Theoretical method for solving a two-level collision system

D. Arora
Division of Radiological Protection, Bhabha Atomic Research Center, Trombay, Bombay-400 085, India

J. E. Turner
Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Collisionally induced transitions between two electronic states during atom-atom collisions are described in the near-adiabatic formalism. The two-level system, in the semiclassical impact-parameter method, is represented by time-dependent coupled differential equations which have been studied by many workers. We present a method of solving the system of equations under the approximation of slow variation of the matrix elements responsible for the transition. A general formula for the transition probability is obtained with special reference to the problem of charge transfer, though the result is applicable to other two-level systems. The formula reduces under various special conditions to other well-known expressions, such as those found by Vainshtein and co-workers, the Landau-Zener formula, and that for resonance charge transfer.

I. INTRODUCTION

In a previous paper[1] (referred to as I), we reported the results of calculations of cross sections for electron transfer between ground- and excited-state alkali-metal atoms and halogen atoms. The computations utilized a near-adiabatic approximation in which the nuclear motion was assumed to be classical and rectilinear. These studies were motivated by a more general interest in two-level systems where transitions are induced by time-dependent perturbations. Such systems occur in studies in radiation research, controlled-thermonuclear-fusion plasmas, and laser-matter interactions. Because of their importance and the need for estimates of cross sections, we have extended our earlier work, presenting here a more general formula for the transition probability appropriate to single-electron two-center systems, in particular. Early investigations of the two-level systems were carried out by Landau,[2] Zener,[3] and Stueckelberg.[4] They obtained an estimate of the two-state transition probability for two potential-energy curves having a crossing or near crossing. Estimates of charge transfer probability have been considered by Gurnee and Magee,[5] Rapp and Francis,[6] and others.[7-10] Recently, Payne and Nayfeh[11] have studied the problem of energy transfer in a two-state model between slowly moving atoms and have obtained a formula for the transition probability. We derive here, for a two-level system, a more general formula for the transition probability, which under special conditions reduces to earlier known formulas. The new formalism is less restrictive and clarifies some assumptions made in the earlier studies.

II. BASIC EQUATIONS

The basic coupled differential equations describing the electron in the quantum-mechanical two-level system can be written in the following form[10,11,13]:

$$i\frac{da}{dt} = V_{ii}a + V_{ij}e^{-i\omega_0 t}b\,, \tag{1}$$

$$i\frac{db}{dt} = V_{ji}e^{i\omega_0 t}a + V_{jj}b\,. \tag{2}$$

Here a and b represent the amplitudes of the initial and final states of the electron undergoing the transition, and ω_0 is the energy difference between the states. The subscripts i and j on the matrix elements V denote the initial and final states. In the case of inelastic atom-atom collisions, which concerns us here, Eqs. (1) and (2) can describe excitation of one of the atoms, excitation transfer and charge transfer. These processes are represented symbolically by writing

$$A+B\rightarrow A^*+B,\quad A^*+B\rightarrow B^*+A\,,\quad A+B\rightarrow A^+ + B^-\,,$$

where A and B are the interacting atoms and the asterisk denotes an excited state.

Recently, Payne and Nayfeh[11] have solved the above system of equations in the case of energy transfer between slowly moving atoms which have nearly resonant energy levels. They point out that their result is also applicable for calculating the probability of leaving an excited atom behind after the passage of a nearly resonant laser pulse through a low-density gas or vapor. Their method is designed to take advantage of the slowness of the interaction, and the final result reduces to the one obtained by Vainshtein *et al.*[13] and others.[10]

In the present treatment we solve the above system of equations with special reference to the charge transfer problem. We find a more general formula than was obtained in I or by Payne and Nayfeh. In the case of excitation, Eqs. (1) and (2) are Hermitian ($V_{ij} = V_{ij}^*$). However, for charge transfer and excitation transfer, where the electron is bound to different atoms before and after the collision, the set is generally not Hermitian ($V_{ij} \neq V_{ij}^*$). This difficulty, which arises due to nonorthogonality of the initial and final states of the electron, can be overcome by suitable transformation.[12] One finally ends up with a similar Hermitian set of equations, though the forms of the coupling matrix elements are not as simple.[1]

III. METHOD OF SOLUTION

Equations (1) and (2) are to be solved for the transition probability $|b(+\infty)|^2$ in the impact-parameter method under the initial conditions $a(-\infty) = 1$ and $b(-\infty) = 0$. We start with a trial solution of the form

$$a = A(t) \exp\left(-i \int_{-\infty}^{t} \omega \, dt'\right), \tag{3}$$

$$b = B(t) \exp\left(-i \int_{-\infty}^{t} (\omega - \omega_0) \, dt'\right), \tag{4}$$

where the lower limit in the integration is the time ($t = -\infty$) when the interaction starts and where A, B, and ω are all real quantities. Substitution into (1) and (2) gives

$$i\dot{A} = (V_{ii} - \omega)A + BV_{ij}, \tag{5}$$

$$i\dot{B} = [V_{jj} - (\omega - \omega_0)]B + AV_{ji}. \tag{6}$$

Comparison of the real and imaginary parts in (5) and (6) implies that

$$i\dot{A} = i\dot{B} = 0$$

(which shows that A and B are constant in this approximation),

$$(V_{ii} - \omega)A + BV_{ij} = 0 \tag{7}$$

and

$$[V_{jj} - (\omega - \omega_0)]B + AV_{ji} = 0. \tag{8}$$

Solution of the homogeneous equations (7) and (8) gives

$$\omega_{\pm} = V_{ii} + \tfrac{1}{2}\alpha \pm \delta, \tag{9}$$

where

$$\alpha = V_{jj} - V_{ii} + \omega_0 \tag{10}$$

and

$$\delta = \tfrac{1}{2}(\alpha^2 + 4V^2)^{1/2} \tag{11}$$

with

$$V^2 = |V_{ij} V_{ji}^*|,$$

V_{ij} being Hermitian. By Eqs. (7) and (8) the two values of A and B are related through $\omega_{\pm}$ and the coupling matrix elements are given by

$$B_1 = [(\omega_+ - V_{ii})/V_{ij}]A_1 \tag{12}$$

and

$$B_2 = [(\omega_- - V_{ii})/V_{ij}]A_2. \tag{13}$$

The most general solution for a and b is a linear combination of the two solutions corresponding to

$$a = A_1 \exp\left(-i \int_{-\infty}^{t} \omega_+ \, dt'\right) + A_2 \exp\left(-i \int_{-\infty}^{t} \omega_- \, dt'\right), \tag{14}$$

$$b = B_1 \exp\left(-i \int_{-\infty}^{t} (\omega_+ - \omega_0) dt'\right) + B_2 \exp\left(-i \int_{-\infty}^{t} (\omega_- - \omega_0) dt'\right). \tag{15}$$

Applying the boundary conditions $a(-\infty) = 1$ and $b(-\infty) = 0$ in Eqs. (14) and (15) and using Eqs. (12) and (13), we have

$$A_1 + A_2 = 1 \tag{16}$$

and

$$\frac{\omega_+ - V_{ii}}{V_{ij}} A_1 + \frac{\omega_- - V_{ii}}{V_{ij}} A_2 = 0. \tag{17}$$

Solving (16) and (17), we obtain

$$A_1 = (\omega_- - V_{ii})/(\omega_- - \omega_+) \tag{18}$$

and

$$A_2 = (V_{ii} - \omega_+)/(\omega_- - \omega_+). \tag{19}$$

From Eqs. (12), (13), (18), and (19) we obtain

$$B_1 = \frac{\omega_+ - V_{ii}}{V_{ij}} \frac{\omega_- - V_{ii}}{\omega_- - \omega_+} \tag{20}$$

and

$$B_2 = \frac{\omega_- - V_{ii}}{V_{ij}} \frac{V_{ii} - \omega_+}{\omega_- - \omega_+}. \tag{21}$$

Substituting the values of A_1 and A_2 in Eq. (14) and using Eq. (9), we find that

$$a \exp\left(i \int_{-\infty}^{t} V_{ii} \, dt'\right) = \frac{1}{2\delta}\left[\left(\frac{\alpha}{2} + \delta\right) \exp\left(i \int_{-\infty}^{t} \delta \, dt'\right) + \left(\delta - \frac{\alpha}{2}\right) \exp\left(-i \int_{-\infty}^{t} \delta \, dt'\right)\right] \times \exp\left(-i \int_{-\infty}^{t} \frac{\alpha}{2} \, dt'\right). \tag{22}$$

We next carry out a unitary transformation by

introducing

$$a = a' \exp\left(-i\int_{-\infty}^{t} V_{ii}\,dt'\right) \tag{23}$$

and

$$b = b' \exp\left(-i\int_{-\infty}^{t} V_{jj}\,dt'\right), \tag{24}$$

which does not alter the main quantity of interest, namely, $|b(t)|^2$. This substitution helps get rid of secular terms in Eqs. (1) and (2) in place of which we now write

$$i\frac{da'}{dt} = V_{ij} b' \exp\left(-i\int_{-\infty}^{t} \alpha\,dt'\right), \tag{25}$$

$$i\frac{db'}{dt} = V_{ji} a' \exp\left(i\int_{-\infty}^{t} \alpha\,dt'\right). \tag{26}$$

The left-hand side of Eq. (22) is a'. Collecting the real and imaginary parts of the expression in the square brackets of (22), we find that

$$a' = \frac{1}{2\delta}\left(i\alpha \sin\int_{-\infty}^{t}\delta\,dt' + 2\delta\cos\int_{-\infty}^{t}\delta\,dt'\right) \times \exp\left(-i\int_{-\infty}^{t}\frac{\alpha}{2}\,dt'\right). \tag{27}$$

Using this expression for a' in Eq. (26) and integrating over the entire range of interaction time with the boundary condition $|b(-\infty)| = |b'(-\infty)| = 0$, we obtain

$$ib'(\infty) = \int_{-\infty}^{\infty} V(t)[\cos x(t) + ip(t)\sin x(t)] \times \exp[iy(t)]\,dt. \tag{28}$$

Here

$$x(t) = \int_{-\infty}^{t}\delta\,dt' = \int_{-\infty}^{t}\frac{1}{2}(\alpha^2+4V^2)^{1/2}\,dt',$$

$$y(t) = \frac{1}{2}\int_{-\infty}^{t}\alpha\,dt',$$

and

$$p(t) = \alpha/2\delta = \alpha/(\alpha^2+4V^2)^{1/2}.$$

We have neglected the small-time variation in the phase $\phi(t)$ of the matrix element V_{ij} (replacing $V \approx V_{ij} = |V_{ij}|e^{-i\phi(t)}$), compared with that obtained from the integrals in the exponents of Eqs. (25) and (26). Since $|b(\infty)|^2 = |b'(\infty)|^2$, it follows from (28) that

$$|b(\infty)|^2 = \left|\int_{-\infty}^{\infty} V\,[\cos x\cos y - p\sin x\sin y + i(\cos x\sin y + p\sin x\cos y)]\,dt\right|^2. \tag{29}$$

The transition probability for a straight-line classical trajectory with impact parameter ρ is given by $T(\rho) = |b(\infty)|^2$. Thus

$$T(\rho) = \left|\int_{-\infty}^{\infty} V\left[\cos\int_{-\infty}^{t}\frac{(\alpha^2+4V^2)^{1/2}}{2}\,dt'\cos\int_{-\infty}^{t}\frac{\alpha}{2}\,dt' - \frac{\alpha}{(\alpha^2+4V^2)^{1/2}}\sin\int_{-\infty}^{t}\frac{(\alpha^2+4V^2)^{1/2}}{2}\,dt'\sin\int_{-\infty}^{t}\frac{\alpha}{2}\,dt'\right.\right.$$
$$+i\left(\cos\int_{-\infty}^{t}\frac{(\alpha^2+4V)^{1/2}}{2}\,dt'\sin\int_{-\infty}^{t}\frac{\alpha}{2}\,dt' + \frac{\alpha}{(\alpha^2+4V^2)^{1/2}}\right.$$
$$\left.\left.\times\sin\int_{-\infty}^{t}\frac{(\alpha^2+4V^2)^{1/2}}{2}\,dt'\cos\int_{-\infty}^{t}\frac{\alpha}{2}\,dt'\right)\right]dt\right|^2. \tag{30}$$

Equations (29) and (30) give a general result for two-state problems when transitions are induced by a slow-time variation of matrix elements. Various special cases of interest follow.

IV. SPECIAL CASES

(i) When $p \sim 1$ in Eq. (29), we obtain for a potential of definite symmetry

$$T(\rho) = \left|\int_{-\infty}^{\infty} V\cos(x+y)\,dt\right|^2 = \left|\int_{-\infty}^{\infty} V\cos\int_{-\infty}^{t}(\alpha^2+4V^2)^{1/2}\,dt'\,dt\right|^2, \quad (V \text{ even}) \tag{31}$$

$$T(\rho) = \left|\int_{-\infty}^{\infty} V\sin(x+y)\,dt\right|^2 = \left|\int_{-\infty}^{\infty} V\sin\int_{-\infty}^{t}(\alpha^2+4V^2)^{1/2}\,dt'\,dt\right|^2, \quad (V \text{ odd}). \tag{32}$$

These results were obtained by Vainshtein *et al.*[13] and by Vora *et al.*[10] by more-complicated methods. Figure 1 shows the behavior of p for the charge transfer reaction[10] $Na + O \rightarrow Na^+ + O^-$. The wave function of Herman and Skillman[15] was used for the 3*s* electron in Na and that of Clementi and McLean[16] for O^-. We see that $p \sim 1$ only at large internuclear distances. Thus the results of the earlier work[10,13] give only the contribution to the transition probability from large internuclear dis-

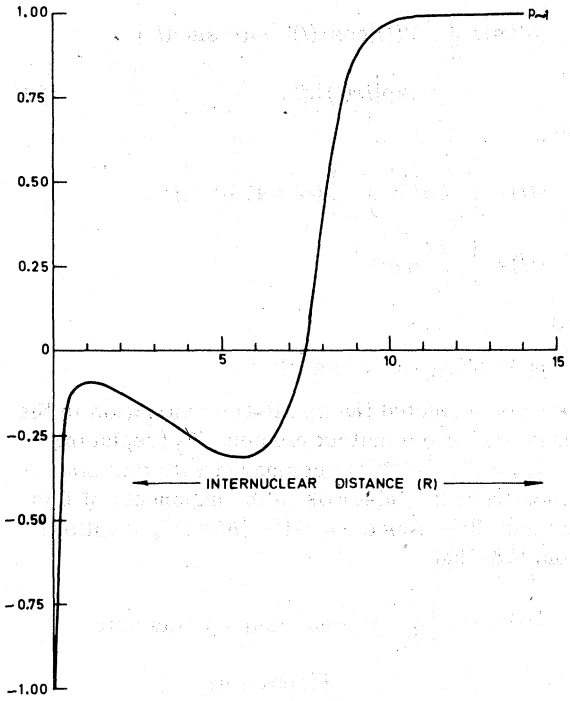

FIG. 1. Variation of p as a function of internuclear distance between the colliding atoms.

tances, a feature that was assumed in I.

(ii) In the charge transfer problem at large internuclear separations R, $V_{jj} \sim -1/R$ represents a Coulomb attraction in the ionic (final) state. If we neglect V_{ii} compared with ω_0, then, to a good approximation,[10]

$$\alpha = \omega_0 - 1/R .$$

If we assume that the main contribution comes from the point $\alpha(R) = 0$, we obtain a condition equivalent to that in the Landau-Zener formulation. For this case the integral in Eq. (31) has been evaluated by Presnyakov,[14] and the final result resembles, in its functional form, the Landau-Zener formula.

(iii) At high velocities, when $|\alpha| \gg V$ and $|V_{jj} - V_{ii}| \ll \omega_0$, Eq. (31) can be written

$$T(\rho) = \left| \int_{-\infty} V(t) \cos\omega_0 t \, dt \right|^2 ,$$

which is identical to the Born-approximation result.

(iv) For near-symmetric or near-resonance charge transfer, $|V_{jj} - V_{ii}| \ll V$ and $\omega_0 \to 0$, which implies $\alpha \sim p \to 0$. The integral in Eq. (29) can be written

$$T(\rho) = \left| \int_{-\infty}^{\infty} V \cos x \, dt \right|^2 = \left| \int_{-\infty}^{\infty} V \cos\left(\int_{-\infty}^{t} V \, dt' \right) dt \right|^2 .$$

This can be evaluated by introducing a change of variable

$$\eta(t) = \int_{-\infty}^{t} V \, dt'$$

to give

$$T(\rho) = \sin^2\eta(\infty) = \sin^2 \int_{-\infty}^{\infty} V \, dt ,$$

which is a well-known formula for resonance charge transfer.[6,8]

V. CONCLUDING REMARKS

The present work is basically exploratory and is aimed at finding a more general formula for the transition probability in a two-level system, where transitions are induced by time-dependent perturbations. More-accurate results could be obtained by taking other levels into account. However, the present two-level treatment offers an initial approach to the solution of a class of collision problems. It has the advantage that it covers the entire interaction region, whereas other existing results give the transition probability only in certain regions, e.g., at large internuclear distances or around a crossing point (Landau-Zener).

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