Short thesis for the degree of doctor of philosophy (PhD)

Light-induced non-adiabatic properties in molecular systems

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Készült a

Debreceni Egyetem

Fizikai Tudományok Doktori Iskolában

I. Introduction

During my research, I studied light-induced non-adiabatic properties in diatomics and polyatomics using theoretical calculations.

The Born-Oppenheimer approximation (BOA) is one of the fundamental methods for investigating atomic and molecular physics. This approximation is based on separating nuclear and electronic motions because the heavy nucleus moves much faster than the light electrons. Although this approximation usually works well and gives reasonable results in molecular dynamical processes, it does lose its validity near degeneracy points between molecules' potential energy surfaces. Such degeneracies between potential energy surfaces give rise to non-adiabatic phenomena in molecules. In non-adiabatic processes, the potential energy surfaces of molecular systems might intersect or approach each other, which are referred to as conical intersections (CIs) and avoided crossings (ACs), respectively. Non-adiabatic effects [P1, P2] play an essential role in investigating the properties of molecules, particularly molecular dynamics and spectroscopy, energy transfer, or topological properties. A large magnitude of non-adiabatic coupling terms (NACTs) near degeneracies (CIs or ACs) allows wave functions to propagate from one adiabatic potential energy surface to another. In such cases, the large magnitude of NACTs can create effective funnels for ultra-fast energy exchange between the electrons and nuclei in molecules.

It has been known that a molecule must hold at least two independent degrees of freedom (DOFs) to form a CI. CIs (occurring in nature) can never be formed in diatomic molecules because of one DOF in diatomics, but only AC can emerge. However,it is possible to get light-induced avoided crossings (LIACs) and light-induced conical intersections (LICIs) by employing external fields like intense laser pulses or optical cavities, even in diatomic molecules. External fields can provide the rotational DOF by rotating the molecule around the polarization direction of the

system's TDMs. Apart from natural non-adiabatic processes, the parameters of light-induced CIs and ACs can be easily modified in light-induced non-adiabatic processes by altering the characteristics of external fields. Therefore, light-induced non-adiabatic dynamics of molecules can be controlled by the external classical or quantized fields.

Light-induced non-adiabatic phenomena can be studied in the presence of light-matter interaction between a molecular system and an applied external field. The non-adiabatic processes can provide the source for a wide-range of interesting phenomena in nature.

II. Objectives

During my research, I investigated light-induced non-adiabatic properties of the NaH and H_2CO molecules. Extensive numerical theoretical investigations have been conducted using an external field to explore the light-induced non-adiabatic characteristics of molecular systems.

Dissociation dynamics in molecules can be essential in energy transfer, molecular spectroscopy and chemical reactions. One of my main goals was to investigate the light-induced dissociation of NaH, together with the fragment kinetic energy release spectra and angular distributions in the presence of LICIs and LIAC formed by an electric field. Another assignment in this research was to study the effect of this system's PDM on dissociation processes.

I studied light-induced degeneracies in the H_2CO molecule by evaluating the non-adiabatic coupling terms and geometric phases in the vicinity of LICI created by a confined cavity quantum light.

III. Results

Below, I provide a summary of my results on the topic of light-induced non-adiabatic properties in molecular systems.

1. I carried out ab initio calculations of electronic orbitals to obtain the potential energy surfaces (PESs) and dipole moments (permanent dipole moments (PDMs) and transition dipole moments (TDMs)) for the NaH system by using the multi-reference configuration interaction (MRCI) at the high-level basis set in the MOLPRO package.

   I prepared the input/output files and carried out various calculations using the multi-configuration time-dependent Hartree (MCTDH) to obtain the dissociation probabilities of individual electronic states. The computational simulations have been performed in the 1D and 2D cases.

   While investigating the dissociation dynamics of NaH, the pump and probe laser pulses that create two LICIs and one LIAC have been applied. These two pulses were utilized in our simulations as follows: first, the pump pulse was applied into the system to transfer some amount of the ground electronic state population to the $V_A(R)$ and $V_B(R)$ states; in the further step, the probe was placed with different starting times (to obtain various delay times) to transfer some amount of the first excited electronic state population to the other two electronic states.

   I studied the influence of the LICIs/LIAC and molecular motion on the dissociation dynamics in the presence of the pump and probe lasers.

   Furthermore, I carried out numerical calculations of the fragment kinetic energy release spectra (KER) and angular distributions of individual electronic states as a function of the delay time using the MCTDH method in order to further analyze the dissociation

dynamics of the NaH molecule. The numerical calculations have been done in 1D and 2D.

In order to study the impact of the system's PDM on dissociation, I performed some calculations in the 1D and 2D frameworks with and without PDM [**P1**].

2. I studied the topological features of light-induced degeneracies of the system in the presence of LICI between the shifted ground and the first excited states created by the single cavity mode.

   Molecular electronic structure calculations have been done for the H_2CO system to acquire the PESs, PDMs and TDMs. The GSL package is used to obtain the interpolation data in the high-level spline type.

   The diagonalization method is used to obtain the polaritonic or adiabatic electronic states in numerical calculations.

   The NACTs between the two (upper and lower) adiabatic surfaces have been calculated to study the geometric features of the system around the point of the polaritonic LICI. Also, the absolute values of the NACTs have been calculated to investigate the effect of polaritonic LICI.

   In addition, I studied the Berry phase for the two various closed paths; one encompassed the point of LICI, while the second did not [**P2**].

Publication list

The short Thesis is based on these publications.

P1. Otabek Umarov, András Csehi, Péter Badankó, Gábor J. Halász, and Ágnes Vibók. Light-induced photodissociation on the lowest three electronic states of NaH molecule. *Physical Chemistry Chemical Physics*, 26,7211, 2024.

P2. Péter Badankó, Otabek Umarov, Csaba Fábri, Gábor J. Halász, and Ágnes Vibók. Topological aspects of cavity-induced degeneracies in polyatomic molecules. *International Journal of Quantum Chemistry*, 122(8):e26750, 2022.

The publications that are NOT included in the Thesis.

P3. Dilfuza Umarova, Otabek Umarov, Attila Tóth and András Csehi. Spectral evidence of vibronic Rabi oscillations in the resonance-enhanced photodissociation of MgH^+. *Physical Review A*, 2024.

Talks

1. O. Umarov: Topological aspects of light-induced degeneracies in polyatomic molecules, "TSRC - Quantum Frontiers in Molecular Science", $6^{th} - 10^{st}$ June 2022, Telluride, USA

2. O. Umarov: Topological aspects of light-induced degeneracies in polyatomic molecules, international scientific conference, 20^{st} May 2023, Jizzakh polytechnical institute, Uzbekistan

3. O. Umarov: Light-induced photodissociation dynamics in NaH, Seminar, 3^{rd} May 2024, Department of Optics and Spectroscopy, Samarkand State University, Uzbekistan

Posters

1. P. Badankó, O. Umarov, C. Fábri, T. Szidarovszky, Á. Vibók, G. J. Halász: Topological aspects of quantum light-induced conical intersections, "Local vs Collective Interactions in Polaritonic Chemistry, CECAM-FR-GSO", $22^{nd} - 24^{st}$ June 2022, University of Bordeaux, France.

2. P. Badankó, O. Umarov, C. Fábri, T. Szidarovszky, Á. Vibók, G. J. Halász: Topological aspects of quantum light-induced conical intersections, "ECAMP14, 14^{th} European Conference on Atoms Molecules and Photons", June 27 - July 1, 2022, Vilnius, Lithuania.

3. O. Umarov, A. Csehi, P. Badankó, G. J. Halász and Á. Vibók: Light-induced photodissociation on the lowest three electronic states of NaH molecule, Attochem conference, February 28 - March 1, 2024, University of La Laguna, Tenerife, Canary Islands (Spain)

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Candidate: Otabek Umarov
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List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. **Umarov, O.**, Csehi, A., Badankó, P., Halász, G. J., Vibók, Á.: Light-induced photodissociation in the lowest three electronic states of the NaH molecule.
   Phys. Chem. Chem. Phys. 26, 7211-7223, 2024. ISSN: 1463-9076.
   DOI: http://dx.doi.org/10.1039/D3CP05402K
   IF: 2.9 (2023)
2. Badankó, P., **Umarov, O.**, Fábri, C., Halász, G. J., Vibók, Á.: Topological aspects of cavity-induced degeneracies in polyatomic molecules.
   Int. J. Quantum Chem. 122 (8), 1-8, 2022. ISSN: 0020-7608.
   DOI: http://dx.doi.org/10.1002/qua.26750
   IF: 2.2

List of other publications

Foreign language scientific articles in international journals (1)

3. Umarova, D., **Umarov, O.**, Tóth, A., Csehi, A.: Spectral evidence of vibronic Rabi oscillations in the resonance-enhanced photodissociation of MgH+.
   Phys. Rev. A. [Epub ahead of print] (-), 1-13, 2024. ISSN: 1050-2947.
   IF: 2.6 (2023)

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The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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A PhD értekezés alapjául szolgáló közlemények

Idegen nyelvű tudományos közlemények külföldi folyóiratban (2)

1. **Umarov, O.**, Csehi, A., Badankó, P., Halász, G. J., Vibók, Á.: Light-induced photodissociation in the lowest three electronic states of the NaH molecule.
   Phys. Chem. Chem. Phys. 26, 7211-7223, 2024. ISSN: 1463-9076.
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   Int. J. Quantum Chem. 122 (8), 1-8, 2022. ISSN: 0020-7608.
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További közlemények

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3. Umarova, D., **Umarov, O.**, Tóth, A., Csehi, A.: Spectral evidence of vibronic Rabi oscillations in the resonance-enhanced photodissociation of MgH+.
Phys. Rev. A. [Epub ahead of print] (-), 1-13, 2024. ISSN: 1050-2947.
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