Symmetry-based tunnelings in high-resolution rovibrational spectra of octahedral molecules

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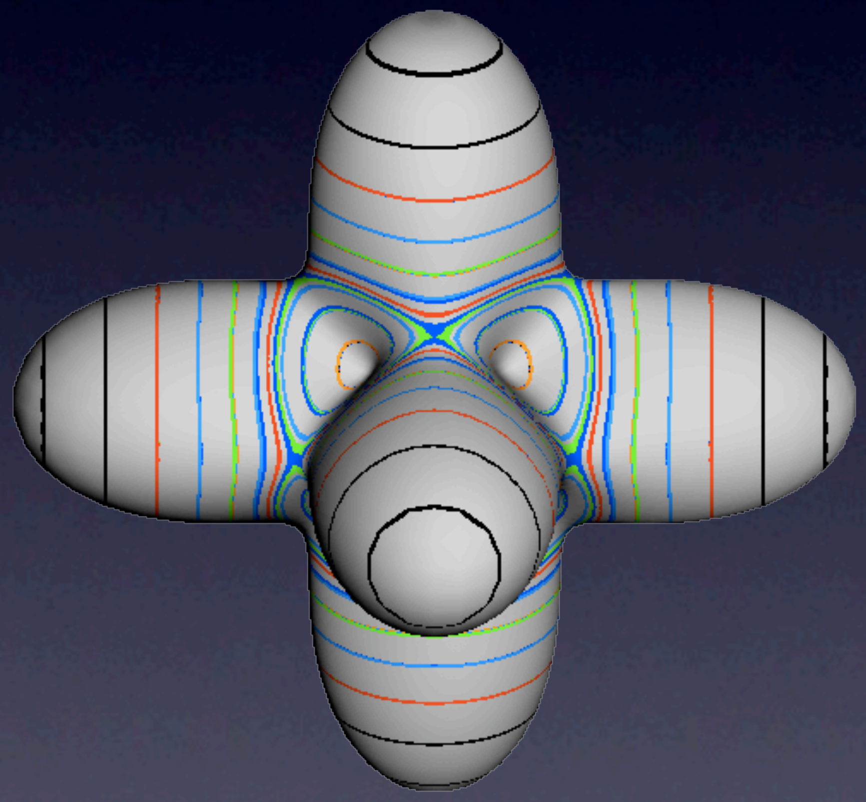
What sort of systems?

- Rotational cluster splitting for spherical top molecules
- Polyads
- Phase space tunneling
- Large amplitude motion in high-symmetry



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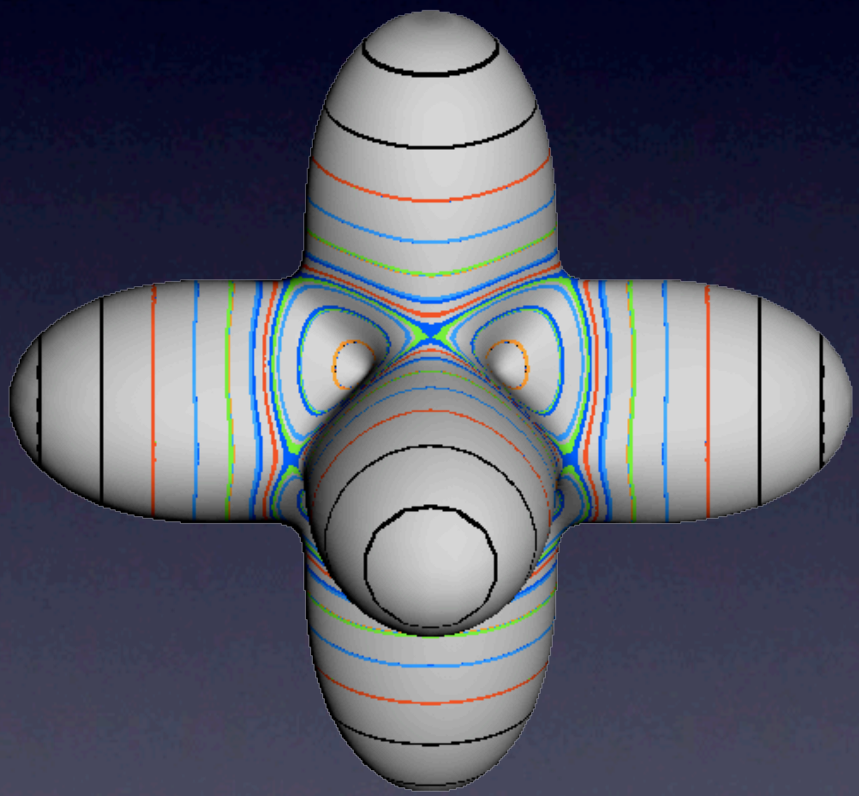
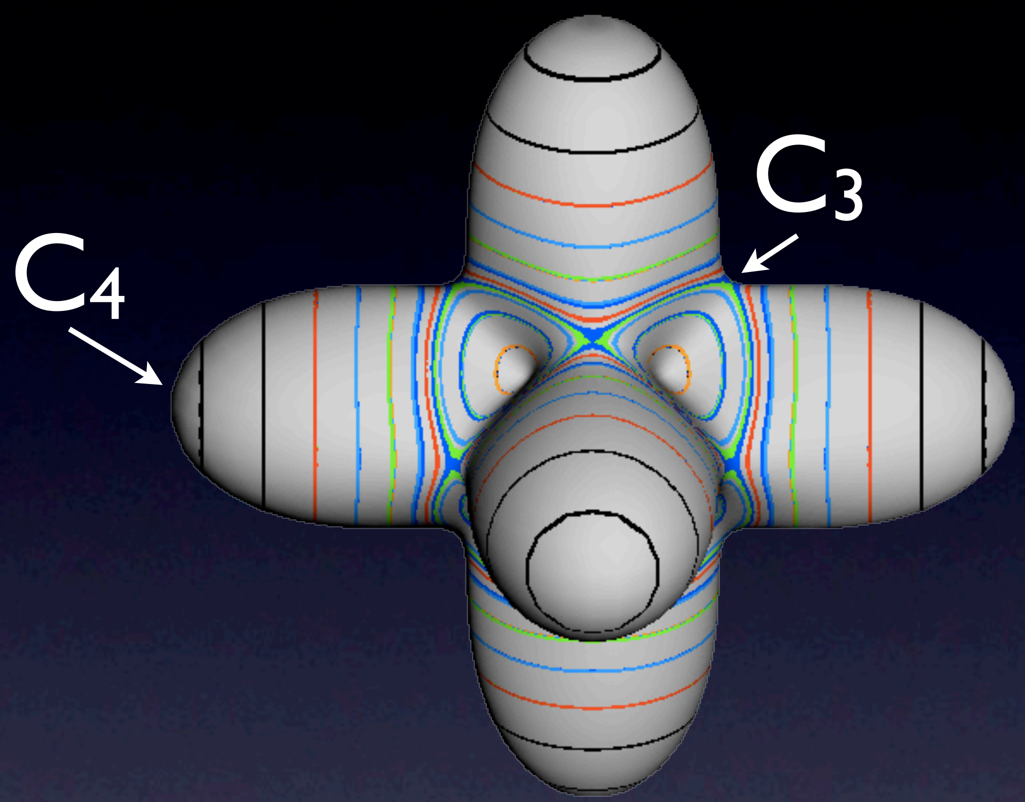


This formalism lets symmetry be your accountant!

Local symmetries

$$H = BJ^2 + c_4 J^4 + c_6 J^6 + c_8 J^8$$



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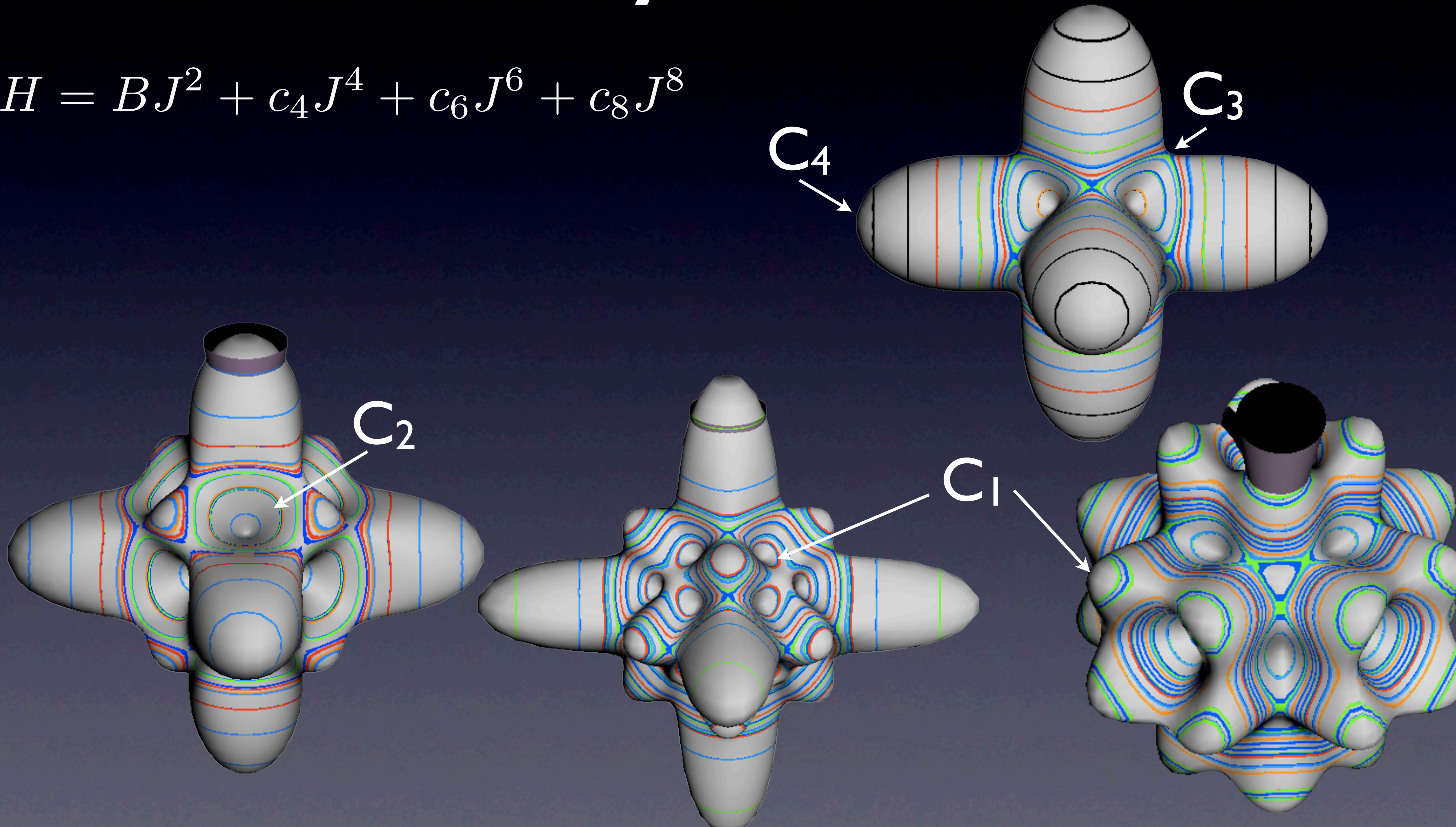
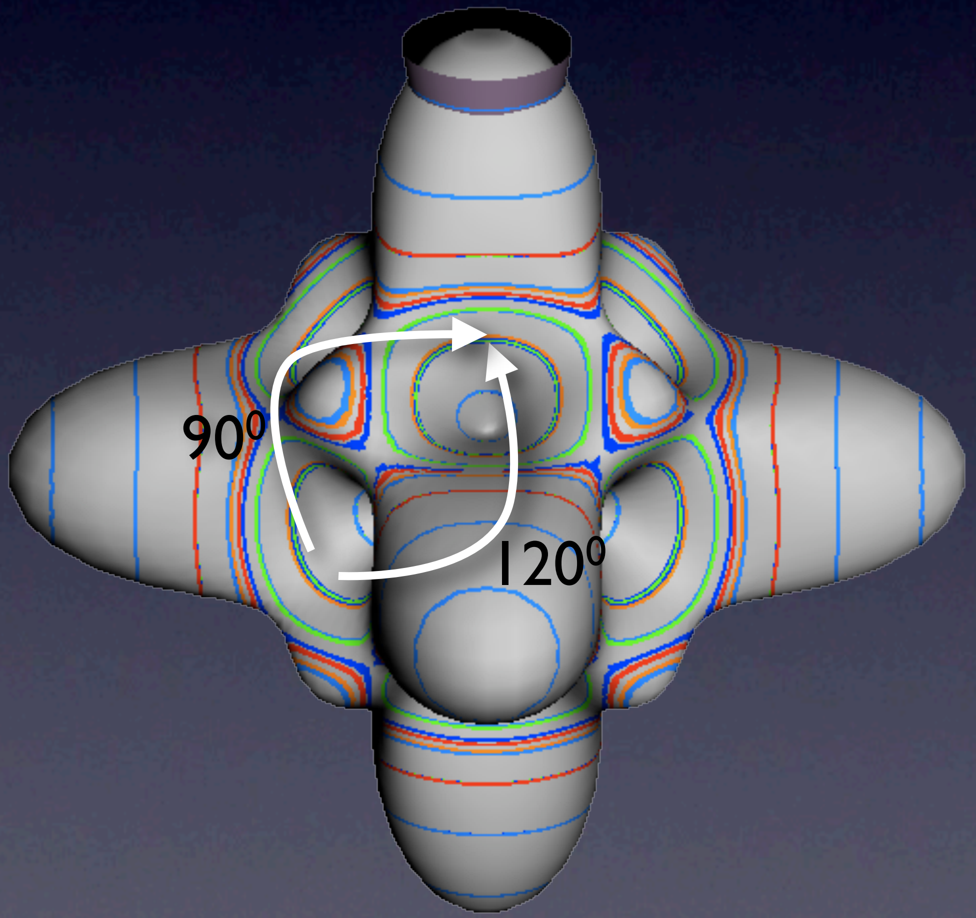


Symmetry-based parameters

- Tunneling parameters should be operations
- Old method
  - Nearest Neighbor, etc
- Symmetric method
  - R, R^2, r, i



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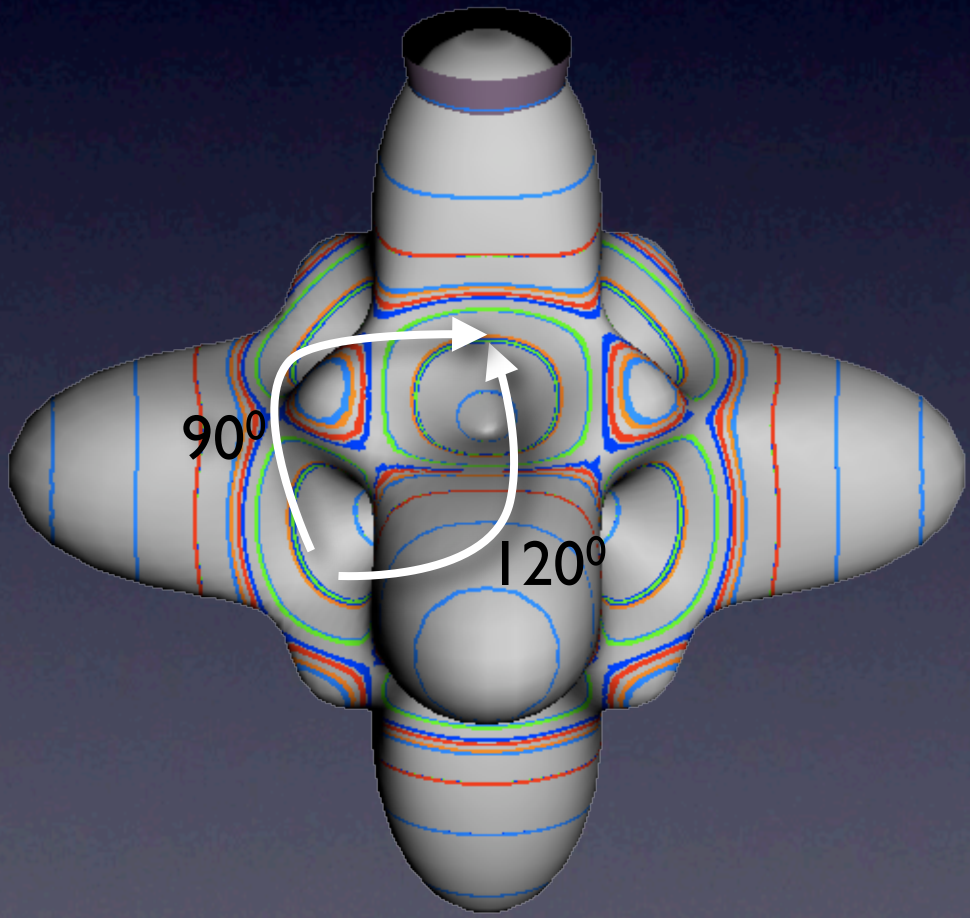

These parameters can handle C_2 and C_1

Predicting the splitting

Look at C_2

$$\varepsilon_n^\alpha = \sum_{c_g} \mathscr{D}^{\alpha *}_{nn}(g_c)^\circ \mathbf{c}_g g_c$$

$O \supset D_4 \supset C_2(i_4)$ H - eigenvals	$\varepsilon^{A_1}_{0_2}$	$\varepsilon^{A_2}_{1_2}$	$\varepsilon^{E}_{0_2}$	$\varepsilon^{E}_{1_2}$	$\varepsilon^{T_1}_{E,0_2}$	$\varepsilon^{T_1}_{E,1_2}$	$\varepsilon^{T_1}_{A_2,1_2}$	$\varepsilon^{T_2}_{E,0_2}$	$\varepsilon^{T_2}_{E,1_2}$	$\varepsilon^{T_2}_{A_1,0_2}$
ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0
$r_{12} = r_1 = \tilde{r_1} = r_2 = \tilde{r_2}$	$4r_{12}$	$4r_{12}$	$-2r_{12}$	$-2r_{12}$	$-2r_{12}$	$2r_{12}$	0	$2r_{12}$	$-2r_{12}$	0
$r_{34} = r_3 = \tilde{r_3} = r_4 = \tilde{r_4}$	$4r_{34}$	$4r_{34}$	$-2r_{34}$	$-2r_{34}$	$2r_{34}$	$-2r_{34}$	0	$-2r_{34}$	$2r_{34}$	0
$\rho_{xy} = \rho_x = \rho_y$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	0	0	$-2\rho_{xy}$	0	0	$-2\rho_{xy}$
ρ_z	ρ_z	ρ_z	ρ_z	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z
$R_{xy} = R_x = \tilde{R}_x = R_y = \tilde{R}_y$	$4R_{xy}$	$-4R_{xy}$	$-2R_{xy}$	$2R_{xy}$	$2R_{xy}$	$2R_{xy}$	0	$-2R_{xy}$	$-2R_{xy}$	0
$R_z = \tilde{R}_z$	$2R_z$	$-2R_z$	$2R_z$	$-2R_z$	0	0	$-2R_z$	0	0	$-2R_z$
$i_{1256} = i_1 = i_2 = i_5 = i_6$	$4i_{1256}$	$-4i_{1256}$	$-2i_{1256}$	$2i_{1256}$	$-2i_{1256}$	$-2i_{1256}$	0	$2i_{1256}$	$2i_{1256}$	0
i_3	i_3	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	i_3
i_4	i_4	$-i_4$	i_4	$-i_4$	i_4	$-i_4$	$-i_4$	i_4	$-i_4$	i_4

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$O \supset D_4 \supset C_2(i_4)$ H - eigenvals	$\varepsilon_{0_2}^{A_1}$	$\varepsilon_{1_2}^{A_2}$	$\varepsilon_{0_2}^{E}$	$\varepsilon_{1_2}^{E}$	$\varepsilon_{E,0_2}^{T_1}$	$\varepsilon_{E,1_2}^{T_1}$	$\varepsilon_{A_2,1_2}^{T_1}$	$\varepsilon_{E,0_2}^{T_2}$	$\varepsilon_{E,1_2}^{T_2}$	$\varepsilon_{A_1,0_2}^{T_2}$
ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0
$r_{12} = r_1 = \tilde{r_1} = r_2 = \tilde{r_2}$	$4r_{12}$	$4r_{12}$	$-2r_{12}$	$-2r_{12}$	$-2r_{12}$	$2r_{12}$	0	$2r_{12}$	$-2r_{12}$	0
$r_{34} = r_3 = \tilde{r_3} = r_4 = \tilde{r_4}$	$4r_{34}$	$4r_{34}$	$-2r_{34}$	$-2r_{34}$	$2r_{34}$	$-2r_{34}$	0	$-2r_{34}$	$2r_{34}$	0
$\rho_{xy} = \rho_x = \rho_y$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	0	0	$-2\rho_{xy}$	0	0	$-2\rho_{xy}$
ρ_z	ρ_z	ρ_z	ρ_z	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z
$R_{xy} = R_x = \tilde{R}_x = R_y = \tilde{R}_y$	$4R_{xy}$	$-4R_{xy}$	$-2R_{xy}$	$2R_{xy}$	$2R_{xy}$	$2R_{xy}$	0	$-2R_{xy}$	$-2R_{xy}$	0
$R_z = \tilde{R}_z$	$2R_z$	$-2R_z$	$2R_z$	$-2R_z$	0	0	$-2R_z$	0	0	$-2R_z$
$i_{1256} = i_1 = i_2 = i_5 = i_6$	$4i_{1256}$	$-4i_{1256}$	$-2i_{1256}$	$2i_{1256}$	$-2i_{1256}$	$-2i_{1256}$	0	$2i_{1256}$	$2i_{1256}$	0
i_3	i_3	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	i_3
i_4	i_4	$-i_4$	i_4	$-i_4$	i_4	$-i_4$	$-i_4$	i_4	$-i_4$	i_4

Predicting the splitting

Look at C_2

$$\varepsilon_n^\alpha = \sum_{c_g} \mathscr{D}_{nn}^{\alpha *}(g_c)^\circ \mathbf{c}_g g_c$$

Splits into sub-classes

$O \supset D_4 \supset C_2(i_4)$ H - eigenvals	$\varepsilon_{0_2}^{A_1}$	$\varepsilon_{1_2}^{A_2}$	$\varepsilon_{0_2}^{E}$	$\varepsilon_{1_2}^{E}$	$\varepsilon_{E,0_2}^{T_1}$	$\varepsilon_{E,1_2}^{T_1}$	$\varepsilon_{A_2,1_2}^{T_1}$	$\varepsilon_{E,0_2}^{T_2}$	$\varepsilon_{E,1_2}^{T_2}$	$\varepsilon_{A_1,0_2}^{T_2}$
ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0
$r_{12} = r_1 = \tilde{r_1} = r_2 = \tilde{r_2}$	$4r_{12}$	$4r_{12}$	$-2r_{12}$	$-2r_{12}$	$-2r_{12}$	$2r_{12}$	0	$2r_{12}$	$-2r_{12}$	0
$r_{34} = r_3 = \tilde{r_3} = r_4 = \tilde{r_4}$	$4r_{34}$	$4r_{34}$	$-2r_{34}$	$-2r_{34}$	$2r_{34}$	$-2r_{34}$	0	$-2r_{34}$	$2r_{34}$	0
$\rho_{xy} = \rho_x = \rho_y$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	0	0	$-2\rho_{xy}$	0	0	$-2\rho_{xy}$
ρ_z	ρ_z	ρ_z	ρ_z	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z
$R_{xy} = R_x = R_x = R_y = R_y$	$4R_{xy}$	$-4R_{xy}$	$-2R_{xy}$	$2R_{xy}$	$2R_{xy}$	$2R_{xy}$	0	$-2R_{xy}$	$-2R_{xy}$	0
$R_z = \tilde{R}_z$	$2R_z$	$-2R_z$	$2R_z$	$-2R_z$	0	0	$-2R_z$	0	0	$-2R_z$
$i_{1256} = i_1 = i_2 = i_5 = i_6$	$4i_{1256}$	$-4i_{1256}$	$-2i_{1256}$	$2i_{1256}$	$-2i_{1256}$	$-2i_{1256}$	0	$2i_{1256}$	$2i_{1256}$	0
i_3	i_3	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	i_3
i_4	i_4	$-i_4$	i_4	$-i_4$	i_4	$-i_4$	$-i_4$	i_4	$-i_4$	i_4

Class splitting is what gives local symmetry

Predicting the splitting

Look at C_2

$$\varepsilon_n^\alpha = \sum_{c_g} \mathscr{D}_{nn}^{\alpha *}(g_c)^\circ \mathbf{c}_g g_c$$

Repetition

$O \supset D_4 \supset C_2(i_4)$ H - eigenvals	$\varepsilon_{0_2}^{A_1}$	$\varepsilon_{1_2}^{A_2}$	$\varepsilon_{0_2}^{E}$	$\varepsilon_{1_2}^{E}$	$\varepsilon_{E,0_2}^{T_1}$	$\varepsilon_{E,1_2}^{T_1}$	$\varepsilon_{A_2,1_2}^{T_1}$	$\varepsilon_{E,0_2}^{T_2}$	$\varepsilon_{E,1_2}^{T_2}$	$\varepsilon_{A_1,0_2}^{T_2}$
ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0
$r_{12} = r_1 = \tilde{r_1} = r_2 = \tilde{r_2}$	$4r_{12}$	$4r_{12}$	$-2r_{12}$	$-2r_{12}$	$-2r_{12}$	$2r_{12}$	0	$2r_{12}$	$-2r_{12}$	0
$r_{34} = r_3 = \tilde{r_3} = r_4 = \tilde{r_4}$	$4r_{34}$	$4r_{34}$	$-2r_{34}$	$-2r_{34}$	$2r_{34}$	$-2r_{34}$	0	$-2r_{34}$	$2r_{34}$	0
$\rho_{xy} = \rho_x = \rho_y$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	0	0	$-2\rho_{xy}$	0	0	$-2\rho_{xy}$
ρ_z	ρ_z	ρ_z	ρ_z	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z
$R_{xy} = R_x = \tilde{R_x} = R_y = \tilde{R_y}$	$4R_{xy}$	$-4R_{xy}$	$-2R_{xy}$	$2R_{xy}$	$2R_{xy}$	$2R_{xy}$	0	$-2R_{xy}$	$-2R_{xy}$	0
$R_z = \tilde{R_z}$	$2R_z$	$-2R_z$	$2R_z$	$-2R_z$	0	0	$-2R_z$	0	0	$-2R_z$
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i_3	i_3	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	i_3
i_4	i_4	$-i_4$	i_4	$-i_4$	i_4	$-i_4$	$-i_4$	i_4	$-i_4$	i_4

Class splitting is what gives local symmetry

Predicting the splitting

Look at C_2

$$\varepsilon^{\alpha}_{n} = \sum_{c_g} \mathscr{D}^{\alpha *}_{nn}(g_c)^{\circ} \mathbf{c}_g g_c$$

Build splitting matrix from these parts

$O \supset D_4 \supset C_2(i_4)$ H - eigenvals	$\varepsilon^{A_1}_{0_2}$	$\varepsilon^{A_2}_{1_2}$	$\varepsilon^{E}_{0_2}$	$\varepsilon^{E}_{1_2}$	$\varepsilon^{T_1}_{E,0_2}$	$\varepsilon^{T_1}_{E,1_2}$	$\varepsilon^{T_1}_{A_2,1_2}$	$\varepsilon^{T_2}_{E,0_2}$	$\varepsilon^{T_2}_{E,1_2}$	$\varepsilon^{T_2}_{A_1,0_2}$
ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0	ε_0
$r_{12} = r_1 = \tilde{r_1} = r_2 = \tilde{r_2}$	$4r_{12}$	$4r_{12}$	$-2r_{12}$	$-2r_{12}$	$-2r_{12}$	$2r_{12}$	0	$2r_{12}$	$-2r_{12}$	0
$r_{34} = r_3 = \tilde{r_3} = r_4 = \tilde{r_4}$	$4r_{34}$	$4r_{34}$	$-2r_{34}$	$-2r_{34}$	$2r_{34}$	$-2r_{34}$	0	$-2r_{34}$	$2r_{34}$	0
$\rho_{xy} = \rho_x = \rho_y$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	$2\rho_{xy}$	0	0	$-2\rho_{xy}$	0	0	$-2\rho_{xy}$
ρ_z	ρ_z	ρ_z	ρ_z	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z	$-\rho_z$	$-\rho_z$	ρ_z
$R_{xy} = R_x = R_x = R_y = R_y$	$4R_{xy}$	$-4R_{xy}$	$-2R_{xy}$	$2R_{xy}$	$2R_{xy}$	$2R_{xy}$	0	$-2R_{xy}$	$-2R_{xy}$	0
$R_z = \tilde{R}_z$	$2R_z$	$-2R_z$	$2R_z$	$-2R_z$	0	0	$-2R_z$	0	0	$-2R_z$
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i_3	i_3	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	$-i_3$	$-i_3$	i_3	i_3
i_4	i_4	$-i_4$	i_4	$-i_4$	i_4	$-i_4$	$-i_4$	i_4	$-i_4$	i_4

Class splitting is what gives local symmetry

Predicting the splitting

Look at C_2

$$\varepsilon_n^\alpha = \sum_{c_g} \mathscr{D}_{nn}^{\alpha *}(g_c)^\circ \mathbf{c}_g g_c$$

0_2	$\mathbf{1}$	r_{12}, i_{1256}	r_{34}, R_{xy}	ρ_{xy}, R_z	ρ_z, i_3
$\varepsilon_{0_2}^{A_1}$	1	4	4	2	1
$\varepsilon_{0_2}^{E}$	1	-2	-2	2	1
$\varepsilon_{0_2}^{T_1}$	1	-2	2	0	-1
$\varepsilon_{E,0_2}^{T_2}$	1	2	-2	0	-1
$\varepsilon_{A_1,0_2}^{T_2}$	1	0	0	-2	1

Splittings will be combinations of these columns

Finding tunneling parameters

$$g_c = \frac{l^\alpha}{{}^\circ\mathcal{G}} \sum_\alpha \sum_n \mathscr{D}^\alpha_{nn}(g_c)\varepsilon^\alpha_n$$

0_2	$\varepsilon^{A_1}_{0_2}$	$\varepsilon^{E}_{0_2}$	$\varepsilon^{T_1}_{0_2}$	$\varepsilon^{T_2}_{E,0_2}$	$\varepsilon^{T_2}_{A_1,0_2}$
$\mathbf{1}$	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
r_{12}, i_{1256}	$\frac{1}{12}$	$-\frac{1}{12}$	$-\frac{1}{8}$	$\frac{1}{8}$	0
r_{34}, R_{xy}	$\frac{1}{12}$	$-\frac{1}{12}$	$\frac{1}{8}$	$-\frac{1}{8}$	0
ρ_{xy}, R_z	$\frac{1}{12}$	$\frac{1}{6}$	0	0	$-\frac{1}{4}$
ρ_z, i_3	$\frac{1}{12}$	$\frac{1}{6}$	$-\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$

Such a transformation will give tunneling parameters given energy splittings

Finding tunneling parameters

Now let's watch it work

$$g_c = \frac{l^\alpha}{\circ\mathcal{G}} \sum_\alpha \sum_n \mathscr{D}^\alpha_{nn}(g_c)\varepsilon^\alpha_n$$

0_2	$\varepsilon^{A_1}_{0_2}$	$\varepsilon^{E}_{0_2}$	$\varepsilon^{T_1}_{0_2}$	$\varepsilon^{T_2}_{E,0_2}$	$\varepsilon^{T_2}_{A_1,0_2}$
$\mathbf{1}$	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
r_{12}, i_{1256}	$\frac{1}{12}$	$-\frac{1}{12}$	$-\frac{1}{8}$	$\frac{1}{8}$	0
r_{34}, R_{xy}	$\frac{1}{12}$	$-\frac{1}{12}$	$\frac{1}{8}$	$-\frac{1}{8}$	0
ρ_{xy}, R_z	$\frac{1}{12}$	$\frac{1}{6}$	0	0	$-\frac{1}{4}$
ρ_z, i_3	$\frac{1}{12}$	$\frac{1}{6}$	$-\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$

Such a transformation will give tunneling parameters given energy splittings

Cluster splitting

Mixing $T^{[4]}$ and $T^{[6]}$

$$H = BJ^2 + c_4 J^4 + c_6 J^6$$

Cluster splitting

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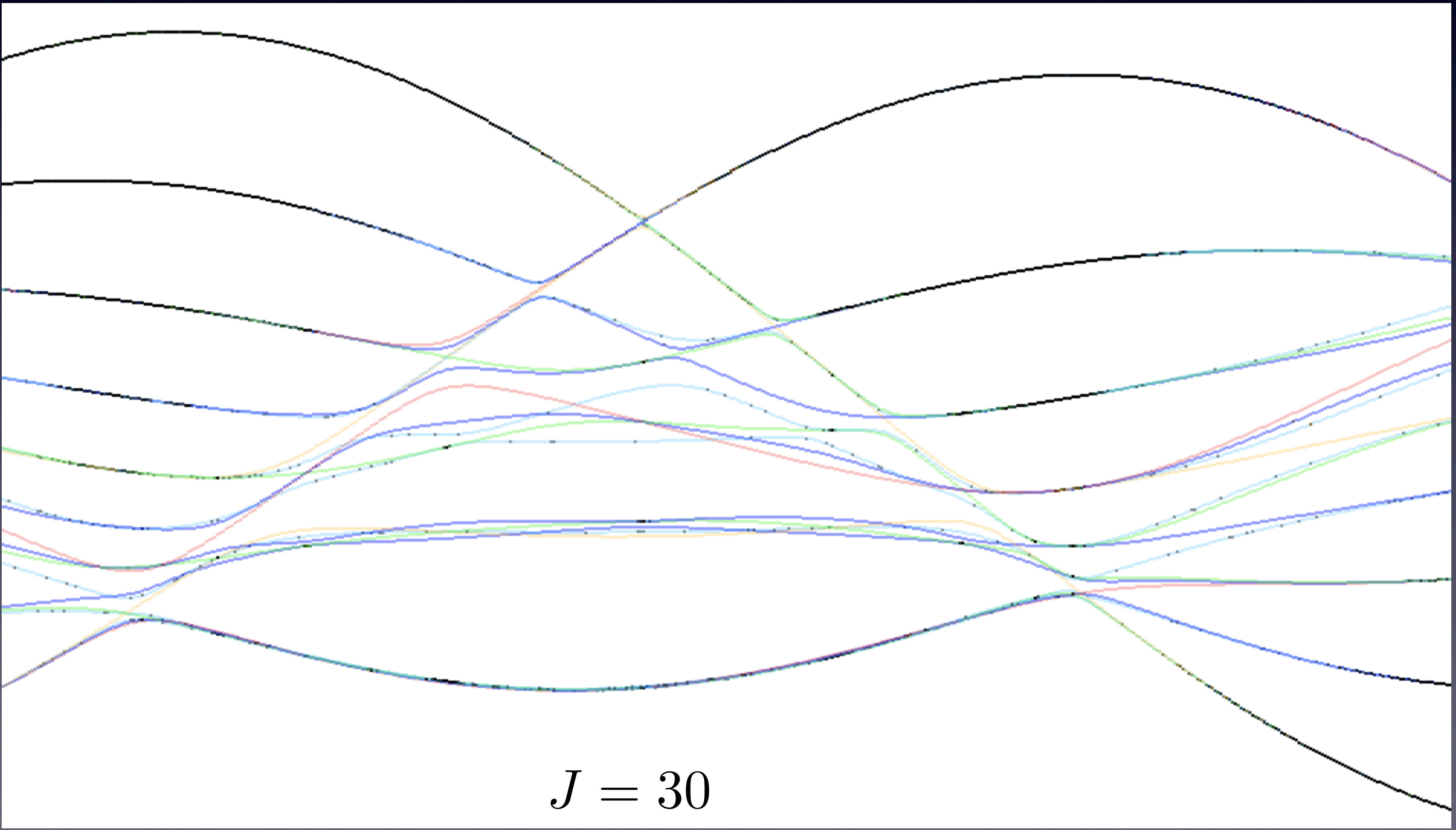

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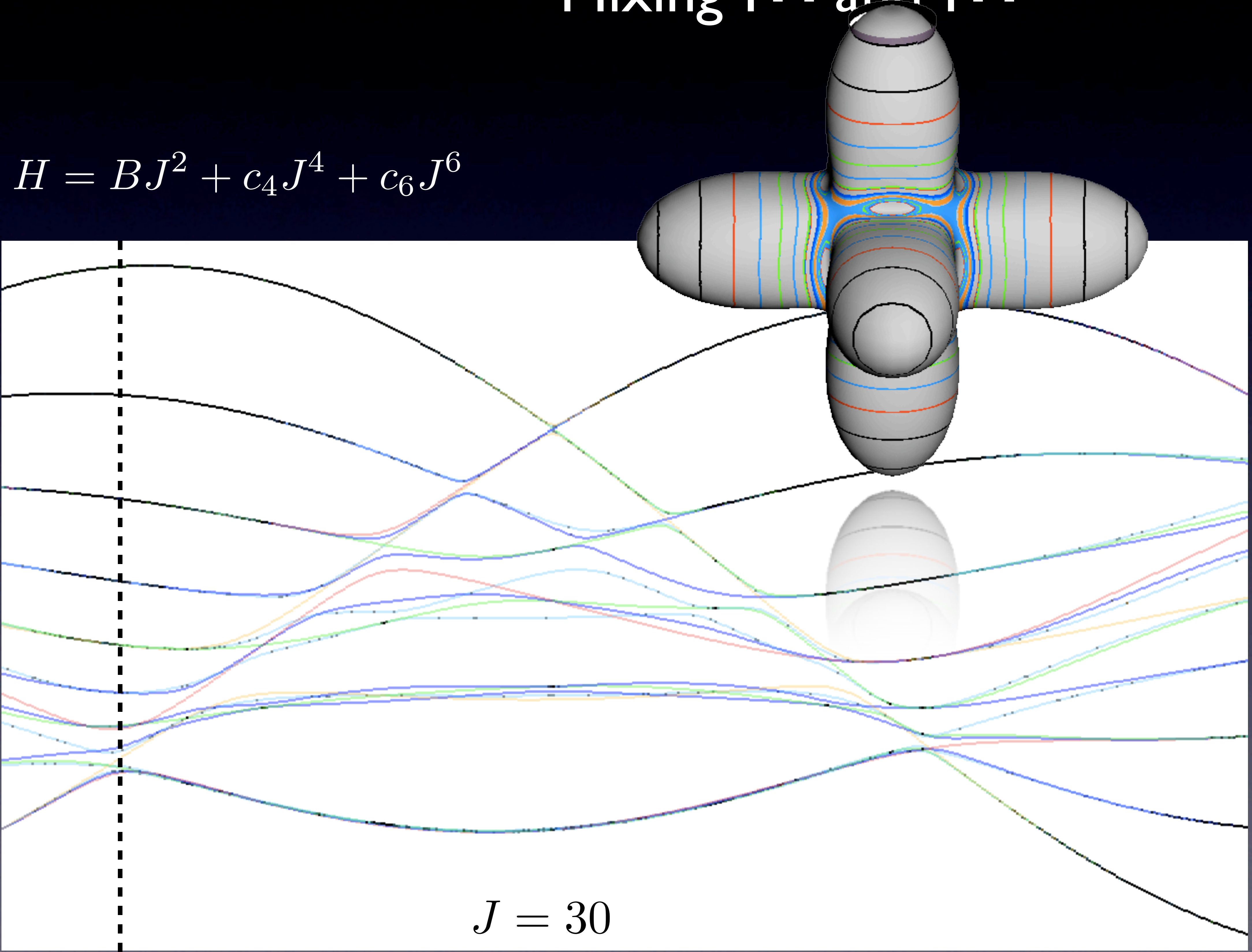

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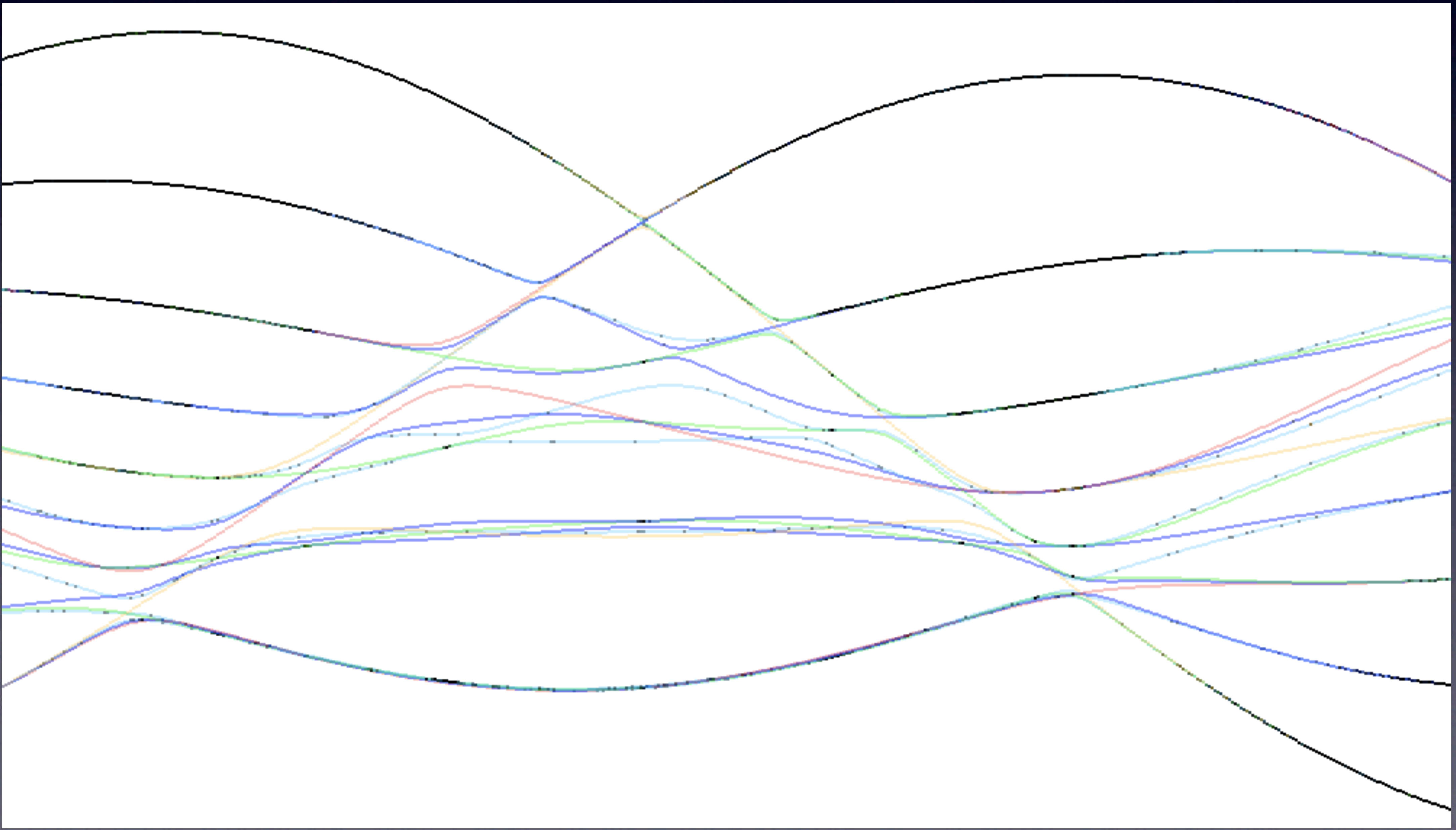

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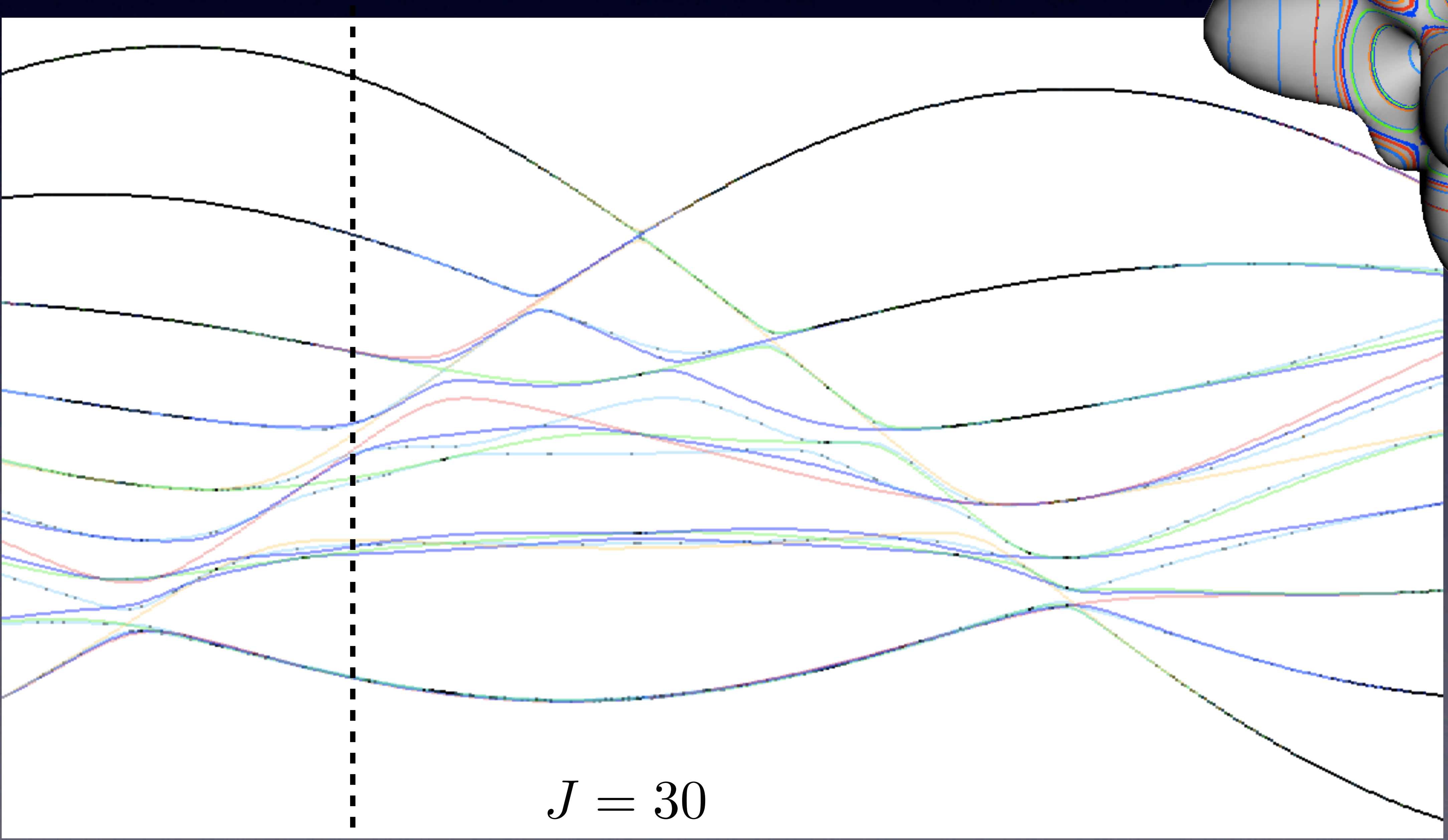

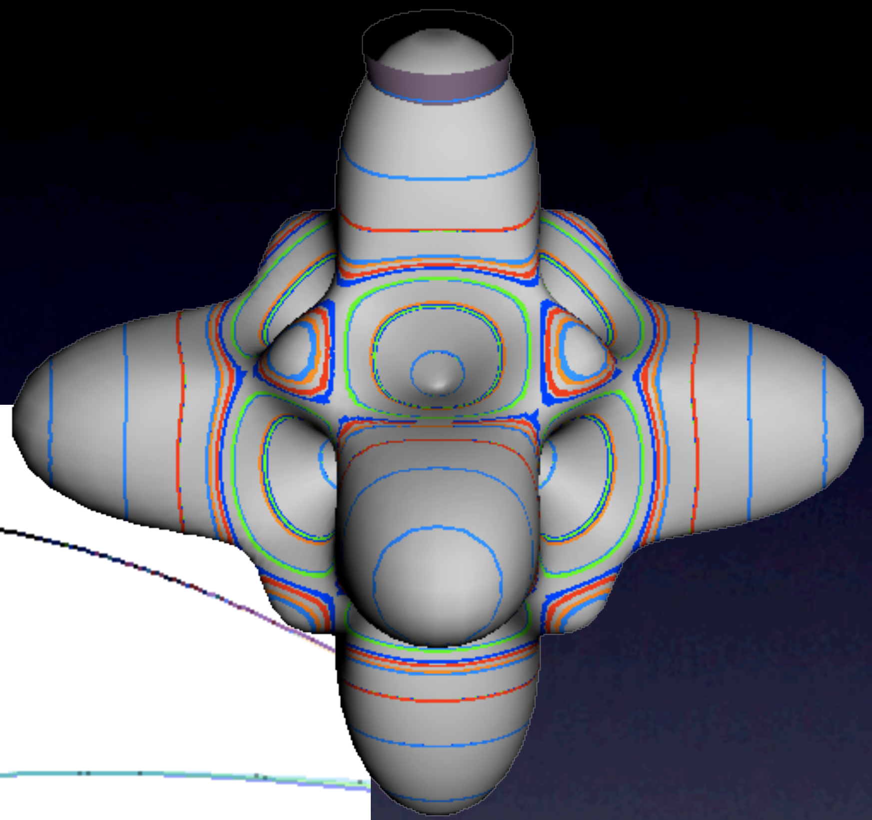

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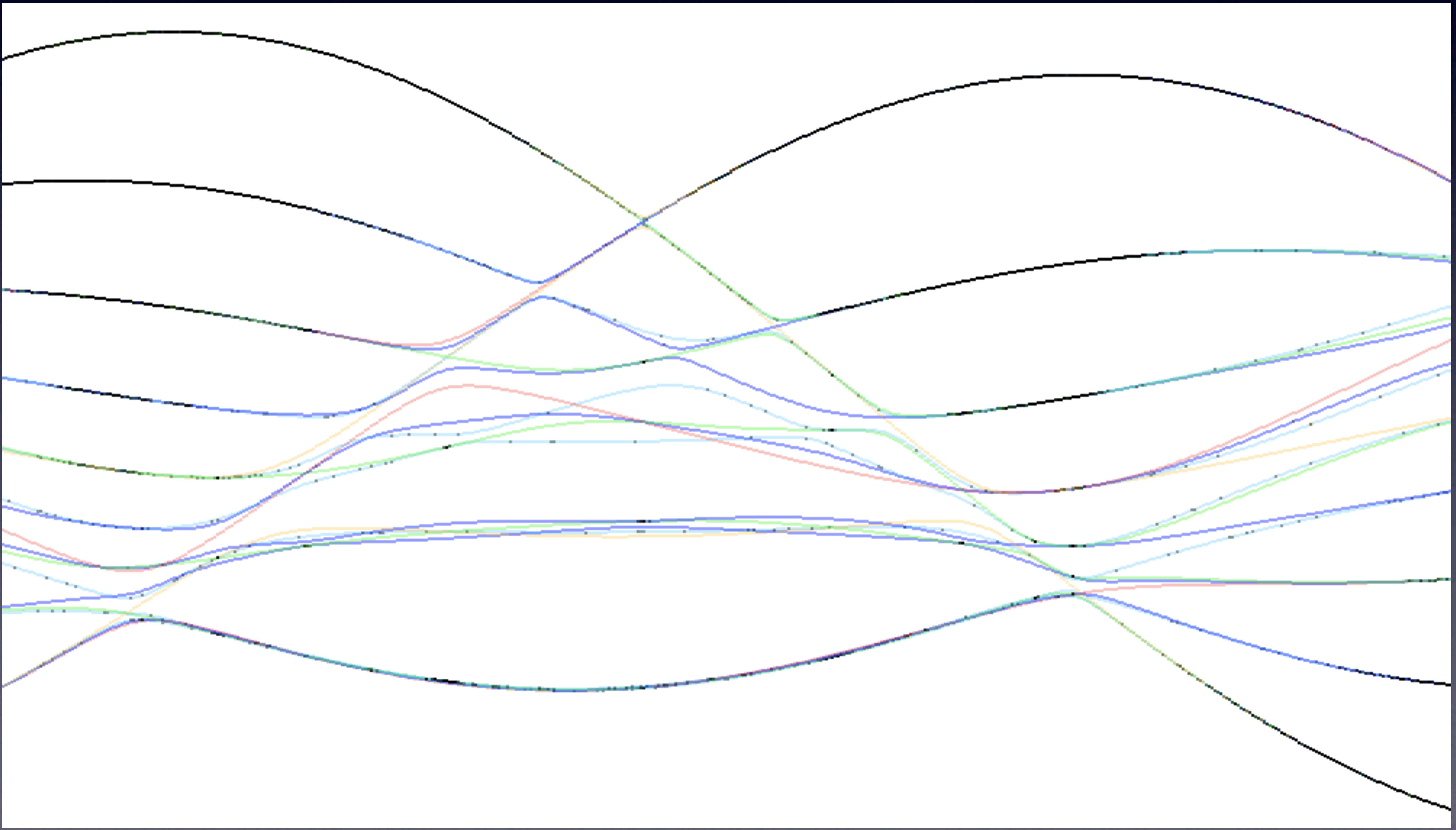

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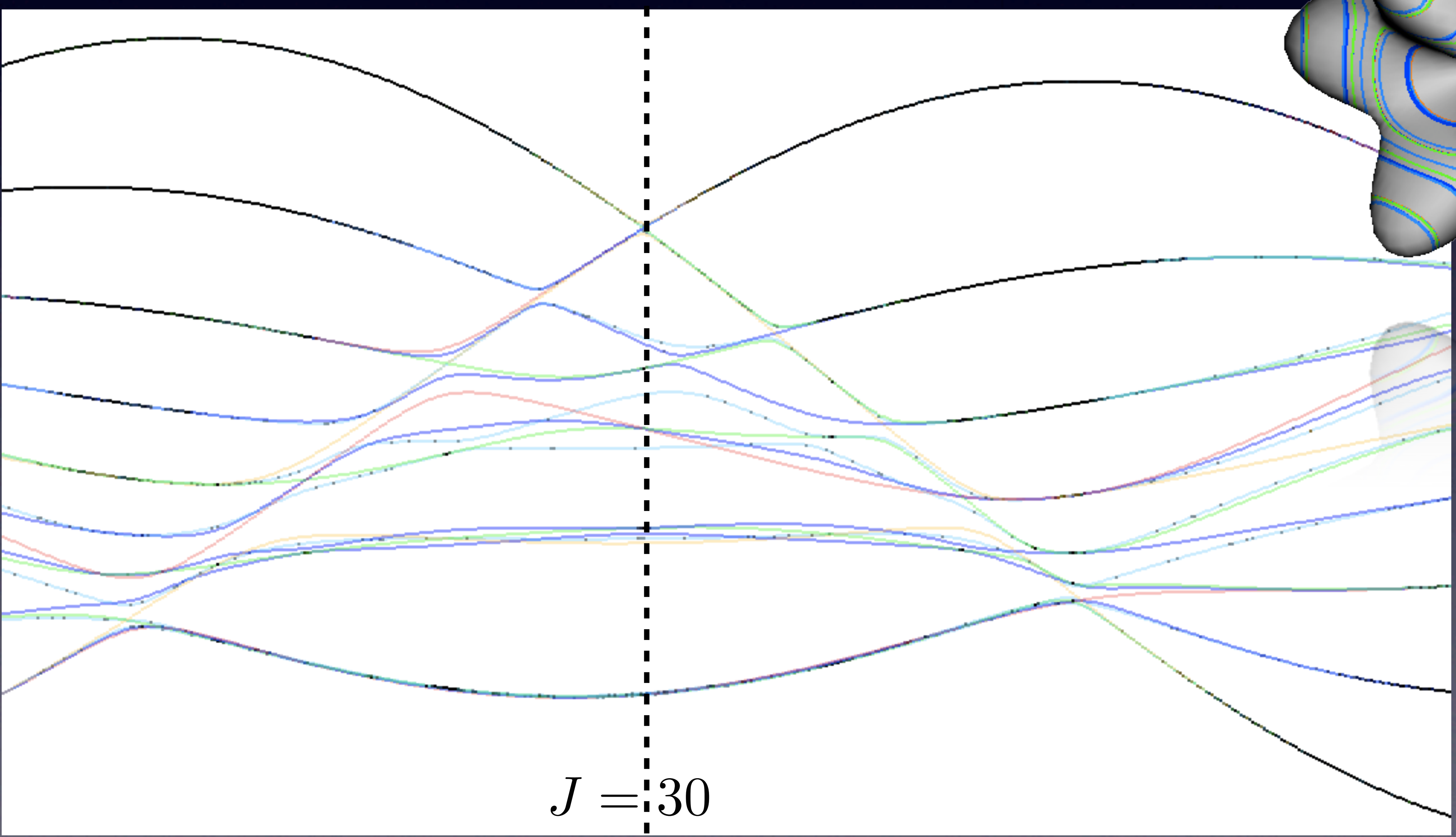
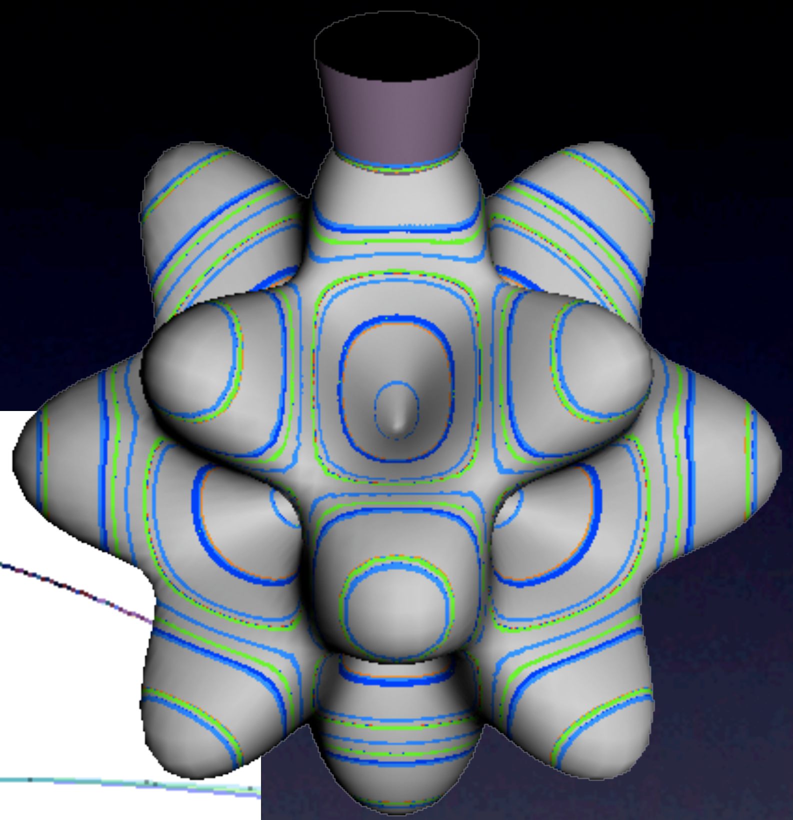
$H = BJ^2 + c_4 J^4 + c_6 J^6$

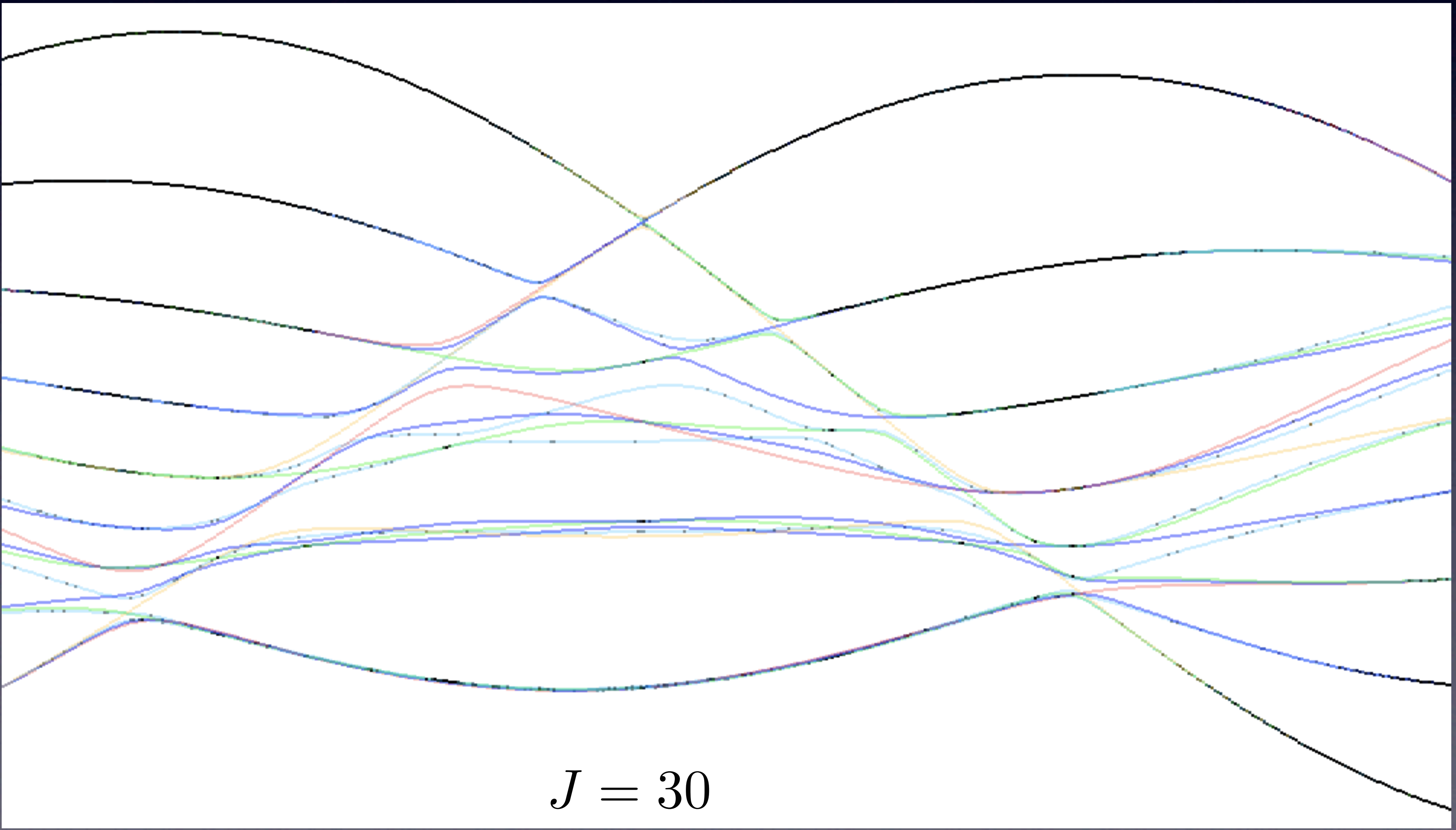




Cluster splitting

Look at the lowest cluster

$H = BJ^2 + c_4J^4 + c_6J^6$



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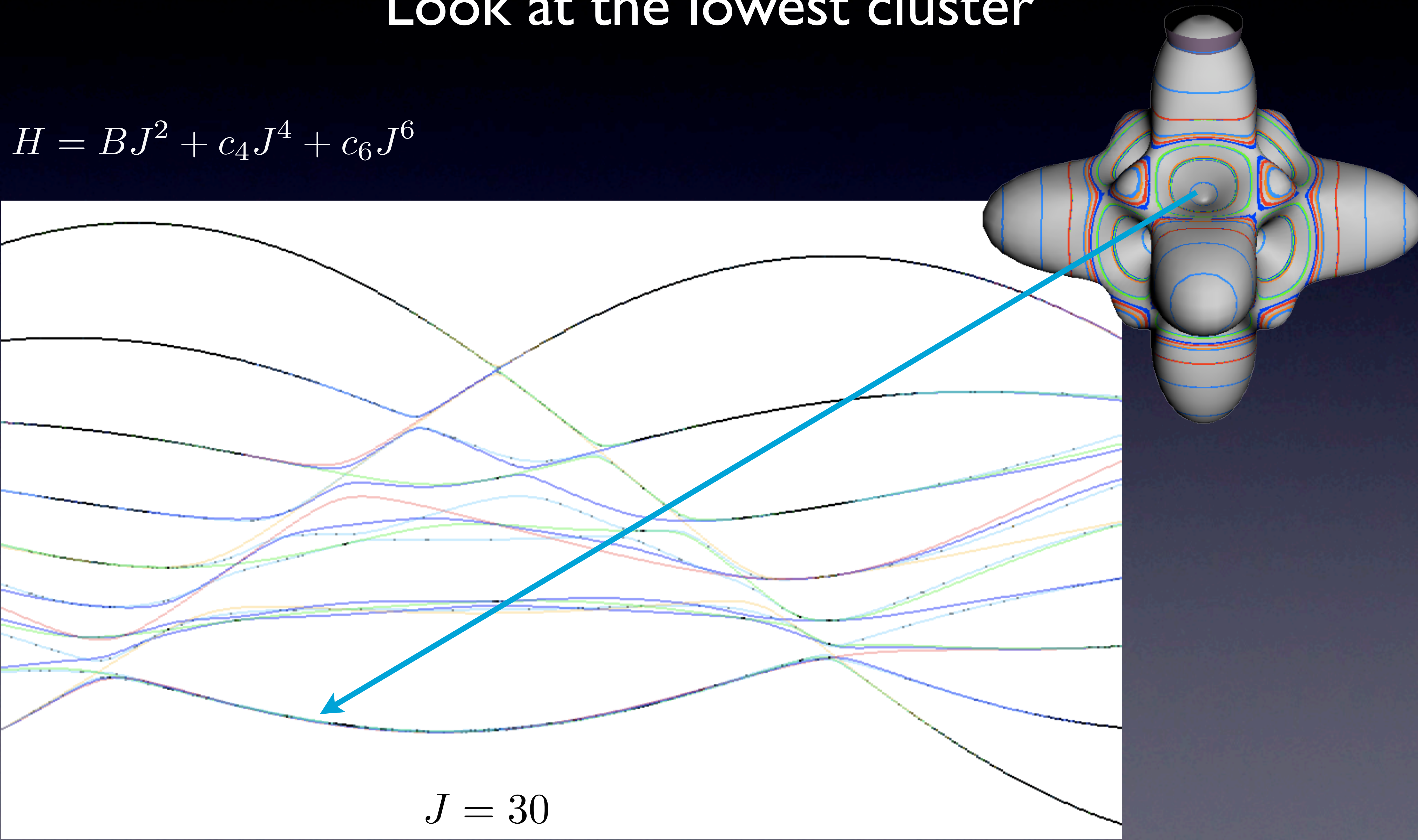
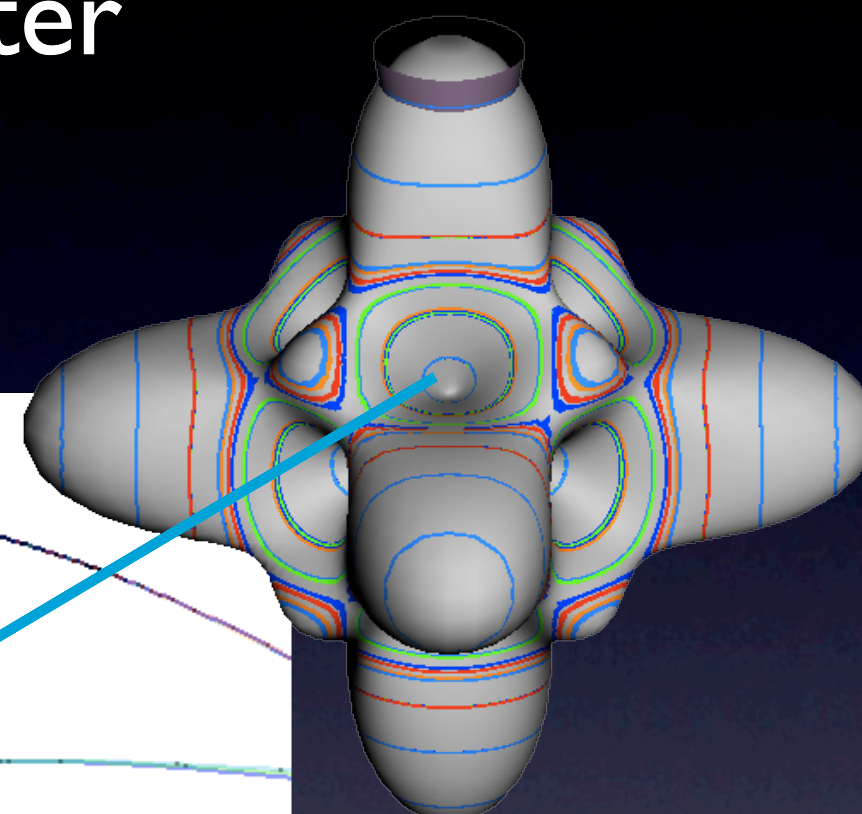
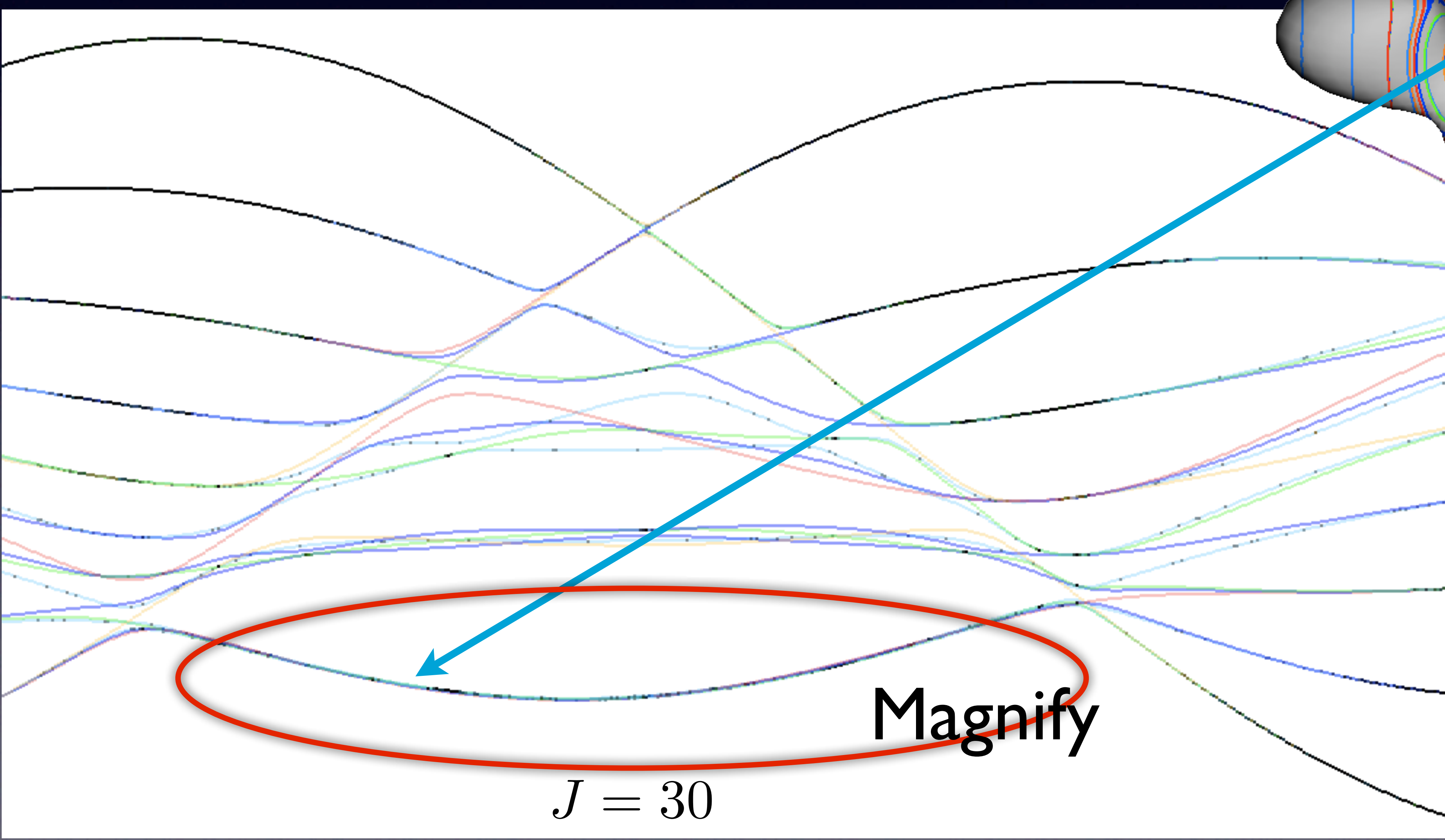


Cluster splitting

Look at the lowest cluster

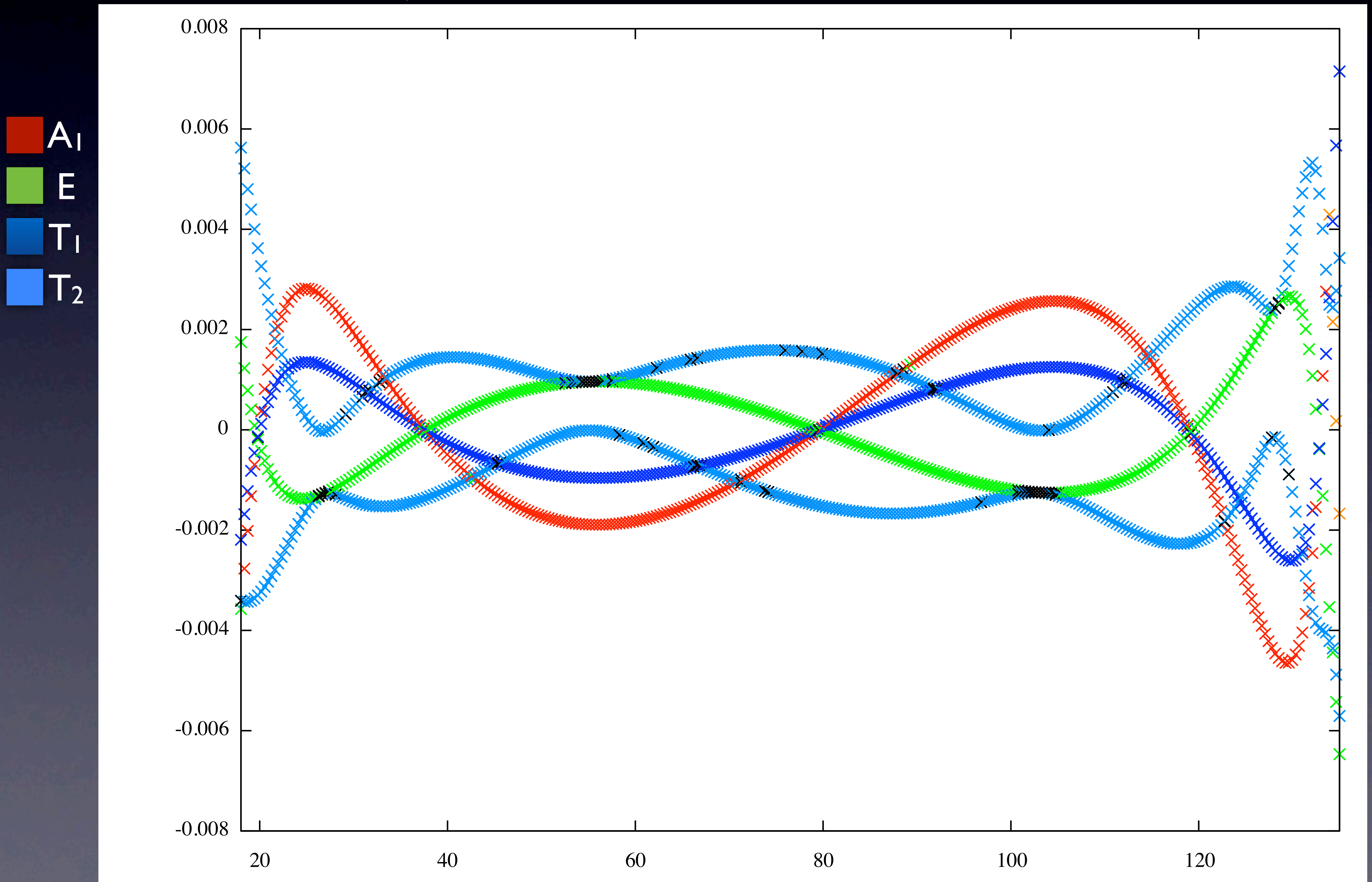
$H = BJ^2 + c_4 J^4 + c_6 J^6$





Magnified x1000

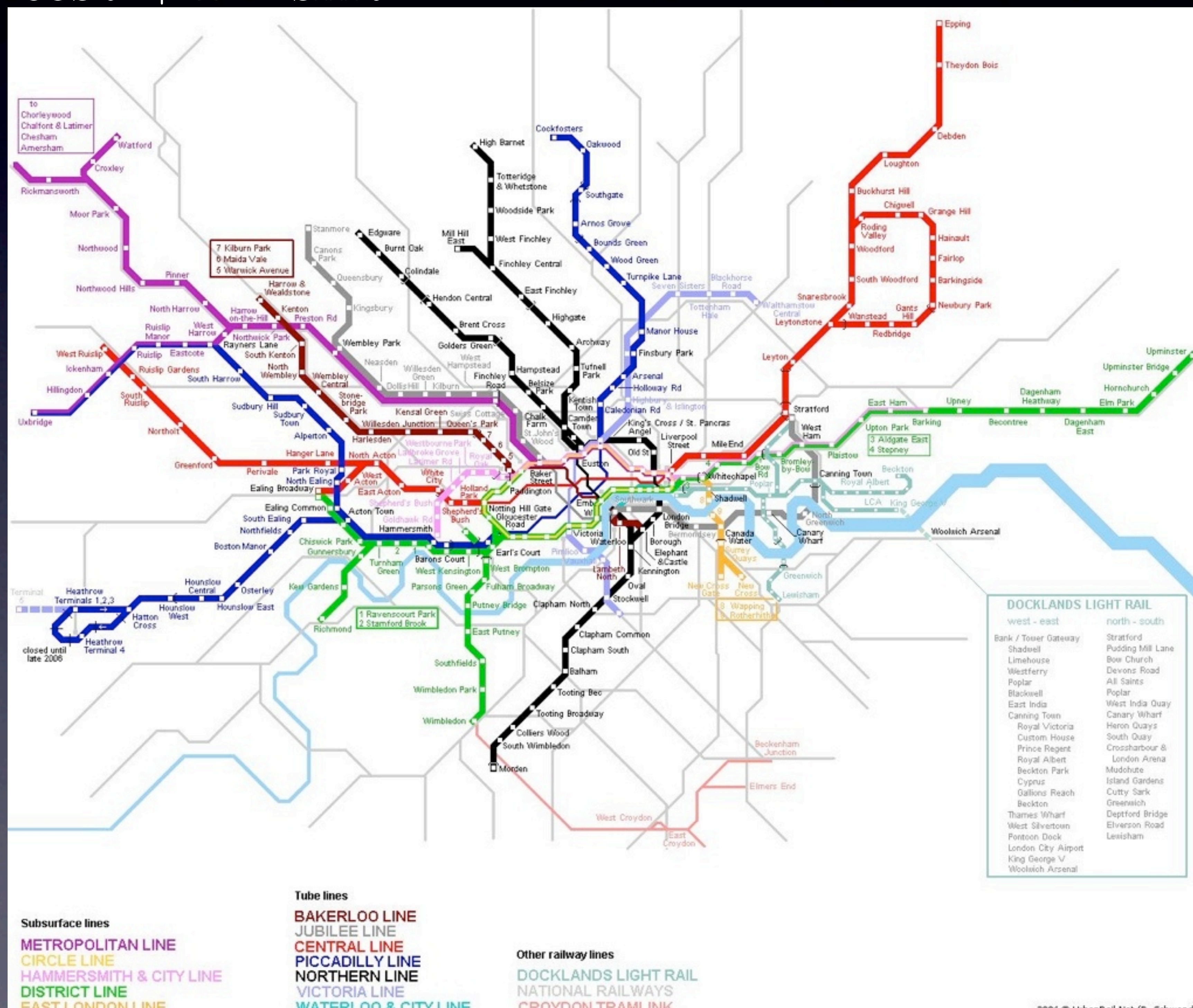
$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



Magnified x1000

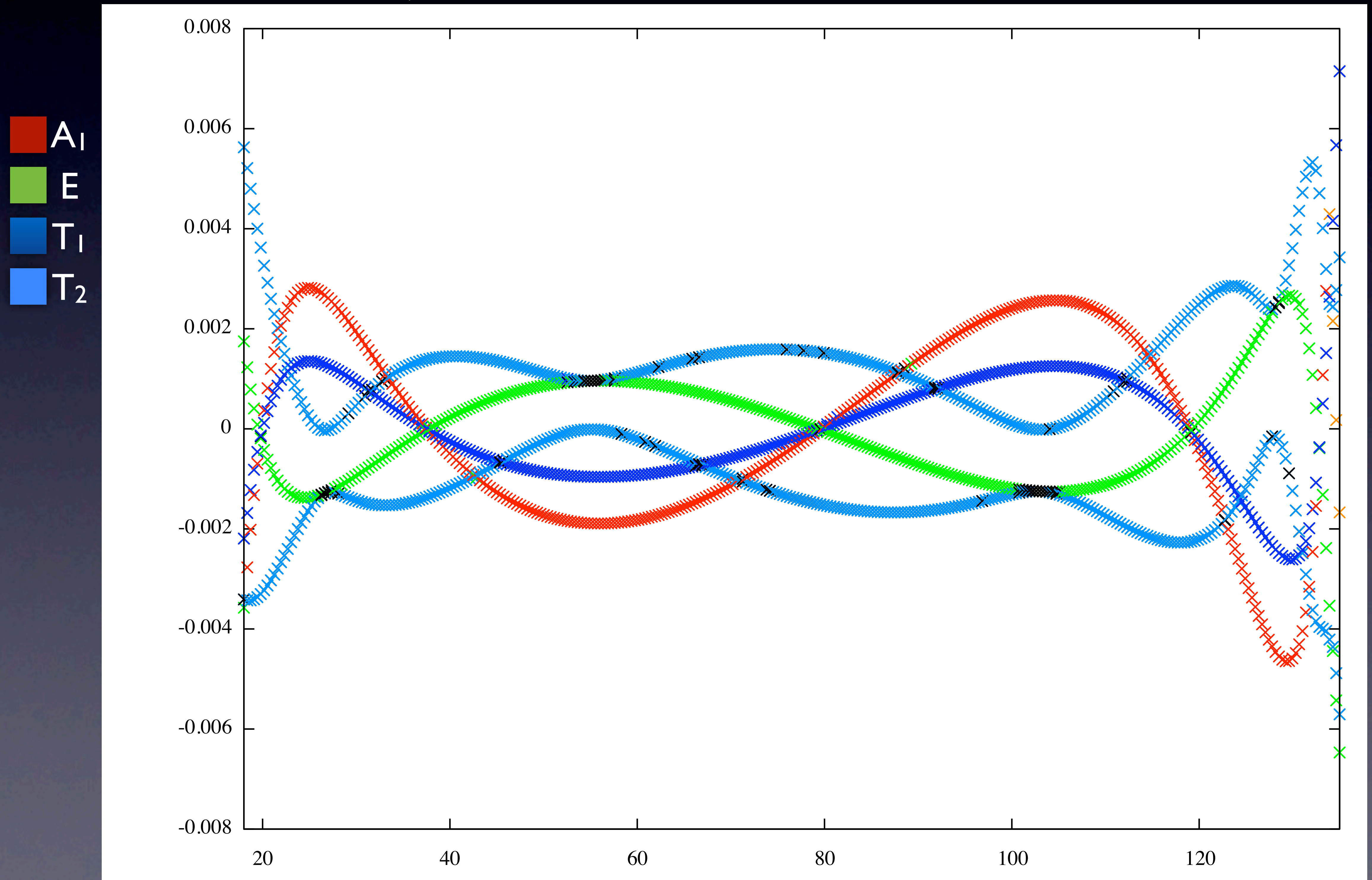
$$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$$

- A_1
- E
- T_1
- T_2



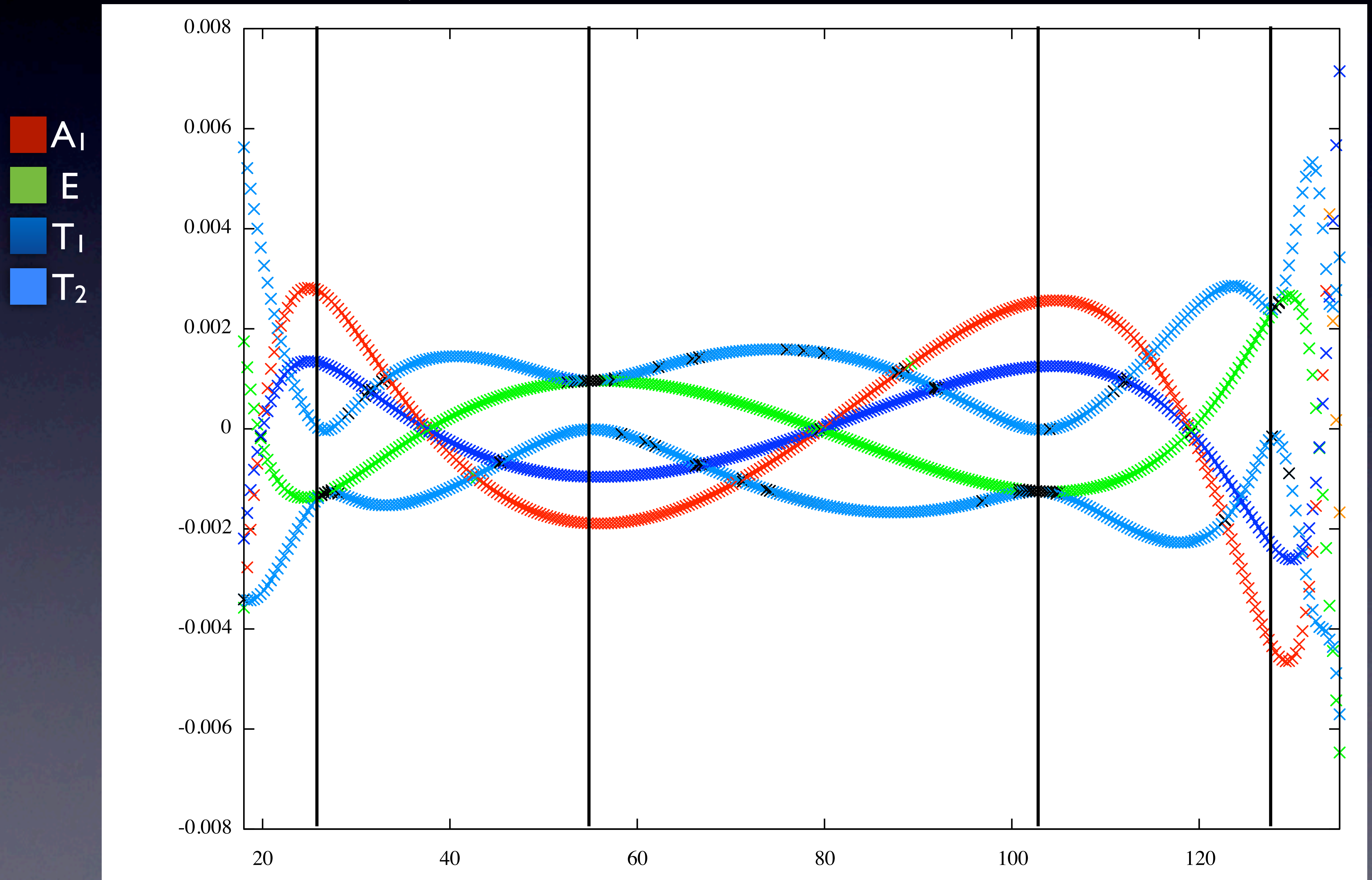
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



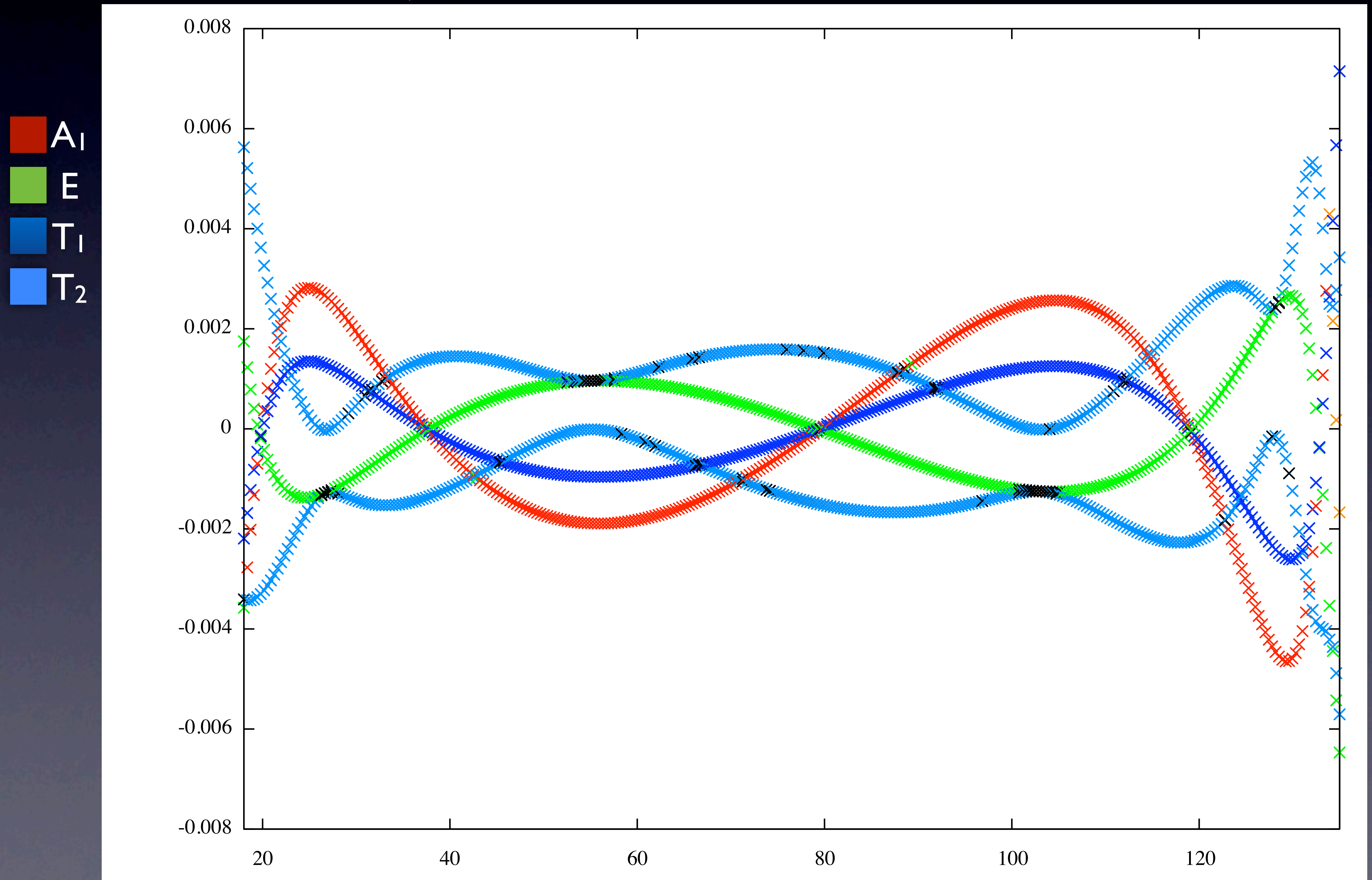
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



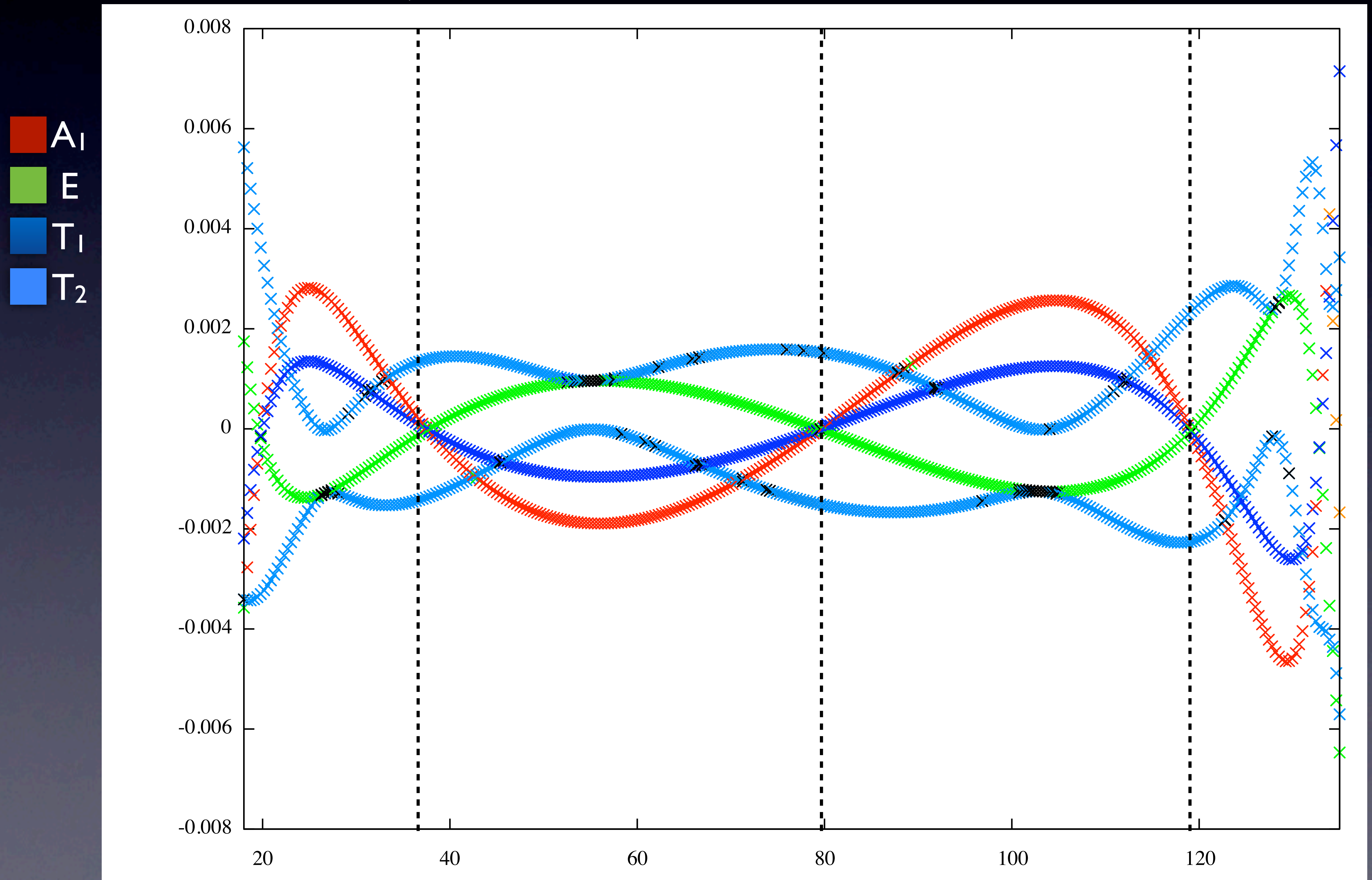
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



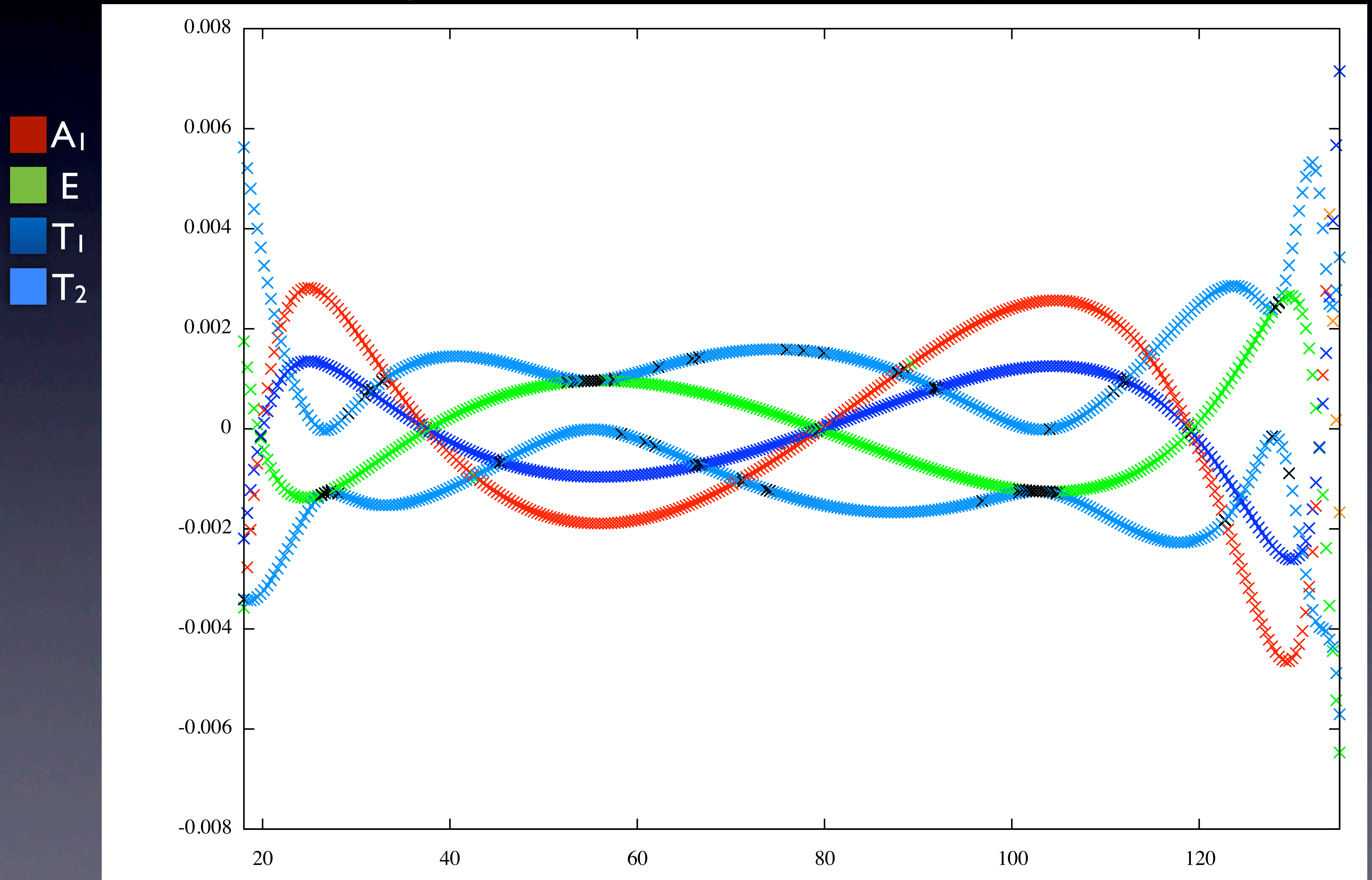
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



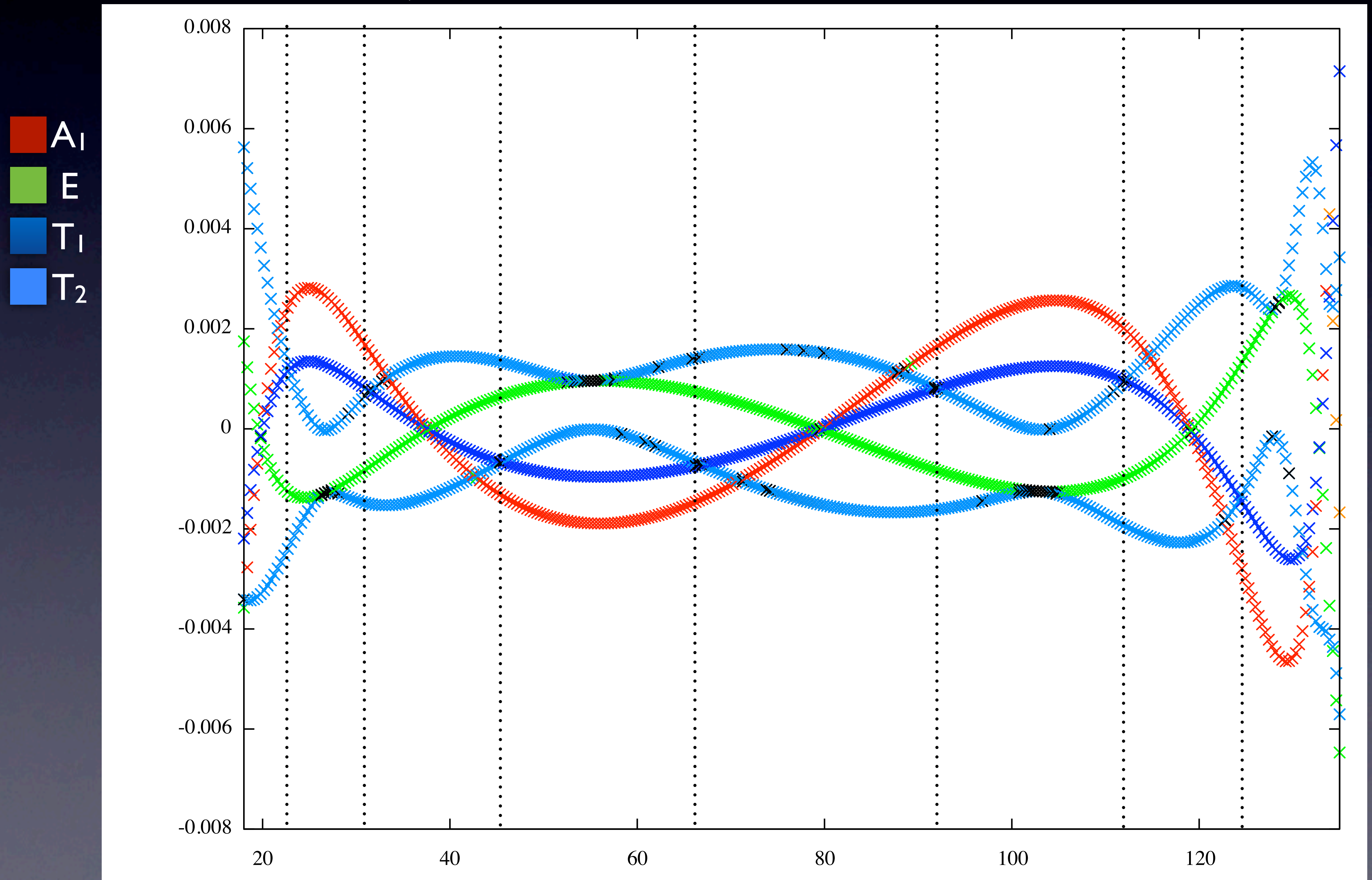
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



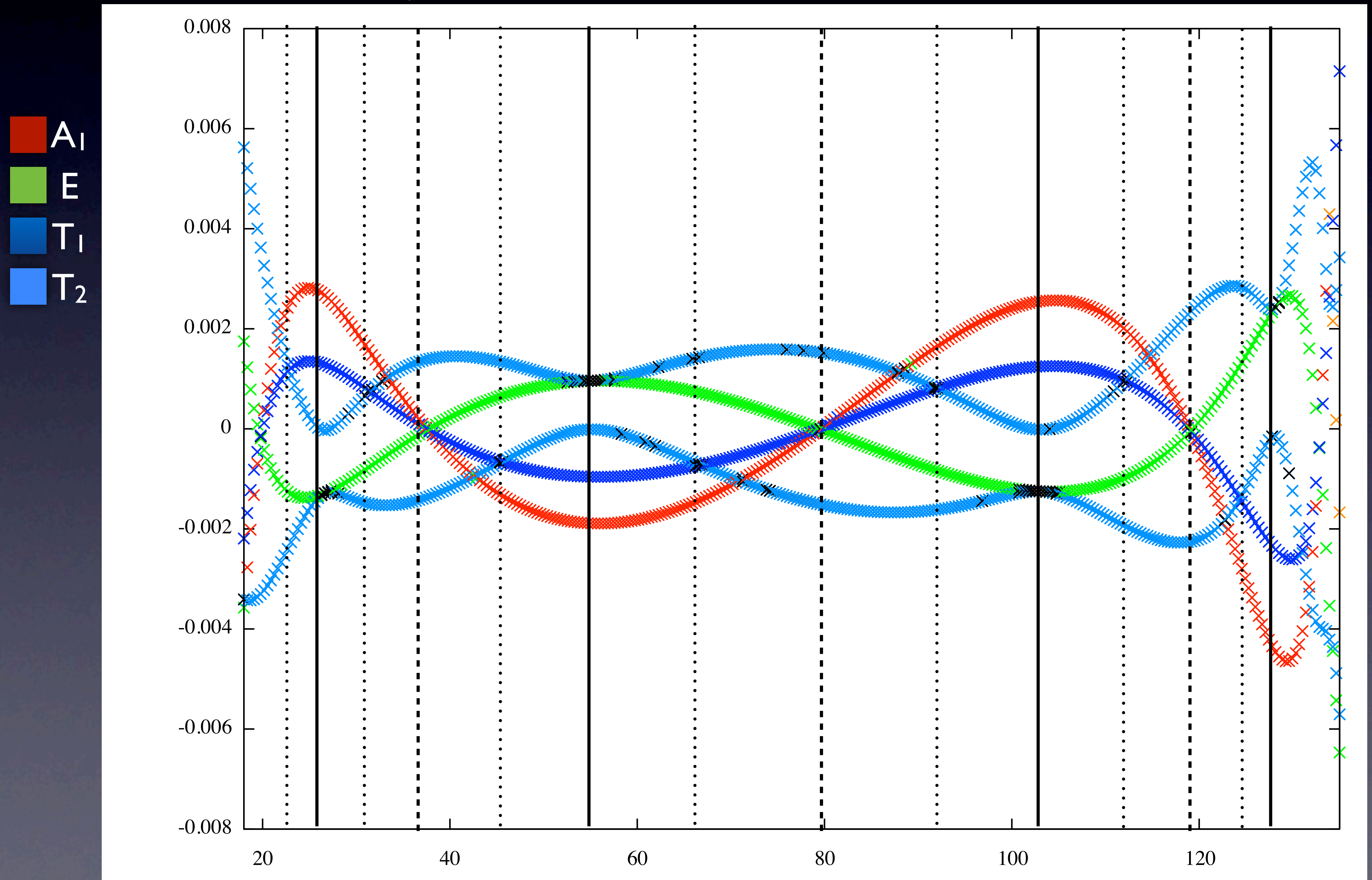
Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$



Magnified x1000

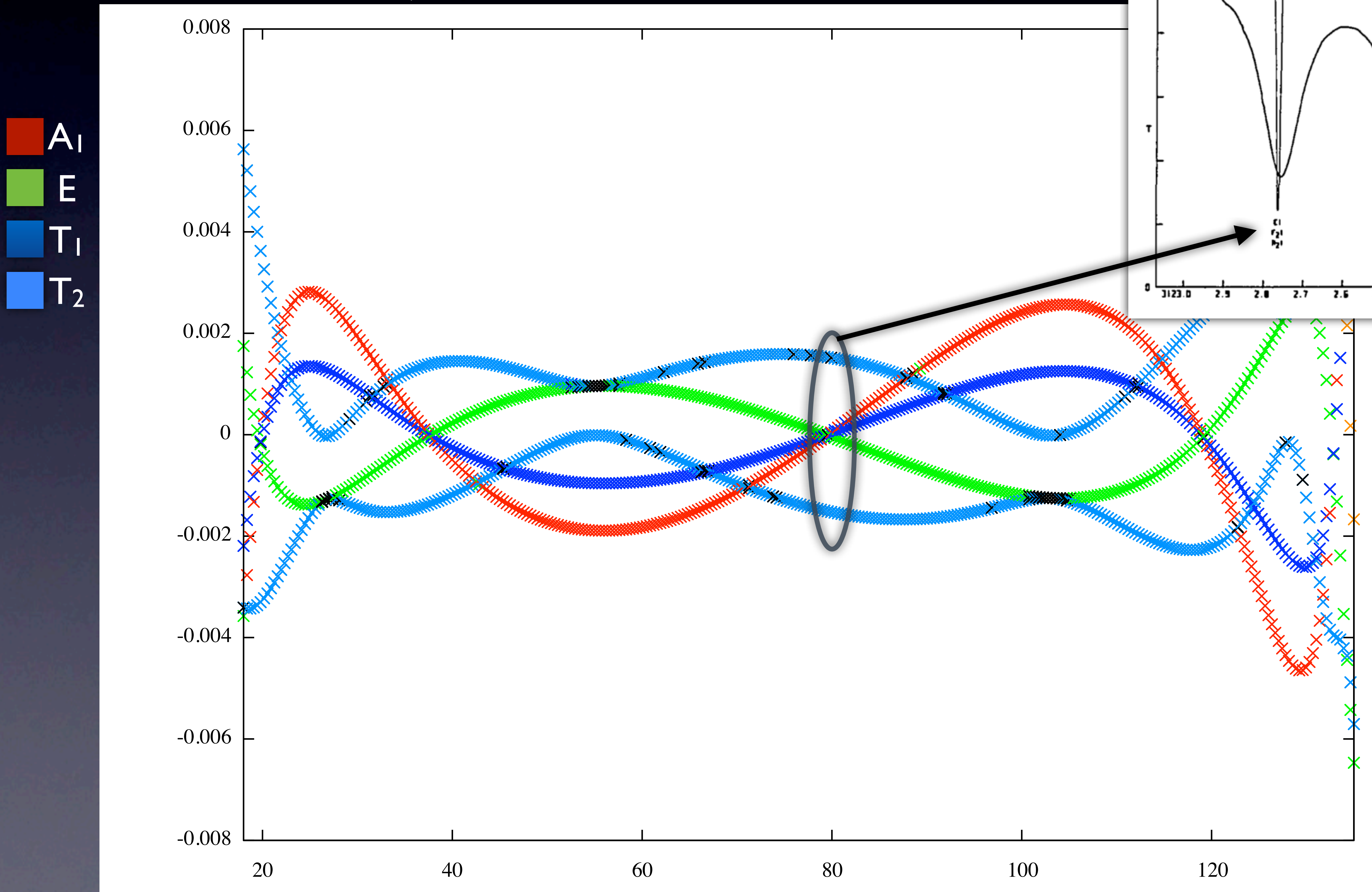
$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$

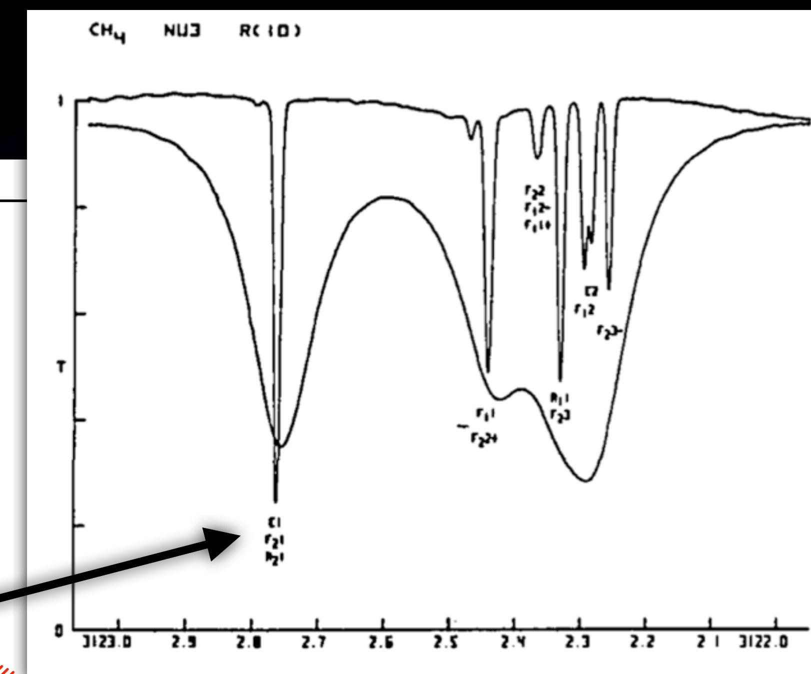


$$\left(\begin{matrix}0\\0\\0\\1\\0\end{matrix}\right) \quad \left(\begin{matrix}0\\1\\-1\\2\\-4\end{matrix}\right) \quad \left(\begin{matrix}0\\1\\1\\2\\-4\end{matrix}\right)$$

Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$

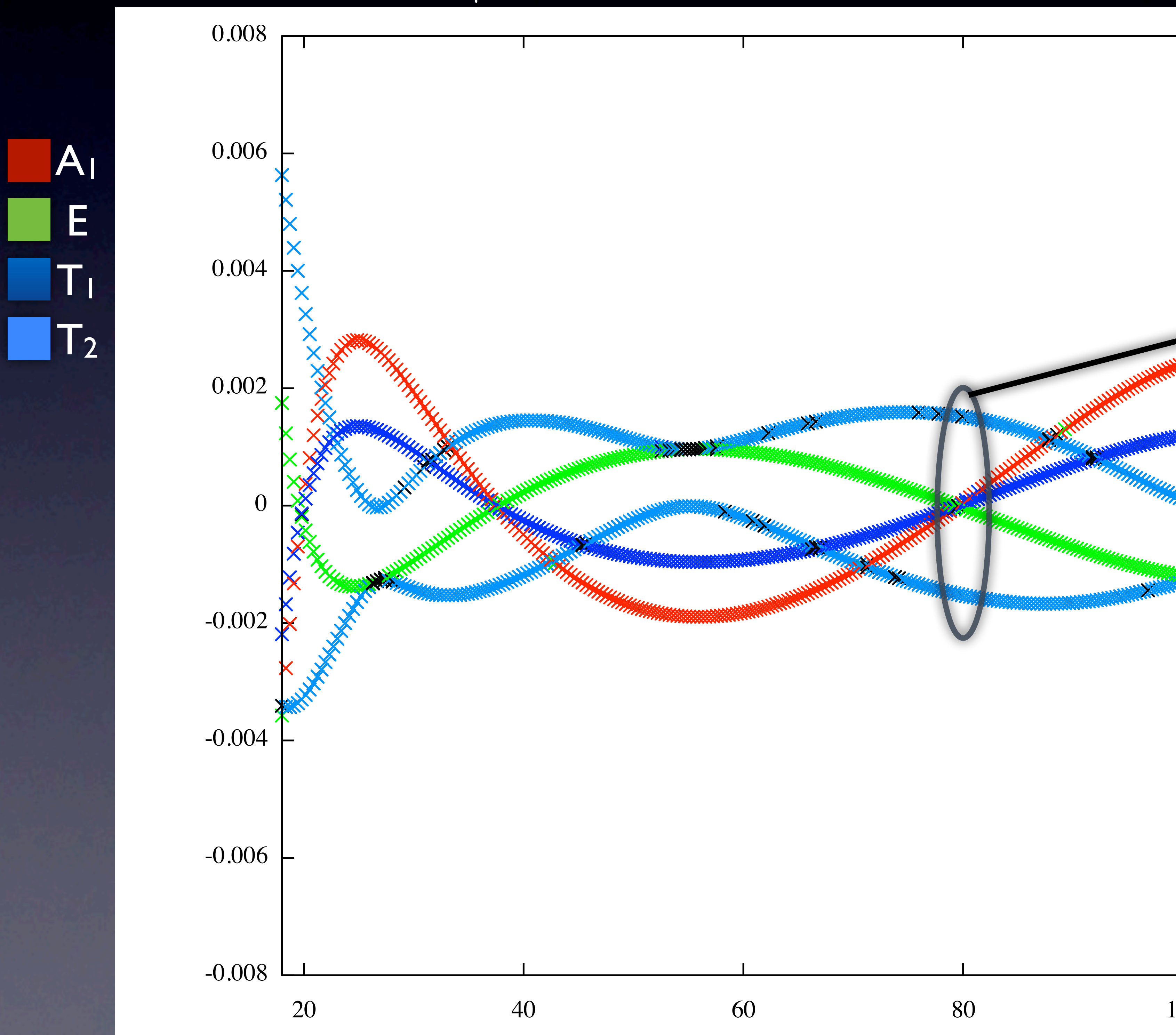


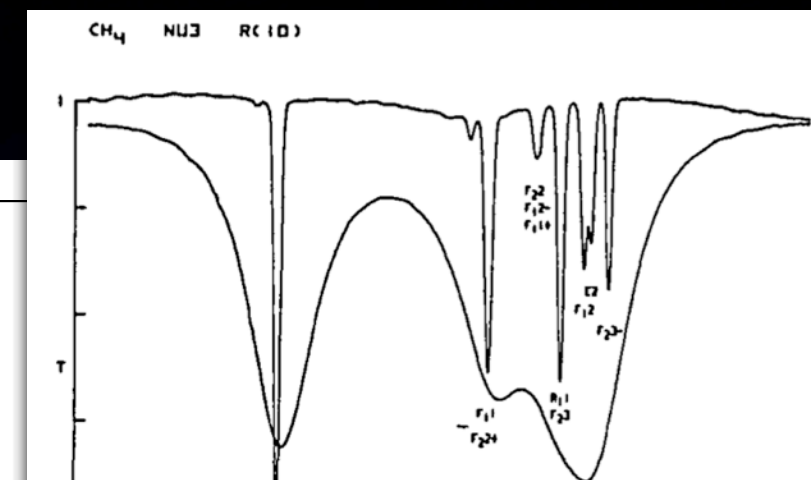


A.S.Pine, J Opt Soc Am, 66 (1976)

Magnified x1000

$H \propto T^{[4]} \cos\theta + T^{[6]} \sin\theta$





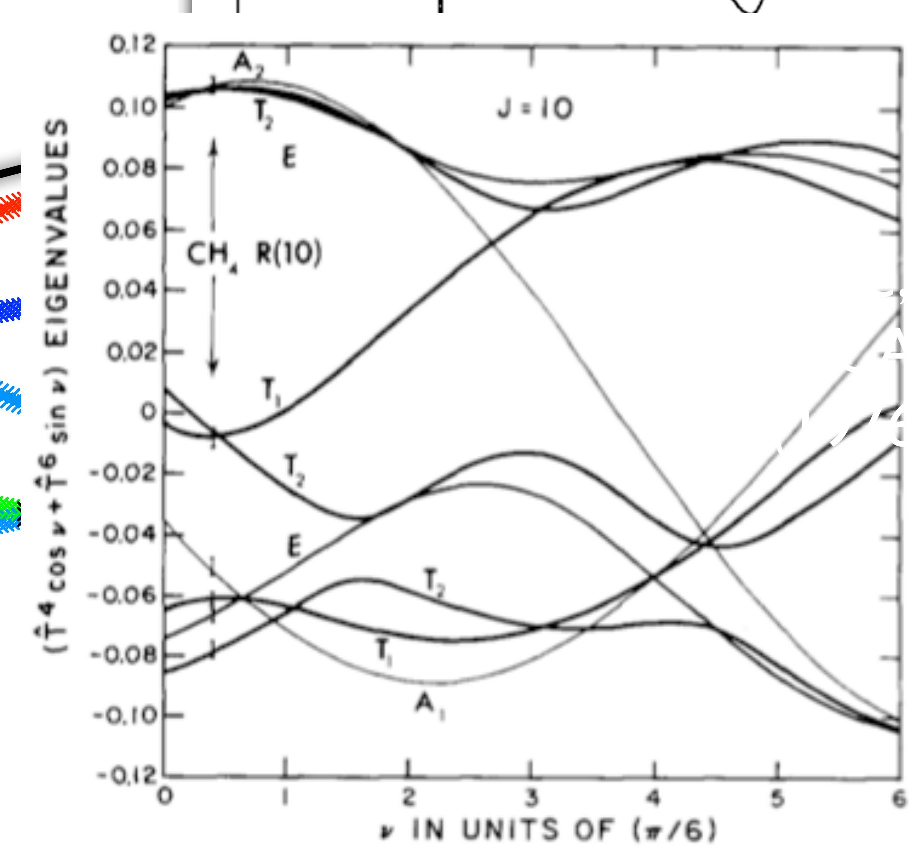
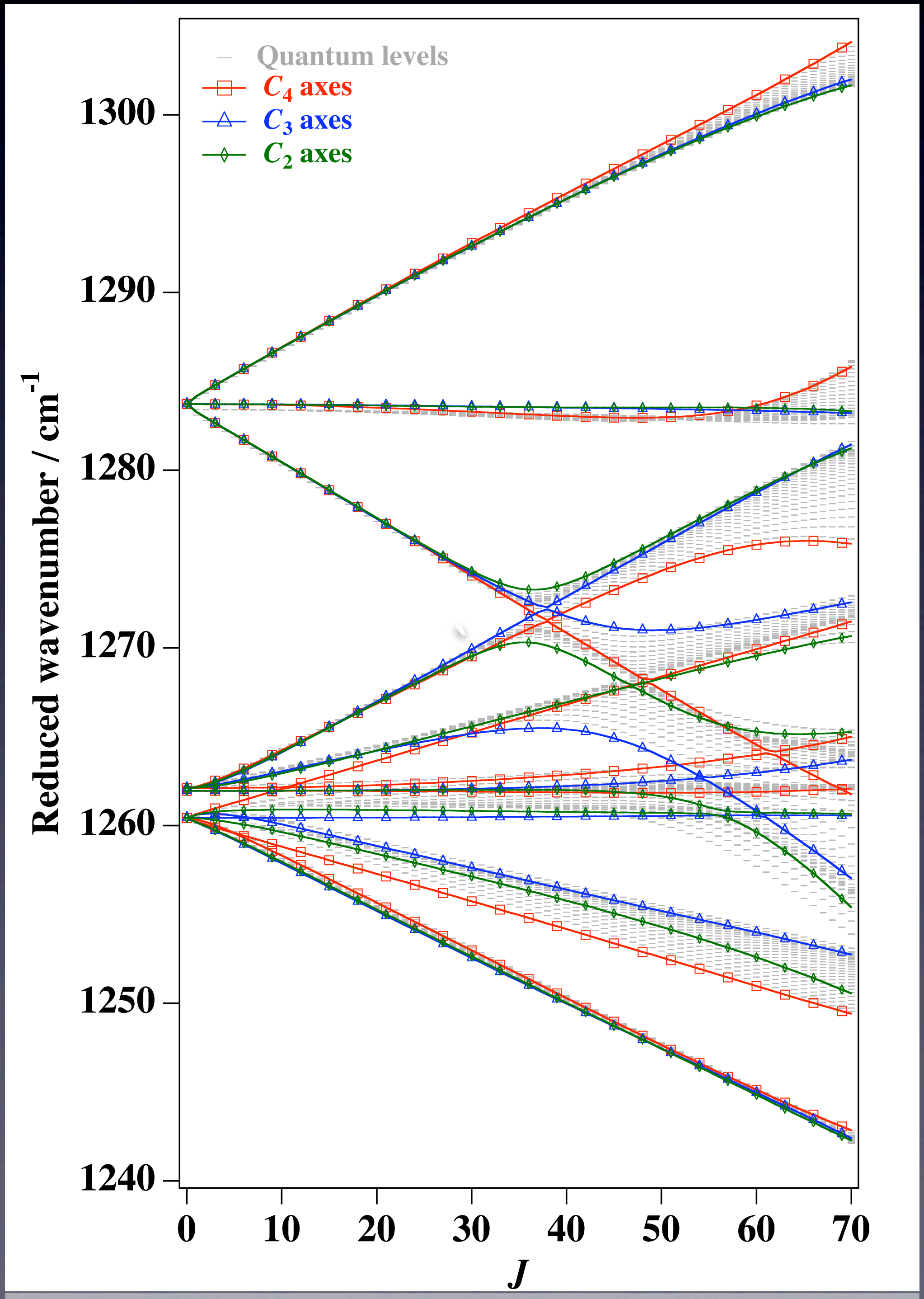


FIG. 6. ($J = 10$) Eigenvalue spectrum of $T(\nu)$.

Do we see this in polyads?

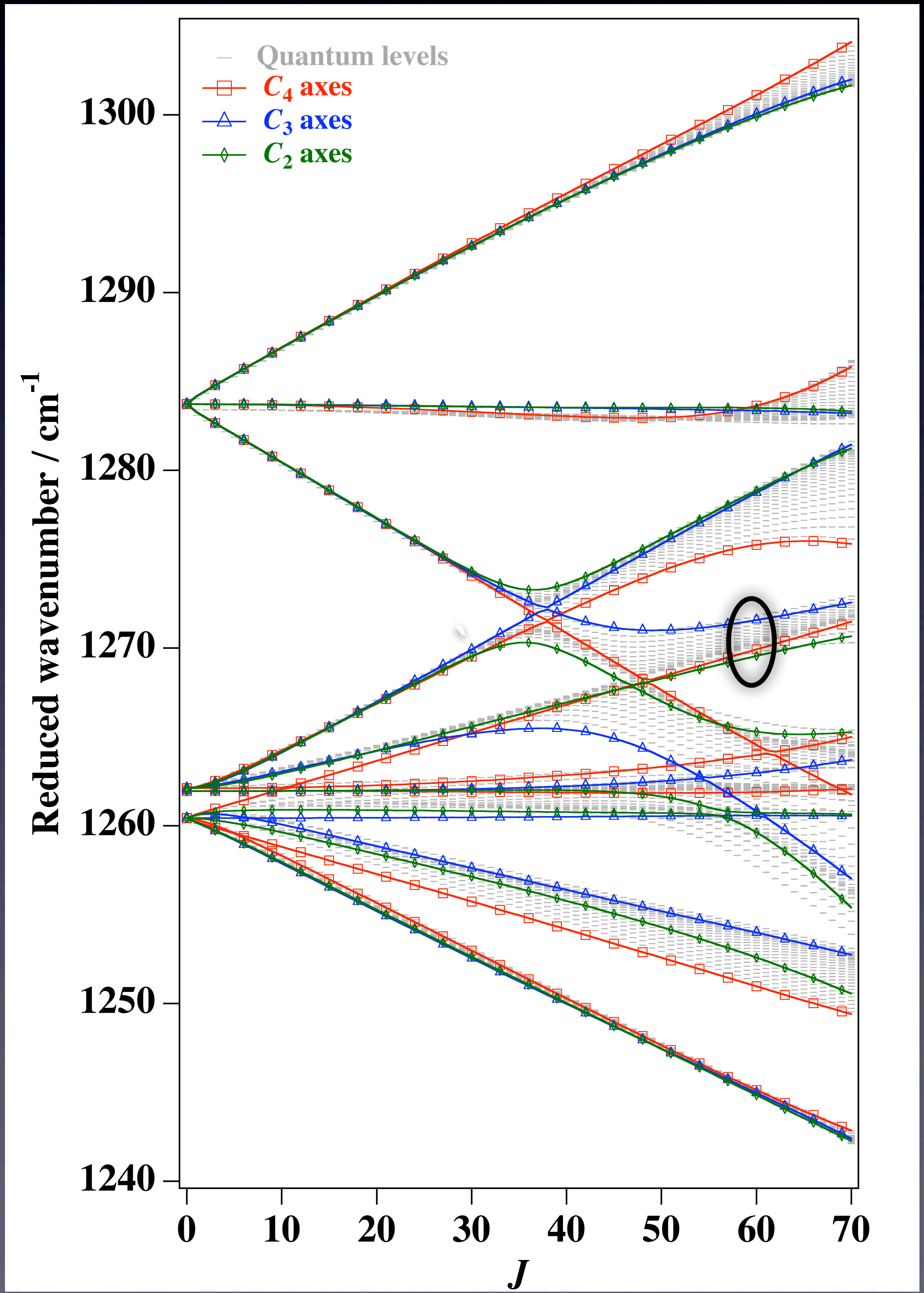
$\nu_3/2\nu_4$ band of CF_4

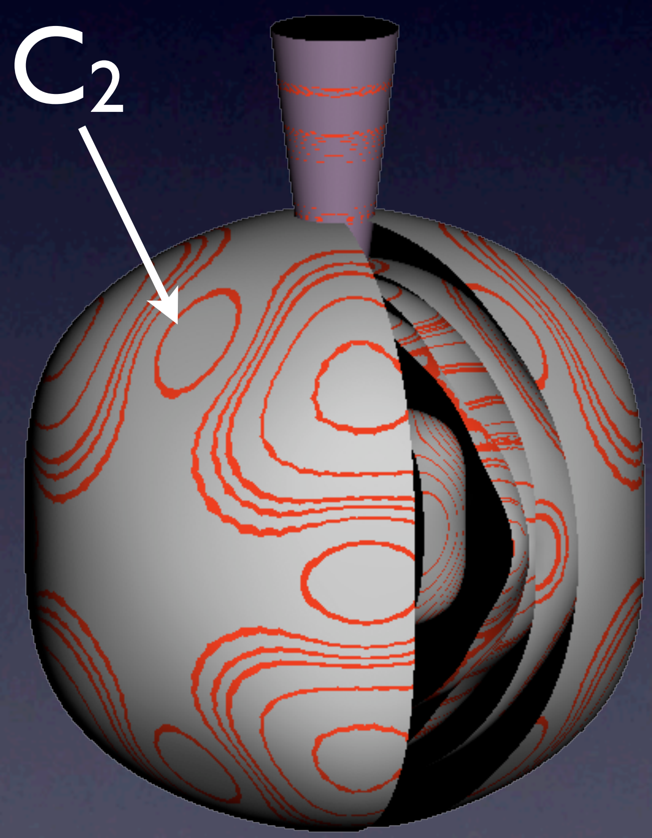


Thanks to V. Boudon of Dijon Group

Do we see this in polyads?

$\nu_3/2\nu_4$ band of CF_4



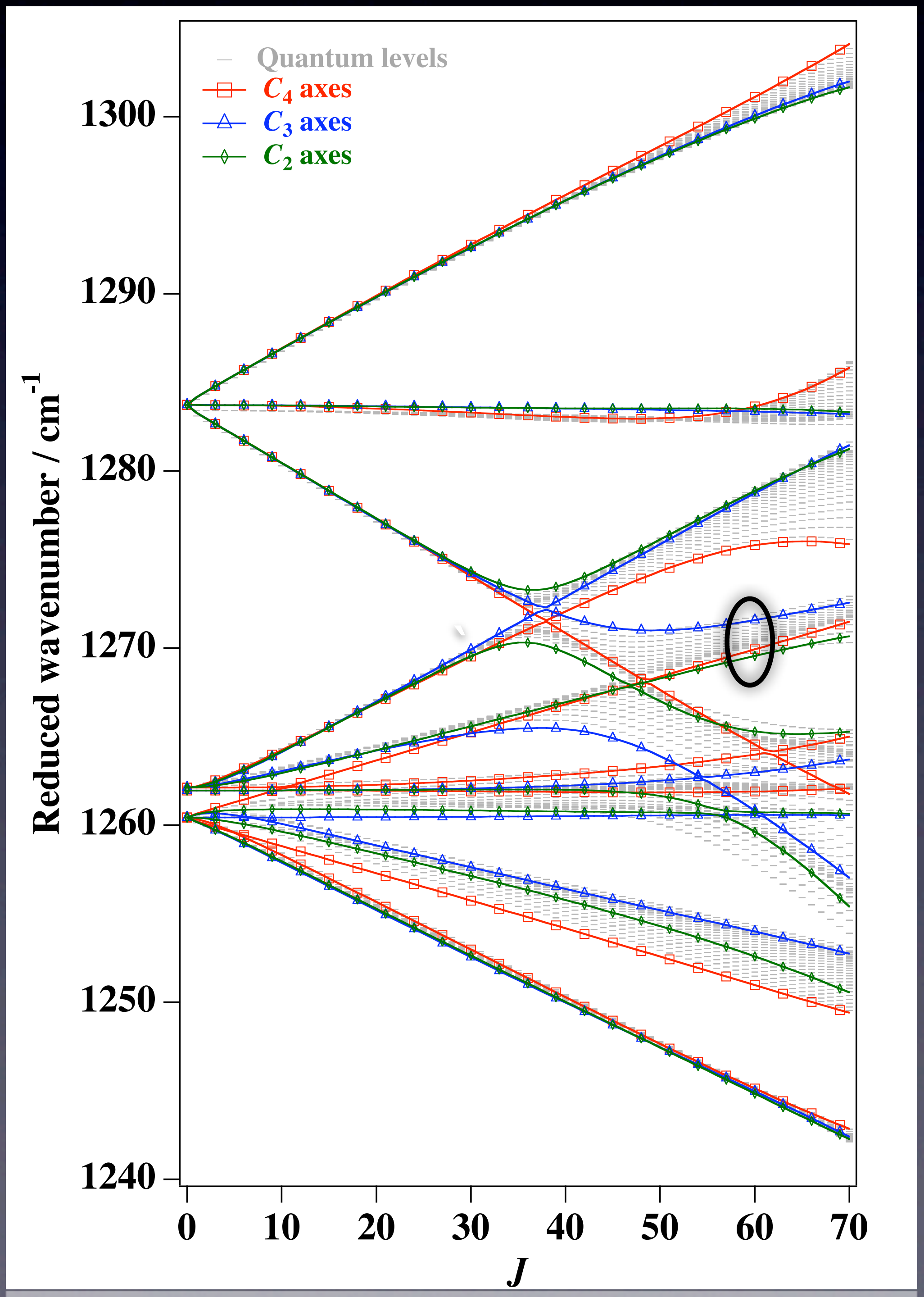


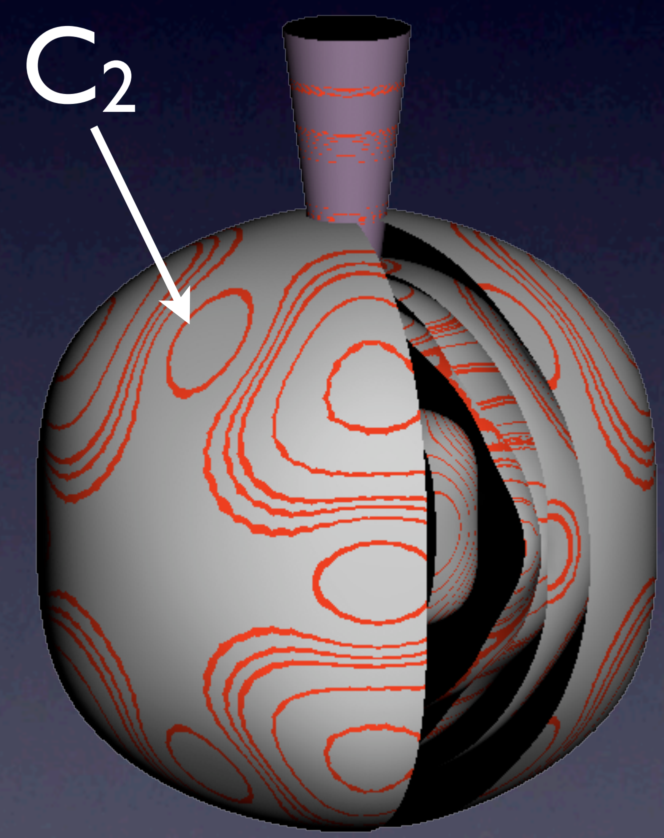
J=60
Surface 6

Thanks to V. Boudon of Dijon Group

Do we see this in polyads?

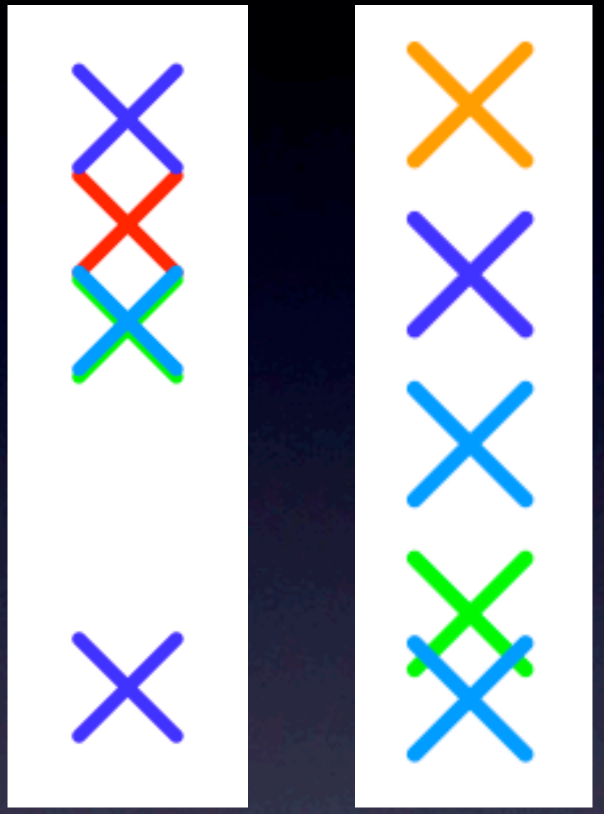
$\nu_3/2\nu_4$ band of CF_4





J=60

Surface 6



O_2 $\sim \begin{pmatrix} 0 \\ 1 \\ -1 \\ 2 \\ -4 \end{pmatrix}$

I_2 $\sim \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$

Thanks to V. Boudon of Dijon Group

Conclusions

- Spectral structure indicates active tunneling by group operations
- Even works for complicated C_1 regions
- Tunneling parameters make a basis for describing tunneling
- Rapid parameter deconvolution
  - Spectra ⇒Phase space ⇒ Tunneling parameters⇒

    Estimate higher resolution splittings

Makes rotational phase space take on analogous role to PES