

# Time-dependent description of electronic predissociation in the LiH molecule

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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.

## 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 adiabatic and diabatic 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 and Fig.2). The quality of our calculations were confirmed in our previous papers [8, 9]. Using adiabatic potentials and split diabatic representation method [10] 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<sub>0</sub>) and  $D_e$  (cm<sup>-1</sup>) for the ground and excited states of LiH molecule.

| State         | $R_e$          | $D_e$ |
|---------------|----------------|-------|
| $1^1\Sigma^+$ | Li(2s) + H(1s) |       |
| Exp.[11]      | 3.015          | 20285 |
| Theory[12]    | 3.003          | 20349 |
| Theory[13]    | 3.007          | 20174 |
| Present work  | 3.000          | 20325 |
| $2^1\Sigma^+$ | Li(2p) + H(1s) |       |
| Exp.[11]      | 4.906          | 8679  |
| Theory[12]    | 4.862          | 8687  |
| Theory[13]    | 4.847          | 8690  |
| Present work  | 4.800          | 8692  |
| $3^1\Sigma^+$ | Li(3s) + H(1s) |       |
| Exp.[14]      | -              | -     |
| Theory[12]    | 10.140         | 8469  |
|               | 3.821          | -     |
| Theory[13]    | 10.181         | 8453  |
|               | 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. 4). These results are also performed by means of the MOLPRO program package [7] and overall agreement with other theoretical data is very reasonable [12, 15, 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 potentials

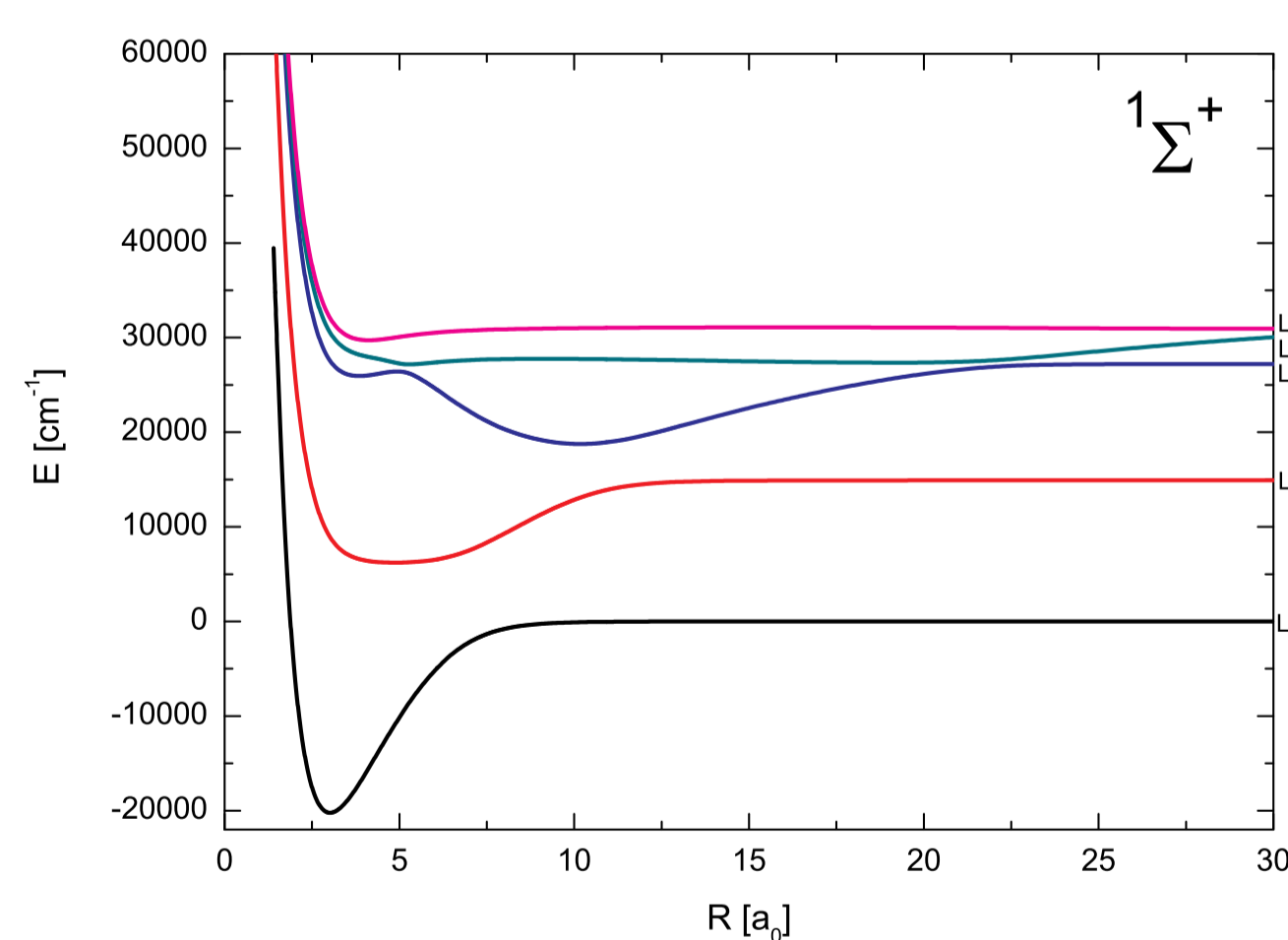


Figure 1. Adiabatic potential energy curves for the ground and 4 excited states in the symmetry  $1^1\Sigma^+$  of the LiH molecule correlating to the Li(2s) + H(1s), Li(2p) + H(1s), Li(3s) + H(1s), Li(3p) + H(1s) and Li(3d) + H(1s) asymptotes.

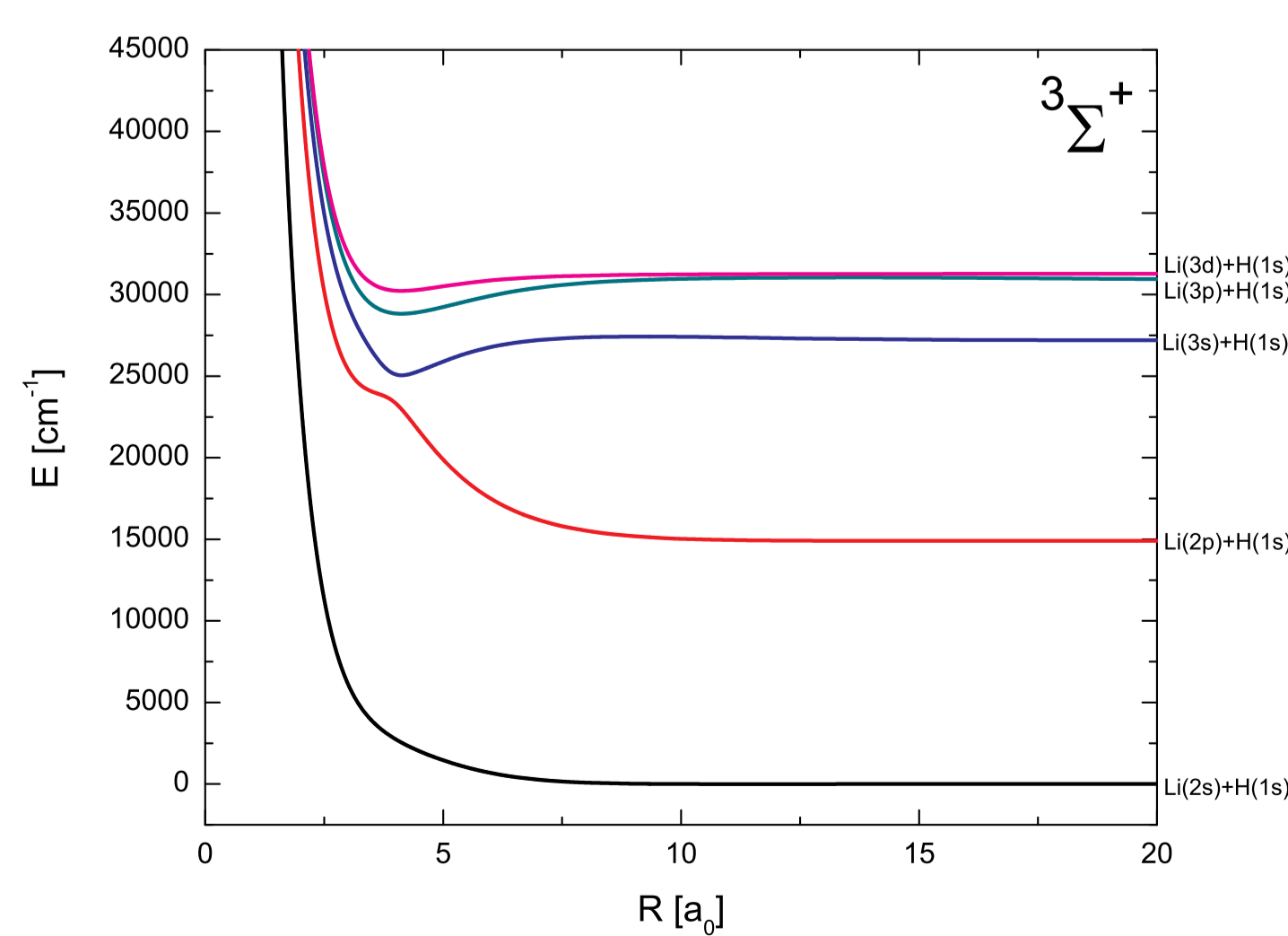


Figure 2. Adiabatic potential energy curves for 5 excited states in the symmetry  $3^1\Sigma^+$  of the LiH molecule correlating to the Li(2s) + H(1s), Li(2p) + H(1s), Li(3s) + H(1s), Li(3p) + H(1s) and Li(3d) + H(1s) asymptotes.

## Non-adiabatic couplings

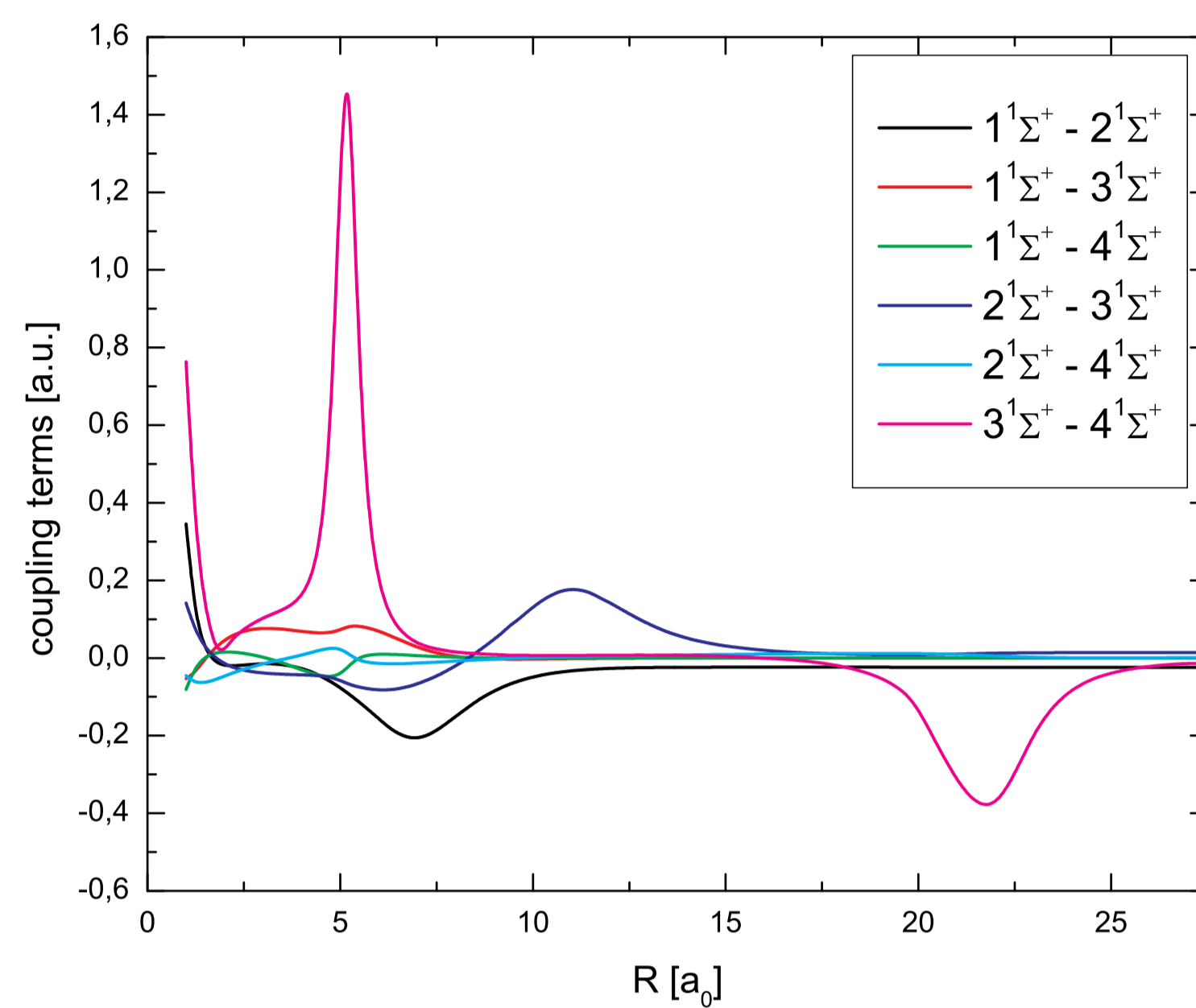


Figure 3. Non-adiabatic couplings between the concerned singlet sigma states of the LiH dimer.

## Transition dipole moments

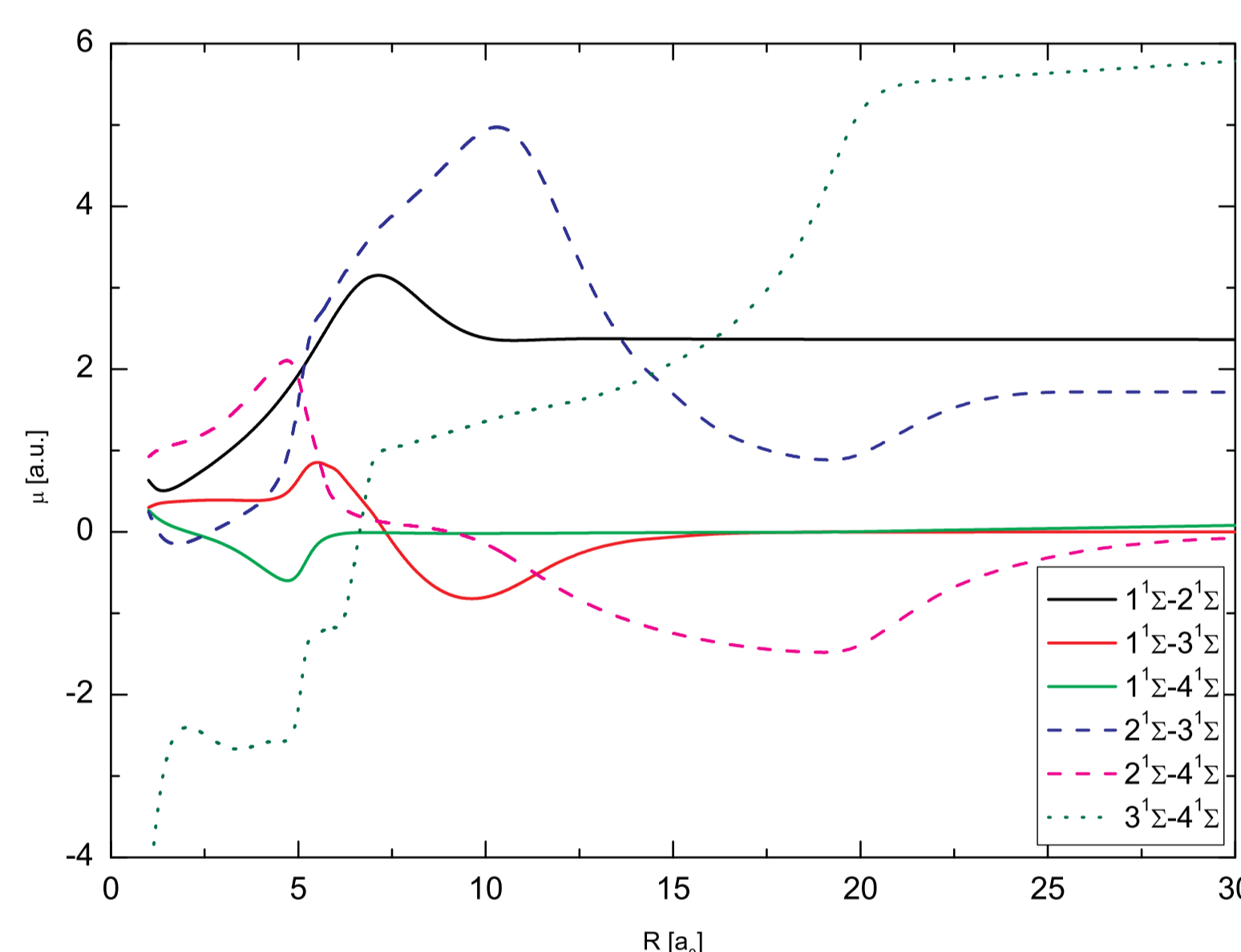


Figure 4. LiH adiabatic  $1^1\Sigma^+$  transition dipole moments

## Diabatic potentials

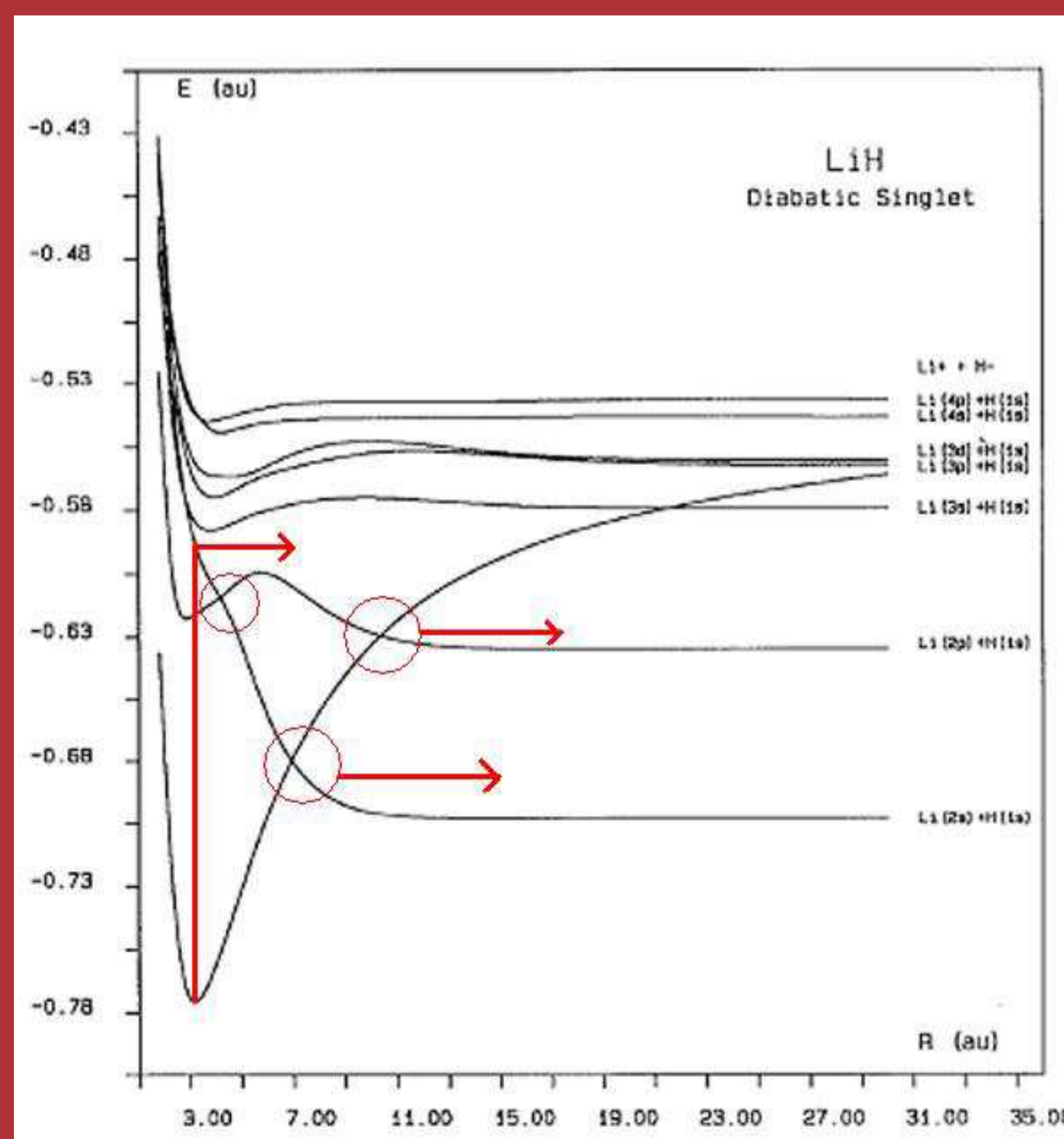


Figure 5. Diabatic potential energy curves for LiH molecule.

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## Photodissociation cross section

Below we present the procedure for calculations of photodissociation cross section in bound-free transitions ( $i$  - initial state,  $f$  - final state) [1]:

- the adiabatic potential energy curves  $E_i^a(R)$  and  $E_f^a(R)$  for the electronic states between which the transition occurs,
- the electronic transition dipole moment function  $\vec{\mu}_{if}^e(\vec{R})$ ,
- the nuclear wavefunctions  $\Psi_i^{\text{nucl}}(\vec{R})$  and  $\Psi_f^{\text{nucl}}(\vec{R})$ ,
- the photodissociation amplitude  $t_{fi} = \langle \Psi_f^{\text{nucl}}(\vec{R}) | \vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e} | \Psi_i^{\text{nucl}}(\vec{R}) \rangle$ .

Following Schinke [1] or Balint-Kurti [18] photodissociation cross section may be given by expression

$$\sigma(\omega) = \frac{\rho\pi}{\hbar\epsilon_0 c} E^{\text{photon}} |t_{fi}|^2, \quad (1)$$

where  $t_{fi}$  is the photodissociation amplitude, the factor  $\rho = (2\pi\hbar)^{-1}$  is a constant and  $E^{\text{photon}}$  is the energy of the photon, provided that the energy in the upper electronic state is always taken as  $E_f = E_i + E^{\text{photon}}$  [19].

## Time-dependent method

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

$$\hbar \frac{\partial}{\partial t} \Phi_f(\vec{R}; t) = \hat{H}_{\text{mol}}(\vec{R}) \Phi_f(\vec{R}; t), \quad (2)$$

where  $\Phi_f(\vec{R}; t)$  is a time-dependent wavepacket evolving on the adiabatic potential energy curve of the excited electronic state and  $\hat{H}_{\text{mol}}(\vec{R})$  is the molecular hamiltonian. We can define the wavepacket as a coherent superposition of stationary states, each being multiplied by the time-evolution factor  $e^{-iE_f^{\text{mol}} t/\hbar}$  [19, 20, 21]. The construction of the time-dependent wavepacket can be given as

$$\Phi_f(\vec{R}; t) = \int c_f(E_f^{\text{mol}}) e^{-iE_f^{\text{mol}} t/\hbar} \Psi_f^{\text{nucl}}(\vec{R}) dE_f^{\text{mol}}, \quad (3)$$

where  $\Phi_f(\vec{R}; t)$  is a solution of (2) because each stationary wavefunction  $\Psi_f^{\text{nucl}}(\vec{R})$  is an eigenfunction of  $\hat{H}_{\text{mol}}(\vec{R})$  with the energy  $E_f^{\text{mol}}$ . In the next step we determine the initial condition in order to calculate coefficients  $c_f(E_f^{\text{mol}})$  [1, 20],

$$\Phi_f(\vec{R}; t=0) = \vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e} \Psi_i^{\text{nucl}}(\vec{R}), \quad (4)$$

The initial condition informs us that the wavepacket at its start in the upper electronic state equals the wavefunction of the parent molecule,  $\Psi_i^{\text{nucl}}(\vec{R})$ , multiplied by the electronic transition dipole moment function  $\vec{\mu}_{if}^e(\vec{R})$ . Using the equation (3) and the initial condition (4) we obtain the relation

$$c_f(E_f^{\text{mol}}) = \frac{1}{2\pi\hbar} \langle \Psi_i^{\text{nucl}}(\vec{R}) | \vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e} | \Psi_i^{\text{nucl}}(\vec{R}) \rangle = \frac{1}{2\pi\hbar} t_{fi}(E_f^{\text{mol}}), \quad (5)$$

where the photodissociation amplitude  $t_{fi}(E_f^{\text{mol}})$  is defined above. Multiplying (3) from the left by  $\Phi_f(\vec{R}; t=0)$  and integrating over all nuclear coordinates gives

$$S(t) = \langle \Phi_f(\vec{R}; t=0) | \Phi_f(\vec{R}; t) \rangle = \frac{1}{2\pi\hbar} \int |t_{fi}(E_f^{\text{mol}})|^2 e^{-iE_f^{\text{mol}} t/\hbar} dE_f^{\text{mol}}, \quad (6)$$

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

$$\sigma(E) = \frac{\rho\pi}{\hbar\epsilon_0 c} E^{\text{photon}} \int_{-\infty}^{\infty} e^{iE_f^{\text{mol}} t/\hbar} S(t) dt, \quad (7)$$

The formal solution of the time-dependent Schrödinger equation (2) is given by

$$\Phi_f(\vec{R}; t) = e^{-\frac{i}{\hbar} \hat{H}_{\text{mol}}(\vec{R}) t} \Phi_f(\vec{R}; t=0), \quad (8)$$

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

$$\hat{U}(t) = \exp\left[-\frac{i}{\hbar} \hat{H}_{\text{mol}}(\vec{R}) t\right], \quad (9)$$

is the time-evolution operator [21, 22, 23]. With (8) inserted into (6) and using the initial condition (4) the autocorrelation function becomes

$$S(t) = \langle \Phi_f(\vec{R}; t=0) | e^{-\frac{i}{\hbar} \hat{H}_{\text{mol}}(\vec{R}) t} | \Phi_f(\vec{R}; t=0) \rangle = \langle \vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e} \Psi_i^{\text{nucl}}(\vec{R}) | e^{-\frac{i}{\hbar} \hat{H}_{\text{mol}}(\vec{R}) t} | \vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e} \Psi_i^{\text{nucl}}(\vec{R}) \rangle. \quad (10)$$

In the beginning of the propagation, the wavepacket is constructed by the product of the nuclear wavefunction  $\Psi_i^{\text{nucl}}(\vec{R})$  and the element of the electronic transition dipole moment function in the direction of the polarization of the electric field  $\vec{\mu}_{if}^e(\vec{R}) \cdot \vec{e}$ . Using the split-operator method SPO, the time-evolution operator (9) is approximated by a symmetric splitting of the kinetic energy operator in the following way [20, 22, 23]

$$\hat{U}(t) = \exp\left[-\frac{i}{\hbar} \hat{T}_{\text{mol}}(\vec{R}) t\right] \approx \exp\left[-\frac{i}{2\hbar} \hat{T}_{\text{mol}}(\vec{R}) t\right] \exp\left[-\frac{i}{\hbar} \hat{V}_{\text{mol}}(\vec{R}) t\right] \exp\left[-\frac{i}{2\hbar} \hat{T}_{\text{mol}}(\vec{R}) t\right]. \quad (11)$$

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  $\exp(-i p^2 t/4 m \hbar)$  and transforming back to the coordinate space, where it is multiplied by  $\exp(-i E_f^{\text{mol}}(R) t/\hbar)$ . The resulting function is Fourier transformed to the momentum space, multiplied by  $\exp(-i p^2 t/4 m \hbar)$  and transformed again back to the coordinate space in order to complete one timestep propagation [20, 22, 23].

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