Coherence effects in radiatively assisted inelastic collisions: General theory

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A radiatively assisted inelastic collision (RAIC) is one in which two atoms collide in the presence of a radiation field to produce a reaction of the form $A^* + B + \hbar\Omega \rightarrow A + B^*$. In this paper, a general theory of RAIC is developed with special attention given to the final-state coherences produced by RAIC. These final-state coherences can be monitored by standard experimental techniques (polarization of fluorescence, quantum beats), enabling one to use such studies to gain information on the interatomic potentials that are relevant to the RAIC under consideration.

I. INTRODUCTION

There has been considerable recent interest in reactions of the form

$$A_i + A_i' + \hbar\Omega \rightarrow A_f + A_f' \tag{1}$$

in which two atoms (A and A') undergo a collision while simultaneously absorbing a photon of energy $\hbar\Omega$ from an external radiation field to take the atoms from some initial state $A_i A_i'$ to a final state $A_f A_f'$. In many cases, the direct transition $A_i + A_i' \rightarrow A_f + A_f'$ is energetically forbidden; consequently, the transition can take place only in the presence of the radiation field, with the photon providing the energy mismatch $(E_f + E_{f'}) - (E_i + E_{i'})$.[1] Such processes have been referred to as radiative collisions[2] (RC), laser-induced collisional energy transfer[3] (LICET), or radiatively assisted inelastic collisions[4] (RAIC) and have been the subject of a large number of theoretical[5] and a lesser number of experimental[3,6] investigations. By studying the RAIC cross section as a function of frequency Ω, one can gain important information about the initial- and final-state AA' interatomic potentials.

Typically, the RAIC cross section can be measured by monitoring the fluorescence from one of the final states (A_f', for example) since the total RAIC cross section can be simply related to the *total* fluorescence rate. It is apparent, however, that additional information is contained in the polarization of the fluorescence, i.e., in the coherence properties of the final states. It is the purpose of this paper to present a general theory of RAIC which allows one to calculate the final-state coherence properties as well as the total RAIC cross section. Experimentally, the final-state coherence can be probed by standard methods (absorption, emission, or quantum beats originating from one of the final states).

A few calculations[7,8] have already appeared which include magnetic degeneracy effects in RAIC and in the related problem of collisionally assisted radiative excitation (CARE). However, these calculations were restricted to specific J values for the various levels and to specific forms for the interatomic potentials; moreover, only total cross sections were obtained.

A more global picture of the collisional process is achieved if levels of arbitrary J and interatomic potentials of a quite general nature are considered. The calculations, including an averaging over different collision orientations, are conveniently carried out using techniques involving irreducible tensor operators. The final-state coherence resulting from RAIC can then be interpreted in terms of the symmetry properties of the interatomic potential and the characteristic properties (polarization, frequency, intensity) of the external light field participating in the RAIC reaction.

A general formalism for RAIC is given in this paper. The physical system is described in Sec. II, the equations of motion are given in Sec. III (and derived in Appendix A), and a formal solution is obtained in Sec. IV. A discussion of the results is given in Sec. V. In Appendix B, I present a diagrammatic interpretation of the operators that appear in the equations of motion.

Solutions of the RAIC equations in the limit where the external field is weak and the collision-induced level shifts of the atomic energy levels can be neglected will be presented in a following paper. In future work, solutions of the RAIC equations will be sought that are valid for arbitrary field strengths and include level-shifting effects.

II. PHYSICAL SYSTEM

The physical system consists of a low density ($\lesssim$ several hundred Torr) atomic vapor containing two types of atoms, A and A', to which a light pulse is applied. The atomic energy levels for

atoms A and A' are shown in Fig. 1. Levels of atom A are designated by unprimed variables and those of atom A' by primed ones. It is assumed that the levels of each atom can be separated into subgroups of levels (see Fig. 1), with the energy separation between sublevels in a given group having some upper bound $\hbar\omega_E$ (to be established below). Specifically, the sublevels within a group are generally different fine structure, hyperfine structure, or Zeeman sublevels of a given electronic state. The atoms are prepared in a linear superposition of states $|ii'\rangle$, where i and i' represent any of the sublevels in the i and i' groups, respectively.

The light pulse is taken to be of the form

$$\vec{\mathcal{E}}(\vec{R},t)=\tfrac{1}{2}[\vec{\mathcal{E}}(\vec{R},t)e^{-i\Omega t}+\vec{\mathcal{E}}(\vec{R},t)^{*}e^{i\Omega t}], \tag{2}$$

where the envelope function $|\vec{\mathcal{E}}(\vec{R},t)|$ is characterized by a duration T and a maximum amplitude $|\mathcal{E}_0|$ (Fig. 2). It is assumed that the pulse envelope varies very slowly in an optical period ($\Omega T \gg 1$) and that the frequency Ω is very far detuned from any transition frequency in atom A or in atom A'. On the other hand, the field is assumed to be in near resonance with the transition in the *composite* AA' system from some initial state $|ii'\rangle$ to a final state $|ff'\rangle$. In other words

$$\hbar\Omega \approx E_f + E_{f'} - (E_i + E_{i'}), \tag{3}$$

where E_α is the energy of a given level α.

Thus, the field can induce transitions only in the composite system AA', implying that excitation can occur only if there is an $A-A'$ collision during the on-time of the light pulse. Let us suppose that such a collision occurs, centered at time $t=t_c$, position $\vec{R}=\vec{R}_c$, and is characterized by a collision duration $\tau_c = b/v$, where b is the impact

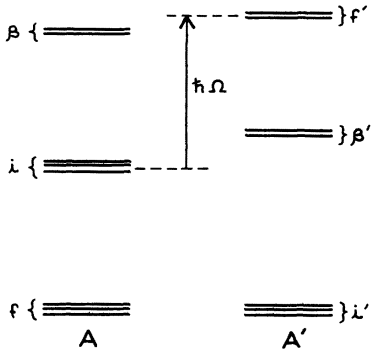

FIG. 1. Energy levels for the atoms A and A' under consideration. The groups of levels represented by a single letter are degenerate or near degenerate, with a maximum frequency separation ω_E such that $\omega_E\tau_c \ll 1$ (τ_c = duration of a collision). The field frequency Ω is such that $\hbar\Omega \approx E_f + E_{f'} - (E_i + E_{i'})$.

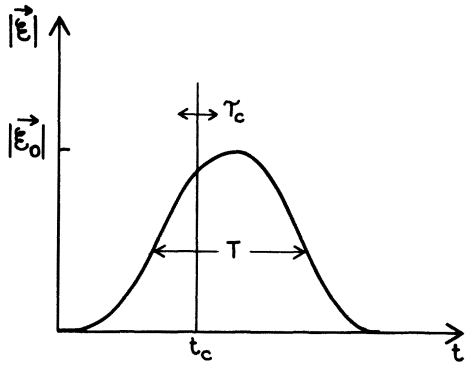

FIG. 2. Field-pulse envelope as a function of time. A collision occurs, centered in time at $t=t_c$, with a duration $\tau_c \ll T$.

parameter and v_r the relative atomic speed associated with the collision. Collision durations are on the order of 10^{-12} sec so that it is reasonable to assume that

$$\tau_c \ll T, \tag{4}$$

since pulse durations $T \gtrsim 1.0$ nsec are typical. Thus, excitation occurs on the time scale τ_c; on this time scale, the field amplitude $\vec{\mathcal{E}}(\vec{R},t)$ is essentially constant and may be evaluated as $\vec{\mathcal{E}}(\vec{R}_c,t_c)$ (Fig. 2). In calculating excitation probabilities, it is generally necessary to average over all possible t_c and $\vec{R}_c$ during the light pulse and to average over all collision impact parameters, orientations, and relative speeds. The average over $\vec{R}_c$ is equivalent to an average over the spatial profile of the light pulse.

The following assumptions are adopted: (1) Collisional excitation exchange between atoms A and A' does not occur in the absence of the light field (i.e., all such exchange processes are assumed to be nonresonant). (2) The frequency ω_E is chosen such that

$$\omega_E\tau_c \ll 1, \tag{5}$$

ensuring that all sublevels in a given group are, in effect, degenerate during a collision. (3) There is no population decay or buildup of Doppler phase during a collision; that is,

$$\gamma\tau_c \ll 1, \quad ku\tau_c \ll 1, \tag{6}$$

where γ is a decay rate associated with the initial or final states, $\vec{k}$ is a wave vector associated with the field, and u is an atomic speed. (4) Each atom undergoes, at most, one collision, on average, during the pulse time T, enabling one to ignore multiple-collision effects [valid for densities $\ll 10^{19}$ atoms/cm^3 T (nsec)]. (5) The collision trajectory is treated classically, which implies that the change in kinetic energy resulting from

RAIC is small, i.e., that

$$|\omega_{fi}+\omega_{f'i'}-\Omega|\tau_c \lesssim 1\,, \tag{7}$$

where

$$\omega_{\alpha\beta}=\omega_\alpha-\omega_\beta\,,\quad \omega_\alpha=E_\alpha/\hbar\,. \tag{7a}$$

If condition (7) were not satisfied, one could not assign a unique classical trajectory to the collision.

To summarize, I am considering the radiatively assisted collisional reaction

$$A_i+A'_{i'}+\hbar\Omega \rightarrow A_f+A'_{f'}$$

from initial states $|ii'\rangle$ to final states $|ff'\rangle$, in which the photon is provided by an electromagnetic pulse. Several assumptions relating to the time scales in the problem have been made which are valid for many systems of practical interest. All information on final-state coherence is contained in the density matrix following the RAIC. The final-state density matrix for one of the atoms can be obtained by taking the trace of the final-state density matrix for the composite system over the final-state variables of the other atom. Experimentally, it is generally such a single-particle density matrix that is monitored (e.g., by fluorescence from the final state of one of the atoms).

III. EQUATIONS OF MOTION

By assumption, the collision trajectory is treated classically. That is, relative to a fixed laboratory frame, a collision is characterized by an impact parameter b, relative speed $v_r=|\vec{v}-\vec{v}'|$ ($\vec{v}$ and $\vec{v}'$ being, respectively, the velocities of atoms A and A'), and orientation Θ relative to the fixed frame. The Hamiltonian for the RAIC can be written

$$H(t;b,v_r,\Theta,\vec{R}_c,t_c)=H_0(\vec{r})+H'_0(\vec{r}') - \tfrac{1}{2}(\vec{\mu}+\vec{\mu}')\cdot[\vec{\mathcal{E}}(\vec{R}_c,t_c)e^{-i\Omega t}+\text{c.c.}] +\mathfrak{u}(\vec{r},\vec{r}',\vec{R}(t))\,, \tag{8}$$

where H_0 and H'_0 are the free-atom Hamiltonians for atoms A and A', respectively, $\vec{\mu}$ and $\vec{\mu}'$ are the dipole-moment operators for atoms A and A', respectively (the atom-field interaction is treated in the dipole approximation), and $\mathfrak{u}$ is the A-A' interaction Hamiltonian. The collision is centered in time at $t=t_c$ and $\vec{R}_c$ is the position of the center of mass of the atoms when $t=t_c$. All effects of atomic motion are contained implicitly in the interatomic separation $\vec{R}(t)$, calculated for a classical trajectory. In writing the approximate Hamiltonian (8), conditions (4), (6), and (7) were used.

According to the assumptions of Sec. II, states $|ii'\rangle$ can be coupled only to states $|i_1i'_1\rangle$ (i_1 is another state in the i group) or to states $|ff'\rangle$. The corresponding equations of motion for the probability amplitudes $a_{ii'}(t)$, $a_{ff'}(t)$ (in the interaction representation), as derived in Appendix A starting from the Schrödinger equation with the Hamiltonian (8), are given by

$$i\hbar\dot{a}_{ii'}=\sum_{i_1i'_1}\langle ii'|\hat{S}(ii';t,b,v_r,\Theta,\vec{R}_c,t_c)|i_1i'_1\rangle a_{i_1i'_1} +\sum_{ff'}\langle ii'|\hat{T}(ff',ii';t,b,v_r,\Theta,\vec{R}_c,t_c)|ff'\rangle e^{i\Delta t}a_{ff'}\,, \tag{9a}$$

$$i\hbar\dot{a}_{ff'}=\sum_{f_1f'_1}\langle ff'|\hat{S}(ff';t,b,v_r,\Theta,\vec{R}_c,t_c)|f_1f'_1\rangle a_{f_1f'_1} +\sum_{ii'}\langle ff'|\hat{T}(ii',ff';t,b,v_r,\Theta,\vec{R}_c,t_c)|ii'\rangle e^{-i\Delta t}a_{ii'}\,, \tag{9b}$$

where the detuning Δ is defined by

$$\Delta=\Omega-(\omega_{fi}+\omega_{f'i'})\,, \tag{10}$$

and the operators $\hat{S}$ and $\hat{T}$ are defined below.

The operator $\hat{S}(\alpha\alpha';t,b,v_r,\Theta,\vec{R}_c,t_c)$ is an operator that acts *only* in the $\alpha\alpha'$ subspace ($\alpha\alpha'=ii'$ or ff'); it shifts and couples levels within that subspace. Explicitly (see Appendix A),

$$\hat{S}(\alpha\alpha';t,b,v_r,\Theta,\vec{R}_c,t_c)=\hat{S}_L+\hat{S}_c\,, \tag{11}$$

$$\hat{S}_L=\frac{-1}{4\hbar}\sum_{\beta\beta'}\left(\frac{\vec{\mu}_T\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c)^*\,|\beta\beta'\rangle\langle\beta\beta'|\,\vec{\mu}_T\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c)}{\omega_{\beta\alpha}+\omega_{\beta'\alpha'}-\Omega}+\frac{\vec{\mu}_T\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c)\,|\beta\beta'\rangle\langle\beta\beta'|\,\vec{\mu}_T\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c)^*}{\omega_{\beta\alpha}+\omega_{\beta'\alpha'}+\Omega}\right), \tag{11a}$$

$$\hat{S}_c=-\hbar^{-1}\sum_{\beta\beta'}\frac{\mathfrak{u}(\vec{R}(t))\,|\beta\beta'\rangle\langle\beta\beta'|\,\mathfrak{u}(\vec{R}(t))}{\omega_{\beta\alpha}+\omega_{\beta'\alpha'}}\,, \tag{11b}$$

where

$$\vec{\mu}_T = \vec{\mu} + \vec{\mu}' . \tag{12}$$

The operator $\hat{S}$ may appear to be complicated, but it has a well-known physical interpretation. The term $\hat{S}_L$ involves only field variables and gives rise to the shifting (light shifts) and coupling of $\alpha\alpha'$ levels produced by an *off-resonant* external electromagnetic field. The summation over intermediate states $\beta\beta'$ represents the virtual excitation of these levels by the field. The term $\hat{S}_c$ [Eq. (11b)] involves only collision variables and gives rise to collisionally induced shifting and coupling of levels in the $\alpha\alpha'$ group. The shift of the levels is the origin of the pressure broadening and shifting of spectral lines, while the coupling within the $\alpha\alpha'$ group leads to collisionally induced relaxation of any alignment, orientation, etc., that may be present in that group of levels. Again one finds a summation over an infinite number of virtual excitations $|\beta\beta'\rangle$.

The transition operator $\hat{T}$ that couples groups of states $|ii'\rangle$ to $|ff'\rangle$ is given by (see Appendix A)

$$\hat{T}(ii',ff';t,b,v_r,\Theta,\vec{R}_c,t_c) = \frac{1}{2\hbar}\sum_{\beta\beta'}\left(\frac{\mathfrak{U}(\vec{R}(t))|\beta\beta'\rangle\langle\beta\beta'|\vec{\mu}_T}{\omega_{\beta f}+\omega_{\beta' f'}} + \frac{\vec{\mu}_T|\beta\beta'\rangle\langle\beta\beta'|\mathfrak{U}(\vec{R}(t))}{\omega_{\beta i}+\omega_{\beta' i'}}\right)\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c) \tag{13}$$

and represents the combined effect of the (field + collision) in producing the transition from initial to final states. The corresponding transition operator which couples states $|ff'\rangle$ to $|ii'\rangle$ is given by[9]

$$\hat{T}(ff',ii';t,b,v_r,\Theta,\vec{R}_c,t_c) = \frac{1}{2\hbar}\sum_{\beta\beta'}\left(\frac{\vec{\mu}_T|\beta\beta'\rangle\langle\beta\beta'|\mathfrak{U}(\vec{R}(t))}{\omega_{\beta f}+\omega_{\beta' f'}} + \frac{\mathfrak{U}(\vec{R}(t))|\beta\beta'\rangle\langle\beta\beta'|\vec{\mu}_T}{\omega_{\beta i}+\omega_{\beta' i'}}\right)\cdot\vec{\mathcal{E}}(\vec{R}_c,t_c)^* . \tag{14}$$

Note that the matrix elements of $\hat{T}$ appearing in Eq. (9) are related by

$$\langle ii'|\hat{T}(ff',ii';t)|ff'\rangle = \langle ff'|T(ii',ff';t)|ii'\rangle^* . \tag{15}$$

A diagrammatic interpretation of $\hat{S}$ and $\hat{T}$ is given in Appendix B.

To obtain the RAIC excitation probability, one must solve Eqs. (9) for $a_{ff'}(t_c^+)$ subject to the initial conditions

$$a_{ii'}(t_c^-) \neq 0, \quad a_{ff'}(t_c^-) = 0 , \tag{16}$$

where $t_c^-(t_c^+)$ are times before (after) the collision. Since $\tau_c \ll T$ [Eq. (4) or Fig. 2], the times $t_c^\pm$ can be set equal to $\pm\infty$ when integrating Eqs. (9) without introducing significant error.

The validity conditions for Eqs. (9) are discussed in detail in Appendix A. If

$$\bar{\omega}\tau_c \gg 1 , \tag{17}$$

where $\bar{\omega}$ is any of the frequency denominators appearing in the operators $\hat{T}$ and $\hat{S}$, and if Eqs. (3)–(7) are satisfied, then Eqs. (9) are valid over a wide range of field strengths.[10] Condition (17) ensures that the intermediate states act only as *virtual* levels in the RAIC problem. The virtual excitations are represented by the summations over β and β' in the $\hat{S}$ and $\hat{T}$ operators, and the problem is reduced to an effective two groups of levels problem for the states $|ii'\rangle$ and $|ff'\rangle$. It should be noted that Eqs. (9) reduce to the corresponding equations derived by other authors in various limiting cases.[5]

IV. FORMAL SOLUTION

It is useful to make use of Eq. (15) and to rewrite Eqs. (9) in matrix form as

$$i\hbar\dot{\vec{a}}_I = S(I,t)\vec{a}_I + [T(IF,t)]^\dagger e^{i\Delta t}\vec{a}_F , \tag{18a}$$

$$i\hbar\dot{\vec{a}}_F = S(F,t)\vec{a}_F + T(IF,t)e^{-i\Delta t}\vec{a}_I , \tag{18b}$$

$$\vec{a}_I(t_c^-) \neq 0, \quad \vec{a}_F(t_c^-) = 0 , \tag{18c}$$

where $\vec{a}_I$ ($\vec{a}_F$) is a vector containing all possible states $|ii'\rangle$ ($|ff'\rangle$) in the initial (final) group of levels and $S(I,t)$, $S(F,t)$, and $T(IF,t)$ are matrix representations of the corresponding operators appearing in Eqs. (9). A solution of the form

$$\vec{a}_K(t) = G_K(t,t_c^-)\vec{A}_K(t), \quad K = I,F \tag{19}$$

is sought, where the matrix $G_K(t,t')$ is chosen to satisfy the equations

$$i\hbar\frac{\partial G_K(t,t')}{\partial t} = S(K,t)G_K(t,t') , \tag{20a}$$

$$G_K(t,t) = 1, \quad K = I,F \tag{20b}$$

and the symbols I and F represent the entire ii' and ff' subspaces, respectively. Substituting Eqs. (19) and (20) into Eqs. (18) and making use of the relations

$$\begin{aligned} &(G_K(t,t'))^{-1} = G_K(t',t) , \\ &G_K(t,t_1)G_K(t_1,t_2) = G_K(t,t_2) , \end{aligned} \tag{21}$$

which follow directly from Eqs. (19) and (20), one obtains

$$i\hbar\dot{\vec{A}}_I = G_I(t_c^-,t)(T(IF,t))^\dagger G_F(t,t_c^-)e^{i\Delta t}\vec{A}_F , \tag{22a}$$

$$i\hbar\dot{\vec{A}}_F = G_F(t_c^-, t)T(IF, t)G_I(t, t_c^-)e^{-i\Delta t}\vec{A}_I, \quad (22b)$$

$$\vec{A}_I(t_c^-) = \vec{a}_I(t_c^-), \quad \vec{A}_F(t_c^-) = 0. \quad (22c)$$

In this form, all effects of shifting and coupling within the ii' and ff' subspaces are contained in the matrices $G_I(t, t')$ and $G_F(t, t')$, respectively.

Once a solution to Eqs. (22) is found, final-state density matrix elements of the form

$$\tilde{\rho}_{ff';f_1f_1'}(t_c^+; b, v_r, \Theta, \vec{R}_c, t_c) = a_{ff'}(t_c^+)[a_{f_1f_1'}(t_c^+)]^* = [G_F(t_c^+, t_c^-)\vec{A}_F(t_c^+)]_{ff'}[G_F(t_c^+, t_c^-)\vec{A}_F(t_c^+)]^*_{f_1f_1'} \quad (23)$$

may be constructed (the tilde is a reminder that results are expressed in the interaction representation). The (complex) rate at which RAIC create density matrix elements $\tilde{\rho}_{ff';f_1f_1'}(t_c^+; v_r, t_c)$ at time t_c during the light pulse for atoms A and A' having relative speed v_r starting from an initial density matrix element $\tilde{\rho}_{ii';i_1i_1'}(t_c^-)$ is given by

$$\Gamma^{II_1}_{FF_1}(v_r, t_c) = \mathfrak{N}_A\mathfrak{N}_{A'}v_r\int_0^\infty 2\pi b\,db\int(8\pi^2)^{-1}d\Theta\int d\vec{R}_c\,\frac{d[\tilde{\rho}_{FF_1}(t_c^+; b, v_r, \Theta, \vec{R}_c, t_c)]}{d[\tilde{\rho}_{II_1}(t_c^-)]}, \quad (24)$$

where $\mathfrak{N}_\alpha$ is the α-atom density (assumed to be independent of position) and the shorthand notation

$$I = ii', \quad F = ff', \quad I_1 = i_1i_1', \quad F_1 = f_1f_1', \quad (25)$$

etc., has been adopted. The integral over $\vec{R}_c$ in Eq. (24) is limited to the interaction region of the atoms and light field; it is essentially an integration over the spatial profile of the light beam.

Thus, *during the light pulse*, the density matrix evolves as

$$\frac{\partial\tilde{\rho}_{FF_1}(\vec{v}, \vec{v}', t_c)}{\partial t_c} = \sum_{II_1}\Gamma^{II_1}_{FF_1}(v_r, t_c)\tilde{\rho}_{II_1}(\vec{v}, \vec{v}', t_c) + [\tilde{X}(t_c)\tilde{\rho}(v, v', t_c)]_{FF_1}, \quad (26)$$

where $\vec{v}_r = \vec{v} - \vec{v}'$. The assumption that an atom undergoes at most one collision during the light pulse is contained implicitly in Eq. (26), otherwise, terms such as

$$\Gamma^{F_2F_3}_{FF_1}\tilde{\rho}_{F_2F_3}$$

would be present. The term with $\tilde{X}(t_c)$ represents changes produced by processes *other* than RAIC (i.e., level decay, other external fields, etc.).[11] It is an equation of the form (26) *plus* a corresponding equation for times when the light pulse is *off* which must be solved in order to make connection with a given experimental situation (of course, there are no RAIC terms in the equations with the field off). For example, if the pulse time T is short enough so that the bracketed term in Eq. (26) may be neglected, then the final-state density matrix following the light pulse is simply

$$\tilde{\rho}_{FF_1}(\vec{v}, \vec{v}', T^+) = \sum_{II_1}\left(\int_{T^-}^{T^+}\Gamma^{II_1}_{FF_1}(v_r, t_c)dt_c\right)\times\tilde{\rho}_{II_1}(\vec{v}, \vec{v}', T^-), \quad (27)$$

where $T^-(T^+)$ indicates a time just before (after) the pulse. One can then monitor the final-state density matrix via absorption or emission experiments to obtain values for the various rates $\Gamma^{II_1}_{FF_1}$. For longer pulse times T, it may be necessary to integrate Eq. (26) to obtain the net effect of the light pulse.

To be consistent with other authors, I define a RAIC transfer rate per pulse from some initial state described by $\tilde{\rho}_{II_1}$ to a final state described by $\tilde{\rho}_{FF_1}$ as

$$\Gamma^{II_1}_{FF_1}(v_r) = \frac{1}{T^+ - T^-}\int_{T^-}^{T^+}\Gamma^{II_1}_{FF_1}(v_r, t_c)dt_c \quad (28)$$

and a RAIC transfer cross section per pulse by

$$\sigma^{II_1}_{FF_1}(v_r) = \Gamma^{II_1}_{FF_1}(v_r)\Big/\left(\mathfrak{N}_A\mathfrak{N}_{A'}v_r\int d\vec{R}_c\right), \quad (29)$$

where the $\vec{R}_c$ integration is over the interaction volume.[12] The rate and cross section for transfer of *population* from some initial state $|I\rangle$ to a final state $|F\rangle$ is obtained by setting $I_1 = I$, $F_1 = F$ in Eqs. (28) and (29). Finally, one can define an average RAIC rate and cross section by

$$\bar{\Gamma}(v_r) = \frac{1}{N_I}\sum_F\Gamma^{II}_{FF}(v_r), \quad (30a)$$

$$\bar{\sigma}(v_r) = \frac{1}{N_I}\sum_F\sigma^{II}_{FF}(v_r), \quad (30b)$$

where N_I is the number of initial states. Equation (30b) defines a quantity that has been typically referred to as the RAIC cross section.[5]

V. DISCUSSION

In general, it is difficult to obtain solutions to Eqs. (22) and perform the necessary averaging

over collision orientations. However, certain general features of the solutions may be understood by examining some of the limiting forms of these equations.

A. Nondegenerate levels

In this limit, the matrices S and T in Eqs. (18) become scalars. Equation (20) is easily integrated and one finds that Eqs. (22) take the form

$$i\hbar\dot{A}_I = T(IF,t)^* \exp\{i[\Delta t - \varphi_c(t)]\}A_F , \tag{31a}$$

$$i\hbar\dot{A}_F = T(IF,t) \exp\{-i[\Delta t - \varphi_c(t)]\}A_I , \tag{31b}$$

where

$$\varphi_c(t) = \int_{t_c^-}^{t} [S(F,t') - S(I,t')]\,dt' \tag{32}$$

and I and F are nondegenerate states. The phase $\varphi_c(t)$ contains the effects of the level shifts produced by the off-resonant light field and the collisional interaction. Equations (31) have been studied by many authors using a variety of analytical and numerical techniques.[5,13] The resulting RAIC profile exhibits a marked asymmetry for large $|\Delta|$, resulting from the action of the level-shifting term. For one sign of Δ, the I-F transition can be brought into instantaneous resonance with the field during a collision, leading to enhanced excitation; for the other sign of Δ, no such instantaneous resonance is possible. Equations (31) also contains saturation effects which can appear for large field strengths or small impact parameters.

B. Perturbation-theory limit

By neglecting the level-shifting terms in Eqs. (22) and taking $\Delta = 0$, one can estimate that a perturbation solution is valid provided

$$\frac{|\mathcal{U}(t=t_c)|\,\tau_c\chi}{\hbar\bar{\omega}} \ll 1 , \tag{33}$$

where $\mathcal{U}(t=t_c)$ is the interatomic potential at the time of closest approach, $\tau_c = b/v_r$ is the collision time, χ is a Rabi frequency (e.g., $\chi = \langle\beta'|\mu'|f'\rangle|\mathcal{E}|/2\hbar$), and $\bar{\omega}$ is some characteristic frequency denominator appearing in the transition operator $\hat{T}$ [Eq. (13)]. For nonzero Δ, Eq. (33) is replaced by a less severe condition. Since $|\mathcal{U}(t=t_c)|\,\tau_c/\hbar \approx 1$ in the range of impact parameters that contributes to excitation,[14] the perturbation theory fails for field strengths $\chi \gtrsim \bar{\omega}$. Regardless of field strength, inequality (33) always fails to hold for sufficiently small impact parameters [$\mathcal{U}(t=t_c)$ varies typically as b^{-n}]; this domain can be treated by using a cutoff procedure.[5]

In the perturbation-theory limit, Eq. (22b) can be integrated directly after setting $\vec{A}_I(t) = \vec{a}_I(t_c^-)$. Using Eqs. (22), (19), and (21), one may obtain

$$\vec{a}_F(t_c^+) = (i\hbar)^{-1} \int_{t_c^-}^{t_c^+} G_F(t_c^+,t')T(IF,t') \times G_I(t',t_c^-)e^{-i\Delta t'}\vec{a}_F(t_c^-)\,dt' . \tag{34}$$

To be consistent with the perturbation-theory limit, the contributions to G_F and G_I arising from the light-shift operator should be neglected. Equation (34) may be given a simple interpretation. Starting in the state represented by $\vec{a}_I(t_c^-)$, one has a mixing and shifting of the initial levels from time $t = t_c^-$ to time $t = t'$ [represented by $G_I(t',t_c^-)$], a transition from initial to final state at time $t = t'$ [represented by $T(IF,t')$] and a mixing and shifting of final-state levels from time $t = t'$ to time $t = t_c^+$ [represented by $G_F(t_c^+,t')$]; an integration over all possible t' is included. Thus, it appears that reorientation effects in the initial and final states are correlated with both the shifting of these levels and the changes that occur in the $I \rightarrow F$ transition. In particular, if there are times at which instantaneous resonances occur for a given detuning $|\Delta|\tau_c \gtrsim 1$, the T matrix can be evaluated at such times and the integral (34) evaluated by a stationary-phase method. This condition can help to simplify the calculations, although the average over collision orientations can still pose considerable problems. Experimentally, one should expect to find a variation-of final-state coherence as a function of detuning.

C. Perturbation theory neglecting level shifts

Additional simplifications of Eq. (34) are possible for a range of impact parameters if one limits the detuning to the impact core of the RAIC profile ($|\Delta|\tau_c \ll 1$). If $|\Delta|\tau_c \ll 1$, the effects of instantaneous resonances are not important, since the phase factor $\exp(i\Delta t)$ is slowly varying; all times t' in the range (t_c^-, t_c^+) contribute to the integral in Eq. (34). Since the matrix S is quadratic in the collision interaction potential while the T matrix is linear in it, there exists a range of impact parameters where one can neglect the collisional contributions to S. Contributions to S from the light field have already been neglected owing to the perturbation-theory limit. Thus, in this limit where all level shifting and mixing in the initial and final states are ignored, $S(I,t) = S(F,t) = 0$ and, $G_I(t,t') = G_F(t,t') = 1$. Equation (34) reduces to

$$\vec{a}_F(t_c^+) = (i\hbar)^{-1} \int_{t_c^-}^{t_c^+} dt'\, T(IF,t')e^{-i\Delta t'}\vec{a}_I(t_c^-) . \tag{35}$$

This expression is evaluated explicitly in the following paper, where the appropriate averaging over collision orientations and impact parameters is carried out. Since the interatomic potential appears linearly in Eq. (35) and, consequently, bilinearly in Eqs. (23) and (24), the averaging over collision orientations is easily performed using techniques involving irreducible tensor operators. One can show that the collsion produces the same type of final-state coherence properties that would be produced by replacing the collision by an unpolarized field having the same multipolar properties as the collision operator (e.g., a dipole collision operator is replaced by an unpolarized electric field). This result is not difficult to understand. Excitation is produced in a single collision; when averaged over all collision orientations, the net effect is similar to that produced by an unpolarized field of the corresponding multipolarity.

It is relatively easy in this case to predict the final-state coherence properties for various polarizations of the external field. The final-state coherence may be observed by monitoring the polarization of fluorescence or the quantum beats originating from one of the final states.

D. General case

If perturbation theory fails (power densities $\gtrsim 10^{10}$ W/cm^2), the solutions of Eqs. (22) exhibit saturation effects. Unless a way can be found to perform the averaging over collision orientations and beam intensity profiles, one is faced with the costly task of integrating Eqs. (22) numerically as a function of collision orientation Θ and field amplitude $\mathcal{E}(\vec{R}_c, t_c)$. There has been limited work in this area, although a few related calculations have appeared.[7]

A general formalism for calculating the final-state coherences produced by radiatively-assisted inelastic collisions has been given. In the following paper, the RAIC transfer cross section is calculated in the perturbation-theory limit, neglecting level-shifting effects. In future work, it is hoped that the more general problem will be addressed.

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APPENDIX A

In this appendix, starting from the Hamiltonian (8) and using the assumptions of Sec. II, I derive Eqs. (9). The wave vector is written as

$$|\Psi(t)\rangle = \sum_M a_M(t) e^{-i\omega_M t} |M\rangle , \tag{A1}$$

where

$$|M\rangle = |mm'\rangle = |m\rangle |m'\rangle' ,$$
$$\omega_M = \omega_m + \omega_{m'} ,$$

and (ω_m and $\omega_{m'}$) and ($|m\rangle$ and $|m'\rangle'$) are eigenfrequencies and eigenkets of free atoms A and A', respectively [i.e., eigenfrequencies and eigenkets of the Hamiltonians $H_0(\vec{r})$ and $H_0'(\vec{r}')$, respectively, appearing in Eq. (8)]. I adopt the notation that a captial Roman letter represents a composite state of the AA' system [e.g., $|I\rangle = |ii'\rangle$, $\omega_{F_1} = \omega_{f_1} + \omega_{f_1'}$, etc.]. Using Schrödinger's equation with the Hamiltonian (8), one can derive the following equation for the probability amplitude (in the interaction representation) $a_M(t)$:

$$i\hbar \dot{a}_M = \{ -\tfrac{1}{2}\langle M|\vec{\mu}_T|B\rangle \cdot [\vec{\mathcal{E}} e^{-i\Omega t} + \vec{\mathcal{E}}^* e^{i\Omega t}] + \langle M|\mathcal{U}(t)|B\rangle \} e^{i\omega_{MB} t} a_B , \tag{A2}$$

where $\vec{\mu}_T = \vec{\mu} + \vec{\mu}'$, $\omega_{MB} = \omega_M - \omega_B$, and the summation convention is used.

According to the assumptions of Sec. II, the only states that are significnatly coupled are $|I\rangle$ and $|F\rangle$. However, this coupling does not yet appear directly in Eq. (A2) since the I-F coupling is via virtual intermediate states. To see the coupling directly, one writes Eq. (A2) for $\dot{a}_F$, replacing the a_B which appears on the right-hand side of this equation by the value obtained by formally integrating Eq. (A2) for $\dot{a}_B$. In this way, one finds

$$i\hbar \dot{a}_F = e^{i\omega_{FB} t} [-\tfrac{1}{2}\langle F|\vec{\mu}_T|B\rangle \cdot (\vec{\mathcal{E}} e^{-i\Omega t} + \vec{\mathcal{E}}^* e^{i\Omega t}) + \langle F|\mathcal{U}(t)|B\rangle] \times \left(a_B(t_c^-) + (i\hbar)^{-1} \int_{t_c^-}^{t} dt' \, e^{i\omega_{BM} t'} [-\tfrac{1}{2}\langle B|\vec{\mu}_T|M\rangle \cdot (\vec{\mathcal{E}} e^{-i\Omega t'} + \vec{\mathcal{E}}^* e^{i\Omega t'}) + \langle B|\mathcal{U}(t')|M\rangle] a_M(t') \right) . \tag{A3}$$

The term proportional to $a_B(t_c^-)$ can be neglected using the assumption that the field and collision must act *simultaneously* to produce a transition. The validity conditions for the neglect of this term are

$$\bar{\omega}_\epsilon T \gg 1 , \quad \bar{\omega}_c \tau_c \gg 1 , \tag{A4}$$

where $\bar{\omega}_\epsilon$ and $\bar{\omega}_c$ are some appropriate frequency

mismatches for the atom-field and atom-atom interactions, respectively.[15]

The integral term in Eq. (A3) is treated as follows: (1) The only terms $a_M(t')$ of importance are assumed to be $a_{F_1}(t')$ and $a_I(t')$, where $|F_1\rangle$ is in the final-state group of levels. This assumption is equivalent to asserting that there is negligible population in all states outside the I and F groups (i.e., that there are only *virtual* excitations of the intermediate states). For this approximation to be valid one must again require conditions (A4) to hold. In addition, one must require that the cross section for transfer within a *given* atom from either its initial or final state to some intermediate state be negligible. This cross section is precisely that associated with collisionally-aided radiative excitation (CARE).[4] For $\bar{\omega}_\epsilon \tau_c \gg 1$ and $\chi \ll \bar{\omega}_\epsilon$, CARE is unimportant. However, CARE may become significant in the strong-field regime $\chi \approx \bar{\omega}_\epsilon$; in that case, one would have to expand the basis to include those states coupled to either $|I\rangle$ or $|F\rangle$ by CARE. (2) Antiresonance terms in Eq. (A3) varying as $\exp[\pm i(\omega_{FI}+\Omega)t]$ or $\exp(\pm 2i\Omega t)$ are neglected. (3) The functions $\langle B|\mathfrak{u}(t')|M\rangle$ and $a_M(t')$ are assumed to be slowly varying with respect to the exponential factors and are evaluated at time $t'=t$. For this assumption to be valid, one must have

$$\bar{\omega}_c \tau_c \gg 1, \quad \omega_\epsilon \tau_c \gg 1. \tag{A5}$$

There is a supplementary condition which must also be satisfied related to the time variation of $a_I(t')$ (see below). (4) Frequency differences $\omega_{FF_1}, \omega_{II_1}$ are neglected with respect to $\bar{\omega}_c$ or $\bar{\omega}_\epsilon$ and factors such as $\exp(i\omega_{II_1}t)$ or $\exp(i\omega_{FF_1}t)$ are set equal to unity. These approximations are valid owing to Eqs. (5) and (A5).

With these assumptions, one can easily carry out the integration in Eq. (A3) and obtain

$$i\hbar\dot{a}_F = \left[-\frac{1}{4\hbar}\left(\frac{\langle F|\vec{\mu}_T|B\rangle\cdot\vec{\mathcal{E}}^*\langle B|\vec{\mu}_T|F_1\rangle\cdot\vec{\mathcal{E}}}{\omega_{BF}-\Omega} + \frac{\langle F|\vec{\mu}_T|B\rangle\cdot\vec{\mathcal{E}}\langle B|\vec{\mu}_T|F_1\rangle\cdot\vec{\mathcal{E}}^*}{\omega_{BF}+\Omega}\right) - \frac{1}{\hbar}\frac{\langle F|\mathfrak{u}(t)|B\rangle\langle B|\mathfrak{u}(t)|F_1\rangle}{\omega_{BF}}\right] a_{F_1}$$
$$+\frac{1}{2\hbar}\left(\frac{\langle F|\vec{\mu}_T|B\rangle\langle B|\mathfrak{u}(t)|I\rangle}{\omega_{BI}} + \frac{\langle F|\mathfrak{u}(t)|B\rangle\langle B|\vec{\mu}_T|I\rangle}{\omega_{BF}-\Delta}\right)\cdot\vec{\mathcal{E}}e^{-i\Delta t}a_I, \tag{A6}$$

where there is no sum on F and Δ is defined by Eq. (10). The quantity Δ appearing in the frequency denominator can be neglected in comparison with ω_{BF} and it should be dropped for consistency (see below). Equation (A6) is then identical to Eqs. (9b), (11), and (13), using the notation $I=ii'$, $F=ff'$, $B=\beta\beta'$, and $F_1=f_1f_1'$. Similarly, Eq. (9a) can be verified.

Finally, one can check to see if $a_I(t)$ is slowly varying compared with $\exp(i\bar{\omega}t)$ as has been assumed ($\bar{\omega}=\bar{\omega}_\epsilon$ or $\bar{\omega}_c$). By examining Eqs. (9), one can deduce that $|\dot{a}_I/a_I|_{\max}$ is given by the largest of either $|\Delta|$, $\omega_c = 1/\tau_c$, or $\hbar\mathfrak{u}(t=t_c)\chi/\bar{\omega}$, where χ is a Rabi frequency in the problem. Thus, in order to neglect all but the groups I and F, one must have

$$\bar{\omega}/|\Delta| \gg 1, \quad \bar{\omega}\tau_c \gg 1,$$
$$\left[\frac{|\mathfrak{u}(t=t_c)|\tau_c}{\hbar}\left(\frac{\chi}{\bar{\omega}}\right)\right]\frac{1}{\bar{\omega}\tau_c} \ll 1. \tag{A7}$$

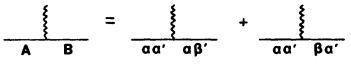
Note that one may retain a consistent solution even in the strong-field limit, $\hbar^{-1}|\mathfrak{u}(t=t_c)|\tau_c\chi/\bar{\omega} \gtrsim 1$, provided that $\bar{\omega}\tau_c$ is large enough to assure the validity of the last inequality in conditions (A7).

APPENDIX B

A simple diagrammatic interpretation of the operators $\hat{T}$ and $\hat{S}$ appearing in Eqs. (9) can be given. The interaction between the field and the atoms is represented by

. (B1)

The field takes the atom from the composite state $A=\alpha\alpha'$ to $B=\beta\beta'$. Actually this diagram may be thought of as the sum of two diagrams,



in which the field acts on each atom separately. The collisional interaction is represented by

(B2)

taking the atoms from states A to B.

With these definitions, it is relatively easy to draw the diagrams corresponding to the operators $\hat{S}_L$, $\hat{S}_c$ and $\hat{T}(IF)$ appearing in Eqs. (11) and (13), and these are shown in Fig. 3. Figure 3(a) corresponds to the light-shift operator $\hat{S}_L(F)$ which acts

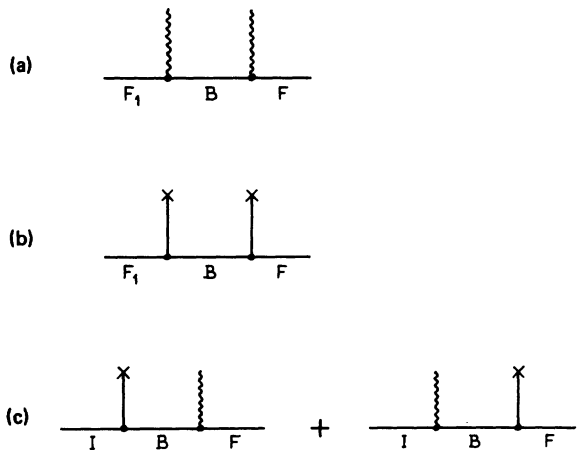


FIG. 3. Diagrammatic interpretation of the operators (a) $\hat{S}_L(F)$, (b) $\hat{S}_c(F)$, and (c) $\hat{T}(IF)$. In each diagram a wavy-line vertex refers to an atom-field interaction and a straight-line vertex to a collisional interaction.

in the final-state subspace [a similar diagram can be drawn for $\hat{S}_L(I)$]. The field excites either of the atoms to some intermediate virtual state and then de-excites the atom back to the final-state manifold. Figure 3(b) corresponds to the collisional operator $\hat{S}_c(F)$; the collision excites the atoms to some intermediate state $B=\beta\beta'$ and then de-excites them to the final-state manifold. Finally, Fig. 3(c) corresponds to the operator $\hat{T}(IF)$. The field and collision combine to excite the atoms from initial state I to final state F via the virtual intermediate state B. These diagrams immediately illustrate the nature of the operators appearing in the RAIC equations (i.e., $\hat{S}_L$ varies as $|\mathcal{E}|^2$, $\hat{S}_c$ as $\mathfrak{u}^2$, and $\hat{T}$ as $\mathfrak{u}\mathcal{E}$).

It is also possible to directly construct the operators from the diagrams. More precisely, the following rules enable one to calculate the matrix representation of the operators in the interaction representation.

(1) Assign a factor $(-1)^{N-1}$ (N=number of vertices) and a factor $e^{i\omega_{GH}t}$ (G=final state, H=initial state) to each diagram.

(2) Each vertex of the form (B1) is assigned the value $-\langle B|\vec{\mu}_T\cdot\vec{E}(t)|A\rangle$, where $\vec{E}(t)$ is given by Eq. (2). Each vertex of the form (B2) is assigned the value $\langle B|\mathfrak{u}(t)|A\rangle$.

(3) In the resulting expression, reject all rapidly varying terms (e.g., terms varying as $\exp(\pm 2i\Omega t)$ or $\exp[\pm i(\Omega+\omega_{FI})t]$).

(4) For a vertex of the form (B1) assign an energy denominator $\hbar(\omega_{BI}\pm\Omega)$, with the (+) sign used if $\vec{\mathcal{E}}$ appears in the B-A matrix element and the (−) sign if $\vec{\mathcal{E}}^*$ appears in the B-A matrix element. For a vertex of the form (B2) assign an energy denominator $\hbar\omega_{BA}$. Energy denominators are assigned for *all but the last vertex* in any diagram.

(5) Sum over all intermediate states.

As an example, I calculate Fig. 3(a) and the second diagram in Fig. 3(c). Following rules (1) and (2) for Fig. 3(a) gives

$$-\tfrac{1}{4}e^{i\omega_{FF_1}t}\langle B|\vec{\mu}_T\cdot(\vec{\mathcal{E}}e^{-i\Omega t}+\vec{\mathcal{E}}^*e^{i\Omega t})|F_1\rangle \times\langle F|\vec{\mu}_T\cdot(\vec{\mathcal{E}}e^{-i\Omega t}+\vec{\mathcal{E}}^*e^{i\Omega t})|B\rangle .$$

Keeping only the slowly varying terms [rule (3)] yields

$$-\tfrac{1}{4}e^{i\omega_{FF_1}t}[\langle F|\vec{\mu}_T\cdot\vec{\mathcal{E}}^*|B\rangle\langle B|\vec{\mu}_T\cdot\vec{\mathcal{E}}|F_1\rangle +\langle F|\vec{\mu}_T\cdot\vec{\mathcal{E}}|B\rangle\langle B|\vec{\mu}_T\cdot\vec{\mathcal{E}}^*|F_1\rangle] . \tag{B3}$$

An energy denominator is assigned only to the first vertex and is $\hbar(\omega_{BF}-\Omega)$ for the first term in (B3) (since $\vec{\mathcal{E}}$ appears in the B-F_1 matrix element) and is $\hbar(\omega_{BF}+\Omega)$ for the second term in (B3) (since $\vec{\mathcal{E}}^*$ appears in the B-F_1 matrix element). Therefore,

$$\langle F|\hat{S}_L|F_1\rangle=-\frac{1}{4\hbar}e^{i\omega_{FF_1}t}\times\left(\frac{\langle F|\vec{\mu}_T\cdot\vec{\mathcal{E}}^*|B\rangle\langle B|\vec{\mu}_T\cdot\vec{\mathcal{E}}|F_1\rangle}{\omega_{BF_1}-\Omega}+\frac{\langle F|\vec{\mu}_T\cdot\vec{\mathcal{E}}|B\rangle\langle B|\vec{\mu}_T\cdot\vec{\mathcal{E}}^*|F_1\rangle}{\omega_{BF_1}+\Omega}\right)$$

in agreement with the first two terms of Eq. (A6) [recall that I set $\exp(i\omega_{FF_1}t)=1$ and $\omega_{BF}\approx\omega_{BF_1}$ in that equation].

Similarly, applying rules (1) and (2) to the second diagram of Fig. 3(c) yields

$$\tfrac{1}{2}e^{i\omega_{FI}t}\langle B|\vec{\mu}_T\cdot(\vec{\mathcal{E}}e^{-i\Omega t}+\vec{\mathcal{E}}^*e^{i\Omega t})|I\rangle\langle F|\mathfrak{u}|B\rangle .$$

Keeping the slowly varying term which varies as $\vec{\mathcal{E}}\exp[i(\omega_{FI}-\Omega)t]=\vec{\mathcal{E}}e^{-i\Delta t}$ and applying rules (3)–(5) gives

$$\frac{1}{2\hbar}e^{-i\Delta t}\frac{\langle F|\mathfrak{u}|B\rangle\langle B|\vec{\mu}_T\cdot\mathcal{E}|I\rangle}{\omega_{BI}-\Omega},$$

which agrees with the last term of Eq. (A6) since $\omega_{BI}-\Omega=\omega_{BF}-\Delta$.

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[1]Part of the energy mismatch can also be compensated for by a change in the translational energy of the atoms.

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[8]S. E. Harris and J. C. White, IEEE J. Quantum Electron. 13, 972 (1977).

[9]The operator appearing in Eq. (14) appears to be the adjoint of the operator in Eq. (13). However, as defined, these operators act in different spaces [i.e., $\hat{T}(ii';ff')$ is defined to couple only states $|ii'\rangle$ to $|ff'\rangle$, implying $\langle ii'|\hat{T}(ii',ff')|ff'\rangle \equiv 0$].

[10]See Eq. (A7) for a more precise statement of the validity conditions.

[11]In situations where one starts from initial states having a nonthermal velocity distribution, effects of velocity-changing collisions may have to be included in Eq. (26). In that case, the first term on the right-hand side of Eq. (26) would be replaced by an integral giving the transfer from initial states with velocities $\vec{v}_1$, $\vec{v}_1'$ to final states with velocities $\vec{v}$, $\vec{v}'$.

[12]As defined, the transfer rates and cross sections are generally complex quantities.

[13]E. J. Robinson, J. Phys. B 12, 1451 (1979); *ibid.* B 13, 2359 (1980).

[14]The impact parameter b_w for which $|\mathcal{U}(t=t_c)|\,\tau_c/\hbar = 1$ is the so-called Weisskopf radius and represents a characteristic length in the problem.

[15]Since some energy mismatch can also be provided by a change in the atom's translational motion, the condition $\bar{\omega}_c\tau_c \gg 1$ can be replaced by the somewhat stronger condition $\hbar\bar{\omega}_c >$ (thermal energy).