Final Research Report (OTKA-NN- 103251)

Laser-Induced nonadiabatic processes in molecular systems: Theory and applications

Our research programme includes of (I) investigation of the impact of light-induced conical intersections in diatomic systems; (ii) Pump - probe numerical experiments and attosecond probing of ultrafast electron dynamics.

Investigation of the impact of light-induced conical intersections in diatomic systems

The light-induced nonadiabaticity couples in a controllable way different electronic states of the molecule and depending on the field intensity this coupling can be strong and extremely large in the vicinity of the light induced conical intersections (LICIs). The nonadiabatic couplings become singular at the LICIs. In contrast to the situation provided by natural conical intersections (CIs) of field-free molecules, the LICI is controllable in the sense that the laser frequency determines its position in nuclear coordinate space and energy and the laser intensity the strength of the couplings. The presence of a CI provides a source for numerous statical and dynamical nonadiabatic phenomena. As is well studied in free polyatomic molecules, the dynamics of the system is highly affected by CIs and becomes strongly nonadiabatic owing to the strong coupling between the nuclei and electrons. Therefore, we investigated the dynamics in the region of laser-induced CI as well.

Nuclear wavepacket propagations have been performed in order to calculate the autocorrelation, the adiabatic and the diabatic population functions. The results undoubtedly demonstrated that LICIs exert strong effects on the quantum dynamics even for weak laser fields [1,2]. The impact of the LICIs on another process of interest has also been studied. We have investigated the spatial alignment of diatomics in fields of moderate intensity (I $\approx 10^8 - 10^{10} W/cm^2$). An important message of our work is that LICIs can substantially influence molecular alignment [3]. Calculating, for example, the population on the first excited electronic state of aligned molecules, there is a large difference between the results obtained in the presence of the LICI and those obtained by employing the 'standard rigid rotor' one-dimensional (1D) model. Since the electronic population is a relevant measurable quantity, we hope that our work concerning the molecular alignment will stimulate experimental investigations in the near future [3].

The phenomenon of LICIs was first demonstrated by us in the framework of the Floquet representation of the nuclear Hamiltonian. This presentation provides a very illustrative picture and is often used to explain various phenomena in the area of strong field physics. The natural question arises: how accurate is the performance of the Floquet approach? More precisely, to what extent do the results produced by the static Floquet picture compared to those obtained from the original Hamiltonian which describes the molecule in a laser pulse? The latter is, of course, explicitely time dependent. To answer this question, we have studied in detail the underlying approximations and compared 'exact' results with those within the Floquet picture in the presence of a LICI. We were able to draw conclusions on the range of validity of the restricted Floquet picture. The restricted Floquet picture has turned out to be of a wide applicability [4]. We have also studied the impact of the LICI on the photodissociation dynamics of the D2+ molecule for realistic laser pulses using the explicit time-dependent Hamiltonian. The kinetic energy release (KER) spectra and the angular distribution of the photodissociation products were calculated with and without LICIs for different initial conditions and for several different laser parameters [5].

Studying the photodissociation process of the D2+ molecule we also reported some novel and observable quantum interference phenomena that arise from the topological singularity induced by a strong laser field. Among others, by means of two-dimensional quantum dynamical calculations, it was shown that the additional rotational degree of freedom in the description of the D2+ photodissociation causes a measurable quantum interference effect [6] due to the very strong nonadiabatic coupling of the electronic, rotational, and vibrational motions. This quantum interference effect has already been experimentally measured by the group of P. H. Bucksbaum [7,8].

Studying the spectra of the D2+ photofragments we have found that fragment energies from certain vibrational eigenstates of the ion are missing in the spectra. To understand and to explain this interesting phenomenon the analysis of the photofragments from single vibrational levels has been required. We found that under very special circumstances, when one of the eigenvalues of the upper adiabatic potential coincides with the energy level of a certain vibrational eigenstate on the diabatic surface, the nuclear wave packet that started from this particular vibrational eigenstate spends a non-negligible amount of time in the upper adiabatic potential before reaching the asymptotic region. The system somehow is being trapped for a while in the upper adiabatic potential [9]. This is the reason that the dissociation probability from this vibrational eigenstate is hardly measurable. Continuing the analysis of this photodissociation process and studying carefully the obtained results, we found a robust effect in the angular distribution of the photofragments that serves as a direct signature of the light-induced conical intersection, providing undoubted evidence of its existence [10]. More recently we concentrated on to initiate the dissociation dynamics of the D2+ molecular ion by using chirped laser pulses [11]. In contrast to the constant frequency (transform limited) laser field, the chirped pulses give rise to LICIs with a varying position according to the temporal frequency change. It has been found that the amplitude of the periodic change in the total dissociation probability rate against the delay time is significantly compressed by the chirped pulse compared to the transform limited case [11]. To understand clearly the physical phenomenon beyond the enhanced and suppressed dissociation process we have performed another set of numerical simulations. Obtained results clearly demonstrate that these effects on the dissociation yields emerge from the broadening of the chirped pulses and the linearly changing frequency is responsible only for the difference between the dissociation rates belonging to the two kind of chirped pulses [12].

Pump - probe numerical experiments and attosecond probing of ultrafast electron dynamics

We proposed a challenging numerical procedures to validate the possible use of cutting-edge attosecond time- and angle-resolved photoelectron spectroscopy to observe in real time the creation of an electronic wave packet and subsequent electronic motion in a neutral molecule photoexcited by a UV pump pulse within a few femtoseconds. Our showcase example was the ozone molecule. As a first step the nonadiabatic coupled electron and nuclear motions have been fully described [13,14]. An initial coherent nonstationary state was prepared as a superposition of the ground state and the excited Hartley state. In this situation neither the electrons nor the nuclei are in a stationary state. The multiconfiguration time-dependent Hartree method (MCTDH) [15] was used to solve the full-dimensional coupled nuclear quantum dynamics in the framework of the adiabatic separation of the time-dependent Schrödinger equation. As a next step to probe the electronic motion, time-dependent Dyson orbitals were computed [16], which are relevant to describe the ionization process starting from the coherent excited states coupled to the continuum. Using these orbitals, time-resolved photoelectron spectra have been calculated [17].

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