Two-level model of charge exchange with Coulomb interaction in one of the channels: quantum and quasiclassical cross sections in the weak-coupling limit

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The differential charge-transfer cross section is calculated for the two-level model in the case of weak coupling, determined by flat and Coulomb diabatic terms with exponential interaction between them. The quasiclassical limit of the quantum-mechanical expression and the conditions for this limit to be identical with the primitive semiclassical approximation used in calculating the transition probability from the Landau-Zener formula are examined. The example of the charge-transfer process $Ar^{++} + He \rightarrow Ar^{+} + He^{+}$ is used to show that the model calculation leads to satisfactory estimates for the cross section, provided the scattering angle is not too small.

INTRODUCTION

There has been recent increased activity in experimental studies of charge-transfer processes of the form

$$A^{++}+B \rightarrow A^{+}+B^{+} \tag{1}$$

at collision energies E of the order of 1 eV (Refs. 1–3). In the initial state, these processes correspond to "covalent" terms with a weak polarizational attraction between A^{++} and B at intermediate and large nuclear separations R, and strong exchange repulsion at small separations. In the final state, they are described by Coulomb terms corresponding to the mutual repulsion between A^{+} and B^{+}. Depending on the ratio of the ionization potentials of B and A^{+}, the covalent and Coulomb terms may cross at different separations R_c. The cross section for process (1) at low collision energies is then determined by the charge-transfer interaction in the crossing region.

A simplified two-level model of charge transfer between Ar^{++} (^3P) and He was examined in Ref. 4. It was shown that, because of the relatively large separation ($R_c \simeq 9$ a.u.), and the correspondingly weak interaction inducing the charge-transfer process, a perturbation theory in this interaction could be used to calculate the transition probability at energyes $E \sim 1$ eV. Satisfactory agreement has been achieved in this model between calculated differential cross sections and charge-transfer rates, on the one hand, and experimental data, on the other.[1,5]

It became clear in the course of these calculations that the weak polarizational attraction at large separations between A^{++} and B, and the strong exchange repulsion at small separations between them, had little effect on the rate constant and the differential cross section when the scattering angle θ was not too small (specifically, for $\theta > 20°$). It is therefore interesting to consider the simple two-level model of (1), in which the covalent term is assumed to be flat. In this model, the quantum-mechanical distorted-wave method can be used to obtain a simple analytic expression for the differential charge-transfer cross section in the quasiclassical limit.

An additional stimulus to the analysis of the quantum-mechanical model was the fact that the well known Landau-Zener formula is not valid near the threshold value of the impact parameter in semiclassical calculations: although a large, clearly incorrect increase in the probability is compensated by the fact that the classical differential cross section tends to zero in this region, it is not clear in advance to what extent the final result is valid (this question is discussed on p. 212 in Ref. 6). However, it turns out that the quasiclassical limit of the quantum-mechanical solution is identical with the semiclassical approximation, which settles the question of whether this approximation can be used.

DISTORTED-WAVE METHOD

We shall consider the two-level model of inelastic scattering, described by flat

$$V_{11}=0 \tag{2}$$

and repulsive Coulomb

$$V_{22}=\alpha/R-\Delta\varepsilon \tag{3}$$

diabatic terms, and the following interaction between the diabatic states:

$$V_{12}=A\exp(-\gamma R). \tag{4}$$

The exponential dependence of V_{12} on R is typical for charge-transfer processes (see, for example, Ref. 7).

For process (1), $\alpha = 1$ (here and henceforth, we shall use atomic units unless otherwise indicated). The terms V_{11} and V_{22} are then found to cross at the separation

$$R_c=1/\Delta\varepsilon. \tag{5}$$

This is the situation to which we shall confine our attention throughout this paper.

We note that analogous results are obtained for $\alpha = -1$, $\Delta\varepsilon < 0$, which corresponds to the process

$$A+B \rightarrow A^{+}+B^{-}. \tag{6}$$

When V_{12} is small, the amplitude $f(\theta)$ for the inelastic transition $1 \rightarrow 2$ can be calculated in the first order of the

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distorted-wave method (see, for example, Ref. 8). However, in the present case, in which the term V_{11} is flat, this method yields

$$f(\theta)=-\frac{\mu}{2\pi}\int d^3\mathbf{R}\,\varphi_{\mathbf{k}_2}^{-*}(\mathbf{R})\,V_{12}(R)\,\varphi_{\mathbf{k}_1}(\mathbf{R}). \tag{7}$$

Where μ is the reduced mass of the system AB, $\varphi_{\mathbf{k}_1}$ is the plane wave corresponding to energy $E=k_1^2/2\mu$, $\varphi_{\mathbf{k}_2}^-$ is the solution of the single-channel Schroedinger equation with potential V_{22} for $k_2^2/2\mu=E+\Delta\varepsilon$, which corresponds to a plane incident and a converging spherical wave in the asymptotic region, and θ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. The functions $\varphi_{\mathbf{k}_1}$ and $\varphi_{\mathbf{k}_2}^-$ are normalized as follows:

$$\int d^3\mathbf{R}\,\varphi_{\mathbf{k}_1}^{*}\varphi_{\mathbf{k}_1'}=(2\pi)^3\delta(\mathbf{k}_1-\mathbf{k}_1'),$$
$$\int d^3\mathbf{R}\,\varphi_{\mathbf{k}_2}^{-*}\varphi_{\mathbf{k}_2'}^{-}=(2\pi)^3\delta(\mathbf{k}_2-\mathbf{k}_2'). \tag{8}$$

The standard approach to the evaluation of $f(\theta)$ from (7) relies on the expansion of $\varphi_{\mathbf{k}_1}$ and $\varphi_{\mathbf{k}_2}^-$ in terms of spherical waves. This approach was adopted in Ref. 9 for the model considered here. However, the authors of Ref. 9 were unable to perform an analytic summation of the resulting series, and used numerical methods and various approximations to determine the total cross section for the inelastic process.

It turns out, however, that a relatively simple analytic expression can be obtained for (7) by using the Coulomb wave functions in expressed parabolic coordinates. Details of this are given in Ref. 10 in another connection. In our terminology, however, the author of Ref. 10 obtained, in the first order of the distorted-wave method, an analytic expression for the amplitude $\tilde{f}(\theta)$ for the inelastic process in the case of the two-level model with

$$V_{11}=(\tilde{\alpha}_1/R),\quad V_{22}=(\tilde{\alpha}_2/R)-\Delta\varepsilon,\quad V_{12}=(A/R)\exp(-\gamma R), \tag{9}$$

for which

$$\tilde{f}(\theta)=-(\mu/2\pi)\exp[-\pi(\tilde{\eta}_1+\tilde{\eta}_2)/2]\Gamma(1+i\tilde{\eta}_1)\Gamma(1+i\tilde{\eta}_2)A\tilde{I}(\theta), \tag{10}$$

$$\tilde{I}(\theta)=\pi\left[\frac{a}{(a+ik_1)(1+\xi)}\right]^{i\tilde{\eta}_1}\cdot\left[\frac{a}{(a+ik_2)(1+\xi)}\right]^{i\tilde{\eta}_2}\times\frac{F(-i\tilde{\eta}_1,-i\tilde{\eta}_2,1,-\xi)}{(a+ik_1)(a+ik_2)(1+\xi)}, \tag{11}$$

where $\tilde{\eta}_i=\mu\tilde{\alpha}_i/k_i$ is the Coulomb interaction parameter, $a=[\gamma-i(k_1+k_2)]/2$, $F(\ldots)$ is the hypergeometric function, and

$$\xi=4k_1k_2[\gamma^2+(k_1-k_2)^2]^{-1}\sin^2(\theta/2). \tag{12}$$

It is clear that the expression for $f(\theta)$ is obtained from (10) by inserting $\tilde{A}=A$, $\tilde{\eta}_1=0$, and $\tilde{\eta}_2=\mu\alpha/k_2=\eta_2$, and, moreover, by replacing $\tilde{I}(\theta)$ with

$$I(\theta)=-\frac{\partial}{\partial\gamma}(\tilde{I}(\theta)|_{\tilde{\eta}_1=0,\,\tilde{\eta}_2=\eta_2}), \tag{13}$$

where $F(0,-i\eta_2,1,-\xi)=1$. Simple rearrangement then yields

$$f(\theta)=-(\mu/2\pi)\exp(-\pi\eta_2)\Gamma(1+i\eta_2)AI(\theta), \tag{14}$$

$$I(\theta)=\pi\left[\frac{a}{(a+ik_2)(1+\xi)}\right]^{i\eta_2}[(a+ik_1)(a+ik_2)(1+\xi)]^{-1}\times\left\{\frac{2\gamma(1+i\eta_2)}{4(a+ik_1)(a+ik_2)(1+\xi)}-\frac{\eta_2(2ia-k_1)}{2a(a+ik_1)}\right\}. \tag{15}$$

The inelastic differential cross section for the process

$$q(\theta)=(k_2/k_1)|f(\theta)|^2 \tag{16}$$

can be written in the form

$$q(\theta)=\sigma_{LZ}\{\sin^2\theta_c[4\pi(1-\cos\theta_c\cos\theta)^2]^{-1}\}\times\Phi[\exp(\pi\eta_2)/2\,\mathrm{sh}\,\pi\eta_2]. \tag{17}$$

The physical meaning of the factors in (17) is as follows. The factor

$$\sigma_{LZ}=8\pi^2R_c^2(2E/\mu)^{-1/2}R_c^2a^2 \tag{18}$$

has the dimensions of area and is the total cross section calculated in the standard semiclassical Landau-Zener model in the weak coupling limit (see, for example, Ref. 6) with off-diagonal matrix element $a=V_{12}(R_c)=A\exp(-\gamma R_c)$ and term slope difference $\Delta F=R_c^{-2}$ at $R_c=\Delta\varepsilon^{-1}$.

The second factor in (17) contains the main angular dependence of the differential cross section, and yields unity when integrated over all angles. This factor includes the parameter

$$\theta_c=\arcsin[\Delta\varepsilon/(\Delta\varepsilon+2E)], \tag{19}$$

whose significance is discussed below.

The factor Φ depends on the scattering angle θ, the angular parameter θ_c, the reduced energy $x=E/\Delta\varepsilon$ (through the latter parameter), and the two parameters $y=\gamma/(2\mu\Delta\varepsilon)^{1/2}$ and $\eta_0=(\mu/2\Delta\varepsilon)^{1/2}$. The explicit form of Φ is

$$\Phi=\exp\{2\gamma R_c[1-{}^1/_2(y^2(1+x))^{-1/2}\operatorname{arctg}(2y(1+x)^{1/2}/(1-y^2))]\}\times\frac{\{[x^{1/2}-(x+1)^{1/2}]^2+4[(1+x)x]^{1/2}\sin^2(\theta/2)\}^2}{\{y^2+[x^{1/2}-(1+x)^{1/2}]^2+4[(1+x)x]^{1/2}\sin^2(\theta/2)\}^2}\left|\frac{1-iy(1+x)^{-1/2}}{1-y^2+2iy(1+x)^{1/2}}+\frac{y\eta_0^{-1}+iy(1+x)^{-1/2}}{y^2+[x^{1/2}-(1+x)^{1/2}]^2+4[(1+x)x]^{1/2}\sin^2(\theta/2)}\right|. \tag{20}$$

It will be shown below that this factor describes the deviation from the Landau-Zener model due to the presence of the second nonadiabatic coupling region localized for distances $R<R_c$, for which the splitting between the diabatic terms becomes comparable with the off-diagonal matrix element. Finally, the last factor in (17) gives the correction to the quasiclassical approximation.

To estimate this correction, and to elucidate the part

played by Φ in the quasiclassical limit, let us suppose that $\eta_0 \gg 1$ and $y \ll 1$ (these conditions are well satisfied under typical conditions for which $\Delta\varepsilon \sim 1$ eV, $\gamma \simeq 1$ a.u., $\mu = 10^4$ a.u.). The first condition ensures that the motion is quasiclassical with respect to the Coulomb term for low initial energies $E < \Delta\varepsilon$ (motion through the flat term is always quasiclassical), and the second ensures that the off-diagonal matrix element varies smoothly. Since $\pi\eta_2 = \pi\eta_0(1+x)^{-1/2}$, it is readily shown that, right up to very high energies, the last factor in (17) may be assumed to be equal to unity (the failure of the quasiclassical approximation at very high energies is due to the appearance of the singularity in the Coulomb potential at $R = 0$).

Analysis of the factor Φ shows that the main parameter governing its magnitude is the product $y(1+x)^{1/2}$. When this product is small, Φ is close to unity but, when the energy x is high enough, so that $y(1+x)^{1/2} \gtrsim 1$ (this occurs when $E > 100$ eV for the adopted values of $\Delta\varepsilon$, γ, and μ), Φ may exceed unity and depends appreciably on angle for small θ. This effect is entirely due to the stronger coordinate dependence of the matrix element of the interaction as compared with the splitting of the diabatic terms: when $R < R_c$, we have the situation where $V_{12}(R)$ becomes comparable with the difference $V_{11} - V_{22}$, so that the adiabatic terms and the corresponding adiabatic functions become very different from the diabatic quantities, which should not occur in the Landau-Zener model. In the region of strong mixing of the diabatic states, there are also possible nonadiabatic transitions, but their probabilities are appreciable only at relatively high energies. The situation here is completely analogous to that encountered in the linear-exponential model (see Section 27 in Ref. 6), which can be completely interpreted in terms of the semiclassical trajectory approximation.

Thus, in a wide range of energies, the quantum-mechanical differential cross section for the charge-transfer process can be represented with high precision by the formula

$$q(\theta) = \sigma_{LZ} \sin^2\theta_c [4\pi(1-\cos\theta_c\cos\theta)^2]^{-1}, \qquad (21)$$

which follows from (17) when the last two factors are set equal to unity.

The particular feature of the inelastic differential cross section, give by (21), is its monotonic dependence on the scattering angle θ. The physical reason for this will be particularly easily understood in terms of the quasiclassical method, which also enables us to determine the range of angles in which the model with the flat term that we are considering reproduces satisfactorily the differential cross section in the realistic situation in which strong repulsion in state 1 appears only for small R.

MULTITRAJECTORY SEMICLASSICAL APPROXIMATION

It is well-known that, in the multitrajectory semiclassical approximation, also referred to as the primitive semiclassical approximation,[6] the scattering amplitude is calculated as the sum of contributions, each of which is associated with the motion of the particle along a particular trajectory. The amplitudes and phases of these contributions are determined from the complete quasiclassical representation of the scattering amplitude by evaluating the integral by the method of stationary phase, where each point of stationary phase determines the deflection function $\chi(b)$ for the corresponding trajectory with initial impact parameter b. In the present case, in which the interaction is weak, these deflection functions correspond to the following two possible paths of the system through the diabatic terms. The first path corresponds to the mutual approach of the particles through the flat term V_{11} to $R = R_c$, the transition to the Coulomb term V_{22} at $R = R_c$, which follows the approach along this term up to the turning point R_2^t, and separation through the term V_{22} to infinity (the cumulative phase at the end of all this is $2\delta^i$). The second path corresponds to the mutual approach of the particles over the term V_{11} up to the turning point R_1^t, separation over this term up to $R = R_c$, transition from the term V_{11} to the Coulomb term V_{22} at $R = R_c$, and separation over the Coulomb term to infinity (the cumulative phase is $2\delta^c$).

In this approximation, the scattering amplitude is

$$f(\theta) = -(k_1/k_2)^{1/2}\{[P(b^i)q^i(\theta)]^{1/2}\exp[-i(k_1 b^i\theta - 2\delta^i)] + [P(b^c)q^c(\theta)]^{1/2}\exp[-i(k_1 b^c\theta - 2\delta^c - \pi/2)]\}, \qquad (22)$$

where

$$q^i(\theta) = (1/\sin\theta)\, b^i \left| d\chi^i/db \right|^{-1}_{b=b^i(\theta)} \qquad (23)$$

is the classical differential cross section corresponding to the deflection function χ^i, and

$$P(b^i) = 4\pi R_c^2 V_{12}^2(R_c)\{(2E/\mu)[1-(b/R_c)^2]\}^{-1/2} \qquad (24)$$

is the probability of a single transition according to the Landau-Zener model. The corresponding expressions for branch c are obtained from (23) and (24) by replacing i with c.

The impact parameter b^i in (22)–(24) is looked upon as the function $b^i(\theta)$, and is found from the equation for the position of the stationary phase, which also establishes the relation between the deflection function χ^i and the corresponding phase δ^i:

$$\chi^i(b) = d\delta^i/d(bk_1) = \theta, \qquad (25)$$

and, analogously,

$$\chi^c(b) = d\delta^c/d(bk_1) = \theta. \qquad (26)$$

These equations already take into account the fact that there is no attraction in channels 1 and 2, so that the angles of deflection cannot be negative.

Since the classical motion over segments of diabatic terms is known, it is readily shown that the deflection function is

$$\chi^i = \arccos\left\{\frac{\cos\theta_c - [1-(b/R_c)^2]^{1/2}}{1-[1-(b/R_c)^2]^{1/2}\cos\theta_c}\right\}, \qquad (27)$$

$$\chi^c = \arccos\left\{\frac{\cos\theta_c + [1-(b/R_c)^2]^{1/2}}{1+[1-(b/R_c)^2]^{1/2}\cos\theta_c}\right\}, \qquad (28)$$

where the angle θ_c is given by (19).

It follows from (27) and (28) that (25) has a solution only for $\theta_c \leqslant \theta \leqslant \pi$, and (26) only for $0 \leqslant \theta \leqslant \theta_c$. Hence, for

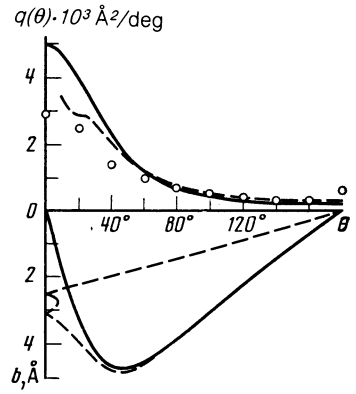

FIG. 1. Moduli of the deflection functions $|\chi(b)| = \theta$ and differential cross sections $q(\theta)$ (in units of 10^{-3} Å^2/deg) at collision energy $E = 0.53$ eV: O—experiment,[1] broken curve—calculated,[4] solid curve—calculated in the present paper.

each value of θ, only one term remains in the sum in braces in (22), which explains the absence of oscillations, mentioned above, on the differential charge-transfer cross section $q(\theta)$.

By analogy with the results in Ref. 4, the function $b^i(\theta)$ passes smoothly into $b^c(\theta)$ at $\theta = \theta_c$ and, in our model, the two branches can be described by the simple single function

$$b(\theta) = R_c(1-\cos\theta_c\cos\theta)^{-1}\sin\theta_c\sin\theta. \qquad (29)$$

In view of the foregoing discussion, and using (16), (22)–(29), we obtain an expression for $q(\theta)$ that is identical with formula (21), obtained by the quantum-mechanical approach.

In relation to the quasiclassical calculation of $q(\theta)$, we know that, strictly speaking, it is not valid near $\theta = \theta_c$, where the transition probability $P(b)$ increases rapidly as $(R_c - b)^{-1/2}$ and the increase is balanced exactly by the reduction in the derivatives $|db^i/d\theta| \sim |db^c/d\theta| \sim (R_c - b)^{1/2}$. Comparison with the quantum-mechanical calculation shows, however, that the quasiclassical calculation leads to the correct result for $q(\theta)$ even at scattering angles near θ_c in the case of the crossing of the flat and Coulomb terms. Hence, we may conclude that, even in the more realistic model of the charge-transfer process (1) that takes into account the long-range dispersive attraction and short-range exchange repulsion on V_{11}, we can still use the primitive semiclassical approximation described in Ref. 4 for angles near θ_c. The criterion for the validity of this approach can be the closeness between θ_c and the deflection functions near θ_c in the realistic model and in the corresponding model with flat and Coulomb diabatic terms. Moreover, the model that includes the flat term may then provide a reasonable approximation to the differential charge-transfer cross section in a relatively wide range of angles.

Let us illustrate this discussion by considering the example

$$Ar^{++}(^3P)+He(^1S)\rightarrow Ar^+(^2P)+He^+(^2S), \quad \Delta\varepsilon = 3 \text{ eV}, \qquad (30)$$

which we previously investigated in terms of the simplifier two-level model. Figure 1 compares the deflection functions and the differential cross sections calculated at $E = 0.53$ eV in Ref. 4, including the polarizational attraction of Ar^{++} and He at large distances and the strong exchange interaction at short distances, with the present calculations based on (21), (27), and (28), in which these effects are neglected.

It is clear that the neglect of the polarizability of He ($\alpha_{He} = 1.38$ a.u.) has practically no effect on R_c and θ_c for $E \gtrsim 0.53$ eV. The ionic branches of the deflection function $\chi^i(b)$ are also practically identical down to $\theta = \theta_c$. The calculations reported in Ref. 4 show that the contribution of the core to the differential cross section at $E = 0.53$ eV falls from 15% at $\theta = 180°$ to 5% at $\theta = \theta_c = 46°$. The corresponding figures for $E = 1.62$ eV are 27% at $\theta = 180°$ and 3% at $\theta = \theta_c = 28°$.

CONCLUSION

It is well-known that the elastic scattering of atoms during their motion over segments of the flat and attractive Coulomb terms is characterized by the so-called giant glory, i.e., total back reflection at a certain particular value of the relative energy.[11] Possible distortions of this effect by the difference between the true potentials and the model potentials, and the nonzero inelastic scattering probability, can be taken into account as corrections to the zero-order approximation.[12] The analytic formula reported here for the differential scattering cross section in the inelastic channel represents other properties of an analogous system whose motion is also determined by segments of the covalent and ionic terms. This formula can be used as the initial approximation for taking these effects into account, including the influence of the curving of the trajectories by the core (their radius is small in comparison with the crossing separation) and the dependence of the charge-transfer matrix element on the separation. The latter effect may become significant not only in the differential but also the integral cross sections. In particular, it may appear as a change in the energy dependence of the cross section (which may become an increasing rather than a decreasing function), and may explain the existence of the cross section minimum. This type of minimum has been found on the energy dependence of the cross section for the neutralization process $H^+ + H^- \rightarrow H^*$ ($n = 2.3$) + H, where, on the low-energy side (less than 20 eV), the cross sections found by numerical solution of the multichannel scattering problem are satisfactorily reproduced by the Landau-Zener formula.[13]

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[1]B. Friedrich and Z. Herman, Chem. Phys. Lett. **107**, 375 (1984).
[2]B. Friedrich *et al.*, Chem. Phys. Lett. (1985).
[3]R. Disch, S. Scherbath, and D. Gerlich, in: Abstracts of 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird, Utah, USA, 1985.
[4]B. Friedrich *et al.*, J. Chem. Phys. **84**, 807 (1986).
[5]D. Smith *et al.*, J. Phys. B **13**, 2790 (1980).
[6]E. E. Nikitin and S. Ya. Umanskiĭ, Neadiabaticheskie perekhody pri medlennykh atomnykh stolknoveniyakh (nonadiabatic transition during slow atomic collisions) Atomizdat, Moscow, 1979.
[7]V. M. Galitskiĭ, E. E. Nikitin, and B. M. Smirnov, Teoriya stolknovenii

atomnykh chastits (Theory of collisions between atomic particles), Nauka, Moscow, 1981.
[8]M. L. Goldberger and K. Watson, *Collision Theory*, Rev. Ed., Krieger, (1975).
[9]D. R. Bates and D. S. F. Crothers, Proc. R. Soc. London Ser. A **315**, 465 (1970).
[10]K. A. Ter-Martirosyan, Zh. Eksp. Teor. Fiz. **29**, 713 (1955).
[11]Yu. N. Demkov and J. Los, Phys. Lett. A **46**, 13 (1973).
[12]V. N. Ostrovsky, J. Phys. B **8**, 2979 (1975).
[13]D. Fussen and C. Kubach, J. Phys. B **19**, L31 (1986).

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