less than gas kinetic cross sections.

In our calculation, r_0 represents a hard-core interaction range, analogous to the classical distance of closest approach for two colliding particles. While a determination of r_0 from cross sections obtained in monoenergetic collision experiments would, in theory, be possible using the equations presented above, in practice it would be difficult since σ_d and σ_e vary within at most only one order of magnitude over the range of expected values of r_0. In the case of Ca*, H^- collisions, for instance, one expects r_0 to be in the neighborhood of 2–3 Å.

From the restrictions placed upon the theory by the approximations employed, it is evident that our method of calculating Penning detachment and photon-emission cross sections will be useful in gaining an order of magnitude estimate of the relative importance of these two processes when negative ions and metastable atoms collide. The cross sections associated with the H*, H^- system indicate that quenching of $H(2^1S)$ by ions, even H^-, is far more important than Penning detachment in regions such as the solar chromosphere where H^- is known to be abundant. In any neutral-ion collision system for which ΔE_{rm} is so small that *diabatic* contributions become dominant, quenching of the metastable state will dominate over Penning detachment even if adiabatic approximation indicates that $\sigma_d > \sigma_e$. On the other hand, interaction of H^- or other negative ion with atoms in metastable excited states associated with large ΔE_{rm} will result in Penning detachment (see Table II) and may be an important channel for deexcitation of such metastables.

ACKNOWLEDGMENTS

We thank Professor U. Fano for his helpful comments. This work was supported by the National Science Foundation under Grant No. GP-10547.

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PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Unitarity in Coulomb Scattering*

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It is demonstrated that the pure-Coulomb t matrix satisfies a modified unitarity condition and that its discontinuity is not zero, as has been asserted elsewhere.

Recently several attempts[1] have been made to evaluate the scattering amplitude for three charged particles via the impulse approximation applied to the Faddeev equations. All of these approaches rely on a result due to Nutt,[2] who contends that the discontinuity of the off-shell–Coulomb t matrix along the unitarity axis is zero. We will demonstrate here that this result is, in fact, wrong, so that those results based upon it are probably also incorrect.

To formulate the problem precisely, we follow Nutt and define the Coulomb t matrix by the integral representation derived by Schwinger[3]:

$$\langle \vec{K}_2 \,|\, T(K^2) \,|\, \vec{K}_1 \rangle = -\frac{e^2}{2\pi^2} \frac{1}{|\vec{K}_2 - \vec{K}_1|^2}$$

$$\times\left(1-\frac{4i\eta}{e^{2\pi\eta}-1}\frac{1}{\epsilon}\int_{C_0}dt\,t^{-i\eta}\frac{1}{(t-t_+)(t-t_-)}\right), \quad (1)$$

where

$$\eta=\frac{me^2}{K},\quad K^2=2mE,\quad \epsilon=\frac{(K^2-K_1^2)(K^2-K_2^2)}{K^2|\vec{K}_1-\vec{K}_2|^2},$$

$$t_+=\frac{1}{t_-}=\frac{(\epsilon+1)^{1/2}-1}{(\epsilon+1)^{1/2}+1}.$$

The integration contour C_0 begins at $t=1+i0$, moves to the origin, circles it once, and continues to $t=1-i0$. With this prescription, $\langle\vec{K}_2|T(K^2)|\vec{K}_1\rangle$ is a mathematically well-defined function of $\vec{K}_1$, $\vec{K}_2$, and K^2. At this point, it is worth noting that while the integrand in Eq. (1) is a multisheeted function of t, the poles at $t=t_\pm$ are present on every sheet. Thus, it is not possible to argue, as is done in Ref. 2, that one of these poles can disappear from the "principal" sheet by sliding through the branch cut, since it will be immediately and continuously replaced by a corresponding pole from another sheet.

The integral in Eq. (1) can be evaluated, as was done by Nutt, to show that

$$\langle\vec{K}_2|T(K^2)|\vec{K}_1\rangle=-\frac{e^2}{\pi}\frac{1}{|\vec{K}_1-\vec{K}_2|^2}\frac{\eta}{e^{2\pi\eta}-1}\times\left(\frac{(K^2-K_1^2)(K^2-K_2^2)}{4K^2|\vec{K}_1-\vec{K}_2|^2}\right)^{-i\eta}$$

$$+\text{analytic function of } K^2 \text{ for } \epsilon\to 0. \quad (2)$$

We will demonstrate that the representations given in Eqs. (1) and (2) satisfy a modified unitarity condition and therefore that the discontinuity of T across the unitarity cut is not zero. The unitarity relation may be written as

$$\langle\vec{K}_2|T(K^2+i\delta)|\vec{K}_1\rangle-\langle\vec{K}_2|T(K^2-i\delta)|\vec{K}_1\rangle=T-T^\dagger$$
$$=\int d^3K'\langle\vec{K}_2|T(K^2+i\delta)|\vec{K}'\rangle\langle\vec{K}'|T(K^2-i\delta)|\vec{K}_1\rangle$$
$$\times 2m[(K^2-K'^2+i\delta)^{-1}-(K^2-K'^2-i\delta)^{-1}], \quad (3)$$

where the limit $\delta\to 0$ is to be taken only after the evaluation of either side has been accomplished. We will evaluate both sides of Eq. (3) exactly and thereby demonstrate that they are, in fact, equal and, moreover, are not equal to zero.

We begin with the left-hand side of Eq. (3) since its evaluation is almost trivial. Using the integral representation, Eq. (1), we find

$$T-T^\dagger=\frac{e}{2\pi^2|\vec{K}_2-\vec{K}_1|^2}\frac{4i\eta}{\epsilon}\times\left(\frac{1}{e^{2\pi\eta}-1}\int_{C_0}dt\,t^{-i\eta}\frac{1}{(t-t_+)(t-t_-)}\right.$$
$$\left.+\frac{1}{e^{-2\pi\eta}-1}\int_{C_0}dt\,t^{i\eta}\frac{1}{(t-t_+^*)(t-t_-^*)}\right). \quad (4)$$

This is almost the same as Eq. (25) in Ref. 2, with the exception that in the second integral we have poles at $t=t_\pm^*$, whereas Nutt has placed them at $t=t_\pm$. A careful examination of the paths of $t_\pm$ as E goes from $K^2+i\delta$ to $K^2-i\delta$ will show that our expression is the correct one. We will suppose, as does Nutt, that we have chosen the labels $t_\pm$ such that $|t_+|<1$ and $|t_-|>1$. Then, taking $0<\arg(t)<2\pi$, we find

$$\arg(t_+^*)=2\pi-\arg(t_+). \quad (5)$$

The contour C_0 may be distorted into an integral around the unit circle plus an integral around the pole at $t=t_+$ in the negative sense. It is easy to show that the integral around the unit circle is zero, so we are left only with the residues at the poles $t=t_+$ and $t=t_+^*$. Since as $\delta\to 0$, $\arg(t_+)\to 0$, we are left with

$$T-T^\dagger=-2\pi i\frac{e^2}{2\pi^2}\frac{1}{|\vec{K}_2-\vec{K}_1|^2}\frac{4i\eta}{\epsilon}\times\left(\frac{1}{e^{2\pi\eta}-1}\frac{(t_+)^{-i\eta}}{t_+-t_-}+\frac{e^{-2\pi\eta}}{e^{-2\pi\eta}-1}\frac{(t_+)^{-i\eta}}{t_+-t_-}\right)$$
$$=\frac{4e^2}{\pi}\frac{\eta}{e^{2\pi\eta}-1}\frac{1}{|\vec{K}_1-\vec{K}_2|^2}\times\frac{1}{\epsilon}\frac{1}{(t_+-t_-)}[(t_-)^{i\eta}-(t_+)^{i\eta}]. \quad (6)$$

It is obvious that this will, in general, not be zero.

To evaluate the right-hand side of Eq. (3), we first realize that the only contributions will come from the product of the singular terms in T and $T^\dagger$. We must therefore consider the integral

$$\frac{2me^4}{\pi^2}\left(\frac{\eta}{e^{2\pi\eta}-1}\right)^2\int d^3K'\frac{1}{|\vec{K}_2-\vec{K}'|^2}\frac{1}{|\vec{K}_1-\vec{K}'|^2}\times\left(\frac{|\vec{K}_2-\vec{K}'|^2}{|\vec{K}_1-\vec{K}'|^2}\right)^{i\eta}\left(\frac{K^2-K_1^2}{K^2-K_2^2}\right)^{i\eta}\left(\frac{K^2-K'^2-i\delta}{K^2-K'^2+i\delta}\right)^{i\eta}$$
$$\times\left(\frac{1}{K^2-K'^2+i\delta}-\frac{1}{K^2-K'^2-i\delta}\right). \quad (7)$$

We have deliberately not replaced the discontinuity of the free-particle resolvent with a δ function, as was done in Ref. 2, since it is not the only factor which is singular near $K'=K$. Rather, both the last two factors are singular in this region and must be treated together in performing the integration. Since the last factor does approach a δ function as $\delta\to 0$, we may rigorously replace K' by K except where it appears in the combination $K'-K$. Thus, we write

$$\left.\begin{aligned} &K^2 - K'^2 + i\delta \to 2K(K-K') + i\delta = -re^{i\theta} \\ &K^2 - K'^2 - i\delta \to 2K(K-K') - i\delta = -re^{2\pi i - i\theta} \end{aligned}\right\} \quad 0<\theta<2\pi\,. \tag{8}$$

Using θ as our variable of integration, the integral over the singular terms becomes

$$\int_0^\infty \left(\frac{K^2-K'^2-i\delta}{K^2-K'^2+i\delta}\right)^{i\eta}\left(\frac{1}{K^2-K'^2+i\delta}-\frac{1}{K^2-K'^2-i\delta}\right) \times K'^2\,dK' = iKe^{-2\pi\eta}\int_\pi^{2\pi} e^{2\eta\theta}\,d\theta = i\pi K\left(\frac{e^{2\pi\eta}-1}{2\pi\eta}\right)\,. \tag{9}$$

We note that when $\eta \to 0$, this becomes the usual factor associated with short-range forces.

When the result in Eq. (9) is inserted in Eq. (7), we are left with

$$i\frac{me^4}{\pi^2}\,\frac{\eta}{e^{2\pi\eta}-1}\,K\int\left(\frac{|\vec{K}_2-\vec{K}|^2}{|\vec{K}_1-\vec{K}|^2}\right)^{i\eta}\frac{1}{|\vec{K}_2-\vec{K}|^2} \times\frac{1}{|\vec{K}_1-\vec{K}|^2}\left(\frac{K^2-K_1^2}{K^2-K_2^2}\right)^{i\eta} d\Omega_{\hat{K}}\,. \tag{10}$$

If we use the definition of η and define a new variable by

$$Z \equiv |\vec{K}_2-\vec{K}|^2/|\vec{K}_1-\vec{K}|^2\,, \tag{11}$$

we can write this as

$$i\frac{e^2}{\pi^2}\,\frac{\eta^2}{e^{2\pi\eta}-1}\,K^2\left(\frac{K^2-K_1^2}{K^2-K_2^2}\right)^{i\eta} \times\int Z^{i\eta}\,\frac{1}{|\vec{K}_2-\vec{K}|^2}\,\frac{1}{|\vec{K}_1-\vec{K}|^2}\,d\Omega_{\hat{K}}\,. \tag{12}$$

From the definition of Z, we have

$$(\vec{K}_2-\vec{K}_1 Z)\cdot\vec{K} = \tfrac{1}{2}(K^2+K_2^2) - \tfrac{1}{2}(K^2+K_1^2)Z\,. \tag{13}$$

For $Z=$ const, this represents a plane normal to $\vec{K}_2-\vec{K}_1 Z$ and at a distance h from the orgin where

$$h = [(K^2+K_2^2)-(K^2+K_1^2)Z]/2|\vec{K}_2-\vec{K}_1 Z|\,. \tag{14}$$

The limits on Z are determined by taking $h=\pm K$ with the result that the extreme values of Z are given by

$$Z = [(K^2-K_2^2)/(K^2-K_1^2)]t_\pm\,. \tag{15}$$

It is not difficult to show that as Z ranges between its limits, the family of planes defined by Eq. (13) all intersect the sphere $|\vec{K}|=K$ and are related to one another by a simple rotation about a fixed axis. If we consider the region of the sphere between planes corresponding to Z and $Z+dZ$, we obtain the situation depicted in Fig. 1. Here $r^2 = K^2-h^2$, $d\alpha$ is the angle between the vectors $\vec{K}_2 - \vec{K}_1 Z$ and $\vec{K}_2-\vec{K}_1(Z+dZ)$ which is determined to be

$$d\alpha = [|\vec{K}_1\times\vec{K}_2|/|\vec{K}_2-\vec{K}_1 Z|^2]dZ\,, \tag{16}$$

and θ is an angular variable which goes from 0 to 2π as we travel once around the strip enclosed by the two planes. The shaded element of area is found to be

$$K^2 d\Omega_{\hat{K}} = K[dh + r\sin\theta\,d\alpha]d\theta\,, \tag{17}$$

where θ is measured in an appropriate fashion. If we use the definition of Z to eliminate $|\vec{K}_2-\vec{K}|^2$ and express $\vec{K}_1\cdot\vec{K}$ in terms of θ and the angle between the vectors $\vec{K}_1$ and $\vec{K}_2-\vec{K}_1 Z$, which we shall call ϕ, we find that the integration over θ may be done rather easily, leaving us with the expression

$$i\frac{2e^2}{\pi}\,\frac{\eta^2}{e^{2\pi\eta}-1}\,K\left(\frac{K^2-K_1^2}{K^2-K_2^2}\right)^{i\eta}\int Z^{i\eta-1}\frac{a\,dh - b\,r\,d\alpha}{(a^2-b^2)^{3/2}}\,,$$

where

$$a = K^2+K_1^2-2hK_1\cos\phi\,, \qquad b = 2rK_1\sin\phi\,. \tag{18}$$

Realizing that

$$|\vec{K}_1\times\vec{K}_2| = |\vec{K}_1\times(\vec{K}_2-\vec{K}_1 Z)| = K_1|\vec{K}_2-\vec{K}_1 Z|\sin\phi \tag{19}$$

we see that

$$r\,d\alpha = [b/2|\vec{K}_2-\vec{K}_1 Z|]dZ\,. \tag{20}$$

Also, using the definition of h and after performing some manipulations, we find that

$$dh = [a/2|\vec{K}_2-\vec{K}_1 Z|]\,dZ\,, \tag{21}$$

so that our integral becomes

$$i\frac{e^2}{\pi}\,\frac{\eta^2}{e^{2\pi\eta}-1}\,K\left(\frac{K^2-K_1^2}{K^2-K_2^2}\right)^{i\eta}\int\frac{Z^{i\eta-1}\,dZ}{|\vec{K}_2-\vec{K}_1 Z|(a^2-b^2)^{1/2}}\,. \tag{22}$$

Using the definitions of a and b, it is not very difficult to show that the denominator in our integrand is independent of Z and is, in fact, given by

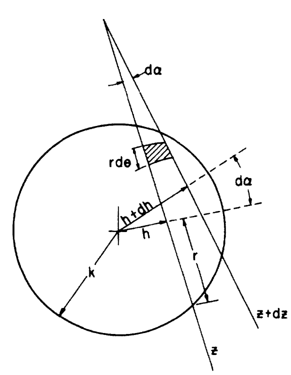

FIG. 1. Intersection of adjacent planes with sphere of radius K. Symbols are described in the text.

$$|\vec{K}_2 - \vec{K}_1 Z|\,(a^2 - b^2)^{1/2} = \tfrac{1}{4} K^2 |\vec{K}_1 - \vec{K}_2|^2 \epsilon (t_+ - t_-) \; . \tag{23}$$

With this fact, the integral over Z becomes trivial and recalling the limits on Z, we finally obtain the expression

$$\frac{4e^2}{\pi} \frac{\eta}{e^{2\pi\eta} - 1} \frac{1}{|\vec{K}_1 - \vec{K}_2|^2} \frac{1}{\epsilon} \frac{1}{(t_+ - t_-)} \left[(t_-)^{i\eta} - (t_+)^{i\eta} \right] \tag{24}$$

which is identical to the result obtained in Eq. (6). It thus appears rather obvious that the Coulomb t matrix does posses a branch cut along the unitarity axis, contrary to previous assertions. The crucial error in Ref. 2 is that the limit $\delta \to 0$ was taken incorrectly to yield the result

$$0 = T(K^2) - T(K^2) \neq \lim \left[T(K^2 + i\delta) - T(K^2 - i\delta) \right] \quad \text{as } \delta \to 0 \; . \tag{25}$$

We note that $T(K^2)$ does not satisfy the usual unitarity condition owing to the singular factor in the integral in Eq. (7) which gives rise to the extra multiplicative factor shown in Eq. (9). We may obtain a relation which looks more like ordinary unitarity if, like Schwinger,[3] we remove a factor $(K^2 - K'^2 + i\delta)^{-i\eta}(2\pi\eta)^{1/2}(e^{2\pi\eta} - 1)^{-1/2}$ from $T(K^2 + i\delta)$ and a similar factor of $(K^2 - K'^2 - i\delta)^{i\eta}(2\pi\eta)^{1/2} \times (e^{2\pi\eta} - 1)^{1/2}$ from $T(K^2 - i\delta)$ before performing the integral in Eq. (3).

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*Work supported in part by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. 71-1979.

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PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Resonance-Coupling Model for Simple Molecular Reactions*

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A strong-coupling model for the simple exchange reaction $A + BC \to AB + C$ is developed by considering the atom-diatom inelastic problems $A + BC$ and $AB + C$ separately and then introducing coupling between these configurations to allow for reaction. The inelastic systems are developed in the form of self-coupled differential-integral equations and are recoupled by the matrix element over internal states of the resonance energy between the adiabatic surfaces for the separate configurations. The model is applied to the $D + H_2 \to DH + H$ system and its isotopes in a two-level approximation. At the threshold energy (0.33 eV) for the $D + H_2 \to DH + H$ system, the calculated reactive total cross section is 1.62 Å^2 and the DH product is backscattered in the center-of-mass system.

I. INTRODUCTION

Advances in the technique of experimental molecular beams has renewed interest in the microscopic theory of chemical kinetics. In the present paper the dynamics of the simple exchange reaction $A + BC \to AB + C$ will be considered. To date, the appropriate equations of motion have been considered mainly in the classical case.[1] Quantum mechanically, the dynamics of the reaction may be considered within the framework of scattering theory. Weak-coupling (e.g., distorted wave) models[2,3] have been developed with the approximation of a linear alignment of A, B, and C; however they tend to underestimate the observable cross sections.

In these models the scattering amplitude is determined in its integral form for the two-state case. In the present paper, a strong-coupling model from the coupled-differential-equations approach will be investigated also using a two-state approximation. The coupled radial Schrödinger equations will be solved exactly and the $\underline{R}$ matrix determined numerically.

To begin our model, the relative motion of both configurations $A + BC$ and $AB + C$ is expressed in a common radial coordinate. The self-coupled sets of radial equations for each configuration are developed similar to the atom-diatom inelastic problem.[4] In Sec. III, coupling is introduced to account for the reactive process. The supposition is made that the self-coupled sets of radial equations for the separate configurations are recoupled by a matrix element over internal states of the resonance en-