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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS:
PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

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COLLISION INDUCED RESONANT STRUCTURES IN SPECTROSCOPIC LINE SHAPES

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Collision - Induced Resonant Structures in Spectroscopic Line Shapes

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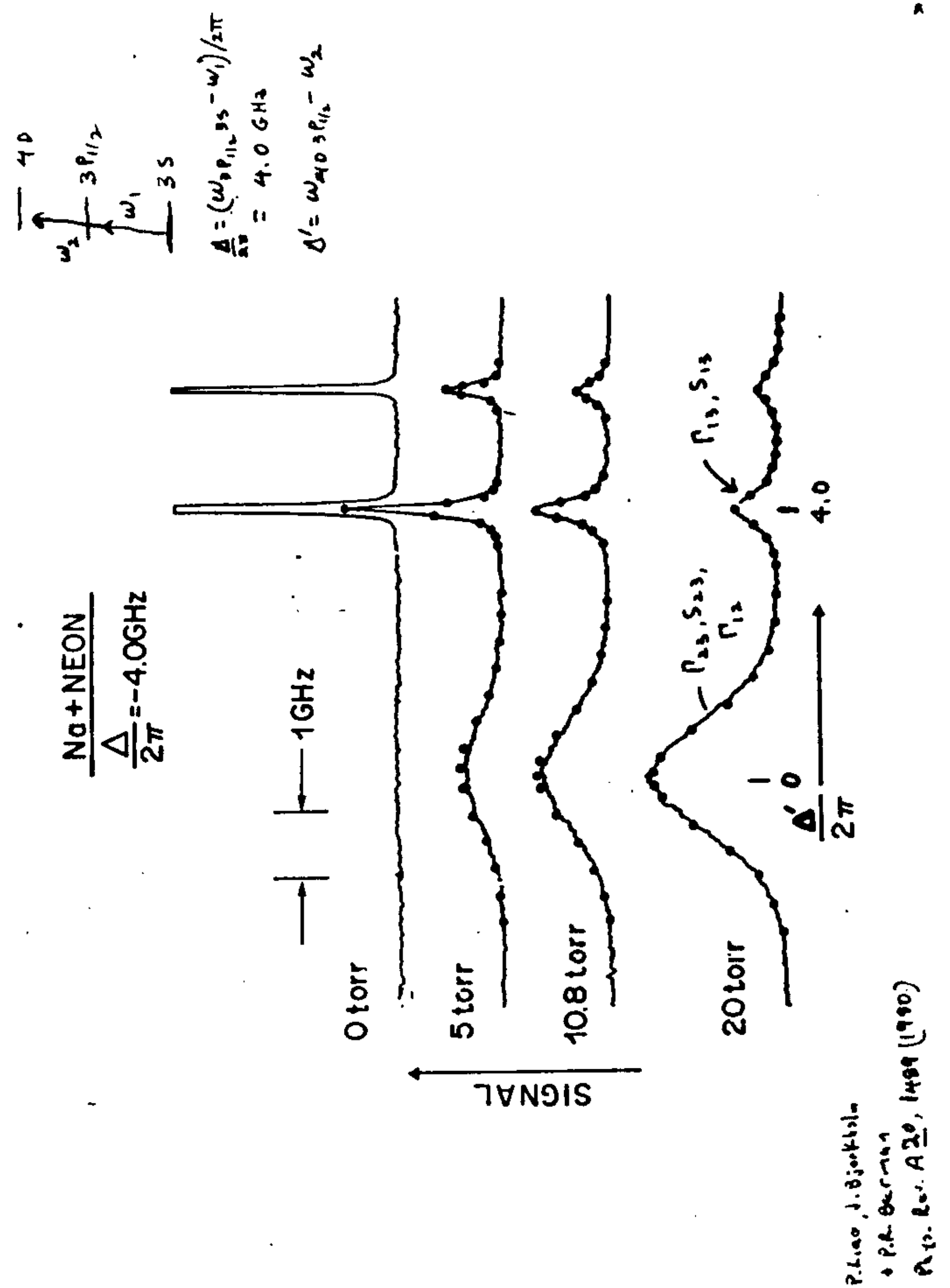
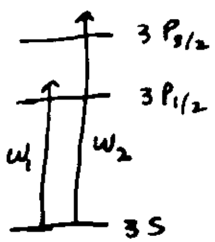
I am going to discuss a number of radiative-collisional processes that lead to resonant structures in spectroscopic line shapes. Experimental situations where such structures are seen are illustrated on the next few pages. Following a discussion of these experiments, I will review the basic concepts involved in describing collisions in atomic vapors whose atoms are also driven by radiation fields. Subsequently, I will describe how combined radiative-collisional processes can lead to enhanced production of atomic state coherence and excited state population in atomic vapors.



Y. Prior et. al. Phys. Rev. Lett. 46, 111 (1981)

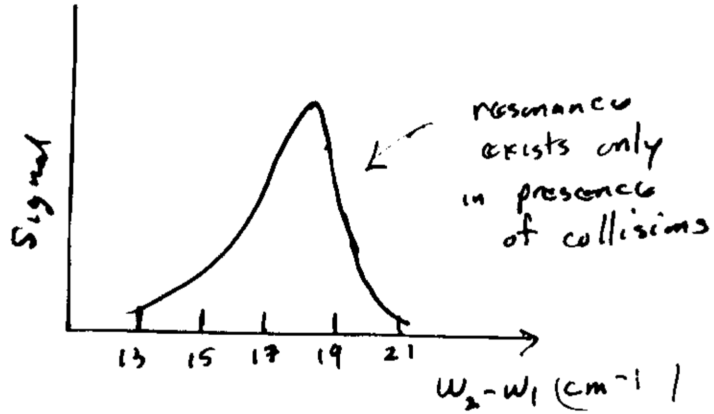
Na
+ 800 Torr
He



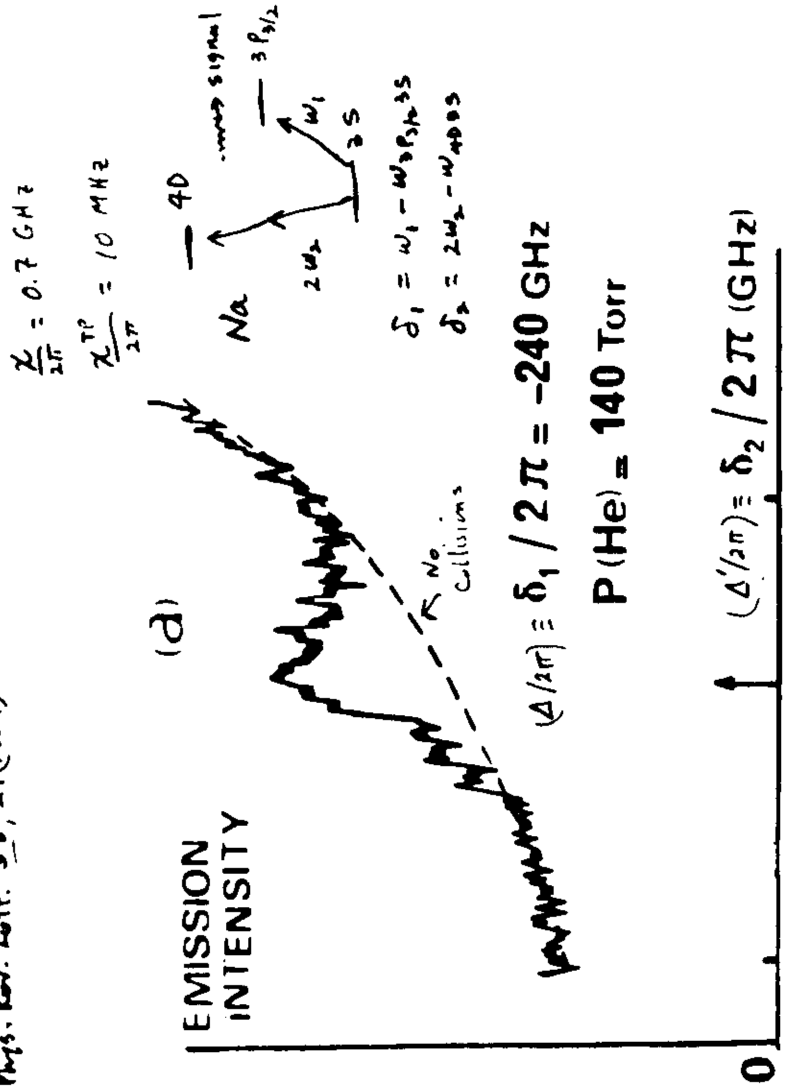
$\omega_{P_{3/2}} - \omega_{P_{1/2}}$
$= 17\,cm^{-1}$

$$\Delta = \omega_1 - \omega_{3P_{1/2}-3S} \simeq 5\,cm^{-1}$$

Four-wave mixing signal generated with
$$\omega_s = 2\omega_1 - \omega_2$$



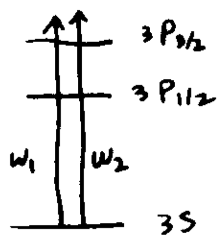
E. Giacobino + P.R. Berman
Phys. Rev. Lett. 58, 21 (1987)



A.R. Bogdan, Y. Prior and N. Bloembergen

Opt. Lett. 6, 82 (1981)

Na + He



$\Delta = \omega_1 - \omega_{3P_{3/2}3S}$

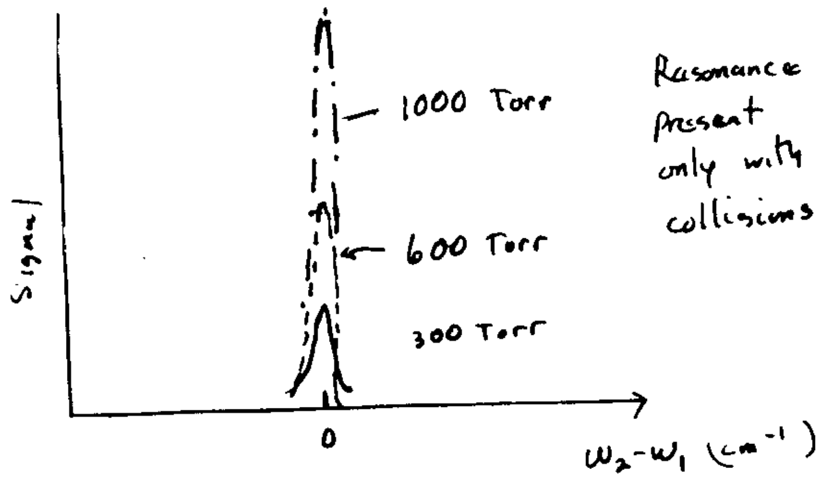
$= 24\,cm^{-1}$

Four wave mixing signal with

$\vec{k}_s = 2\vec{k}_1 - \vec{k}_2 \qquad \Omega_s = 2\omega_1 - \omega_2$

Actually – two beams for ω_1

$\vec{k}_s = (\vec{k}_1)_{\omega_1} + (\vec{k}_1')_{\omega_1} - \vec{k}_2$

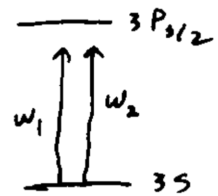


Resonance present only with collisions

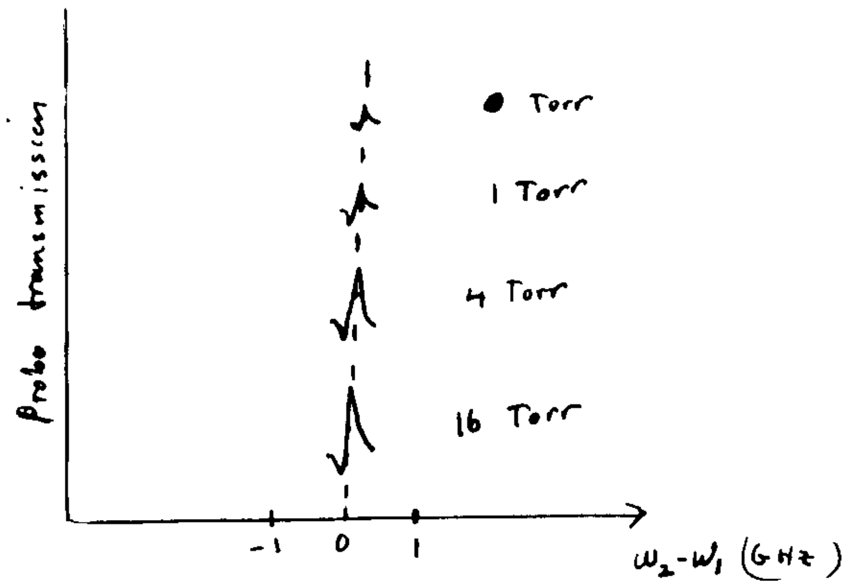
M.T. Gruneisen, K.R. MacDonald and R.W. Boyd

J.O.S.A. 5, 123 (1988)

Na + He



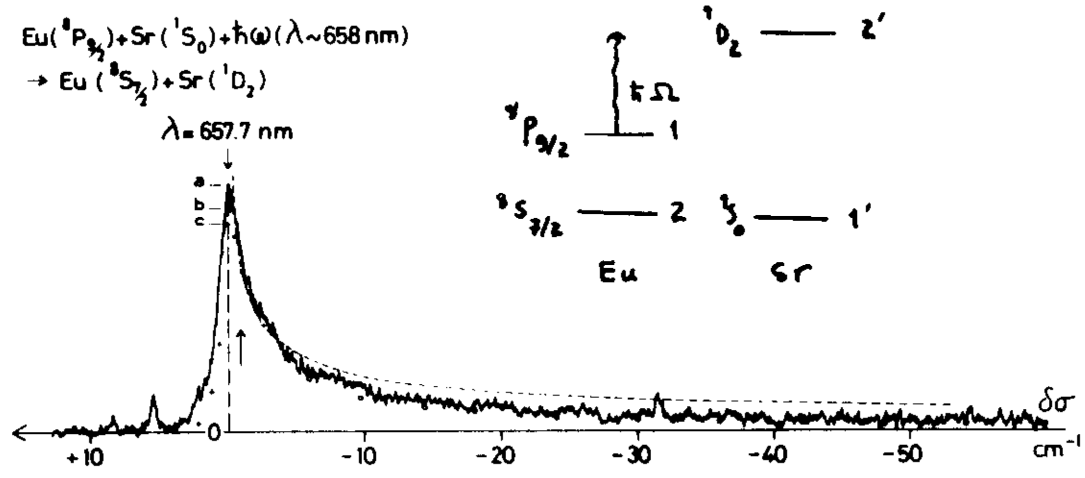
Measure probe absorption of field with frequency ω_2



D. Grandclément, G. Grynberg and M. Pinard

Phys. Rev. Lett. 59, 40 (1987).

Observed gain and oscillation which they attributed in part to collisional processes. The experiment is similar to the pump-probe experiment with gain on ω_2 in the region $\omega_2 \simeq \omega_1$. Gain was observed only with He buffer gas in the cell.



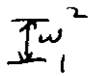
σ = 50 Å^2/MW/cm^2 at line center

C. Brechignac, Ph. Cahuzac and P. E. Toschek, Phys. Rev. A 21, 1969 (1980).

A. Débarre, J. Phys. B 15 1693 (1982) remeasured this spectrum and also measured final-state magnetic polarization.

I. Review of Basic Concepts

A. Radiation Alone

Consider a two-level atom 

subjected to a driving field $\vec{E} = \vec{E}_0 \cos(\vec{k}\cdot\vec{R} - \Omega t)$. This field produces a linear combination of states 1 and 2. If the field acts on an ensemble of such atoms, there will be a macroscopic dipole moment for the sample owing to the presence of the field. In terms of density matrix elements, the field produces atomic state populations ρ_{11}, ρ_{22} and atomic-state coherences ρ_{12} and ρ_{21}.

B. Collisions Alone

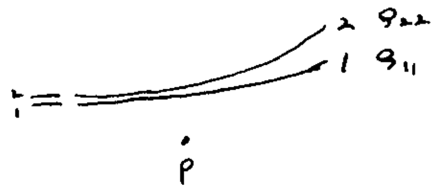
Let us imagine that the "active" atoms (the ones which will interact with the field) undergo collisions with perturber atoms. The energy $\hbar\omega$ is large enough to neglect any inelastic collisions. In that case, collisions are conveniently described by the scattering amplitude $f_1(\theta)$ and differential scattering cross section $|f_1(\theta)|^2$.

In a vapor, one speaks of a collision kernel $W_1(\vec{v}\,' \to \vec{v})$ giving the probability density per unit time that collisions change the active atom velocity of atoms in state 1 from $\vec{v}\,'$ to $\vec{v}$. One also speaks of a collision rate $\Gamma_1(\vec{v}\,')$ for such processes.

If the atoms were in state 2, corresponding quantities could be defined related to $|f_2(\theta)|^2$, the differential cross section for active atom – perturber collisions when the active atoms are in state 2.

C. Combined Radiation and Collisions

The atoms are now described by density matrix elements ρ_{11}, ρ_{22}, and ρ_{12}. In a collision with a perturber P, one could assign a trajectory with ρ_{11} and ρ_{22}, but what about ρ_{12}?



$\rho_{12} = ?$

If the collision-interaction is state-dependent as it is for electronic transitions, the collision acts as a good state selector (much in the same way as a Stern-Gerlach magnet) and $\rho_{12} = 0$ following a collision, owing to the trajectory separation for states 1 and 2. In this limit

$$\dot{\rho}_{12} = -\Gamma_{12}\,\rho_{12}$$

where Γ_{12} is the collision rate. Actually, it turns out that ρ_{12} is not totally destroyed in collisions as a result of quantum-mechanical, diffractive scattering; however, for the purpose of this discussion, such effects can be neglected. The velocity associated with each level population changes in collisions but the total (velocity-integrated) populations are constant.

D. Approximations

The following approximations will be made throughout the discussion:

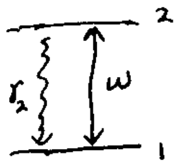
1. Impact approximation: On the time scale of a collision duration τ_c, nothing much happens (with the exception of electronic state oscillations). In other words, all decay rates, collision rates, atom-field detunings, and Rabi frequencies are much smaller than τ_c^{-1}. This allows one to write time evolution equations for $\dot{\rho}$ with separate contributions from atom-field and collisional interactions.
2. Neglect of inelastic collisions: $\omega\tau_c \gg 1$
3. Large detuning limit: $|\Delta| \gg$ any Doppler width or decay rate (Δ = atom-field detuning). A large $|\Delta|$ is assumed such that radiative processes alone (without collisions) cannot induce transitions.
4. Weak fields: all processes calculated to lowest order perturbation theory in the applied fields.

From assumption (3), the atoms are sufficiently detuned that it is unimportant what velocity they have. Consequently, velocity-changing collisions for level populations is unimportant and one need consider only the effects of collisions on off-diagonal density matrix elements given by

$$\dot{\rho}_{12}\Big)_{\text{collisions}} = -\Gamma_{12}\,\rho_{12}.$$

II. Pressure-Induced Excited-State Population

A. Two-Level Atom - One field



$$\vec{E} = \frac{\hat{x}}{2}\left[E_0 e^{i(\vec{k}\cdot\vec{R}-\Omega t)} + E_0^* e^{-i(\vec{k}\cdot\vec{R}-\Omega t)}\right]$$

$$\Delta = \omega - \Omega$$

$|\Delta| >> ku$ $\quad u =$ most probable atomic speed

$$\chi = \frac{\mu_{21} E_0^*}{2\hbar}$$

$$\underline{H} = \frac{\hbar}{2}\begin{pmatrix} -\omega & 2\chi^* e^{-i(\vec{k}\cdot\vec{R}-\Omega t)} \\ 2\chi e^{i(\vec{k}\cdot\vec{R}-\Omega t)} & \omega \end{pmatrix}$$

resonance approximation $\left|\frac{\Omega-\omega}{\Omega+\omega}\right| << 1$

$$\rho_{21} = \tilde{\rho}_{21} e^{i(\vec{k}\cdot\vec{R}-\Omega t)}$$

1. Density-matrix equations with relaxation

$$\dot{\rho}_{22} = -\gamma_2 \rho_{22} - i(\chi^* \tilde{\rho}_{21} - \chi \tilde{\rho}_{12})$$

$$\dot{\tilde{\rho}}_{12} = -\left(\frac{\gamma_2}{2} + \Gamma_{12}\right)\tilde{\rho}_{12} + i\Delta\tilde{\rho}_{12} + i\chi^*(\rho_{22} - \rho_{11})$$

$\Gamma_{12} =$ collisional dephasing rate

$$\tilde{\rho}_{21} = (\tilde{\rho}_{12})^*$$

$$\rho_{11} + \rho_{22} = W_0(\vec{v})$$

$$W_0(\vec{v}) = \left(\frac{1}{\pi u^2}\right)^{3/2} e^{-v^2/u^2}$$

Solution to second order in χ

$$\rho_{22} \simeq \frac{|\chi|^2}{\Delta^2}\left(1 + \frac{2\Gamma_{12}}{\gamma_2}\right) W_0(v)$$

↑ will lead to a pressure induced resonance.

If the calculation were done for a pulse of radiation

$|\Delta T| >> 1$

$\gamma_2 T << 1$

then, following the pulse at time $t = t^+$

$$\rho_{22}(t^+) = \frac{2\Gamma_{12}}{\Delta^2}\int_{\text{pulse}} |\chi(t)|^2 dt .$$

Population would vanish in the absence of collisions.

2. Semiclassical Dressed Atom Approach to this Problem

If $\left|\frac{\chi}{\Delta}\right| << 1$ then set

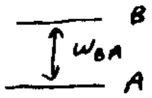
$$|A\rangle = |1\rangle + \frac{\chi}{\Delta}|2\rangle$$

$$|B\rangle = -\frac{\chi^*}{\Delta}|1\rangle + |2\rangle$$

With this basis, the original Hamiltonian in the field interaction representation $\quad \tilde{H} = \frac{\hbar}{2}\begin{pmatrix} -\Delta & 2\chi^* \\ 2\chi & \Delta \end{pmatrix}$

becomes

$$H_0 = \frac{\hbar}{2}\begin{pmatrix} -\omega_{BA} & 0 \\ 0 & \omega_{BA}\end{pmatrix} \qquad \omega_{BA} = [\Delta^2 + 4|\chi|^2]^{1/2} \approx |\Delta|$$



In the absence of relaxation, and for slowly varying envelope functions of the applied fields,

$$\dot\rho_{AA} = 0 \qquad \dot\rho_{BB} = 0 \qquad \dot\rho_{AB} = i\omega_{BA}\rho_{AB}$$

If an atom starts in dressed state A, it will stay there.

When collisions are included, they mix the dressed states (which are linear combinations of the bare states). For $\frac{\gamma_2}{|\Delta|} \ll 1$ and $\frac{\Gamma_{12}}{|\Delta|} \ll 1$ (secular approximation), one finds

$$\dot\rho_{BB} \approx 2\Gamma_{12}\frac{|\chi|^2}{\Delta^2}\rho_{AA} - \gamma_2\rho_{BB} \qquad \rho_{AA} + \rho_{BB} = W_0(\vec v)$$

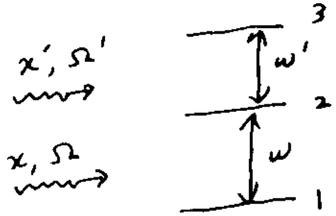
$$\dot\rho_{AB} \approx i\omega_{BA}\rho_{AB}$$

Collisions populate dressed state B. Of course, if we transform back to the bare-state basis, we again find $\rho_{22} \approx \frac{|\chi|^2}{\Delta^2}\left(1 + \frac{2\Gamma_{12}}{\gamma_2}\right)$ as the steady state solution.

We could have equally well used a quantized-field dressed atom approach with basis states $|1;n\rangle$ and $|2;n-1\rangle$ in the product basis (n = photon occupation number) and states $|A;n\rangle$ and $|B;n-1\rangle$ in the dressed basis.

To <u>observe</u> the collision induced effects, some sort of detection scheme must be used. For example, with pulsed excitation, there is no fluorescence following the excitation pulse in the absence of collisions. With collisions present, there <u>would</u> be fluorescence following the excitation pulse. This fluorescence can be identified with either (a) the collision-induced increase in ρ_{22} in the bare state picture or (b) the collision induced creation of ρ_{BB} in the dressed state picture.

Another way of probing the collision-induced population is to probe the second level with a second field. An example of such a technique is shown below.



$\Delta' = \omega' - \Omega'$

$\Delta = \omega - \Omega$

$|\Delta| \gg \gamma_2, ku$

Neglect atomic motion for the time being.

For fixed Δ, one monitors the population ρ_{33} as a function of Δ'.

a. Bare-State Calculation

One can ask, "where are the resonances?" It might appear that there are resonances at $\Delta' \doteq 0$ $(\omega \doteq \Omega')$ and $\Delta' + \Delta = 0$ $(\Omega + \Omega' = \omega + \omega')$. This conclusion is reinforced by looking at the density-matrix perturbation chains leading to ρ_{33}.

$$\begin{tikzcd}[column sep=small]
 & \rho_{21} \arrow[dr, "\chi^*"] & & \rho_{32} \arrow[dr, "\chi'^*"] & \\
\rho_{11} \arrow[ur, "\chi"] \arrow[dr, "\chi^*"'] & & \rho_{22} \arrow[ur, "\chi'"] \arrow[dr, "\chi'^*"'] & & \rho_{33} \\
 & \rho_{12} \arrow[ur, "\chi"'] & & \rho_{23} \arrow[ur, "\chi'"'] &
\end{tikzcd} \qquad \text{SW}$$

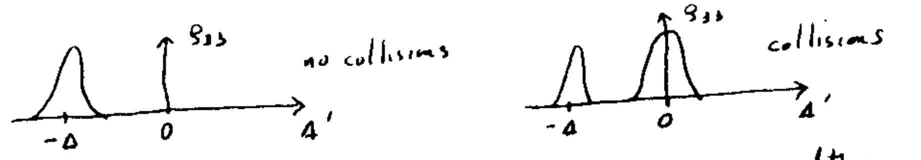
This is a step-wise (SW) chain involving the intermediate state population ρ_{22}. It contains a resonance at $\Delta' \doteq 0$.

Another chain also contributes

$$\begin{tikzcd}[column sep=small]
 & \rho_{21} \arrow[r, "\chi'"] & \rho_{31} \arrow[r, "\chi^*"] & \rho_{32} \arrow[dr, "\chi'^*"] & \\
\rho_{11} \arrow[ur, "\chi"] \arrow[dr, "\chi^*"'] & & & & \rho_{33} \\
 & \rho_{12} \arrow[r, "\chi'^*"'] & \rho_{13} \arrow[r, "\chi"'] & \rho_{23} \arrow[ur, "\chi'"'] &
\end{tikzcd} \qquad \text{TQ}$$

This is a "two-quantum" chain containing the two-photon resonance condition $(\Delta + \Delta' = 0)$ through the dependence on ρ_{13} (or ρ_{31}).

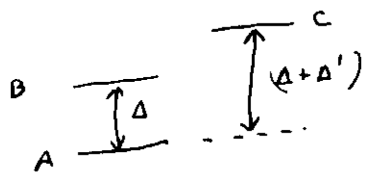
Thus it appears that both $\Delta' \doteq 0$ and $\Delta' + \Delta = 0$ resonances are present. However, when one adds the chains, the $\Delta' \doteq 0$ resonance disappears in the absence of collisions. That is



(Both resonances are Doppler broadened with widths $|\vec{k} - \vec{k}'|u$ for the TQ resonance and $k'u$ for the $\Delta' \doteq 0$ resonance). There is no simple physical picture for the disappearance of the $\Delta' \doteq 0$ resonance in this approach.

b. Dressed-State Calculation

Dressed states $|A\rangle$ and $|B\rangle$ are as before, while dressed state $|C\rangle$ is just equal to state $|3\rangle$. Since each of states $|A\rangle$ and $|B\rangle$ contains an admixture of state $|2\rangle$, both states $|A\rangle$ and $|B\rangle$ are coupled to state $|C\rangle$. An energy level diagram in the dressed picture is



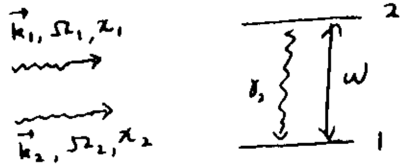
$\left|\frac{\chi}{\Delta}\right| \ll 1$

As Δ' is varied, resonances occur when state $|C\rangle$ is degenerate with state $|A\rangle$ or $|B\rangle$.

For $|C\rangle$ to be degenerate with $|A\rangle$, one must have $\Delta+\Delta'=0$ (two-photon resonance). For $|C\rangle$ to be degenerate with $|B\rangle$, one must have $\Delta'=0$ (one-photon resonance). The absence of the $\Delta'=0$ resonance in the absence of collisions is now easily understood in this dressed-atom picture. In the absence of collisions, only dressed state $|A\rangle$ is populated (assuming the atoms start in level 1 and the fields are turned on slowly). There is no mechanism to couple state $|A\rangle$ to $|B\rangle$ to make up the energy difference $\hbar\Delta$. Consequently only the C-A resonance ($\Delta+\Delta'=0$) occurs in the absence of collisions. With collisions present, the collisions provide the necessary energy to compensate for the difference $\hbar\Delta$ and to populate dressed state $|B\rangle$. Since state $|B\rangle$ is now populated, one also has the one-photon, $\Delta'=0$, resonance when state $|C\rangle$ is degenerate with state $|B\rangle$. In this picture, the $\Delta'=0$ resonance arises from a collisionally produced population of dressed state $|B\rangle$ — in the absence of collisions state $|B\rangle$ is not populated owing to conservation of energy (no mechanism to compensate for the separation $\hbar\Delta$).

B. Two-Level Atom - Two Fields

Fluorescence beats - an example of collision-induced coherence.



$\Delta_1 = \omega - \Omega_1 \qquad \left|\frac{\Delta_1}{k_1 u}\right| \gg 1$

$\Delta_2 = \omega - \Omega_2 \qquad \left|\frac{\Delta_2}{k_2 u}\right| \gg 1$

Take

$$\Omega_1 = \Omega$$
$$\Omega_2 = \Omega + \delta$$

Will calculate the "steady-state" response ρ_{22}. The population ρ_{22} can be monitored by measuring the total fluorescence from level 2. This experiment could be done using either pulsed or cw lasers. Using pulsed lasers could eliminate some background (non-collision induced terms). I will carry out the cw calculation - in principle one could also eliminate the non-collision terms in the cw case by filtering the signal and looking only for fluorescence at frequencies close to the laser frequency Ω and not close to ω. Again, both bare- and dressed atom approaches are used.

1. Bare-atom calculation

To second order in the applied fields and keeping only terms proportional to $\chi_1 \chi_2^*$ (or $\chi_1^* \chi_2$) (experimentally one can use modulation techniques to detect only this component of the signal), it is easy to use perturbation theory to derive

$$\rho_{22}(\chi_1 \chi_2) \simeq \rho_{22}(\tilde{\delta})\, e^{-i(\vec{K}\cdot\vec{R} - \delta t)} + c.c.$$

where
$$\vec{K} = \vec{k}_2 - \vec{k}_1$$
$$\tilde{\delta} = \delta - \vec{K}\cdot\vec{v}$$
$$\rho_{22}(\tilde{\delta}) = \frac{\chi_1 \chi_2^* W_0(\vec{v})}{\Delta^2}\left[1 + \frac{2\Gamma_{12}}{\gamma_2 + i\tilde{\delta}}\right]$$

It is implicitly assumed that $|\delta| \lesssim \gamma_2$. ~~Average this over space, assuming that~~ Average this over space, assuming $|\vec{K}|L \ll 1$ (L = sample length) and over velocity assuming that $|\vec{K}|u \ll \gamma_2$. Then one finds

$$\langle \rho_{22}(\chi_1 \chi_2) \rangle = \frac{\chi_1 \chi_2^*}{\Delta^2}\left(1 + \frac{2\Gamma_{12}}{\gamma_2 + i\delta}\right) e^{i\delta t} + c.c.$$

This results reminds one of the analogous result for population if δ is set equal to zero. The signal again consists of a "background" term (present in the absence of collisions) and a collision induced term proportional to Γ_{12}. The collision-induced term now exhibits a resonant structure as a function of δ. One can try to understand the physical origin of the collision-induced term. In a density matrix picture, the contribution to ρ_{22} proportional to $\chi_1 \chi_2^*$ is formed as follows:

$$\begin{tikzcd} & \rho_{12} \arrow[dr, "\chi_1"] & \\ \rho_{11} \arrow[ur, "\chi_2^*"] \arrow[dr, "\chi_1"'] & & \rho_{22} \\ & \rho_{21} \arrow[ur, "\chi_2^*"'] & \end{tikzcd}$$

top path $\dfrac{\chi_1 \chi_2^*}{\gamma_2 + i\delta}\,\dfrac{1}{\left(\frac{\gamma_2}{2} + \Gamma_{12}\right) - i(\Delta - \delta)}$

bottom path $\dfrac{\chi_1 \chi_2^*}{\gamma_2 + i\delta}\,\dfrac{1}{\left(\frac{\gamma_2}{2} + \Gamma_{12}\right) + i}$

Both the top and bottom paths lead to resonance denominators which vary as $\frac{1}{\gamma_2 + i\delta}$. However, in the absence of collisions, these two contributions just cancel one another (destructive interference). With collisions present the destructive interference is no longer complete and the resonant structure $\frac{1}{\gamma_2 + i\delta}$ emerges. This mechanism has led Bloembergen and coworkers to attribute the resonant structure to a "destruction of destructive interference."

If one measures the modulation depth of the signal $\langle \rho_{22}(\chi_1 \chi_2) \rangle_{max} - \langle \rho_{22}(\chi_1 \chi_2) \rangle_{min} = M(\chi_1 \chi_2)$, he finds

$$M(\chi_1 \chi_2) = \frac{8 |\chi_1 \chi_2^*| \Gamma_{12}}{\Delta^2 (\gamma_2^2 + \delta^2)^{1/2}}$$

valid for $\Gamma_{12} \gg \gamma_2$ or if just those fluorescence photons with frequency $\simeq \omega$ are monitored. The modulation depth has a resonant structure centered at $\delta = 0$ with FWHM equal to $2\sqrt{3}\,\gamma_2$.

2. Dressed-atom calculation

Some additional insight into the physical origin of the resonances may be obtained by using a dressed-atom approach. In a semiclassical picture, the easiest way to introduce the dressed states is to write the sum of the incident fields as a single field with a slowly-varying amplitude. In other words, let the two field frequencies be

$$\Omega_1 = \Omega - \frac{\delta}{2} \quad ; \quad \Omega_2 = \Omega + \frac{\delta}{2}$$

Then

$$\vec{E}(t) = \tfrac{1}{2} \underset{\substack{\uparrow \\ \text{polarization}}}{\hat{\epsilon}_1} E_1 e^{-i\Omega_1 t} + \tfrac{1}{2} \hat{\epsilon}_2 E_2 e^{-i\Omega_2 t} + \text{c.c.}$$

$$= \tfrac{1}{2} \vec{\mathcal{E}}(t)\, e^{-i\Omega t} + \text{c.c.}$$

where $\quad \mathcal{E}(t) = \hat{\epsilon}_1 E_1 e^{-i\frac{\delta}{2}t} + \hat{\epsilon}_2 E_2 e^{i\delta/2\, t}$.

The total field has an average frequency Ω and an amplitude that is modulated at frequency $\delta/2$.

As long as $|\delta| \ll |\Delta|$, one can still introduce dressed states in the same manner as was done for the case of constant amplitude fields. (Actually one can always define semiclassical dressed states as in the constant amplitude case; however, only for $|\delta| \ll \sqrt{\Delta^2 + |E_1|^2 + |E_2|^2}$

(secular approximation) does the dressed-atom method prove to be particularly convenient.) The calculation proceeds as for the constant amplitude case, except that the (slow) time dependence of $\mathcal{E}(t)$ must be accounted for. To second order in the applied fields one finds dressed state populations with both dc and modulated components.

$$\rule{2em}{0.4pt}\ B \qquad \rho_{BB} \sim \rho_{BB}(0) + \rho_{BB}^{+} e^{i\delta t} + \rho_{BB}^{-} e^{-i\delta t}$$

$$\rule{2em}{0.4pt}\ A \qquad \rho_{AA} \sim \rho_{AA}(0) + \rho_{AA}^{+} e^{i\delta t} + \rho_{AA}^{-} e^{-i\delta t}$$

State $|B\rangle$ is populated <u>only</u> when collisions are present. The modulated part of ρ_{BB} is proportional to $x_1 x_2^*$ (or $x_1^* x_2$) and is responsible for the collision-induced fluorescence beats. Since state A has an admixture of bare state $|2\rangle$, it also contributes to fluorescence. However, to second order in the fields, ρ_{22} varies as ρ_{AA} times a term of second order in the fields — thus, only ρ_{AA} to <u>zero</u> order in the fields contributes (to zero order in the fields, $\rho_{AA} \simeq 1$). This contribution is modulated at frequency δ, but has no resonance about $\delta = 0$ (the resonance arises only when the signal depends on a dressed state population which is itself of second order in the applied fields).

In this semiclassical picture, the resonance in the fluorescence beats arises from a collision-induced modulated population of dressed state |B>. The background term results from fluorescence from dressed state |A>.

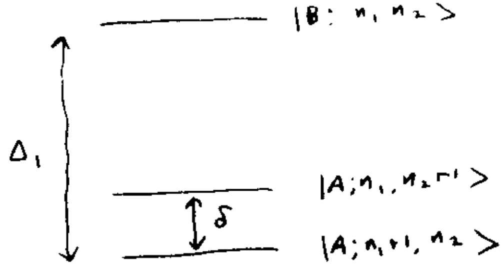
It should be noted that the fluorescence beat resonance is proportional to the product $\chi_1 \chi_2^*$. For a non-vanishing signal, the two fields must be relatively coherent. This is a feature that exists in some, but by no means all, cases of pressure-induced extra resonances.

The importance of the relative coherence of the fields is seen immediately if one uses a quantized-field dressed-atom approach to the problem. As an aside, I outline such a method. If n_1 and n_2 are photon occupation numbers for fields 1 and 2, respectively, one can define dressed states to first order in the fields as

$$|A; n_1+1, n_2\rangle = |1; n_1+1, n_2\rangle + \frac{i\chi_1}{\Delta_1}|2; n_1, n_2\rangle + \frac{i\chi_2}{\Delta_2}|2; n_1+1, n_2-1\rangle$$

$$|B; n_1, n_2\rangle = |2; n_1, n_2\rangle - \frac{i\chi_1^*}{\Delta_1}|1; n_1+1, n_2\rangle - \frac{i\chi_2^*}{\Delta_2}|1; n_1, n_2+1\rangle$$

The dressed-state energy-level diagram is

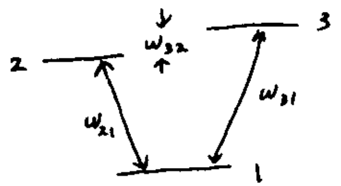


The fluorescence beat resonance now arises from the creation of excited state population $\rho_{B n_1 n_2; B n_1 n_2}$ from an initial-state coherence $\rho_{A; n_1 n_2+1; A n_1+1 n_2}$ — excitation of state |B> occurs only in the presence of collisions. The background beat signal results from fluorescence from the (zeroth-order) coherence $\rho_{A n_1 n_2+1; A n_1+1 n_2}$ since this term is linked to the bare-state population $\rho_{2 n_1 n_2; 2 n_1 n_2}$ via a second-order transformation (from bare to dressed state) matrix element. This background term appears even in the absence of collisions since it depends only on the zeroth order coherence $\rho_{A n_1 n_2+1; A n_1 n_2+1}$ which has amplitude of unity and oscillates at frequency δ.

III. Pressure-Induced Extra Resonances

Although I have discussed only collision-induced creation of populations, the fluorescence beat calculation actually serves as a prototype for most other examples of so-called pressure-induced extra resonances. For example, if the two-fields in the previous example excited a state having magnetic degeneracy, they could create a collisionally-induced Zeeman or magnetic-state coherence. Listed below are a number of situations in which pressure-induced extra resonances can be observed.

a) Four-wave mixing – 3-level atom



Fields 1+2 act on the 1-2 transition and field 3 on the 1-3 transition

Three incident fields

$\chi_1, \vec{k}_1, \Omega_1$

$\chi_2, \vec{k}_2, \Omega_2$

$\chi_3, \vec{k}_3, \Omega_3$

Take

$\Omega_1 = \Omega_2 = \Omega$

$\Omega_3 = \Omega'$

$|\Delta| = |\omega_{21} - \Omega| >> k_1 u$

$|\Delta'| = |\omega_{31} - \Omega'| >> k_3 u$

A four-wave mixing signal can be generated in the direction

$$\vec{k}_s = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$$

with frequency

$$\Omega_s = \Omega_1 + \Omega_2 - \Omega_3$$

provided phase matching $k_s = \Omega_s/c$ is satisfied.

As Ω' is varied with Ω held fixed, a pressure induced resonance is produced centered at

$$\Omega' - \omega_{31} = \Omega - \omega_{21} \quad \text{i.e.} \quad \Omega' - \Omega = \omega_{32}$$

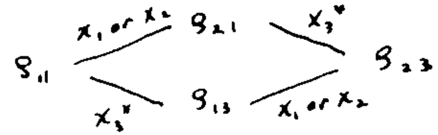
having width $\frac{\gamma_2 + \gamma_3}{2} + \Gamma_{32}$ (plus any Doppler broadening associated with the 2-3 transition). In terms of dressed states

$$|A\rangle = |1\rangle + \frac{\chi_1 \text{ or } \chi_2}{\Delta}|2\rangle + \frac{\chi_3}{\Delta'}|3\rangle$$

$$|B\rangle = |2\rangle - \frac{\chi_1^* \text{ or } \chi_2^*}{\Delta}|1\rangle$$

$$|C\rangle = |3\rangle - \frac{\chi_3^*}{\Delta'}|1\rangle ,$$

the extra-resonance can be attributed to a creation of a coherence between dressed states $|B\rangle$ and $|C\rangle$. In the bare-state picture it arises from a collisional contribution to density matrix element ρ_{23} that is proportional to $\chi_1 \chi_3^*$ (or $\chi_2 \chi_3^*$). The density matrix chain responsible for this



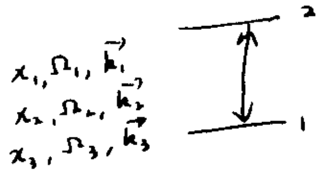
is similar to that encountered in fluorescence beats.

This is the type of resonance observed by Bloembergen and coworkers and termed a PIER4 resonance. The transition ω_{32} was a fine structure transition in Na. Since the final signal varies as $|\rho_{13}|^2$ or as $|\chi_1 \chi_2 \chi_3^*|^2$, the fields do not have to be relatively coherent for this signal to be emitted (spatial coherence over the sample length is still required). Evidence for this is seen in a quantum calculation where a four-wave mixing signal is achieved if one starts from a totally phase-incoherent Fock state $|\{n_1, n_2, n_3\}\rangle$. The four-wave mixing signal is essentially the same as that calculated using coherent states for the fields.

A modification of this experiment was carried out by E. Giacobino. The 1-3 transition was taken to be a two-photon transition in Na so that the 3-2 transition was an allowed optical transition (4D-3P). Direct emission on the 3-2 transition was produced which had a resonant structure at Ω' (two-photon transition frequency) $- \Omega = \omega_{32}$. This resonant structure occurred only in the presence of collisions.

b. Four-wave mixing – 2-level atom

A modification of the above situation occurs if one considers 4-wave mixing in a 2-level atom.



$\Omega_1 = \Omega_2 = \Omega$

$\Omega_3 = \Omega + \delta$

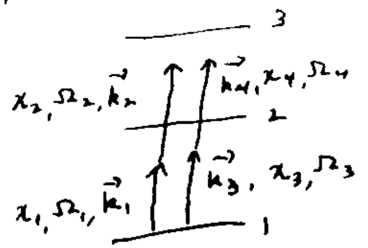
$|\Delta| = |\omega - \Omega| >> ku$

$|\delta| \lesssim \gamma_2$

A four-wave mixing signal can be produced with $\Omega_s = \Omega_1 + \Omega_2 - \Omega_3 = \Omega - \delta$ and $\vec{k}_s = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$. A collision-induced resonant structure in the four-wave mixing signal occurs at $\delta = 0$ having width equal to $2\gamma_2$. The origin of this resonance is the same as that in fluorescence beats – fields χ_1 (or χ_2) and χ_3 produce a modulated dressed-state population which, in turn, is the origin of the pressure-induced resonance. As in case (a), the fields need not be relatively coherent to produce a signal since the signal varies as $|\chi_1 \chi_2 \chi_3^*|^2$.

c. Three-level atom – four fields.

Just as it was possible to probe the upper state population using a second laser on a coupled transition, it is possible to probe the collision-induced resonances by a similar method using the level scheme below.



$\Omega_1 = \Omega \quad \Omega_3 = \Omega + \delta \quad \Omega_2 = \Omega' \quad \Omega_4 = \Omega' - \delta$

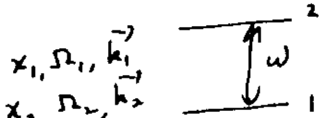
$$|\Delta| = |\omega_{21} - \Omega| >> k_1 u$$
$$|\Delta'| = |\omega_{32} - \Omega'| >> k_2 u$$
$$|\Delta + \Delta'| = |\omega_{31} - (\Omega + \Omega')| >> |\vec{k}_1 + \vec{k}_2| u$$

If one monitors the upper state population ρ_{33} as a function of δ (where $|\delta| \lesssim \gamma_2$), there is a collision-induced resonance centered at $\delta = 0$ having width $2\gamma_2$. The origin of this resonance is the same as in fluorescence beats. This method differs from 4-wave mixing in that the signal $\rho_{33} \sim \chi_1 \chi_2 \chi_3^* \chi_4^*$ — the fields must be relatively coherent to produce a nonvanishing signal. The population is spatially modulated with wave vector $\vec{k} = \vec{k}_4 - (\vec{k}_1 + \vec{k}_2 - \vec{k}_3)$. Thus, a type of "phase-matching" is achieved if $\vec{k}_4 = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$.

A variation of this scheme is to allow the fields 2 and 4 to take the atom into the continuum. Then there would be a pressure-induced resonance in the photoionization signal. To date, such 4-field experiments have not been carried out.

d. Pump-probe spectroscopy - two-level atom

One can also measure the probe absorption on a given transition driven by a "pump" field.

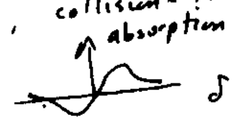


$\Omega_1 = \Omega \quad \Omega_2 = \Omega + \delta$

$|\Delta| = |\omega - \Omega| >> k_1 u$

$|\delta| \lesssim \gamma_2$

If one considers the contribution to ρ_{12} of order $|\chi_1|^2 \chi_2$, the calculation is similar to that of 4-wave mixing. In this case, however, we are calculating probe field absorption and the relative phase of the induced polarization at frequency Ω_2 to the external field χ_2 must be calculated. In the region near $\delta = 0$, collision-induced gain or absorption can be achieved



with a width of order $2\gamma_2$. Oscillation on such collision-induced gain has been seen by Grandclément et al. As in 4-wave mixing, the origin of the collision induced component is related to the creation of a modulated dressed-state population produced by fields χ_1 and χ_2.

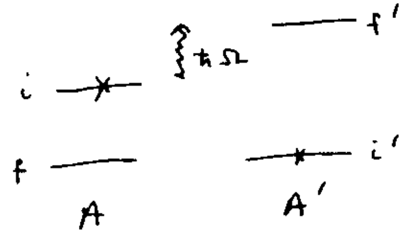
IX Laser-Assisted Collisions

CARE

Many of the collision-induced effects are really multiple-field variations of a laser-assisted collision. The process has been termed "optical collisions" or "collisionally-aided radiative excitation" CARE. The general CARE reaction is of the form $A_i + X + \hbar\Omega \to A_f + X$, where the $i \to f$ transition in atom A occurs only in the presence of collisions. The perturber-active atom translational energy compensates for the detuning Δ between the applied field and atomic transitions. One can calculate both the excited state population and magnetic polarization induced by the collisional-radiative process. It will be noted that CARE occurs for all the pressure-induced resonance level schemes discussed above – one cannot have pressure-induced resonances without CARE – they are interrelated. Those interested in a discussion of CARE are referred to the review article of Burnett. Typically, detunings in the range $|\Delta|\tau_c \gtrsim 1$ are considered (τ_c = collision duration) – that is collisions within and outside of the impact region.

LICET

In this discussion, I focus on another type of collisionally-assisted reaction, which has been termed "radiative collision," "radiatively-assisted collisional interaction" (RAIC) and "light-induced collisional energy transfer" (LICET). A typical LICET reaction is pictured below:



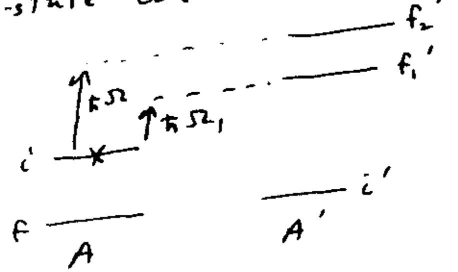
$$A_i + A'_{i'} + \hbar\Omega \to A_f + A'_{f'}$$

This is a true collisional-radiative process, requiring both the collision and field to be present simultaneous for the reaction to go. Although excitation can occur outside the impact limit [$|\Delta|\tau_c >> 1$ $\Delta = \Omega - \omega_{f'i'}$], I will restrict the discussion to the impact limit $|\Delta|\tau_c$ Also, the calculations are carried out to lowest order in the applied radiation fields.

It is possible to create either electronic or magnetic-state coherence in LICET reactions. Basically, it is the applied fields that are coherent.

Some of this coherence can be transferred to the atomic ensemble if the collision does not totally destroy the coherence that is created in the LICET reaction. In other words LICET allows some of the coherence of the fields to be transferred to the atomic medium.

An example in which LICET can create electronic-state coherence is shown below

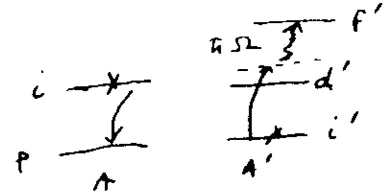


$$A_i + A'_{i'} + \hbar\Omega_1 + \hbar\Omega_2 \to A_f + A'(f_1', f_2')$$

where atom A' is left in a coherent superposition of states f_1' and f_2'. This coherence could then be monitored by applying a probe field to the atoms. An interesting question is whether or not one can excite a coherence between final states having opposite parity by this method.

The creation of final-state magnetic coherence also leads to some interesting physics. This problem is discussed in detail in my 1980 paper - for the present, I look at one specific

example of the creation of magnetic coherence via LICET. Consider the level scheme below



state f' has a number of magnetic sublevels

State d' is nearly-resonant with state i, but not so resonant as to maintain $|\omega_{id'}|\tau_c \gg 1$ (no transfer from i to d' as a result of collisions). State d' does provide the dominant channel in the LICET reaction. In a first step, the collisional interaction takes atom A from state i to f and atom A' from state i' to (virtual) state d'. The LICET reaction is completed when the applied field takes atom A' from state d' to f'! If the atoms start in an unpolarized state, then the collisional interaction, on average, produces an unpolarized intermediate state. Thus the unpolarized excitation of state f' is the same as that produced by a field acting on an unpolarized initial state d' exciting the $d'f'$ transition. Explicit calculations confirm this prediction.

Other limiting cases can be discussed in a similar way. The collisional interaction is viewed as two unpolarized multipolar fields (e.g. dipole fields for a dipole-dipole interaction) incident from all directions.

⋮

I have discussed several examples of radiative-collisional processes in which population and coherence can be produced as a result of the combined action of a collision and an applied radiation field. Some of these processes are finding applications in increasing excitation rates, providing collision-induced gain, and (possibly) explaining some features of cooled and trapped atoms.

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For general reviews of this subject area, see

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