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Analytic solutions to two-state collision problems for the case of exponential coupling

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Analytic solutions to two-state collision problems are obtained for systems in which the interaction matrix element of the Hamiltonian displays an exponential variation with time. When the difference in the diagonal matrix elements is either constant or governed by the same exponential function, exact analytic solutions can be found. When it is in the form of a constant plus an exponential term, the case of practical importance, an approximate solution is obtained based upon these exact solutions. The solution is used to calculate cross sections for fine-structure transitions in atomic collisions (Na-He, F-Xe, F-H^+).

I. INTRODUCTION

A semiclassical treatment of a two-state collision problem leads inevitably to the following coupled equations for the probabiliy amplitudes $c_1(t)$ and $c_2(t)$ for the two states $|1\rangle$ and $|2\rangle$:[1]

$$i\hbar\frac{dc_1}{dt}=H_{11}c_1+H_{12}c_2 \ , \tag{1a}$$

$$i\hbar\frac{dc_2}{dt}=H_{21}c_1+H_{22}c_2 \ , \tag{1b}$$

with the initial condition

$$|c_1(t=-\infty)|=1,\ \ c_2(t=-\infty)=0 \ . \tag{2}$$

For a realistic collision system, the matrix elements $H_{ij}\equiv\langle i\,|H\,|j\rangle$ of the Hamiltonian H show a complicated dependence on the internuclear distance of the colliding partners and thus on time t. It is this time dependence of the matrix elements H_{ij} that makes it difficult to obtain an exact solution of Eqs. (1). Various models with simple forms of H_{ij} have been proposed in an attempt to simulate the actual collision process as accurately as possible (see Table I). If the difference $H_{22}-H_{11}$ is assumed to be independent of time, the problem becomes formally equivalent to that of a stationary two-level system whose levels are coupled by a time-dependent interaction. This problem has recently been considered by Bambini and Berman,[6] Thomas,[7] and Robiscoe.[8] There, however, exist many collision systems for which the time variation of $H_{22}-H_{11}$ needs to be taken into account.

The simplest nontrivial case for which an exact solution of Eqs. (1) can be found is the case of resonance scattering, i.e., when

$$H_{22}-H_{11}=0 \ \ (H_{12}\text{ arbitrary}) \ . \tag{3}$$

If a phase transformation

$$c_j=a_j\exp\left[-\frac{i}{\hbar}\int^t H_{jj}dt_1\right] \tag{4}$$

is applied to Eqs. (1), we obtain

$$i\hbar\frac{da_1}{dt}=H_{12}a_2\exp\left[-\frac{i}{\hbar}\int^t(H_{22}-H_{11})dt_1\right] , \tag{5a}$$

$$i\hbar\frac{da_2}{dt}=H_{21}a_1\exp\left[\frac{i}{\hbar}\int^t(H_{22}-H_{11})dt_1\right] , \tag{5b}$$

which, for the case $H_{22}-H_{11}=0$, immediately yields

TABLE I. Various models for a two-state collision problem.

Model	$H_{22}-H_{11}$	$H_{12}(H_{21})$	Refs.
Rosen-Zener	$\Delta\epsilon$	$\beta\,\text{sech}(\gamma t)$	Rosen and Zener (Ref. 2)
Landau-Zener	$\alpha(t-t_0)$	β	Landau, Zener (Ref. 3)
Demkov	$\Delta\epsilon$	$\beta e^{-\gamma\|t\|}$	Demkov (Ref. 4), this work
Nikitin	$\alpha e^{-\gamma\|t\|}+\Delta\epsilon$	β	Nikitin (Ref. 5)
Exponential	$\alpha e^{-\gamma\|t\|}$	$\beta e^{-\gamma\|t\|}$	This work
Demkov-exponential	$\alpha e^{-\gamma\|t\|}+\Delta\epsilon$	$\beta e^{-\gamma\|t\|}$	This work

$$a_1(t)=\cos\left[\frac{1}{\hbar}\int^t H_{12}dt_1\right],$$
$$a_2(t)=-i\sin\left[\frac{1}{\hbar}\int^t H_{12}dt_1\right]. \tag{6}$$

Here and throughout the paper we assume that $H_{12}=H_{21}$.

There exist several other cases for which an exact or approximate solution is known. Here we mention those which bear importance in a collision problem. Rosen and Zener[2] have shown that Eqs. (1) [or Eqs. (5)] have an exact solution for the case

$$H_{22}-H_{11}=\Delta\epsilon,\ \ H_{12}=\beta\,\mathrm{sech}(\gamma t);\ \ \Delta\epsilon,\beta,\gamma\ \text{const}. \tag{7}$$

Being an exact solution, the Rosen-Zener solution can be used as a basis to obtain approximate solutions for collision systems for which the matrix elements H_{ij} take a different form.[9] The model of considerable importance in collision physics is the Landau-Zener model,[3] which provides an approximate solution to Eqs. (1) under the assumption that

$$H_{22}-H_{11}=\alpha(t-t_0),\ \ H_{12}=\beta;\ \ \alpha,\beta,t_0\ \text{const}. \tag{8}$$

This model has been widely used with success to describe collision processes involving curve crossings.[10] Another model of importance in collision physics is the Demkov model,[4] which provides a solution for the case

$$H_{22}-H_{11}=\Delta\epsilon,\ \ H_{12}=\beta e^{-\gamma|t|};\ \ \beta,\gamma,\Delta\epsilon\ \text{const}. \tag{9}$$

While the Landau-Zener model is useful for curve-crossing problems, the Demkov model has been found useful for describing collisions with two potential curves lying parallel to each other.[11] Finally, Nikitin[5] has obtained a solution for the case where

$$H_{22}-H_{11}=\alpha e^{-\gamma|t|}+\Delta\epsilon,\ \ H_{12}=\beta;\ \ \alpha,\beta,\gamma,\Delta\epsilon\ \text{const}. \tag{10}$$

In this paper we consider collision systems for which the interaction matrix element H_{12} is given by an exponential function $H_{12}=\beta e^{-\gamma|t|}$. Such systems are of practical importance because, for a large number of collision systems, the variation of H_{12} with respect to the internuclear distance can be well fit by an exponentially decreasing function.[12] If $H_{22}-H_{11}$ is independent of time, then we have the Demkov model. We first look at that model and derive an exact solution which is more general than the solution given by Demkov. We next consider the case

$$H_{22}-H_{11}=\alpha e^{-\gamma|t|},\ \ H_{12}=\beta e^{-\gamma|t|};\ \ \alpha,\beta,\gamma\ \text{const} \tag{11}$$

and show that an exact solution exists for this case. We call the model characterized by Eq. (11) the exponential model. We then consider the case of considerable practical importance, i.e., where

$$H_{22}-H_{11}=\alpha e^{-\gamma|t|}+\Delta\epsilon,\ \ H_{12}=\beta e^{-\gamma|t|};\ \ \alpha,\beta,\gamma,\Delta\epsilon\ \text{const}. \tag{12}$$

An approximate solution for this case is found in the form of the combination of the solutions for the Demkov and exponential models, thus the name Demkov-exponential model. Applications of the Demkov-exponential model to fine-structure transitions in Na-He, F-Xe, and F-H^+ collisions are also described.

It should be mentioned that Crothers[13] has obtained a solution for the Demkov-exponential model in terms of the confluent hypergeometric function. His solution, however, has a limited value due to difficulties associated with asymptotic expansions of the confluent hypergeometric function. Our approximate solution, on the other hand, is simple enough to allow determination of collision cross sections without much difficulty.

II. THE DEMKOV AND RELATED MODELS

In this section we find solutions to Eqs. (1) [or equivalently, Eqs. (5)] for the following three different models: (a) the Demkov model, characterized by Eq. (9); (b) the exponential model, characterized by Eq. (11); and (c) the Demkov-exponential model, characterized by Eq. (12). For our purpose we first obtain from Eqs. (5) second-order differential equations for a_1 and a_2:

$$\frac{d^2a_1}{dt^2}+\left[\frac{i}{\hbar}(H_{22}-H_{11})-\frac{\dot H_{12}}{H_{12}}\right]\frac{da_1}{dt}+\frac{H_{12}H_{21}}{\hbar^2}a_1=0 \tag{13}$$

and a similar equation for a_2. With a phase transformation

$$a_1=u_1\exp\left[-\frac{i}{2\hbar}\int^t(H_{22}-H_{11})dt_1+\tfrac{1}{2}\int^t\frac{\dot H_{12}}{H_{12}}dt_1\right], \tag{14a}$$

$$a_2=u_2\exp\left[\frac{i}{2\hbar}\int^t(H_{22}-H_{11})dt_1+\tfrac{1}{2}\int^t\frac{\dot H_{21}}{H_{21}}dt_1\right], \tag{14b}$$

the first-order derivative term in Eq. (13) can be eliminated to yield

$$\frac{d^2u_1}{dt^2}+\left[\frac{H_{12}H_{21}}{\hbar^2}+\frac{d}{dt}\left[-\frac{i}{2\hbar}(H_{22}-H_{11})+\frac{1}{2}\frac{\dot H_{12}}{H_{12}}\right]-\left[-\frac{i}{2\hbar}(H_{22}-H_{11})+\frac{1}{2}\frac{\dot H_{12}}{H_{12}}\right]^2\right]u_1=0, \tag{15a}$$

$$\frac{d^2u_2}{dt^2}+\left[\frac{H_{12}H_{21}}{\hbar^2}+\frac{d}{dt}\left[\frac{i}{2\hbar}(H_{22}-H_{11})+\frac{1}{2}\frac{\dot{H}_{21}}{H_{21}}\right]-\left[\frac{i}{2\hbar}(H_{22}-H_{11})+\frac{1}{2}\frac{\dot{H}_{21}}{H_{21}}\right]^2\right]u_2=0\,. \quad (15b)$$

Equations (15) are our working equations.

A. Demkov model

Demkov[4] has found a solution to Eq. (1) for the case given by Eq. (9) under the assumption that $\beta/\hbar\gamma \gg 1$. Here we derive an exact solution without making this assumption. Substituting Eq. (9) into Eqs. (15), we obtain, for the first half of the collision, i.e., for $t<0$,

$$\frac{d^2u_1}{dt^2}+\left[\frac{\beta^2}{\hbar^2}e^{2\gamma t}-\frac{1}{4}\left[\gamma-\frac{i}{\hbar}\Delta\epsilon\right]^2\right]u_1=0\,, \quad (16a)$$

$$\frac{d^2u_2}{dt^2}+\left[\frac{\beta^2}{\hbar^2}e^{2\gamma t}-\frac{1}{4}\left[\gamma+\frac{i}{\hbar}\Delta\epsilon\right]^2\right]u_2=0\,. \quad (16b)$$

Equations (16) are recognized as a varied form of the Bessel equation. The solution of Eqs. (16) which satisfies the initial condition, Eq. (2), is given by

$$u_1=\left[\frac{\pi\beta}{2\hbar\gamma}\operatorname{sech}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}e^{\gamma t}\right]\,. \quad (17a)$$

$$u_2=-i\left[\frac{\pi\beta}{2\hbar\gamma}\operatorname{sech}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{\nu_2}\left[\frac{\beta}{\hbar\gamma}e^{\gamma t}\right]\,, \quad (17b)$$

where

$$\nu_1=\tfrac{1}{2}-i\frac{\Delta\epsilon}{2\hbar\gamma},\quad \nu_2=\tfrac{1}{2}+i\frac{\Delta\epsilon}{2\hbar\gamma}\,. \quad (18)$$

In deriving Eqs. (17), the lower limit of the integrals that appear in Eqs. (14) has been chosen to be zero for convenience. We note that the unitarity of the system is ensured at all times by the Bessel function identity,

$$J_{-1/2+ix}(y)J_{-1/2-ix}(y)+J_{1/2+ix}(y)J_{1/2-ix}(y)=\frac{2}{\pi y}\cosh(\pi x)\,. \quad (19)$$

Equations (17) provide the initial condition,

$$u_1(0)=\left[\frac{\pi\beta}{2\hbar\gamma}\operatorname{sech}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]\,, \quad (20a)$$

$$u_2(0)=-i\left[\frac{\pi\beta}{2\hbar\gamma}\operatorname{sech}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]\,, \quad (20b)$$

for the second half of collision, $t\geq 0$, where Eqs. (15) read as

$$\frac{d^2u_1}{dt^2}+\left[\frac{\beta^2}{\hbar^2}e^{-2\gamma t}-\frac{1}{4}\left[\gamma+\frac{i}{\hbar}\Delta\epsilon\right]^2\right]u_1=0\,, \quad (21a)$$

$$\frac{d^2u_2}{dt^2}+\left[\frac{\beta^2}{\hbar^2}e^{-2\gamma t}-\frac{1}{4}\left[\gamma-\frac{i}{\hbar}\Delta\epsilon\right]^2\right]u_2=0\,. \quad (21b)$$

A general solution to Eqs. (21) is given by

$$u_1=A_1J_{\nu_2}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]+B_1J_{-\nu_2}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]\,, \quad (22a)$$

$$u_2=A_2J_{\nu_1}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]+B_2J_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]\,. \quad (22b)$$

The constants A_1, B_1, A_2, and B_2 can be determined by requiring that the solution satisfy Eqs. (1) and the initial condition, Eqs. (20). We then obtain with the help of the identity Eq. (19),

$$A_1=iB_2=\left[\frac{\pi\beta}{2\hbar\gamma}\right]^{3/2}\operatorname{sech}^{3/2}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\times\left[J_{\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]J_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]+J_{\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]J_{-\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]\right]\,, \quad (23a)$$

$$B_1=-iA_2=\left[\frac{\pi\beta}{2\hbar\gamma}\right]^{3/2}\operatorname{sech}^{3/2}\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\times\left[J^2_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]-J^2_{\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]\right]\,. \quad (23b)$$

The transition probability P is given in terms of a gamma function as

$$P=|c_2(t=\infty)|^2=\lim_{t\to\infty}e^{-\gamma t}|u_2(t)|^2=|B_2|^2\frac{2\hbar\gamma}{\beta}\frac{1}{\left|\Gamma\left[\frac{1}{2}+i\frac{\Delta\epsilon}{2\hbar\gamma}\right]\right|^2}\,. \quad (24)$$

Substituting Eq. (23a) into Eq. (24), we obtain

$$P=\left[\frac{\pi\beta}{2\hbar\gamma}\right]^2\operatorname{sech}^2\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\times\left[J_{\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]J_{-\nu_1}\left[\frac{\beta}{\hbar\gamma}\right]+J_{\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]J_{-\nu_2}\left[\frac{\beta}{\hbar\gamma}\right]\right]^2\,. \quad (25)$$

Equation (25) is an exact expression for the transition probability for the Demkov model. If $\beta/\hbar\gamma\gg 1$, then Eq. (25) is reduced to the formula derived by Demkov,[4]

$$P\cong\operatorname{sech}^2\left[\frac{\pi\Delta\epsilon}{2\hbar\gamma}\right]\sin^2\left[\frac{2\beta}{\hbar\gamma}\right]\,. \quad (26)$$

In order to see the importance of Eq. (25), we first note that the interaction matrix element H_{12} is equal to β at time $t=0$, i.e., at the time of the closest approach. This means that β represents the interaction matrix element at the time when the internuclear distance R is equal to impact parameter b. Assuming a straight-line trajectory with a constant velocity v, we then have

$$\beta \cong \beta_0 e^{-\lambda b} , \qquad (27)$$

where β_0 represents the value of H_{12} at $R=0$, and

$$\lambda \cong \gamma v . \qquad (28)$$

Thus, at large b, the parameter β is small and no longer satisfies the inequality $\beta/\hbar\gamma \gg 1$. In this case, Eq. (25) should be used instead of Eq. (26) for the evaluation of the transition probability. This is important because the behavior of the transition probability at large impact parameters often plays an essential role in determining the collision cross section σ according to the formula

$$\sigma = 2\pi \int_0^\infty P(b) b\, db . \qquad (29)$$

B. Exponential model

If both $H_{22}-H_{11}$ and H_{12} are given by an exponential function with the same decay constant γ,

$$H_{22}-H_{11} = \alpha e^{-\gamma|t|}, \quad H_{12} = \beta e^{-\gamma|t|} , \qquad (11)$$

an exact solution to Eqs. (1) can be found. The solution can be easily obtained by rewriting Eqs. (1) in terms of $\tau \equiv e^{-\gamma|t|}$. For use in our discussion of the Demkov-exponential model, however, we find it more convenient to derive the solution without introducing the new variable τ. Substituting Eq. (11) into Eqs. (15), we obtain, for $t<0$,

$$\frac{d^2 u_{1,2}}{dt^2} + \left[\left[\frac{\beta^2}{\hbar^2} + \frac{\alpha^2}{4\hbar^2} \right] e^{2\gamma t} - \frac{\gamma^2}{4} \right] u_{1,2} = 0 . \qquad (30)$$

The solution to Eq. (30), subject to the initial condition Eq. (2), is

$$u_1 = \frac{i\alpha}{2\hbar\gamma} \left[\frac{\pi}{2x} \right]^{1/2} J_{1/2}(x e^{\gamma t}) + \left[\frac{\pi x}{2} \right]^{1/2} J_{-1/2}(x e^{\gamma t}) , \qquad (31a)$$

$$u_2 = -\frac{i\beta}{\hbar\gamma} \left[\frac{\pi}{2x} \right]^{1/2} J_{1/2}(x e^{\gamma t}) , \qquad (31b)$$

where

$$x = \left[\frac{\beta^2}{\hbar^2\gamma^2} + \frac{\alpha^2}{4\hbar^2\gamma^2} \right]^{1/2} . \qquad (32)$$

At $t=0$ we have

$$u_1(0) = \frac{i\alpha}{2\hbar\gamma} \left[\frac{\pi}{2x} \right]^{1/2} J_{1/2}(x) + \left[\frac{\pi x}{2} \right]^{1/2} J_{-1/2}(x) , \qquad (33a)$$

$$u_2(0) = -\frac{i\beta}{\hbar\gamma} \left[\frac{\pi}{2x} \right]^{1/2} J_{1/2}(x) . \qquad (33b)$$

Equations (33) constitute the initial condition for $t \geq 0$ where Eqs. (15) read as

$$\frac{d^2 u_{1,2}}{dt^2} + \left[\left[\frac{\beta^2}{\hbar^2} + \frac{\alpha^2}{4\hbar^2} \right] e^{-2\gamma t} - \frac{\gamma^2}{4} \right] u_{1,2} = 0 . \qquad (34)$$

Thus

$$u_1 = C_1 J_{1/2}(x e^{-\gamma t}) + D_1 J_{-1/2}(x e^{-\gamma t}) , \qquad (35a)$$

$$u_2 = C_2 J_{1/2}(x e^{-\gamma t}) + D_2 J_{-1/2}(x e^{-\gamma t}) . \qquad (35b)$$

The constants C_1, D_1, C_2, and D_2 can be determined by requiring that the solution satisfies Eqs. (1) and the initial condition, Eqs. (33). Among these the constant D_2 is of our most interest because the transition probability P is given by

$$P = |c_2(\infty)|^2 = \lim_{t\to\infty} e^{-\gamma t} |u_2(t)|^2 = |D_2|^2 \frac{2}{\pi x} . \qquad (36)$$

Through straightforward algebra we obtain

$$P = \frac{\beta^2}{\hbar^2\gamma^2 x^2} \sin^2(2x) = \frac{\beta^2}{\beta^2+\alpha^2/4} \sin^2 \left[2 \left[\frac{\beta^2}{\hbar^2\gamma^2} + \frac{\alpha^2}{4\hbar^2\gamma^2} \right]^{1/2} \right] . \qquad (37)$$

Equation (37) is an exact expression for the transition probability for the exponential model. It coincides with the expression for the transition probability for a stationary two-level system subject to a constant interaction. This is not surprising because it can be shown, by expressing Eqs. (1) in terms of $\tau \equiv e^{-\gamma|t|}$, that the exponential model is formally equivalent to such a two-level system. In τ space, the interaction time is 2, from $\tau=0$ ($t=-\infty$) through $\tau=1$ ($t=0$) back to $\tau=0$ ($t=\infty$), thus the appearance of the sine term in Eq. (37). The parameter β/γ plays the role of the interaction strength, whereas α/γ represents detuning.

C. Demkov-exponential model

For many collision systems the matrix elements H_{ij} can be approximated as

$$H_{22}-H_{11} = \alpha e^{-\gamma|t|} + \Delta\epsilon, \quad H_{12} = \beta\epsilon^{-\gamma|t|} . \qquad (12)$$

In this case Eqs. (15) become, for $t<0$,

$$\frac{d^2 u_1}{dt^2} + \left[\left[\frac{\beta^2}{\hbar^2} + \frac{\alpha^2}{4\hbar^2} \right] e^{2\gamma t} + \frac{\alpha\Delta\epsilon}{2\hbar^2} e^{\gamma t} - \frac{1}{4} \left[\gamma - \frac{i}{\hbar}\Delta\epsilon \right]^2 \right] u_1 = 0 , \qquad (38)$$

and a similar equation for u_2. Through a change of variable, Eq. (38) can be put in the form of the Whittaker equation. The solution to this equation can then be obtained in terms of the derivative of the confluent hypergeometric function,[13] whose evaluation is rather difficult. We therefore look for an approximate solution.

From Eq. (12) we immediately see that if $|t|$ is sufficiently large, $H_{22}-H_{11} \cong \Delta\epsilon$. On the other hand, when $|t|$ is small, $H_{22}-H_{11} \cong \alpha e^{-\gamma|t|}$, assuming $\alpha \gg \Delta\epsilon$. This suggests that a collision system characterized by Eq. (12) can be regarded approximately as a combination of the Demkov and exponential models. Thus we can approximate Eq. (12) as

$$H_{22}-H_{11}=\Delta\epsilon,\ H_{12}=\beta e^{-\gamma|t|} \text{ if } |t|\geq|t_m| \quad (39a)$$

$$H_{22}-H_{11}=\alpha e^{-\gamma|t|},\ H_{12}=\beta e^{-\gamma|t|} \text{ if } |t|\leq|t_m| \quad (39b)$$

where t_m is defined through the expression

$$\alpha e^{-\gamma|t_m|}=\Delta\epsilon\ , \quad (40a)$$

which yields

$$|t_m|=\frac{1}{\gamma}\ln\frac{\alpha}{\Delta\epsilon}\ . \quad (40b)$$

One drawback of the approximation represented by Eqs. (39) is that it constantly underestimates the value of $H_{22}-H_{11}$. In order to make up for this, we introduce a parameter $p\geq 1$ and modify Eqs. (39) as

$$H_{22}-H_{11}=p\Delta\epsilon,\ H_{12}=\beta e^{-\gamma|t|} \text{ if } |t|\geq|t_m| \quad (41a)$$

$$H_{22}-H_{11}=\alpha e^{-\gamma|t|},\ H_{12}=\beta e^{-\gamma|t|} \text{ if } |t|\leq|t_m| \quad (41b)$$

where t_m is now determined by

$$\alpha e^{-\gamma|t_m|}=p\Delta\epsilon\ , \quad (42a)$$

or

$$|t_m|=\frac{1}{\gamma}\ln\frac{\alpha}{p\Delta\epsilon}\ . \quad (42b)$$

The choice of p is arbitrary to a certain degree. For fine-structure transitions in atomic collisions, we have found the choice $p=1.5$ to yield reasonably accurate cross sections, as will be shown in Sec. III. In this section we leave the value of p unspecified.

The approximation given by Eqs. (41) allows us to discuss the collision process in four different time regions: (I) $t\leq-|t_m|$, (II) $-|t_m|\leq t\leq 0$, (III) $0\leq t\leq|t_m|$, and (IV) $|t_m|\leq t$. In regions I and IV the Demkov model is applicable, whereas in regions II and III the exponential model can be used. Referring to our previous discussion of the Demkov model, the expression for u_1 and u_2 in region I can be immediately written. It is identical with Eqs. (17) except that $\Delta\epsilon$ should now be replaced by $p\Delta\epsilon$. The initial condition for u_1 and u_2 in region II is then given by

$$u_1(-|t_m|)=\left[\frac{\pi\beta}{2\hbar}\operatorname{sech}\left[\frac{\pi p\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{-\mu_1}\left[\frac{\beta p\Delta\epsilon}{\hbar\gamma\alpha}\right]\ , \quad (43a)$$

$$u_2(-|t_m|)=-i\left[\frac{\pi\beta}{2\hbar\gamma}\operatorname{sech}\left[\frac{\pi p\Delta\epsilon}{2\hbar\gamma}\right]\right]^{1/2}J_{\mu_2}\left[\frac{\beta p\Delta\epsilon}{\hbar\gamma\alpha}\right]\ , \quad (43b)$$

where

$$\mu_1=\tfrac{1}{2}-i\frac{p\Delta\epsilon}{2\hbar\gamma},\ \ \mu_2=\tfrac{1}{2}+i\frac{p\Delta\epsilon}{2\hbar\gamma}\ . \quad (44)$$

The solution for u_1 and u_2 in region II is that of the exponential model,

$$u_1=E_1J_{1/2}(xe^{\gamma t})+F_1J_{-1/2}(xe^{\gamma t})\ , \quad (45a)$$

$$u_2=E_2J_{1/2}(xe^{\gamma t})+F_2J_{-1/2}(xe^{\gamma t})\ . \quad (45b)$$

The constants E_1, F_1, E_2, and F_2 can be determined by requiring that Eqs. (45) satisfy Eqs. (1) and the initial condition, Eqs. (43). Equations (45) then provide the initial condition for region III,

$$u_1(0)=E_1J_{1/2}(x)+F_1J_{-1/2}(x)\ , \quad (46a)$$

$$u_2(0)=E_2J_{1/2}(x)+F_2J_{-1/2}(x)\ . \quad (46b)$$

The general solution for u_1 and u_2 in region III is given by

$$u_1(t)=G_1J_{1/2}(xe^{-\gamma t})+H_1J_{-1/2}(xe^{-\gamma t})\ , \quad (47a)$$

$$u_2(t)=G_2J_{1/2}(xe^{-\gamma t})+H_2J_{-1/2}(xe^{-\gamma t})\ , \quad (47b)$$

subject to the initial condition, Eqs. (46). After the constants G_1, H_1, G_2, and H_2 are determined as before, Eqs. (47) provide the initial condition

$$u_1(|t_m|)=G_1J_{1/2}\left[\frac{xp\Delta\epsilon}{\alpha}\right]+H_1J_{-1/2}\left[\frac{xp\Delta\epsilon}{\alpha}\right]\ , \quad (48a)$$

$$u_2(|t_m|)=G_2J_{1/2}\left[\frac{xp\Delta\epsilon}{\alpha}\right]+H_2J_{-1/2}\left[\frac{xp\Delta\epsilon}{\alpha}\right]\ , \quad (48b)$$

for region IV, where the general solution for u_1 and u_2 can be written as

$$u_1(t)=K_1J_{\mu_2}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]+L_1J_{-\mu_2}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]\ , \quad (49a)$$

$$u_2(t)=K_2J_{\mu_1}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]+L_2J_{-\mu_1}\left[\frac{\beta}{\hbar\gamma}e^{-\gamma t}\right]\ . \quad (49b)$$

The constants K_1, L_1, K_2, and L_2 can again be determined by requiring that Eqs. (49) satisfy Eqs. (1) and the initial condition, Eqs. (48).

Finally, the transition probability is given by

$$P=|c_2(\infty)|^2=\lim_{t\to\infty}e^{-\gamma t}|u_2(t)|^2 = |L_2|^2\frac{2\hbar\gamma}{\beta}\frac{1}{\left|\Gamma\left[\frac{1}{2}+i\frac{p\Delta\epsilon}{2\hbar\gamma}\right]\right|^2}\ . \quad (50)$$

The algebra necessary to determine the constants E_1,F_1 through K_2,L_2 is lengthy but straightforward. Here we only write the final expression for the transition probability P:

$$P=[A\cos(2x-2xp\Delta\epsilon/\alpha)+B\sin(2x-2xp\Delta\epsilon/\alpha)]^2\ , \quad (51a)$$

where

$$A=2\rho_1\rho_2\cos(\phi_1-\phi_2)/(\rho_1^2+\rho_2^2)\ , \quad (51b)$$

$$B=\left[\frac{\alpha}{2\hbar x\gamma}2\rho_1\rho_2\sin(\phi_1-\phi_2)+\frac{\beta}{\hbar x\gamma}(\rho_2^2-\rho_1^2)\right]\Big/(\rho_1^2+\rho_2^2)\ , \tag{51c}$$

and ρ_1, ρ_2, ϕ_1, and ϕ_2 are defined through the expressions

$$J_{\mu_2}\left[\frac{\beta p\Delta\epsilon}{\hbar\gamma\alpha}\right]=\rho_1 e^{i\phi_1},\ J_{-\mu_1}\left[\frac{\beta p\Delta\epsilon}{\hbar\gamma\alpha}\right]=\rho_2 e^{i\phi_2}\ . \tag{52}$$

Equations (51) provide the main result of the this paper, giving an approximate transition probability for the Demkov-exponential model. A few remarks on Eqs. (51) are in order.

(1) The basic assumption behind Eqs. (51) is the division of the time region into the Demkov and exponential regions as indicated in Eqs. (41). It is clear from Eqs. (42) that this division is possibly only if

$$\alpha\geq p\Delta\epsilon\ . \tag{53}$$

If α is smaller than $p\Delta\epsilon$, t_m cannot be defined and the system should be described entirely by the Demkov model within our approximation scheme.

(2) Owing to Eq. (19), the term $\rho_1^2+\rho_2^2$ that appears in Eqs. (51) can be identified as $(2\hbar\gamma\alpha/\pi\beta p\Delta\epsilon)\times\cosh(\pi p\Delta\epsilon/2\hbar\gamma)$. This provides a valuable check on our calculation because, in most of the examples described in Sec. III, ρ_1, ρ_2, ϕ_1, and ϕ_2 were evaluated numerically using either the series expansion or the asymptotic expansion of the Bessel function. Note that we need to evaluate Bessel functions of complex indices μ_1 and μ_2.

(3) In the limit $\Delta\epsilon\to 0$, we have $\rho_2\gg\rho_1$ and thus $P\to(\beta^2/\hbar^2\gamma^2x^2)\sin^2(2x)$. This is identical with the probability for the exponential model, Eq. (37), as it should be.

(4) In the limit $\alpha\to p\Delta\epsilon$, we have $P\to A^2=[2\rho_1\rho_2\cos(\phi_1-\phi_2)/(\rho_1^2+\rho_2^2)]^2$. It can be easily seen, with the help of Eqs. (52) and (19), that this probability is identical with the probability for the Demkov model, Eq. (25), if $\Delta\epsilon$ in Eq. (25) is replaced by $p\Delta\epsilon$. This is expected because, as α approaches $p\Delta\epsilon$, $|t_m|$ approaches zero and the collision process is described entirely by the Demkov model.

The collision cross section for the Demkov-exponential model can now be determined according to Eq. (29). The parameters that give the b dependence of P are β, α, and x. Recalling that β and α refer to values at the time of the closest approach, we may set $\beta\cong\beta_0e^{-\lambda b}$, $\alpha\cong\alpha_0e^{-\lambda b}$, and $x\cong x_0e^{-\lambda b}$, where β_0, α_0, and x_0 denote the values at $R=0$. Since β, α, and x show the same b dependence, the coefficients A and B are independent of b. Thus, we may write

$$\begin{aligned}P=P(b)&=[A\cos(2x_0e^{-\lambda b}-2xp\Delta\epsilon/\alpha)\\&\quad+B\sin(2x_0e^{-\lambda b}-2xp\Delta\epsilon/\alpha)]^2\\&=(A^2+B^2)\sin(2x_0e^{-\lambda b}-2xp\Delta\epsilon/\alpha+\phi)\ ,\end{aligned} \tag{54}$$

where ϕ satisfies

$$\tan\phi=A/B\ . \tag{55}$$

For typical collision systems, P oscillates between its maximum value of A^2+B^2 and minimum value of zero at small impact parameters, finally decaying to zero at large impact parameters. Following Rapp and Francis,[9] we define R_* as the largest value of b that yields $P=(A^2+B^2)/4$, i.e., R_* satisfies

$$2x_0e^{-\lambda R_*}-2xp\Delta\epsilon/\alpha+\phi=\frac{\pi}{6}\ . \tag{56}$$

The cross section is then estimated as

$$\sigma\cong(A^2+B^2)\pi R_*^2/2\ . \tag{57}$$

We note that the determination of R_* according to Eq. (56) assumes that the system can be described by the Demkov-exponential model even at high impact parameters, $b\sim R_*$. Referring to Eq. (53), this means that Eq. (56) cannot be used when $\alpha_0e^{-\lambda R_*}<p\Delta\epsilon$. In this case, collisions at large impact parameters are better described by the Demkov model, and R_* should be estimated accordingly, i.e., a reasonable definition of R_* in this case is the largest value of b that yields a quarter of the maximum value, A^2+B^2, when the probability is calculated from the Demkov formula. Since near R_* the parameter $\beta/\hbar\gamma$ is typically small, one should use Eq. (25), not Eq. (26), to find R_*. For this purpose, it is convenient to rewrite Eq. (25), using the series expansion of the Bessel function, as

$$P=\left[\sum_{k=0}^{\infty}\frac{(-1)^k\left[\dfrac{\beta}{2\hbar\gamma}\right]^{2k+1}(2k+1)!}{(k!)^2\left[(\frac{1}{2}+k)^2+\left[\dfrac{p\Delta\epsilon}{2\hbar\gamma}\right]^2\right]\left[(\frac{1}{2}+k-1)^2+\left[\dfrac{p\Delta\epsilon}{2\hbar\gamma}\right]^2\right]\cdots\left[(\frac{1}{2})^2+\left[\dfrac{p\Delta\epsilon}{2\hbar\gamma}\right]^2\right]}\right]^2\ . \tag{58}$$

In accordance with the approximation of Eqs. (41), $\Delta\epsilon$ in Eq. (25) was replaced by $p\Delta\epsilon$ before the series expansion was performed. R_* can now be estimated by performing a perturbative calculation on Eq. (58).

III. APPLICATIONS TO FINE-STRUCTURE TRANSITIONS

In this section we evaluate cross sections for fine-structure transitions in the following systems, using the Demkov-exponential model described in the preceding section:

$$Na(^2P_{1/2})+He \rightarrow Na(^2P_{3/2})+He\ , \tag{59}$$

$$F(^2P_{3/2})+Xe \rightarrow F(^2P_{1/2})+Xe\ , \tag{60}$$

$$F(^2P_{1/2})+H^+ \rightarrow F(^2P_{3/2})+H^+\ . \tag{61}$$

Some accurate and/or approximate calculations on these systems already exist.[14–17] For the above processes the matrix element can be written as[14]

$$H_{22}-H_{11}=\tfrac{1}{3}\Delta W+\Delta\epsilon\ , \tag{62a}$$

$$H_{12}=\frac{\sqrt{2}}{3}\Delta W\ , \tag{62b}$$

where $\Delta\epsilon$ is the energy of the fine-structure splitting, and ΔW represents the difference in energy of potential energy curves for the Σ and Π states without spin-orbit coupling. Since ΔW can be reasonably well approximated by an exponential function of the form

$$\Delta W \cong Ce^{-\lambda R}\ , \tag{63}$$

the Demkov-exponential model is particularly useful for a description of fine-structure transitions. Atomic units will be used in this section unless specified otherwise.

A. Na + He collision

For a numerical calculation of cross sections for the Na-He system based on an impact-parameter treatment, Masnou-Seeuws[17] assumed the following form for $\Delta W = W_\Sigma - W_\Pi$:

$$\Delta W = 0.1R^{2.2}e^{-0.94R}\ . \tag{64}$$

In order to apply the Demkov-exponential model to this system, however, we need to express ΔW in the form of Eq. (63). We find that the expression

$$\Delta W = 3.54e^{-0.79R} \tag{65}$$

approximates Eq. (64) well in the region of importance, $R \sim 8-15$. Equation (65) is the form that we choose because we wish to compare our cross sections with those of Masnou-Seeuws. From Eqs. (62) we then have $\alpha_0=3.54/3$, $\beta_0=3.54\sqrt{2}/3$. Other parameters we need for the evaluation of P are $\Delta\epsilon=17.19\ \mathrm{cm}^{-1}=7.83\times10^{-5}$ a.u., $\lambda=0.79$, i.e., $\gamma=0.79v$ (v is the relative velocity of the colliding partners), and the parameter p introduced in Eqs. (41) is taken to be $p=1.5$.

A major part of our calculation consists of evaluating Bessel functions to obtain ρ_1, ρ_2, ϕ_1, and ϕ_2 defined by Eqs. (52). At the velocity range of our interest ($v=5\times10^{-4}$–5×10^{-3}), this turns out to be readily achieved by the series expansion of the Bessel functions. Once ρ_1, ρ_2, ϕ_1, and ϕ_2 are evaluated, the value of A^2+B^2 can be easily obtained using Eqs. (51b) and (51c). Next, R_* can be estimated using Eq. (56) or based on Eq. (58) depending upon whether $\alpha_0 e^{-\lambda R_*}$ is greater or smaller than $p\Delta\epsilon=(1.5)\Delta\epsilon$. Since, within the approximation of the Demkov-exponential model, R_* is a decreasing function of the velocity v, Eq. (56) can be used at relatively high collision velocities, whereas Eq. (58) forms the basis of our evaluation of R_* at low collision velocities. For example, at four values of velocity chosen for our calculation (v=0.0005, 0.001, 0.002, and 0.005), we needed to refer to Eq. (58) at v=0.0005 while Eq. (56) was used at other velocities. Finally, with A^2+B^2 and R_* being evaluated, the cross section σ is obtained using Eq. (57).

The results of our calculation are summarized in Table II. Note that R_* is a decreasing function of v whereas A^2+B^2 increases with v. Also shown in the table are the cross sections $\sigma_{\text{M-S}}$ of Masnou-Seeuws[17] obtained by an impact-parameter treatment with a two-state approximation neglecting rotational coupling. The agreement between the two is fair, although the Demkov-exponential model indicates a peak at a lower value (<0.0005) of the velocity.

B. F + Xe collisions

Preston, Sloan, and Miller[15] have made cross-section calculations on the process (60) using a complex-valued semiclassical trajectory approach. For the F-Xe system, they approximated $\Delta W = W_\Pi - W_\Sigma$ as

$$\Delta W = 48.2e^{-1.65R}\ , \tag{66}$$

which is the form we have chosen for our calculation. Thus, we have $\alpha_0=48.2/3$, $\beta_0=48.2\sqrt{2}/3$, $\lambda=1.65$, and $\gamma=1.65v$. Other parameters for the F-Xe system are $\Delta\epsilon=0.001\,842$ and $p=1.5$. Since the method of calculation is the same as that for Na + He collisions, we simply present our results, which are summarized in Table III. Also shown in the table are semiclassical cross sections σ_{PSM} calculated by Preston *et al.*[15] Although the agreement is reasonable, it is difficult to assess the accuracy of the Demkov-exponential model here because the semiclassical approach of Preston *et al.* itself is approximate. We note here that the cross sections shown in Table III represent the values summed over final states and averaged over initial states, i.e.,

$$\sigma=\tfrac{1}{2}\sigma(j=\tfrac{3}{2},m_j=\tfrac{1}{2}\rightarrow j=\tfrac{1}{2},m_j=\tfrac{1}{2})\ .$$

C. F + H$^+$ collisions

The accuracy of the Demkov-exponential model depends largely on the validity of the constant-velocity straight-line trajectory approximation. Therefore, the model is expected to be more accurate at high collision velocities. For the F-H$^+$ system, an accurate quantum-mechanical calculation of Mies[14] exists, which prompted

TABLE II. Cross sections for Na + He collisions.

	Velocity v (a.u.)			
	0.0005	0.001	0.002	0.005
A^2+B^2	0.807	0.869	0.884	0.888
R_* (a_0)	12.3	11.5	10.6	9.4
σ (a_0^2)	192	179	155	124
$\sigma_{\text{M-S}}$ (a_0^2)	180	220	210	190

TABLE III. Cross sections for F + Xe collisions.

Collision energy (eV)=	0.3	0.5	0.7
Velocity v (a.u.)=	0.000 85	0.0011	0.0013
A^2+B^2	0.001 93	0.0251	0.0773
R_* (a_0)	7.7	7.0	5.2
σ (a_0^2)	0.09	0.95	1.63
σ_{PSM} (a_0^2)	0.1	0.42	1.0

TABLE IV. Cross sections for F + H^+ collisions.

	Velocity v (a.u.)		
	0.0018	0.0026	0.0032
A^2+B^2	0.003 26	0.0783	0.474
R_* (a_0)	9.4	7.8	7.2
σ (a_0^2)	0.46	7.4	15.5
σ_M (a_0^2)	1.5	7	17

us to try the Demkov-exponential model on this system. However, the collision-energy range at which Mies's cross sections were reported is low, on the order of the energy of the fine-structure splitting of F, or slightly higher. This, together with the strong attractive potential wells of the potential energy curves of the F-H^+ system, invalidates the constant-velocity approximation. Thus the Demkov-exponential model cannot be expected to yield as accurate cross sections for F + H^+ collisions as for Na + He or F + Xe collisions. The potential energy difference $\Delta W = W_\Sigma - W_\Pi$ for the F-H^+ system calculated from the potential curves of Wahl, Julienne, and Krauss[18] can be adequately fit by an exponential function

$$\Delta W = 0.6612 e^{-0.86R} . \tag{67}$$

The parameters for the Demkov-exponential model of the F-H^+ system are $\alpha_0 = 0.6612/3$, $\beta_0 = 0.6612\sqrt{2}/3$, $\lambda = 0.86$, $\gamma = 0.86v$, $\Delta\epsilon = 0.001\,842$, and $p = 1.5$.

The results of our calculations are summarized in Table IV. Also shown in Table IV are quantum-mechanical cross sections σ_M calculated by Mies.[14] Surprisingly, the agreement between the two sets of the cross sections is not bad. We point out, however, that, if we had used a larger value of v in our calculation in order to account for the strong attractive wells of the potential energy curves involved, the agreement would not have been as good. One therefore should exercise caution when applying the Demkov-exponential model to a low-velocity collision, especially if the potential energy curves involved show a strong variation with respect to the internuclear distance.

IV. SUMMARY AND DISCUSSION

Exact solutions to the first-order coupled differential equations [Eq. (1)] which appear frequently in collision physics have been derived for the Demkov model [Eq. (9)] and for the exponential model [Eq. (11)]. Based upon these exact solutions, an approximate expression for the transition probability [Eqs. (51)] has been obtained for the case where $H_{22} - H_{11} = \alpha e^{-\gamma|t|} + \Delta\epsilon$ and $H_{12} = \beta e^{-\gamma|t|}$. This expression has been found useful in describing fine-structure transitions in atomic collisions. We believe that this model, the Demkov-exponential model, is of practical value, as it is expected to approximate a larger number of actual collision systems that undergo fine-structure transitions, charge exchange, or chemical reactions.

An advantage of the Demkov-exponential model over other models is that the transition probability is given in an analytic form [Eqs. (51)] and the calculational effort required is minimal. Cross sections can be determined without the help of a computer. Because of the constant-velocity approximation implicit in the Demkov-exponential model, it is expected to work better at high collision energies and thus is complementary to the quantum-mechanical coupled-channel approach.

One drawback of the model is that the parameter p is arbitrary to a certain degree. Although the examples discussed in the previous sections show that the choice $p = 1.5$ leads to reasonably accurate cross-section values, it still is desirable to have a reliable recipe by which to predetermine p. This is particularly so because the transition probability seems to vary with p in a nontrivial way.

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