INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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

(30 January - 24 February 1989)

TWO-PHOTON RADIATIVE COLLISIONS
PART II

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Two-photon Radiative Collisions

Intensity Induced phase Resonance

"Two-Atom" Coherence

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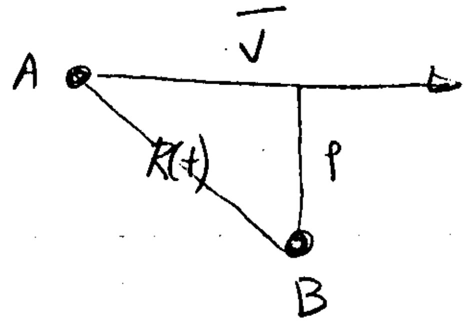
Semi-classical Treatment

Impact parameter calculation



1) Apply perturbation at fixed R or otherwise

2) Integrate over $R(t)$ for fixed ρ, $\bar{V}$

3) Integrate over ρ and $\bar{V}$

Assumptions

1) Collision must be slow compared to orbiting velocity of an outer shell electron ($10^7 - 10^8$ cm/s)

For atomic weight 1, this corresponds to KE of

$$5 \times 10^3 \text{ eV} \sim 5 \text{ KV}$$

2) Classical path validity

$$\lambda = \frac{h}{p} \ll \rho_c$$

The particle can be considered localized

Since $l = \frac{m\bar{v}\rho}{\hbar} = 2\pi\rho/\lambda$

Thus

$\rho/\lambda \gg 1$ means

$$\underline{l \gg 1}$$

In this region, quantization of the motion by the method of partial waves is most difficult to apply.

3) The change in the energy ΔE during the collision is small compared to the initial incident energy

$$\Delta E \ll E$$

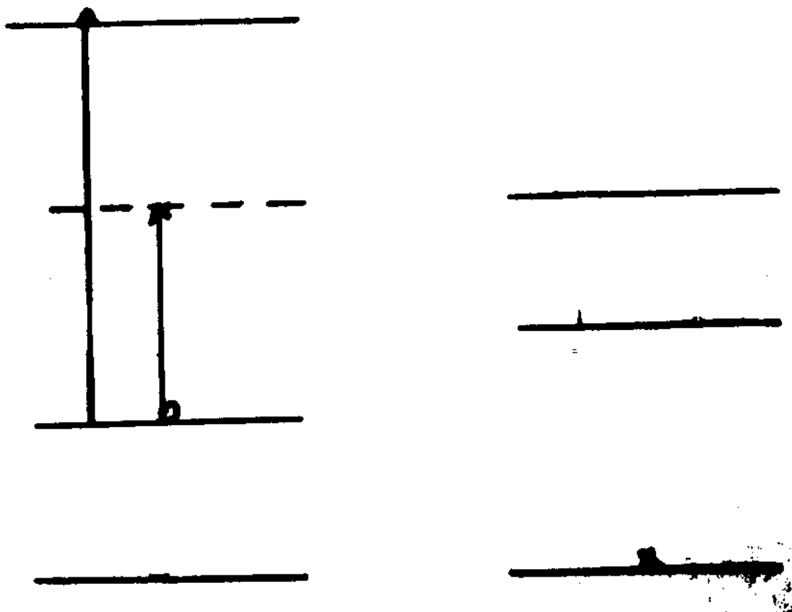
No perturbation to the orbit.

Collisions in presence of Radiation

1) Optical : Radiation is in near resonance with a transition in one of the atoms

2) Radiative : Radiation is in near resonance with difference or sum of transitions of the two atoms

There is no near resonance with any single transition of either one of them.



Atom A
initially excited

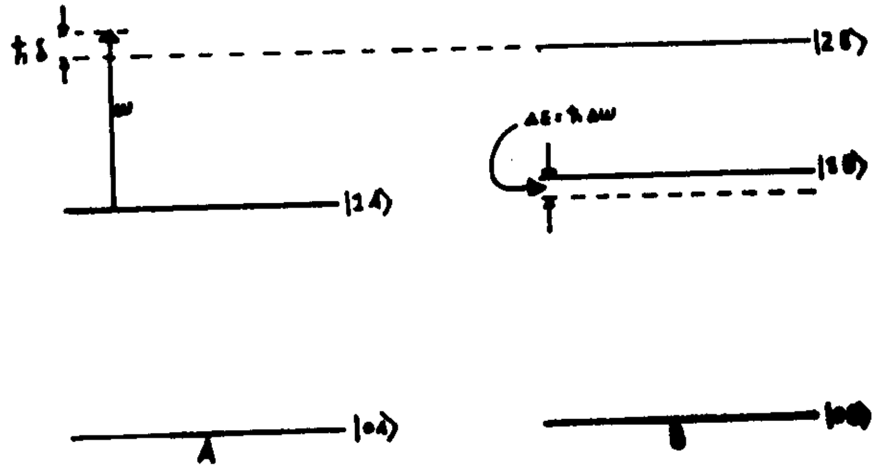
Atom B

Red : optical collision

Green :- Radiative collision

Radiative collision
Single photon

Type I



Process: Virtual collision followed by real
absorption
energy non conserving

energy non conserving
But causes final energy conservation

Expand in product states:

$u_0 \equiv |1A\rangle|0B\rangle$ $\quad \omega_0 \equiv \omega_{1A}+\omega_{0B}$

$u_1 \equiv |0A\rangle|1B\rangle$ $\quad \omega_1 \equiv \omega_{0A}+\omega_{1B}$

$u_2 \equiv |0A\rangle|2B\rangle$ $\quad \omega_2 \equiv \omega_{0A}+\omega_{2B}$

Then: $\psi(t) = a_0 e^{-i\omega_0 t} u_0 + a_1 e^{-i\omega_1 t} u_1 + a_2 e^{-i\omega_2 t} u_2$

and: $\hat{\mathcal{H}} = \hat{\mathcal{H}}_A + \hat{\mathcal{H}}_B + \hat{V}_{AB}(t) - 2\hat{\mu}_B \cdot \vec{E}_0 \cos\omega t$

so: $\mathcal{H}\psi = i\hbar \frac{d\psi}{dt}$

$$\rightarrow \quad \frac{da_0}{dt} = \frac{2i\mu_1\mu_2}{\hbar R^3(t)} e^{-i\omega_0 t} a_1$$

$$\frac{da_1}{dt} = \frac{i\mu_3 E_0}{2\hbar} e^{i(\omega-\delta)t} a_2 + \frac{2i\mu_1^*\mu_2^*}{\hbar R^3(t)} e^{i\omega_0 t} a_0$$

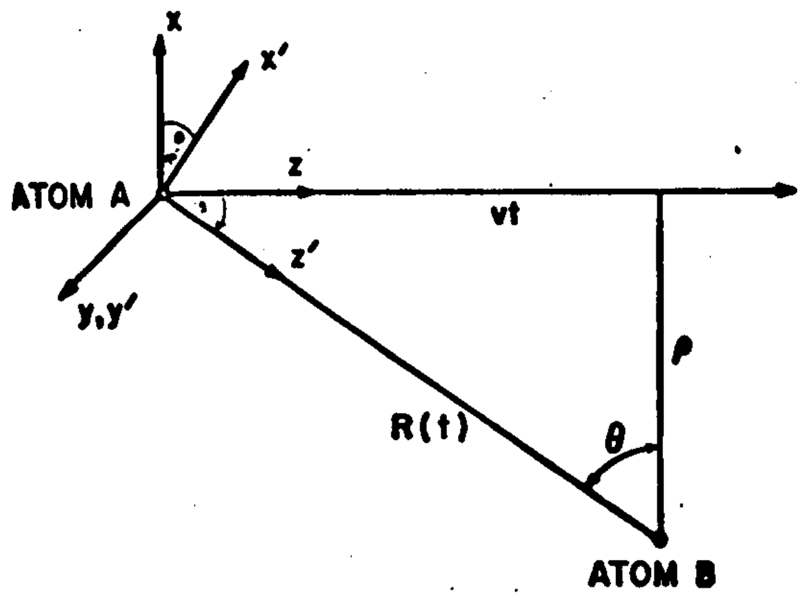
$$\frac{da_2}{dt} = \frac{i\mu_3^* E_0}{2\hbar} e^{-i(\omega-\delta)t} a_1$$

where: $\mu_1 = \langle 1A|\mu_{A}|0A\rangle$

$\mu_2 = \langle 0B|\mu_{B}|1B\rangle$

$\mu_3 = \langle 1B|\mu_{B}|2B\rangle$

$R(t) = (b^2 + v^2t^2)^{1/2}$



—Coordinate system for analysis. Atom A moves with velocity V along the Z axis. The unprimed coordinate system is fixed in space, while in the primed system the z' axis points along the internuclear axis and therefore rotates during the course of the collision.

Dipole – Dipole interaction

$$V_{AB} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{R^3}\left(x_A' x_B' + y_A' y_B' - 2 z_A' z_B' \right)$$

1) Fixed atom approximation – assumes random orientations of the two atoms – occupation of the degenerate m states is assumed to be equally probable.

2) Rotating atom approximation – P_1 and P_2 are fixed along the atom's internuclear axis.

$$V_{AB} = \frac{-2 \mu_1 \mu_2}{R^3}$$

Type of Collision	Interaction Energy	σ_{max}
dipole – dipole	$1/R^3$	$10^{-12}\ cm^2$
dipole – quadrupole	$\frac{1}{R^4}$	
quadrupole – quadrupole	$1/R^5$	$10^{-14}\ cm^2$

Adiabatic Approximation

1) Intermediate States enter through energy nonconserving interactions.

2) Their amplitudes, therefore have slow dependences on t.

3) Equations for an "Effective Two Level system" between initial and Final states can be derived by eliminating the intermediate states.

Integrate by parts

$$a_1 = \int \frac{da_1}{dt}\, dt \Longrightarrow$$

$$a_1 \cong \frac{\mu_0 E_0}{2\hbar(\Delta\omega+\delta)} e^{i(\Delta\omega+\delta)t} a_0 + \frac{2\mu_1^* \mu_2^*}{\hbar R^3(t)\,\Delta\omega} e^{i(\Delta\omega)t} a_0 + \text{terms}$$

involving derivatives of a_0, a_1 or the couplings

Van de Waal shift

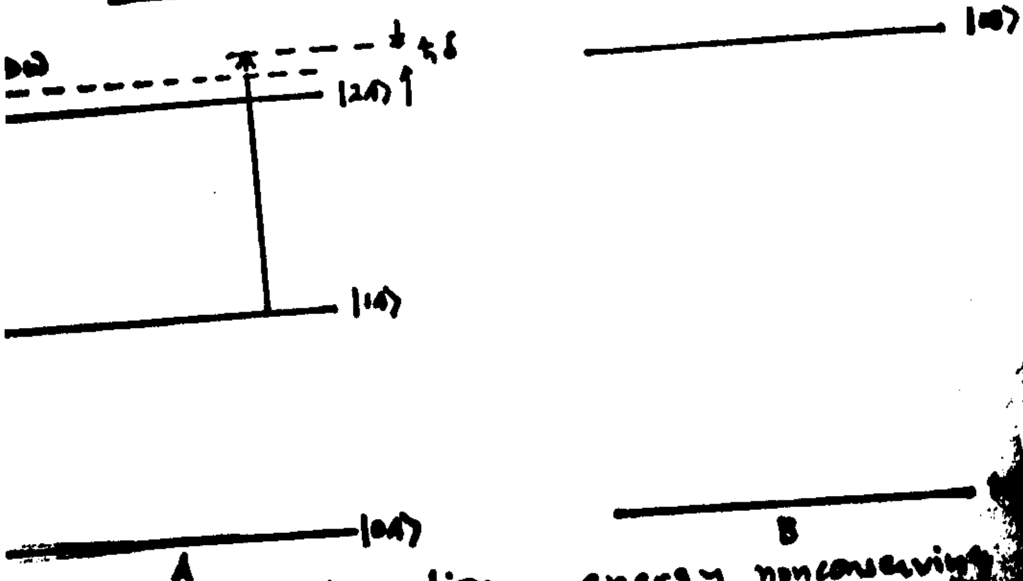
$$\frac{da_0}{dt} = \frac{4i|\mu_1|^2|\mu_2|^2}{\hbar^2\Delta\omega R^6(t)} a_0 + \frac{[illegible]\,\omega_p}{\hbar\Delta\omega R^3(t)} e^{i\delta t} a_1$$

$$\frac{da_1}{dt} = \frac{i|\omega_p|^2}{\Delta\omega} a_1 + \frac{2i\mu_1^*\mu_2^*\omega_p^*}{\hbar\Delta\omega R^3(t)} e^{-i\delta t} a_0$$

a.c Stark shift

where $\omega_p = \mu_0 E_0/2\hbar$ and $(\Delta\omega+\delta) \approx \Delta\omega$

Type 2



1) virtual absorption - energy nonconserving
2) Real colision - energy nonconserving, but causes conservation of the final energy
Following the same procedure we get:

$$\frac{da_0}{dt} = \frac{i\mu_0^* E_0}{2\hbar} e^{-i(\Delta\omega+\delta)t} a_1$$

$$\frac{da_1}{dt} = \frac{2i\mu_1^*\mu_2^*}{\hbar R^3(t)} e^{i\Delta\omega t} a_2 + \frac{i\mu_0 E_0}{2\hbar} e^{i(\Delta\omega+\delta)t} a_0$$

$$\frac{da_2}{dt} = \frac{2i\mu_1\mu_2}{\hbar R^3(t)} e^{-i\Delta\omega t} a_1$$

Integrate by parts

$$a_1 = \frac{2\mu_1^*\mu_2^*}{\hbar R^3 \Delta\omega} e^{i\Delta\omega t} a_2 + \frac{\mu_0 E_0}{2\hbar(\Delta\omega+\delta)} e^{i(\Delta\omega+\delta)t} a_0 + \text{Terms involving derivatives}$$

$$\Downarrow$$

ac Stark shift

$$\frac{da_0}{dt} = \frac{i|\Omega_p|^2}{\Delta\omega} a_0 + \frac{2i\mu_1^*\mu_2^*\,\omega_p^*}{\hbar\,\Delta\omega\,R^3(t)} e^{-i\delta t} a_2$$

$$\frac{da_2}{dt} = \frac{2i|\mu_1|^2|\mu_2|^2}{\hbar^2 R^6(t)\,\Delta\omega} a_2 + \frac{2i\mu_1\mu_2\,\omega_p}{\hbar\,\Delta\omega\,R^3(t)} a_0$$

Van de Waal shift $= \frac{1}{\hbar}\frac{C_6}{R^6}$

ak Field limit:

$$\frac{da_0}{dt} = \frac{4i|\mu_1|^2|\mu_2|^2}{\hbar^2 \Delta\omega R^6(t)} a_0$$

$$\frac{da_2}{dt} = \frac{2i\mu_1^*\mu_2^*\omega_p^*}{\hbar \Delta\omega R^3(t)} e^{-i\delta t} a_0$$

olving:

$$|a_2(\infty,b,\delta,v)|^2 = \frac{C_6|\omega_p|^2}{\hbar\Delta\omega}\left|\int_0^\infty \frac{dt'}{R^3(t')}\cos\left[\frac{C_6}{\hbar}\int_0^{t'}\frac{dt''}{R^6(t'')} - \delta t'\right]\right|^2$$

ross section:

$$\sigma(v,\delta,B_0) = \int_0^\infty 2\pi b\,|a_2(\infty,b,\delta,v)|^2\,db$$

ually This cross section is averaged over a oltzman distribution and Then The resulting rmula reduced To a dimensionless form itable for numerical work.

1) $|a_2|^2 \propto I$ one photon process

2) $\frac{1}{R^3}$ amplitude term gets larger as the impact parameter gets smaller since $R^2 = \rho^2 + v^2t^2$

3) The phase $\phi(t') = \frac{C_6}{\hbar}\int^{t'}\frac{dt''}{R^6(t'')}$ grows as ρ decreases.

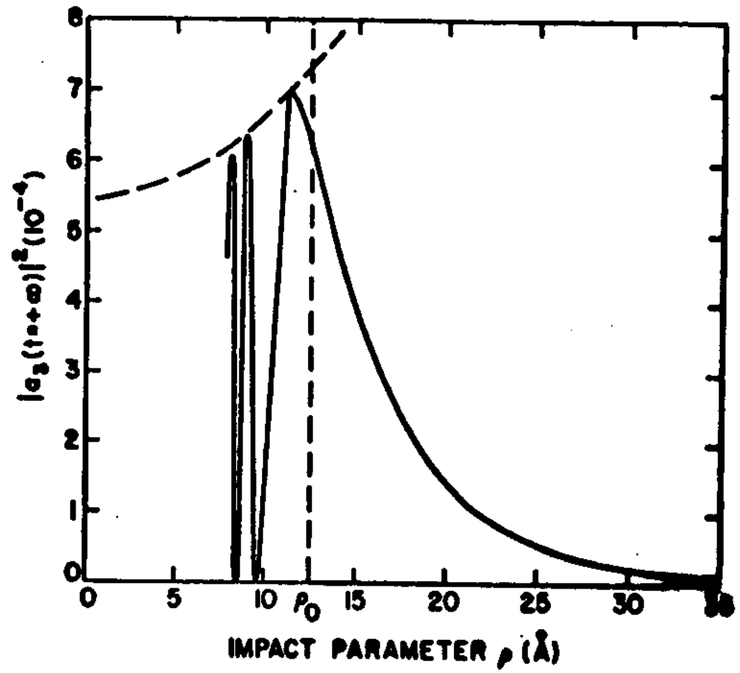
$\phi(t')$ is the phase accumulated with respect to the initial state as a result of the collision.

4) For a given $\delta \neq 0$ and ρ_0 $(\phi - \delta t) = \phi'$ vanishes at one instant of time. ϕ' of atoms approaching at other impact parameters will not vanish at this time.

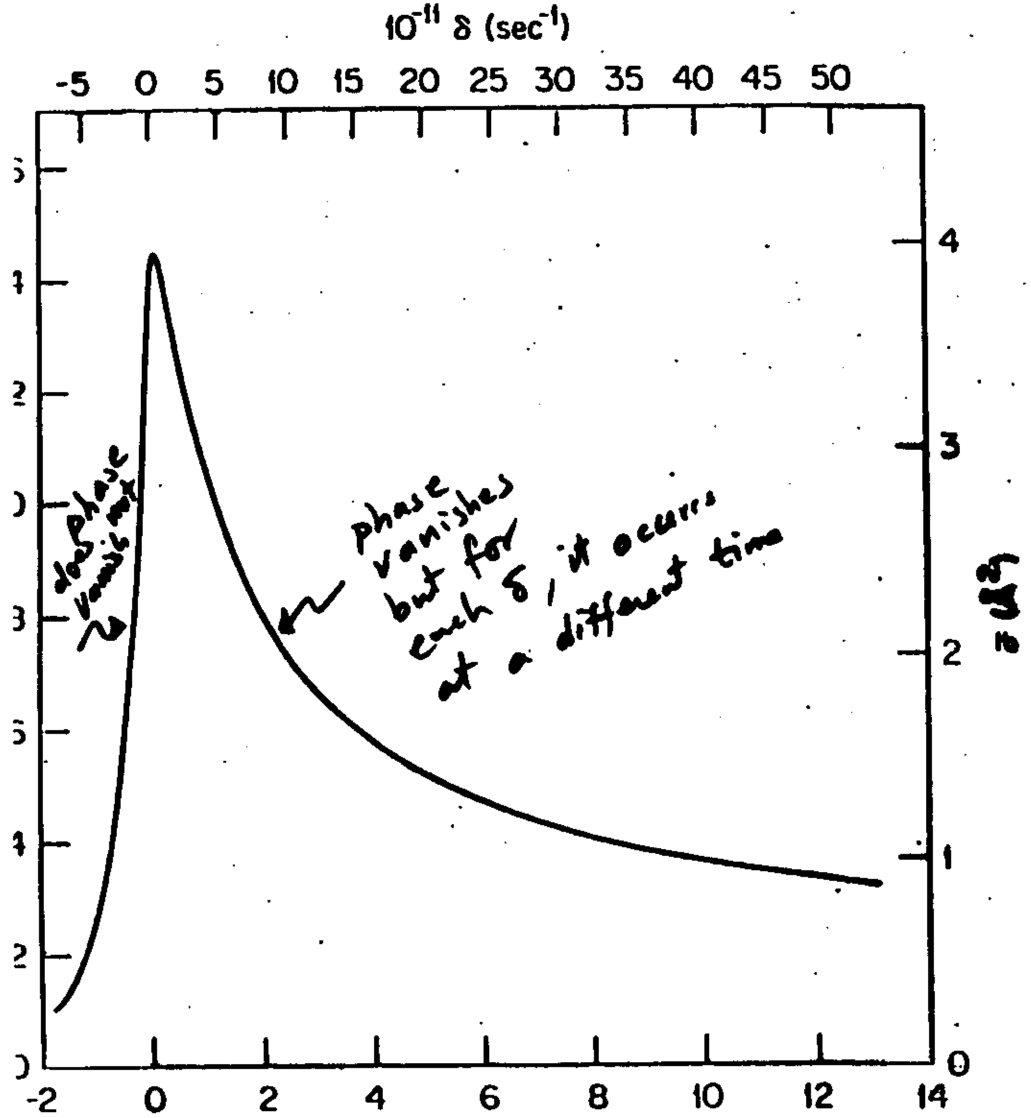
5) The atoms interact much more strongly when the phase difference $\phi' = \phi - \delta t$ vanishes.

6) For negative δ, there is no possibility for ϕ' to vanish.

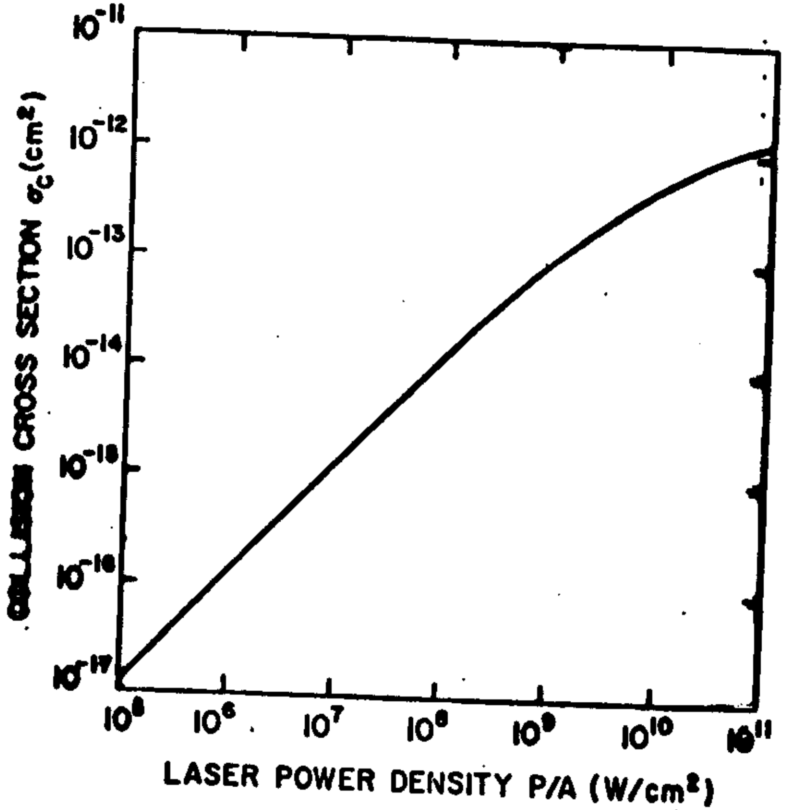
7) For a given δ, the cross section or $|a_2|^2$ behaves as follows as a function of impact parameter.



—Collision transition probability as a function of impact parameter ρ for the Sr-Ca system of Eq. (2.17). The laser is assumed to be tuned to line center ($\delta\omega = 0$), and to have a power density of $P/A = 5 \times 10^5$ W/cm^2. The dotted line shows the position of the relative Weisskopf radius ρ_0



Power Dependence



—Collision cross section versus laser power density. The incident laser is assumed to be tuned to line center. Constants used are those of the Sr-Ca example.

A quick estimate

otal phase accumulated :

$$\frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{C_6}{R^6(t)}\,dt = \frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{C_6}{(\rho_{om}^2+v^2t^2)^3}\,dt$$

$$= \frac{3\pi}{8\hbar}\,\frac{1}{\rho_{om}^5\,\bar{v}}$$

Weisskopf Radius

$\phi \leq 1$ radian $\Longrightarrow \rho_{om} = \left(\frac{3\pi}{8}\,\frac{1}{v}\,\frac{C_6}{\hbar}\right)$

* $\rho \gg \rho_{om}$ Cross section is not oscillatory and maximizes at $\sim \rho_{om}$
* $\rho < \rho_{om}$ cross section oscillates

Weisskopf Radius

Minimum impact parameter such that the accumulated phase retardation during a single transit of atoms is no greater than one radian

$$\frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{C_6}{R^6(t)}\,dt = \frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{C_6}{(\rho_{om}^2+v^2t^2)^3}\,dt \leq 1$$

But $\displaystyle\int_{-\infty}^{\infty}\frac{C_6}{R^6}\,dt = \frac{3\pi}{8}\,\frac{1}{\rho_{om}^5\,v}$

We find that

$$\rho_{om} = \left(\frac{3\pi}{8}\,\frac{1}{v}\,\frac{C_6}{\hbar}\right)^{1/5}$$

Radiative Collisions

Two-photons

1) Type I : one collisional interaction

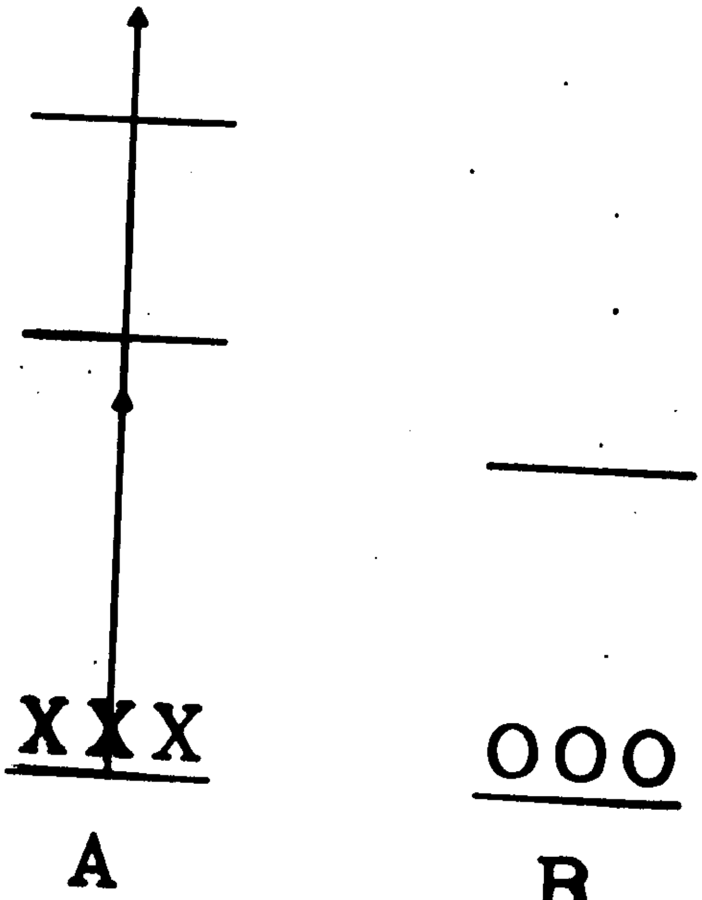
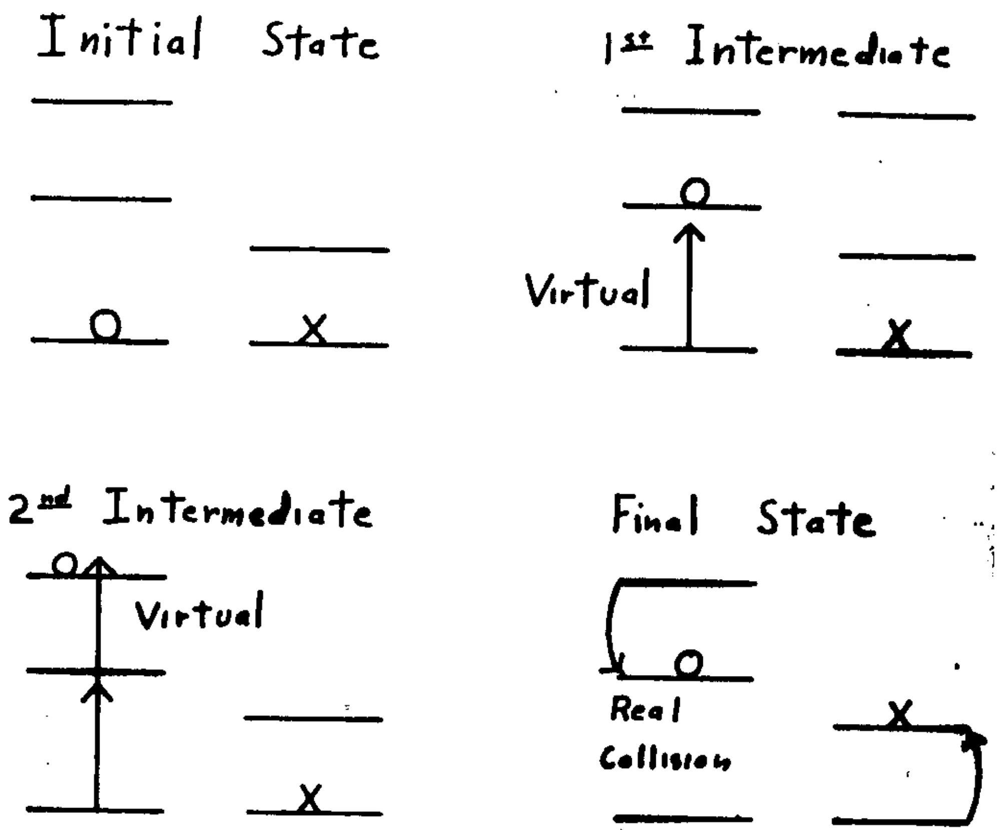


Fig 1(a)

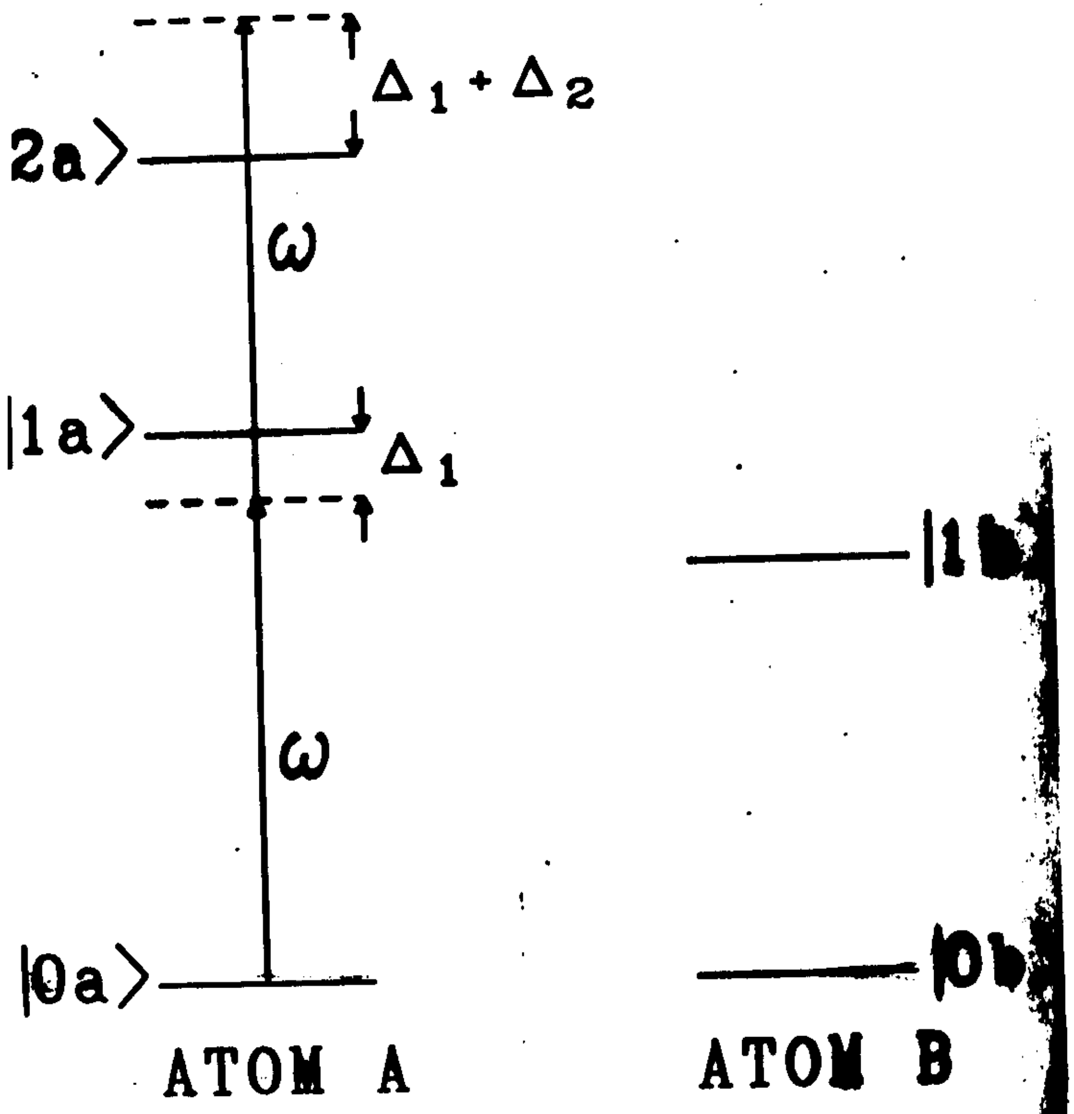


1) 4 states are involved

2) 1 atom is radiatively active

3) 1 collisional interaction - real

4) Both atoms are initially in their ground

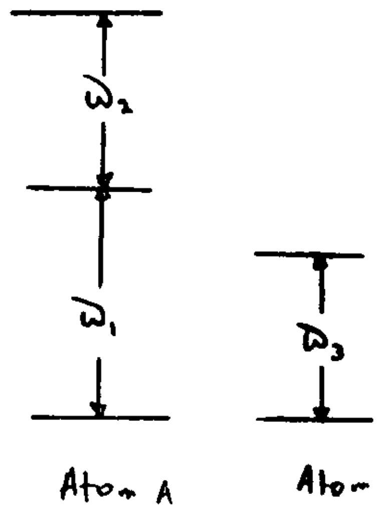


Radiatively active Fig 2(a)

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB} - \hat{\mu}_A \cdot \vec{\mathcal{E}} - \hat{\mu}_B \cdot \vec{\mathcal{E}}$$

<u>Product states</u>   <u>One collision case</u>

$$\begin{aligned} |\psi(t)\rangle = {} & a_0(t)|0a\rangle|0b\rangle \\ & + a_1(t)|1a\rangle|0b\rangle\, e^{i\omega_1 t} \\ & + a_2(t)|2a\rangle|0b\rangle\, e^{i(\omega_1+\omega_2)t} \\ & + a_3(t)|1a\rangle|1b\rangle\, e^{i(\omega_1+\omega_3)t} \end{aligned}$$



$$\frac{da_0}{dt} = i\mu_{1A}E_0 e^{i\Delta_1 t} a_1$$

$$\frac{da_1}{dt} = i\mu_{1A}^* E_0 e^{-i\Delta_1 t} a_0 + i\mu_{2A}E_0 e^{i\Delta_2 t} a_2$$

$$\frac{da_2}{dt} = i\mu_{2A}^* E_0 e^{-i\Delta_2 t} a_1 + iV_2 e^{i\Delta_0' t} a_3$$

$$\frac{da_3}{dt} = iV_2^* e^{-i\Delta_0' t} a_2$$

Adiabatic following of a_1 and a_2 :

$$a_1 \cong -\frac{\mu_{1A}^* E_0}{\Delta_1} e^{-i\Delta_1 t} a_0 + \frac{\mu_{2A}E_0}{\Delta_2} e^{i\Delta_2 t} a_2 + \cdots$$

$$\frac{da_2}{dt} = i\overbrace{\frac{|\mu_{2A}|^2 E_0^2}{\Delta_2}}^{S_2} a_2 - i\frac{\mu_{1A}^*\mu_{2A}^*}{\Delta_1} E_0^2 e^{-i(\Delta_1+\Delta_2)t} a_0 + iV_2 e^{i\Delta_0' t} a_3$$

$$a_2 \cong \frac{\mu_{1A}^*\mu_{2A}^* E_0^2}{\Delta_1+\Delta_2+S_2} e^{-i(\Delta_1+\Delta_2)t} a_0 + \frac{V_2}{\Delta_0'-S_2} e^{i\Delta_0' t} a_3 + \cdots$$

Two-photon - One Collision

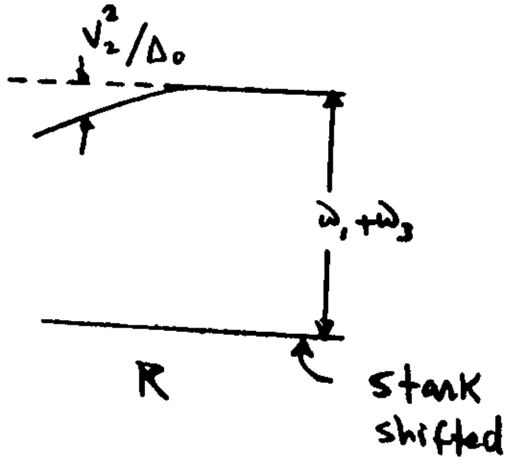
a.c Stark

$$\frac{da_0}{dt} + i(b_1' E_0^2 + b_2' E_0^4) a_0 = i c_0' E_0^2 V_2 e^{i\delta t} a_3$$

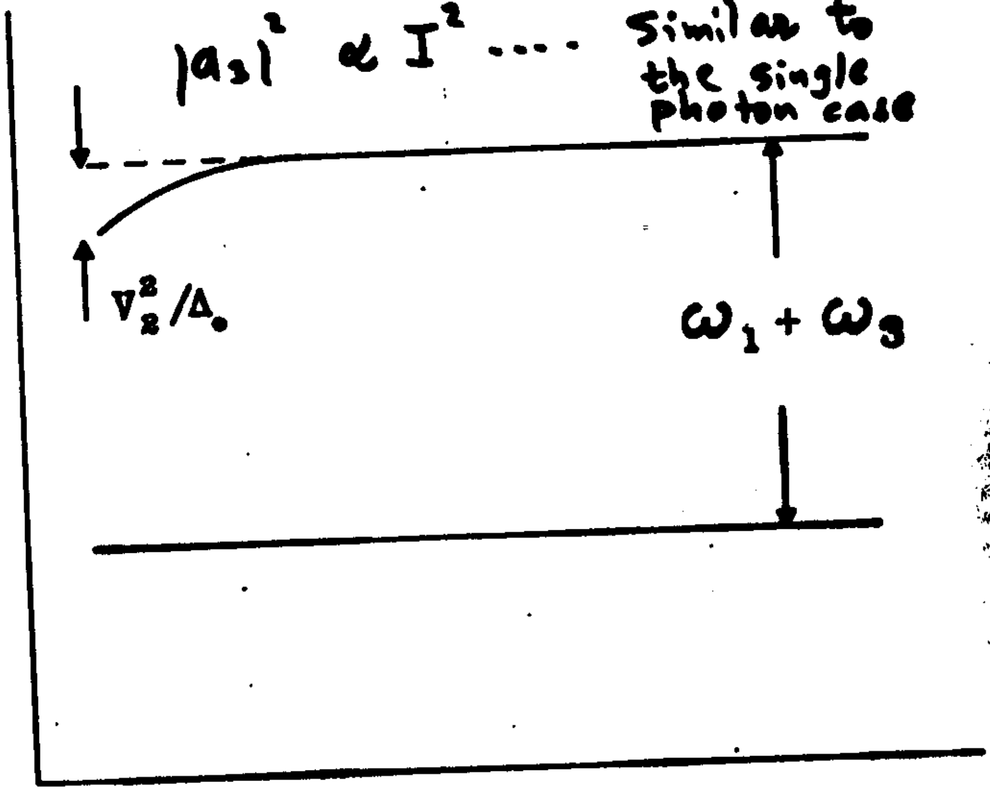
Van der Waal

$$\frac{da_3}{dt} + i\left(\frac{V_2^2}{\Delta_0}\right) a_3 = i c_3' E_0^2 V_2 e^{-i\delta t} a_0$$

$$V_2 = 2\frac{\mu_{2A}\,\mu_{1B}}{\hbar R^3(t)}$$ dipole-dipole



$$|a_3|^2 = 4\alpha^2 E_0^4 \left| \int_0^\infty \frac{1}{R^3(t')} \cos\left[\int_0^{t'} \left(\frac{C_6}{\hbar R^6} - \delta \right) d\bar{t} \right] dt' \right|^2$$



INTERATOMIC RADIUS, R

Fig 3

Type 2 : Two collisional interactions

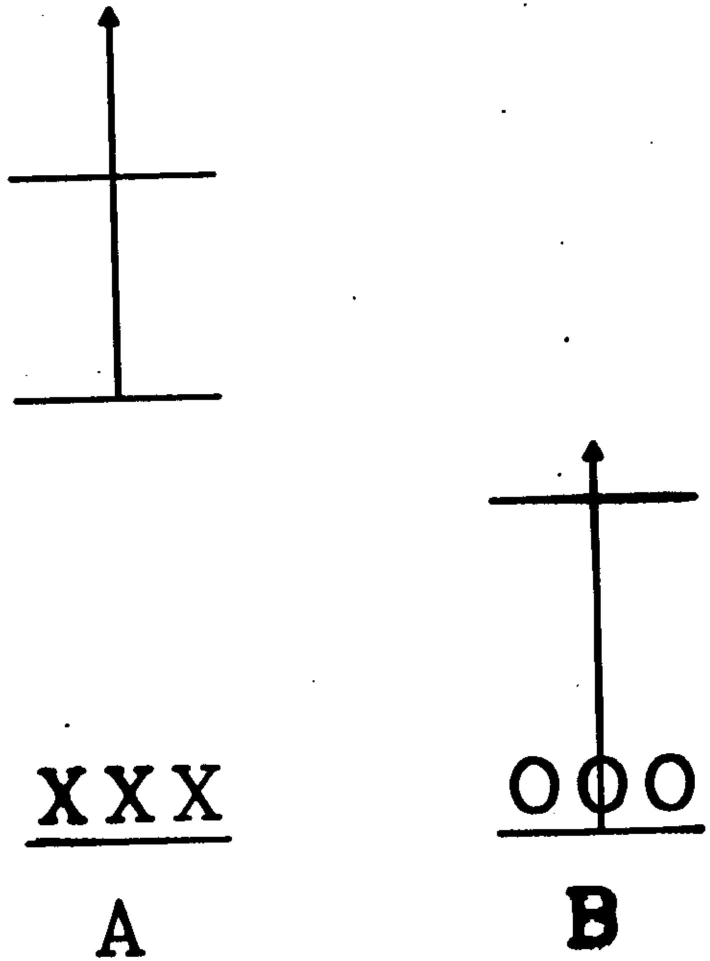


Fig 1 (b)

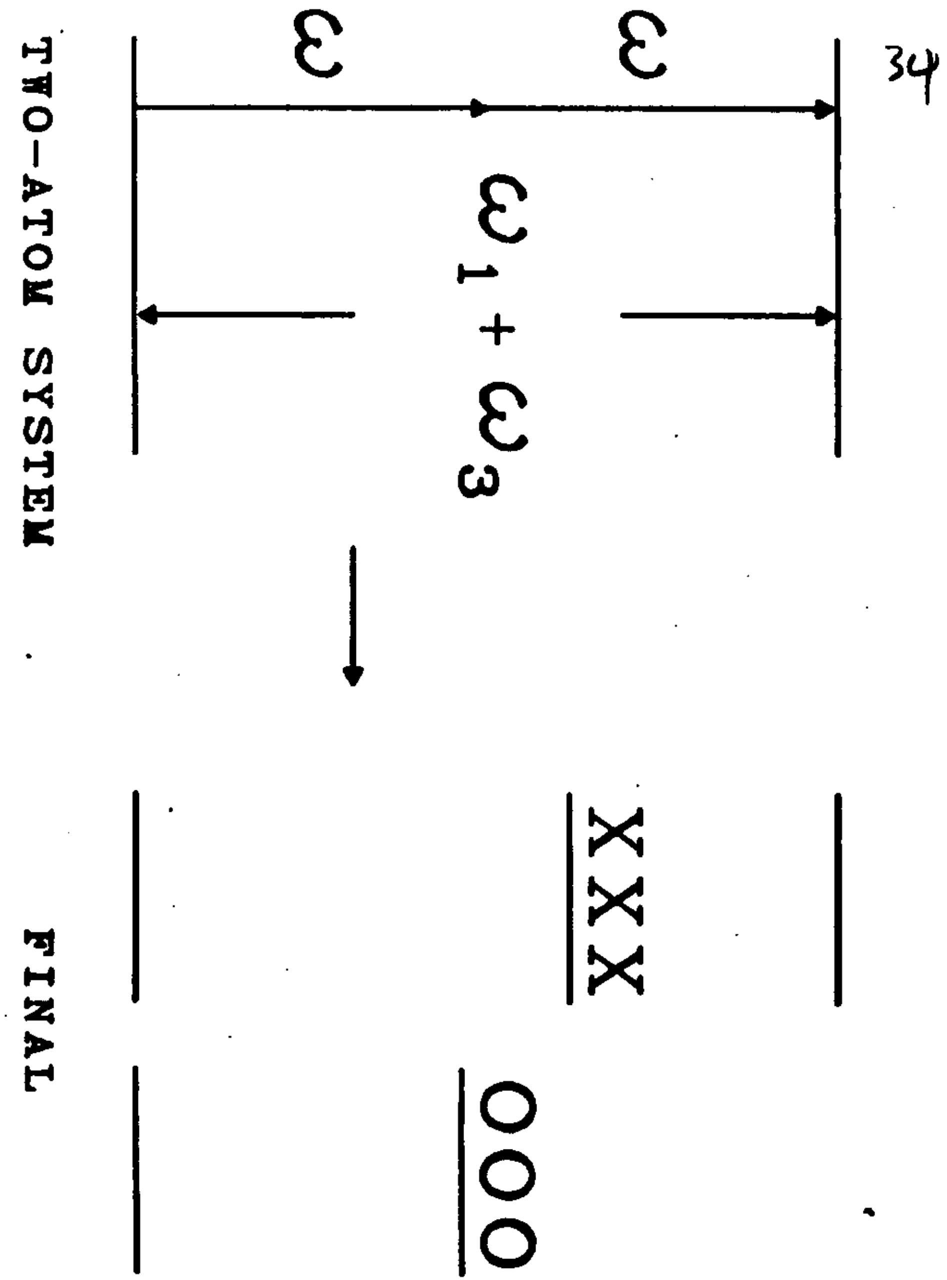
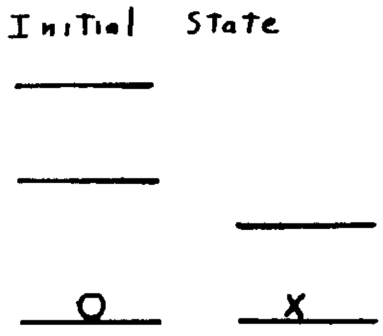
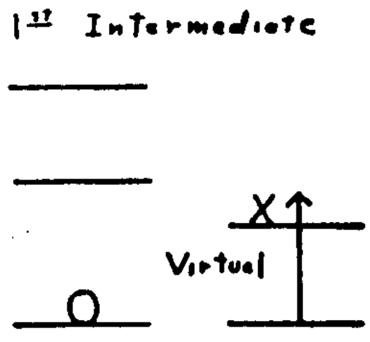
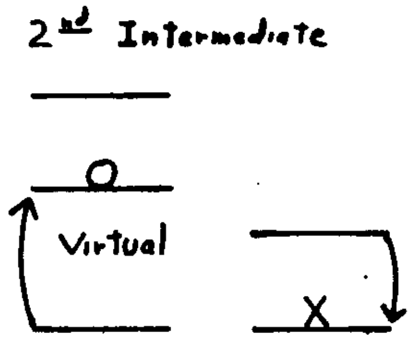
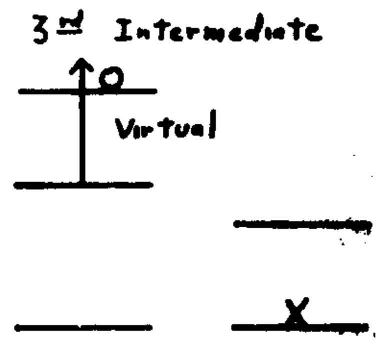


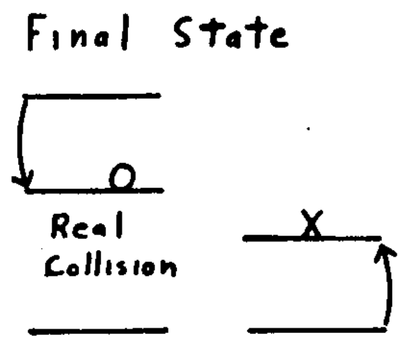
Fig 12











Both atoms are initially unexcited

1) 5 States

2) 2 atoms Radiatively active

3) 2 Collisonal Interactions
1 Real and 1 Virtual

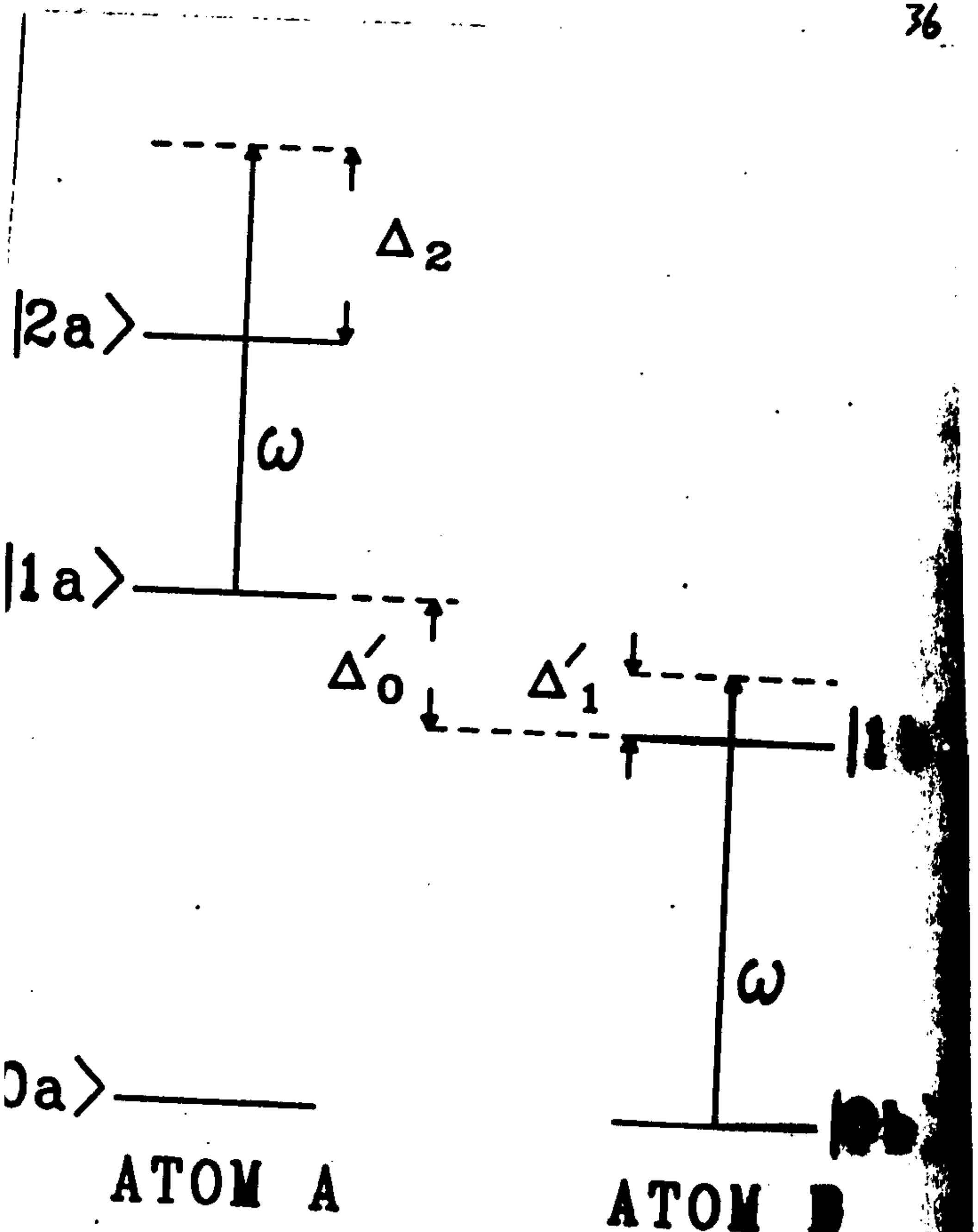


Fig 4 (a)

$$a_1 \cong -\frac{\mu_{1B}^* E_0}{\Delta_1'} e^{-\Delta_1' t} a_0 - \frac{V_1}{\Delta_0'} e^{-i\Delta_0' t} a_2$$

$$\frac{da_2}{dt} = -i\overbrace{\frac{|V_1|^2}{\Delta_0'}}^{W_2} a_2 - i\frac{\mu_{1B}^* E_0 V_1^*}{\Delta_1'} e^{i(\Delta_0'-\Delta_1')} a_0$$

$$+ i\mu_{2A} E_0 e^{i\Delta_2 t} a_2'$$

$$a_2 \cong -\frac{\mu_{1B}^* E_0 V_1^*}{\Delta_1'(\Delta_0'-\Delta_1'-W_2)} e^{i(\Delta_0'-\Delta_1')} a_0$$

$$+ \frac{\mu_{2A} E_0}{\Delta_2+W_2} e^{i\Delta_2 t} a_2'$$

$$\frac{da_2'}{dt} = \overbrace{i\frac{|\mu_{2A}|^2 E_0^2}{\Delta_2+W_2}}^{S_2'} a_2' - \frac{i\mu_{1B}^* \mu_{2A}^* E_0^2 V_1^*}{\Delta_1'(\Delta_0'-\Delta_1'-W_2)} e^{i(\Delta_0'-\Delta_1'-\Delta_2)t} a_0$$

$$+ iV_2 e^{-i\Delta_0 t} a_3$$

$$a_2' \cong \frac{-\mu_{1B}^* \mu_{2A}^* E_0^2 V_1^*}{\Delta_1'(\Delta_0'-\Delta_1'-W_2)(\Delta_0'-\Delta_1'-\Delta_2+S_2')} e^{i(\Delta_0'-\Delta_1'-\Delta_2)t} a_0$$

$$- \frac{V_2}{\Delta_0+S_2'} e^{-i\Delta_0 t} a_3$$

$$\Psi = |0a\rangle|0b\rangle\, a_0(t)$$
$$+\, |0a\rangle|1b\rangle\, e^{i\omega_3 t}\, a_1(t)$$
$$+\, |1a\rangle|0b\rangle\, e^{i\omega_1 t}\, a_2(t)$$
$$+\, |2a\rangle|0b\rangle\, e^{i(\omega_1+\omega_2)t}\, a_2'(t)$$
$$+\, |1a\rangle|1b\rangle\, e^{i(\omega_1+\omega_3)t}\, a_3(t)$$

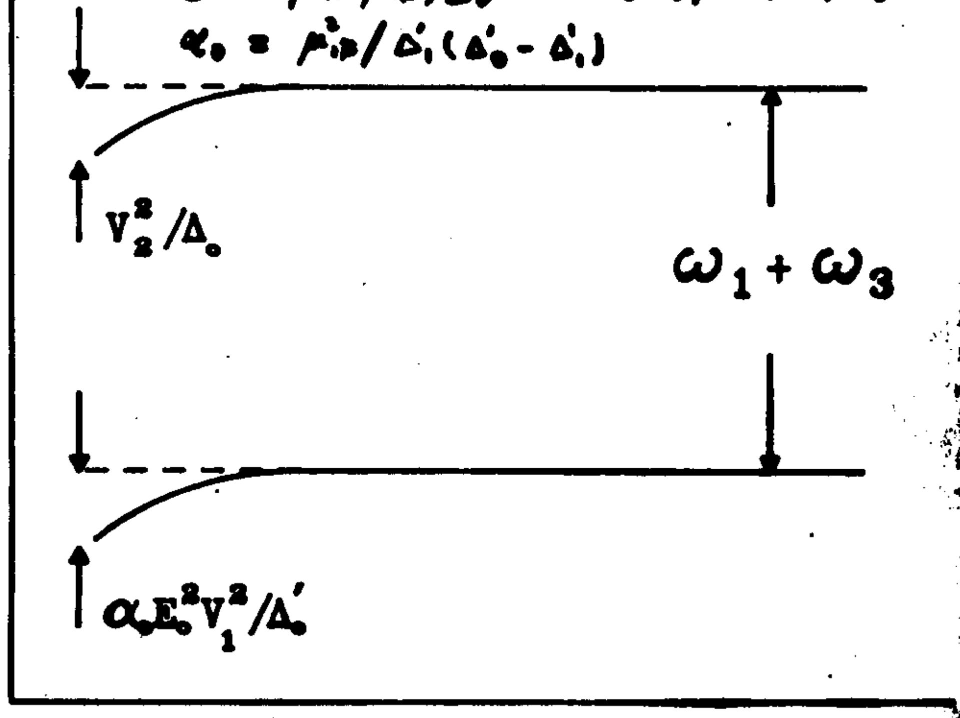
Substituting Ψ in Schrödinger Eq.

$$\frac{da_0}{dt} = i\mu_{1B} E_0\, e^{i\Delta_1' t}\, a_1$$
$$\frac{da_1}{dt} = i\mu_{1B}^* E_0\, e^{-i\Delta_1' t}\, a_0 + iV_1\, e^{-i\Delta_0' t}\, a_2$$
$$\frac{da_2}{dt} = iV_1^*\, e^{i\Delta_0' t}\, a_1 + i\mu_{2A} E_0\, e^{i\Delta_2 t}\, a_2'$$
$$\frac{da_2'}{dt} = i\mu_{2A}^* E_0\, e^{-i\Delta_2 t}\, a_2 + iV_2\, e^{-i\Delta_0 t}\, a_3$$
$$\frac{da_3}{dt} = iV_2^*\, e^{i\Delta_0 t}\, a_2'$$

$$\sigma = 4\alpha'^2 E_0^4 \left| \int_0^\infty R^{-6} \cos\left[\int_0^t (c' R^{-6} - \delta)\, dt' \right] dt \right|^2$$

$$c' = \hbar^{-1} \mu_{0A}^2 \mu_{1B}^2/\Delta_0 - \hbar^{-2} \alpha_0 E_0^2 \mu_{1B}^2 \mu_{1A}^2/\Delta_0'$$

$$\alpha_0 = \mu_{1B}^2/\Delta_1'(\Delta_0' - \Delta_1')$$



INTERATOMIC RADIUS, R

Fig 5

Nature of phase-Resonance

1) Energy nonconserving electromagnetic interactions → a.c Stark shifts

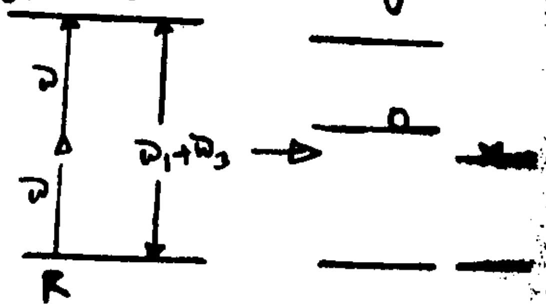
2) Energy nonconserving collisional interactions → Collisional dephasing shift (e.g $\frac{C_6}{R^6}$)

3) A sequence of these two oc coherently (Such as that in two-Colli case) → mixed a.c Stark and Collisional shift (e.g $\frac{\alpha E_0^2}{R^6}$)
Intensity modulated collisional shift

"Two-Atom" Coherence

At phase Resonance, the dephasing effects in the "two-atom" system caused by the collisional interactions are eliminated.

1) Potential curves become parallel
2) Transition frequency of the system becomes independent of R.
3) The "two-atom" system, then interacts coherently with the E.M. field over a wide range of R.
4) Enhansment of σ
5) The line shape becomes symmetric

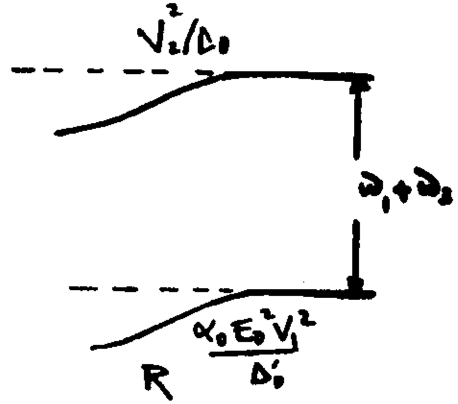


Two-photon – Two Collision

intensity modulated

$$\frac{da_0}{dt} + i\left(S_1 + \frac{\alpha_0 E_0^2 V_1^2}{\Delta_0'}\right)a_0 = i C_0 E_0^2 V_1 V_2 e^{i\delta t} a_2$$

$$\frac{da_3}{dt} + i\left(\frac{V_2^2}{\Delta_0}\right)a_3 = C_1 E_0^2 V_1^* V_2^* e^{-i\delta t} a_0$$



Phase Resonance

$$\alpha_0 E_0^2 \frac{V_1^2}{\Delta_0'} = \frac{V_2^2}{\Delta_0} \longrightarrow \text{Parallel potential curves}$$

Provided: ~~both~~ V_1 and V_2 are dipole-dipole ~~or~~ dipole-quadrupole, etc.

Intensity dependence of absolute cross section

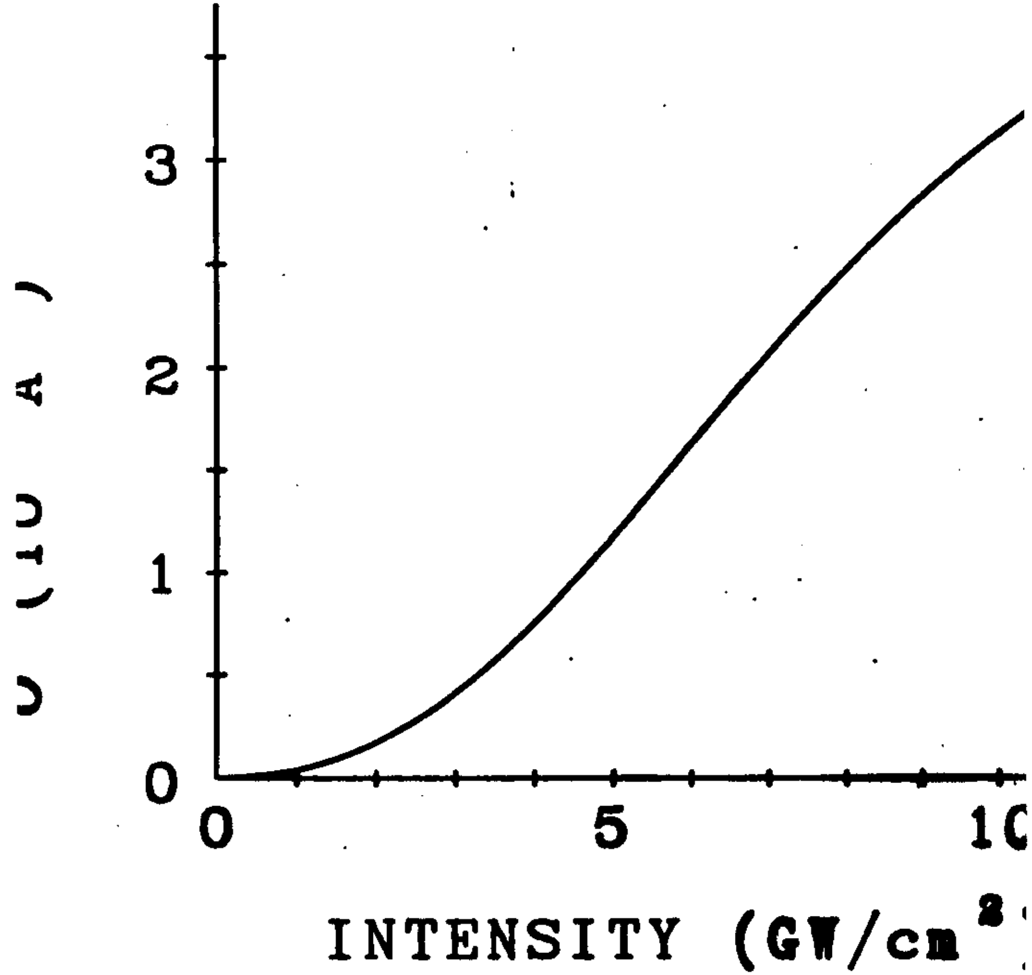


Fig 9

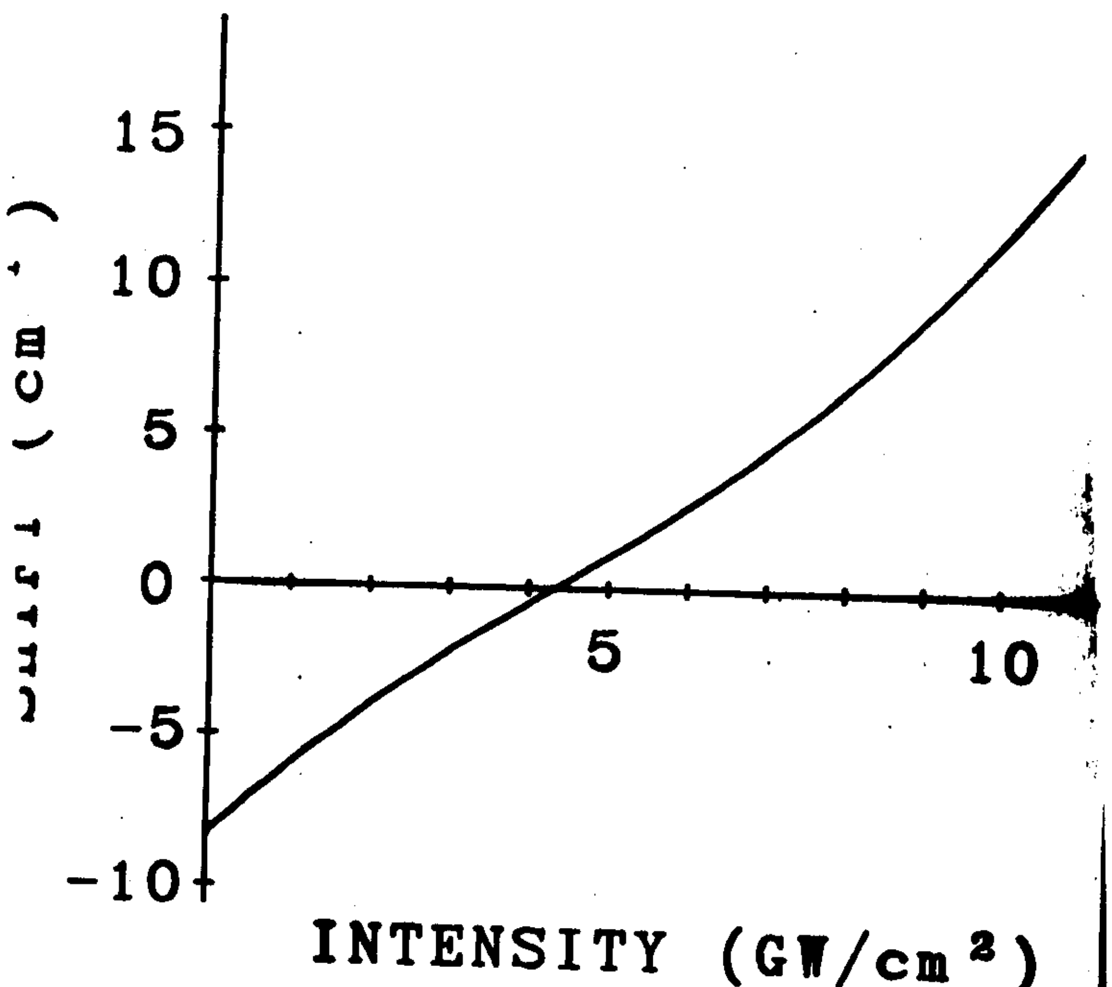


Fig 8

Intensity dependence
of normalized crossection

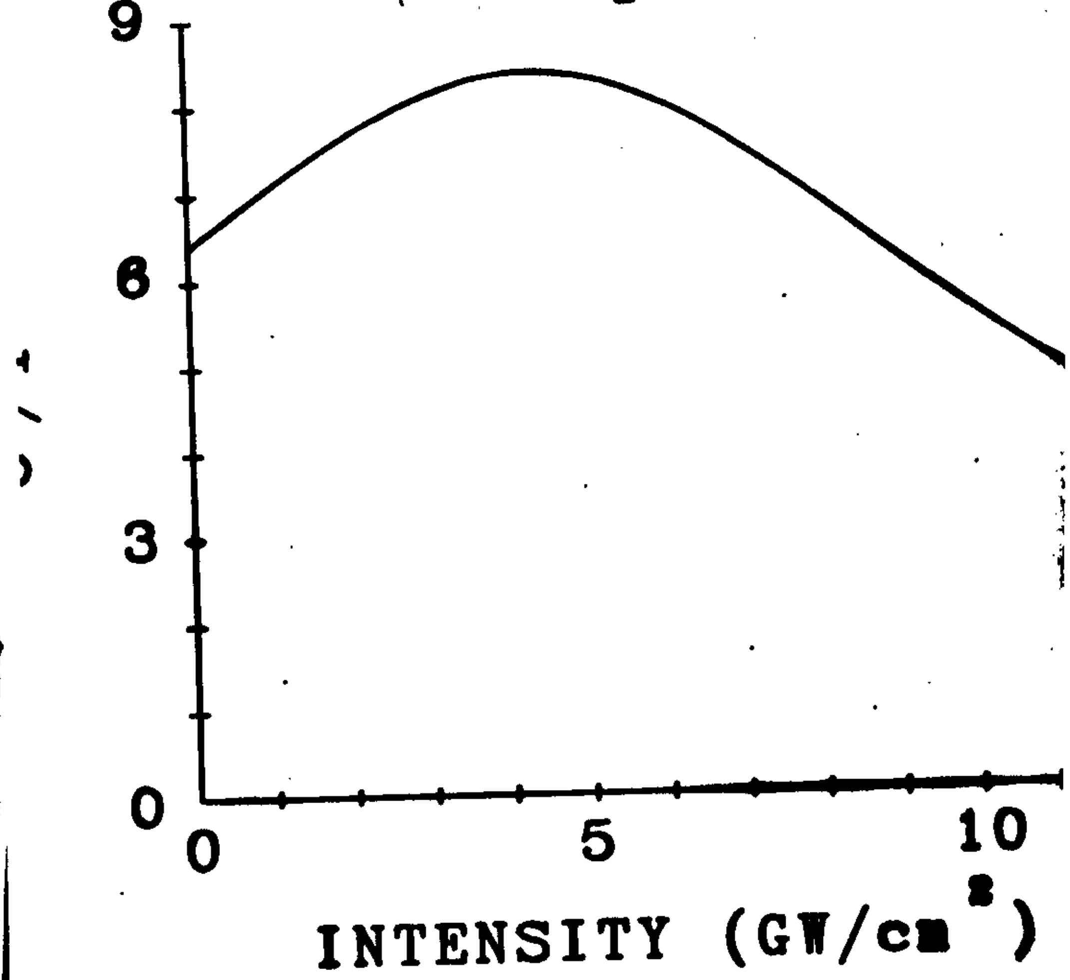


Fig 10

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$$\sigma = 4 d'^2 E_0^4 \left| \int_p^{\infty} \frac{1}{R^6} \cos \int_0^t \left(\frac{C'}{R^6} - \delta \right) dt \right|^2$$

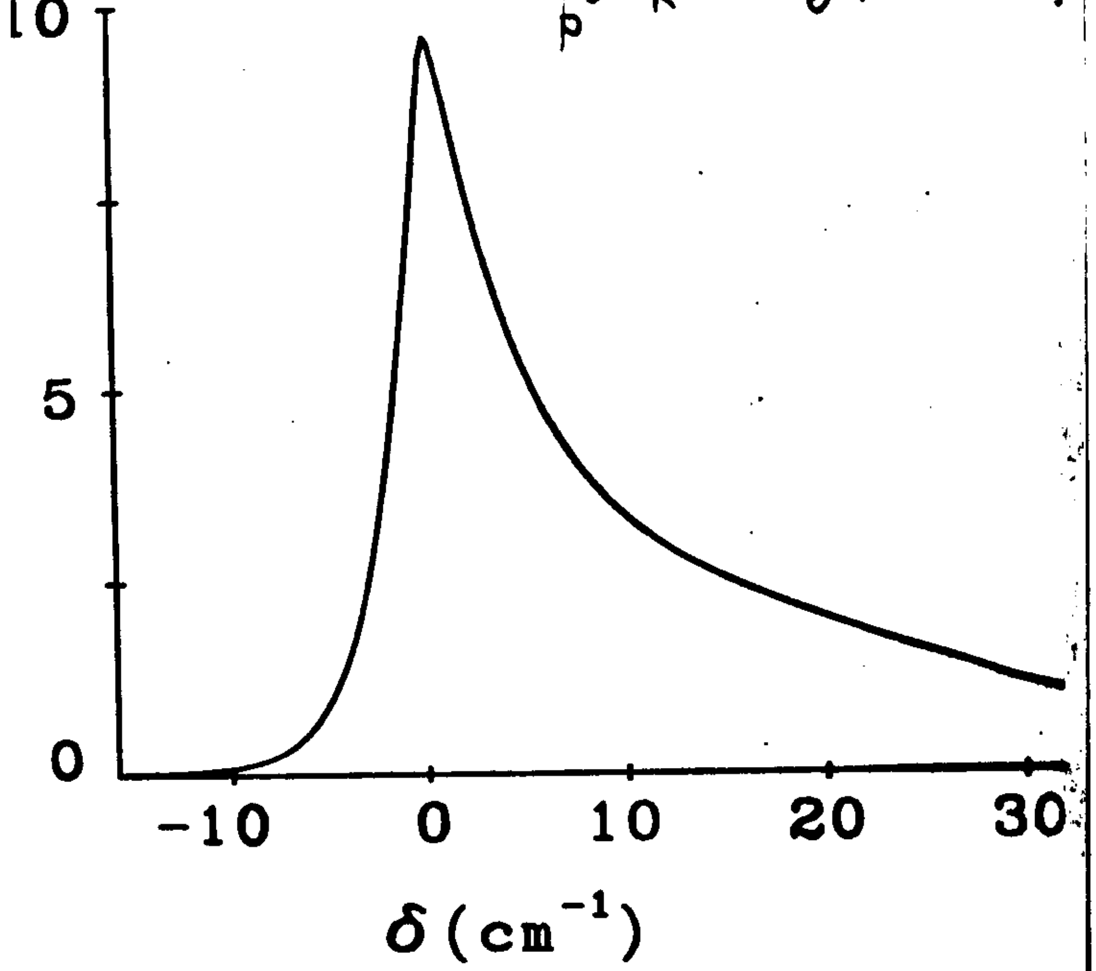

Fig 6

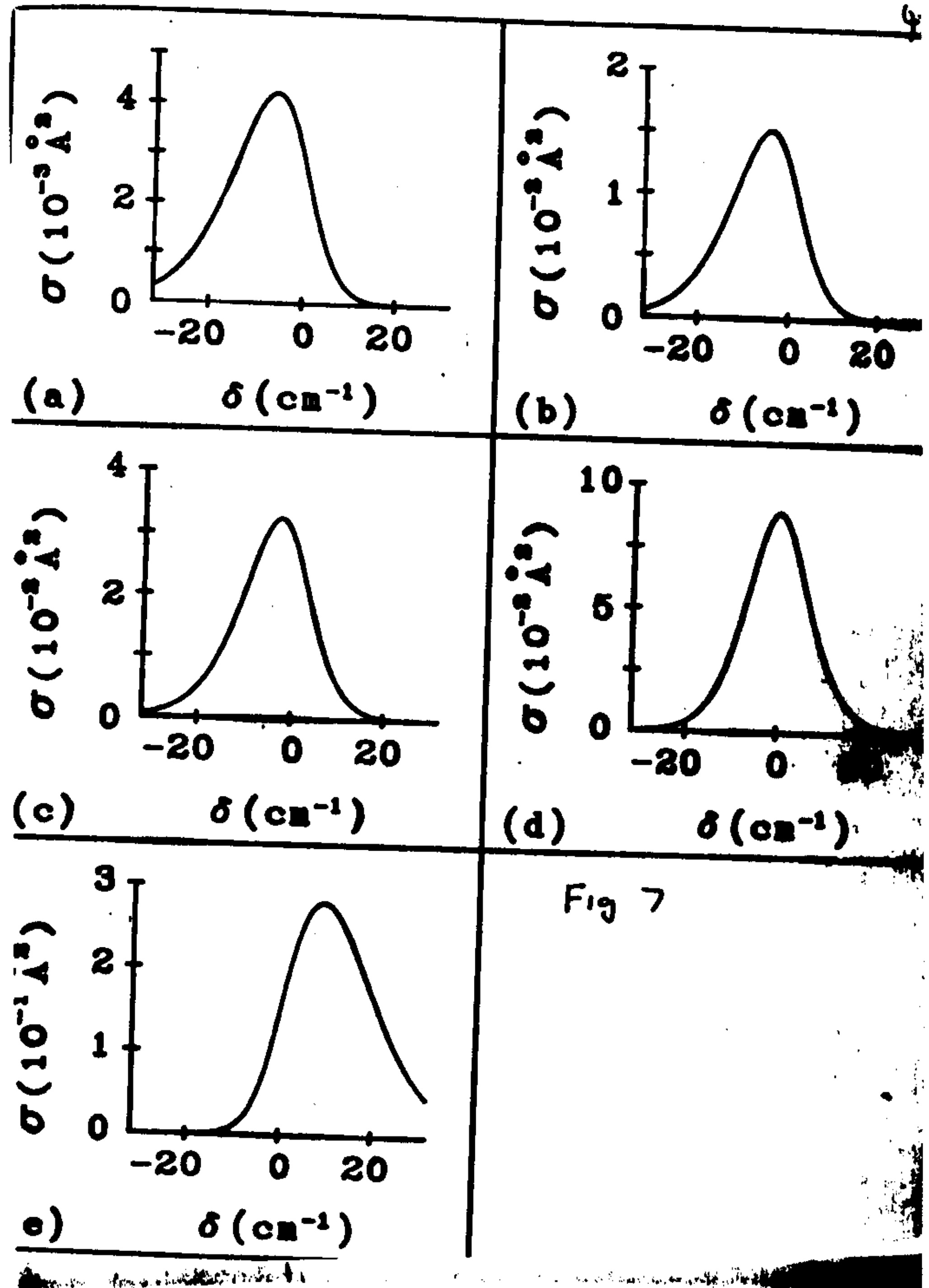

Fig 7

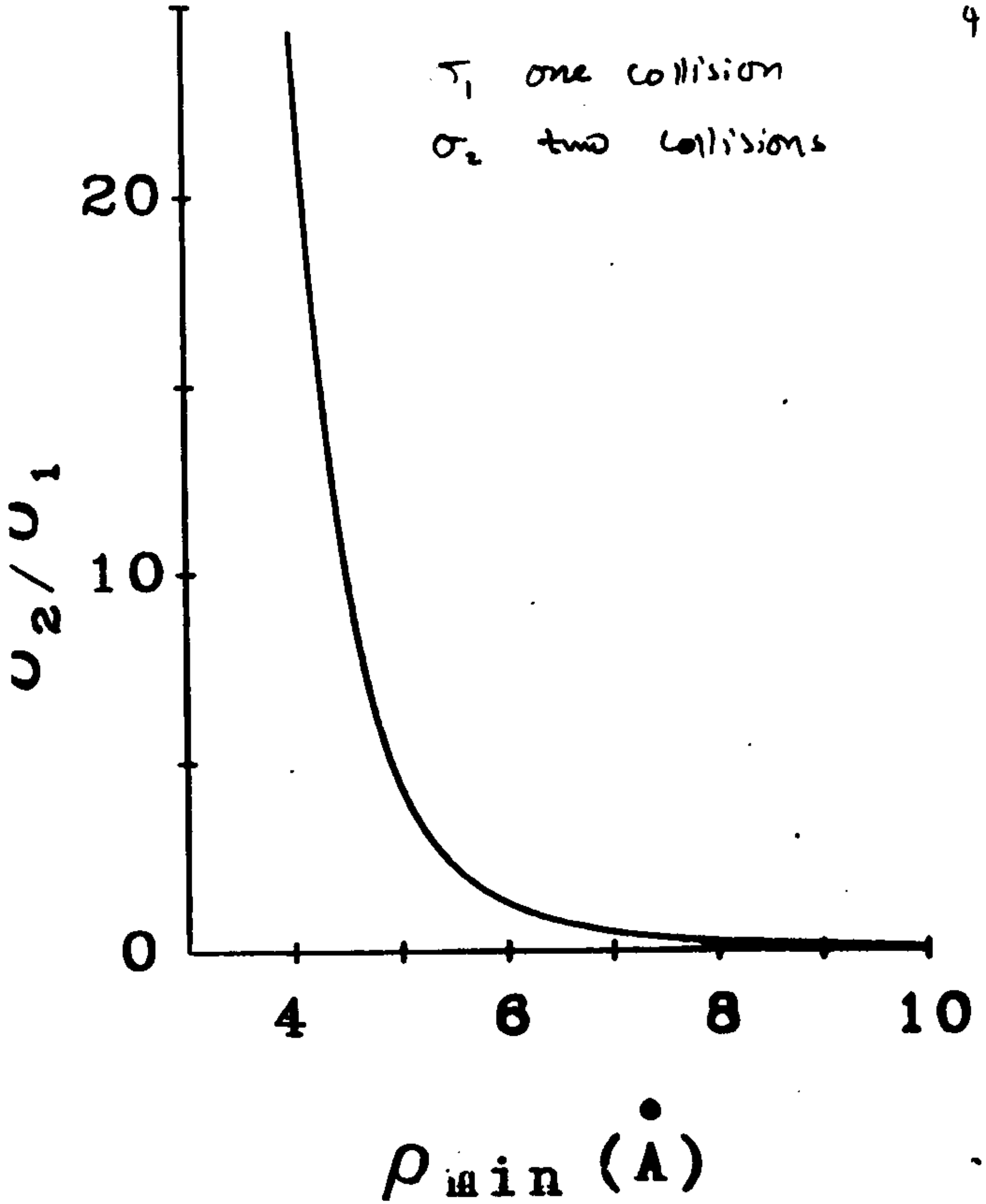

Fig 11