Direct nonadiabatic quantum dynamics in the moving crude adiabatic representation

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Résumé

Conical intersections (CIs) play a central role in photochemistry by allowing radiationless electronic transitions. Unfortunately, CIs are synonymous of the Born-Oppenheimer approximation breakdown. Indeed, in the adiabatic representation, the Hamiltonian exhibits singularities at CIs prevent a straightforward numerical treatment of dynamical processes involving CIs. Furthermore, a Berry phase appears in the corresponding electronic states, which imposes additional non-trivial boundary conditions. These difficulties are in fact a failure of the adiabatic representation. Transforming the representation to diabatic is key to solve this problem. However, such a transformation is not known and is necessarily approximate. Therefore, we shall follow a different path.
The recently introduced moving crude adiabatic representation circumvents this difficulty by introducing time-dependent crude adiabatic states. This representation is a formally exact diabatic basis, and thus, the aforementioned difficulties do not occur. This approach is combined with the use of local Gaussian basis functions to design an exact method for simulating molecular processes involving few intersecting potential energy surfaces. Another major advantage of the method comes from the fact that expressions of the Hamiltonian terms in this representation can all be evaluated exactly without resorting to any approximations or model.

References:

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Mots-Clés: Nonadiabatic, Conical intersection, Direct quantum dynamics

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