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PHYSICAL REVIEW A VOLUME 4, NUMBER 6 DECEMBER 1971

Inversion Problem for Ion-Atom Differential Elastic Scattering*

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(Received 12 July 1971)

An inversion procedure to recover the intermolecular potentials from low-energy (4–14 eV) differential scattering data for the systems HeH$^+$, NeH$^+$, ArH$^+$, and KrH$^+$ is presented. The first step in this procedure is to construct the phase shifts $\{\eta(l)\}$ from the experimental differential cross section $\sigma(\theta)$ and, for reasons of intuition, the corresponding classical deflection function. This is accomplished by employing a new technique developed recently by Remler which involves singularities in the S matrix. The Remler method is as accurate as, but less cumbersome than, the frequently employed standard partial-wave sum and in addition leads to an intuitive connection between $\eta(l)$ and $\sigma(\theta)$. Having found $\{\eta(l)\}$, the intermolecular potential may be determined by means of the transformation method of Vollmer. To test the entire inversion procedure, the intermolecular potential obtained from the H$^+$+He scattering data is compared to the *ab initio* calculation by Wolniewicz of the ground-state potential for HeH$^+$. This method should be applicable to any spherically symmetric scattering system.

I. INTRODUCTION

The role of differential elastic scattering in the determination of intermolecular forces has increased considerably in the past decade. This has been due to continuous improvements in experimental techniques associated with atom-atom and ion-atom collisions and to a desire to complete a theoretical problem which had its genesis in the early days of quantum mechanics but which had relatively little effort devoted to it until recently. The fundamental problem is the formal inversion of differential elastic scattering data to obtain the corresponding intermolecular potential. Some of the basic difficulties which can be encountered in the inversion problem have been discussed previously[1] and will not be elaborated here.

Calculations based on phenomenological potentials (and the JWKB approximation) have been used in various iterative schemes to fit calculated differential cross sections (or perhaps total elastic cross sections) to those experimentally observed.[2] Numerical calculations of the differential cross section which utilize up to several thousand partial waves are common. Approximations such as those by Ford and Wheeler,[3] Berry,[4] and Miller[5] simplify the numerical problem of calculating the differential cross sections and give physical insight into the origin of oscillatory behavior observed in some differential cross sections. These various approximations coupled with phenomenological potentials have proved extremely valuable in semiquantitative interpretations of low-resolution experimental observations. However, the ambiguities which are inherent in the "matching" of low-resolution experiments to various approximation schemes (or to the results of partial-wave calculations) have been pointed out.[6]

Recently, Buck and Pauly[7] have been able to treat high-resolution molecular-beam data with various approximation techniques and consequently construct the classical deflection function associated with the intermolecular potential of the Na-Hg system. Utilizing these results and employing the method of Vollmer[8] (in which the JWKB approximation is assumed valid) in the inversion procedure, they have directly obtained the intermolecular potential. This method represents a considerable improvement over some iterative schemes since restrictive constraints associated with the shapes of phenomenological potentials are no longer present.

The purpose of this paper is to report the practical applications of a new method by which one constructs a set of phase shifts from our high-resolution measurements of the differential elastic scattering of protons by rare-gas atoms. These JWKB phase shifts are then formally inverted to determine the corresponding intermolecular potentials. The validity of this method, is demonstrated by comparing the HeH^+ intermolecular potential obtained by direct inversion of the experimental data to that potential due to an *ab initio* calculation for HeH^+ by Wolniewicz,[9] which is believed to be quite accurate. It will be assumed that the adiabatic calculation is adequate for describing the intermolecular potential at the collision energies investigated.

The molecular systems which are reported (HeH^+, NeH^+, ArH^+, KrH^+) are all bound by several eV. The collision energies for which the differential scattering measurements are made are sufficiently low such that either the elastic scattering channel is the only one available (HeH^+ and NeH^+) or is the only important channel (ArH^+ and KrH^+). However, the collision energies are above the minimum for which barrier penetration and hence (classical) orbiting can occur.

II. DESCRIPTION OF TECHNIQUES UTILIZED IN INTERPRETING DATA

A. Phase Shifts from Data

The standard partial-wave sum which relates the phase shifts to the scattering amplitude may be written in the case of elastic scattering as

$$f(\theta) = (1/2ik)\sum_l (2l+1) P_l(\cos\theta)(e^{2i\eta_l} - 1) \ . \qquad (1)$$

Taking the appropriate S-matrix elements to be

$$S_l = e^{2i\eta_l} \ ,$$

the differential cross section may be written

$$\sigma(\theta) = (1/4k^2)\left| \sum_l (2l+1) P_l(\cos\theta)(S_l - 1) \right|^2 .$$

If one presumes an intermolecular potential, either an *ab initio* calculation or a parametrized model, the JWKB phase shifts $\{\eta(l)\}$ may be calculated and thereby $\sigma(\theta)$ is completely determined. Unfortunately this method has two major disadvantages. First, the actual calculation of the partial-wave sum may necessitate the inclusion of several thousand terms, and second, many important features in the differential cross section cannot be intuitively connected with the form of the summand in Eq. (1). One way of dealing with both of these difficulties is to employ the semiclassical method which is briefly outlined as follows. The sum in Eq. (1) is replaced by an integral and the assumption of stationary phase is used [i.e., the only contributions to $f(\theta)$ are assumed to come from regions where the summand in Eq. (1) has a stationary value as a function of l]. Such considerations have allowed the scattering amplitude to be written as an analytic function[4,5] involving $\eta(l)$ and its derivatives at various points. Further, one of the results of the stationary phase argument relates the phase shifts to the classical deflection function $\Theta(l)$,

$$\Theta(l) = 2\,\frac{\partial\eta(l)}{\partial l} \ .$$

This deflection function, whose magnitude is equal to the center-of-mass scattering angle, is of great value in discussing and interpreting the features of the differential cross section. Alternatively, one may employ the Remler-Regge[10] method of calculating the differential cross section. This method obviates the necessity of calculating many terms in the partial-wave sum, and it allows one to apply his intuition about semiclassical processes to scattering experiments without making the explicit semiclassical approximations such as stationary phase, etc. The actual computation of the differential cross section using this method is not limited to the semiclassical regime; and yet, if the semiclassical theory is applicable to a particular experiment, the phase shifts and deflection function used in the calculation may be viewed in the conventional fashion. For a sufficiently well-resolved differential scattering experiment, the phase shifts may be determined from the data without recourse to any semiclassical approximations. It is this observation that provides the basis and starting point for the inversion procedure discussed in this paper. A description of the Remler-Regge method follows.

Regge[11] noted that if one multiplies the summand in Eq. (1) by a factor which contains first-order poles (e.g., $1/\sin l\pi$ for integer l) and integrates the product over a contour along the positive real l axis, a result identical to Eq. (1) is obtained. Further if the S-matrix element contains a finite number of singularities N which are in the first quadrant of the complex l plane, the contour of integration may be deformed to include only this finite set of poles, and $f(\theta)$ may then be written as a sum over this finite set (in calculations reported here $5 \leq N \leq 16$). Remler[10] has parametrized the (diagonal) S-matrix elements in the angular momentum representation such that they are unitary, symmetric, and contain only first-order poles. That is, we have

$$S_A = \prod_{p=1}^{N} S_p \ ,$$

with

$$S_p = (\lambda^2 - \lambda_p^{*2})/(\lambda^2 - \lambda_p^2) \ ,$$

where λ is the real angular momentum $l + \frac{1}{2}$ and λ_p is the position of the pth pole in the complex plane. Details of the explicit form of the scattering amplitude in this representation will be deferred until later in this section. The set of phases $\{\eta(l)\}$, which are necessary to predict the intermolecular potential, is derivable from the poles. At this point it is enlightening and desirable to connect the Remler-Regge method with "semiclassical thinking."

Remler has shown that the phase shift $\eta_p(l)$ corresponding to a particular pole located at λ_p in the first quadrant of the complex l plane may be written as

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

and is plotted in Fig. 1. The deflection function arising from this pole is

$$\Theta_p(l)$$

$$=2\left(\frac{\mathrm{Im}\lambda_p}{(\lambda+\mathrm{Re}\lambda_p)^2+(\mathrm{Im}\lambda_p)^2}-\frac{\mathrm{Im}\lambda_p}{(\lambda-\mathrm{Re}\lambda_p)^2+(\mathrm{Im}\lambda_p)^2}\right).$$

This function (essentially a pulse centered at l $l=\mathrm{Re}\lambda_p-\frac{1}{2}$ with depth $\approx 2/\mathrm{Im}\lambda_p$) and width $\approx 2\,\mathrm{Im}\lambda_p$ is plotted in Fig. 1. The attractive portion of a set of phases (or corresponding deflection function) may be simply constructed by the superposition of a few such η_p (or Θ_p) obtained by adding additional poles in the first quadrant of the complex l plane. In practice N poles are placed on a small circle of radius ρ ($\rho\approx 1$) centered at λ_p in the complex plane. This has the phenomenological effect of one Nth-order pole positioned at λ_p without entailing the mathematical complication that higher-order poles in S would necessitate. The value of ρ can be mathematically demonstrated to make little difference in the calculations of $\eta(l)$, $\Theta(l)$, or $f(\theta)$ provided it is chosen within reasonable limits. It should be emphasized that $\Theta(l)$ is not actually the basis for calculating $f(\theta)$; rather, the poles are. However, retrieving $\Theta(l)$ from the calculation allows one to use all of his intuition about semiclassical processes in manipulating the pole parameters (N and λ_p) to achieve rapid and accurate agreement between the experimental data and the Remler-Regge calculated cross section.

Since the experimental differential cross section contains interference between both attractive and repulsive components of the deflection function, the method described thus far is not complete. To include the effect of repulsive scattering one could place poles in the fourth quadrant of the complex l plane. Instead it is more convenient to account for the repulsive scattering by going to the partial-wave expression for $f(\theta)$ and summing over the small range of l for which repulsive effects may occur. For example, if the repulsion were due to a hard core, the maximum l (say, l_{core}) in the restricted sum would be that l corresponding to the impact parameter $b=\hbar l_{\mathrm{core}}/(2mE)^{1/2}$, which equals the core radius. In practice, a parametrized function, which goes smoothly to zero at l_{core} and is large and negative at $l=0$, is used to represent the (repulsive) phase shifts because it allows more flexibility in fitting the finer points of the experimental differential cross section.

If one assumes an analytic function for the core phase shifts η_c, which rapidly go to zero, and adds to them the pole phases η_p, a total phase shift η results (see Fig. 1). That is, we have

$$\eta=\eta_c+\eta_A\ ,\quad S=e^{2i(\eta_c+\eta_A)}=S_cS_A\ ,$$

with

$$\eta_A=\sum_{p=1}^{N}\eta_p\simeq N\eta_p\ ,\qquad f(\theta)=f_c(\theta)+f_A(\theta)\ ,$$

where

$$f_c(\theta)=\frac{1}{2ik}\sum_l(2l+1)P_l(\cos\theta)[S_A(S_c-1)]\ ,$$

$$f_A(\theta)=\frac{1}{2ik}\sum_l(2l+1)P_l(\cos\theta)[S_A-1]\ .$$

The term $f_A(\theta)$ is the pole contribution to $f(\theta)$ and can be evaluated by simply summing over the poles

$$f_A(\theta)=\frac{1}{2ik}\sum_{p=1}^{N}\frac{\pi}{\cos\pi\lambda_p}\,[P_{\lambda_p-1/2}(-\cos\theta)]\,(\lambda_p^2-\lambda_p^{*2})$$

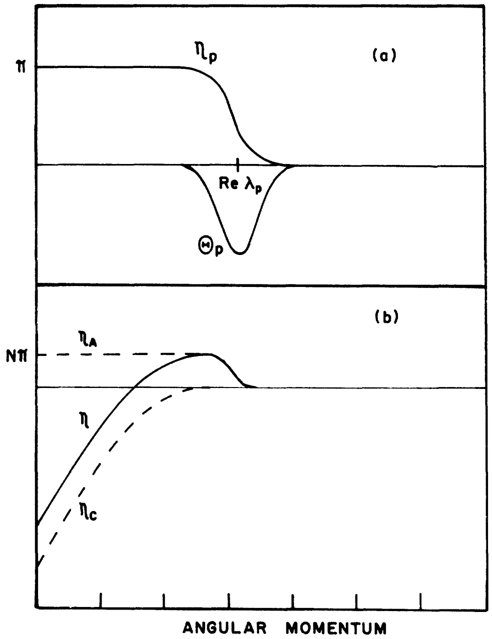

FIG. 1. (a) Phase shift η_p and deflection function Θ_p for a single pole located at λ_p. (b) Core phase shift η_c, pole phase shift η_A, and the total phase shift η for a typical attractive scattering system.

$$\times\left[\prod_{\substack{i=1\\ i\neq p}}^{N}\left(\frac{\lambda_p^2-\lambda_i^{*2}}{\lambda_p^2-\lambda_i^2}\right)\right]$$

For $l > l_c$, $\eta_c = 0$ and $S_c = e^{2i\eta_c} = 1$. Thus, we have

$$f_c(\theta) = \frac{1}{2ik}\sum_{l=0}^{l_{\rm core}}(2l+1)P_l(\cos\theta)[S_A(S_c-1)] \ .$$

The simplicity of the application of the Remler-Regge method is very impressive. This is due to the close connection that can be drawn between this method and the semiclassical idea of a deflection function. Explicit relationships between the deflection function and the pole parameters of the Remler-Regge model will be given. It is instructive to digress briefly and qualitatively discuss the differential cross section in terms of semiclassical ideas. As an example, consider the deflection function for the $H^+ + Ar$ system (collision energy = 5 eV) shown in Fig. 2. Semiclassically, the oscillations seen in the data are attributable to the interference at the same angle θ of partial waves corresponding to scattering from the three branches of the deflection function (i.e., from the two attractive branches at l_a and l_b and from the repulsive branch at l_c). The maximum attractive scattering angle is θ_R, and for $\theta > \theta_R$ no further interference phenomena should be seen in the differential cross section. The number of low-frequency oscillations between 20° and θ_R increases with increasing width of the attractive well of $\Theta(l)$ (or alternatively, decreasing its curvature). The period of the high-frequency oscillations in this same angular range is a very sensitive function of l_R (increasing with decreasing l_R). Finally, at low scattering angles the cross section should contain three different frequency components. The lowest, which is dominant, has periodicity[12]:

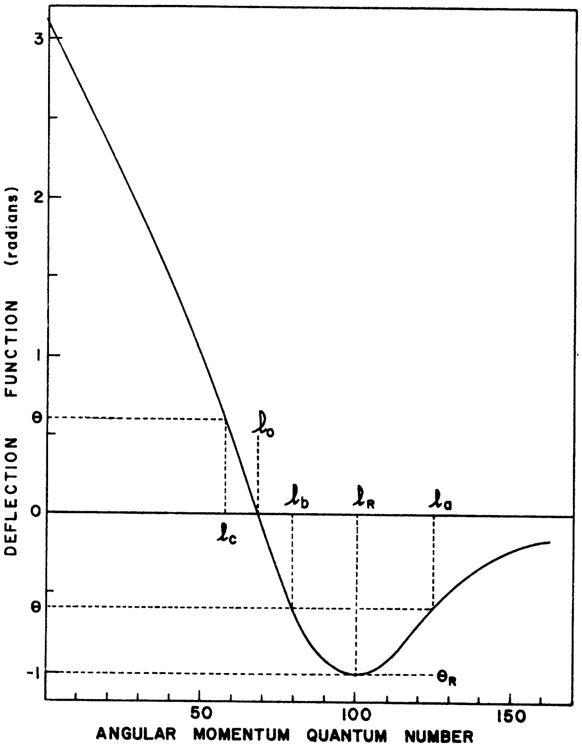

FIG. 2. Deflection function for $H^+ + Ar$ at a collision energy of 5 eV.

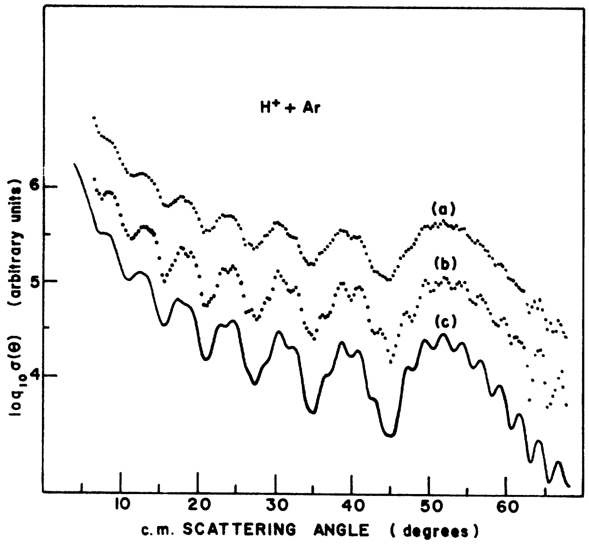

FIG. 3. Differential elastic scattering cross section for $H^+ + Ar$ at 5 eV. (a) Experimental data, (b) deconvoluted experimental data, (c) Remler-Regge fit utilizing pole parameters of Table I.

$$\Delta\theta = 2\pi/(l_a - l_0) \ . \tag{2a}$$

The intermediate, which is more quickly damped out at small angles, has

$$\Delta\theta = \pi/l_0 \ , \tag{2b}$$

while the periodicity of the highest frequency term is

$$\Delta\theta = 2\pi/(l_a + l_0) \ . \tag{2c}$$

It is of interest to note that the first and last terms just discussed are clearly visible in the deconvolution of our 5-eV $H^+ + Ar$ experiment for angles less than 20° (see Fig. 3).

The deflection function parameters just discussed may be closely connected with the pole and core parameters of the Remler-Regge method. The rainbow angle θ_R, its location l_R, and the full width of the deflection function $\Gamma_{1/2}$ at $\theta = \frac{1}{2}\theta_R$ are given by

$$\theta_R = 2N\left(\frac{{\rm Im}\lambda_p}{({\rm Re}\lambda_p)^2 + ({\rm Im}\lambda_p)^2} - \frac{1}{{\rm Im}\lambda_p}\right) \simeq \frac{2N}{{\rm Im}\lambda_p} \ , \tag{3}$$

$$l_R = \mathrm{Re}\lambda_p, \quad \Gamma_{1/2} \simeq 2\,\mathrm{Im}\lambda_p .$$

The zero of the deflection function, l_0, is an adjustable parameter in the analytic expression which represents the repulsive core.

Using these semiclassical considerations, the values for N, $\mathrm{Re}\lambda_p$, $\mathrm{Im}\lambda_p$, and l_0 may be fairly well approximated by inspection of the experimental data. The Remler-Regge method may then be used to predict the differential cross section. On the basis of this calculation the set of parameters may be adjusted and this procedure repeated until satisfactory agreement between data and calculation is achieved.

In conclusion, the decoupling of the parameters $\mathrm{Re}\lambda_p$ and $\mathrm{Im}\lambda_p$ as well as the simple relation between $\mathrm{Im}\lambda_p$ and N [seen in Eqs. (3)] makes the iterative procedure to obtain $\eta(l)$ from $\sigma_{\mathrm{expt}}(\theta)$ quick and efficient. It has been shown[6] that in the case of well-resolved experimental data the deflection function, the phase shifts, and the intermolecular potential thereby obtained are reliably determined.

B. Intermolecular Potential from Phase Shifts

If the phase shifts can be obtained by methods such as those outlined above, then the intermolecular potential (within the realm of the validity of the JWKB approximation) can be uniquely determined. Vollmer and Krüger[8] have reduced this problem to that of solving for the "quasipotential" $Q(t)$:

$$Q(t) = \frac{4E}{\pi k}\,\frac{1}{t}\,\frac{d}{dt}\int_t^\infty \frac{B\eta(B)\,dB}{(B^2 - t^2)^{1/2}} ,$$

where E = collision energy, k = wave number,

$$B = (l + \tfrac{1}{2})/k , \quad \eta = \text{JWKB phase shift} ,$$

and where the intermolecular potential $V(r)$ is related to $Q(t)$ through the expressions

$$V(r) = E(1 - e^{-Q(t)/E}) , \quad r(t) = t e^{Q(t)/2E} .$$

The expression for $Q(t)$ is evaluated by numerical integration after a variable change, $B = t/\cos\alpha$ is made. It should be pointed out that for small values of t [the region where $Q(t)$ is positive], extremely accurate integration schemes are necessary in order to obtain satisfactory values for $r(t)$. Double precision arithmetic is employed throughout for evaluating $Q(t)$.

The validity of the JWKB approximation for the phase shifts has been discussed by numerous authors. Marchi and Mueller[13] have compared JWKB approximated phase shifts to those found by direct integration of the radial Schrödinger equation for a Lennard-Jones-type intermolecular potential. They conclude that, for cases where classical "orbiting" is excluded, the JWKB phase shifts are quite reliable and give differential cross sections nearly identical to those calculated by the exact method.

Although the quantitative construction of the intermolecular potential can be accomplished as outlined above, it is intuitively pleasing to have a way of visualizing some aspects of the qualitative relation between $V(r)$ and $\Theta(l)$. The general shape of the potential is closely related to that of the deflection function. The width and depth of the potential well are correlated with the width and depth of the attractive portion of the deflection function. In our analysis of the proton + rare-gas systems we have noted that the value of l for which the classical turning point equals the equilibrium separation (r_m) is in the vicinity of l_0, while l_R is similarly associated with the intermolecular separation that corresponds to the maximum attractive intermolecular force. Consequently if a differential scattering experiment determines $\Theta(l)$ accurately over the range $l > l_0$, one would have similar confidence in the inverted $V(r)$ for $r > r_m$.

III. APPLICATION

A. $H^+ + Ar$

The 5-eV $H^+ + Ar$ experimental elastic differential cross section shown in Fig. 3(a) has the necessary resolution to be a good candidate for the inversion procedure discussed in Sec. II. Even though the experimental differential cross section does show the high-frequency structure mentioned in Sec. IIA and in Ref. 6, the data has been deconvoluted using the technique of Ioup[14] in order to more clearly present the scattering features for the inversion procedure. It should be noted that the deconvolution is used as a mathematical tool and in this case is acceptable insofar as it reproduces the fine oscillations already observed in the data. The deconvoluted data is much easier to work with in the inversion procedure as it is necessary to make a good fit to the fine oscillations as well as to other features of the data in order to best determine the shape of the deflection function (and thereby the intermolecular potential).

The first step in the inversion is to bring the Remler-Regge calculation, Fig. 3(c), into good agreement with the deconvoluted data, Fig. 3(b). The initial choice of pole parameters is clearly motivated by semiclassical considerations. The rainbow angle θ_R and the width $\Gamma_{1/2}$, may be quickly approximated by fitting the low-frequency oscillatory term of the Ford and Wheeler rainbow approximation

$$\mathrm{Ai}^2[(\theta - \theta_R)/q^{1/3}] ,$$

where

$$\Gamma_{1/2} = (2\theta_R/q)^{1/2} ,$$

TABLE I. Pole parameters used to fit the calculated cross section to the experimental cross section. The phase shifts obtained by using these parameters were inverted to find the intermolecular potentials for the various molecular ions. The resulting dissociation energies D_e and the equilibrium separations r_m are also given.

System	Collision energy (eV)	$\mathrm{Re}\lambda_p$	$\mathrm{Im}\lambda_p$	N	l_0	D_e (eV)	r_m (a_0)
ArH^+	5.0	100.2	25.78	13	67	4.22	2.35
NeH^+	5.71	78	23.24	6	50.1	2.27	1.90
KrH^+	6.0	138.2	33.6	16	91.2	4.6	2.9
HeH^+	4.0	44	15.04	5	29.5	2.18	1.41

to the low-frequency oscillations in the experimental data in the vicinity of the rainbow angle. The large-angle high-frequency term in the expression for the cross section determines the value of $l_R + l_c$. That is, we have

$$\Delta\theta = 2\pi/(l_R + l_c)\ ,$$

where $\Delta\theta$ is the angle between adjacent maxima of the high-frequency component of the cross section. The value of l_0 is originally approximated as the average of l_R and l_c. In the actual calculations, however, l_0 is adjusted until the two frequency components seen at low angles $[2\pi/(l_a \pm l_0)]$ agree with those resolved in the experiment. Using the initial estimates for θ_R, $l_R + l_c$, l_0, and $\Gamma_{1/2}$, an approximate deflection function is determined. The deflection function may then be related to the pole parameters via Eqs. (3), and the Remler-Regge method may be used for a prediction of the cross section. This technique gives a reasonable first approximation of the pole parameters, and only slight variation of these parameters is necessary to bring the Remler-Regge calculated differential cross section into very good agreement with the experimental data. Figure 3(c) is a plot of this calculation, and the agreement between it and the data is seen to be excellent. Parameter values used in this calculation are given in Table I.

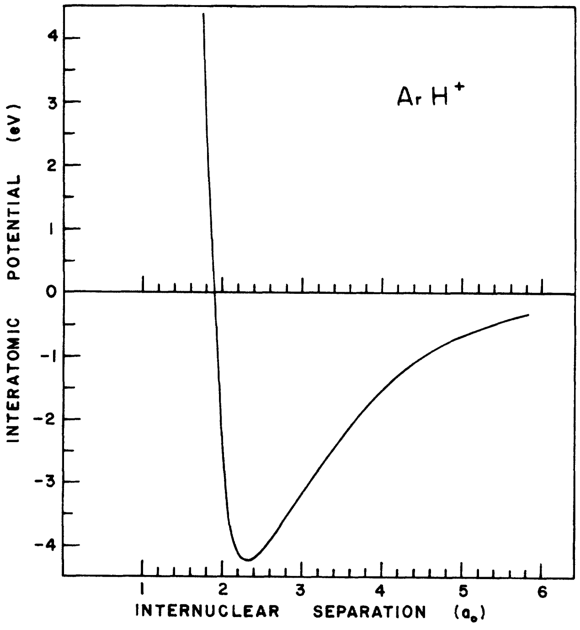

FIG. 4. Interatomic potential for the ArH^+ molecular ion from the inversion of 5-eV $\mathrm{H}^+ + \mathrm{Ar}$ experiment.

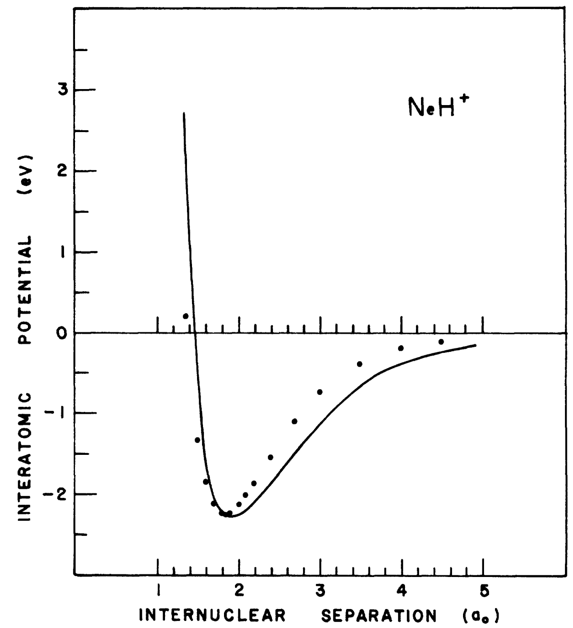

FIG. 5. Interatomic potential for the NeH^+ molecular ion from the inversion of 5.71-eV $\mathrm{H}^+ + \mathrm{Ne}$ experiment (solid line) and results of Peyerimhoff (dots).

The method outlined in Sec. IIB was used to construct the intermolecular potential using the phase shifts retrieved from the Remler-Regge calculation. Since the 5-eV $(\mathrm{ArH})^+$ data presents little information on the dark side of the rainbow (i.e., θ greater than θ_R), the potential can not be accurately predicted for $V(r) \gtrsim 0$ in this case. In order to check (and possibly improve) the calculation for the repulsive portion of the potential, a higher-energy (14 eV) experiment, which did not contain as much bright side information but contained considerable information for θ greater than θ_R, was analyzed. The repulsive portion of $V(r)$ was found to be very sensitive to the large negative slope of the differential cross section in this region. The resulting inverted intermolecular potential which reproduces all the observed features in the 5- and 14-eV experiments is shown in Fig. 4. It was indeed gratifying to see that the interference scattering as well as the dark side features observed in

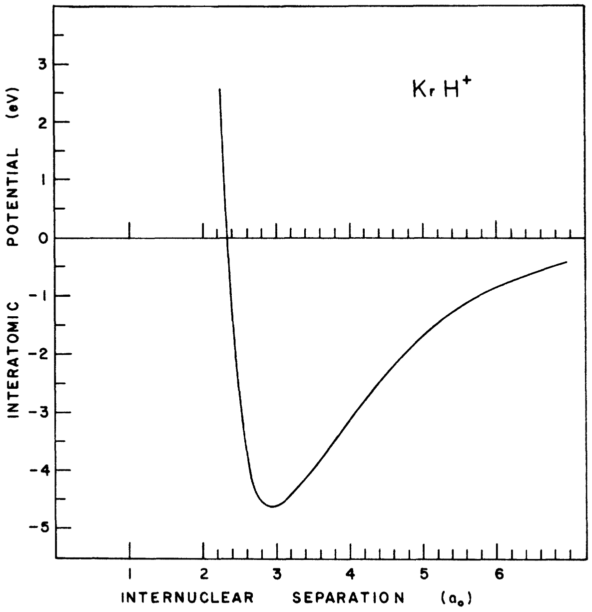

FIG. 6. Interatomic potential for the KrH$^+$ molecular ion from the inversion of 6-eV H$^+$ + Kr experiment.

the 14-eV data and all the details observed in the 5-eV experiment were well reproduced by a single intermolecular potential.

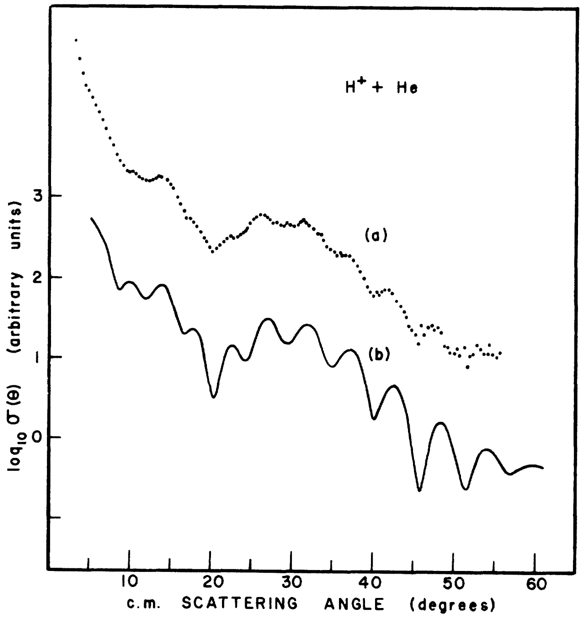

FIG. 7. Differential elastic scattering cross section for H$^+$ + He at 4 eV; (a) experimental data, (b) Remler-Regge fit utilizing pole parameters of Table I.

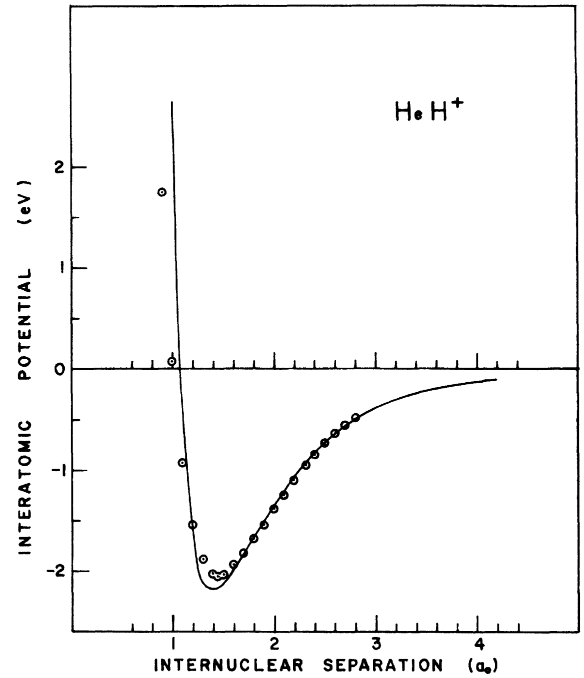

FIG. 8. Interatomic potential for the HeH$^+$ molecular ion. The solid line is the result of the inversion of the 4-eV H$^+$ + He experiment; the circles are values of a function (Ref. 17) which has been fit to the calculation of Wolniewicz.

B. H$^+$ + Ne

The H$^+$ + Ne system has been discussed in some detail earlier,[6] and it was shown that the differential cross section predicted by an *ab initio* calculation of the intermolecular potential due to Peyerimhoff[15] was in good agreement with the experimental results. Since the low-frequency oscillations at small angles are not clearly identifiable in the differential cross section, Eqs. (2) can not be used to determine l_0 for the deflection function. However, the very distinct fine oscillations observed in the experimental data serve to fix the value of $l_R + l_c$ while the low-frequency rainbow structure determines the rainbow angle as well as the curvature of $\Theta(l)$. Thus, one can obtain initial values for the pole parameters. The Remler-Regge method is then iteratively employed to bring the calculation into close agreement with the experimental differential cross section. These final pole parameters and resulting phase shifts have been inverted yielding the intermolecular potential which is seen in Fig. 5 along with the calculation of Peyerimhoff.

C. H$^+$ + Kr

The H$^+$ + Kr experiment [the results can be seen in Ref. 2(d)] does not resolve any fine oscillations in the differential cross section. Therefore a direct determination of l_R in the deflection function is not possible. However, the large number of low-frequency oscillations seen in the data does allow the construction of the attractive well of the deflection function utilizing the methods of Sec. II B. In order to fix the scale of l for $\Theta(l)$, it is assumed that the ratio of l_a to l_0 for the last few well-resolved large oscillations at low scattering angles is approximately 2; therefore $l_0 = 2\pi/\Delta\theta$. Although this assumption has not been theoretically justified, it has been observed that such is the case for the other proton–rare-gas-atom deflection functions which were constructed from data exhibiting fine oscillations. Basing the initial estimate for the pole parameters on this deflection function, several iterations suffice to bring the calculated differential cross section into agreement with the (low-resolution) experimental cross section. The final pole parameters (Table I) were then used for determining the intermolecular potential and that result is seen in Fig. 6. In this case the intermolecular potential is obviously less reliable than that for ArH^+ and NeH^+, where high-frequency oscillations are observed.

D. $H^+ + He$

Extensive *ab initio* calculations of the intermolecular potential of HeH^+ have been made, and the recent calculations of Wolniewicz[9] are believed to be the most accurate to date. In a previous paper,[16] comparison was made between the measured differential elastic cross section at 4 eV for the proton-helium system and a JWKB calculation of the cross section which utilized the *ab initio* HeH^+ potential of Wolniewicz. The agreement between the calculated and measured cross sections is very satisfactory. Therefore, it would seem appropriate to use the experimental data for HeH^+ to test the operational validity of the scheme outlined in Sec. II which is designed to recover the intermolecular potential directly from the scattering data.

The experimental cross section for $H^+ + He$ at 4 eV collision energy along with the Remler-Regge fit (see Table I for pole parameters) is seen in Fig. 7. The agreement between the two potentials can be seen in Fig. 8 where the inverted intermolecular potential is compared to an analytic function[17] which has been fit to the results of Wolniewicz. Although the dynamic scattering situation may not be best characterized by the well depth D_e and the equilibrium separation r_m, it is of interest to compare the values of Wolniewicz to those recovered by inversion procedure, viz., 2.04 eV vs 2.18 eV for D_e and $1.46a_0$ vs $1.41a_0$ for r_m, where the former values are those of Wolniewicz.

IV. CONCLUSIONS

The methods outlined in this paper can, when used in conjunction with sufficiently high-resolution experimental data, yield accurate intermolecular potentials over the internuclear distance which is effectively sampled by the particular experiment. The analysis and inversion techniques presented here should be applicable to any spherically symmetric scattering system for which the JWKB approximated phase shifts are thought to be adequate.

Recently, Mittmann and co-workers[18] have performed a series of high-resolution experiments on the systems reported in this paper. They have used various potential models with adjustable parameters to calculate $\sigma(\theta)$ in order to match their experimental data. Their results for the intermolecular potentials of ArH^+, NeH^+, and KrH^+ are in good agreement with those reported herein.

ACKNOWLEDGMENT

We would like to thank Professor E. A. Remler for many valuable discussions relevant to his work.

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[*] Work supported in part by the National Science Foundation and by NASA Grant No. NGL-47-006-055.

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