

RECENT PROGRESSES TOWARDS THE TIME-DEPENDENT CALCULATION OF VIBRONIC SPECTRA OF FLEXIBLE AND (OR) NONADIABATIC SYSTEMS

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In recent years a number of user friendly methods for the computation of the line shapes of electronic spectra have been developed. Calculation of vibronic spectra for rigid harmonic systems with negligible nonadiabatic couplings accounting for temperature, Duschinsky and Herzberg-Teller effects is nowadays rather standard and it can be performed with little computational cost with either time-independent (TI) or time-dependent (TD) methods.

However, many systems with interesting optical properties are flexible, in the sense that the optical transition triggers large-amplitude curvilinear distortions, and this challenges the applicability of harmonic approximation. Here we show that switching from adiabatic to vertical models of the potential energy surfaces, or moving to a description of the normal modes in internal coordinates it is possible to remarkably extend the applicability of the available methodologies [1-2]. For cases where this is not sufficient, we illustrate the potentiality of hybrid quantum-classical (QC) approaches that are able to describe even the room temperature spectra of systems with severe anharmonicities along curvilinear motions, if these latter are characterized by a low-frequency. Such QC protocols are based on an approximate partition of the vibrational motions in two sets (harmonic and anharmonic) and they obtain the spectrum from the convolution of the TD quantum spectrum of the harmonic set [3] and a classical approximation of the spectrum of the anharmonic set [4]. We show some applications to flexible oligo-thiophenes [4] but we also point out that the same formalism provides a natural framework for the simulation of the solvent inhomogeneous broadening by explicit solvent models [5].

Finally, for systems where nonadiabatic couplings cannot be treated in a perturbative way, the calculation of vibronic spectra requires the direct quantum dynamical propagation of suitable initial wavepackets. In these cases, hierarchical representations of the Hamiltonian offer an effective route to reduce the dimensionality of the system and the computational cost [6-7], allowing the description of fairly large systems. Here we show that using these techniques it is possible to compute fully-converged vibronic lineshapes of the circular dichroism spectra of exciton coupled dimers of large (anthracene [8], oligothiophenes) chromophores.

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