teraction (see Fig. 1).

We conclude that intrachannel interaction in the continuum gives significant improvement in calculated photoionization cross sections near threshold. Interchannel interaction so far seems to have a minor influence on the gross spectral shape of the cross section. Possibly, the sizable remaining discrepancies between experiment and length and velocity results for the cross section can be accounted for by ground-state correlations, by interchannel interactions with series of doubly excited levels, and by the development of consistent formulas for the transition matrix element in approximate calculations.

ACKNOWLEDGMENTS

I would like to thank Professor U. Fano for numerous valuable discussions and suggestions. I am also indebted to Professor P. L. Altick for very helpful suggestions and for providing me with two of his computer programs.

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*Work supported in part by U. S. Atomic Energy Commission under Contract No. COO-1674-28.

†National Science Foundation Graduate Fellow.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 1 JULY 1970

Two-State Stueckelberg-Landau-Zener Theory Applied to Oscillatory Inelastic Total Cross Sections*

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(Received 6 January 1970)

The two-state Stueckelberg-Landau-Zener theory of curve crossings can be utilized to explain qualitatively many of the observed asymmetric-inelastic total cross sections. It predicts not only a broad maximum in the inelastic total cross sections as a function of velocity, but also a rapid rise to this maximum followed by a slow decline past the maximum. If the difference in the potentials between the two states possesses an extremum, oscillations superimposed upon the general velocity dependence of the inelastic total cross sections may also be expected because of the existence of a stationary phase. At high velocities, the spacing of these oscillations will be proportional to v^{-1}.

I. INTRODUCTION

The recent measurements of total charge-transfer cross sections by Perel *et al.*[1-3] on the alkali-alkali systems in the 0.5–10$\times 10^2$-cm/sec velocity range have shown prominent regularly spaced oscillations superimposed upon a smooth energy dependence of the cross sections. These oscillations occur in the asymmetric systems

$(A^+ + B \rightarrow A + B^+)$ where the process is inelastic as well as in the symmetric elastic systems $(A^+ + A \rightarrow A + A^+)$ where the effect is now well understood. An example of one set of measurements by Perel and Yahiku[2] is illustrated in Fig. 1. Several other authors[4] have also observed oscillations of a similar nature.

For the case of resonant symmetric charge-transfer systems, Smith[5] pointed out that the existence of an extremum in the difference between the g and u electronic states dissociating to an unexcited ion-atom pair would provide a natural source for prominent oscillations of the sort seen in these total cross sections. This prediction has been substantiated by *ab initio* calculations on the Li^+ - Li system by Peek, Green, Perel, and Michels.[6] Formulas for deriving the difference potential from the experimental data have also been set up.[7]

It is the purpose of this paper to point out that the same feature, namely, an extremum in the difference potential between the two electronic states involved in the charge exchange, is the source of the oscillations observed in asymmetric cases, as well as those seen in symmetric cases. This is substantiated by detailed calculations for a hypothetical example, the results of which are closely comparable with the experimental measurements of Perel *et al.* The principal difference between the symmetric and asymmetric cases is that in the former the two states involved do not cross each other, but have different symmetries (g and u), and they become degenerate when the particles are very far apart. In the asymmetric case, the two ion-atom pairs involved in the charge transfer have different energies at infinity,

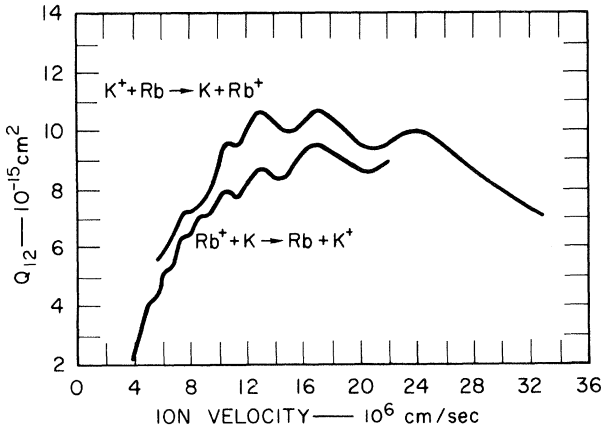

FIG. 1. Reproduction of the data of Perel and Yahiku (Ref. 2) on the asymmetric systems $K^+ + Rb \rightarrow K + Rb^+$ and $Rb^+ + K \rightarrow Rb + K^+$.

but there may be a crossing (in the diabatic sense), or a point of closest approach (a pseudocrossing in the adiabatic sense) between the two electronic states at some finite distance R_x. If the difference between the potentials has an extremum at some position inside the crossing or pseudocrossing, the conditions necessary for generating oscillations of this type exist just as much as they do in the symmetric system (which can be considered as a limiting case in which the crossing point has moved to infinity).

Qualitatively, this point of view is related also to an idea put forth by Lichten[8] who suggested that certain oscillations seen in symmetric ion-atom scattering would appear almost as strongly in asymmetric scattering, because the molecular wave functions appropriate to a description of the asymmetric systems have approximately g or u character when the internuclear distance becomes sufficiently small. There is, therefore, a transition between an outer domain in which the states are best described as an ion and an atom with the charge distribution well localized, and an inner domain, where the states are best described in a molecular framework with a delocalized charge, but with approximate g or u symmetry. The transition region between these domains can be approximately treated as a crossing, although it is perhaps better to consider it as a region where the nature of the coupling changes. Since the details of this description are probably not very important in establishing the major features under consideration, we have chosen to use the simple description of a curve crossing for illustrative purposes. The important factor is the extremum in the difference potential inside R_x, not the nature of the transition near R_x.

The oscillations in question here should be carefully distinguished from some other types of oscillations that have been seen and discussed recently. First, there is the feature that the existence of two or more electronic states, connected either by a curve crossing or a degeneracy at infinity, will lead to strong oscillations in the differential cross sections even in the absence of an extremum in the difference potential.[9] However, when these differential cross sections are integrated over angle (or when the contributions from all impact parameters are summed) to obtain a total cross section, the oscillations disappear or become very weak unless special phase relationships are favored in the summation or integration. An extremum in the difference potential provides the source for such a special phase relationship and results in strong oscillations.

Another situation, involving oscillations of a different type in inelastic total cross sections, has

been pointed out by Rosenthal.[10] He shows that the rapid oscillations in the inelastic cross sections for such systems as He^+ by He arise from the interaction of two or more crossings at very large internuclear distances. These effects are seen in the optical spectra of the states produced, but they would not be seen in simple charge-transfer scattering; and the Rosenthal mechanism does not explain the oscillations seen by Perel.

In Sec. II, the Stueckelberg-Landau-Zener (SLZ) curve crossing theory[11] for inelastic collisions is utilized to explain the source of the oscillations. The effect on the total cross sections by an extremum in the difference between potential states is described both theoretically and via a calculation of a hypothetical example.

II. THEORY

In the region where the two-state SLZ theory is applicable, the inelastic total cross section is given by[12]

$$Q_{12}=\frac{4\pi}{k_1^2}\sum_{l=0}^{l_x}(2l+1)P_l(1-P_l)\sin^2\tau_l \quad , \tag{1}$$

where k_1 is the wavenumber of the incident particles, and

$$P_l=\exp(-2v_x/v_l), \tag{2}$$

in which the probability P_l of transfer from one state to the other at the crossing is a function of a characteristic velocity v_x and the radial velocity at the crossing point v_l. The characteristic velocity is related to the parameters of the crossing point R_x by

$$v_x=\frac{\pi V_{12}^2(R_x)}{\hbar\,|\,V_{11}'(R_x)-V_{22}'(R_x)\,|} \quad , \tag{3}$$

where V_{12} is the interaction matrix and V_{11}' and V_{22}' are the first derivatives of V_{11} and V_{22} with respect to R. The phase factor τ_l is determined by the quadratures

$$\tau_l=\int^{R_x} g_+^{1/2}dR-\int^{R_x} g_-^{1/2}dR \quad , \tag{4}$$

where

$$g_\pm=\tfrac{1}{2}(f_1+f_2)\pm\tfrac{1}{2}[(f_1-f_2)^2+(8\mu/\hbar^2)V_{12}^2(R)]^{1/2} \, , \tag{5}$$

$$\text{with} \quad f_{1,2}=k_{1,2}^2-\frac{2\mu}{\hbar^2}V_{11,22}(R)-\frac{(l+\frac{1}{2})^2}{R^2} \quad . \tag{6}$$

Since V_{12} is usually small with respect to V_{11} and V_{22}, then

$$\tau_l=\int^{R_x} f_1^{1/2}dR-\int^{R_x} f_2^{1/2}dR \quad . \tag{7}$$

At high velocities, where $v_1\cong v_2=v$ and small impact parameters $b=(l+\frac{1}{2})/k$, Eq. (7) may be approximated by

$$\tau(b)=-\frac{1}{\hbar v_1}\int_b^{R_x}\frac{RV_{11}(R)\,dR}{(R^2-b^2)^{1/2}}+\frac{1}{\hbar v_2}\int_b^{R_x}\frac{RV_{22}(R)\,dR}{(R^2-b^2)^{1/2}} \quad . \tag{8}$$

Then Eq. (8) becomes

$$\tau(b)=-\frac{1}{\hbar v}\int_b^{R_x}\frac{R[\,V_{11}(R)-V_{22}(R)\,]\,dR}{(R^2-b^2)^{1/2}} \quad , \tag{9}$$

so that if the difference potential $\Delta V(R)=V_{11}(R)-V_{22}(R)$ possesses an extremum within R_x, it is possible for $\tau(b)$ to have an extremum.

If we replace the summation of Eq. (1) by an integral and use the classical analog which specifies that the impact parameter $b=(l+\frac{1}{2})/k$, then

$$Q_{12}=2\pi\int_0^{b_x} b\,\mathcal{P}(b)\,db \, , \tag{10}$$

where $\mathcal{P}(b)$ is the over-all transition probability from state 1 to state 2.

If we substitute for $\mathcal{P}(b)$, then

$$Q_{12}=8\pi\int_0^{b_x} bP(b)[1-P(b)]\sin^2\tau(b)\,db \quad . \tag{11}$$

Equation (11) may be reduced to a tabulated function if we replace the rapidly oscillating $\sin^2\tau(b)$ by its average value of 0.5 (the random-phase approximation). Equation (11) may then be rewritten

$$Q_{12}=4\pi R_x^2[1-V_{11}(R_x)/E]G(\lambda) \quad , \tag{12}$$

where $G(\lambda)$ is the tabulated integral

$$G(\lambda)=\int_1^\infty e^{-\lambda x}(1-e^{-\lambda x})x^{-3}dx \quad , \tag{13}$$

which has a maximum value of 0.113 when

$$\lambda=2V_x/v[1-V_{11}(R_x)/E]^{1/2}=0.424 \quad . \tag{14}$$

When an extremum in $\tau(b)$ exists, so will a stationary point[13] exist and an interference effect will be set up. [In other words, there will be nonrandom contributions to Eq. (10) about the stationary-point impact parameter giving rise to oscillations in the inelastic total cross sections.] The stationary-phase approximation may then be employed to determine Eq. (1) to yield a smoothly varying and an oscillatory term

$$Q_{12}=\overline{Q}-\frac{4P(1-P)\pi^{3/2}b_0}{|d^2\tau(b)/db^2|_{b=b_0}^{1/2}}\cos[\,2\tau(b_0)+\tfrac{1}{4}\pi] \quad , \tag{15}$$

where b_0 is the impact parameter at the stationary point. (If the difference potential inside R_x has a minimum, then the $\frac{1}{4}\pi$ within the cosine brackets will be $-\frac{1}{4}\pi$.) The smooth over-all behavior $\overline{Q}$ of Q_{12} is simply given by Eq. (12) and may be conveniently expressed in terms of the reduced parameter

$$Q_{max} = \tfrac{1}{2}\pi R_x^2 \quad . \tag{16}$$

At the stationary-point impact parameter and at high velocities where $V_{11}(R_x)/E$ is small, the radial velocity of Eq. (2) is a constant (less than unity) times the incident velocity. Thus, the quantity P of Eq. (15) is

$$P = \exp(-2v_x/av), \tag{17}$$

where a is a constant less than unity and is equal to $(1 - b_0^2/R_X^2)^{1/2}$.

From Eqs. (9) and (15), we see that the oscillations superimposed upon the smooth behavior will have a frequency proportional to v^{-1} in the high velocity limit. Since the stationary-point impact parameter is invariant with velocity, Eq. (9) may be written

$$\tau(b_0) = \text{const} \times v^{-1} \quad . \tag{18}$$

As the velocity is varied, extrema will occur when the difference in the phase factor at the stationary-point impact parameter proceeds through multiples of $\frac{1}{2}\pi$. Specifically, the extrema of the inelastic cross sections and phase factor may be parametrized as

$$\tau(b_0) = \pm(N - \tfrac{3}{8})\pi \quad , \tag{19}$$

where $N = 1, 2, 3, \ldots$ are indices for the maxima and $N = 1.5, 2.5, 3.5, \ldots$ refer to the minima. [The plus or minus sign of Eq. (18) refers to difference potentials that have a minimum or maximum, respectively.] If the extrema of the inelastic total cross sections are plotted versus v^{-1} and sequenced in the order above, a plot of N versus v^{-1} will have an intercept of $\frac{3}{8}$, and the slope will determine the constant of Eq. (18) which is composed of all the potential parameters. It is interesting to note, also, that an identical plot has been used for several years to retrieve potential information from the glories in low-energy atom-atom total cross sections.[14] In turn, the amplitude of the oscillations will be proportional to $P(1-P)v^{1/2}$.

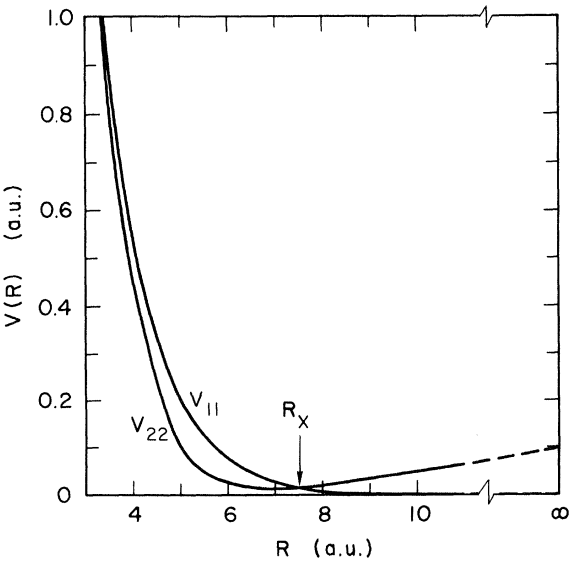

FIG. 2. Potentials used for the calculation. Here, $V_{11} = 29.7\exp(-R)$ and V_{22} was constructed so that $\Delta V = V_{11} - V_{22}$ has a maximum of 0.1 a.u. at 5 a.u. and zeros at $R = 0$ and R_x. At $R = \infty$, $\Delta V = -0.1$ a.u.

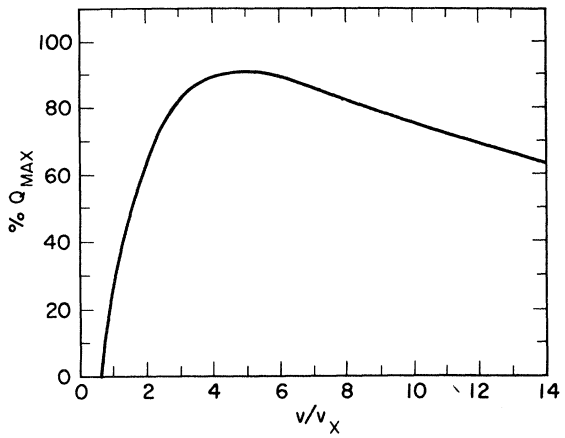

FIG. 3. General shape expected for the inelastic total cross sections as predicted by SLZ theory.

Equations (7)–(15) are based upon a number of approximations. Therefore, in Sec. III a hypothetical example has been set up and calculated via Eqs. (1)–(6) so that a comparison can be made with the predictions. It must be remembered also, that any agreement with experiment can only be qualitative because of the limitations on the SLZ theory itself.

III. EXAMPLE

A hypothetical example has been set up to test the predictions made in Sec. II. The inelastic total cross sections were computed by means of Eqs. (1)–(6), not via the stationary-phase approximation. The $V_{11}(R)$ potential was chosen to be a simple repulsive potential of the form $V_{11}(R) = 29.7\exp(-R)$. $V_{22}(R)$ was then constructed so that $\Delta V(R) = V_{11}(R) - V_{22}(R)$ was equal to -0.1 a.u. at $R = \infty$, and equal to 0.0 a.u. at $R = 0$ and $R = R_x = 7.5$ a.u. A broad maximum with a magnitude of 0.1 a.u. was positioned at 5.0 a.u. Figure 2 illustrates the two potentials used. The interaction potential V_{12} was set equal to 0.0122 a.u. for all R.

The predicted smooth shape of the inelastic total cross sections $\overline{Q}$ may be calculated from Eq. (12). This shape is illustrated in Fig. 3. Here the assumption is made that $V_{11}(R)/E = 0$. The re-

duced units v_x of Eq. (3) and Q_{max} of Eq. (16) are employed (in this case, $v_x = 0.0166$ a.u. and $Q_{max} = 87.8$ a.u.). Note the rapid rise of the inelastic total cross sections with velocity to a broad maximum and then a generally slow decrease with increasing velocity.

We next examine the result when the full treatment of Eqs. (1)–(6) is employed with the calculation of all quadratures. Figure 4 displays the resulting inelastic cross sections with very pronounced oscillations. As shown in the theory section above, these oscillations are simply a result of the difference potential possessing a maximum within R_x. The oscillations have been indexed and plotted versus v^{-1} (Fig. 5). There is a distinct energy dependence which is expected. Equation (9) is only the first term in an expansion with the next term proportional to v^{-3}. Also, at lower velocities as the threshold is approached, the approximation $v_1 = v_2$ is invalid. The high velocity theoretical intercept of $\frac{3}{8}$ is obtained.

IV. DISCUSSION

A qualitative comparison of the calculations with the experimental measurements of Perel *et al.*[1-3] can be made. On Fig. 1 are representative inelastic total cross sections for only one of the many

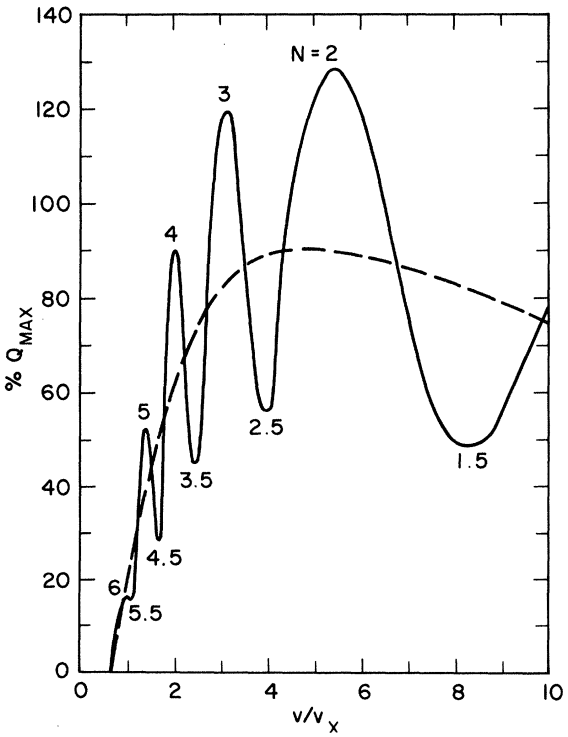

FIG. 4. Calculated reduced inelastic total cross sections for the potentials of Fig. 1. The reduced parameters are defined in Eqs. (3) and (15). The indexing numbers N are also included.

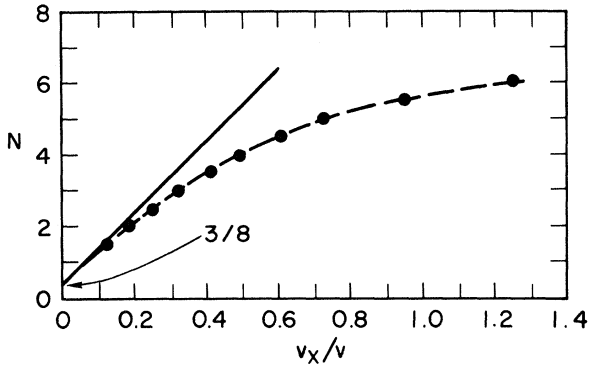

FIG. 5. Plot of the indexing numbers versus v^{-1} showing the energy dependence and the theoretical $\frac{3}{8}$ intercept.

alkali-alkali systems measured by these workers. As in most of their other cases the smooth portion of the cross sections is similar to that predicted by the two-state theory (Fig. 3). The oscillations in turn are also proportional to v^{-1}. In Fig. 6, the experimental oscillations of several systems have been indexed and plotted versus v^{-1}. The oscillations are linear in v^{-1}. However, the experimental intercept is $\frac{7}{8}$, which indicates that there is a phase constant missing in Eq. (1). The experimental phase factor is therefore $\frac{1}{2}\pi$ which is not in accord with the work of Thorson and Boorstein[15] who found $\frac{1}{4}\pi$ or our work here[16] in which we find the phase factor to vary between 0 and $\frac{1}{4}\pi$. The Stueckelberg phase factor tends to change with the system studied and so the experimental $\frac{1}{2}\pi$ is not too surprising.

Also, the SLZ theory does predict identical cross sections for $A^+ + B \rightarrow A + B^+$ and $B^+ + A \rightarrow B + A^+$. The work of Perel, however, indicates that there are slight differences in the magnitude of the cross sections for the above reactions. This may be seen in Fig. 2. The positions of the extrema, nevertheless, remain fixed. This may indicate another inadequacy of the SLZ theory.

V. SUMMARY

The SLZ two-state theory has been utilized to show that if the difference between the potentials of the two states possesses an extremum, oscillatory structure may be observed on the inelastic total cross sections. In the high-velocity limit, the frequency of these oscillations will be proportional to v^{-1}.

Qualitative agreement between experiment and theory can be obtained with the measurements of Perel *et al.*[1-3] who investigated alkali-alkali asymmetric charge exchange scattering of the type $A^+ + B \rightarrow A + B^+ + \Delta E$. Here the magnitude of the

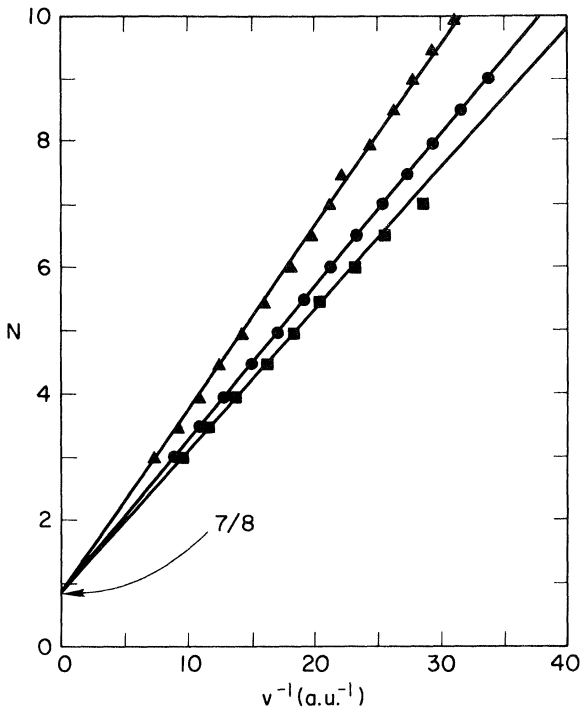

FIG. 6. Plots of the indexing numbers N versus v^{-1} for some of the experimental data of Perel *et al.* The solid triangles refer to the $Na^+ + K \rightarrow Na + K^+$ data,[2] the solid circles refer to the $Rb^+ + K \rightarrow Rb + K^+$ data,[2] and the solid squares refer to the $Rb^+ + Cs \rightarrow Rb + Cs^+$ data.[1]

inelastic cross sections indicates that the transfer of charge occurs at large internuclear distances, approximately 15 a.u. The polarizabilities for the various alkali atoms are very large and vary greatly among themselves.[17] The difference between the polarizabilities of the atoms would yield a long-range R^{-4} difference potential that would rapidly increase with decreasing R values. Ultimately, however, the short-range forces would dominate and for both initial and final states the same Coulomb potential would apply. It is thus not unreasonable to expect a maximum in the difference potential for these reactions. Also, an extremum may occur because of unusual features in the correlation diagram. The applicability of the two-state approximation is inferred by the fact that the general shape is similar to that predicted and the oscillations have a v^{-1} dependence. The amplitude of the oscillations are also compatible with theory.

It must be remembered that the SLZ is qualitative in nature and may be employed only to better understand the observed phenomena. It encompasses only two states and at high velocities predicts an incorrect v^{-1} dependence in the inelastic total cross sections.[18]

ACKNOWLEDGMENT

The author wishes to thank Dr. Felix T. Smith for helpful discussions and comments on this manuscript.

*Work supported in part by an Atholl McBean Fellowship at the Stanford Research Institute.

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