Formal derivation of nonadiabatic couplings from time-dependent density functional theory and the extension within modified linear response

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Most of modern ab initio theories rely on the Born-Oppenheimer approximation to separate the electronic and nuclear motion, due to the fact that the smallness of the mass ratio between electrons and nuclei drastically scales down the nonadiabatic coupling (NAC) terms, which can thus be assumed to be negligible. However, this approximation will break down if there exists degenerate states, i.e. the crossing of potential energy surfaces, which are involved in numerous and rather diverse phenomena. NACs become infinite at the degeneracy points and needs to be seriously considered in the vicinity of these points.

For the computation of NACs, it has been long carried out using wavefunction-based methods, whereas the density-based ones, in particular time-dependent density functional theory (TDDFT), are desired for more efficient calculations. Here we present a formal derivation of NACs between the electronically ground and excited states of molecules, within the framework of TDDFT linear response theory. Based on the comparison of dynamic polarizability formulated both in the many-body wavefunction form and the Casida formalism [1], a rigorous expression is established for NACs, which is similar to the calculation of oscillator strength in the Casida formalism. Implemented in the ABINIT program package [2], our approach is demonstrated to work well. The adiabatic local density approximation (ALDA) gives results in reasonable accuracy as long as the conical intersection is not approached too closely, which is consistent with the real-time TDDFT calculation [3].

In order to improve the ALDA performance on NACs near the conical intersections, we have incorporated modified linear response theory [4, 5] through use of the ground-state-component separation scheme. In this scheme, the excitation energy is computed from the response of the mid-excited state, while the nonadiabatic strength term (the numerator in the formula of nonadiabatic couplings) is obtained from the response of the pure-state configuration, which uses the occupation number of the ground state while keeping other quantities of the mid-excited state. This scheme has been demonstrated to give NACs with an accuracy comparable to that of wavefunction-based methods, not only in the vicinity of conical intersections, but also for Rydberg and charge-transfer excitations [6].

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