

Time-dependent description of electronic predissociation in the LiH molecule - preliminary results

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Introduction

During the last 20 years, the physics of dilute gases has seen major advances in two fields: laser cooling of atomic and molecular samples and femtosecond chemistry. In both cases, a strong motivation is to use laser light in order to achieve a better control of the system by reducing the energy distribution of the various degrees of freedom. In this context, two fundamental processes, i.e., photoassociation and photodissociation, or in other words formation and breaking of the chemical bond, have motivated a lot of theoretical and experimental studies. Photodissociation of diatomic and small polyatomic molecules is an ideal field for investigating molecular dynamics at a high level of precision [1]. In this poster we present the preliminary theoretical description of the photodissociation process.

Our attention is focused on the theoretical treatment of electronic predissociation processes in the lithium hydride molecule. We base our considerations on the NaI dimer, which is an interesting and well studied prototype molecule in femtochemistry [2, 3, 4, 5, 6]. We propose to investigate the LiH molecule which shows similar interesting behavior as NaI. Our project is divided into two parts: electronic structure calculations and nuclear wave packet dynamics induced by femtosecond laser pulses.

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Calculation details

To calculate adiabatic potential energy curves of the LiH dimer we use multiconfigurational self-consistent field/complete active space self-consistent field (MCSCF/CASSCF) method and multi-reference configuration interaction (MRCI) method. In this approach we do not include spin-orbit interaction. All calculations are performed by means of the MOLPRO program package [7]. In order to describe the two-channel electronic predissociation in the lithium hydride molecule, we have decided to consider five the lowest lying singlet sigma states and diatomic potential energy curves for singlet and triplet sigma states, which correlate to the Li(2s) + H(1s) ground atomic asymptote and Li(2p) + H(1s), Li(3s) + H(1s), Li(3p) + H(1s), Li(3d) + H(1s) excited atomic asymptotes (Fig. 1). The quality of our calculations were confirmed in our previous papers [8]. Using adiabatic potentials and diabaticization methods [9, 10, 11] we calculated the diabatic potential energy curves. Equilibrium positions R_e and depths of the potential wells D_e are in very good agreement with other theoretical and experimental results (Table 1) and it confirms high quality of our calculations.

Table 1. Spectroscopic parameters R_e (a.u.) and D_e (cm⁻¹) for the ground and excited states of LiH molecule.

State	R_e	D_e
$1^1\Sigma^+$	Li(2s) + H(1s)	
Exp.[12]	3.015	20285
Theory[13]	3.003	20349
Theory[14]	3.007	20174
Present work	3.000	20325
$2^1\Sigma^+$	Li(2p) + H(1s)	
Exp.[12]	4.906	8679
Theory[13]	4.862	8687
Theory[14]	4.847	8690
Present work	4.800	8692
$3^1\Sigma^+$	Li(3s) + H(1s)	
Exp.[15]	-	-
	10.140	8469
Theory[13]	3.821	-
	10.181	8453
Theory[14]	3.825	1277
	10.206	8444
Present work	3.800	1267
	10.250	8440

In order to present the nuclear wave packet dynamics induced by (ultraviolet) femtosecond laser pulses, we have to also calculate non-adiabatic couplings between considered states (Fig. 3) and transition dipole moments (Fig. 2). These results are also performed by means of the MOLPRO program package [7] and overall agreement with other theoretical data is very reasonable [13, 16].

Calculated adiabatic and diabatic potentials, non-adiabatic couplings and transition dipole moments allow us to present and describe the two-channel electronic predissociation in lithium hydride molecule. We have decided to consider the transition from the $1^1\Sigma^+$ ground state, to $3^1\Sigma^+$ excited state. After transition we will investigate the propagation of the wave packet in the system of three crossings between the three lowest lying singlet sigma states of the LiH dimer (Fig. 5). Using the above described results and WavePacket 4.6, a program package for quantum-mechanical wavepacket propagation and time-dependent spectroscopy [17], we will be able to display the nuclear as well as the electronic dynamics on the femtosecond (and attosecond) time scale. I.e., to observe electronic excitation and subsequent nuclear motion. And in the next step, we will present investigation of how laser pulse shaping might influence the expected non-adiabatic dissociation dynamics. Thus, this project considers a lot of interesting problems of femtochemistry.

Adiabatic states

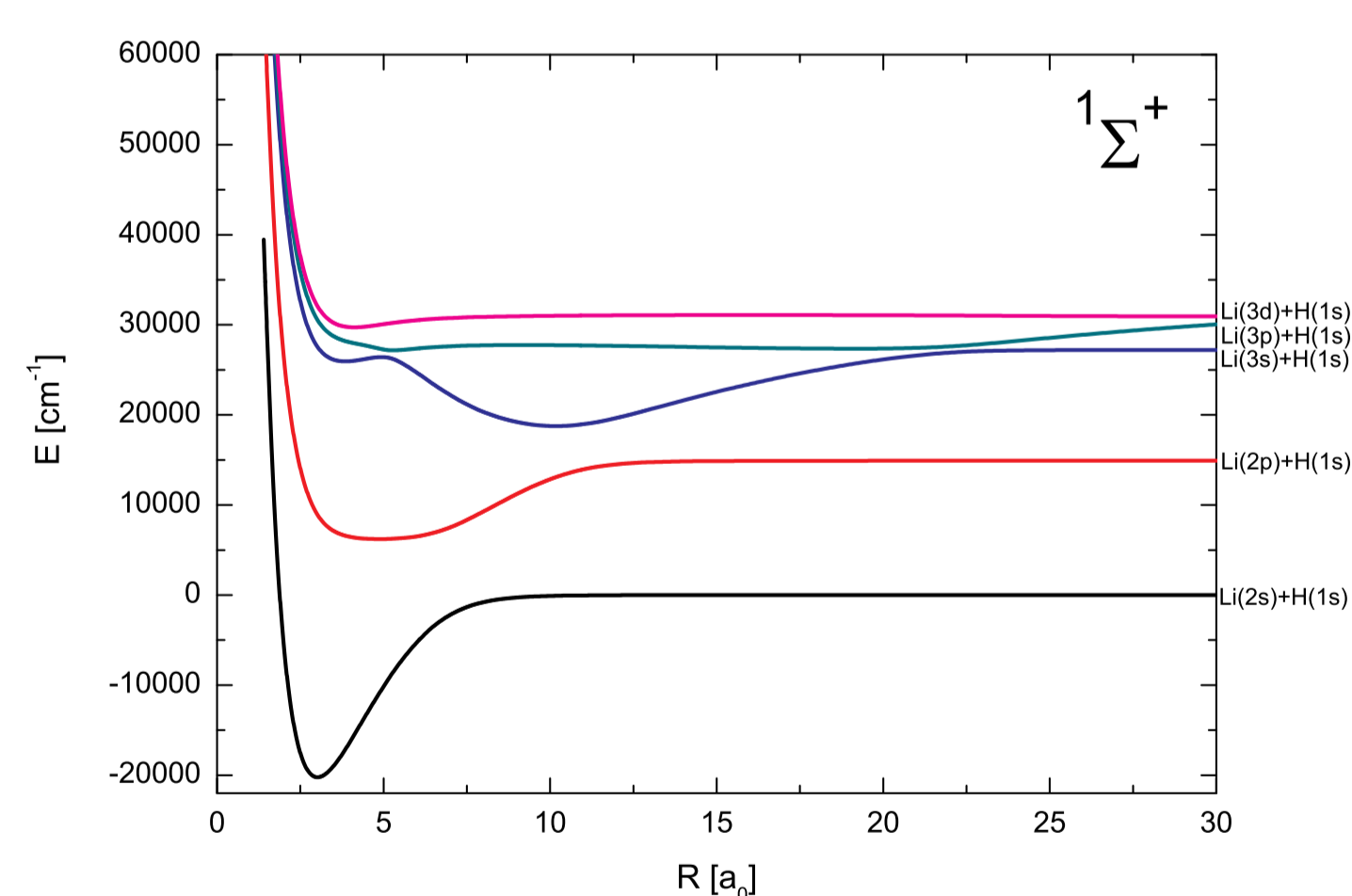


Figure 1. Adiabatic potential energy curves for the ground and 4 excited states in the symmetry $1^1\Sigma^+$ of the LiH molecule correlating to the Li(2s) + H(1s), Li(2p) + H(1s), Li(3s) + H(1s), Li(3p) + H(1s) and Li(3d) + H(1s) asymptotes.

Transition dipole moments

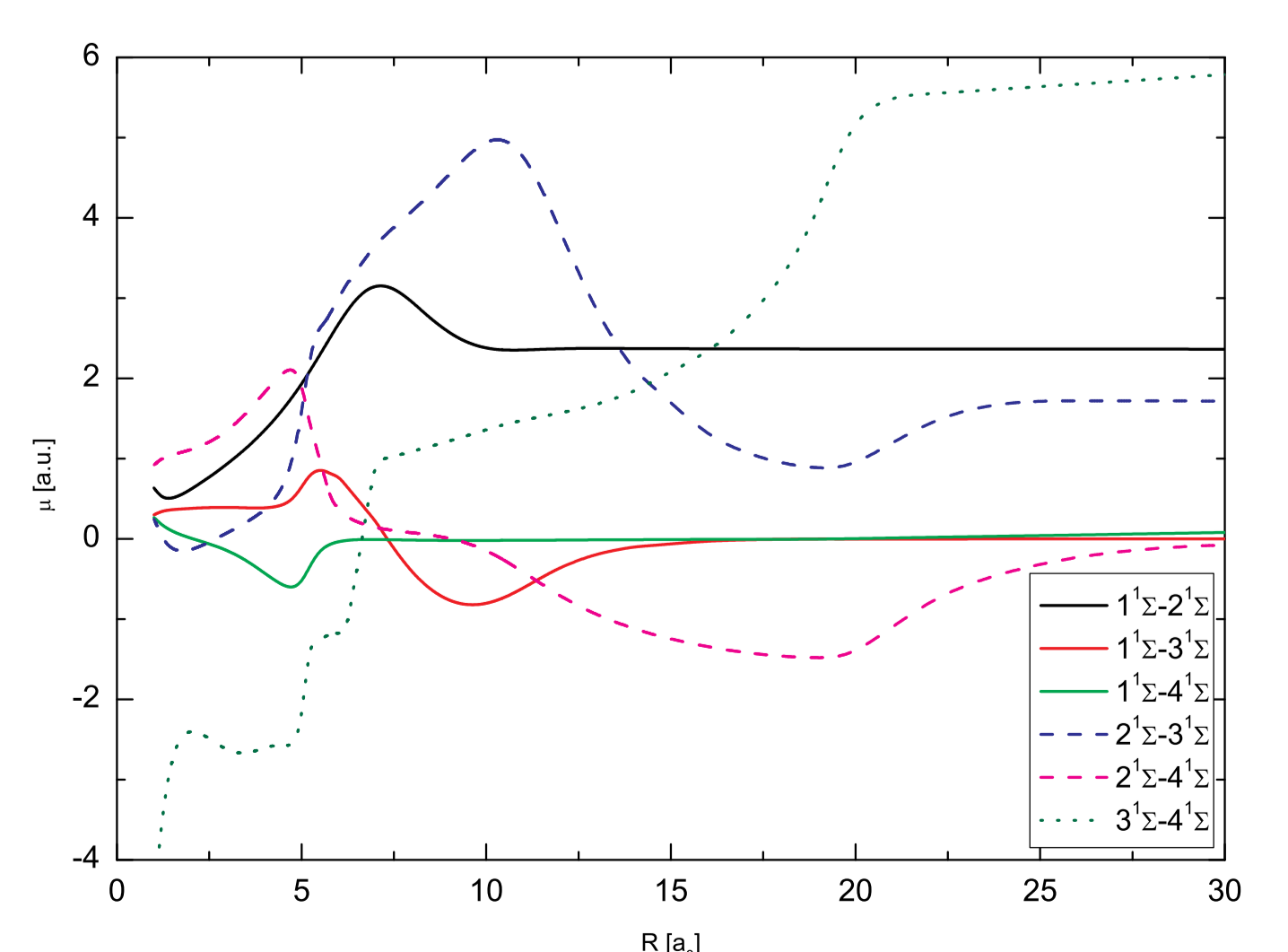


Figure 2. LiH adiabatic $1^1\Sigma^+$ transition dipole moments.

Non-adiabatic couplings

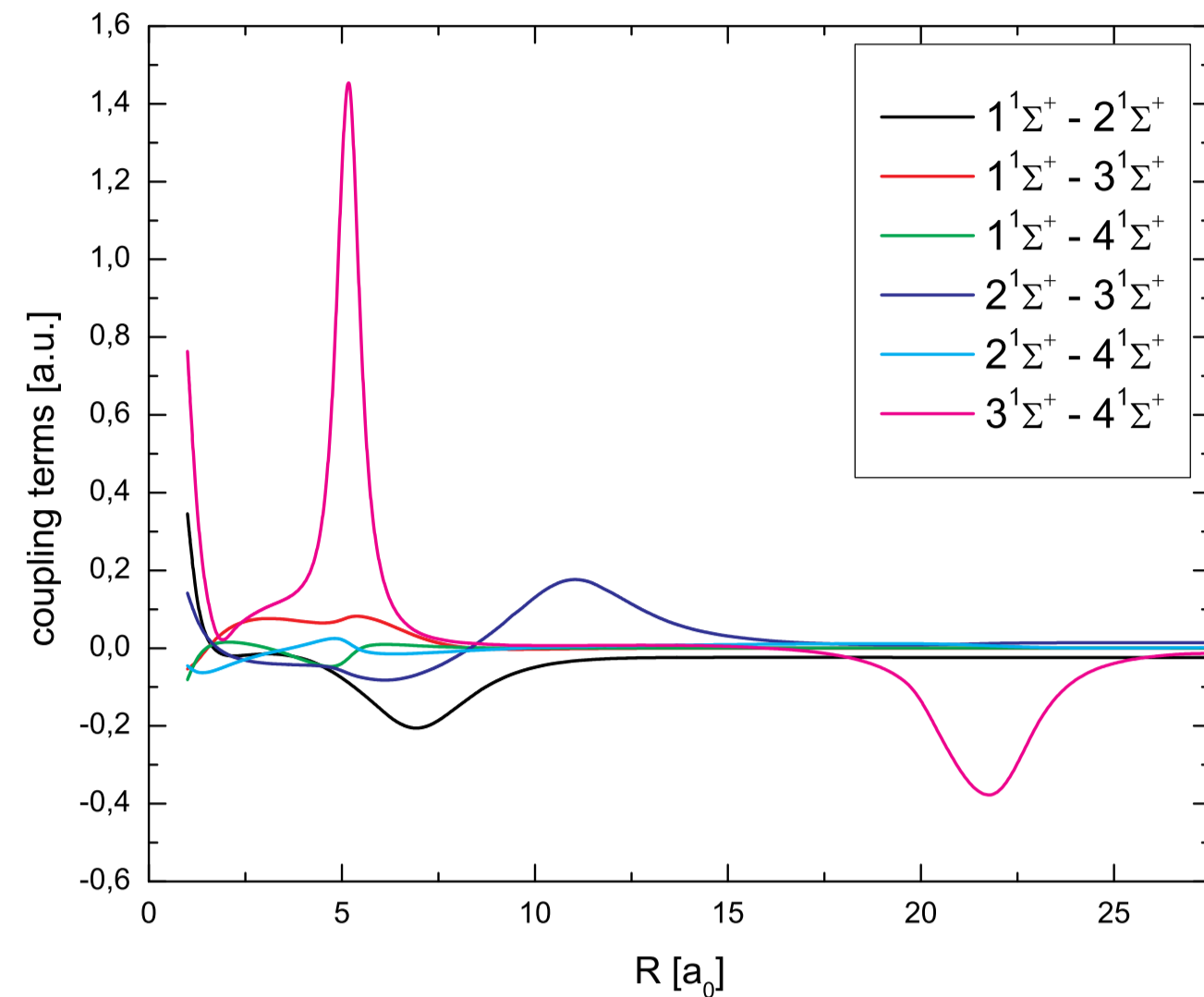


Figure 3. Non-adiabatic couplings between the concerned singlet sigma states of the LiH dimer.

Diabatic states

It is well known, that two adiabatic states interact in the vicinity of an avoided crossing. In the two-state model, the adiabatic potential matrix V with matrix elements $V_{ij} = V_i(R)\delta_{ij}$ can be transformed into the diabatic potential matrix U using transformation matrix P . The diagonal elements of U are the diabatic potentials and the off-diagonal elements correspond to the electronic couplings. The transformation is given by

$$U = P^{-1} \cdot V \cdot P, \quad (1)$$

where the unitary, orthogonal transformation matrix, in the two-state problem can be written as

$$P = \begin{pmatrix} \cos[\theta(R)] & -\sin[\theta(R)] \\ \sin[\theta(R)] & \cos[\theta(R)] \end{pmatrix}. \quad (2)$$

Asymptotically, far from avoided crossing, we assume that the adiabatic and diabatic potential energy curves are identical. Following Roos et al. [10], the two-state model can be extended for more states. In order to do that, we treat each crossing as a two-by-two transformation P_i , a rotation where only two states are included and the rest are left unchanged. If we take into consideration n crossings, the diabatic potential matrix U is given by

$$U = P_n^{-1} \cdot \dots \cdot P_2^{-1} \cdot P_1^{-1} \cdot V \cdot P_1 \cdot P_2 \cdot \dots \cdot P_n, \quad (3)$$

where the matrices P_i for rotations between states 1 and 2 take the form

$$P_i = \begin{pmatrix} \cos[\theta_i(R)] & -\sin[\theta_i(R)] & 0 & 0 & \dots \\ \sin[\theta_i(R)] & \cos[\theta_i(R)] & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (4)$$

The rotational angles are calculated by integration non-adiabatic couplings $C_{ij}^{(nl)}(R)$ connecting with considered adiabatic states [11]

$$\theta_i(R) = \int_R^\infty C_{ij}^{(nl)}(R') dR'. \quad (5)$$

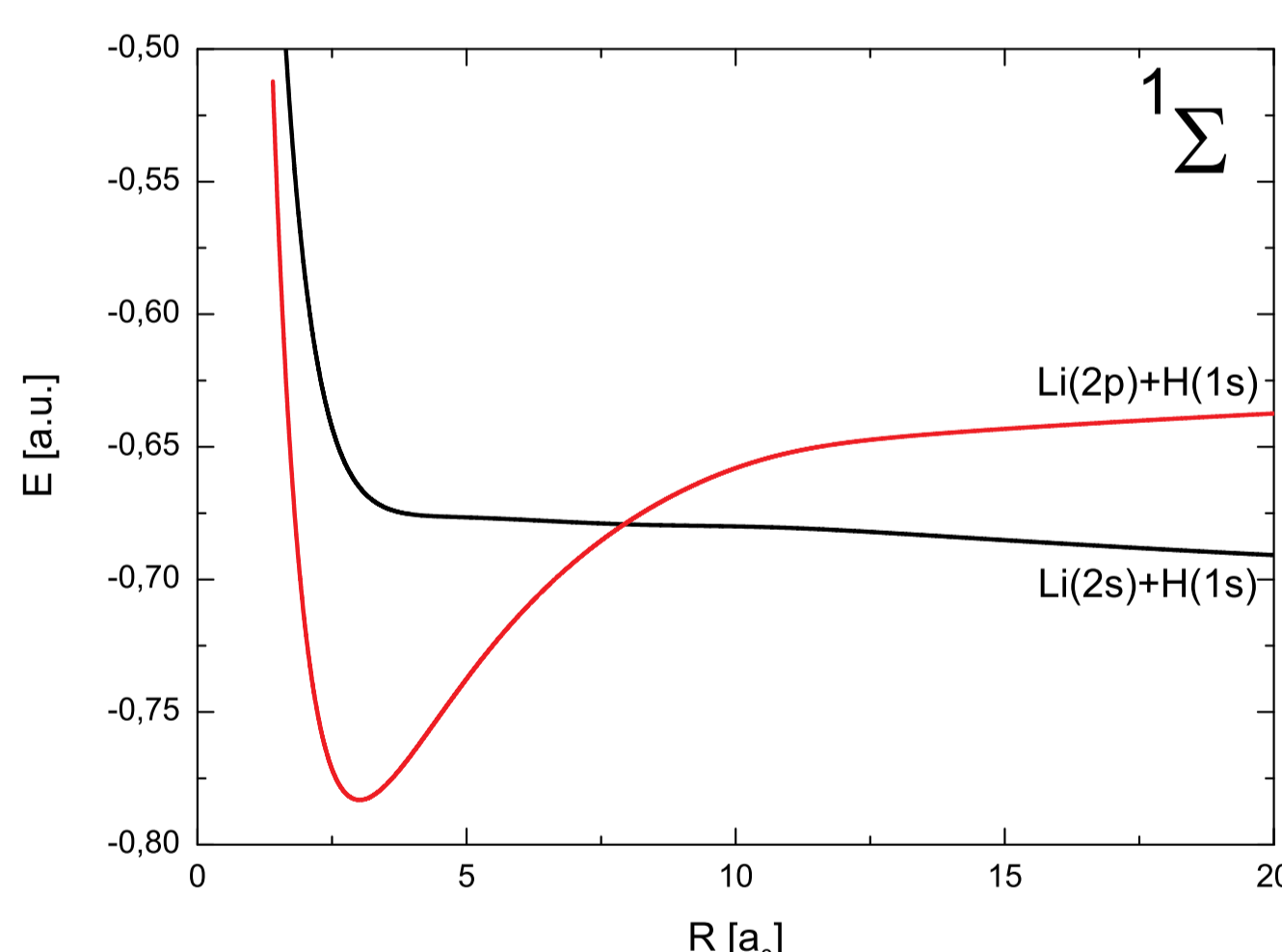


Figure 4. Diabatic potential energy curves in symmetry $1^1\Sigma$ for LiH molecule.

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Electronic predissociation

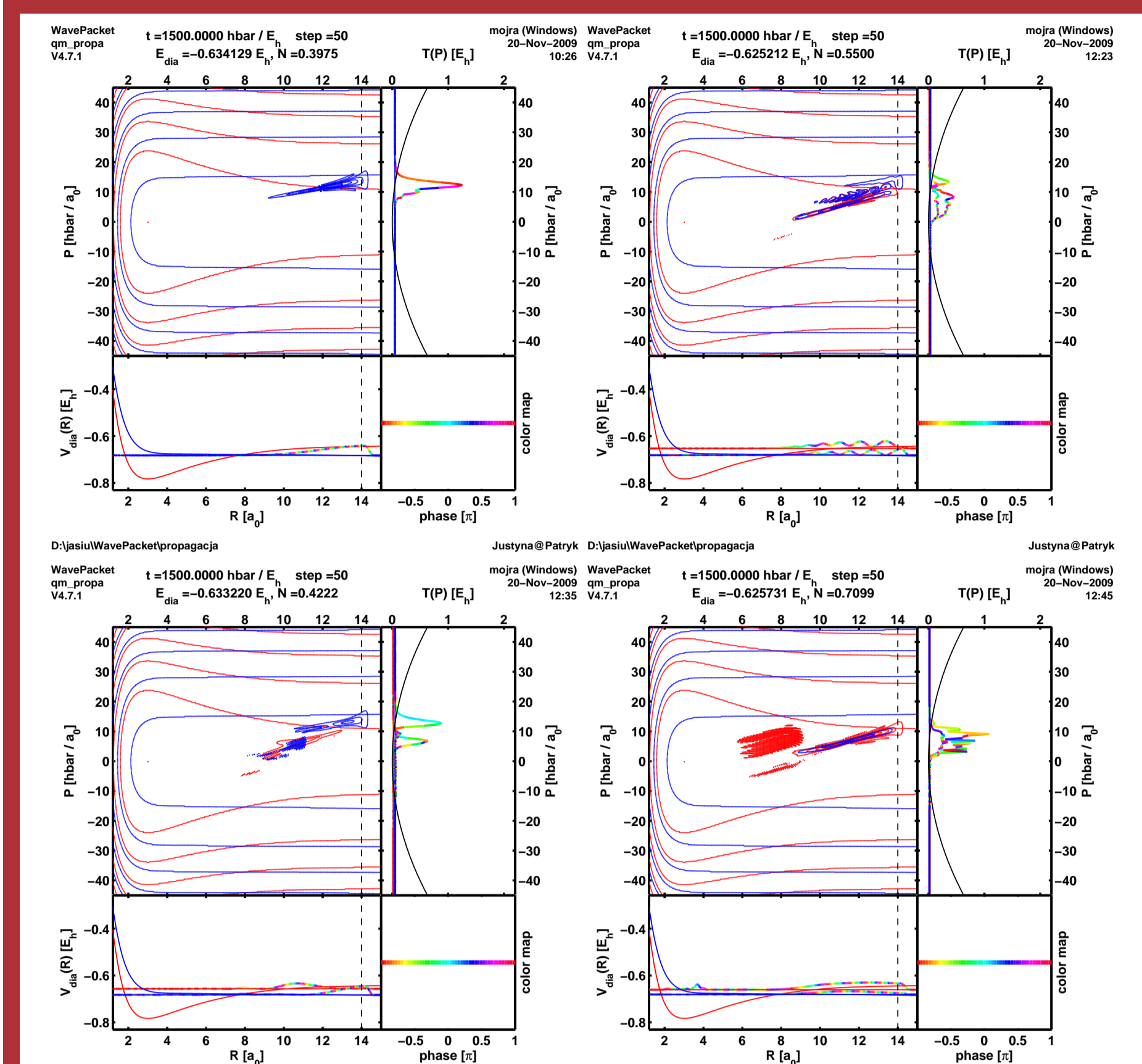


Figure 5. Propagation of the wavepacket on the two coupled diabatic states.

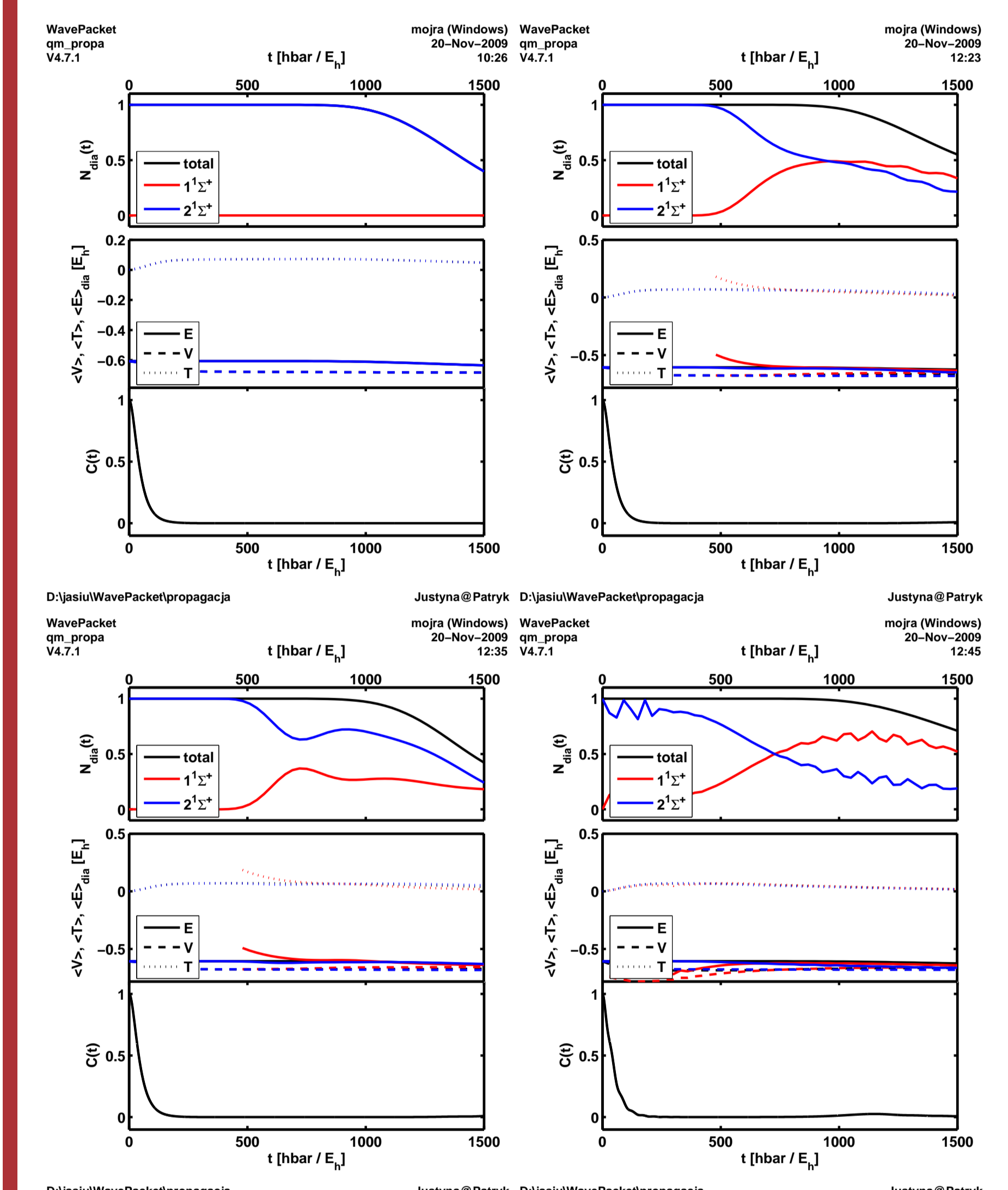


Figure 6. Change of the population in the system of the two coupled diabatic states.

Time-dependent method

We consider the time-dependent nuclear Schrödinger equation in the form

$$i\hbar \frac{\partial}{\partial t} \Phi_f(\vec{R}; t) = \hat{H}_{mod}(\vec{R}) \Phi_f(\vec{R}; t), \quad (6)$$

where $\Phi_f(\vec{R}; t)$ is a time-dependent wavepacket evolving on the adiabatic potential energy curve of the excited electronic state and $\hat{H}_{mod}(\vec{R})$ is the molecular hamiltonian. We can define the wavepacket as a coherent superposition of stationary states, each being multiplied by the time-evolution factor $e^{-iE_j^{mod}t/\hbar}$ [18]. The construction of the time-dependent wavepacket can be given as

$$\Phi_f(\vec{R}; t) = \int c_f(E_j^{mod}) e^{-iE_j^{mod}t/\hbar} \Psi_j^{mod}(\vec{R}) dE_j^{mod}, \quad (7)$$

where $\Psi_j^{mod}(\vec{R})$ is a solution of (6) because each stationary wavefunction $\Psi_j^{mod}(\vec{R})$ is an eigenfunction of $\hat{H}_{mod}(\vec{R})$ with the energy E_j^{mod} . In the next step we determine the initial condition in order to calculate coefficients $c_f(E_j^{mod})$ [1].

$$\Phi_f(\vec{R}; t=0) = \vec{\mu}_f^i(\vec{R}) \cdot \vec{e} \Psi_i^{mod}(\vec{R}). \quad (8)$$

The initial condition informs us that the wavepacket at its start in the upper electronic state equals the wavefunction of the parent molecule, $\Psi_i^{mod}(\vec{R})$, multiplied by the electronic transition dipole moment function $\vec{\mu}_f^i(\vec{R})$. Multiplying (7) from the left by $\Phi_f(\vec{R}; t=0)$ and integrating over all nuclear coordinates gives

$$S(t) \equiv \langle \Phi_f(\vec{R}; t=0) | \Phi_f(\vec{R}; t) \rangle = \frac{1}{2\pi\hbar} \int |c_f(E_j^{mod})|^2 e^{-iE_j^{mod}t/\hbar} dE_j^{mod}, \quad (9)$$

where $S(t)$ is the autocorrelation function. Following Schinke [1] yields the final expression for the total photodissociation cross section,

$$\sigma(E) = \frac{\rho\pi}{\hbar c \nu} E^{photon} \int_{-\infty}^{+\infty} e^{iE\nu t/\hbar} S(t) dt, \quad (10)$$

The formal solution of the time-dependent Schrödinger equation (1) is given by

$$\Phi_f(\vec{R}; t) = e^{-i\hat{H}_{mod}(\vec{R})t/\hbar} \Phi_f(\vec{R}; t=0), \quad (11)$$

where $\Phi_f(\vec{R}; t=0)$ is the wavepacket at the start of the propagation process for $t=0$ and operator

$$\hat{U}(t) = \exp\left[-\frac{i\hat{H}_{mod}(\vec{R})t}{\hbar}\right], \quad (12)$$

is the time-evolution operator [19, 20]. With (11) inserted into (9) and using the initial condition (8) the autocorrelation function becomes

$$S(t) = \langle \Phi_f(\vec{R}; t=0) | e^{-i\hat{H}_{mod}(\vec{R})t/\hbar} | \Phi_f(\vec{R}; t=0) \rangle = \left\langle \vec{\mu}_f^i(\vec{R}) \cdot \vec{e} \Psi_i^{mod}(\vec{R}) \left| e^{-i\hat{H}_{mod}(\vec{R})t/\hbar} \right| \vec{\mu}_f^i(\vec{R}) \cdot \vec{e} \Psi_i^{mod}(\vec{R}) \right\rangle. \quad (13)$$

In the beginning of the propagation, the wavepacket is constructed by the product of the nuclear wavefunction $\Psi_i^{mod}(\vec{R})$ and the element of the electronic transition dipole moment function in the direction of the polarization of the electric field $\vec{\mu}_f^i(\vec{R}) \cdot \vec{e}$. Using the split-operator method SPO, the time-evolution operator (12) is approximated by a symmetric splitting of the kinetic energy operator in the following way [19, 20]

$$\hat{U}(t) = \exp\left[-\frac{i\hat{H}_{mod}(\vec{R})t}{\hbar}\right] \approx \exp\left[-\frac{i\hat{T}_{mod}(\vec{R})t}{2\hbar}\right] \exp\left[-\frac{i\hat{V}_{mod}(\vec{R})t}{\hbar}\right] \exp\left[-\frac{i\hat{T}_{mod}(\vec{R})t}{2\hbar}\right]. \quad (14)$$

The propagation of the wavepacket involves the following steps: the Fourier transformation of the wavepacket to the momentum space, multiplying it by the free particle propagator $\exp(-i\hat{p}^2 t/4m\hbar)$ and transforming back to the coordinate space, where it is multiplied by $\exp(-iE_j^{mod} t/\hbar)$. The resulting function is Fourier transformed to the momentum space, multiplied by $\exp(-i\hat{p}^2 t/4m\hbar)$ and transformed again back to the coordinate space in order to complete one timestep propagation [19, 20].