

# Pairing Equation-of-Motion Coupled Cluster and the Reflection Principle: Constructing Photodissociative Absorption Spectra from Quantum Chemical Calculations

Megan R. Bentley and John F. Stanton

*Department of Chemistry, Quantum Theory Project, University of Florida, Gainesville, FL,  
USA*

The reflection principle, originally proposed by Edward Condon in 1928, is a special case of the more familiar Franck-Condon principle. It is built on the premise that when a molecule is excited from a bound lower state to a repulsive excited state, the resulting continuous absorption spectra depends only on the (vertical) slope of the upper potential and the form of the lower-state wavefunction. This method has been shown to be surprisingly successful in reproducing experimental photodissociation spectra, although it is often used erroneously. Here, excited-state properties are calculated via Equation-of-Motion Coupled-Cluster (EOM-CC) theory to test the performance of the reflection principle in constructing calculated photodissociation spectra for various diatomic test cases. Extensions of the classical reflection principle model towards incorporating semiclassical corrections are also discussed.