The MP/SOFT methodology for simulations of quantum dynamics: Model study of the photoisomerization of the retinyl chromophore in visual rhodopsin

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Abstract

Rigorous simulations of excited-state nonadiabatic quantum dynamics in polyatomic chromophores are particularly challenging since they require solving the multichannel time-dependent Schrödinger equation describing nuclear wavepackets evolving on electronically coupled potential energy surfaces. This paper presents an overview of the matching-pursuit/split-operator-Fourier-transform (MP/SOFT) method for simulations of nonadiabatic quantum dynamics [X. Chen, V.S. Batista, Matching-pursuit split operator Fourier transform simulations of excited-state nonadiabatic quantum dynamics in pyrazine. J. Chem. Phys., 125 (2006) Art. No. 124313] and its application to the description of the 11-*cis*/all-*trans* photoisomerization of the retinyl chromophore in rhodopsin. The underlying nonadiabatic dynamics is described by a 2-state 25-dimensional wave-packet evolving according to an empirical model Hamiltonian with frequencies and excited-state gradients parameterized to reproduce the observed resonance Raman excitations of rhodopsin. The reported results show that the MP/SOFT method is a valuable tool to simulate nonadiabatic dynamics in polyatomic systems and to assess the validity of mixed quantum-classical approaches as applied to simulations of complex (nonintegrable) quantum dynamics in multidimensional systems.
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1. Introduction

Understanding ultrafast photoinduced reactions in excited electronic states of polyatomic chromophores is a problem common to a wide range of systems in chemistry, biology, physics and beyond. Many experimental techniques implementing ultrafast time-resolved pump-probe spectroscopy (besides various types of transient absorption experiments) have been developed to study a variety of ultrafast photoinduced processes, including isomerization reactions, excited state intramolecular proton transfer, direct dissociation, vibrational energy redistribution and electronic internal conversion, among others. The unambiguous interpretation of these highly multiplexed pump-probe experiments, however, often requires theoretical simulations since the signals result from complicated nonadiabatic dynamics involving multiple potential energy surfaces (PESs). This paper presents an overview of the matching-pursuit/split-operator-Fourier-transform (MP/SOFT) method for simulations

of nonadiabatic quantum dynamics [1] and its illustration as applied to modeling the ultrafast 11-*cis*/all-*trans* photoisomerization of the retinyl chromophore in rhodopsin, described by the structural diagram of Fig. 1.

The photoisomerization of the retinyl chromophore in rhodopsin constitutes the primary step in the vertebrate vision process [2–9] and has been the subject of extensive experimental and theoretical studies. Femtosecond pump-probe spectroscopic measurements have provided detailed time-resolved information on the photoisomerization and interconversion dynamics, indicating that the all-*trans* photoproduct is formed within 200 fs with high efficiency (67%) [10–12]. However, due to the complexity of the problem, the complete theoretical description of the underlying nonadiabatic dynamic has yet to be reported with an explicit treatment of the rhodopsin environment. In this paper, the description of dynamics is based on an approximate empirical model Hamiltonian with frequencies and excited-state gradients parameterized to reproduce the observed resonance Raman excitations of rhodopsin.

Most previous theoretical studies were performed long before the crystallographic structure of rhodopsin was available [13–18]. However, the recently reported X-ray crystal
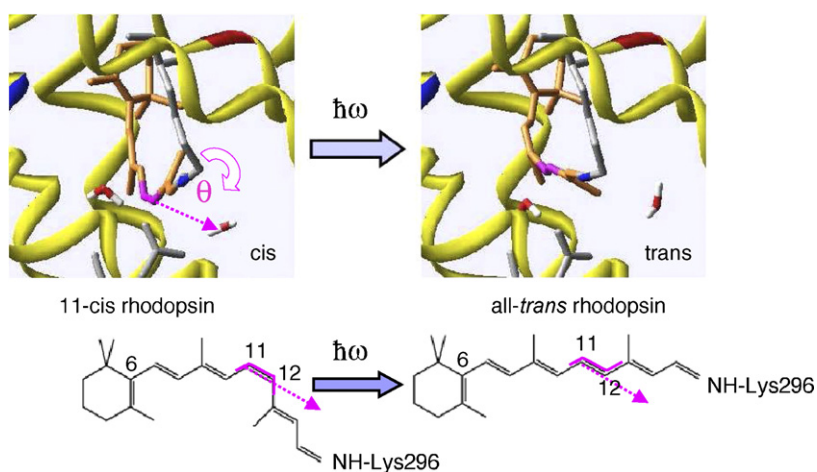
Fig. 1. Structural diagram of the 11-*cis*/all-*trans* photoisomerization of the retinyl chromophore in visual rhodopsin. The C_{11}–C_{12} bond and the dihedral angle $\theta(C_{11}$–$C_{12})$ are highlighted in magenta.

structures of bovine rhodopsin [19–21] have motivated several computational studies that focused on the analysis of the geometry and electronic excitation of the retinyl chromophore [22–26], the underlying molecular rearrangements, and the mechanism of energy storage by 11-*cis*/all-*trans* isomerization [27–31]. In addition, several studies based on reduced dimensional model systems have investigated the underlying nonadiabatic dynamics associated with the photoisomerization of the chromophore [32–37], including studies based on approximate mixed quantum-classical techniques applied in conjunction with an empirical 2-state 2-mode model Hamiltonian, coupled to a classical bath of 23 vibrational modes of rhodopsin [38,39]. This model Hamiltonian is thus particularly suited for detailed investigations based on newly developed computational methods since it allows for direct comparisons with previous studies and recent theoretical work on related systems [40,41]. This paper reports simulations of the photoisomerization dynamics treating the 2-state 25-mode model fully quantum mechanically. This includes the two coordinates accounting for the collective torsion about the C_{11}–C_{12} bond and its coupling to the delocalized stretching mode of the polyene chain, evolving on 2 electronically coupled potential energy surfaces. The quantum bath includes 23 vibrational modes with frequencies and excited-state gradients parameterized to reproduce the experimental resonance Raman excitations of rhodopsin [42].

Numerically exact simulations of excited-state nonadiabatic quantum dynamics are particularly challenging since they require solving the multi-channel time-dependent Schrödinger equation for the description of nuclear motion on multiple coupled potential energy surfaces. This problem can be rigorously solved by applying methods for wave-packet propagation [43–55], such as approaches based on the split-operator-Fourier transform (SOFT) method [56–58], the Chebyshev expansion [59] and the short iterative Lanczos algorithms [60]. While rigorous, these approaches demand storage space and computational effort that scale exponentially with the number of coupled degrees of freedom in the system, limiting their applicability to molecular systems with very few atoms (e.g., less than three or

four atoms). Due to this scalability problem, studies of nonadiabatic dynamics in polyatomic systems have been usually based on approximate methods built around semi-classical and mixed quantum-classical treatments [61–75]. However practical, these popular mixed quantum-classical approaches rely upon *ad hoc* approximations whose resulting consequences are often difficult to quantify in applications to complex (*i.e.*, nonintegrable) dynamics. It is, thus, imperative to develop practical, yet rigorous, methods to validate approximate approaches and gain insight into the nature of quantum dynamics [1,76–87].

The MP/SOFT method [1,82–87] is a time-dependent propagation scheme for numerically exact simulations of quantum processes. The method is based on the propagation of multidimensional time-dependent wave-packets, represented in matching-pursuit coherent-state expansions, by analytically applying the time-evolution operator as defined by the Trotter expansion to second order accuracy. The resulting propagation scheme thus bypasses the 'exponential scaling problem' of the standard grid-based SOFT approach [56–58], usually limited by the capabilities of the fast-Fourier transform FFT algorithm [88]. Furthermore, the MP/SOFT method overcomes the 'truncation problem', natural to propagation schemes where the basis set is defined *a priori*, by dynamically adapting the coherent-state expansion according to the desired propagation accuracy. When compared to alternative time-dependent methods, including the MCTDH method [89,90] and approaches based on coherent-state expansions [78,79,91–105], the MP/SOFT method is usually easier to implement since it has the advantage of avoiding the need of propagating time-dependent expansion coefficients, a task that would require solving a coupled system of differential equations. The main drawback of the MP/SOFT method is that it requires generating a new coherent-state expansion for each propagation step. However, such a computational task can be trivially parallelized, overcoming the limitations of memory/storage bandwidth in terms of readily available computational processing power.

The accuracy and efficiency of the MP/SOFT method have already been demonstrated in several applications to multidimensional quantum dynamics, including recent studies