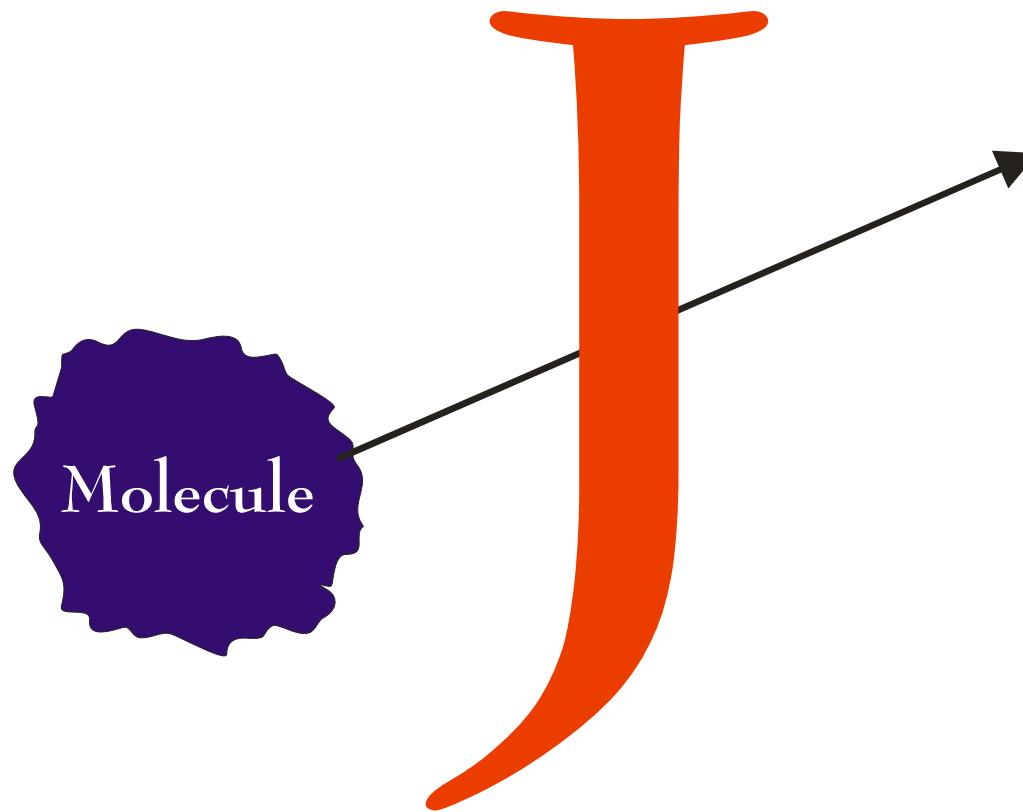
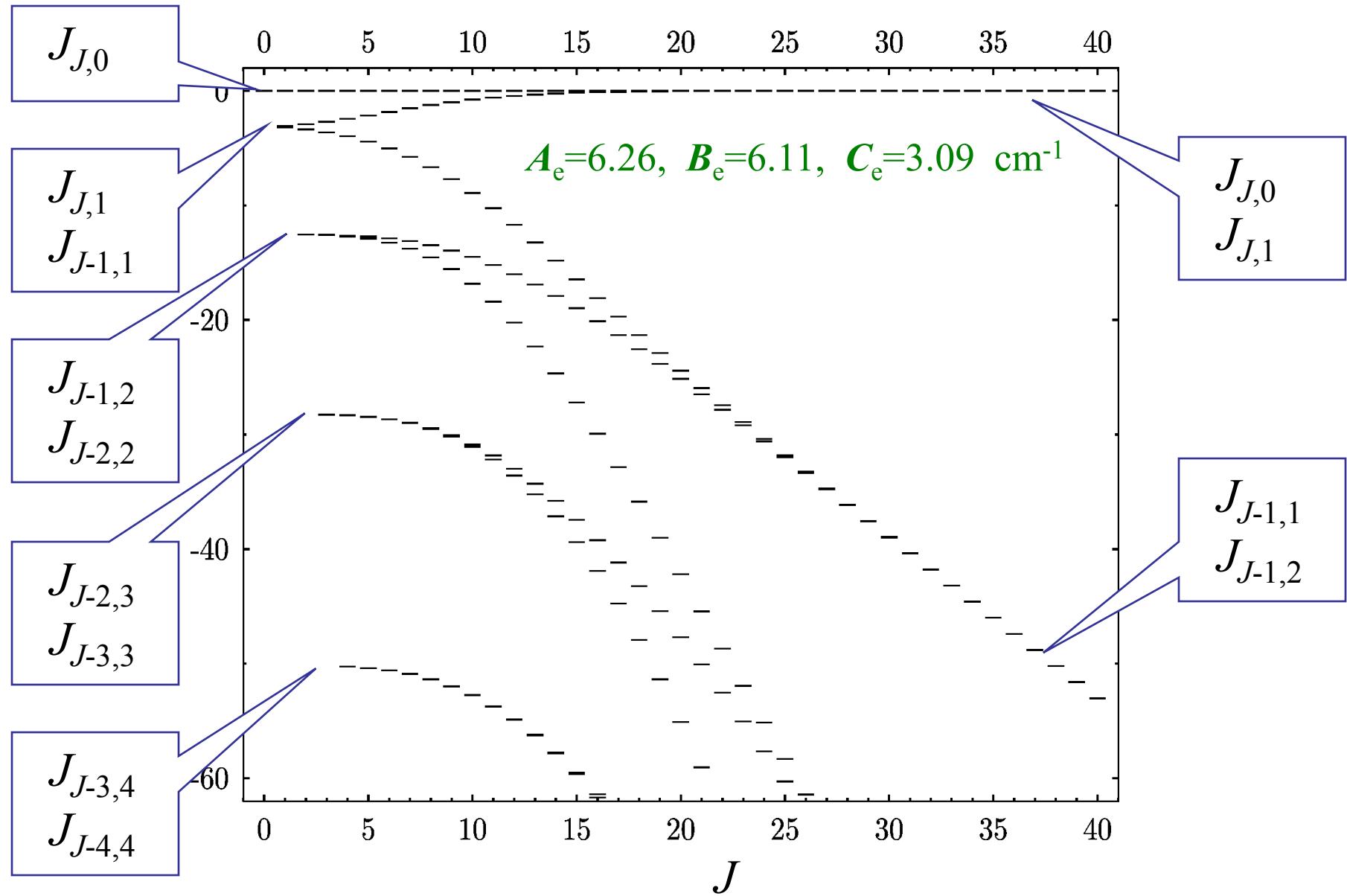


Molecules in highly excited rotational states

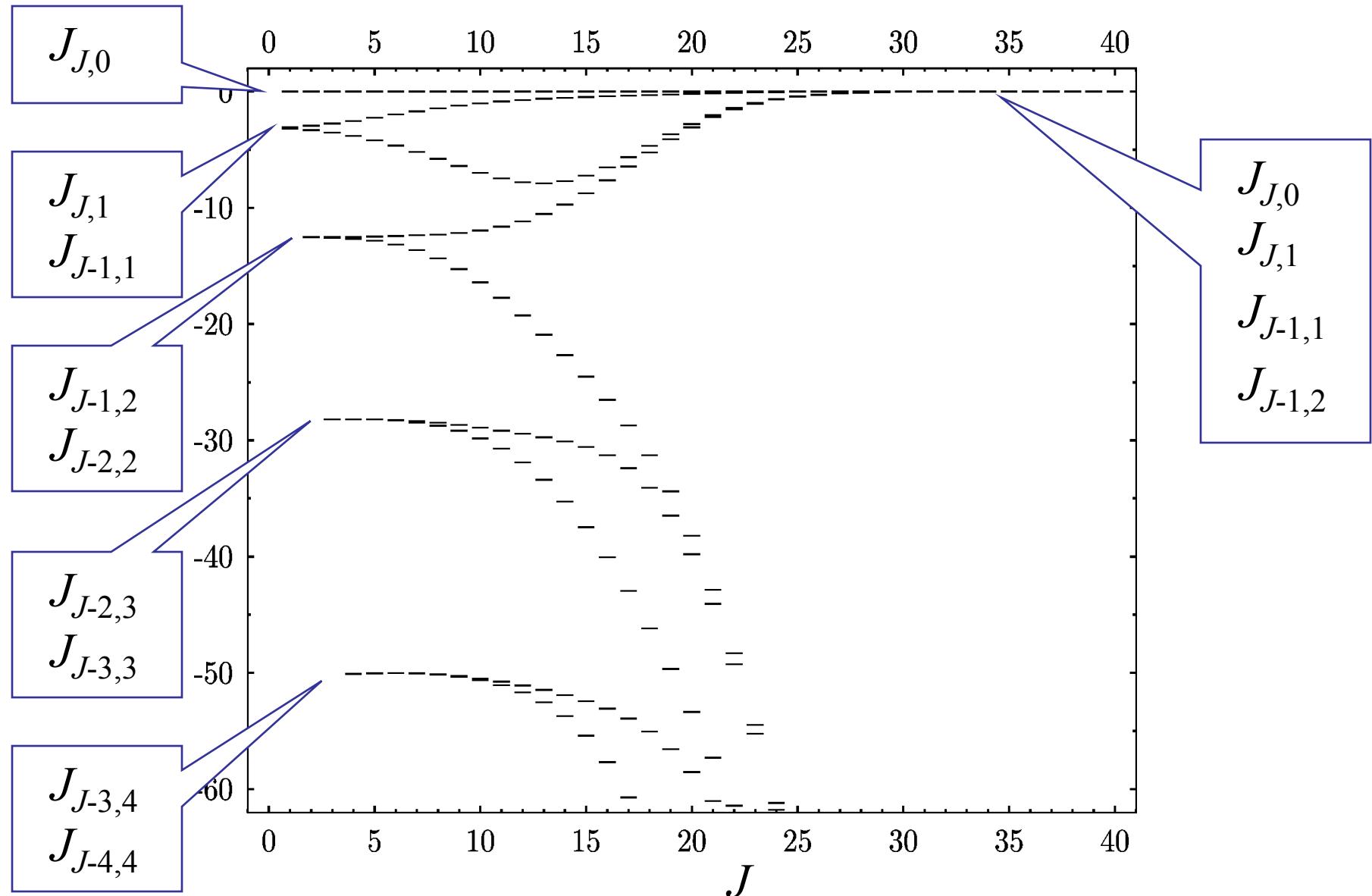


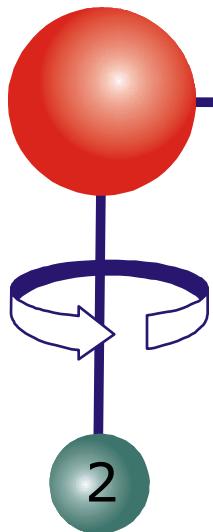
$J \sim 100$

H₂Te Rigid Rotor Energy Levels [$E(J_{KaKc}) - E(J_{J0})$]

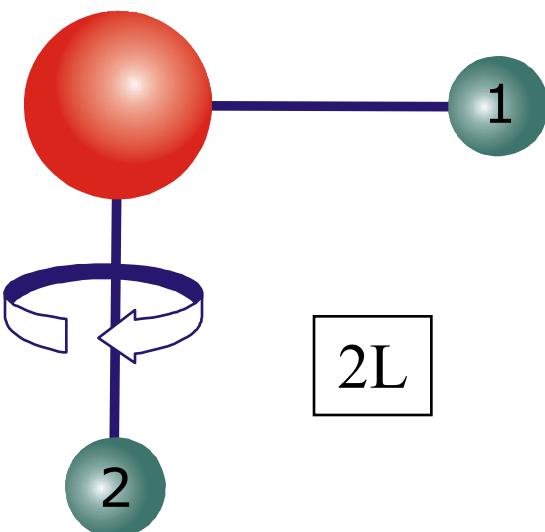


Actual H₂Te Energy Levels [$E(J_{KaKc}) - E(J_{J0})$]

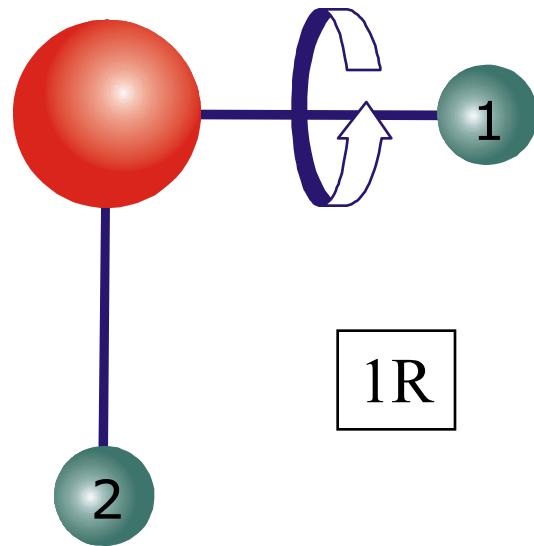




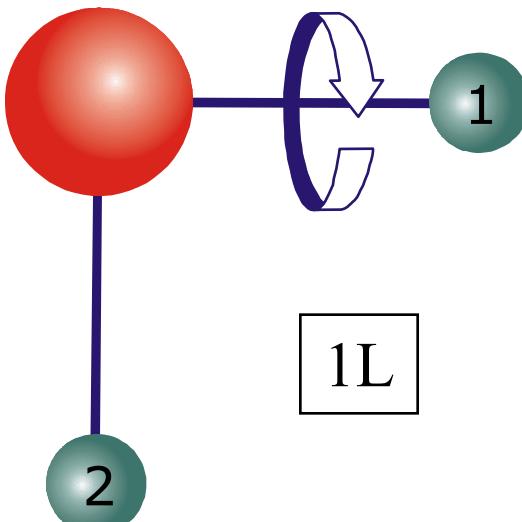
2R



2L



1R



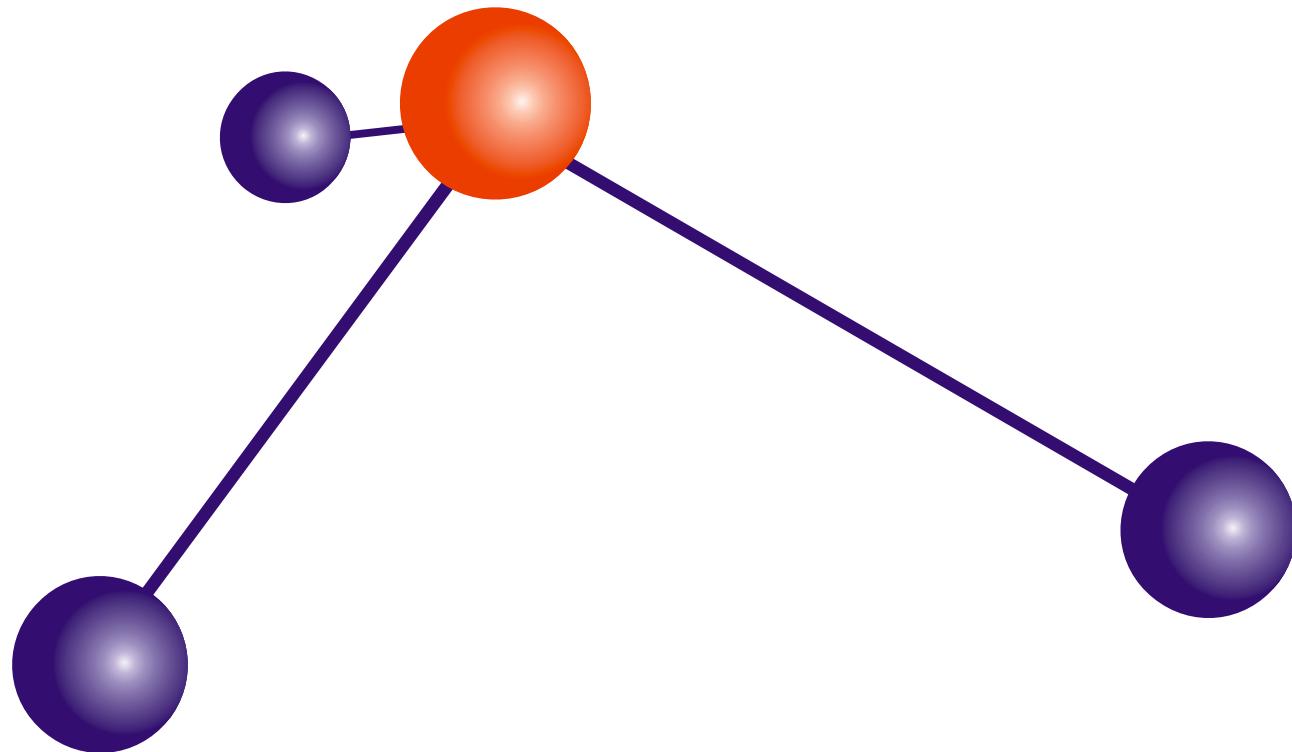
1L

$$\left. \begin{array}{c} J_{J,0} \\ J_{J,1} \\ J_{J-1,1} \\ J_{J-1,2} \end{array} \right\} \equiv$$

$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad C_{2v}(\mathbf{M})$$

Rotational Energy Level Clusters

1972	Dorney and Watson	CH ₄	8-fold and 6-fold clusters
1978	Zhilinskii and Pavlichenkov	H ₂ O	4-fold clusters (E_{rb})
1978	Harter and Patterson		Rotational energy surfaces and clusters
1991	Lehmann		Local mode theory and clusters
1992	Kozin et al	H ₂ Se	4-fold clusters observed
1993	Kozin and Jensen	H ₂ Se	4-fold cluster theory (E_{rbs})
1994	Jensen and Bunker	H ₂ X	4-fold cluster symmetry
1996	Kozin et al	H ₂ Te	4-fold clusters (exp and theory)
1997	Jensen et al		Review paper on 4-fold clusters
2000	Jensen		Review paper on LMT and clusters [Mol. Phys. 98 , 1253-1285 (2000)]



**Are there similar effects for
XH₃ molecules – say PH₃?**

We investigate by variational rotation-vibration calculations

Basis functions:

$$|\Psi_{Basis}\rangle = |J, K, m\rangle |v_{inv}, J, K\rangle \Psi_{v_1}^{MO}(\xi_1) \times \Psi_{v_2}^{MO}(\xi_2) \times \Psi_{v_3}^{MO}(\xi_3) \times \Psi_{V,l}^{HO}(\xi_{4a}, \xi_{4b})$$

Rigid rotor
eigenfunctions

Morse oscillators

Two-dimensional
isotropic harmonic
oscillators for doubly
degenerate bending
vibrations

Numerov-Cooley
solution of inversion
Schrödinger
equation for

$$V_0(\rho) = V(\rho, \xi_\lambda = 0)$$

**Hougen-Bunker-Johns theory:
Eckart & Sayvetz conditions**
 $\Rightarrow \widehat{T}_{\text{nuc}} = \text{expansion in the } \xi_i$

[1] H. Lin *et al.*, *J. Chem. Phys.* **117**, 11265 (2002)

[2] S.N. Yurchenko *et al.*, *Mol. Phys.* **103**, 359 (2005) and references given there.

Variational rotation-vibration calculations for PH₃

$J \leq 80$

Vibrational basis set:

$$2(\nu_1 + \nu_2 + \nu_3) + \nu_{inv} + V_{bend} \leq 6$$

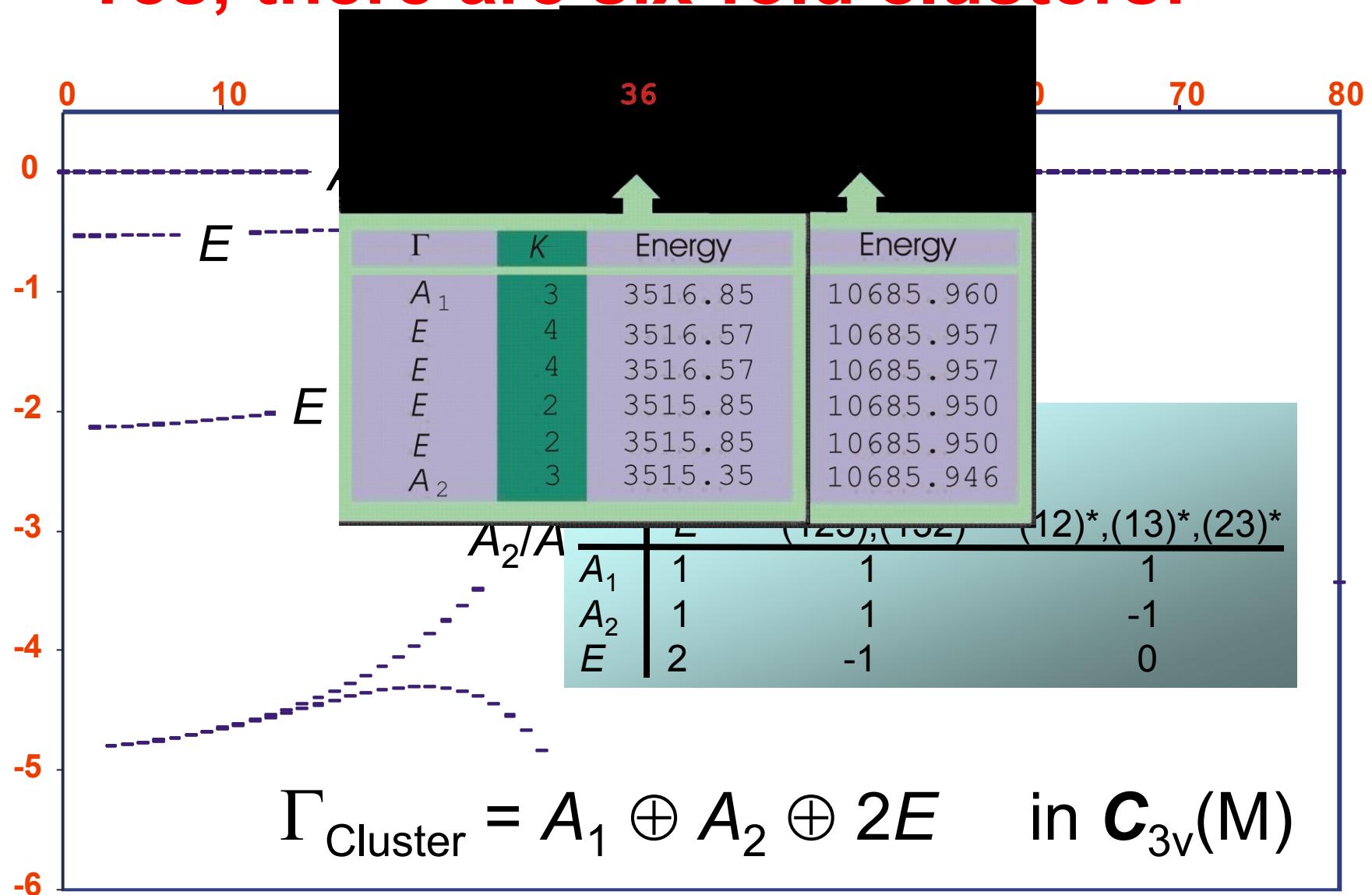
Potential energy surface:

cc-pwCVTZ [1]
refined by fitting to experimental
vibrational term values [2]

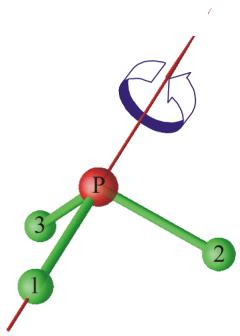
[1] D. Wang, Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.*, **112**, 9624 (2000)

[2] S.N. Yurchenko *et al.*, *Chem. Phys.* **290**, 59 (2003)

Yes, there are six-fold clusters!

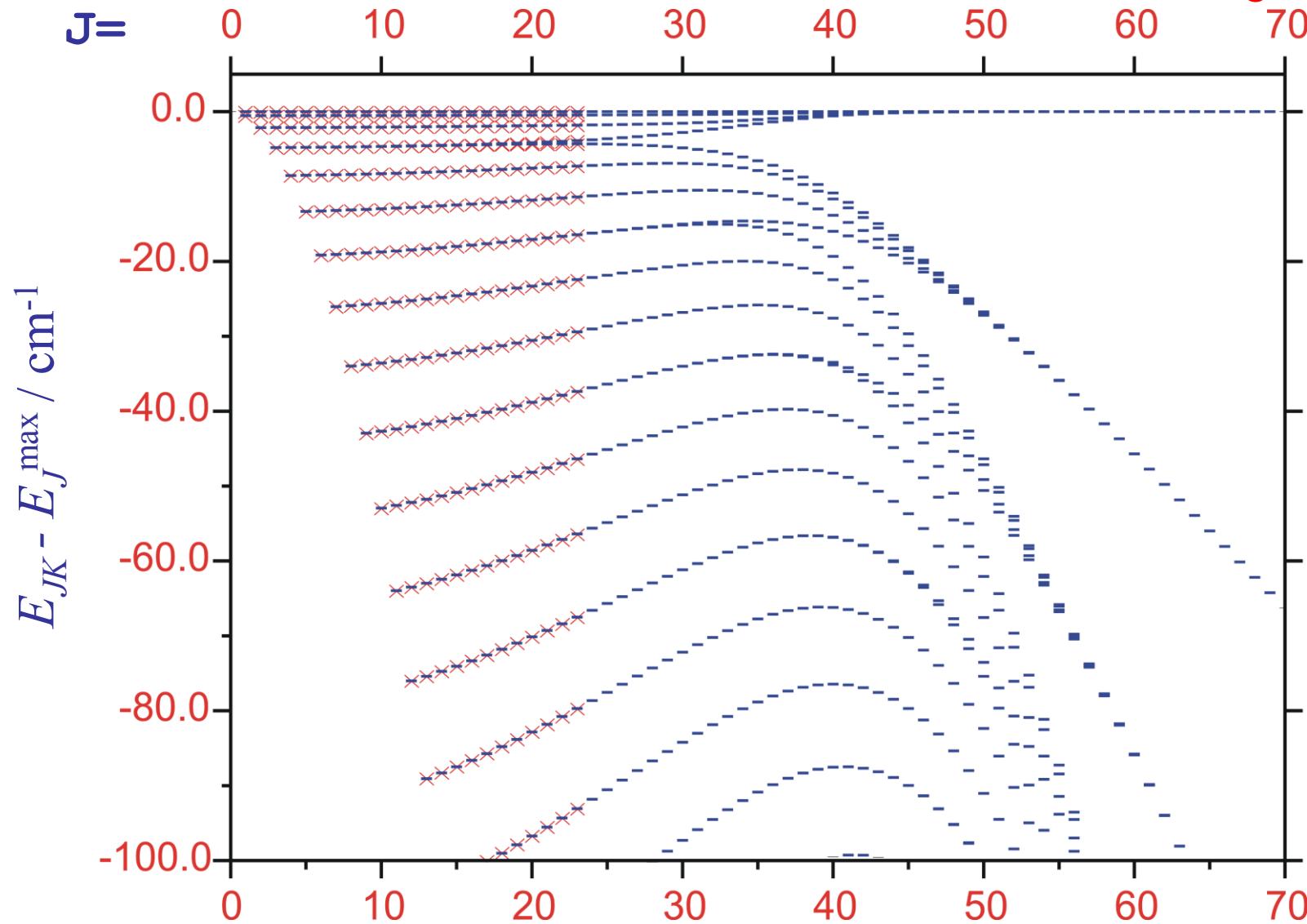


$$|1 \text{ PCS}\rangle = E |1 \text{ PCS}\rangle$$

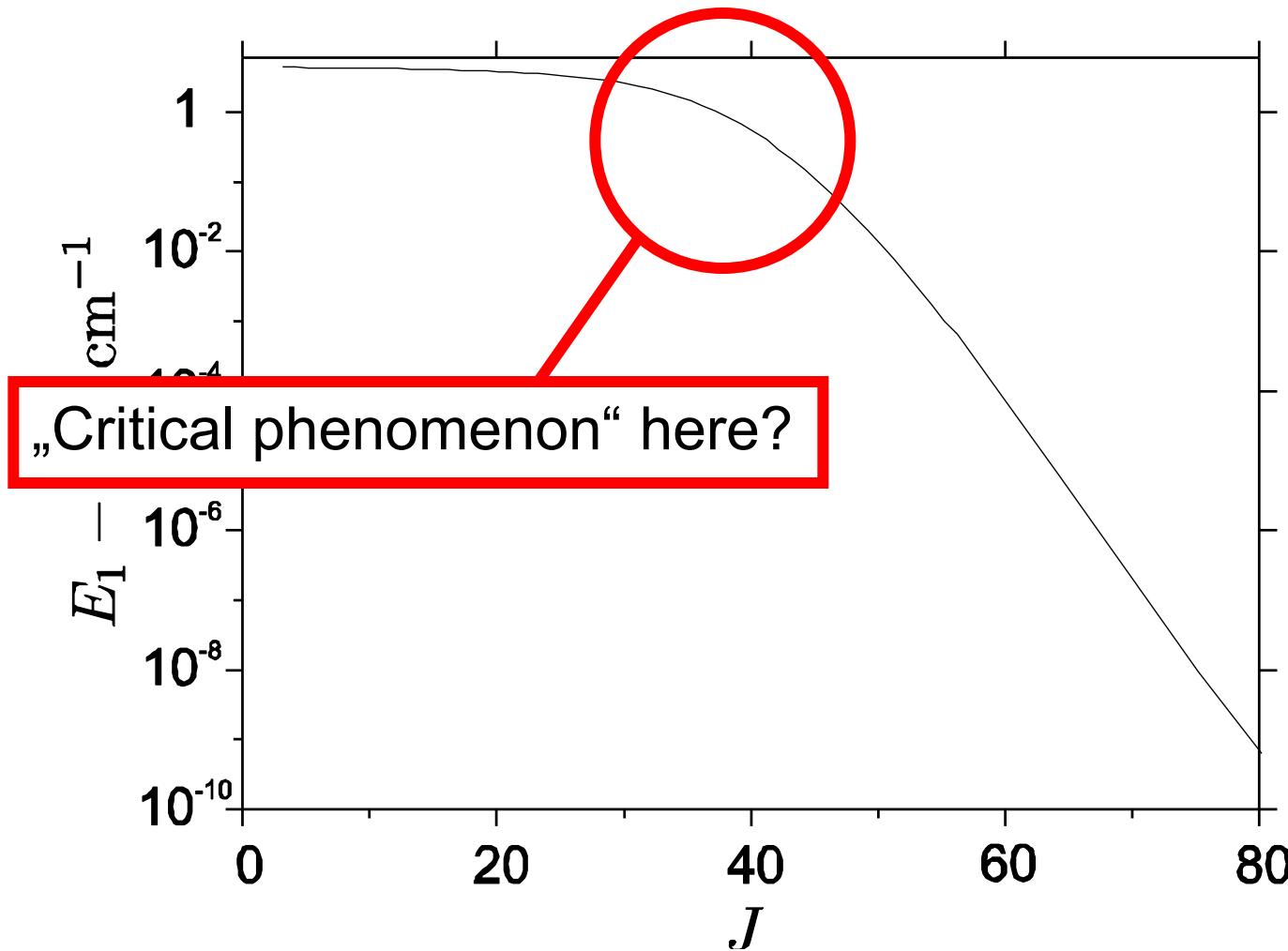


$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M)$$

Watson-type Hamiltonian for PH₃

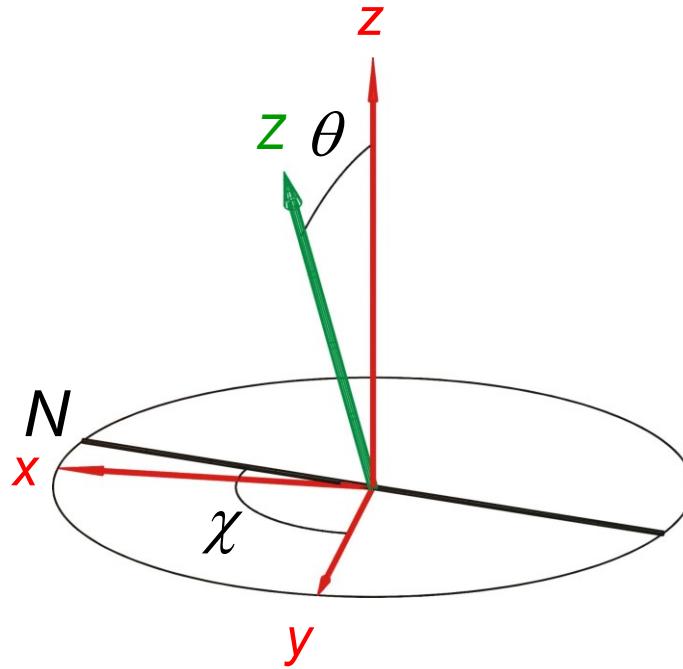
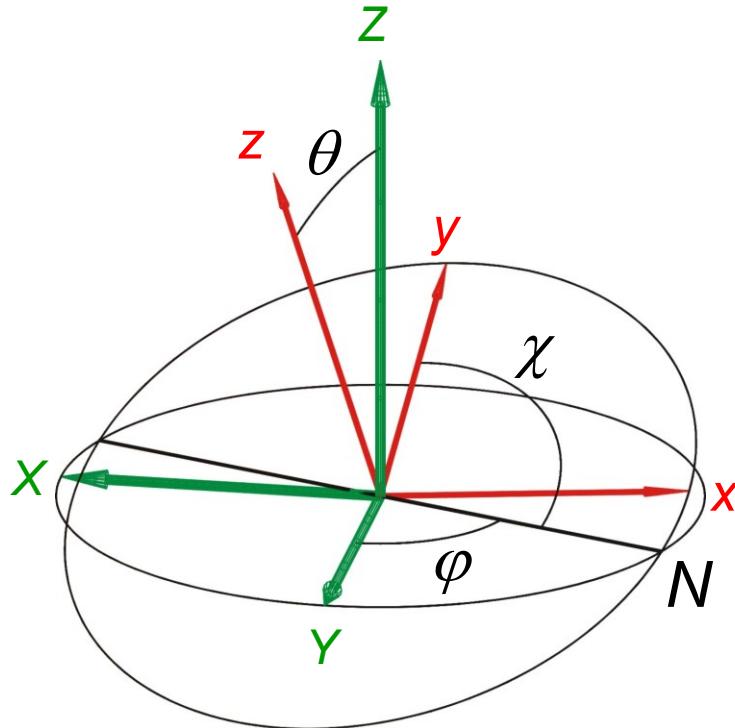


“Cluster spread”, vibrational ground state of PH₃



Rotational coordinates

xyz is molecule-fixed; XYZ is space-fixed



- (θ, φ, χ) define orientation of molecule (xyz) relative to laboratory (XYZ).
- (θ, χ) define orientation of Z axis relative to molecule (xyz).

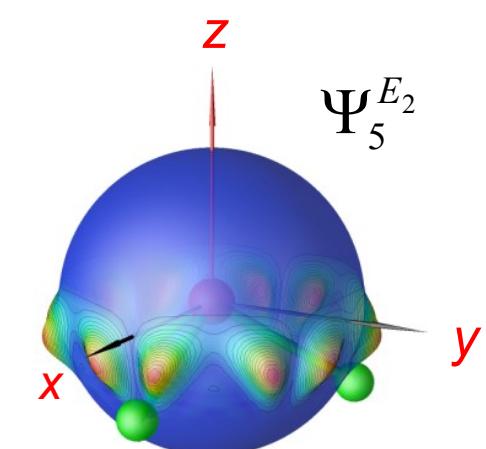
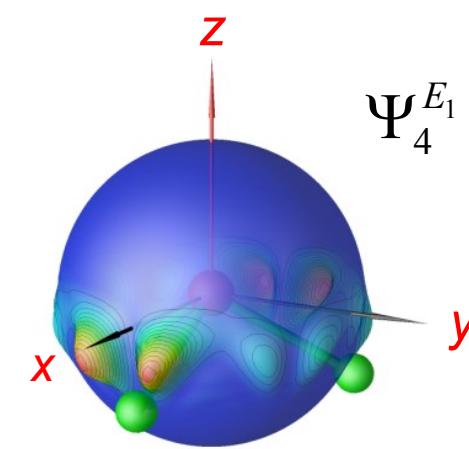
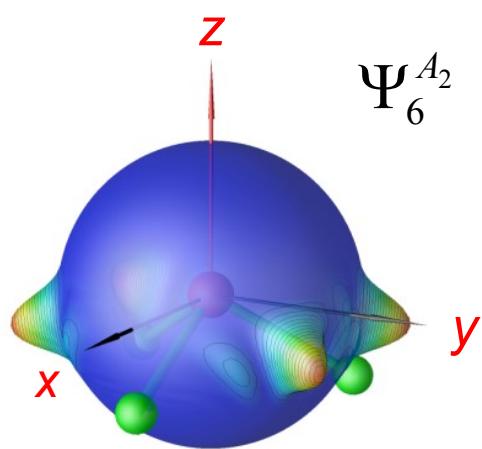
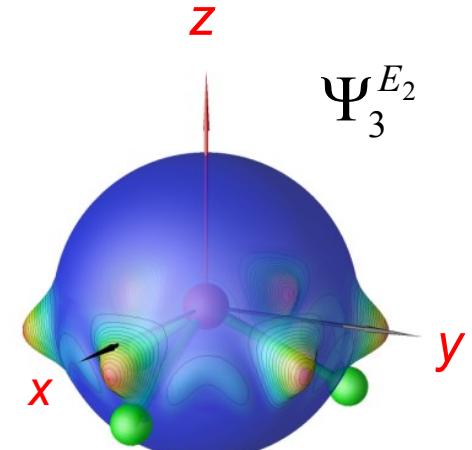
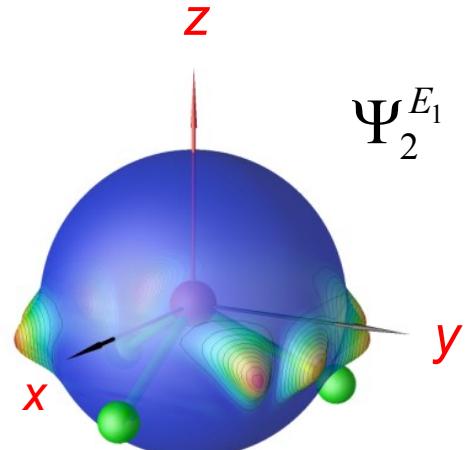
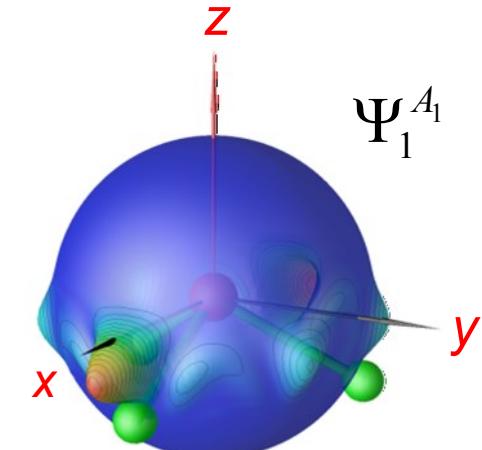
For a rovibronic eigenstate Φ_i

$$F_{J,m}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta dV$$

Integration over all vibronic coordinates and φ

is the probability distribution for the orientation of the Z axis relative to the molecule.

$$F_{J,m}(\theta, \chi)$$



**“Top cluster states” for $J = m = 40$,
vibrational ground state of PH_3**

Primitive cluster states $|j \text{ PCS}\rangle$

First symmetrize, e.g.

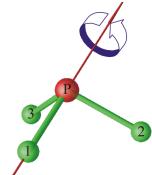
$$\Psi_1^{A_1} = \frac{1}{\sqrt{6}} (|1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle + |4 \text{ PCS}\rangle + |5 \text{ PCS}\rangle + |6 \text{ PCS}\rangle)$$

$$\Psi_6^{A_2} = \frac{1}{\sqrt{6}} (|1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle - |4 \text{ PCS}\rangle - |5 \text{ PCS}\rangle - |6 \text{ PCS}\rangle)$$

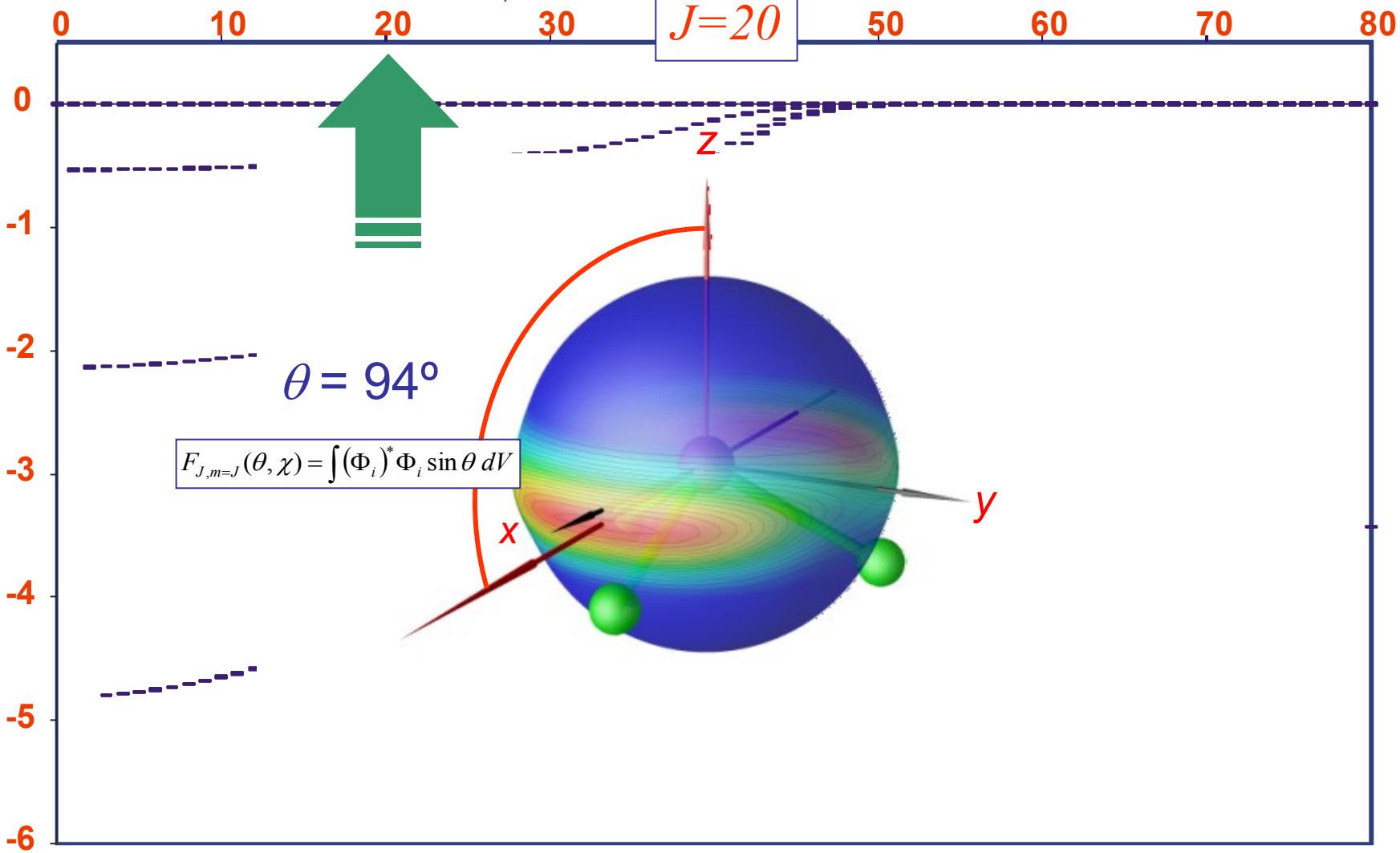
with similar expressions for the E functions....



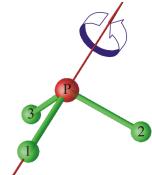
$| 1 \text{ PCS} \rangle$



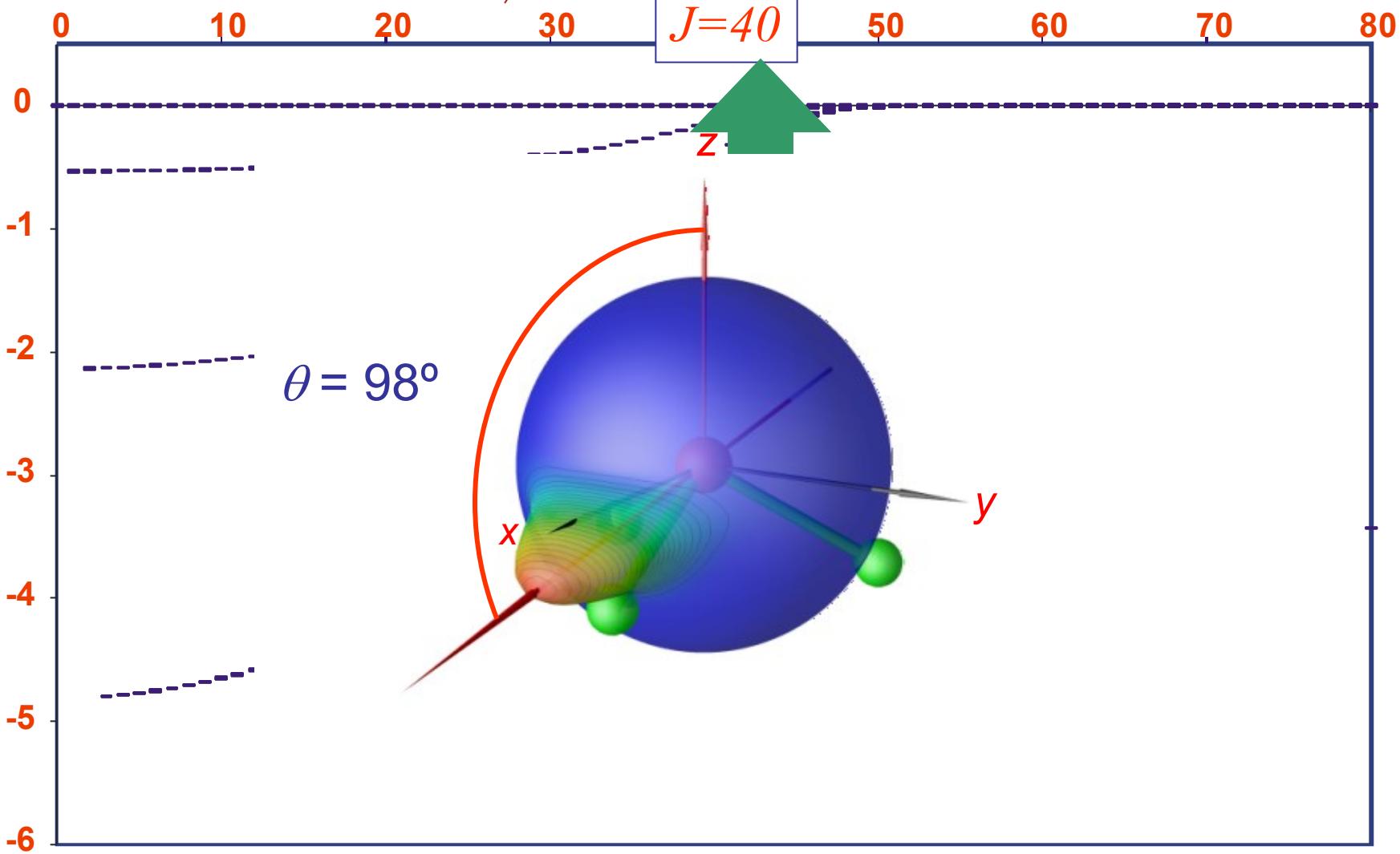
$J=20$



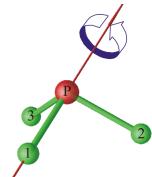
$| 1 \text{ PCS} \rangle$



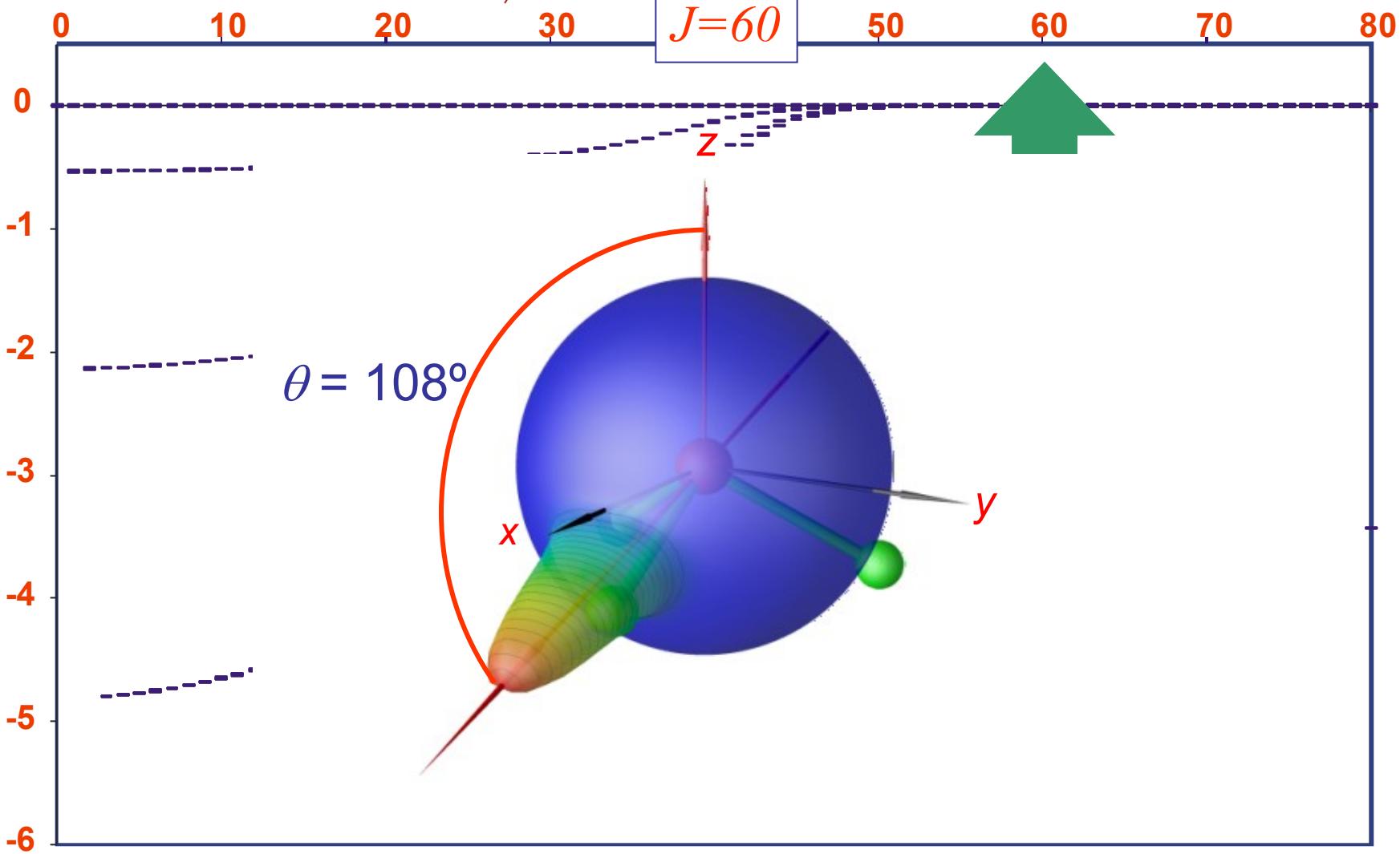
$J=40$



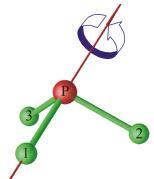
$| 1 \text{ PCS} \rangle$



$J=60$

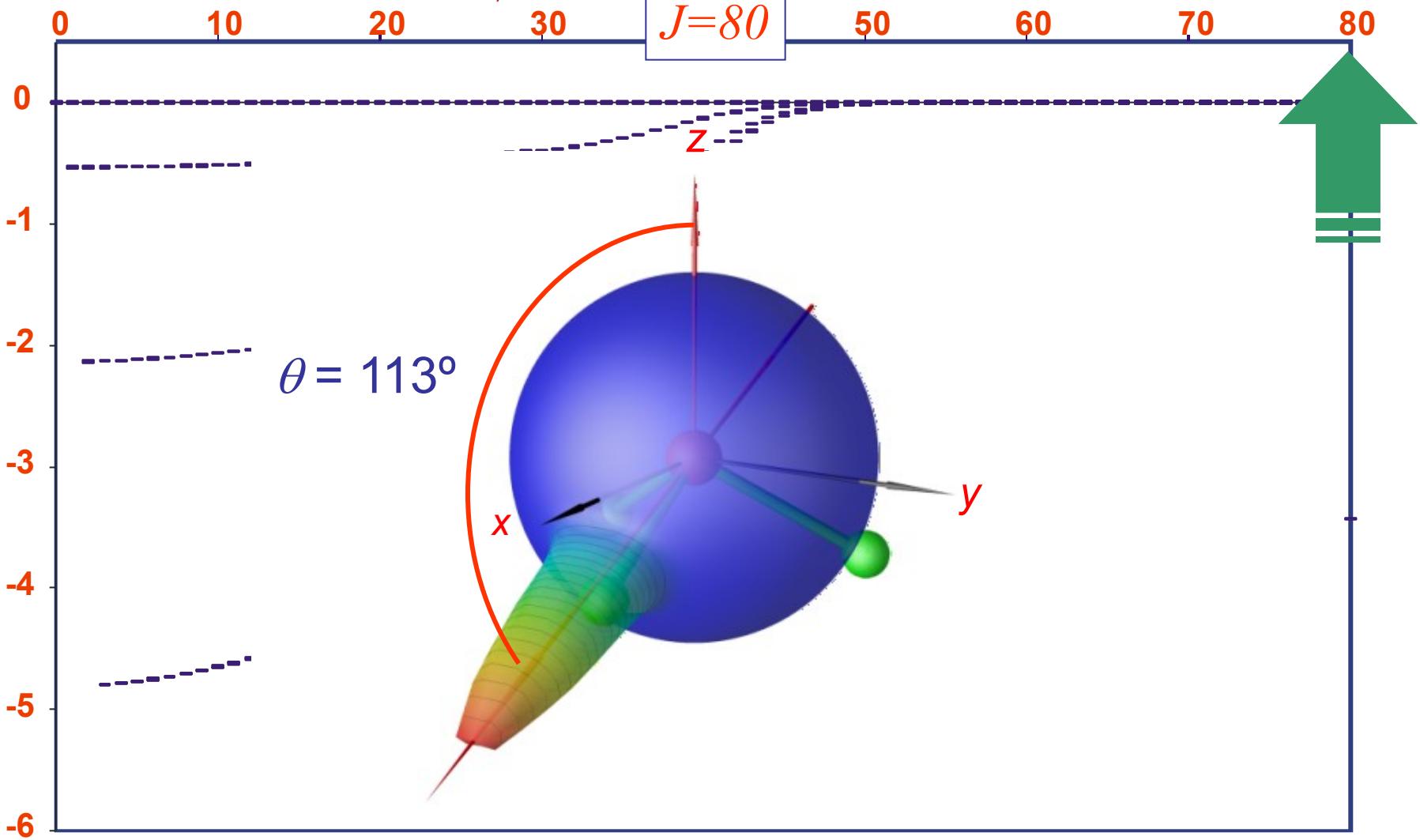


$| 1 \text{ PCS} \rangle$

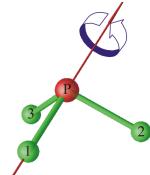


$\theta_{\text{eq}} = 123^\circ$

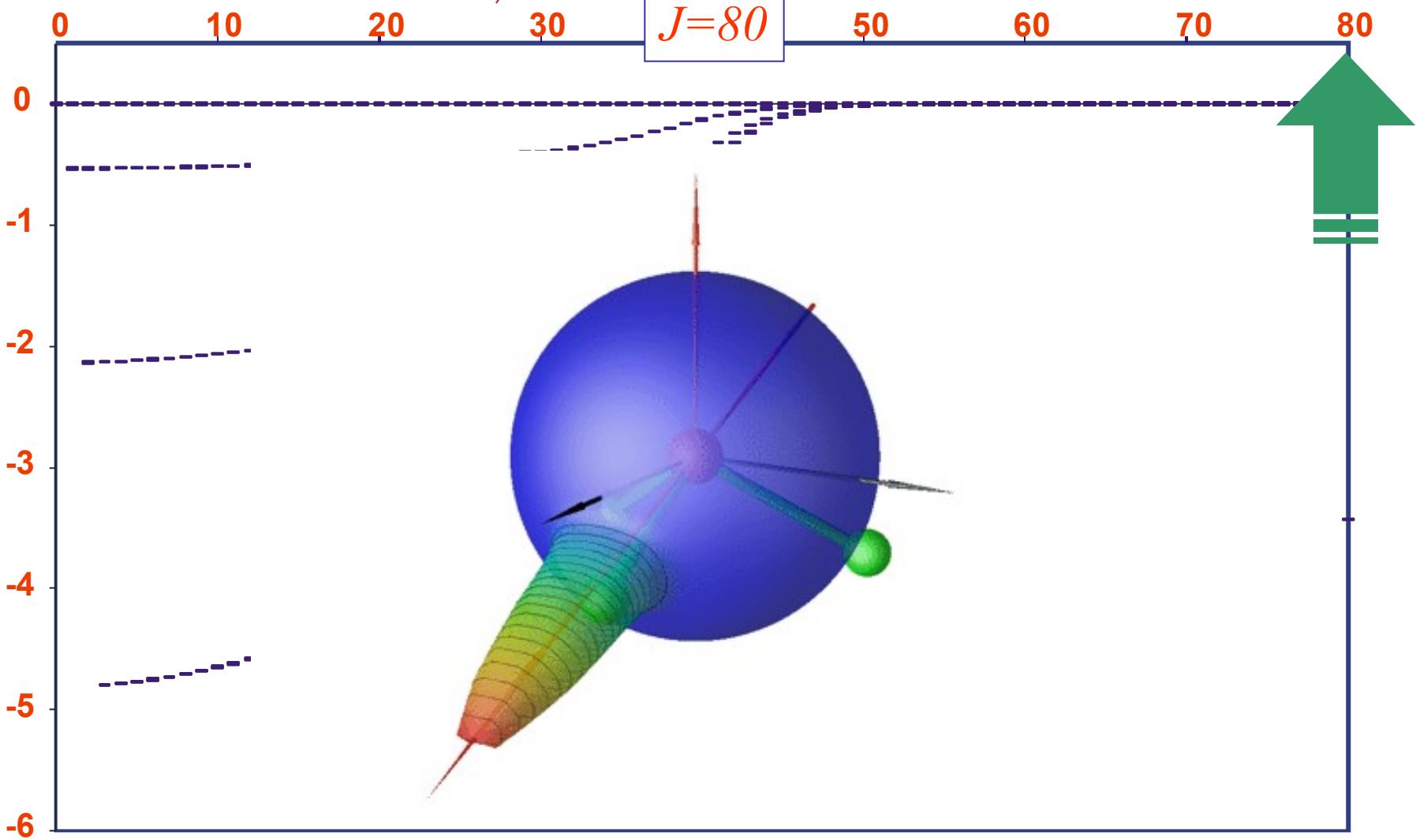
$J=80$



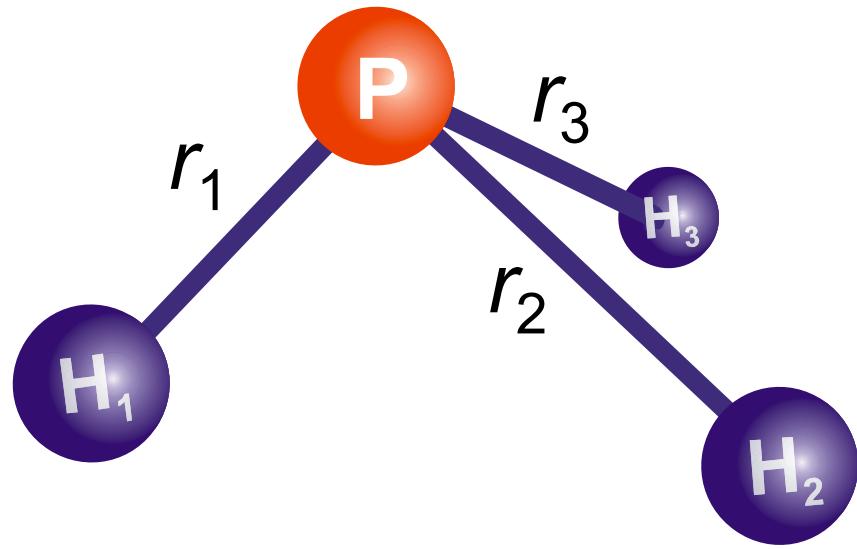
$| 1 \text{ PCS} \rangle$



$J=80$



Expectation value analysis



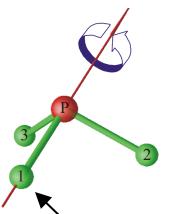
$$\alpha_1 = \angle(H_2PH_3)$$
$$\alpha_2 = \angle(H_1PH_3)$$
$$\alpha_3 = \angle(H_1PH_2)$$

$$\bar{r}_i = \langle 1 \text{ PCS} | r_i | 1 \text{ PCS} \rangle$$

$$\bar{\alpha}_i = \langle 1 \text{ PCS} | \alpha_i | 1 \text{ PCS} \rangle$$

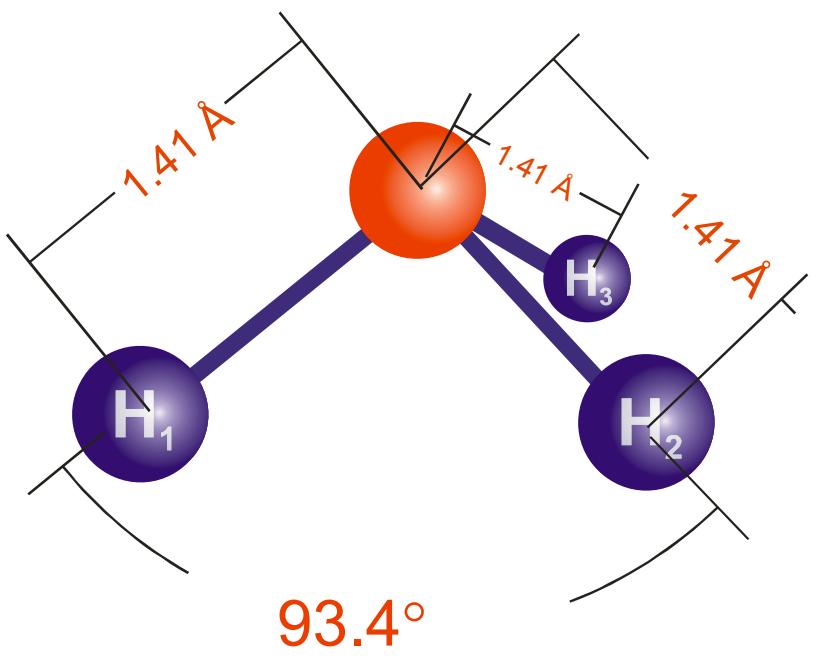
$| 1 \text{ PCS} \rangle$

$J=0$

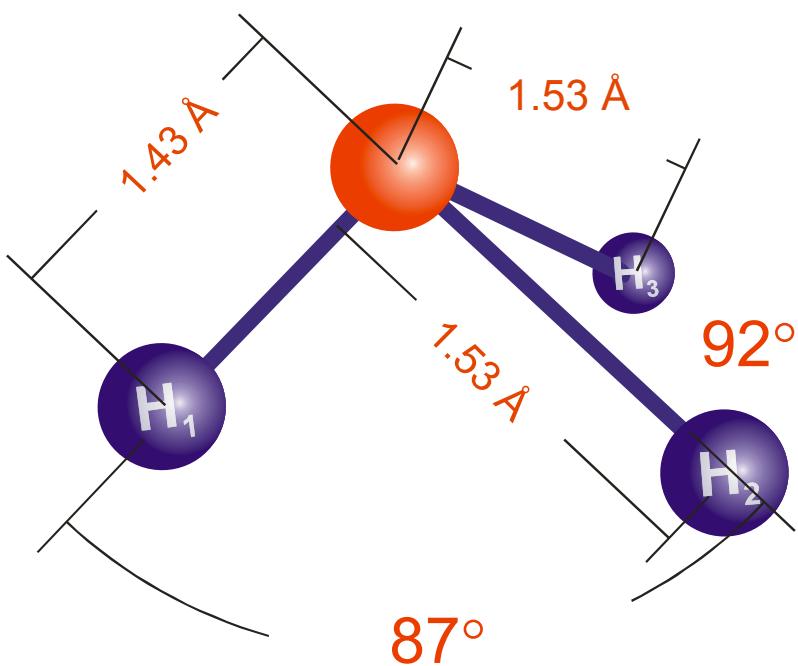


average geometry

$J=80$

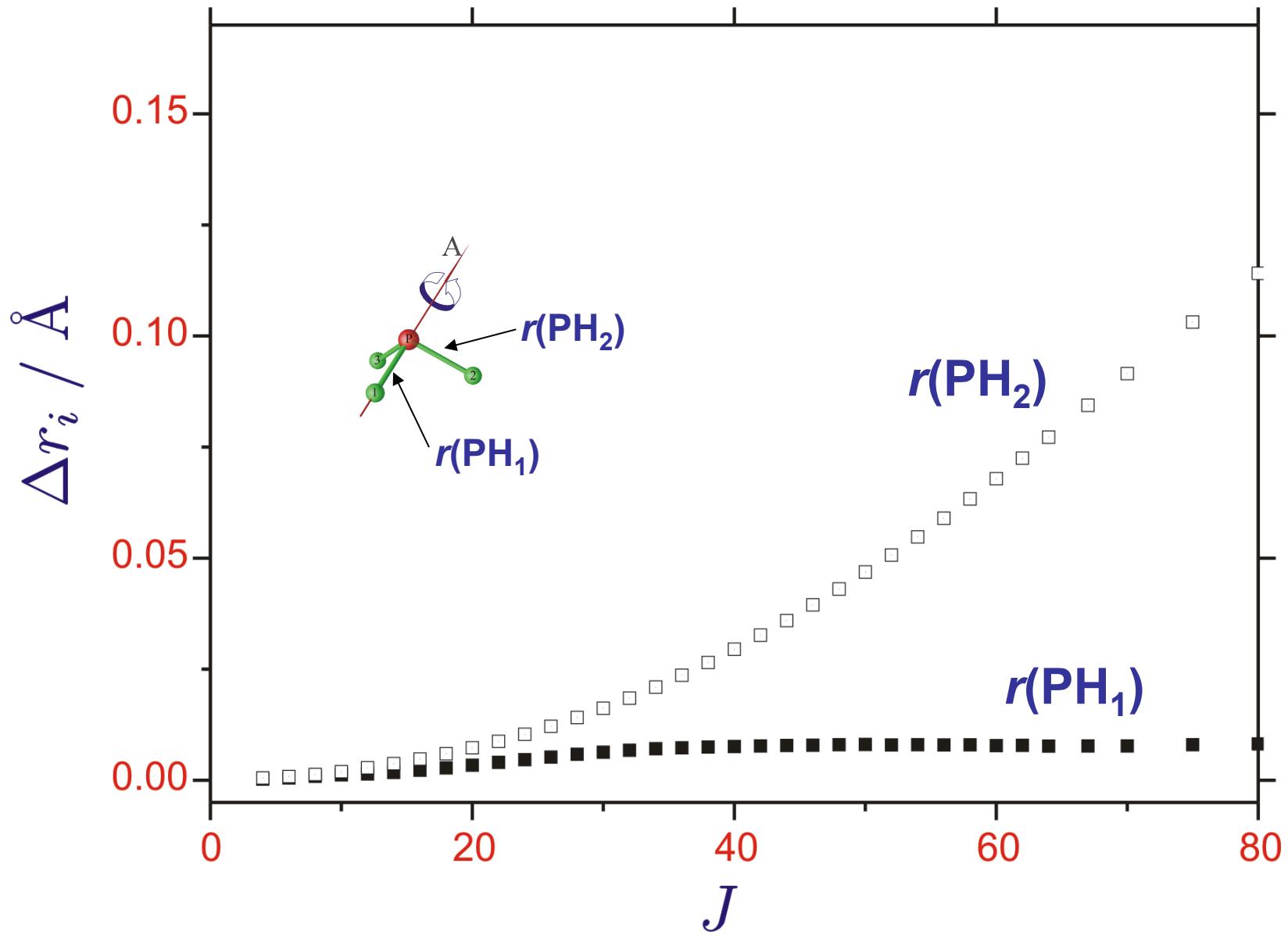


C_{3v} geometrical symmetry

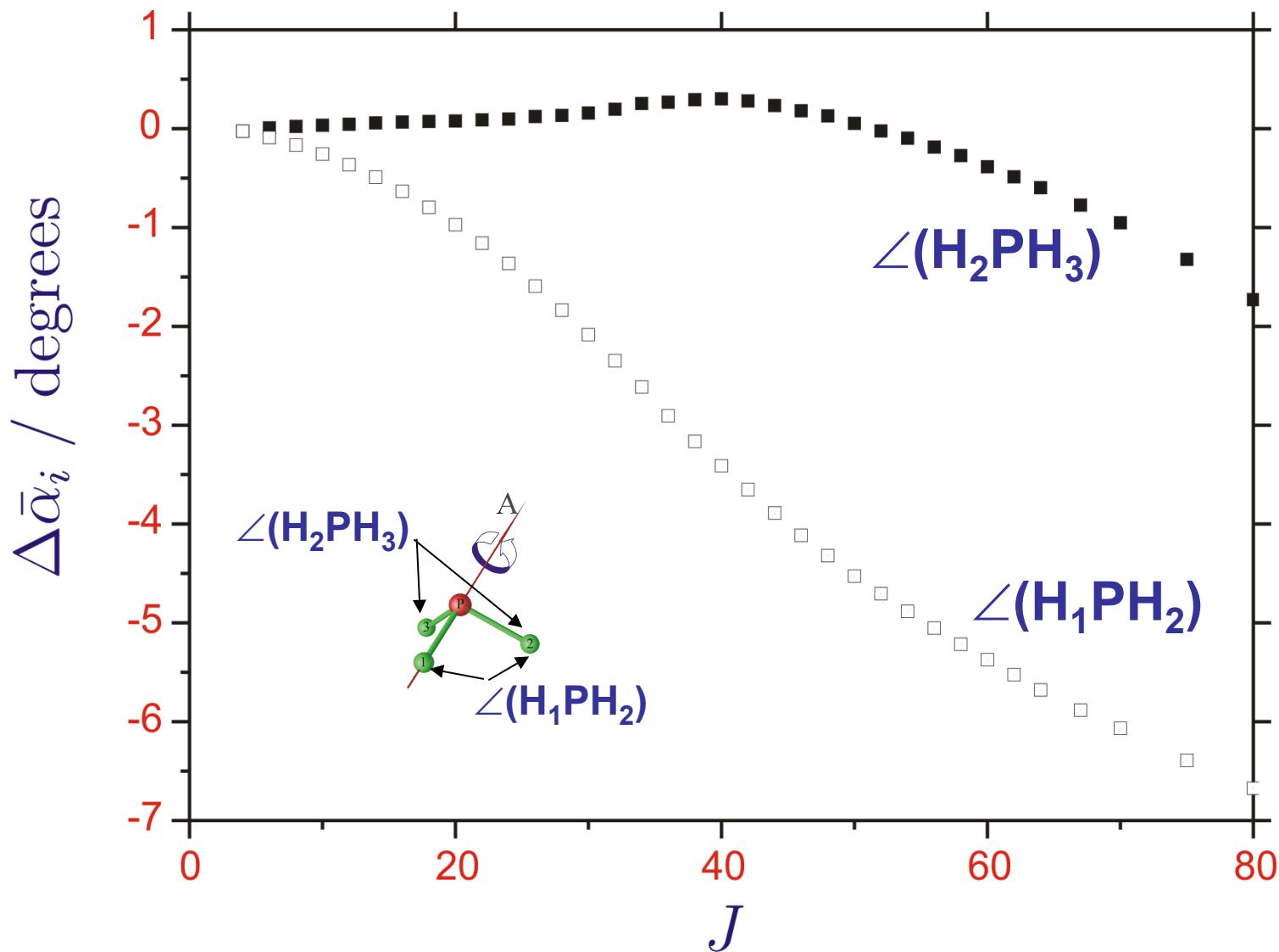


C_s geometrical symmetry

$$\Delta r_i = \langle 1 \text{ PCS} | r_i | 1 \text{ PCS} \rangle - 1.41 \text{ \AA}$$



$$\Delta \bar{\alpha}_i = \langle 1 \text{ PCS} \mid \alpha_i \mid 1 \text{ PCS} \rangle - 93.4^\circ$$



Semi-classical theory

$$\begin{aligned}\dot{q}_n &= \boxed{\partial H_{\text{rv}} / \partial p_n}, \\ \dot{p}_n &= -\partial H_{\text{rv}} / \partial q_n, \\ \dot{J}_\alpha &= \{J_\alpha, H_{\text{rv}}\}\end{aligned}$$

Stationary states

=0

$$J_x = \sqrt{J(J+1)} \sin \theta_J \cos \phi_J$$

$$J_y = \sqrt{J(J+1)} \sin \theta_J \sin \phi_J$$

$$J_z = \sqrt{J(J+1)} \cos \theta_J.$$

Rotational energy surface

$$E_J(\theta_J, \phi_J) = H_{\text{rv}}(J, q_n = q_n^s, p_n = p_n^s, \theta_J, \phi_J)$$

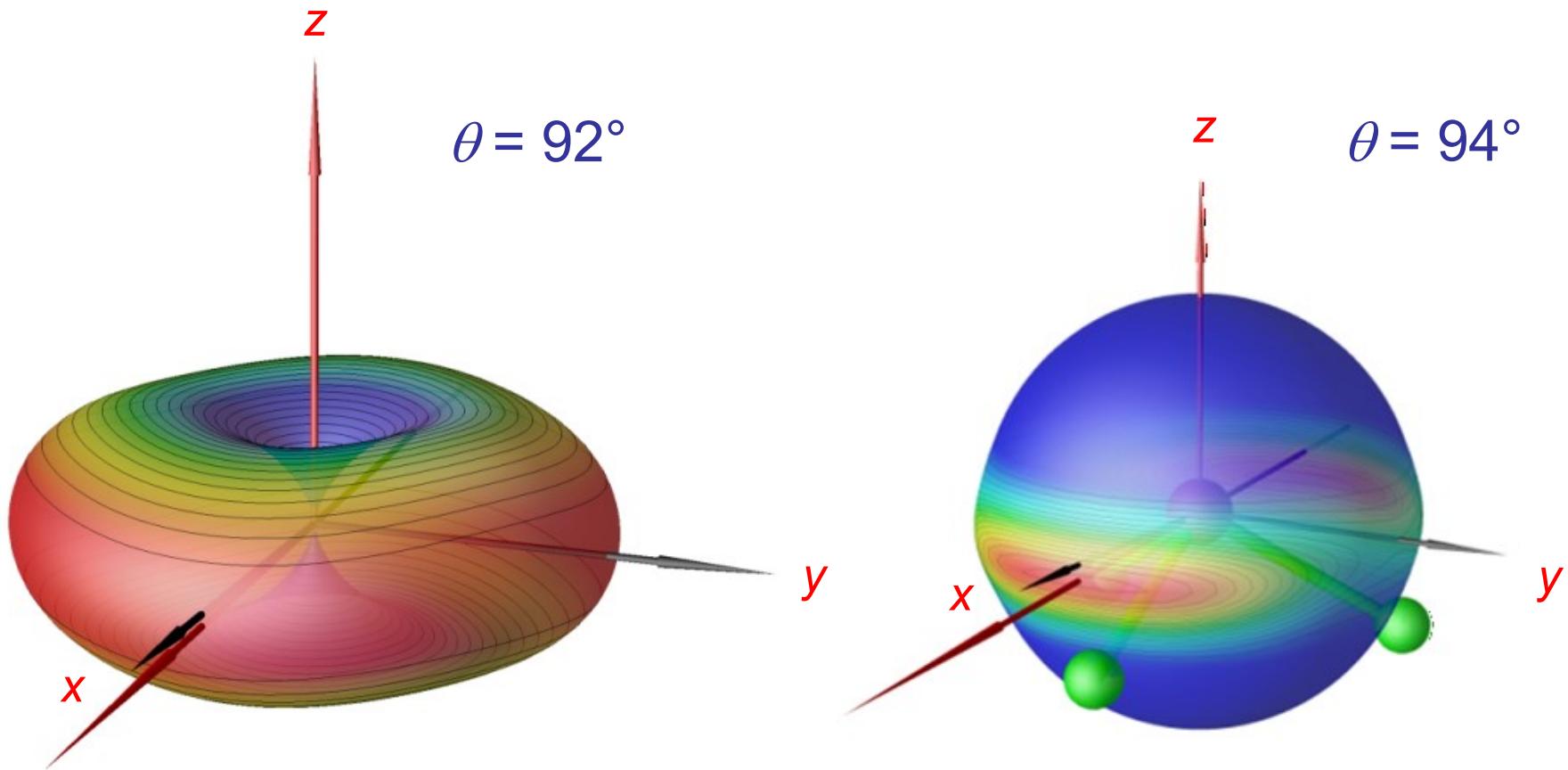
$$J_x = \sqrt{J(J+1)} \sin \theta_J \cos \phi_J$$

$$J_y = \sqrt{J(J+1)} \sin \theta_J \sin \phi_J$$

$$J_z = \sqrt{J(J+1)} \cos \theta_J.$$

The rotational energy surface is a radial plot of $E_J - E_J^{(\min)}$ as a function of θ_J, ϕ_J

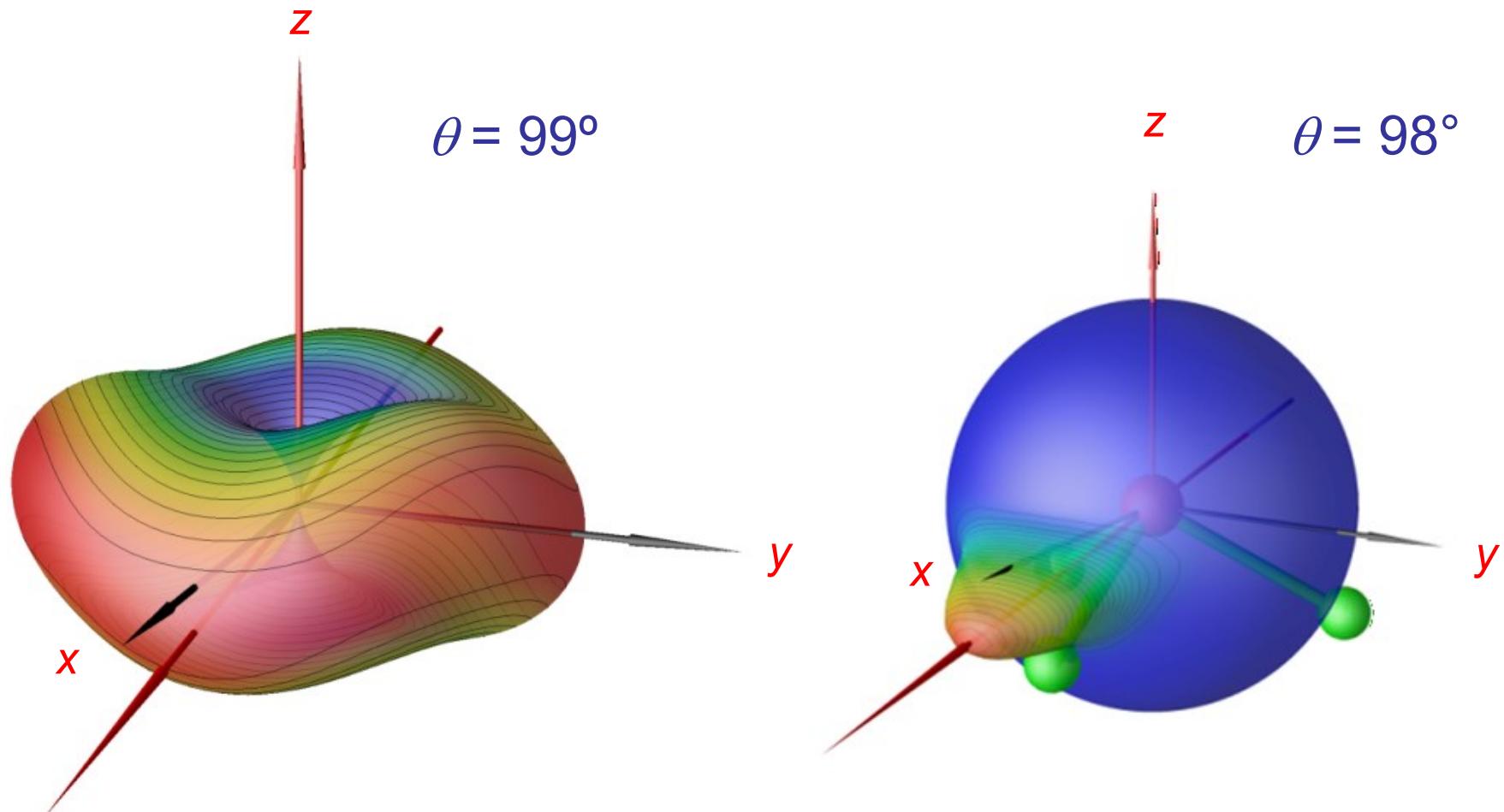
Rotational energy surface, $J = 20$



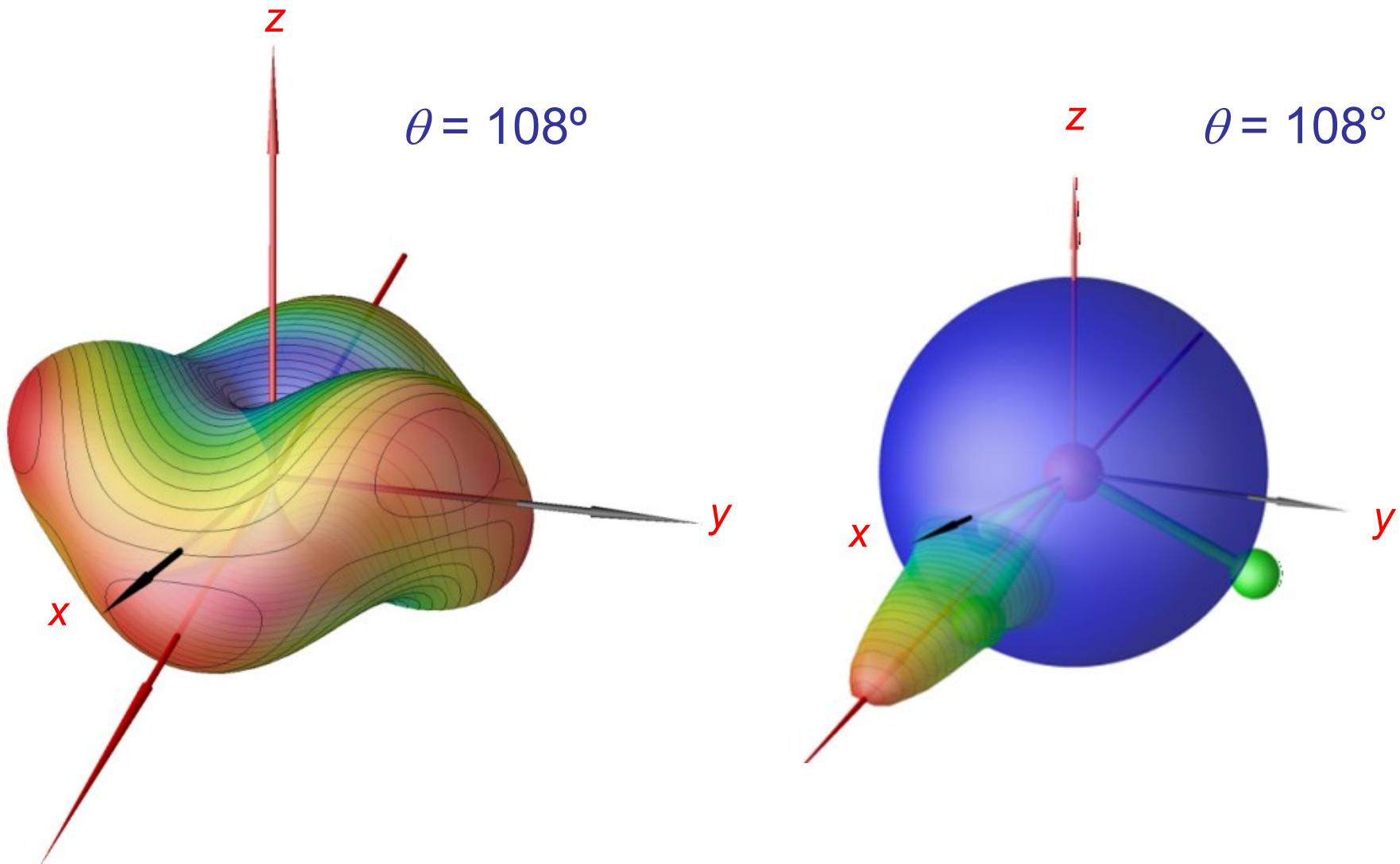
For a rigid PH_3 molecule:

$$E_J^{(\text{rigid})}(\theta_J, \phi_J) - E_J^{(\text{rigid})}(\theta_{\min}, \phi_{\min}) = |B_e - C_e| J(J + 1) \sin^2 \theta_J$$

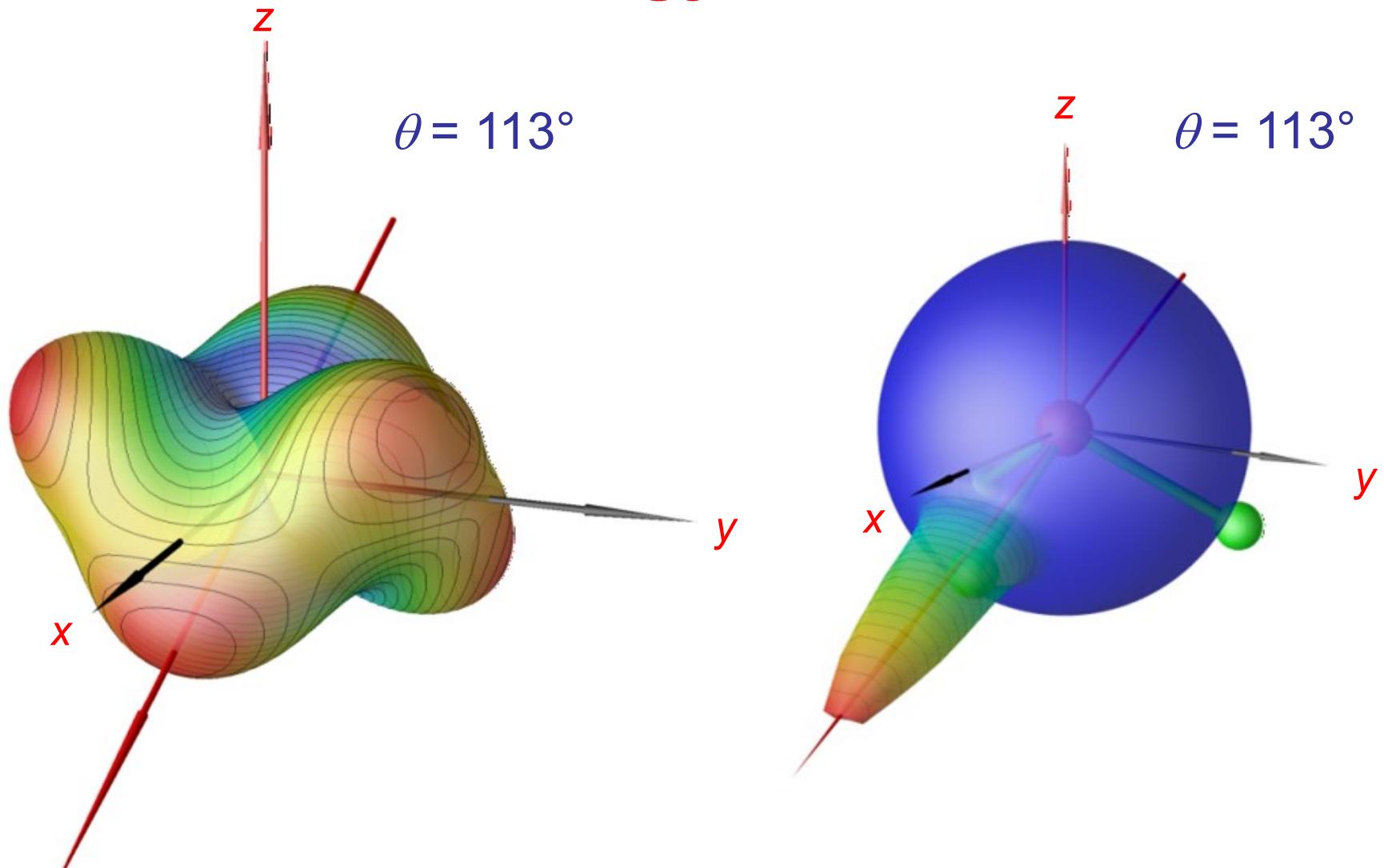
Rotational energy surface, $J = 40$



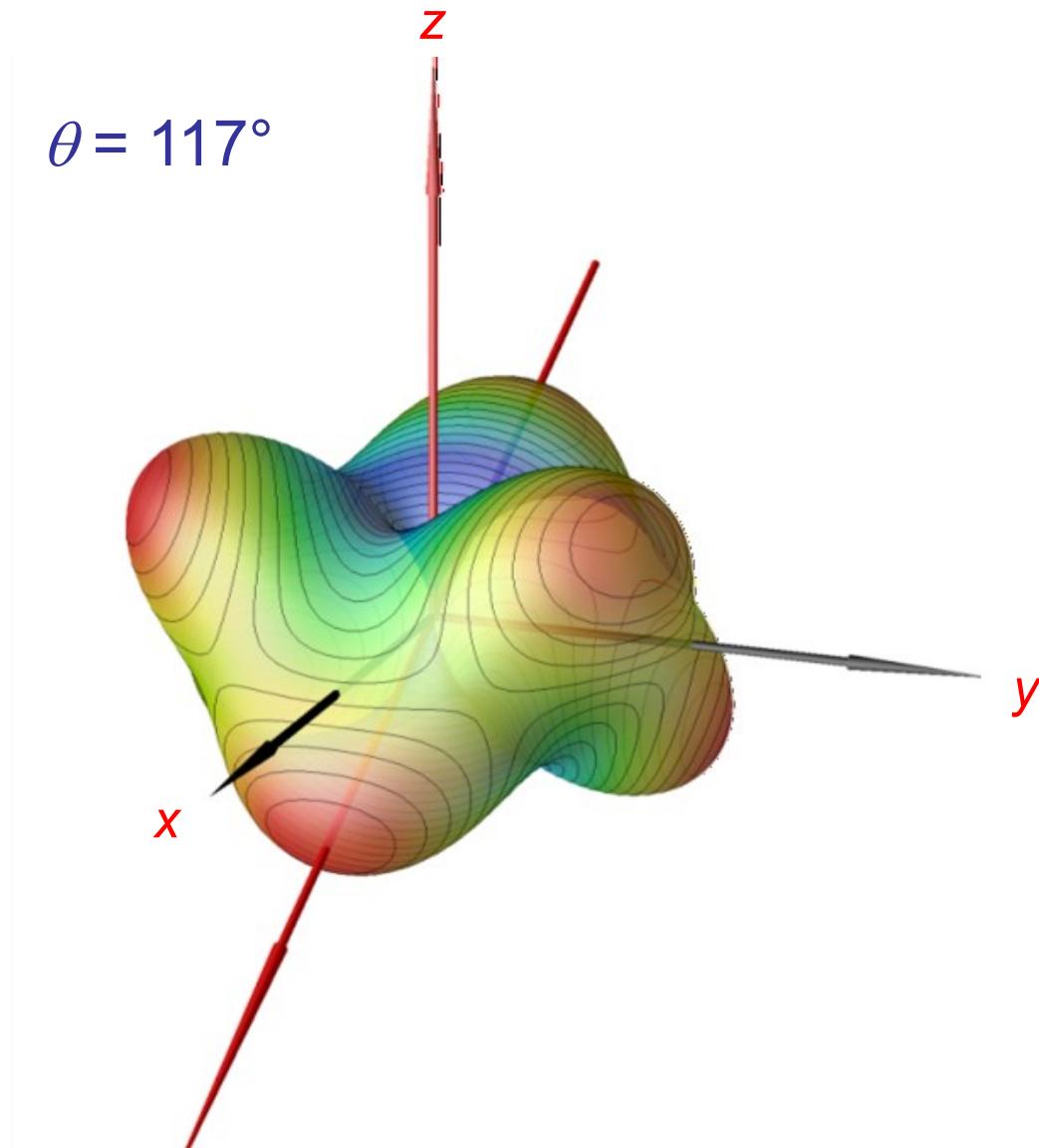
Rotational energy surface, $J = 60$



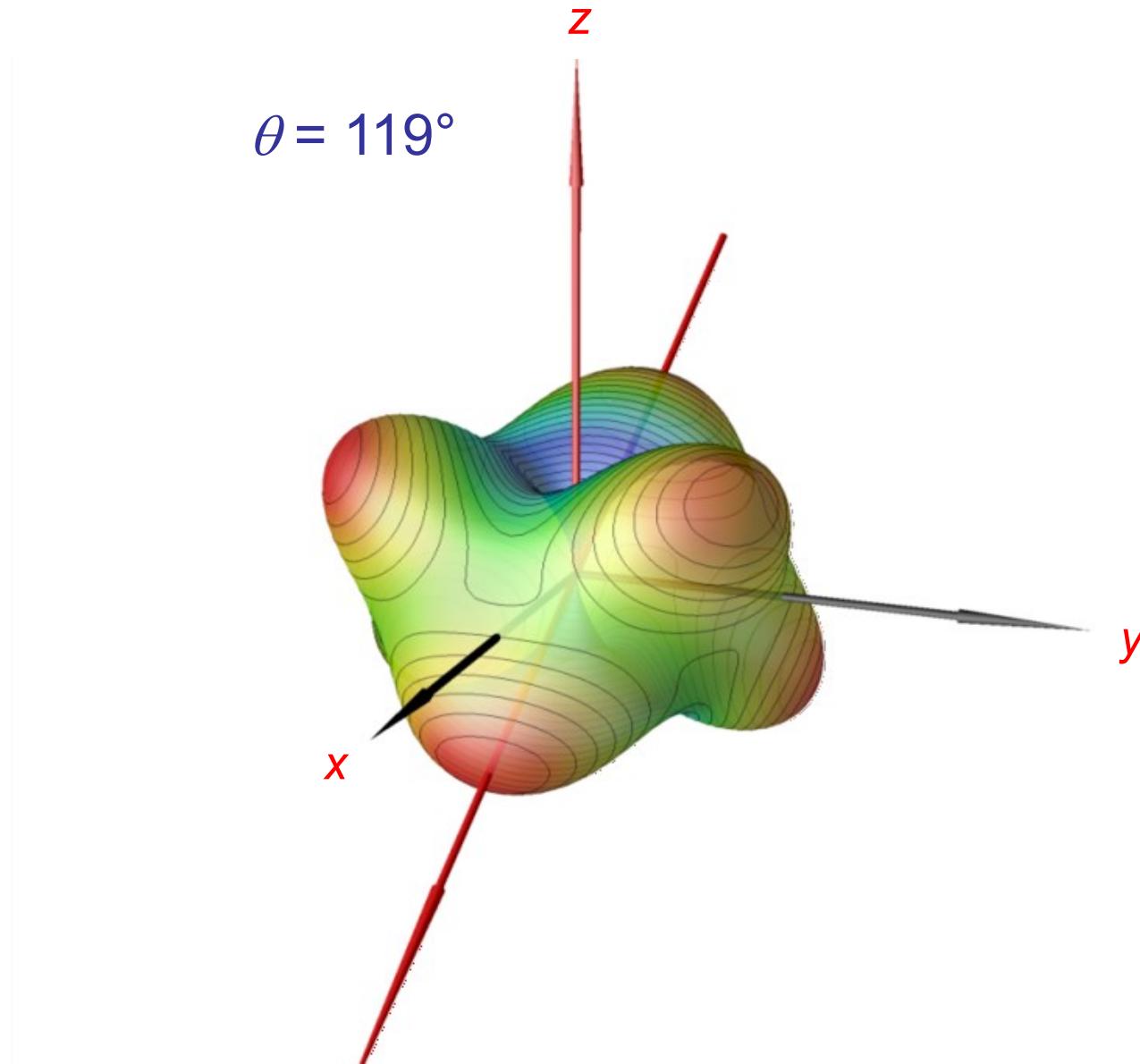
Rotational energy surface, $J = 80$



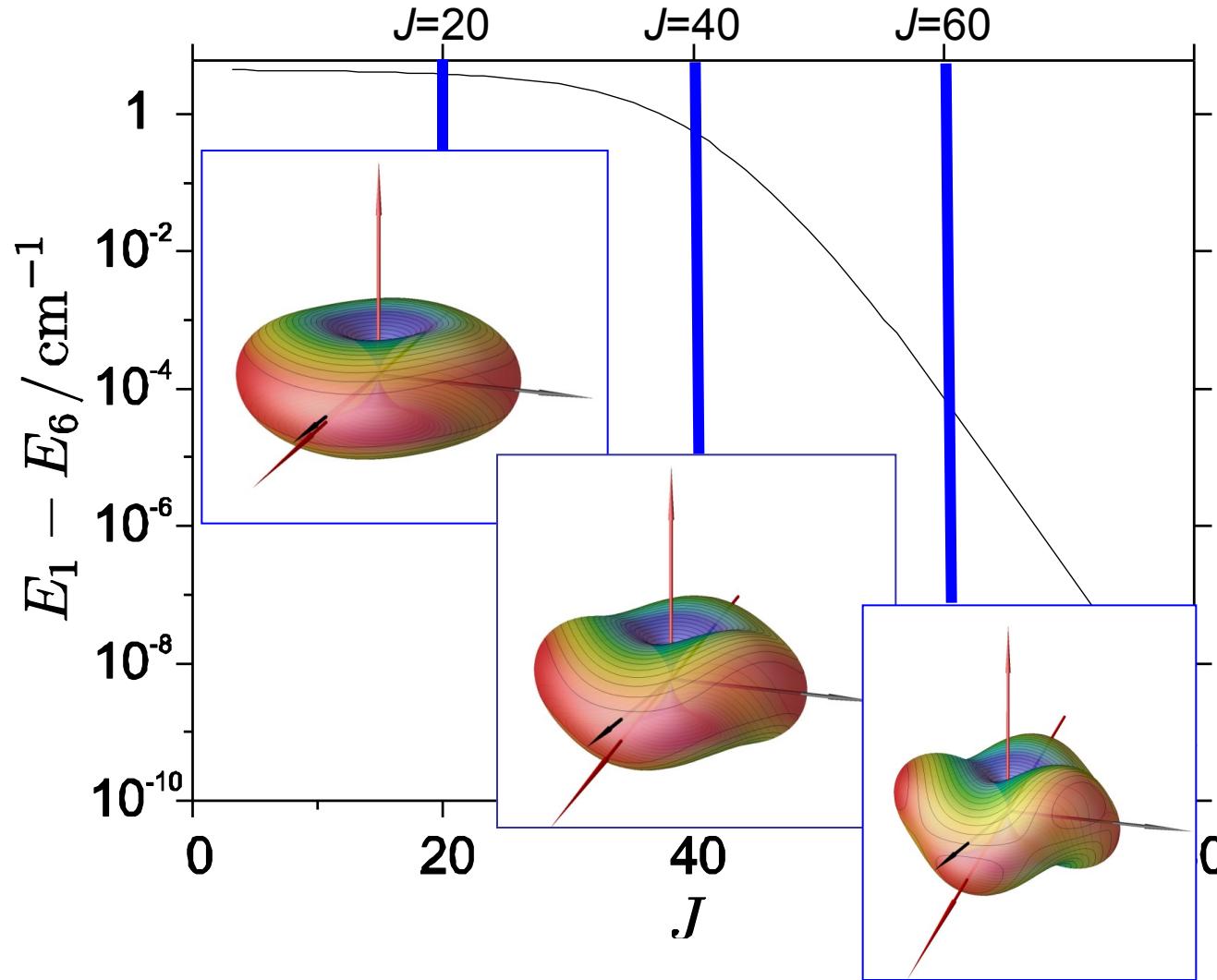
Rotational energy surface, $J = 100$



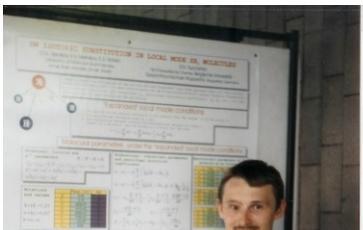
Rotational energy surface, $J = 120$



“Cluster spread”, vibrational ground state of PH₃



Thanks & Acknowledgments



The principal doer:

Sergei N. Yurchenko, Wuppertal, Ottawa,
Mülheim

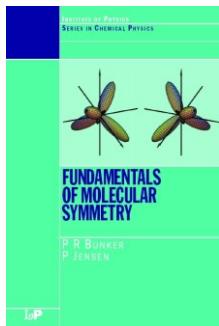
Posters related to this talk:

- H20 NH₃⁺ Tuesday 1700 hrs
 - J25 BiH₃, SbH₃ Wednesday 1100 hrs
 - L29 NH₃ Thursday 1100 hrs

Walter Thiel, Mülheim

Thanks for support from the European Commission,
the German Research Council (DFG), and the Foundation
of the German Chemical Industry (Fonds der Chemie).

You are cordially invited to ...



... buy a copy of “Fundamentals of Molecular Symmetry” by P. R. Bunker and PJ

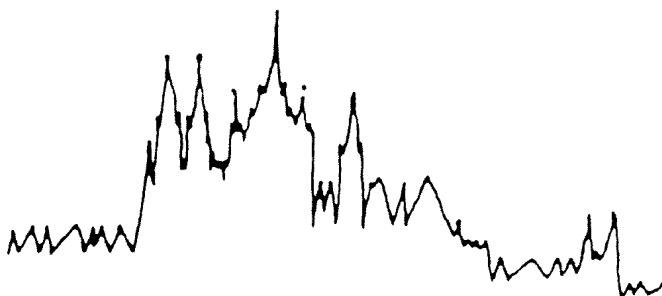
[http://www.crcpress.com/shopping_cart/products/
product_contents.asp?id=&parent_id=&sku=IP298&pc](http://www.crcpress.com/shopping_cart/products/product_contents.asp?id=&parent_id=&sku=IP298&pc)

... apply for a young-researcher position in the
EU Marie Curie research training network
QUASAAR



<http://www.chem.uni-wuppertal.de/quasaar>

... PRAHA2006



<http://www.chem.uni-wuppertal.de/conference>