Density Matrix Treatment of Optical Response with Combined Instantaneous and Delayed Dissipations: Adsorbates on Solid Surfaces

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Abstract
The interaction of light with a localized (primary) region in a many-atom system undergoing electronic and vibrational transitions leads to energy dissipation and fluctuations through both nearly instantaneous and delayed processes. A fast dissipation typically occurs due to electronic energy relaxation in the medium, while a delayed dissipation arises from vibrational energy relaxation. A theoretical and computational treatment of these phenomena has been done in terms of a reduced density matrix (RDM) satisfying a generalized Liouville-von Neumann equation.[1] Instantaneous dissipation is described by a Lindblad term containing electronic transition rates,[2] while the delayed dissipation is given by a time integral derived from the time-correlation function (TCF) of atomic displacements in the medium.[3] We consider cases where the TCF decays exponentially (fast) or as an inverse power (slowly). An initial thermal equilibrium can not be assumed when there are long lasting interactions between the primary region and the medium. We describe a general procedure that provides the optical response in this case by calculating the difference between solutions for the RDM with and without excitation by a light pulse. We present examples for slow relaxation of optical excitation in CO/Cu(001) and Ag3/Si(111).[4]


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