

# Effects of Molecular Symmetry on Quantum Reaction Dynamics: Novel Aspects of Photo-Induced Non-Adiabatic Dynamics

Salih Al-Jabour<sup>(1)</sup> and Monika Leibscher<sup>(2)\*</sup>

<sup>(1)</sup>*Institut für Chemie und Biochemie,*

*Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany*

<sup>(2)</sup> *Institut für Theoretische Physik, Leibniz Universität Hannover,*

*Appelstr. 2, 30167 Hannover, Germany*

## Generalization of the symmetry rules from a three-state system to a N-state system

Here, we present a generalization of the symmetry rules for the irreducible representations of the NACTs<sup>1</sup>, as shown in Eq.(3) of the original paper to a system with  $N$  electronic states. For real electronic wavefunction the matrix  $\tau_k$  which contains the non-adiabatic coupling terms with respect the symmetry adapted nuclear coordinate  $s_k$  is anti-symmetric and the diagonal elements are zero [see Eq.(10) of the original paper]. Therefore, the coupling between those  $N$  states is determined by  $N(N-1)/2$  different NACTs. It has been shown<sup>1</sup> that by a loop constructed from three electronic sates  $i, j, k$  one can determine the irreducible representation of the third NACT if two are known via

$$\Gamma(\tau_k^{ij}) \times \Gamma(\tau_k^{jk}) \times \Gamma(\tau_k^{ik}) = \Gamma\left(\frac{\partial}{\partial s_k}\right). \quad (1)$$

In a N-state system, one can construct a sequence of  $N-2$  of such loops between subsequent electronic states:

$$\begin{aligned} \Gamma(\tau_k^{01}) \times \Gamma(\tau_k^{12}) \times \Gamma(\tau_k^{02}) &= \Gamma\left(\frac{\partial}{\partial s_k}\right), \\ \Gamma(\tau_k^{12}) \times \Gamma(\tau_k^{23}) \times \Gamma(\tau_k^{13}) &= \Gamma\left(\frac{\partial}{\partial s_k}\right), \\ &\vdots \\ \Gamma(\tau_k^{N-3,N-2}) \times \Gamma(\tau_k^{N-2,N-1}) \times \Gamma(\tau_k^{N-3,N-1}) &= \Gamma\left(\frac{\partial}{\partial s_k}\right). \end{aligned} \quad (2)$$

In the first loop, the irreducible representations of two NACTs are required to determine the third one. For each of the subsequent loops, the irreducible representation of one additional NACT has to be known to obtain the third one. That is, for the  $N-2$  loops presented in Eq.(2), the symmetries of  $N-1$  NACTs are required in order to obtain the remaining ones. The sequence of loops in Eq.(2) contains all NACTs between subsequent states  $\tau_k^{i,i+1}$  and all NACTs  $\tau_k^{i,i+2}$ . Knowing their irreducible representations allows the determination of the transformation properties of all remaining NACTs by constructing further loops of the form

$$\Gamma(\tau_k^{i,i+2}) \times \Gamma(\tau_k^{i+1,i+3}) \times \Gamma(\tau_k^{i,i+3}) = \Gamma\left(\frac{\partial}{\partial s_k}\right) \quad (3)$$

an so on. Therefore, one only has to determine the irreducible representations of  $N-1$  NACTs to obtain the remaining  $(N-1)(N-2)/2$  NACTs. For the three state system considered here, the irreducible representation of two states are required to get the third

one. For system with more electronic states, this scheme becomes more powerful: for  $N = 6$  electronic states, for example, 15 different NACTs exist and the irreducible representations of 10 of them can be obtained if only five are known.

---

<sup>1</sup> Al-Jabour, S.; Baer, M.; Deeb, O.; Leibscher, M.; Manz, J.; Xu, X.; Zilberg, S. Molecular Symmetry Properties of Conical Intersections and Nonadiabatic Coupling Terms: Theory and Quantum Chemical Demonstration for Cyclopenta-2,4-dienimine (C<sub>5</sub>H<sub>4</sub>NH). *J. Phys. Chem. A* **2010**, *114*, 2991 - 3010.