

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

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Introduction

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 [1, 2]. 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 diatomic molecule we use multiconfigurational self-consistent field/complete active space self-consistent field (MCSCF/CASSCF) method and multi-reference configuration interaction (MRCI) method. All calculations are performed by means of the MOLPRO program package [3]. Using these computational methods we obtained adiabatic potential energy curves for singlet and triplet sigma, pi and delta 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. The quality of our calculations can be confirmed by the comparison of experimental and theoretical asymptotic energies for different electronic states, which is shown in Table 1. Obtained by us asymptotic energies for ground and excited states are in very good agreement with experimental and other theoretical values.

Table 1. The comparison of asymptotic energies with other theoretical and experimental results. Energies are shown in cm⁻¹ units.

Atomic asymptotes	Experiment Moore [4]	Theory Boutalib [5]	Theory Gadea [6]	Theory Jasik
Li(2p)+H(1s)	14904	14905	14898	14904
Li(3s)+H(1s)	27206	27210	27201	27202
Li(3p)+H(1s)	30925	30926	30920	30921
Li(3d)+H(1s)	31283	31289	31278	31276

Equilibrium positions R_e and depths of the potential wells D_e are in very good agreement with other theoretical and experimental results (Table 2) and it confirms high quality of our calculations.

Table 2. Spectroscopic parameters R_e [a₀] and D_e [cm⁻¹] for the ground and excited states of LiH molecule.

State	Dissociation	Author	R_e	D_e
$1^1\Sigma^+$	Li(2s)+H(1s)	Jasik 2009 (theory)	3.000	20325
		Boutalib 1992 (theory) [5]	3.007	20174
		Gadea 2006 (theory) [6]	3.003	20349
		Stwalley 1993 (exp.) [7]	3.015	20285
		Aymar 2009 (theory) [8]	3.002	20167
Dolg 1996 (theory) [9]	3.000	20123		
$2^1\Sigma^+$	Li(2p)+H(1s)	Jasik 2009 (theory)	4.800	8692
		Boutalib 1992 (theory) [5]	4.847	8690
		Gadea 2006 (theory) [6]	4.862	8687
		Stwalley 1993 (exp.) [7]	4.906	8679
		Aymar 2009 (theory) [8]	4.820	8698
Vidal 1982 (theory) [10]	4.910	8686		
$1^1\Pi$	Li(2p)+H(1s)	Jasik 2011 (theory)	4.496	286
		Boutalib 1992 (theory) [5]	4.524	258
		Aymar 2009 (theory) [8]	4.520	251
		Velasco 1957 (exp.) [11]	-	284
		Vidal 1984 (theory) [12]	4.500	289

In Fig. 1 we present selected adiabatic potentials. Our main aim is the description of the two kinds of photodissociation processes in the LiH molecule. First is the rotational predissociation in the system of adiabatic $1^1\Pi$ - $1^1\Sigma^+$ potentials and second one is the two-channel electronic predissociation in the system of four the lowest lying adiabatic and diabatic potential energy curves for singlet sigma states. In order to present in this process the nuclear wave packet dynamics induced by femtosecond laser pulses, we also calculated non-adiabatic couplings between considered states and transition dipole moment functions (Fig. 2).

Adiabatic states

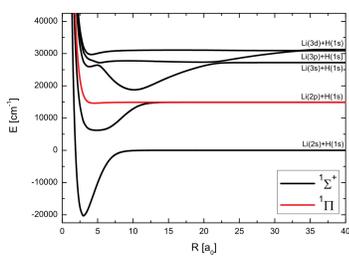


Fig. 1. Adiabatic potential energy curves for the first five $1^1\Sigma^+$ states and $1^1\Pi$ state of the LiH molecule.

Transition dipole moments

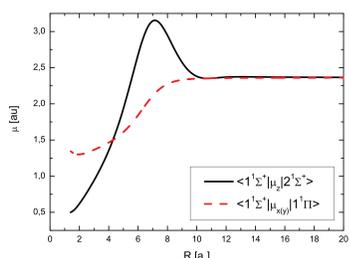


Fig. 3. The electronic transition dipole moment functions for $2^1\Sigma^+ - 1^1\Sigma^+$ and $1^1\Pi - 1^1\Sigma^+$ transitions.

Non-adiabatic couplings and diabatic states

Using calculated adiabatic potentials, non-adiabatic couplings between them and one of the available diabaticization procedures [13, 14], we will obtain diabatic potential energy curves. We have chosen a split diabatic representation method [13], which generates the diabatic potentials with the maximal physical content. Using the adiabatic representation of the molecular wave function in the form

$$\Psi^{mod}(\vec{r}, R) = \sum_i \Psi_i^{mod}(\vec{r}, R) = \sum_i \Psi_i^a(\vec{r}, R) \Psi_i^{osc}(R), \quad (1)$$

the molecular Schrödinger equation can be written in the following matrix form

$$\left[-\frac{1}{2\mu} \left(\frac{d}{dR} + \mathbf{P} \right)^2 + \mathbf{E}_d^a \right] \Psi^{osc} = E^{mod} \Psi^{osc}, \quad (2)$$

where \mathbf{I} is the unit matrix, \mathbf{E}_d^a is the diagonal matrix of adiabatic potentials and Ψ^{osc} is the vector of radial channel functions. The non-adiabatic coupling matrix \mathbf{P} , representing the residual coupling between the fast and slow coordinates, such as the electronic and nuclear coordinates in molecules respectively, is given by

$$\mathbf{P} = P_{ij}(R) = \left\langle \Psi_i^a(\vec{r}, R) \left| \frac{d}{dR} \right| \Psi_j^a(\vec{r}, R) \right\rangle. \quad (3)$$

The strict diabatic representation can be defined from the unitary transformation that diagonalizes the kinetic energy in the molecular Schrödinger equation

$$\frac{d}{dR} \mathbf{C} = -\mathbf{P} \mathbf{C}. \quad (4)$$

The radial equations in the strict diabatic representation are

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + \mathbf{E}_d^d \right] \Psi_D^{osc} = E^{mod} \Psi_D^{osc}, \quad (5)$$

with the diabatic radial functions and diabatic potential matrix

$$\Psi_D^{osc} = \mathbf{C}^T \Psi^{osc}, \quad \mathbf{E}_d^d = \mathbf{C}^T \mathbf{E}_d^a \mathbf{C}. \quad (6)$$

In order to calculate diabatic potential energy curves, the diabaticization procedure requires a solution of the first-order differential matrix equation, which is realized by the Crank-Nicolson propagation method [13], which can be written in the following way

$$\mathbf{C}(R + \Delta R) = e^{-\mathbf{P} \Delta R} \mathbf{C}(R). \quad (7)$$

A transformation propagator, akin to the Cayley-Hamilton time evolution operator, is employed to obtain the diabatic states while preserving unitarity

$$e^{-\mathbf{P} \Delta R} = \frac{\mathbf{I} - \mathbf{P} \frac{\Delta R}{2}}{\mathbf{I} + \mathbf{P} \frac{\Delta R}{2}}. \quad (8)$$

Finally we obtain the Crank-Nicolson-like equation for the transformation matrix propagation

$$\left(\mathbf{I} + \mathbf{P} \frac{\Delta R}{2} \right) \mathbf{C}(R + \Delta R) = \left(\mathbf{I} - \mathbf{P} \frac{\Delta R}{2} \right) \mathbf{C}(R). \quad (9)$$

Using this procedure we are able to obtain the transformation matrix $\mathbf{C}(R)$ and next the set of diabatic potentials E_D^d . In Fig. 3 we present two pairs of adiabatic and diabatic potential energy curves for the ground molecular state $1^1\Sigma^+$ and first excited state $2^1\Sigma^+$, which correlate to Li(2s)+H(1s) and Li(2p)+H(1s) atomic asymptotes, respectively.

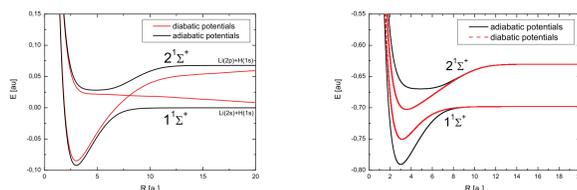


Fig. 3. Adiabatic and diabatic potentials for the ground molecular state $1^1\Sigma^+$ and first excited state $2^1\Sigma^+$. (on the right panel) Potentials calculated with radial couplings scaled to 0 in the long distances between atoms.

Next figure (Fig. 4) is the complement of the previous one, because presents adiabatic and diabatic couplings between considered states of the LiH diatomic molecule. We are able to find a peaks of the adiabatic coupling in this figure, which represents the position of avoided crossing between adiabatic potentials. The coupling seems to be strong in this region, but the distance between considered electronic states is quite large, so these states don't repel each other very strong. Using described above diabaticization procedure we are also able to calculate the diabatic couplings. These one shown in the Fig. 4 are very smooth and slowly varying through the crossing region. This behaviour is characteristic for the diabatic couplings.

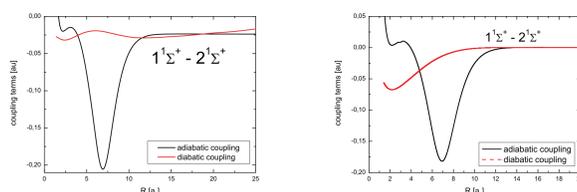


Fig. 4. Adiabatic and diabatic couplings between the ground molecular state $1^1\Sigma^+$ and first excited state $2^1\Sigma^+$.

Franck-Condon factors

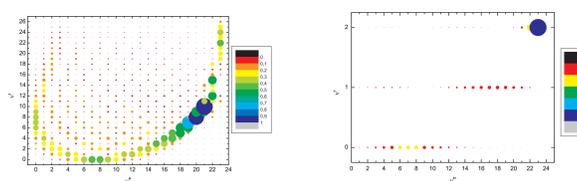


Fig. 5. Franck-Condon factors of the $1^1\Sigma^+$ ground-state levels with all $2^1\Sigma^+$ and $1^1\Pi$ excited-states levels.

Photodissociation

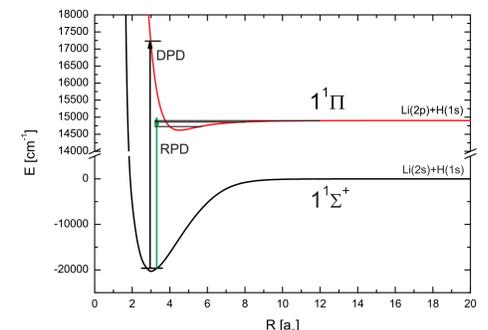


Fig. 6. Two possible photodissociation process in the $1^1\Pi - 1^1\Sigma^+$ band system. DPD (black arrow) is the direct photodissociation reaction and RPD (green arrow) is the rotational predissociation. DPD laser parameters: duration of the pulse 40 [fs], the amplitude 0.6 [TW] and the frequency 4.57 [eV].

Table 3. Vibration-rotation levels of the $1^1\Pi$ excited state. Energies are shown in cm⁻¹ units.

J	$\nu = 0$	$\nu = 1$	$\nu = 2$
0	14727.65	14857.43	14900.25
1	14733.44	14861.01	14901.62
2	14744.94	14868.01	14903.92
3	14761.98	14878.10	14907.21
4	14784.31	14890.73	
5	14811.55	14904.83	
6	14843.18	14918.43	
7	14878.40		
8	14915.85		
9	14952.54		

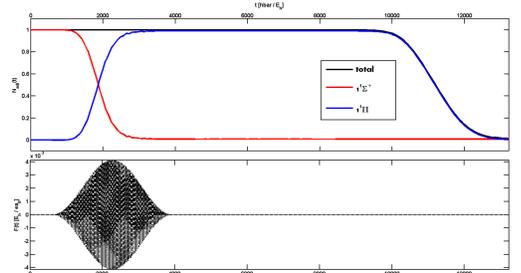


Fig. 7. The change of the population in the direct photodissociation process (transition above the dissociation limit).

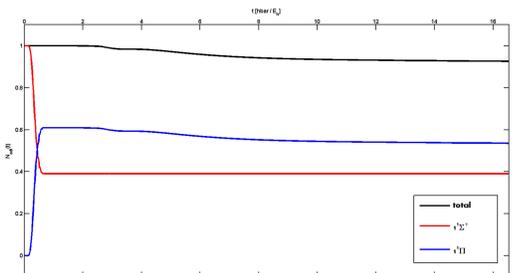


Fig. 8. The change of the population in the rotational predissociation process (transition to the $\nu' = 0, J' = 8$ vibration-rotation level of the $1^1\Pi$ excited state).

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