

SECTION SEMINAR MEETING

3:30 PM, Thursday, April 28
University of Miami, Cox Science Center, room 318
Coral Gables Campus



Dr. Rigoberto Hernandez

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"Obtaining exact transition state theory rates without perturbation theory"

The rates of chemical reactions (or any activated process) are by definition determined by the flux of reactants (or initial states) that end up as products (or final states). Through the last hundred years of studies on reaction rate theory, it has become clear that this can be equated to the flux through any surface that divides reactants from products as long as only those trajectories that end up as products are included in the flux. Transition state theory (TST) ignores this last clause. It thereby overestimates the rate if any of the trajectories recross the dividing surface. However, its advantage is that it replaces a dynamical calculation with a geometric one. Through the variational principle or perturbation theory, however, one can construct non-recrossing dividing surfaces that lead to exact rates. These approaches are limited by the nature of the search space of surfaces and the reference dividing surface, respectively. We have recently discovered that the Lagrangian descriptor can be used to resolve the dividing surface directly. [G. T. Craven and R. Hernandez, Phys. Rev. Lett. 115, 148301 (2015)] We will further show the accuracy of the approach for barrierless reactions, model reactions, ketene isomerization and LiCN isomerization.