A Quantum Leap Into the Future of Chemistry

What's New in Q-Chem

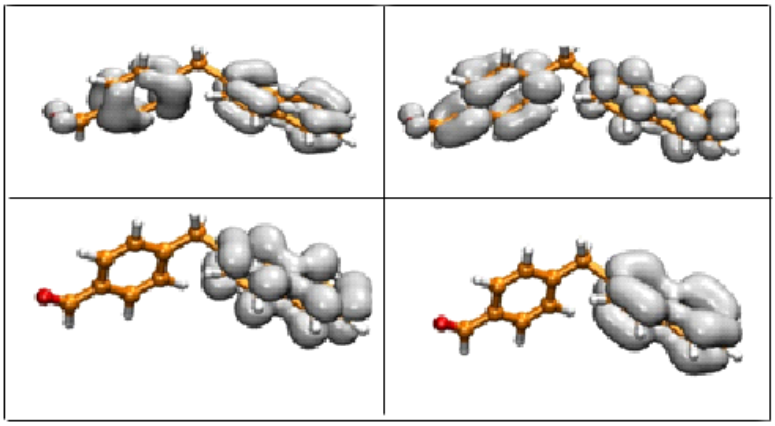
Feature 18

Boys and Edmiston-Ruedenberg Localized Diabatization

Developers: Joseph Subotnik, Ryan Steele, Neil Shenvi, Alex Sodt

Calculating stable diabatic states is crucial for predicting rates of electron or energy transfer, and this feature's techniques allows one to calculate the diabatic couplings that enter Marcus theory rates. Boys and Edmiston-Ruedenberg localization are unique tools for constructing diabatic states because they can be derived from physical models of system-solvent interactions and they don't require fragment definitions or any other parameterization. This feature should be applied post CIS/TD-DFT calculations. The adiabatic excited states are rotated to create a diabatic Hamiltonian with off-diagonal elements

The diagram to the right shows diabatic and adiabatic electronic detatchment and attachment densities for one electronic state near a crossing point. Note how the "exciton" is localized in the diabatic picture.



For more new features, visit:
www.q-chem.com/whatsNew4.html

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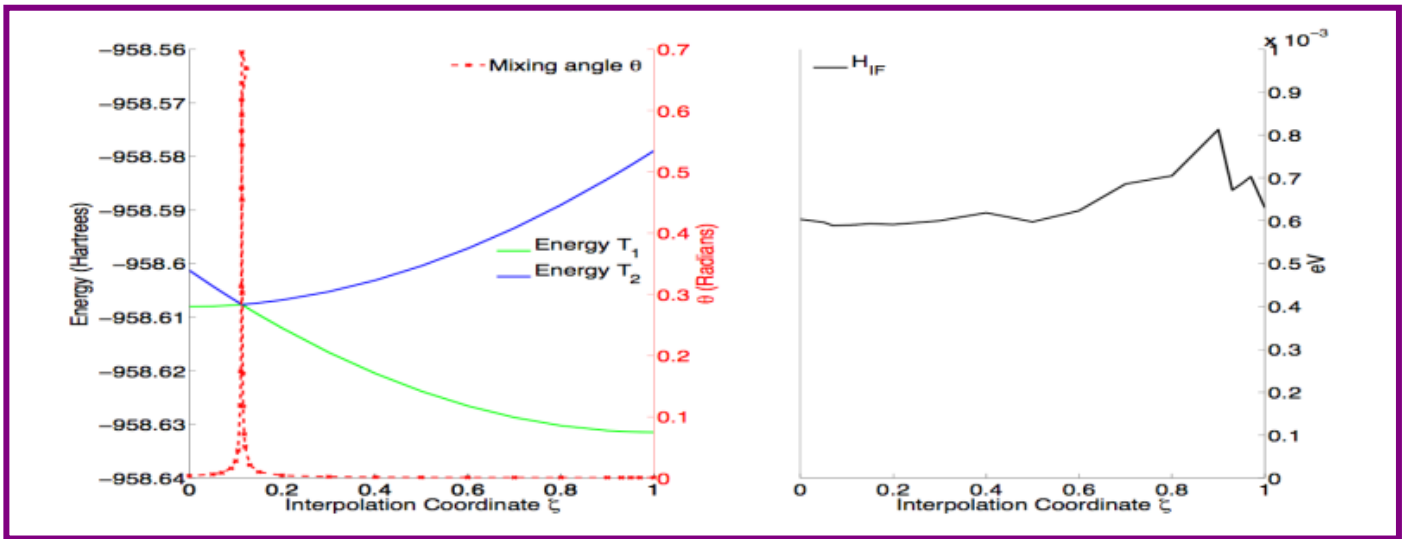
Boys and Edmiston-Ruedenberg Localized Diabatization (continued)



This picture above shows the diabatic coupling as a function of nuclear geometry for the famous Closs molecules. The diabatic coupling does not change as a function of nuclear coordinate, which validates the so-called Condon approximation which is assumed in Marcus theory. On the left, we show the same electronic states now from an adiabatic perspective with an avoided crossing.

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Ryan Steele


Neil Shenvi


Alex Sodt


Joe Subotnik

For more information on how to use this feature, refer to the Q-Chem Manual, Section _____

Publications:

J. Subotnik, S. Yeganhe, R. Cave, and M. Ratner, "Constructing diabatic states from adiabatic states: Extending generalized Mulliken-Hush to multiple charge centers with Boys localization" J. Chem. Phys., **129**, 244101 (2008)

J. Subotnik, R. Cave, R. Steele, N. Shenvi, "The initial and final states of electron and energy transfer processes: Diabatization as motivated by system-solvent interactions" J. Chem. Phys., **130**, 234102, (2008)

J. Subotnik, J. Vura-Weis, A. Sodt, M. Ratner, "Predicting Accurate Electronic Excitation Transfer Rates via Marcus Theory with Boys or Edmiston-Ruedenberg Localized Diabatization" J. Phys. Chem. A, 114, 8665, (2010)

J. Vura-Weis, M. Newton, M. Wasielewski, J. Subotnik, "Characterizing the Locality of Diabatic States for Electronic Excitation Transfer By Decomposing the Diabatic Coupling" J. Phys. Chem C 2010, 114, 20449-20460

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