

# **First principles simulations of electronic spectroscopy**

**Marcel Nooijen**  
**University of Waterloo**

Over the past decade various methodologies have been developed that can calculate the electronic structure of excited states and radicals to high accuracy. A detailed description of UV absorption, resonance Raman, Circular Dichroism, or photo-electron spectra of course requires a consideration of nuclear motion. In the past years we have developed a routine diabaticization procedure to extract linear, quadratic, or even quartic, vibronic models from Coupled Cluster type of electronic structure calculations for excited states (EOMCC and STEOM), and a similar procedure is available for time-dependent DFT methods. These vibronic models use a diabatic basis and they allow a convenient inclusion of non-Born-Oppenheimer effects in the simulations. Diagonalization of the vibronic model potential matrix as a function of nuclear geometry provides adiabatic potential energy surfaces that yield qualitative insight in the nuclear dynamics in the excited states, and which can be a basis for Born-Oppenheimer based Franck-Condon calculations, including high-order Hertzberg-Teller effects. Classical simulations based on the vibronic model can be used to effectively account for the geometry dependence of transition dipoles and can be particularly important for the description of CD spectra.

For small molecules the UV absorption or photoelectron spectra, including non-adiabatic effects, can be obtained by solving for the full vibrational-electronic (or vibronic) eigenstates in a harmonic oscillator basis using the Lanczos algorithm. For larger systems, solving for the high-dimensional vibronic eigenstates rapidly becomes prohibitively expensive. I will describe how coupled cluster techniques can be used to transform the vibronic Hamiltonian at the level of second quantization (a kind of CC theory for bosons). The transformed Hamiltonian is far simpler than the original model Hamiltonian and it can be diagonalized more easily. The efficiency of the approach is remarkable as the number of cluster amplitudes scales essentially as the classical degrees of freedom, while the dimensionality of the full quantum problem explodes exponentially with the number of normal modes in the system. This approach is still in its infancy, and preliminary results will be discussed.