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Electron–nuclear correlations in mixed quantum–classical calculations of laser-induced ionization and dissociation

Mathias Uhlmann, Frank Großmann *, Thomas Kunert, Rüdiger Schmidt

Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

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Abstract

Mixed quantum–classical methods, in which the electronic system is described quantum mechanically and the nuclear system classically, allow an efficient theoretical description of molecular systems in intense laser fields. In standard mean field approaches, the missing correlation between the nuclear and the electronic system may lead to a source of error, however. Here, we present an approximate treatment of this correlation for strongly perturbed single electron systems. The performance of the methodology is demonstrated by the qualitative reproduction of full quantum results for the ionization as well as the dissociation probability of the H_2^+ molecule interacting with an intense laser field.

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The experimental and theoretical investigations of the interaction mechanisms of atoms, molecules and clusters with intense laser fields represent one of the most challenging problems of present day research. In strong dependence on the laser parameters, very different phenomena can be observed. In atoms these are e.g. high harmonic generation [1,2], above threshold ionization [3,4] and stabilization against ionization [4,5]. In molecules, due to the nuclear degrees of freedom (DOF), additional mechanisms do occur, like molecular stabilization against dissociation [6–9], bond softening [10–12] and charge resonance enhanced ionization [13–17], to name but a few effects.

The theoretical understanding of these mechanisms requires, in principle, the solution of the time-dependent Schrödinger equation (TDSE) for all electrons and all nuclear DOF. However, only for the smallest molecular systems, like laser aligned H_2^+ [9], laser aligned H_2 with fixed nuclei [18,19], and since very recently also for all electronic and vibrational degrees of H_2 [20] exact numerical solutions of the TDSE exist. In order to treat more complex systems, approximations are necessary due to the exponential scaling of the computational effort with the number of DOF. Promising approaches for an approximate description of the laser driven dynamics are mixed quantum–classical calculations, where the nuclear system is described classically, whereas the electronic system is treated quantum mechanically, see e.g. [21–25]. Among them is the so-called nonadiabatic quantum molecular dynamics (NA-QMD) [22,25]. The applicability of this method to a laser driven system was e.g. demonstrated in [22] and [26], where results from mixed quantum–classical calculations were compared to those from a full quantum mechanical calculation [9]. Recently NA-QMD has been extended to describe realistically ionization, including so-called charge resonance effects [25]. Yet, to obtain a classical description of the nuclear system, several approximations had to be made. Among them is the neglect of electron–nuclear correlations. The method thus is a so-called “mean field” method. The nuclear coordinates are evolving on an effective potential energy surface, which is an average over all electronic states.

Several attempts to include electron–nuclear correlation in quantum–classical simulations have been made so far. The most prominent approach is the so-called Tully surface-hopping method [27,28]. In the more recent version, the nuclear system is propagated on single Born–Oppenheimer (BO) potential en-

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* Corresponding author. Tel.: +49 351 46333863; fax: +49 351 46337297.
E-mail address: frank@physik.tu-dresden.de (F. Großmann).

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ergy surfaces at each instant of time with instantaneous hopping according to the fewest switches algorithm. Recently a model study comparing surface hopping with mean field results has been performed for different potentials of the heavy (in our context the nuclear) particle [29]. Surface hopping is seen to be well suited in cases of considerably different potential energy surfaces, whereas a mean field approach turns out to be superior in cases of rather similar surfaces.

In this Letter, we will focus on the accurate description of ionization and dissociation processes in the laser driven molecular hydrogen ion benchmark system. Based on previous work using an electronic two level model [8], it has been shown by full quantum calculations [9], that for appropriate initial conditions and moderate laser intensities around 3×10^{13} W/cm^2 a stabilization of the system against dissociation does occur. For these parameters, a major part of the nuclear wave-function is caught in an adiabatic laser-induced electronic potential. As a consequence, in the full quantum calculation, this leads to a plateau in the dissociation probability after around 20 fs. As will be shown in the following, in order to reproduce the plateau formation, we have to extend the NA-QMD by (approximately) including electron–nuclear correlations. Due to the very different nuclear dynamics expected for trajectories that stay bound in comparison to those that are undergoing Coulomb explosion in the fully ionized case, we expect that an extension of the NA-QMD approach beyond the mean field approximation is necessary. Work along similar lines has been performed for single [30] as well as for many electron systems using a so-called surface hopping time-dependent Kohn–Sham (TDKS) approach [31], for a critical review of which we refer to [32].

For the formulation of the working equations of standard NA-QMD, including the description of ionization processes, we refer to previous publications [22,25]. For the present discussion we stress that the electronic problem is described by time-dependent density functional theory. Using an expansion of the electronic wave-function in localized basis functions leads to the TDKS equations in basis representation. The many-body aspect of the theory is not relevant for the present Letter that deals exclusively with H_2^+. Very important for the following, however, is the fact that the classical equations of motion for the nuclei are governed by an effective, averaged potential in the standard NA-QMD approach.

In order to extend NA-QMD by going beyond the mean field approach, the quantum solutions are analyzed at fixed times $t_n = n\Delta t$. The norm $N(t)$ of the wave function is between zero and one due to the absorbing boundary conditions that have been incorporated in the quantum equations recently [25]. Thus, at any time t the probability that the molecule is in the bound or in the ionized channel can be determined. The first probability is given by $P_{\text{bound}} = N(t_n)$, whereas the latter then follows to be $P_{\text{I}} = 1 - N(t_n)$ by conservation of the total probability. These probabilities are used to randomly determine whether the molecular system is to be propagated in the bound or in the ionized channel. In the first case, the population of all states is rescaled so that the norm of the wave function is again one. In the second case, the molecule undergoes Coulomb explosion. Within a certain window, the numerical results will not depend on the "channel separation parameter" Δt which is typically chosen to be an order of magnitude larger than the integration time step. Clearly, it is necessary to average over a large number of trajectories using this approach.

Similar to standard surface hopping, the extended NA-QMD methodology lined out above is "ad hoc" and thus only approximately accounts for correlation effects. However, some basic differences to surface hopping should be noted. Firstly, and most importantly, neither BO-surfaces nor (in general many-electron) Floquet like states in laser fields with varying shape have to be known. Secondly, in contrast not only to standard surface hopping but also to the work by Craig et al. [31], the approach presented here does not distribute the trajectories over *all* possible channels but retains the mixing over all bound states and only separates the ionization channel and the bound motion from each other. Therefore, momentum corrections are probably not necessary (and have not been applied in this Letter) because the system does not jump on a single surface but on all bound state surfaces and, thus, the gradient corrections on the nuclei are canceling each other to a large extend. In particular in laser driven systems, this issue, however, must be studied in more detail in future investigations.

The extended NA-QMD procedure described above is now applied to the hydrogen molecular ion aligned along the polarization direction of an intense laser field. Although general pulse shapes could be treated, for reasons of comparison, we use the quasi-cw laser parameters of [9] for the following investigations. The laser field thus has a short linear turn-on period of 1 fs, after which its envelope is kept constant. For the initial conditions to be defined below, a laser frequency of $\omega = 0.21$ a.u. $= 5.71$ eV and an intensity of 3.5×10^{13} W/cm^2 lead to the plateau formation for the dissociation probability in the full quantum results.

For the NA-QMD implementation of the dynamics, the basis set consists of uncontracted Gaussians with angular momenta up to $l = 2$ located at the nuclei and additional s-type Gaussians arranged in a chain-like manner along the laser polarization axis [26]. The basis set is described in more detail in [25]. Initially the electron is assumed to be in its ground state, while the nuclei are chosen to be in the 6th vibrationally excited state [9]. The vibrational state was determined using the Bohr–Sommerfeld formula $\oint p\,dx = (n + 1/2) \times h$ and it was sampled using 1000 trajectories. The standard as well as the extended NA-QMD results will be compared to full quantum calculations, that we have performed, in the following. The quantities we consider are the ionization probability $P_{\text{I}} = 1 - \int_0^{R_{\max}} f_1(R,t)\,dR$ and the dissociation probability $P_{\text{D}} = \int_{R_{\text{D}}}^{R_{\max}} f_1(R,t)\,dR$ *without* ionization. Here R is the inter-nuclear separation and in the full quantum calculations f_1 is obtained through integration of the absolute square of the electron–nuclear wave-function only over electronic positions, given by z and ρ, inside a finite cylinder of radius $L = 8$ a.u. and height $2 \times z_I$. For $|z| > z_I$, the system is considered to be ionized [9]. The nuclear separation defining the onset of dissociation into the $\text{H} + \text{H}^+$ channel is taken as $R_D = 9.5$ a.u. In the corresponding NA-QMD calculations, which are not grid based but use a basis expansion of the electronic wave function, the ionization probability is de-