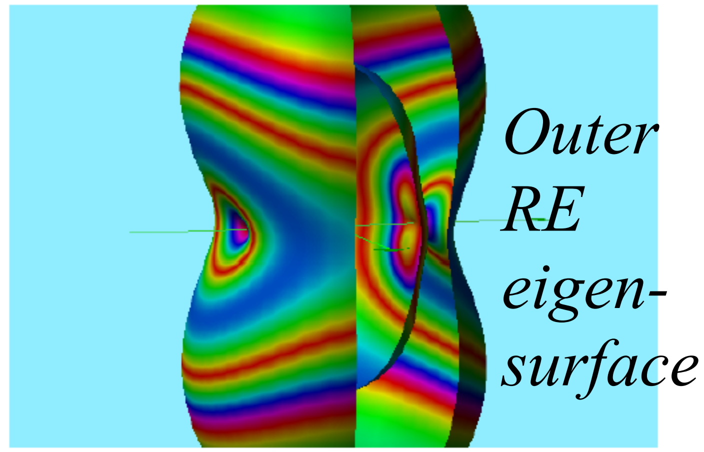
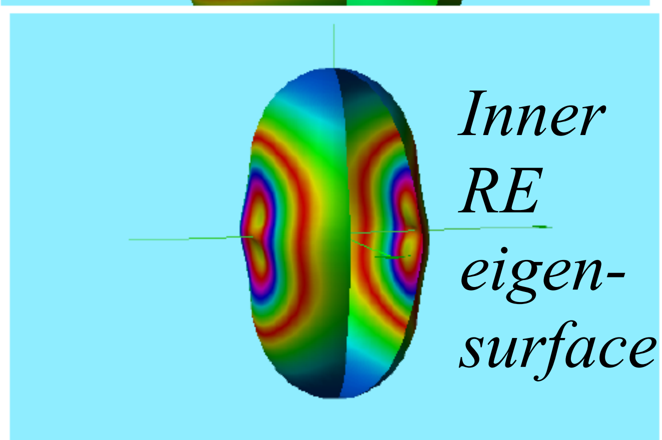
# ROVIBRONIC ENERGY TOPOGRAPHY

## II: Molecular internal-momentum effects and multi-RES resonance in high symmetry molecules.




Bill Harter , Justin Mitchell - University of Arkansas

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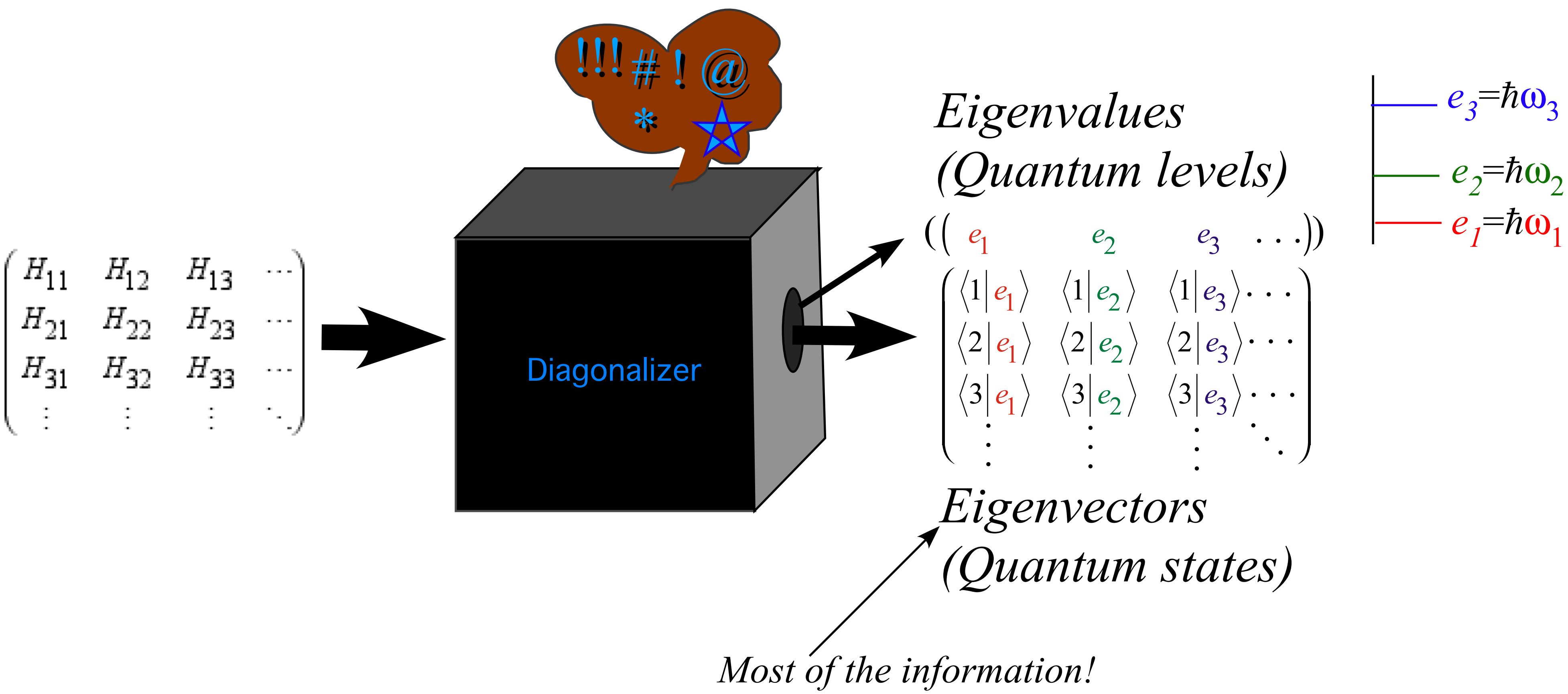
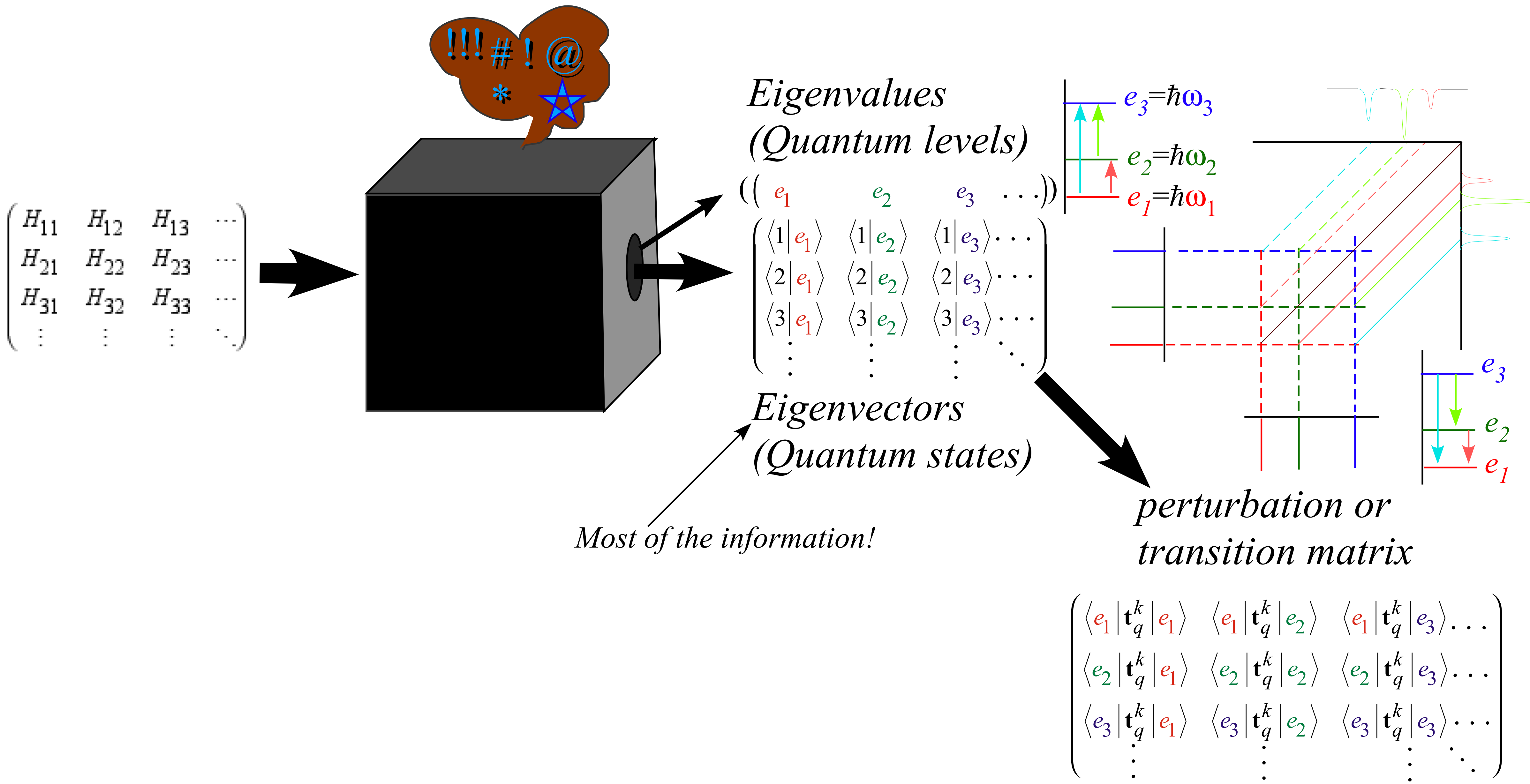
# *Matrix Diagonalization:*
# *The* **BLACK BOX** *of quantum physics, chemistry, and spectroscopy*

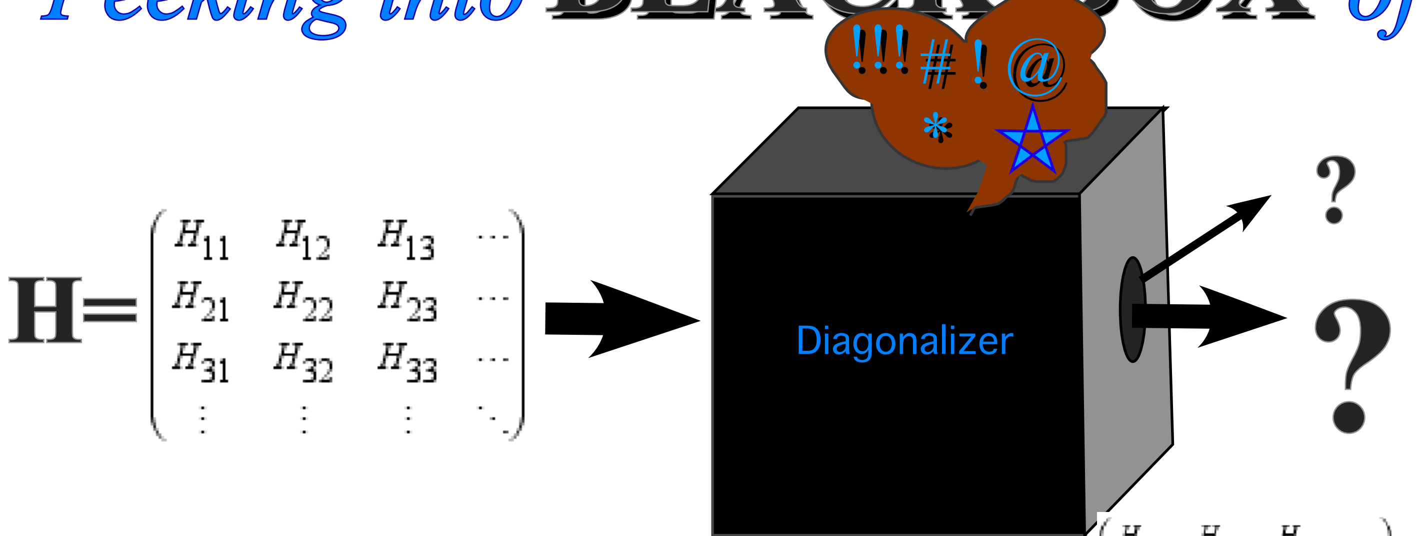


## *Matrix Diagonalization*

# *The* **BLACK BOX** *of quantum physics, chemistry, and spectroscopy*



# *Peeking into* **BLACK BOX** *of matrix diagonalization:*

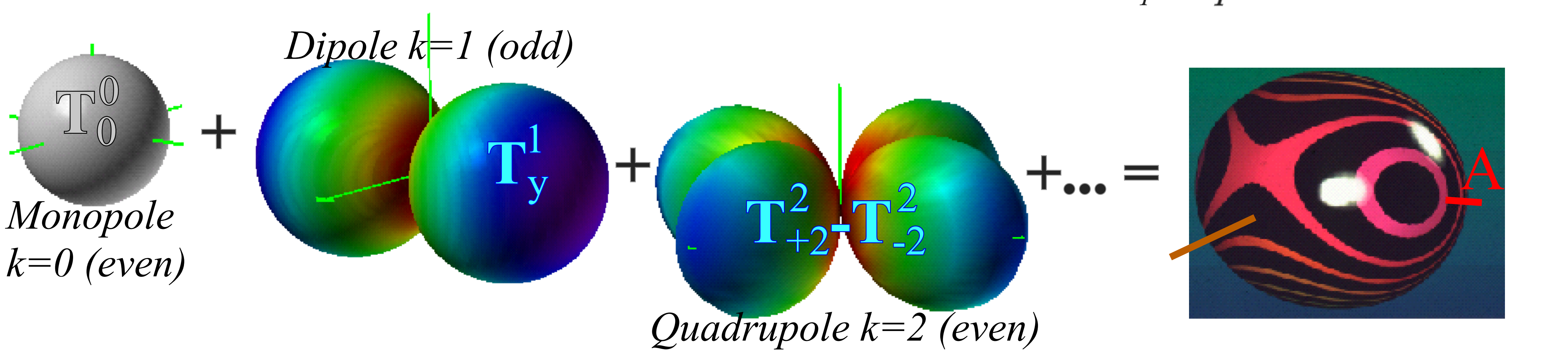



## *Plotting $2^k$-pole expansion of* $\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$ *into Fano-Racah tensors*

*scalar+* *+ vector+* *+ $2^2$-tensor +...* *+ $2^k$-tensor +..*

*Generators of group U(n)*

$$\mathbf{H}= a\mathbf{T}^0_{\;0}+b\mathbf{T}^1_{\;0}+c\mathbf{T}^1_{\;1}+\ldots+d\mathbf{T}^2_{\;0}+e\mathbf{T}^2_{\;1}+\ldots=\Sigma c^k_{\;q}\,\mathbf{T}^k_{\;q}$$



# *Expansion of $C_n$ symmetric* $\mathbf{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$ *by $C_n$ operator powers* $\mathbf{r}^n$

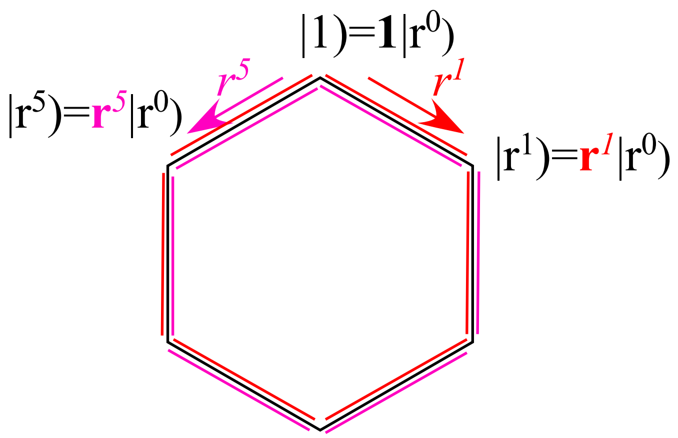
$$\mathbf{H}= r_0\mathbf{r}^0+r_1\mathbf{r}^1+r_2\mathbf{r}^2+\ldots+r_{n-1}\mathbf{r}^{n-1}=\Sigma\, r_q\,\mathbf{r}^k$$

## *$C_6$ example:*

$$\mathbf{H} = r_0\mathbf{r}^0 + r_1\mathbf{r}^1 + r_2\mathbf{r}^2 + r_3\mathbf{r}^3 + r_4\mathbf{r}^4 + r_5\mathbf{r}^5$$

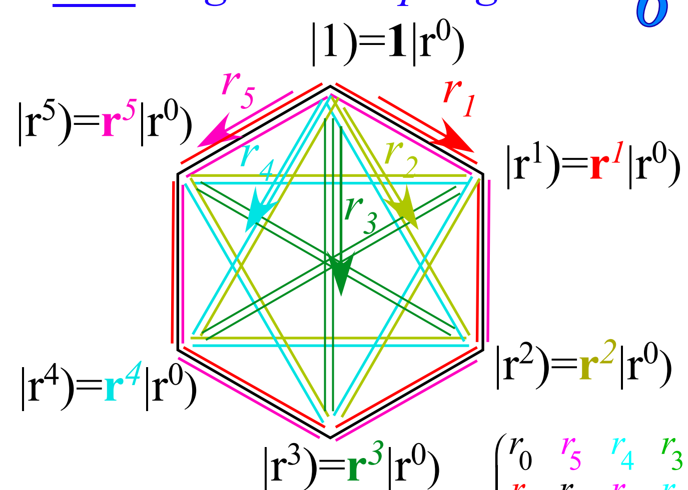
$$\begin{pmatrix} r_0 & r_5 & r_4 & r_3 & r_2 & r_1 \\ r_1 & r_0 & r_5 & r_4 & r_3 & r_2 \\ r_2 & r_1 & r_0 & r_5 & r_4 & r_3 \\ r_3 & r_2 & r_1 & r_0 & r_5 & r_4 \\ r_4 & r_3 & r_2 & r_1 & r_0 & r_5 \\ r_5 & r_4 & r_3 & r_2 & r_1 & r_0 \end{pmatrix} = r_0\begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} + r_1\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} + r_2\begin{pmatrix} \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \end{pmatrix} + r_3\begin{pmatrix} \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \end{pmatrix} + r_4\begin{pmatrix} \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + r_5\begin{pmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

*Nearest neighbor coupling*




$$\begin{pmatrix} r_0 & r_5 & & & & r_1 \\ r_1 & r_0 & r_5 & & & \\ & r_1 & r_0 & r_5 & & \\ & & r_1 & r_0 & r_5 & \\ & & & r_1 & r_0 & r_5 \\ r_5 & & & & r_1 & r_0 \end{pmatrix}$$

*<u>ALL</u> neighbor coupling*




$$\begin{pmatrix} r_0 & r_5 & r_4 & r_3 & r_2 & r_1 \\ r_1 & r_0 & r_5 & r_4 & r_3 & r_2 \\ r_2 & r_1 & r_0 & r_5 & r_4 & r_3 \\ r_3 & r_2 & r_1 & r_0 & r_5 & r_4 \\ r_4 & r_3 & r_2 & r_1 & r_0 & r_5 \\ r_5 & r_4 & r_3 & r_2 & r_1 & r_0 \end{pmatrix}$$

## *$C_6$ group table gives* **r**-*matrices...*

## *...$C_6$-allowed* **H**-*matrices...*

| $C_6$ | 1 | $\mathbf{r}^5$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ | $\mathbf{r}$ |
|---|---|---|---|---|---|---|
| **1** | 1 | $\mathbf{r}^5$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ | $\mathbf{r}$ |
| $\mathbf{r}$ | $\mathbf{r}$ | 1 | $\mathbf{r}^5$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ |
| $\mathbf{r}^2$ | $\mathbf{r}^2$ | $\mathbf{r}$ | 1 | $\mathbf{r}^5$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ |
| $\mathbf{r}^3$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ | $\mathbf{r}$ | 1 | $\mathbf{r}^5$ | $\mathbf{r}^4$ |
| $\mathbf{r}^4$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ | $\mathbf{r}$ | 1 | $\mathbf{r}^5$ |
| $\mathbf{r}^5$ | $\mathbf{r}^5$ | $\mathbf{r}^4$ | $\mathbf{r}^3$ | $\mathbf{r}^2$ | $\mathbf{r}$ | 1 |

$$\mathbf{H} = r_0\mathbf{r}^0 + r_1\mathbf{r}^1 + r_2\mathbf{r}^2 + r_3\mathbf{r}^3 + r_4\mathbf{r}^4 + r_5\mathbf{r}^5$$

# *To diagonalize* $\mathbf{H}$ *just diagonalize* $\mathbf{g} = \mathbf{r}, \mathbf{r}^2, \ldots$ *(All obey:* $\mathbf{g}^6 = 1$*)*

*Eigenvalues* $D_m^p = \psi_m^*(\mathbf{r}^p)$ *of* $\mathbf{r}^p$ *are 6 th roots of 1:*

*Eigenfunctions* $\psi_m(\mathbf{r}^p) = D_m^{*p}$ *of* $\mathbf{r}^p$ *are 6 th roots of 1:*

$$\psi_m(\mathbf{r}) = (1^m)^{1/6} = (e^{2\pi i m})^{1/6} = e^{2\pi i m/6}$$

$$\psi_m(\mathbf{r}^2) = (e^{2\pi i m/6})^2$$

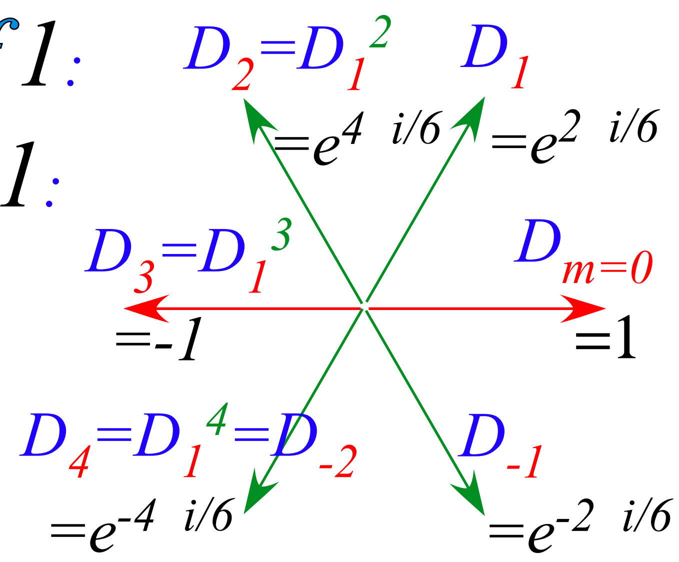
$$\psi_m(\mathbf{r}^3) = (e^{2\pi i m/6})^3$$

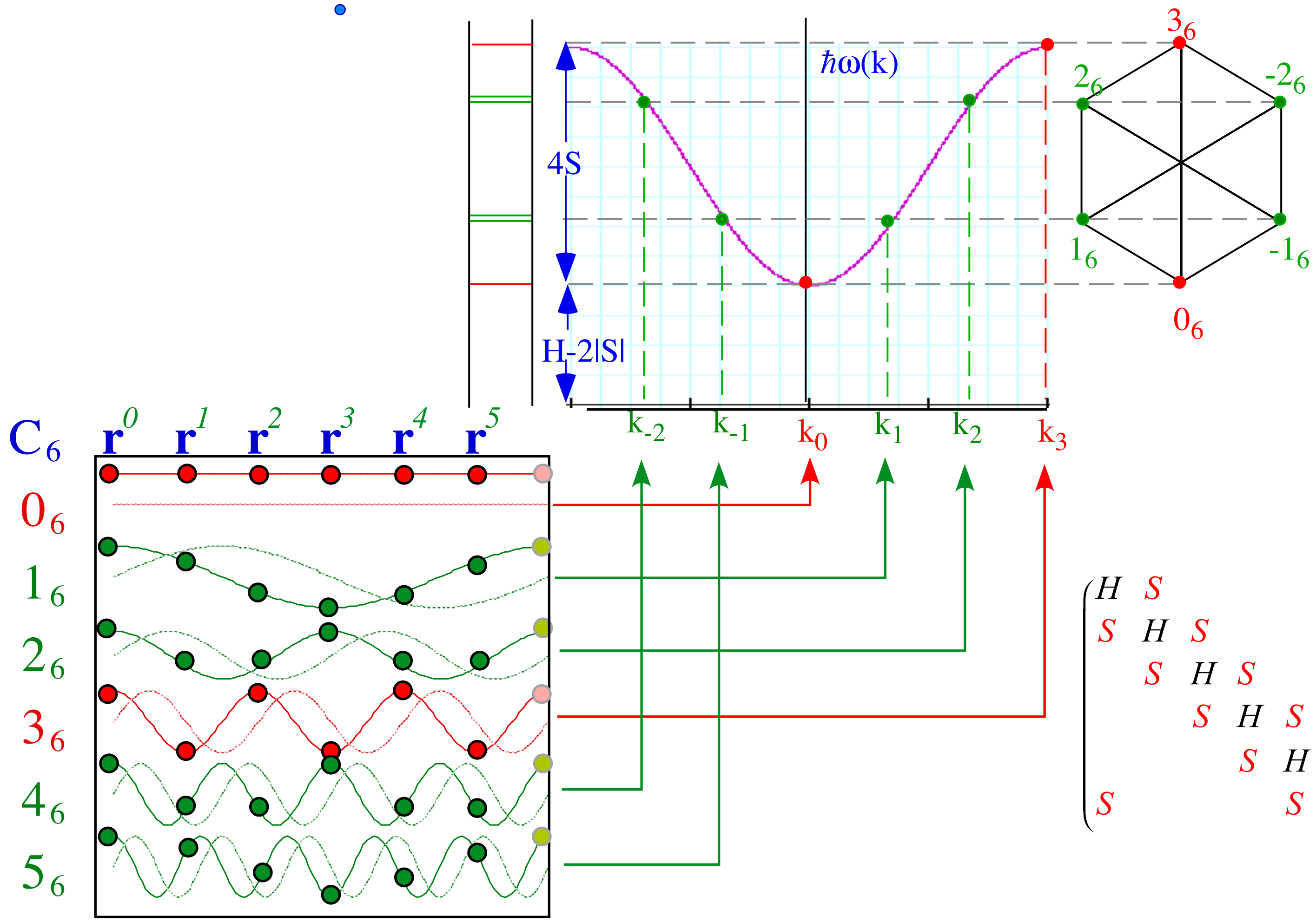
$\vdots$

power or position point $p$

$$\boxed{\psi_m(\mathbf{r}^p) = (e^{2\pi i m/6})^p = e^{2\pi i m \cdot p/6} = D_m^{*p}}$$

momentum number $m$



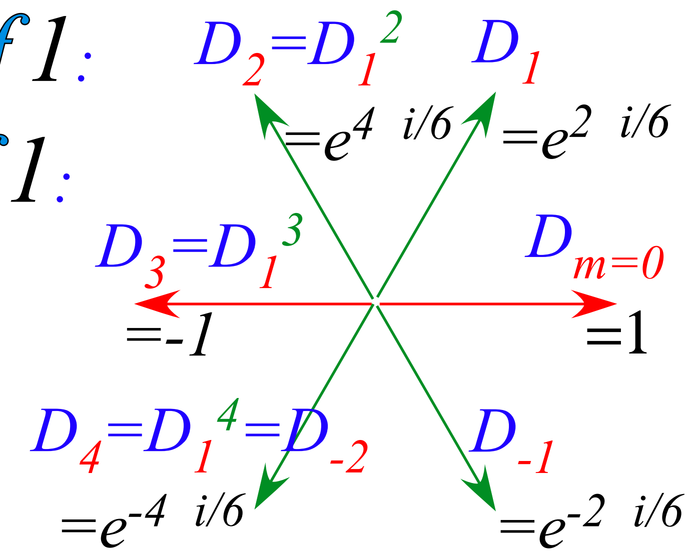

$$\begin{pmatrix} H & S & & & & S \\ S & H & S & & & \\ & S & H & S & & \\ & & S & H & S & \\ & & & S & H & S \\ S & & & & S & H \end{pmatrix}$$

$$\mathbf{H} = r_0\mathbf{r}^0 + r_1\mathbf{r}^1 + r_2\mathbf{r}^2 + r_3\mathbf{r}^3 + r_4\mathbf{r}^4 + r_5\mathbf{r}^5$$

# *To diagonalize* $\mathbf{H}$ *just diagonalize* $\mathbf{g} = \mathbf{r}, \mathbf{r}^2, \ldots$ *(All obey:* $\mathbf{g}^6 = 1$*)*

*Eigenvalues* $D^p_m = \psi^*_m(\mathbf{r}^p)$ *of* $\mathbf{r}^p$ *are 6th roots of 1:*

*Eigenfunctions* $\psi_m(\mathbf{r}^p) = D^{*p}_m$ *of* $\mathbf{r}^p$ *are 6th roots of 1:*




$$\psi_m(\mathbf{r}) = (1^m)^{1/6} = (e^{2\pi i m})^{1/6} = e^{2\pi i m/6}$$

$$\psi_m(\mathbf{r}^2) = (e^{2\pi i m/6})^2$$

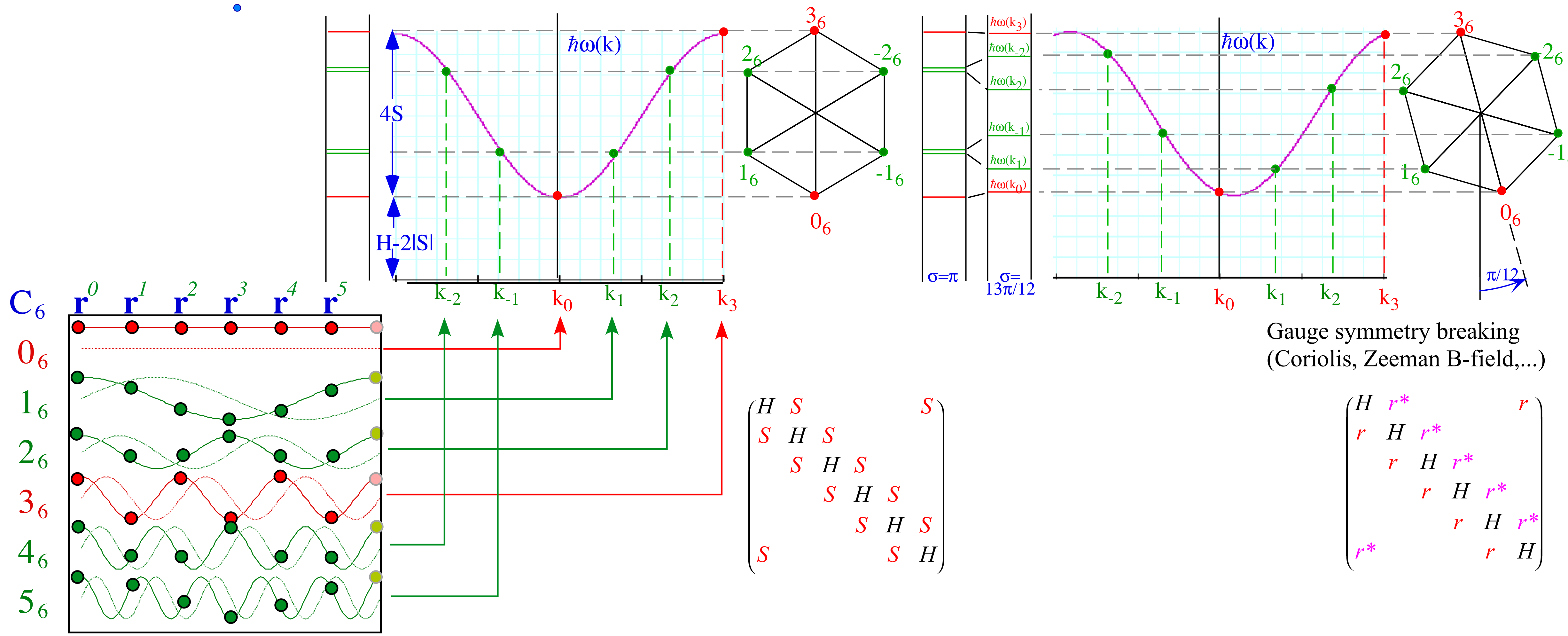
$$\psi_m(\mathbf{r}^3) = (e^{2\pi i m/6})^3$$

$\vdots$

power or position point $p$

$$\psi_m(\mathbf{r}^p) = (e^{2\pi i m/6})^p = e^{2\pi i m \cdot p/6} = D^{*p}_m$$

momentum number $m$

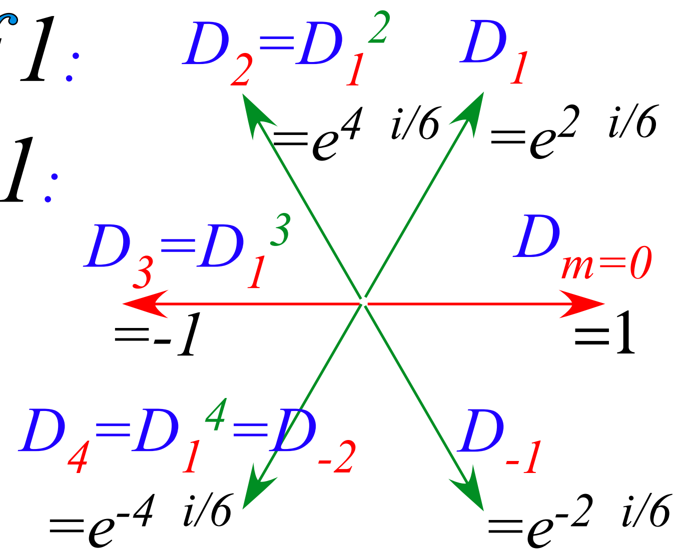


$\mathbf{H} = r_0 \mathbf{r}^0 + r_1 \mathbf{r}^1 + r_2 \mathbf{r}^2 + r_3 \mathbf{r}^3 + r_4 \mathbf{r}^4 + r_5 \mathbf{r}^5$

# *To diagonalize* $\mathbf{H}$ *just diagonalize* $\mathbf{g} = \mathbf{r}, \mathbf{r}^2, \ldots$ *(All obey:* $\mathbf{g}^6 = 1$*)*

*Eigenvalues* $D_m^p = \psi_m^*(\mathbf{r}^p)$ *of* $\mathbf{r}^p$ *are 6th roots of 1:*

*Eigenfunctions* $\psi_m(\mathbf{r}^p) = D_m^{*p}$ *of* $\mathbf{r}^p$ *are 6th roots of 1:*




$\psi_m(\mathbf{r}) = (1^m)^{1/6} = (e^{2\pi i m})^{1/6} = e^{2\pi i m/6}$

$\psi_m(\mathbf{r}^2) = (e^{2\pi i m/6})^2$

$\psi_m(\mathbf{r}^3) = (e^{2\pi i m/6})^3$

⋮

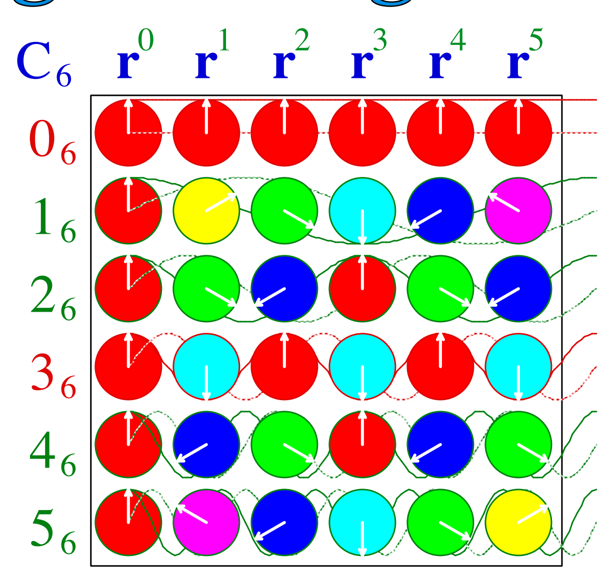
power or position point $p$

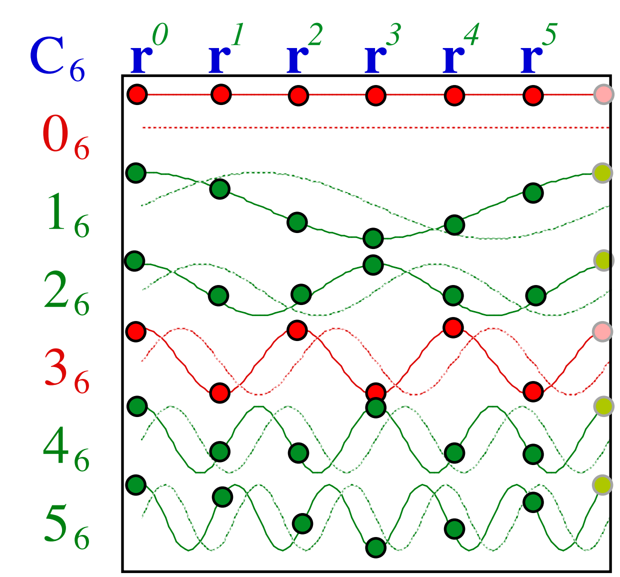
$$\psi_m(\mathbf{r}^p) = (e^{2\pi i m/6})^p = e^{2\pi i m \cdot p/6} = D_m^{*p}$$

momentum number $m$

## $D_m^p = \psi_m^*(\mathbf{r}^p)$ *give Fourier diagonalizing transform matrix*

| $\rho_m^{p*} = \psi_m^p$ | $\mathbf{r}^0$ | $\mathbf{r}^1$ | $\mathbf{r}^2$ | $\mathbf{r}^3$ | $\mathbf{r}^4$ | $\mathbf{r}^5$ |
|---|---|---|---|---|---|---|
| $m=(0)$ | 1 | 1 | 1 | 1 | 1 | 1 |
| (1) | 1 | $\psi_1$ | $(\psi_1)^2$ | $(\psi_1)^3$ | $(\psi_1)^4$ | $(\psi_1)^5$ |
| (2) | 1 | $\psi_2$ | $(\psi_2)^2$ | $(\psi_2)^3$ | $(\psi_2)^4$ | $(\psi_2)^5$ |
| (3) | 1 | $\psi_3$ | $(\psi_3)^2$ | $(\psi_3)^3$ | $(\psi_3)^4$ | $(\psi_3)^5$ |
| (4) | 1 | $\psi_4$ | $(\psi_4)^2$ | $(\psi_4)^3$ | $(\psi_4)^4$ | $(\psi_4)^5$ |
| (5) | 1 | $\psi_5$ | $(\psi_5)^2$ | $(\psi_5)^3$ | $(\psi_5)^4$ | $(\psi_5)^5$ |



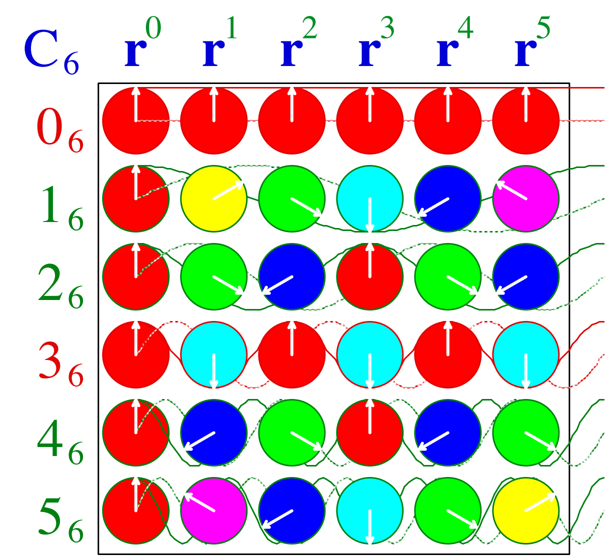



# *H diagonalized by spectral resolution of $r, r^2, \ldots, r^6 = 1$*

$$(\mathbf{r})^p = D_0^p \mathbf{P}^{(0)} + D_1^p \mathbf{P}^{(1)} + D_2^p \mathbf{P}^{(2)} + D_3^p \mathbf{P}^{(3)} + D_4^p \mathbf{P}^{(4)} + D_5^p \mathbf{P}^{(5)}$$

$$\begin{pmatrix} D_0^p & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & D_1^p & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & D_2^p & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & D_3^p & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & D_4^p & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & D_5^p \end{pmatrix} = D_0^p \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + D_1^p \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + D_2^p \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + D_3^p \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + D_4^p \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} + D_5^p \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix}$$

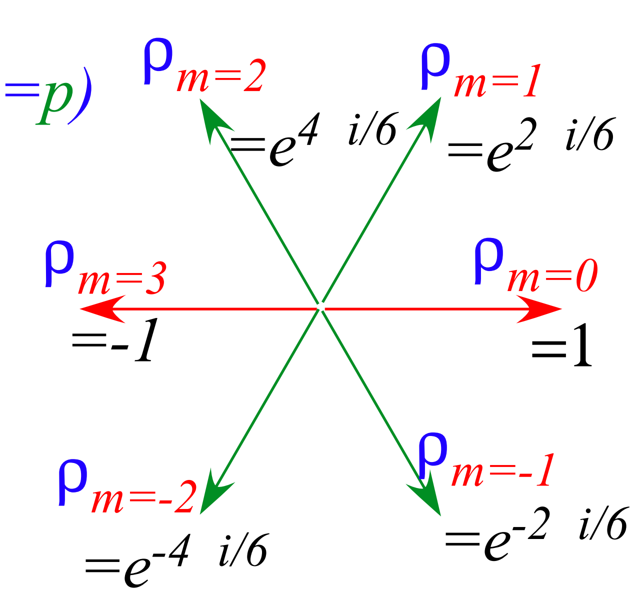
| $\rho_m^p{}^* = \chi_m^p$ | $\mathbf{r}^0$ | $\mathbf{r}^1$ | $\mathbf{r}^2$ | $\mathbf{r}^3$ | $\mathbf{r}^4$ | $\mathbf{r}^5$ |
|---|---|---|---|---|---|---|
| $m$=(0) | 1 | 1 | 1 | 1 | 1 | 1 |
| (1) | 1 | $\chi_1$ | $(\chi_1)^2$ | $(\chi_1)^3$ | $(\chi_1)^4$ | $(\chi_1)^5$ |
| (2) | 1 | $\chi_2$ | $(\chi_2)^2$ | $(\chi_2)^3$ | $(\chi_2)^4$ | $(\chi_2)^5$ |
| (3) | 1 | $\chi_3$ | $(\chi_3)^2$ | $(\chi_3)^3$ | $(\chi_3)^4$ | $(\chi_3)^5$ |
| (4) | 1 | $\chi_4$ | $(\chi_4)^2$ | $(\chi_4)^3$ | $(\chi_4)^4$ | $(\chi_4)^5$ |
| (5) | 1 | $\chi_5$ | $(\chi_5)^2$ | $(\chi_5)^3$ | $(\chi_5)^4$ | $(\chi_5)^5$ |

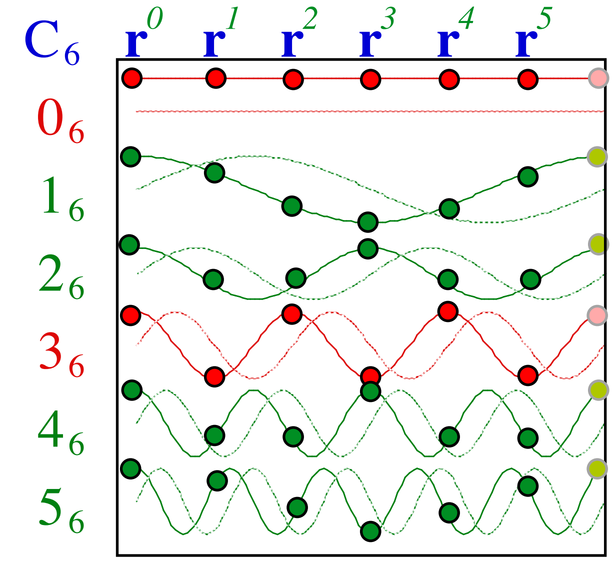



*$\rho_m^p$ give "quantized" $\psi(x)=e^{ik\cdot x}$ wavefunctions:*

$$\psi_m(x_p) = e^{2\pi i m\cdot p/6} = e^{ik_m \cdot x_p} \quad (\text{let: } k_m = 2\pi m/6 \text{ and } x_p = p)$$

wavelength $\lambda_m = \frac{2}{k_m} = \frac{6}{m}$




*$\rho_m^p$ give Fourier transformation matrices:*

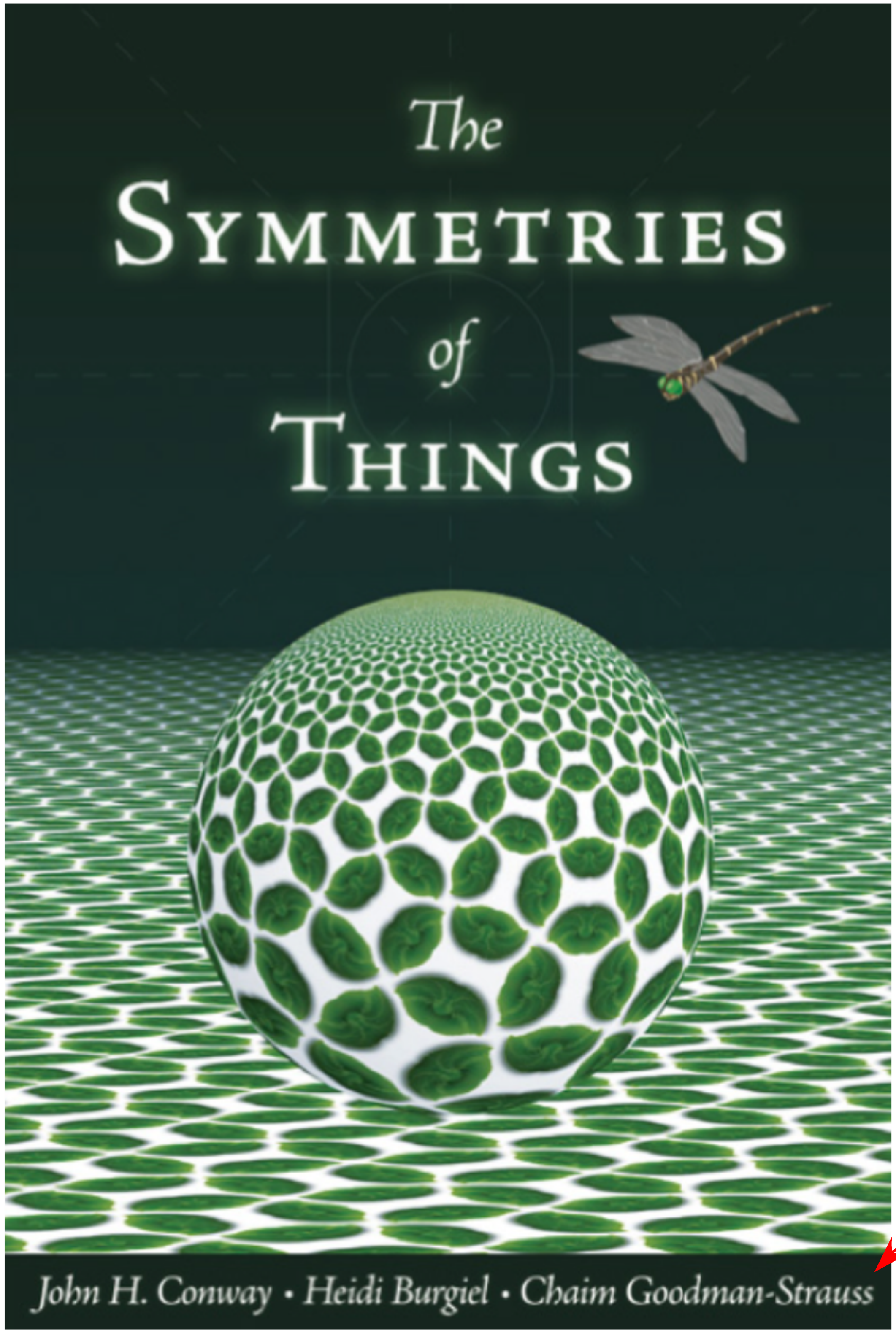
$$(x_p|k_m) = e^{2\pi i m\cdot p/6} = (k_m|x_p)^*$$

*We interrupt this program to bring an important announcement from the makers of PURE and APPLIED group theory...*

*(drum-roll, Please...)*

# ...from PURE group theory...

*A revolutionary simplification to classify all groups and their algebras*




Disclosure:
*Chaim G-S is a colleague at University of Arkansas (He's in math across the street.)*

## *...from APPLIED group theory...*

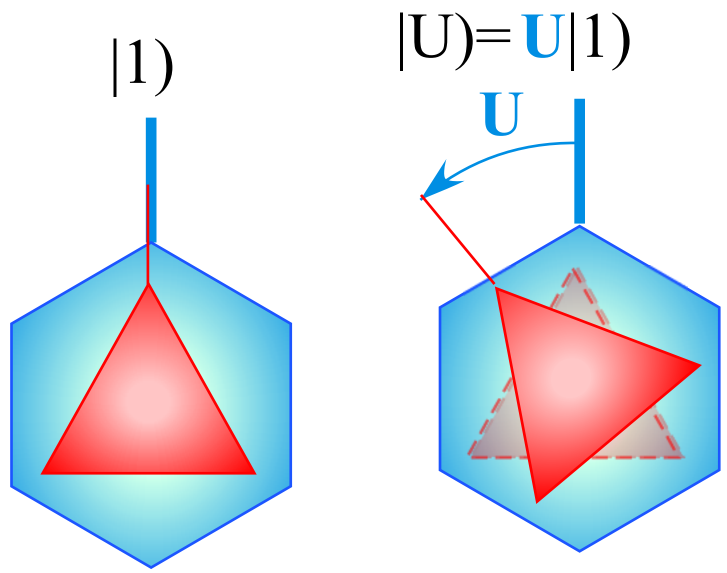
*Group theory of wave mechanics is twice as big as you might think...*

# *...from APPLIED group theory...*

*Group theory of wave mechanics is twice as big as you might think...*

*APPLIED RELATIVITY-DUALITY THEOREM:*

For each *external* group $\{..\mathbf{T},\mathbf{U},\mathbf{V},...\}$ there is an *internal* group $\{..\bar{\mathbf{T}},\bar{\mathbf{U}},\bar{\mathbf{V}},...\}$




satisfing *duality:*

$\mathbf{T}|1)=|T)=\bar{\mathbf{T}}^{-1}|1)$,

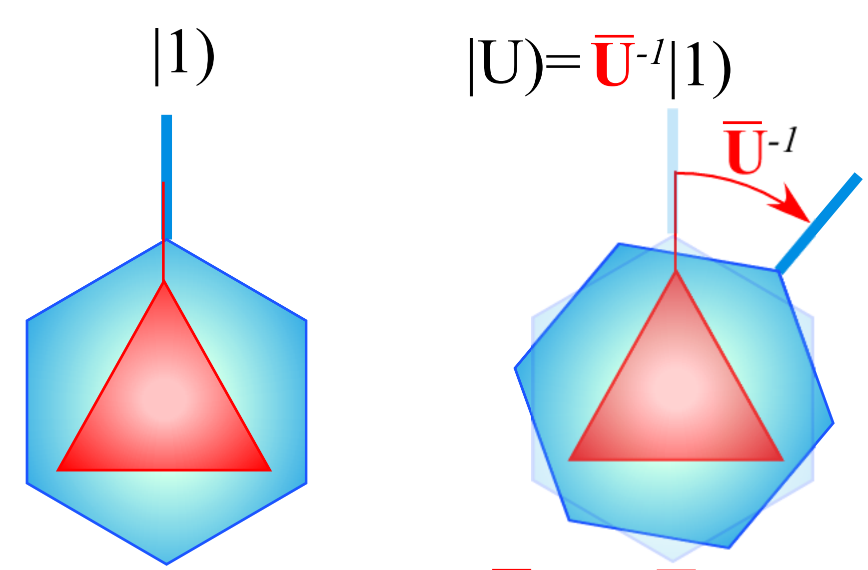
$\mathbf{U}|1)=|U)=\bar{\mathbf{U}}^{-1}|1)$,

*etc.*,

and *commutivity:*

$\mathbf{T}\bar{\mathbf{U}}=\bar{\mathbf{T}}\mathbf{U}$, $\mathbf{T}\bar{\mathbf{V}}=\bar{\mathbf{V}}\mathbf{U}$,..

$\mathbf{U}\bar{\mathbf{V}}=\bar{\mathbf{V}}\mathbf{U}$, *..etc.*,




|1) moved by **U** to **U**|1) yields same *relative* position |U) as |1) moved by $\bar{\mathbf{U}}^{-1}$ to $\bar{\mathbf{U}}^{-1}|1)$

...and wave interference depends on *relative* position only.

# *...from APPLIED group theory...*

*Group theory of wave mechanics is twice as big as you might think...*

*APPLIED RELATIVITY-DUALITY THEOREM:*

For each *external* group {..**T**,**U**,**V**,... }there is an *internal* group{..$\mathbf{\bar{T}}$,$\mathbf{\bar{U}}$,$\mathbf{\bar{V}}$,... }

satisfing *duality:*

$\mathbf{T}|1)=|T)=\mathbf{\bar{T}}^{-1}|1)$,

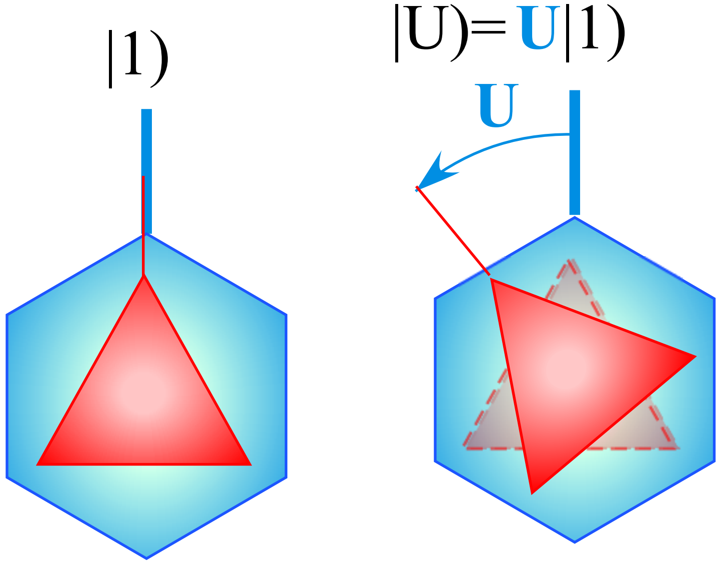
$\mathbf{U}|1)=|U)=\mathbf{\bar{U}}^{-1}|1)$,

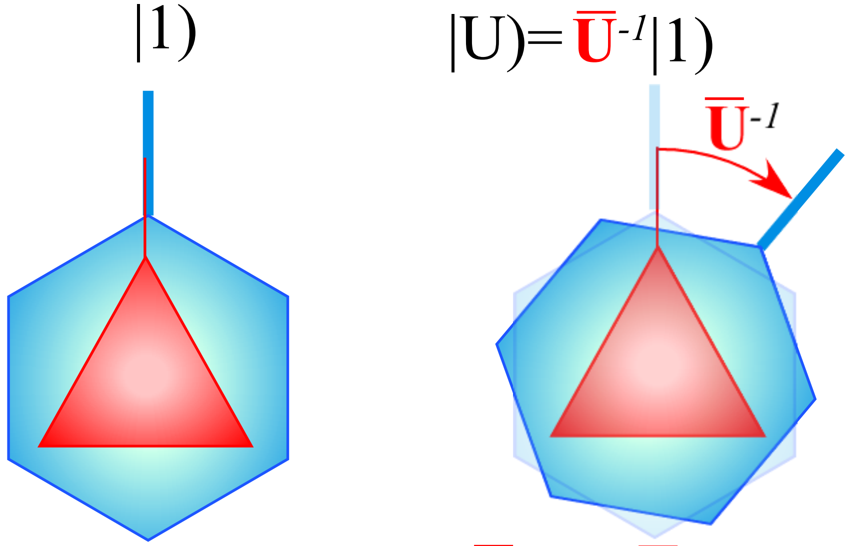
*etc.*,

and *commutivity:*

$\mathbf{T\bar{U}}=\mathbf{\bar{T}U}$, $\mathbf{T\bar{V}}=\mathbf{\bar{V}U}$,..

$\mathbf{U\bar{V}}=\mathbf{\bar{V}U}$, ..*etc.*,




|1) moved by **U** to **U**|1) yields same *relative* position |U) as |1) moved by $\mathbf{\bar{U}}^{-1}$ to $\mathbf{\bar{U}}^{-1}|1)$

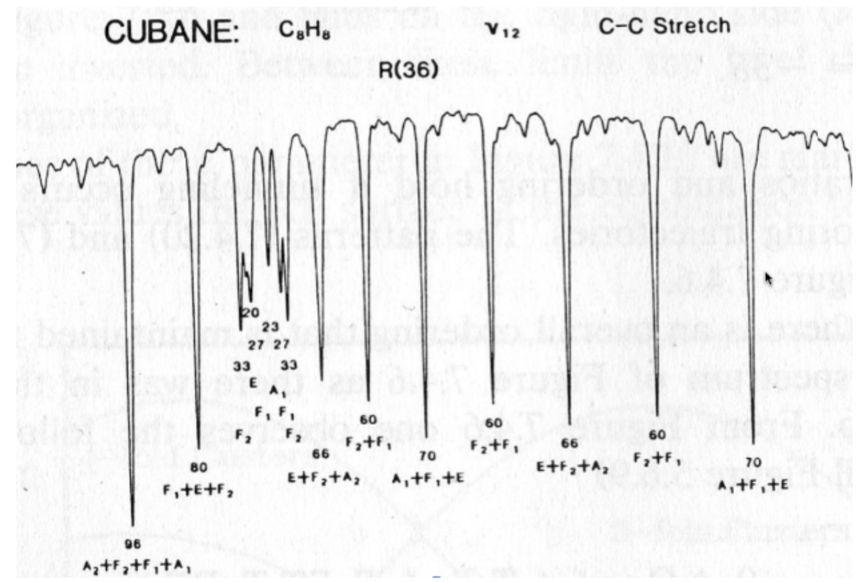
...and wave interference depends on *relative* position only.

*RELATIVITY-DUALITY also known as:*

*LAB vs BODY (molecular theory)*

*STATE vs PARTICLE (nuclear shell theory)*

*GLOBAL vs LOCAL (gauge theory)*


CUBANE: $C_8H_8$
$\nu_{12}$
C–C Stretch
R(36)
20
23
27 27
33 33
E $A_1$
$F_1$ $F_1$
$F_2$ $F_2$
66
$E+F_2+A_2$
60
$F_2+F_1$
70
$A_1+F_1+E$
60
$F_2+F_1$
66
$E+F_2+A_2$
60
$F_2+F_1$
70
$A_1+F_1+E$
80
$F_1+E+F_2$
96
$A_2+F_2+F_1+A_1$

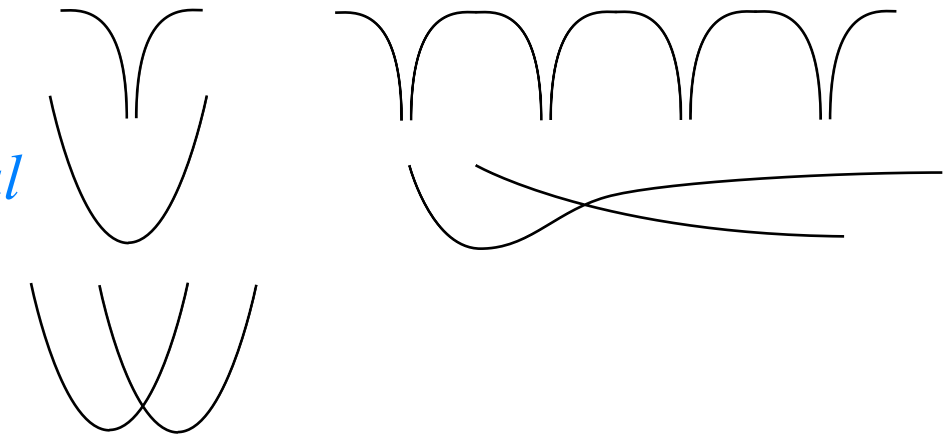
# *Some ways to picture AMO eigenstates*

- *Potential Energy Surfaces (PES)*

  *electronic*

  *vibrational*

  *vibronic*

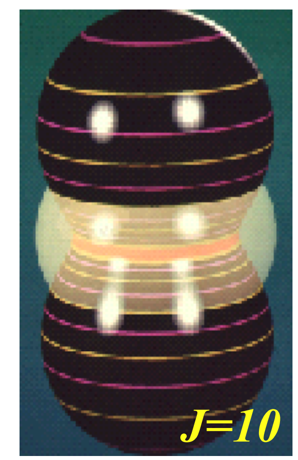


- *Rotational Energy Surfaces (RES)*

  *pure rotational (centrifugal) effects*

  *rovibrational (centrifugal and Coriolis) effects*

  *rovibronic (centrifugal, Coriolis, and Jahn-Teller) effects*



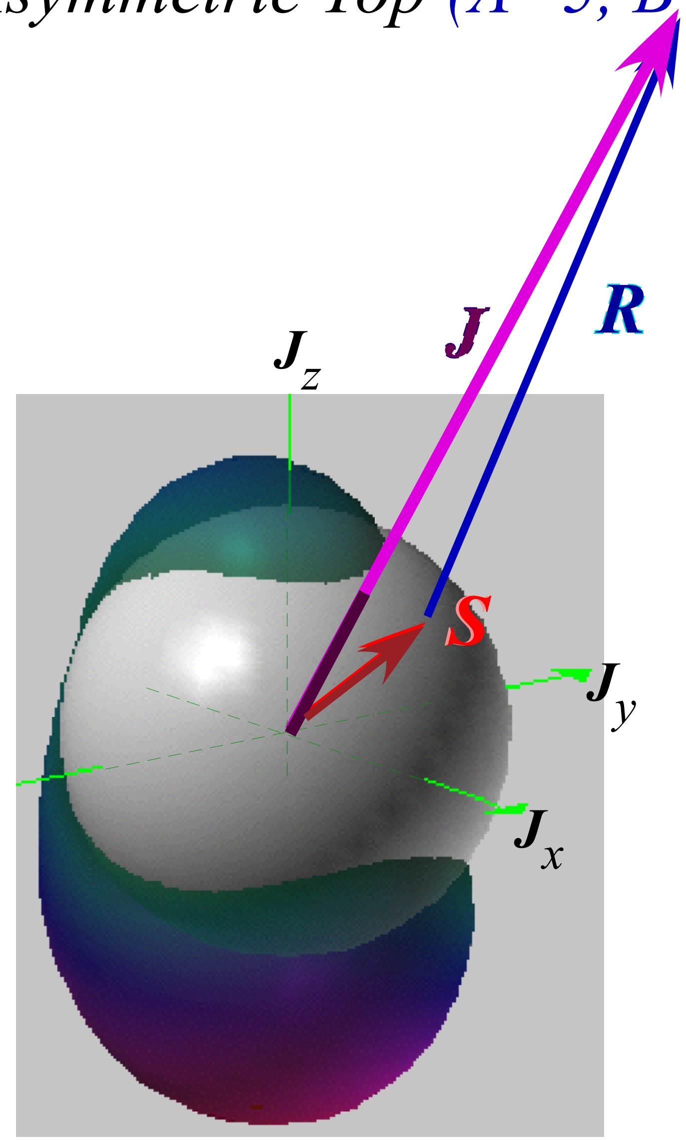


- *Generalized phase spaces*

  *vibrational polyad sphere*

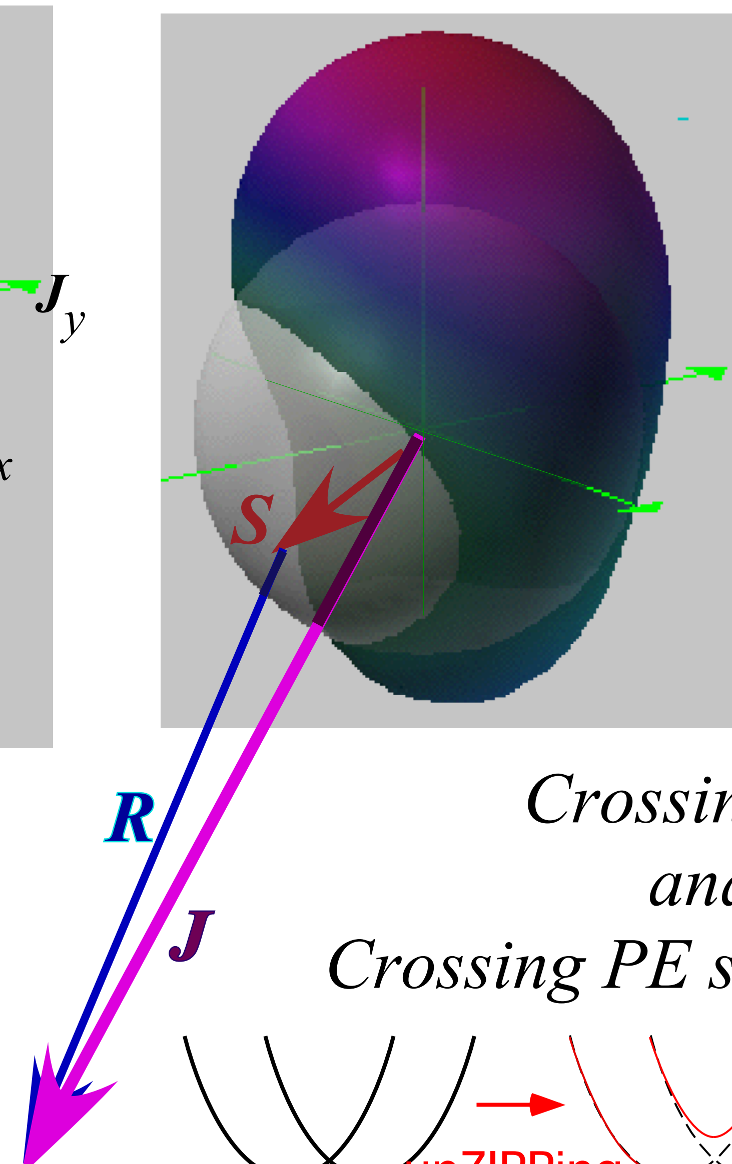
  *high energy pulse state space*

*Spin gyro S=(1,1,1) attached (ZIPPed) to*
*Asymmetric Top (A=5, B=10, C=15)*

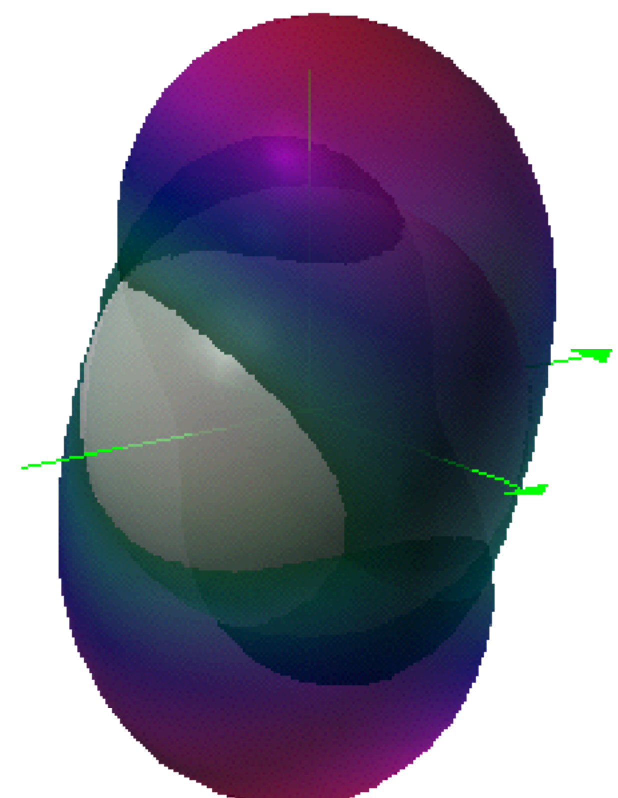



*"Sherman" (The shark)*

*Time reversed*
*gyro -S=(-1,-1,-1)*




*The two together*



*Crossing RE surfaces*
*analogous to*
*Crossing PE surfaces (Jahn-Teller)*

*Two or more RE's beg to be unZIPPed.* $\langle \mathbf{H} \rangle = \begin{pmatrix} \text{Spin-up } RE(\beta,\gamma) & \text{Coupling}(\beta,\gamma) \\ \text{Coupling}(\beta,\gamma)^* & \text{Spin-down } RE(\beta,\gamma) \end{pmatrix}$

*Base RE surfaces are eigenvalues of matrix.*

*Classical RE*

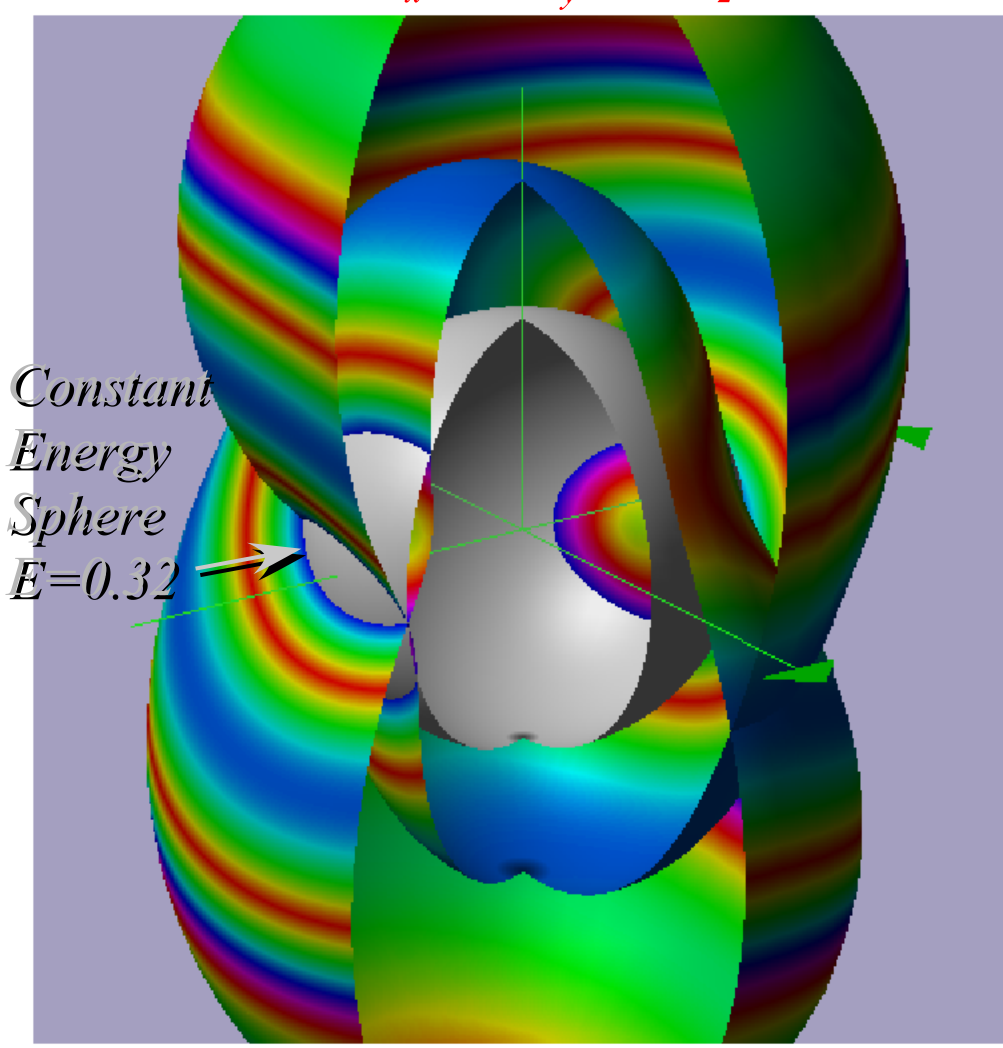
$$H = AJ_x{}^2 + BJ_y{}^2 + CJ_z{}^2 + \ldots - 2AJ_x S_x - 2BJ_y S_y - 2CJ_z S_z + \ldots + \textit{(more constant terms)}$$

*Semi-Classical Spin-1/2 RE* $\quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ *makes matrix*

$$\mathbf{H} = (AJ_x{}^2 + BJ_y{}^2 + CJ_z{}^2)\mathbf{1} \ldots - AJ_x s_x \sigma_x \; - BJ_y s_y \sigma_y \; - CJ_z s_z \sigma_z + \ldots + \mathbf{1}\textit{(more constant terms)}$$

*Classical ZIPP* $A=0.2, B=0.8, C=1.4$

$S_x=0.0, S_y=0.1, S_z=0.2$




*Semi-Classical spin-1/2 unZIPP* $A=0.2, B=0.8, C=1.4$

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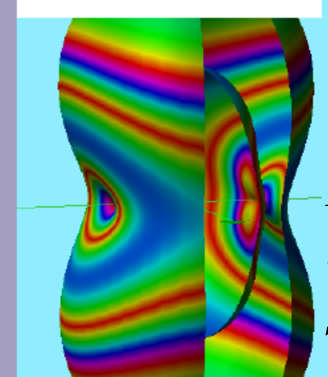
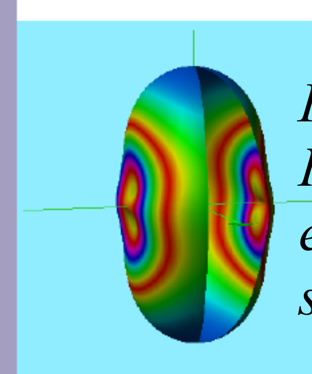
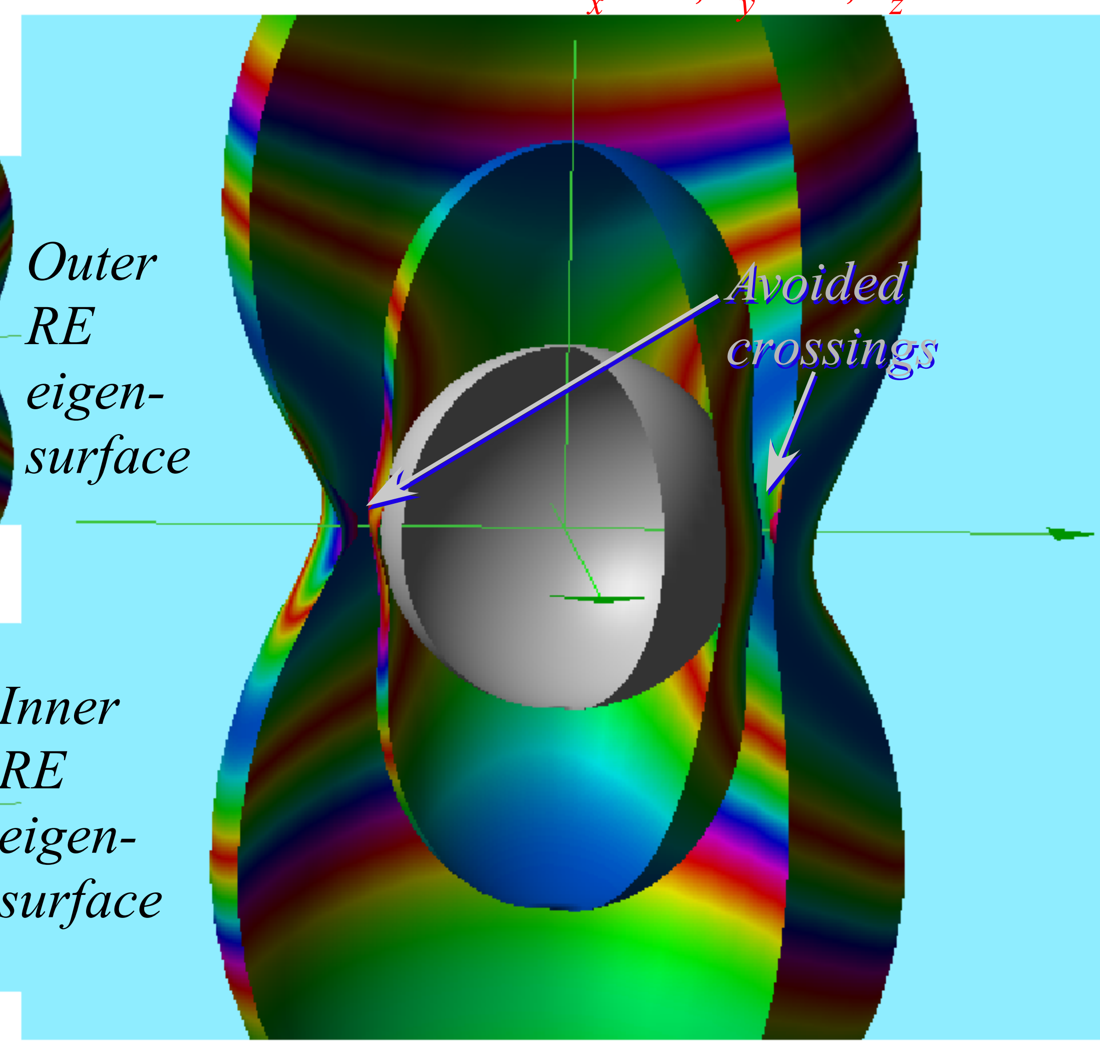
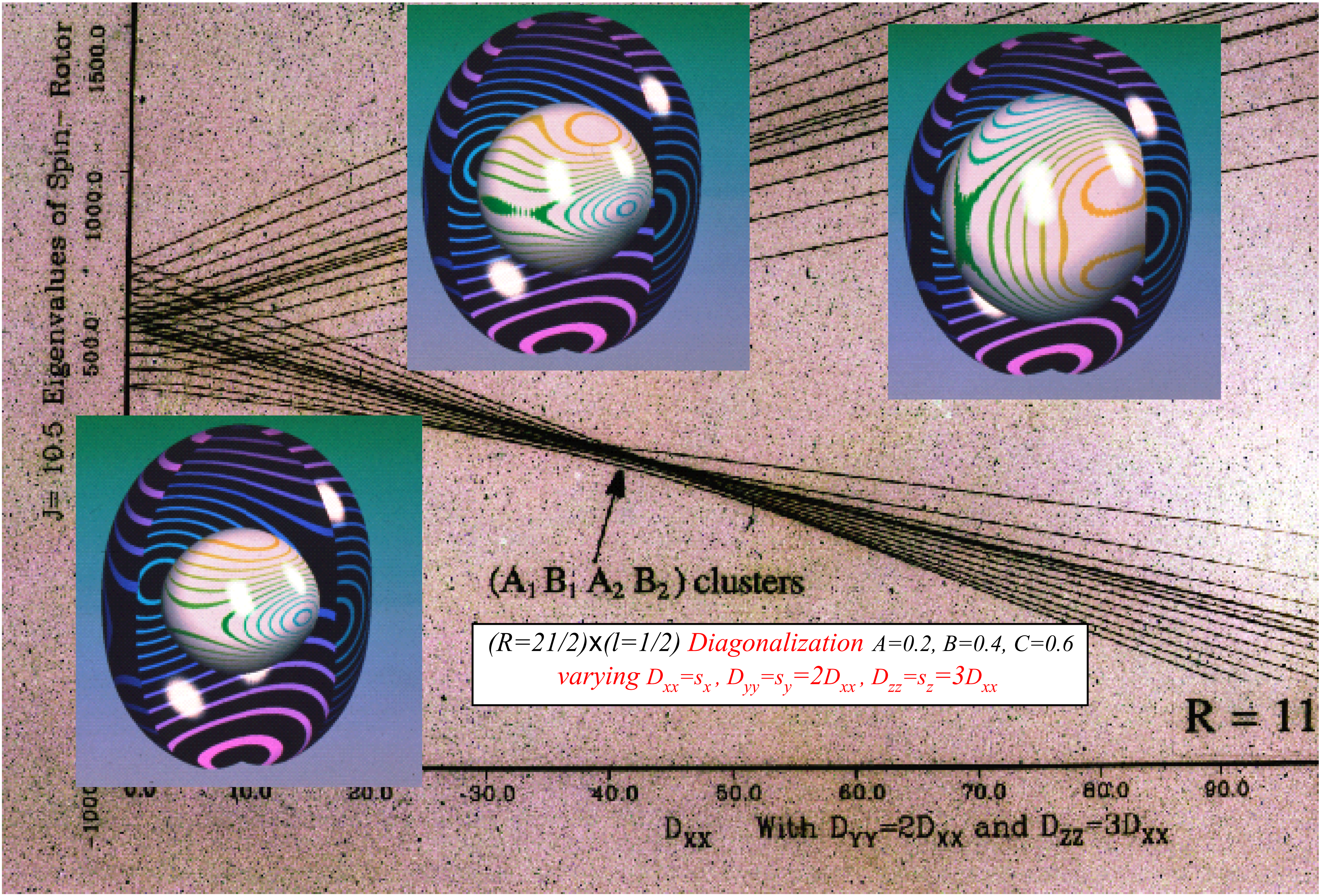


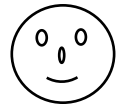




J= 10.5 Eigenvalues of Spin- Rotor
1500.0
1000.0
500.0
(A1 B1 A2 B2) clusters
(R=21/2)x(l=1/2) Diagonalization A=0.2, B=0.4, C=0.6
varying $D_{xx}=s_x$, $D_{yy}=s_y=2D_{xx}$, $D_{zz}=s_z=3D_{xx}$
R = 11
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
$D_{XX}$ With $D_{YY}=2D_{XX}$ and $D_{ZZ}=3D_{XX}$

## *Good news*

*Rotational energy surfaces (RES) may help visualize matrix eigensolutions in general, but rotational and vibrational-polyad states in particular.*

## *Good news* 

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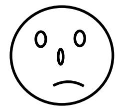
## *Bad news* 

*Well, not every matrix! If your RES looks like a potato, you may be in trouble!*

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*RES can help expose new phenomena and suggest new experiments.*

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*That takes some thought and work. Let us know how you do.*

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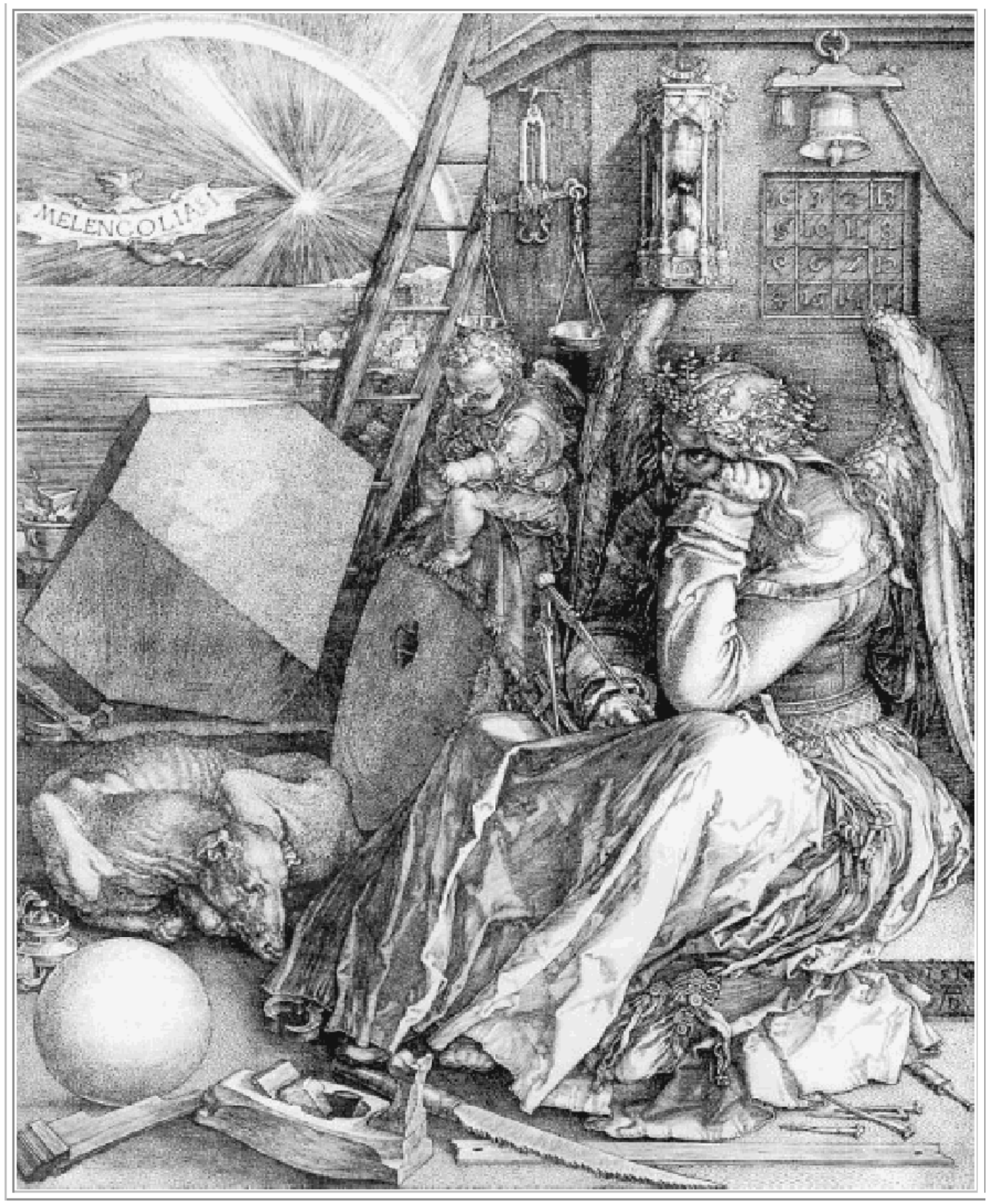
*Don't count on it.*




What's up, Doc?

Durer's "Melancholia"
1514