

Optical Bloch Equations

To discuss coherent spectroscopy, we need a formalism that includes coherence:

Optical Bloch Equations

The Optical Bloch Equations:

are basically the equations of motion for the elements of the density matrix

explicitly include both

coherence – **off** diagonal elements of the density matrix

population – diagonal elements of the density matrix

Outline:

- 1) Review density matrix
- 2) Derive equations of motion (from Schrödinger's Equation)
- 3) Mixed case density matrix (ensembles)
- 4) Dipole moment operator
- 5) Decay/relaxation

Density matrix

Why use the density matrix?

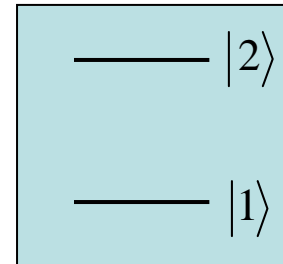
- it is bilinear in the wave function, as are most of the physical quantities of interest
- allows ensemble averages to be conveniently introduced
- decay/relaxation is easier to handle

Consider a two-level system

Write the wavefunction

$$|\psi\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle$$

(in the Schrödinger picture: time dependence in ψ , not operators)



Physical quantities of interest:

$|C_1(t)|^2$ probability of being in the lower state

$|C_2(t)|^2$ probability of being in upper state

$C_1(t)C_2^*(t) = C_1^*(t)C_2(t)$ probability of being in a coherent superposition state

Density matrix definition

$$\rho = |\psi\rangle\langle\psi|$$

(note: this is the “pure” case)

What does this mean?

It is an outer product, in matrix notation:

$$|\psi\rangle = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad \langle\psi| = (C_1^* \quad C_2^*)$$

$$\rho = |\psi\rangle\langle\psi| = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} (C_1^* \quad C_2^*) = \begin{pmatrix} C_1 C_1^* & C_1 C_2^* \\ C_2 C_1^* & C_2 C_2^* \end{pmatrix}$$

We can identify

ρ_{11} probability of being in the lower state

ρ_{22} probability of being in upper state

$\rho_{12} = \rho_{21}^*$ probability of being in a coherent superposition state

Mathematical definition of pure case:

$$\rho^2 = \rho$$

Check:

$$\rho^2 = |\psi\rangle\langle\psi| \underbrace{|\psi\rangle\langle\psi|}_{=1} = |\psi\rangle\langle\psi|$$

for normalized wavefunction

Calculation of expectation values using ρ

Recall, the expectation value for operator \mathbf{A} is

$$\langle \mathbf{A} \rangle = \langle \psi | \mathbf{A} | \psi \rangle$$

and the projection operator

$$\mathbf{P} = \sum_i |i\rangle\langle i| = \mathbf{1}$$

if $\{|i\rangle\}$ is an orthonormal basis set

Then

$$\langle \mathbf{A} \rangle = \langle \psi | \mathbf{A} | \psi \rangle$$

$$\langle \mathbf{A} \rangle = \sum_i \langle \psi | \mathbf{A} | i \rangle \langle i | \psi \rangle$$

$$\langle \mathbf{A} \rangle = \sum_i \langle i | \psi \rangle \langle \psi | \mathbf{A} | i \rangle$$

$$\langle \mathbf{A} \rangle = \sum_i \langle i | \rho \mathbf{A} | i \rangle$$

$$\langle \mathbf{A} \rangle = \text{Tr}(\rho \mathbf{A})$$

(recall: $\text{Tr}(\mathbf{M}) = \sum_i M_{ii}$)

Check for 2-level system:

$$\langle \mathbf{A} \rangle = \langle \psi | \mathbf{A} | \psi \rangle = \begin{pmatrix} C_1^* & C_2^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$= \begin{pmatrix} C_1^* & C_2^* \end{pmatrix} \begin{pmatrix} A_{11}C_1 + A_{12}C_2 \\ A_{21}C_1 + A_{22}C_2 \end{pmatrix}$$

$$= A_{11}|C_1|^2 + A_{12}C_1^*C_2 + A_{21}C_1C_2^* + A_{22}|C_2|^2$$

$$\text{Tr}(\rho \mathbf{A}) = \text{Tr} \left(\begin{pmatrix} |C_1|^2 & C_1C_2^* \\ C_2C_1^* & |C_2|^2 \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \right)$$

$$= A_{11}|C_1|^2 + A_{12}C_1^*C_2 + A_{21}C_1C_2^* + A_{22}|C_2|^2$$

checks

Equations of motion

The Schrödinger equation is the equation of motion for the wavefunction

$$i\dot{|\psi\rangle} = -\frac{i}{\hbar} \mathbf{H}|\psi\rangle$$

where \mathbf{H} is the Hamiltonian. For ρ

$$\dot{\rho} = |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}| = -\frac{i}{\hbar} \mathbf{H}|\psi\rangle\langle\psi| + \frac{i}{\hbar} |\psi\rangle\langle\psi| \mathbf{H} = -\frac{i}{\hbar} [\mathbf{H}\rho - \rho\mathbf{H}]$$

$$\dot{\rho} = -\frac{i}{\hbar} [\mathbf{H}, \rho]$$

Check

Schrödinger equation: $\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$ $\psi = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$ Eqn. of motion for ρ :

$$\begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$\dot{\rho} = -\frac{i}{\hbar} \left[\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} - \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \right]$$

$$\dot{C}_1 = -\frac{i}{\hbar} (H_{11}C_1 + H_{12}C_2)$$

$$\dot{\rho}_{11} = -\frac{i}{\hbar} [H_{11}\rho_{11} + H_{12}\rho_{21} - \rho_{11}H_{11} - \rho_{12}H_{21}]$$

$$\begin{aligned} \dot{\rho}_{11} &= \dot{C}_1 C_1^* + C_1 \dot{C}_1^* \\ &= -\frac{i}{\hbar} (H_{11}C_1 + H_{12}C_2) C_1^* + \frac{i}{\hbar} C_1 (H_{11}^* C_1^* + H_{12}^* C_2^*) \end{aligned}$$

$$= -\frac{i}{\hbar} [H_{12}\rho_{21} - \rho_{12}H_{21}]$$

$$= -\frac{i}{\hbar} (H_{12}\rho_{21} - H_{21}\rho_{12})$$

Mixed case density matrix I

Let $|\psi\rangle$ be the wavefunction of the “universe”

Divide the universe into a “system” (part we care about) with eigenfunctions $|\phi_i\rangle$ and the rest (we don't care about) with eigenfunctions $|\theta_i\rangle$

The most general $|\psi\rangle$ is $|\psi\rangle = \sum_{ij} C_{ij} |\phi_i\rangle |\theta_j\rangle$

Consider an operator \mathbf{A} that only acts on the system, i.e.,

$$\mathbf{A}|\theta_i\rangle|\phi_j\rangle = |\theta_i\rangle\mathbf{A}|\phi_j\rangle$$

For the system, \mathbf{A} can be written

$$\mathbf{A} = \sum_{i,j} A_{ij} |\phi_i\rangle\langle\phi_j|$$

where

$$A_{ij} = \langle\phi_i|\mathbf{A}|\phi_j\rangle$$

For the universe

$$\mathbf{A} = \sum_{i,j,k} A_{ij} |\phi_i\rangle|\theta_k\rangle\langle\theta_k|\langle\phi_j|$$

Mixed case density matrix II

What is the expectation value $\langle \mathbf{A} \rangle$?

$$\begin{aligned} \langle \mathbf{A} \rangle &= \langle \psi | \mathbf{A} | \psi \rangle = \sum_{\substack{n,m,n',m', \\ i,j,k}} C_{nm}^* C_{n'm'} \langle \theta_m | \langle \phi_n | A_{ij} | \phi_i \rangle | \theta_k \rangle \langle \theta_k | \langle \phi_j | \phi_{n'} \rangle | \theta_{m'} \rangle \\ &= \sum_{\substack{n,m,n',m', \\ i,j,k}} C_{nm}^* C_{n'm'} \underbrace{\langle \theta_m | \theta_k \rangle}_{\delta_{mk}} \underbrace{\langle \phi_n | \phi_i \rangle}_{\delta_{ni}} \underbrace{\langle \theta_k | \theta_{m'} \rangle}_{\delta_{km'}} \underbrace{\langle \phi_j | \phi_{n'} \rangle}_{\delta_{jn'}} A_{ij} \end{aligned}$$

(δ -functions arise because θ 's and ϕ 's are an orthonormal basis set)

$$= \sum_{i,j,k} C_{ik}^* C_{jk} \langle \phi_i | \mathbf{A} | \phi_j \rangle = \sum_{ij} \langle \phi_i | \mathbf{A} | \phi_j \rangle \rho_{ij} = \text{Tr}(\mathbf{A}\rho)$$

where

$$\rho_{ij} = \sum_k C_{ik}^* C_{jk}$$

Look closer at this definition:

$$\begin{aligned} \rho_{ij} &= \sum_k C_{ik}^* C_{jk} = \sum_k \langle \psi | \phi_i \rangle \langle \theta_k | \langle \phi_j | \psi \rangle = \sum_k \langle \theta_k | \langle \phi_j | \psi \rangle \langle \psi | \phi_i \rangle \langle \theta_k | \\ &= \sum_k \langle \phi_j | \underbrace{\langle \theta_k | \psi \rangle \langle \psi | \theta_k \rangle}_{w_k} | \phi_i \rangle = \sum_k w_k \langle \phi_i | \psi_k \rangle \langle \psi_k | \phi_j \rangle \end{aligned}$$

probability that rest of universe is described by $|\theta_k\rangle$

recall

$$|\psi\rangle = \sum_{ij} C_{ij} |\phi_i\rangle |\theta_j\rangle$$

$$\mathbf{A} = \sum_{i,j,k} A_{ij} |\phi_i\rangle \langle \theta_k | \langle \theta_k | \langle \phi_j |$$

interpret w_k as the probability that the system is described by $|\psi_k\rangle$. $|\psi_k\rangle$ is not an eigenfunction, but a state vector for the system.

Mixed case density matrix III

This yields the definition of the mixed case density matrix:

$$\rho = \sum_k w_k |\psi_k\rangle\langle\psi_k|$$

The same formulas hold for mixed case as pure case:

$$\dot{\rho} = -\frac{i}{\hbar} [\mathbf{H}, \rho]$$

$$\langle \mathbf{A} \rangle = \text{Tr}(\rho \mathbf{A})$$

(proofs left as exercise for the student...)

Dipole moment

Need to calculate how an atom responds to an applied electric field

Evolution of ρ given by Hamiltonian \rightarrow need energy of atom-field interaction:

$$V = -e\mathbf{E} \cdot \mathbf{r}$$

\mathbf{E} – applied field

\mathbf{r} – position of electron (in atom)

(note: this is in the dipole approximation, $\lambda \gg$ size of atom)

We will treat \mathbf{E} classically, need to compute expectation value of dipole moment $e\mathbf{r}$

$$\langle e\mathbf{r} \rangle = e\langle \psi | \mathbf{r} | \psi \rangle$$

i.e., all we have to calculate is $\langle \mathbf{r} \rangle$

Let's consider the dipole moment of various states of the simplest atom, hydrogen

Dipole moment of S states of H

The 1S wave function is

$$\psi_{10} \sim e^{-r/a_0}$$

where a_0 is the Bohr radius

Simplify to one dimension, x , $r = \sqrt{x^2 + y^2 + z^2}$ so $r \rightarrow |x|$

$$\begin{aligned}\langle x \rangle_{10} &= \langle \psi_{10} ||x| \psi_{10} \rangle = \int_{-\infty}^{\infty} e^{-|x|/a_0} |x| e^{-|x|/a_0} dx \\ &= \int_{-\infty}^0 e^{2x/a_0} (-x) dx + \int_0^{\infty} e^{-2x/a_0} x dx \\ &= -\frac{e^{2x/a_0}}{\frac{1}{2a_0}} (x - 2a_0) \Big|_{-\infty}^0 + \frac{e^{-2x/a_0}}{\frac{1}{-2a_0}} (-x + 2a_0) \Big|_0^{\infty} = 4a_0^2 - 4a_0^2 = 0\end{aligned}$$

Therefore the 1S state has no dipole moment because it has even symmetry

The 2S state is $|\psi_{20}\rangle \sim 1 - \frac{r}{a_0}$ which also has even symmetry and thus no dipole moment

Dipole moment of P states of H

What about the 2P states?

$$|\psi_{21}\rangle \sim \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

this has odd symmetry along x ($\theta = 0$ for $+x$, $\theta = \pi$ for $-x$) so

$$|\psi_{21}\rangle \sim \frac{x}{a_0} e^{-|x|/2a_0}$$

$$\begin{aligned} \langle x \rangle_{21} &= \langle \psi_{21} | |x| | \psi_{21} \rangle = \int_{-\infty}^{\infty} \frac{x}{a_0} e^{-|x|/2a_0} |x| \frac{x}{a_0} e^{-|x|/2a_0} dx \\ &= - \int_{-\infty}^0 \frac{x^3}{a_0^2} e^{x/a_0} dx + \int_0^{\infty} \frac{x^3}{a_0^2} e^{-x/a_0} x dx \end{aligned}$$

⋮ ← algebra happens here

$$= 6a_0^2 - 6a_0^2 = 0$$

so even for a P state there is no dipole moment.

How, you might ask, do we get a dipole moment???

Dipole moment of a superposition state (between S and P)

Consider a superposition state

$$|\psi\rangle = C_1|\psi_{10}\rangle + C_2|\psi_{21}\rangle$$

Calculate

$$\begin{aligned} \langle\psi|r|\psi\rangle &= C_1C_1^*\langle\psi_{10}|r|\psi_{10}\rangle + C_2C_2^*\langle\psi_{21}|r|\psi_{21}\rangle \longleftarrow \text{We know both of these are 0} \\ &\quad + C_1C_2^*\langle\psi_{21}|r|\psi_{10}\rangle + C_1^*C_2\langle\psi_{10}|r|\psi_{21}\rangle \end{aligned}$$

calculate these off-diagonal dipole moments

$$\begin{aligned} \langle\psi_{21}|r|\psi_{10}\rangle &\Rightarrow \langle\psi_{21}||x||\psi_{10}\rangle = \int_{-\infty}^{\infty} \frac{x}{a_0} e^{-|x|/2a_0} |x| e^{-|x|/a_0} dx \\ &\quad \vdots \\ &= \frac{1}{a_0} \left(-\frac{16a_0^3}{27} - \frac{16a_0^3}{27} \right) = -\frac{32a_0^2}{27} \neq 0 \end{aligned}$$

Conclusion: To have dipole moment, must be in a superposition state, $\rho_{ij} \neq 0$ ($i \neq j$)

Time dependence of dipole moment

Levels are eigenfunctions of Hamiltonian with eigenvalue E_i so

$$|\psi_i(t)\rangle = e^{i\frac{E_i t}{\hbar}} |\psi_i\rangle$$

thus

$$|\psi(t)\rangle = C_1 e^{i\frac{E_1 t}{\hbar}} |\psi_{10}\rangle + C_2 e^{i\frac{E_2 t}{\hbar}} |\psi_{21}\rangle$$

$$\begin{aligned} \langle \psi | r | \psi \rangle &= C_1 C_2^* e^{i\frac{(E_1 - E_2)t}{\hbar}} \langle \psi_{21} | r | \psi_{10} \rangle + c.c. \\ &= C_1 C_2^* e^{i\omega t} \mu_{12} \end{aligned}$$

where

$$\omega = \frac{E}{\hbar} \quad \mu_{12} = \langle \psi_{21} | r | \psi_{10} \rangle$$

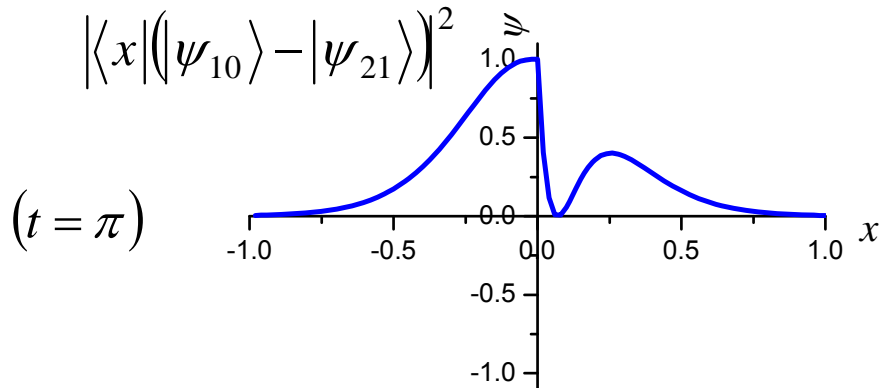
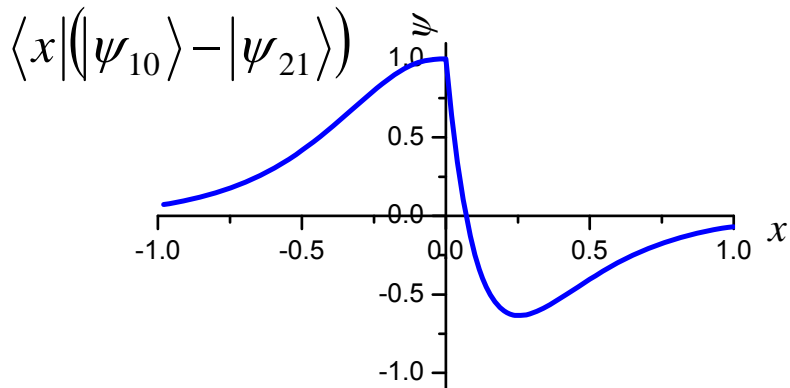
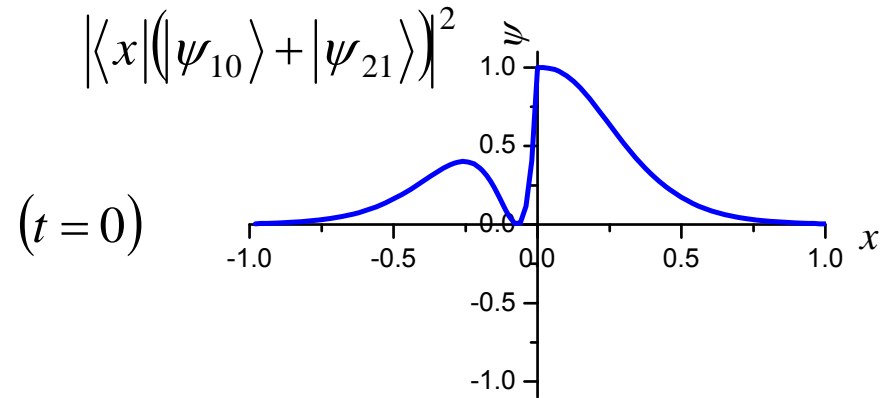
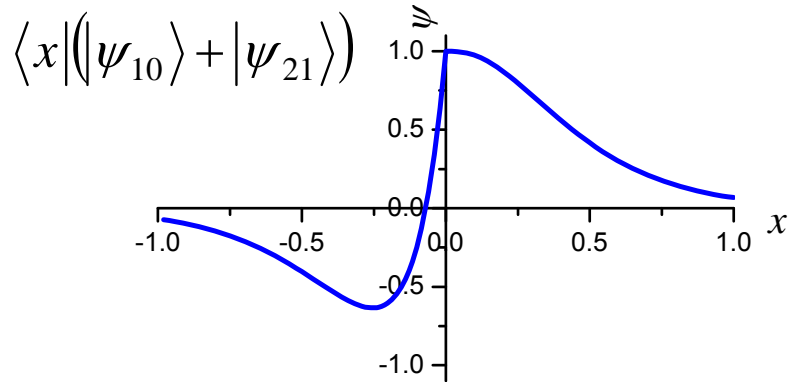
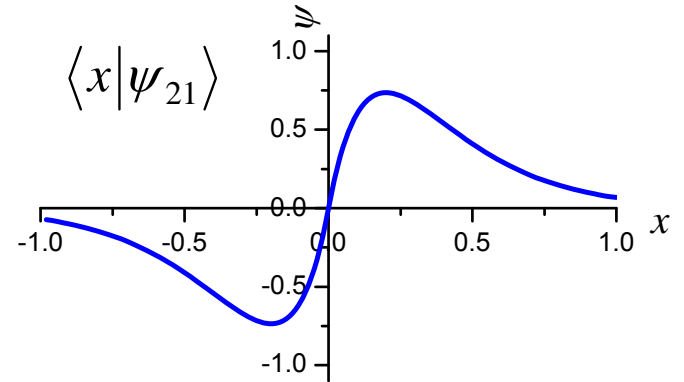
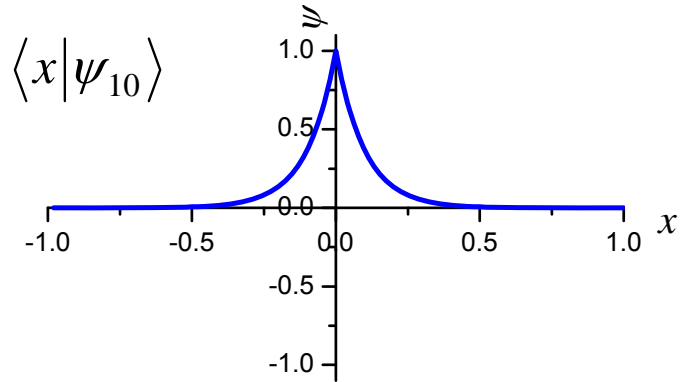
For a two level system, the dipole moment operator in matrix form is

$$\boldsymbol{\mu} = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} \quad \text{where} \quad \mu_{12} = -e \langle \psi_1 | r | \psi_2 \rangle$$

Notes:

- 1) In principle $\boldsymbol{\mu}$ is a tensor to include polarization
- 2) Typical values $\sim 0.3 \text{ nm} \cdot e$

In pictures....



Relaxation/Decay Phenomena

If the **probability** that the system is in state $|i\rangle$ decays exponentially at rate γ_i , then the equation of motion for C_i must have a term

$$\dot{C}_i = \dots - \frac{\gamma_i}{2} C_i \dots$$

since the probability $\propto |C_i|^2$

For ρ_{ii} there will be a term ($\rho_{ii} = C_i^* C_i$)

$$\dot{\rho}_{ii} = \dots - \gamma_i \rho_{ii} \dots$$

For ρ_{ij} there will be a term ($\rho_{ij} = C_i^* C_j$)

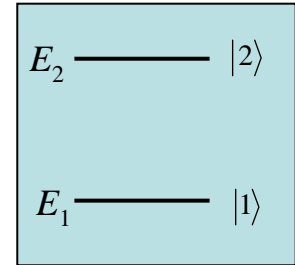
$$\dot{\rho}_{ij} = \dots - \gamma_{ij} \rho_{ij} \dots$$

where $\gamma_{ij} = \frac{1}{2}(\gamma_i + \gamma_j)$

Relaxation/Decay Phenomena in 2 Level system

Consider a 2-level system without an external field

$$H = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \quad (\hbar\omega = E_2 - E_1)$$



How do we include decay in the equation of motion for ρ ?

$$\dot{\rho} = -\frac{1}{2}[\Gamma\rho - \rho\Gamma] - \frac{i}{\hbar}[\mathbf{H}, \rho]$$

$$\text{where } \Gamma = \begin{pmatrix} \gamma_1 & 0 \\ 0 & \gamma_2 \end{pmatrix}$$

Writing this out

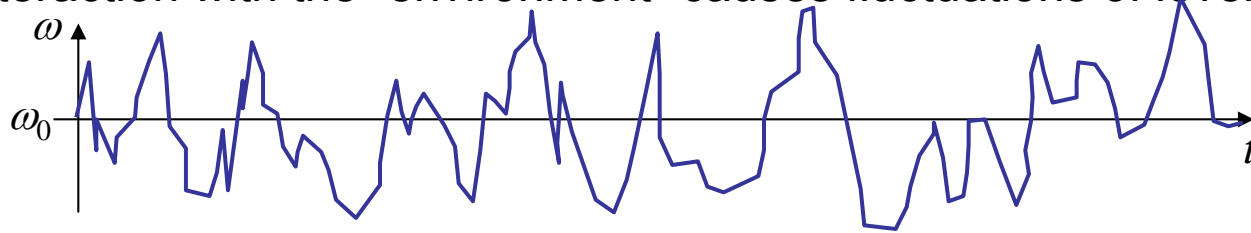
$$\dot{\rho}_{11} = -\gamma_1\rho_{11}$$

$$\dot{\rho}_{22} = -\gamma_2\rho_{22}$$

$$\dot{\rho}_{12} = -i\omega\rho_{12} - \gamma_{12}\rho_{12}$$

Relaxation/Decay of off-diagonal elements I

Interaction with the “environment” causes fluctuations of levels



For example, during a collision a transient molecular orbital forms

Write $\omega = \omega_0 + \delta\omega(t)$ then

$$\dot{\rho}_{12} = -i[\omega_0 + \delta\omega(t)]\rho_{12} - \gamma_{12}\rho_{12}$$

We can integrate this

$$\rho_{12}(t) = \rho_{12}(0)\exp\left[-(i\omega_0 + \gamma_{12})t - i\int_0^t \delta\omega(t')dt'\right]$$

now ensemble average over realizations of random function $\delta\omega(t)$

$$\left\langle \exp\left[-i\int_0^t \delta\omega(t')dt'\right] \right\rangle =$$

$$\left\langle 1 - i\int_0^t \delta\omega(t')dt' - \frac{1}{2}i\int_0^t \int_0^t \delta\omega(t')\delta\omega(t'')dt'dt'' + \dots + \frac{(-i)^{2n}}{(2n)!} \int_0^t \dots \int_0^t \delta\omega(t_1)\dots\delta\omega(t_{2n})dt_1\dots dt_{2n} + \dots \right\rangle$$

Relaxation/Decay of off-diagonal elements II

$$\left\langle \exp \left[-i \int_0^t \delta\omega(t') dt' \right] \right\rangle = \left\langle 1 - i \int_0^t \delta\omega(t') dt' - \frac{1}{2} i \int_0^t \int_0^t \delta\omega(t') \delta\omega(t'') dt' dt'' + \dots + \frac{(-i)^{2n}}{(2n)!} \int_0^t \dots \int_0^t \delta\omega(t_1) \dots \delta\omega(t_{2n}) dt_1 \dots dt_{2n} + \dots \right\rangle$$

Bring ensemble average inside integrals, $\langle \delta\omega(t) \rangle = 0$

The second term will average to zero for t different from t' , take the limit of this and set

$$\langle \delta\omega(t) \delta\omega(t') \rangle = 2\gamma_{ph} \delta(t - t')$$

This is called the Markoff (a.k.a. Markov) approximation, it means the finite duration of the collisions don't matter

Higher order terms in the expansion can be factored into pairs, for an odd number of terms, they average to zero, for an even number terms the possible permutations of breaking up the integral give a prefactor $(2n)!/2^n n!$ so the $2n$ term is

$$\frac{(-i)^{2n}}{(2n)!} (2\gamma_{ph})^n \frac{(2n)!}{2^n n!} \int_0^t \dots \int_0^t \delta\omega(t_1) \dots \delta\omega(t_{2n}) dt_1 \dots dt_{2n} = \frac{(-\gamma_{ph})^n}{n!}$$

hence

$$\left\langle \exp \left[-i \int_0^t \delta\omega(t') dt' \right] \right\rangle = \sum_{n=0}^{\infty} \frac{(-\gamma_{ph} t)^n}{n!} = \exp[-\gamma_{ph} t]$$

thus

$$\rho_{12}(t) = \rho_{12}(0) \exp[-(i\omega_0 + \gamma_{12} + \gamma_{ph})t]$$

We have a new decay rate

$$\gamma_{12}^{ph} = \gamma_{12} + \gamma_{ph}$$

Optical Bloch Equations (OBE)

The Optical Bloch Equations, which are the equations of motion for the elements of the density matrix

$$\dot{\rho} = -\frac{1}{2}[\Gamma\rho + \rho\Gamma] - \frac{i}{\hbar}[H, \rho]$$

where $\Gamma = \gamma_i \delta_{ij}$

write

$$H = H_0 + V$$

H_0 is the Hamiltonian for a 2-level system

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

V is the coupling to the EM field (later treat as small perturbation)

$$V = \underline{\mu}_{12} E = E(t) \mu_{12} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

dipole moment operator

Plugging these into the equation of motion for ρ gives

$$\dot{\rho}_{11} = -\gamma_1 \rho_{11} + \frac{i}{\hbar} \mu_{12} E(t) (\rho_{12} - \rho_{21}) \quad (1)$$

$$\dot{\rho}_{22} = -\gamma_2 \rho_{22} - \frac{i}{\hbar} \mu_{12} E(t) (\rho_{12} - \rho_{21}) \quad (2)$$

$$\dot{\rho}_{12} = -\gamma_{12}^T \rho_{12} + i\omega_0 \rho_{12} - \frac{i}{\hbar} \mu_{12} E(t) (\rho_{22} - \rho_{11}) \quad (3)$$

where

$$\omega_0 = \frac{E_2 - E_1}{\hbar}, \quad \gamma_{12}^T = \frac{1}{2}(\gamma_1 + \gamma_2) + \gamma_{ph}$$