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Chem 249

# Density Matrix Description of Absorption

## I. Equations of Motion for $\rho$

We are interested in the time evolution of the density matrix for a two level system:

$$|2\rangle \;\text{———}\; E_2 \qquad\qquad \hbar\omega_0 = E_2 - E_1 \qquad\qquad |1\rangle \;\text{———}\; E_1$$

$$H_0|1\rangle = E_1|1\rangle$$
$$H_0|2\rangle = E_2|2\rangle$$

The density matrix for this system is a $2\times 2$ matrix with elements $\rho_{11}$, $\rho_{22}$, $\rho_{21}$ & $\rho_{12}$. Remember that for a wavefunction $|\Psi\rangle$:

$\rho_{nm} = \langle n|\Psi\rangle\langle\Psi|m\rangle$.

In general, recall that the expectation value of an operator $\langle A\rangle$ is given by: $\quad \langle A\rangle = tr(\rho A)$

and the time evolution of $\rho$ is given by:

$$\frac{\partial\rho}{\partial t} = \frac{i}{\hbar}[\rho, H]$$

We are interested in the case where

$$H = H_0 + H'(t)$$

$$H'(t) = -\mu E(t)$$

This is a one-dimensional picture of the dipole interaction. The dipole moment operator's matrix elements are assumed to be:

$$\mu_{11} = \mu_{22} = 0 \qquad \text{(no dipole moment in grd. or excited state)}$$

$$\mu_{21} = \mu_{12} = \mu \qquad \text{(sets the phases of } |1\rangle \text{ \& } |2\rangle\text{)}$$

Thus, $H'$ only has off-diagonal elements $H'_{12}$ & $H'_{21}$
For any given time (or wavefunction) $\langle\mu\rangle$ is given by:

$$\langle\mu\rangle = tr(\rho\mu) = \rho_{12}\mu_{21} + \rho_{21}\mu_{12} + \rho_{11}\mu_{11} + \rho_{22}\mu_{22}$$

$$= \mu(\rho_{12} + \rho_{21})$$

$\langle\mu\rangle \neq 0$ only in the non-eigenstate wavefunction.

II. Time Evolution of $\rho$ for a two level system

To calculate the time evolution of $\rho$, we use the eqn. of motion for each matrix element $\rho_{nm}$:

$$\frac{d\rho_{21}}{dt} = -\frac{i}{\hbar}\left[(H_0 + H'), \rho\right]_{21} = -\frac{i}{\hbar}\left\{H'_{21}\rho_{11} + E_2\rho_{21} - E_1\rho_{21} - \rho_{22}H'_{21}\right\}$$

$$= -\frac{i}{\hbar}\left[H'_{21}(\rho_{11} - \rho_{22}) + (E_2 - E_1)\rho_{21}\right]$$

$$\frac{d\rho_{21}}{dt} = +i\frac{\mu}{\hbar}E(t)(\rho_{11} - \rho_{22}) - i\omega_0\rho_{21}$$

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And in a similar fashion:

$$\frac{d\rho_{22}}{dt} = -i\frac{\mu}{\hbar}E(t)\left(\rho_{21} - \rho_{21}^*\right)$$

$$\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i\frac{\mu}{\hbar}E(t)\left(\rho_{21} - \rho_{21}^*\right)$$

This is because $\rho_{11} + \rho_{22} = 1$

III. Relaxation Times $T_1$ & $T_2$

For an ensemble of atoms or molecules, collisions and other interactions will eventually lead to a loss of "phase coherence". This means that $\rho_{21}$ will eventually approach zero with some time constant $T_2$:

$$\frac{d\rho_{21}}{dt} = -i\omega_0\rho_{21} + i\frac{\mu}{\hbar}(\rho_{11} - \rho_{22})E(t) - \frac{\rho_{21}}{T_2}$$

Likewise, if $E(t)$ were turned off, then $\rho_{11}$ & $\rho_{22}$ would return to a Boltzmann equilibrium distribution with a time constant $T_1$:

$$\frac{d}{dt}(\rho_{11} - \rho_{22}) = \frac{2i\mu E(t)}{\hbar}\left(\rho_{21} - \rho_{21}^*\right) - \frac{(\rho_{11} - \rho_{22}) - (\rho_{11} - \rho_{22})_0}{T_1}$$

IV. Interaction Representation & Rotating Wave Approximation

We now let $E(t) = E_0 \cos\omega t = \frac{1}{2}E_0\left(e^{i\omega t} + e^{-i\omega t}\right)$

Now, if $E(t) = 0$, then $\rho_{21} = \rho_{21}(0)\exp\left[\left(-i\omega_0 - \frac{1}{T_2}\right)t\right]$

(oscillation at frequency $\omega_0$ with a decay time of $T_2$)

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To factor this behavior out, we define new "slowly" varying variables $\sigma_{21}$ & $\sigma_{12}$:

$$\rho_{21}(t) = \sigma_{21}(t)\, e^{-i\omega t}$$

$$\rho_{12}(t) = \sigma_{12}(t)\, e^{i\omega t} = \rho_{21}^*$$

for $\omega \approx \omega_0$, $\sigma_{21}$ is slowly varying.

Thus:
$$\frac{d\sigma_{21}}{dt} = i(\omega - \omega_0)\sigma_{21} + \frac{i\mu E_0}{2\hbar}(\rho_{11} - \rho_{22}) - \frac{\sigma_{21}}{T_2} \qquad (a)$$

$$\frac{d}{dt}(\rho_{11} - \rho_{22}) = \frac{i\mu E_0}{\hbar}(\sigma_{21} - \sigma_{21}^*) - \frac{(\rho_{11} - \rho_{22}) - (\rho_{11} - \rho_{22})_0}{T_1} \qquad (b)$$

In (a) we have only kept terms with an $e^{-i\omega t}$ dependence, and in (b) we have only kept terms with no exponential time dependence. The neglected non-synchronous terms average out to zero for times longer ~~than~~ than $2\pi/\omega$. This approximation is sometimes called the "Rotating Wave Approximation".

Using ~~equation~~ the definition of $\sigma_{21}$ we can calculate $\langle \mu(t) \rangle$:

$$\langle \mu \rangle = \mu\left(\sigma_{12}\, e^{i\omega t} + \sigma_{21}\, e^{-i\omega t}\right)$$

$$= 2\mu \left\{ \mathrm{Re}\,\sigma_{21}(t) \cos\omega t + \mathrm{Im}\,\sigma_{21}(t) \sin\omega t \right\}$$

since $\sigma_{21} = \sigma_{12}^*$

Thus if we know $\sigma_{21}$, we know $\langle \mu(t) \rangle$.

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## V. Steady State Solutions

We can obtain the steady state solutions for $\sigma_{21}$ & $(\rho_{11}-\rho_{22})$ by setting $\frac{d\sigma_{21}}{dt} = \frac{d(\rho_{11}-\rho_{22})}{dt} = 0$ in equations (a) & (b). These solutions (after a bit of algebra) look like:

$$\operatorname{Im}\sigma_{21} = \frac{\Omega T_2 (\rho_{11}-\rho_{22})_0}{1+(\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

where $\Omega \equiv \frac{\mu E_0}{2\hbar}$ "precession frequency"

$$\operatorname{Re}\sigma_{21} = \frac{(\omega_0-\omega) T_2^2 \Omega (\rho_{11}-\rho_{22})_0}{1+(\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$(\rho_{11}-\rho_{22}) = (\rho_{11}-\rho_{22})_0 \frac{1+(\omega-\omega_0)^2 T_2^2}{1+(\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

From $\sigma_{21}$ we can get $\langle \mu(t)\rangle$. The total macroscopic oscillating polarization is $P(t) = N\langle\mu\rangle$ where $N$ is just the # of molecules/atoms.

$$P = \frac{\mu^2 \Delta N_0 T_2}{\hbar} E_0 \left[\frac{\sin\omega t + (\omega_0-\omega) T_2 \cos\omega t}{1+(\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}\right]$$

$$\Delta N = \Delta N_0 \frac{1+(\omega-\omega_0)^2 T_2^2}{1+(\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

population difference (per unit volume)

where $\Delta N = N(\rho_{11}-\rho_{22})$ & $\Delta N_0 = N(\rho_{11}-\rho_{22})_0$

$\Delta N_0$ is the population difference when $E(t)=0$.

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Note that:

1) $P(t)$ is proportional to $\mu^2$, the square of the transition dipole moment (as in the TDPT theory)

2) $P(t) \propto E_0$, the intensity of the applied field. This linear relationship between $P$ & $E$ is quite general, and the proportionality constant is called the linear susceptibility $\chi$:

$$\underline{P}(t) = \varepsilon_0 \chi \underline{E}(t)$$

3) $P(t)$ has a $\sin\omega t$ & a $\cos\omega t$ part. Remember that $E(t) = E_0 \cos\omega t$.

Thus, $P(t)$ has components both in and out of phase with $E(t)$.

These components are expressed as the real & imaginary parts of the linear susceptibility: $\chi \equiv \chi' - i\chi''$

$$P(t) = \varepsilon_0 E \left( \chi' \cos\omega t + \chi'' \sin\omega t \right)$$

We will talk about $\chi'$ & $\chi''$ more later (classically).

4) $\chi'$ & $\chi''$ are functions of $\omega$:

$$\chi''(\omega) = \frac{\mu^2 T_2 \Delta N_0}{\varepsilon_0 \hbar} \frac{1}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

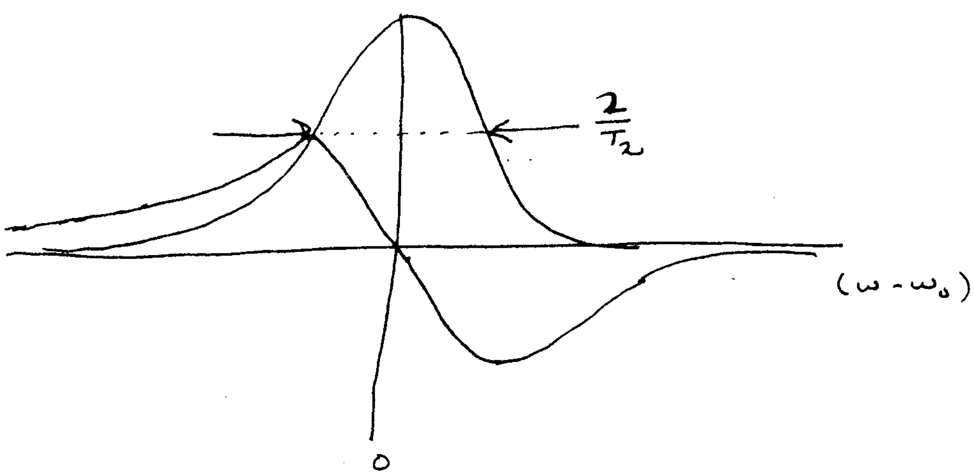
$$\chi'(\omega) = \frac{\mu^2 T_2 \Delta N_0}{\varepsilon_0 \hbar} \frac{(\omega_0 - \omega) T_2}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

If $E_0$ is small, then the $4\Omega^2 T_2 T_1$ term in the denominator can be neglected, $\chi'$ & $\chi''$ can then be related to the Lorentzian lineshape function $g(\omega)$:

$$g(\omega) = \frac{2T_2}{1 + (\omega-\omega_0)^2 T_2^2}$$

$$\chi''(\omega) = \frac{\mu^2 \Delta N_0}{2\varepsilon_0 \hbar}\, g(\omega)$$

$$\chi'(\omega) = \frac{\mu^2 T_2 \Delta N_0}{2\varepsilon_0 \hbar}(\omega_0-\omega)\, g(\omega)$$




$\chi''$ is a Lorentzian with a half width of $\frac{2}{T_2}$, and $\chi'$ is a dispersive lineshape with maxima at $\omega_0 \pm \frac{1}{T_2}$. We will see later in our classical equations that $\chi''(\omega)$ is directly proportional to the absorption lineshape, and $\chi'(\omega)$ is the change in the index of refraction with absorption.

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5) Both $\Delta N$ and $\chi(\omega)$ decrease as $E_0$ gets large. This is called saturation, and is just the result of the de-population of the ground state. Saturation effects will be important when:

$$4\Omega^2 T_2 T_1 > 1 + (\omega - \omega_0)^2 T_2^2$$

Not only will the intensity of the absorption decrease, but the effective half width of the resonance in $\chi''(\omega)$ will become larger. This is called saturation broadening, and is approximately given by:

$$\Delta\omega_{sat} \simeq \Delta\omega \left[ 1 + 4\Omega^2 T_2 T_1 \right]^{1/2}$$

where $\Delta\omega = \frac{1}{T_2}$, the linewidth in the absence of saturation effects.

## VI. Perturbation Calculation of P(t)

The preceding calculation of $P(t)$ & $\chi(\omega)$ was for a two level system when $\omega$ is near resonance @ $\omega_0$. We can also use a perturbation calculation similar to that employed in TDPT to obtain $P(t)$:

$$P(t) = \frac{\mu^2 E_0}{2\hbar}\left[\left(\frac{1}{\omega_0+\omega-iT_2}\right)+\left(\frac{1}{\omega_0-\omega+iT_2}\right)\right]e^{i\omega t}$$

$$+\frac{\mu^2 E_0}{2\hbar}\left[\left(\frac{1}{\omega_0-\omega-iT_2}\right)+\left(\frac{1}{\omega_0+\omega+iT_2}\right)\right]e^{-i\omega t}$$

Note that:

1) There are resonances at both $\omega=\omega_0$ & $\omega=-\omega_0$ (absorption & emission)

2) There is no saturation term in this perturbation calculation.

A complete derivation of $P(t)$ using a perturbation calculation has been written out by D. Higgins (of my group), and is ~~[illegible]~~ reproduced for you in the following pages.

① 

# $\alpha + \beta$ Derivation

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(D16)

DAH

## (Two States (g,l) ONLY)

Dan Higgins

## Definitions:

① $\vec{P} = \text{Trace}(\rho \cdot \vec{\mu})$

② $\vec{E}(\omega) = \vec{E}^{o}\cos\omega t = \frac{1}{2}\vec{E}^{o}(e^{i\omega t} + e^{-i\omega t})$

Thus, since $\beta$ involves $E^2$:

③ $$E^2(\omega) = \frac{E^{o}}{2}(1 + \cos 2\omega t)$$

④ $\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] + \left(\frac{d\rho}{dt}\right)_{relax}$

References:

$\boxed{\text{R. Carlson Thesis} \quad \text{Y.R. Shen} \quad \text{Zyss, Chemla}}$

⑤ $H = H^{o} + V$

$V = -\frac{1}{2}\vec{\mu}\cdot\vec{E}^{o}(e^{i\omega t} + e^{-i\omega t})$

⑥ $V^{+} = -\frac{1}{2}\vec{\mu}\cdot\vec{E}^{o}e^{i\omega t}$

⑦ $V^{-} = -\frac{1}{2}\vec{\mu}\cdot\vec{E}^{o}e^{-i\omega t}$

[these are the raising and lowering operators]

⑧ $\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \ldots$

As in the case of $\vec{E}(\omega)$, a given $\rho^{(n)}$ can also be expanded in a Fourier Series:

⑨ $\rho^{(0)} = \rho^{(0)}$ (thermal equilibrium)

⑩ $\rho^{(1)} = \rho^{+(1)}e^{i\omega t} + \rho^{-(1)}e^{-i\omega t}$ (the perturbations of $V^{+}$ or $V^{-}$ act once)

⑪ $\rho^{(2)} = \rho^{+(2)}e^{i2\omega t} + \rho^{-(2)}e^{-i2\omega t}$ (the perturbations $V^{+}$ or $V^{-}$ act twice)

Note in ⑪ that the perturbation is $V^{+}V^{+}$ or $V^{-}V^{-}$ and that $V^{+}V^{-}$ or $V^{-}V^{+}$ lead to DC terms.

⑫ $H^{o} = \hbar\omega_n = E_n$ ($E_n$ = energy of $n^{th}$ state)

The expansion ⑧ is then inserted into ④ and like terms are collected, i.e., terms with the same time dependence, for example, in $\frac{d\rho^{\pm(2)}}{dt}$, $\rho^{\pm(2)}$ has a time dependence of $e^{\pm i2\omega t}$ so this will be collected with terms like $V^{\pm}\rho^{\pm(1)}$ having time dependence $e^{\pm i\omega t}e^{\pm i\omega t} = e^{\pm i2\omega t}$.

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Derivation:

④ $$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] + \left(\frac{d\rho}{dt}\right)_{relax}$$

using ⑤

⑬ $$\frac{d\rho}{dt} = \frac{i}{\hbar}\left([\rho, H^0] + [\rho, V]\right) + \left(\frac{d\rho}{dt}\right)_{relax}$$

$$[\rho, H^0] = \rho \cdot H^0 - H^0 \cdot \rho = \begin{bmatrix} \rho_{gg} & \rho_{g1} \\ \rho_{1g} & \rho_{11} \end{bmatrix}\begin{bmatrix} H^0 & 0 \\ 0 & H^0 \end{bmatrix} - \begin{bmatrix} H^0 & 0 \\ 0 & H^0 \end{bmatrix}\begin{bmatrix} \rho_{gg} & \rho_{g1} \\ \rho_{1g} & \rho_{11} \end{bmatrix}$$

⑭ $$[\rho, H^0] = \begin{bmatrix} 0 & \rho_{g1}(\hbar(\omega_1 - \omega_g)) \\ \rho_{1g}(\hbar(\omega_g - \omega_1)) & 0 \end{bmatrix} = \begin{bmatrix} 0 & \rho_{g1}\hbar\omega_{1g} \\ \rho_{1g}\hbar\omega_{g1} & 0 \end{bmatrix}$$

NOTE ⟶ $$\left( = \begin{bmatrix} 0 & -\rho_{g1}\hbar\omega_{g1} \\ -\rho_{1g}\hbar\omega_{1g} & 0 \end{bmatrix} \right)$$

$$[\rho, V] = [\rho, -\vec{\mu}\cdot\vec{E}] = \rho\cdot(-\vec{\mu}\cdot\vec{E}) - (-\vec{\mu}\cdot\vec{E})\cdot\rho$$

$$= \begin{bmatrix} \rho_{gg} & \rho_{g1} \\ \rho_{1g} & \rho_{11} \end{bmatrix} \begin{bmatrix} -\vec{\mu}_{gg}\cdot\vec{E} & -\vec{\mu}_{g1}\cdot\vec{E} \\ -\vec{\mu}_{1g}\cdot\vec{E} & -\vec{\mu}_{11}\cdot\vec{E} \end{bmatrix} - \begin{bmatrix} -\vec{\mu}_{gg}\cdot\vec{E} & -\vec{\mu}_{g1}\cdot\vec{E} \\ -\vec{\mu}_{1g}\cdot\vec{E} & -\vec{\mu}_{11}\cdot\vec{E} \end{bmatrix} \begin{bmatrix} \rho_{gg} & \rho_{g1} \\ \rho_{1g} & \rho_{11} \end{bmatrix}$$

$$= \begin{bmatrix} -\rho_{gg}\vec{\mu}_{gg}\cdot\vec{E} - \rho_{g1}\vec{\mu}_{1g}\cdot\vec{E} & -\rho_{gg}\vec{\mu}_{g1}\cdot\vec{E} - \rho_{g1}\vec{\mu}_{11}\cdot\vec{E} \\ -\rho_{1g}\vec{\mu}_{gg}\cdot\vec{E} - \rho_{11}\vec{\mu}_{1g}\cdot\vec{E} & -\rho_{1g}\vec{\mu}_{g1}\cdot\vec{E} - \rho_{11}\vec{\mu}_{11}\cdot\vec{E} \end{bmatrix} -$$

$$\begin{bmatrix} -\vec{\mu}_{gg}\cdot\vec{E}\rho_{gg} - \vec{\mu}_{g1}\cdot\vec{E}\rho_{1g} & -\vec{\mu}_{gg}\cdot\vec{E}\rho_{g1} - \vec{\mu}_{g1}\cdot\vec{E}\rho_{11} \\ -\vec{\mu}_{1g}\cdot\vec{E}\rho_{gg} - \vec{\mu}_{11}\cdot\vec{E}\rho_{1g} & -\vec{\mu}_{1g}\cdot\vec{E}\rho_{g1} - \vec{\mu}_{11}\cdot\vec{E}\rho_{11} \end{bmatrix}$$

(15) $$[\rho, V] = \begin{bmatrix} \vec{\mu}_{g1}\cdot\vec{E}\rho_{1g} - \rho_{g1}\vec{\mu}_{1g}\cdot\vec{E} & \rho_{g1}(\vec{\mu}_{gg}\cdot\vec{E} - \vec{\mu}_{11}\cdot\vec{E}) + \vec{\mu}_{g1}\cdot\vec{E}(\rho_{11} - \rho_{gg}) \\ \rho_{1g}(\vec{\mu}_{11}\cdot\vec{E} - \vec{\mu}_{gg}\cdot\vec{E}) + \vec{\mu}_{1g}\cdot\vec{E}(\rho_{gg} - \rho_{11}) & \vec{\mu}_{1g}\cdot\vec{E}\rho_{g1} - \rho_{1g}\vec{\mu}_{g1}\cdot\vec{E} \end{bmatrix}$$

(16) $$\left(\frac{d\rho}{dt}\right)_{relax} = -\Gamma_{1g}\rho_{1g}\ (\text{for } \rho_{1g}),\ -\Gamma_{g1}\rho_{g1}\ (\text{for } \rho_{g1}),\ 0\ (\text{for } (\rho_{gg} \text{ or } \rho_{11})),$$

[note that terms like $\Gamma_{11}$ and $\Gamma_{gg}$ and their respectiv feeding terms are set to zero as in general, $T_1$ is long, and also, perturbative treatments do not call for large population changes when these terms would be importa

Taking (15), (16), (14), and (13):

(17) $$\frac{d\rho_{11}^{(n)}}{dt} = \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\vec{E}\rho_{g1}^{(n-1)} - \rho_{1g}^{(n-1)}\vec{\mu}_{g1}\cdot\vec{E}\right)$$

(18) $$\frac{d\rho_{1g}^{(n)}}{dt} = -i\omega_{1g}\rho_{1g}^{(n)} + \frac{i}{\hbar}\left(\rho_{1g}^{(n-1)}(\vec{\mu}_{11}\cdot\vec{E} - \vec{\mu}_{gg}\cdot E) + \vec{\mu}_{1g}\cdot\vec{E}(\rho_{gg}^{(n-1)} - \rho_{11}^{(n-1)})\right) - \Gamma_{1g}\rho_{1g}^{(n)}$$

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Calculation of Linear Polarizability ($\alpha_{ij}$):

$$\vec{P}^{(1)} = \mathrm{Trace}(\rho^{(1)} \cdot \vec{\mu}) = \rho_{gg}^{(1)}\mu_{gg} + \rho_{1g}^{(1)}\mu_{g1} + \rho_{g1}^{(1)}\mu_{1g} + \rho_{11}^{(1)}\mu_{11}$$

<u>for $\rho_{1g}^{(1)}$, using $V^+$, $\rho_{1g}^{+(1)}e^{i\omega t}$ and (18):</u>

$$\frac{d(\rho_{1g}^{+(1)}e^{i\omega t})}{dt} = -i\omega_{1g}\rho_{1g}e^{i\omega t} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}}{2}e^{i\omega t}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right) - \Gamma_{1g}\rho_{1g}^{+(1)}e^{i\omega t}$$

note $\rightarrow$ $(\rho_{1g}^{(0)} = 0)$

$$\Rightarrow \cancel{e^{i\omega t}}\frac{d\rho_{1g}^{+(1)}}{dt} + i\omega\rho_{1g}^{+(1)}\cancel{e^{i\omega t}} = -i\omega_{1g}\rho_{1g}^{+(1)}\cancel{e^{i\omega t}} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}\cancel{e^{i\omega t}}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right) - \Gamma_{1g}\rho_{1g}^{+(1)}\cancel{e^{i\omega t}}$$

$$\Rightarrow \frac{d\rho_{1g}^{+(1)}}{dt} + i\omega\rho_{1g}^{+(1)} = -i\omega_{1g}\rho_{1g}^{+(1)} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right) - \Gamma_{1g}\rho_{1g}^{+(1)}$$

$\frac{d\rho_{1g}^{+(1)}}{dt} = 0$ in steady state
(ie, slowly varying $\rho_{1g}^{+(1)}$)

$$\Rightarrow \rho_{1g}^{+(1)}(i\omega + i\omega_{1g} + \Gamma_{1g}) = \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\Rightarrow \rho_{1g}^{+(1)}(\omega + \omega_{1g} - i\Gamma_{1g}) = \frac{1}{2\hbar}\left(\vec{\mu}_{1g}\cdot\vec{E}^{\circ}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\boxed{\rho_{1g}^{+(1)} = \frac{1}{2\hbar}\vec{\mu}_{1g}\cdot\vec{E}^{\circ}\left(\frac{1}{\omega_{1g}+\omega-i\Gamma_{1g}}\right)}$$

<u>assuming $\rho_{gg}^{(0)} = 1$, $\rho_{11}^{(0)} = 0$</u>

Similarly, for $\rho_{1g}^{(1)}$, using $V^-$, $\rho_{1g}^{-(1)}e^{-i\omega t}$ and (18):

$$\frac{d(\rho_{1g}^{-(1)}e^{-i\omega t})}{dt} = -i\omega_{1g}\rho_{1g}^{-(1)}e^{-i\omega t} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}e^{-i\omega t}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right) - \Gamma_{1g}\rho_{1g}^{-(1)}e^{-i\omega t}$$

using $\frac{d\rho_{1g}^{-(1)}}{dt} = 0$ :

$$\Rightarrow -i\omega\rho_{1g}^{-(1)}\cancel{e^{-i\omega t}} = -i\omega_{1g}\rho_{1g}^{-(1)}\cancel{e^{-i\omega t}} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}\cancel{e^{-i\omega t}}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right) - \Gamma_{1g}\rho_{1g}^{-(1)}\cancel{e^{-i\omega t}}$$

$$\Rightarrow -i\omega\rho_{1g}^{-(1)} = -i\omega_{1g}\rho_{1g}^{-(1)} + \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{gg}^{(0)}-\rho_{11}^{(0)}\right) - \Gamma_{1g}\rho_{1g}^{-(1)}$$

$$\Rightarrow \rho_{1g}^{-(1)}(-i\omega + i\omega_{1g} + \Gamma_{1g}) = \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\Rightarrow \rho_{1g}^{-(1)}(\omega - \omega_{1g} + i\Gamma_{1g}) = \frac{-1}{2\hbar}\left(\vec{\mu}_{1g}\cdot\vec{E}^{\circ}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\boxed{\rho_{1g}^{-(1)} = \frac{1}{2\hbar}\vec{\mu}_{1g}\cdot\vec{E}^{\circ}\left(\frac{1}{\omega_{1g}-\omega-i\Gamma_{1g}}\right)}$$

For $\rho_{g1}^{(1)}$, using $V^+$, $\rho_{g1}^{+(1)}e^{i\omega t}$ and (18):

$$\frac{d(\rho_{g1}^{+(1)}e^{i\omega t})}{dt} = i\omega_{1g}\rho_{g1}^{+(1)}e^{i\omega t} + \frac{i}{\hbar}\left(\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}e^{i\omega t}(\rho_{11}^{(0)}-\rho_{gg}^{(0)})\right) - \Gamma_{g1}\rho_{g1}^{+(1)}e^{i\omega t}$$

(used $\omega_{g1} = -\omega_{1g}$ above)

$$\Rightarrow \cancel{e^{i\omega t}}\frac{d\rho_{g1}^{+(1)}}{dt}\rightarrow 0 + i\omega\rho_{g1}^{+(1)}\cancel{e^{i\omega t}} = i\omega_{1g}\rho_{g1}^{+(1)}\cancel{e^{i\omega t}} + \frac{i}{\hbar}\left(\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}\cancel{e^{i\omega t}}(\rho_{11}^{(0)}-\rho_{gg}^{(0)})\right) - \Gamma_{g1}\rho_{g1}^{+(1)}\cancel{e^{i\omega t}}$$

$$\Rightarrow \rho_{g1}^{+(1)}(i\omega - i\omega_{1g} + \Gamma_{g1}) = \frac{i}{\hbar}\left(\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{11}^{(0)}-\rho_{gg}^{(0)})\right)$$

$$\Rightarrow \rho_{g1}^{+(1)}(\omega - \omega_{1g} - i\Gamma_{g1}) = \frac{-1}{2\hbar}\left(\vec{\mu}_{g1}\cdot\vec{E}^{\circ}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\boxed{\rho_{g1}^{+(1)} = \frac{1}{2\hbar}\vec{\mu}_{g1}\cdot\vec{E}^{\circ}\left(\frac{1}{\omega_{1g}-\omega+i\Gamma_{g1}}\right)}$$

$(\Gamma_{g1} = \Gamma_{1g})$

For $\rho_{g1}^{(1)}$, using $V^-$, $\rho_{g1}^{-(1)}e^{-i\omega t}$ and (18):

$$\frac{d(\rho_{g1}^{-(1)}e^{-i\omega t})}{dt} = i\omega_{1g}\rho_{g1}^{-(1)}e^{-i\omega t} + \frac{i}{\hbar}\left(\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}e^{-i\omega t}(\rho_{11}^{(0)}-\rho_{gg}^{(0)})\right) - \Gamma_{g1}\rho_{g1}^{-(1)}e^{-i\omega t}$$

$$\Rightarrow -i\omega\rho_{g1}^{-(1)} = i\omega_{1g}\rho_{g1}^{-(1)} + \frac{i}{\hbar}\left(\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}(\rho_{11}^{(0)}-\rho_{gg}^{(0)})\right) - \Gamma_{g1}\rho_{g1}^{-(1)}$$

$$\Rightarrow \rho_{g1}^{-(1)}(-i\omega - i\omega_{1g} + \Gamma_{g1}) = -\frac{i}{2\hbar}\left(\vec{\mu}_{g1}\cdot\vec{E}^{\circ}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\Rightarrow \rho_{g1}^{-(1)}(\omega + \omega_{1g} + i\Gamma_{g1}) = \frac{1}{2\hbar}\left(\vec{\mu}_{g1}\cdot\vec{E}^{\circ}(\rho_{gg}^{(0)}-\rho_{11}^{(0)})\right)$$

$$\boxed{\rho_{g1}^{-(1)} = \frac{1}{2\hbar}\vec{\mu}_{g1}\cdot\vec{E}^{\circ}\left(\frac{1}{\omega_{1g}+\omega+i\Gamma_{g1}}\right)}$$

For $\rho_{11}^{(1)}$, using $V^+$, $\rho_{11}^{+(1)}e^{i\omega t}$ and (17):

$$\frac{d(\rho_{11}^{+(1)}e^{i\omega t})}{dt} = \frac{i}{\hbar}\left(\vec{\mu}_{1g}\cdot\frac{\vec{E}^{\circ}}{2}e^{i\omega t}\overset{0}{\cancel{\rho_{g1}^{(0)}}} - \overset{0}{\cancel{\rho_{1g}^{(0)}}}\vec{\mu}_{g1}\cdot\frac{\vec{E}^{\circ}}{2}e^{i\omega t}\right)$$

$$i\omega\rho_{11}^{+(1)}e^{i\omega t} = 0 \quad , \quad \boxed{\begin{array}{ll} \rho_{11}^{+(1)} = 0 , & \rho_{gg}^{+(1)} = 0 \\ \rho_{11}^{-(1)} = 0 , & \rho_{gg}^{-(1)} = 0 \end{array}}$$

$$\vec{P}^{(1)} = \rho_{1g}^{(1)}\vec{\mu}_{g1} + \rho_{g1}^{(1)}\vec{\mu}_{1g} = \left(\rho_{1g}^{+(1)}e^{i\omega t} + \rho_{1g}^{-(1)}e^{-i\omega t}\right)\vec{\mu}_{g1} + \left(\rho_{g1}^{+(1)}e^{i\omega t} + \rho_{g1}^{-(1)}e^{-i\omega t}\right)\vec{\mu}_{1g}$$

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$$\vec{P}^{(1)} = \frac{1}{2\hbar}\Big(\vec{\mu}_{1g}\cdot\vec{E}^{o}\Big[\Big(\frac{1}{\omega_{1g}+\omega-i\Gamma_{1g}}\Big)e^{i\omega t}+\Big(\frac{1}{\omega_{1g}-\omega-i\Gamma_{1g}}\Big)e^{-i\omega t}\Big]\vec{\mu}_{g1}+$$
$$\vec{\mu}_{g1}\cdot\vec{E}^{o}\Big[\Big(\frac{1}{\omega_{1g}-\omega+i\Gamma_{1g}}\Big)e^{i\omega t}+\Big(\frac{1}{\omega_{1g}+\omega+i\Gamma_{1g}}\Big)e^{-i\omega t}\Big]\vec{\mu}_{1g}$$

By <u>inspection</u> of the above equation, it is <u>immediately</u> apparent that $\alpha_{ij}$ will be as follows:

$$\boxed{RE(\alpha_{ij}) = \frac{1}{2\hbar}\Big(\mu^{j}_{1g}\mu^{i}_{g1}\Big(\frac{1}{\omega_{1g}+\omega-i\Gamma_{1g}}+\frac{1}{\omega_{1g}-\omega-i\Gamma_{1g}}\Big)+\mu^{j}_{g1}\mu^{i}_{1g}\Big(\frac{1}{\omega_{1g}-\omega+i\Gamma_{1g}}+\frac{1}{\omega_{1g}+\omega+i\Gamma_{1g}}\Big)}$$

$$\boxed{IM(\alpha_{ij}) = \frac{i}{2\hbar}\Big(\mu^{j}_{1g}\mu^{i}_{g1}\Big(\frac{1}{\omega_{1g}+\omega-i\Gamma_{1g}}-\frac{1}{\omega_{1g}-\omega-i\Gamma_{1g}}\Big)+\mu^{j}_{g1}\mu^{i}_{1g}\Big(\frac{1}{\omega_{1g}-\omega+i\Gamma_{1g}}-\frac{1}{\omega_{1g}+\omega+i\Gamma_{1g}}\Big)}$$

<u>note that $\mu = -er$</u>