LOCATING MINIMUM ENERGY CROSSING POINTS USING EOM-CC METHODS

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Non-adiabatic and spin-forbidden processes involve transitions between electronic states through potential energy surface (PES) crossings. They are often found in atmospheric and combustion chemistry, photochemistry and photobiology. To describe the kinetics of such processes, a version of transition state theory can be applied.

Locating the minimum energy crossing point of the PESs is the first step of characterizing a spin-forbidden reaction. The point corresponds to the transition state of the process.

This work presents a computational procedure for minimizing singlet-triplet crossings of PESs, which is applied to a benchmark series of methylene-related radicals, formaldehyde, and oxybenzene, an intermediate in atmospheric formation of phenol. The intersection minimum in the studied methylene-related radicals is located very close to the excited state minimum, singlet for CH_2 and triplet for CHF and CF_2. The crossing in oxybenzene is found along the CO wagging coordinate. In the case of para-benzyne, which has a singlet-triplet adiabatic excitation energy of less than 0.2 eV, the crossing minimum is unexpectedly located 0.65 eV above the ground state equilibrium energy and corresponds to a distorted ring geometry.