PHYSICAL REVIEW A VOLUME 22, NUMBER 4 OCTOBER 1980

Theory of collisionally aided radiative excitation in three-level systems

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(Received 18 March 1980)

A theory of collisionally aided radiative excitation (CARE) for three-level systems in the weak-field limit is presented. Cross sections for the excitation of three-level atoms by two off-resonant pulsed radiation fields in the presence of collisions with structureless perturbers are calculated. Analytic expressions for the cross sections as functions of atom-field detunings are obtained under usual classical-trajectory and rotating-wave approximations using perturbation theory for various regions of detunings. Examples for the resulting excitation line shapes are given mostly for van der Waals potentials. A dressed-atom picture of the CARE processes is discussed. Emphasis is put on an interesting effect arising from the interference between the "stepwise" and the "direct" channel of excitation. Such an interference effect manifests itself as modulations in the total excitation cross section as a function of relative interatomic speed in some cases.

I. INTRODUCTION

In this paper, we present a theory of collisionally aided radiative excitation (CARE) for three-level systems in the weak-field limit. CARE in two-level systems has been the subject of many recent studies.[1] Approximation schemes, valid in different regions of atom-field detunings, have been used and verified by numerical calculations.[2] In three-level systems, however, calculations have been limited to a narrow range of detunings.[3] It is thus desirable to have a theory which is free from such limitations.

In Sec. II, we state the problem to be investigated and define the conditions under which the treatment of this paper are applicable. The complexity of a three-level CARE problem over its two-level counterpart is due partly to the fact that there are two detunings which can be independently varied. In addition, the collision-induced energy shifts of these three levels can be of either a positive or a negative sign (relative to the detunings), leading to different physical situations. It becomes necessary, for the convenience of presentation, to classify the cases according to the sizes and signs (relative to those of the collision-induced energy-level shifts) of the detunings. This is done in Sec. III. A "dressed-atom" picture of the physical processes will be given in Sec. IV with discussions of interesting interference effects for some cases. In Sec. V, the basic equations involved are given. The solutions and results for cases as classified in Sec. III are obtained in Sec. VI. In Sec. VII, we discuss the advantages of using CARE over conventional atom-atom collision techniques to study the atom-atom interactions. The paper is concluded in Sec. VIII. Appendices A and B provide some calculational details.

II. THE PROBLEM

Consider a three-level active atom, which may have one of the configurations shown in Fig. 1 with level separations $\hbar\omega_{21}$ and $\hbar\omega_{32}$, subjected to two off-resonant incident pulsed radiation fields of frequencies ω and ω' and amplitudes $E(t)$ and $E'(t)$. The atom simultaneously undergoes a collision with a structureless perturber. Under some conditions to be stated in this section, we calculate the $1 \rightarrow 3$ excitation cross section as a function of detunings.

The fields $E(t)$ and $E'(t)$ are assumed to drive only 1-2 and 2-3 transitions, respectively, with interactions characterized by the coupling strengths $\chi(t) = \mu_{12}E/2\hbar$ and $\chi'(t) = \mu_{23}E'/2\hbar$, respectively, where μ_{12} and μ_{23} are the dipole matrix elements of the respective transitions. The collisions are assumed only to shift the energies of the active-atomic levels without coupling them (sometimes referred to as adiabatic approximation), a generally good assumption in the case of electronic transitions in the optical regime because of the lack of interatomic potential curve crossings (except perhaps at extremely small internuclear distance which cannot be reached with ordinary thermal energy).

If the atom-field detunings Δ and Δ', defined as $\Delta = \omega - \omega_{21}$ and $\Delta' = \omega' - \omega_{32}$, are larger than the Doppler width, and/or if the incident pulsed fields are adiabatic, the excitation cross section are negligibly small in the absence of collisions. In both cases, the collision can greatly enhance the excitation by either breaking the adiabaticity or shifting the energy levels of the active atom into resonance (instantaneously) with the external fields. We shall confine the discussion of this paper to detunings larger than the Doppler width and assume that the pulses are slow enough such

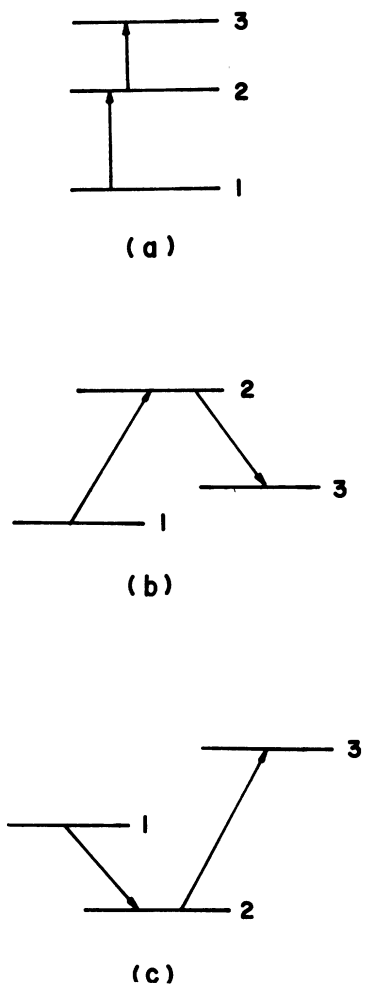

FIG. 1. Configurations of a three-level active atom for CARE. (a) Upward cascade, (b) inverse V, and (c) V.

that the pulse durations are much larger than the collision time, and that during a collision the field amplitudes are constants; that is,

$$|\Delta|, |\Delta'| > W_D, \tag{2.1}$$

where W_D is the Doppler width,

$$\lim_{t\to\pm\infty} \chi(t), \chi'(t) \to 0, \tag{2.2}$$

$$\frac{d\chi}{dt}, \frac{d\chi'}{dt} \to 0, \tag{2.3}$$

and

$$\chi(t) \to \chi_0, \chi'(t) \to \chi_0' \tag{2.4}$$

during a collision.

In addition to conditions (2.1)–(2.4), the perturber density is assumed to be low enough that the time between collisions is much longer than the inverse of the detunings and the pulse durations. In such a pressure regime, one can take the CARE rate to be linear in the perturber density and calculate the CARE cross section for a single collision, from which the CARE rate is obtained by averaging over all possible collisions. This procedure is followed throughout this paper.

The conditions on the pulsed radiation [Eqs. (2.1)–(2.4)] can be met by ordinary laser pulses which have typical pulse lengths ($\gtrsim 10^{-9}$ sec) much longer than the collision time ($\sim 10^{-12}$ sec). The pressure range we are considering is typically of the order of 10 Torr or less in order to satisfy the conditions stated above.

III. CLASSIFICATION

For the convenience of presentation, the three-level atom is assumed to have a configuration shown in Fig. 1(a), unless otherwise stated. The theory to be presented is equally applicable to other configurations with suitable changes of the signs of detunings and of the relative energy-level shifts.

Consider such a three-level active atom [Fig. 1(a)] undergoing a collision with a structureless perturber. The energy levels are shifted during a collision, as shown schematically in Fig. 2, for some specific collision impact parameter b and relative velocity v in a manner depending on the assumed interatomic potential. The relative shifts of these levels can lead to an increase or decrease in the atomic transition frequencies over their unperturbed values. In the case shown in Fig. 2(a), both the 1-2 and 2-3 transition frequencies decrease (shift toward the red), and one speaks of (relative) attractive interatomic potentials. Conversely, the transition frequencies increase for repulsive potentials. Although different combinations of attractive and repulsive potentials for the 1-2, 2-3, and 1-3 (two-photon) transitions may occur in a three-level system, we shall be concerned only with attractive interatomic potentials. This restriction (to the attractive relative interatomic potentials) is for the convenience of the presentation; the theory to be presented is, nevertheless, applicable to all types of interatomic potentials.

What is essential in the theory is the existence (or lack thereof) of the collision-induced instantaneous resonances during a collision. When the detunings equal (both in signs and in magnitudes) the relative energy-level shifts, resonances occur. In Fig. 2(a), instantaneous resonances occur at $\pm\tau_0$ for 1-2 transitions, $\pm\tau_0'$ for 2-3 transition, and $\pm\tau_0''$ for 1-3 two-photon transition. Such instantaneous resonances enhance the absorption of radiation, especially in the case of large detunings.

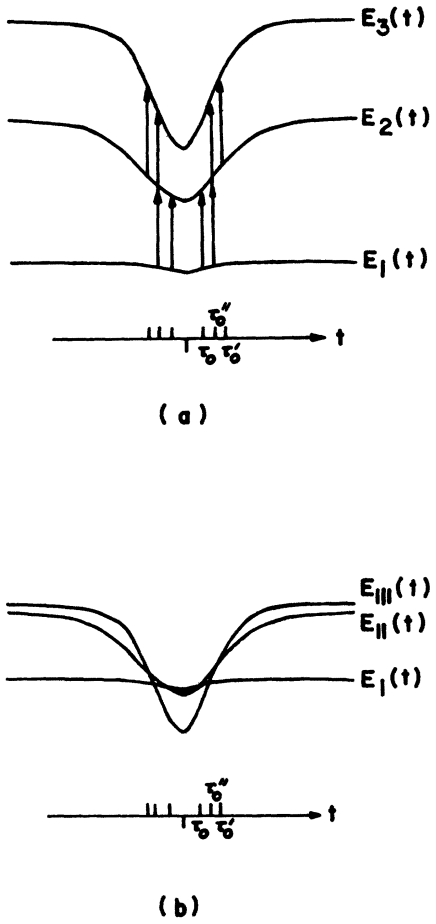

FIG. 2. Energy levels of a three-level active atom during a collision, schematically shown for a relatively attractive interatomic potential. (a) In a bare-state–classical-field picture, the energy levels, thus the detunings, are time dependent. As shown, resonances occur at $\pm\tau_0$ for 1-2 transition, $\pm\tau_0'$ for 2-3 transition, and $\pm\tau_0''$ for 1-3 two-photon transition. (b) In a dressed-state picture, the resonance points in (a) are transformed into level crossings of the dressed states.

The studies of two-level CARE (Ref. 2) have led to the understanding that the instantaneous resonances are important when the detunings are much larger than the inverse collision time τ_c^{-1}, i.e., $|\text{detuning}|\tau_c \gg 1$. For $|\text{detuning}|\tau_c \ll 1$ [impact region (I)], the existence or lack thereof of instantaneous resonances is unimportant, and the absorption cross section varies as $|\text{detuning}|^{-2}$ irrespective of the sign of the detuning. The case of $|\text{detuning}|\ \tau_c \gg 1$ can be divided into two regions according to the sign of the detuning relative to the interatomic potential: the quasistatic (Q) region where the instantaneous resonances can occur (e.g., red detunings for attractive potentials), and the antistatic (A) regions where *no* instantaneous resonance can occur (e.g., blue detunings for attractive potentials).[4] In the three-level problem, classification of the cases is complicated by the possible combinations of I, Q, and A regions for Δ, Δ', and $\Delta+\Delta'$. If there is no constraint, there would be a total of 27 cases to be discussed; the fact that $\Delta+\Delta'$ cannot be independently varied and that we restrict our discussion to attractive potentials reduces the number to 13 cases.

The cases to be considered are listed in Table I according to the region of each detuning. In the third column, the conditions, appropriate for attractive potentials only, are also listed to help clarify the cases considered. In subsequent sections, results are given mainly for attractive van der Waals potentials, although the treatments are generally applicable to other types of potentials. Table I exhausts all possible cases where attractive potentials only are considered. It does not, however, include all cases for a general interatomic potential. We choose not to include all possible cases because it is impractical to do so and may lead to confusion. At any rate, for the cases *not* included, one can find applicable treatments in one of the cases included.

It is natural to group together the cases in Table I for which the mathematical treatments are similar. In Sec. VI, we present the solutions and the results according to these groups. We group cases A, B, and C (Δ in the I region), cases D and E (Δ' in the I region), and cases F and G ($\Delta+\Delta'$ in the I region). Cases H and I, which have two of the three detunings in the Q region and the third detuning in the A region, will be grouped together. Case J, with all three detunings in the Q region, is the last and the most interesting case to be treated. Cases K, L, and M will not be discussed since at least two of the detunings are in the A region, leading to exponentially small excitation cross sections. Although numerical calculations can be performed to obtain cross sections for these cases, reliable analytic approximation schemes have yet to be developed.

IV. THE DRESSED-ATOM PICTURE AND GENERAL CONSIDERATIONS

In this section we shall give a general description of the physical processes in terms of the "dressed-atom" picture[5] (sometimes referred to as the atom-field diabatic representation)[6] in which the eigenstates of the Hamiltonian of free atom + free fields + atom-field interactions (i.e.,

TABLE I. Classification of cases.

Δ	Δ'	$\Delta+\Delta'$	Conditions appropriate for attractive potentials	Case
I	I	I	$\lvert\Delta\rvert\tau_c\ll1$, $\lvert\Delta'\rvert\tau_c\ll1$, $\lvert\Delta+\Delta'\rvert\tau_c\ll1$	A
I	Q	Q	$\lvert\Delta\rvert\tau_c\ll1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta'<0,\Delta+\Delta'<0$	B
I	A	A	$\lvert\Delta\rvert\tau_c\ll1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta'>0,\Delta+\Delta'>0$	C
Q	I	Q	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\ll1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta<0,\Delta+\Delta'<0$	D
A	I	A	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\ll1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta>0,\Delta+\Delta'>0$	E
Q	A	I	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\ll1$, $\Delta<0,\Delta'>0$	F
A	Q	I	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\ll1$, $\Delta>0,\Delta'<0$	G
Q	A	Q	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta<0,\Delta'>0,\Delta+\Delta'<0$	H
A	Q	Q	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta>0,\Delta'<0,\Delta+\Delta'<0$	I
Q	Q	Q	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta<0,\Delta'<0,\Delta+\Delta'<0$	J
Q	A	A	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta<0,\Delta'>0,\Delta+\Delta'>0$	K[a]
A	Q	A	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta>0,\Delta'<0,\Delta+\Delta'>0$	L[a]
A	A	A	$\lvert\Delta\rvert\tau_c\gg1$, $\lvert\Delta'\rvert\tau_c\gg1$, $\lvert\Delta+\Delta'\rvert\tau_c\gg1$, $\Delta>0,\Delta'>0,\Delta+\Delta'>0$	M[a]

[a] Not treated in this paper.

atomic dressed states) are taken as stationary states and the collision, which couples the dressed states as well as shifts their energies, is treated as a perturbation. The dressed states are generally linear combinations of the "bare states" (i.e., eigenstates of free atom + free-field Hamiltonian) and, in the weak-field limit, can be approximated as

$$
\begin{aligned}
|\mathrm{I}\rangle &= (1-\chi^2/2\Delta^2)\,|1,n,n'\rangle + (\chi/\Delta)\,|2,n-1,n'\rangle + [\chi\chi'/\Delta(\Delta+\Delta')]\,|3,n-1,n'-1\rangle,\\
|\mathrm{II}\rangle &= (-\chi/\Delta)\,|1,n,n'\rangle + (1-\chi^2/2\Delta^2-\chi'^2/2\Delta'^2)\,|2,n-1,n'\rangle + (\chi'/\Delta')\,|3,n-1,n'-1\rangle,\\
|\mathrm{III}\rangle &= [\chi\chi'/\Delta'(\Delta+\Delta')]\,|1,n,n'\rangle - (\chi'/\Delta')\,|2,n-1,n'\rangle + (1-\chi'^2/2\Delta'^2)\,|3,n-1,n'-1\rangle,
\end{aligned}
\tag{4.1}
$$

with eigenenergies

$$
\begin{aligned}
E_{\mathrm{I}} &= E_1 + n\hbar\omega + n'\hbar\omega' + \chi^2/\Delta,\\
E_{\mathrm{II}} &= E_2 + (n-1)\hbar\omega + n'\hbar\omega' - \chi^2/\Delta + \chi'^2/\Delta',\\
E_{\mathrm{III}} &= E_3 + (n-1)\hbar\omega + (n'-1)\hbar\omega' - \chi'^2/\Delta',
\end{aligned}
\tag{4.2}
$$

where E_1, E_2, and E_3 are energies of the atomic states 1, 2, and 3, respectively, with separations $E_2-E_1=\hbar\omega_{21}$ and $E_3-E_2=\hbar\omega_{32}$; the fields are represented by number states with photon numbers n and n' for fields E and E', respectively. For adiabatic pulses χ and χ', n and n' take on the instantaneous values.

In the weak-field limit, from Eqs. (4.1), the dressed states $|\mathrm{I}\rangle$, $|\mathrm{II}\rangle$, and $|\mathrm{III}\rangle$ are composed almost entirely of only states $|1,n,n'\rangle$, $|2,n-1,n'\rangle$, and $|3,n-1,n'-1\rangle$, respectively, with some small corrections; their energy separation are approximately $E_{\mathrm{II}}-E_{\mathrm{I}}\simeq-\Delta$, $E_{\mathrm{III}}-E_{\mathrm{II}}=-\Delta'$, and $E_{\mathrm{III}}-E_{\mathrm{I}}\simeq-(\Delta+\Delta')$; during a collision, the time dependence of E_{I}, E_{II}, and E_{III} are almost the same as E_1, E_2, and E_3. Thus, the instantaneous resonance points in Fig. 2(a) (i.e., $\pm\tau_0$, $\pm\tau_0'$, and $\pm\tau_0''$) are transformed into crossing points as shown in Fig. 2(b), and a physical picture of CARE can be established similar to that of ordinary (radiationless) inelastic atomic collision, which has been under active research for several decades.

The coupling between the dressed states by the collision is characterized by the off-diagonal matrix elements

$$
\begin{aligned}
&\langle\mathrm{I}|U(t)|\mathrm{II}\rangle = \langle\mathrm{II}|U(t)|\mathrm{I}\rangle \simeq (\chi/\Delta)V(t),\\
&\langle\mathrm{II}|U(t)|\mathrm{III}\rangle = \langle\mathrm{III}|U(t)|\mathrm{II}\rangle \simeq (\chi'/\Delta')V'(t),\\
&\langle\mathrm{I}|U(t)|\mathrm{III}\rangle = \langle\mathrm{III}|U(t)|\mathrm{I}\rangle\\
&\qquad \simeq [\chi\chi'/\Delta(\Delta+\Delta')]V'(t) - [\chi\chi'/\Delta'(\Delta+\Delta')]V(t),
\end{aligned}
\tag{4.3}
$$

where $U(t)$ is the collision interaction which is diagonal in the atomic bare-state basis. $V(t) = \langle 2|U(t)|2\rangle - \langle 1|U(t)|1\rangle$ and $V'(t) = \langle 3|U(t)|3\rangle - \langle 2|U(t)|2\rangle$ are the collision-induced relative energy-level shifts between states 1,2 and states 2,3, respectively. The off-diagonal matrix element $\langle\mathrm{I}|U(t)|\mathrm{III}\rangle$ is responsible for the "direct" (I→III) excitation corresponding to two-photon absorption in the bare-state picture, while $\langle\mathrm{I}|U(t)|\mathrm{II}\rangle$ and $\langle\mathrm{II}|U(t)|\mathrm{III}\rangle$ form the chain for "stepwise" (I→II→III) excitation. By studying these matrix elements we can better understand dominant excitation processes in different regions of detunings. It is clear that when $|\Delta+\Delta'| \ll |\Delta|, |\Delta'|$, the direct process is the dominant one. When $|\Delta|$ (or $|\Delta'|$) is smaller than the other two detunings, Eq. (4.3) suggest that the "direct"

and the "stepwise" processes have comparable contributions. However, as we shall see later, cancellation between the two processes occurs, and the stepwise process remains dominant. This will be seen when the detailed calculations are given.

In the above discussion, the effects of the collision-induced curve crossings (i.e., of the collision-induced shifts of the dressed states) have not been included. As discussed earlier, the crossings are particularly important when the detunings are large, corresponding to large separations between the dressed states. When the detunings are small (corresponding to small-level separations between the dressed states), however, the crossings do not provide major contributions to the excitation, since Fourier frequencies are induced by the collision to cover the energy mismatch. To show the importance of curve crossings, we choose, in the remainder of this section, to discuss only the case where all the detunings are in the Q region, since an interesting interference effect occurs in this limit.

The interference effect is better described using a classical-trajectory approximation of the collision event. In this approximation, crossings, as shown in Fig. 2(b) in the time domain, occur at corresponding internuclear distances $R(\tau_0) = R_0$, $R(\tau_0') = R_0'$, and $R(\tau_0'') = R_0''$. For collision impact parameters such that the closest approach between the active atom and the perturber is smaller than R_0, R_0', and R_0'', all the crossings occur during the collision. For larger impact parameters, some or all of the crossings are not induced, and the excitation probability is reduced (as compared to the all-crossing case) by orders of magnitude. Hence, collisions with larger impact parameters do not contribute significantly to the excitation cross section and can be ignored. Consequently, we consider only the collisions with impact parameters small enough to induce all the crossings. Furthermore, since the radiation pulses are assumed to be adiabatic, the atom-field system is in its dressed state $|\mathrm{I}\rangle$ before the collision (which comes from adiabatic following of bare atomic state 1), and only the dressed state $|\mathrm{III}\rangle$ will adiabatically follow the pulses back to bare atomic state 3. Hence, calculating the $|\mathrm{I}\rangle \rightarrow |\mathrm{III}\rangle$ transition probability is equivalent to calculating the $1 \rightarrow 3$ transition probability.

When the detunings are large ($|\Delta|$, $|\Delta'|$, $|\Delta + \Delta'| \gg$ inverse collision time), all the transitions occur well localized near the crossings. It is not difficult to see that there are four channels for the $|\mathrm{I}\rangle \rightarrow |\mathrm{III}\rangle$ transition to occur, two from the stepwise process ($\mathrm{I} \rightarrow \mathrm{II} \rightarrow \mathrm{III}$) and two from the direct process ($\mathrm{I} \rightarrow \mathrm{III}$). With reference to Fig. 2(b), these four channels are

$$\left.\begin{array}{l} |\mathrm{I}\rangle \xrightarrow[\tau_0]{} |\mathrm{II}\rangle \xrightarrow[\tau_0']{} |\mathrm{III}\rangle \\ |\mathrm{I}\rangle \xrightarrow[\tau_0]{} |\mathrm{II}\rangle \xrightarrow[\tau_0']{} |\mathrm{III}\rangle \end{array}\right\} \text{stepwise}$$

$$\left.\begin{array}{l} |\mathrm{I}\rangle \xrightarrow[\tau_0'']{} |\mathrm{III}\rangle \\ |\mathrm{I}\rangle \xrightarrow[\tau_0'']{} |\mathrm{III}\rangle \end{array}\right\} \text{direct},$$

where the times below the arrows correspond to the crossing times shown in Fig. 2(b) and indicate when each transition takes place. Each of these four channels contributes to the $|\mathrm{I}\rangle \rightarrow |\mathrm{III}\rangle$ transition amplitude, and interference between them can exhibit interesting phenomena. In a recent article,[7] we have demonstrated that this interference effect gives rise to an oscillatory structure in the total excitation cross section as a function of the active-atom-perturber relative speed when the crossings are well separated and the interatomic potentials are such that the "stepwise" and "direct" processes have comparable contributions to the transition amplitude. This effect is similar to that discussed by Rosenthal and Foley[8,9] regarding He-He$^+$ charge-exchange inelastic collision in which the atom-ion interatomic potential curves are similar to those of CARE in the dressed-atom diabatic representation discussed here. In this paper, we provide a detailed calculation to supplement the discussion in Ref. 7. This interference phenomena is quite general and should be expected to occur in many systems where excitation is possible *via* several channels.

The interference effect discussed above requires a special crossing configuration, i.e., three well-separated crossings occurring at R_0, R_0', and R_0''. Since the existence of crossings and their positions and slopes depend on the interatomic potential as well as the detunings, other crossing configurations may occur leading to different manifestations of the interference effect in the total excitation cross section. In this paper, a treatment for the general case is given, and results for special cases follow.

We note that the interference between the stepwise and the direct processes occurs even in the case of small detunings. However, the interference does not give rise to interesting effects such as the oscillatory total excitation cross sections discussed above for the case of large detunings because, in the case of small detunings, the transitions do not occur at well-defined instants, which is required to obtain a definite phase relationship between amplitudes arising from the stepwise and the direct processes.

V. THE HAMILTONIAN AND THE EQUATIONS OF MOTION

The equations of motion to be derived in this section do not differ for quantized or classical fields. To be more in line with the discussion in the dressed-atom picture given earlier, we take the fields to be quantized and use the photon-number representation; however, the calculation is carried out in the bare-atom picture. Let us consider a system consisting of a three-level active atom interacting with two external fields and a perturber atom. The Hamiltonian of this system can be written as

$$H=H_A+H_R+H_{AR}+U(t), \tag{5.1}$$

where the following hold. (i) The free-atom Hamiltonian H_A has three eigenstates $|1\rangle$, $|2\rangle$, $|3\rangle$ with eigenenergies E_1, E_2, and E_3; $E_2-E_1=\hbar\omega_{21}$ and $E_3-E_2=\hbar\omega_{32}$. (ii) $H_R=\hbar\omega a_\omega^+ a_\omega+\hbar\omega' a_{\omega'}^+ a_{\omega'}$ is the quantized free-field Hamiltonian describing a two-mode external field with photon energies $\hbar\omega$ and $\hbar\omega'$, where a_ω^+, $a_{\omega'}^+$, and $a_\omega, a_{\omega'}$ are the usual creation and annihilation operators of the photons for each mode. (iii) The active-atom-field interaction is given in the rotating-wave approximations by

$$H_{AR}=\hbar\xi_\omega(a_\omega R_{12}^+ + a_\omega^+ R_{12}) + \hbar\xi_{\omega'}(a_{\omega'} R_{23}^+ + a_{\omega'}^+ R_{23}), \tag{5.2}$$

where R_{12}^+, R_{23}^+ and R_{12}, R_{23} are the raising and lowering operators of the active-atomic states, the indices referring to the transition involved, and ξ_ω and $\xi_{\omega'}$ are the coupling constants related to the interaction strengths introduced in Sec. I by $\chi=n^{1/2}\xi_\omega$ and $\chi'=n'^{1/2}\xi_{\omega'}$ with n,n' the photon numbers. (iv) The effective interaction with the perturber $U(t)$ is taken to be time dependent, since the internuclear motion is not quantized, and is diagonal in the basis of $|1,n,n'\rangle$, $|2,n-2,n'\rangle$, and $|3,n-1,n'-1\rangle$ (eigenstates of H_A+H_R),

$$V_1(t)=\langle 1,n,n'|U(t)|1,n,n'\rangle,$$
$$V_2(t)=\langle 2,n-1,n'|U(t)|2,n-1,n'\rangle,$$
$$V_3(t)=\langle 3,n-1,n'-1|U(t)|3,n-1,n'-1\rangle \tag{5.3}$$
$$\langle 1,n,n'|U(t)|2,n-1,n'\rangle=\langle 2,n-1,n'|U(t)|3,n-1,n'-1\rangle=\langle 3,n-1,n'-1|U(t)|1,n,n'\rangle=0,$$

owing to the absence of inelastic collisions.

The wave function of the system

$$|\Psi(t)\rangle=C_1(t)e^{-i(E_1+n\hbar\omega+n'\hbar\omega')t/\hbar} + C_2(t)e^{-i[E_2+(n-1)\hbar\omega+n'\hbar\omega']t/\hbar} + C_3(t)e^{-i[E_3+(n-1)\hbar\omega+(n'-1)\hbar\omega']t/\hbar}$$

satisfies the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle=H|\Psi(t)\rangle,$$

from which the equation of motion for the probability amplitudes $C_1(t)$, $C_2(t)$, and $C_3(t)$ are obtained,

$$\begin{aligned} i\dot{C}_1&=C_1V_1(t)+\chi C_2e^{i\Delta t},\\ i\dot{C}_2&=\chi C_1e^{-i\Delta t}+C_2V_2(t)+\chi'C_3e^{i\Delta' t},\\ i\dot{C}_3&=\chi'C_2e^{-i\Delta' t}+C_3V_3(\quad. \end{aligned} \tag{5.4}$$

With the substitution

$$C_1=\tilde{C}_1\exp\left(-i\int_{-\infty}^t V_1(t')dt'\right),$$

$$C_2=\tilde{C}_2\exp\left(-i\int_{-\infty}^t V_2(t')dt'\right),$$

and

$$C_3=\tilde{C}_3\exp\left(-i\int_{-\infty}^t V_3(t')dt'\right),$$

the equations become

$$\begin{aligned} i\dot{\tilde{C}}_1&=\chi\tilde{C}_2\exp\left[i\left(\Delta t-\int_{-\infty}^t V(t')dt'\right)\right],\\ i\dot{\tilde{C}}_2&=\chi\tilde{C}_1\exp\left[-i\left(\Delta t-\int_{-\infty}^t V(t')dt'\right)\right] + \chi'\tilde{C}_3\exp\left[i\left(\Delta' t-\int_{-\infty}^t V'(t')dt'\right)\right],\\ i\dot{\tilde{C}}_3&=\chi'\tilde{C}_2\exp\left[-i\left(\Delta' t-\int_{-\infty}^t V'(t')dt'\right)\right], \end{aligned} \tag{5.5}$$

where $V(t)=V_2(t)-V_1(t)$ and $V'(t)=V_3(t)-V_2(t)$ are the relative energy shifts of the active-atomic levels during a collision. All the relaxation rates are neglected in this equation owing to the condition of large detunings in Eqs. (2.1)–(2.4).

Equations (5.5) will be solved using the perturbation theory with the initial conditions $\tilde{C}_1(t=-\infty)=1$, $\tilde{C}_2(t=-\infty)=0$, and $\tilde{C}_3(t=-\infty)=0$ corresponding to a three-level atom initially prepared in state 1. The probability of exciting the atom to state 3 is given by $|\tilde{C}_3(t=\infty)|^2$, and the corresponding total cross section is obtained by integrating over the impact parameter b,

$$\sigma=\int_0^\infty |\tilde{C}_3(t=\infty)|^2 2\pi b\,db. \tag{5.6}$$

VI. SOLUTIONS AND RESULTS

In the perturbation limit, Eqs. (5.5) are easily solved to obtain a formal expression for $\tilde{C}_3(t=\infty)$,

$$\tilde{C}_3(t=\infty) = -\int_{-\infty}^{\infty} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t V'(t')dt'\right)\right] \int_{-\infty}^{t} \chi(t_1) \exp\left[i\left(\Delta t_1 - \int_0^{t_1} V(t')dt'\right)\right] dt_1 dt , \tag{6.1}$$

where an overall phase factor has been suppressed since it does not change the probability $|\tilde{C}_3(t=\infty)|^2$.

Equation (6.1) has to be evaluated using different techniques in different regions of detunings corresponding to different physical situations. We follow the classification of Table I.

A. Cases A, B, C

In this group, Δ is in the I region. We integrate by parts the t_1 integral in Eq. (6.1), neglecting the term containing $d\chi/dt$ owing to the conditions (2.1)–(2.4), and obtain

$$\tilde{C}_3(t=\infty) = \frac{1}{i\Delta}\left\{\int_{-\infty}^{\infty} \chi(t)\chi'(t) \exp\left[-i\left((\Delta+\Delta')t - \int_0^t [V(t')+V'(t')]dt'\right)\right] dt \right.$$
$$\left. - i\int_{-\infty}^{\infty} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t V'(t')dt'\right)\right] \int_{-\infty}^{t} \chi(t_1) V(t_1) \exp\left[-i\left(\Delta t_1 - \int_0^{t_1} V(t')dt'\right)\right] dt_1 dt \right\} . \tag{6.2}$$

Since $\chi(t)$ is a constant χ_0 over the range of $V(t)$, and $|\Delta|\tau_c \ll 1$, we can take $\chi(t_1)$ out of the t_1 integral in the second term of Eq. (6.2) and set $e^{-i\Delta t_1} \simeq 1$. One finds

$$\tilde{C}_3(t=\infty) = \frac{1}{i\Delta}\left\{ \int_{-\infty}^{\infty} \chi(t)\chi'(t) \exp\left[-i\left((\Delta+\Delta')t - \int_0^t [V(t')+V'(t')]dt'\right)\right] dt \right.$$
$$- \chi_0 \int_{-\infty}^{\infty} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t [V(t')+V'(t')]dt'\right)\right] dt$$
$$\left. + \chi_0 \int_{-\infty}^{\infty} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t V'(t')dt'\right)\right] dt \right\} . \tag{6.3}$$

Up to this point, we have used the assumptions that the field, $E(t)$, is a slow pulse and that Δ is in the I region, which are common to all three cases A, B, and C. Further evaluation of Eq. (6.3) involves the other field, $E'(t)$, and the other detunings, Δ' and $\Delta+\Delta'$.

1. Case A

In this case, all the detunings are in the I region. We use the same technique used to obtain Eq. (6.3) from Eq. (6.2) to evaluate the integrals in Eq. (6.3). Namely, we integrate by parts once on each of these integrals, neglect the terms containing the derivatives of $\chi(t)$ and $\chi'(t)$, replace $e^{-i\Delta t}$, $e^{-\Delta' t}$, and $e^{-i(\Delta+\Delta')t}$ by 1, and set $\chi'(t) = \chi_0'$ to obtain the excitation amplitude

$$\tilde{C}_3(t=\infty) = -\chi_0\chi_0'\left(\frac{1-e^{i\theta'}}{\Delta\Delta'} - \frac{1-e^{i(\theta+\theta')}}{\Delta'(\Delta+\Delta')}\right) , \tag{6.4}$$

where $\theta = \int_{-\infty}^{\infty} V(t')dt'$ and $\theta' = \int_{-\infty}^{\infty} V'(t')dt'$ are the usual impact phases associated with pressure broadening theories.[10] The amplitude depends on the collision impact parameter b, implicitly through $V(t)$ and $V'(t)$.

The excitation probability is obtained by squaring Eq. (6.4):

$$|\tilde{C}_3(t=\infty)|^2 = \chi_0^2\chi_0'^2\left(\frac{2(1-\cos\theta)}{\Delta\Delta'^2(\Delta+\Delta')} + \frac{2(1-\cos\theta')}{\Delta^2\Delta'(\Delta+\Delta')} - \frac{2(1-\cos\theta'')}{\Delta\Delta'(\Delta+\Delta')^2}\right) , \tag{6.5}$$

with $\theta'' = \theta + \theta'$. Equation (6.5) exhibits some interesting features. The first term dominates when $|\Delta'| \ll |\Delta|, |\Delta+\Delta'|$, and only the impact phase associated with the 1-2 transition θ appears. This suggests that the collisionally enhanced excitation to state 3 is determined by the collision rate associated with the 1-2 transition only. When $|\Delta| \ll |\Delta'|, |\Delta+\Delta'|$, the second term dominates, and the only relevant collision rate is that associated with the 2-3 transition. From the point of view of CARE, these two terms can be regarded as "stepwise," since no collision rate associated with 1-3 transition is involved. When $|\Delta+\Delta'| \ll |\Delta|, |\Delta'|$, however, the third term dominates, indicating that the "direct" process is responsible for the excitation. When $|\Delta|$, $|\Delta'|$ and $|\Delta+\Delta'|$ are comparable, contributions from both the "direct" and the "stepwise" processes interfere with each other.

The excitation cross section is obtained by integrating Eq. (6.5) over the impact parameter [i.e., Eq. (5.6)]:

$$\sigma = \frac{4\pi\chi_0^2\chi_0'^2}{\Delta\Delta'(\Delta+\Delta')}\left(\frac{A}{\Delta'} + \frac{B}{\Delta} + \frac{C}{\Delta+\Delta'}\right) , \tag{6.6}$$

where

$$A=\int_0^\infty (1-\cos\theta)b\,db\,,$$

$$B=\int_0^\infty (1-\cos\theta')b\,db\,,$$

$$C=\int_0^\infty (\cos\theta''-1)b\,db\,.$$

This result does not specify the type of interatomic potential. For a given potential, A, B, and C can be calculated analytically or numerically. For van der Waals potentials with the straight-line-trajectory approximation

$$V(t)=C_{\mathrm{VDW}}/[R(t)]^6$$

and

$$V'(t)=C'_{\mathrm{VDW}}/[R(t)]^6$$

with $R(t)=(b^2+v^2t^2)^{1/2}$, analytic results can be obtained,

$$\sigma=\frac{4\pi\chi_0^2\chi_0'^2}{\Delta\Delta'(\Delta+\Delta')}\left(\frac{3\pi}{8v}\right)^{2/5}(-\Gamma(-\tfrac{2}{5})\cos\tfrac{1}{5}\pi)\times\left(\frac{|C_{\mathrm{VDW}}|^{2/5}}{\Delta'}+\frac{|C'_{\mathrm{VDW}}|^{2/5}}{\Delta}-\frac{|C''_{\mathrm{VDW}}|^{2/5}}{\Delta+\Delta'}\right),\tag{6.7}$$

with

$$-\Gamma(-\tfrac{2}{5})\cos(\tfrac{1}{5}\pi)\simeq 3\,,$$

where v is the active-atom-perturber relative speed and $C''_{\mathrm{VDW}}=C_{\mathrm{VDW}}+C'_{\mathrm{VDW}}$.

2. Case B

Since Δ' and $\Delta+\Delta'$ are in the Q region, the integrals appearing in Eq. (6.3) can be evaluated by the stationary-phase method.[11] The first term and the second term in Eq. (6.3) cancel each other approximately because of the condition $|\Delta|\tau_c \ll 1$. The third term yields

$$\tilde{C}_3(t=\infty)=(-i\chi_0\chi_0'/\Delta)(\pi/\alpha')^{1/2}2\cos(\phi'+\tfrac{1}{4}\pi)\,,\tag{6.8}$$

where

$$\alpha'=\frac{1}{2}\left|\left(\frac{dV'}{dt}\right)_{\tau_0'}\right|,\quad \phi'=-\Delta'\tau_0'+\int_0^{\tau_0'}V'(t')dt'$$

and τ_0' is the stationary-phase point defined to be the positive solution of $V'(t')=\Delta'$.

In obtaining Eq. (6.8), we have assumed that the impact parameter b is small enough such that the crossings are induced during a collision (i.e., we neglect collisions with large impact parameter which do not contribute significantly to the total cross section since no crossing is induced), and that $t=0$ is the time of closest approach between the active atom and the perturber.

Apart from the factor χ_0/Δ, Eq. (6.8) takes the form of the two-level result,[12] and a standard treatment for obtaining the total excitation cross section can be used. The excitation probability is obtained by taking the square of Eq. (6.8)

$$|\tilde{C}_3(t=\infty)|^2=(\chi_0^2\chi_0'^2/\Delta^2)(\pi/\alpha')4\cos^2(\phi'+\tfrac{1}{4}\pi)\,,\tag{6.9}$$

from which the total excitation cross section is calculated using

$$\sigma=\int_0^{R_0'}|\tilde{C}_3(t=\infty)|^2 2\pi b\,db\,.\tag{6.10}$$

The upper limit in this integral has been changed to R_0', the internuclear distance at which the instantaneous resonance for the 2-3 transition occurs, since for collision impact parameter larger than R_0', the excitation is negligibly small due to lack of crossings and Eq. (6.9) fails to be valid. Equation (6.9) diverges as the impact parameter approaches R_0'; however, Eq. (6.10) remains finite since α' varies as $(b^2-R_0'^2)^{1/2}$. The cutoff at R_0' may lead to an error of up to 15%, depending on the detuning. Better results can be achieved by numerical calculations for impact parameters near $b\simeq R_0'$, or by a uniform approximation[13] specially designed to overcome the difficulty of divergence.

For van der Waals potentials, $R_0'=(C'_{\mathrm{VDW}}/\Delta')^{1/6}$, and Eq. (6.10) leads to the total excitation cross section

$$\sigma=\frac{4\pi^2\chi_0^2\chi_0'^2|C'_{\mathrm{VDW}}|^{1/2}}{3\Delta^2 v|\Delta'|^{3/2}},\tag{6.11}$$

where $\cos^2(\phi'+\frac{1}{4}\pi)$ has been approximated by $\frac{1}{2}$, and v is the active-atom-perturber relative speed.

This result shows that the line shape varies as Δ^{-2} (since Δ is in the I region) and varies as $|\Delta'|^{-3/2}$, reflecting the fact that Δ' is in the Q region.[12]

3. Case C

In this case, Δ' and $\Delta+\Delta'$ are both in the A region. No crossing occurs for the 2-3 transition and the 1-3 two-photon transition at any collision impact parameter. Since Δ is in the I region ($|\Delta|\tau_c\ll 1$), the first two terms in Eq. (6.3) approximately cancel each other as in case B, leading to the excitation amplitude

$$\tilde{C}_3(t=\infty)=\frac{-i\chi_0}{\Delta}\times\int_{-\infty}^{\infty}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]dt\,.\tag{6.12}$$

This equation is easily recognized as simply a two-level excitation amplitude (2-3 transition) multiplied by a factor χ_0/Δ. Results for the two-level excitation probability are available from the numerical study of Yeh and Berman[2] for van der Waals potentials and Lennard-Jones–type potentials. Also available are approximate analytic results of Tvorogov and Fomin[14] and Szudy and Baylis[15] using saddle-point methods.[11] We now give only the essential features of the results. For details, the readers are referred to Refs. 2, 14, and 15.

The cross section, obtained by integrating $|\bar{C}_3(t=\infty)|^2$ over the impact parameter b, shows a Δ^{-2} dependence as is clear from Eq. (6.12). The dependence on Δ' follows the antistatic wing behavior. For a van der Waals potential, Fig. 6 of Yeh and Berman[7] exhibits a line shape going as

$$|\Delta'|^{-7/3}\exp(-\beta|\Delta'|^{5/6})$$

with β a constant, which is in agreement with asymptotic results[14,15] to within a multiplicative factor of order 1.

B. Cases D, E

In these cases, Δ' is in the I region, while Δ and $\Delta+\Delta'$ are in the Q region (case D) or A region (case E). Since Δ' is in the I region, the integration-by-parts technique used in cases A, B, and C can be applied to the t integral in Eq. (6.1) for its evaluation.

We write Eq. (6.1) in the following form:

$$\bar{C}_3(t=\infty)=-\int_{-\infty}^{\infty}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]G(t)dt\,, \tag{6.13}$$

where

$$G(t)=\int_{-\infty}^{t}\chi(t_1)\exp\left[-i\left(\Delta t_1-\int_0^{t_1}V(t')dt'\right)\right]dt_1\,. \tag{6.14}$$

An integration by parts is performed on Eq. (6.13), neglecting the term containing $d\chi'/dt$, setting $\chi'(t)=\chi_0'$ over the range of $V'(t)$, and setting $e^{-\Delta' t}\simeq 1$ to obtain

$$\begin{aligned}\bar{C}_3(t=\infty)=\frac{-i\chi_0'}{\Delta'}\Bigg\{&e^{i\theta'}\int_{-\infty}^{\infty}\chi(t)\exp\left[-i\left(\Delta t-\int_0^t V(t')dt'\right)\right]dt\\&-\int_{-\infty}^{\infty}\chi(t)\exp\left[-i\left(\Delta t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt\\&+\int_{-\infty}^{\infty}\chi(t)\exp\left[-i\left((\Delta+\Delta')t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt\Bigg\}\,.\end{aligned} \tag{6.15}$$

The second and the third terms approximately cancel each other because of the condition $|\Delta'|\tau_c \ll 1$, and we get

$$\bar{C}_3(t=\infty)=\frac{-i\chi_0'}{\Delta'}e^{i\theta'}\times\int_{-\infty}^{\infty}\chi(t)\exp\left[-i\left(\Delta t-\int_0^t V(t')dt'\right)\right]dt\,, \tag{6.16}$$

where $\theta'=\int_{-\infty}^{\infty}V'(t')dt'$ is the impact phase[10] associated with the 2-3 transition.

Equation (6.16) is simply the 1-2 two-level transition amplitude multiplied by the factor $(\chi_0'/\Delta')e^{i\theta'}$. Its evaluation depends on the region of Δ. For case D (Δ in Q region) a stationary phase method[11] is used, and for case E (Δ in the A region) a method of steepest descent[16] or a numerical calculation[2] can be carried out.

1. Case D

The integral in Eq. (6.16) is evaluated using a stationary-phase method to yield

$$\bar{C}_3(t=\infty)=(-i\chi_0\chi_0'/\Delta')e^{i\theta'}(\pi/\alpha)^{1/2}2\cos(\phi+\tfrac{1}{4}\pi)\,, \tag{6.17}$$

where

$$\alpha=\frac{1}{2}\left|\left(\frac{dV}{dt}\right)_{\tau_0}\right|\,,$$

$$\phi=-\Delta\tau_0+\int_0^{\tau_0}V(t')dt'\,,$$

and τ_0 is the stationary-phase point of the integrand in Eq. (6.16), i.e., the solution of the equation $\Delta=V(t)$. τ_0 is taken to be positive, and we have taken $t=0$ to be the time of closest approach so that $\pm\tau_0$ are both stationary-phase points.

Equation (6.17) holds only for collision impact

parameter small enough such that potential curve crossings (in the dressed-atom picture) are induced during a collision. In the straight-line-path approximation, this amounts to restricting the impact parameter to values smaller than R_0, the internuclear distance at which the resonance between the 1-2 transition and the field E occurs. For $b \geq R_0$, Eq. (6.17) is not valid, and the contribution to the total excitation cross section is negligible due to lack of induced resonance.

The excitation probability is given by

$$|\tilde{C}_3(t=\infty)|^2 = (\chi_0^2\chi_0'^2/\Delta'^2)(\pi/\alpha)4\cos^2(\phi+\tfrac{1}{4}\pi). \quad (6.18)$$

To obtain the total excitation cross section, Eq. (6.18) is integrated over the impact parameter from $b=0$ to $b=R_0$ according to the discussion leading to Eq. (6.10). For a van der Waals potential $R_0=(C_{\mathrm{VDW}}/\Delta)^{1/6}$, an analytic result can be obtained provided that $\cos^2(\phi+\frac{1}{4}\pi)$ is approximated by its average value $\frac{1}{2}$, which is a good approximation since $\cos^2(\phi+\frac{1}{4}\pi)$ is rapidly oscillating as a function of b. We get

$$\sigma = \int_0^{R_0} |\tilde{C}_3(t=\infty)|^2 2\pi b\, db = \frac{4\pi^2\chi_0^2\chi_0'^2}{3\Delta'^2 v}\frac{|C_{\mathrm{VDW}}|^{1/2}}{|\Delta|^{3/2}}. \quad (6.19)$$

The Δ'^{-2} and $|\Delta|^{-3/2}$ dependences in this equation are expected because Δ' is in the I region and Δ is in the Q region.

2. Case E

Since Δ is in the A region, Eq. (6.16) has to be evaluated using saddle-point methods or numerical methods. We do not have to reiterate the discussion given in case C. Let us just state the results for van der Waals potentials: Both the numerical method and the saddle-point method give a total excitation cross section going as

$$\Delta'^{-2}|\Delta|^{-7/3}\exp(-\beta|\Delta|^{5/6}),$$

with a difference of a multiplicative factor of order 1.

C. Cases F, G

In these cases, Δ and Δ' are large ($|\Delta|\tau_c \gg 1$, $|\Delta'|\tau_c \gg 1$) and $\Delta+\Delta'$ is in the I region. This can occur when Δ and Δ' are of opposite signs and differ by at most $1/\tau_c$ in magnitude. According to the discussions in Sec. IV, the direct excitation process is expected to be dominant. Since $\Delta+\Delta'$ is in the I region, large contributions to the total excitation cross section come from collisions with impact parameters near the Weisskopf radius[17] associated with the 1-3 interatomic potential. Near such impact parameters, $V(t)/\Delta \ll 1$, so that approximations can be made to neglect terms containing such a factor in evaluating Eq. (6.1). When an integration by parts is performed on the t_1 integral in Eq. (6.1), such as the one leading to Eq. (6.2), a factor of $V(t)/\Delta$ is produced in the second term of Eq. (6.2) and is subsequently neglected. Further integrations by parts produce additional factors of $V(t)/\Delta$. Hence, to a good approximation, the 1-3 excitation amplitude can be written as

$$\tilde{C}_3(t=\infty) = \frac{1}{i\Delta}\int_{-\infty}^{\infty}\chi(t)\chi'(t)\exp\left[-i\left((\Delta+\Delta')t - \int_0^t [V(t')+V'(t')]dt'\right)\right]dt. \quad (6.20)$$

Since $\Delta+\Delta'$ is in the I region, Eq. (6.20) can be evaluated easily by integrating by parts once, neglecting terms containing $d(\chi\chi')/dt$, setting $e^{-i(\Delta+\Delta')t} \approx 1$, and evaluating $\chi(t)\chi'(t)$ as $\chi_0\chi_0'$. One obtains

$$\tilde{C}_3(t=\infty) = [\chi_0\chi_0'/\Delta(\Delta+\Delta')](1-e^{i\theta''}), \quad (6.21)$$

where

$$\theta'' = \theta+\theta' = \int_{-\infty}^{\infty}[V(t')+V'(t')]dt'.$$

In this approximation, the region of Δ (Q or A) does not play an important role, because the contribution to the total excitation cross section comes mainly from collision with impact parameters near the Weisskopf radius associated with the 1-3 direct transition. At such (large) impact parameters, no instantaneous resonance can be induced during a collision, even in the Q region. This suggests that when $\Delta+\Delta'$ is in the I region and Δ, Δ' are large ($|\Delta|\tau_c \gg 1$, $|\Delta'|\tau_c \gg 1$), the direct excitation process dominates, and the collision-induced potential curve crossings for the 1-2 and 2-3 transitions, which occur at much smaller internuclear distances than the Weisskopf radius, have only higher-order effects on the excitation cross section. Consequently, cases F and G are equivalent in this approximation.

The excitation probability is given by

$$|\tilde{C}_3(t=\infty)|^2 = [\chi_0^2\chi_0'^2/\Delta^2(\Delta+\Delta')^2]2(1-\cos\theta''), \quad (6.22)$$

and the total excitation cross section by

$$\sigma = [4\pi\chi_0^2\chi_0'^2/\Delta^2(\Delta+\Delta')^2]\int_0^{\infty}(1-\cos\theta'')b\,db. \quad (6.23)$$

For a van der Waals potential, the total excita-

tion cross section is given by

$$\sigma=\frac{4\pi\chi_0^2\chi_0'^2}{\Delta^2(\Delta+\Delta')^2}\left(\frac{3\pi|C''_{\mathrm{VDW}}|}{8v}\right)^{2/5}\left(\frac{-\Gamma(-\frac{2}{5})\cos\frac{1}{5}\pi}{5}\right), \tag{6.24}$$

where $C''_{\mathrm{VDW}}=C_{\mathrm{VDW}}+C'_{\mathrm{VDW}}$ is the van der Waals constant for the 1-3 relative potential, and $-\Gamma(-\frac{2}{5})\cos\frac{1}{5}\pi\approx 3$.

The line shape varying as $\Delta^{-2}(\Delta+\Delta')^{-2}$ is typical of the impact region when the direct excitation process is dominant over the stepwise process. The line exhibits a Δ^{-2} rather than exponential Δ dependence, even though Δ is in the A region; in some sense, the direct excitation serves to break the adiabatic following of the field $\chi(t)$ on the 1-2 transition and changes the dependence from exponential to power law.

D. Cases H, I

In these two cases, Δ and Δ' are large ($|\Delta|\tau_c \gg 1$, $|\Delta'|\tau_c \gg 1$) and of opposite signs, and their sum $(\Delta+\Delta')$ is still in the Q region. We further focus our attention to the region of $|\Delta+\Delta'| \ll |\Delta|$, $|\Delta'|$. This region is of particular interest because the direct two-photon excitation process is dominant over the stepwise process and, by varying $|\Delta+\Delta'|$, the effects of stepwise process on the direct two-photon line shape can be determined. Moreover, this further restriction of detunings makes the mathematical treatment to be given below much simplified and equally applicable to both case H and case I.

If the condition $|\Delta+\Delta'| \ll |\Delta|, |\Delta'|$ holds, the instantaneous resonance for the direct $(1\rightarrow 3)$ transition occurs at an internuclear distance (R_0'') much larger than that for the 1-2 transition (R_0) or the 2-3 transition (R_0') (i.e., $R_0'' \gg R_0, R_0'$). Thus, in the straight-line-path approximation, for collisions with impact parameter b such that $R_0'' > b > R_0, R_0'$, only the 1-3 instantaneous resonances occur during a collision. Collisions within this range of impact parameters give a major contribution to the total excitation cross section because of the condition $R_0'' \gg R_0, R_0'$, the weighting factor $b\,db$ in the definition of the total cross section [Eq. (5.6)], and the fact that collisions with impact parameters b larger than R_0'' do not contribute, due to lack of collision-induced resonance. Hence, we can do repeated integrations by parts on the t_1 integral in Eq. (6.1), each integration by parts producing a factor $|V(t)/\Delta| \ll 1$ for the range of impact parameters of importance determined by the $(\Delta+\Delta')$ crossing. The excitation amplitude is thus given, keeping only terms up to first order in $V(t)/\Delta$, by

$$\tilde{C}_3(t=\infty)=\frac{-i}{\Delta}\left\{\int_{-\infty}^{\infty}\chi(t)\chi'(t)\exp\left[-i\left((\Delta+\Delta')t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt + \int_{-\infty}^{\infty}\chi(t)\chi'(t)[V(t)/\Delta]\exp\left[-i\left((\Delta+\Delta')t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt\right\}. \tag{6.25}$$

Since $\Delta+\Delta'$ is in the Q region, Eq. (6.25) is evaluated using the stationary-phase method to obtain

$$\tilde{C}_3(t=\infty)=(-i\chi_0\chi_0'/\Delta)(\pi/\alpha'')^{1/2}2\cos(\phi''+\tfrac{1}{4}\pi)[1+V(\tau_0'')/\Delta], \tag{6.26}$$

where

$$\alpha''=\frac{1}{2}\left|\left(\frac{d(V+V')}{dt}\right)_{\tau_0''}\right|,$$

$$\phi''=-(\Delta+\Delta')\tau_0''+\int_0^{\tau_0''}[V(t')+V'(t')]dt',$$

with $\tau_0''>0$ satisfying $\Delta+\Delta'=V(\tau_0'')+V'(\tau_0'')$. As before, we have taken $t=0$ to be the time of closest approach between the active atom and the perturber.

The first term in Eq. (6.26) represents the direct two-photon process since it contains only quantities relevant to the 1-3 transition α'' and ϕ''. The second term represents the correction due to stepwise process, which affects the line shape somewhat, and may become important when $|\Delta+\Delta'|$ is increased, as will be shown below.

The excitation probability is given by

$$|\tilde{C}_3(t=\infty)|^2=(4\pi\chi_0^2\chi_0'^2/\Delta^2\alpha'')\cos^2(\phi''+\tfrac{1}{4}\pi)\times[1+2V(\tau_0'')/\Delta]. \tag{6.27}$$

The excitation cross section is obtained as usual by integrating over the impact parameter, cutting off the integral at $b=R_0''$, and approximating $\cos^2(\phi''+\frac{1}{4}\pi)$ by its average value $\frac{1}{2}$. For van der Waals potentials, we obtain

$$\sigma=\frac{4\pi^2\chi_0^2\chi_0'^2}{3\Delta^2 v}\frac{|C''_{\mathrm{VDW}}|^{1/2}}{|\Delta+\Delta'|^{3/2}}\times\left[1+2\left(\frac{C_{\mathrm{VDW}}}{C''_{\mathrm{VDW}}}\right)\left(\frac{\Delta+\Delta'}{\Delta}\right)\right], \tag{6.28}$$

where v is the active-atom-perturber relative speed and C_{VDW} and C''_{VDW} are the van der Waals constants corresponding to the 1-2 and 1-3 relative interatomic potentials, respectively.

This equation has been obtained in a recent

paper by Nayfeh[3] using a Landau-Zener–type approximation and discussed in connection with the collision-induced three-photon ionization in which two photons are used to excite the atom, *via* CARE, to a bound excited state. A third photon then ionizes the atom. The present discussion makes clear the conditions under which Eq. (6.28) is valid.

The correction term in Eq. (6.28) shows the effect of the stepwise process on the direct two-photon process. It falls off as $|\Delta+\Delta'|^{-1/2}$ for fixed Δ, which is slower then the main part going as $|\Delta+\Delta'|^{-3/2}$. It is thus easier to observe such an effect at a larger $|\Delta+\Delta'|$; however, the correction term cannot become larger than the main part, since the treatment presented here ceases to be valid.

Digression. Before we go on to present the next case, it is advisable to show a spectrum so that we can have a better overall view of all the cases presented so far. In Fig. 3, the total excitation cross section is shown as a function of Δ' for a fixed $\Delta=-1.5\times10^{12}\,\mathrm{sec}^{-1}$ and an attractive van der Waals potential with constants $C_{\mathrm{VDW}}=-1.2\times10^{18}$ Å^6 sec^{-1}, $C'_{\mathrm{VDW}}=-1.5\times10^{18}$ Å^6 sec^{-1}. In showing such a "complete" spectrum, we cannot avoid regions where *none* of the approximations employed in cases A through I is good (i.e., regions with |detunings| $\sim 1/\tau_c$). Hence, the line shape from numerical integrations of Eqs. (5.5) and Eq. (5.6) is also shown for comparison and to aid in gaining an appreciation of regions of each case. Since there are many curves on Fig. 3, and each curve only has a limited region of validity (for some cases the regions do not fall within this figure), the following points will help in reading this graph:

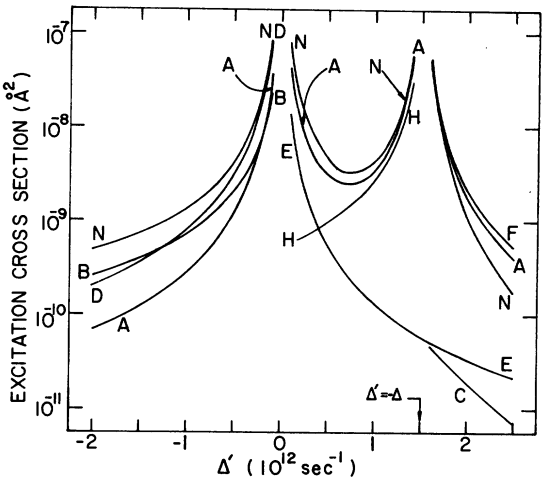

FIG. 3. Excitation cross sections versus Δ' for a fixed $\Delta=-1.5\times10^{12}$ sec^{-1} and an attractive van der Waals potential of constants $C_{\mathrm{VDW}}=-1.2\times10^{18}$ Å^6 sec^{-1}, $C'_{\mathrm{VDW}}=-1.5\times10^{18}$ Å^6 sec^{-1}, and $v=10^5$ cm sec^{-1}, $\chi_0=\chi'_0=10^9$ sec^{-1}. Curve N is the result of numerical integrations of Eqs. (5.5) and (5.6); others are plotted according to the equations in Table II. Only the regions, where at least the signs of the detunings are correct, are shown. See the text for discussion.

(1) Curves A, B, C, D, E, F, and H, representing cases covered so far, are plotted according to equations shown in Table II, and curve N is from numerical integrations of Eqs. (5.5) and Eq. (5.6). For curves B, C, D, E, and F, only the

TABLE II. Line shapes.

Case	Excitation cross section
A	$\frac{4\pi\chi_0^2\chi_0'^2}{\Delta\Delta'(\Delta+\Delta')}\left(\frac{3\pi}{8v}\right)^{2/5}\left(\frac{-\Gamma(-\frac{2}{5})\cos\frac{1}{5}\pi}{5}\right)\left(\frac{\lvert C_{\mathrm{VDW}}\rvert^{2/5}}{\Delta'}+\frac{\lvert C'_{\mathrm{VDW}}\rvert^{2/5}}{\Delta}-\frac{\lvert C''_{\mathrm{VDW}}\rvert^{2/5}}{\Delta+\Delta'}\right)$
B	$\frac{4\pi^2\chi_0^2\chi_0'^2}{3v\Delta^2}\frac{\lvert C'_{\mathrm{VDW}}\rvert^{1/2}}{\lvert\Delta'\rvert^{3/2}}$
C[a]	$\frac{\chi_0^2\chi_0'^2\pi^{5/2}}{0.952\Delta^2}\lvert C'_{\mathrm{VDW}}\rvert^{1/3}\lvert\Delta'\rvert^{-7/3}e^{-1.2(\lvert C'_{\mathrm{VDW}}\rvert^{1/6}/v)\lvert\Delta'\rvert^{5/6}}$
D	$\frac{4\pi^2\chi_0^2\chi_0'^2}{3v\Delta'^2}\frac{\lvert C_{\mathrm{VDW}}\rvert^{1/2}}{\lvert\Delta\rvert^{3/2}}$
E[a]	$\frac{\chi_0^2\chi_0'^2\pi^{5/2}}{0.952\Delta'^2}\lvert C_{\mathrm{VDW}}\rvert^{1/3}\lvert\Delta\rvert^{-7/3}e^{-1.2(\lvert C_{\mathrm{VDW}}\rvert^{1/6}/v)\lvert\Delta\rvert^{5/6}}$
F, G	$\frac{4\pi\chi_0^2\chi_0'^2}{\Delta^2(\Delta+\Delta')^2}\left(\frac{3\pi\lvert C''_{\mathrm{VDW}}\rvert}{8v}\right)^{2/5}\left(\frac{-\Gamma(-\frac{2}{5})\cos\frac{1}{5}\pi}{5}\right)$
H, I	$\frac{4\pi^2\chi_0^2\chi_0'^2}{3v\Delta^2}\frac{\lvert C''_{\mathrm{VDW}}\rvert^{1/2}}{\lvert\Delta+\Delta'\rvert^{3/2}}\left[1+2\left(\frac{C_{\mathrm{VDW}}}{C''_{\mathrm{VDW}}}\right)\left(\frac{\Delta+\Delta'}{\Delta}\right)\right.$

[a] The exponential line shape from the two-level asymptotic calculation of Tvorogov and Fomin (Ref. 14) is adopted.

portions, where at least the signs of detunings are correct, are shown.

(2) The conditions in the fourth column of Table I should be kept in mind in reading this figure.

(3) The detuning, $\Delta = -1.5\times10^{12}$ sec^{-1} ($|\Delta|\tau_c \sim 1$), is in neither the impact region nor the quasistatic region. Hence, only in the cases when Δ is unimportant, does the agreement with the numerical result become good, e.g., cases A, F, and G near $|\Delta+\Delta'|\tau_c \ll 1$.

(4) Curve B has the tendency of having the same Δ' dependence with the numerical result, if we extend the value of Δ' well into Q region. The numerical difference comes from the Δ^{-2} variation in case B, which is not a very good approximation for $\Delta = -1.5\times10^{12}$ sec^{-1}. The same statement holds for case C if we extend the value of Δ' well into the A region of $\Delta+\Delta'$.

(5) Curve E does not have any region of validity in this figure because of the sign and size of Δ. We show it for comparison.

E. Case J

We return now to case J, which is perhaps the most interesting case, since all the detunings are in the Q region and the curve crossings can interfere with each other, leading to a new type of interference effect. For the convenience of presentation, we give some of the details of the calculation in the Appendices and separate the discussions to calculations on (1) the amplitude and (2) the cross section. Since the detunings involved are large (typically of the order of 10^{13} sec^{-1}) in this case, a large amount of energy per collision ($\sim10^{-1}$ eV) is transferred from the atomic motion to the internal degrees of freedom. Some consideration of the energetics seems to be advisable to ensure the validity of the calculations below.

For such large kinetic energies, a temperature higher than the room temperature ($\gtrsim$100°C) is required, which in turn reduces the atomic collision time ($\tau_c \propto 1/v$). This, however, will not violate the condition for the Q region ($|\text{detunings}|\tau_c \gg 1$) in general, since one can keep this condition with a thermal energy ($\propto v^2$) $> \hbar|\text{detunings}|$. To be more specific, an estimate of the relevant quantities ($\hbar|\Delta|, E_{\text{thermal}}, v, |\Delta|\tau_c$) is given. For the largest detuning considered in case J ($\Delta = -8\times10^{13}$ sec^{-1}) and an atomic mass of forty times proton mass, $\hbar|\Delta| = 5.31\times10^{-2}$ eV, $T = 410$ K, $v = 5.04\times10^{4}$ cm/sec, $\tau_c = 9.85\times10^{-13}$ sec, and $|\Delta|\tau_c \simeq 79 \gg 1$. Hence, at a temperature higher than 137 °C, the kinetic energy will be large enough to overcome the energy mismatch ($\hbar|\Delta|$) while simultaneously maintaining the condition of the Q region ($|\Delta|\tau_c \gg 1$).

1. The amplitude

In this case, the instantaneous resonances for 1-2, 2-3, and 1-3 two-photon transitions occur at internuclear distances R_0, R_0', and R_0'', respectively, during a collision if the impact parameter is such that the distance of closest approach between the active atom and the perturber is smaller than the smallest of R_0, R_0', or R_0''. At such impact parameters, radiative excitation is enhanced owing to the collision-induced instantaneous resonances. At larger impact parameters, some of the instantaneous resonances cannot be induced, giving rise to a negligible contribution (compared with contributions from collisions with smaller b) to the total cross section. Therefore, in the straight-line-path approximation, it is sufficient to consider collisions with impact parameter $b < R_0$, R_0', or R_0''.

The instantaneous resonance points in the time domain correspond to the stationary-phase points of the integrals appearing in Eq. (6.1) and, owing to the conditions $|\Delta|\tau_c \gg 1$, $|\Delta'|\tau_c \gg 1$, and $|\Delta+\Delta'|\tau_c \gg 1$, major contributions to these integrals are from the neighborhood of these points. Hence, a stationary-phase method, of which the details are shown in Appendix A, is used to evaluate Eq. (6.1).

Assuming that the time of instantaneous resonances are all far from $t=0$, where the collision is centered, the amplitude is given by

$$\bar{C}_3(t=\infty) = -\tfrac{1}{2}\chi_0\chi_0'(\pi/\alpha)^{1/2}[A_1+A_2+A_3], \quad (6.29)$$

where

$$A_1 = (\pi/\alpha')^{1/2} e^{-i(\phi+\phi'+s\pi/4+s'\pi/4)}[1 - s_1 - i\sqrt{2}\,s' s_1 (f_1^2+g_1^2)^{1/2} e^{is'\theta_1 + i\pi/4) - is'\pi Z_1^2/2}]$$
$$- i\sqrt{2}\,s s_2 (\pi/\alpha'')^{1/2}(f_0^2+g_0^2)^{1/2} e^{is\theta_0 - i(\phi''+s''\pi/4)}[1 + i\sqrt{2}\,s''(f_2^2+g_2^2)^{1/2} e^{is''(\theta_2+\pi/4) - is''\pi Z_2^2/2}], \quad (6.30)$$

$$A_2 = (\pi/\alpha')^{1/2} e^{i(\phi+\phi'+s\pi/4+s'\pi/4)}[1 + s_1 - i\sqrt{2}\,s' s_1 (f_1^2+g_1^2)^{1/2} e^{-is'(\theta_1+\pi/4) + is'\pi Z_1^2/2}]$$
$$- i\sqrt{2}\,s s_2 (\pi/\alpha'')^{1/2}(f_0^2+g_0^2)^{1/2} e^{-is\theta_0 + i(\phi''+s''\pi/4)}[1 - i\sqrt{2}s''(f_2^2+g_2^2)^{1/2} e^{-is''(\theta_2+\pi/4) + is''\pi Z_2^2/2}], \quad (6.31)$$

$$A_3 = 2(\pi/\alpha')^{1/2} e^{-i(\phi-\phi'+s\pi/4-s'\pi/4)}, \quad (6.32)$$

$$\alpha = \frac{1}{2}\left|\left(\frac{dV}{dt}\right)_{\tau_0}\right|, \quad \alpha' = \frac{1}{2}\left|\left(\frac{dV'}{dt}\right)_{\tau_0'}\right|, \quad \alpha'' = \frac{1}{2}\left|\left(\frac{d(V+V')}{dt}\right)_{\tau_0''}\right|, \quad (6.33)$$

where

$$s=\mathrm{sgn}\left(\frac{dV}{dt}\right)_{\tau_0},\quad s'=\mathrm{sgn}\left(\frac{dV'}{dt}\right)_{\tau_0'},\quad s''=\mathrm{sgn}\left(\frac{d(V+V')}{dt}\right)_{\tau_0''},\tag{6.34}$$

$$\phi=-\Delta\tau_0+\int_0^{\tau_0}V(t)dt,\quad \phi'=-\Delta'\tau_0'+\int_0^{\tau_0'}V'(t)dt,\quad \phi''=-(\Delta+\Delta')\tau_0''+\int_0^{\tau_0''}[V(t)+V'(t)]dt,\tag{6.35}$$

$$\theta_i=\tan^{-1}(g_i/f_i);\tag{6.36}$$

g_i, f_i are the auxiliary functions of Fresnel integrals evaluated at z_i,

$$z_0=\left|(2\alpha/\pi)^{1/2}(\tau_0''-\tau_0)\right|,\quad z_1=\left|(2\alpha'/\pi)^{1/2}(\tau_0'-\tau_0)\right|,\quad z_2=\left|(2\alpha''/\pi)^{1/2}(\tau_0''-\tau_0)\right|,\tag{6.37}$$

$$s_1=\mathrm{sgn}(\tau_0'-\tau_0),\quad s_2=\mathrm{sgn}(\tau_0''-\tau_0),\tag{6.38}$$

and $\tau_0, \tau_0', \tau_0''$ are the positive solutions of

$$\Delta=V(t),\quad \Delta'=V'(t),\quad \Delta+\Delta'=V(t)+V'(t),\tag{6.39}$$

respectively. If any of the times of instantaneous resonances is near $t=0$ (i.e., $\tau_0\simeq 0$, $\tau_0'\simeq 0$, or $\tau_0''\simeq 0$), the corresponding time derivative of the potential (α, α', or α'') approaches 0, and Eq. (6.29) becomes singular and is a poor approximation to the amplitude. Apart from this, Eqs. (6.29)–(6.39) provide good approximations for the amplitude, regardless of the type of potentials and the ordering of τ_0, τ_0', and τ_0'', as long as the conditions for this case (case J) hold. The essential difference between various types of potentials in determining the transition amplitude lies in the derivatives and their signs at the times of instantaneous resonance, which are given by α, α', and α'' and s, s', and s''. The ordering of τ_0, τ_0', and τ_0'' determines the values of s_1 and s_2. For given interatomic potentials and detunings, these parameters can be determined, and Eqs. (6.29)–(6.39) are greatly simplified.

In Eq. (6.29), it is natural to interpret the terms containing α' as the contribution coming from the stepwise process and the terms containing α'' as that from the direct process, since α' and α'' are associated with resonances of 2-3 transition and 1-3 transition, respectively.

Equations (6.29)–(6.39) represent the general form of the transition amplitude under the conditions of case J. They have been compared with the results of direct numerical integration of Eqs. (5.5) using attractive van der Waals potentials of constants $C_{\mathrm{VDW}}=-1.2\times10^{18}$ Å^6 sec^{-1}, $C'_{\mathrm{VDW}}=-1.5\times10^{18}$ Å^6 sec^{-1}, and several detunings of the order of 10^{13} sec^{-1}. For impact parameters smaller than the smallest of R_0, R_0', and R_0'', Eqs. (6.29)–(6.39) give very accurate results (see Fig. 4); for impact parameters outside this region, which contribute little to the total cross section, Eqs. (6.29)–(6.39) are not applicable as discussed above. There are two cases (*a* and *b*) of special interest in which Eqs. (6.29)–(6.39) can be very much simplified.

a. Exactly coinciding times of instantaneous resonance, $\tau_0=\tau_0'=\tau_0''$. All the times of instantaneous resonance coincide. In this case, $z_i=0$, $f_i=g_i=\frac{1}{2}$, and $\theta_i=\frac{1}{4}\pi$ so we obtain from Eqs. (6.29)–(6.39),

$$A_1=(\pi/\alpha')^{1/2}e^{-i(\phi+\phi'+3\pi/4+s'\pi/4)},\tag{6.40}$$

$$A_2=(\pi/\alpha')^{1/2}e^{i(\phi+\phi'+3\pi/4+s'\pi/4)},\tag{6.41}$$

$$A_3=2(\pi/\alpha')^{1/2}e^{-i(\phi-\phi'+3\pi/4-s'\pi/4)}.\tag{6.42}$$

The amplitude is given by Eqs. (6.40), (6.41), (6.42), and (6.29). The contributions from the

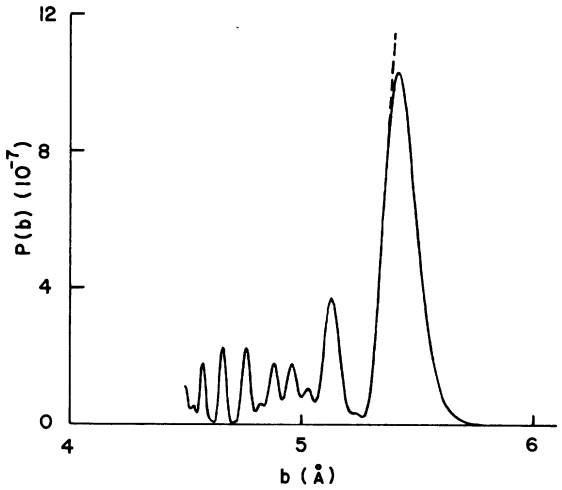

FIG. 4. Comparison of $P(b)$ vs b curves from the analytic expression [Eqs. (6.29)–(6.39)] and the numerical calculation [integration of Eqs. (5.5)] for an attractive van der Waals potential with $\chi_0=\chi_0'=10^{11}$ sec^{-1}, $\Delta=-4.0\times10^{13}$ sec^{-1}, and $\Delta'=-5.05\times10^{13}$ sec^{-1}. Other parameters are the same as those in Fig. 3. The analytic expression, which is singular at $b=5.57$ Å, was cut off at $b=5.40$ Å, where it begins to diverge. The agreement at smaller impact parameters is near perfect. —— numerical integration of Eqs. (5.5); ----- analytic expression [Eqs. (6.29)–(6.39)].

direct process are *absent*, leaving a very simple form involving only the stepwise contributions.

For given interatomic potential and Δ, the condition $\tau_0=\tau_0'=\tau_0''$ corresponds to a particular value of Δ' (e.g., $\Delta'=(C'_{\rm VDW}/C_{\rm VDW})\Delta$, for van der Waals potentials). Near this value of Δ', according to Eqs. (6.41)–(6.42), one would expect that the direct process would be less important than the stepwise process, which should be reflected in the line shape. We find this result when we numerically evaluate Eqs. (6.29)–(6.39) to obtain the total cross section, as will be shown later.

b. Well-separated times of instantaneous resonance. In this case, the arguments of f_i and g_i in Eq. (6.36) become large, and since f_i and g_i are rapidly decreasing functions with maximum values $f_i(0)=g_i(0)=\frac{1}{2}$, we can, to a good approximation, neglect terms containing factors $\sqrt{2}\,(f_i^2+g_i^2)^{1/2}$, as compared with 1 in Eqs. (6.30) and (6.31). We obtain

$$A_1=(\pi/\alpha')^{1/2}e^{-i(\phi+\phi'+s\pi/4+s'\pi/4)}(1-s_1) - i\sqrt{2}\,ss_2(\pi/\alpha'')^{1/2}(f_0^2+g_0^2)^{1/2}e^{is\theta_0-i(\phi''+s''\pi/4)}, \tag{6.43}$$

$$A_2=(\pi/\alpha')^{1/2}e^{i(\phi+\phi'+s\pi/4+s'\pi/4)}(1+s_1) - i\sqrt{2}\,ss_2(\pi/\alpha'')^{1/2}(f_0^2+g_0^2)^{1/2}e^{-is\theta_0+i(\phi''+s''\pi/4)}. \tag{6.44}$$

The amplitude as given by Eqs. (6.43), (6.44), (6.32)–(6.39), and (6.29) contains contributions from the stepwise and the direct process that interfere with each other.

It is not difficult to understand the physical meaning of each term in Eqs. (6.32), (6.43), and (6.44) by tracing back the calculations leading to them in Appendix A. Term A_1 [Eq. (6.43)] contains the contributions from the instantaneous resonance points before $t=0$; term A_2 [Eq. (6.44)] contains the contributions from the instantaneous resonance points after $t=0$; and term A_3 [Eq. (6.32)] contains the contribution from the *stepwise process* in which 1-2 resonance occurs before $t=0$ and 2-3 resonance occurs after $t=0$. Terms A_1 and A_2 contain both stepwise and direct contributions. For a given ordering of τ_0, τ_0', and τ_0'' some stepwise contributions will be absent. For example, when $\tau_0<\tau_0'$, $s_1=1$ and the first term in Eq. (6.43) vanishes, indicating that no stepwise process is occuring before $t=0$, since the 1-2 resonance happens at a later time than the 2-3 transition ($-\tau_0>-\tau_0'$). The first term in Eq. (6.44) does not vanish because $\tau_0<\tau_0'$ and the stepwise process can occur after $t=0$. The situation is reversed when $\tau_0>\tau_0'$ ($s_1=-1$). However, A_3 always survives since the 1-2 transition occurs before $t=0$ and the 2-3 transition occurs after $t=0$. In any case, there are *four* terms in the amplitude corresponding to the *four* excitation channels discussed in Sec. IV.

2. The total cross section

It is straightforward to obtain the excitation probability by taking the modulus of Eq. (6.29). The resulting expressions are lengthy and are given in Appendix B. Only for the two special cases ($\tau_0=\tau_0'=\tau_0''$ and τ_0,τ_0',τ_0'' far apart) are the analytic expressions given in this subsection.

To demonstrate the success of the stationary-phase method used in Appendix A, we compare in Fig. 4 two $|\bar{C}_3(t=\infty)|^2$ vs b curves, one from numerically integrating Eqs. (5.5), the other from squaring Eq. (6.29) for an attractive van der Waals potential with $C_{\rm VDW}=-1.2\times10^{18}$ Å^6 sec^{-1}, $C'_{\rm VDW}=-1.5\times10^{18}$ Å^6 sec^{-1}, $\Delta=-4.0\times10^{13}$ sec^{-1}, and $\Delta'=-5.05\times10^{13}$ sec^{-1}. The agreement is near perfect except for $b\gtrsim5.40$ Å, which is close to $R_0=(C_{\rm VDW}/\Delta)^{1/6}=5.57$ Å, at which Eqs. (6.29)–(6.39) become singular. The values of detunings used are large ($|\Delta|\tau_c\gg1$, $|\Delta'|\tau_c\gg1$); however, for smaller values of detunings ($\sim10^{12}$ sec^{-1}), good agreement (to within 10%) is still obtained.

To obtain accurate cross sections, we have to do numerical integrations of Eqs. (5.5) for impact parameters b near and larger than the smallest of R_0, R_0', and R_0'' and to use Eqs. (6.29)–(6.39) for smaller impact parameters. This procedure is used to obtain the total cross section as a function of Δ' in a range including the point $\Delta'=(C'_{\rm VDW}/C_{\rm VDW})\Delta$ at which all the times of instantaneous resonance coincide, for the attractive van der Waals potential used in Fig. 4, and for $\Delta=-2.0\times10^{13}$ sec^{-1}. The results are shown in Fig. 5 along with two curves, one with a $(\Delta+\Delta')^{3/2}$ dependence, the other with a $\Delta'^{-3/2}$ dependence. The calculated cross section lies between the two curves, which are normalized to the same value as the calculated one at $\Delta'=(C'_{\rm VDW}/C_{\rm VDW})\Delta$ ($=-2.5\times10^{13}$ sec^{-1} in this case).

From the discussion earlier, the contributions from the $(1\rightarrow3)$ direct process disappear at this point, since $\tau_0=\tau_0'=\tau_0''$. The calculated line shape shows no marked structure due to this "interference" effect; the line profile is a smooth curve exhibiting the influence of both the stepwise and the direct processes. If the stepwise process is the only contributing one, the line shape would have followed the $\Delta'^{-3/2}$ curve; if, on the other hand, the direct process is the predominant one, the line shape should go as $(\Delta+\Delta')^{-3/2}$. Since the calculated curve on Fig. 5 tends to follow more closely the $\Delta'^{-3/2}$ curve, it suggests that at the

vicinity of $\Delta' = (C'_{\rm VDW}/C_{\rm VDW})\Delta$, the stepwise process is more important than the direct process, as previously discussed.

Simple analytic results can be obtained for the following two special cases (*i* and *ii*)

i. Exactly coinciding times of instantaneous resonance, $\tau_0 = \tau'_0 = \tau''_0$. Using Eqs. (6.29), (6.40), (6.41), and (6.42), we obtain

$$|\bar{C}_3(t=\infty)|^2 = (\pi^2\chi_0^2\chi_0'^2/\alpha\alpha')[\cos^2(\phi+\phi'+s\pi/4+s'\pi/4)+1 + 2\cos(\phi+\phi'+s\pi/4+s'\pi/4)\cos(\phi-\phi'+s\pi/4-s'\pi/4)]. \quad (6.45)$$

Although this is a simple expression, it cannot be used to obtain an accurate value for the total cross section for reasons to be discussed below. The time derivatives of the interatomic potentials α and α' can be expressed in terms of the internuclear distance and the impact parameter,

$$\alpha = (v/2R_0)(R_0^2 - b^2)^{1/2}\left|\left(\frac{dV}{dR}\right)_{R_0}\right|, \quad (6.46)$$

$$\alpha' = (v/2R'_0)(R_0'^2 - b^2)^{1/2}\left|\left(\frac{dV'}{dR}\right)_{R'_0}\right|. \quad (6.47)$$

When $R_0 = R'_0$ (as in this case), both α and α' approach 0 as b approaches $R_0(=R'_0)$, and Eq. (6.45) is singular, varying as $(R_0^2 - b^2)^{-1}$. An approximate formula for obtaining the total cross section, such as Eq. (6.10), is not applicable since it leads to a logarithmic divergence. Therefore, for a certain range of impact parameter b near R_0, numerical integration of Eqs. (5.5) and of $\int |\bar{C}_3(t=\infty)|^2 2\pi b\, db$ are required to obtain an accurate value for the total cross section. The result for a specific van der Waals potential and a given Δ is represented by a point on the line-shape curve, such as the one in Fig. 5 [the point $\Delta' = \Delta(C'_{\rm VDW}/C_{\rm VDW})$].

ii. Well-separated times of instantaneous resonance. The probability can be obtained from Eqs. (6.43), (6.44), (6.32)–(6.39), and (6.29). Since the amplitude contains contributions from both the stepwise and the direct processes, there will be interference terms in the probability. The interference effect is best illustrated using a specific order of instantaneous resonances (e.g., $\tau'_0 > \tau''_0 > \tau_0$). For this order ($\tau'_0 > \tau''_0 > \tau_0$), the excitation probability is obtained as

$$|\bar{C}_3(t=\infty)|^2 = (\pi\chi_0\chi'_0)^2(P_S + P_D + P_{\rm INT}), \quad (6.48)$$

with

$$P_S = 2(1 - s\sin 2\phi)/\alpha\alpha', \quad (6.49)$$

$$P_D = (f_0^2 + g_0^2)[1 - s''\sin 2(\phi'' - s\theta_0)]/\alpha\alpha'', \quad (6.50)$$

$$P_{\rm INT} = -s\left(\frac{2(f_0^2+g_0^2)}{\alpha^2\alpha'\alpha''}\right)^{1/2}\{\sin[\phi+\phi'-\phi''+(s+s'-s'')\pi/4+s\theta_0] + \sin[\phi+\phi'+\phi''+(s+s'+s'')\pi/4-s\theta_0] + \sin[\phi'+\phi''-\phi+(s'+s''-s)\pi/4-s\theta_0] + \sin[\phi'-\phi''-\phi+(s'-s''-s)\pi/4+s\theta_0]\}, \quad (6.51)$$

where all the quantities have been defined in Eqs. (6.29)–(6.39). Equations (6.48)–(6.51) clearly show the contributions to the total cross section from the stepwise process, the direct process, and the interference between the two. This result has been obtained and discussed in a recent paper,[7] and we summarize only the essential features.

All the sine functions in Eqs. (6.48)–(6.51) oscillate rapidly as functions of impact parameter b, except the one varying as

$$\sin[\phi+\phi'-\phi''+(s+s'-s'')\pi/4+s\theta_0]$$

(the first term in $P_{\rm INT}$), which is a slowly varying function of b. On integrating over b to obtain the total cross section, only this term survives to yield a term representing the interference of the stepwise and the direct processes which oscillates as a function of inverse active-atom-perturber relative speed $1/v$.

An approximation such as Eq. (6.10) is used to calculate the total cross section, yielding

$$\sigma=\frac{(\pi\chi_0\chi_0')^2R_0}{v^2\left|\left(\frac{dV}{dR}\right)_{R_0}\right|}\left[\frac{4R_0'}{\left|\left(\frac{dV'}{dR}\right)_{R_0'}\right|}\ln\frac{R_0'+R_0}{R_0'-R_0}+\frac{2R_0''(f_0^2+g_0^2)}{\left|\left(\frac{d(V+V')}{dR}\right)_{R_0''}\right|}\ln\frac{R_0''+R_0}{R_0''-R_0}\right.$$
$$\left.-2s\left[\frac{2R_0'R_0''(f_0^2+g_0^2)}{\left|\left(\frac{dV'}{dR}\right)_{R_0'}\left(\frac{d(V+V')}{dR}\right)_{R_0''}\right|}\right]^{1/2}\ln\frac{R_0'+R_0''+2R_0}{R_0'+R_0''-2R_0''}\sin\left(\frac{A}{v}+\phi_0\right)\right], \tag{6.52}$$

where A is the area enclosed by the three crossings on the interatomic potential curves in a dressed-atom picture, and

$$\phi_0=(s+s'-s'')\pi/4+s\theta_0$$

is a constant phase.

Equation (6.52) is not restricted to any specific type of potential, and the calculation of total excitation cross section using it is remarkably simple. For given interatomic potential curves and detunings, one can graphically obtain the slopes at the crossing points and the area A enclosed by them. Substitution of these values into Eq. (6.52) yields σ. A comparison of this cross section with the corresponding one obtained from computer solutions indicates that Eq. (6.52) is accurate to within 15%.

The third term in Eq. (6.52), which represents the interference between the stepwise and the direct processes, contains a sine function which will oscillate as the relative speed v is varied. It is clear from Eq. (6.52) that the area A determines the oscillation frequency, while the slopes at the crossing points determine the amplitudes of the oscillations. For given interatomic potential curves, these quantities (A and slopes) can be changed by varying the detunings, and hence the frequency and the amplitude of the oscillation in the total cross section.

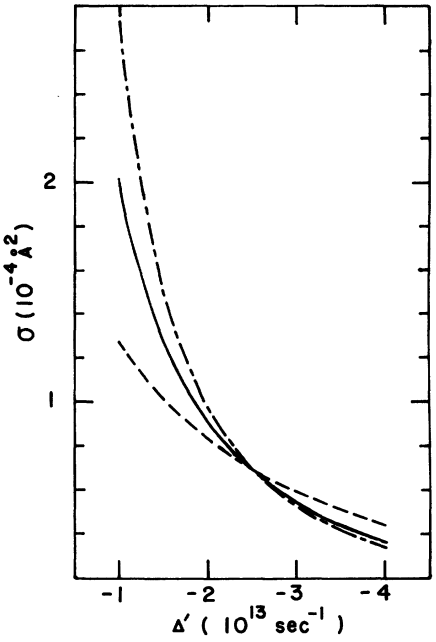

FIG. 5. The total excitation cross section as a function of Δ' near $\Delta'=(C'_{VDW}/C_{VDW})\Delta$ for a fixed $\Delta=-2.0\times10^{13}$ sec^{-1}. The interatomic potential and other parameters used are the same as those in Fig. 4. —— this calculation; ------ $\propto(\Delta+\Delta')^{-3/2}$; - · - · - · $\propto\Delta'^{-3/2}$. The three curves are normalized to the same value at $\Delta'=\Delta(C'_{VDW}/C_{VDW})$.

The restriction to a specific ordering of the crossing times (i.e., $\tau_0'>\tau_0''>\tau_0$) corresponds to confining the detunings in certain regions depending on the given interatomic potential. For detunings in different regions, the ordering will be different. However, it would be just as easy to obtain the excitation probability and the total cross section from Eqs. (6.43), (6.44), (6.32)–(6.39), and (6.29).

To illustrate this interference effect and to investigate the feasibility of its experimental observation, we use a specific potential, as shown in Figs. 6(a) and 6(b), instead of van-der-Waals-type potentials for detunings $\Delta=-8.0\times10^{13}$ sec^{-1} and $\Delta'=-3.0\times10^{13}$ sec^{-1}. The resulting total excitation cross section as a function of inverse relative speed $1/v$ is shown in Fig. 7, with $\chi_0=\chi_0'=10^{11}$ sec^{-1}. The curve rises as $(1/v)^2$ with equally spaced peaks when the speed is varied from 10^5 to 4×10^5 cm sec^{-1}. In terms of the laser power, the excitation cross sections are of the order of $(10^{-34}I_0I_0')$ cm^2, with I_0, I_0' the peak power density in W/cm^2. Thus, the interference effect should be observable with moderate laser power. Although a specific potential [Figs. 6(a) and 6(b)] is used to demonstrate this effect, we emphasize that the oscillatory feature occurs regardless of the form of the potential as long as three conditions are satisfied. First, there must be three crossings, as shown in Fig. 6(b). Second, the area enclosed by the crossings must be large enough to produce a phase change of order π when the speed is varied in a convenient range. Third, the stepwise and the direct excitation contributions must be comparable. The first condition is required for there to be four excitation channels interfering with each other. This condition allows for a phase factor that is nearly independent of

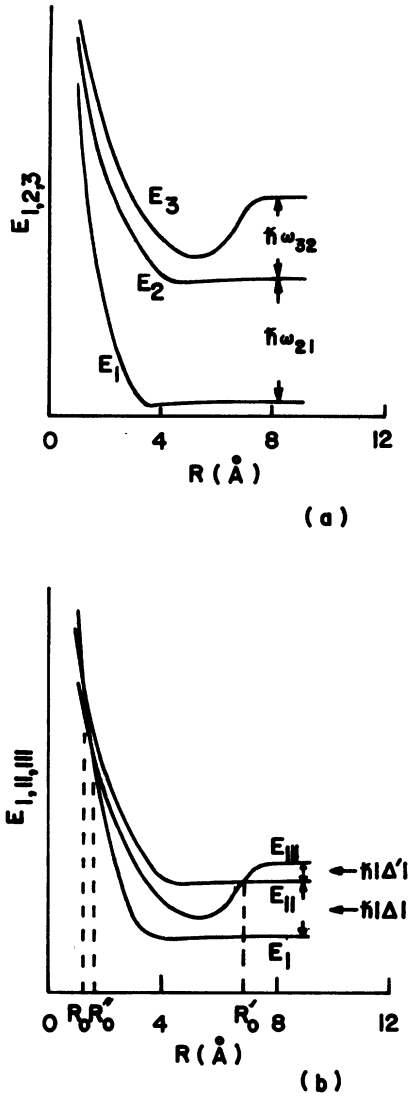

FIG. 6. Interatomic potential used to demonstrate the interference effect discussed in case J. (a) Bare-state-classical-field picture. (b) Dressed-atom picture. The dressed-state energies $E_{I,II,III}$ are related to the bare-state energies $E_{1,2,3}$ by Eqs. (4.2). In (a), the level separations are not drawn to scale; in (b), the energies $\hbar|\Delta|$ and $\hbar|\Delta'|$ set the energy scale. $\Delta = -8.0\times10^{13}$ sec^{-1}, $\Delta' = -3.0\times10^{13}$ sec^{-1}.

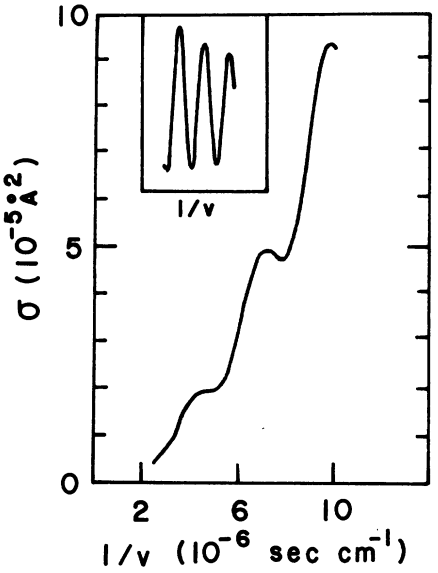

FIG. 7. Total excitation cross section as a function of inverse relative speed $1/v$ for a potential shown in Fig. 6, with $\chi_0 = \chi_0' = 10^{11}$ sec^{-1}, $\Delta = -8.0\times10^{13}$ sec^{-1}, and $\Delta' = -3.0\times10^{13}$ sec^{-1}. The curve rises as $(1/v)^2$. As the speed varies from 10^5 to 4×10^5 cm sec^{-1}, equally spaced peaks are clearly seen. In the inset, the product of the total cross section and v^2 as a function of $1/v$ is shown.

impact parameter b. The second and third conditions determine the frequency and amplitude of the oscillatory term.

VII. DISCUSSION

CARE, as presented in the dressed-atom picture, is similar to radiationless inelastic collisions. However, there is an important difference between the two. In the radiationless inelastic atomic collision, the process, and hence the cross section, is determined by the interatomic potential of the atom-atom system, which cannot be controlled once the system is chosen. In CARE, on the other hand, the corresponding interatomic potential (in the dressed-atom picture) depends not only on the atom-atom system, but also on the atom-field detunings as well as the field intensities. In the weak-field limit, one can vary the detunings to change the level spacings of the dressed states and the positions of, and the slopes at, the potential curve crossings (if any) which are the essential parameters determining the CARE cross section. Hence, the interaction between the two colliding atoms can be probed in a controlled fashion by using CARE, a great advantage over the ordinary radiationless atomic collisions. The three-level problem discussed in this paper provides a good example of the relationship between CARE and inelastic collisions. The oscillatory features obtained in case J of the previous section for the total CARE cross section as a function of active-atom-perturber relative speed are of similar nature to those obtained by Rosenthal and Foley[8] for He-He$^+$ charge-exchange inelastic collisions. The He-He$^+$ atom-ion interatomic potential curves are analogous to those of the three-level CARE in the dressed-atom picture [Fig. 6(b)]. The frequency and amplitude of oscillation in CARE can be varied by changing the detunings and thus the

potential-curve crossing properties (positions and slopes); such a variation is not possible in charge-exchange inelastic collisions. Although oscillation of this type continue to be discovered[18,19] for charge-exchange inelastic collisions in alkali-ion-noble-gas systems such as Na^+-Ne, K^+-Ar, Cs^+-Ar, they are confined in systems with atom-ion interatomic potentials bearing a resemblance to Fig. 6(b), and thus have limited value in investigating the atom-atom or atom-ion interactions. With CARE, the scope of such studies can be extended.

In case J of the previous section, we mentioned that the interference effect should be observable with moderate laser powers, without referring to any specific experimental setup. The experiment can be performed using crossed atomic beams or a beam interacting with a gas sample. The beam-gas sample method works only if the active-atom-perturber relative velocity is approximately equal to the beam velocity. In cases when better detection efficiency is required, one can use a third laser to ionize the active atom from the upper excited state (state 3) and thus detect the ions instead of the fluorescence.

Finally, let us mention another type of oscillation which can occur in a two-level system and should be distinguished from the present one. The modulation in the absorption coefficient as a function of *detuning* for atoms in a collisional environment was discussed by Mies,[20] Carrington *et al.*,[21] Shlyapnikov and Shmatov,[22] and observed by Scheps *et al.*[23] and Bergeman and Liao.[24] This has been attributed to the oscillatory structure of the vibrational wave function of the quasimolecule formed by the colliding atoms. Such an effect does not involve interference of different channels of excitation, and is due to oscillation in the transition matrix elements.

VIII. CONCLUSION

We have presented a theory of collisionally aided radiative excitation for three-level systems in the weak-fields limit. Attempts are made to cover as many cases as possible and to be as general as possible, although results are given for some specific potentials only. Because of the complexity of a three-level system and the distinct physical features and mathematical treatments in different limiting cases, we classified the problem into thirteen cases according to the sizes and the signs of the detunings. These cases were treated in detail, except the last three cases (K, L, M) which give rise to exponentially small excitation cross sections for which reliable analytic approximations are lacking at the present time.

A dressed-atom picture was also given which brought the CARE problem into complete parallel with the problem of radiationless inelastic atomic (or molecular) collisions. In this picture, the collision-induced instantaneous resonances between the atomic transitions and the external fields are transformed into interatomic potential curve crossings. Such curve crossings enhance the excitation, especially in the large detuning cases, and interfere with each other, leading to effects reflecting the crossing configurations. Some special crossing configurations yield particularly interesting interference effects (e.g., the modulation of the total excitation cross section discussed in case J). A quantitative examination indicates that experimental observations of such effects are feasible.

The theory does not include the cases of strong fields which are of increasing importance and interest with the advent of high-power lasers. The dressed-atom approach seems to be most suitable for attacking such cases, and numerical calculations may be inevitably needed. The established numerical method used in two-level CARE problems and the analytic methods presented in this paper can be combined to form useful tools in the investigation of these cases.

ACKNOWLEDGMENTS

This work was supported by the U. S. ONR through contract number N00014-77-C-0553. The authors thank Professor E. J. Robinson for many discussions during the course of the work.

APPENDIX A

In this appendix we give the details of calculations leading to Eqs. (6.29)–(6.39) from Eq. (6.1). Assuming that the collision trajectories are symmetric about $t=0$, the time of closest approach between the active atom and the perturber, we break the t integral of Eq. (6.1) into two parts, $t>0$ and $t<0$,

$$\tilde{C}_3(t=\infty) = -\int_{-\infty}^{0} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t V'(t')dt'\right)\right] Q(t)\,dt - \int_0^{\infty} \chi'(t) \exp\left[-i\left(\Delta' t - \int_0^t V'(t')dt'\right)\right] Q(t)\,dt, \tag{A1}$$

where

$$Q(t)=\int_{-\infty}^{t}\chi(t_1)\exp\left[-i\left(\Delta t_1-\int_0^{t_1}V(t')dt'\right)\right]dt_1 .$$

Because of the condition $|\Delta|\tau_c\gg 1$, the contributions to Q are from the neighborhood of the crossing points $\pm\tau_0$, satisfying $\Delta=V(t)$ only. Thus, for the first term (restricted to $t<0$), we expand the exponent of the integrand in Q in Taylor series about $t_1=-\tau_0$, and for the second term (restricted to $t>0$), we break the Q integral into two parts, from $-\infty$ to 0 and from 0 to t, and expand the exponent about $t_1=-\tau_0$ and $t_1=\tau_0$ for each region, respectively. The factor $\chi(t_1)$ is evaluated at $\chi(\pm\tau_0)\equiv\chi_0$. The Taylor series is terminated at terms $\propto(t_1\pm\tau_0)^2$, and the integrals obtained are evaluated exactly to yield

$$Q(t)=\chi_0 e^{-i(\phi+s\pi/4)}\tfrac{1}{2}(\pi/\alpha)^{1/2}\{1+\mathrm{erf}[\alpha^{1/2}(t+\tau_0)e^{is\pi/4}]\}\quad\text{for } t<0 \tag{A2}$$

and

$$\begin{aligned}Q(t)=\chi_0 e^{-i(\phi+s\pi/4)}\tfrac{1}{2}(\pi/\alpha)^{1/2}&[1+\mathrm{erf}(\alpha^{1/2}\tau_0 e^{is\pi/4})]\\&+\chi_0 e^{i(\phi+s\pi/4)}\tfrac{1}{2}(\pi/\alpha)^{1/2}\{\mathrm{erf}[\alpha^{1/2}(t-\tau_0)e^{-is\pi/4}]-\mathrm{erf}(-\alpha^{1/2}\tau_0 e^{-is\pi/4})\}\quad\text{for } t>0\end{aligned} \tag{A3}$$

where erf is the error function and ϕ, s, α are defined in Eqs. (6.29)–(6.39). Putting Eqs. (A2) and (A3) into Eq. (A1), using the relation $\mathrm{erf}(z)=1-\mathrm{erfc}(z)$, and combining terms, we can write $\bar{C}_3(t=\infty)$ as a sum of four terms. Under the assumption that the crossing points are far from $t=0$ ($\alpha^{1/2}\tau_0\gg 1$), one of the four terms, which contains a factor $\mathrm{erfc}[\alpha^{1/2}\tau_0 e^{-is\pi/4}]$, can be neglected. Thus,

$$\begin{aligned}\bar{C}_3(t=\infty)=-\frac{\chi_0}{2}(\pi/\alpha)^{1/2}\Bigg\{&e^{-i(\phi+s\pi/4)}\int_{-\infty}^{0}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]\mathrm{erfc}[-\alpha^{1/2}(t+\tau_0)e^{is\pi/4}]dt\\&+e^{i(\phi+s\pi/4)}\int_0^{\infty}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]\mathrm{erfc}[-\alpha^{1/2}(t-\tau_0)e^{-is\pi/4}]dt\\&+e^{-i(\phi+s\pi/4)}\mathrm{erfc}[-\alpha^{1/2}\tau_0 e^{is\pi/4}]\int_0^{\infty}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]dt\Bigg\}.\end{aligned} \tag{A4}$$

This, again, is to be evaluated using the stationary-phase method. Since the error functions with complex arguments are oscillatory functions, their presence in the integrands of the first two terms in Eq. (A4) will modify the stationary-phase positions of these integrals. To cope with this, we use Eqs. 7.1.2, 7.1.9, 7.1.10, 7.3.9, 7.3.10, and 7.3.22 of Abramowitz and Stegun[25] to express the error functions in terms of an exponential (oscillating) part and the auxiliary functions f,g of the Fresnel's integrals, which are slowly varying functions. By doing this, the integrals are written in a form suitable for the stationary-phase method. We shall now demonstrate the method by evaluating the first term in the curly bracket of Eq. (A4), to be called W. The evaluation of the second term follows exactly the same procedure.

In terms of f,g and the exponential function, W can be written as a sum of three terms. In two of these terms a phase of the form $\phi+s\alpha(t+\tau_0)^2$ appears which is simply the Taylor-series expansion of $\Delta t-\int_0^t V(t')dt'$ at $t=-\tau_0$. We transform this term back to its original form and find

$$\begin{aligned}W=&2e^{-i(\phi+s\pi/4)}\int_{-\tau_0}^{0}\chi'(t)\exp\left[-i\left(\Delta' t-\int_0^t V'(t')dt'\right)\right]dt\\&+is\sqrt{2}\int_{-\tau_0}^{0}\chi'(t)(f^2+g^2)^{1/2}e^{is\theta}\exp\left[-i\left((\Delta+\Delta')t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt\\&-is\sqrt{2}\int_{-\infty}^{-\tau_0}\chi'(t)(f^2+g^2)^{1/2}e^{is\theta}\exp\left[-i\left((\Delta+\Delta')t-\int_0^t[V(t')+V'(t')]dt'\right)\right]dt,\end{aligned} \tag{A5}$$

where $\theta=\tan^{-1}g/f$ and the argument of f,g is

$$\left|(2\alpha/\pi)^{1/2}(t+\tau_0)\right| .$$

Other parameters are defined in Eqs. (6.29)–(6.39). The integrals in Eq. (A5) can be evaluated using the stationary-phase method. Since $\chi'=\chi_0'$, a constant during the collision, and f,g,θ are slowly varying functions compared with the rapidly oscillating exponential part, we can evaluate them at the stationary-phase points, $-\tau_0'$ for the first term, $-\tau_0''$ for the second and the third term, and take them out of the integrals. The remaining integrals are evaluated using the same method as that leading to Eqs. (A2) and (A3) for Q. Then, the error functions can again be written in terms of f,g functions, which leads to Eq. (6.30).

The same procedure applied to the second term in Eq. (A4) yields Eq. (6.31). The evaluation of the

third term in Eq. (A4) is particularly simple. For stationary-phase point τ_0 far from 0, the erfc function can be approximated by 2, and the integral is done by the stationary-phase method. This method yields Eq. (6.32).

APPENDIX B

The excitation probability can always be written as a sum of three terms, P_S, D_D, and $P_{\rm INT}$ representing the stepwise, the direct, and the interference contributions, respectively. In the most general case, they are

$$\begin{aligned}P_S=\frac{(\chi_0\chi_0'\pi)^2}{\alpha\alpha'}\{&2-(1+s_1)s\sin2\phi-(1-s_1)s'\sin2\phi'\\&+(f_1^2+g_1^2)[1-s\sin2(\phi+\phi'_{\tau_0}-s'\theta_1)]\\&+[2(f_1^2+g_1^2)]^{1/2}[s\sin(2\phi+\phi'+\phi'_{\tau_0}-s'\pi/4-s'\theta_1)-\cos(\phi'-\phi'_{\tau_0}-s'\pi/4+s'\theta_1)]\\&+s_1[2(f_1^2+g_1^2)]^{1/2}[s\sin(2\phi-\phi'+\phi'_{\tau_0}+s'\pi/4-s'\theta_1)-\cos(\phi'+\phi'_{\tau_0}-s'\pi/4-s'\theta_1)]\},\end{aligned}\tag{B1}$$

$$\begin{aligned}P_D=[(\chi_0\chi_0'\pi)^2/\alpha\alpha'']&(f_0^2+g_0^2)\{1-s''\sin2(\phi''-s\theta_0)+2(f_2^2+g_2^2)[1-\cos2(\phi''_{\tau_0}-s\theta_0-s''\theta_2)]\\&+2[2(f_2^2+g_2^2)]^{1/2}[\cos(\phi''+\phi''_{\tau_0}-2s\theta_0-s''\theta_2-s''\pi/4)-\cos(\phi''_{\tau_0}-\phi''-s''\theta_2+s''\pi/4)]\},\end{aligned}$$

$$P_{\rm INT}=\frac{(\chi_0\chi_0'\pi)^2}{\alpha}\left(\frac{2(f_0^2+g_0^2)}{\alpha'\alpha''}\right)^{1/2}\tag{B2}$$

$$\begin{aligned}\times(&-s_1s_2\{\cos[\phi+\phi'+\phi''-(s-s'-s'')\pi/4-s\theta_0]+\cos[\phi+\phi'-\phi''-(s-s'+s'')\pi/4+s\theta_0]\}\\&+s_2\{\cos[\phi-\phi'+\phi''-(s+s'-s'')\pi/4-s\theta_0]\\&\quad+\cos[\phi-\phi'-\phi''-(s+s'+s'')\pi/4+s\theta_0]\}\\&+s_1s_2s''[2(f_2^2+g_2^2)]^{1/2}\{\sin[\phi+\phi'-\phi''_{\tau_0}-(s-s')\pi/4+s\theta_0+s''\theta_2]\\&\qquad-\sin[\phi+\phi'+\phi''_{\tau_0}-(s-s')\pi/4-s\theta_0-s''\theta_2]\}\\&-s_2s''[2(f_2^2+g_2^2)]^{1/2}\{\sin[\phi-\phi'-\phi''_{\tau_0}-(s+s')\pi/4+s\theta_0+s''\theta_2]\\&\qquad-\sin[\phi-\phi'+\phi''_{\tau_0}-(s+s')\pi/4-s\theta_0-s''\theta_2]\}\\&-s_1s_2s'[2(f_1^2+g_1^2)]^{1/2}\{\sin[\phi+\phi''+\phi'_{\tau_0}-(s-s'')\pi/4-s\theta_0-s'\theta_1]\\&\qquad+\sin[\phi-\phi''+\phi'_{\tau_0}-(s+s'')\pi/4)+s\theta_0-s'\theta_1]\}\\&+2s_1s_2s's''[(f_1^2+g_1^2)(f_2^2+g_2^2)]^{1/2}[\cos(\phi+\phi'_{\tau_0}+\phi''_{\tau_0}-s\pi/4-s\theta_0-s'\theta_1-s''\theta_2)\\&\qquad-\cos(\phi+\phi'_{\tau_0}-\phi''_{\tau_0}-s\pi/4+s\theta_0-s'\theta_1+s''\theta_2)]),\end{aligned}\tag{B3}$$

where

$$\phi'_{\tau_0}=-\Delta'\tau_0+\int_0^{\tau_0}V'(t')dt',\quad \phi''_{\tau_0}=-(\Delta+\Delta')\tau_0+\int_0^{\tau_0}[V(t')+V'(t')]dt',$$

and all the other quantities have been defined in Eqs. (6.29)–(6.39).

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