Chem 564 NOTES 14

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TIME EVOLUTION OF DENSITY (Continued)

A. Getting to Know F.V.H Equations

1. The 3 Cases from NOTES

Case 1 $H_{11} = H_{22}$, $H_{12} = H_{21}$ = real & positive

(Resonance), $\psi(0) = |1\rangle$, $\rho_{11}(0) = 1$

Ω_x = Positive $\qquad \rho_{22}(0) = 0$

$\Omega_y = 0 \qquad \rho_{12}^{(0)} = \rho_{21}^{(0)} = 0$

$\Omega_z = H_{11} - H_{22} = 0$

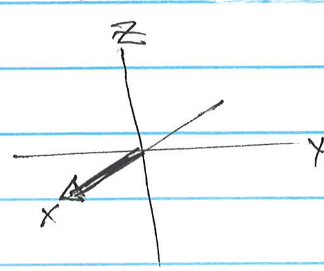
$\rho_x = \rho_{12} + \rho_{21} = 0$

$\rho_y = -i(\rho_{12} - \rho_{21}) = 0$

$\rho_z = \rho_{11} - \rho_{22} = 1$

$$\rho(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$\vec{\Omega} =$



from NOTES 8, p. 4

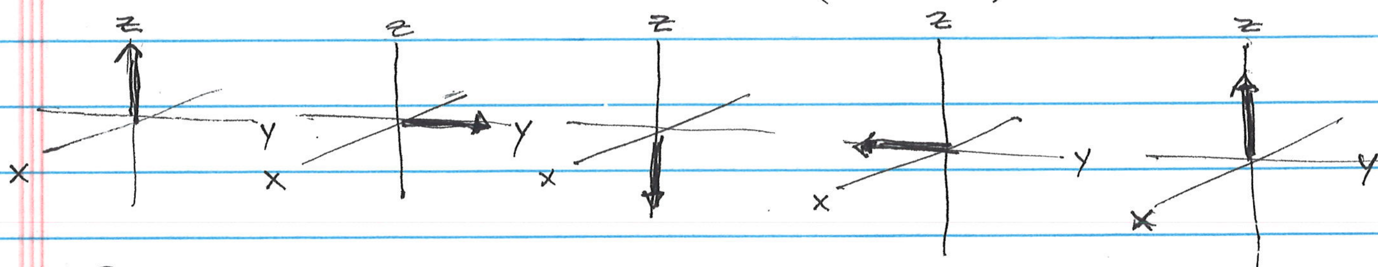
Case 1

$\psi = c_1|1\rangle + c_2|2\rangle \qquad c_1 = \cos\omega t \qquad -i\sin\omega t$

$\omega = \dfrac{H_{12}}{\hbar}$

ωt:	0	$\pi/4$	$\frac{\pi}{2}$	$\frac{3\pi}{4}$	π
$\psi =$	$\|1\rangle$	$\frac{\|1\rangle - i\|2\rangle}{\sqrt{2}}$	$-i\|2\rangle$	$\frac{-\|1\rangle - i\|2\rangle}{\sqrt{2}}$	$-\|1\rangle$
$\underset{\approx}{\rho}$	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1/2 & +i/2 \\ -i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$

$\vec{\rho}$



	$\rho_z = 1$	$\rho_y = 1$	$\rho_z = -1$	$\rho_y = -1$	$\rho_z = 1$
$2\omega t$	0	$\pi/2$	π	$\frac{3\pi}{2}$	2π

Notes: • Density is periodic with frequency $= 2\omega t$

Rabi frequency $= 2\omega = \dfrac{2H_{12}}{\hbar} = \omega_1$

• a "$\frac{\pi}{2}$ pulse" equalizes population

• a "π pulse" inverts population

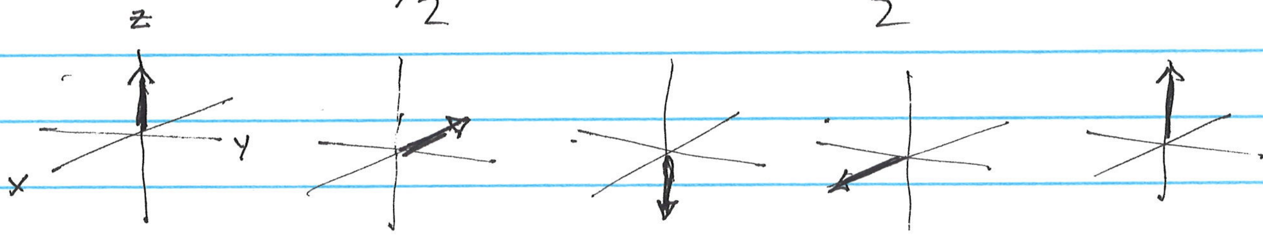
where ρ_{11} & ρ_{22} = population of states 1 & 2

Case 2: $H_{11} = H_{22}$ $\quad H_{12} =$ pure imaginary.

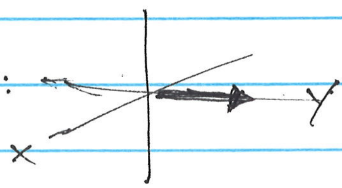
$\Omega_y =$ positive $\quad \Omega_x = \Omega_z = 0$

$\psi(0) = |1\rangle$

$2\omega t \quad 0 \quad \pi/2 \quad \pi \quad \frac{3\pi}{2} \quad 2\pi$



$\vec{\Omega}$:



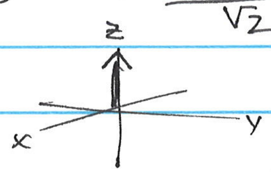
Case 1 & 2 = pure nutation

Case 3 $\quad H_{11} - H_{22} > 0 \quad H_{12} = 0$

$\Omega_z =$ positive $\quad \Omega_x = \Omega_y = 0$

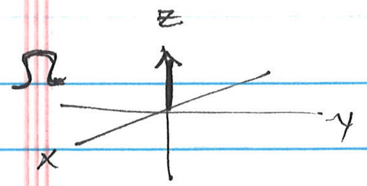
$\psi(0) = \frac{|1\rangle + |2\rangle}{\sqrt{2}} \qquad e_x = 1 \quad e_z = e_y = 0$

Ω



$$\rho_{12} = C_1^{(0)} C_2^{*(0)}\, e^{-i\frac{(E_1 - E_2)t}{\hbar}} = \tfrac{1}{2} e^{-i\omega t}$$

$\omega =$ Larmor Frequency

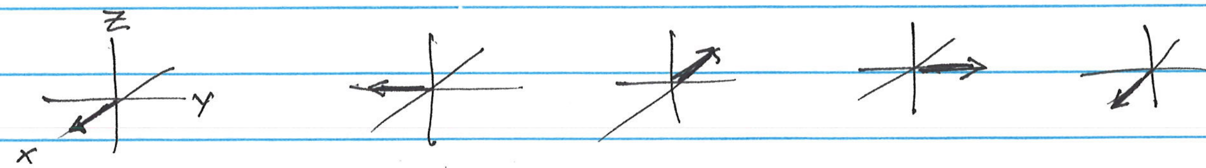


$H_{12} = H_{21} = 0 \quad \Omega_x = \Omega_y = 0$

Free Precession

ωt	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$	2π
$\underset{\sim}{\rho}$	$\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & i/2 \\ -i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$
ρ_x	1	0	−1	0	1
ρ_y	0	−1	0	1	0
ρ_z	0	0	0	0	0

$\vec{\rho}$



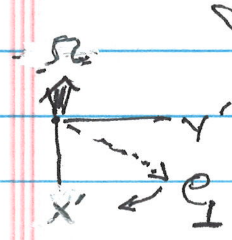
General Case.

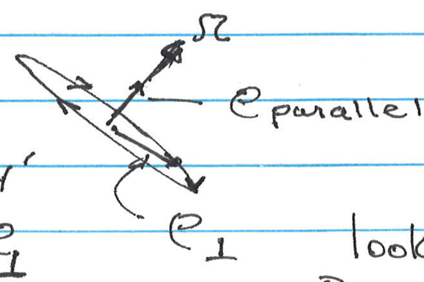
$H_{11} \neq H_{22}$

$H_{12} = a + ib$

$$\vec{\Omega} = 2a\,\vec{i} + 2b\,\vec{j} + (H_{11} - H_{22})\,\vec{k}$$

$\vec{\rho}$ has a component $\perp$ to $\vec{\Omega}$ and a component parallel to $\vec{\Omega}$





precession of $\rho_\perp$ is by LEFT HAND RULE (in most books), i.e., looking in $-\vec{\Omega}$ direction the $\rho_\perp$ moves clockwise