

- 1) rotate by  $\alpha$  about  $z$
- 2) rotate by  $\beta$  around  $y$
- 3) rotate by  $\gamma$  around  $x$



Euler angles  $\alpha / \beta / \gamma$

- now consider any orbiting molecule, defined by the

use  $2J+1$  vectors span a space  $E(t)$  - since  
 $J_+, J_-, \pm J_z$  turn these vectors into one another,  
any vector of  $E(t)$  is transformed into another  
vector in  $E(t)$  — they leave  $E(t)$  invariant.

- we can construct all  $2J+1$  vectors of well-defined  
angular momentum by operating on the state  $|Jm\rangle$   
repeatedly with  $J_+$  &  $J_-$  operators.

- consider a quantum system with angular momentum  $J$

TRIGONOMETRIC BASIS OPERATORS

$$\langle \tilde{M} | e^{-i\alpha \hat{T}_z} e^{-i\beta \hat{T}_y} | \tilde{M} \rangle =$$

$$R(\alpha, \beta) \equiv \langle \tilde{M} | R(\alpha, \beta) | \tilde{M} \rangle$$

We can define rotation matrices

$\Rightarrow$  irreducible with respect to rotations.

$R(u)$  span the whole space  $\mathcal{G}(T)$

i.e. if  $|u\rangle$  is an arbitrary vector of  $\mathcal{G}(T)$ , then

$\mathcal{G}(T)$  is invariant under rotation.

non-commuting operations.

- so rotations can always be described in terms of angular

$$= e^{-i\alpha \hat{T}_z} e^{-i\beta \hat{T}_y} e^{i\gamma \hat{T}_z}$$

$$R(\alpha, \beta, \gamma) = e^{-i\gamma \hat{T}_z} e^{-i\beta \hat{T}_y} e^{i\alpha \hat{T}_z}$$

one can show that this can be described by the rotation

$$= R^{i_1} R^{j_2} [A \otimes B]^{k_2}$$

$$[A \otimes B]^{k_2} = A^{i_1} B^{j_2} = R^{i_1} R^{j_2} A^{k_2} B^{k_2}$$

under notation

$$\underline{A} \otimes \underline{B} = A^i B^j$$

- another example - consider tensor product of 2 vectors

$$\text{then } u_m = \sum_{i_1, i_2} R^{(i_1, i_2)} u_{i_1} u_{i_2}$$

$$\text{if } u_m = \langle \cdot | M | u \rangle \quad (2 \times 1 \text{ component of } | u \rangle)$$

so for example

vector is represented by a  $n \times n$  matrix

- choose a basis set of vectors in  $\mathbb{R}^n$

so vectors of  $\mathbb{R}^n$  are  $2 \times 1$  - component tensors.

By definition, the vectors are  $n$ -component tensors.

vectors in  $\mathbb{R}^n$ .

tensors of the vectors in  $\mathbb{R}^n$  transform like other

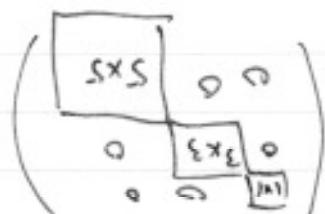
- consider an  $n$ -dimensional space  $\mathbb{R}^n$ , such that

tensor operator.  
defines the  $2k+1$  components of an irreducible  $k^{\text{th}}$ -order

$$R T_{(k)} R^{-1} = \sum_{g=1}^{2k+1} T_{(k)}^{(g)} P_{(k)}^{(g)}$$

a formal definition:

The 3 subspaces are defined by  $A \cdot B$ ,  $A \times B$  is a  
S component tensor.



can write  $9 \times 9$  which is some choice of basis as:

- the 9-D space is the sum of 3 irreducible subspaces with 1, 3, 5 dimensions

but  $A \otimes B$  is reducible

- e.g. ~~closure~~ the vecors of  $\mathbb{C}^n$  are irreducible

!+ is defined is irreducible with respect to reflections.

- a tensor is irreducible if the space  $\mathbb{C}^n$  in which

- certain tensors are special - "irreducible tensors"

$\frac{\partial}{\partial \bar{z}} \text{ dependence}$  on  $w$

reduced mechanics  
element

Clebsch-Gordan  
coupling

$$\langle \bar{n}, \bar{J}_M | T_{(k)}^g | \bar{n}, \bar{J}_M \rangle = C(\bar{J}_M; M^g, J_{(k)})$$

- the Wigner-Eckart Theorem:

$$K_{(1)} = -\frac{1}{2} (K_x + iK_y) \quad K_{(2)} = K_x - \frac{1}{2} (K_x - iK_y)$$

- vector operators are rank-1

- scalar operators are 0-th-order irreducible tensor operators.

- they have standard commutation relations with  $J_i$ .

$$[J_z, T_{(k)}^g] = g T_{(k)}^g$$

$$[J_z, T_{(k)}^g] = \sqrt{k(k+1)} [T_{(k)}^g, T_{(k)}^g]$$

- a complete valid alternative definition:

$$\Delta m = 0, \pm 1$$

$$\Delta J = 0, \pm 1$$

dipole transitions:

$\Leftarrow$  this yields the selection rules for electric

$$z = 3$$

( $b_1^+ b_1^- + b_2^+ b_2^- + b_3^+ b_3^-$ ) and irreducible tensor operators

where  $Y_0^k(\theta, \phi)$  are spherical harmonics (and are

$$e^{-\frac{r}{a}} = e^{-\left[\frac{1}{4}kr\right]} \left[ Y_1^1, Y_1^{-1}, -Y_0^0, Y_1^2, Y_1^{-2} \right]$$

e.g. expand the dipole operator in spherical harmonics

$$m + g = m$$

and

$$|J, m_J \rangle = |J, m_J \rangle$$

from transition rules for Clebsch-Gordan coefficients

$$[\psi]_{\mu} = \langle \psi | \mu | \psi \rangle \stackrel{\text{min}}{\geq} = \langle \mu \rangle \quad \text{thus}$$

$$|\psi\rangle \langle \psi| \stackrel{?}{\geq} \frac{N}{1} = \underbrace{\langle \psi | \mu | \psi \rangle}_{\text{define the density matrix } \rho} = \langle \mu \rangle = \frac{\text{the elements}}{N}$$

$$\langle \psi | \mu | \psi \rangle \stackrel{?}{\geq} \frac{N}{1} =$$

$$\langle \psi | \mu | \psi \rangle \stackrel{?}{\geq} \frac{N}{1} = \langle \mu \rangle$$

usually we average over the ensemble to find the value of  $\mu$

$$\langle \psi | \mu | \psi \rangle \stackrel{?}{\geq} \frac{N}{1} =$$

$$\langle \psi | \mu | \psi \rangle \stackrel{?}{\geq} \frac{N}{1} = \langle \psi | \mu | \psi \rangle \quad \text{so}$$

any physical ensemble corresponds to the expectation value of the operator  $\mu$

$$\langle \psi | \mu | \psi \rangle \stackrel{?}{\geq} \frac{N}{1} = \langle \psi | \mu | \psi \rangle$$

comes a general quantum state for the  $i^{\text{th}}$  atom

the density matrix:

$$T_{(2)}^{\circ} = \left( 3J_z^2 - J_x^2 \right) / 2 \quad T_{(2)}^{\pm} = \pm (J_z^2 \mp J_x^2) / 2 \quad T_{(2)}^{z^2} = (J_z^2) / 2$$

$$T_{(0)}^{\circ} = \frac{J_z}{\sqrt{2}} \quad T_{(1)}^{\pm} = \pm \frac{J_x}{\sqrt{2}} \quad T_{(1)}^{z^2} = \frac{J_z^2}{2}$$

for  $J=1$

(degenerate to  $C-G_3$ )

$\rightarrow$  3-j symbol

$$|g-m> <\bar{m}|m-g> \left[ \begin{array}{c} g-m \\ \bar{m}-g \\ k \end{array} \right] \left[ \begin{array}{c} g-m \\ \bar{m}-g \\ k+1 \end{array} \right] = \sum_{k=0}^m (-1)^k P_k^g T_{(k)}^{\circ}$$

moment of the density matrix.

where  $P_k^g$  are the components of the  $2^k$ -multiple

$$(-1)^g P_k^g T_{(k)}^{\circ} = d$$

the density matrix in terms of irreducible tensor operators:

For an atom with angular momentum  $J$ , expand

- We need to use the density matrix formalism.

decoherence.

a wave fn.  $\Rightarrow$  they are not pure states, due to

- Many quantum systems cannot be described by

quadratic polynomials were

— for fluorescence or absorption, may dipole;

the others, and each has a characteristic decay rate.

When a polarized ensemble relaxes (e.g. desensitizing acidic sites), each molecule is decoupled from

— when a polarized ensemble relaxes (e.g. desorbing

- Spherical or oscillating magnetic fields cannot change the multipolarity of a distribution

$\frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5}$	.....	—	—	—
$\frac{1}{2} + \frac{1}{3}$	.....	—	—	.....
$\frac{1}{2} + \frac{1}{3} + \frac{1}{4}$	.....	—	—	—
$\frac{1}{2}$	—	—	—	—

for a spin-3/2 charm

$$(\text{absolute moment}) + \text{age moment} \leftarrow \frac{g}{2} d$$

(3 components of  $\underline{\underline{f}}$ )

8  
P  
1  
arithmetic

$$w_{45} / \ln \rho_0 \leq \frac{1}{\rho}$$

$$(\partial L + [J^a H] \frac{\partial}{\partial J^a}) = \frac{\delta S}{\delta e}$$

Including relaxation, dissipation etc. (not in  $H$ )

$$[J^a H] \frac{\partial}{\partial J^a} = \frac{\delta S}{\delta e}$$

Schrodinger Eq.  $\Rightarrow$  Liouville equation

Evolution of the density matrix

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$\Leftrightarrow$  This reduces a possible relaxation rate to  $(2\zeta + 1)$

If this was not true, an initially spherically symmetric distribution would convert to a preferred direction in space which would decay to something asymmetric,

If this was not true, an initially spherically symmetric

$$\frac{\delta}{\delta J^a} L = \frac{\delta S}{\delta e}$$

to account at the same rate:

requires all  $2k+1$  components of the  $L^a$  will have

cancel on average since - isotope of space

- the density matrix is constant except for pumping and relaxation.

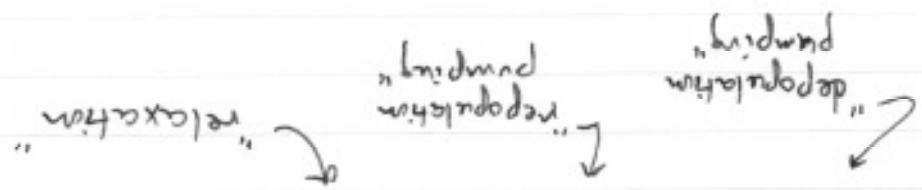
$$(d) \bar{\rho} = \int \frac{\partial P}{P}$$

then the Liouville equation becomes

$$\dot{\rho} = e^{-\frac{H}{\hbar}} - e^{\frac{H}{\hbar}}$$

dense density matrix is time-averaging picture (defined by  $\sim$ )

Note: quite often one uses the hierarchical picture to remove time dependence due to  $H_0$ .



$$\dots + \int_{(3)} \frac{\partial P}{P} + \int_{(2)} \frac{\partial P}{P} + \int_{(1)} \frac{\partial P}{P} = (d) \bar{\rho}$$

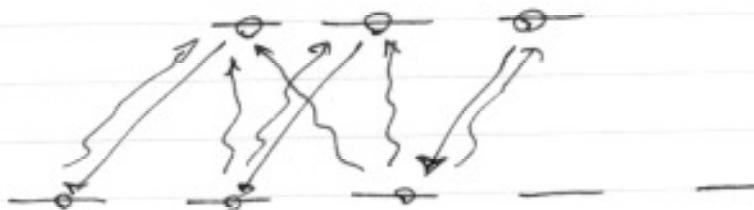
The Liouville operator for optical pumping is written as

$T = M = \Gamma$ , when is pumped all population



transitions given by C-C scattering.

The excited states decay, with  $\Delta M = 0, \pm 1$  and



apply C + light sees  $\Delta M = 0, \pm 1$



$J = 2$  e.s.

light of given polarization and frequency.

in some particular distribution of states with

"Optical pumping" - preparation of atoms

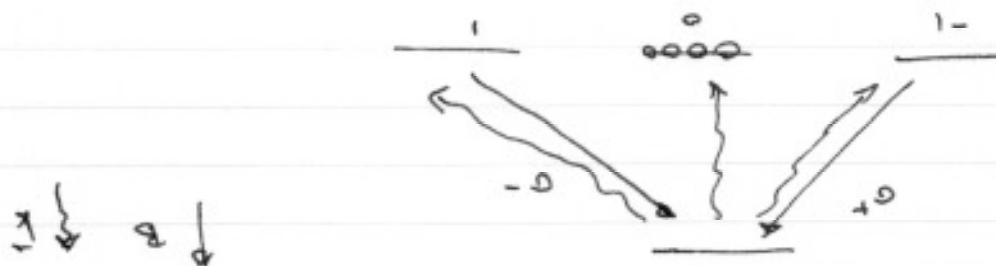
$$\frac{d\langle \rangle}{dt} / P_{\text{par}} = - g \int_{\text{par}} P_{\text{par}} d\omega$$

changes in qd. state due to  $\omega$ :

exchanges was weak because there is no field at  $\omega_2$ ,  
atoms accumulate in 2, in this case because the

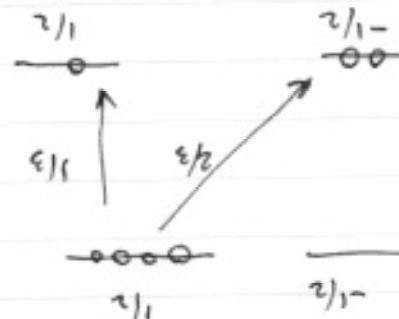


exchange rates.  
accumulate in the states with the weakest  
shifts at depopulation  $\Rightarrow$  atoms tend to  
atoms accumulate in  $m=0$ , because the  $m=1$



Depopulation Pumping

- transfer of polarization from an excited state to a ground state.



- "Depopulation pumping"

$$P_{nm} = \sum_i R_{nm} / P_{nn}$$

- now in the excited state,

Note: quite often there is no depopulation pumping for a broad spectral source.

$\tau = \text{excited state width}$

$D_{nm} = \text{dipole operator from n to m}$

$$R_{nm} = \frac{1}{\tau} \left| \vec{E}_{nm} \cdot \vec{P}_{nm} \right|^2 + \text{c.c.}$$

where  $S_{nm} = \sum_m R_{nm}$

$m = \text{excited state sublevel}$

different multiplets

- various relaxation mechanisms may couple to

random walk electrons,  
with nucleons

wall relaxation

collisions

nuclear quadrupole

spin - spin ( $S_A \cdot S_B$ )

dipole - dipole interaction

relaxation, which can come from many sources:

The last piece of the Liouville operator is

pumping is important

- in general both depolarization ; repopulation

$$\langle n | \bar{\rho} | m \rangle = \langle m | \bar{\rho} | n \rangle \geq \frac{4\pi^2 c^3 \hbar}{3m^2} =$$

$$A_{mn} / \rho_{mn} = \sum_m C_m / \rho_{mn}$$

- in general than can be more reasonably rather

$\mu \neq \bar{\mu}$

$$\text{"1"} \quad \mu/\bar{\mu} = \frac{1}{P_{\text{out}}(s)P_{\text{in}}}$$

$$\text{"1"} \quad \cancel{\mu/\bar{\mu}} = \frac{1}{P_{\text{out}}(s)P_{\text{in}}}$$

Relaxation may act differently in parallel and off-diagonal parts of the density matrix