

Constructing effective hamiltonians for multiple electronic states and their intersections

Bastiaan J. Braams

Centrum Wiskunde en Informatica (CWI), Amsterdam, Netherlands

Potential energy surfaces represent the total energy of a system of nuclei and electrons as a function of the nuclear configuration. These surfaces (and property surfaces, such as the dipole moment) are key tools for quasi-classical trajectory calculations, molecular spectroscopy, quantum scattering and other applications in molecular science. In the talk I will first review methods developed and used in collaboration with Joel Bowman at Emory University [1] to fit full-dimensional potential energy and dipole moment surfaces for small molecules and molecular reaction complexes, with up to about eight nuclei depending on the application. The methods take full account of permutational symmetry among like nuclei, and this required extensive use of computer algebra through the Magma system.

Proper treatment of electronic excited states and their interactions, including conical intersections, requires fitting a small effective hamiltonian of which the leading eigenvalues and eigenvectors represent the states of interest. However, a priori the invariance or covariance properties of such an effective hamiltonian are quite obscure and it is not clear how to obtain suitable training data for fitting. In the talk I outline a solution to those problems.

- [1] Braams, Bastiaan J., and Joel M. Bowman. "Permutationally invariant potential energy surfaces in high dimensionality." *International Reviews in Physical Chemistry* 28, no. 4 (2009): 577-606. Online: <https://doi.org/10.1080/01442350903234923>.