

Ultrafast Laser Driven Proton Dynamics in Gas- and Condensed Phase

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Ultraschnelle Lasergetriebene Protonendynamik in Gas- und Kondensierter Phase

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Zusammenfassung

In dieser Arbeit werden verschiedene Methoden der Behandlung des multidimensionalen, lasergetriebenen intramolekularen Protonentransfers in Gasphase und dissipativer Umgebung untersucht. Dabei wird zuerst die Methodik des “Cartesian Reaction Surface” (CRS) Hamilton-Operators und seine Herleitung aus *ab initio* Daten dargestellt. Dieser Ansatz erlaubt die näherungsweise Berechnung von Potentialenergieflächen für die Kernbewegung größerer molekularer Systeme in vollständiger Dimensionalität. Zur Lösung der durch diesen Operator definierten Schrödinger Gleichung wird die für hochdimensionale Systeme besonders geeignete “Multi Configuration Time Dependent Hartree” (MCTDH) Methode genutzt.

Zur Einbeziehung dissipativer Effekte wurde das Lösungsmittel störungstheoretisch mit Hilfe der Redfield Theorie modelliert. Zusätzlich wurde das Bad durch klassische Molekulardynamik-Simulationen untersucht, um direkt den Einfluss eines klassisch behandelten Lösungsmittels auf den CRS Hamiltonoperator zu bestimmen.

Mit Hilfe dieser numerischen Methoden zur Berechnung der Quantendynamik wurden verschiedene Strategien zur Kontrolle des Protonentransfers durch ultrakurze Laserpulse verglichen. Dazu werden Modellsysteme, die an *ab initio* Daten angepasst wurden, sowohl isoliert als auch in kondensierter Phase mit Dissipation untersucht. Die Kontrollmethoden die benutzt wurden, reichen von der Parameteranpassung analytischer Pulse in einem zwei Puls Pump-Dump Modell über die Parameteroptimierung durch genetische Algorithmen und lokale Kontrollstrategien für das elektrische Feld bis zur Anwendung der Theorie zur optimaler Kontrolle.

Abstract

In this work different models for the treatment of laser driven, multidimensional intramolecular proton dynamics in gas phase and dissipative surroundings are examined. First the method of the “Cartesian Reaction Surface” (CRS) Hamiltonian and its derivation from *ab initio* data is presented. This approximation allows the modeling and calculation of potential energy surfaces for the nuclear motion of larger molecular systems in full dimensionality. The solution of the Schrödinger equation for this operator is then calculated via the “Multi Configuration Time Dependent Hartree” (MCTDH) method, which is especially suited for calculations dealing with systems of high dimensionality.

The dissipative effects were modeled within perturbation theory with the Redfield approach. In addition to that the solvent was simulated using classical molecular dynamics, to determine the interaction of the bath with the CRS Hamiltonian.

Using these numerical methods for the quantum dynamics, different control strategies for the proton transfer, using ultra-short laser pulses are compared. To this end, model systems, which were fitted to *ab initio* data, were calculated isolated and in condensed phase with dissipation. The control methods used range from fitting the parameters of analytical pulses in a simple two pulse pump–dump model, to parameter fits with genetic algorithms and local control schemes for the electrical field, and up to the application of optimal control theory.

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