Molecular electronic transitions: turning linear algebraic considerations into physical insights

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ABSTRACT

During this contribution we would like to introduce a new linear algebraic theorem inspired from inequalities in matrix perturbation theory. Combining this theorem with some known perturbation bounds for matrix eigenvalues we will provide the exact boundary value for the amount of charge transferred during a light-induced molecular electronic transition. Such matrix inequalities are derived in the case where orbital relaxation is accounted for in the representation of an electronic transition through the addition of the so-called Z-vector to the unrelaxed TDDFT one-body reduced difference density matrix. Few interesting matrix equalities in the case where the D/A machinery is applied to unrelaxed/relaxed difference density matrix instead of ground/excited-state difference density matrix will be introduced in order to measure and visualize the global effects of orbital relaxation on the electronic-structure reorganization occurring during the electronic transition.

Besides, we will reveal the ambiguity of the picture of a molecular electronic transition considering the canonical tools that are still currently used for visualizing a molecular electronic transition and quantifying its nature. Without the disambiguation we suggest to introduce, and considering the possibility to imply auxiliary many-body wavefunctions as a possible picture, the representation of an unrelaxed TDDFT electronic transition would be either incomplete, arbitrary, or equivocal.

References

[1] All relevant information and references are available at thibaudetienne.wordpress.com