

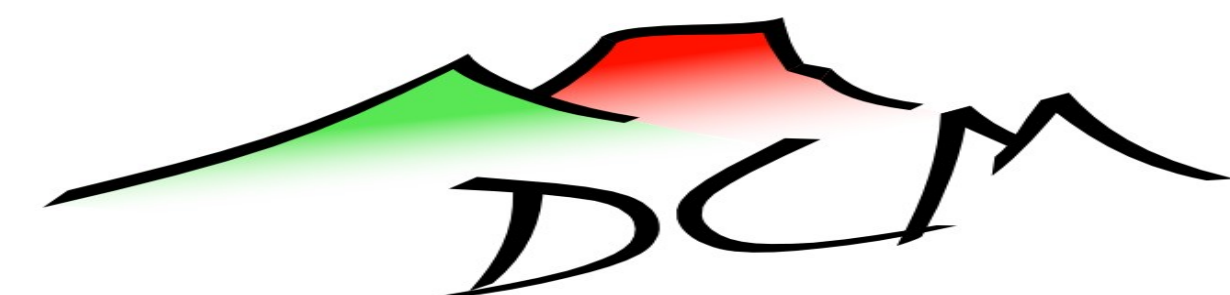
Behaviour of Conical Intersections within Noncollinear Spin-Flip Time-Dependent Density-Functional Theory: Oxirane as Test Case

* Bhaarathi Natarajan^{1,2}, Miquel Huix-Rotllant¹, Andrei Ipatov¹, C. Muhavini Wawire¹, Thierry Deutsch², and Mark E. Casida¹

¹Département de Chimie Moléculaire, Université Joseph Fourier, Grenoble, France and

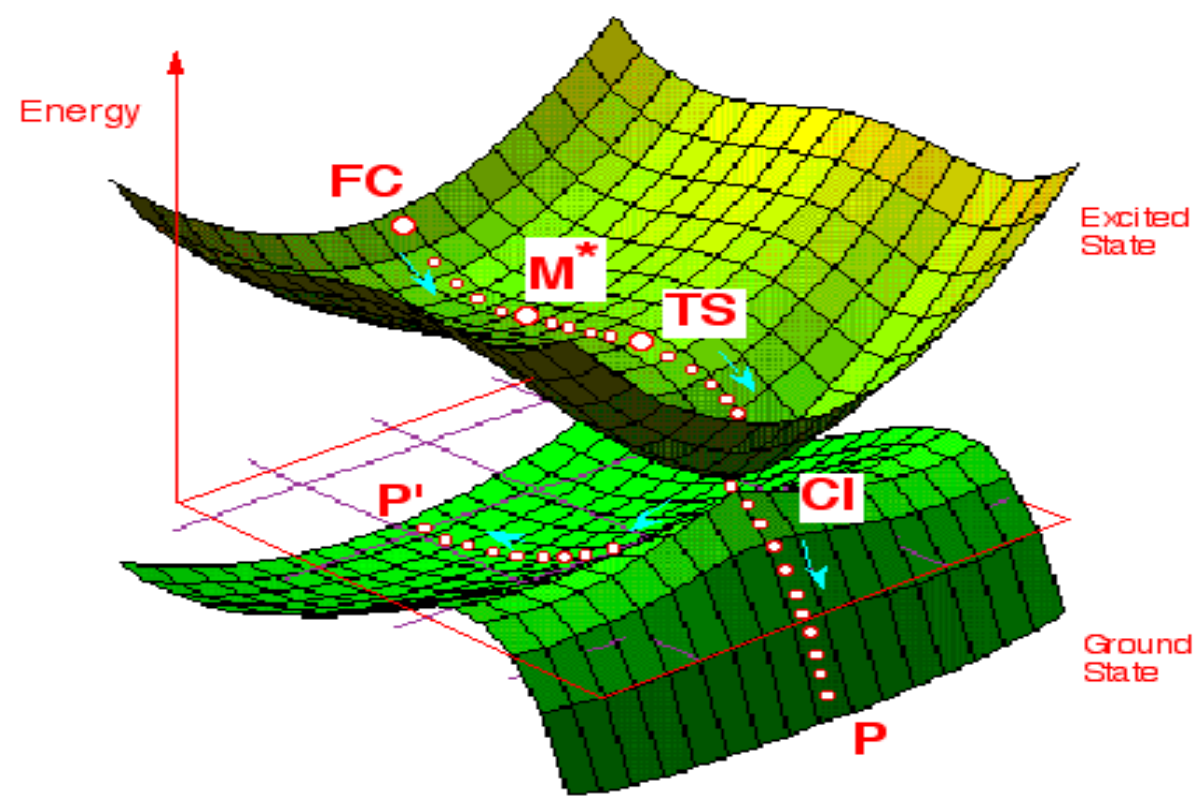
²INAC, CEA-Grenoble, Grenoble, France

*email:bhaarathi.natarajan@ujf-grenoble.fr



Conical Intersections and Photochemistry

The concept of a conical intersection (CX) goes back to the 1930s. [1] However their importance as very fast funnels for non-radiative relaxation in photochemical reactions was only fully recognized in the 1990s.



$$H = \begin{bmatrix} E_1(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & E_2(\mathbf{R}) \end{bmatrix}$$

$$E_1(\mathbf{R}) = E_2(\mathbf{R})$$

$$V(\mathbf{R}) = 0$$

(Image taken from the website of Prof. M. Olivucci)

Interest in taking advantage of the efficiency of TDDFT calculations to investigate photochemical reactions has been increasing. A potential obstacle to this application is the nonexistence of a CX in adiabatic TDDFT [2], though an approximate CX can be found in at least some cases. [3] The fundamental difficulty is the lack of double excitations in adiabatic TDDFT. In this work we try to surmount this problem by using spin-flip (SF) TDDFT.

The Trouble With Adiabatic TDDFT

Adiabatic approximation (AA)

$$v_{xc}(\mathbf{r}, t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})}$$

This means that the potential reacts instantaneously and without memory to any temporal change in the charge density.

TDDFT working equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$\mathbf{A}_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \frac{\partial F_{ia}}{\partial P_{jb}} \quad \mathbf{B}_{ia,bj} = \frac{\partial F_{ia}}{\partial P_{bj}}$$

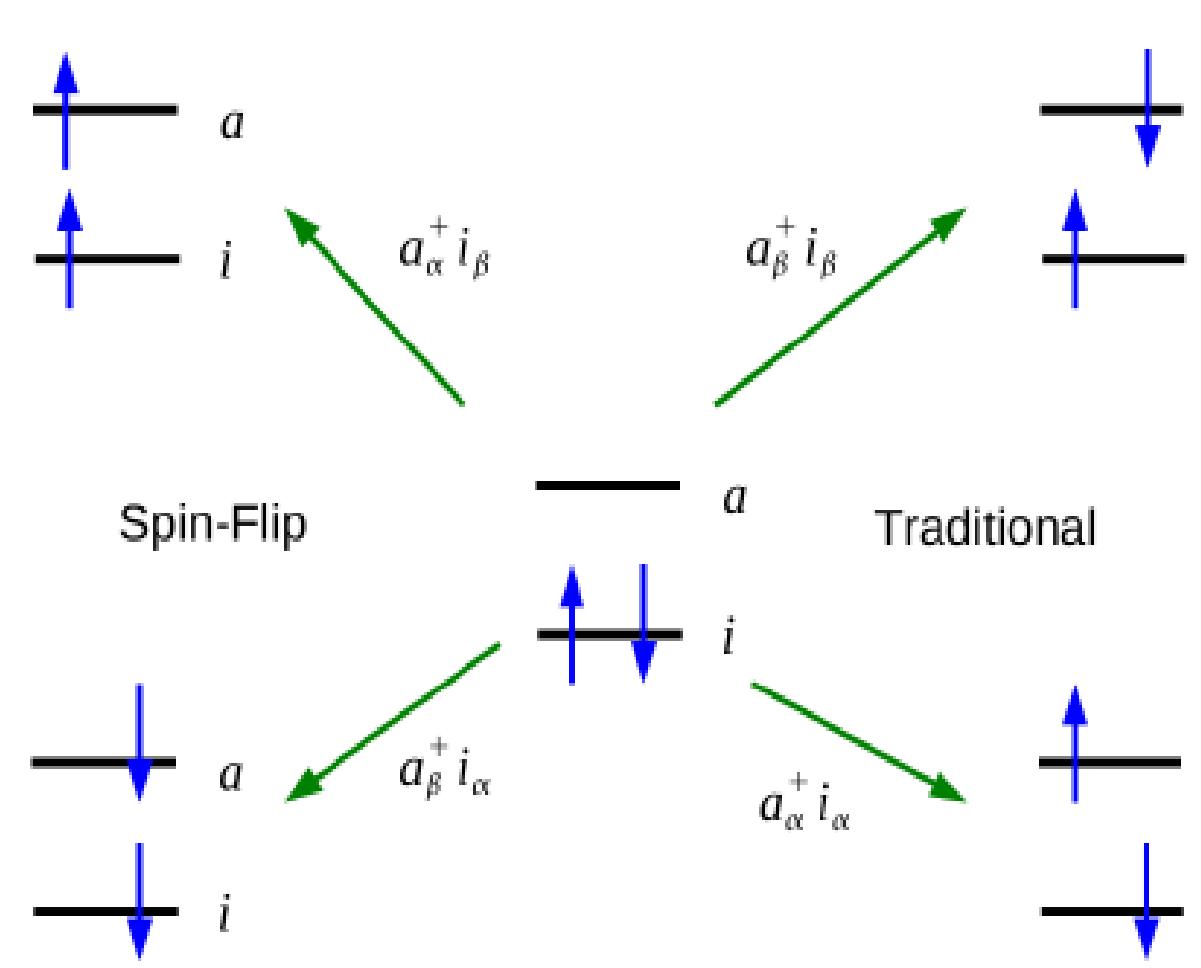
AA => A and B are independent of ω .

TDDFT/TDA

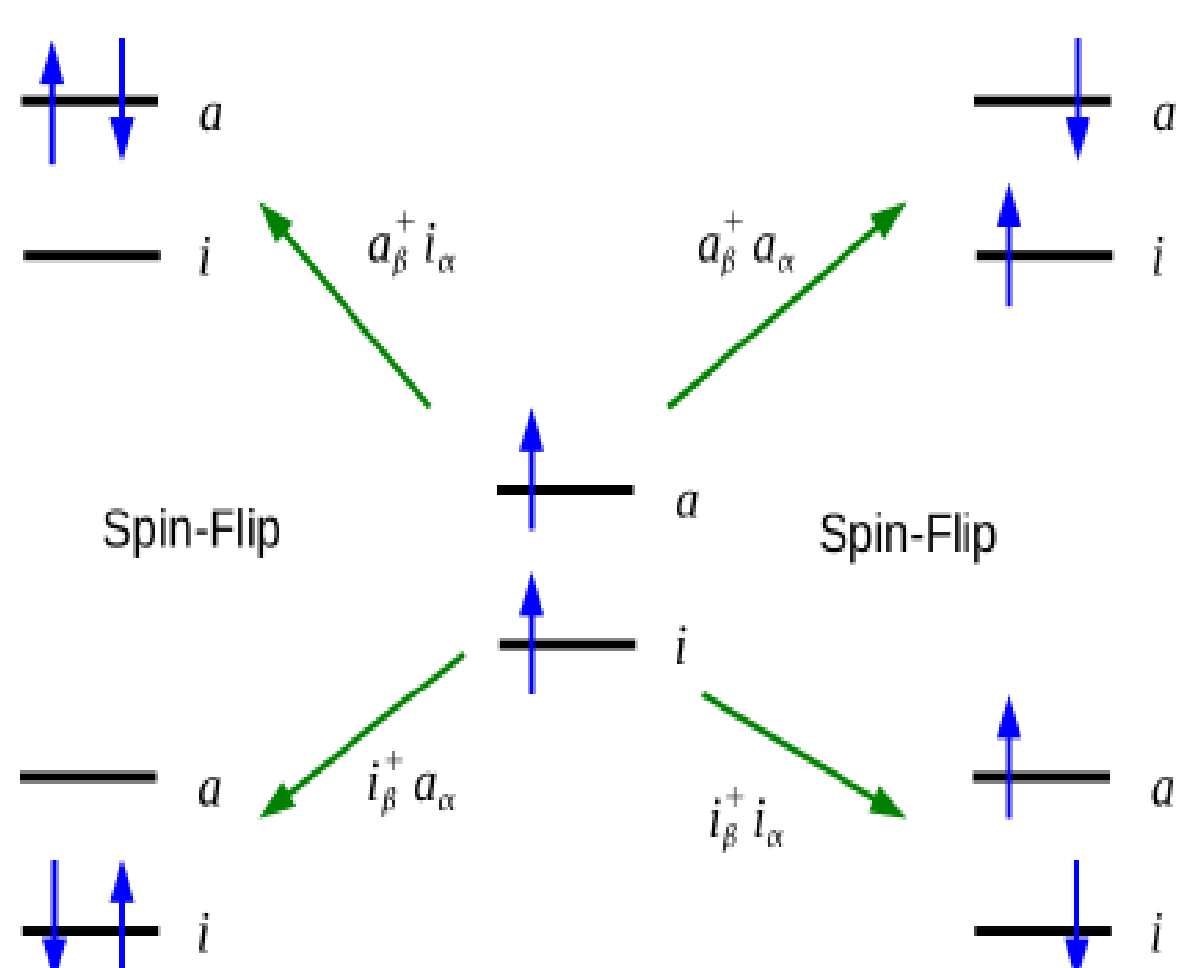
$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}$$

A => number of solutions is size of matrix = number of single excitations

Two-orbital model for TDDFT excitations



Two-orbital model for SF-TDDFT excitations



Note: TDDFT and SF-TDDFT generate different sets of configurations.

Pros: SF-TDDFT calculations give access to some double excitations

Cons: SF-TDDFT (i) may miss some interesting configurations
(ii) may lead to impure spin states.

Noncollinear SF-TDDFT [4]

Allow spins to have an arbitrary direction

$$E_{xc} = E_{xc}[\rho_+, \rho_-] \quad \rho_{\pm} = \frac{1}{2}(\rho \pm s)$$

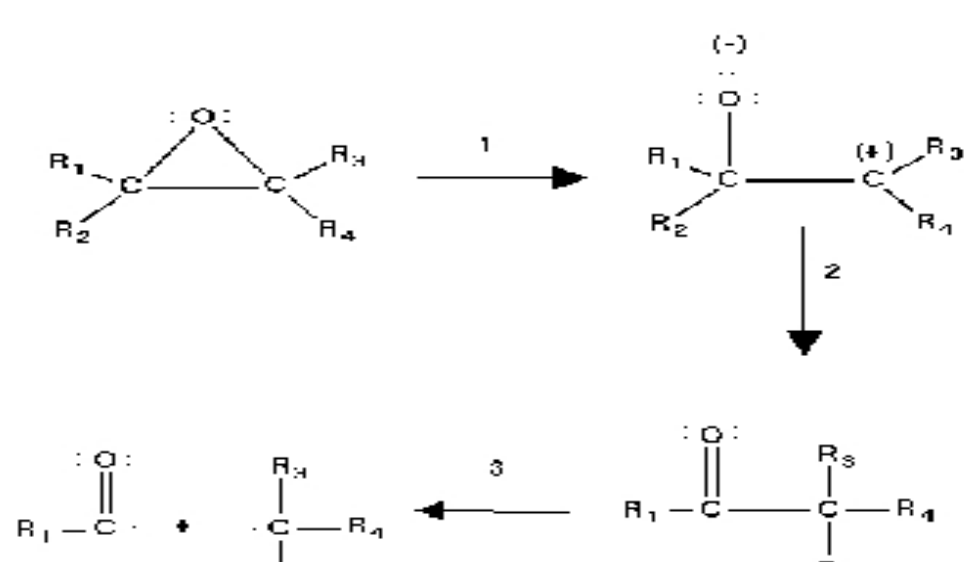
$$\rho = \begin{bmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{bmatrix} \quad \rho = \rho_{\alpha} + \rho_{\beta} \quad s = \rho_{\alpha} - \rho_{\beta}$$

Can now treat spin-flipping perturbations. Final result is expressed in terms of collinear DFT.

$$(K_{xc}^{\sigma\sigma,\tau\tau})_{ia,jb} = (ia|f_{xc}^{\sigma,\tau}|jb) \quad (K_{xc}^{\sigma\tau,\sigma\tau})_{ia,jb} = (ia|\frac{v_{xc}^{\sigma} - v_{xc}^{\tau}}{\rho_{\sigma} - \rho_{\tau}}|jb)$$

Choice of Test Case: Oxirane

Oxirane was chosen because photodynamics has been studied and CASSCF calculation of CX already available. [3]



E. Gomer and W.A. Noyes, Jr., *J. Am. Chem. Soc.* **72**, 101 (1950)

Computational details

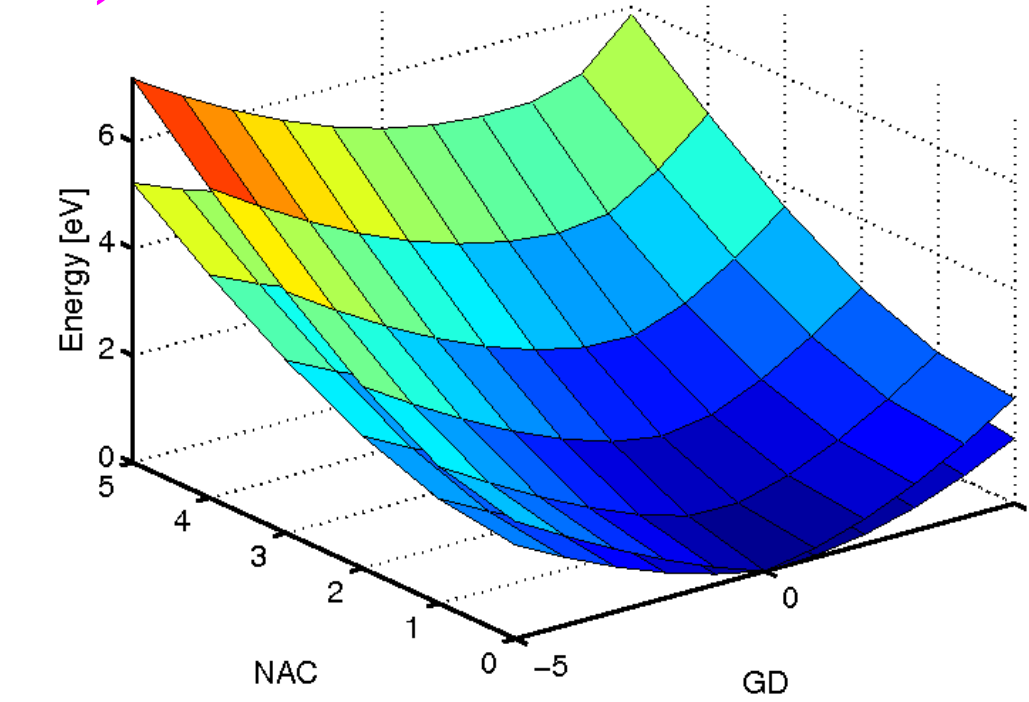
* **Gaussian03** [5] was used to generate CX branching coordinates for the plotting of PESs. CASSCF calculations were carried out [3] for an active space of four electrons in five orbitals in 6-31G** basis set.

* SF-TDDFT has been implemented in the Grenoble development version of **deMon2k**. [6]

Results and discussion

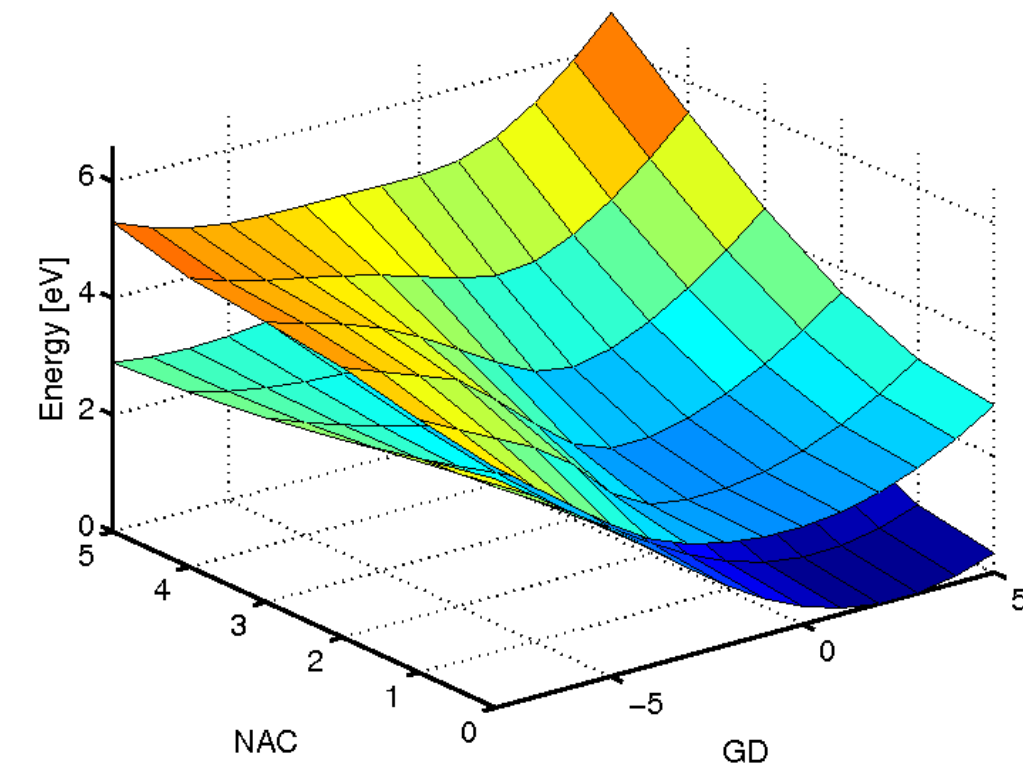
- Reference calculation to know exactly where CX is located.
- Shows hyperline instead of hyperpoint.
- Shows more or less CX with interpenetrating surfaces
- No surface interpenetration but CX is displaced from CASSCF and TDDFT/TDA CX

a) CASSCF

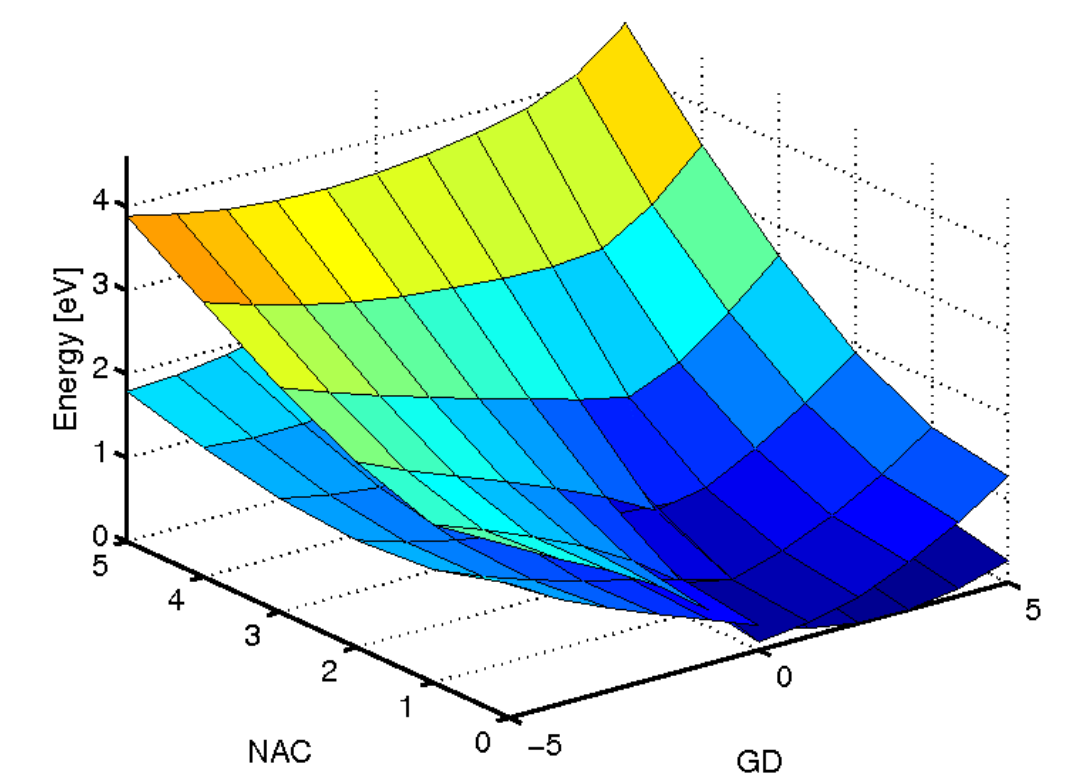


Fig(4) shows the PESs computed for the first excited state (S1) and ground state (S0) around the CX obtained using different methods. (For a,b,c [3] and d[7])

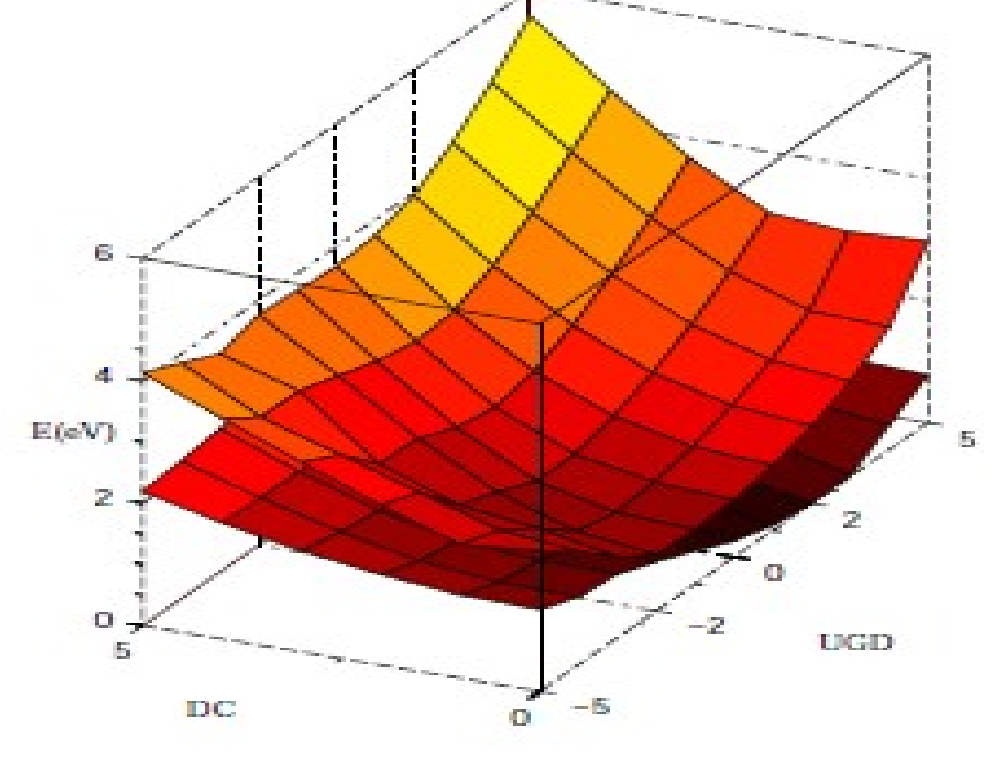
b) CIS



c) TDDFT/TDA



d) SF-TDDFT/TDA



For plotting, two branching coordinates namely energy difference gradients ($g_q^{(I,J)}$) and non-adiabatic coupling vectors ($h_q^{(I,J)}$) are computed using the relations

$$g_q^{(I,J)} = C_I^{\dagger} \frac{\partial H}{\partial q} - C_J^{\dagger} \frac{\partial H}{\partial q} C_J \quad h_q^{(I,J)} = C_I^{\dagger} \frac{\partial H}{\partial q} C_J$$

Comparing of Fig. 4b-d with Fig. 4a, the SF-TDDFT/TDA most resembles a true CX, but is displaced from the CASSCF CX.

* Due to the lack of explicit inclusion of two-electron excitations in CIS calculations, a true CX is absent in Fig. 4b.

* Somehow TDDFT is able to approximate a CX in Fig. 4c, but convergence is difficult due to noninteracting v-representability problems and the local behaviour very close to the CX is incorrect.

* Even though the dimensionality of the intersection space and the rapid variation of the S1 energy near the CX is not described correctly, inclusion of some doubly-excited character allows the formation of a true CX (Fig. 4d.)

* Our results show the suggestion of Levine *et al.* [2] that the SF-TDDFT/TDA method could be used for locating CXs has its strong points (existence of a true CX, ease of convergence) and its weak points (position of the CX, lack of potentially important configurations.)

* To understand the performance of SF-TDDFT, calculations have been done for another choice of triplet reference state. The result (not shown) is that the ground state minimum shifts towards the origin, however the quality of the excited-state potential energy surfaces is degraded.

CONCLUSIONS

* TDDFT could be an inexpensive alternative to *ab initio* methods, but conventional adiabatic TDDFT fails to describe correctly the doubly-excited states.

* Calculations has done using the SF-TDDFT/TDA method in the CX region. There does indeed appear to be a CX in roughly the right place but the accuracy needs improving.

* Our implementation of SF-TDDFT in **deMon2k** uses the LDA. Use of GGAs might give better results (but we do not know this).

* A general method is needed for the inclusion of double excitations and at the same time have all possible excited state configurations.

References

- E. Teller, *J. Phys. Chem.* **4**, 109 (1937).
- B.G. Levine *et al.*, *Mol. Phys.* **104**, 1039 (2006).
- E. Tapavicza *et al.*, *J. Chem. Phys.* **129**, 124108 (2008); F. Cordova *et al.*, *J. Chem. Phys.* **127**, 164111 (2007).
- F. Wang and T. Ziegler, *J. Chem. Phys.* **121**, 12191 (2004).
- Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- deMon2k, Andreas M. Koester, Patrizia Calaminici, Mark E. Casida, Roberto Flores, Gerald Geudtner, Annick Gourso, Thomas Heine, Andrei Ipatov, Florian Janetzko, Serguei Patchkovskii, J. Ulises Reveles, Alberto Vela, Dennis R. Salahub, deMon developers, 2006 deMon@Grenoble, <http://dcm.ujf-grenoble.fr/PERSONNEL/CT/casida/deMonaGrenoble/>
- M. Huix-Rotllant *et al.*, *in preparation*.

Acknowledgements

C.M.W. would like to acknowledge a scholarship from the French Embassy in Kenya. M.H.R. would like to acknowledge an *Allocation de Recherche* from the French Ministry of Education. B.N. would like to acknowledge a scholarship from the *Fondation Nanosciences*. A.I. would like to acknowledge postdoctoral funding from the *Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité (LEDSS)* which has now become part of the *Département de Chimie Moléculaire (DCM)*. Those of us at the *Université Joseph Fourier* would like to thank Pierre Vatton, Denis Charapoff, Régis Gras, Sébastien Morin, and Marie-Louise Dheu-Andries for technical support at the DCM and for technical support in the context of the *Centre d'Expérimentation du Calcul Intensif en Chimie (CECIC)* computers used for the calculations reported here. This work has been carried out in the context of the French Rhône-Alpes Réseau thématique de recherche avancé (RTRA): *Nanosciences aux limites de la nanoelectronique* and the Rhône Alpes Associated Node of the European Theoretical Spectroscopy Facility (ETSF).

