



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



INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2940-1
CABLE: CENTRATOM - TELEX 460392-1

H4.SMR/381-44

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

(30 January - 24 February 1989)

COLLISION DYNAMICS OF COLD COLLISIONS

J. WEINER

University of Maryland
Department of Chemistry
Maryland, U.S.A.

Collision Dynamics of Cold Collisions

1. *Review of Absorption & Emission of Radiation*
2. *Interaction of Radiation and Matter*
3. *Review of Classical & Quantum Collision Theory*
4. *Cooling and Trapping*

Why are cold-atom collisions interesting?

1. Nuclear motion quantal at long range
e.g. deBroglie wavelength 400 a.u
for Na @ 1mK
2. Doppler width very narrow:
 $kT = 20$ MHz @ 1mK
 $kT = 2$ GHz @ 300K: precise free-bound spectroscopy possible.
3. Long-range potentials and couplings control collision dynamics--orientation of colliding partners very important.
4. Light field directly modifies collision dynamics--potential curves become dressed states

Properties of the Interaction of Radiation & Matter

A Classical Relation

In a bulk dielectric medium the energy density w is related to the polarization $\vec{P}$ of the medium and an external field $\vec{E}_0$ by

$$w = -\frac{1}{2} \vec{P} \cdot \vec{E}(\vec{r}, t)$$

The force on the dielectric medium is given by

$$\vec{F} = -\vec{\nabla} w = +\frac{1}{2} \vec{P} \cdot \vec{\nabla} \cdot \vec{E}_0 \cos(\omega t + \phi(r))$$

$$\vec{F} = +\frac{1}{2} \vec{P} \cdot \left[\nabla E_0 \cos(\omega t + \phi(r)) - E_0 \nabla \phi \sin(\omega t + \phi(r)) \right]$$

Now, $\vec{P}(t)$, the polarization can be expressed in terms of the susceptibility of the medium and the field

$$\vec{P}(t) = \text{Re}(\epsilon_0 \chi E_0 e^{i\omega t}) ; \chi = \chi' - i\chi'' \text{ is the complex susceptibility}$$

$$\vec{P}(t) = \text{Re}[\epsilon_0 (\chi' - i\chi'') E_0 (\cos \omega t + i \sin \omega t)]$$

$$\vec{P}(t) = \underbrace{\epsilon_0 E_0 \chi' \cos \omega t}_{\text{in phase with } \vec{E}(r, t)} + \underbrace{\epsilon_0 E_0 \chi'' \sin \omega t}_{\text{in quadrature with } \vec{E}(r, t)}$$

in phase with $\vec{E}(r, t)$ in quadrature with $\vec{E}(r, t)$

$$\text{Now } \vec{F} = +\frac{1}{2} \epsilon_0 E_0 [\chi' \cos \omega t + \chi'' \sin \omega t] [\nabla E_0 \cos(\omega t) - E_0 \nabla \phi \sin \omega t]$$

note that $\phi(r) \equiv 0$ although $\nabla \phi \neq 0$ necessarily.

Now we want to average the force over a period in the field oscillation: The cross terms vanish and we note that $\int_0^T \cos^2(\omega_1 t) dt = \int_0^T \sin^2(\omega_1 t) dt = \frac{T}{2}$

Note also that $\frac{1}{T} \int_0^T \cos^2(\omega_1 t) dt = \frac{1}{2}$ because $\frac{1}{T} = \nu$ & $\omega = 2\pi\nu$

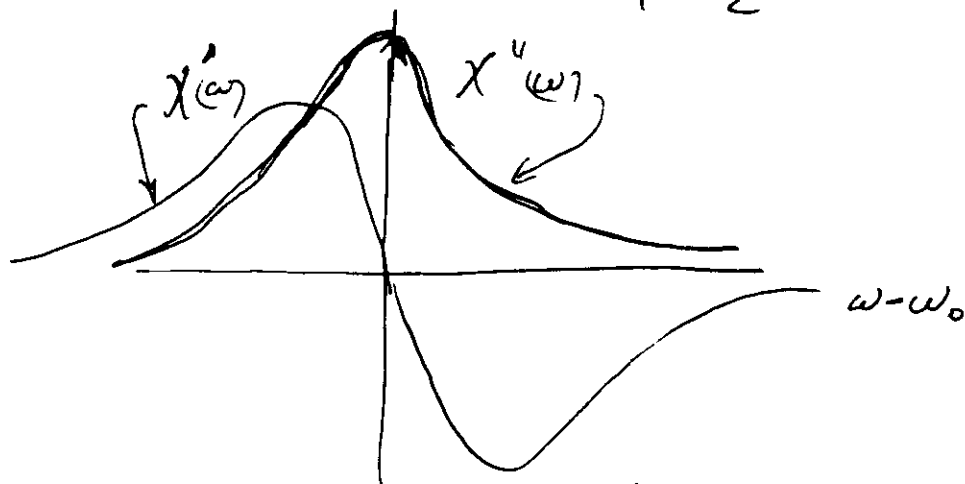
$$\text{so: } \vec{F} = +\frac{1}{4} \epsilon_0 \epsilon_0 \left[\underbrace{X' \vec{\nabla} E_0}_{\text{term proportional to gradient of the field}} - \underbrace{X'' E_0 \vec{\nabla} \phi}_{\text{term proportional to gradient of the phase}} \right]$$

term proportional
to gradient of
the field

term proportional
to gradient of
the phase

Now X' & X'' are frequency dependent. If the dielectric medium has a resonance at ω_0

$$X'(\omega) \sim \frac{\omega_0 - \omega}{(\omega - \omega_0)^2 + \frac{\Gamma^2}{4} + \frac{\Omega^2}{2}} ; X''(\omega) \sim \frac{-\Omega^2/2}{(\omega - \omega_0)^2 + \frac{\Gamma^2}{4} + \frac{\Omega^2}{2}}$$



Note that the gradient force changes sign through the resonance $\vec{F}$ & $\vec{\nabla} E$ are in the same direction (strong field seeking) when $(\omega - \omega_0) < 0$ (red detuning). But force is in opposite direction on blue side of the resonance.

The first term is called the gradient force. Note that the gradient force is zero for a plane wave.

The second term is called the scattering force because it has a line shape identical to absorption.

Suppose we take a plane wave $E(x, t) = E_0 e^{i(\omega t - kx)}$

$$\vec{\nabla} \phi = -\vec{k} \quad \text{so}$$

$$\vec{F} = +\frac{1}{4} \epsilon_0 E_0^2 \chi'' k = +\frac{1}{4} \epsilon_0 E_0^2 k \frac{-\Omega_1^2 / 2}{(\omega - \omega_0)^2 + \frac{\Gamma^2}{4} + \frac{\Omega_1^2}{2}}$$

$$-\Omega_1 = -\frac{N \langle \mu \rangle E_0}{\hbar} = \text{constant for dipole moment } \langle \mu \rangle \text{ and field field}$$

Significance of $-\Omega_1$ discussed later.

Note that the gradient force does not change sign and that $\vec{F}$ and $\vec{k}$ (propagation vector) are in the same direction.

Now consider interaction of radiation & matter at the atomic level.

Force on an atom is given by, $\vec{F} = \int \langle \mu_i \rangle \vec{\nabla} \vec{E}(x, t)$
 where $\langle \mu_i \rangle$ is the ^{time} average dipole induced in the atom by the field

now it can be shown by analysis of the optical Bloch equation that

$$\langle \mu_i \rangle = 2 \vec{\mu} [u_{\text{at}} \cos \omega_L t - v_{\text{at}} \sin \omega_L t]$$

$$\text{where } u_{\text{at}} = \frac{S}{\Omega_1} \left(\frac{a}{1+a} \right); \quad v_{\text{at}} = \frac{\Gamma}{2\Omega_1} \left(\frac{a}{1+a} \right)$$

$$a = \frac{\Omega_1^2 / 2}{\delta^2 + \Gamma^2 / 4}; \quad -\Omega_1 = -\frac{\vec{\mu} E_0}{\hbar}; \quad \vec{E}(x, t) = \vec{E}_0 \cos(\omega t + \phi)$$

$$\text{then } \vec{F}_i = 2\vec{\mu} \left[\frac{\delta}{-\Omega_1} \left(\frac{A}{1+A} \right) \cos \omega t - \frac{\Gamma}{2-\Omega_1} \left(\frac{A}{1+A} \right) \sin \omega t \right] \times \nabla_i \epsilon_0 \cos(\omega t + \phi)]$$

A is called the saturation parameter $= \frac{-\Omega_1^2/2}{\delta^2 + \Gamma^2/4}$; $\delta = \omega - \omega_0$
 $-\Omega_1$ is called the Rabi frequency
 $\Gamma = \frac{1}{\tau}$ is the inverse of the radiative lifetime of the atom

$$\vec{F}_i = 2\vec{\mu} \left(\frac{A}{1+A} \right) \frac{1}{-\Omega_1} \left[\delta \cos \omega t - \frac{\Gamma}{2} \sin \omega t \right] [\nabla \epsilon \cos \omega t - \epsilon_0 \sin \omega t + \phi]$$

where we take $\phi(\vec{r}) = 0$: average over an optical period for the $\cos^2 \omega t$ & $\sin^2 \omega t$ terms

$$\langle \vec{F}_i \rangle = \vec{\mu} \left(\frac{A}{1+A} \right) \frac{1}{-\Omega_1} \left[\underbrace{\delta \nabla \epsilon}_{\text{gradient field force}} + \underbrace{\frac{\Gamma \epsilon_0}{2} \nabla \phi}_{\text{gradient phase force}} \right]$$

Note first term, gradient field force, changes sign just as the two-level susceptibility does

phase force for a plane wave $\epsilon_0 e^{i(\omega t - \vec{k} \cdot \vec{r})}$
 $\nabla \phi = -\vec{k}$

$$\langle \vec{F} \rangle \text{ for the gradient of the phase} = \vec{\mu} \left(\frac{A}{1+A} \right) \frac{1}{-\Omega_1} \frac{\Gamma \epsilon_0}{2} \vec{k}$$

note that $-\Omega_1 = -\frac{\vec{\mu} \cdot \vec{E}_0}{\hbar}$

$$\boxed{\langle \vec{F} \rangle_{\text{phase}} = \hbar \frac{\Gamma}{2} \left(\frac{A}{1+A} \right) \vec{k}}$$

(1)

COLLISIONS

REVIEW of CLASSICAL COLLISION THEORY

$$\begin{array}{ccc} m_2 & & m_1 \\ \bullet & & \bullet \end{array} \quad \vec{F}_1 = -\vec{F}_2$$

$$\left. \begin{array}{l} m_1 \ddot{\vec{r}}_1 = \vec{F}_1 \\ m_2 \ddot{\vec{r}}_2 = \vec{F}_2 \end{array} \right\} \text{Newton's 2nd law}$$

Introduce a coordinate change

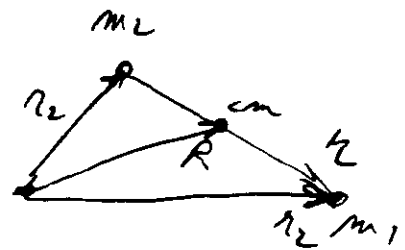
$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

Inverse Transformation

$$\vec{r}_1 = \vec{R} + \frac{m_2}{m_1 + m_2} \vec{r}$$

$$\vec{r}_2 = \vec{R} - \frac{m_1}{m_1 + m_2} \vec{r}$$



Now

$$\begin{array}{l} m_2 m_1 \ddot{\vec{r}}_1 = m_2 \vec{F}_1 \\ m_1 m_2 \ddot{\vec{r}}_2 = m_1 \vec{F}_2 \end{array}$$

$$\ddot{\vec{r}}(m_1, m_2) = \vec{F}_i(m_1 + m_2)$$

$$\vec{F}_1 = \left(\frac{m_1 m_2}{m_1 + m_2} \right) \ddot{\vec{r}} \quad ; \quad \text{Define } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\underline{\mu \ddot{\vec{r}} = \vec{F}} \quad \text{Equation of motion for relative vector + reduced mass.}$$

(2)

Now the relative particle is subject to a radial potential

Conservation of Energy

Initial kinetic energy = radial kinetic energy + angular kinetic + pot. e.

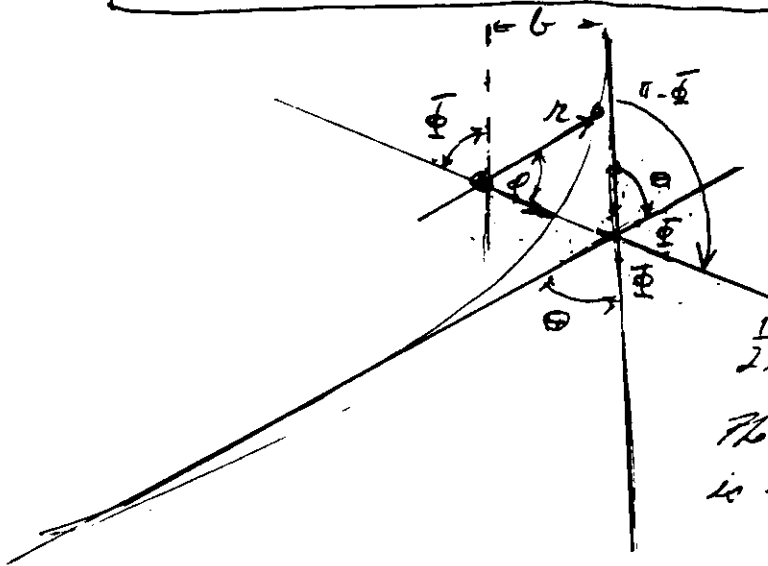
$$\frac{1}{2} \mu v_0^2 = \frac{1}{2} \mu v_r^2 + \frac{L^2}{2I} + V(r)$$

L = angular momentum

$$= \mu v_0 b$$

I = moment of inertia

$$= \mu r^2$$



$$\frac{1}{2} \mu v_0^2 = \frac{1}{2} \mu v_r^2 + \frac{\mu v_0^2 b^2}{2 \mu r^2} + V(r)$$

The second term on the right is the 'centrifugal' potential:

$$V_{\text{eff}} = V(r) + \left(\frac{\mu v_0^2}{2} \right) \frac{b^2}{r^2}$$

Scattering angle relation

$$\Theta = \pi - 2\Phi$$

$$\text{Now } \pi - \Phi = \int_{r_0}^{\infty} \frac{d\phi}{dr} dr$$

$$-2\Phi = 2 \int_{r_0}^{\infty} \frac{d\phi}{dr} dr - \pi$$

$$\Theta = -\pi + 2 \int_{r_0}^{\infty} \frac{d\phi}{dr} dr ; \quad \Theta = \pi - 2 \int_{r_0}^{\infty} \frac{d\phi}{dr} dr$$

ATTRACTIVE POTENTIAL

REPULSIVE POTENTIAL

⑧

Now it can be shown that $\frac{d\phi}{dr} =$

$$\frac{1}{r^2} \frac{G}{\left[1 - \frac{V(r)}{\frac{1}{2}\mu v_0^2} - \frac{G^2}{r^2}\right]^{\frac{1}{2}}}$$

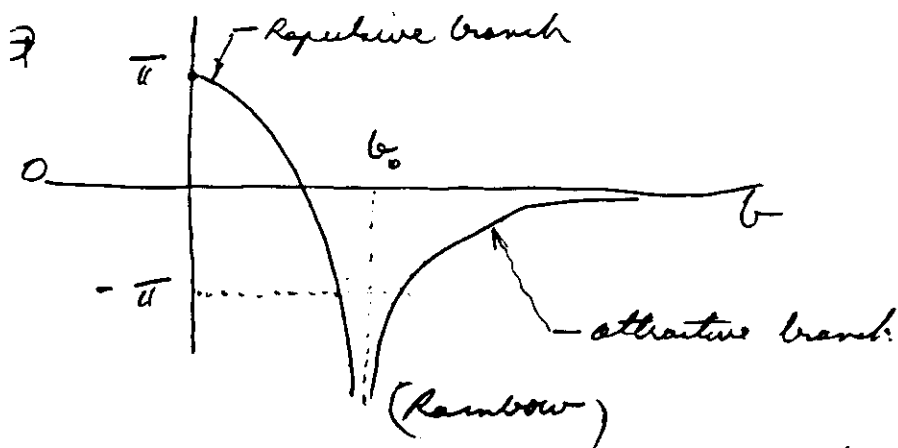
The total deflection function $\Theta = \pi - 2 \int_{r_c}^{\infty} \frac{d\phi}{dr} dr$

$$\Theta = \pi - 2G \int_{r_c}^{\infty} \frac{dr}{r^2 \left[1 - \frac{V(r)}{\frac{1}{2}\mu v_0^2} - \frac{G^2}{r^2}\right]^{\frac{1}{2}}}$$

$$E_{\text{tot}} = \frac{1}{2}\mu v_0^2$$

Note: when denominator goes to zero $\Theta \rightarrow \infty$; the orbit condition:

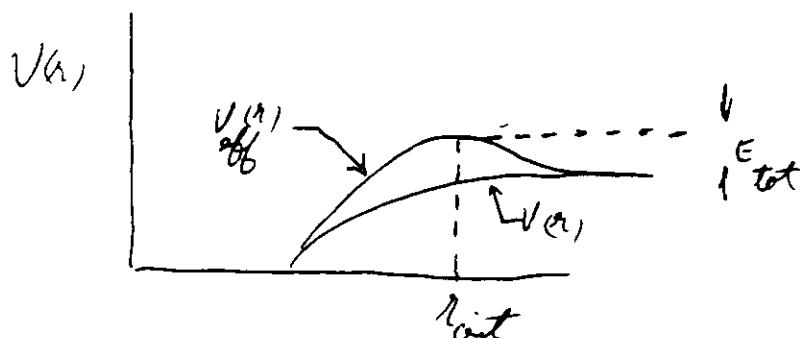
Plot deflection function vs impact parameter



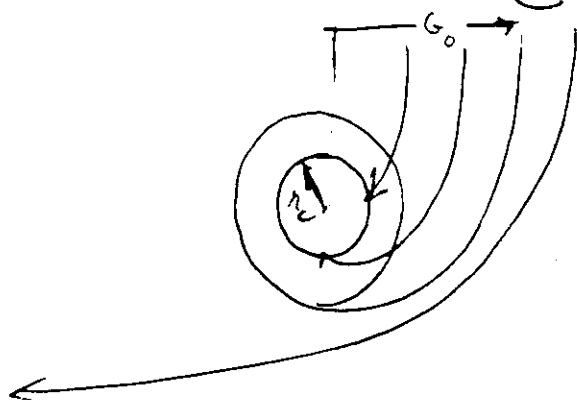
Note that at orbit position, the radial velocity is zero

$$E_{\text{tot}} = V_{\text{eff}} = V(r_{\text{crit}}) + E_{\text{tot}} \frac{G^2}{r_{\text{crit}}^2}$$

$$\text{or } E_{\text{tot}} \left(1 - \frac{G_0^2}{r_{\text{crit}}^2} \right) = V(r_{\text{crit}})$$



LANSDOWN MODEL: Below a CRITICAL RADIUS, R_c , THE "COLLISION" (INELASTIC PROCESS) OCCURS WITH UNIT PROBABILITY. For a fixed E_{tot} & R_c , there is a max G (G_0) at which the incoming particle will reach r_c



G_0 corresponds to the zero of the denominator in the deflection function ($\Theta \rightarrow \infty$)

or the point at which the radial energy $\rightarrow$ zero

$$V_{\text{eff}} = E_{\text{tot}} \frac{G^2}{r^2} - \frac{C_n}{r^n}$$

at maximum, $\frac{dV_{\text{eff}}}{dr} = 0 = -2E_{\text{tot}} \frac{G_0^2}{r_c^3} + n \frac{C_n}{r_c^{n+1}}$

General Relation between r_c & G_0 :

$$G_0 = \left(\frac{n C_n}{2 E_{\text{tot}}} \right)^{\frac{1}{n-2}}$$

for the case of $n=4$
(From two conditions: (i) extremum in V_{eff} and (ii) $\Theta \rightarrow \infty$)

$$\sigma = \pi G_0^2 = 2\pi \left(\frac{C_4}{E_{\text{tot}}} \right)^{\frac{1}{2}}$$

(5)

Rate Constant Definition -- Velocity averaged cross section

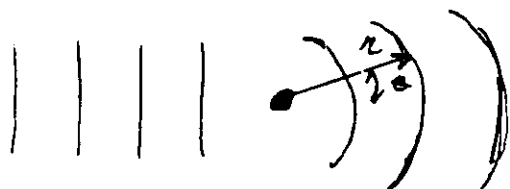
$$k = \int_0^{\infty} \sigma(v) v f(v) dv$$

For the case of con-molecule reaction

$$\sigma(v) = \frac{2\pi}{(\frac{\mu}{2})^{\frac{1}{2}}} (C_4)^{\frac{1}{2}}$$

$$k = \int_0^{\infty} \frac{2\pi C_4^{\frac{1}{2}}}{(\frac{\mu}{2})^{\frac{1}{2}} v} \cdot v f(v) dv = \frac{2\pi C_4^{\frac{1}{2}}}{(\frac{\mu}{2})^{\frac{1}{2}}} \quad (\text{independent of energy})$$

Quantum Theory of Scattering - The Scattering of Waves



Wave function must have the form $\psi \approx e^{ikz} + \frac{e^{ikr}}{r} f(\theta)$

First term, the incoming plane wave, e^{ikz}

Second term, scattered spherical wave, $\frac{e^{ikr}}{r}$

The $f(\theta)$ modulate the amplitude of the wave w.r.t. the scattering angle

If has cylindrical symmetry and can be written as

$$\psi = \sum_{l=0}^{\infty} A_l P_l(\cos\theta) L_l(r) \quad (\text{sum of partial waves})$$

A_l arbitrary constant $L_l(r)$ is solution of the radial equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL_l}{dr} \right) + \left(k^2 - U(r) - \frac{l(l+1)}{r^2} \right) L_l^{(r)} = 0$$

(Schrödinger equation in cylindrical coordinates)

$L_l(r)$ takes the simple form $\frac{1}{r} G_l(r)$

and then

$$\frac{d^2 G_l}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2} \right] G_l = 0$$

$U(r)$ is related to the scattering potential $U(r) = \frac{2m}{\hbar^2} V(r)$

$$k = \frac{m v}{\hbar}; \quad (\vec{p} = \hbar \vec{k})$$

Note that $\lim_{r \rightarrow \infty} \left[U(r) + \frac{l(l+1)}{r^2} \right] = 0$; so the asymptotic

solution G_l should look like the plane-wave solution.

$$G_l \sim A (\sin(kr) + \text{phase shift})$$

$$\text{we find } \frac{G_l}{r} \sim \frac{1}{kr} \sin(kr - \frac{1}{2} l\pi + \eta_l)$$

The $\frac{l(l+1)}{r^2}$ comes from centrifugal potential & η_l comes from specific nature of the potential.
radial

$$\psi = \sum_{l=0}^{\infty} (2l+1) i^l e^{i\eta_l} \frac{1}{r} L_l(r) P_l(\cos\theta)$$

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) [e^{2i\eta_l} - 1] P_l(\cos\theta)$$

The definition of cross section for elastic scattering

$$\sigma = 2\pi \int_0^\pi |f(\theta)|^2 \sin \theta d\theta$$

Introduce S_{ℓ} matrix = $e^{2i\eta_{\ell}}$

$$f(\theta) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} (2\ell+1) [S_{\ell} - 1] P_{\ell}(\cos \theta)$$

$$\sigma = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \eta_{\ell}$$

Rate content

$$\int \sigma(\omega) \omega f(\omega) d\omega = \frac{1}{\Phi_T} \cdot \frac{1}{k} \int \sum (2\ell+1) |S_{\ell}|^2 e^{-\epsilon/kT} d\epsilon$$

COOLING & TRAPPING

COOLING FORCE

We have seen that the gradient force is given by

$$\vec{F}_g = -\frac{1}{2} \frac{\epsilon_0}{\hbar} \nabla \phi ; E(r, t) = E_0 \cos(\omega t + \phi)$$

$$\vec{F}_g = -\frac{1}{2} \frac{\epsilon_0}{\hbar} \vec{k}$$

$$E(r, t) = E_0 e^{i(\omega t - k r)}$$

Photon relation: $E = \hbar \omega$

$$p = \hbar k = \frac{\hbar \omega}{c} = \frac{\hbar}{\lambda}$$

$$\langle \vec{F} \rangle_{\text{grad}} = \hbar \frac{\Gamma}{2} \left(\frac{a}{1+a} \right) \vec{k} \quad \text{where } a = \frac{\Omega^2/2}{\delta^2 + \Gamma^2/4}$$

This could be a decelerating force on the atoms. How long does it take to slow down a thermal Na atom?

$$\langle \vec{F} \rangle = m a ; \text{ take } \lambda = 5890 \text{ \AA}, m = 23 \text{ amu (sodium)}$$

$$a = \frac{\langle \vec{F} \rangle}{m} = -10^6 \text{ m sec}^{-2}$$

$$v_i = 10^3 \text{ m sec}^{-1} \quad v_f = 0 \quad a = -10^6 \text{ m sec}^{-2}$$

$$v_i - v_f = \int_0^t a dt \quad ; \quad v_i = 10^3 \text{ m sec}^{-1}$$

$$v_i - v_f = a t ; \quad t = \frac{10^3 \text{ m sec}^{-1}}{10^6 \text{ m sec}^{-2}} = 1 \text{ msec}$$

What distance is required

$$x = \int \frac{dx}{dt} dt = \int_0^t v dt = \frac{1}{2} a t^2 = \frac{1}{2} \text{ meter}$$

How many ^{absorption} photons required? At saturation, absorption and emission of one photon ≈ 32 msec. Deceleration to zero vel. takes 1 msec

$$\# \text{ photon} = \frac{1 \times 10^{-3} \text{ sec}}{32 \text{ msec/photon}} = 3100 \text{ photon}$$

$$\text{note also that } \Delta v / \text{photon} = 0.03 \text{ m sec}^{-1}$$

However, what about Doppler shift? We cannot pick one frequency to slow down atoms, because of shifting out of resonance

Need to get spatial variation of velocity as atom decelerates down beam path so as to calculate spatial variation of atomic frequency

$$z = \int_0^t dz = \int_0^t v_0 dt - \int_0^t a t dt = v_0 t - \frac{1}{2} a t^2$$

$$z = v_0 \left[\frac{v_0 - v}{a} \right] - \frac{1}{2} a \left[\frac{v_0 - v}{a} \right]^2$$

$$z = \frac{1}{2a} (v_0^2 - v^2)$$

$$v^2 = v_0^2 - 2az \quad \text{or} \quad \boxed{v(z) = (v_0^2 - 2az)^{1/2}}$$

Now the Doppler shift: $\Delta v = \frac{v}{\lambda_0}$

$$\text{so } \boxed{\Delta v(z) = \frac{1}{\lambda_0} (v_0^2 - 2az)^{1/2}}$$

(3)

Two ways to solve problem:

1. Vary Atom FREQ.
 2. Vary Laser FREQ
- } Compensation for $\Delta\gamma(z)$ due to Doppler

First solution: SPATIALLY VARYING ^{ATOMIC} ZEEMAN SHIFT.

$$\Delta V_B(z) = \left[\frac{\Delta\gamma}{B_0} \right] B(z)$$

fixed for atom $\rightarrow$ ↑ spatially varying field

Set $\Delta\gamma_B = \Delta\gamma_D$

$$\left[\frac{\Delta\gamma}{B} \right] B(z) = \frac{1}{\lambda_0} (\nu_0^2 - 2az)^{\frac{1}{2}}$$

$$B(z) = \left(\frac{B}{\Delta\gamma \lambda_0} \right) [\nu_0^2 - 2az]^{\frac{1}{2}} = \frac{B}{\Delta\gamma \lambda_0} \left[1 - \frac{2az}{\nu_0^2} \right]^{\frac{1}{2}}$$

$$= \frac{B_0}{\Delta\gamma_0} \cdot \Delta\gamma_0 \left[1 - \frac{2az}{\nu_0^2} \right]^{\frac{1}{2}}$$

Define $\Delta\gamma_0 = \frac{\nu_0}{\lambda_0}$ &

$$\Delta\gamma_0 = \left(\frac{\Delta\gamma}{B} \right) B_0$$

$$\therefore \frac{B}{\Delta\gamma} = \frac{B_0}{\Delta\gamma_0}$$

$$B(z) = B_0 \left[1 - \frac{2az}{\nu_0^2} \right]^{\frac{1}{2}}$$

$\sqrt{2}$ Na $\frac{\Delta\gamma_0}{B_0} = \frac{144 \text{ Hz}}{\text{Tesla}}$; comes from $E_B =$ energy shift ^{due} to Zeeman interaction

$$E_B = \beta B \frac{g_J}{J} M_J; \beta = \frac{e\hbar}{2mc} \text{ (Bohr magneton)}$$

$$^2P_{3/2} \rightarrow J_{3/2} = 4/3$$

$$E_B^{P_{3/2}} = \beta \frac{4}{3} B M_J$$

$$^2S_{1/2} \rightarrow J_{1/2} = 2$$

$$E_B^{S_{1/2}} = \beta 2 B M_J$$

$$\boxed{\Delta E_B = 2\beta B - \beta B = \beta B} = 14.6 \text{ Hz/T} \quad (\beta = 9.274 \times 10^{-24} \text{ J/T})$$

Need 1.75 Hz for B_0 $\frac{1.75 \text{ Hz}}{14.6 \text{ Hz/T}} = 120 \text{ gauss}$

Vary LASER Frequency (Frequency Chirping)

④

Laser cooling by Frequency Chopping - Want to get $\gamma_L(t)$

Change in velocity per photon absorbed. unit time, assuming saturation:

$$\frac{\Delta P}{\Delta t} = - \frac{h\nu}{2\gamma c}$$

$$\dot{v} = \frac{dv}{dt} = - \frac{h\nu_L(t)}{mc 2\gamma} ; \quad \begin{array}{l} \gamma = \text{natural life time} \\ m = \text{atom mass} \\ \nu_L(t) = \text{frequency of laser} \end{array}$$

Frequency shift due to Doppler slowing.

$$\nu_L(t) = \nu_0 \left(1 - \frac{v(t)}{c} \right)$$

$$\text{or } \frac{v(t)}{c} = 1 - \frac{\nu_L(t)}{\nu_0}$$

$$v(t) = c \left[1 - \frac{\nu_L(t)}{\nu_0} \right]$$

$$\dot{v}(t) = - \frac{\dot{\nu}_L(t) c}{\nu_0}$$

$$- \frac{\dot{\nu}_L(t) c}{\nu_0} = - \frac{h\nu_L(t)}{mc 2\gamma}$$

$$\dot{\nu}_L(t) - \frac{h\nu_0}{mc 2\gamma} \nu_L(t) = 0$$

by inspection: $\boxed{\nu_L(t) = \nu_s \cdot e^{-\frac{mc 2\gamma}{h} t}}$ ν_s starting frequency

(6)

$$\dot{V}_L - \alpha V_L = 0$$

$$V_L(t) = e^{\alpha t}$$

$$\dot{V}_L(t) = \alpha e^{\alpha t}$$

Practical size of α : $\alpha = \frac{\hbar \nu_0}{mc^2 \tau}$

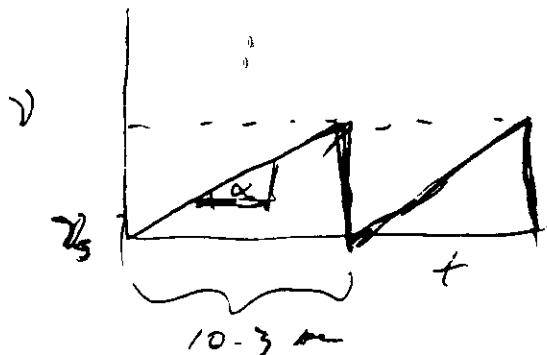
$$\left. \begin{array}{l} \nu_0 = 5.1 \times 10^{14} \text{ sec}^{-1} \\ \hbar = 6.63 \times 10^{-27} \text{ erg} \cdot \text{sec} \\ m = 23 \times 1.66 \times 10^{-24} = 3.81 \times 10^{-23} \\ c = 3 \times 10^{10} \\ \tau = 16 \text{ msec} \end{array} \right\} \alpha = .0031 \text{ sec}^{-1}$$

We already know that $t = 3 \times 10^{-3} \text{ sec}$ will stop Ne

$$\alpha t = 3.1 \times 10^{-3} \times 3 \times 10^{-3} \approx 10^{-5}$$

$\therefore$ argument of $e^{\alpha t}$ always small

$$V_L(t) = V_5 e^{\alpha t} \approx V_5 (1 + \alpha t)$$



$$\frac{dV_L}{dt} = \alpha (1 + \alpha t) \approx \alpha V_5 \alpha t$$

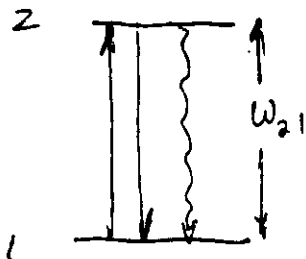
$$\text{Let } V_5 \approx 5 \times 10^{14} \quad \alpha = 7.1 \times 10^{-3} \quad t = 10^{-3}$$

$$\boxed{\frac{dV_L}{dt} = 15 \times 10^8 = 1.5 \times 10^9 \text{ /sec} = 1.5 \text{ GHz} = \text{freq. Frequency per sec } V}$$

Review of Basic Concepts and Vocabulary

A. Absorption and Emission of Radiation

1. Einstein Coefficients



ω_{12}^i = rate of absorption (induced by field)

ω_{21}^i = rate of emission (induced by field)

ω_{21}^s = rate of spontaneous emission from state 2 to state 1

$$\omega_{12}^i = B_{12} \rho_{\omega} N_1 ; B_{12} = \text{Einstein "B" coefficient}$$

ρ_{ω} = energy density per unit angular frequency
 N_1 = population in level 1.

$$\omega_{21}^i = B_{21} \rho_{\omega} N_2$$

Relations: $B_{21}^{\omega} g_2 = B_{12}^{\omega} g_1$ ^{induced} rate constants per state are equal. Note g_2, g_1 are level degeneracy factors

Units: ρ has units of energy density per unit angular frequency:
 (joules $\text{m}^{-3} \text{Hz}^{-1}$)

$$B_{12}, B_{21} \quad (\text{m}^3 \text{Hz} / \text{joule sec})$$

$$N_1, N_2 \quad (\text{unitless})$$

Spontaneous Emission: $A_{21} = \frac{1}{\tau}$; τ is the lifetime of the excited state
 $\tau \equiv \frac{1}{\gamma} \text{ (sec}^{-1}\text{)}$

Relations between $B_{12}, B_{21}, + A_{21}$

$$B_{21}^{\omega} = \frac{\pi^2 c^3}{\hbar \omega_{21}^3} A_{21} ; B_{12}^{\omega} = \frac{g_2}{g_1} B_{21}^{\omega}$$

N.B. Einstein Relations assume ρ_{ω} is constant over the line-width.

N.B. The relation between B & A depends on the definition of ρ . For example, suppose ρ defined as energy density per unit frequency ν instead of angular frequency $\omega = 2\pi\nu$

The rate must be the same so: $B_{21}^{\omega} \rho_{\omega} = B_{21}^{\nu} \rho_{\nu}$
and $\rho_{\omega} d\omega = \rho_{\nu} d\nu$

$$\text{and } d\omega = 2\pi d\nu$$

$$\text{so } \rho_{\nu} = \rho_{\omega} \frac{d\omega}{d\nu} = \rho_{\omega} 2\pi$$

$$\text{so } B_{21}^{\omega} \rho_{\omega} = B_{21}^{\nu} \rho_{\omega} 2\pi$$

$$\text{and } \boxed{\frac{B_{21}^{\omega}}{B_{21}^{\nu}} = 2\pi}$$

Emitted B coefficients must be consistent with definition of ρ

2. Linewidth:

If an excited state decays exponentially we can derive its linewidth by a Fourier transform:

$$f(t) = e^{-t/\tau}$$

$$f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-t/\tau} e^{-i(\omega-\omega_0)t} dt$$

$$f(\omega) = \frac{\tau/2}{\pi} \frac{1}{(\omega-\omega_0)^2 + \tau^2/4} \quad (\text{Lorentzian})$$

Then $\Gamma_{12}(\omega) = B_{12}^{\omega} f(\omega)$; must use emission $\Gamma_{12}(\omega)$ when light source is narrow compared to natural atom linewidth

$$\text{Then } \omega_{12}^i = \int_{-\infty}^{+\infty} f(\omega - \omega_0) N_1 B_{12}(\omega) d\omega$$

$$= P \omega_0 N_1 \int_{-\infty}^{+\infty} B_{12} f(\omega) d\omega$$

What is a typical natural width

$$\frac{1}{2} f(\omega_0) = \frac{1}{4} \Gamma = \text{half maximum}$$

$$\frac{1}{4\pi\Gamma} = \frac{2\Gamma}{\pi} \cdot \frac{1}{(\omega - \omega_0)^2 + \Gamma^2}$$

$$\pi\Gamma = \frac{\pi[(\omega - \omega_0)^2 + \Gamma^2]}{2\Gamma}$$

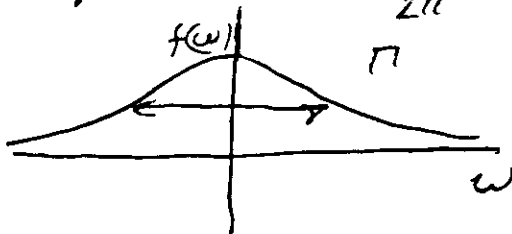
$$2\pi\Gamma^2 - \pi\Gamma^2 = \frac{1}{4} (\omega - \omega_0)^2_{FWHM}$$

$$\Gamma^2 = \frac{(\omega - \omega_0)^2_{FWHM}}{4}$$

$$\boxed{\Gamma = \frac{(\omega - \omega_0)_{FWHM}}{2}}$$

Thus, Γ is the full width at half max of the transition.

$$\Gamma = \frac{1}{\tau} ; \Delta\nu = \frac{\Gamma}{2\pi} = 10 \text{ MHz (in the case of Na)}$$



3. The Measure of Probability of a Transition.

Relation between A_{21} and transition dipole:

$$A_{21} = \frac{2}{3\epsilon_0 \hbar c^3} \omega_{21}^3 \mu_{21}^2 \quad ; \quad \omega_{21} = \text{angular frequency of transition}$$

$\hbar$ = planck's constant

ϵ_0 = permittivity of free space

c = speed of light

μ_{21} = transition dipole

From Q.M.

$$\underline{\mu_{21} = e \langle 1 | \vec{r} | 2 \rangle}$$

$$\underline{\text{line strength } S_{21} = S_{12} = \gamma_2 \mu_{21}^2}$$

$$\text{and } S_{21} = \frac{3\epsilon_0 \hbar c^3}{2\omega_{21}^3} \gamma_2 A_{21}$$

Oscillator strength - a measure of the "strength" of a transition compared to a classical oscillator.

Consider harmonically oscillating charge:

It is accelerated by harmonics force and therefore radiatively damped.

The time constant γ of the radiative damping:

$$-\frac{dU}{dt} = \text{rate of energy loss by radiation} = \frac{e^2 \omega_0^2}{12\pi\epsilon_0 c^3} A^2 e^{-\gamma t}$$

A = amplitude of oscillation

$$\gamma = \frac{e^2 \omega_0^2}{6\pi\epsilon_0 c^3 m}$$

So if we were to consider the atom as a classical oscillator:

$$\gamma = \frac{e^2 \omega_{12}^2}{6\pi\epsilon_0 c^3 m_e}$$

Now Oscillator strength defined:

$$\boxed{f_{21} = -\frac{1}{3} A_{21} \gamma^{-1}} \quad (\text{dimensionless})$$

Absorption oscillator strength: $f_{12} \equiv -g_2 f_{21} \equiv g_f$

$$\therefore f_{12} = \frac{g_2}{g_1} \frac{1}{3} A_{21} \tau^{-1}$$

For α $\bar{\nu} = 0 \rightarrow \bar{\nu} = 1$ transition

$$g_1 = 1 \quad g_2 = 3$$

$$f_{12} = A_{21} \tau^{-1} \cdot \text{Note that } A_{21} \text{ will be } \leq \text{unity}$$

Note the sum rule: $\sum_i f_{i1} = 1$ THOMAS KUNN SUM RULE

Summary: Measure of transition probability:

$$A_{21}, \mu_{21}, S_{21}, f_{21}$$

We have not mentioned the cross section. We give the relation between the absorption cross section and the Einstein B_{12} without proof development

$$\sigma_0 = \frac{\pi \omega_{21} B_{12} \omega}{c}$$

a table of conversions follows:

	A_{21}	B_{12}	B'_{12}	σ_0	f_{12}	μ_{21}^2	S_{21}
A_{21}	1						
B_{12}	$\frac{8\pi^2 \omega_{21}^3}{81 \hbar \omega_{21}^3}$	1					
B'_{12}	$\frac{8\pi^2 \omega_{21}^3}{81 \hbar \omega_{21}^3}$	$\frac{1}{2\pi}$	1				
σ_0	$\frac{1}{4} \frac{8\pi^2 \omega_{21}^3}{81 \hbar \omega_{21}^3}$	$\frac{\hbar \omega_{21}}{c}$	$\frac{\hbar \omega_{21}}{c}$	1	f_{12}		
f_{12}	$\frac{8\pi^2 \omega_{21}^3}{81 \hbar \omega_{21}^3}$	$\frac{2\epsilon_0 \hbar \omega_{21}}{\pi^2}$	$\frac{4\epsilon_0 \hbar \omega_{21}}{\pi^2}$	$\frac{2\epsilon_0 \hbar \omega_{21}}{\pi^2}$	1	μ_{21}^2	
μ_{21}^2	$\frac{3\epsilon_0 \hbar^2 c^3}{2\omega_{21}^3}$	$3 \frac{8\pi^2 \epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$6 \frac{8\pi^2 \epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$3 \frac{8\pi^2 \epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$\frac{3}{2} \frac{8\pi^2 \epsilon_0 \hbar^2}{81 \omega_{21}^3}$	1	S_{21}
S_{21}	$\frac{3\epsilon_0 \hbar^2 c^3}{2\omega_{21}^3}$	$\frac{3\epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$\frac{6\epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$\frac{3\epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$\frac{3\epsilon_0 \hbar^2}{81 \omega_{21}^3}$	$\frac{3\epsilon_0 \hbar^2}{81 \omega_{21}^3}$	1

last relation very important for future discussion:
the Rabi frequency

$$\Omega_1 = \frac{\mu_{21} E_0}{\hbar} \quad \text{where } E_0 \text{ is the amplitude of a field incident on the atom}$$

$$\vec{E}(\vec{r}, t) = \vec{e} E_0(\vec{r}) \cos[\omega_L t + \phi(\vec{r})]$$

$\vec{e}$ is the polarization vector

$E_0(\vec{r})$ the field amplitude (not necessarily constant)

ω_L the incident frequency - we think of it coming from the laser (L)

$\phi(\vec{r})$ is a phase factor indicating spatial propagation.

e.g. $\phi(\vec{r}) = \vec{k} \cdot \vec{r}$