SEMICLASSICAL MODELLING OF FINITE-PULSE EXCITATION EFFECTS ON THE PREDISSOCIATION DYNAMICS OF NaI

MODELACIÓN SEMICLÁSICA DE LOS EFECTOS DE LA EXCITACIÓN MEDIANTE PULSOS DE DURACIÓN FINITA SOBRE LA DINÁMICA DE PREDISOCIACIÓN DE NaI

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During the last decades, pump-probe spectroscopy has placed itself among the most powerful tools available to investigate, at a microscopic level, the underlying mechanisms of many phenomena in physics, chemistry and biology. On the other hand, addressing fundamental processes taking place in many-body systems from the time-resolved spectroscopy perspective, often requires auxiliary theoretical calculations to support the interpretation of empirical data. However, rigorous time-dependent quantum mechanical calculations are computationally very demanding for systems with more than a few degrees of freedom. At present, simulations of pump-probe spectra for many-body molecular systems appear to be out of reach, unless a theoretical treatment relying on a classical (or semiclassical) approximation is used.

An additional source of complexity in the simulation of photochemical events is the nearly ubiquitous presence of conical intersections or avoided crossings, giving rise to the manifestation of non-adiabatic effects. Starting from the pioneering experiments of Zewail and co-workers on probing the real-time dynamics of NaI predissociation using (femtosecond) electromagnetic fields [1, 2], this reaction has evolved into a paradigm of ultrafast dynamics involving strong non-adiabatic couplings. The Landau-Zener transitions at the crossing region of the two electronic states involved in the process give rise to marked interference patterns. Moreover, the relative phase between the wavepackets moving on the dissociative and on the bound potential energy curves can be engineered to inhibit (or enhance) the fragmentation channel [3, 4].

The theoretical investigation of electronic transitions induced by finite-length pulses demands the actual profile of the exciting electromagnetic field to be explicitly incorporated into the model. Nevertheless, it makes more difficult to carry out numerically converged simulations based on semiclassical schemes such as surface-hopping techniques. The reason is

that field-induced couplings may be appreciably delocalized in space, rendering the application of Tully's fewest switches scheme [5] inefficient. A possible route to overcome these difficulties would be to handle these couplings within the initial conditions of the semiclassical calculations, i.e., to implicitly account for the effects of the various pump pulse parameters (e.g, the pulse width and chirp) via a suitable sampling function. This simple procedure, though approximate, has a fairly lower computational cost compared to more sophisticated simulation techniques, what makes it very appealing concerning its extension to the analysis of non-adiabatic dynamics in large molecular systems. In this work, we aim to assess the validity of this approach to study photoinduced phenomena in presence of strong non-adiabatic effects. By using the electronic predissociation of NaI as a numerical example, we undertake the modelling of dynamical phenomena where interference between the wavepackets evolving on different electronic states plays a major role.
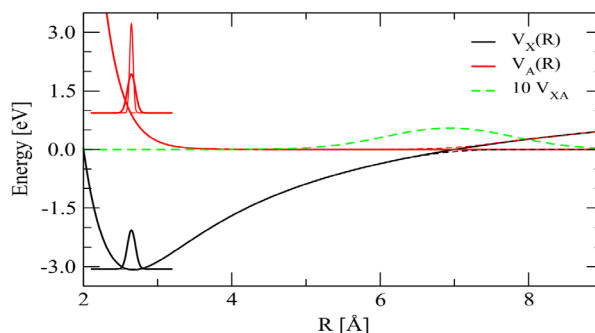

Figure 1. Diabatic potential energy curves V_X, V_A and non-adiabatic coupling element V_{XA} for a NaI molecule. The probability distribution corresponding to the vibrational ground state on the ionic diabatic state is also shown. On the upper potential energy curve, the thick solid line represents the initial wavefunction corresponding to the photoexcitation by a zero-width laser pulse. The thin solid line is the wavepacket promoted by a finite-width pulse with FWHM of 5 fs.

We consider the promotion of a NaI molecule from the $X(^1\Sigma^+)$ ionic state to $A(0^+)$ neutral state, upon absorption of photons

from a (weak) ultrashort laser pulse. The diabatic states V_X and V_A are also coupled by a non-adiabatic matrix element V_{XA}. The explicit functions defining the potential energy curves V_X, V_A and V_{XA} were taken from the literature [6]. These potential energy curves, together with the vibrational ground state on the electronic state X, are represented in figure 1. For an infinitely short laser pulse, the wavepacket promoted onto the neutral diabatic state is the exact copy of that in the vibronic ground state. However, as it is shown in this diagram, even for narrow finite-width pulses acting on the molecule during a few femtoseconds, the spatial extent of the initial wavefunction on the excited state gets strongly suppressed. Such contraction owes to the resonant-filtering of the phase space density, within the limits imposed by the spectral width of the electromagnetic field.

To asses the influence of the finite pulse duration on the subpicosend dynamics of the target system, the time evolution of the wavepackets evolving on the dissociative $\Psi_A(R, t)$ and the bound $\Psi_X(R, t)$ channels was analysed by numerically solving the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\Psi_X \\ \Psi_A\end{pmatrix} = \left[\begin{pmatrix}\hat{T}+\hat{V}_X & \hat{V}_{XA} \\ \hat{V}_{XA} & \hat{T}+\hat{V}_A\end{pmatrix}+\hat{W}\right]\begin{pmatrix}\Psi_X \\ \Psi_A\end{pmatrix} \qquad (1)$$

In equation (1), $\hat{T}$ is the kinetic energy operator and $W(t) = -\mu(R)\,E(t)\left(|X\rangle\langle A|+|A\rangle\langle X|\right)$ is the field-molecule interaction within the dipole approximation, whereas $\mu(R)$ stands for the transition dipole function which is assumed to be constant, and $E(t)=f(t;\tau)\cos(\omega t)$ is the component of the external electric field along the molecular axis. The function $f(t;\tau)$ is the envelope of the laser pulse of length τ (Full Width at Half Maximum, FWHM), while ω designates the central frequency of the electromagnetic field.

The time-dependent propagation scheme employed in the simulation of the non-adiabatic dynamics is based on the decomposition of the time evolution operator according to the Trotter expansion [7, 8], combined with a finite-difference representation of the molecular Hamiltonian on a uniform mesh containing 4096 points. The initial wavefunction $\Psi_X(R, t)$ corresponds to the vibrational ground state of the of the diabatic state X, computed using a Numerov's scheme [9]. Cayley's form of the matrix exponential [10] was found to be accurate enough to represent the effect of the kinetic energy operator on the evolution of the molecular wavefunction. On the other hand, the modification of the wavepacket as a consequence of the interactions (including non-adiabatic couplings) is calculated utilizing the second-order approximation to the exponential of the potential energy introduced in Ref. [11].

The surface-hopping calculations of the predissociation dynamics are based in the numerical implementation of the Tully's fewest switches algorithm [5], i.e., the time evolution of the electronic degrees of freedom is treated quantum mechanically while the forces driving the classical nuclear dynamics are derived from the diabatic potential energy curves

V_X and V_A. A swarm of N independent trajectories resembling the nuclear wavepacket at every point in time, was propagated according to the classical equations of motion. Individual trajectories are allowed to hop between the potential energy curves in order to match the time-dependent occupation probability of the electronic states. Observables are calculated as statistical averages over this ensemble of trajectories.

In order to start the propagation of the nuclear trajectories, initial conditions need to be specified. During the generation of the initial positions and momenta, the energetic constraints following from the finite spectral width of the laser pulse have to be taken into account. The classical limit $\rho(R, t)$ of the probability distribution, consistent with the initial excited state wavefunction calculated within first-order perturbation theory is:

$$\rho(R,P,\mathrm{t}) = e^{-\mathcal{L}t}\rho_A(R,P,\mathrm{t}=0) \qquad (2)$$

where $\mathcal{L}$ is the classical Liouville operator. Following the procedure outlined in [12], the distribution $\rho_A(R, P, t=0)$ can be straightforwardly derived to be:

$$\rho_A(R,P,\mathrm{t}=0) \sim \int dt' e^{-\mathcal{L}t'}W_g(t', D_{AX}-\hbar\omega)\rho_X(R,P,\mathrm{t}=0) \qquad (3)$$

where W_g denotes the Wigner transform of the pulse envelop $f(t;\tau)$ and $D_{AX}=V_A - V_X$ is the energy difference between the two electronic states.

Equation (3) can be translated into a simulation scheme with three main steps:

(i) generate an ensemble of trajectories which sample the phase space density ρ_X associated with the initial quantum-mechanical state,

(ii) randomly choose the "promoted" phase space points at time t' from the distribution given by W_g, and

(iii) undertake the propagation of the nuclear trajectories, governed by the state-specific potentials V_X and V_A as well as the non-adiabatic couplings V_{XA}, starting on the excited electronic state at time t'.

It is obvious that this implementation allows to incorporate the explicit shape of the excitation pulse, while retaining the simplicity of standard surface-hopping calculations (i.e., those carried out assuming vertical excitations exclusively).

First we consider the performance of the semiclassical surface-hopping method for this specific problem by considering a δ-like excitation, i.e., the case where, after the initial electronic transition, the two electronic states are solely coupled by the non-adiabatic matrix element V_{XA}. As it is shown in figure 2, the population instantaneously transferred to the electronic stay A evolves on this potential energy surface for about 100 fs. At this point in time, the wavepacket approaches the

degeneracy region of the diabatic potentials and, as a result of the non-adiabatic couplings, around 98% of the population is brought back on the electronic state *X*. It can be seen, that the the surface-hopping model also predicts an extensive re-population of the *X* state (95%) but somewhat lower than the quantum mechanical calculations. Up to 3 ps after the photoexcitation, it becomes striking that the semiclassical hopping algorithm systematically predicts the correct timing of the non-adiabatic events, but the semiclassical transition probability underestimates its quantum counterpart. Such behaviour can be attributed to frustrated hops, where the trajectories do not change the electronic state due to violation of energy conservation. Though several prescriptions have being devised and tested to alleviate this deficiency, such as the fewest-switches with time-uncertainty method, for the time being we just ignored classically forbidden transitions. If they are necessary to attain an accurate description of specific phenomena, they can be incorporated into the surface-hopping simulations at the same computational expense than for the standard algorithm.
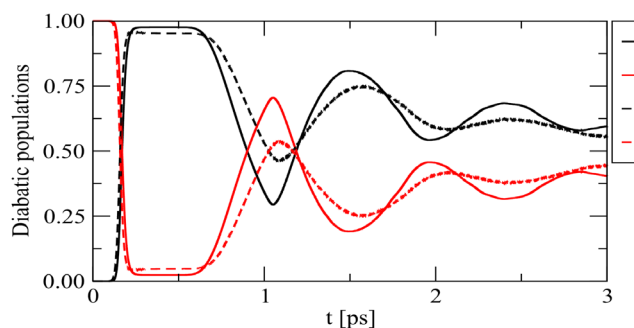

Figure 2. Transient diabatic state populations computed via quantum wavepacket propagation, $P^{qm}_X(t)$ and $P^{qm}_A(t)$, and the surface-hopping scheme, $P^{sh}_X(t)$ and $P^{sh}_A(t)$. The influence of the finite-width of the pump pulse on the non-adiabatic dynamics was neglected in these calculations.

The time-dependent density distribution, corresponding to the vibrations of salt molecules triggered by a 20 fs pump pulse, is depicted in figure 3. It can be seen, that upon the photoexcitation the wavepacket stays localized in space, oscillating back and forth between the inner and outer turning points. The overall agreement of the quantum and the semiclassical density distributions is striking, the latter exhibiting a somewhat larger vibrational amplitude. Hence, the vibrational period obtained in the semiclassical calculations is 12% smaller than the quantum mechanical result. Globally, the application of the surface-hopping algorithm combined with the filtering of finite pulse effects into the initial conditions is found to yield a qualitatively correct picture of the predissociation dynamics for pulse lengths up to a few tens of femtoseconds. In general, the level of correspondence between the quantum and the semiclassical calculations is similar for other pulse shapes considered and for rather large pulse chirps.

In summary, the filtering of the influence of the waveform of the pump pulse into the initial conditions can be applied to the simulation of photoinduced dynamical processes where the use of a δ-function pulse may become a severe drawback for the

quantitative analysis. The time-dependent predissociation rates of NaI molecules are largely governed by strong interference effects, so the target system is intended to provide lower bounds of the applicability of the method for the numerical simulation of non-adiabatic dynamics. The proposed semiclassical methodology predicts precise branching ratios between the bound and the dissociative channels, whereas it gives a correct qualitative picture of the dynamics of the excited wavepacket.
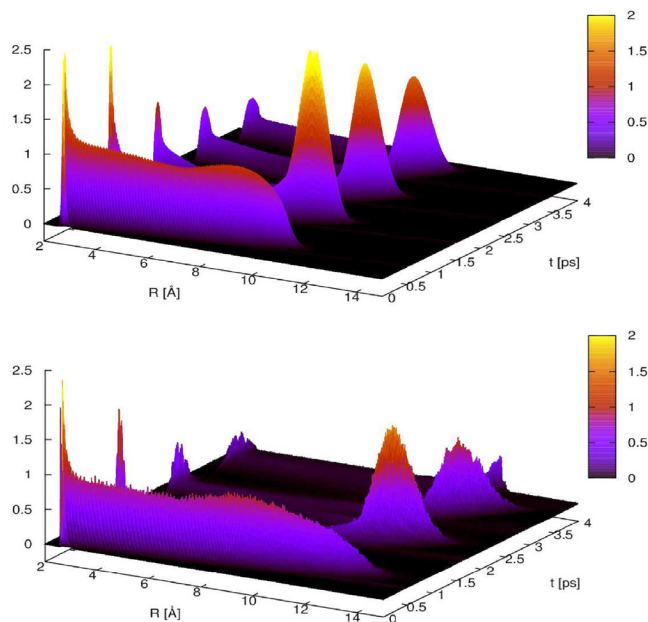

Figure 3. Time-dependent density distribution, as evaluated via quantum wavepacket propagation (upper panel) and semiclassical surface-hopping calculations (bottom panel). The initial wavepacket is promoted onto the *A* electronic state by a Gaussian laser pulse with FWHM of 20 fs.

The present analysis paves the way to employ the mapping of the influence of the finite pulse width into the initial conditions for surface-hopping simulations, to investigate the possibility to achieve a limited control of the non-adiabatic dynamics by tailoring the pump pulse.

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