4) **on resonance** \( (\phi = 0) \) rotates in a circle at frequency \( \omega_R \), always \( 1 \) to \( \vec{w} \). If it starts in the \( y-z \) plane, it remains there:

\[
\begin{align*}
V_y &= \cos \omega_R t \\
V_z &= -\sin \omega_R t
\end{align*}
\]

always along \( \hat{x} \)

5) **off resonance**, traces out a cone whose circular base is \( 1 \) to \( \vec{w} \):

\( \vec{V} \) is always at angle \( \theta \) from \( \vec{w} \)

\[
\theta = \text{(constant)}
\]

Here \( V_3 = 1 - 2 \rho_{bb} = 1 - \frac{2 \omega_R^2}{\omega^2} \sin^2 \left( \frac{\omega t}{2} \right) \).

Just like the precession of a magnetic moment around \( \vec{B} \).

6) \( \pi \)-**pulse on resonance** \( \vec{V} \rightarrow -\vec{V} \)

(always an orthogonal state)

\( \pi/2 \)-**pulse on resonance**: rotate \( \vec{V} \) by \( \pi/2 \), etc.
Relaxation

In statistical mechanics, the density matrix evolves towards thermal equilibrium and is described by
\[ \rho_T = \frac{1}{Z} e^{-\mathcal{H}_0/kT}. \]

However, the details of how it gets there depend on the specific situation. Frequently, it's useful to introduce decay processes phenomenologically, omitting the details of the interactions causing the decay.

Ex: Relaxation in a closed system

Decay of \( 1b \rightarrow 1a \) can be introduced by taking
\[
\dot{\rho}_{bb} = \frac{d\rho_{bb}}{dt} = \frac{1}{i\hbar} [\mathcal{H}_0, \rho]_{bb} - \frac{\rho_{bb}}{T_b}
\]
\( \mathcal{H}_0 = \) Hamiltonian without decay inducing term(s)
\( T_b = \) lifetime of \( 1b \rightarrow 1a \)

Since \( \rho_{aa} + \rho_{bb} = 1 \)
\[
\dot{\rho}_{aa} = \frac{1}{i\hbar} [\mathcal{H}_0, \rho]_{aa} + \frac{\rho_{bb}}{T_b}
\]
\[
= \frac{1}{i\hbar} [\mathcal{H}_0, \rho]_{aa} + (1 - \rho_{aa})/T_b
\]
(assuming \( 1a \) lives indefinitely)

The off-diagonal coherences will in general decay at a different rate, the "transverse" or "\( T_2 \)" relaxation time. If the decay of \( 1a \) and \( 1b \) is purely radiative, with lifetimes \( T_a \) and \( T_b \), one can show that this rate is
\[
T_2^{-1} = \frac{1}{2} (T_a^{-1} + T_b^{-1}) + \gamma \phi
\]
where \( \gamma \phi \) describes interactions that perturb only the phase of the system, but not the populations.
For the example at hand, where $T_a \rightarrow \infty$, if we assume for the moment that $\gamma_0 = 0$, we have:

\[ \Gamma_b = \frac{1}{T_b}, \quad \Gamma_2 = \frac{1}{T_2} = \frac{1}{2} \Gamma_b. \tag{30} \]

If $a, b$ are the zero-field eigenstates, then $\rho_{aa}$ and $\rho_{bb}$ give the populations, while $\rho_{ab} = \rho_{ba}^*$ gives the induced dipole (more on this later).

We have:

\[
\frac{d\rho}{dt} = \frac{i}{\hbar} \left[ H, \rho \right] - \begin{pmatrix} -\Gamma_b \rho_{bb} & \frac{\Gamma_2}{2} \rho_{ab} \\ \frac{\Gamma_2}{2} \rho_{ba} & -\Gamma_b \rho_{bb} \end{pmatrix} \tag{31}
\]

In the RWA, the Hamiltonian is:

\[ H = \frac{\hbar}{2} \begin{pmatrix} -\omega_0 & \omega_R e^{i\omega t} \\ \omega R e^{-i\omega t} & \omega_0 \end{pmatrix} \left( \omega_0 = \omega_b - \omega_a \right) \]

with $\omega_R = \frac{eE_0}{\hbar} |\langle \alpha | \vec{E} \cdot \vec{r} | \alpha \rangle |$ as usual.

For low power, or when $t$ is large enough to damp transients, we can find a steady-state solution by setting $\frac{d\rho_{aa}}{dt} = 0$ (see more on p. DM-111).

First we need to find:

\[
\left[ H, \rho \right] = \frac{\hbar}{2} \begin{pmatrix} -\omega_0 & \omega_R e^{i\omega t} \\ \omega R e^{-i\omega t} & \omega_0 \end{pmatrix} \left( \begin{array}{c} \rho_{aa} \\ \rho_{ab} \end{array} \right)
- \frac{\hbar}{2} \left( \begin{array}{cc} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{array} \right) \begin{pmatrix} -\omega_0 & \omega_R e^{i\omega t} \\ \omega R e^{-i\omega t} & \omega_0 \end{pmatrix} \tag{33}
\]

\[
= \frac{\hbar}{2} \begin{pmatrix} \omega_R (e^{i\omega t} \rho_{ba} - e^{-i\omega t} \rho_{ab}) & -2\omega_0 \rho_{ab} + \omega_R e^{i\omega t} (\rho_{bb} - \rho_{aa}) \\ 2\omega_0 \rho_{ba} + \omega_R e^{-i\omega t} (\rho_{ab} - \rho_{bb}) & \omega_R (e^{-i\omega t} \rho_{ab} - e^{i\omega t} \rho_{ba}) \end{pmatrix}
\]
We expect $P_{ab}$ to be stationary in the rotating frame. Thus we will guess that,

$$\dot{P}_{ab} = (\dot{A} + i\omega A) e^{i\omega t}$$

This simplifies (31) greatly. We get two independent equations:

$$\dot{P}_{aa} = \frac{1}{2i} \left[ w_k (A^* - A) - \frac{1}{b} (P_{aa} - 1) \right]$$

$$\dot{P}_{bb} = (\dot{A} + i\omega A) e^{i\omega t} = \frac{1}{2i} \left( -2w_k A e^{i\omega t} + w_k e^{i\omega t} \dot{P}_{bb} - \dot{P}_{aa} \right) - \frac{1}{2} A e^{i\omega t}$$

As expected, the $e^{i\omega t}$ terms cancel.

**Steady-state solution.** Set $\dot{P}_{aa} = 0$ and $\dot{A} = 0$.

After some algebra,

$$\begin{align*}
\dot{P}_{aa} &= \frac{1 + \frac{x^2}{2}}{1 + x} \\
\text{with } x &= \frac{w_k^2 \Gamma_1}{\Gamma_b (\omega - \omega_0)^2 + \Gamma_2^2} \\
\dot{P}_{bb} &= \frac{s}{2(1+s)}
\end{align*}$$

Using (29), write $\Gamma_b = \gamma = \frac{1}{k}$ and $\Gamma_2 = \pm \gamma$.

Then,

$$\begin{align*}
P_{aa} &= \frac{1 + \frac{s^2}{2}}{1 + s} \\
\text{saturation parameter } s &= \frac{w_k^2}{2} \frac{1}{\omega^2 + \left(\frac{\gamma}{2}\right)^2 + \frac{w_k^2}{2}}
\end{align*}$$

And

$$\begin{align*}
P_{bb} &= \frac{s}{2(1+s)} \\
&= \frac{w_k^2}{4} \frac{1}{\omega^2 + \left(\frac{\gamma}{2}\right)^2 + \frac{w_k^2}{2}}
\end{align*}$$

At high irradiance (large $w_k$), $P_{aa} \approx P_{bb} \approx \frac{1}{2}$, the limit of strong saturation.

We can now find a general expression for the rate of light scattering:

In equilibrium, decay rate = rate of absorption, not including cycles of absorption -> stimulated emission.

Thus the photon scattering rate is $R = \gamma P_{bb}$
This gives a general expression for absorption of monochromatic light in the RWA:

\[
R = \left( \frac{w_R}{2} \right)^2 \frac{\delta}{\delta^2 + (\frac{\gamma}{2})^2 + \frac{w_R^2}{2}}
\]

Rate for scattering monochromatic light (RWA, 19) assumed stable

At low power, this is the excitation rate per atom. More generally, it is the rate at which photons are lost from the electromagnetic field (not including stimulated emission cycles.)

Lorentzian lineshape:

Eq. (30) predicts a Lorentzian lineshape for absorption spectroscopy with monochromatic light:

\[
\Delta w = \sqrt{\gamma^2 + 2w_R^2}
\]

\(w_0 = w_b - w_a\)

At low power the width is just \(\Delta w = \gamma\). \(\gamma_a + \gamma_b\).

This natural linewidth is ubiquitous in physics. On the following page I’ve appended a real experimental spectrum for the 4f, \(Y=3\) state of the NO molecule, showing the Lorentzian shape with a little deviation due to laser power drift.

At higher power, we see power broadening. The effective lifetimes of \(1a^2\) and \(1b^2\) are both reduced by Rabi cycling. For large \(w_R\) the width becomes \(\Delta w \approx \sqrt{2} w_R\). Experimentally this is very hard to distinguish from natural linewidth except by careful extrapolation.
$^2P_{3}(1)$ branch to 4f, $v=3$, ND 0.0

FILE: no22185.6
$\chi^2 = 0.251$

$A = 34723 \pm 239.6$
$B = 238 \pm 4.4$
WIDTH = 746.85 \pm 6.47$ MHz

CENTER:
5477.1 \pm 2.0$ MHz
= 23637.995$ cm$^{-1}$

![Fit to Lorentzian](image-url)
Also, note that since \( \omega R \propto E \) and the field irradiance is \( \frac{1}{2} \epsilon_0 |E_0|^2 \), then \( \omega R \propto \sqrt{E} \) and the power dependence of a power-broadened resonance is weak,
\[
\Delta \omega \propto \sqrt{E}.
\]

All of this fails for very high powers, where a variety of higher-order effects emerge. This can be important for \( P > 10^6 \text{ W/cm}^2 \) for a typical optical transition, and will be a major subject next semester.

Finally, note that the Lorentzian lineshape, while a very good approximation, cannot be truly exact—it has infinite area! It can be shown using QED that at very short and very long times, spontaneous decay is not quite exponential, explaining the apparent paradox.

**Ex 26: Bloch Relaxation** (borrowed from NMR)

The saturation behavior of (29) is actually somewhat unusual. A more typical situation is to let \( \rho \) relax to equilibrium with two different rates \( \frac{1}{\tau_1} \) and \( \frac{1}{\tau_2} \), a good model for a system involving collisions or other strong interactions. The equation of motion becomes,
\[
\frac{d\rho}{dt} = \frac{i}{\hbar} \left[ H, \rho \right] = \begin{pmatrix}
\Gamma_1 (\rho_{aa} - \rho_{00}) & \Gamma_2 \rho_{ab} \\
\Gamma_2 \rho_{ba} & \Gamma_1 (\rho_{bb} - \rho_{00})
\end{pmatrix}
\]

where \( \rho_{00}, \rho_{0a} \) are equilibrium values.

From problem set #2, the steady-state solution is,
\[
(\rho_{0b} - \rho_{aa})_{ss} = (\rho_{00} - \rho_{aa}) \left( 1 - \frac{\omega_R^2 \rho_{bb}/\rho_{00}}{\omega^2 + \rho_{bb}/\rho_{00}} \right)
\]
and
\[
(\rho_{ab})_{ss} = -\frac{\omega_R^2}{2} \frac{1}{\sqrt{\omega^2 + \rho_{bb}/\rho_{00}}} e^{i\omega t} (\rho_{bb} - \rho_{aa})_{ss}
\]

As always, \( \Delta \equiv \omega - (\omega_b - \omega_a) = \omega - \omega_0 \).

\[\text{Width} = 2 \sqrt{\frac{\rho_{bb}}{\rho_{00}} + \frac{\omega_R^2}{\omega}}\]

\( \omega \) power broadening, slightly generalized.
Note: We can also allow sources to decay out of the system, for example,

\[
\frac{dp}{dt} = \frac{1}{i\hbar} \left[ H, \rho \right] - \left( \begin{array}{cc} \Gamma_{1a} & \Gamma_{1b} \\ \Gamma_{2b} & \Gamma_{2a} \end{array} \right) + \Gamma_{W_0} (\rho_{aa} 0 \ 0)
\]

But in general, trace is not preserved (the present example maintains it manually).

This allows for decay out of the system, drifting out of the laser beam, etc. Collisions are a little more complex due to phase effects.

Absorption & cross section

Let's stay with monochromatic illumination: 2-level system with \( \Gamma_0 = 0 \)

We define, for an unsaturated transition,

\[
\sigma = \frac{\text{Absorption rate}}{\text{Incident photon flux}} = \frac{\text{photons s}^{-1}}{\text{photons cm}^{-2} \text{ s}^{-1}}
\]

\[
\sigma = \frac{R_{ab}}{I/\hbar w} = \frac{\hbar w}{\frac{1}{2}E_0 E_o^2} R_{ab}
\]

\[
\sigma = \frac{2\hbar w}{E_0 E_o^2} \frac{c^2 E_0^2}{\hbar^2} |<b|E_0^{-}\cdot\n|a>|^2 \frac{\Gamma_b/4}{(w-w_0)^2 + (\Gamma_b/2)^2}
\]

\[
\sigma = \frac{\pi w e^2}{E_0 c^2} \frac{\hbar^2}{x^2} |<b|E_0^{-}\cdot\n|a>|^2 \frac{\Gamma_b/4}{(w-w_0)^2 + (\Gamma_b/2)^2}
\]

If \( |b> \) decays only to \( |a> \) and \( \gamma_a = \gamma_b \), then

\[
\Gamma_b = A_{ba} = \frac{w^3}{3\pi\varepsilon_0 \hbar c^3} |<b|E_0^{-}\cdot\n|a>|^2
\]

\[\text{factor of 3?} = \frac{2}{\pi\Gamma_b} \text{ on res.}\]
So in this "true 2-level" limit, on resonance,

\[
\sigma = \frac{\pi \cal W e^2}{\cal E_0 \cal E_b}  \frac{2 \left| \frac{3 \pi \cal E_0 e^2 c^3}{\cal W^3} \langle b | \cal E_0 \cdot \nabla | a \rangle \right|^2}{\pi} = \frac{2}{\pi \cal E_b}
\]

\[= 2 \pi \left( \frac{c}{\cal W} \right)^2 \left( \times 3 \text{ ?} \right) = \frac{3 \lambda^2}{2 \pi}\]

But it's necessary to treat the angular momentum/polarization aspects a little more carefully. We will learn to do this shortly. For now, refer to Budker, Kimball & DeMille, pp. 148-149 (2nd Ed.)

\[
\sigma_{ab} = \frac{\lambda^2}{2 \pi} \frac{2 J' + 1}{2 J + 1} \quad J = \text{excited state}, \quad J' = \text{lower state}
\]

This is easily generalized to the case where \( |e> \) decays not only to \( |g> \), but to other states:

\[
\sigma = \frac{\lambda^2}{2 \pi} \frac{2 J' + 1}{2 J + 1} \delta \rho_{\text{tot}}
\]

\( \delta \rho = \text{spontaneous decay rate from } |e> \rightarrow |g> \).

Note: several prominent texts give \( \sigma = \frac{3 \lambda^2}{2 \pi} \); this is not accurate except for \( S \leftrightarrow P \) transitions (as in alkali atom ground-state transitions).

Note 2: Our density matrix solution depended only on the fact that \( V \propto e^{i \omega t} + c.c. \)

\( \Rightarrow (40) \) is also valid for \( M_1, E2 \) transitions! (assuming source linewidth \( \ll \) natural width).

The corresponding absorption coefficient is

\[
\alpha = \sigma_{ab} (N_a - N_b) \quad \text{densities}
\]

We need \( \sigma_{ba} = -\sigma_{ab} \) since radiation field gains a photon with stimulated emission.