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

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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 $\text{C}_5\text{H}_4\text{NH}$ 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**

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2v&lt;/sub&gt;</th>
<th>E</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>σ&lt;sub&gt;v&lt;/sub&gt;</th>
<th>σ'&lt;sub&gt;v&lt;/sub&gt;</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>y</td>
</tr>
</tbody>
</table>

**Molecular symmetry group**

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2v&lt;/sub&gt;(M)</th>
<th>E</th>
<th>(12)</th>
<th>E*</th>
<th>(12)*</th>
<th>MS adapted coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>?</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>?</td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>?</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>?</td>
</tr>
</tbody>
</table>

- 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<sub>1</sub> symmetry"

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

"q has A<sub>2</sub> MS symmetry"

1<sup>st</sup>. 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 ($\phi$) describing cis-trans isomerization reaction.
One can show that $P^{A_1} r = r \iff r$ has $A_1$ symmetry

$P^{A_2} \phi, (\mathbf{R}_\phi) \iff \phi$ has $A_2$ symmetry

$P^{B_1} y = y \iff y$ has $B_1$ symmetry

$P^{B_2} x = x \iff x$ has $B_2$ symmetry

Frozen geometry of (3N-6-1 coordinates) : near CI $\Rightarrow$ need quantum chemistry to locate CI
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.*

Locating the Cl 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.
Close to

- trans anti-

Cl (S\textsubscript{0}/S\textsubscript{1})

cis syn-

Cl (S\textsubscript{0}/S\textsubscript{1})

trans Anti-
\[
| \psi(r, \varphi) | = | \psi(r, -\varphi) | = | \psi(r, \pi - \varphi) | = | \psi(r, -\pi + \varphi) |
\]

NACTs

\[ \left\langle \psi_i \left| \frac{\partial}{\partial \varphi} \psi_j \right. \right\rangle \]

Pole property*

### Determination of the irreducible representations (IREPs) of NACTs

- **Step 1: sign and nodal patterns**

<table>
<thead>
<tr>
<th>(\text{C}_2r(M))(^{(a)})</th>
<th>E</th>
<th>(12)</th>
<th>(E^*)</th>
<th>(12)*</th>
<th>coord.</th>
<th>deriv.</th>
<th>rel. signs and nodes(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\hat{S}_g)</td>
<td>(S_1)</td>
<td>(S_2)</td>
<td>(S_3)</td>
<td>(S_4)</td>
<td>rotation</td>
<td>(\partial/\partial r)</td>
<td>(\partial/\partial \phi)</td>
</tr>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(r)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>(\phi (\hat{R}_\phi))</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(B_1)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>(y)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(B_2)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>(x)</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

**Application to**

\(\text{C}_5\text{H}_4\text{NH}\)

\((r, \phi) \rightarrow \hat{S}_g(r, \phi)\)

\((x, y) \rightarrow \hat{S}_g(x, y)\)

\((r, \phi) (r, -\pi + \phi) (r, -\phi) (r, \pi - \phi) (d)\)

\((x, y) (-x, -y) (x, -y) (-x, y) (e)\)
Step 2: theorem of NACTs in $C_{2v}(M)$

Example:

\[
\text{IREP } (\tau^{i,j}_r) \cdot \Gamma_r \left( \frac{\partial}{\partial r} \right) \cdot \Gamma_\phi \left( \frac{\partial}{\partial \phi} \right) = IREP \left( \left\langle \psi_i \left| \frac{\partial}{\partial r} \right| \psi_j \right\rangle \right) \cdot \Gamma_r \left( \frac{\partial}{\partial r} \right) \cdot \Gamma_\phi \left( \frac{\partial}{\partial \phi} \right)
\]

\[
= \Gamma_i \cdot A_1 \cdot \Gamma_j \cdot A_1 \cdot A_2
\]

\[
= \text{IREP} \left( \left\langle \psi_i \left| \frac{\partial}{\partial \phi} \right| \psi_j \right\rangle \right)
\]

\[
= \tau^{i,j}_\phi
\]

In general:

\[
\text{IREP } \tau^{i,j}_k = \text{IREP } \tau^{i,j}_l \cdot \Gamma \left( \frac{\partial}{\partial k} \right) \cdot \Gamma \left( \frac{\partial}{\partial l} \right)
\]
### Character table

<table>
<thead>
<tr>
<th>$C_{2v}(M)^{(a)}$</th>
<th>E</th>
<th>(12)</th>
<th>$E^*$</th>
<th>$(12)^*$</th>
<th>coord. (rotation)</th>
<th>deriv.</th>
<th>rel. signs and nodes$^{(b)}$</th>
<th>${c}$</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_\sigma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$r$</td>
<td>$\partial/\partial r$</td>
<td>$+</td>
<td>+$</td>
<td>$+</td>
<td>+$</td>
<td>$\tau_\phi$</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$\phi$ ($R_\phi$)</td>
<td>$\partial/\partial \phi$</td>
<td>$-</td>
<td>+$</td>
<td>$+</td>
<td>-$</td>
<td>$\tau_\tau$</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$y$</td>
<td>$\partial/\partial y$</td>
<td>$+</td>
<td>+$</td>
<td>$+</td>
<td>-$</td>
<td>$\tau_x$</td>
</tr>
<tr>
<td></td>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x$</td>
<td>$\partial/\partial x$</td>
<td>$-</td>
<td>+$</td>
<td>$+</td>
<td>+$</td>
<td>$\tau_y$</td>
</tr>
</tbody>
</table>

Application to $C_5H_4NH$:

$(r, \phi) \rightarrow \hat{S}_g(r, \phi)$

$(x, y) \rightarrow \hat{S}_g(x, y)$

Sym.-related locations $\hat{S}_g(x, y)$:

- $(r, \phi)$
- $(r, -\pi + \phi)$
- $(r, -\phi)$
- $(r, \pi - \phi)$

- $(x, y)$
- $(-x, -y)$
- $(x, -y)$
- $(-x, y)$

<table>
<thead>
<tr>
<th>${c}$</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>${d}$</td>
<td>$\tau_{K_{12}}$</td>
<td>$\tau_{K_{01}}$</td>
<td>$\tau_{K}$</td>
<td>$\tau_{K_{02}}$</td>
</tr>
</tbody>
</table>

| $\{e\}$ | $\tau_{K_{12}}$ | $\tau_{K_{01}}$ | $\tau_{K}$ | $\tau_{K_{02}}$ |

| $\{f\}$ | $\tau_{K_{12}}$ | $\tau_{K_{01}}$ | $\tau_{K}$ | $\tau_{K_{02}}$ |
* 2nd possibility: \( \oint = 0 \) contradiction

* 4th possibility: \( \oint = 0 \) contradiction

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

\[
\oint ds \cdot \tau^{i,i+1}(s \mid L_g) = \begin{cases} 
\pm \pi & \text{if } L_g \text{ contains CI} \\
0 & \text{else}
\end{cases}
\]

* Pole property: \( \tau^{i,i+1}_k(s) \rightarrow \pm \infty \) for \( s \rightarrow (s^{i,i+1}) \)

* We are left with the 3rd possibility

## Character table

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<tr>
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<th>$E^*$</th>
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<th>coord.</th>
<th>deriv.</th>
<th>rel. signs and nodes ((b))</th>
<th>({c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_2$</td>
<td>$S_1$</td>
<td>$S_2$</td>
<td>$S_3$</td>
<td>$S_4$</td>
<td>(rotation)</td>
<td>(\partial/\partial r)</td>
<td>(\tau_\phi)</td>
<td>(\tau_r)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(r)</td>
<td>(\partial/\partial r)</td>
<td>(+)</td>
<td>(+)</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>(\phi (R_\phi))</td>
<td>(\partial/\partial \phi)</td>
<td>(-)</td>
<td>(+)</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>(y)</td>
<td>(\partial/\partial y)</td>
<td>(+)</td>
<td>(-)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>(x)</td>
<td>(\partial/\partial x)</td>
<td>(-)</td>
<td>(+)</td>
</tr>
</tbody>
</table>

### Application to $C_5H_4NH$

- \((r, \phi) \rightarrow \tilde{S}_g(x, y)\)
- \((x, y) \rightarrow \tilde{S}_g(x, y)\)

\[\begin{align*}
(r, \phi) & \rightarrow \tilde{S}_g(r, \phi) \\
(x, y) & \rightarrow \tilde{S}_g(x, y)
\end{align*}\]

Sym.-related locations $\tilde{S}_g(x, y)$

- $x$
- $y$
- $-x$
- $-y$

\[\begin{align*}
\text{sym.-related locations } \tilde{S}_g(x, y) & \\
& \begin{cases}
\ast & \ast & \ast & \ast \\
\end{cases}
\end{align*}\]
NACTs $\tau^{0,1}_\phi$ and $\tau^{0,2}_\phi$ interchange at $\phi$ near CI ($S_1 / S_2$),
$\Rightarrow$ they also interchange at $\pi - \phi, -\pi + \phi, -\phi$

$\Rightarrow \tau^{0,1}_\phi$ and $\tau^{0,2}_\phi$ have the same IREP = $B_1$
Example

\[ \text{IREP} (\tau^{0,1}_\phi) \cdot \text{IREP} (\tau^{1,2}_\phi) \cdot \text{IREP} (\tau^{2,0}_\phi) \]

\[ = B_1 \cdot \text{IREP} (\tau^{1,2}_\phi) \cdot B_1 \]

\[ = \text{IREP} \left( \psi_0 \left| \frac{\partial}{\partial \phi} \right| \psi_1 \right) \cdot \text{IREP} \left( \psi_1 \left| \frac{\partial}{\partial \phi} \right| \psi_2 \right) \cdot \text{IREP} \left( \psi_2 \left| \frac{\partial}{\partial \phi} \right| \psi_0 \right) \]

\[ = \Gamma_0 \cdot A_2 \cdot \Gamma_1 \cdot \Gamma_1 \cdot A_2 \cdot \Gamma_2 \cdot \Gamma_2 \cdot A_2 \cdot \Gamma_0 = A_2 \]

\[ \Rightarrow \text{IREP} (\tau^{1,2}_\phi) = A_2 \]

In general

\[ \text{IREP} (\tau^{0,1}_k) \cdot \text{IREP} (\tau^{1,2}_k) \cdot \ldots \cdot \text{IREP} (\tau^{z,0}_k) \]

\[ = \Gamma_k \text{ if ungerade loop} \]

else

\[ = A_1 \text{ if gerade loop} \]
\begin{align*}
|\psi(r, \varphi)| &= |\psi(r, -\varphi)| = |\psi(r, \pi - \varphi)| = |\psi(r, -\pi + \varphi)|
\end{align*}

NACTs
\begin{align*}
\left\langle \psi_i \left| \frac{\partial}{\partial \varphi} \psi_j \right. \right\rangle
\end{align*}

\begin{align*}
\text{ok} & \quad \text{wrong}
\end{align*}
Charges and IREPs of conical intersections

If \( \int ds \tau^{i,i+1}(s \mid L_g) = \pm \pi = e_i \cdot \pi \)

Then charge \( e_i \) of CI is \( \pm 1 \)

Example: CI (S\(_0\)/S\(_1\))

\( e_{1}^{0,1} = +1 \)  Arbitrary choice

Due to IREP of NACTs
\( \Rightarrow \) CI (S\(_0\)/S\(_1\)) has IREP B\(_1\)
\( \Rightarrow \) 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

\[ \int \varphi = +\pi \Rightarrow 2\pi \quad \text{contradiction} \]
Seam of CIs

CI \((S_1/S_2)\) for all \(\phi\)

CI \((S_0/S_1)\) only for \(\phi = \pi/2\)
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 $C_5H_4NH$
Effect of NACTs on Quantum Reaction Dynamics


\[ i \hbar \dot{\psi}_{ad} = \frac{1}{2I(r)}(-i\hbar \frac{\partial}{\partial \varphi} - \tau)^2 + V_{ad} \psi_{ad} \]

\[ \psi_{dia}(r, \varphi) = A(r, \varphi)\psi_{ad}(r, \varphi) \]

\[ i \hbar \dot{\psi}_{dia} = \left(-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \varphi^2} + W_{dia}\right) \psi_{dia} \]

Quantization:

\[ W_{dia}(r, \varphi) = A(r, \varphi) V_{ad}(r, \varphi) A^+(r, \varphi) \]

\[ W(r,0) = W(r,2\pi) \]

\[ \frac{\partial}{\partial \varphi} A + \tau A = 0 \]

\[ \Rightarrow A(r, \varphi) = \exp \left( \int_{\phi_0}^{\phi} d\varphi \cdot \tau_{\phi}(r, \varphi) \right) A_0(r, \varphi) \]

\[ A_0 = 1 \]

Adiabatic to diabatic potential

Diabatic potentials are not MS symmetric! W is only a mathematical tool, no physical meaning.
Initial state: ground torsional state $S_0$ of syn-C$_5$H$_4$NH
Short laser pulse excites wavepacket $S_0 \rightarrow S_2$
(Franck-Condon excitation)
Wavepacket propagation in diabatic representation with split-operator-method

Diabatic versus adiabatic presentation

Initial wavepacket localized in "syn" geometry

Initial wavepacket localized in "anti" geometry

For $W_{00}$, $W_{11}$, $W_{22}$

Diabatic

Adiabatic

$r = 1.0 \, \text{Å}$

Interpretation maybe misleading

consistent
Does IREP of NACTs effects reaction dynamics?! 

- Small ring, two cases 
  \( r = 0.8 \, \text{Å} \) 

---

**Case A** 

**Case B** 

hypothetical
* 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
Peace is in the waves at sea.
Peace must begin with you and me
To tell the world
no more violence
- **Nuclear Hamiltonian (1D)**

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

\[ \tau^{i,j}_\phi = \left\langle \psi_i(\phi) \left\{ \frac{\partial}{\partial \phi} \psi_j(\phi) \right\} \right\rangle = -\tau^{j,i}_\phi \]

- **Numerical calculation of** \( \tau^{i,j}_\phi \)** by finite difference**

\[ \tau^{i,j}_\phi = \frac{1}{2*\Delta \phi} \left( \langle \psi_i(\phi) | \psi_j(\phi + \Delta \phi) \rangle - \langle \psi_i(\phi) | \psi_j(\phi - \Delta \phi) \rangle \right) \]