was poor, since they were weak and situated on an upward-sloping background. Although in the transmission experiment structures 5 and 6 appeared to belong to different series from band c, our five resonances, to within experimental accuracy, could belong to a single vibrational series, with an average spacing in excellent agreement with the 0.23-eV[5] spacing for the $A\,^2\Pi_u$ state of N_2^+. In Fig. 2 we have sketched as a broken line a possible potential curve for the resonant state of N_2^-. This has been drawn on the assumption that it has the same shape as the N_2^+ grandparent $A\,^2\Pi_u$, and that, as suggested by Sanche and Schulz,[5] the lowest vibrational resonance is at 12.6 eV. The relative intensities (see Table I) of the observed series can be understood in terms of Franck–Condon factors for excitation from the ground $X\,^1\Sigma_g^+$ state of N_2, and the resonances would then autoionize into appropriate vibrational levels of metastable $A\,^3\Sigma_u^+$ and $a\,^1\Pi_g$.

ACKNOWLEDGMENTS

The establishment of our electron spectrometer in Amherst would have been impossible without the advice and technical help of the Electron Physics Section of the National Bureau of Standards. We are grateful to George Schulz and Walter Borst for stimulating discussions and for making available material prior to publication.

*Work supported in part by the University of Massachusetts, the National Bureau of Standards, and the Air Force Office of Scientific Research under Contract No. F44620-70-C-0042.

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PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Semiclassical Collision Theory within the Feynman Path-Integral Formalism*

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(Received 29 August 1972)

A multichannel semiclassical collision theory, based on Feynman's path-integral formulation of quantum mechanics and developed by Pechukas, is discussed. The theory is applied to low-energy, elastic and inelastic, collisions between He^+ and Ne. The calculation involves the solution of a boundary-value problem, and a numerical method for obtaining this solution is presented. The numerical results and the qualitative interpretation of them are compared with the predictions of other available theories.

I. INTRODUCTION

One of the more serious problems encountered in collision theory is that of finding experimental information of sufficient quality and detail to allow one to critically evaluate a particular theoretical interpretation. Not only must the experimental information be quantitatively reproducible, but it should also, ideally, display qualitatively new features. In the area of low-energy atomic scattering this type of information has recently been produced by Lorents and Aberth[1] and has been given an extensive theoretical analysis by Smith and co-workers.[2] The present calculation is an attempt to supplement the existing interpretation of some of this information. We present the results of elastic and inelastic scattering of He^+ off Ne, at an impact energy of 70.9 eV, using a two-state electronic representation, together with a classical nuclear model. The impact energy is sufficiently low so

that the exact nature of the nuclear model is quite important for both elastic and inelastic processes. This therefore allows one to critically test the value of the nuclear model used here even though the comparison with experimental results is only a qualitative one.

The main experimental feature in which we are interested is a perturbation[3] in the elastic scattering differential cross section which has been observed for He^+-Ne, as well as for other systems. It has been associated with the onset of inelastic processes due to a curve crossing of diabatic energy surfaces. A number of theoretical discussions of this perturbation have already been given.[4-7] They have been successful in qualitatively explaining the fact that the perturbation is localized in the threshold region where the classical turning point is close to the point at which the energy levels cross. However, they suffer from the fact that the interpretation is based on a Landau-Z ener-Stueckelberg (SLZ)[8-10] model of electronic behavior. The present calculation is an attempt to find out whether the same interpretation is obtained when SLZ theory is not appealed to. In the course of the calculation it was found that the precise nature of the nuclear model was crucial in determining the form of this perturbation, and therefore the theory presented here concentrates only on the nuclear motion, assuming that the electronic interactions are known in some sense. The formal aspects of our nuclear model have been developed by Pechukas[11] using the Feynman[12] path-integral formulation of quantum mechanics. The classical equations of motion are retrieved by performing a stationary-phase approximation to a reduced[11] Feynman propagator. As a result, one obtains an interpretation of the electronic motion which is qualitatively quite similar to the impact-parameter interpretation, although the nuclear equations of motion are quite different. In the present theory it is found that the nuclear trajectory can only be determined through the solution of a boundary-value problem. The reason for this is that the force law governing nuclear motion has a dependence on the future behavior of the electrons, as well as their past behavior. In special cases it has been shown[11,13] that this difficulty can be removed if one is willing to make analytical approximations (such as SLZ) in the electronic equations of motion. In general, however, one is left with a boundary-value problem whose numerical solution is nontrivial.

Before discussing this theory we will briefly mention two other "classical" nuclear models which at a first glance might seem to be applicable to the He^+-Ne system. It was found that neither of these two models yielded worthwhile information in the present case, but both were helpful in the qualitative interpretation of the electronic motion. The simplest model is obtained from impact-parameter theory where the nuclei follow a stationary, or local, energy surface (i.e., the energy surface has no velocity or time dependence). The applicability of this theory to low-energy scattering has been discussed by Bates and Holt.[14] They conclude that it is properly applicable only when the differences between the various possible nuclear trajectories, corresponding to different electronic eigenstates, can be ignored. In the present case, therefore, the stationary-energy-surface–impact-parameter (SESIP) theory is of no value. We will use it in Sec. IV as a first approximation in an iterative procedure and as an aid in the qualitative interpretation of results, but not as a quantitatively reliable theory. Another theory which could be used is obtained when an average[15] energy surface replaces the stationary energy surface in the impact-parameter theory. This energy surface is obtained by averaging the Hamiltonian matrix over the existing electronic state at any time t. Intuitively, one would hope that this procedure would allow the nuclei to respond correctly to any particular electronic rearrangement. Formally, however, if one attempts to motivate this nuclear model using the method of Bates and Holt, it is found that the average-energy-surface theory is plagued by the same theoretical shortcomings as SESIP theory. From a more practical point of view it has recently been shown[16] that this theory is incapable of correctly predicting the energy dependence of the rainbow-scattering angle for H^+-Kr and H^+-Ar.

Both of the above theories suffer from the fault that they employ nuclear models which do not follow naturally from the fully quantum-mechanical equations for low-energy scattering. The electronic behavior which they predict is clearly acceptable, but the nuclear equations of motion are not generally valid. For inelastic processes this can be most easily seen by noting that the post-collision energy surfaces do not behave as they should. If one is interested in the electronic transition $\alpha \to \beta$, one would expect the precollision and post-collision energy surfaces to be given, respectively, by the αth and βth eigenenergies, regardless of what the intermediate behavior is. Neither of the above theories satisfies this requirement since the nuclear-force law does not explicitly recognize the final state β. From this point of view it is reasonable that a good classical nuclear model should involve some kind of boundary-value calculation.

In Sec. II we present the formal theory used in this calculation together with a qualitative discussion of the nuclear model. The interpretation used here differs somewhat from existing interpretations,[6,7] especially as it relates to the perturbation

in the elastic scattering cross section, and these differences will be mentioned.

II. MODEL

We define the reduced Feynman propagator[11,13] for the scattering problem by the relation[17]

$$K_{\beta\alpha}(\vec{R}''t'', \vec{R}'t') = \int_{t'}^{t''} e^{iS_0[\vec{R}(t)]} \underline{U}_{\beta\alpha}(t'', t') \mathfrak{D}\vec{R}(t). \tag{1}$$

This can be regarded as a probability amplitude that the state defined at t' ($t' \to -\infty$) will lead to the state defined at t'' ($t'' \to \infty$). The state at time t' is given by the relative nuclear position $\vec{R}'$ and the electronic state α. At time t'' it is defined analogously. (A general discussion of the reduced propagator, in the context of formal scattering theory, has already been given.[11]) The quantity $S_0[\vec{R}(t)]$ is a functional of the nuclear trajectory

$$S_0[\vec{R}(t)] = \int_{t'}^{t''} \tfrac{1}{2} m \dot{\vec{R}}^2 dt \ .$$

The quantity $P_{\alpha\beta} = |\underline{U}_{\beta\alpha}(t'', t')|^2$ is an electronic transition probability from the state α (prepared at t') to the state β (observed at t'') and is also a functional of the nuclear path. Within the diabatic[9,18–20] representation the matrix $\underline{U}(t, t')$ satisfies the equation

$$\frac{d}{dt}\underline{U}(t, t') = -i[\underline{H}(R(t), t) - \underline{E}]\underline{U}(t, t') \ , \tag{2}$$

where $\underline{H}(R(t), t)$ is the diabatic Hamiltonian, $\underline{E} = \underline{H}(\infty, t)$, and the function $R(t)$ is assumed to be determined by some external criterion, such as a stationary-phase constraint. $\underline{U}(t, t')$ satisfies the identities

$$\begin{aligned} &\underline{U}(t', t') = \underline{1}, \quad \underline{U}(t'', t') = \underline{U}(t'', t)\underline{U}(t, t'), \\ &\underline{U}^{-1}(t, t') = \underline{U}^{\dagger}(t, t') = \underline{U}(t', t) \ . \end{aligned} \tag{3}$$

In order to obtain a classical nuclear model we perform a quadratic expansion of the full path integral in Eq. (1) about "classical" paths, where each classical path satisfies a stationary-phase constraint. The phase of the integrand of Eq. (1) is given by

$$S_0[\vec{R}(t)] + \mathrm{Im} \ln \underline{U}_{\beta\alpha}(t'', t') \ .$$

If this phase is extremized[21] with respect to first-order variations in the nuclear path, the following equation of motion is obtained after some manipulation:

$$m\ddot{\vec{R}} = -\,\mathrm{Re}\left(\frac{[\underline{U}(t'', t)\nabla_R \underline{H}(R, t)\underline{U}(t, t')]_{\beta\alpha}}{\underline{U}_{\beta\alpha}(t'', t')} \right) \ . \tag{4}$$

This result is comparable to that obtained by Pechukas[11] [E$_\perp$. (3.3)], after allowing for differences in notation. It is a force law governing (classical) nuclear motion for a collision where the electrons are prepared in state α and observed in state β.

In order to complete the theory one should at this point calculate the effect of the second-order variation about classical paths. Instead we will appeal to an approximate result obtained by Pechukas. In Sec. V, Ref. 11, the statement is made: "The cross section for scattering in a given direction and with a given quantum transition is simply the classical cross section for scattering of the atoms in that direction times the probability for the quantum transition." This statement is quantitatively reliable only if the magnitude of $\underline{U}_{\beta\alpha}(t'', t')$ varies much more slowly than its phase as the nuclear path is varied about the classical path (see Eqs. 3.5–3.7 in Ref. 11). However, we will use this result since it seems to be qualitatively quite reasonable and since we are interested predominantly in the nuclear paths themselves, not in quantitative accuracy. This completes the formal theory.

Two problems which must be dealt with before the numerical results can be understood are how to interpret the force law obtained above and how to numerically solve the boundary-value problem represented by Eqs. (2) and (4). The numerical method will be discussed in Sec. III. The discussion of the force law centers around this question: How many trajectories contribute to any particular experimental event and how are they interrelated? We mention here three ways in which multiple nuclear trajectories can occur in the present model. The first way can be seen by noting that the trajectory for the $\alpha \to \alpha$ (elastic) electronic event is in general not the same as that for the $\alpha \to \beta$ (inelastic) event. It is at this point that the present calculation differs from both the stationary- and the average-energy-surface theories since they do not make this distinction. An example of the second type of multiplicity is the rainbow-scattering phenomenon, where two or more trajectories with different impact parameters lead to the same scattering angle. This type of multiplicity did not occur in the present calculation, although it could have, if the matrix elements and impact energy had been different. As a result, our interpretation of the perturbation in the elastic cross section states that it is not a rainbow-scattering effect, in contrast to the interpretation given by other workers.[6,7] In order to understand the rainbow-scattering interpretation,[6] one must consider a third type of multiplicity of trajectories. This occurs when the same impact parameter leads to two different scattering angles. For a two-state curve-crossing problem, if SLZ theory is used, it occurs for the following reason: It is assumed that the electronic transition occurs instantaneously. Once this assumption is made it is natural to treat the region inside the crossing point separately from the outside region. In the

inside region the nuclear motion is decomposed into two components, each following a different diabatic energy surface. These two components are regarded as representing two distinct physical situations, whose relative probability is given by SLZ theory. As a result of this decomposition one finds a single impact parameter leading to two different scattering angles. In special cases[6] this decomposition incidentally leads one to conclude that rainbow scattering will occur. (Note that the numerical results obtained by Olson and Smith do not depend on this assumption, although their interpretation does.) An interesting formal motivation for this procedure has been given by Pechukas.[22] However, we emphasize that this procedure is valid only if one is willing to make the (SLZ) assumption that the transition at the crossing point occurs instantaneously. In the present calculation we have not made this assumption and therefore observe only one trajectory corresponding to any particular impact parameter.

A closely related problem, which also can display two scattering angles at a common impact parameter, is resonant charge exchange. In this case we feel that the decomposition procedure (into gerade and ungerade modes of scattering) is valid since it does not involve any additional assumptions about the electronic motion; it merely appeals to a symmetry argument which is equally applicable to all systems displaying resonant charge exchange.

III. NUMERICAL METHOD

The numerical method used in this calculation consists of changing the boundary-value problem into a sequence of initial-value problems which ultimately converge to a boundary-value solution. This is done by isolating all of the dependence on the future within a single constant matrix $\underline{U}(t'', t')$. Given Eq. (3), the force law [Eq. (4)] is rewritten

$$m\ddot{\vec{R}} = -\mathrm{Re}\left(\frac{[\underline{U}(t'', t')\underline{U}^{\dagger}(t, t')\nabla_R \underline{H}(R, t)\underline{U}(t, t')]_{\beta\alpha}}{\underline{U}_{\beta\alpha}(t'', t')}\right). \tag{5}$$

The form of this force law suggests the following procedure: Guess an energy surface and perform a SESIP calculation, using it to obtain an approximate estimate of $\underline{U}(t'', t')$. Given this estimate one can then calculate an improved force law using Eq. (5) and eventually an improved value of $\underline{U}(t'', t')$. In this way a sequence of initial-value problems is solved until two estimates of $\underline{U}(t'', t')$ agree. The specific form of the force law which was used was, therefore,

$$m\ddot{\vec{R}} = -\mathrm{Re}\left(\frac{[\underline{U}^{n-1}(t'', t')\underline{U}^{n\dagger}(t, t')\nabla_R \underline{H}(R, t)\underline{U}^{n}(t, t')]_{\beta\alpha}}{\underline{U}^{n-1}_{\beta\alpha}(t'', t')}\right). \tag{6}$$

Equation (2), which determines $\underline{U}^n(t, t')$, is solved simultaneously with Eq. (6). The label n refers to the nth initial-value collision. The force law for the nth collision recognizes the future electronic behavior through the matrix $\underline{U}^{n-1}(t'', t')$, obtained from the previous collision. The first question which must be answered is the following: Does the fact that two successive estimates of $\underline{U}(t'', t')$ agree necessarily imply that we have converged to a true solution of the boundary-value problem represented by Eqs. (2) and (4)? This can be quickly answered by setting $n = n - 1$ in Eq. (6). We might also ask whether this algorithm necessarily converges or how quickly it converges, or even whether it converges to a unique solution. None of these questions have been given a general answer here, but they will be partially answered in Secs. IV and V.

It is of some interest to note the behavior of the potential energy, both exact and approximate, before and after the collision. First of all, we note that if convergence has been obtained, then an energy conservation law can be proven, in the sense that

$$\tfrac{1}{2}m\dot{\vec{R}}^2 + \mathrm{Re}\left(\frac{[\underline{U}(t'', t)\underline{H}(R, t)\underline{U}(t, t')]_{\beta\alpha}}{\underline{U}_{\beta\alpha}(t'', t')}\right) = \text{const.} \tag{7}$$

Second, it can be shown that even if convergence has not been obtained, one still has the identity

$$\tfrac{1}{2}m\dot{\vec{R}}^2 + \mathrm{Re}\left(\frac{[\underline{U}^{n-1}(t'', t')\underline{U}^{n\dagger}(t, t')\underline{H}(R, t)\underline{U}^{n}(t, t')]_{\beta\alpha}}{\underline{U}^{n-1}_{\beta\alpha}(t'', t')}\right) = \text{const.} \tag{8}$$

This last identity is very useful in practice since it provides one with a sensible criterion with which to determine the time interval in the Runge–Kutta–Gill[15] procedure used to solve the initial-value problem. Equation (7) is of formal interest but is of no value in the actual numerical calculation. Formally, Eq. (7) shows that at time t' the potential energy is given by $\underline{H}_{\alpha\alpha}(\infty, t)$ and at time t'' it is given by $\underline{H}_{\beta\beta}(\infty, t)$, as was anticipated in Sec. I. Equation (8), on the other hand, shows that at time t' the potential energy is given by $\underline{H}_{\alpha\alpha}(\infty, t)$, and at time t'' the potential energy could be anything, depending on how close one is to convergence. When convergence is obtained Eq. (8) reduces to Eq. (7).

The program used to solve this problem is a modified version of one developed for use with the average-energy-surface[15] theory. The main difference is the presence of a new force law [Eq. (6)]. In addition, the original program was modified so that it automatically performed a whole series of collisions with the same initial conditions but with a revised estimate of $\underline{U}(t'', t')$. The calculation was initiallized by choosing the diabatic energy surface $\underline{H}_{11}(R)$ and performing one SESIP calculation. The succeeding collisions at that impact parameter were

then performed using Eq. (6) to generate the force law. The most sensitive criterion for convergence was found to be the scattering angle. The iterative procedure was normally continued until two successive scattering angles differed by less than 0.001°. An additional convergence criterion was the final value of the potential energy, since this value is known for any particular electronic event.

The matrix $\underline{H}(R,t)$, which governs the electronic interaction between He^+ and Ne, was identical to that already used by Olson and Smith[6] and will not be repeated here. The impact energy was 70.9 eV, with an excitation energy of 16.8 eV for the inelastic collisions. The pseudocrossing occurs at $R_x = 2.02$ a.u. A slight discrepancy between the present calculation of matrix elements and that of Olson and Smith was observed. They state (Ref. 6, Table I) that $H_{11}(R_x) = H_{22}(R_x) = 0.530$ a.u. Our calculation of this quantity yielded a value of 0.533 a.u. They also quote a value of 0.00819 a.u. for $H_{12}(R_x)$, compared to our value of 0.00823 a.u. These discrepancies are presumably due to a trivial numerical error which has gone undetected. They were ignored in the present calculation since we are interested mostly in qualitative behavior.

IV. ELASTIC SCATTERING

The elastic differential cross section was obtained by performing a series of collisions with a constant spacing of 0.02 a.u. between neighboring impact parameters. At any given impact parameter b, less than five initial-value collisions were required in order to obtain convergence. The reason for this was that the diabatic surface $H_{11}(R)$ provided a very good initial estimate of the true energy surface, at least for elastic scattering. However, the deviations of the true energy surface from the diabatic surface led to pronounced effects in the differential cross section.

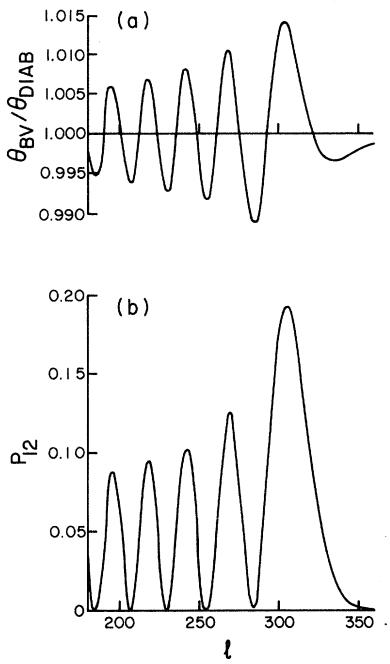

FIG. 1. (a) $\theta_{BV}/\theta_{DIAB}$ as a function of angular momentum l for elastic collisions. (b) P_{12} as a function of l for the same collisions as in (a).

Figure 1(b) shows the quantity P_{12} plotted as a function of angular momentum. The angular momentum l is obtained by the relation $l = bp$, where p is the initial momentum (178.76 a.u.). It can be seen that P_{12} shows the usual oscillations associated with a curve crossing. A rough estimate of the threshold for these oscillations is given by $l_x = 322$. If $l > l_x$, then the nuclei will not reach the crossing point at $R = R_x$. The results in Fig. 1(b), however, do not explicitly recognize this threshold since SLZ theory is not being used. It is of some interest to compare Fig. 1(b) with the distorted-wave (DW) result (Ref. 6, Fig. 4). Qualitatively, the two results are very similar, although there are quantitative differences. The present calculation displays a spacing of about $25l$ units between successive peaks, whereas the DW spacing is approximately $16l$ units. This discrepancy is presumably due to the fact that P_{12} in Fig. 1(b) has been calculated using an elastic trajectory. In Sec. V, where P_{12} is obtained using an inelastic scattering trajectory, the comparison is much more encouraging. Another feature of Fig. 1(b) is the fact that the value of P_{12} was essentially the same regardless of whether the diabatic surface or the final (dynamic) surface was used. That is, the electronic behavior for elastic scattering was quite insensitive to changes in the nuclear model.

We now consider the effect of the electronic behavior on the nuclear motion. It is this effect which is particularly dramatic in the present calculation and in fact provides the only justification for taking the trouble to solve the full boundary-value problem in the first place. It can be seen by an inspection of the deflection function (scattering angle θ vs impact parameter). For elastic scattering, θ was invariably very close to the diabatic prediction, which excludes the possibility of rainbow scattering. The difference between the two angles was never more than 0.5°. Instead of plotting θ directly we have shown in Fig. 1(a) a plot of $\theta_{BV}/\theta_{DIAB}$ vs l. θ_{BV} is obtained from the boundary-value calculation and θ_{DIAB} is the diabatic prediction. The most striking (and unexpected) feature of Fig. 1(a) is the fact that $\theta_{BV}/\theta_{DIAB}$ is oscillatory and can be correlated closely with the oscillations of P_{12}. The only exception to the correlation is the shallow minimum at $l = 334$. This minimum comes from a collision where the turning point is greater than

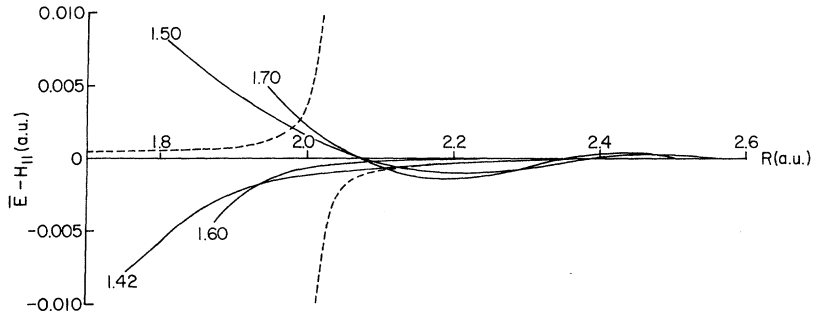

FIG. 2. Difference between the dynamic energy surface $\bar{E}(R, t)$ obtained from the boundary-value calculation and the diabatic surface $H_{11}(R)$, plotted as a function of internuclear separation, for elastic collisions at impact parameters 1.42, 1.50, 1.60, and 1.70 a.u. The dashed lines are the corresponding adiabatic surfaces.

the crossing point and is therefore in the "subexcitation" region. It can be qualitatively understood by noting that the nuclei display a tendency to follow the bottom adiabatic, not the diabatic, surface in this region. For collisions where $l < 322$, this initial tendency towards adiabatic behavior is quickly replaced by a tendency to follow the diabatic prediction instead. The interpretation of the scattering angle can best be done by an inspection of the energy surfaces for these collisions. Figure 2 shows the energy surfaces for collisions at impact parameters 1.42, 1.50, 1.60, and 1.70 a.u. The quantity $\bar{E}(R,t)$-$H_{11}(R)$ has been plotted vs R, where $\bar{E}(R,t)$ is the potential energy obtained in the boundary-value calculation. For comparison, the adiabatic surfaces, which display an avoided crossing, have also been shown. The impact parameters 1.50 and 1.70 correspond to the first two maxima in Fig. 1. The other two impact parameters generate minima in Fig. 1. One can see that the energy surface for any particular collision is very smooth (nonoscillatory), but that the surface as a whole displays an oscillatory dependence on b. It is this dependence on b which generates the oscillatory behavior in the function $\theta_{BV}/\theta_{DIAB}$. The fact that this oscillation is correlated with P_{12} can be analytically understood by an inspection of Eq. (7). However, we have not been able to analytically explain why it is that the energy surfaces at $b = 1.50$ and 1.70 are above instead of below the other two surfaces (i.e., the existence of the correlation is reasonable but there is a plus or minus ambiguity as to which way it should affect the energy surface). Another feature seen in Fig. 2 is the fact that the surfaces corresponding to a zero in P_{12} fall completely between the two adiabatic limits, whereas those corresponding to $P_{12} \neq 0$ do not. This can be easily understood by setting $P_{12} = 0$ in Eq. (7) and making use of the unitarity of $\underline{U}(t,t')$. A final feature of Fig. 2 is the fact that the energy surface is a unique function of R, i.e., the incoming and outgoing surfaces are reflections of each other. This reflection symmetry is presumably a consequence of the fact that the formal theory satisfies the detailed balance[11] requirement. Computationally, it provides a nontrivial test of numerical accuracy, since the symmetry exists only after good convergence to a boundary-value solution has been obtained.

As has already been pointed out,[11,13] it is difficult to obtain mathematical assurance that any particular solution at a given b is unique. We have numerically searched for other possible solutions by using an initial estimate different from the one given above. The collisions at $b = 1.16$, 1.22, 1.60, 1.70, and 1.86 a.u. were recalculated using the bottom adiabatic, instead of the diabatic, surface as an initial estimate. In every case it was found that the final solution obtained was the same as the one shown above, even for those values of b where the adiabatic and diabatic predictions of θ differ greatly. We therefore feel justified in regarding the above solution as unique.

Having rationalized the behavior of θ in terms of the energy surfaces one can now consider the effect that this behavior of θ will have on the cross section. The reduced[6] differential cross section is given by the quantity $b\theta(db/d\theta)P_{11}$. If this were calculated using SESIP theory then the quantity $b\theta(db/d\theta)$ would be a monotonic function of θ and the only source of oscillations would be the term P_{11}. In the boundary-value calculation, however, both terms can now contribute oscillations since Fig. 1(a) implies that $db/d\theta$ is an oscillatory function of θ. Figure 3 shows the results of a SESIP calculation of the cross section, as well as the boundary-value result. Both are compared to the DW result.[6] The DW result shows two major features, an isolated peak at 1450 eV deg and a smooth series of oscillations between 3000 and 5000 eV deg. Essentially the same features are seen experimentally [Fig. 3(c) and Ref. 2]. The SESIP result does not display any peaks in the threshold region, although it does qualitatively reproduce the smooth oscillations at large θ. The boundary-value calculation shows the same oscillations at large θ, but they are strongly accentuated due to the fact that $db/d\theta$ is also oscillatory. The main new feature of the boundary-value result is that the peaks in the differential cross section rise above the single-

channel prediction. These peaks are predominantly due to peaks in the function $db/d\theta$ and can be easily understood if one considers the behavior of θ_{BV} in Fig. 1(a). It can be seen that the boundary-value theory used here generates a perturbation in the elastic cross section which looks quite different from the perturbation that one would expect if the rainbow-scattering interpretation were used. In particular, the numerical results presented here are not compatible with those obtained by Kotova and Ovchinnikova.[7] On the basis of the comparison with experimental results it would appear that their results[7] are superior to ours, at least for elastic processes. This is presumably due to the fact that the decomposition procedure, which leads to rainbow scattering, yields a more detailed picture of nuclear motion inside the crossing region than our approach does. The relative merits of the two interpretations, for those systems where SLZ theory is not necessarily reliable,[19] remain to be seen.

A feature of the elastic cross section, which has not been mentioned above, is a shallow isolated peak occurring at 1600 eV deg in Fig. 3(b). This peak is situated in the subexcitation region ($l > 322$) and is due to a maximum in $db/d\theta$ which is generated by the tail shown in Fig. 1(a) for $l > 334$. It serves as a reference point defining the onset of the elastic perturbation. Had this peak been more pronounced, it would have provided an ideal interpretation of the experimental results, since it is isolated and is definitely a threshold effect, not a member of a continuing series of oscillations. However, it is too small to be of any experimental interest in the present case.

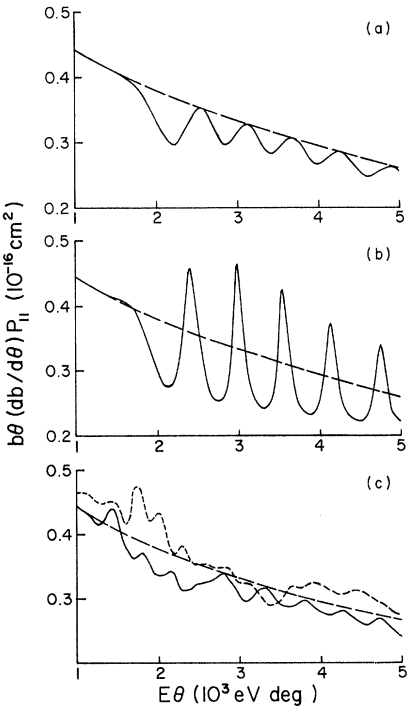

FIG. 3. Comparison of three theoretical calculations of the reduced differential cross section for elastic scattering at 70.9 eV. The long dashed lines are the single-channel (diabatic) predictions. The theories used are (a) SESIP, (b) boundary-value, and (c) distorted-wave (Ref. 6). The short dashed line in (c) is the experimental result at 83.5 eV, raised by 0.2 units (Refs. 2 and 6).

V. INELASTIC SCATTERING

The inelastic scattering calculation was performed using the same set of impact parameters and initiallization procedure as for elastic scattering. The only difference was that the force law was altered to correspond to the $1 \rightarrow 2$ electronic event. From a qualitative point of view the results are not particularly exciting since the behavior of the differential cross section is very similar to the DW prediction. The main difference between the boundary-value and SESIP calculations for inelastic scattering is that the angular threshold predicted by the boundary-value calculation is considerably lower than the SESIP prediction since the final energy surface is 16.8 eV higher than the initial energy surface. From a numerical point of view some interesting problems were encountered in the inelastic calculation. The main one was that of initiallizing the iterative procedure reasonably. The present calculation used the elastic diabatic surface as an initial estimate, even though this surface does not possess the correct long-range behavior after the collision. For strongly inelastic collisions a more sophisticated procedure would probably be required. Another difficulty was encountered for those collisions which display a transition probability P_{12} which is close to zero. In this case the force law [Eq. (6)] consists of a ratio of two arbitrarily small terms and the calculation is numerically ill conditioned. The main effect of these two problems was simply to decrease the efficiency of the calculation. It was found that ten iterations were normally required to obtain convergence to a boundary-value solution.

We begin the discussion of the inelastic results by considering P_{12} as a function of l. As expected, the qualitative behavior is the same as for elastic scattering, although significant quantitative differences were observed since the trajectories are different. When P_{12} for inelastic scattering was compared to the DW prediction (Ref. 6, Fig. 4), it was found that the agreement was so close that the differences could probably be attributed to plotting errors. This is quite encouraging since it implies that a single trajectory calculation may be capable of providing a quantitatively, as well as qualitatively, reasonable account of inelastic processes.

The next feature of the inelastic collisions is the

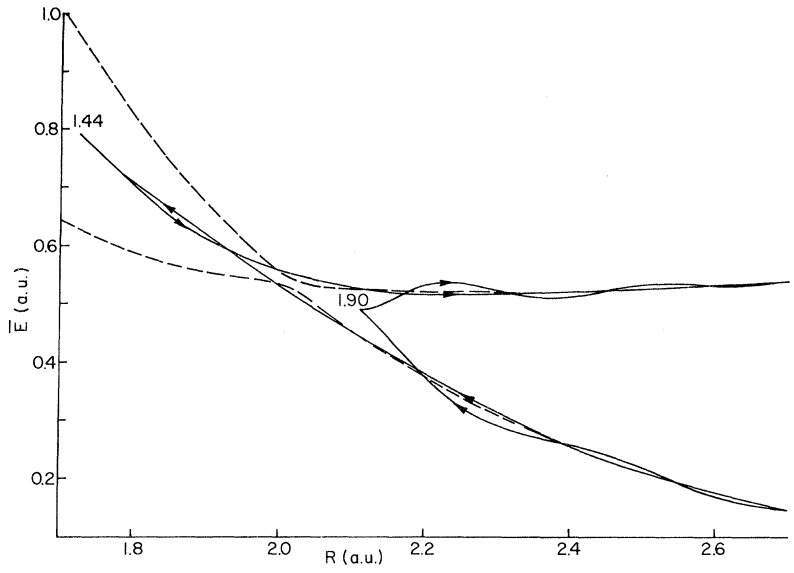

FIG. 4. Energy surfaces $\bar{E}(R, t)$ obtained from the boundary-value calculation, as a function of internuclear separation, for inelastic collisions at impact parameters 1.44 and 1.90 a.u. The dashed lines are the adiabatic surfaces.

behavior of the energy surface. Figure 4 presents energy surfaces for collisions at $b = 1.44$ and 1.90 a.u. The collision at $b = 1.44$ corresponds to the top of the third excitation peak ($P_{12} = 0.115$). The one at $b = 1.90$ corresponds to a collision where the nuclei do not even reach the crossing point ($P_{12} = 0.005$). The arrows indicate the direction in which the nuclei move along the surface since the energy is a two-valued function of R. The adiabatic surfaces are shown for comparison. In both collisions the nuclei originally follow the bottom and finally follow the top adiabatic (or diabatic) surface. In the intermediate region they follow a surface which smoothly switches over from the bottom to the top eigensurface. It was found that the energy surfaces for other collisions had essentially the same shape as the ones shown here. In every case the energy near the nuclear turning point was roughly the average value of the two adiabatic surfaces. As already observed for elastic collisions, the energy surface is not necessarily bounded by the two adiabatic extremes, especially near the pseudocrossing.

A test of detailed balancing was performed at $b = 1.44$ a.u., mostly as a check on numerical accuracy. This was done by changing the force law to correspond to the electronic event $2 \rightarrow 1$, as well as changing the initial conditions on the nuclear motion to correspond to the final behavior observed for the $1 \rightarrow 2$ electronic event. It was found that the transition probability and scattering angle for the two runs were identical. In addition to this, the two events followed the same energy surface, but in opposite directions.

Figure 5 shows the reduced differential cross section for inelastic scattering, given by the quantity $b\theta(db/d\theta)P_{12}$, as well as the DW result.[6] The over-all shapes of the two results are quite similar. The main difference is that the present calculation is shifted to the right by about 200 eV deg

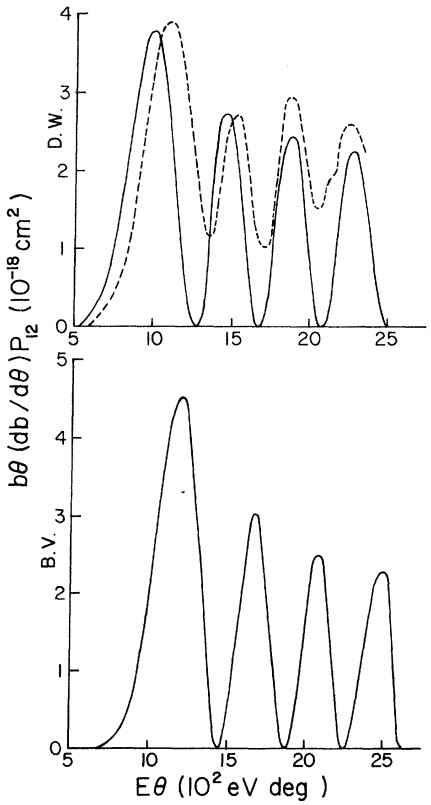

FIG. 5. Comparison of the boundary-value and the distorted-wave (Ref. 6) calculations of the reduced differential cross section for inelastic scattering at 70.9 eV. The dashed line is the experimental result (Refs. 2 and 6).

compared to the DW result. This shift is not enough to seriously affect the comparison with the experimental results. A certain amount of ambiguity as to the exact behavior of the differential cross section near the minima exists in the present calculation. This is because of the zero-over-zero problem mentioned earlier. It is possible that these minima may not rigorously approach zero although we know them to be quite small. This ambiguity was not felt to be of any great importance in the present calculation and was ignored.

VI. CONCLUSIONS

The present calculation is an attempt to develop a three-dimensional classical nuclear model applicable to low-energy multichannel atomic collisions. In particular, we have attempted to show what happens in a two-state curve-crossing calculation, if one does not make the usual SLZ approximations. The emphasis has been on those features which are experimentally observable and which are due to the effect of the electronic rearrangement on the nuclear motion. It was found that a realistic account of this effect requires the solution of a boundary-value problem. The comparison of the present results with a distorted-wave calculation[6] indicates that our theory is capable of producing reasonable inelastic scattering information. For elastic scattering, the interpretation obtained here differs from that obtained in the classical model developed by Smith and co-workers,[2,6] especially as it relates to the perturbation[3] induced in elastic scattering caused by inelastic events. It is not completely clear which of these two interpretations is the better one, although possibly a fully quantal calculation would display a combination of both types of "classical" perturbation.

As presented above, the theory we have used has some limitations which will be mentioned here. For example, we have assumed throughout that the calculation is being done within the diabatic representation. The equations of motion, as given above, are not valid within any other representation. They can, however, be easily generalized to other representations simply by making use of the known transformation properties[9,18,19] of the various matrices which enter into a general derivation. It is clear that the theory is not restricted to two-state calculations, nor is it restricted to curve-crossing problems. However, it could easily become an impractical theory if applied indiscriminately to a multistate calculation. In this case it would probably be necessary to develop a more sophisticated algorithm to solve the numerical problem. Another shortcoming of the present calculation is the assumption (Sec. II) that the classical expression for the differential cross section can be used directly. This assumption would have to be carefully reexamined before the theory could be expected to yield quantitatively reliable results.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Dr. G. Luss for helpful discussions and to M. B. Labatt for instigating this research.

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*Work supported by a grant in aid of research by the National Research Council of Canada.

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