Chem 564

NOTES 15

29 Apr 03
25 Apr 05
1 May 07 27 Apr 09

TIME DEPENDENT QUANTUM MECHANICS OF ENSEMBLES OF WEAKLY COUPLED (INDEPENDENT) SYSTEMS (TWO-LEVEL)

A. PURE STATES VS MIXED STATES (Ensembles)

Most experiments are carried out on a large number of molecules at the same time, i.e., on an ensemble (it is now possible to observe single molecules, but difficult).

When speaking of a single system or an ensemble of systems in identical states the ensemble is said to be in a

pure state

If the individual systems are in different states (do not have identical density matrices) the ensemble is said to be in a

mixed state

$\langle \rho(t) \rangle = \sum_k P_k \rho_k(t)$ where P_k is the probability to find a system with $\rho = \rho_k$ and $\sum P_k = 1$

<u>Note</u>: We are assuming that the members of the ensemble are interacting so weakly with each other as to be effectively <u>independent</u>

If there is a continuum of states

$$\langle \rho(t) \rangle = \int P(k)\, \rho(k,t)\, dk \qquad \text{with} \int P(k)\, dk = 1$$

The use of brackets $\langle \quad \rangle$ is commonly used to indicate an ensemble average.

Note that $P(k)$ is the density of states with units of probability per index k

B. <u>ENSEMBLE AVERAGE</u> (Expectation value)

1. <u>pure state case</u>: For a system in state ψ the expectation value for operator $\hat{A}$ is.

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

If $|\psi\rangle = \sum_k c_k |k\rangle$

$$\langle A \rangle = \sum_{k,l} c_k c_l^* \langle l | \hat{A} | k \rangle = \sum_{k,l} \rho_{kl} A_{lk}$$

$$\langle A \rangle = \sum_k (\hat{\rho} \hat{A})_{kk} = \text{trace}(\rho A)$$

If A is Hermitian, then

$$\langle A \rangle = \sum_{k\ell} \rho_{k\ell} A^*_{k\ell}$$ which may be evaluated much like a scalar projection if one thinks of the dual index k,ℓ as a single index.

2. Ensemble expectation value. $\langle\langle A \rangle\rangle$

$$\langle\langle A \rangle\rangle = \sum_k P_k \, \text{tr}(\rho_k A) = \text{tr}\left(\sum_k P_k \rho_k A\right)$$

3. Equilibrium Density Matrix

At equilibrium, the distribution of energies of the independent systems of an ensemble will be such that

$$\frac{C_m C_m^*}{C_n C_n^*} = e^{\frac{-(E_m - E_n)}{k_B T}} = \frac{\langle \rho_{mm} \rangle}{\langle \rho_{nn} \rangle}$$

i.e., the Boltzmann distribution.

For the two-state system ensemble

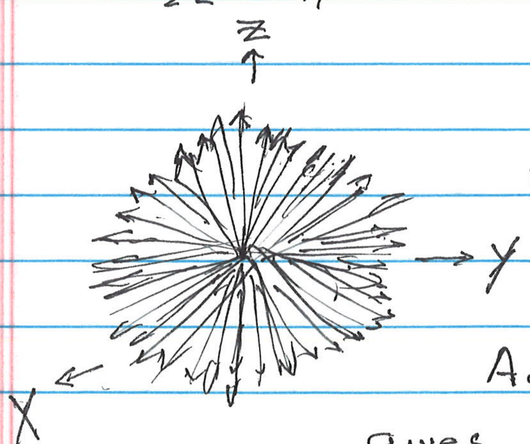
$$\frac{\langle |C_2|^2 \rangle}{\langle |C_1|^2 \rangle} = \frac{\langle \rho_{22} \rangle}{\langle \rho_{11} \rangle} = e^{-\frac{(H_{22}-H_{11})}{k_B T}} \quad \text{when } H_{12}=0$$

The relative phases of C_1 and C_2, however, are completely random. This means that.

$$\langle \rho_{12} \rangle = \langle \rho_{21} \rangle = 0$$

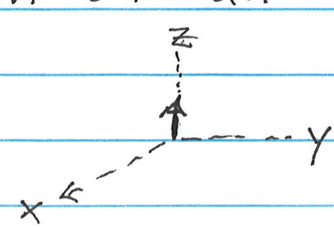
and $\langle \rho_x \rangle = \langle \rho_y \rangle = 0$

Pictorially, if we draw an arrow for the value of $\vec{\rho}$ for each member of the ensemble for a case where $H_{22}-H_{11} << k_B T$, i.e., $\langle \rho_{22} \rangle \cong \langle \rho_{11} \rangle$



The density of arrows is nearly the same for every direction in ρ space.

Addition of all the arrows gives



For a *large* number of systems, $\vec{e}$ points in the z direction if $H_{11} < H_{22}$. The random phases make $\langle e_x \rangle = \langle e_y \rangle = 0$

At equilibrium only $\langle \Omega_z \rangle \neq 0$, and since $\langle e_x \rangle = \langle e_y \rangle = 0$,

$$\langle \dot{e}_z \rangle = \langle \dot{e}_x \rangle = \langle \dot{e}_y \rangle = 0$$

But *each* system $\vec{e}$ is *dynamically* obeying $\dot{\vec{e}} = \vec{e} \times \vec{\Omega}$.

C. PULSE SPECTROSCOPY ON ENSEMBLES

1. $(\pi/2)_x$ pulse

This means we suddenly make

$H_{12} \gg |H_{22} - H_{11}|$ and real & positive

i.e. the eigenstates suddenly become $|1\rangle \pm |2\rangle$ with eigenvalues

$$E_{\pm} \cong H_{11} \pm H_{12}$$

$$\Omega_x \gg \Omega_z$$

<u>Each</u> system independently obeys $\dot{\vec{e}} = \vec{e} \times \vec{\Omega}$ but the <u>net</u> effect is what you deduce from $\langle \dot{\vec{e}} \rangle$

Initially
$$\langle \dot{\vec{e}}_z \rangle = \langle e_x \rangle \Omega_y - \langle e_y \rangle \Omega_x = 0$$
$$\langle \dot{\vec{e}}_x \rangle = \langle e_y \rangle \Omega_z - \langle e_z \rangle \Omega_y = 0$$
$$\langle \dot{\vec{e}}_y \rangle = \langle e_z \rangle \Omega_x - \langle e_x \rangle \Omega_z$$
$$= \langle e_z \rangle \Omega_x \cong \left(\frac{\Omega_z}{2K_B T} \right) (2H_{12})$$

i.e. $\langle \vec{e} \rangle$ starts tipping from pointing along z towards the $+y$ direction

<u>Note</u> $\langle e_{11} - e_{22} \rangle \cong \dfrac{\Omega_z}{K_B T}$ because

$$\frac{\langle e_{22} \rangle}{\langle e_{11} \rangle} = e^{-\frac{(H_{22}-H_{11})}{K_B T}} = e^{\frac{\Omega_z}{K_B T}}$$

and $\langle e_{11} \rangle + \langle e_{22} \rangle = 1$

This is solved by
$$e_{11} = \tfrac{1}{2} e^{\frac{\Omega_z}{2K_B T}}$$
$$e_{22} = \tfrac{1}{2} e^{-\frac{\Omega_z}{2K_B T}}$$

$$e_{11} - e_{22} \cong \tfrac{1}{2} \left[1 + \frac{\Omega_z}{2K_B T} - \left(1 - \frac{\Omega_z}{2K_B T} \right) \right] = \frac{\Omega_z}{2K_B T}$$

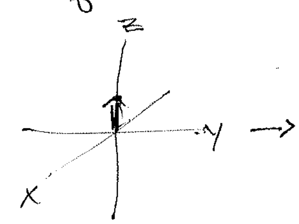
The *net* result is: a $\left(\frac{\pi}{2}\right)_x$ pulse takes $\langle \rho \rangle$ from pointing in the $+z$ direction to pointing in the $+y$ direction.

But the length is unchanged, so $\langle \rho \rangle$ evolves as

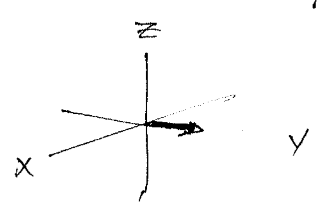
$$\begin{pmatrix} \langle \rho_{11} \rangle_{eq} & 0 \\ 0 & \langle \rho_{22} \rangle_{eq} \end{pmatrix} \xrightarrow{(\pi/2)_x} \frac{1}{2} \begin{pmatrix} \langle \rho_{11} \rangle_{eq} + \langle \rho_{22} \rangle_{eq} & i\left(\langle \rho_{11} \rangle_{eq} - \langle \rho_{22} \rangle_{eq}\right) \\ -i\left(\langle \rho_{11} \rangle_{eq} - \langle \rho_{22} \rangle_{eq}\right) & \langle \rho_{11} \rangle_{eq} + \langle \rho_{22} \rangle_{eq} \end{pmatrix}$$

i.e. $\langle \rho_z \rangle = 0$, $\langle \rho_x \rangle = 0$, $\langle \rho_y \rangle = \langle \rho_{11} \rangle_{eq} - \langle \rho_{22} \rangle_{eq}$.

The net ensemble $\vec{\rho}$ tips from



to



This is because of the *slight* excess of $\vec{\rho}$ vectors pointing in $+z$ compared to $-z$ i.e. slightly larger population of $|1\rangle$ compared to $|2\rangle$

Recall $|1\rangle \rightarrow \frac{|1\rangle - i|2\rangle}{\sqrt{2}}$ points in $\vec{y}$ $\rho_{12} = \frac{+i}{2}$

but $|2\rangle \rightarrow \frac{|2\rangle - i|1\rangle}{\sqrt{2}}$ $\rho_{12} \rightarrow -i/2$ points in $-y$

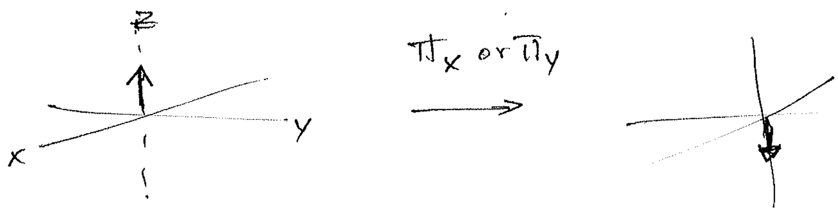
2. π_x pulse

Likewise the effect of a π_x pulse can be deduced as for the effect on individual systems

$$\begin{pmatrix} \langle \rho_{11}\rangle_{eq} & 0 \\ 0 & \langle\rho_{22}\rangle_{eq}\end{pmatrix} \xrightarrow{\pi_x \text{ or } \pi_y} \begin{pmatrix} \langle\rho_{22}\rangle_{eq} & 0 \\ 0 & \langle\rho_{11}\rangle_{eq}\end{pmatrix}$$

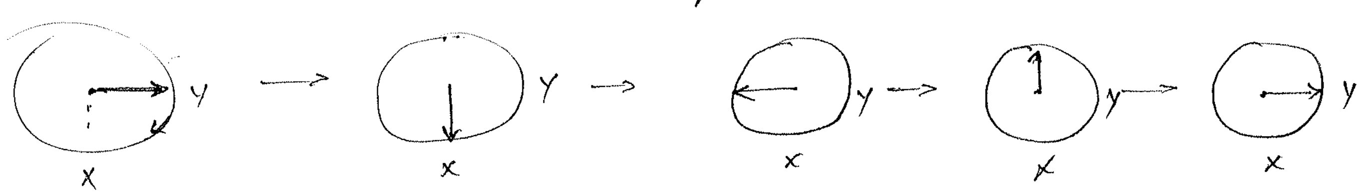
i.e. net population is inverted

$\langle \vec{\rho} \rangle$:



3. Free Precession & Coherence

As for individual systems if $H_{12} = 0$ after the $\pi/2$ pulse the $\langle \vec{\rho} \rangle$ precesses about z



at the Larmor frequency $\omega_0 = \dfrac{H_{22} - H_{11}}{\hbar}$

This oscillating density is called coherence between $|1\rangle$ and $|2\rangle$. It can be detected, often as an oscillating dipole (emission of light)