CSD6

The Jahn-Teller theorem for graphs

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Outline

- Symmetry breaking and the Jahn-Teller effect
- Jahn-Teller distortion of a triangle
- Jahn-Teller distortions of a simplex molecule
- Jahn-Teller distortions of a complete graph
- Conclusions

References and coauthors

• with Erwin Lijnen:

Electronic degeneracy and vibrational degrees of
freedom: The permutational proof of the Jahn-Teller theorem
In: The Jahn-Teller-effect, fundamentals and implications for physics
and chemistry, H. Köppel, D. R. Yarkony, H, Barentzen (eds.) Springer, 2009

• with Erwin Lijnen, Patrick W. Fowler, Roger B. Mallion, and Tomaž Pisanski

- Graph Theory and the Jahn-Teller effect
Proc R Soc A 468:971-989 (2012)

- S5 graphs as model systems for icosahedral Jahn–Teller problems
Theor. Chem. Acc. 131:1246 (2012)

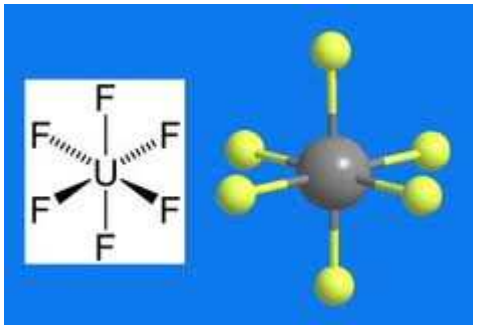
Notwithstanding the TCA aims and scope:

In many cases, theorists and computational chemists have special concerns which reach either across the vertical borders of the special disciplines in chemistry or else across the horizontal borders of structure, spectra, synthesis, and dynamics. TCA is especially interested in papers that impact upon multiple chemical disciplines.

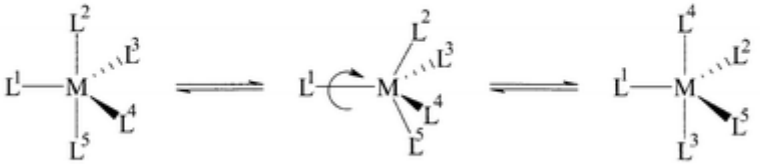
Papers focusing on graph theoretical work and quantitative structure-activity relationships are generally judged to fall outside the scope of the journal.

The concept of symmetry breaking

The symmetry breaking term of the molecular Schrödinger equation, giving rise to molecular structure, is not in the equation, but in the Born-Oppenheimer boundary conditions.



UF_6
$S_6 = 6!$: 720 operations
O_h : 48 operations



$Fe(CO)_5$
Fluxional at higher temperature
Coalescence of NMR signals.

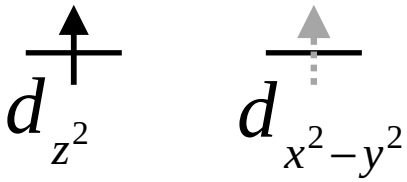
The Jahn-Teller (further) symmetry breaking for electronic degeneracies

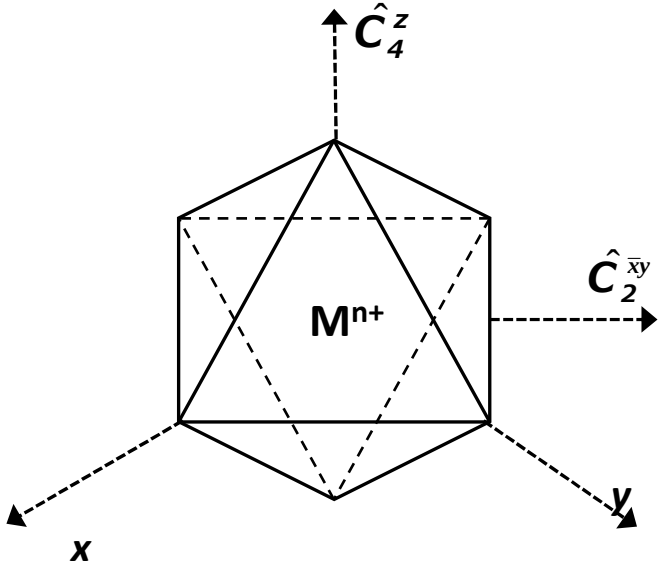
Electronic degeneracy is a typical quantum phenomenon.
It means that the wavefunction describing a given state of the system is not unique, but part of a manifold.

According to the Jahn-Teller theorem (1937):
Non-linear molecules in an orbitally degenerate electronic state are unstable. Their nuclear configuration is subject to <u>spontaneous</u> distortion forces which lower the symmetry to a geometry where the electronic degeneracy is lifted.

The Jahn-Teller (further) symmetry breaking for electronic degeneracies

Example: d^7 low-spin (or a $d^{9)}$ transition-metal octahedral complex. The highest filled orbital set is twofold ***degenerate***.



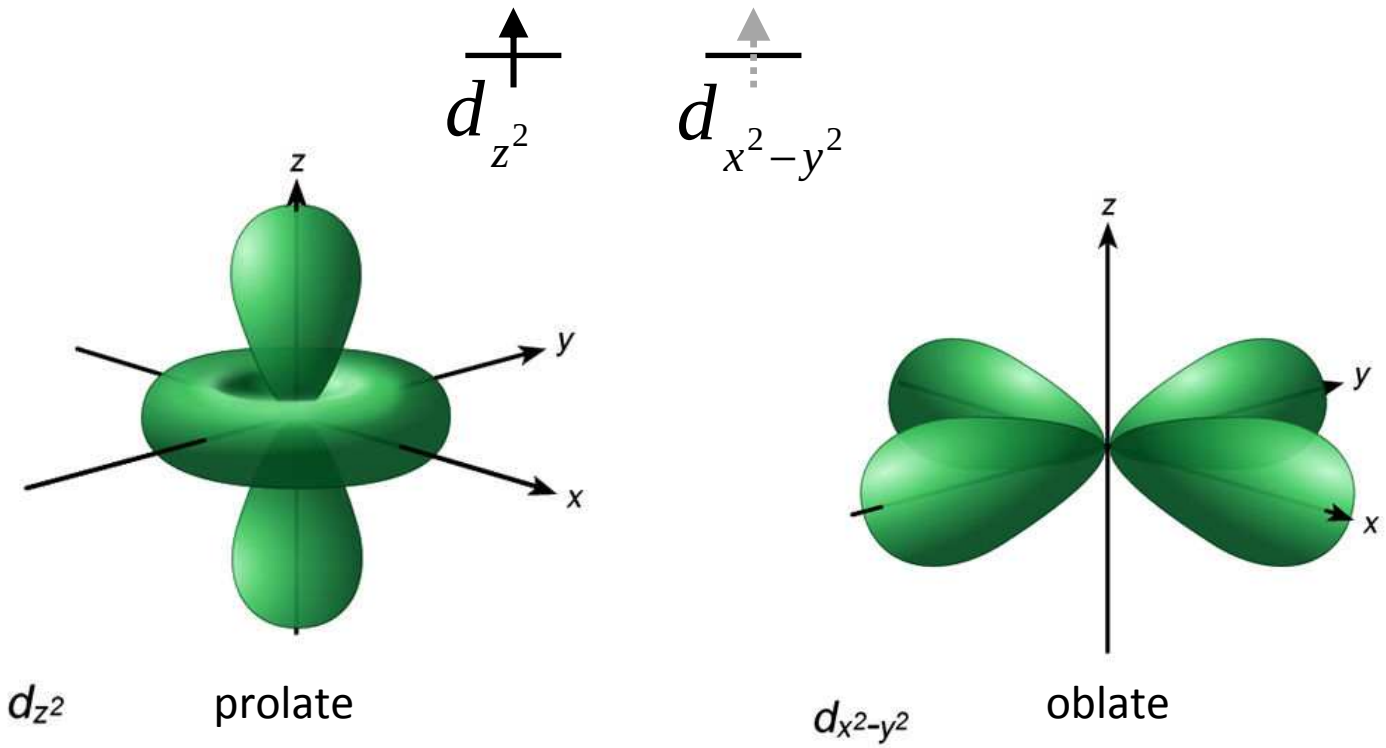


Q: In which orbital is the electron?

A: The electron cannot be assigned to an orbital, only to a space of two orbitals. Any (complex) linear combination of these functions is a valid eigenstate.

The Jahn-Teller symmetry breaking for electronic degeneracies

As a result, the shape of the central metal ion is elongated (or shortened) in the z-direction. The imbalance between electronic charge distribution and nuclear charge distribution must lead to a spontaneous breaking of symmetry.



d_{z^2} prolate

$d_{x^2-y^2}$ oblate

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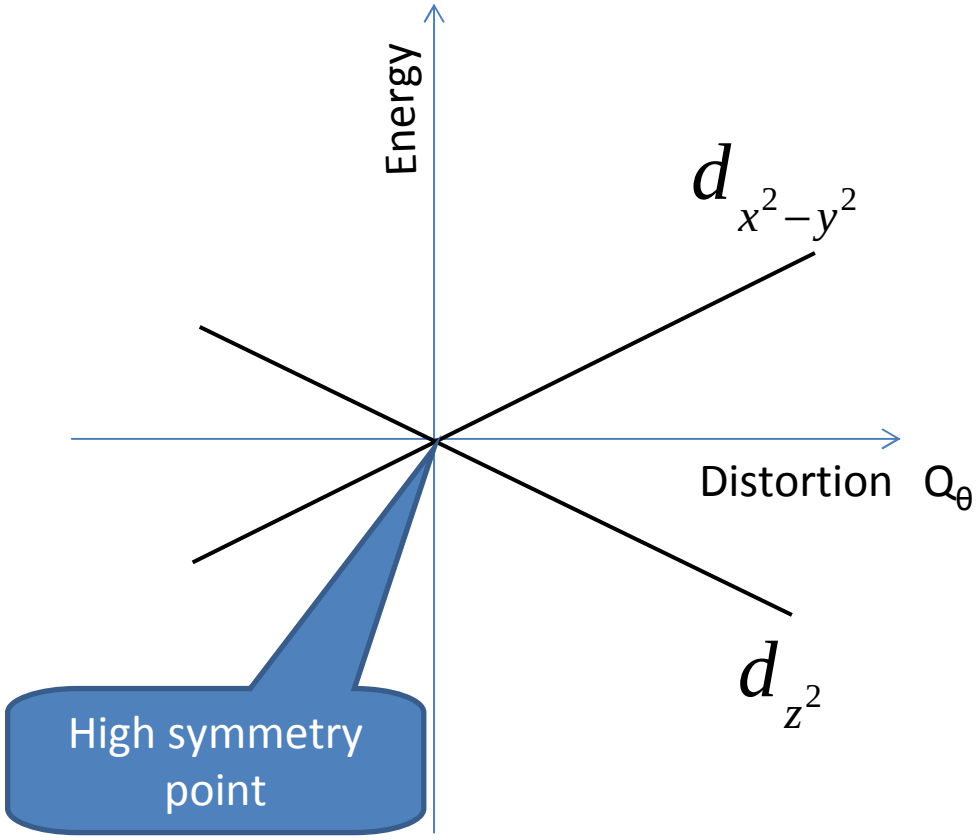
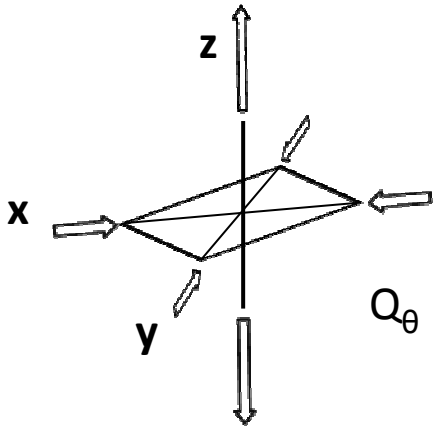
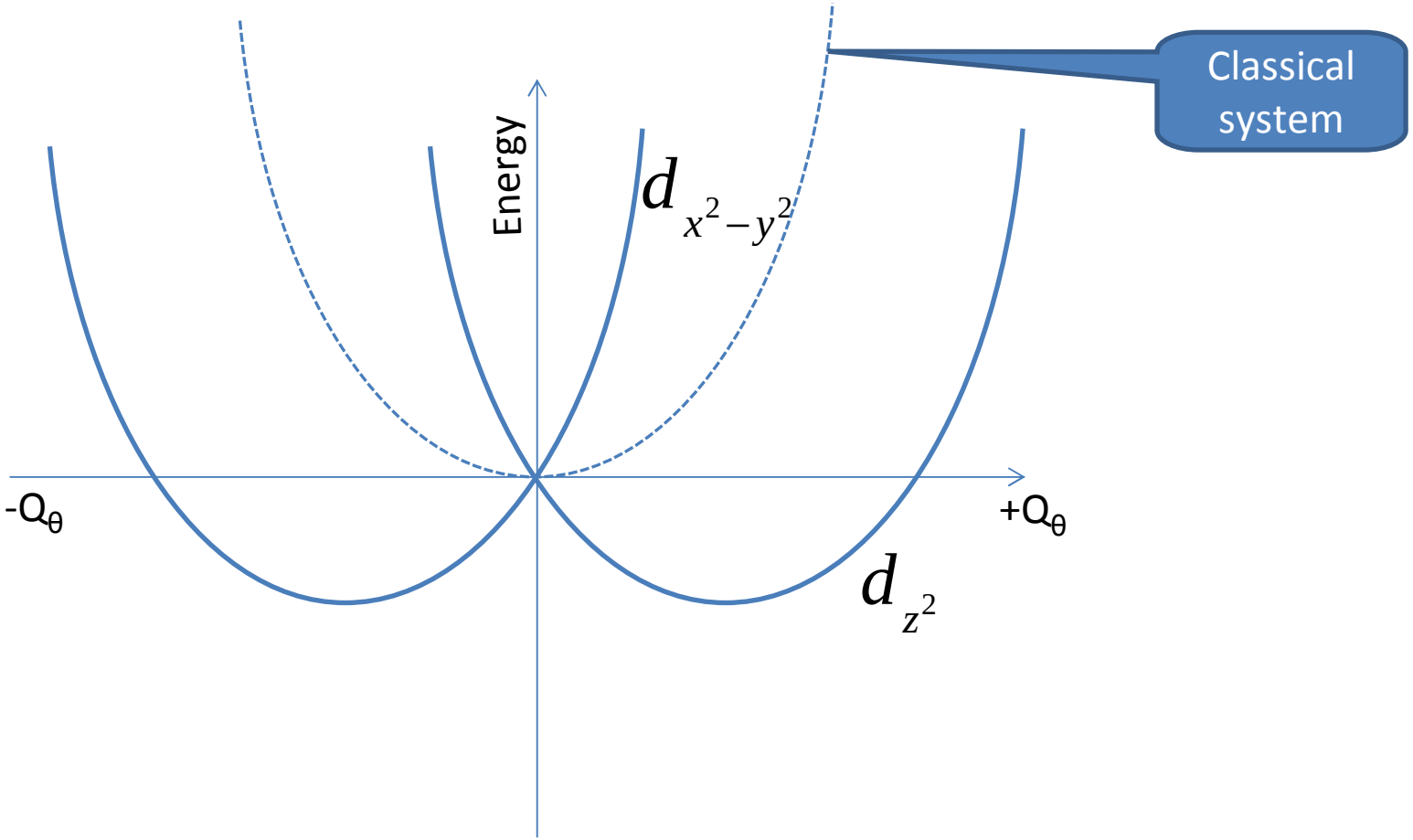
- The symmetry breaking is carried by the nuclei. Excitations of nuclear motions are **bosons**. Hence, the Jahn-Teller symmetry breaking is due to the coupling of the electrons (fermions) with bosons.

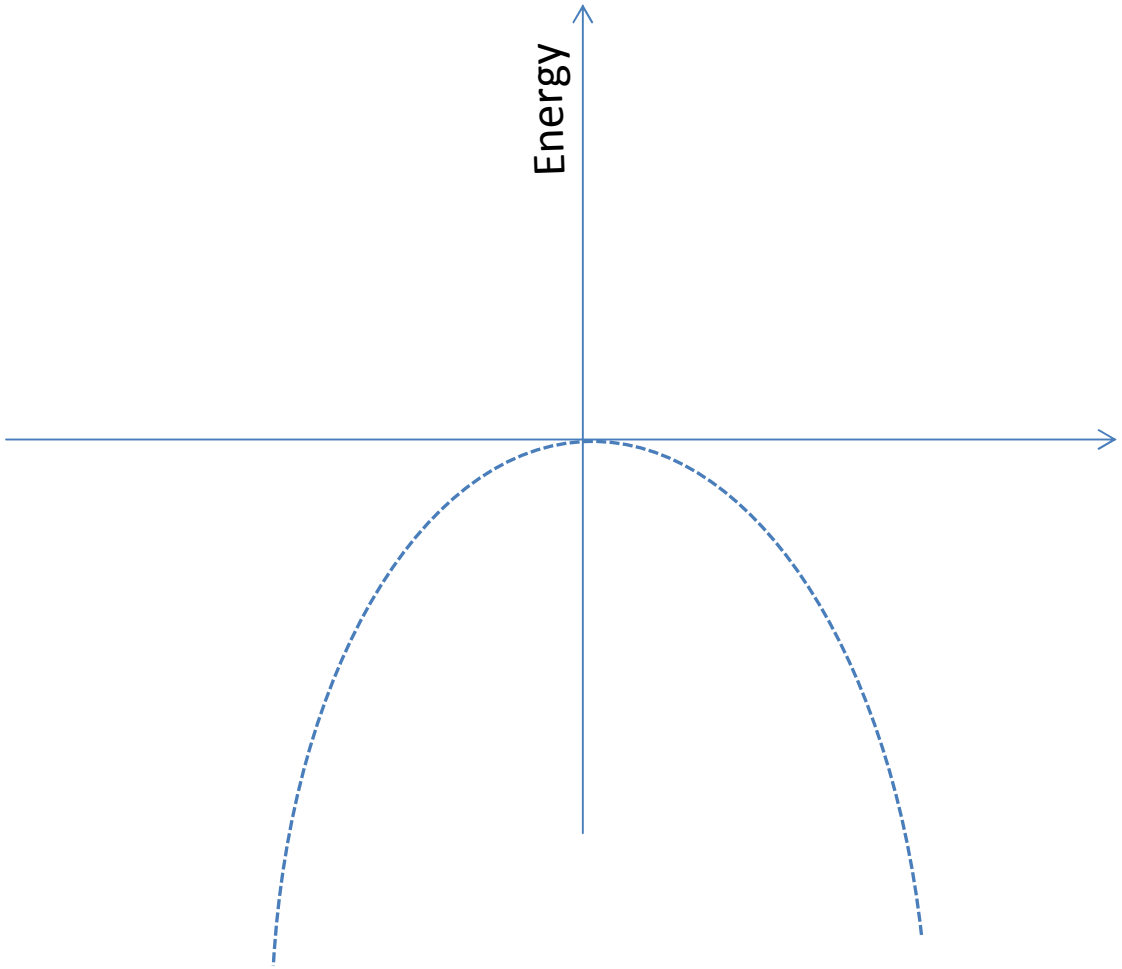
- The nuclear motion that couples to the anisotropic shape of the central metal ion is Q_θ : tetragonal elongation.





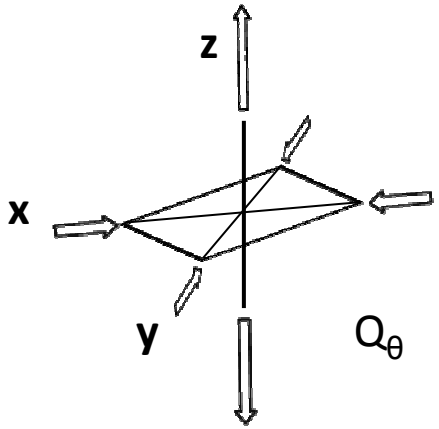
-The distortion cannot carry on for ever. At some point the harmonic restoring forces induce a new symmetry broken equilibrium.

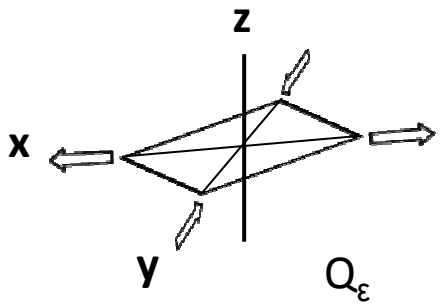


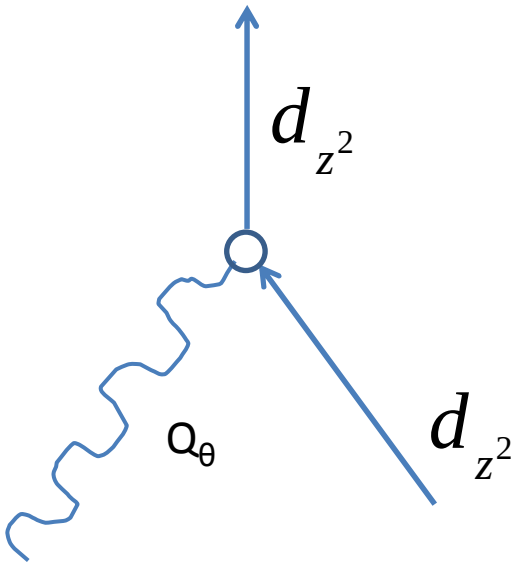


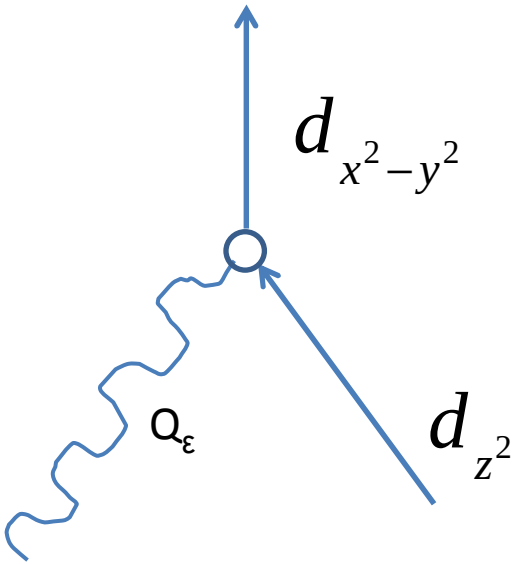
Alternative classical system: the fall of the pencil

Coupling really consists of two kinds:
-A splitting field which discriminates both orbitals: Q_θ
-A mixing field which mixes the two orbitals: Q_ε.

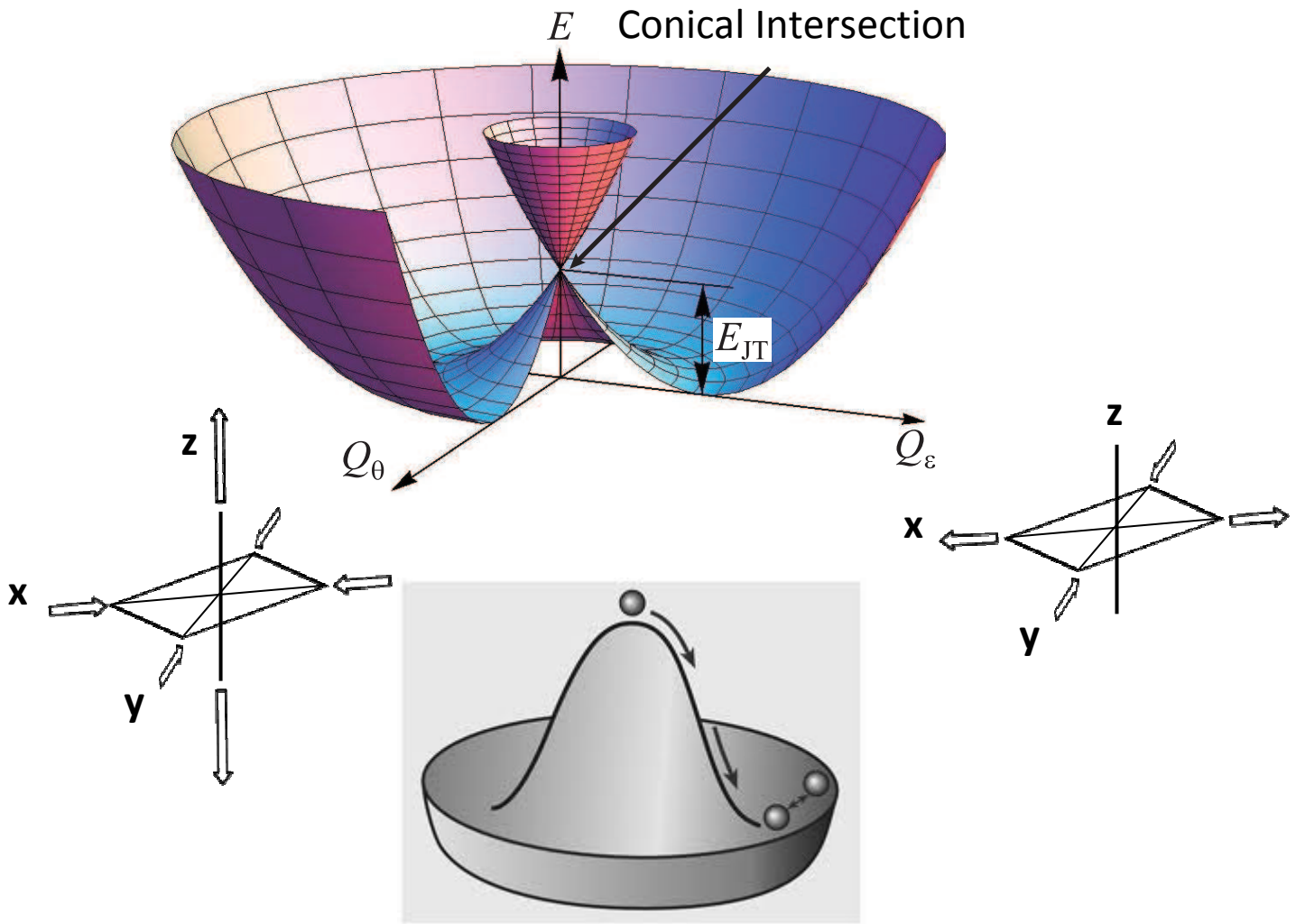




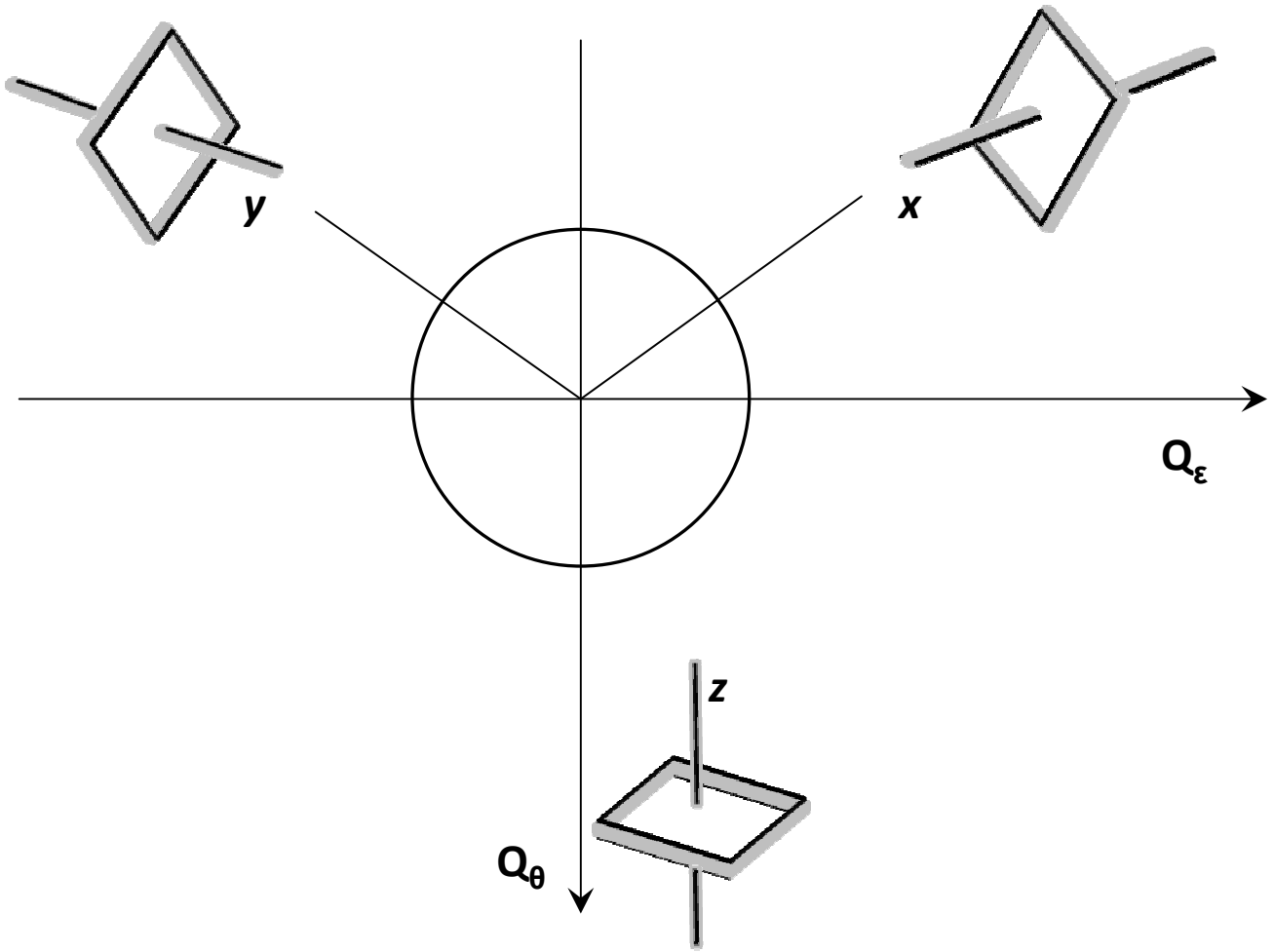




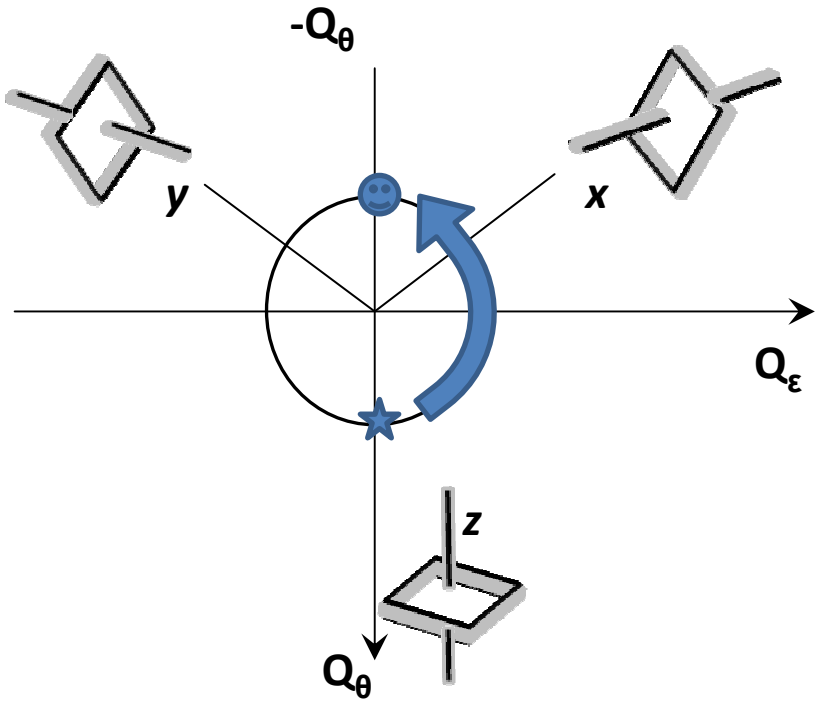
The potential energy surface is thus a surface of revolution in a two-dimensional space.
This is the famous 'Mexical hat' Jahn-Teller surface.

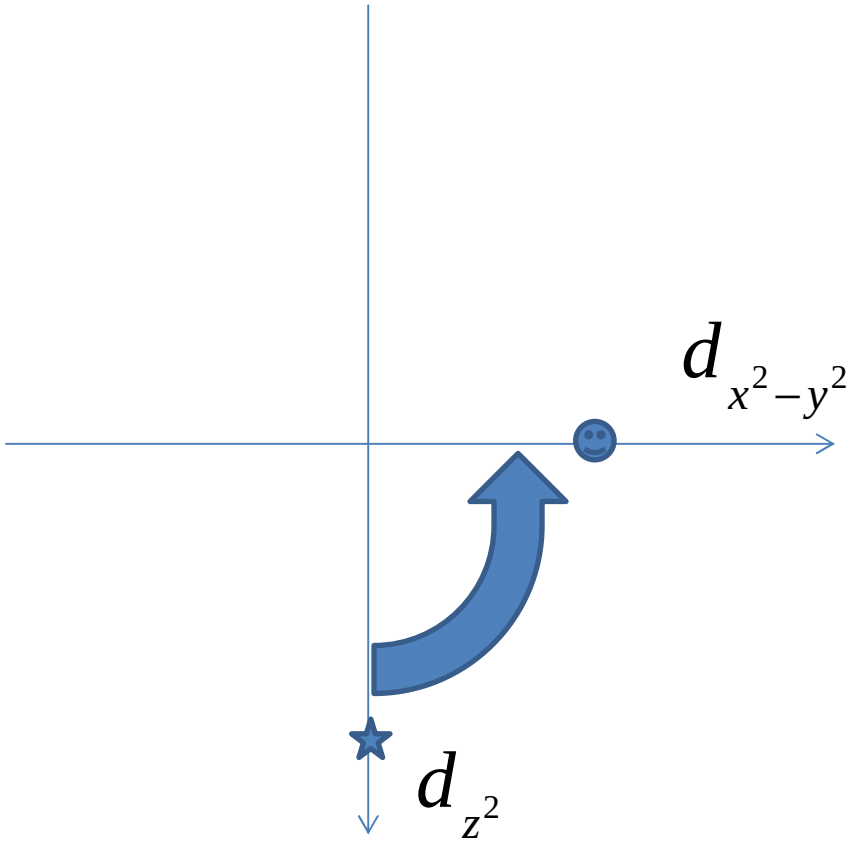


As we go around the trough of the hat, what is rotating is not the complex itself, but the distortion.

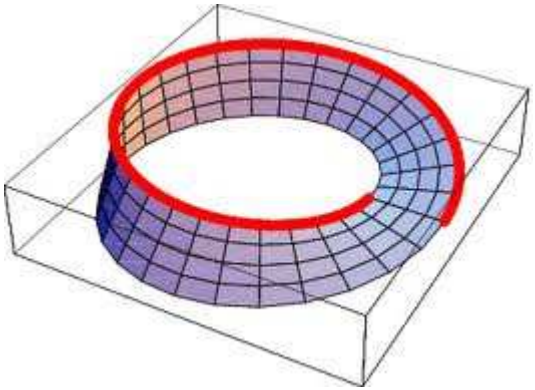


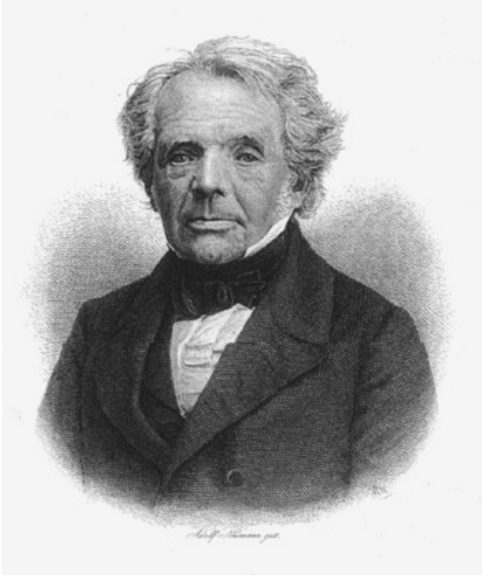
As we turn around in distortion space, the wavefunction gradually turns from d_{z2} into d_{x2-y2}, but only at half the speed.



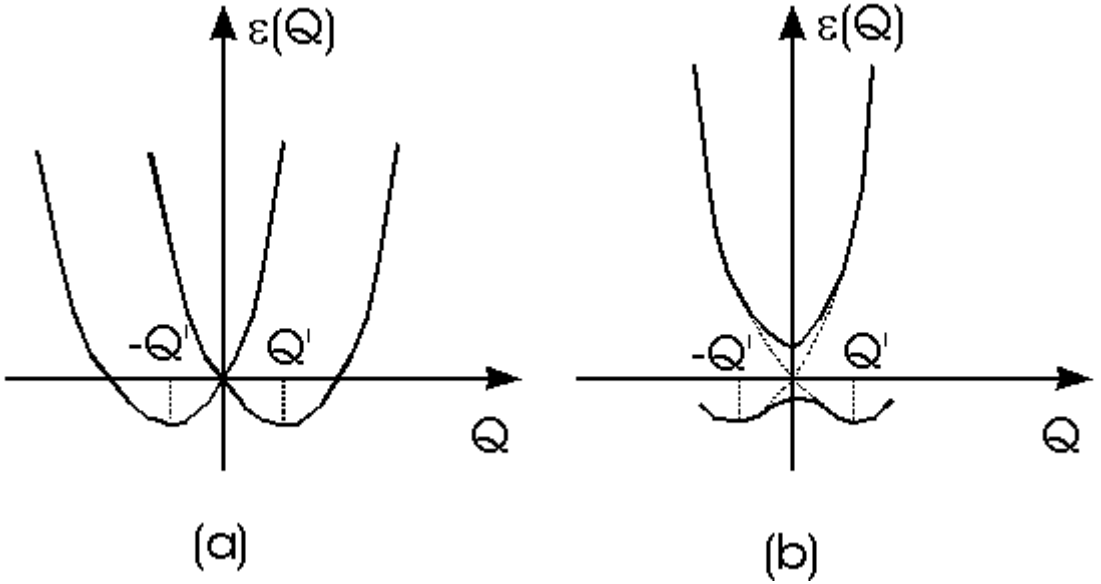


Emergent feature:
The coupling between the electronic state and the distortion is topologically equivalent to a Möbius ring topology. We have to turn around twice to reach the initial state again.





Second-order symmetry breaking

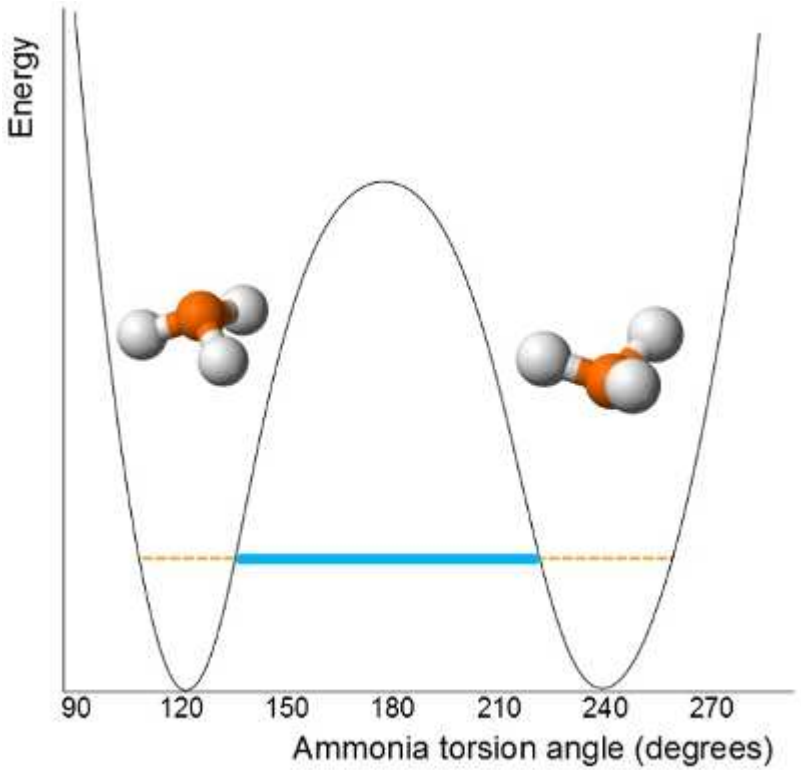


Jahn-Teller

pseudo Jahn-Teller

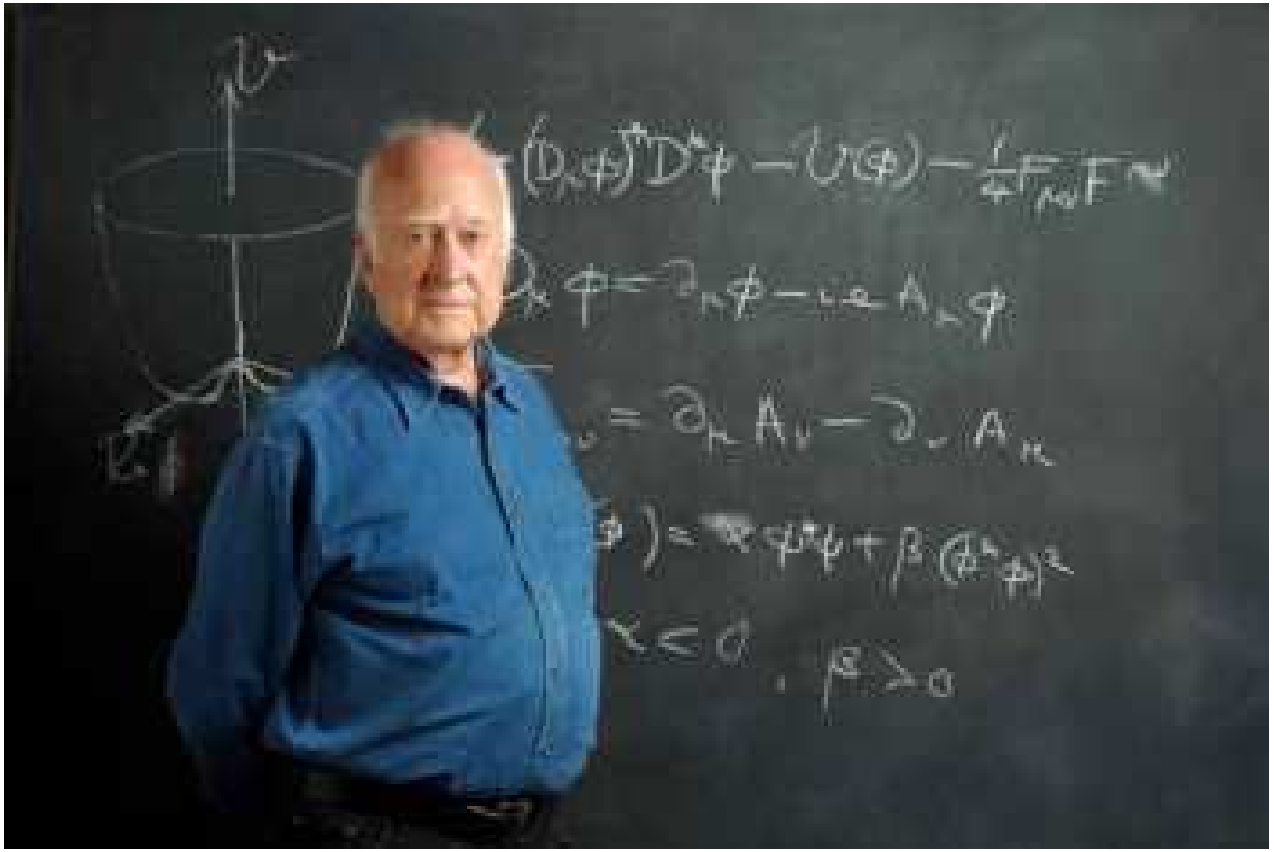
$$E(Q) = AQ^2 + BQ^4$$

with: $A < 0$



Example: tunneling states of ammonia

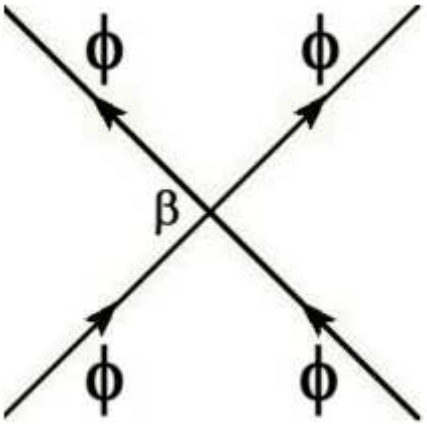
Analogues in physics: the Englert-Brout-Higgs boson



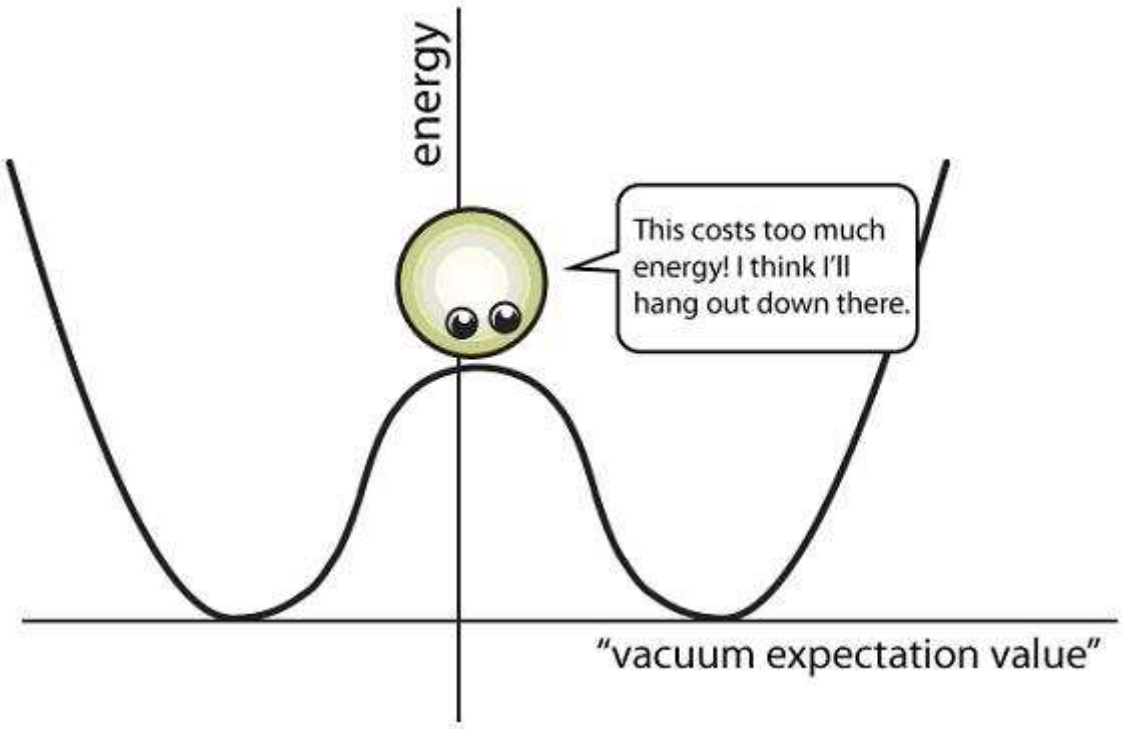
$$E = \alpha\, \Phi^{*}\Phi + \beta\, \left(\Phi^{*}\Phi\right)^{2}$$

The quadratic term in field theory is the energy cost of producing a Higgs particle. This is the symmetry breaking term. (α<0)

The quartic term is the strength with which two particles interact with each other.



Nicholas Mee, The Higgs force, Lutterworth Press, 2012



'The cooling universe undergoes a phase transition, in which the Higgs field reaches a symmetry broken state, with a non-zero expectation value.' The interaction of particles with this background field gives us 'the sensation of mass'.

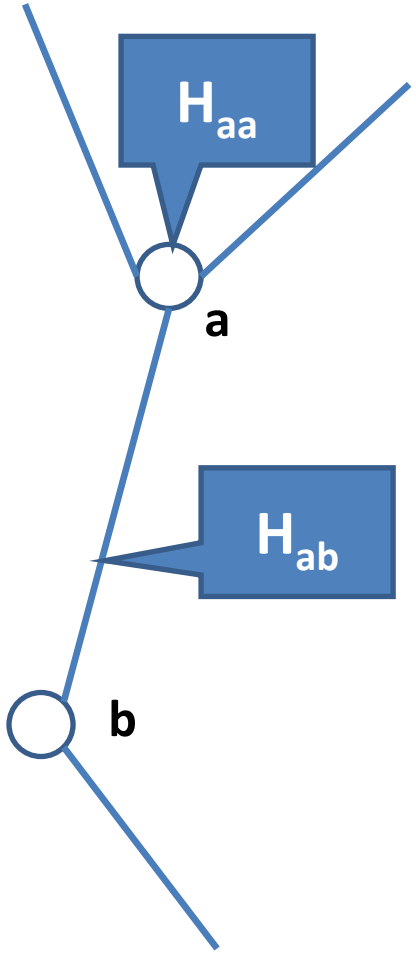
Molecular graphs

H_{aa} : Coulomb integral (on-site interaction) (unit=α)
H_{bb}: Exchange integral (inter-site interaction) (unit=β)

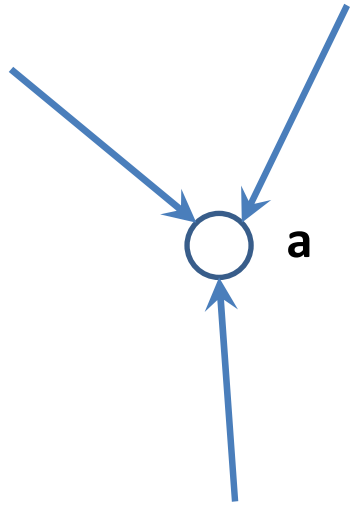
E_k: eigenenergy of level k

Density: $$\frac{\delta E_k}{\delta H_{aa}} = \left(c_a^k\right)^2$$

Coulson bond order: $$\frac{1}{2}\frac{\delta E_k}{\delta H_{ab}} = c_a^k c_b^k$$



$$\frac{\beta}{2}\left(\sum_{j\in v_a}\frac{\delta E_k}{\delta H_{aj}}\right)=(E_k-\alpha)\frac{\delta E_k}{\delta H_{aa}}$$



v_a is the neighbourhood of a

Except for a level which is non-bonding, the change in the on-site interaction can be expressed by a change in the weights of the edges which connect the given site to the network. Hence, we can limit the treatment to edge distortivity.

Jahn-Teller distortion of a graph

ψ_k

Level *k* is non-degenerate:

$$\Delta E_k = \sum_{i<j} \Delta H_{ij} \frac{\delta E_k}{\delta H_{ij}} = 2 \sum_{i<j} \Delta H_{ij} c_i^k c_j^k$$

Equivalent edges have the same k^{th}-bond-order and thus influence the energy to the same extent.
As a result, non-degenerate levels can only couple to totally-symmetric modes of distortion.

Jahn-Teller distortion of a graph

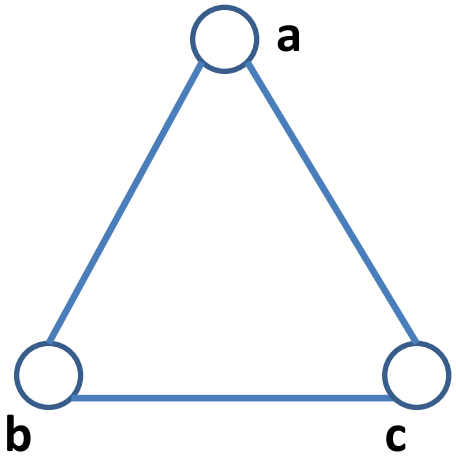
Ψ_k Ψ_l

Levels *k* and l are degenerate:

$$H = \sum_{i<j} H^{JT}(\Delta H_{ij}) = \begin{pmatrix} 2c_i^k c_j^k & c_i^k c_j^l + c_j^k c_i^l \\ c_i^l c_j^k + c_j^l c_i^k & 2c_i^l c_j^l \end{pmatrix}$$

The trace of the hamiltonian still is totally-symmetric, but the individual energy levels depend on two symmetry lowering coordinates:
a splitting mode (Qθ) and a mixing mode (Qε).

Example: triangle



Ψ_k Ψ_l

$$\Psi_k = \frac{1}{\sqrt{2}}\left(|b\rangle - |c\rangle\right)$$

$$\Psi_l = \frac{1}{6}\left(2|a\rangle - |b\rangle - |c\rangle\right)$$

$$\begin{pmatrix} -\Delta H_{bc} & \frac{1}{\sqrt{3}}\Delta H_{ab} - \frac{1}{\sqrt{3}}\Delta H_{ac} \\ \frac{1}{\sqrt{3}}\Delta H_{ab} - \frac{1}{\sqrt{3}}\Delta H_{ac} & \frac{1}{3}\Delta H_{bc} - \frac{2}{3}\Delta H_{ab} - \frac{2}{3}\Delta H_{ac} \end{pmatrix}$$

$$Q_\theta = \frac{1}{\sqrt{6}}\left(2\Delta H_{bc} - \Delta H_{ab} - \Delta H_{ac}\right) \qquad Q_\varepsilon = \frac{1}{\sqrt{2}}\left(\Delta H_{ab} - \Delta H_{ac}\right)$$

Jahn-Teller distortions of molecules versus graphs: the complete symmetry case

We carry out two proofs of the Jahn-Teller theorem:

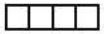
1. **For a simplex molecule, with n+1 atoms, as a geometric structure in n-dimensional space.**

2. **For the complete graph, K_{n+1}, containing (n+1) nodes.**

Jahn-Teller distortions: 1. Simplex molecule

Simplex molecule: e.g. the tetrahedron

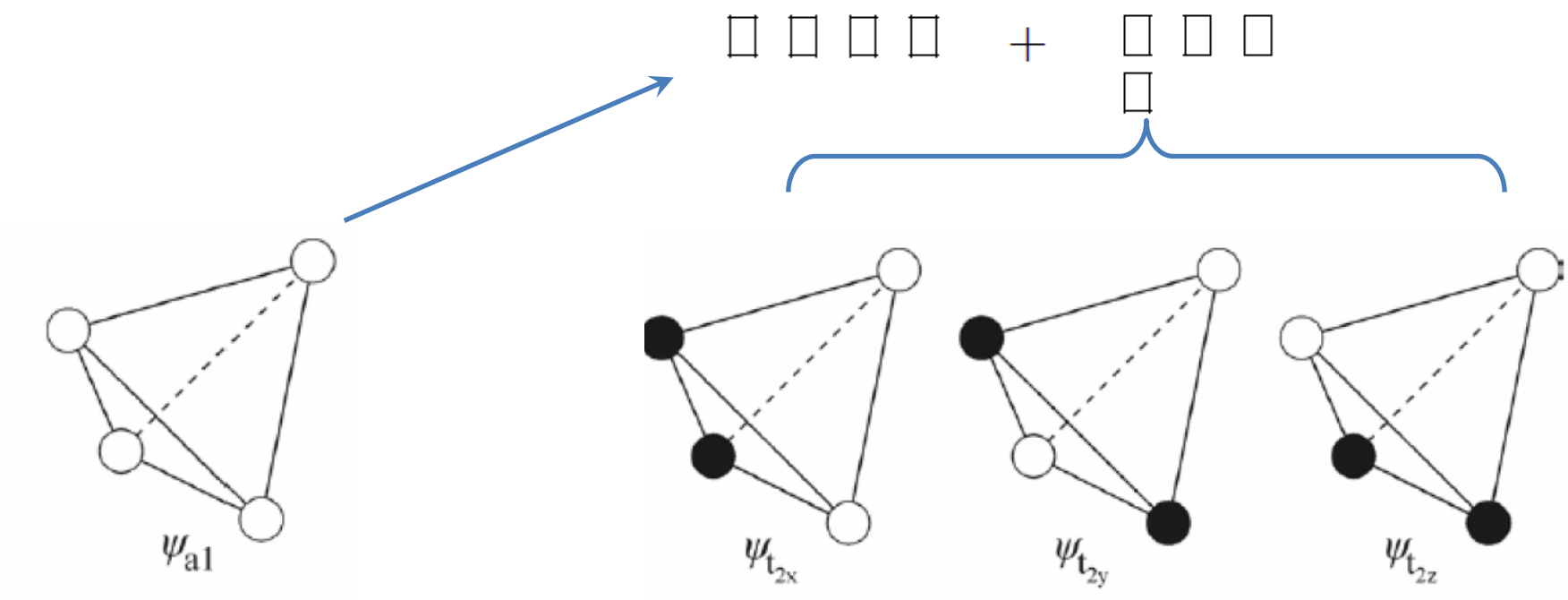
Table 1 Isomorphism relations between the elements of the groups T_d and S_4

		T_d S_4	E 1^4	$8C_3$ $1^1 3^1$	$3C_2$ 2^2	$6S_4$ 4^1	$6\sigma_d$ $1^2 2^1$
A_1	(4)		1	1	1	1	1
A_2	(1^4)		1	1	1	−1	−1
E	(2^2)		2	−1	2	0	0
T_1	$(2, 1^2)$		3	0	−1	1	−1
T_2	(3, 1)		3	0	−1	−1	1

n-dimensional space:

- Simplex has n+1 nodes, and symmetry S_{n+1}
- Eigenlevels:

$$\Gamma_v(S_n \uparrow S_{n+1}) = (n+1) + (n,1)$$



Eigenlevels:

$$\psi_{a_1} = \frac{1}{2}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)$$

$$\psi_{t_2 x} = \frac{1}{2}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)$$

$$\psi_{t_2 y} = \frac{1}{2}(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4)$$

$$\psi_{t_2 z} = \frac{1}{2}(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4)$$

→ simple rationale of the Jahn-Teller theorem

The elementary JT hamiltonian can be expressed
in this carrier space as the set
of inter-site operators.

$$H = \sum_{k<l} k\left(\left|\varphi_k\right\rangle\left\langle\varphi_l\right| + \left|\varphi_l\right\rangle\left\langle\varphi_k\right|\right)$$

inter-site operators → normal modes

The JT Hamiltonian is time-even. The active modes will transform as the symmetrized square of the orbital representation:
Mode symmetry belongs to: $[\Gamma]^2 - A_1$

Symmetry of inter-site operators:

$$(n,1)\times(n,1) = [(n+1)+(n,1)+(n-1,2)] + \{(n-1,1^2)\}$$

Symmetry of atomic displacements:

$$\Gamma\left(S_n \uparrow S_{(n+1)}\right)\times(n,1) \quad = \quad (n+1)+2(n,1)+(n-1,2)+(n-1,1^2)$$

Fibre representation

$$\begin{aligned}\Gamma_T &= (n,1)\\ \Gamma_R &= \Gamma_T\times\Gamma_T = (n-1,1^2)\end{aligned}$$

Symmetry of normal modes:

$$\Gamma\left(S_n \uparrow S_{(n+1)}\right)\times(n,1) - \Gamma_T - \Gamma_R = (n+1)+(n,1)+(n-1,2) \equiv [(n,1)]^2$$

Jahn-Teller distortions: 2. Graph analogue: the complete graph

Complete graph: K_{n+1}

Symmetric group of n+1 sites:

$$H = S_n \ , G = S_{n+1}$$

$$\Gamma(S_n \uparrow S_{n+1}) = (n+1) + (n,1)$$

Symmetric group of inter-site interactions:

$$\Gamma(\Delta H) = \left\{ \sum_{i \neq j}^{n+1} \left| r_i - r_j \right| \right\}$$

$$= \left[(n+1) + (n,1) \right]^2 - \left((n+1) + (n,1) \right)$$

$$= \left\{ (n+1) + (n,1) + \left[(n,1) \right]^2 \right\} - \left((n+1) + (n,1) \right)$$

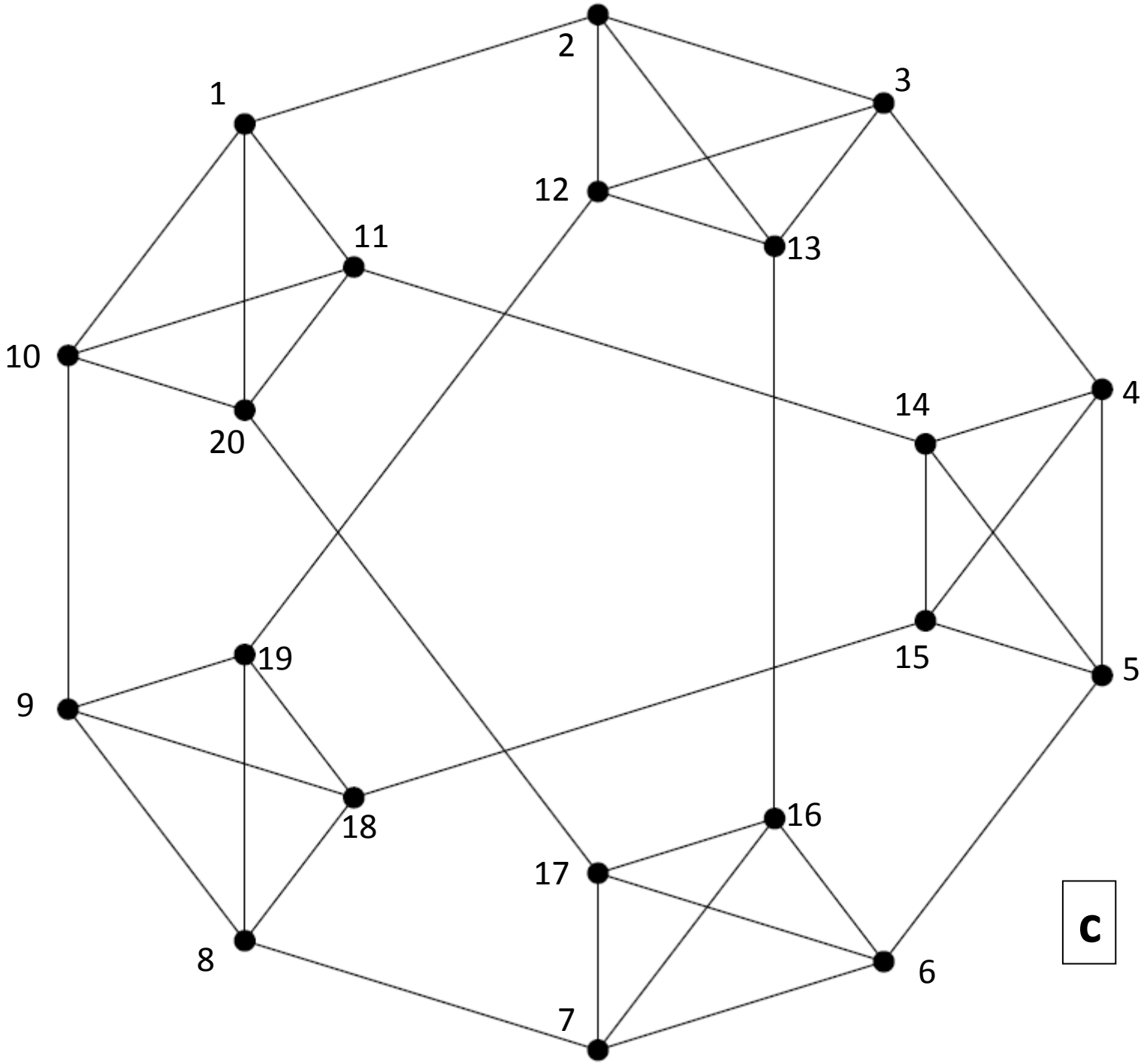
$$= \left[(n,1) \right]^2$$

1. The proof for molecules with S_n symmetries, can be extended to almost all cases of point group degenerate irreducible representations, due to a theorem by Hall:

   A doubly transitive permutation representation of a group G over the complex field is the sum of the identical representation and an absolutely irreducible representation.

2. The exceptions are the two threefold degeneracies in the icosahedral symmetry group: T_1 and T_2 . These follow the JT theorem, but the permutational proof cannot be hosted in the icosahedral group, because it does not contain a subgroup of order 120/4.

   Pisanski provided us with a graph with S_5 symmetry, which has a sixfold degenerate eigenlevel, that moreover subduces $T_1 + T_2$.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S_5	$\{1^5\}$ 1	$\{1^3,2\}$ 10	$\{1^2,3\}$ 20	$\{1,2^2\}$ 15	$\{1,4\}$ 30	$\{2,3\}$ 20	$\{5\}$ 24
A_1 (5)	1	1	1	1	1	1	1
G_1 (4,1)	4	2	1	0	0	−1	−1
H_1 (3,2)	5	1	−1	1	−1	1	0
I (3,1^2)	6	0	0	−2	0	0	1
H_2 (2^2,1)	5	−1	−1	1	1	−1	0
G_2 (2,1^3)	4	−2	1	0	0	1	−1
A_2 (1^5)	1	−1	1	1	−1	−1	1

Jahn-Teller active modes:

$[I \times I]^2 = A_1 + \mathbf{A_2} + G_1 + 2H_1 + H_2$

Available edge modes:

$\Gamma_{10}(e) = A_1 + G_1 + H_1$

$\Gamma_{30}(e) = A_1 + 2G_1 + 2H_1 + H_2 + I$

The symmetry breaking, $S_5 \rightarrow A_5$, splits the sixfold degeneracy into $T_1 + T_2$, but requires an A_2 mode, which is not provided by the edge distortions.

Conclusions and outlook

- Degenerate levels in graphs show a linear dependence on non-totally symmetric distortions of edge weights, which as a result will remove the degeneracy. This is the graph analogue of the molecular JT effect.
- For the case of the complete graph there is an exact correspondence to the JT effect of the simplex molecule.
- Unlike the molecular JT effect, there are cases where not all JT symmetry breakings can be activated by edge distortions. This has no counterpart in 3D molecules, but can occur in higher dimensions, as well as in linear molecules.

- Time-odd (electrodynamic) interactions are unexplored territory.

Thanks to my coauthors for many discussions, and thanks to you all for your attention.