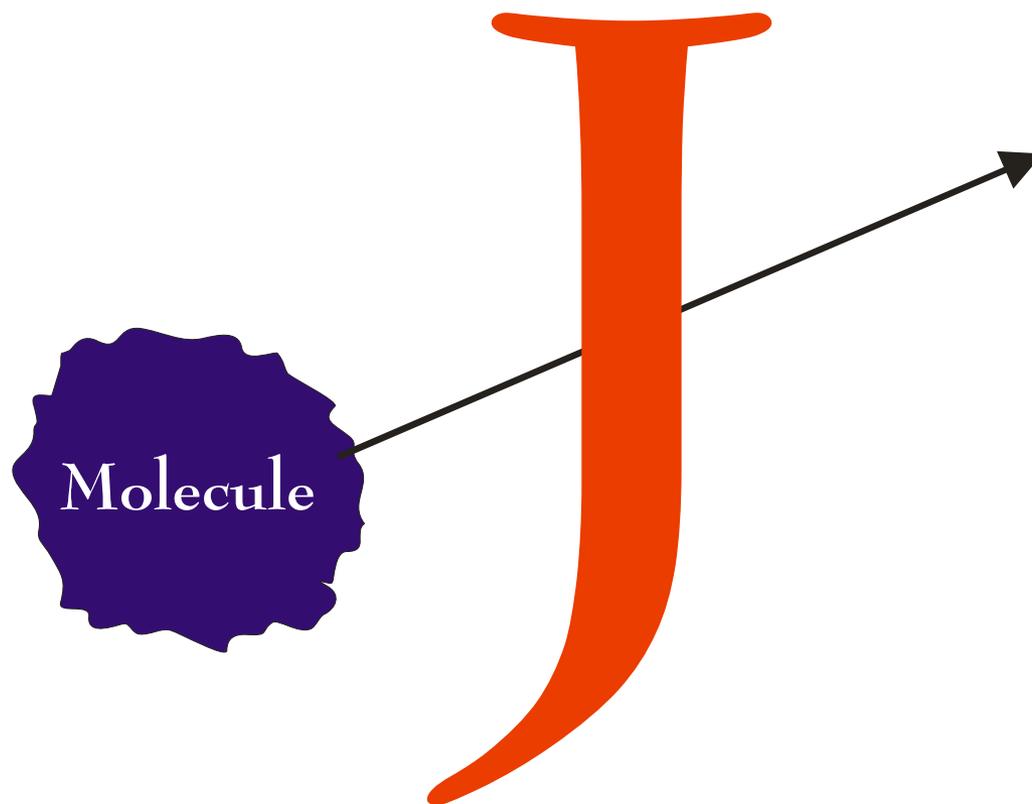
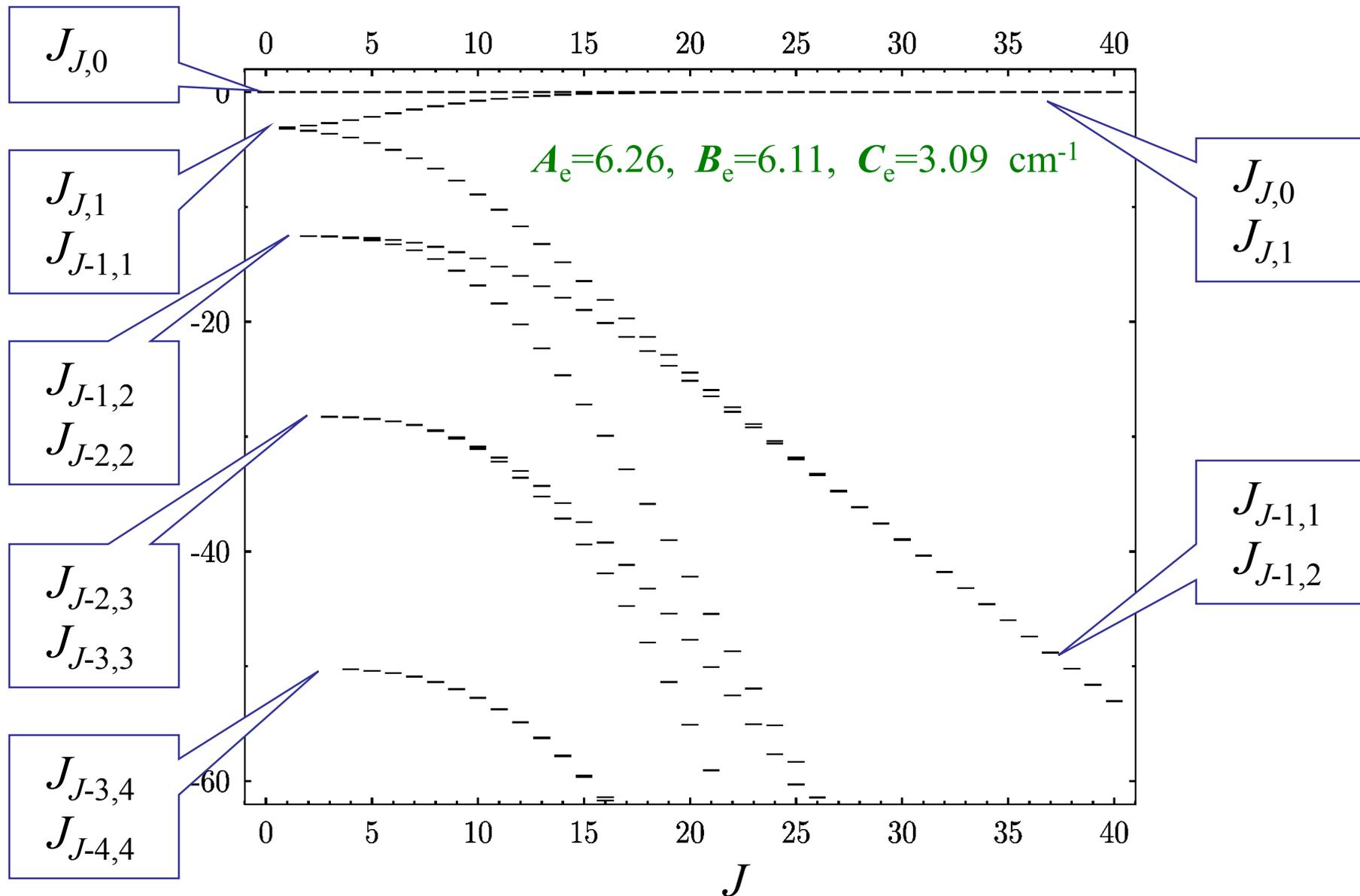


Molecules in highly excited rotational states

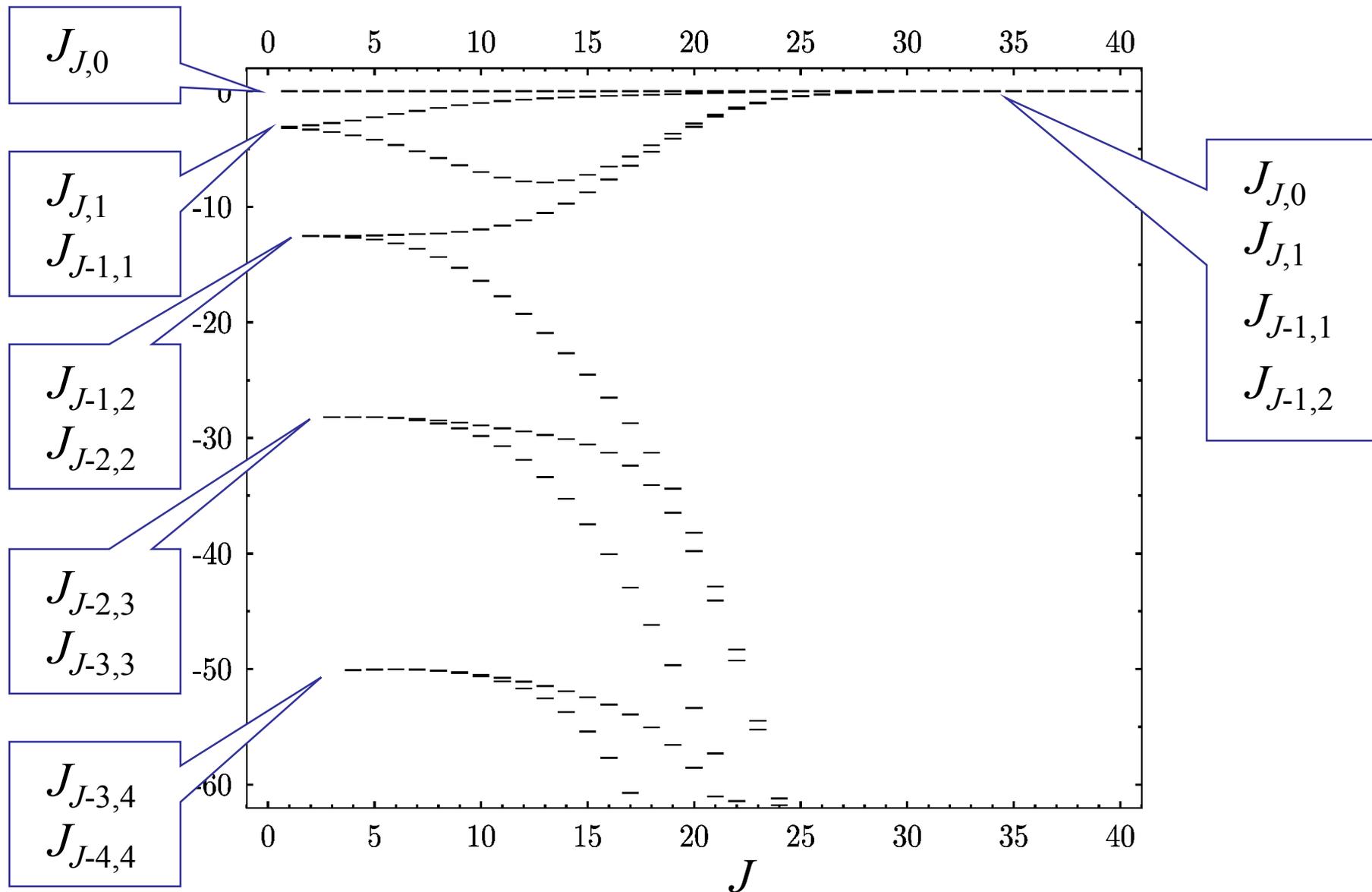


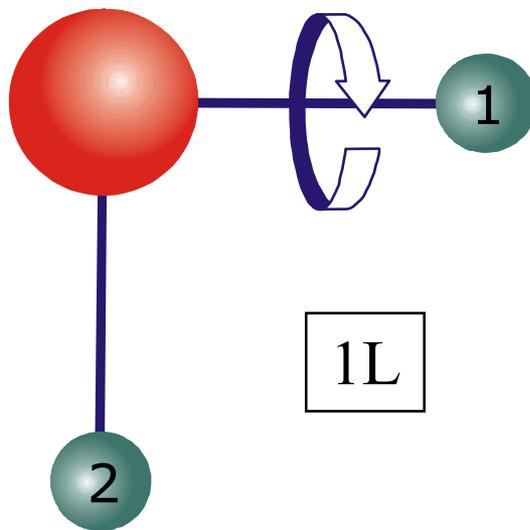
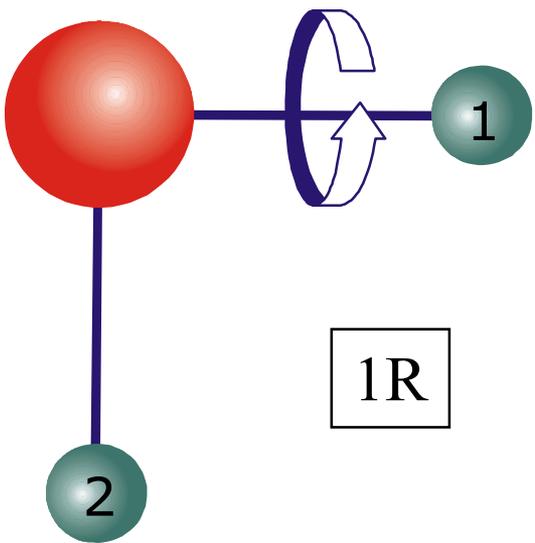
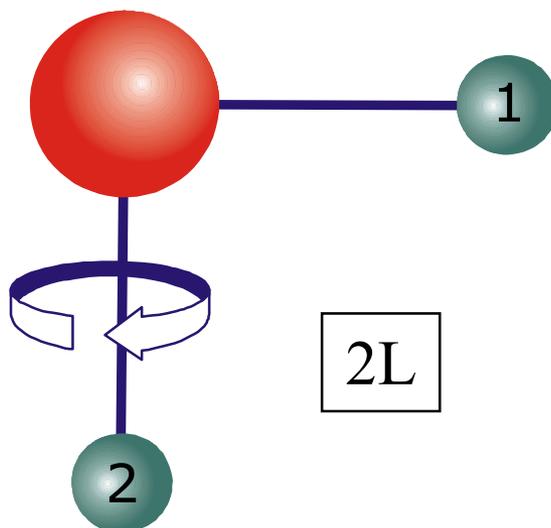
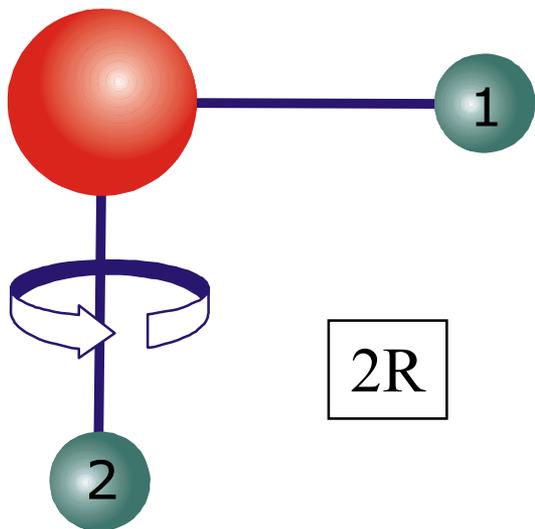
$$J \sim 100$$

H₂Te Rigid Rotor Energy Levels [$E(J_{K_a,K_c})-E(J_{J,0})$]



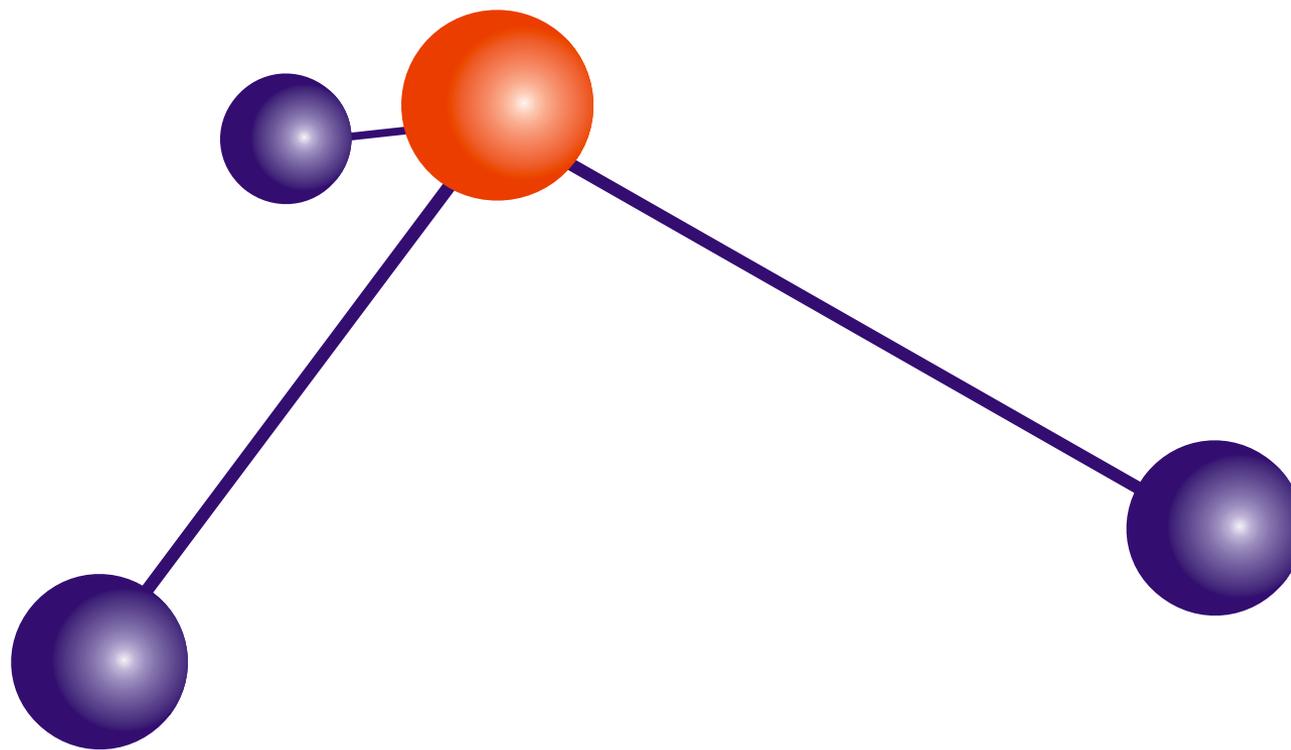
Actual H₂Te Energy Levels [$E(J_{K_a,K_c})-E(J_{J,0})$]





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

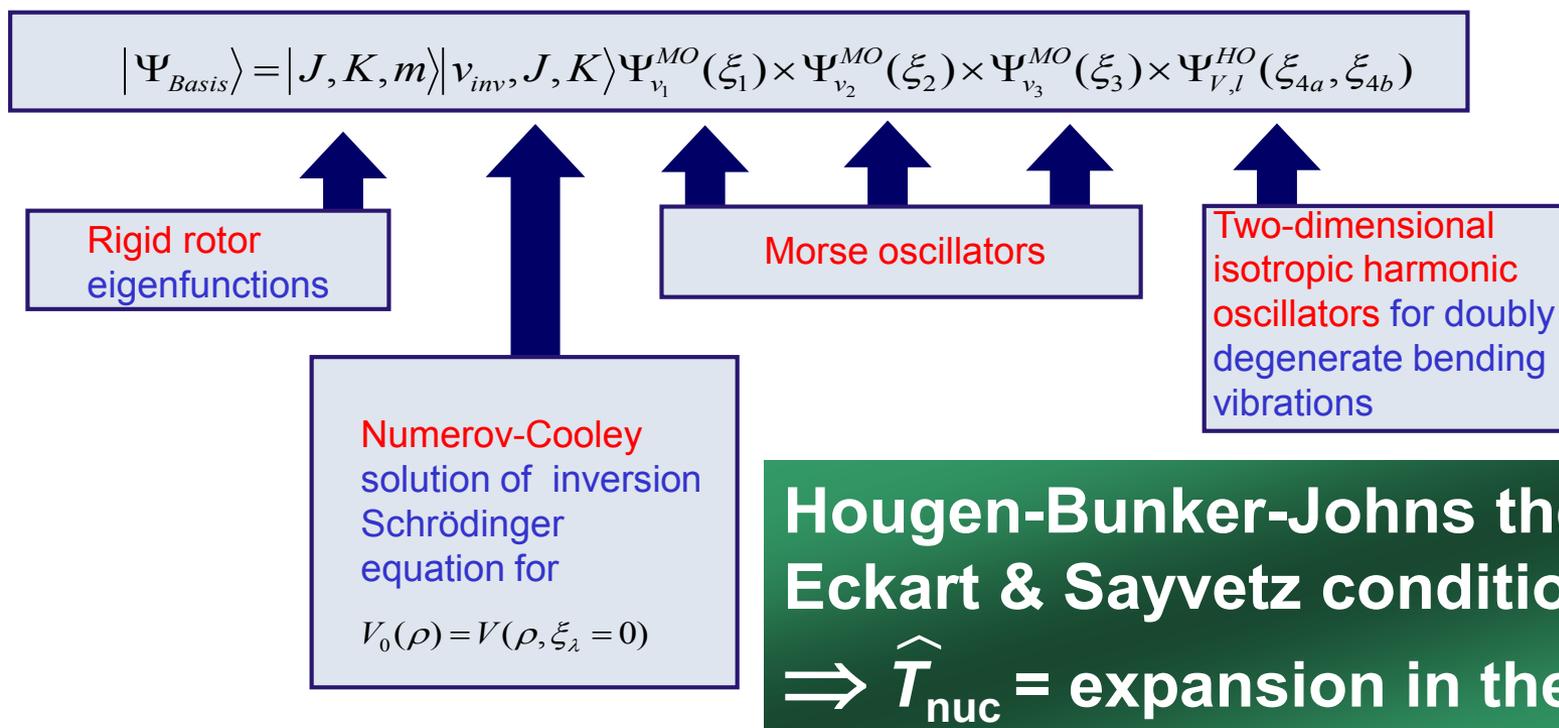
$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in } C_{2v}(M)$$



Are there similar effects for XH_3 molecules – say PH_3 ?

We investigate by variational rotation-vibration calculations

Basis functions:



[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:

$$2(v_1 + v_2 + v_3) + v_{inv} + V_{bend} \leq 6$$

Potential energy surface:

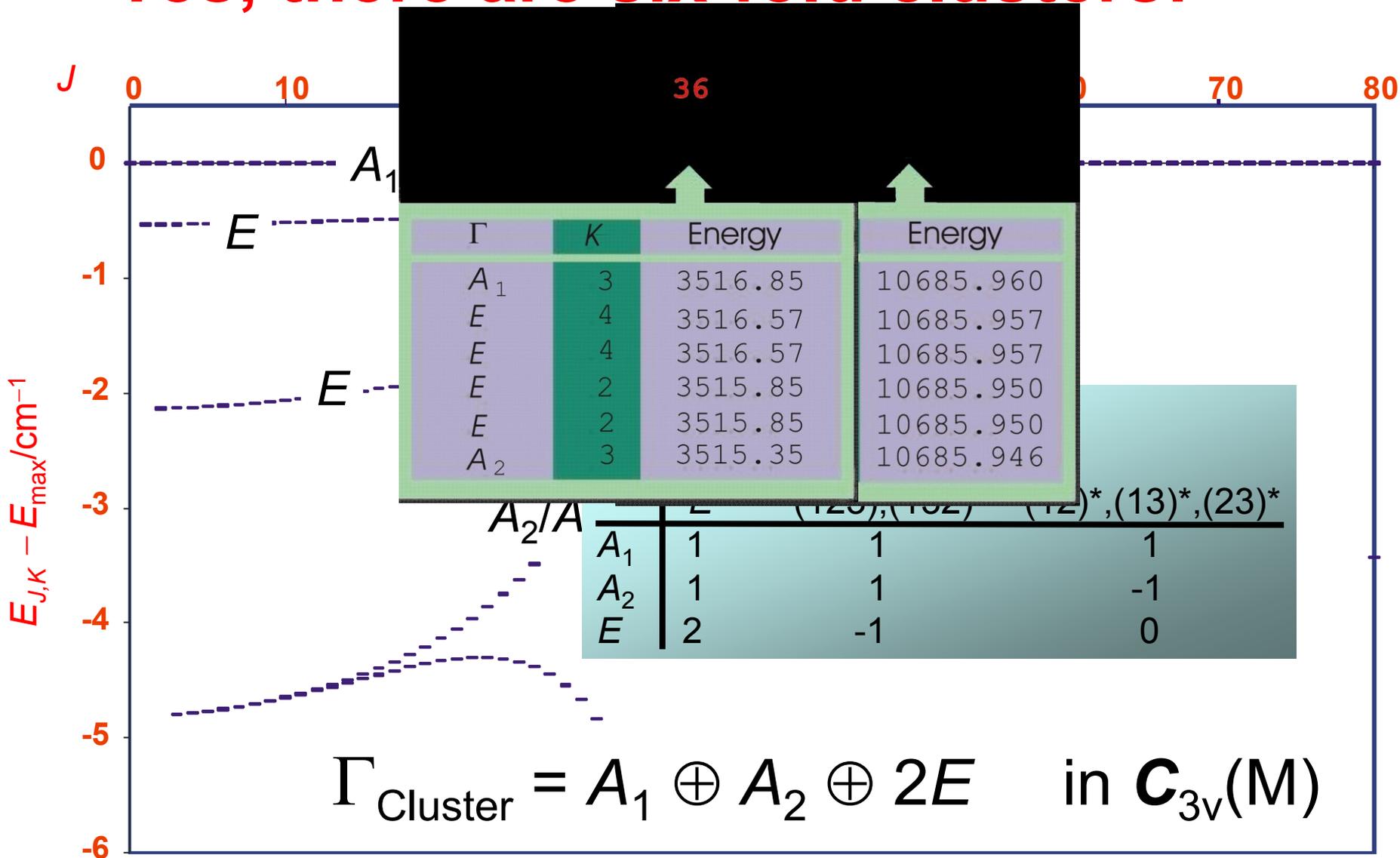
cc-pwCVTZ [1]

refined by fitting to experimental
vibrational term values [2]

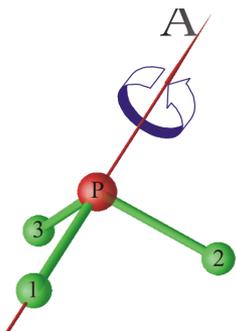
[1] D. Wang, Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.*, **112**, 9624 (2000)

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

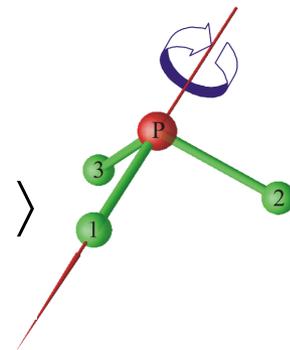
Yes, there are six-fold clusters!



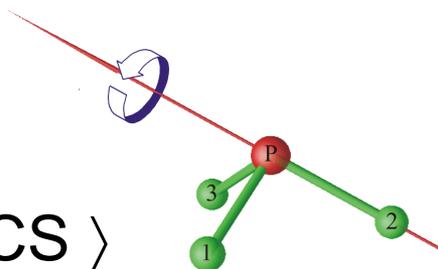
$$|1 \text{ PCS} \rangle = E |1 \text{ PCS} \rangle$$



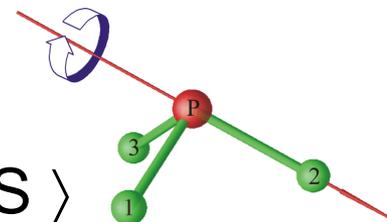
$$|4 \text{ PCS} \rangle = (23)^* |1 \text{ PCS} \rangle$$



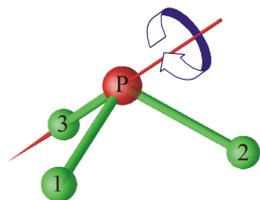
$$|2 \text{ PCS} \rangle = (123) |1 \text{ PCS} \rangle$$



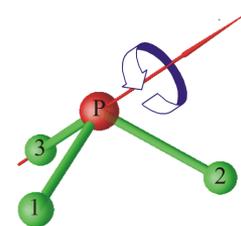
$$|5 \text{ PCS} \rangle = (12)^* |1 \text{ PCS} \rangle$$



$$|3 \text{ PCS} \rangle = (132) |1 \text{ PCS} \rangle$$

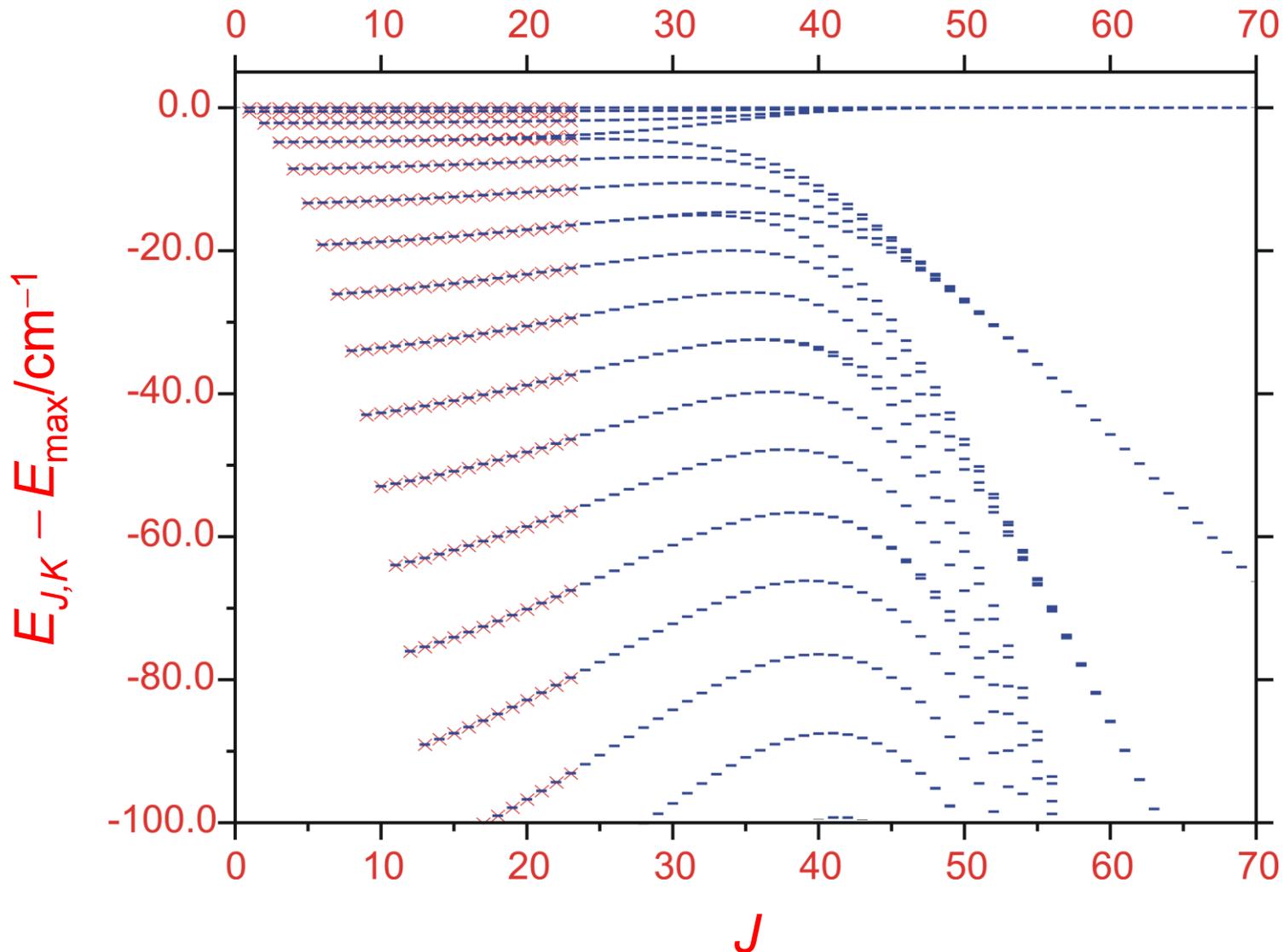


$$|6 \text{ PCS} \rangle = (13)^* |1 \text{ PCS} \rangle$$



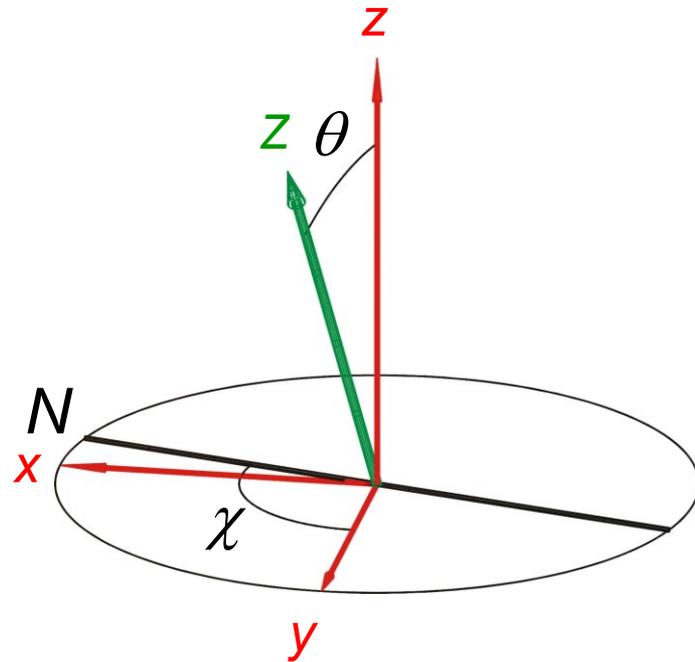
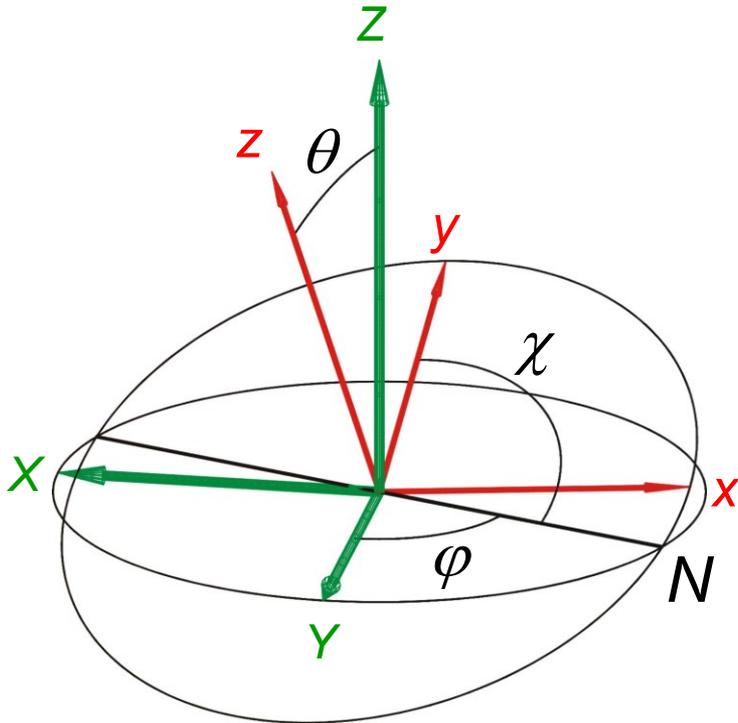
$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M)$$

Watson-type Hamiltonian for PH₃



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).

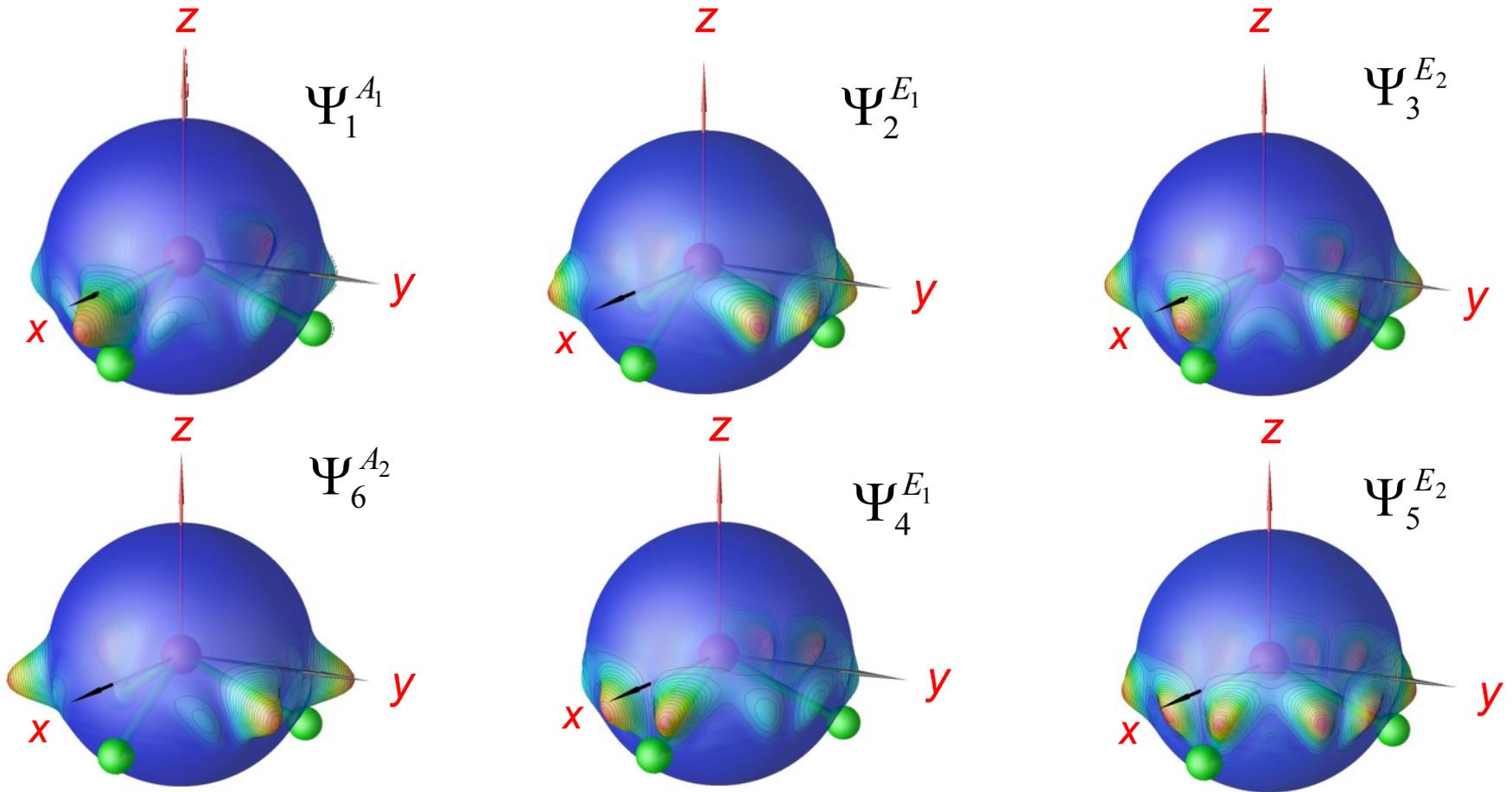
For a rovibronic eigenstate Φ_i

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

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 PH₃**

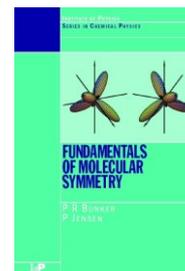
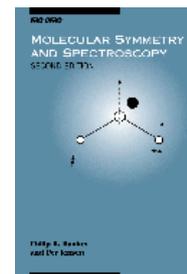
Primitive cluster states $|j \text{ PCS} \rangle$

First symmetrize, e.g.

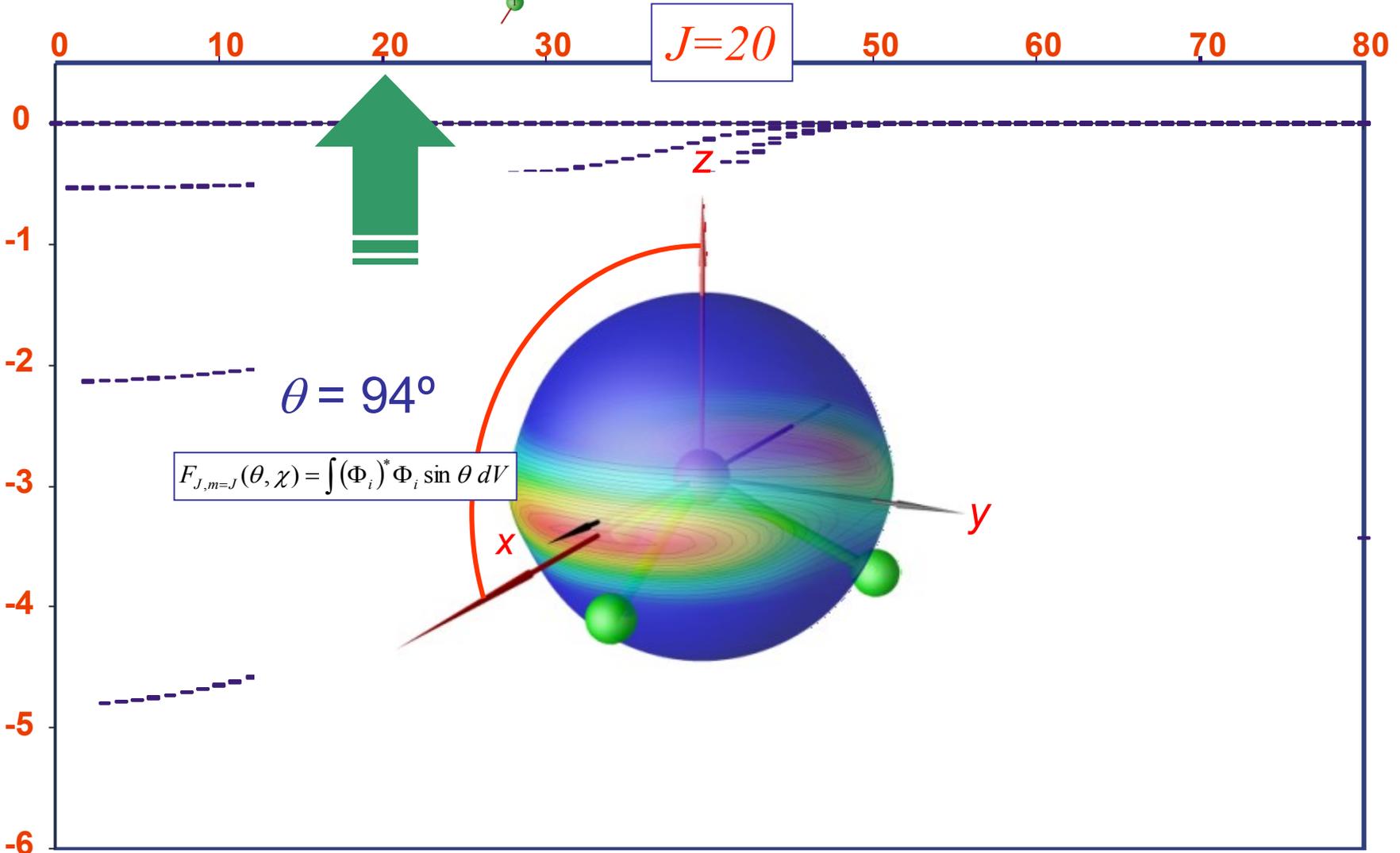
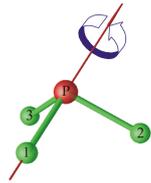
$$\Psi_1^{A_1} = \frac{1}{\sqrt{6}} \left(|1 \text{ PCS} \rangle + |2 \text{ PCS} \rangle + |3 \text{ PCS} \rangle + |4 \text{ PCS} \rangle + |5 \text{ PCS} \rangle + |6 \text{ PCS} \rangle \right)$$

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

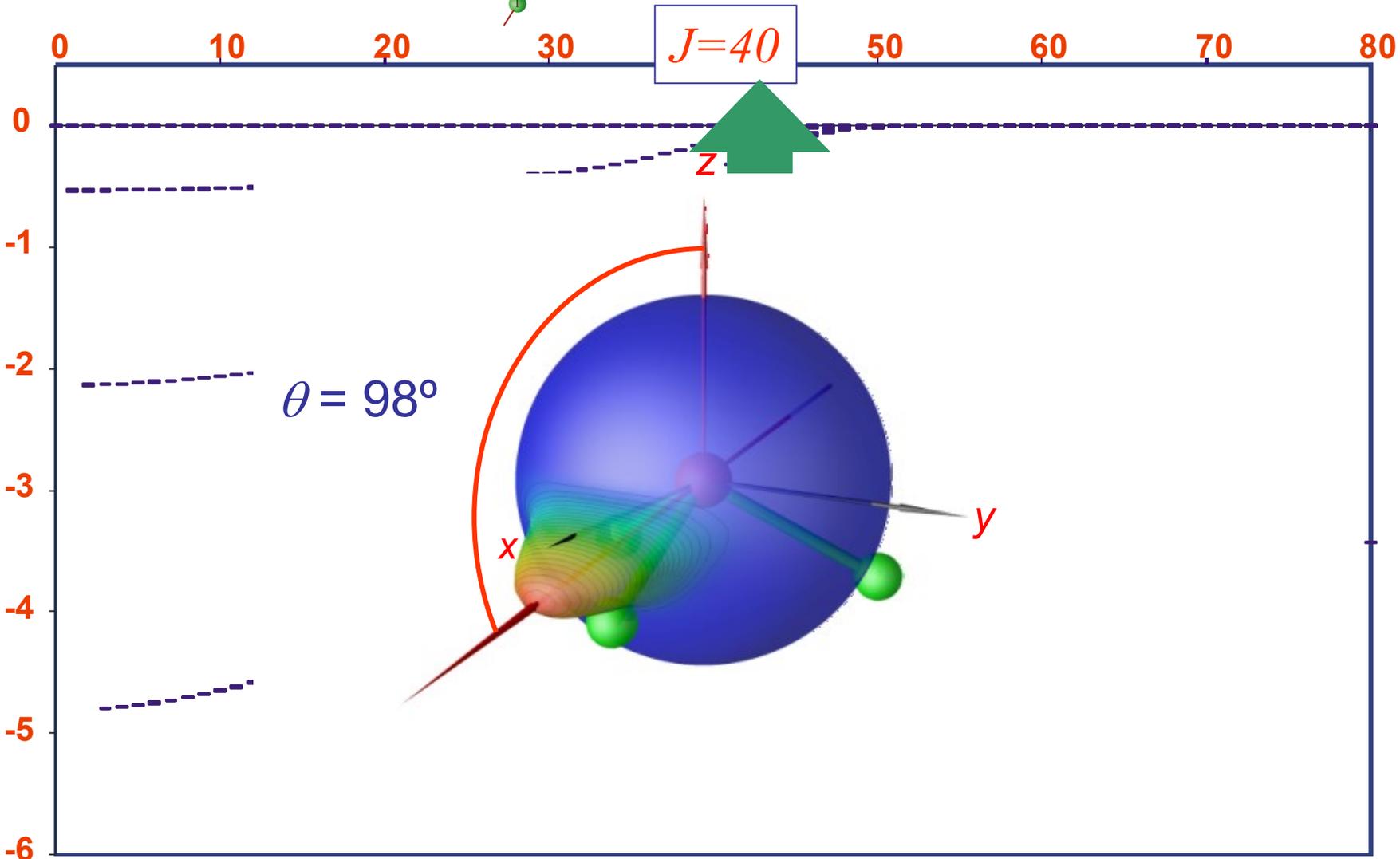
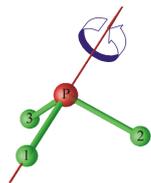
with similar expressions for the E functions....



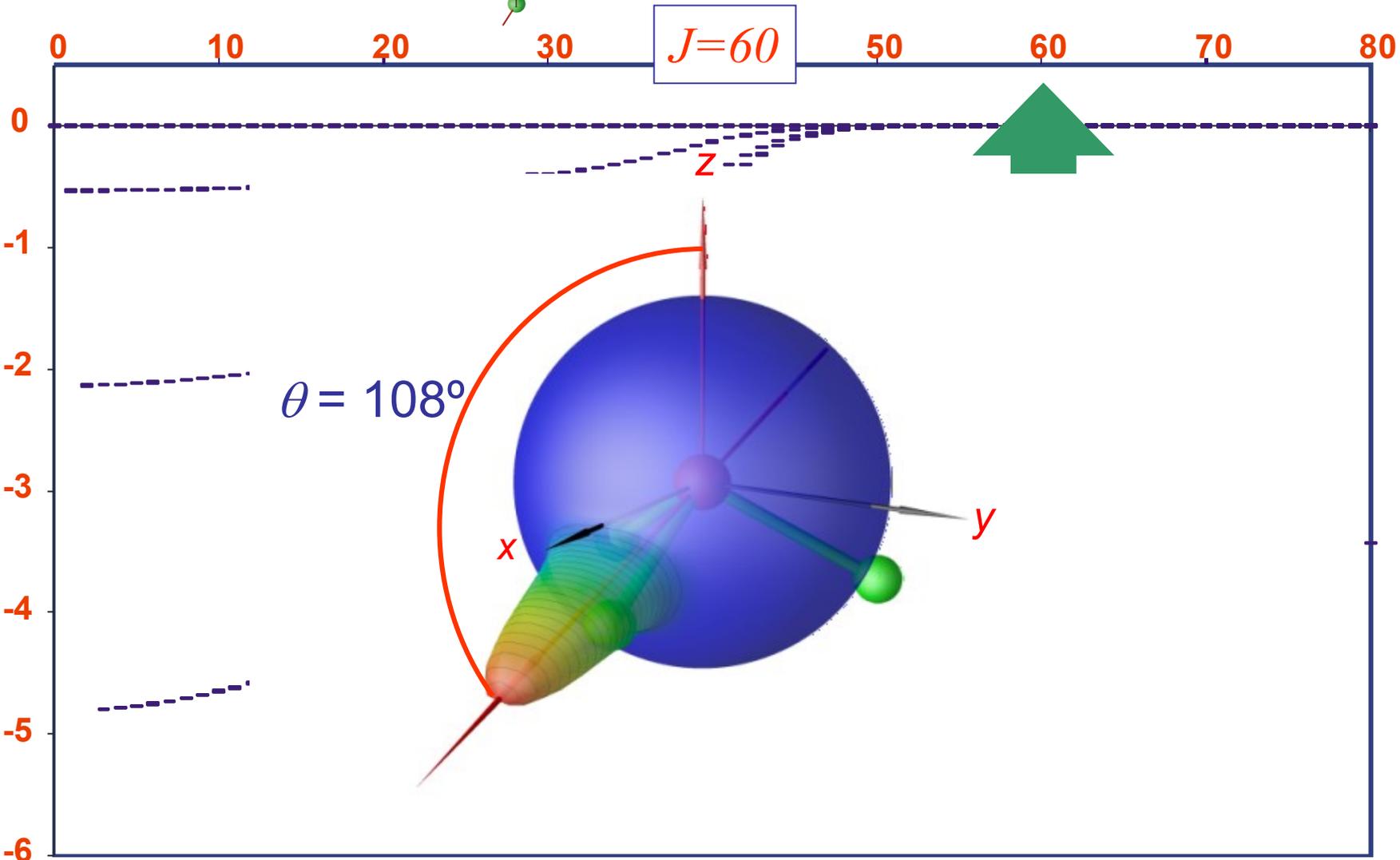
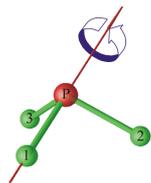
$|1 \text{ PCS} \rangle$



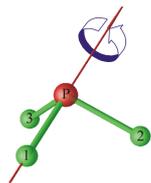
$|1 \text{ PCS} \rangle$



$|1 \text{ PCS} \rangle$

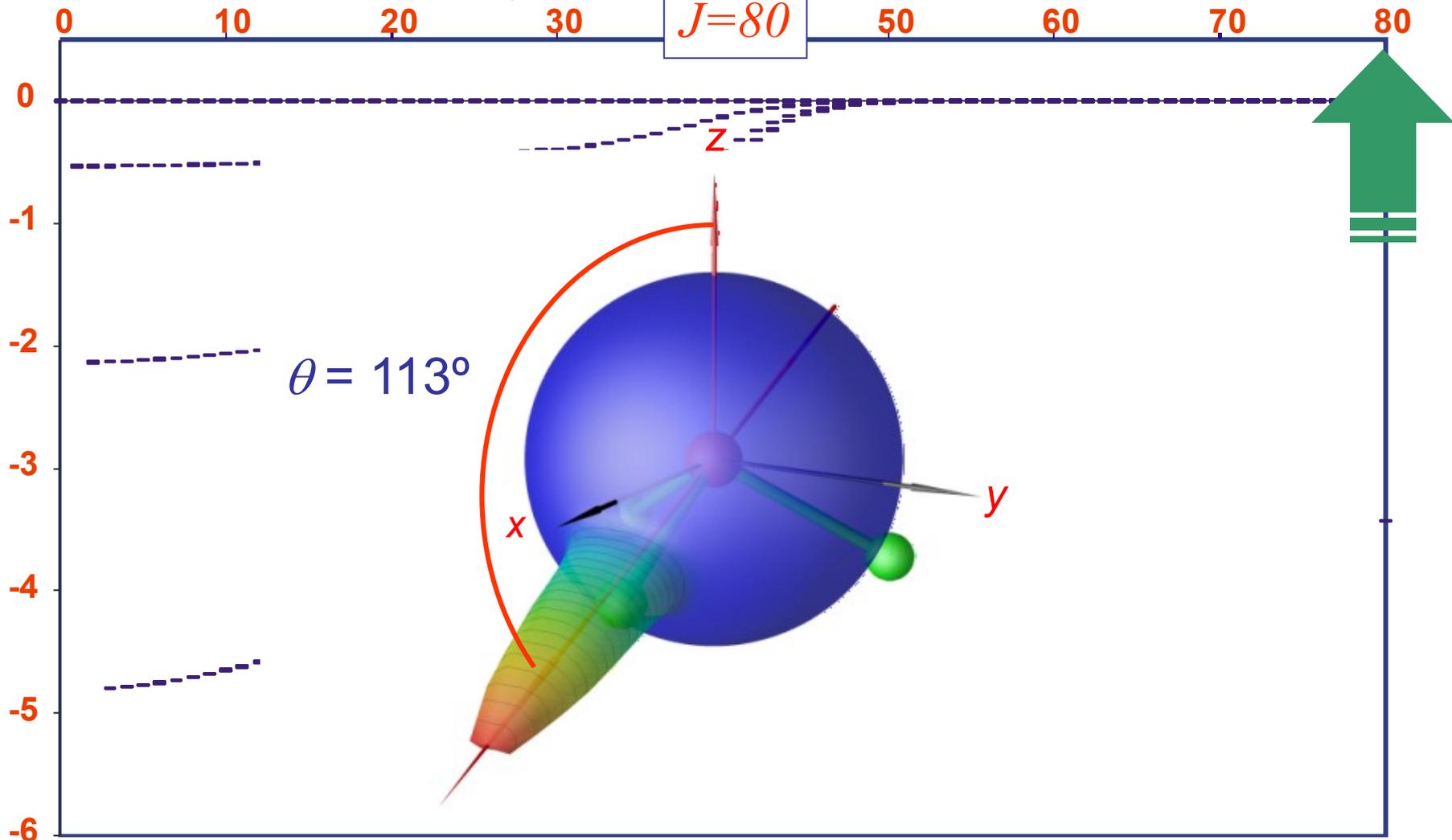


$|1 \text{ PCS} \rangle$

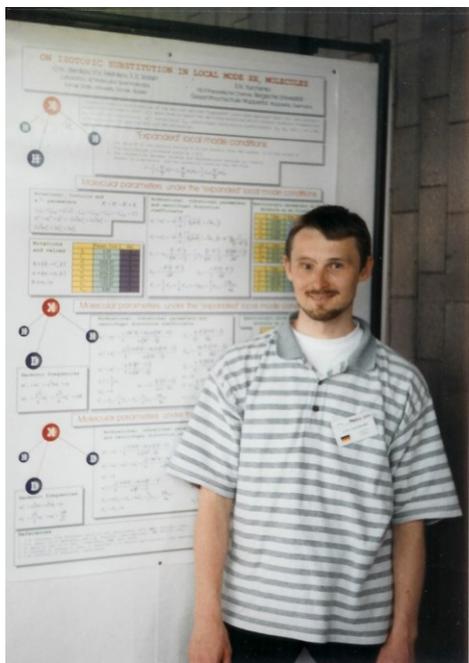


$$\theta_{\text{eq}} = 123^\circ$$

$J=80$



Thanks & Acknowledgments



The principal doer:

← **Sergei N. Yurchenko**, Wuppertal, Ottawa,
Mülheim

Other doers:

Miguel Carvajal, Huelva

Hai Lin, Minneapolis

Serguei Patchkovskii, Ottawa

A fellow ponderer:

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**).

Simulations of absorption spectra of NH_3 :

MF09 in 1153 Smith Hall at 4:01 p.m.

i.e., in 34 minutes if we're on schedule