Rovibronic Energy Topography I:

Tensor Eignvalue Structure and Tunneling Effects in Low-Symmetry Species-Clusters of High Symmetry Molecules

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Understanding Eigensolutions

- We want to interpret physically numerical solutions and begin to understand dynamics.

$$H = \begin{pmatrix} H11 & H12 & \dots \\ H21 & H22 & \dots \\ \dots & & \end{pmatrix}$$

$$\begin{pmatrix} e_1 \\ e_2 \\ \dots \end{pmatrix}$$

How to get more information

1. Write Hamiltonian in Tensor Expansion
2. Phase Space Plots of Tensors
3. Topography of Level Clustering (fine structure)
4. Symmetry Analysis of Cluster Splitting (super-fine structure)

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Clustering in Rotational Sub-Levels

- Level Clusters Appear in Diagonalization of 4th, 6th, 8th Rank Rotational Hamiltonian.

$$H = BJ^2 + c_4 T^{[4]} + c_6 T^{[6]} + c_8 T^{[8]}$$
$$H = BJ^2 + c_{4,6,8} T^{[4,6,8]}$$

- Spontaneous Symmetry Breaking of Octahedral O_h to Cyclic C_4, C_3, C_2 and C_1.
    - Rotational Energy Surface display 4th, 6th and 8th rank tensors combinations.

$$T^{[4,6,8]} = \left(T^{[4]}\cos\mu + T^{[6]}\sin\mu\right)\cos\nu + T^{[8]}\sin\nu$$

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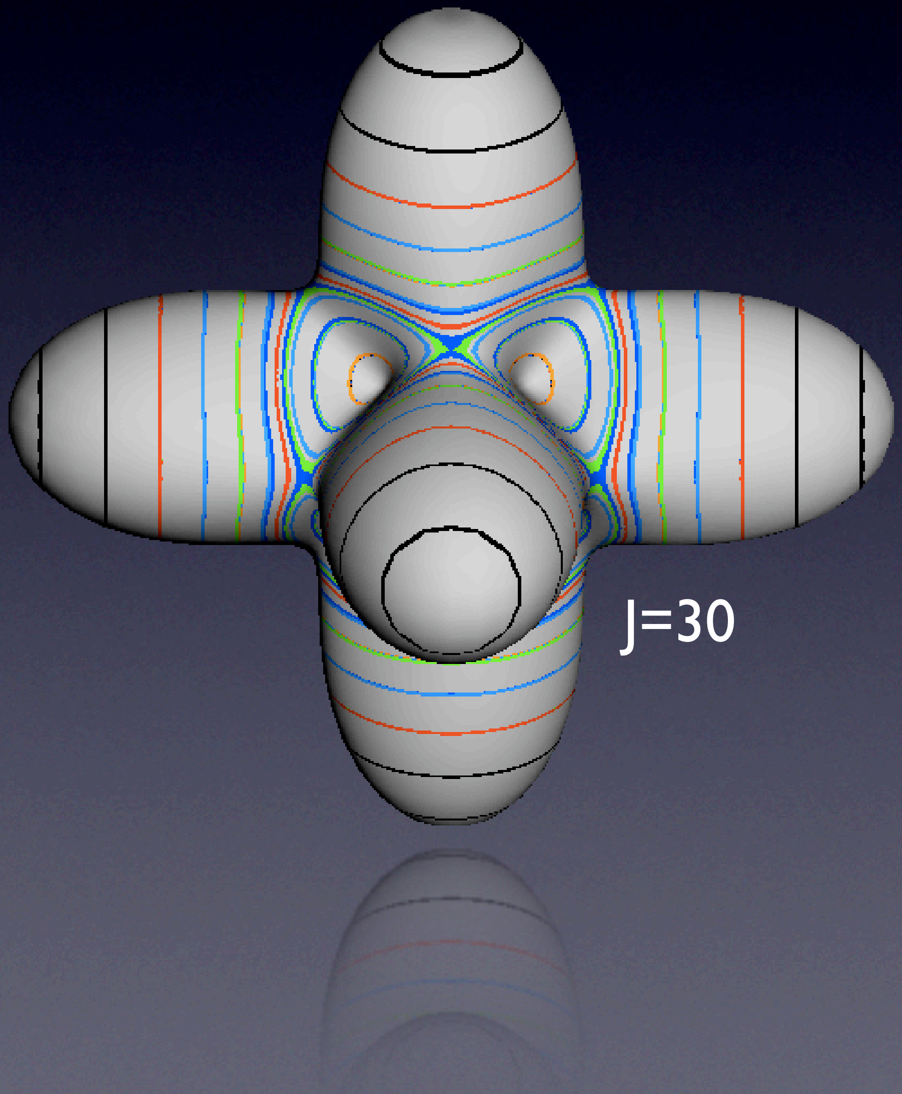
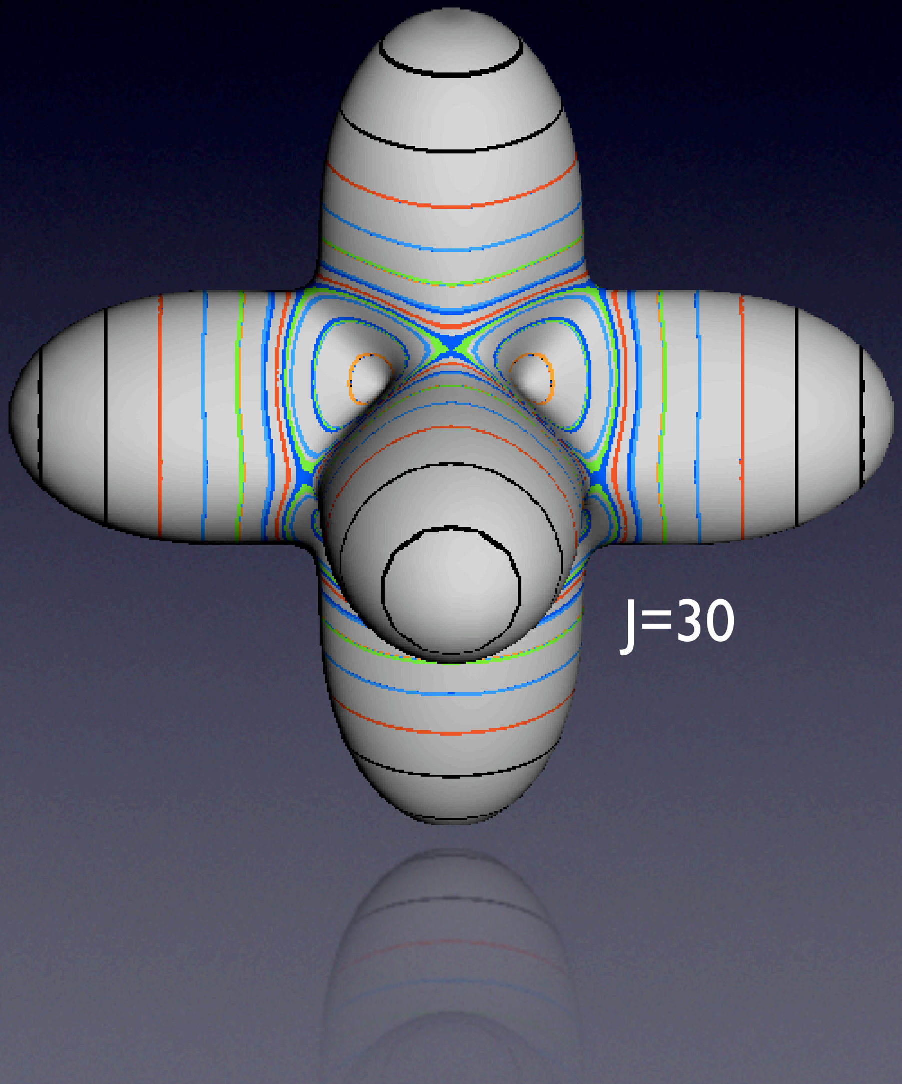
Rotational Energy Surface

- Phase Space Plot.
- Constant Total Angular Momentum, J.
- Angular momentum follows constant energy contours in molecular frame.
- Contours are Eigenvalues



Level Clustering

- Fewer Levels Than Expected.
- Level clusters may contain 6, 8, 12, 24 or 48 rotational levels.
- Phase Space Pockets have Local Symmetry C_4, C_3, C_2, C_v or C_1.
- Resonance or tunneling occurs between the equivalent phase space regions.



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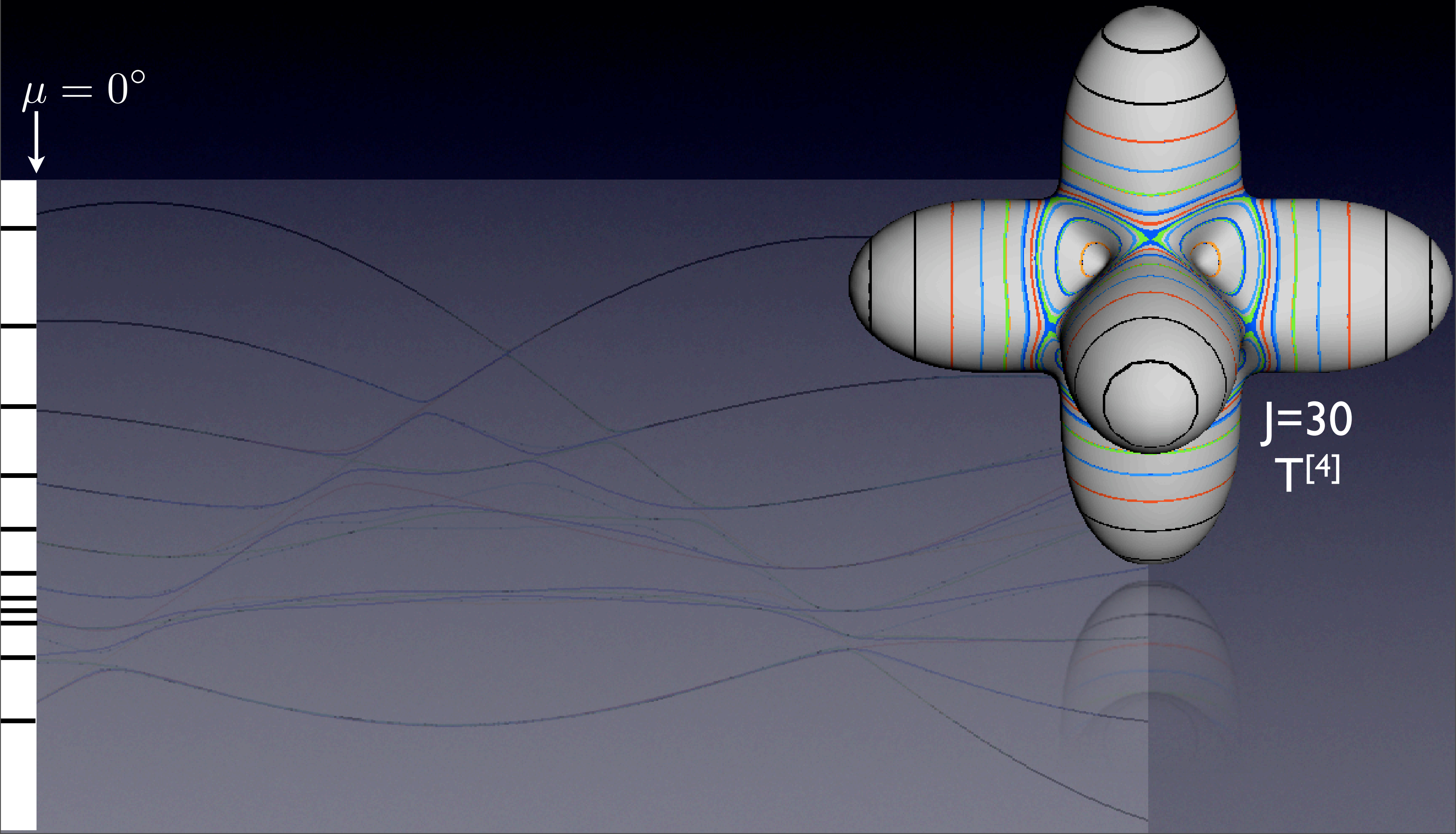
All $T^{[4]}$ - C_3 and C_4 Clusters

$T^{[4]} \cos\mu + T^{[6]} \sin\mu$

$\mu = 0^\circ$



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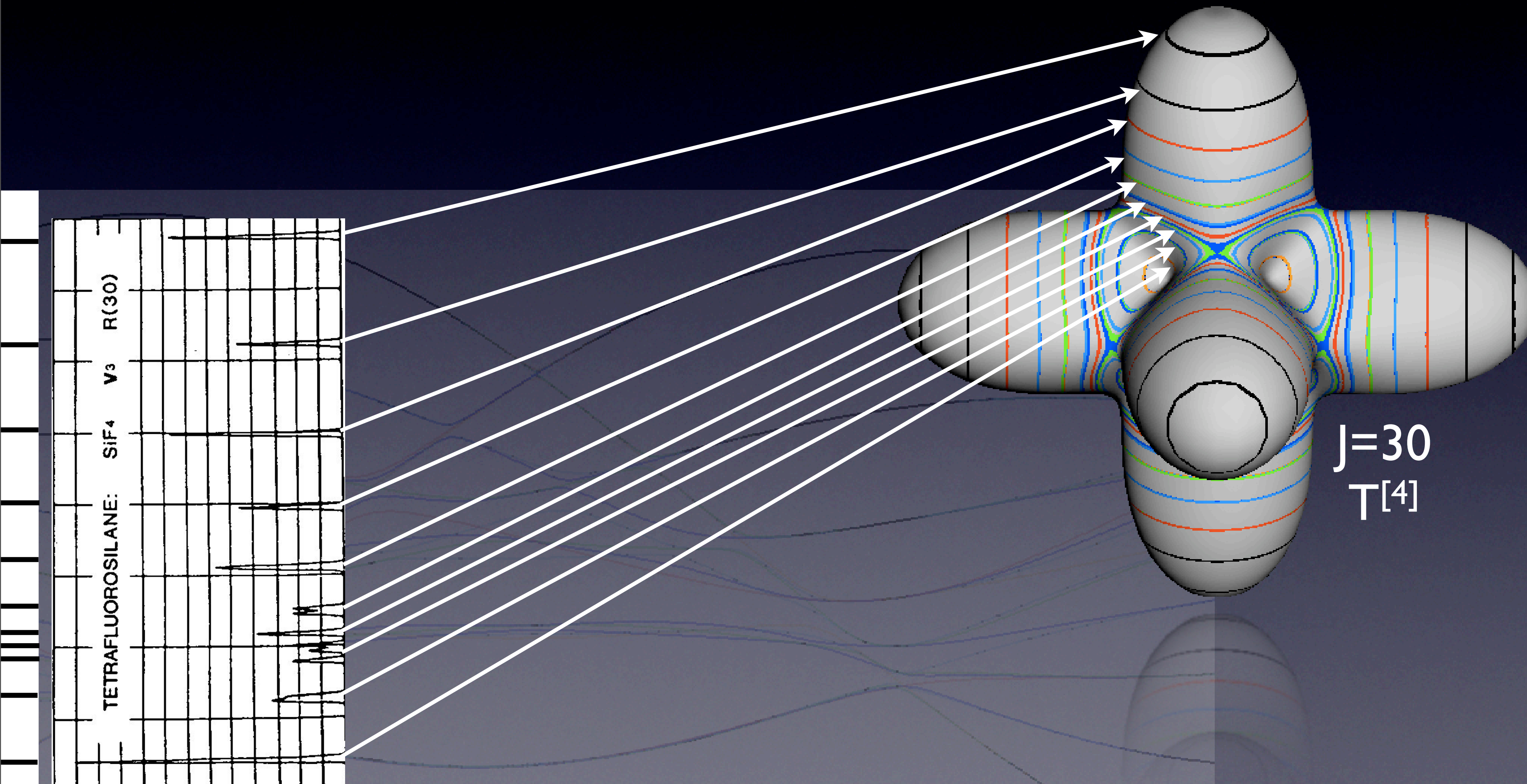
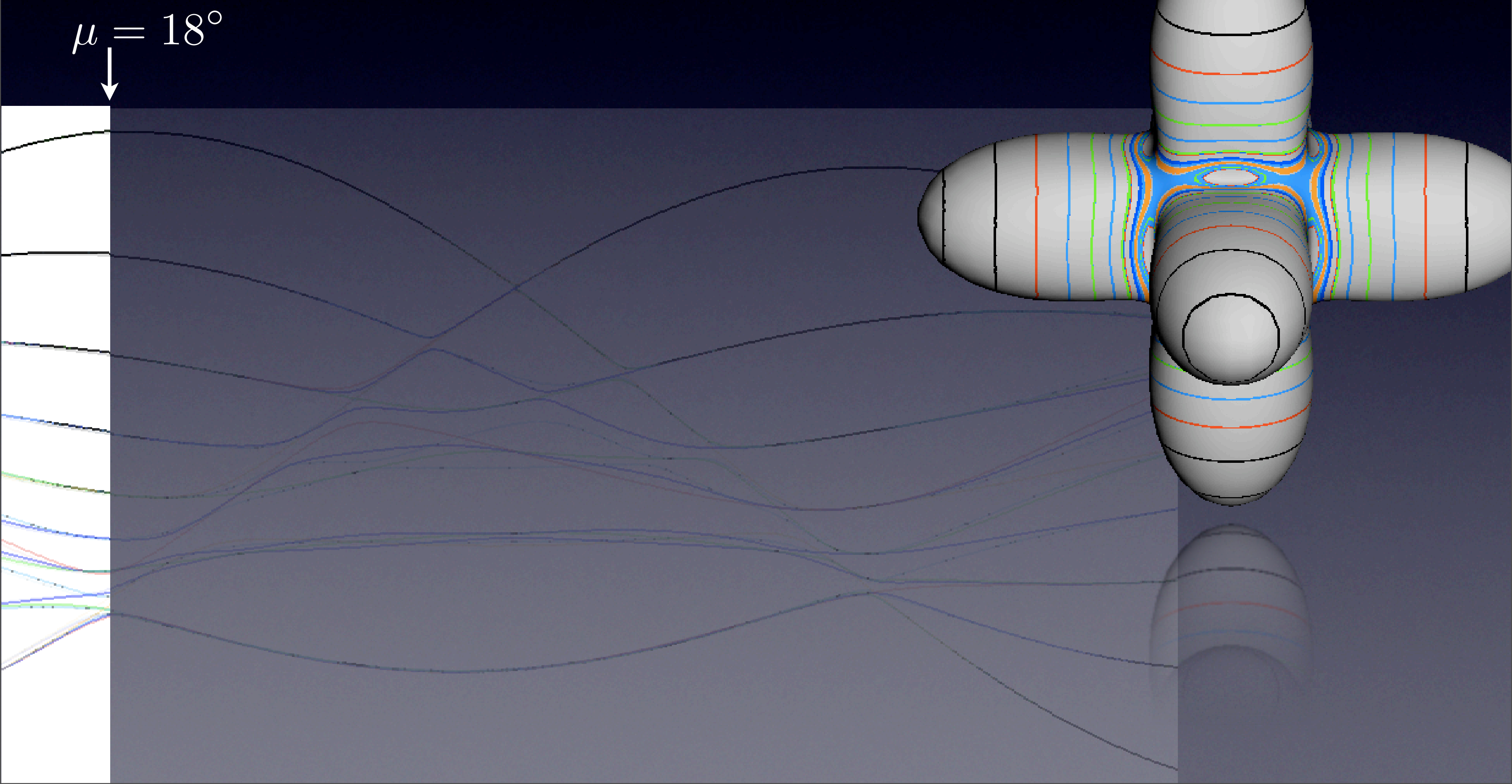


C.W. Patterson, R.S. McDowell, N.G. Nereson, B.J. Krohn, J.S.Wells, and F.R.Peterson, J. Mol. Spec. **91**, 416 (1982)

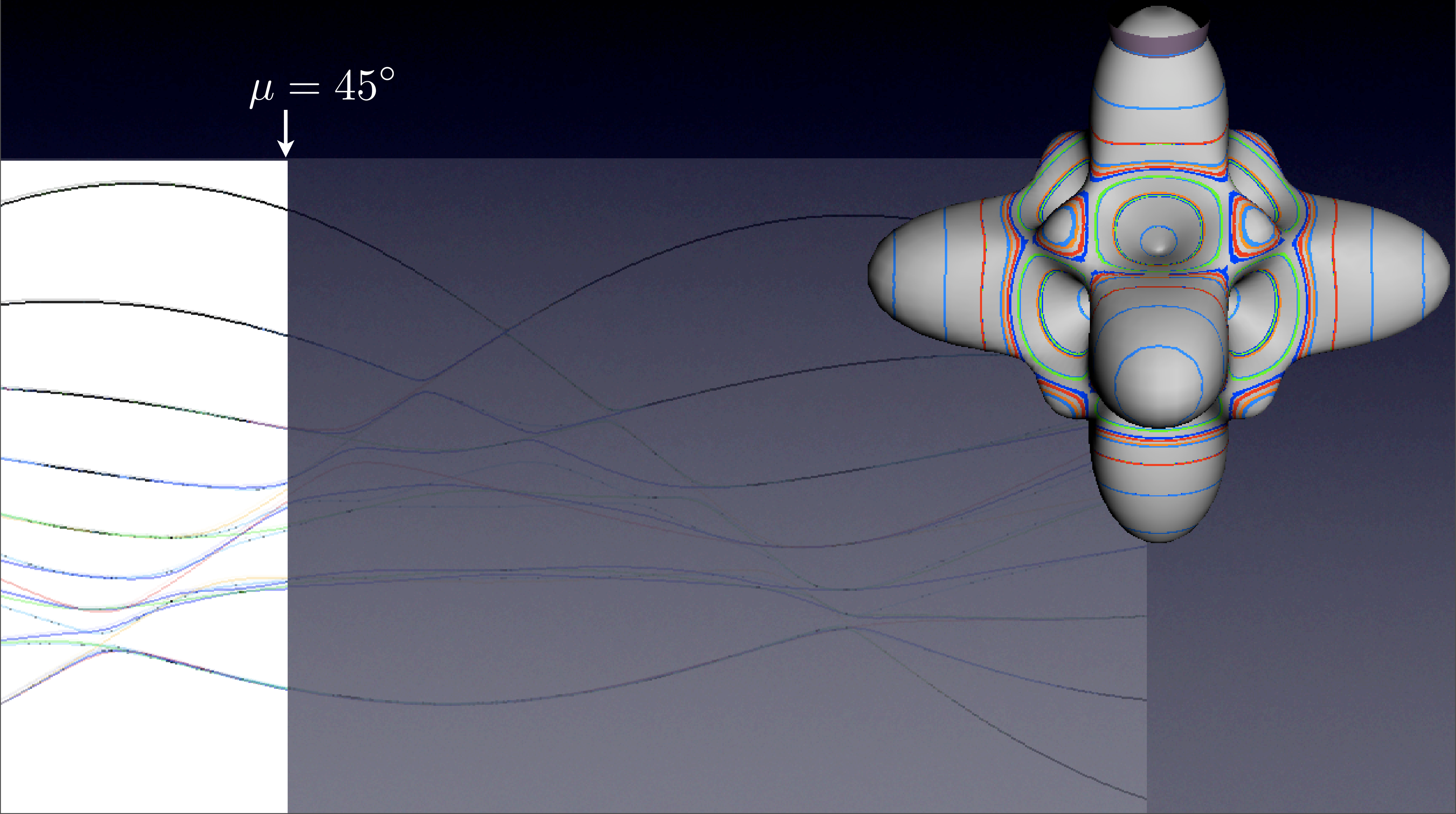
No C_3, Start C_2 Clusters

$T^{[4]} \cos\mu + T^{[6]} \sin\mu$



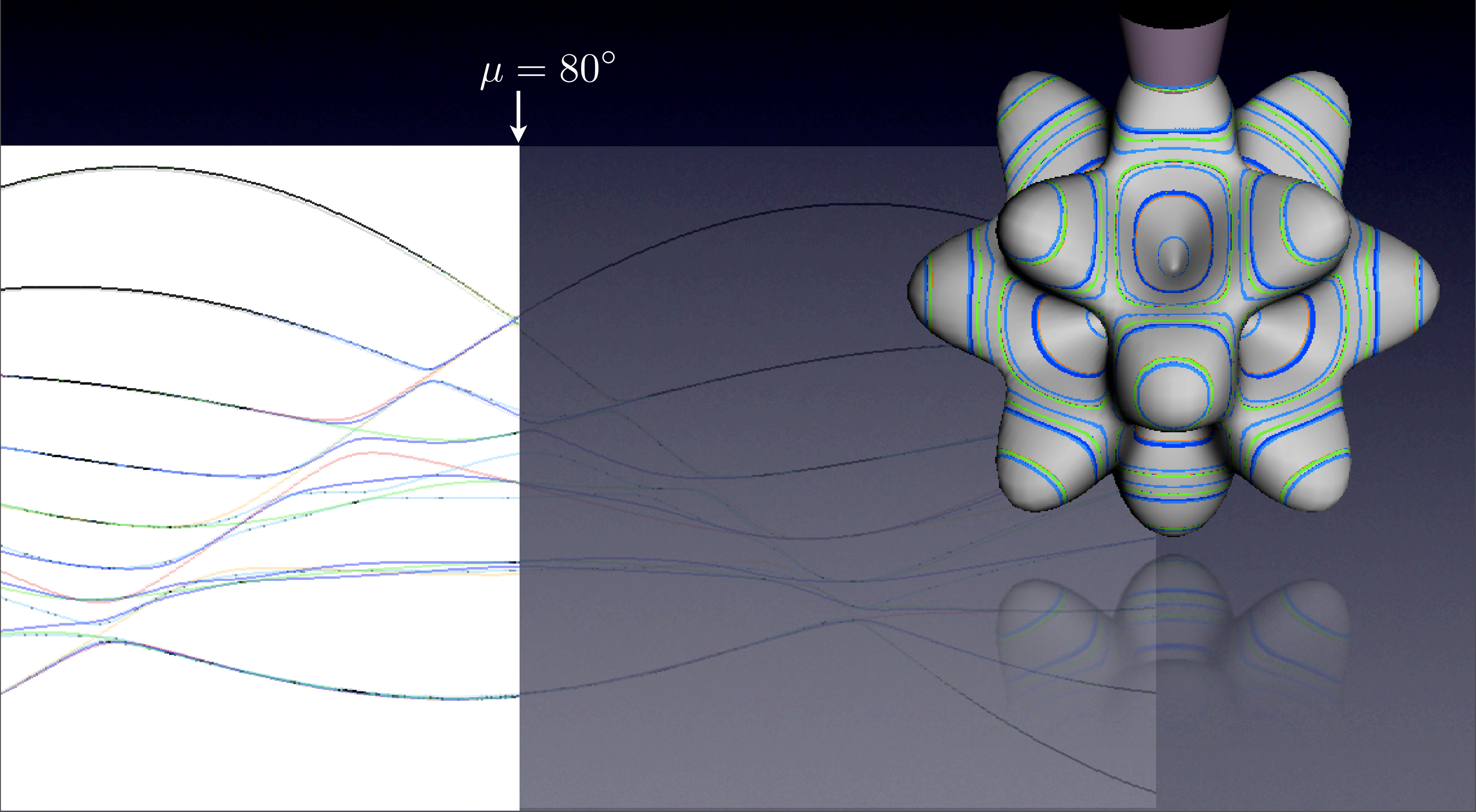
Even T[4], T[6]

$T^{[4]} \cos\mu + T^{[6]} \sin\mu$



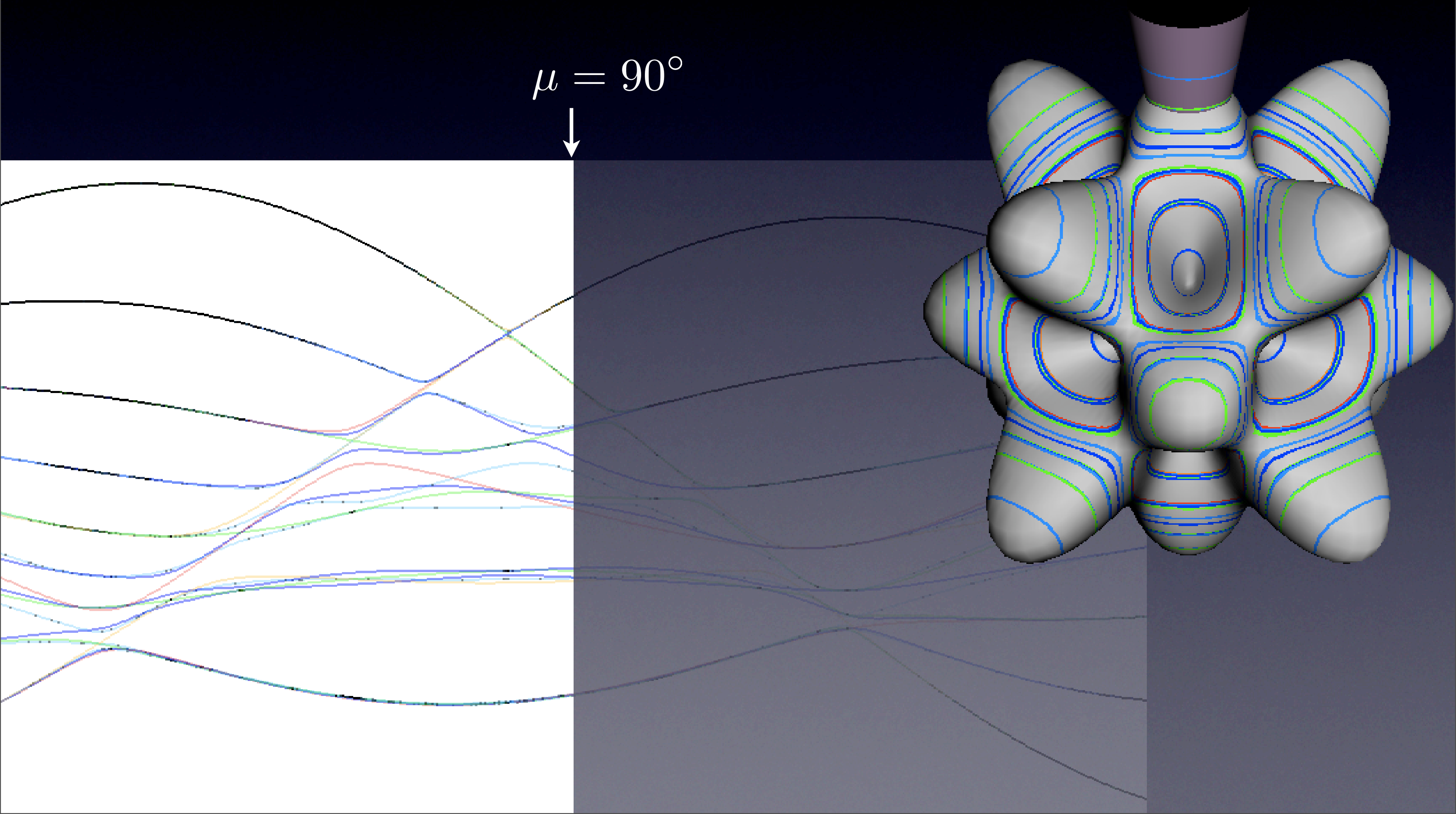
C_4 Equal C_3 Clusters

$T^{[4]} \cos \mu + T^{[6]} \sin \mu$



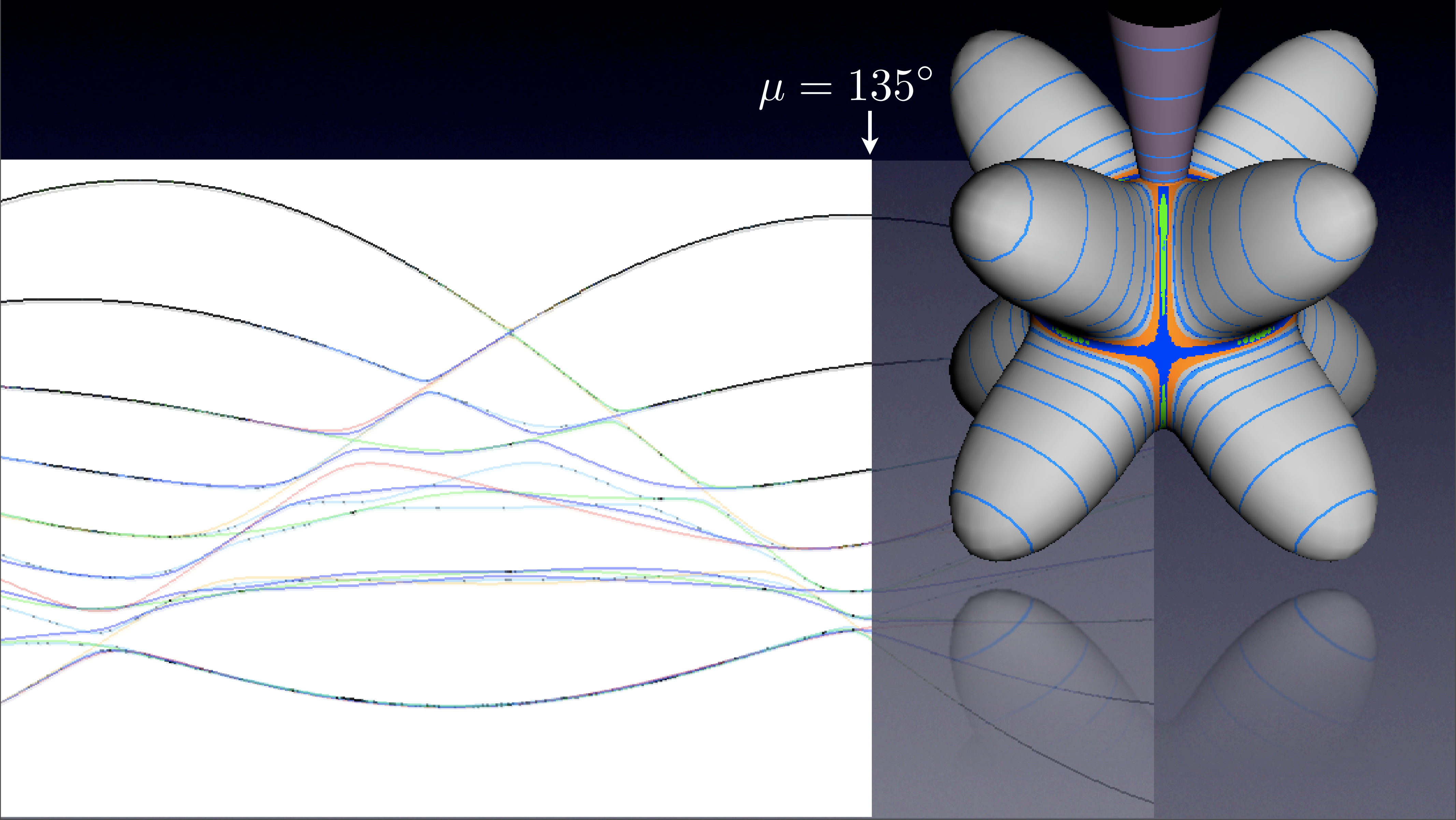
All T[6]

$T^{[4]} \cos \mu + T^{[6]} \sin \mu$



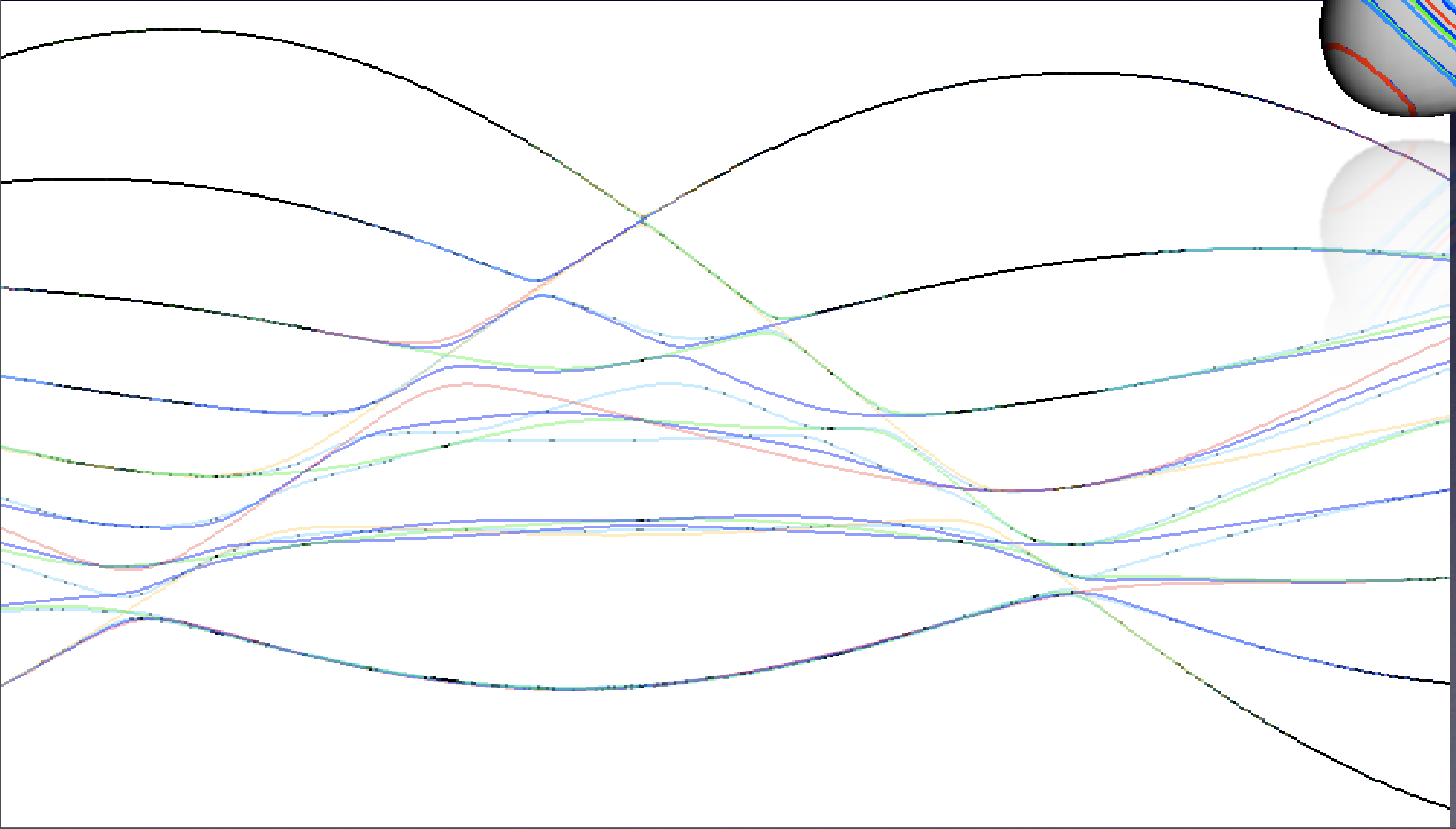
No C_2, C_4 Clusters

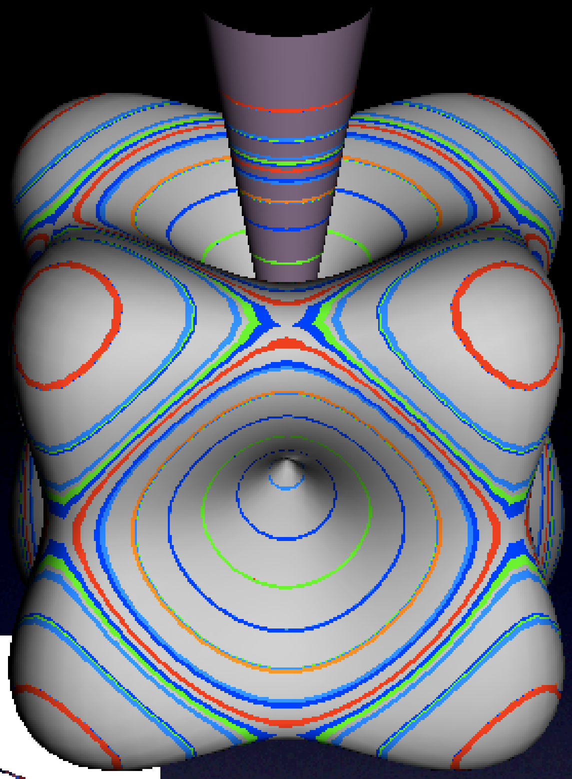
$T^{[4]} \cos \mu + T^{[6]} \sin \mu$



All $T^{[4]}$ - C_3 and C_4 Clusters

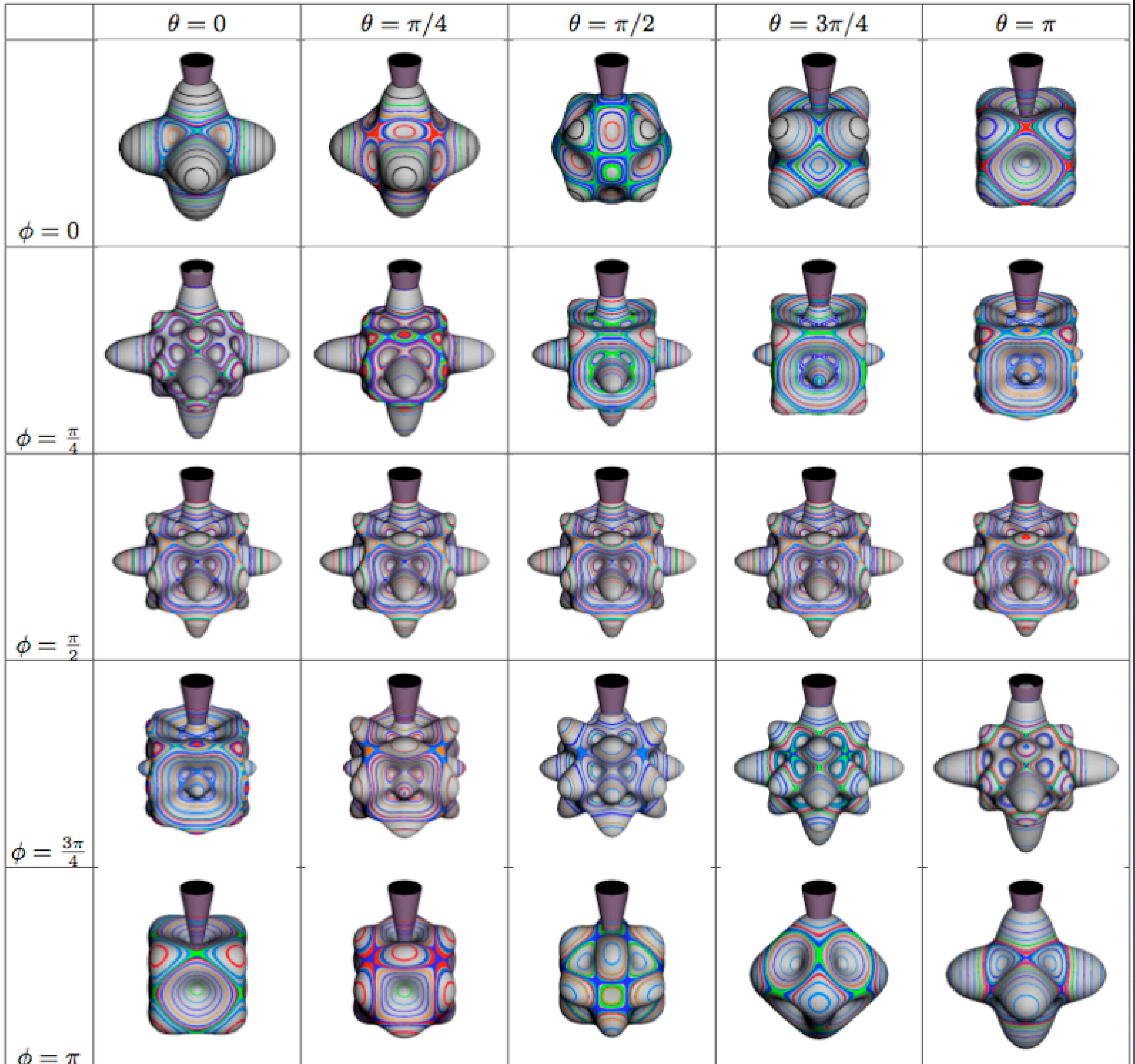
$$T^{[4]}\cos\mu + T^{[6]}\sin\mu$$





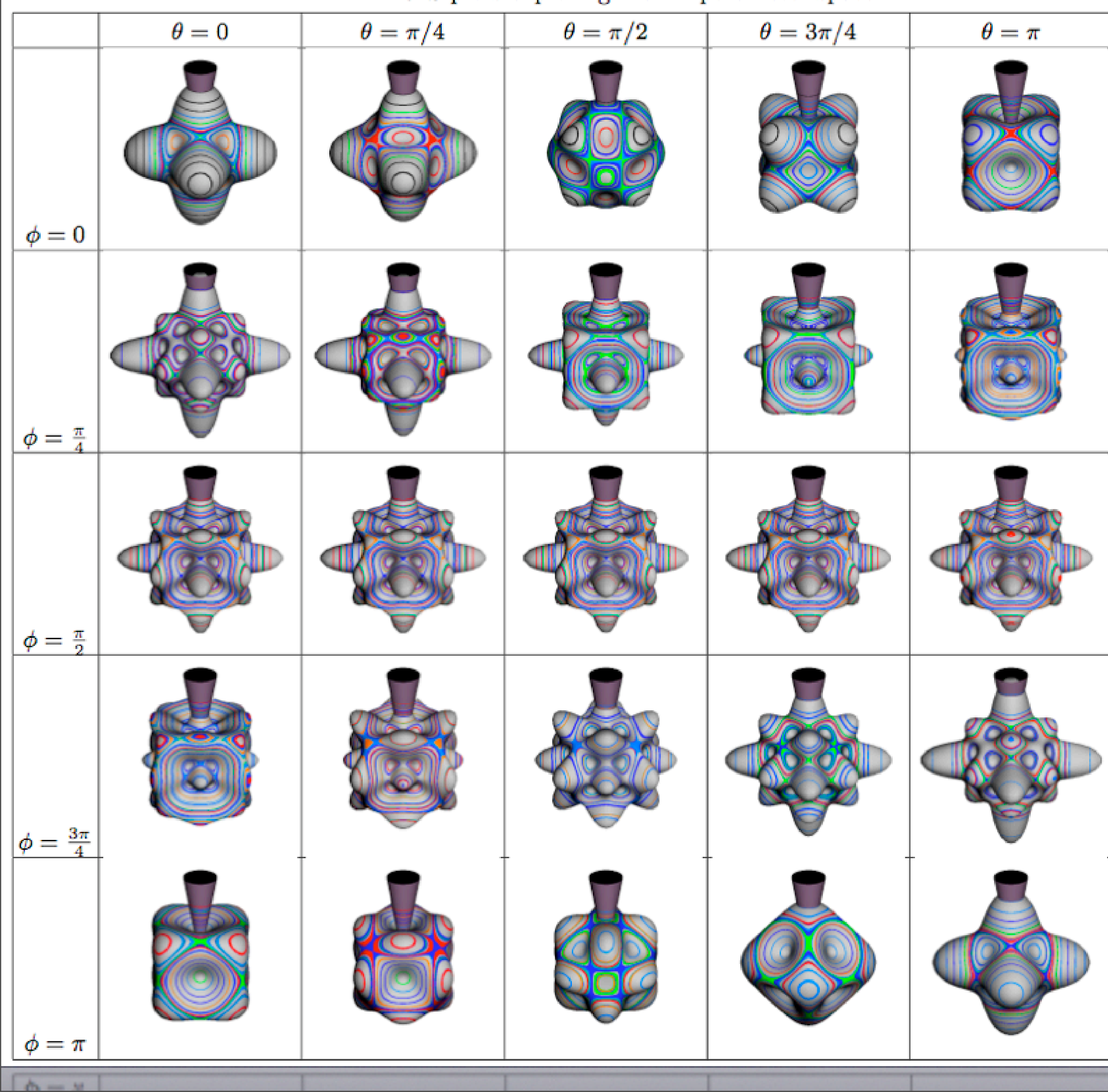
Include $T^{[4]}, T^{[6]}, T^{[8]}$

TABLE XII: RES plots exploring the 2D parameter space



Include $T^{[4]}, T^{[6]}, T^{[8]}$

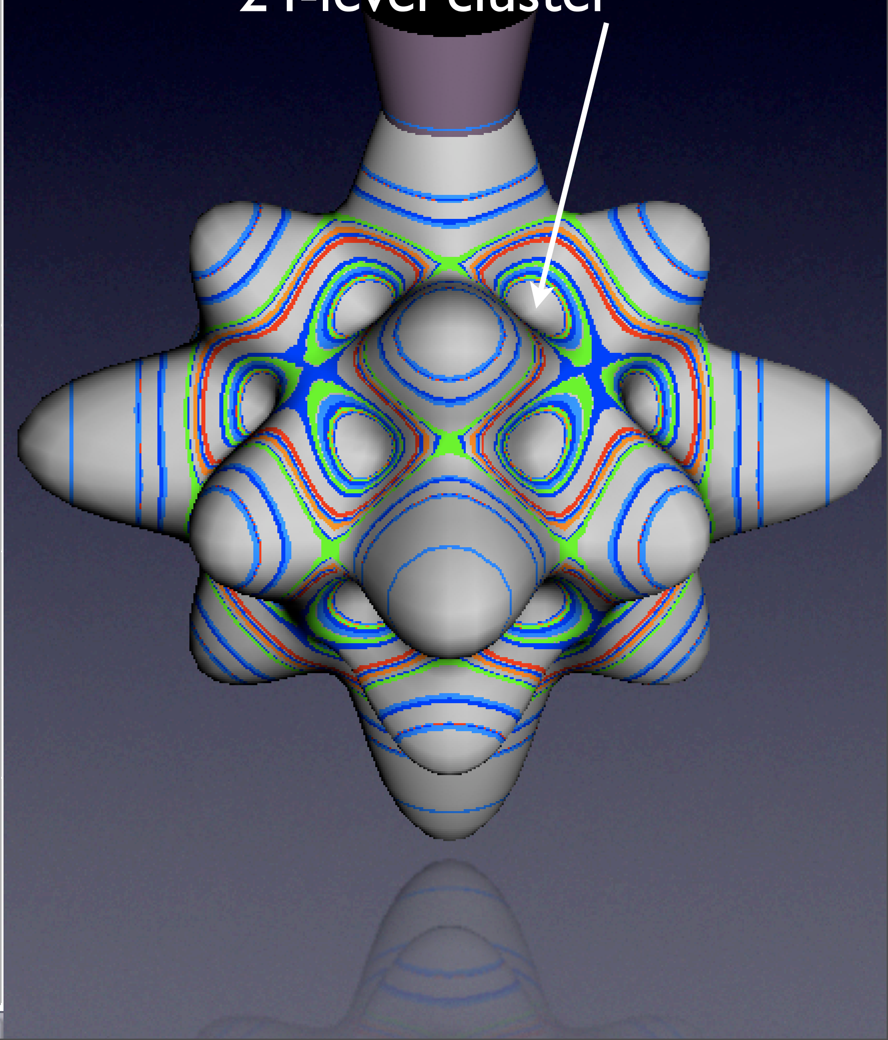
TABLE XII: RES plots exploring the 2D parameter space



<u>Big level cluster!</u>

24 Equivalent valleys

24-level cluster



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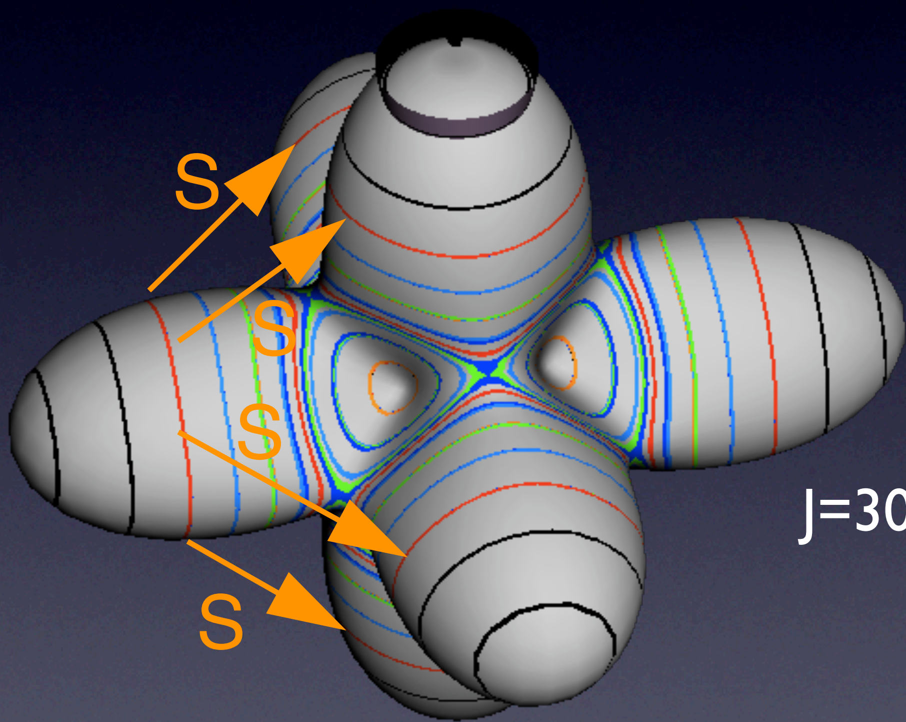
Analyze Splitting

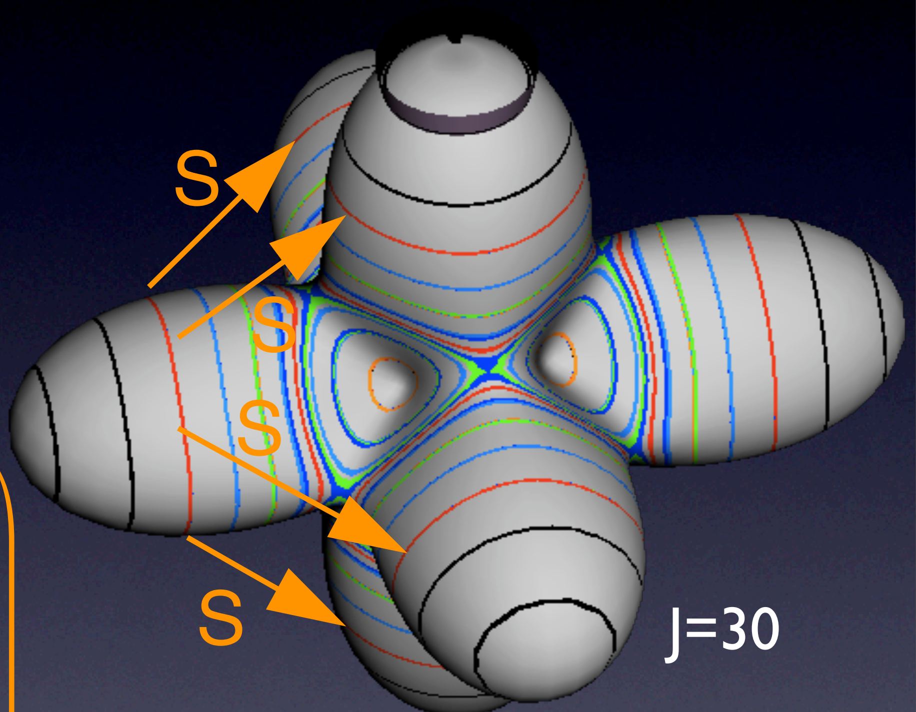
- Start With Octahedral Hamiltonian.
- Write All Tunnelings Between Equivalent Local Symmetry Regions.
- Use This Hamiltonian with Known Eigenvectors.



Tunneling “paths”

Analyze Splitting

$$H_{Tunnel} = \begin{pmatrix} H & 0 & S & S & S & S \\ 0 & H & S & S & S & S \\ S & S & H & 0 & S & S \\ S & S & 0 & H & S & S \\ S & S & S & S & H & 0 \\ S & S & S & S & 0 & H \end{pmatrix}$$



$$E(2_4) = \begin{pmatrix} 1 \\ 1 \\ \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \quad T_2(2_4) = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad A_2(2_4) = \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \\ -1 \\ -1 \end{pmatrix}$$

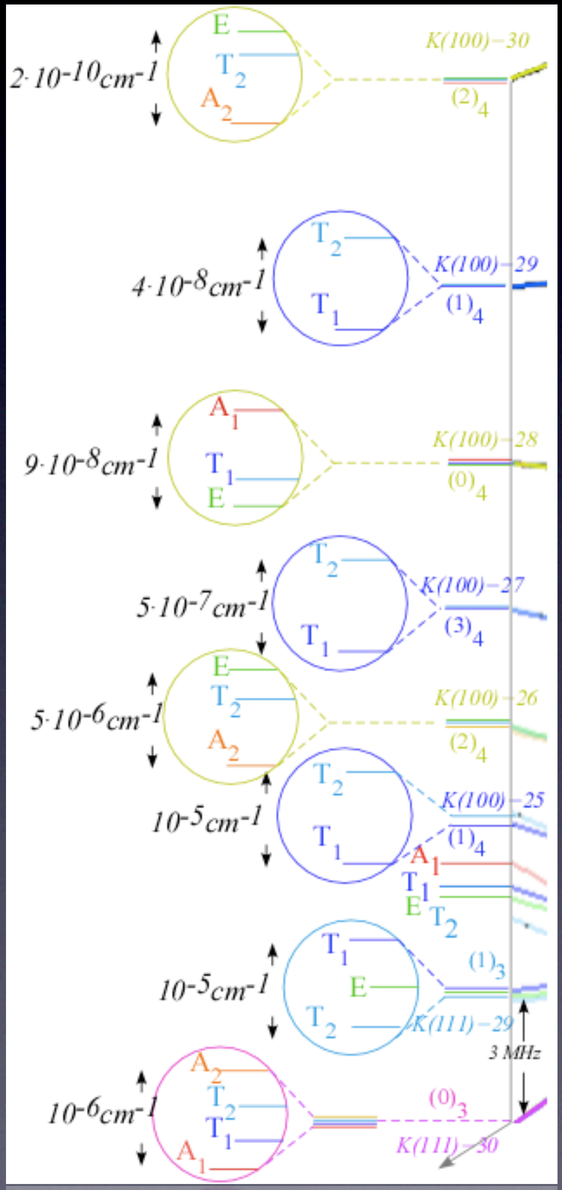
$$e^{E}(2_4) = H + 2S$$

$$e^{T_2}(2_4) = H$$

$$e^{A_2}(2_4) = H - 4S$$

Analyze Splitting

$$H_{Tunnel} = \begin{pmatrix} H & 0 & S & S & S & S \\ 0 & H & S & S & S & S \\ S & S & H & 0 & S & S \\ S & S & 0 & H & S & S \\ S & S & S & S & H & 0 \\ S & S & S & S & 0 & H \end{pmatrix}$$



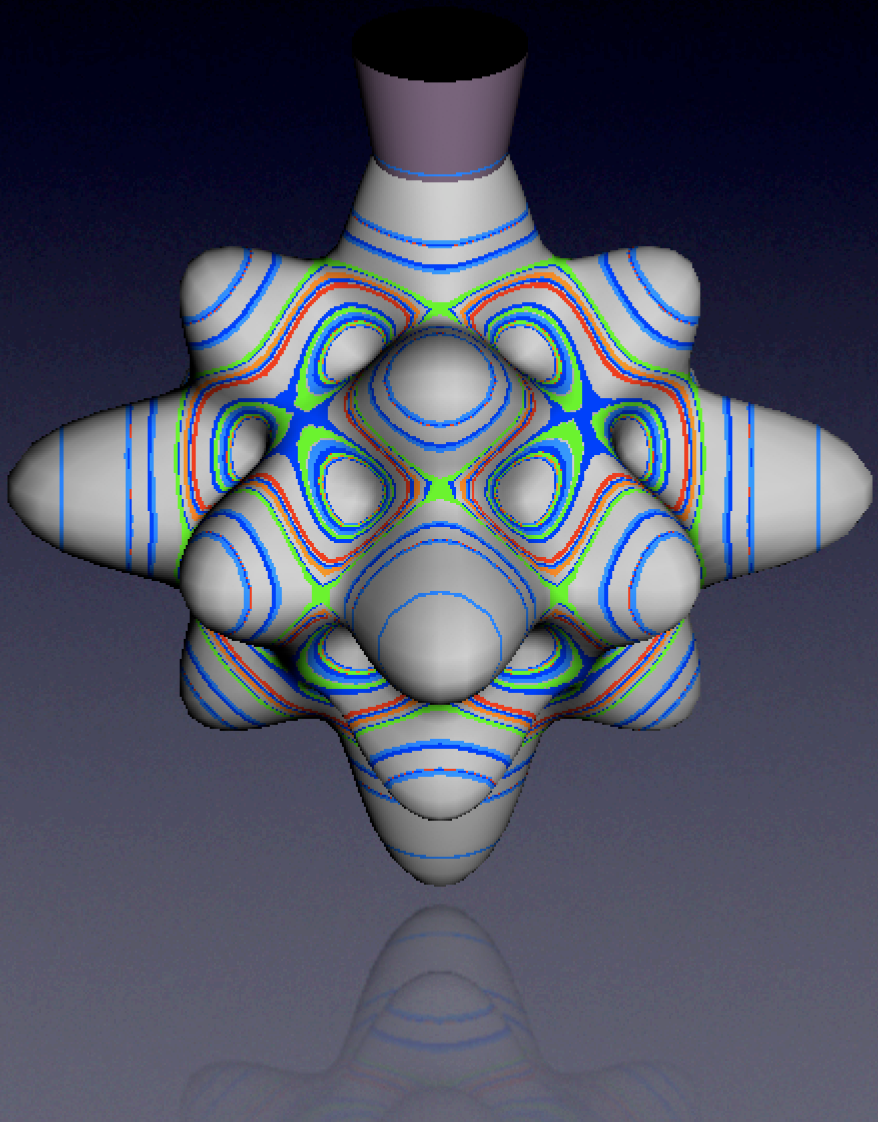
$e^{A_1}(0_4) = H + 4S$ $\quad$ $e^{T_1}(0_4) = H$ $\quad$ $e^{E}(0_4) = H - 2S$

$e^{T_2}(1_4) = H + 2S$ $\quad$ $e^{T_1}(1_4) = H - 2S$

$e^{E}(2_4) = H + 2S$ $\quad$ $e^{T_2}(2_4) = H$ $\quad$ $e^{A_2}(2_4) = H - 4S$

Next Talk

- Similar Splittings, More Sophisticated Method
- Keep Track of Tunneling Paths with Group Parameters
- Method To Find What Tunneling Paths Spoil the Local Symmetry



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