **226**, 423.

Vollmer, G., 1971, Z. Phys. **243**, 92.

Vollmer, G., and H. Krüger, 1968, Phys. Lett. **28**, 165.

Vollmer, G., and S. Flügge, 1971, Z. Phys. **248**, 1.

Weise, H. P., H. U. Mittmann, A. Ding, and H. Henglein, 1971, Z. Naturforsch. A **26**, 1122.

Wheeler, J. A., 1955, Phys. Rev. **99**, 630.

Zener, C., 1933, Proc. R. Soc. A **137**, 696.