First-Principles Calculations of Excited-State Decay Rate Constants in Molecular Systems

In this lecture, I will delve into recent advances made to evaluate from first-principles the excited-state decay rate constants of molecular systems, focusing on the so-called static strategy. In this strategy, one essentially takes advantage of Fermi’s golden rule (FGR) to evaluate rate constants at key points of the potential energy surfaces, a procedure that can be refined in a variety of ways. In this way, the radiative rate constant can be straightforwardly obtained by integrating the fluorescence line shape, itself determined from vibronic calculations. Likewise, FGR allows for a consistent calculation of the internal conversion (related to the non-adiabatic couplings) in the weak-coupling regime and intersystem crossing rates, therefore giving access to estimates of the emission yields when no complex photophysical phenomenon is at play. Beyond outlining the underlying theories, I will showcase in detail benchmarks performed for various types of rates, highlighting that both the quality of the vibronic calculations and the accuracy of the relative energies are crucial to reaching semiquantitative estimates.

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