Chem 564 $\boxed{\text{NOTES 13}}$ TIME EVOLUTION OF DENSITY: Feynman-Vernon-Hellworth Equations

22 Apr 03
24 Apr 05
27 Apr 09

Liouville Equation: follows easily from the Schroedinger Eq:

$$|\dot{\psi}\rangle = -i\mathcal{H}|\psi\rangle$$

$$\langle\dot{\psi}| = i\langle\psi|\mathcal{H}^{\dagger} \qquad \text{Hermitian Conjugate}$$

$$\dot{\rho} = \frac{d|\psi\rangle\langle\psi|}{dt} = |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}|$$

$$= -i\mathcal{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\mathcal{H}$$

$$= -i\mathcal{H}\rho + i\rho\mathcal{H}$$

$$= -i(\mathcal{H}\rho - \rho\mathcal{H}) = -i[\mathcal{H},\rho]$$

$$\equiv -i\mathcal{L}\rho$$

Definition of Liouvillean $\equiv -i$ commutator with $\mathcal{H}$

Equivalently

$$\dot{\rho} = i[\rho,\mathcal{H}] = i(\rho\mathcal{H} - \mathcal{H}\rho)$$

$$\frac{d\rho}{dt} = i(\rho\mathcal{H} - \mathcal{H}\rho)$$

$$= \dot{\rho}_{11}|1\rangle\langle 1| + \dot{\rho}_{12}|1\rangle\langle 2| + \dot{\rho}_{21}|2\rangle\langle 1| + \dot{\rho}_{22}|2\rangle\langle 2|$$

$$\dot{\rho}_{11} = i\langle 1|\rho H - \mathcal{H}\rho|1\rangle = i\left((\rho H)_{11} - (H\rho)_{11}\right)$$

$$= i\left(\cancel{\rho_{11}H_{11}} + \rho_{12}H_{21} - \cancel{H_{11}\rho_{11}} - H_{12}\rho_{21}\right)$$

$$\boxed{\dot{\rho}_{11} = i\left(\rho_{12}H_{21} - H_{12}\rho_{21}\right)}$$

$$\dot{\rho}_{22} = i\left(\rho_{21}H_{12} + \rho_{22}H_{22} - H_{21}\rho_{12} - H_{22}\rho_{22}\right)$$

$$\boxed{\dot{\rho}_{22} = i\left(\rho_{21}H_{12} - H_{21}\rho_{12}\right)} = \underline{\underline{-\dot{\rho}_{11}}}$$

So $\dot{\rho}_{11} + \dot{\rho}_{22} = 0$ <u>Conservation of Probability</u>

$$\dot{\rho}_{12} = i\left(\rho_{11}H_{12} + \rho_{12}H_{22} - H_{11}\rho_{12} - H_{12}\rho_{22}\right)$$

$$\boxed{\dot{\rho}_{12} = i\left((\rho_{11} - \rho_{22})H_{12} - \rho_{12}(H_{11} - H_{22})\right)}$$

$$\dot{\rho}_{21} = i\left(\rho_{21}H_{11} + \rho_{22}H_{21} - H_{21}\rho_{11} - H_{22}\rho_{21}\right)$$

$$\boxed{\dot{\rho}_{21} = i\left(-(\rho_{11} - \rho_{22})H_{21} + \rho_{21}(H_{11} - H_{22})\right)}$$

Feynman - Vernon - Hellwarth saw that three independent combinations of the four density elements behave as the components of an <u>ordinary 3-space vector</u>. as do the corresponding combinations of $\mathcal{H}$

$$\rho_x = 2 * \text{Real part of } \rho_{12} = \rho_{12} + \rho_{21}$$

$$(\text{since } \rho_{21} = \rho_{12}^*)$$

$$\rho_y = 2 \cdot \text{Imaginary Part of } \rho_{12} = -i(\rho_{12} - \rho_{21})$$

$$\rho_z = \text{Population Difference.} = \rho_{11} - \rho_{22}$$

$$\Omega_x = H_x = 2 * \text{Real part of } H_{12} = H_{12} + H_{21}$$

$$\Omega_y = H_y = 2 * \text{Imaginary part of } H_{12} = -i(H_{12} - H_{21})$$

$$\Omega_z = H_z = \text{Energy Difference} = H_{11} - H_{22}$$

Thus

Identity op.

$$\dot{\rho}_{11} + \dot{\rho}_{22} = \dot{E} = 0 \qquad \text{Conservation of prob.}$$

$$\dot{\rho}_{11} - \dot{\rho}_{22} = \dot{\rho}_z = (\rho_{12}+\rho_{21})\{-i(H_{12}-H_{21})\}$$
$$- \{-i(\rho_{12}-\rho_{21})(H_{12}+H_{21})\}$$

or $$\boxed{\dot{\rho}_z = \rho_x \Omega_y - \rho_y \Omega_x}$$

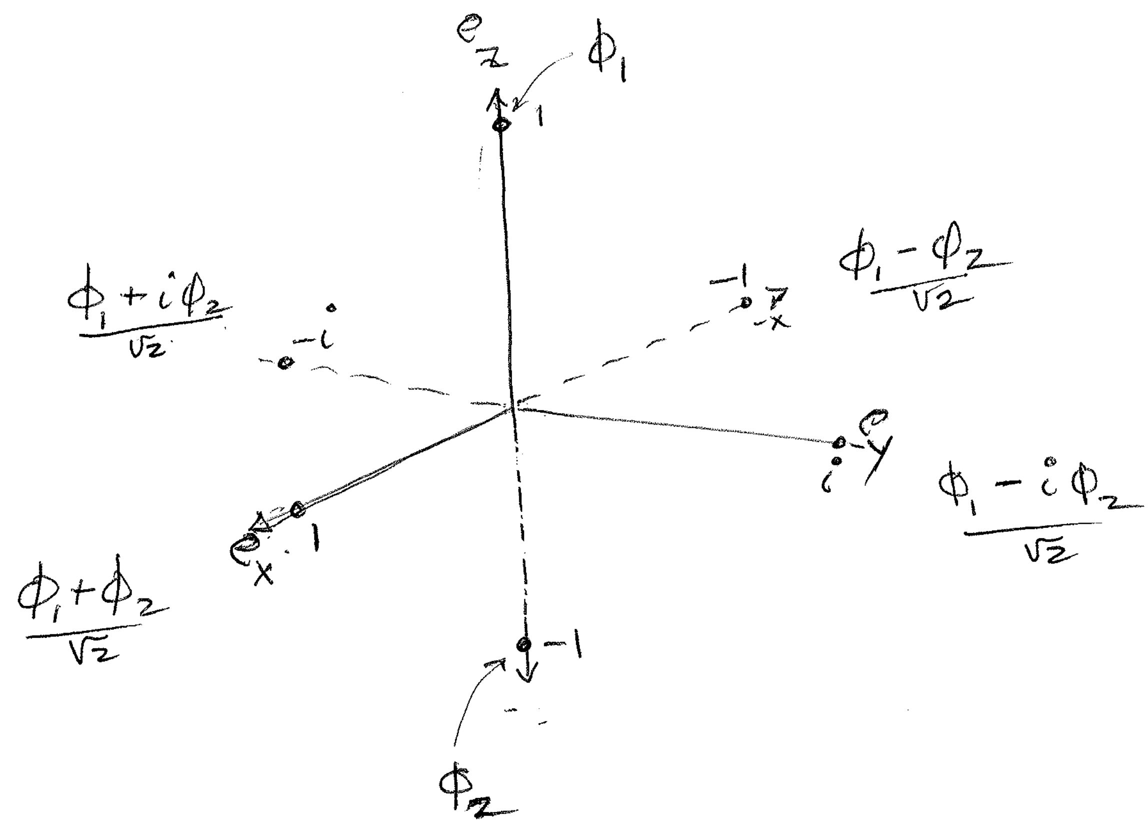
$$\dot{\rho}_{12} + \dot{\rho}_{21} = \dot{\rho}_x = -i(\rho_{12}-\rho_{21})(H_{11}-H_{22}) -$$
$$(\rho_{11}-\rho_{22})(-i(H_{12}-H_{21}))$$

or $$\boxed{\dot{\rho}_x = \rho_y \Omega_z - \rho_z \Omega_y}$$

$$-i(\dot{\rho}_{12} - \dot{\rho}_{21}) = \dot{\rho}_y = (\rho_{11}-\rho_{22})(H_{12}+H_{21}) - (\rho_{12}+\rho_{21})(H_{11}-H_{22})$$

or $$\boxed{\dot{\rho}_y = \rho_z \Omega_x - \rho_x \Omega_z}$$

$$\boxed{\dot{\vec{\rho}} = \vec{\rho} \times \vec{\Omega}}$$



$\psi = c_1 \phi_1 + c_2 \phi_2$ at the extreme points in density space,

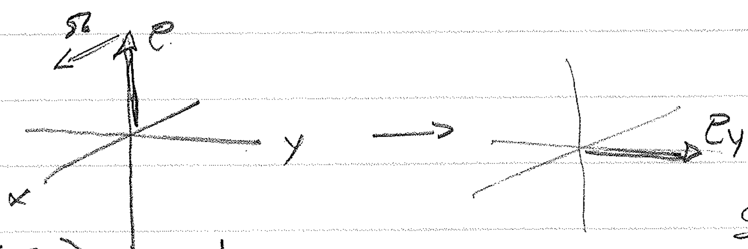
Starting with $\psi = \phi_1 \equiv |1\rangle$ with H_{12} = real & +
and with $H_{11} = H_{22}$

gives $\Omega_x = +$ $\qquad \rho_x = 0$
$\Omega_y = 0$ $\qquad \rho_y = 0$
$\Omega_z = 0$ $\qquad \rho_z = 1$

Thus, only $\dot{\rho}_y = \rho_z \Omega_x - \rho_x \Omega_z$ is $\neq 0$
$= +$

ρ evolves from $\rho_z \rightarrow \rho_y$

ψ evolves from $|1\rangle \longrightarrow \dfrac{|1\rangle - i\,|2\rangle}{\sqrt{2}}$



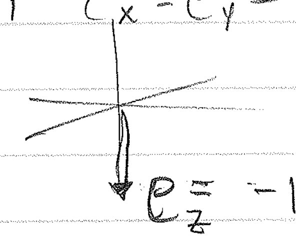
Now $\rho_z = 0$, $\rho_y = 1$
Ω still $= \Omega_x = +$

a $(\pi/2)_x$ pulse

Now $\dot{\rho}_y = 0$ by $\dot{\rho}_z = \rho_x \Omega_y - \rho_y \Omega_x$ = neg.

Density further evolves $\rightarrow$ $\rho_z = -1$ $\quad \rho_x = \rho_y = 0$

π_x pulse (inversion)



Note that $\vec{\rho}$ precesses clockwise about $\vec{\Omega}$
view from + z direction.