Molecular symmetry effects on non-adiabatic coupling terms and quantum reaction dynamics via conical intersections

Jörn Manz

Freie Universität Berlin

Acknowledgments

- Freie Universität Berlin group

M. Leibscher, PhD.

Prof. D. Haase

- Al Quds University group

Prof. O. Deeb

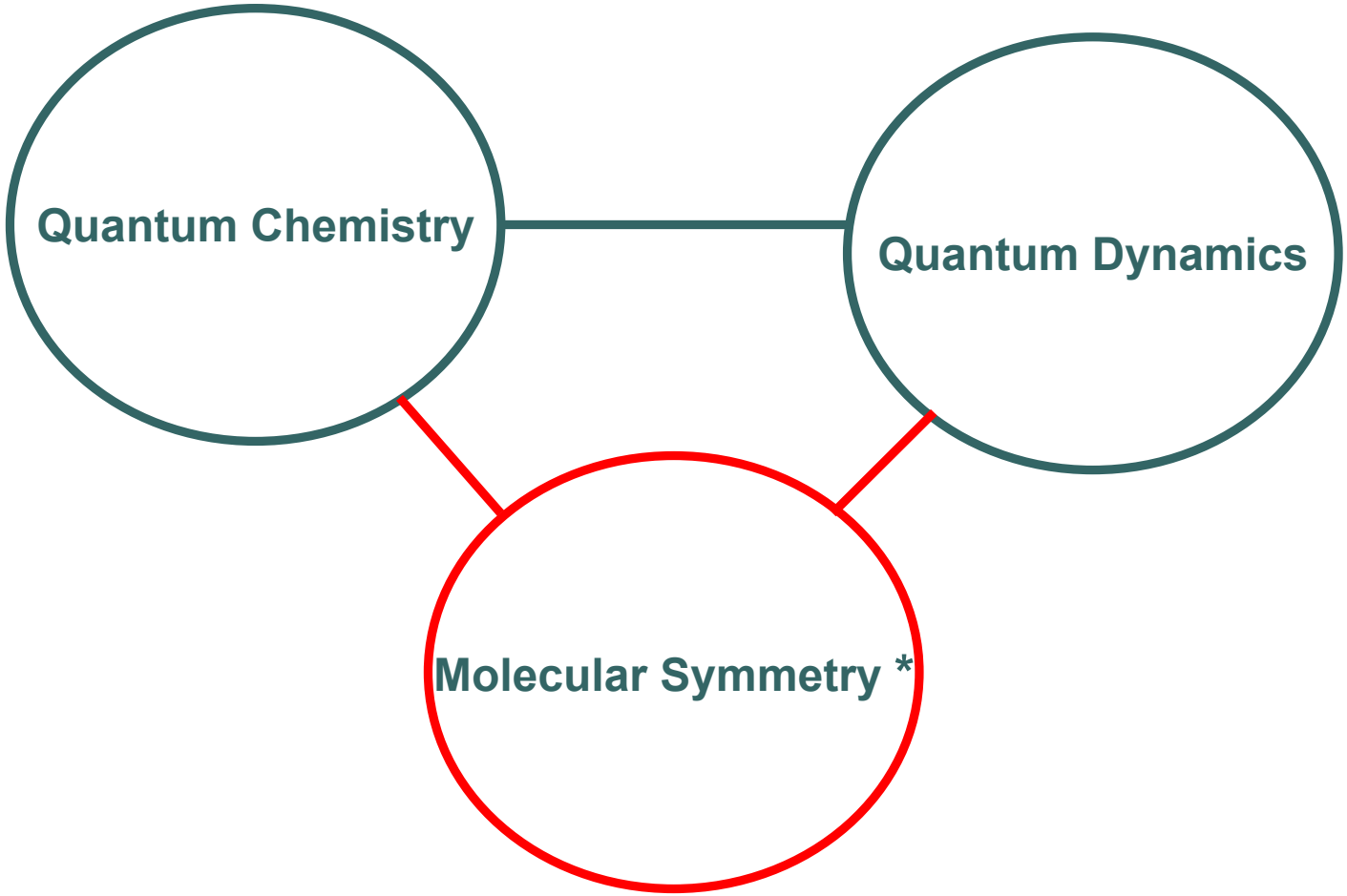
S. Al-Jabour

- Hebrew University Jerusalem group

Prof. M. Baer

Prof. S. Zilberg

Dr. X. Xu



* NOT molecular point group

Bunker, P. R.;Jensen, P., Molecular Symmetry and Spectroscopy; NRC Research Press, Ottawa 1998.
S. Al-Jabour, M. Baer, O. Deeb, M. Leibscher, J. Manz, X. Xu, S. Zilberg; J. Phy. Chem. A, *in press*

Outline:

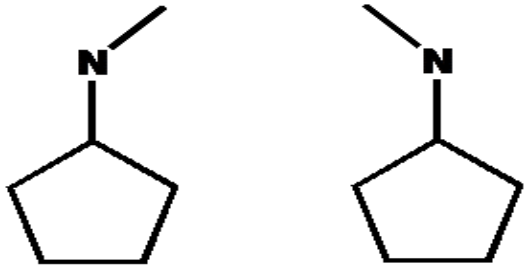
- Molecular point group versus molecular symmetry group
- MS- adapted coordinates
- Locating the CIs using Longuet-Higgins loops
- Determination of the irreducible representations (IREPs) of NACTs
- Applying molecular Symmetry rule on C_5H_4NH NACT
- Charges and IREPs of conical intersections
- Seam of conical intersections
- Effects of NACTs on Quantum Reaction Dynamics

Molecular point group versus molecular symmetry group

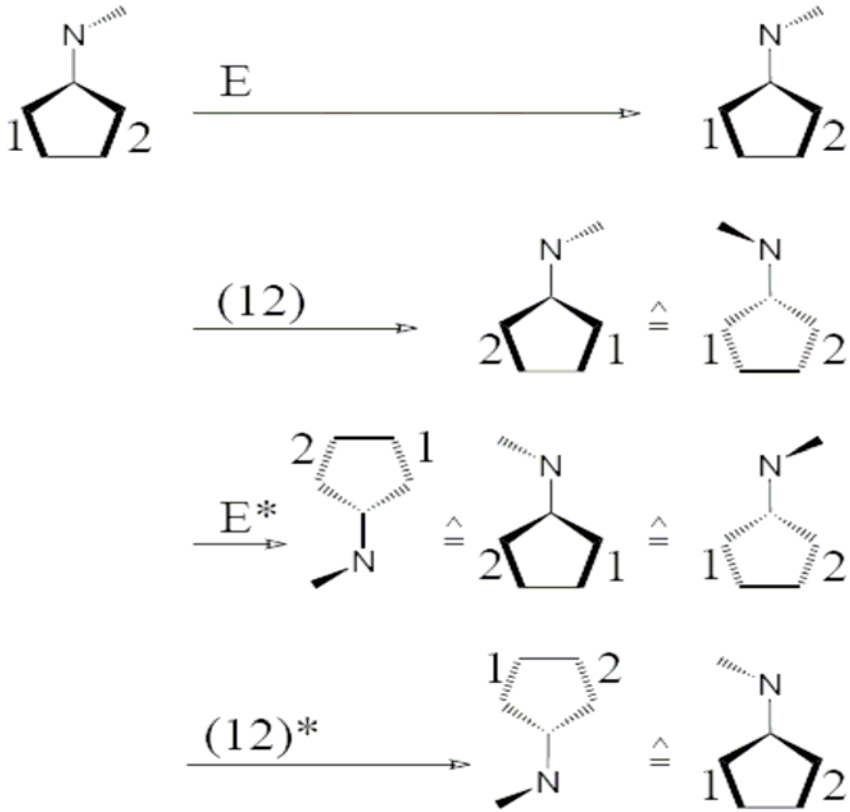
- **Molecular point group**: only for local structures (minima, transition states, conical intersection)

- **Molecular symmetry group**: global (all feasible inversion and permutation which commute with the Hamiltonian)

Example: Cyclopenta-2,4-dienimine



cis **“syn”** **trans** **“anti”**



Character table

Molecular point group

C_{2v}	E	C_2	σ_v	σ'_v	coordinates
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Molecular symmetry group

$C_{2v}(M)$	E	(12)	E*	(12)*	MS adapted coordinates
A_1	1	1	1	1	?
A_2	1	1	-1	-1	? "q"
B_1	1	-1	1	-1	?
B_2	1	-1	-1	1	?

- Symmetry projection operators and symmetry adapted coordinates

Example:

$$P^{B_1} x = \frac{1}{4}(E - C_2 + \sigma_V - \sigma_V^{'})x = x$$

"x has B_1 symmetry"

$$P^{A_2} q = \frac{1}{4}(E + (12) - E^{*} - (12)^{*})q = q$$

"q has A_2 MS symmetry"

1st. Goal: construct MS- adapted coordinates

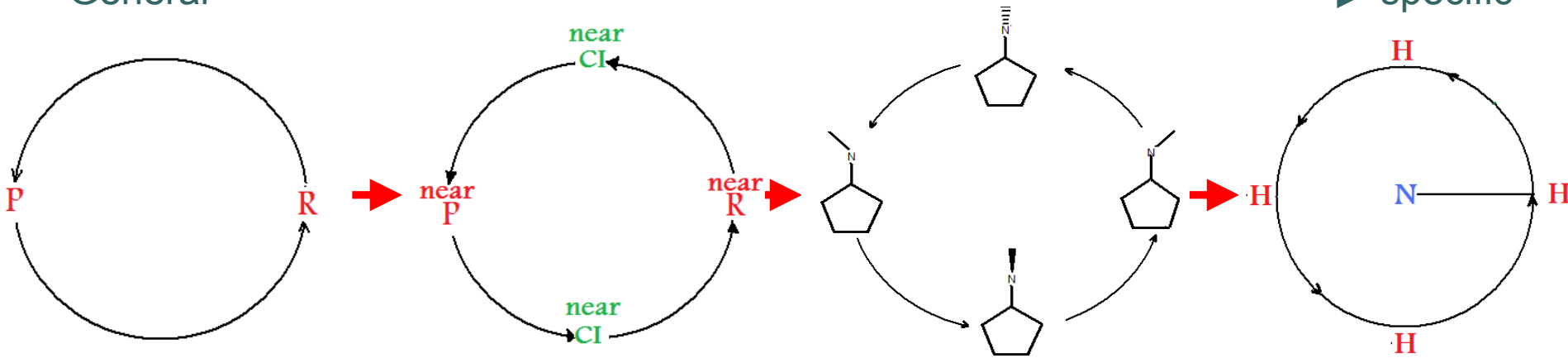
- In general: 3N-6 symmetry adapted coordinates, these describe feasible motions of large and small amplitudes

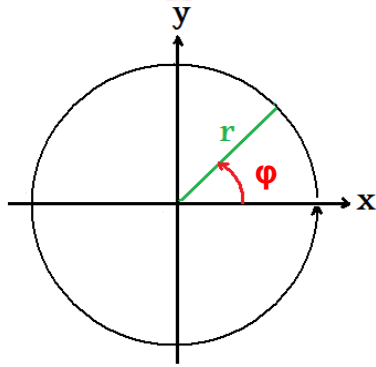
- Model: small amplitudes: frozen
  large amplitude: moving

Example:

torsion angle (φ) describing cis-trans isomerization reaction.

General → specific





$C_{2v}(M)$	E	(12)	E*	(12)*	MS adapted coordinates	MS adapted derivatives
A_1	1	1	1	1	$P^{A_1} r = r \Leftrightarrow r$	has A_1 symmetry
A_2	1	1	-1	-1	$P^{A_2} \varphi = -\varphi \Leftrightarrow \varphi$	has A_2 symmetry
B_1	1	-1	1	-1	$P^{B_1} y = y \Leftrightarrow y$	has B_1 symmetry
B_2	1	-1	-1	1	$P^{B_2} x = x \Leftrightarrow x$	has B_2 symmetry

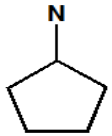
One can show that

r d/dr

φ, (R φ) d/dφ

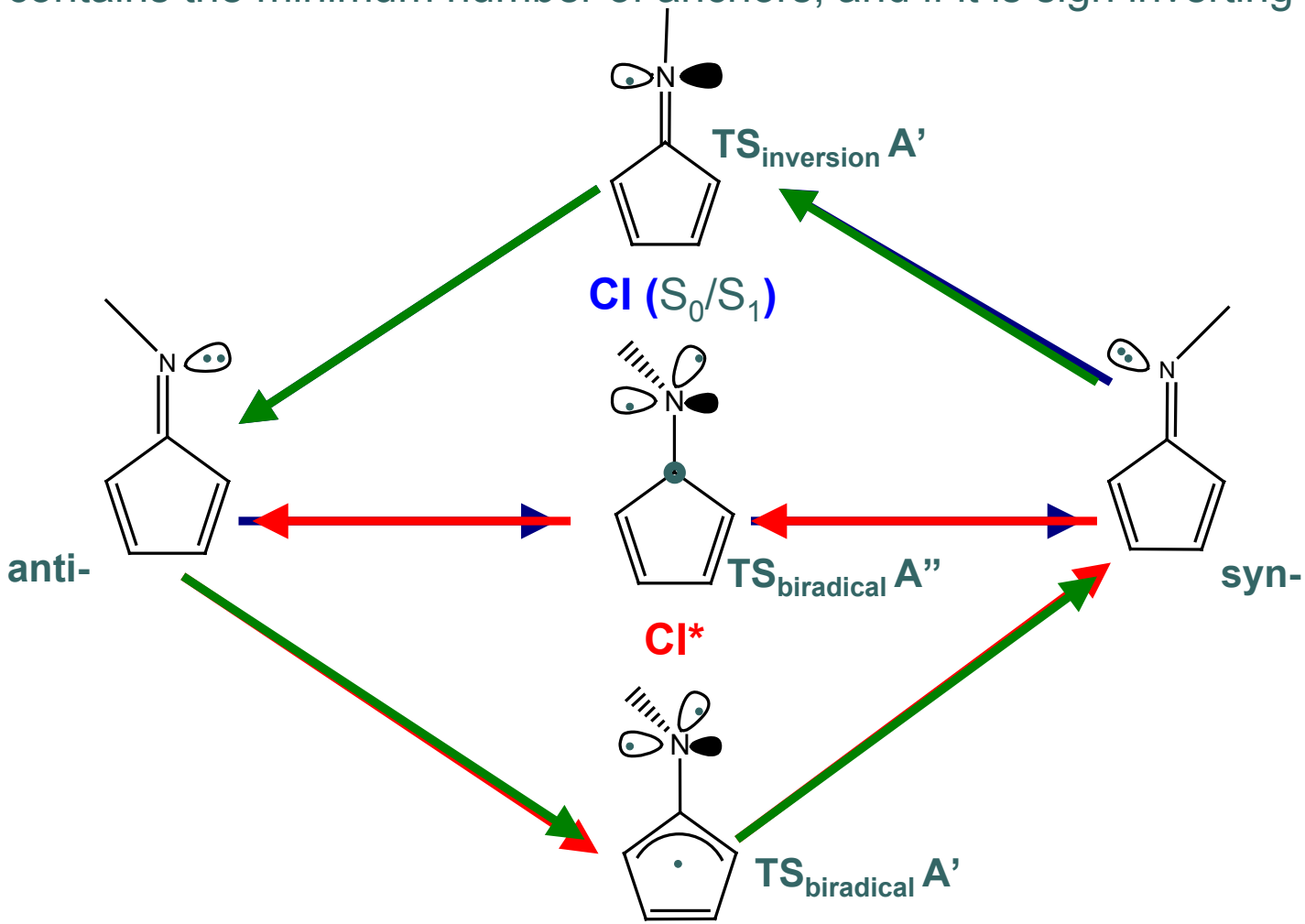
y d/dy

x d/dx

Frozen geometry of  (3N-6-1 coordinates) : near CI ➔ need quantum chemistry to locate CI

Locating the CIs using Longuet-Higgins loops

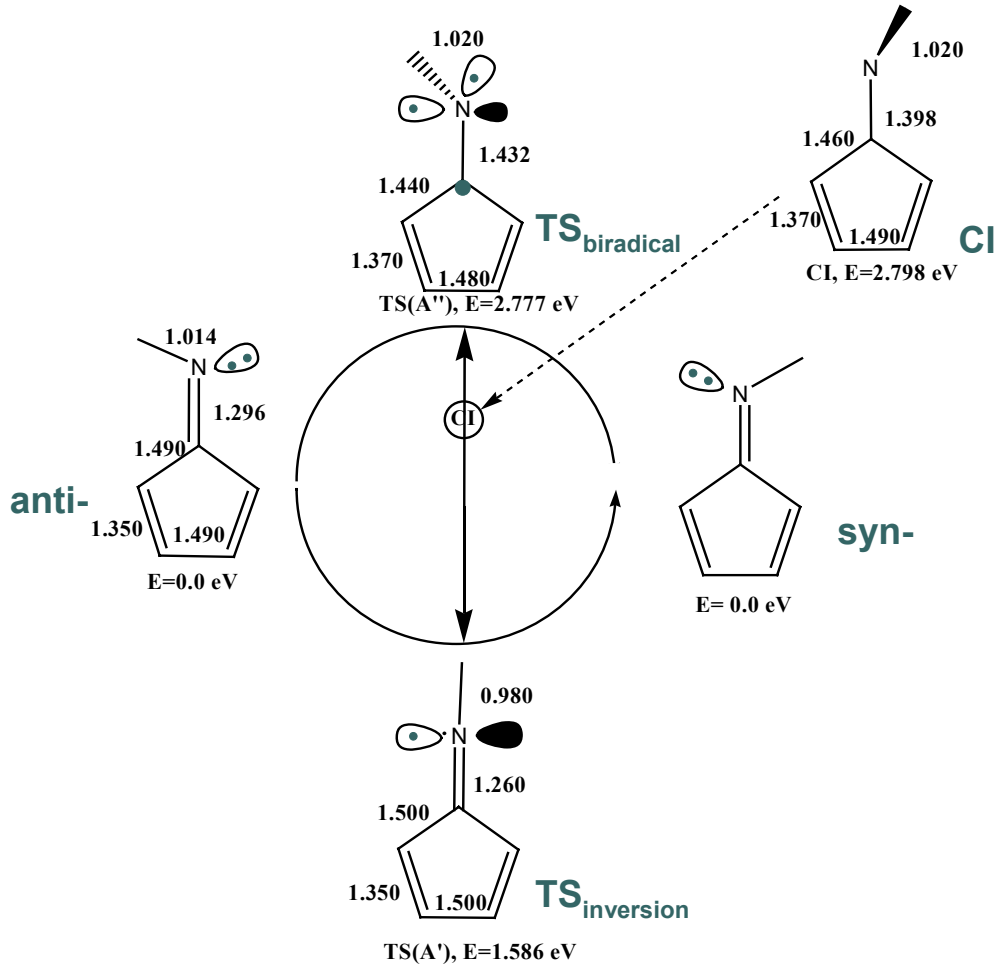
According to LH theorem, a single CI exists within any LH loop if the loop contains the minimum number of anchors, and if it is sign inverting*

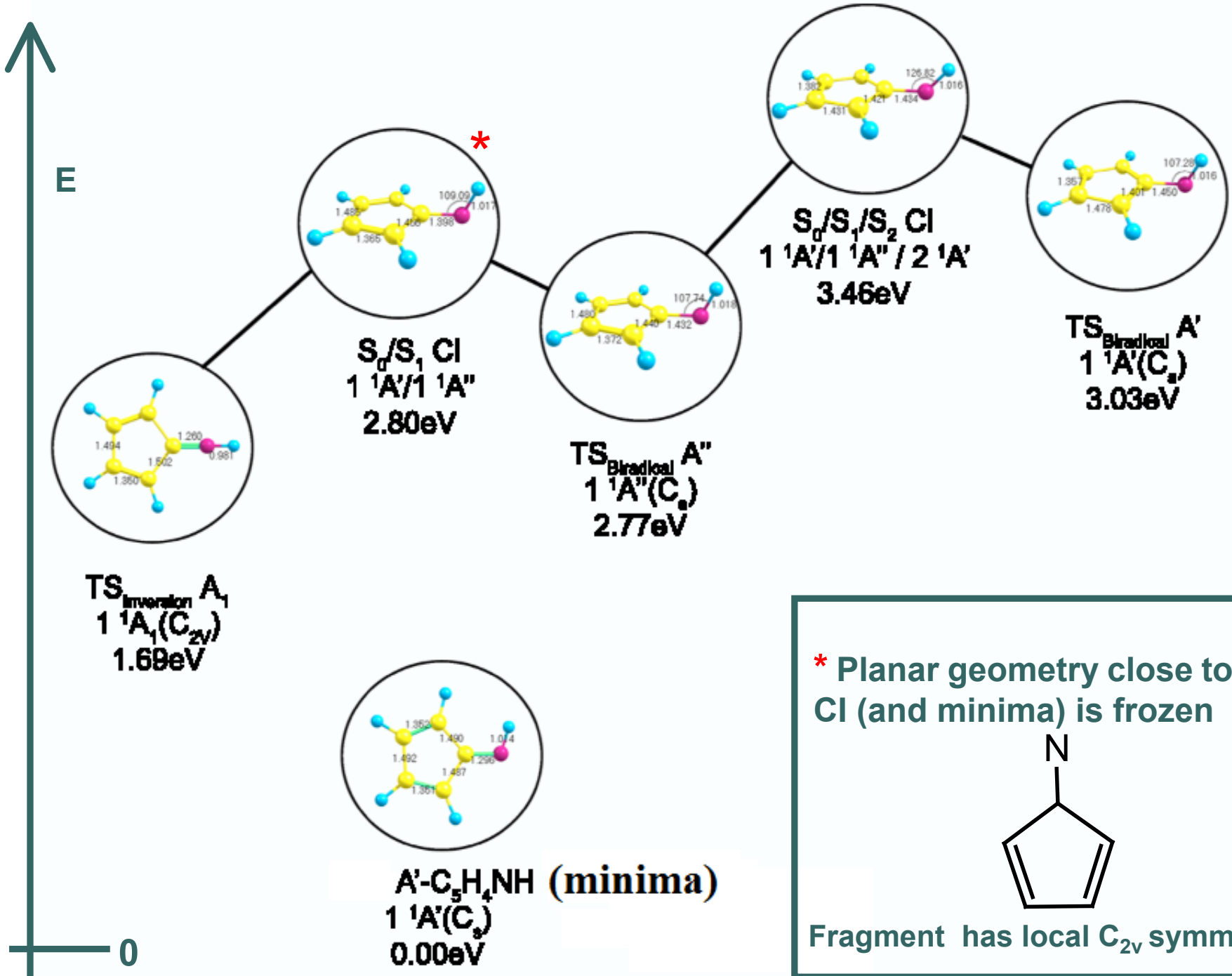


LH_2 ⟹ syn- — TS$_{inversion}$ A'' — anti- — TS$_{biradical}$ A'' — syn- → Sign inverting

* Haas, Y.; Zilberg, S.; Adv. Chem. Phys. 2002, 124, 433.

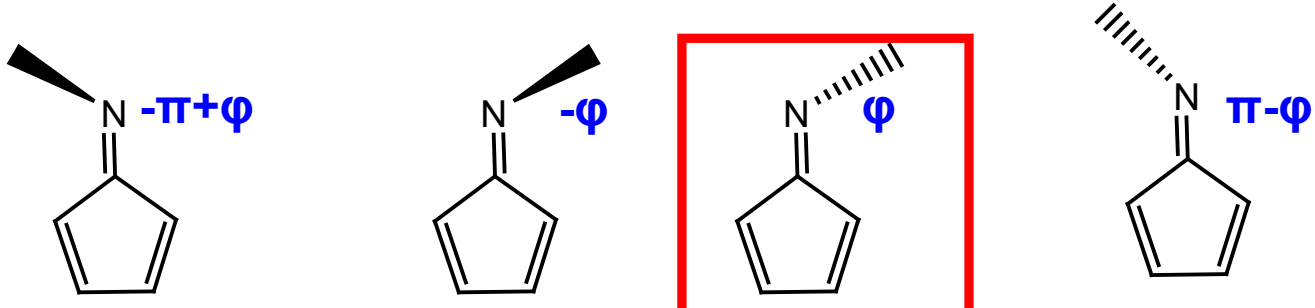
Locating the CI using Longuet-Higgins loops, cont'd



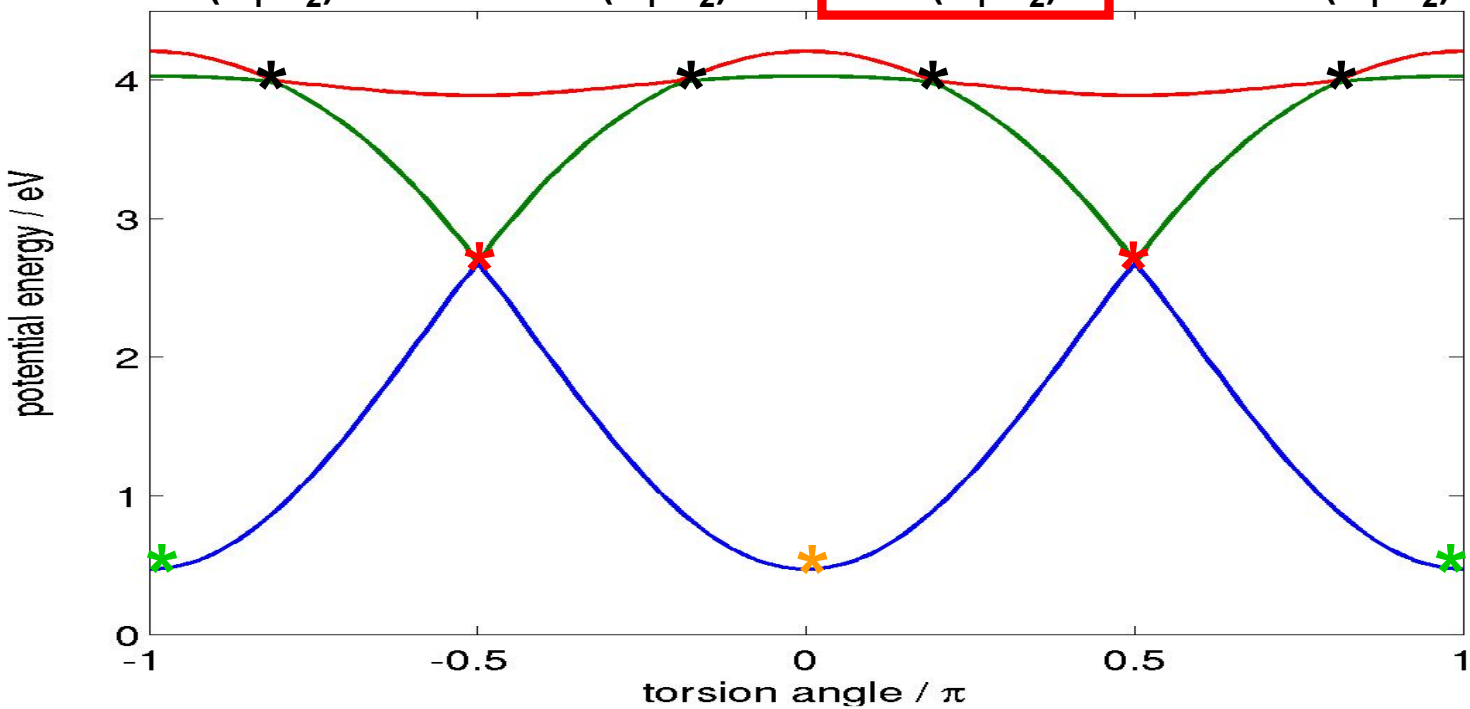


* Planar geometry close to S_0/S_1 CI (and minima) is frozen

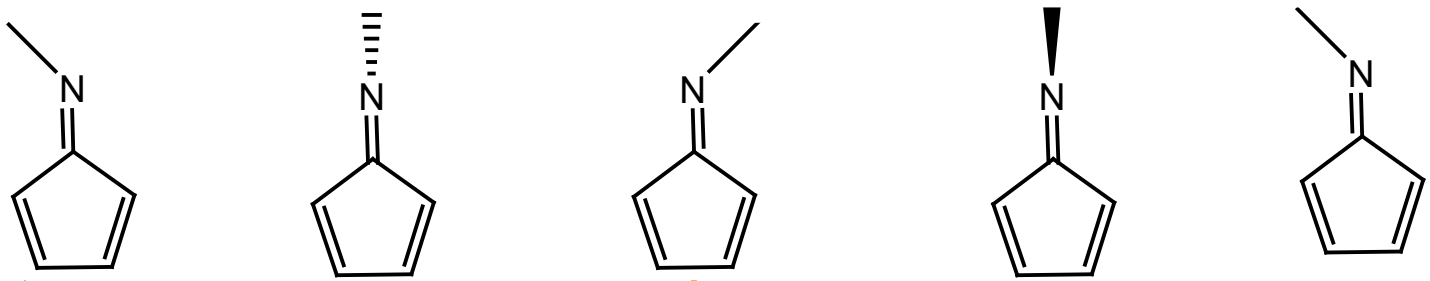
Fragment has local C_{2v} symmetry



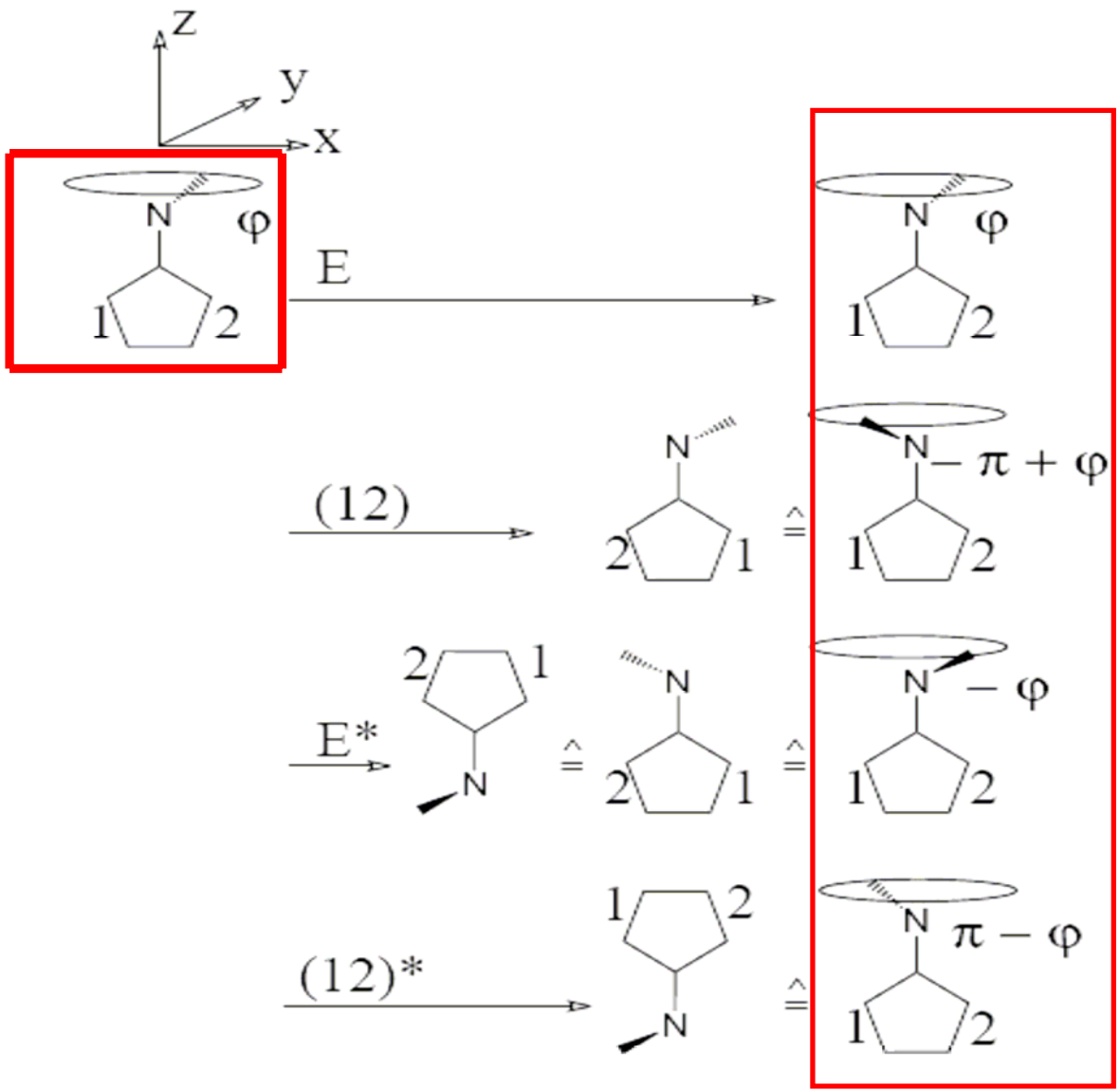
CI (S_1/S_2) CI (S_1/S_2) CI (S_1/S_2) CI (S_1/S_2)



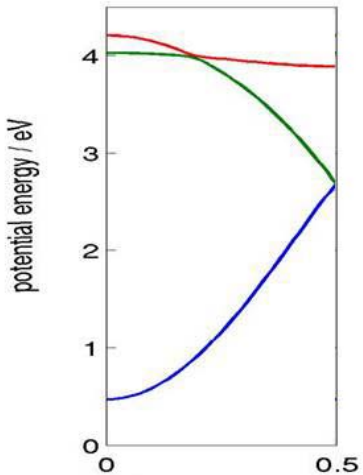
Close to

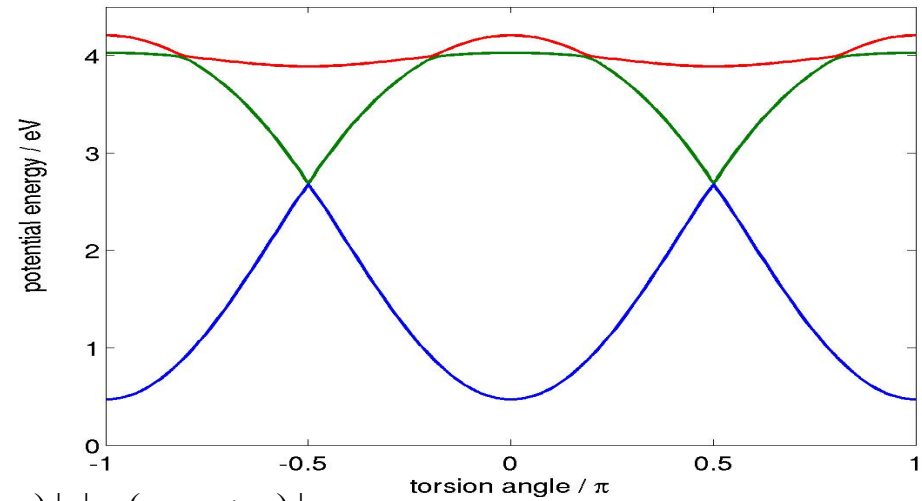


trans anti- CI (S_0/S_1) cis syn- CI (S_0/S_1) trans Anti-


z
y
x
N
φ
1
2
E
(12)
N
2
1
≙
N
− π + φ
1
2
E*
2
1
N
≙
N
2
1
≙
N
− φ
1
2
(12)*
1
2
N
≙
N
π − φ
1
2

PES

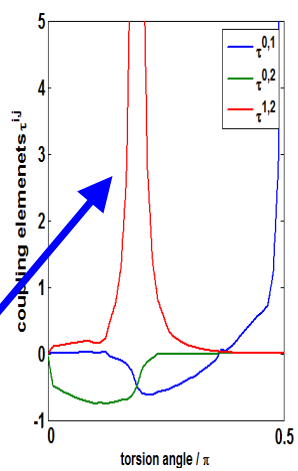




$$|\psi(r,\varphi)| = |\psi(r,-\varphi)| = |\psi(r,\pi-\varphi)| = |\psi(r,-\pi+\varphi)|$$

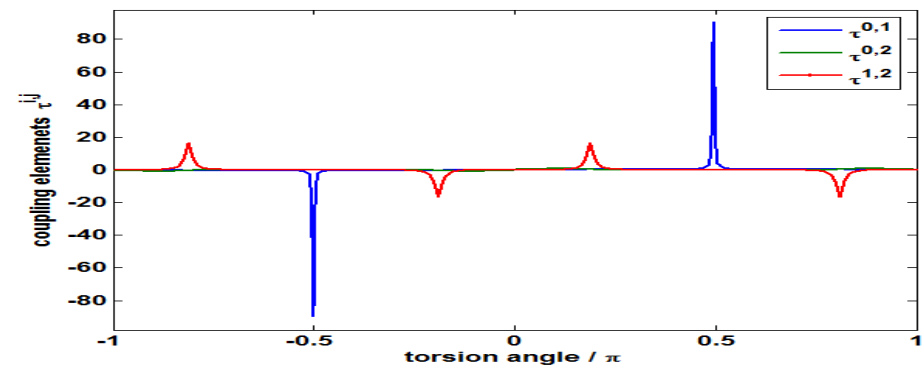
NACTs

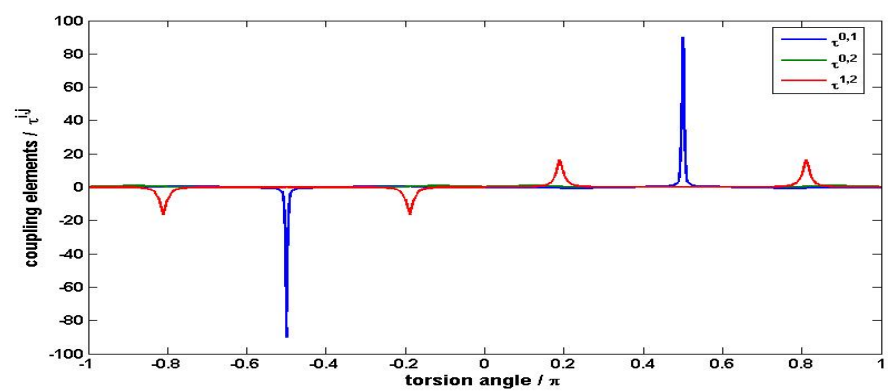
$$\left\langle \Psi_i \left| \frac{\partial}{\partial \varphi} \Psi_j \right. \right\rangle$$



?

?



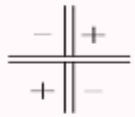


Pole property*

* Baer, *Beyond Born Oppenheimer: Electronic non- adiabatic coupling terms and conical intersections*, Wiley (2006).

Determination of the irreducible representations (IREPs) of NACTs

- Step 1: sign and nodal patterns

$C_{2v}(M)^{(a)}$ $\hat{S}_g$	E $\hat{S}_1$	(12) $\hat{S}_2$	E* $\hat{S}_3$	(12)* $\hat{S}_4$	coord. (rotation)	deriv.	rel. signs and nodes$^{(b)}$
A_1	1	1	1	1	r	$\partial/\partial r$	
A_2	1	1	-1	-1	ϕ ($\hat{R}_\phi$)	$\partial/\partial\phi$	
B_1	1	-1	1	-1	y	$\partial/\partial y$	
B_2	1	-1	-1	1	x	$\partial/\partial x$	
application to C_5H_4NH							
$(r,\phi) \rightarrow \hat{S}_g(r,\phi)$	(r,ϕ)	$(r,-\pi+\phi)$	$(r,-\phi)$	$(r,\pi-\phi)$	(d)		
$(x,y) \rightarrow \hat{S}_g(x,y)$	(x,y)	$(-x,-y)$	$(x,-y)$	$(-x,y)$	(e)		

Step 2: theorem of NACTs in $C_{2v}(M)$

Example:

$$\mathbf{IREP}\ (\tau_r^{i,j})\cdot\Gamma_r(\frac{\partial}{\partial r})\cdot\Gamma_\varphi(\frac{\partial}{\partial \varphi})$$

$$=\mathbf{IREP}\ (\left\langle \psi_i \left| \frac{\partial}{\partial r} \right| \psi_j \right\rangle)\cdot\Gamma_r(\frac{\partial}{\partial r})\cdot\Gamma_\varphi(\frac{\partial}{\partial \varphi})$$

$$= \qquad \Gamma_i\cdot\mathbf{A_1}\cdot\Gamma_j \quad \cdot\mathbf{A_1} \qquad \cdot\mathbf{A_2}$$

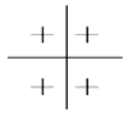
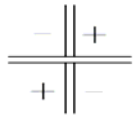
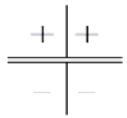
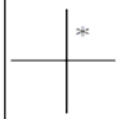
$$=\mathbf{IREP}\ (\left\langle \psi_i \left| \frac{\partial}{\partial \varphi} \right| \psi_j \right\rangle)$$

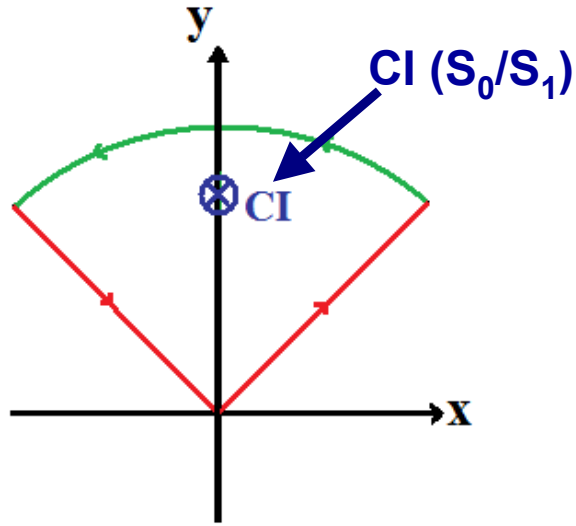
$$=\tau_\varphi^{i,j}$$

In general: $$\mathbf{IREP}\ \tau_k^{i,j}=\mathbf{IREP}\ \tau_l^{\mathbf{i,j}}\cdot\Gamma(\frac{\partial}{\partial k})\cdot\Gamma(\frac{\partial}{\partial l})$$

Character table

Four possibilities

$C_{2v}(M)^{(a)}$ $\hat{S}_g$	E $\hat{S}_1$	(12) $\hat{S}_2$	E^* $\hat{S}_3$	$(12)^*$ $\hat{S}_4$	coord. (rotation)	deriv.	rel. signs and nodes$^{(b)}$	(c) 1st	2nd	3rd	4th
A_1	1	1	1	1	r	$\partial/\partial r$		τ_ϕ	τ_r	τ_x	τ_y
A_2	1	1	-1	-1	ϕ $(\hat{R}_\phi)$	$\partial/\partial\phi$		τ_r	τ_ϕ	τ_y	τ_x
B_1	1	-1	1	-1	y	$\partial/\partial y$		τ_x	τ_y	τ_ϕ	τ_r
B_2	1	-1	-1	1	x	$\partial/\partial x$		τ_y	τ_x	τ_r	τ_ϕ
application to C_5H_4NH								—	τ_k^{12}	τ_k^{01} τ_k^{02}	—
$(r,\phi) \to \hat{S}_g(r,\phi)$ $(x,y) \to \hat{S}_g(x,y)$	(r,ϕ) (x,y)	$(r,-\pi+\phi)$ $(-x,-y)$	$(r,-\phi)$ $(x,-y)$	$(r,\pi-\phi)$ $(-x,y)$	(d) (e)						
sym.-related locations $\hat{S}_g(x,y)$					(f)						



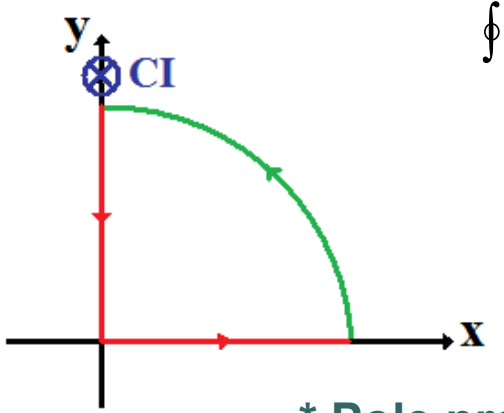
* 2nd possibility: $\oint \quad = 0$ contradiction

* 4th possibility: $\oint \quad = 0$ contradiction

* Quantization rule *: $\oint ds \cdot \tau^{i,i+1}(s \mid L_g) = \pm\pi$ **if** L_g **contains CI**

else

$\oint ds \cdot \tau^{i,i+1}(s \mid L_g) = 0$



* 1st possibility: $\oint \quad \neq 0$ contradiction

* Pole property: $\tau_k^{i,i+1}(s) \to \pm\infty \quad \text{for } s \to (s^{i,i+1})$

*** We are left with the 3rd possibility**

* Baer, *Beyond Born Oppenheimer: Electronic non- adiabatic coupling terms and conical intersections*, Wiley (2006).

Character table

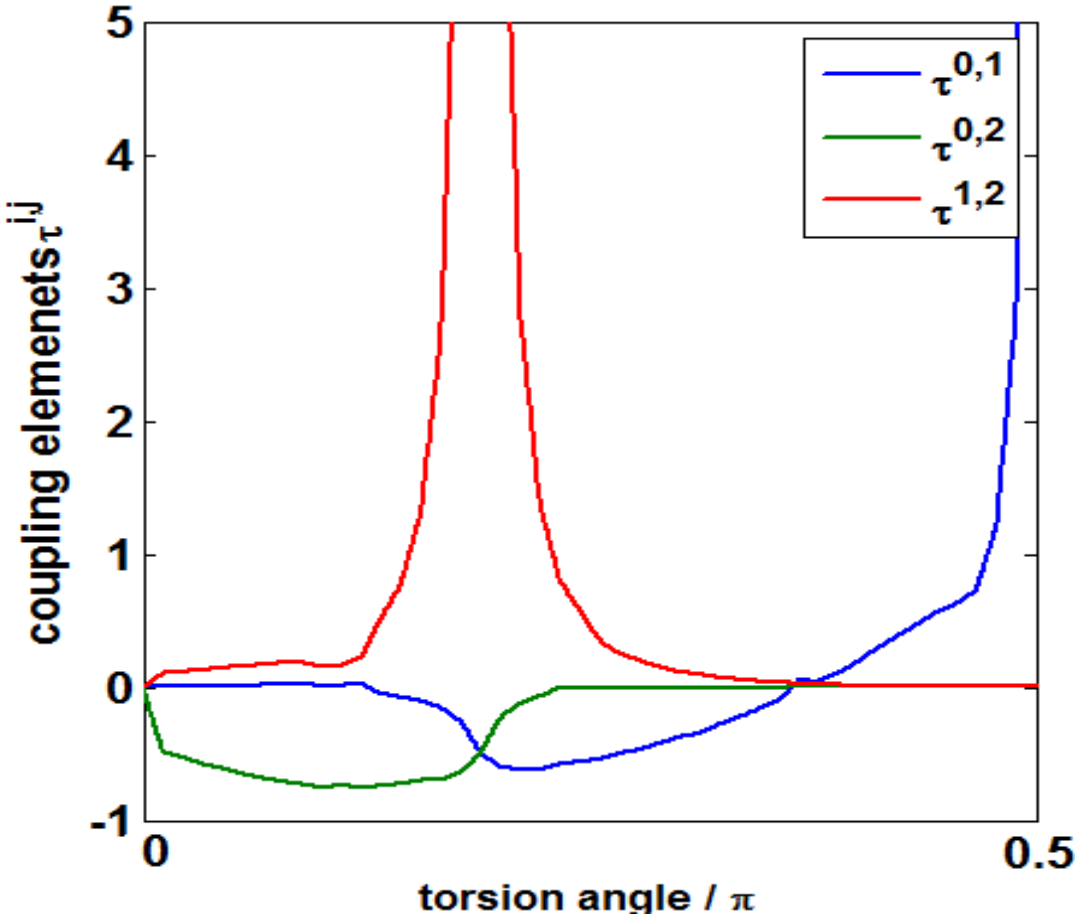
Four possibilities

$C_{2v}(M)^{(a)}$ $\hat{S}_g$	E $\hat{S}_1$	(12) $\hat{S}_2$	E^* $\hat{S}_3$	$(12)^*$ $\hat{S}_4$	coord. (rotation)	deriv.	rel. signs and nodes$^{(b)}$	(c) 1st	2nd	3rd	4th
A_1	1	1	1	1	r	$\partial/\partial r$	$\begin{array}{c\|c} + & + \\ \hline + & + \end{array}$	τ_ϕ	τ_r	τ_x	τ_y
A_2	1	1	-1	-1	ϕ $(\hat{R}_\phi)$	$\partial/\partial\phi$	$\begin{array}{c\|c} - & + \\ \hline + & - \end{array}$	τ_r	τ_ϕ	τ_y	τ_x
B_1	1	-1	1	-1	y	$\partial/\partial y$	$\begin{array}{c\|c} + & + \\ \hline - & - \end{array}$	τ_x	τ_y	τ_ϕ	τ_r
B_2	1	-1	-1	1	x	$\partial/\partial x$	$\begin{array}{c\|c} - & + \\ \hline - & + \end{array}$	τ_y	τ_x	τ_r	τ_ϕ
application to C_5H_4NH								—	τ_k^{12}	τ_k^{01} τ_k^{02}	—
$(r,\phi) \to \hat{S}_g(r,\phi)$ $(x,y) \to \hat{S}_g(x,y)$	(r,ϕ) (x,y)	$(r,-\pi+\phi)$ $(-x,-y)$	$(r,-\phi)$ $(x,-y)$	$(r,\pi-\phi)$ $(-x,y)$	(d) (e)						
sym.-related locations $\hat{S}_g(x,y)$	$\begin{array}{c\|c} & * \\ \hline & \end{array}$	$\begin{array}{c\|c} & \\ \hline * & \end{array}$	$\begin{array}{c\|c} & \\ \hline & * \end{array}$	$\begin{array}{c\|c} * & \\ \hline & \end{array}$	(f)						

NACTs $\tau_{\varphi}^{0,1}$ and $\tau_{\varphi}^{0,2}$ interchange at φ near CI (S_1 / S_2),

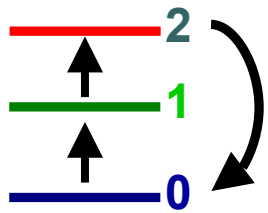
$\Rightarrow$ they also interchange at $\pi-\varphi, -\pi+\varphi, -\varphi$

$\Rightarrow \tau_{\varphi}^{0,1}$ and $\tau_{\varphi}^{0,2}$ have the same IREP = B_1



2nd theorem for NACTs

- Example



$$\mathbf{IREP}\,(\tau_{\varphi}^{0,1})\cdot\mathbf{IREP}\,(\tau_{\varphi}^{1,2})\cdot\mathbf{IREP}\,(\tau_{\varphi}^{2,0})$$

$$= \quad \mathbf{B_1}\cdot\mathbf{IREP}\,(\tau_{\varphi}^{1,2})\cdot\mathbf{B_1}$$

$$=\mathbf{IREP}\left\langle\psi_0\,|\,\frac{\partial}{\partial\varphi}\,|\,\psi_1\right\rangle\cdot\mathbf{IREP}\left\langle\psi_1\,|\,\frac{\partial}{\partial\varphi}\,|\,\psi_2\right\rangle\cdot\mathbf{IREP}\left\langle\psi_2\,|\,\frac{\partial}{\partial\varphi}\,|\,\psi_0\right\rangle$$

$$= \quad \Gamma_0\cdot\mathbf{A_2}\cdot\Gamma_1 \quad\cdot\quad \Gamma_1\cdot\mathbf{A_2}\cdot\Gamma_2 \quad\cdot\quad \Gamma_2\cdot\mathbf{A_2}\cdot\Gamma_0=\mathbf{A_2}$$

$$\Rightarrow\mathbf{IREP}\,(\tau_{\varphi}^{1,2})=\mathbf{A_2}$$

In general

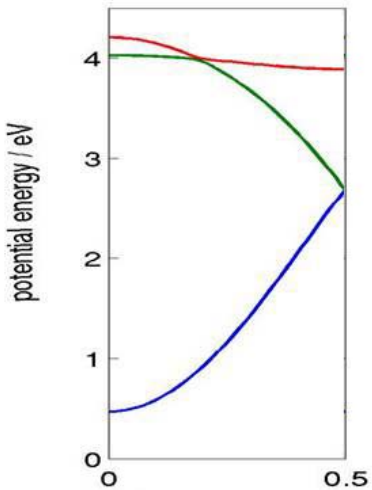
$$\mathbf{IREP}\,(\tau_{\mathbf{k}}^{0,1})\cdot\mathbf{IREP}\,(\tau_{\mathbf{k}}^{1,2})\cdot\ldots\cdot\mathbf{IREP}\,(\tau_{\mathbf{k}}^{z,0})$$

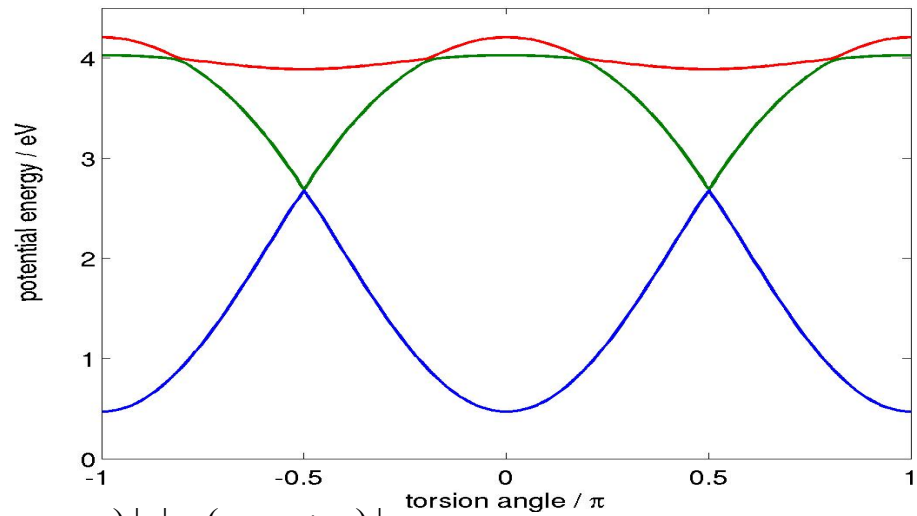
$$=\Gamma_k \;\; \textbf{if ungerade loop}$$

else

$$=\mathbf{A_1}\;\textbf{if gerade loop}$$

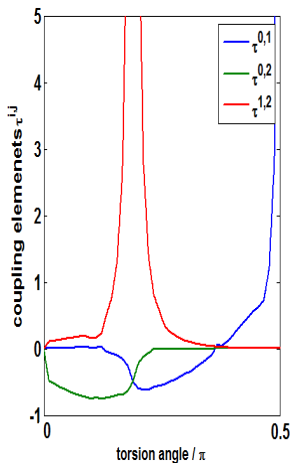
PES



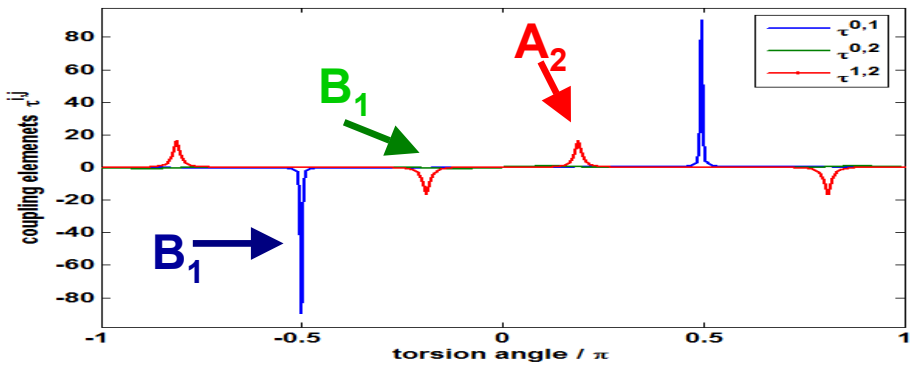


$$|\psi(r,\varphi)| = |\psi(r,-\varphi)| = |\psi(r,\pi-\varphi)| = |\psi(r,-\pi+\varphi)|$$

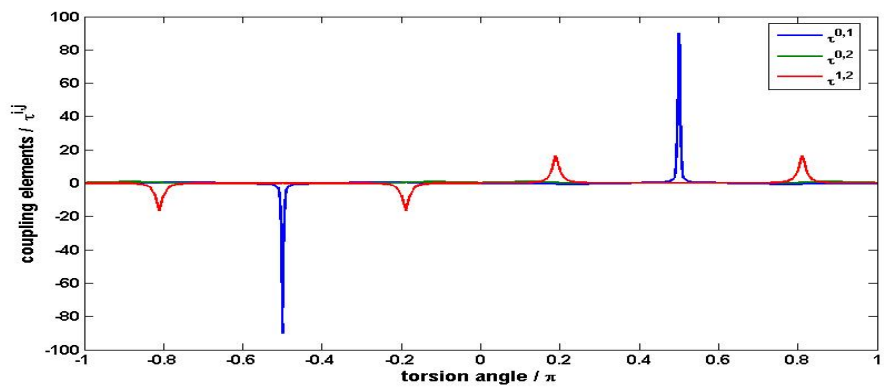
NACTs $\left\langle \psi_i \left| \frac{\partial}{\partial \varphi} \psi_j \right. \right\rangle$



ok



wrong

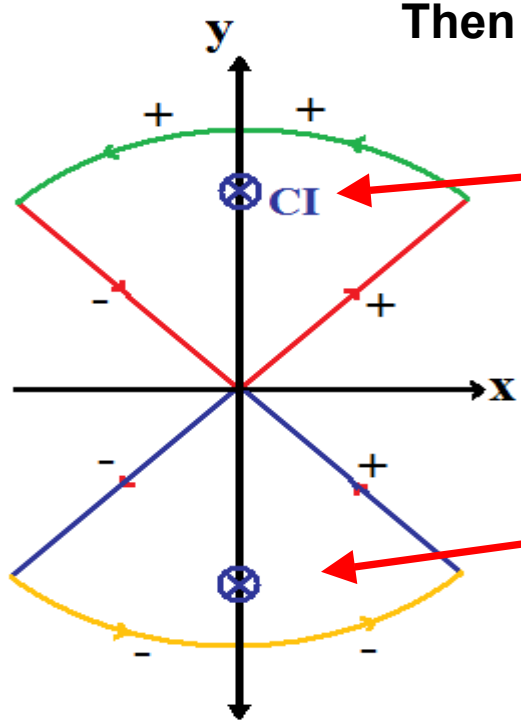


Charges and IREPs of conical intersections

$$\text{if} \oint ds\, \tau^{i,i+1}(s \mid L_g) = \pm\pi = e_i \cdot \pi$$

Then charge e_i of CI is ±1

Example: CI (S_0/S_1)



$e_1^{0,1} = +1$ **Arbitrary choice**

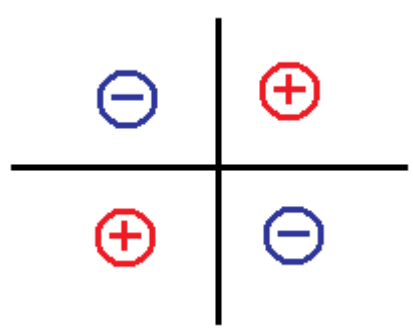
$e_2^{0,1} = -1$

Due to IREP of NACTs

➔ CI (S_0/S_1) has IREP B_1

➔ CI (S_1/S_2) has IREP A_2

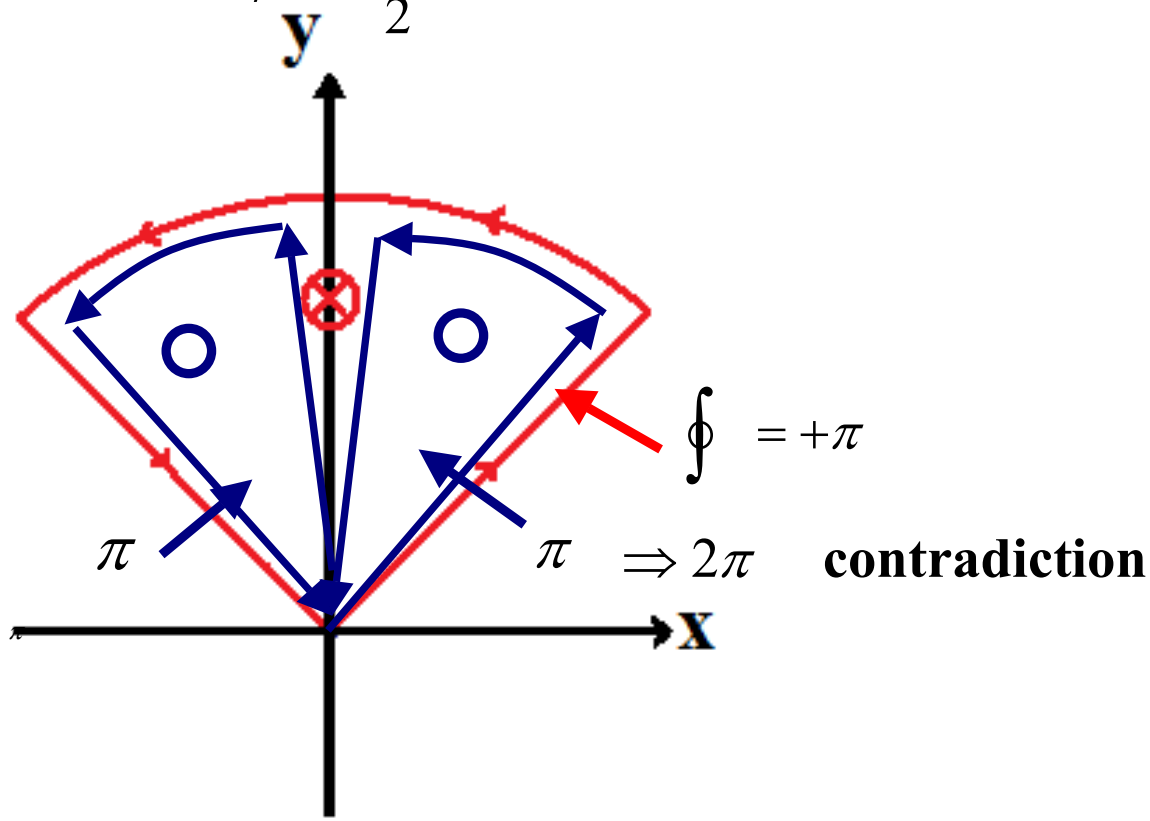
Example: CI (S_1/S_2)



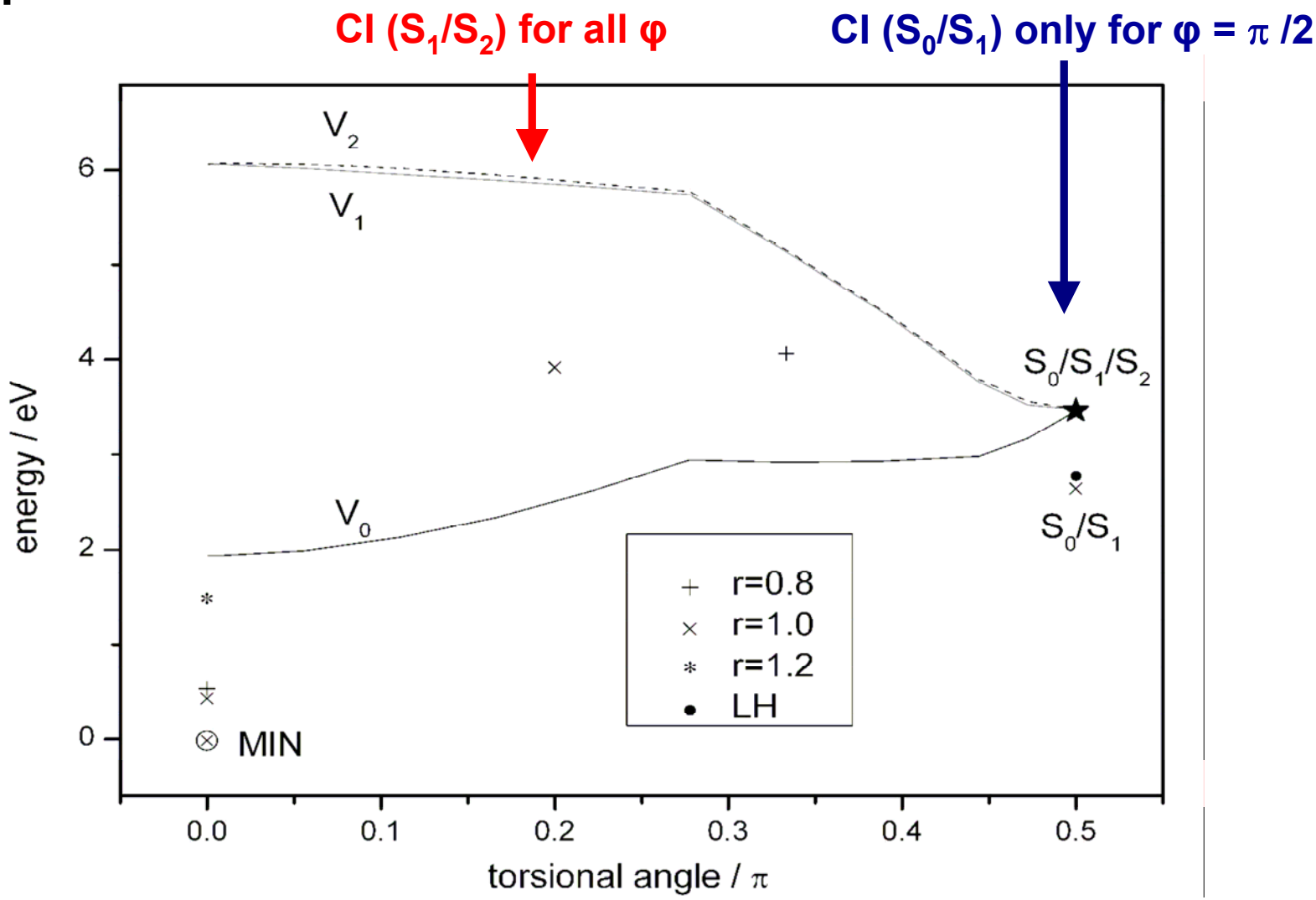
Seam of conical intersection

Example: CI (S_0/S_1) is restricted to $\varphi = \pm\frac{\pi}{2}$

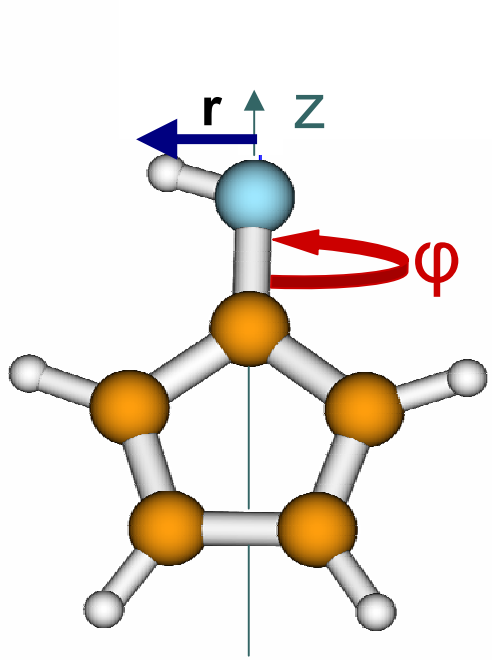
Proof: assume

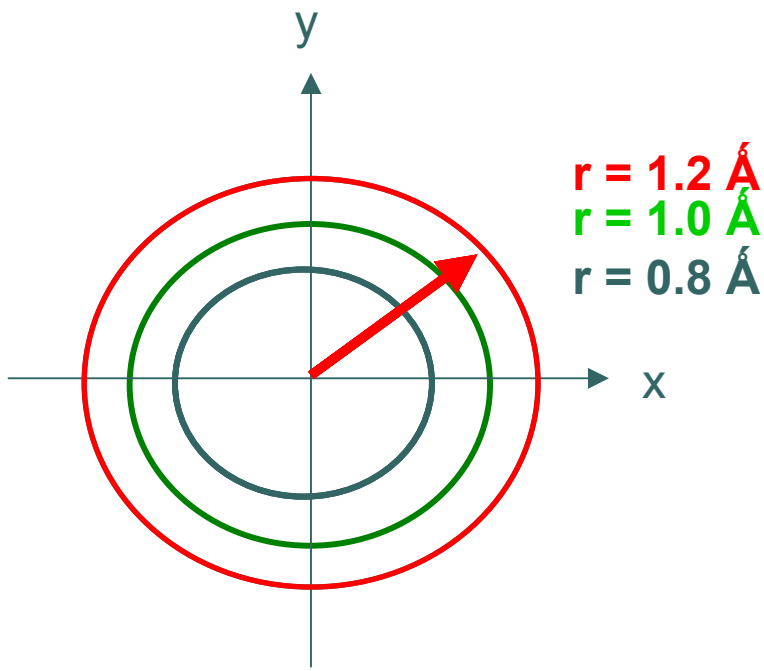


Seam of CIs


CI (S_1/S_2) for all φ
CI (S_0/S_1) only for φ = π /2
V_2
V_1
V_0
$S_0/S_1/S_2$
S_0/S_1
MIN
r=0.8
r=1.0
r=1.2
LH
energy / eV
torsional angle / π
0
2
4
6
0.0
0.1
0.2
0.3
0.4
0.5

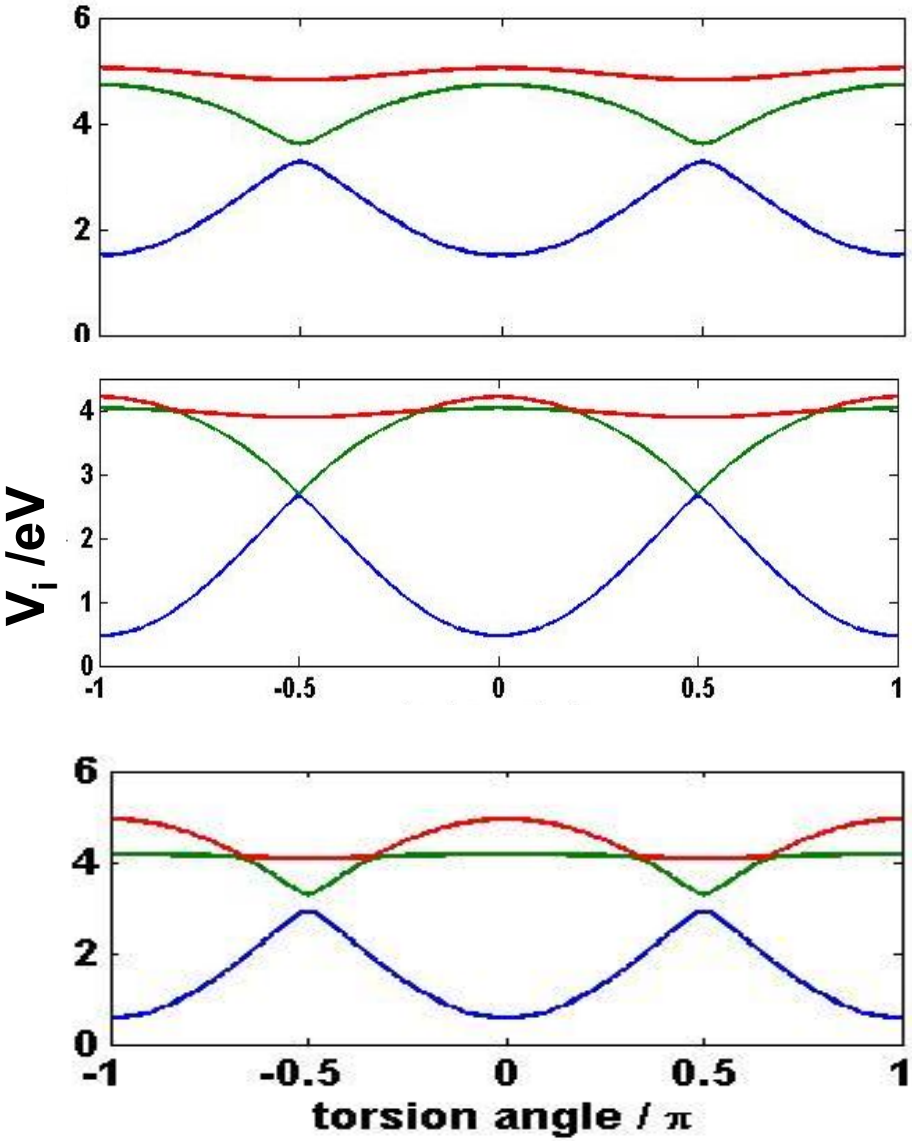
Quantum calculation for three different rings



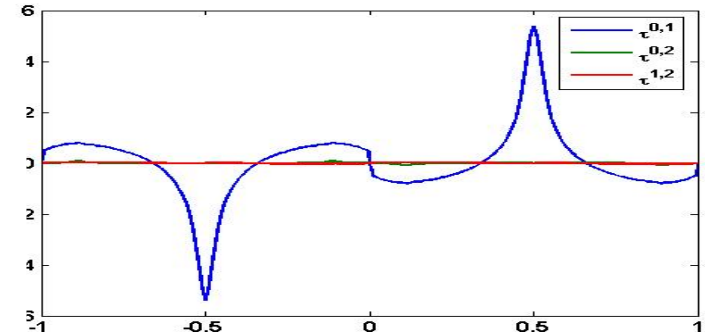


Quantum chemistry calculation carried out using MOLPRO (or Gamess) with CASS (10,9)/cc-pVDZ level of theory

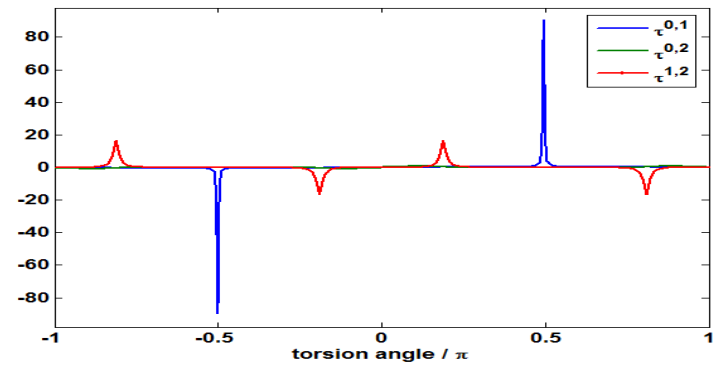
Adiabatic potentials and NACTs of C_5H_4NH



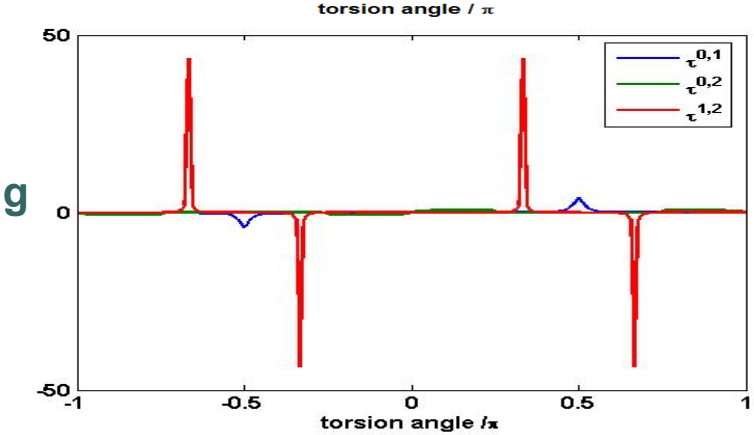
Large ring



middle ring



Small ring



Effect of NACTs on Quantum Reaction Dynamics

Baer, M., *Beyond Born Oppenheimer: Electronic non- adiabatic coupling terms and conical intersections*, Wiley (2006).

Adiabatic : $$i\hbar\,\dot{\boldsymbol{\psi}}_{ad} = \frac{1}{2I(r)}\left(-i\hbar\frac{\partial}{\partial\varphi} - \boldsymbol{\tau}\right)^2 + \mathbf{V}_{ad}\,\boldsymbol{\psi}_{ad}$$

$$\psi_{dia}(r,\varphi) = \mathrm{A}(r,\varphi)\psi_{ad}(r,\varphi)$$

diabatic : $$i\hbar\,\dot{\psi}_{dia} = \left(-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\varphi^2} + \mathrm{W}_{dia}\right)\psi_{dia}$$

quantization :

$$\mathrm{W}_{dia}(r,\varphi) = \mathrm{A}(r,\varphi)\,\mathrm{V}_{ad}(r,\varphi)\,\mathrm{A}^{\dagger}(r,\varphi)$$

$$\mathrm{W}(r,0) = \mathrm{W}(r,2\pi)$$

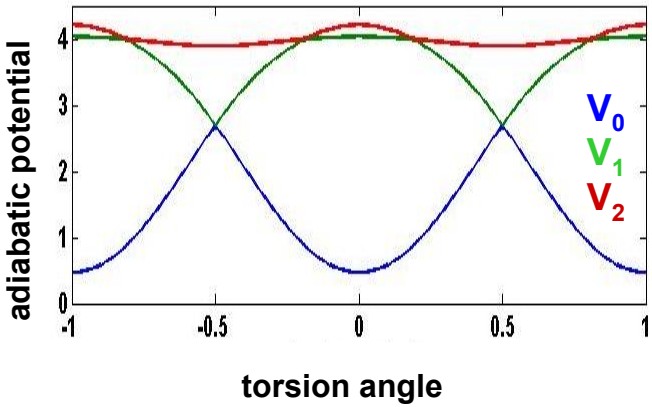
$$\frac{\partial}{\partial\varphi}\mathbf{A} + \boldsymbol{\tau}\,\mathbf{A} = \mathbf{0}\ *$$

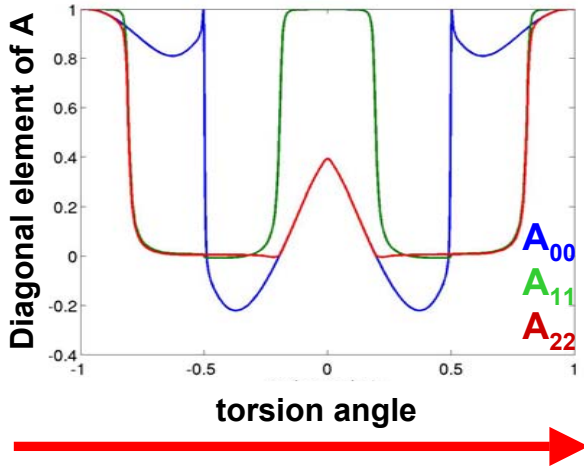
$$\Rightarrow \mathbf{A}(r,\varphi) = \mathbf{exp}\left(\int_{\varphi_0}^{\varphi} d\tilde{\varphi}\cdot\boldsymbol{\tau}_{\varphi}(r,\tilde{\varphi})\right)\mathbf{A_0}(r,\varphi_0)$$

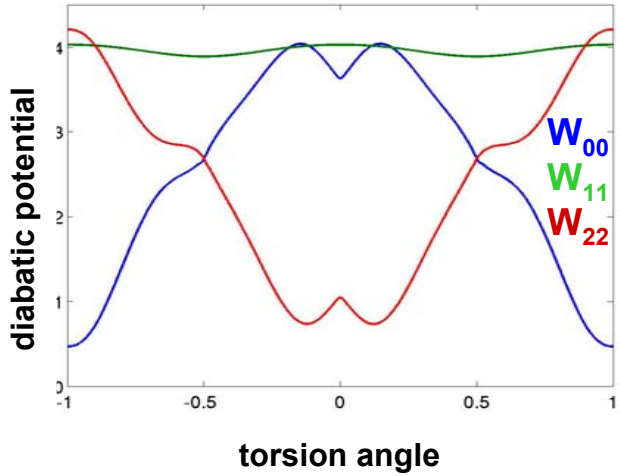
$$\mathbf{A_0} = \mathbf{1}$$

* Baer, M.; Chem. Phys. Lett. 1975, 35,112.

Adiabatic to diabatic potential

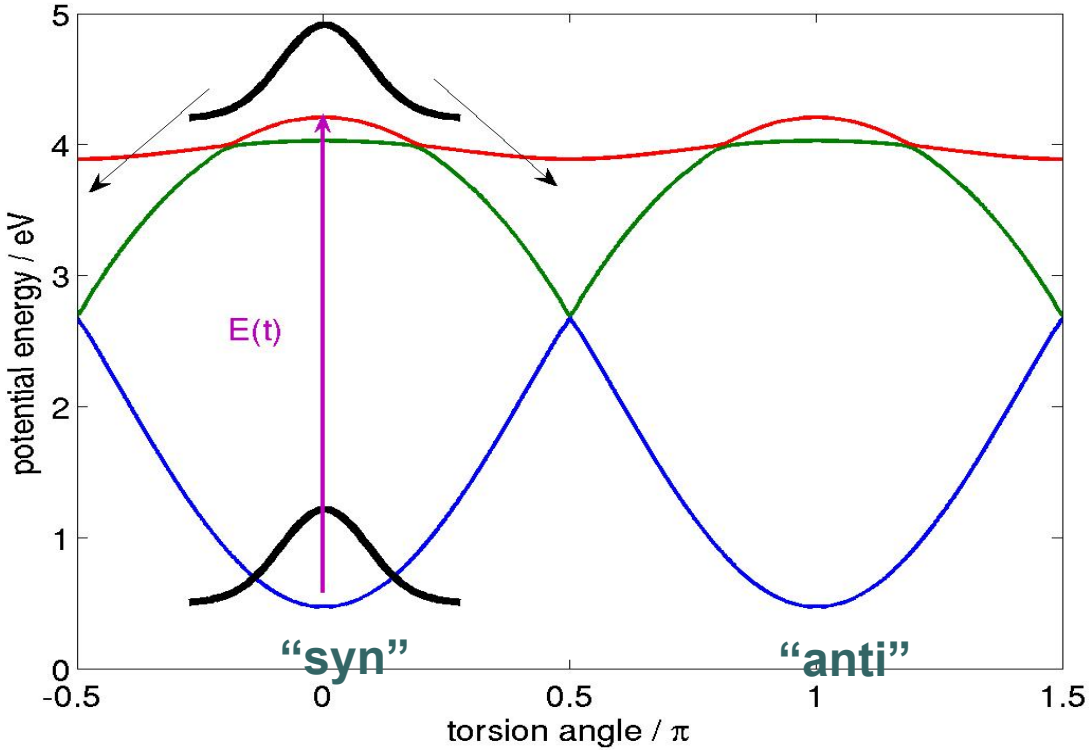






Diabatic potentials are not MS symmetric !
W is only a mathematical tool, no physical meaning

Photoinduced Dynamics

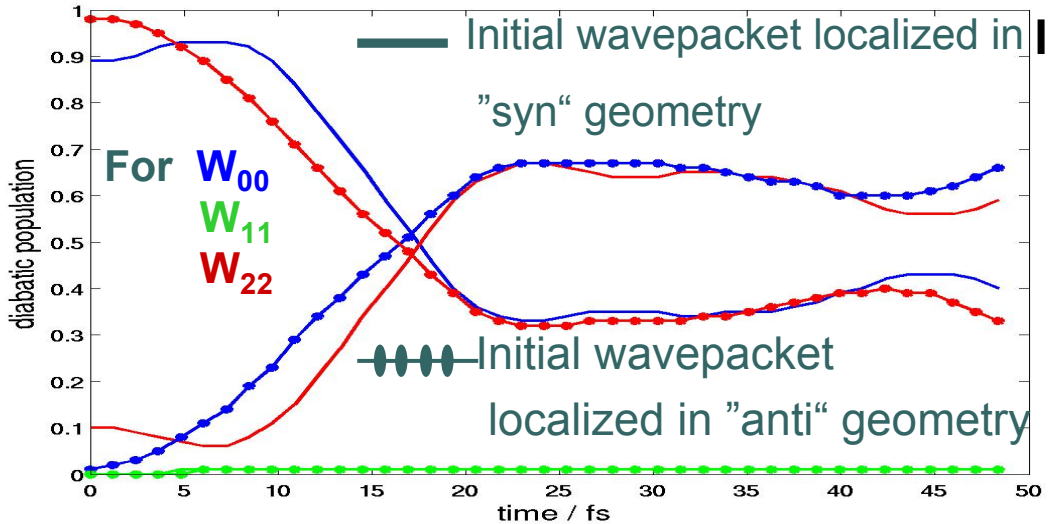


- Initial state: ground torsional state S_0 of syn-C_5H_4NH
- Short laser pulse excites wavepacket $S_0 \rightarrow S_2$ (Franck-Condon excitation)
- Wavepacket propagation in diabatic represntation with split-operator-method*

* Schmidt, Lorenz, WavePacket 4.5 (2008).

Diabatic versus adiabatic presentation

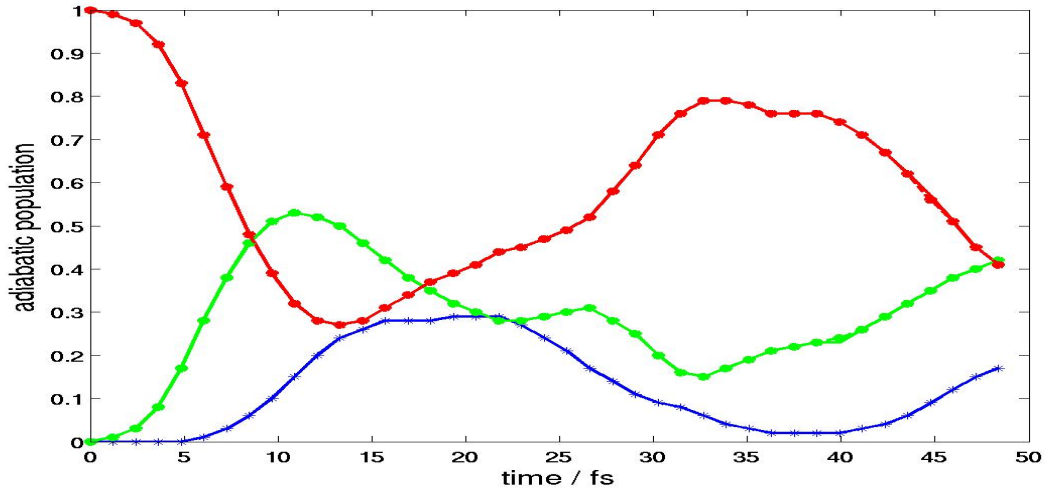
Diabatic



Interpretation maybe

misleading

Adiabatic

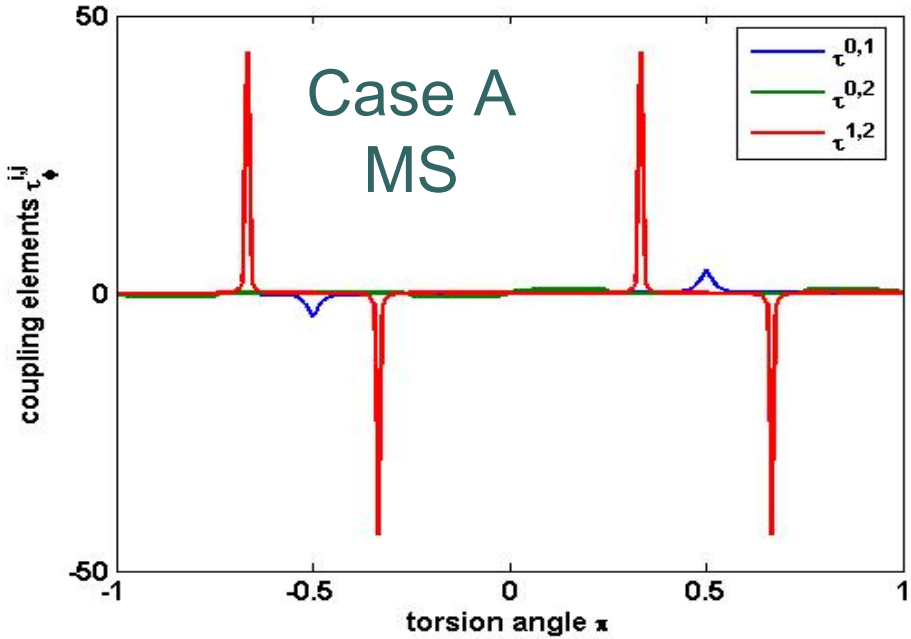


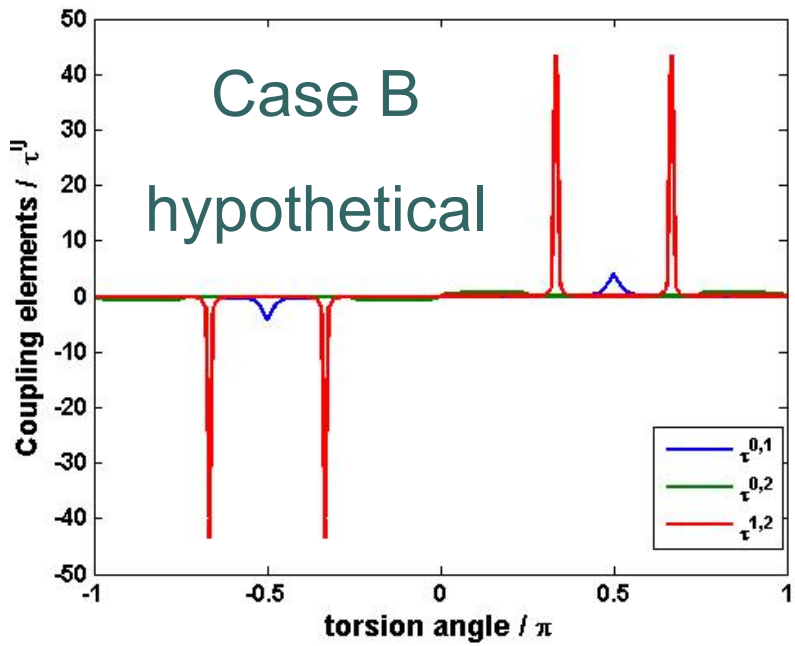
consistent

r = 1.0 Å

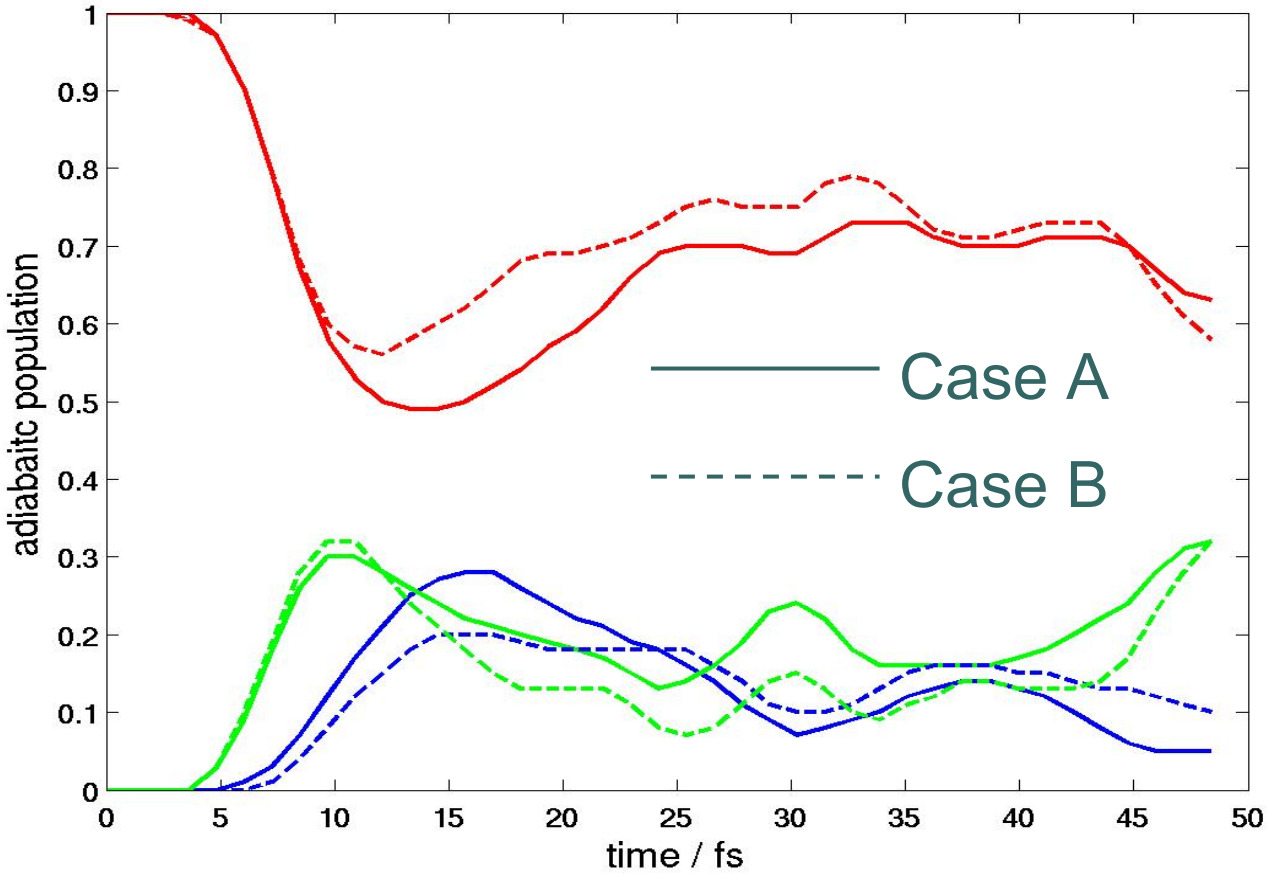
Does IREP of NACTs effects reaction dynamics?!

- Small ring, two cases
  r= 0.8 Å





Reaction dynamics propagation result



*** Radiationless decay depends on IREP of NACTs**

Conclusions:

- IREP of NACTs and CIs can be assigned according to MS group.
- New result beyond traditional quantum chemistry
- Photoinduced dynamics, e.g. radiationless decay depends on IREP of NACTs
- New result beyond traditional quantum reaction dynamics

Berlin group

Peace is in the waves at sea.
Peace must begin with you and me
To tell the world
no more violence

- **Nuclear Hamiltonian (1D)**

$$H^{ad} = -\frac{\hbar^2}{2m_H r^2}\left(\frac{\partial}{\partial\varphi} + \tau\right)^2 + V$$

$$\tau_\varphi^{i,j} = \left\langle \psi_i(\varphi) \middle| \frac{\partial}{\partial\varphi}\psi_j(\varphi) \right\rangle = -\tau_\varphi^{j,i}$$

- **Numerical calculation of $\tau_\varphi^{i,j}$ by finite difference**

$$\tau_\varphi^{i,j} = \frac{1}{2*\Delta\varphi}\left\langle \psi_i(\varphi) \middle| \psi_j(\varphi+\Delta\varphi) \right\rangle - \left\langle \psi_i(\varphi) \middle| \psi_j(\varphi-\Delta\varphi) \right\rangle$$