Extension of the Optimal Control Theory to Solvated Systems

Marta Rosa[a] , Gabriel Gil Perez[a], Stefano Corni[a,b] and Roberto Cammi[c]

[a]Università degli Studi di Padova, [b]Center S3, CNR Institute of Nanoscience, Modena, [c]Università degli Studi di Parma

Optimal control is a quantum theory designed to selectively guide a (molecular) quantum system from an initial state towards a final target state with desired properties (e. g. a given pure excited state), through the interaction of the system with an external laser pulse.
Many efforts have been devoted to the control of nuclear dynamics, allowing to successfully control products ratios of chemical reactions and crystallization processes, photodissociation of molecules in the gas phase, energy flow optimization in light-harvesting complex, and generally proving the method valuable in the conception of effective experiments .
Optimal control theory is widely applied to the study of molecular electronic states with ultrashort laser pulses, which require a short time scale (fs) to avoid nuclear relaxation and energy level rearrangements; with the application of optimal control theory it is possible to compute perfectly suited laser fields able to drive the system to the desired target state. Once the final shape of the pulse is obtained, the analysis of its polarization and frequencies can allow to understand the molecular behaviour and excitation mechanism.
Optimal control theory has been widely applied to in vacuo systems, but only few studies tried to include environmental effects into the calculations (e. g. dissipative coupling with the external bath, molecular geometry fluctuations). Nevertheless, none of them accounted for the modification in the molecular electronic and optical properties due to the dielectric nature of the solvent.
Electronic and optical properties of a molecule embedded in solution (or more generally, in a polarizable environment) can differ substantially from the ones of the same molecule in vacuo, therefore the optimal control of a solvated molecule needs a special consideration.
Electonic dynamics for a molecule in solution is coupled with the dynamics of the surrounding polarizable environment, i.e. the solvent. The Polarizable Continuum Model (PCM) provides a reliable description of the solvent dielectric properties, including polarization effects [1, 2]
Concerning optimal control pulses, two effects influences the optimal driving field: first, the presence of the molecule induces a polarization in the solvent (the reaction field) which influences the molecule itself; second, the effective field acting on the molecule is different from the external applied field, which in fact induces a further polarization of the environment (the so called cavity field effect) [3, 4].
Both these effects must be included in the Hamiltonian describing the system when deriving the optimal control problem for a molecule immersed in a solvent.
In this study we developed an optimal control theory for a molecule in solution subject to ultrashort laser pulses and applied it to quinolone and LiCN molecules, to understand how the effect of the solvent modifies the optimal control process itself.

References

1 - Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev. 2005, 105, 2999–3094.
2 - Cammi, R.; Corni, S.; Mennucci, B.; Tomasi, J. J. Chem. Phys. 2005, 122, 104513.
3- Pipolo, S.; Corni, S.; Cammi, R. J. Chem. Phys. 2017, 146, 064116.
4 - Gil, G.; Pipolo, S.; Delgado, A.; Rozzi, C. A.; Corni, S. JCTC 2019