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# CSC/WCPM joint seminar

## Diabatization strategies for non-adiabatic dynamics: photodissociation of acetylene and NO/$Au_3$ scattering

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Monday, 5th December, 1 p.m.
P5.23 Seminar room, Department of Physics, 5th Floor

**Abstract:** Despite the success of the Born-Oppenheimer approximation (BOA) when applied to the description of a vast number of problems in chemistry, it reaches an impasse when the energy of systems enable electronic transitions. This breakdown predominates in scattering and photodissociation experiments and respective examples will be provided in this presentation. The immediate challenge when stepping beyond BOA is that the electronic adiabatic representation becomes ill-equipped to handle the evaluation of the non-adiabatic (NA) coupling operator (neglected in BOA). This has prompted the use of diabatic representations which minimise NA coupling operator contributions. We present two strategies for obtaining such representations and which obviate the need to evaluate the NA coupling operator, recovering vibronic coupling through the choice of diabatic-adiabatic transformation.
The first approach is an extension of the diabatization by ansatz applied to molecules with non-Abelian symmetries; an approach for generating non-Abelian symmetry-invariant polynomials is used to construct a 10-state 7D Acetylene model describing the vibrationally-mediated photodissociation experiment. The distribution of geometries at the time of dissociation are provided for a number of IR+UV pulses.
The second, more general approach can be used for an arbitrary number of state/coordinates for which one can perform CAS/RAS-SCF or CASPT2 calculations. It generalises a known method that perform rotations on the orbital and CI vectors to maximise the overlap of the multiconfigurational wavefunction states to that of some reference geometry. The advantages and generality of this approach is demonstrated in the generation of a 12-state 2D model of electron-transient NO scattering of an $Au_3$ cluster. The relevance of such a simple model to the non-adiabatic scattering off Au(111) surfaces will be discussed.

A festive buffet lunch is available from 12:45 pm.

More info: http://warwick.ac.uk/wcpm/seminars

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