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Time-propagation of the reduced density matrix for fast and transient phenomena

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This contribution extends a generalization of our previous "***relax-and-drive***" procedure to propagate reduced density matrices (RDMs) [1,2] developed here for the ***dissipative dynamics*** of a many-atom structure in a medium, undergoing a ***fast and transient evolution*** during excitation by a light pulse or an atomic collision. This involves two types of excitations (fast electronic and slow atomic) entangling with ***very different time scales***. Time-propagation of the RDM can be done as a sequence of long intervals of dissipative relaxation of fast variables, driven in each interval by slow variables. Electronic relaxation in each interval can be extracted from solutions of eigenvalue equations for local RDMs, which provide time-dependent electronic densities [3,4], while bypassing the need to integrate the RDM equations of motion over short time intervals. This shortens computational times for propagation of the RDM. A numerical integration procedure can be implemented for the one-electron RDM with a basis set of many-atom orbitals generated by a density functional, and can incorporate ab initio non-adiabatic treatments [5,6]. Recent DFT/RDM descriptions (which include accurate energy band gaps) have been applied to electronic relaxation of nanostructured surfaces of Si [7] and TiO_2 [8].

[1] K. Runge, D. A. Micha, and E. Q. Feng, Int. J. Quantum Chem. (1990) *38 S24*, 781.
[2] D. A. Micha and K. Runge, Phys. Rev. A **50**, 322 (1994)
[3] D. S. Kilin and D. A. Micha, J. Phys. Chem. Letters 2010, *1*, 1073
[4] D. A. Micha, Adv. Quantum Chem. **71**, 195 (2015)
[5] R. Long and O. V. Prezhdo, JACS 2014, *136*, 4343.
[6] Y. Han, S. Tretiak and D. Kilin, Mol. Phys. (2014) *112*, 474
[7] T. Vazhappilly and D. A. Micha, J. Phys. Chem. C 2014, *118*, 4429
[8] T. Vazhappilly, M. P. de Lara-Castells, and D. A. Micha, Mol. Phys. (2019) *117*, 2267 (DOI: 10.1080/00268976.2018.1533651)

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