THE JAHN-TELLER EFFECT

Arnout Ceulemans, Jülich, September 18, 2023

Hermann Arthur Jahn
(Colchester, 1907 - Southampton, 1979

Edward Teller (Budapest, 1908 – Stanford 2003)

Teller and Wigner are two members of the famous group of five Jewish Hungarian scientists designated informally as "the Martians," (Teller, Wigner, Leo Szilard, John von Neumann, and Theodore von Karman).

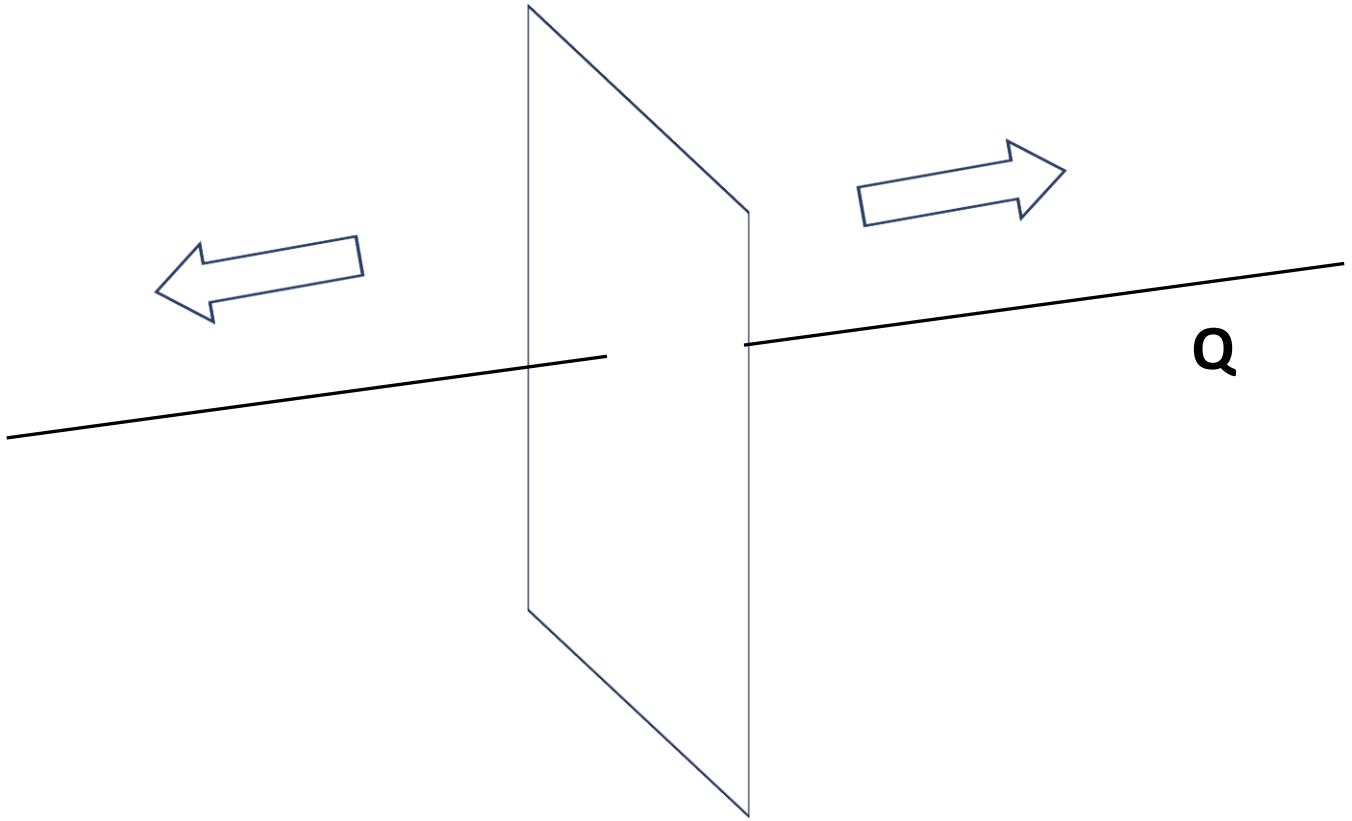
PART I: Jahn-Teller Potential Energy Surface

In the following we investigate the conditions under which a polyatomic molecule can have a stable equilibrium configuration when its electronic state has orbital degeneracy, i.e. degeneracy not arising from the spin. We shall show that stability and degeneracy are not possible simultaneously unless the molecule is a linear one, i.e. unless all the nuclei in the equilibrium configuration lie on a straight line. We shall see also that the instability is only slight if the degeneracy is due solely to electrons having no great influence on the binding of the molecule.

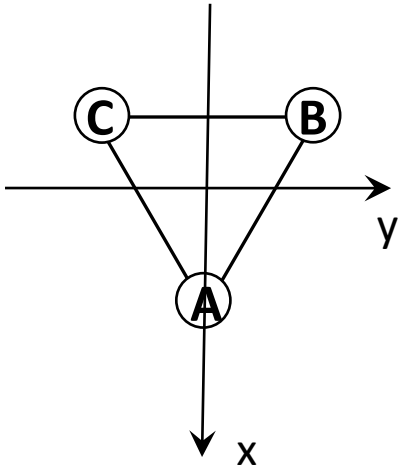
Jahn and Teller: On the stability of polyatomic molecules in degenerate electronic states. Proc. Roy. Soc., 1937

In a classical system:

$$\left.\frac{\partial E}{\partial Q}\right|_{o} = 0$$

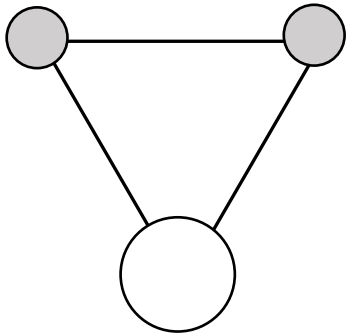


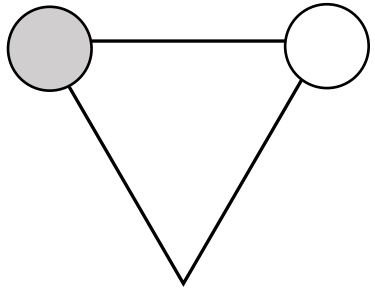
Toy model triangle of hydrogen atoms: the C3v symmetry group



C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2,xy)(xz,yz)$

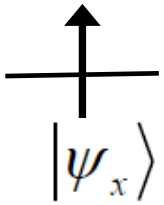
Toy model triangle of hydrogen atoms: the orbitals



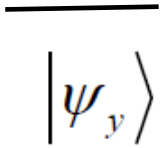


$$\Psi x = \frac{1}{\sqrt{6}}(2A - B - C)$$

$$\Psi y = \frac{1}{\sqrt{2}}(B - C)$$



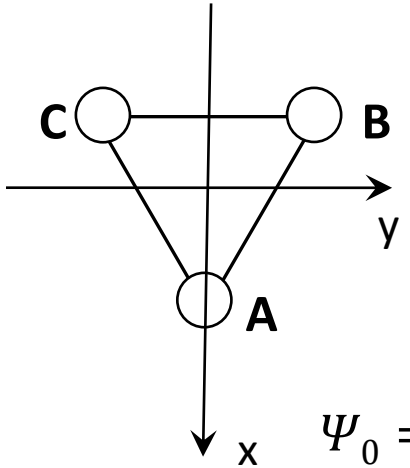
$|\psi_x\rangle$

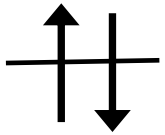


$|\psi_y\rangle$

E

MO energy



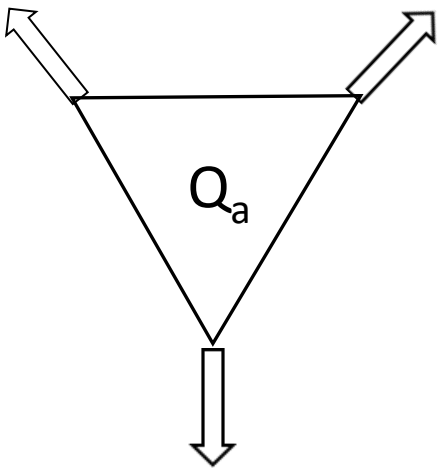


$|\psi_0\rangle$ A_1

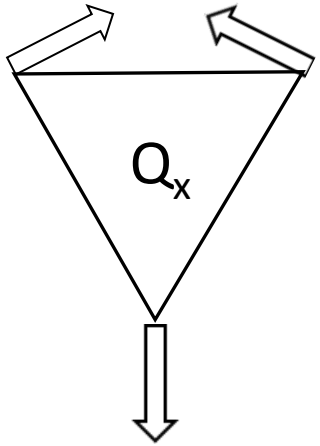
$$\Psi_0 = \frac{1}{\sqrt{3}}(A + B + C)$$

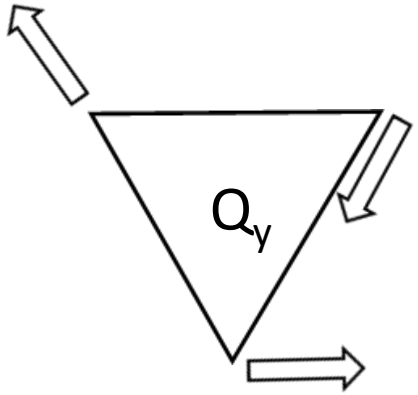
Toy model triangle of hydrogen atoms: normal modes

ν_{a1} breathing mode



ν_e asymmetric stretch





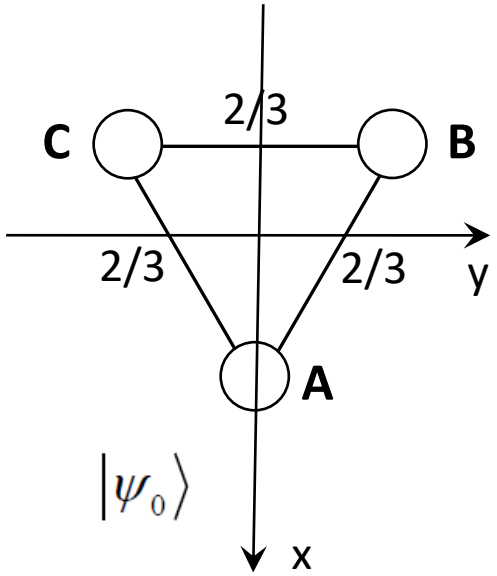
$$Q_x = \frac{1}{\sqrt{3}}\left[Q_A^x + \left(-\frac{\sqrt{3}}{2}Q_B^y - \frac{1}{2}Q_B^x\right) + \left(\frac{\sqrt{3}}{2}Q_C^y - \frac{1}{2}Q_C^x\right)\right]$$

$$Q_y = \frac{1}{\sqrt{3}}\left[Q_A^y + \left(-\frac{1}{2}Q_B^y + \frac{\sqrt{3}}{2}Q_B^x\right) + \left(-\frac{1}{2}Q_C^y - \frac{\sqrt{3}}{2}Q_C^x\right)\right]$$

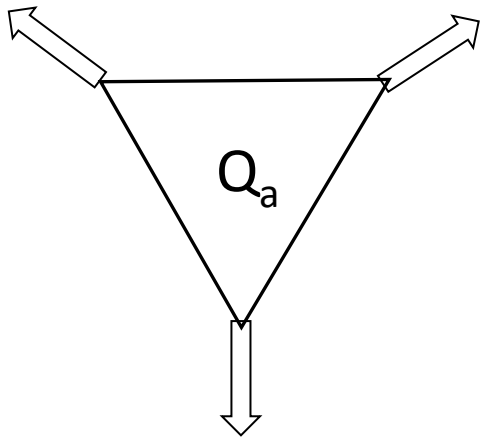
Toy model triangle of hydrogen atoms: the coupling

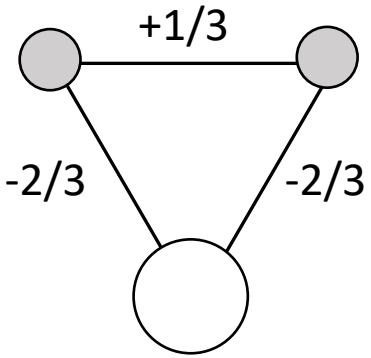
Orbital bond indices:

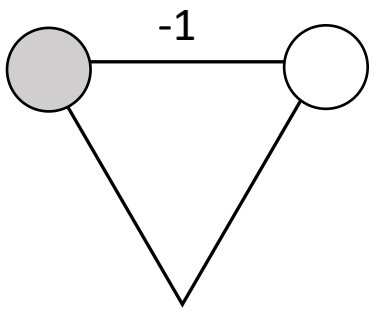
$$\langle I|J\rangle = \bar{c}_I c_J + \bar{c}_J c_I$$



$$\Psi_0 = \frac{1}{\sqrt{3}}(A + B + C)$$



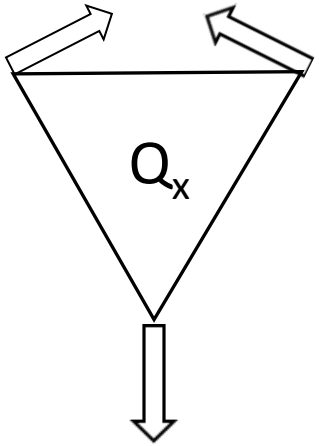


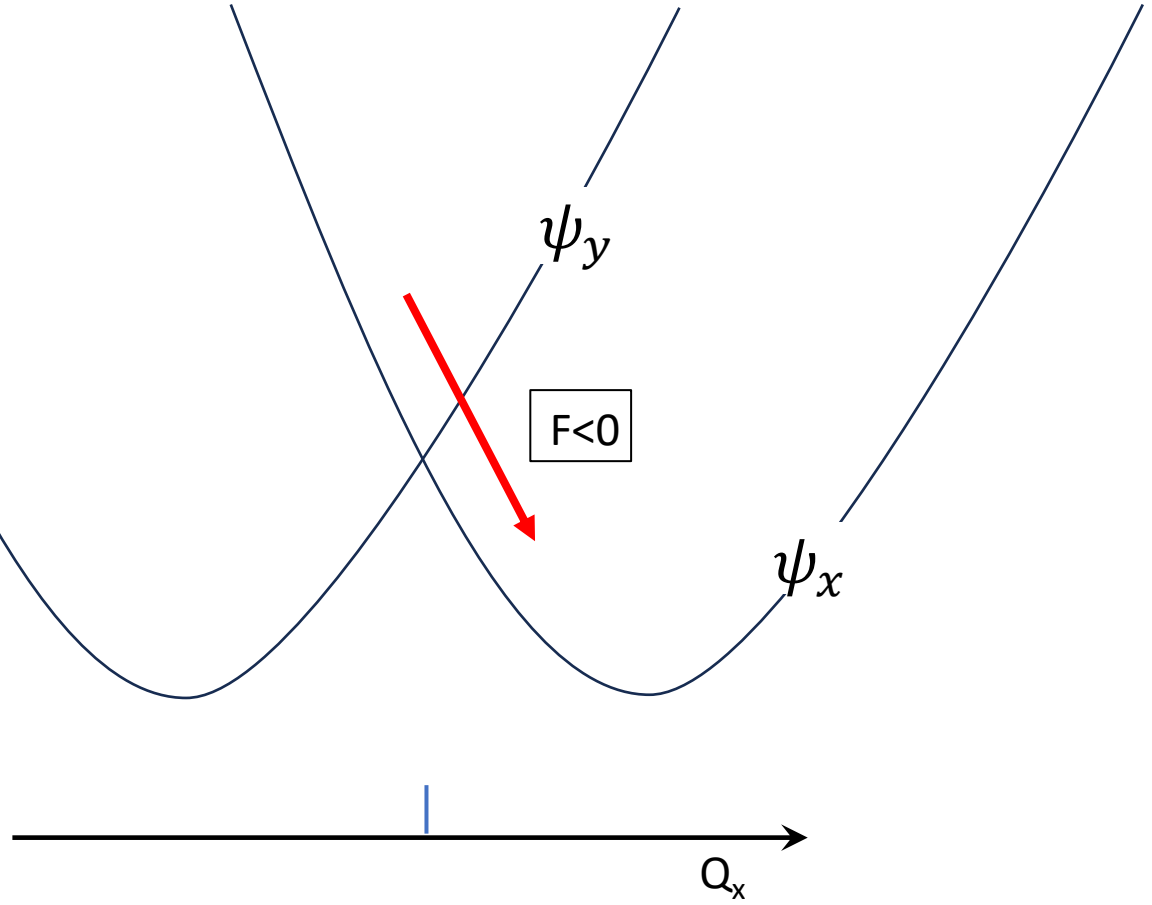


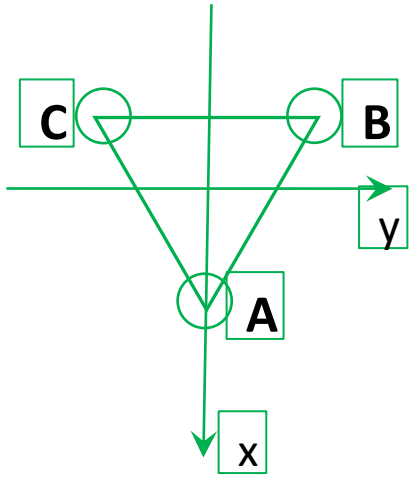
$$\Psi x = \frac{1}{\sqrt{6}}(2A - B - C)$$

$$\Psi y = \frac{1}{\sqrt{2}}(B - C)$$

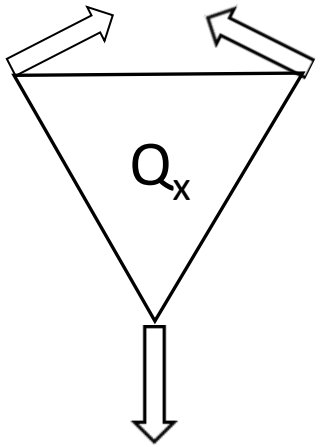
$$\frac{F}{\sqrt{2}}\begin{pmatrix} Qx & \dots \\ \dots & -Qx \end{pmatrix}$$



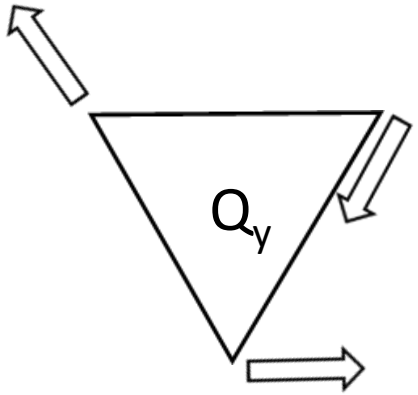




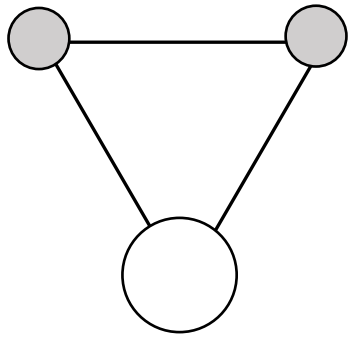
~ x^2-y^2



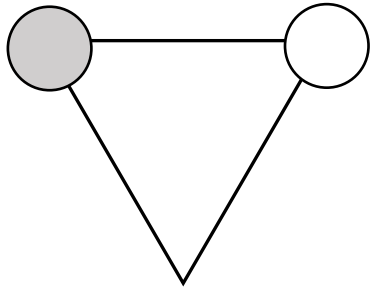
~ xy



~ x



~ y



$$\hat{C}_3 \begin{pmatrix} Q_x & Q_y \end{pmatrix} = \begin{pmatrix} Q_x & Q_y \end{pmatrix} \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$\hat{\sigma}_x \begin{pmatrix} Q_x & Q_y \end{pmatrix} = \begin{pmatrix} Q_x & Q_y \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{C}_3 \begin{pmatrix} |\psi_x\rangle & |\psi_y\rangle \end{pmatrix} = \begin{pmatrix} |\psi_x\rangle & |\psi_y\rangle \end{pmatrix} \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$\hat{\sigma}_x \begin{pmatrix} |\psi_x\rangle & |\psi_y\rangle \end{pmatrix} = \begin{pmatrix} |\psi_x\rangle & |\psi_y\rangle \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Toy model triangle of hydrogen atoms: the Hamiltonian

$$\mathcal{H} = H_0 + \sum_{\Lambda\lambda} \left(\frac{\partial H}{\partial Q_{\Lambda\lambda}}\right)_0 Q_{\Lambda\lambda} + \frac{1}{2}\sum_{\Lambda\lambda} K_\Lambda Q_{\Lambda\lambda}^2$$

$$\left\langle \Psi_{\gamma_a}^{\Gamma} \left| \left(\frac{\partial H}{\partial Q_{\Lambda\lambda}}\right)_0 \right| \Psi_{\gamma_b}^{\Gamma} \right\rangle = F_\Lambda \langle \Gamma\gamma_a | \Lambda\lambda\Gamma\gamma_b \rangle$$

Γ= E_1
γ= x,y
Λ= E_2
λ= x^2-y^2, xy

$$\mathcal{H} = \frac{K}{2}\left(Q_x^2 + Q_y^2\right) + \frac{F_e}{\sqrt{2}} \begin{pmatrix} Q_x & Q_y \\ Q_y & -Q_x \end{pmatrix}$$

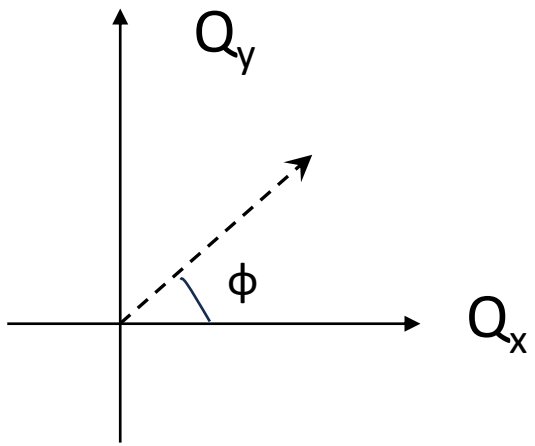
Coupling table

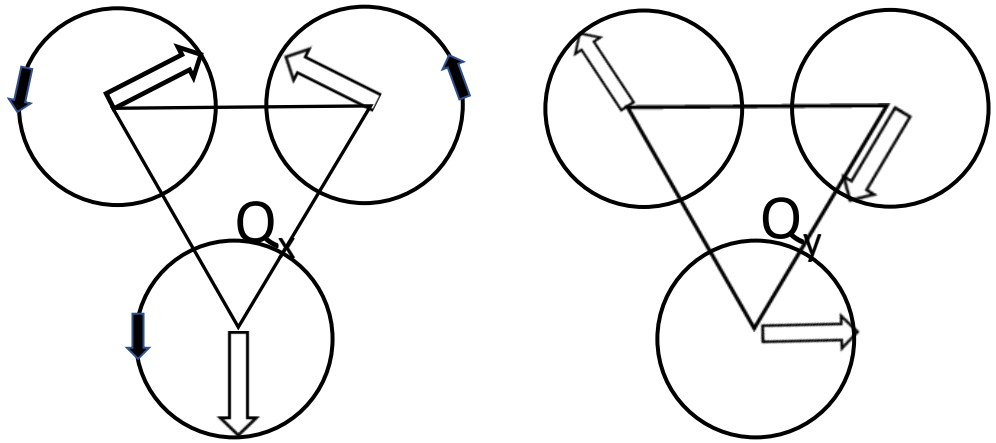
$E_1 \times E_2$	E_1		E_2	
	x	y	c	s
x c	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0
y s	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
x s	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$
y c	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$

Toy model triangle of hydrogen atoms: Coordinate space (Qx,Qy)

$Q_x = \rho \cos(\phi)$

$Q_y = \rho \sin(\phi)$

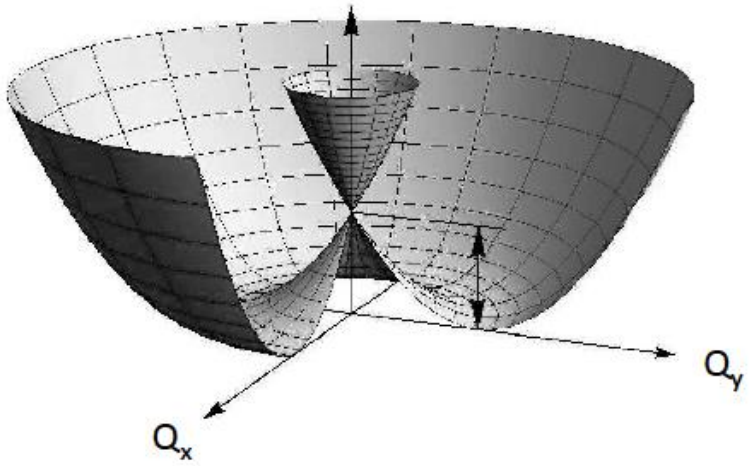




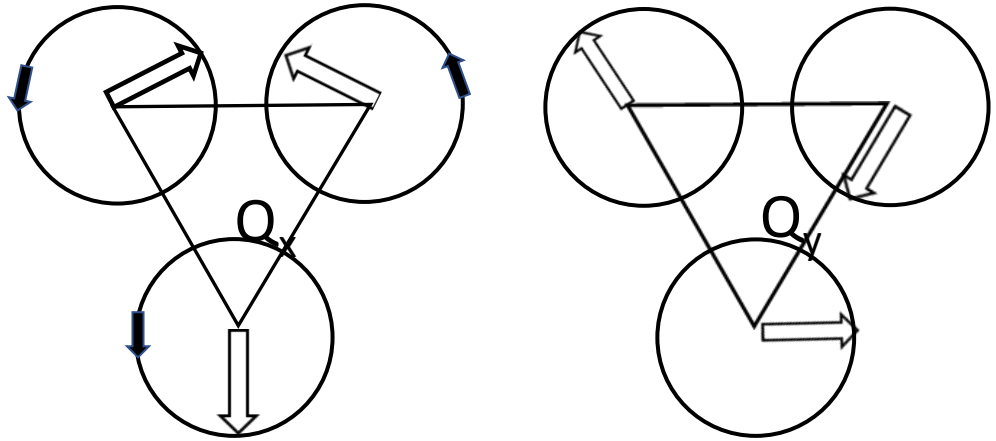
ϕ=0 ϕ=π/2

Toy model triangle of hydrogen atoms: the potential energy surface

$$E_{\pm} = \frac{K}{2}\left(Q_x^2 + Q_y^2\right) \pm \frac{F_e}{\sqrt{2}}\sqrt{Q_x^2 + Q_y^2}$$



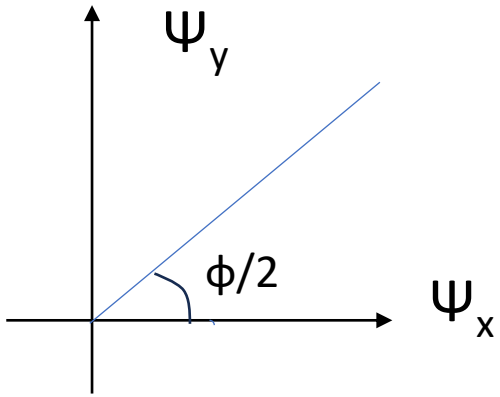
$$E_{JT} = -\frac{1}{2}\frac{F_e^2}{K}$$



Toy model triangle of hydrogen atoms: Function space (Ψx,Ψy)

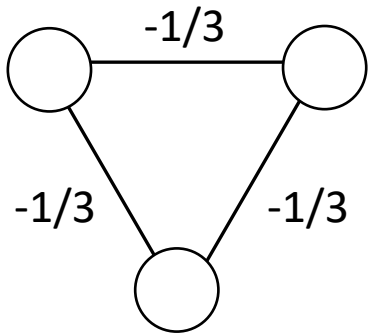
Force matrix: lower root for $F_e<0$

$$\frac{\rho F}{\sqrt{2}}\begin{pmatrix} -1+\cos\phi & \sin\phi \\ \sin\phi & -1-\cos\phi \end{pmatrix}\begin{pmatrix} c_x \\ c_y \end{pmatrix} = 0$$



$$|\psi_-\rangle = \cos\frac{\phi}{2}|x\rangle + \sin\frac{\phi}{2}|y\rangle$$

By the way:



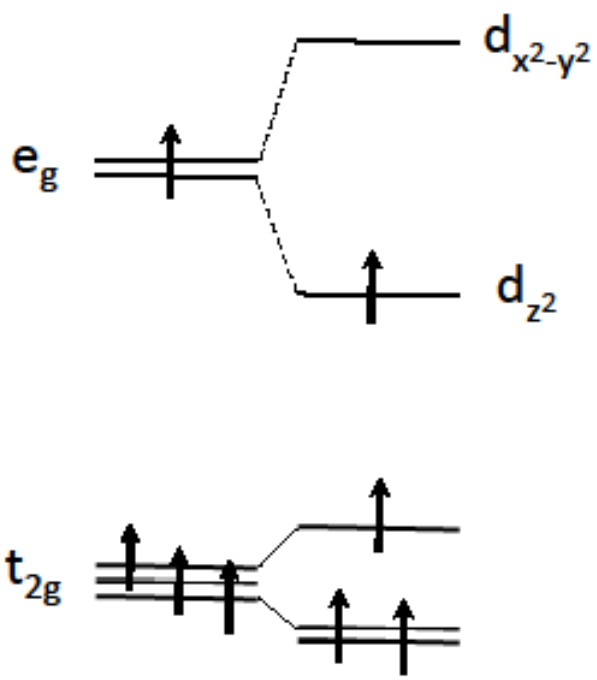
$$\frac{1}{\sqrt{2}}\left(\Psi x + i\,\Psi y\right) = \frac{1}{\sqrt{3}}\left(A + \varepsilon B + \varepsilon^{*} C\right)$$

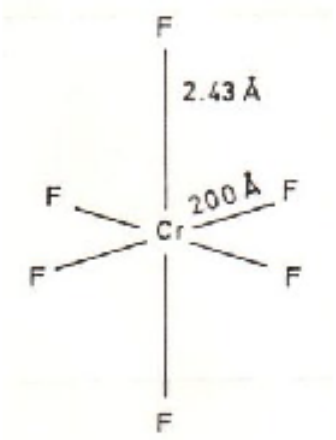
$$\frac{1}{\sqrt{2}}\left(\Psi x - i\,\Psi y\right) = \frac{1}{\sqrt{3}}\left(A + \varepsilon^{*} B + \varepsilon C\right)$$

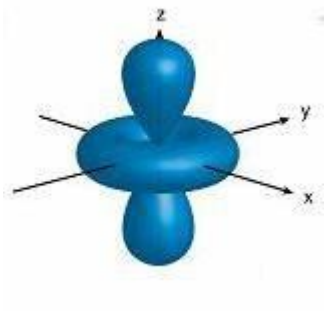
$$\varepsilon = \exp\left(\frac{2\pi i}{3}\right)$$

$$\frac{F}{\sqrt{2}}\begin{pmatrix} 0 & Qx - iQy \\ Qx + iQy & 0 \end{pmatrix}$$

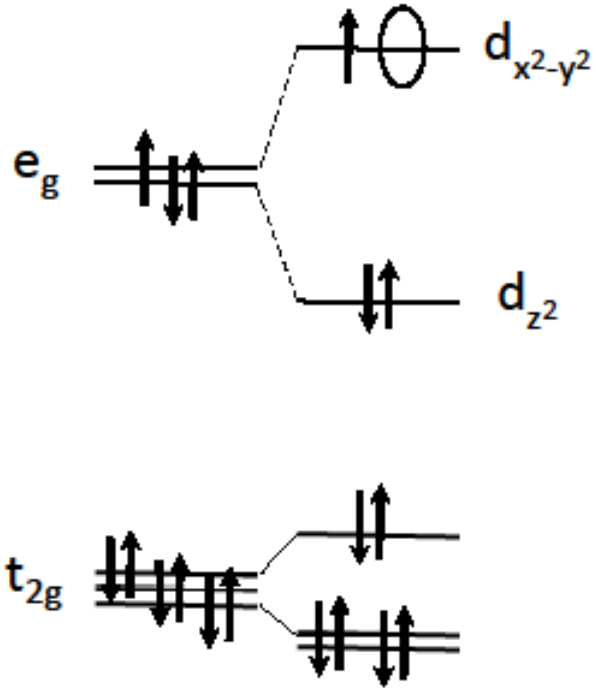
The E x e potential in octahedral symmetry

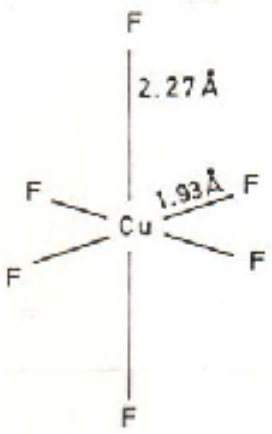


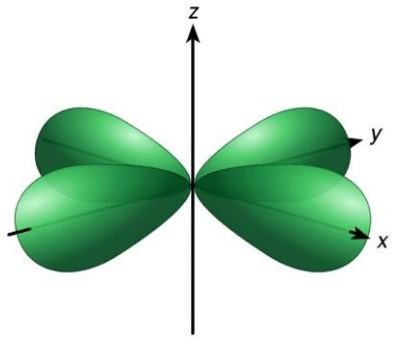




CrF_2



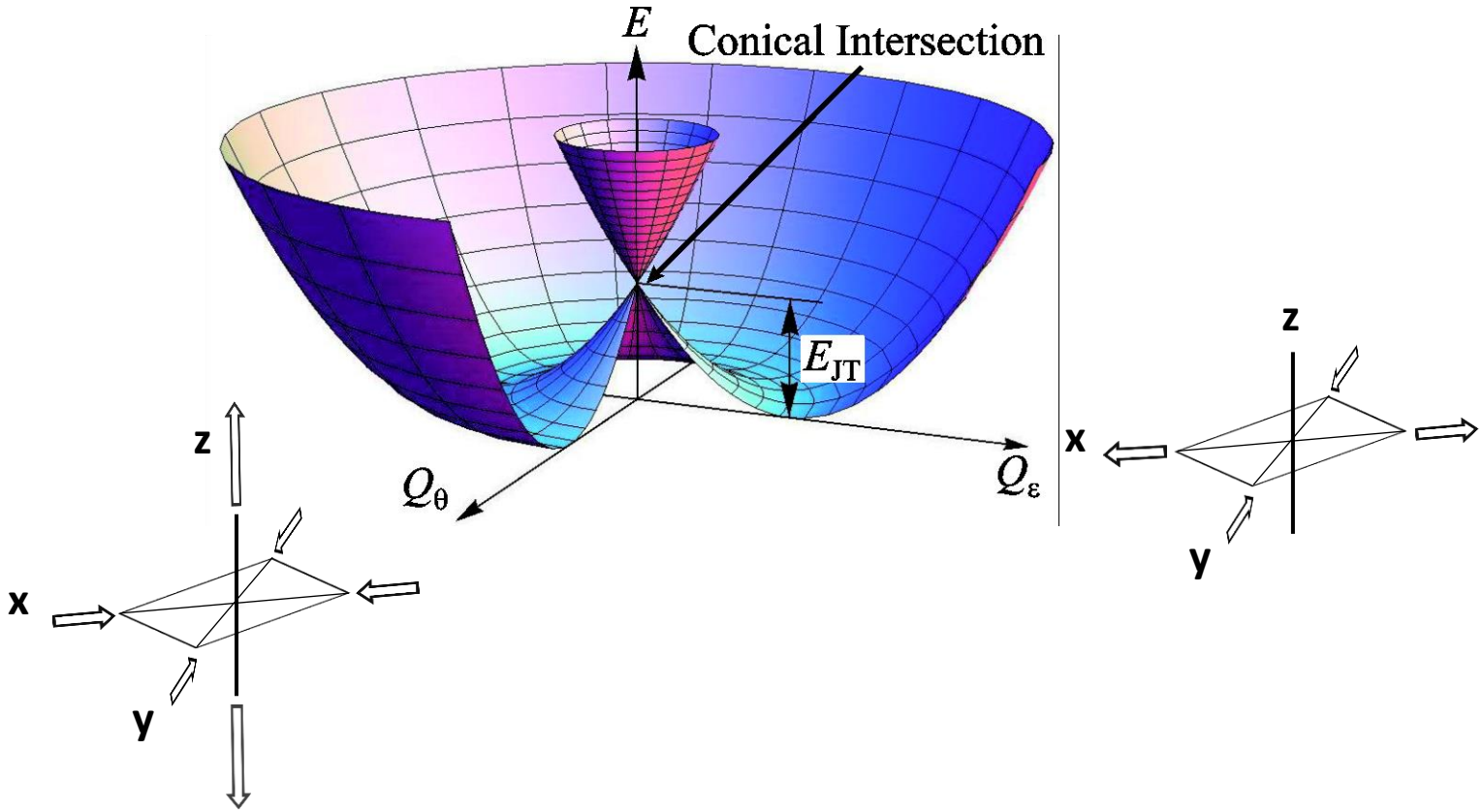




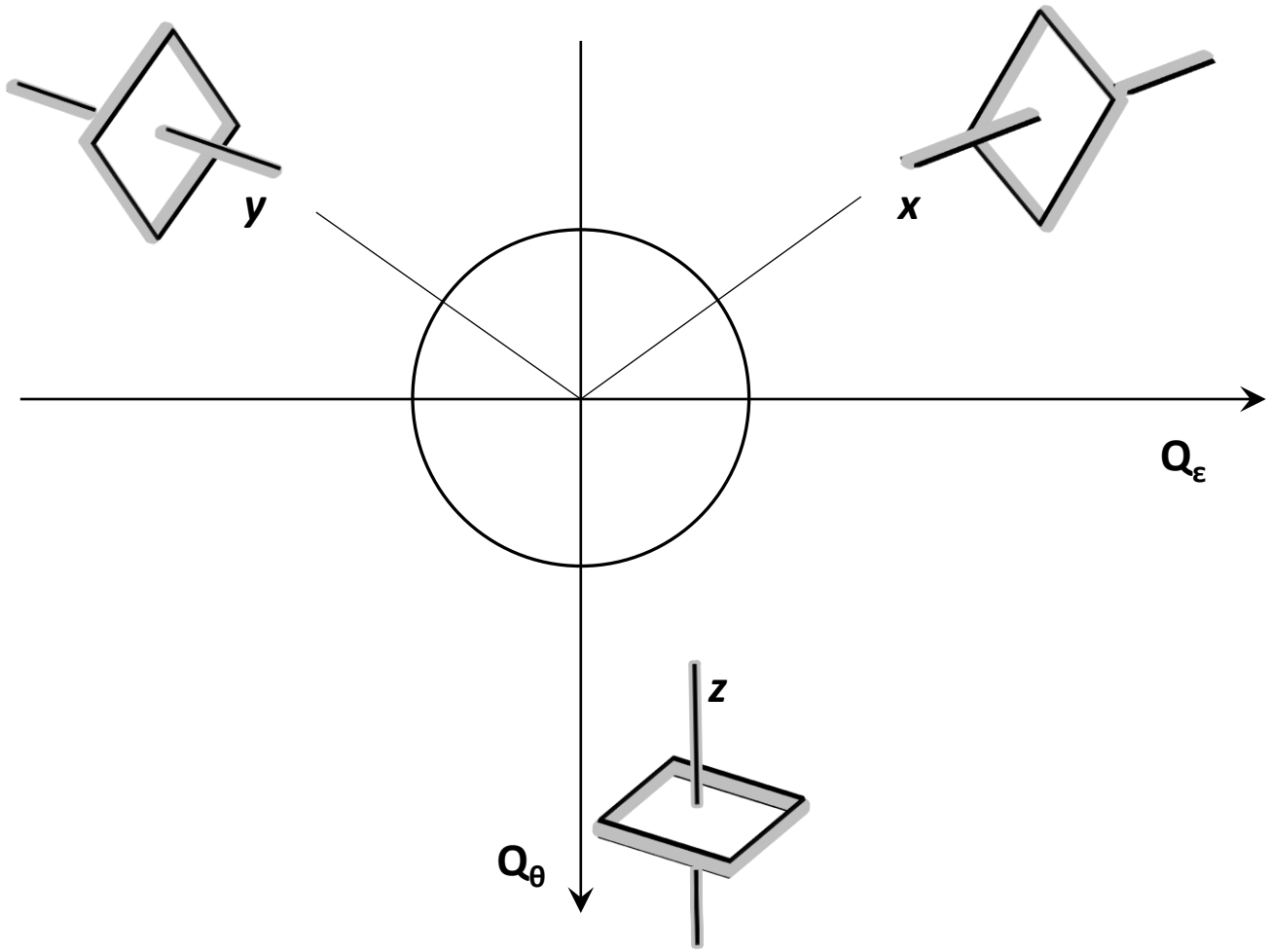
CuF_2

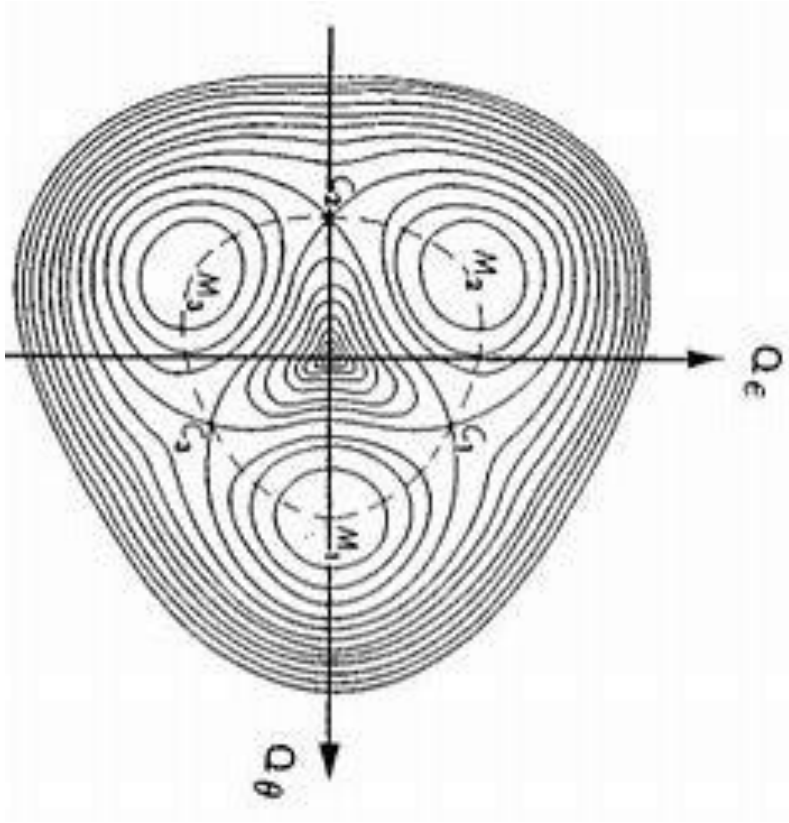
$d_{x^2-y^2}$

The E x e potential in octahedral symmetry

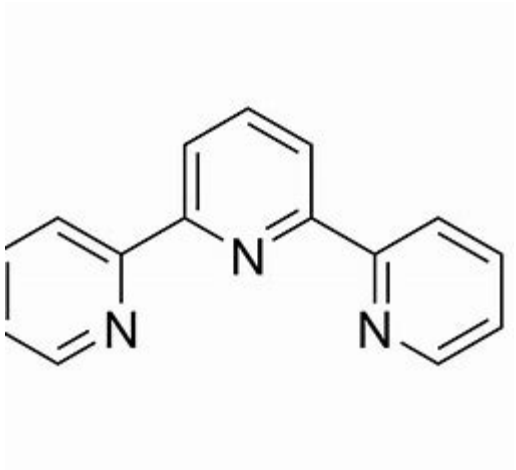


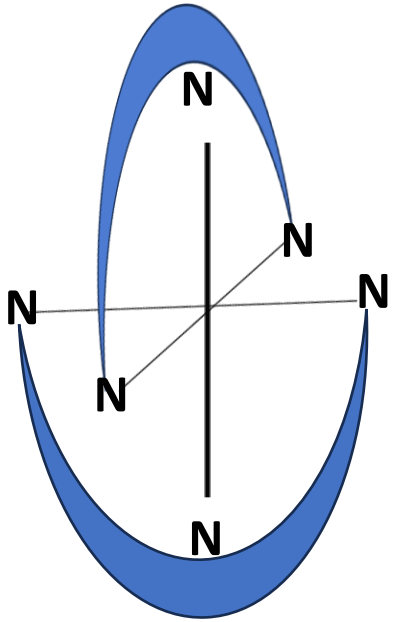
Effect of non-linear terms



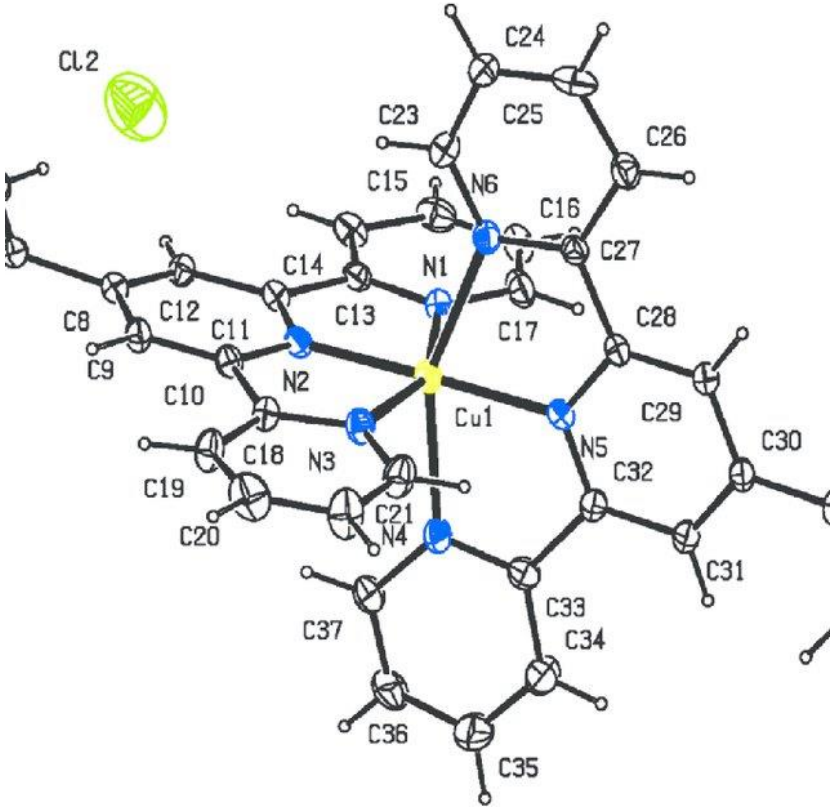


Effect of strain via molecular design: terpyridine ligand





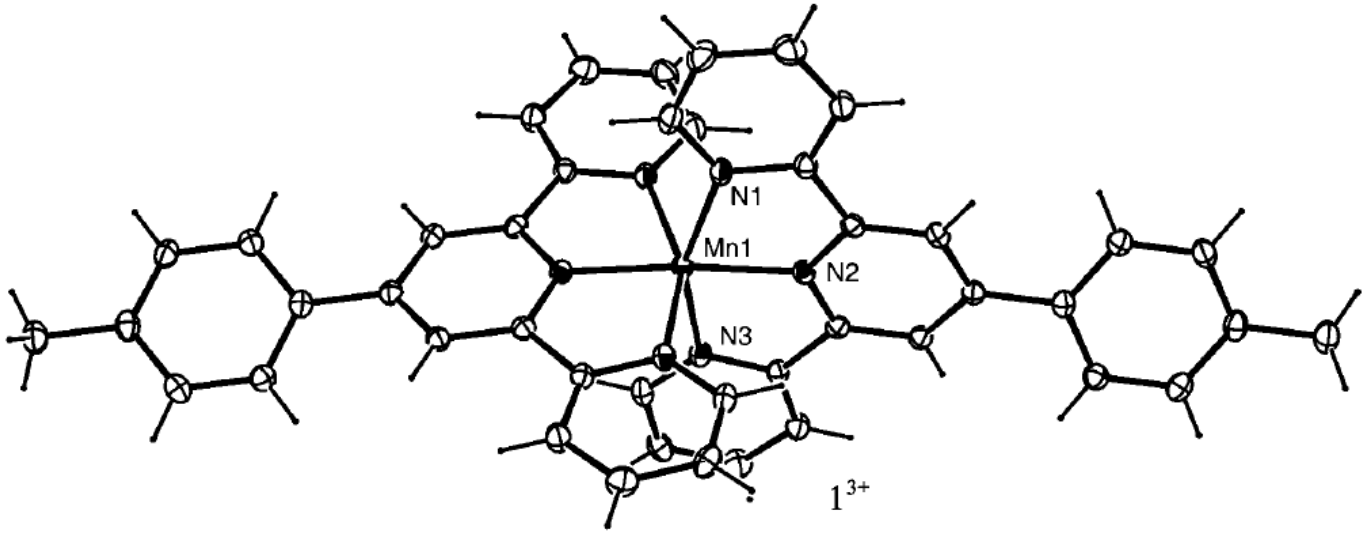
Meridional isomer: D2d

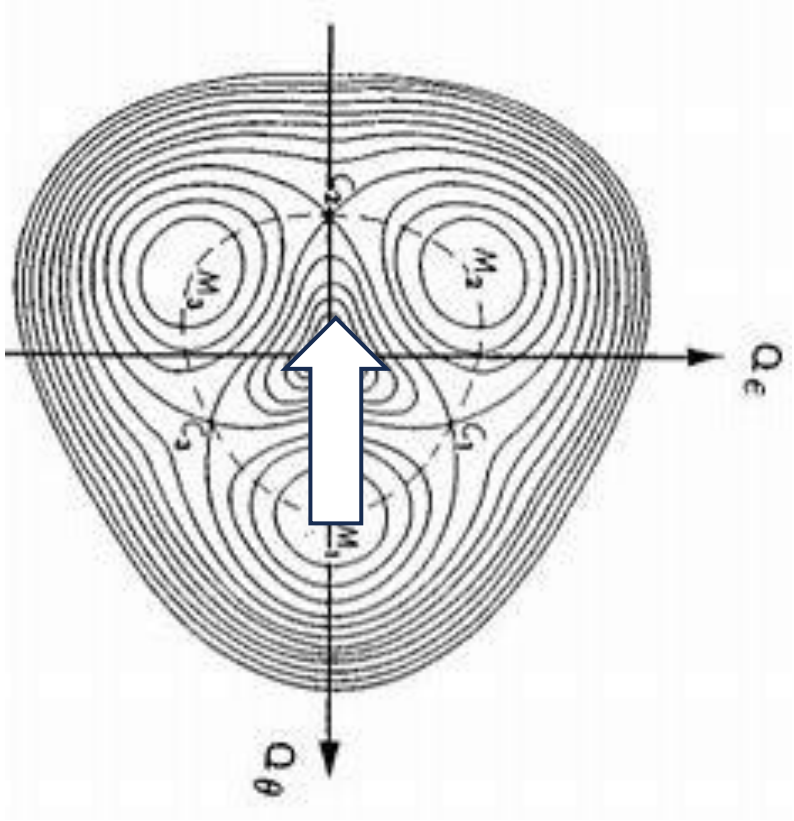


$Cu(terpy)_2^{2+}$

Effect of strain via molecular design: JT frustration

(S. Romain et al, Chem. Eur. J. 2009, 15, 980 – 988)

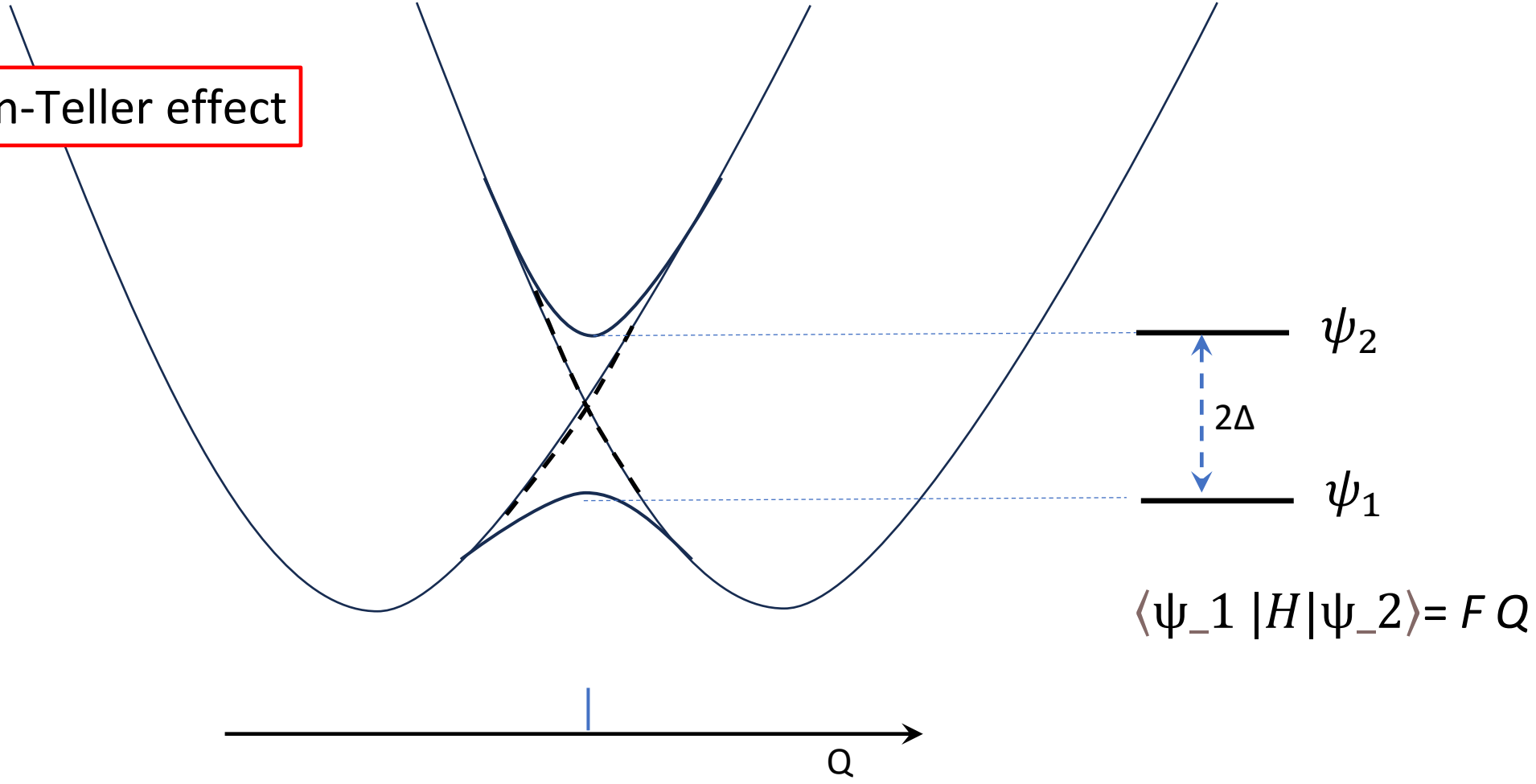




$Mn(terpy)_3^{3+}$: facial isomer C_{2h}

High spin d^4 weak plane.

Pseudo-Jahn-Teller effect

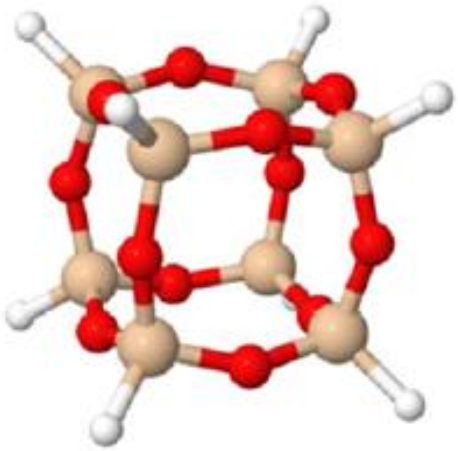


$\langle \psi\_1 | H | \psi\_2 \rangle = F\,Q$

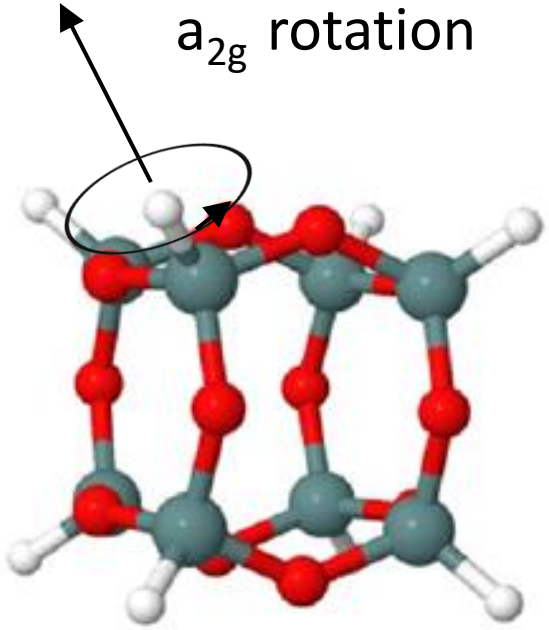
$$E_{\pm} = \frac{1}{2}K_0Q^2 \pm \left(\Delta^2 + F^2Q^2\right)^{1/2} = \frac{1}{2}\left(K_0 \pm \frac{F^2}{\Delta}\right)Q^2 \pm \Delta \mp \left(\frac{F^4}{\Delta^3}\right)Q^4 \pm \ldots \tag{19}$$

Rare Oh to Th symmetry breaking in a Germanium cluster

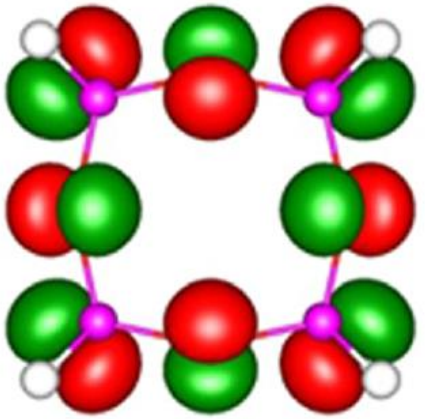
Muya, S.T. et al, J. Chem. Phys., 154, 164305



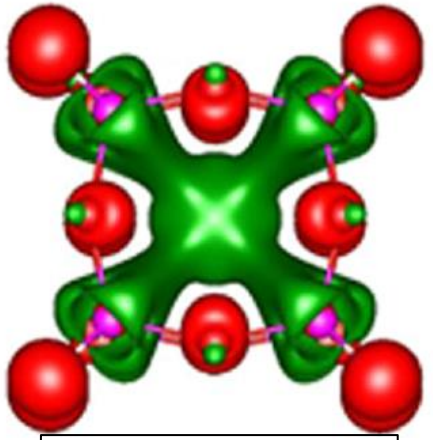
$Si_8H_8O_{12}$ (O_h)



$Ge_8H_8O_{12}$ (T_h)



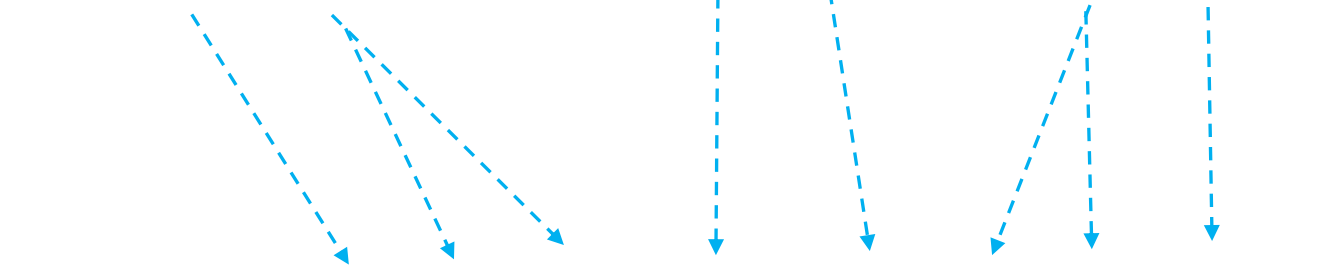
HOMO $1a_{2g}$



LUMO $11a_{1g}$

Symmetry breaking of Oh by an A_{2g} distortion

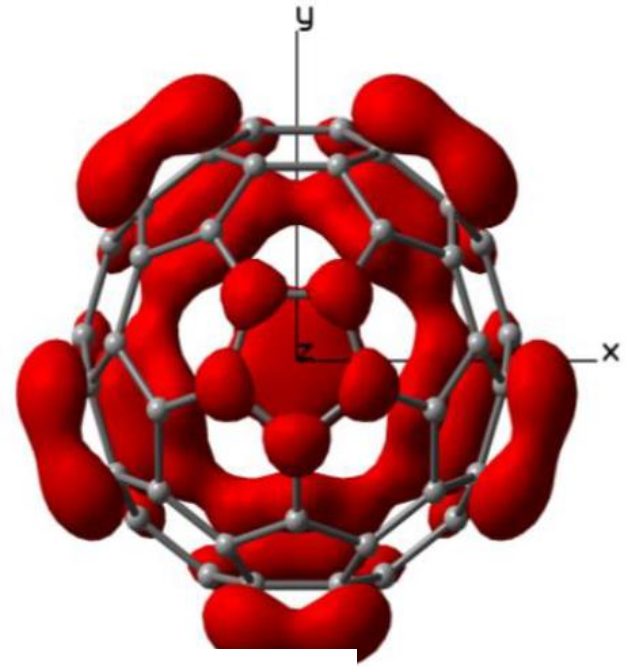
O_h	$\hat{E}$	$8\hat{C}_3$	$6\hat{C}_2$	$6\hat{C}_4$	$3\hat{C}_2$	$\hat{\imath}$	$6\hat{S}_4$	$8\hat{S}_6$	$3\hat{\sigma}_h$	$6\hat{\sigma}_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1



T_h	$\hat{E}$	$4\hat{C}_3$	$4\hat{C}_3^2$	$3\hat{C}_2$	$\hat{\imath}$	$4\hat{S}_6^5$	$4\hat{S}_6$	$3\hat{\sigma}_h$

Pseudo JT effect in C70 cation: upon ionization C70 distorts from
D5h to Cs symmetry. This introduces a permanent dipole moment (of e'1 symmetry),
with implications for radio-astronomy.
Nemes, L. Proceedings Jahn-Teller conference, York (2023)

b3lyp/6-311+g		b3lyp/ccpvdz	
a1"	-0.13793	a1"	-0.12557
e1"	-0.13946	e1"	-0.12876
e1"	-0.13946	e1"	-0.12876
a2"	-0.23878	e1"	-0.22673
e1"	-0.24013	e1"	-0.22673
e1"	-0.24013	a2"	-0.22712



$\mathbf{D_5}$	A_1	A_2	E_1	E_2
A_1	A_1	A_2	E_1	E_2
A_2	A_2	A_1	E_1	E_2
E_1	E_1	E_1	$[A_1 + E_2] + \{A_2\}$	$E_1 + E_2$
E_2	E_2	E_2	$E_1 + E_2$	$[A_1 + E_1] + \{A_2\}$

Part II: Dynamic Jahn-Teller Effect

We now rewrite the Hamiltonian in a second quantization form:

- The electronic part is isolated from the force matrix
  and expressed as a coupling of fermion operators
- The vibrational part is likewise expressed in boson form
- The Hamiltonian then reappears as a scalar product of both parts

Force matrix: Switch from matrix to operator expression

$$\langle \Psi^{\Gamma}_{\gamma_a} \left| \left(\frac{\partial H}{\partial Q_{\Lambda\lambda}} \right)_0 \right| \Psi^{\Gamma}_{\gamma_b} \rangle = F_\Lambda \langle \Gamma\gamma_a | \Lambda\lambda\Gamma\gamma_b \rangle$$

$$\left(\frac{\partial H}{\partial Q_{\Lambda\lambda}} \right)_0 = \sum_{\gamma_a\gamma_b} F_\Lambda |\Gamma\gamma_a\rangle \langle \Gamma\gamma_a | \Lambda\lambda\Gamma\gamma_b \rangle \langle \Gamma\gamma_b|$$

$$\left(\frac{\partial H}{\partial Q_{\Lambda\lambda}} \right)_0 = \sum_{\gamma_a\gamma_b} F_\Lambda f^\dagger_{\gamma_a} \langle \Gamma\gamma_a | \Lambda\lambda\Gamma\gamma_b \rangle f_{\gamma_b}$$

$f^\dagger_{\gamma_a}$: creation operator -> creates a particle in a (spin)orbital with symmetry $\Gamma\gamma_a$

f_{γ_a} : annihilation operator -> removes a particle from a (spin)orbital with symmetry $\Gamma\gamma_a$

Recoupling

$$\langle \Gamma\gamma_a|\Lambda\lambda\Gamma\gamma_b\rangle = \left(\frac{\dim\Gamma}{\dim\Lambda}\right)^{1/2}\langle \Gamma\gamma_a\Gamma\overline{\gamma_b}|\Lambda\lambda\rangle$$

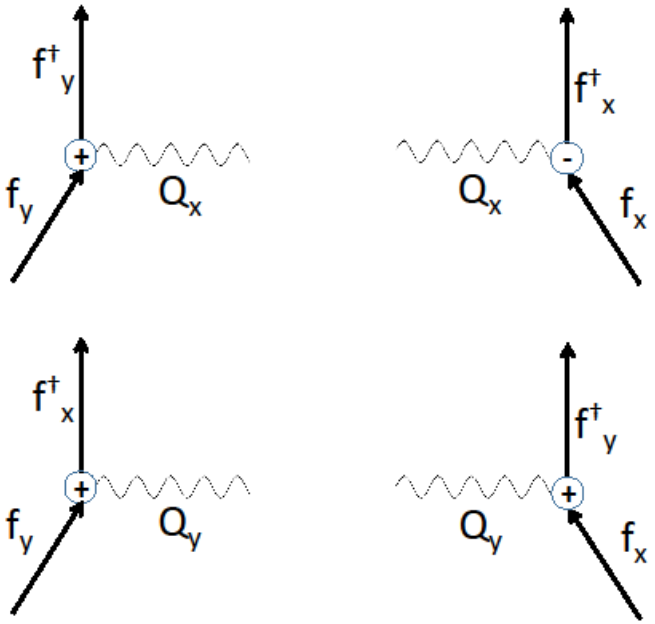
$$k_\Lambda = \left(\frac{\dim\Gamma}{\dim\Lambda}\right)^{1/2} F_\Lambda$$

$$\begin{aligned} H'_\Lambda &= k_\Lambda \sum_{\gamma_a\gamma_b}\langle \Gamma\gamma_a\Gamma\overline{\gamma_b}|\Lambda\lambda\rangle f^\dagger_{\gamma_a} f_{\gamma_b} \\ &= k_\Lambda \sum_{\gamma_a\gamma_b}\langle \Gamma\gamma_a\Gamma\gamma_b|\Lambda\lambda\rangle f^\dagger_{\gamma_a} \tilde{f}_{\gamma_b} \\ &= k_\Lambda \left(\mathbf{f}^\dagger\mathbf{f}\right)^\Lambda_\lambda \end{aligned}$$

$E_1 \times E_2$	E_1		E_2	
	x	y	c	s
$x\ \ c$	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0
$y\ \ s$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
$x\ \ s$	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$
$y\ \ c$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$

$E_1 \times E_1$	A_1	A_2	E_2	
	a_1	a_2	c	s
$x\ \ x$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
$y\ \ y$	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0
$x\ \ y$	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$
$y\ \ x$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$

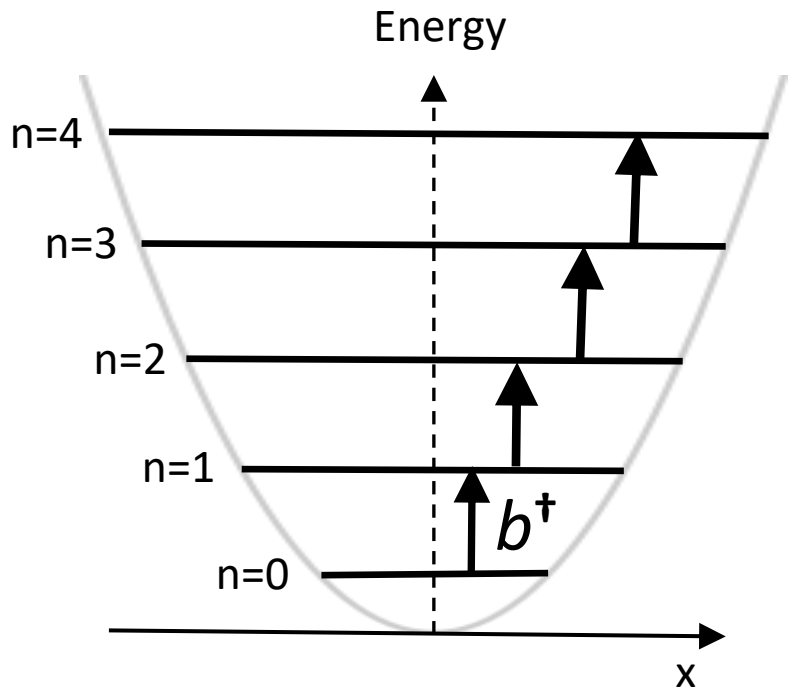
Coupled operator, $(\mathbf{f}^\dagger \mathbf{f})^\wedge$
corresponding to a Λ excitation



Boson part:

$$Q_{\Lambda\lambda} = \frac{1}{\sqrt{2}}\left(b^{\dagger}_{\Lambda\lambda} + \tilde{b}_{\Lambda\lambda}\right)$$

$$H_0 = \sum_{\Lambda\lambda} \hbar\omega_{\Lambda}\left(b^{\dagger}_{\Lambda\lambda} b_{\Lambda\lambda} + \frac{1}{2}\right)$$



Scalar product

$$\sum_{\Lambda\lambda}\left(\frac{\partial H}{\partial Q_{\Lambda\lambda}}\right)_0 Q_{\Lambda\lambda}=\sum_{\Lambda}\kappa_\Lambda\left(\mathbf{f}^\dagger\mathbf{f}\right)^\Lambda\odot\left(\mathbf{b}^\dagger+\mathbf{b}\right)_\Lambda$$

$$\left(\mathbf{f}^\dagger\mathbf{f}\right)^l\odot\left(\mathbf{b}^\dagger+\mathbf{b}\right)_l=\sum_m(-1)^m\left(\mathbf{f}^\dagger\mathbf{f}\right)^l_m\left(b^\dagger_{l,-m}+\tilde{b}_{l,-m}\right)$$

$$\mathcal{H}=\sum_{\Lambda}\kappa_\Lambda\left(\mathbf{f}^\dagger\mathbf{f}\right)^\Lambda\odot\left(\mathbf{b}^\dagger+\mathbf{b}\right)_\Lambda+\sum_{\Lambda\lambda}\hbar\omega_\Lambda\left(b^\dagger_{\Lambda\lambda}b_{\Lambda\lambda}+\frac{1}{2}\right)$$

$$\mathcal{H} = \sum_{\Lambda} \kappa_{\Lambda} \left(\mathbf{f}^{\dagger}\mathbf{f}\right)^{\Lambda} \odot \left(\mathbf{b}^{\dagger} + \mathbf{b}\right)_{\Lambda} + \sum_{\Lambda\lambda} \hbar\omega_{\Lambda} \left(b^{\dagger}_{\Lambda\lambda} b_{\Lambda\lambda} + \frac{1}{2}\right)$$

$$\mathcal{H} = \begin{pmatrix} b_x^{\dagger} b_x + b_y^{\dagger} b_y + 1 + \kappa\left(b_x^{\dagger} + b_x\right) & \kappa\left(b_y^{\dagger} + b_y\right) \\ \kappa\left(b_y^{\dagger} + b_y\right) & b_x^{\dagger} b_y + b_y^{\dagger} b_y + 1 - \kappa\left(b_x^{\dagger} + b_x\right) \end{pmatrix}$$

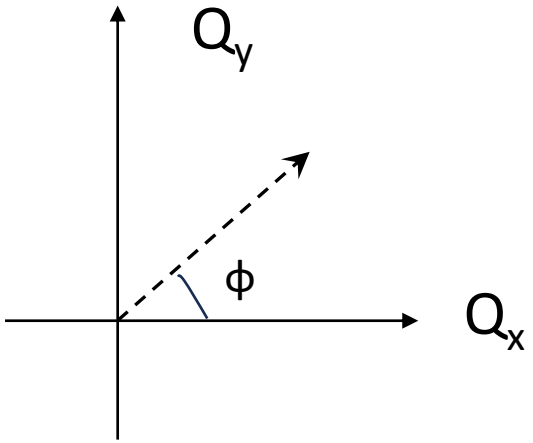
Selection rules

Orbital representations : $\Lambda \in [\Gamma \times \Gamma] - A_1$

Spin representations: $\Lambda \in \{\Gamma \times \Gamma\} - A_1$

$\mathbf{D_3}$				
C3v	A_1	A_2	E	
	a_1	a_2	x	y
$x\ \ x$	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0
$y\ \ y$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
$x\ \ y$	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$
$y\ \ x$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$

Towards an Ansatz: rotational symmetry analysis in boson space

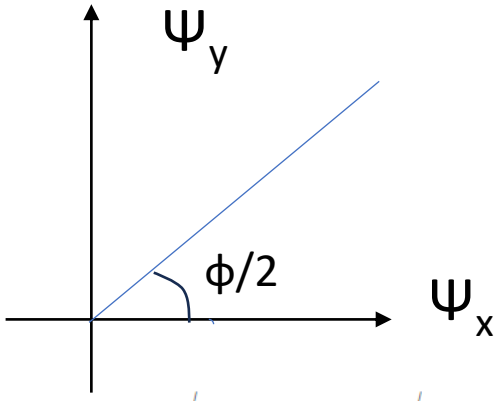


$$
\begin{aligned}
Q_x &= \frac{1}{\sqrt{2}}\left(b_x^\dagger + b_x\right) \\
P_x &= \frac{i}{\sqrt{2}}\left(b_x^\dagger - b_x\right)
\end{aligned}
$$

$$
\begin{aligned}
\hat{\mathcal{L}}_z &= Q_x P_y - Q_y P_x \\
&= \frac{i}{2}\left[\left(b_x^\dagger + b_x\right)\left(b_y^\dagger - b_y\right) - \left(b_y^\dagger + b_y\right)\left(b_x^\dagger - b_x\right)\right] \\
&= i\left(b_y^\dagger b_x - b_x^\dagger b_y\right)
\end{aligned}
$$

$$
\left[\hat{\mathcal{L}}_z, \mathcal{H}\right] = i\begin{pmatrix} \kappa\left(b_y^\dagger + b_y\right) & -\kappa\left(b_x^\dagger + b_x\right) \\ -\kappa\left(b_x^\dagger + b_x\right) & -\kappa\left(b_y^\dagger + b_y\right) \end{pmatrix}
$$

Towards an Ansatz: rotational symmetry analysis in fermion space



$$|\psi_-\rangle = \cos\frac{\phi}{2}|x\rangle + \sin\frac{\phi}{2}|y\rangle$$

$$\hat{\mathcal{S}}_z = \frac{i}{2}\left(f_y^\dagger f_x - f_x^\dagger f_y\right)$$

$[\mathcal{S}z,\mathcal{H}] = -[\mathcal{L}z,\mathcal{H}]$ → $[\mathcal{S}z + \mathcal{L}z,\mathcal{H}] = 0$

$$\hat{\mathcal{J}}_z = \hat{\mathcal{L}}_z + \hat{\mathcal{S}}_z$$

$\mathcal{J}_z$ and $\mathcal{H}$ commute.

Construction of symmetry adapted boson and fermion operators

$$b_{\pm}^{\dagger} = \frac{1}{\sqrt{2}}\left(b_x^{\dagger} \pm i b_y^{\dagger}\right) \qquad \left[\hat{\mathcal{L}}_z, b_{\pm}^{\dagger}\right] = \pm b_{\pm}^{\dagger}$$

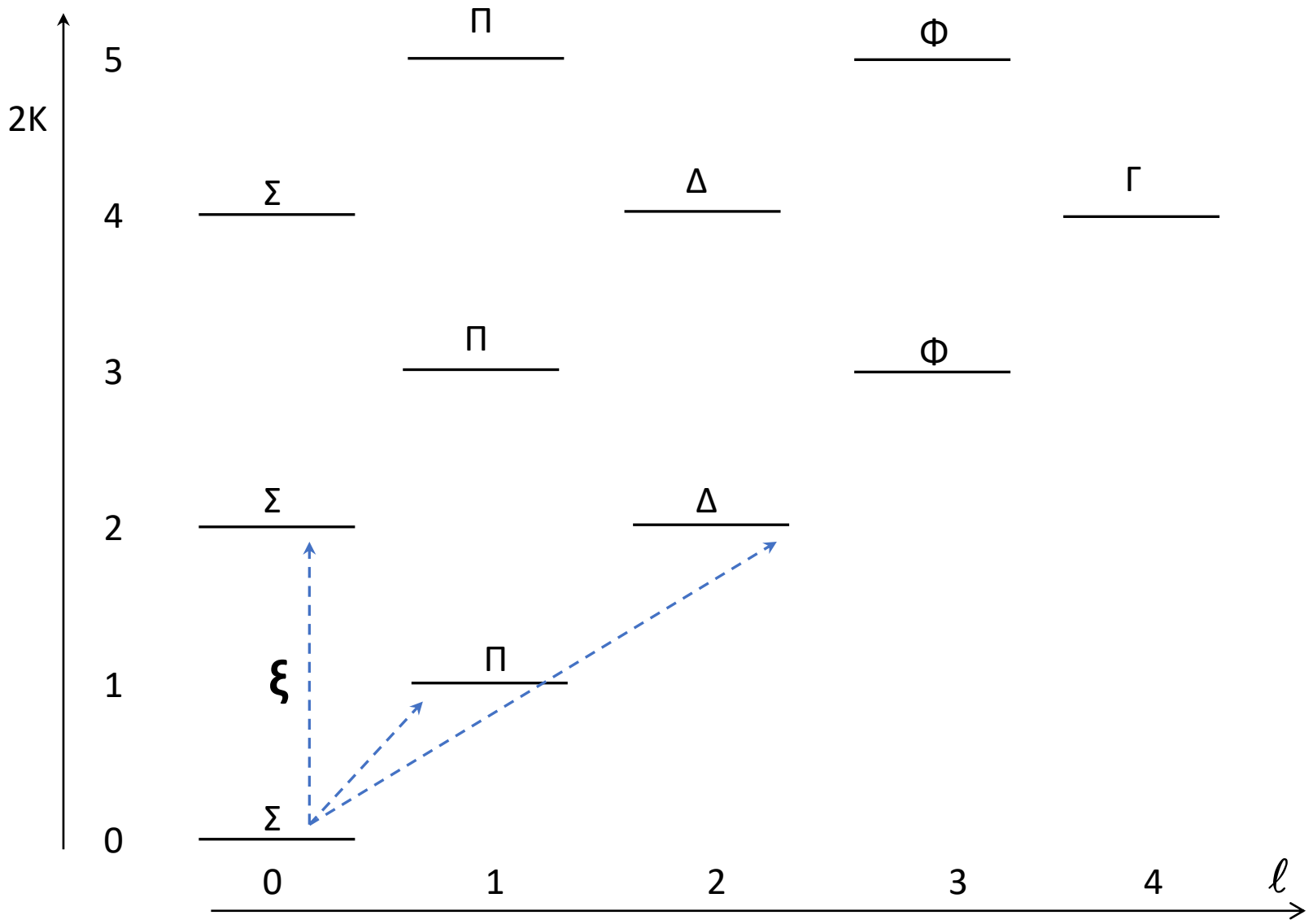
$$b_{\pm} = \frac{1}{\sqrt{2}}\left(b_x \mp i b_y\right) \qquad \left[\hat{\mathcal{L}}_z, b_{\pm}\right] = \mp b_{\pm}$$

$$|\uparrow\rangle = \frac{1}{\sqrt{2}}\left(|x\rangle + i|y\rangle\right) \qquad \hat{\mathcal{S}}_z|\uparrow\rangle = +\frac{1}{2}|\uparrow\rangle$$

$$|\downarrow\rangle = \frac{1}{\sqrt{2}}\left(|x\rangle - i|y\rangle\right) \qquad \hat{\mathcal{S}}_z|\downarrow\rangle = -\frac{1}{2}|\downarrow\rangle$$

Cylindrical (Qx,Qy) oscillator:
Angular momentum content

$$\xi = b_+^\dagger b_-^\dagger$$



Boson-fermion products with definite angular momentum *j=l+1/2 can be obtained in two ways:*

- *as the addition of an l oscillator state with a spin-up electron state*
- *as the subtraction of an l+1 oscillator state with a spin-down electronic state.*

Hence the Ansatz:

$$|\Psi\rangle_{l+1/2} = (b_+^\dagger)^l \Phi_1(\xi)|\uparrow\rangle + (b_+^\dagger)^{l+1} \Phi_2(\xi)|\downarrow\rangle$$

… and its time reversed partner:

$$|\Psi\rangle_{-l-1/2} = (b_-^\dagger)^l \Phi_1(\xi)|\downarrow\rangle + (b_-^\dagger)^{l+1} \Phi_2(\xi)|\uparrow\rangle$$

This means we take leave from the Born-Oppenheimer approximation!

Hamiltonian in the rotational symmetry basis:

$$\mathcal{H} = \begin{pmatrix} b_+^\dagger b_+ + b_-^\dagger b_- & \kappa\sqrt{2}\left(b_-^\dagger + b_+\right) \\ \kappa\sqrt{2}\left(b_+^\dagger + b_-\right) & b_+^\dagger b_+ + b_-^\dagger b_- \end{pmatrix} \begin{pmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{pmatrix}$$

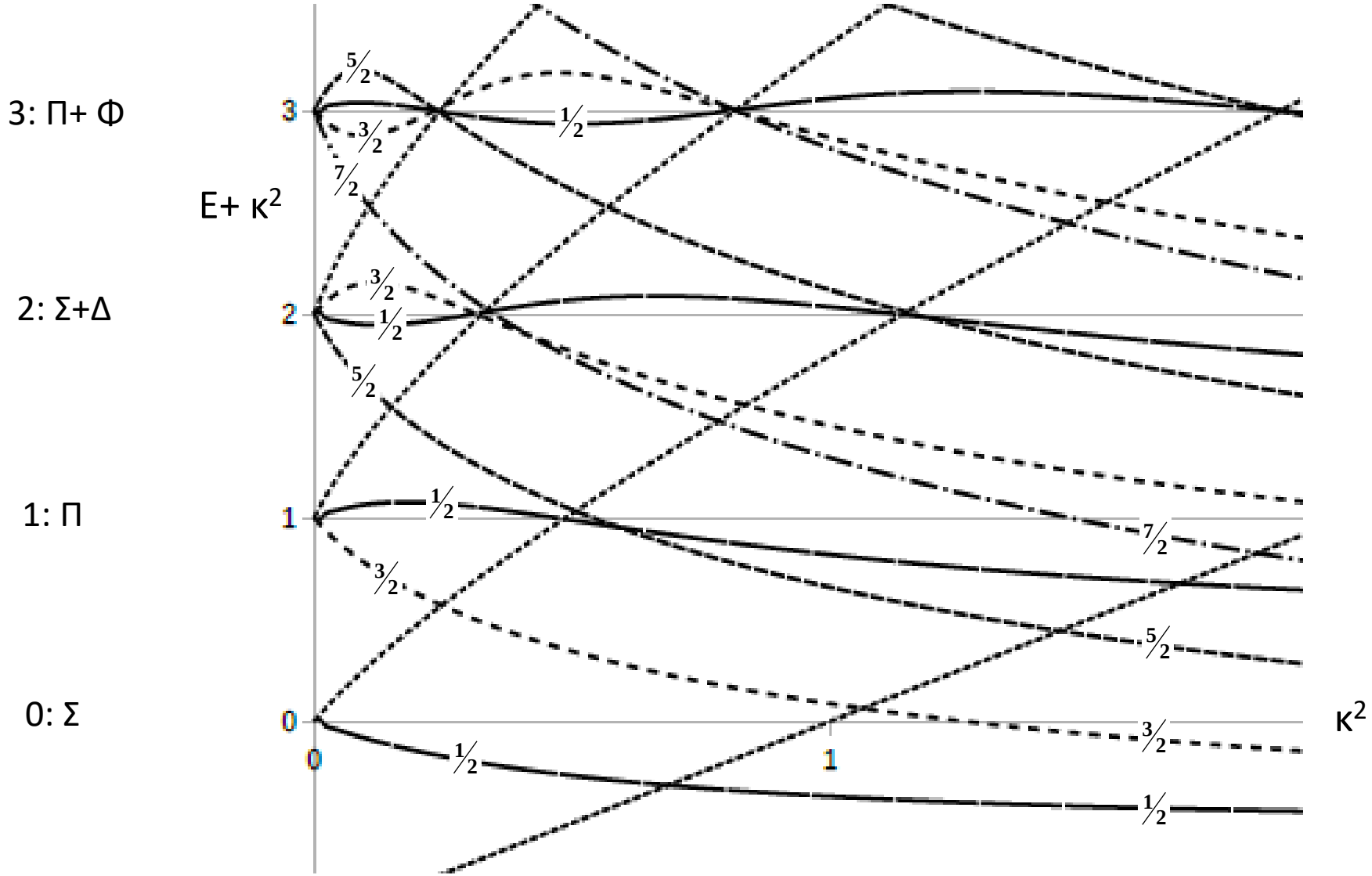
Set up the Schrödinger equation, using the Ansatz wavefunction

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle = \begin{pmatrix} b_+^\dagger b_+ + b_-^\dagger b_- & \kappa\sqrt{2}\left(b_-^\dagger + b_+\right) \\ \kappa\sqrt{2}\left(b_+^\dagger + b_-\right) & b_+^\dagger b_+ + b_-^\dagger b_- \end{pmatrix} \begin{pmatrix} (b_+^\dagger)^l \Phi_1(\xi) \\ (b_+^\dagger)^{l+1} \Phi_2(\xi) \end{pmatrix}$$

The angular part is completely factored out!

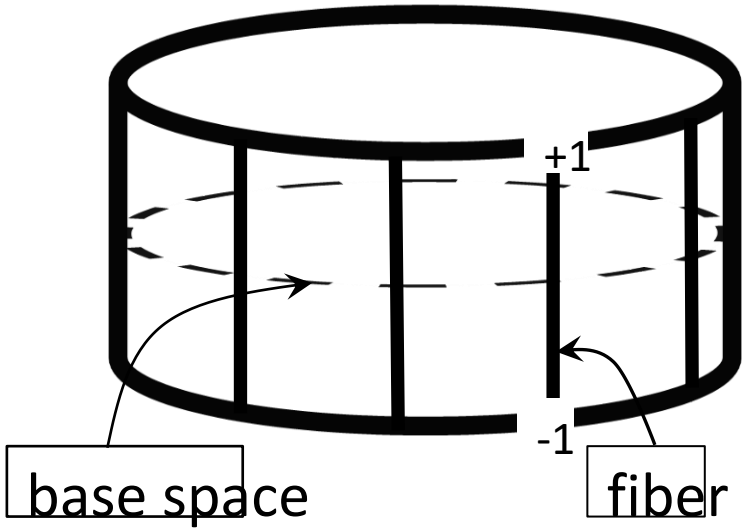
$$(l - E)\Phi_1 + 2\xi\frac{\partial}{\partial\xi}\Phi_1 + \kappa\sqrt{2}\left(\xi + (l+1) + \xi\frac{\partial}{\partial\xi}\right)\Phi_2 = 0$$

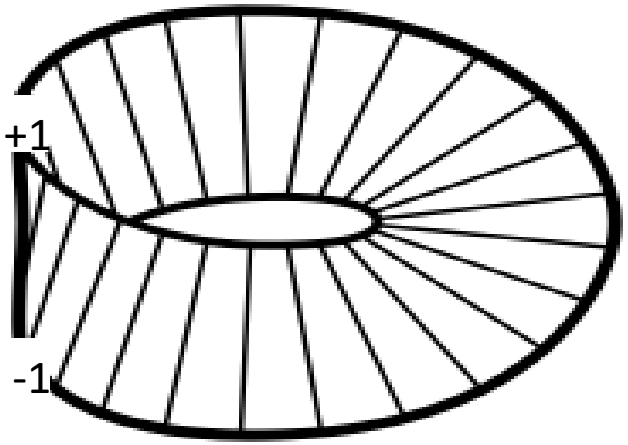
$$(l + 1 - E)\Phi_2 + 2\xi\frac{\partial}{\partial\xi}\Phi_2 + \kappa\sqrt{2}\left[1 + \frac{\partial}{\partial\xi}\right]\Phi_1 = 0$$


3: Π+ Φ
2: Σ+Δ
1: Π
0: Σ
E+ κ2
κ2
3
2
1
0
0
1
5/2
3/2
7/2
1/2

The Berry phase

Holonomy is what is observed in the fiber bundle when a closed loop is performed in the base space.





The connection between both is provided by the time dependent Schrödinger equation under adiabatic constraints

$$\mathcal{H}(\mathbf{R})|n(\mathbf{R})\rangle = E_n(\mathbf{R})|n(\mathbf{R})\rangle$$

|n(R)> differentiable and single valued

$$|\Psi\rangle = \exp\left(-\frac{iE_n}{\hbar}t\right)\exp\Big(i\gamma_n(t)\Big)|n(\mathbf{R}(t))\rangle$$

$$i\hbar\frac{d}{dt}|\Psi\rangle = E_n|\Psi\rangle - \hbar\frac{d\gamma_n}{dt}|\Psi\rangle + i\hbar\exp\left(-\frac{iE_n}{\hbar}t\right)\exp\Big(i\gamma_n(t)\Big)\frac{d}{dt}|n(\mathbf{R}(t))\rangle$$

$$-\frac{d\gamma_n}{dt}|\Psi\rangle + i\exp\left(-\frac{iE_n}{\hbar}t\right)\exp\left(i\gamma_n(t)\right)\frac{d}{dt}|n(\mathbf{R}(t))\rangle = 0$$

$$\begin{aligned} d\gamma_n &= i\langle n(\mathbf{R})|dn(\mathbf{R})\rangle \\ &= i\langle n(\mathbf{R})|\nabla_R|n(\mathbf{R})\rangle\cdot \mathrm{d}\mathbf{R} \end{aligned}$$

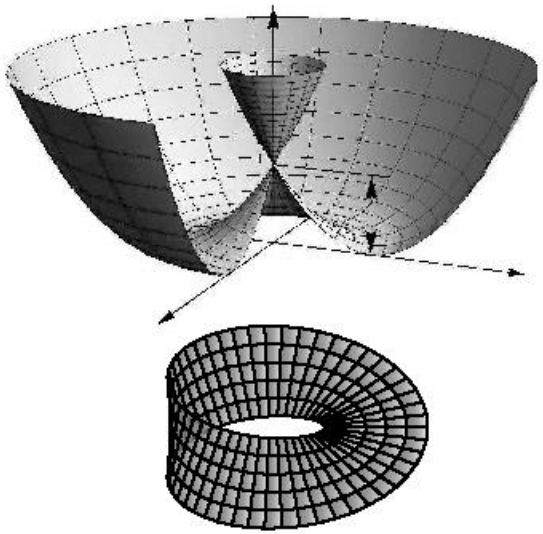
$$\gamma_n(C) = \oint_C d\gamma_n = i\oint\langle n|dn\rangle,$$

Application to the Jahn-Teller system

$$|n(\mathbf{R})\rangle = \exp -\frac{i\phi}{2}|\psi_-(\phi)\rangle = \exp -\frac{i\phi}{2}\left(\cos\phi/2|E_x\rangle + \sin\phi/2|E_y\rangle\right)$$

$$\begin{aligned} d|n(\mathbf{R})\rangle &= \exp -\frac{i\phi}{2}\left(-\frac{id\phi}{2}|\psi_-(\phi)\rangle + d|\psi_-(\phi)\rangle\right) \\ \langle n(\mathbf{R})|dn(\mathbf{R})\rangle &= -\frac{id\phi}{2} \end{aligned}$$

$$\gamma_n(C) = \oint_C d\gamma_n = i\oint\langle n|dn\rangle = i\oint(-\frac{i}{2}d\phi = \pi$$



As Berry writes, one might say that the dynamical phase factors give the system's best answers to two questions about its adiabatic circuit. For the dynamical phase the question is: how long did your journey take? For $\Upsilon n(C)$ it is: where did you go to?

Did we require this additional field term in our Hamiltonian?

$$\mathbf{A} = i\langle n(\mathbf{R})|\nabla_R|n(\mathbf{R})\rangle$$

$$\gamma_n(C) = \oint_C \mathbf{A}\cdot \mathrm{d}\mathbf{R}$$

This field term is a vector potential which changes the momentum operator:

P → **P** – q **A**

$$A_\phi = i\langle n|\frac{\delta}{\delta\phi}|n\rangle = \frac{1}{2} \qquad \rightarrow \qquad \mathbf{R}\wedge(\mathbf{P}-q\mathbf{A}) = \mathcal{L} - q\frac{1}{2} = \mathcal{J}_z$$

The field term affects the angular momentum, precisely as designed in the Ansatz!