Energy transfer between slowly moving atoms—the case of no crossing point*

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(Received 11 August 1975)

The classical path treatment of a collision between an excited atom and another atom with a nearly resonant energy level leads to coupled differential equations which have been discussed previously by many workers. Here we present an elementary procedure for solving this system of equations in the case of no crossing point and in the limit where $\Delta E\tau \gg \hbar$, with ΔE being the energy discrepancy and $\tau = b/v$ being a measure of the time of collision. Even though the method is designed to take advantage of the slowness of the collision, it is also shown to be exact if $\Delta E = 0$. The form of the solution is very similar to that of Vainshtein *et al.*, but the present derivation avoids several of their approximations which individually are not as accurate as their final result. It is also pointed out that the coupled equations which arise for the energy-transfer problem also arise in connection with the interaction of laser pulses with atoms. Hence, the method has application to a wide class of multistate problems. A simple laser-interaction problem is discussed as a second example of the method.

In many situations where transitions are induced by nearly resonant time-dependent perturbations, a two-state model of the problem predicts much of the essential physics.[1-4] In such a case the amplitude $a_0(t)$ for remaining in the initial state and the amplitude $a_1(t)$ for making a transition to the second state usually satisfy the following pair of equations [for proper choice of $V_0(t)$, $V(t)$, $V_1(t)$, and ω]:

$$i\hbar \frac{da_0}{dt} = V_0(t)a_0 + V(t)e^{-i\omega t}a_1 ,$$
$$i\hbar \frac{da_1}{dt} = V_1(t)a_1 + V^*(t)e^{i\omega t}a_0 . \tag{1}$$

We will now review for the reader two situations where Eqs. (1) apply before proceeding to an approximate solution of the system.

Consider first a collision between an excited atom of type 1 (in state $|e1\rangle$) and a ground-state atom (i.e., in state $|02\rangle$) of type 2. If the energy of excitation of the type-1 atom is nearly equal to that required to excite a particular state (say state $|e2\rangle$) of atom 2 and if the atoms 1 and 2 have dipole-allowed transitions to the ground state from $|e1\rangle$ and $|e2\rangle$, respectively, energy transfer can occur at large internuclear separations due to dipole-dipole coupling.[3] Assuming that the relative velocity of collision v and the impact parameter b are sufficiently large, we can use a classical path treatment of the nuclear motion and a multipole expansion of the long-range atom-atom interaction and write

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + [e^2/R^3(t)](x_1x_2 + y_1y_2 - 2z_1z_2) , \tag{2}$$

where $\hat{H}_1$ and $\hat{H}_2$ are Hamiltonians for the isolated atoms 1 and 2, respectively; x_1, x_2, y_1, y_2, z_1, and z_2 are sums of electronic coordinates for atoms 1 and 2 (relative to the center of mass); and $R(t) = (b^2 + v^2t^2)^{1/2}$ is the internuclear separation evaluated along the classical path. A straight-line orbit has been assumed and only the dipole-dipole interaction has been retained. If the ground states are S states and the excited states P, there will actually be three states of the isolated excited atom with equal energies. However, this situation can be simplified by following Bates[4] in assuming that the transition dipole moments align themselves along the line joining the nuclei (i.e., the rotating atom approximation) and retain this configuration during the collision. Thus, with this approximation

$$\hat{H} = \hat{H}_1 + \hat{H}_2 - 2e^2z_1z_2/R^3(t) , \tag{3}$$

where the electronic wave functions are expressed in terms of the coordinates of the rotating frame with the z axis being along the line joing the nuclei. In this approximation only the $m_z = 0$ magnetic substate is populated, and if at $t = -\infty$ the composite state is $|e1\rangle_{m_z=0}|02\rangle$, the state at $t = \infty$ will be a linear combination of $|e1\rangle_{m_z=0}|02\rangle$ and $|e2\rangle_{m_z=0}|01\rangle$. Thus, the rotating atom approximation has the effect of reducing the complicated multistate problem to a two-state problem with state vector (we suppress the $m_z = 0$ subscript)

$$|\psi(t)\rangle = a_0(t)e^{-i(\omega_{e1}+\omega_{02})t}|e1\rangle|02\rangle + a_1(t)e^{-i(\omega_{01}+\omega_{e2})t}|01\rangle|e2\rangle , \tag{4}$$

where $\hat{H}_1|01\rangle = \hbar\omega_{01}|01\rangle$, $\hat{H}_1|e1\rangle = \hbar\omega_{e1}|e1\rangle$, $\hat{H}_2|02\rangle = \hbar\omega_{02}|02\rangle$, and $\hat{H}_2|e2\rangle = \hbar\omega_{e2}|e2\rangle$. Since $i\hbar\,\partial|\psi\rangle/\partial t = \hat{H}|\psi\rangle$, we find

$$i\hbar \frac{da_0}{dt} = -2e^2 \frac{z_1(0\to e)z_2(e\to 0)}{R^3(t)} e^{-i\omega t}a_1 ,$$
$$i\hbar \frac{da_1}{dt} = \frac{-2e^2z_1(e\to 0)z_2(0\to e)}{R^3(t)} e^{i\omega t}a_0 , \tag{5}$$

where $\omega = \omega_{01} + \omega_{e2} - \omega_{e1} - \omega_{02}$ and $\hbar\omega \equiv \Delta E$ is sometimes called the energy discrepancy for energy transfer. Equations (5) are obviously a special case of the system in Eq. (1). When ω is small, the predicted energy transfer cross section can be very large compared with gas kinetic cross sections so that errors due to a breakdown of the dipole-dipole expansion and the assumption of straight-line orbits at small impact parameters are negligible compared with the very large contributions that arise from large b where all of the assumptions (except for the rotating atom approximation which in some situations gives 30% errors[3]) are very accurate.

We choose as a second example a ground-state atom located at (x_0, y_0, z_0) and having velocity (v_x, v_y, v_z) at $t = 0$ interacting with a laser beam whose frequency at line center matches very well with that emitted by the atom in question in a dipole allowed transition from an excited to the ground state. Assume further that the laser frequency is not resonant for transitions from the latter excited state to any state other than the ground state or for any two-photon absorption processes. In such a situation the atom state vector should be approximately of the form

$$|\psi\rangle = a_0(t)e^{-i\omega_0 t}|0\rangle + a_1(t)e^{-i\omega_e t}|e\rangle , \tag{6}$$

where $|0\rangle$ is the ground-state vector, $|e\rangle$ is the state vector of the nearly resonant excited state, and if $\hat{H}_0$ is the Hamiltonian for the isolated atom, $\hat{H}_1|0\rangle = \hbar\omega_0|0\rangle$ and $\hat{H}_0|e\rangle = \hbar\omega_e|e\rangle$. We treat the electromagnetic field classically so that the Hamiltonian becomes[5]

$$\hat{H} = \hat{H}_0 - P_x E(z,t) , \tag{7}$$

where P_x is the x component of the electric dipole operator for the atom and the laser beam is assumed to be a pulse propagating in the z direction, peaking at the position of the atom at time $t = 0$ and having its polarization in the x direction. In Eq. (7) the electric field is evaluated at the z coordinate of the atom whose motion is treated in the classical path approximation. Thus, $z = z_0 + v_z t$. We take the electric field intensity E as

$$E(z,t) = \frac{E_0}{\{1 + [(z - ct - z_0)/b]^2\}^n}\cos(\omega t - kz)$$
$$= E_0\{1 + [(c - v_z)/b]^2 t^2\}^{-n}\cos(\omega' t - \alpha) , \tag{8}$$

where $\omega' = \omega(1 - v_z/c)$, $\alpha = kz_0$, n is a postive integer, and b is a parameter with units of length such that b/c determines the length of the pulse. Equation (8) specifies the type of laser pulse we are talking about, but the amplitude could vary with z and t in a more general way without destroying most of our arguments which will follow. We write more simply

$$E(z,t) = F(t)\cos(\omega' t - \alpha) , \tag{9}$$

where $F(t)$ is defined through Eq. (8). Equation (9) represents a beam whose line width would be zero save for the finite pulse length. Using Eqs. (6), (7), and (9) with $P_{0e} = \langle 0|P_x|e\rangle$, we find from the time-dependent Schrödinger equation

$$i\hbar\frac{da_0}{dt} = F(t)e^{-i(\omega_e - \omega_0)t}\cos(\omega' t - \alpha)\, a_1 P_{0e} ,$$
$$i\hbar\frac{da_1}{dt} = F(t)e^{i(\omega_e - \omega_0)t}\cos(\omega' t - \alpha)\, a_0 P_{0e}^* . \tag{10}$$

Following Rabi[6] and others, we note that $\cos x = \frac{1}{2}(e^{ix} + e^{-ix})$. Thus, the right-hand side of each equations of Eqs. (10) is made up of the sum of two terms, one oscillating slowly (i.e., with angular frequency $\omega_e - \omega_0 - \omega'$) and one oscillating very rapidly (i.e., with angular frequency $\omega_e - \omega_0 + \omega'$). The rapidly oscillating term produces little time-integrated effect, and further, since it is not resonant it would be in a sense inconsistent with the two-state approximation to keep it [i.e., only states which resonant for single-photon processes have been retained in Eq. (6)]. Thus, we make the rotating wave approximation and keep only the part of $\cos(\omega' t - \alpha)$ which gives rise to the slowly varying term. We have

$$i\hbar\frac{da_0}{dt} = [e^{-i\alpha}F(t)/2]e^{-i(\omega_e - \omega_0 - \omega')t}a_1 P_{0e} ,$$
$$i\hbar\frac{da_1}{dt} = [e^{i\alpha}F(t)/2]e^{i(\omega_e - \omega_0 - \omega')t}a_0 P_{0e}^* . \tag{11}$$

We have assumed further that the natural lifetime of $|e\rangle$ is long compared with the length of the pulse (i.e., b/c). Equations (11) are again a special case of Eqs. (1). If spontaneous emission from $|e\rangle$ had been included phenomenologically by inserting $-i\hbar\gamma a_1(t)/2$ on the right-hand side of the second equation, we would have found $V_1(t)$ to also be nonzero. Thus, as stated before, many physical situations are described approximately by way of Eqs. (1).

Much of the remainder of the paper will focus on the problem of collisional energy transfer as discussed first by Stuckelberg[1] and more recently by Vainshtein *et al.*[2] However, the results are equally applicable to the problem of 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. In the latter problem the averaging over the velocity distribution and over the initial positions of the atoms in

order to predict a total population has been discussed elsewhere[7] for constant $F(t)$ and will not be considered here.

In order to solve Eqs. (1), we let $U(t)=V(t)/\hbar$, $U_0(t)=V_0(t)/\hbar$, $U_1(t)=V_1(t)/\hbar$, and

$$a_1(t)=A_1(t)\exp\left(-i\int_0^t U_1(t')dt'\right). \tag{12}$$

From Eqs. (1)

$$\frac{d^2A_1}{dt^2}-\left(i\omega+\frac{d}{dt}\ln U+i(U_1-U_0)\right)\frac{dA_1}{dt}+U^2A_1=0. \tag{13}$$

Equation (13) could be solved immediately if we find

$$\left(\frac{d}{dt}+g_1(t)\right)\left(\frac{d}{dt}+g_2(t)\right)A_1=0. \tag{14}$$

Obviously, $g_1(t)$ and $g_2(t)$ must satisfy

$$g_1+g_2=-i\omega-\frac{d}{dt}\ln U-i(U_1-U_0),$$

$$g_1g_2+\frac{dg_2}{dt}=U^2.$$

The easiest case for finding g_1 and g_2 occurs when U, U_1, and U_0 vary slowly with time (i.e., for energy transfer the relative velocity in the collision is very small). In the latter situation we note that g_1 and g_2 can be written as

$$g_1=g_{10}+\epsilon_1,\quad g_2=g_{20}+\epsilon_2,$$

where

$$g_{10}+g_{20}=-i(\omega+U_1-U_0),$$

$$g_{10}g_{20}=U^2,$$

and $|\epsilon_1|\ll|g_{10}|$, $|\epsilon_2|\ll|g_{20}|$ if the ω of Eq. (1) times the time over which U_1, U_0, or U is of substantial amplitude is much greater than unity, and $\omega+U_1-U_0\neq 0$. We have

$$g_1\cong-i(\alpha+J)+\frac{1}{2J}\frac{d}{dt}(\alpha-J)-\frac{(J+\alpha)}{2J}\frac{d}{dt}\ln U, \tag{15}$$

$$g_2\cong-i(\alpha-J)-\frac{1}{2J}\frac{d}{dt}(\alpha+J)+\frac{(\alpha-J)}{2J}\frac{d}{dt}\ln U,$$

where $\alpha=\frac{1}{2}(\omega+U_1-U_0)$ and $J=(U^2+\alpha^2)^{1/2}$. The above expressions for g_1 and g_2 are accurate if the ω in Eqs. (1) times the time over which $U(t)$ remains appreciable is very large compared with unity or if one has exact resonance. Higher-order corrections involve higher-order derivatives of α, J, and U as well as higher powers of the derivatives. It should be noted that the first-order derivative corrections to g_{10} and g_{20} can never be dropped because integrals of g_1 and g_2 over time determine the solution to Eq. (3), and consequentially these terms are not negligible for nonconstant U, U_0, and U_1 even as the rate of change of these functions becomes arbitrarily small. Further corrections do approach zero, however, for sufficiently slow variations providing α is never zero.

Let $h_i(t)=\int_0^t g_i(t')\,dt'$, $i=1,2$. If $Z=dA_1/dt+g_2(t)A_1$, we find $Z(t)=Z(-\infty)\exp[-h_1(t)+h_1(-\infty)]$. Thus,

$$A_1(t)=e^{h_1(-\infty)}Z(-\infty)\int_{-\infty}^t\exp[-h_1(t')+h_2(t')-h_2(t)]\,dt'. \tag{16}$$

In Eq. (16) it is important to interpret $Z(-\infty)\times\exp[h_1(-\infty)]$ as a limit of $Z(t)\exp[h_1(t)]$ as $t\to-\infty$.

To understand better the nature of the solution, we let $U_0=U_1=0$ as in the dipole-dipole energy transfer case discussed earlier where the excited state in each atom has an allowed electric dipole transition to the ground state so that the R^{-3} dipole-dipole interaction dominates at large R. We find

$$h_1(t)=\int_0^t g_{10}(t')\,dt'+\tfrac{1}{2}\ln\left(\frac{1+\omega/2J}{U^2}\right)+C,$$

where C is chosen so that $h_1(0)=0$. Further,

$$h_2(t)=\int_0^t g_{20}(t')\,dt'-\tfrac{1}{2}\ln[1+\omega/2J]+C',$$

and C' is chosen so as to make $h_2(0)=0$. After a bit of algebra, we find

$$|A_1(\infty)|^2=\left(1+\frac{\omega}{2J(-\infty)}\right)\left(1+\frac{\omega}{2J(\infty)}\right)\times\left|\int_{-\infty}^{\infty}\frac{U(t')\cos[2\int_0^{t'}J(t'')dt'']dt'}{1+\omega/2J(t')}\right|^2. \tag{17}$$

In the case of energy transfer, expression (17) reduces to the result of Vainshtein *et al.*[2] if $\frac{1}{2}\omega\gg U(t)$ for all t. Further, this relation is an exact solution at resonance ($\omega=0$), or when $U(t)=$ constant and when U_1, U_0, and U are sufficiently small, it reduces to the Born approximation. The quantity being interpreted in Eq. (17) is always within a factor of 4 of the result given by Vainshtein *et al.*[2] with the largest differences occurring when our result is valid, but $U(0)\gtrsim\frac{1}{2}\omega$. Thus, we conclude that despite some of the crude approximations made by the latter authors, there are (as they claimed) compensating errors which make their results reasonably accurate for very slow collisions.

The simple technique applied here has also been used by the present authors to solve several other two- or three-state problems related to the inter-

action of laser pulses with gases. In the case of the laser pulse interaction problem described here, Eq. (17) gives the probability of the atom remaining in the excited state just after the laser pulse has passed, providing $|\omega_e - \omega_0 - \omega'|b/c \gg 1$. In the latter case, evaluation of $A_1(t)$ at finite times can be made in order to predict the probability of being in the excited state at various times during the pulse. At times when the pulse is present, the integrals in the expression for $A_1(t)$ can be evaluated by integrating by parts and neglecting the remaining integral which can be shown to be small. At larger times when the amplitude of the laser pulse becomes small, the integration-by-parts technique fails because the neglected integral becomes comparable to or larger than the part that has been retained. At times when the laser pulse is present, the results described here reduce to a special case of those derived from a multiple-time-scale perturbation theory treatment of a related problem by Nayfeh and Nayfeh.[8] However, the latter treatment which is accurate while the pulse is present fails at sufficiently large times.

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*Research sponsored by the U.S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

†Postdoctoral research appointment through the University of Kentucky supported by Los Alamos Scientific Laboratory.

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