Time-dependent approaches for the calculation of intersystem crossing rates

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Abstract

We present three formulas for calculating intersystem crossing (ISC) rates in the Condon approximation by means of a time-dependent approach: an expression using the full time correlation function which is exact for harmonic oscillators, a second-order cumulant expansion, and a short-time approximation of this expression. While the exact expression and the cumulant expansion require numerical integration of the time correlation function, the integration of the short-time expansion can be performed analytically. To insure convergence in the presence of large oscillations of the correlation function, we use a Gaussian damping function. The strengths and weaknesses of these approaches as well as the dependence of the results on the choice of the technical parameters of the time integration are assessed on four test examples, i.e. the nonradiative $S_1 \rightsquigarrow T_1$ transitions in thymine, phenalenone, flavone, and porphyrin. The obtained rate constants are compared with previous results of a time-independent approach. Very good agreement between the literature values and the integrals over the full time correlation functions are observed. Furthermore, the comparison suggests that the cumulant expansion approximates the exact expression very well while allowing the interval of the time integration to be significantly shorter. The short-time approximation typically yields rates that are about an order of magnitude larger than the results of the exact formula and the cumulant expansion. A great advantage of the time-dependent approach over the time-independent approach is its excellent computational efficiency making it the method of choice in cases of large energy gaps, large numbers of normal modes and high densities of final vibrational states.

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