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Non-adiabatic quantum molecular dynamics: General formalism and case study H_2^+ in strong laser fields

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Abstract. A general formalism of the so-called non-adiabatic quantum molecular dynamics is presented, which applies to atomic many-body systems in external laser fields. The theory treats the nuclear dynamics and electronic transitions simultaneously and self-consistently in a mixed classical-quantum approach. The equations of motion are derived from a general action principle by combining time-dependent density functional theory in *basis-set-expansion* with classical molecular dynamics. Structure and properties of the resulting equations of motion as well as the energy and momentum balance equations in this formalism are discussed in detail. For the model system H_2^+, the classical-quantum equations of motion are solved. The results agree very well with that of full quantum mechanical calculations. Moreover, from the present calculation a transparent physical interpretation of the mechanisms of energy absorption and dissociation dynamics can be obtained. Future applications and approximations of the formalism presented here are briefly outlined.

PACS. 36.40.-c Atomic and molecular clusters – 31.15.Ew Density-functional theory – 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.)

1 Introduction

The non-adiabatic dynamics of electronic and nuclear degrees of freedom in atomic many-body systems represents one of the fundamental processes in different areas of physics and chemistry.

Experimentally, exceptional large progress has been made during the last decade in studying non-adiabatic processes, in particular in molecules and atomic clusters. So, experiments with intense femto-second laser pulses interacting with molecules [1] or atomic clusters [2–8] have revealed a variety of fascinating new, typical non-adiabatic phenomena like the production of keV electrons [2], MeV ions [3] and intense X-rays [4]; the Coulomb explosion [5] connected even with nuclear fusion [6]; the multiple plasmon excitation and relaxation in metallic clusters [7], or the unexpected enhanced ionization with decreasing laser intensity [8]. Moreover, pump-probe experiments allow now to investigate the time-resolved non-adiabatic dynamics, *e.g.* of photoinduced isomerization processes (for a review see [9]). Finally, refined scattering experiments involving metal clusters [10] and fullerenes [11] revealed detailed insight into electronic and vibronic excitation mechanisms, as well as their coupling and related fragmentation processes in those complex systems.

Theoretically, the non-adiabatic coupling of electronic and nuclear dynamics is one of the most challenging problems of atomic many-body theory and, in principle, requires the solution of the full time-dependent electron-nuclear Schrödinger equation. At present, however, a full-scale numerical solution is barely feasible for the smallest possible molecular system, the H_2^+ molecule [12]. Thus, for larger systems like atomic clusters, phenomenological models, based on classical mechanics and/or hydrodynamics [13–18] have been developed to investigate the mechanism of the intense laser-cluster interaction. More microscopic approaches are based on electronic time-dependent Thomas-Fermi theory [19–21] or related semi-classical (meanfield) approximations [22,23] coupled with molecular dynamics (MD) for the nuclear motion. The most advanced microscopic theory to study the coupled electronic and ionic dynamics in intense laser-cluster interaction developed so far, is based on time-dependent (TD) density functional theory (DFT) in local density approximation (LDA) for the treatment of the electronic system coupled with classical MD for the nuclear (ionic) dynamics [24,25]. In this approach, the TD-Kohn-Sham equations are numerically solved on a grid with the consequence that full 3D calculations [24] are still on the edge of available computational facilities. Therefore, the upper most applications of this theory have been obtained within an effective two-dimensional approximation [25] (see [26] for a review).

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An alternative fully microscopic approach to the nonadiabatic dynamics in atomic many-body systems is the so-called nonadiabatic quantum molecular dynamics (NA-QMD), developed recently [27]. In this method, electronic and vibrational degrees of freedom are treated simultaneously and self-consistently by combining classical MD with TD-DFT in a *finite basis set expansion* of the Kohn-Sham-orbitals. The formalism [27] has been worked out for conservative systems, in particular to investigate adiabatic and non-adiabatic collisions involving molecules and atomic clusters.

The NA-QMD theory has been successfully applied so far for the description and interpretation of fragment correlations in collision-induced dissociation [28], charge transfer cross-sections [29–31], as well as the excitation and fragmentation processes in collisions of atoms (ions) with small sodium clusters [32] and systems as large as fullerenes [33].

In this work, we present a general NA-QMD formalism suitable to describe also the interaction of large, but still finite atomic many-body systems with external laser fields. Whereas in previous work [27] approximate classical forces taken from energy conservation have been used, here we present a rigorous derivation of generalized forces from the action principle.

In order to make this paper self-contained, we derive and discuss the equations of motion in a systematic way, starting from a general mixed classical-quantum action principle (Sect. 2.1), specified then for an atomic many body system (Sect. 2.2) and formulated finally in TD-DFT *without basis set expansion* for the Kohn-Sham-orbitals (Sect. 2.3). The central equations of motion of the present general NA-QMD formalism, however, are derived by using a *finite basis set expansion* for the Kohn-Sham-orbitals (Sect. 2.4). Their general properties, in particular that of the resulting force corrections, including their physical interpretation in terms of classical mechanics, are discussed in detail, too (Sect. 2.5). In addition, the energy (Sect. 2.6) and momentum (Sect. 2.7) balance equations in this basis set formalism are derived.

For the model system H_2^+, all equations of motion are solved without any further assumptions or approximations (Sect. 3). The results of these calculations are in reasonable, and to some extend quantitative, agreement with full quantum mechanical calculations [12]. Moreover the present treatment allows to obtain a very transparent interpretation of the excitation and fragmentation mechanisms in this fundamental atomic system.

Future applications of the formalism to larger systems are briefly outlined.

2 Theory

2.1 General mixed classical-quantum treatment

We consider first the general case of a mixed classical-quantum system consisting of interacting particles [34]. The N_i classical particles are described by their trajectories $\mathbf{R} \equiv \{\mathbf{R}_1(t), \ldots, \mathbf{R}_{N_\mathrm{i}}(t)\}$. They are determined by an explicit time-dependent potential $U(\mathbf{R}, t)$ as well as the interaction with a system of N_e quantum-mechanical particles, described by their many-body wave function $\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\mathrm{e}}, t)$ (We omit the spin index). This is determined by an explicit time-dependent Hamiltonian $\hat{H}(\mathbf{R}, t)$ which on its part depends parametrically on $\mathbf{R}$. The action of such a system consists of a classical and a quantum part

$$A = A_\mathrm{c} + A_\mathrm{q} \tag{1}$$

with

$$A_\mathrm{c} = \int_{t0}^{t1} \left\{ \sum_{A}^{N_\mathrm{i}} \frac{M_A}{2} \dot{\mathbf{R}}_A^2 - U(\mathbf{R}, t) \right\} \mathrm{d}t \tag{2}$$

and (atomic units $\hbar = e = m_e = 1/4\pi\varepsilon_0 = 1$ are used)

$$A_\mathrm{q} = \int_{t0}^{t1} \left\langle \Psi \left| \mathrm{i}\frac{\partial}{\partial t} - \hat{H}(\mathbf{R}, t) \right| \Psi \right\rangle \mathrm{d}t \tag{3}$$

with M_A the mass of the classical particles and the brackets $\langle \ldots \rangle$ denote integration over all coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_{N_\mathrm{e}}$. The equations of motion for the trajectories $\mathbf{R}$ and the many body state $|\Psi\rangle$ are obtained by making the total action stationary, leading to

$$\frac{\delta A}{\delta \langle \Psi(t)|} = 0 \;\Rightarrow\; \mathrm{i}\frac{\partial}{\partial t} |\Psi\rangle = \hat{H}(\mathbf{R}, t) |\Psi\rangle \tag{4}$$

$$\begin{aligned} \frac{\delta A}{\delta \mathbf{R}_A(t)} = 0 \;\Rightarrow\; M_A \ddot{\mathbf{R}}_A = &-\frac{\partial}{\partial \mathbf{R}_A} U(\mathbf{R}, t) \\ &- \left\langle \Psi \left| \frac{\partial}{\partial \mathbf{R}_A} \hat{H}(\mathbf{R}, t) \right| \Psi \right\rangle \\ &A = 1, \ldots, N_\mathrm{i}. \end{aligned} \tag{5}$$

Equations (4, 5) have to be solved simultaneously. They represent the general equations of motion of the mixed classical-quantum system defined above. Classical motion $\mathbf{R}(t)$ and quantum dynamics $|\Psi(t)\rangle$ are coupled self-consistently owing to the action principle.

In the next section, the potential U and the Hamiltonian $\hat{H}$ will be specified for an atomic many body system, we are interested in.

2.2 Atomic many body system

Considering now N_i ions (nuclei) with charge Z_A ($A = 1, \ldots, N_\mathrm{i}$) and N_e electrons exposed to an external laser potential (usually, but not necessarily, described in dipole approximation $V_\mathrm{L}(\mathbf{x}, t) = -\mathbf{x} \cdot \mathbf{E}(t)$, with $\mathbf{E}(t)$ the electric field strength) the potential energy of the nuclei reads

$$U(\mathbf{R}, t) = \sum_{A<B}^{N_\mathrm{i}} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{A=1}^{N_\mathrm{i}} Z_A V_\mathrm{L}(\mathbf{R}_A, t) \tag{6}$$

and the Hamiltonian becomes

$$\hat{H}(\mathbf{R}, t) = \sum_{i=1}^{N_\mathrm{e}} \hat{t}_i + \sum_{i=1}^{N_\mathrm{e}} V(\mathbf{r}_i, \mathbf{R}, t) + \sum_{i<j}^{N_\mathrm{e}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{7}$$

with the single particle kinetic energy operator $\hat{t} = -\Delta/2$. The external single particle potential $V(\mathbf{r}, \mathbf{R}, t)$ contains the laser field $V_{\mathrm{L}}(\mathbf{r}, t)$ and the electron-ion interaction $V_{\mathrm{int}}(\mathbf{r}, \mathbf{R})$

$$\begin{aligned} V(\mathbf{r}, \mathbf{R}, t) &= V_{\mathrm{int}}(\mathbf{r}, \mathbf{R}) + V_{\mathrm{L}}(\mathbf{r}, t) && \text{(8a)} \\ &= -\sum_{A=1}^{N_{\mathrm{i}}} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} + V_{\mathrm{L}}(\mathbf{r}, t). && \text{(8b)} \end{aligned}$$

The first term in (8) is time dependent *via* $\mathbf{R}(t)$ and the second one explicitly depends on time. Using the definition of the single particle density

$$\rho(\mathbf{r}, t) = N_{\mathrm{e}} \int \mathrm{d}^3 r_2 \ldots \mathrm{d}^3 r_{N_{\mathrm{i}}} \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_{\mathrm{e}}}, t) \times \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_{\mathrm{e}}}, t) \quad (9)$$

it becomes apparent that the general Newton-type equation (5) drastically simplifies with equations (7–9) leading to

$$M_A \ddot{\mathbf{R}}_A = -\frac{\partial U(\mathbf{R}, t)}{\partial \mathbf{R}_A} - \int \mathrm{d}^3 \mathbf{r} \rho(\mathbf{r}, t) \frac{\partial V_{\mathrm{int}}(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_A} \qquad A = 1, \ldots, N_{\mathrm{i}}. \quad (10)$$

Thus, the electronic forces acting on the nuclei are determined by the single particle density $\rho(\mathbf{r}, t)$ alone, which is the key quantity in DFT. So, in the next section we will reformulate the whole problem using TD-DFT to describe the electronic system.

2.3 TD-DFT coupled with MD

According to the basic theorems of TD-DFT [35] any observable of a many body system can be expressed as functional of the single particle density (9) and this density can be obtained from a non-interacting reference system according to the ansatz

$$\rho(\mathbf{r}, t) = \sum_{j=1}^{N_{\mathrm{e}}} \Psi^{j*}(\mathbf{r}, t) \Psi^j(\mathbf{r}, t) \quad (11)$$

with $\Psi^j(\mathbf{r}, t)$ the time dependent Kohn-Sham-functions. The quantum mechanical part of the action (1) now reads

$$A_{\mathrm{q}} = \int_{t0}^{t1} \sum_{j=1}^{N_{\mathrm{e}}} \left\langle \Psi^j \middle| \mathrm{i}\frac{\partial}{\partial t} - \hat{t} \middle| \Psi^j \right\rangle \mathrm{d}t - A_{\mathrm{pot}} \quad (12)$$

where the brackets $\langle \ldots \rangle \equiv \int_V \mathrm{d}^3 r$ denote integration over the single particle coordinate. The potential part in (12)

$$A_{\mathrm{pot}} = \int_{t0}^{t1} \int \rho(\mathbf{r}, t) \Bigg(V(\mathbf{r}, \mathbf{R}, t) + \frac{1}{2} \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3 r' \Bigg) \mathrm{d}^3 r \, \mathrm{d}t + A_{\mathrm{xc}}[\rho] \quad (13)$$

is a functional of the density $\rho(\mathbf{r}, t)$ and contains the exchange-correlation contribution A_{xc}. In concrete applications of TD-DFT, the latter is subject of adequate approximations, like the time dependent local density approximation (TD-LDA) or the time dependent optimized potential method [36]. In this paper we will not specify A_{xc} and, thus, are dealing with general equations of motion.

In this sense, variation of equations (12, 13) with respect to the KS-orbitals leads to

$$\frac{\delta A}{\delta \Psi^{j*}(\mathbf{r}, t)} = 0 \Rightarrow \quad \mathrm{i}\frac{\partial}{\partial t}\Psi^j = (\hat{t} + V_{\mathrm{eff}}(\mathbf{r}, \mathbf{R}, t))\Psi^j, \qquad j = 1, \ldots, N_{\mathrm{e}} \quad (14)$$

whereas, variation of equations (2, 12, 13) with respect to the trajectories gives

$$\frac{\delta A}{\delta \mathbf{R}_A(t)} = 0 \Rightarrow \; M_A \ddot{\mathbf{R}}_A = -\frac{\partial}{\partial \mathbf{R}_A} U(\mathbf{R}, t) - \sum_{j=1}^{N_{\mathrm{e}}} \left\langle \Psi^j \middle| \frac{\partial}{\partial \mathbf{R}_A} V_{\mathrm{int}}(\mathbf{r}, \mathbf{R}) \middle| \Psi^j \right\rangle \qquad A = 1, \ldots, N_{\mathrm{i}}. \quad (15)$$

In (14), the effective single particle potential $V_{\mathrm{eff}}(\mathbf{r}, \mathbf{R}, t)$ is defined as

$$\begin{aligned} V_{\mathrm{eff}}(\mathbf{r}, \mathbf{R}, t) &= \frac{\delta A_{\mathrm{pot}}[\rho]}{\delta \rho(\mathbf{r}, t)} \\ &= V(\mathbf{r}, \mathbf{R}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3 r' + \frac{\delta A_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r}, t)}. \end{aligned} \quad (16)$$

In (15), the interaction potential $V_{\mathrm{int}}(\mathbf{r}, \mathbf{R})$, as part of $V(\mathbf{r}, \mathbf{R}, t)$, is defined according to (8).

The resulting equations of motion (14, 15) are completely equivalent to (4, 5) and accordingly to (10). So, with the help of (11) one immediately realizes that (15) is identical to (10). The many body Schrödinger equation (4), however, is now replaced by a set of N_{e} coupled integro-differential single particle KS-equations (14). In the present form, these equations have to be solved numerically on a grid, which still is very demanding (if not impossible, at present, for large systems in intense laser fields; see also discussion in the next section). A drastic simplification can be achieved, if the (3+1)-dimensional KS-orbitals $\Psi^j(\mathbf{r}, t)$ are represented in a finite basis set. This, however, complicates the classical equations of motion (15) considerably as will be discussed in the next section.

2.4 TD-DFT in basis set expansion coupled with MD

In this section, we derive the equations of motion of the actual general NA-QMD formalism which is based on a *finite basis set expansion* of the KS-orbitals. We discuss in detail their properties, in particular that of the resulting force corrections. It will be shown, that these force corrections can be interpreted as "constrained quantum forces" known from ordinary classical mechanics for systems with boundary conditions.

The central starting point is to expand the time dependent KS-orbitals $\Psi^j(\mathbf{r},t)$ in a local basis $\{\phi_\alpha\}$

$$\Psi^j(\mathbf{r},t) = \sum_\alpha a^j_\alpha(t)\phi_\alpha(\mathbf{r}-\mathbf{R}_{A_\alpha}) \tag{17}$$

with the expansion coefficients $a^j_\alpha(t)$ and the symbol A_α denotes the atom to which the atomic orbital ϕ_α is attached.

Although technical details are not the topic of this paper, we note in passing, that the use of the linear combination of atomic orbitals (LCAO-ansatz (17)) has clear advantages as compared to a direct numerical solution of the Kohn-Sham-equations (14). First of all (and obviously), the (3+1)-dimensional problem (14)) will be reduced to a one-dimensional one for the determination of the coefficients $a^j_\alpha(t)$. Second (and especially important, if intense laser fields are considered), electrons with basically different spatial extensions (strongly bound core electrons, binding valence electrons as well as practically free electrons in the continuum) can be naturally included in the dynamical treatment, provided appropriate basis functions ϕ_α are taken into account [37].

With the ansatz (17) the explicit expression of the density is given by

$$\rho(\mathbf{r},t) = \sum_{j=1}^{N_\mathrm{e}}\sum_{\alpha\beta} a^{j*}_\alpha(t)a^j_\beta(t)\phi^*_\alpha(\mathbf{r}-\mathbf{R}_{A_\alpha})\phi_\beta(\mathbf{r}-\mathbf{R}_{A_\beta}). \tag{18}$$

Owing to the implicit time-dependence of the basis $\phi_\alpha(\mathbf{r}-\mathbf{R}_{A_\alpha})$, the partial time derivative $\partial/\partial t$ in the action (12) has to be replaced by

$$\frac{\partial}{\partial t} \quad\Rightarrow\quad \frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \sum_{A=1}^{N_\mathrm{i}} \dot{\mathbf{R}}_A \frac{\partial}{\partial \mathbf{R}_A}\cdot \tag{19}$$

For the following considerations it is convenient to introduce the following matrices:

the kinetic energy matrix

$$T_{\alpha\beta} := \left\langle \phi_\alpha \left| \hat{t} \right| \phi_\beta \right\rangle, \tag{20}$$

the Hamilton matrix

$$H_{\alpha\beta} := \left\langle \phi_\alpha \left| \hat{t} + V_\mathrm{eff} \right| \phi_\beta \right\rangle \tag{21}$$

containing the effective potential V_eff defined in (16), the overlap matrix

$$S_{\alpha\beta} := \left\langle \phi_\alpha \left| \phi_\beta \right.\right\rangle, \tag{22}$$

the non-adiabatic coupling matrix

$$B_{\alpha\beta} := \left\langle \phi_\alpha \left| \frac{\mathrm{d}}{\mathrm{d}t}\phi_\beta \right.\right\rangle \tag{23}$$

which due to (19) contains the vector matrices

$$\mathbf{B}^A_{\alpha\beta} := \left\langle \phi_\alpha \left| \frac{\partial}{\partial \mathbf{R}_A}\phi_\beta \right.\right\rangle, \tag{24}$$

and finally, the double differential matrices

$$\mathbf{C}^A_{\alpha\beta} := \left\langle \frac{\mathrm{d}}{\mathrm{d}t}\phi_\alpha \left| \frac{\partial}{\partial \mathbf{R}_A}\phi_\beta \right.\right\rangle\cdot \tag{25}$$

In addition, we define the transposed matrices

$$B^+_{\alpha\beta} := \left\langle \frac{\mathrm{d}}{\mathrm{d}t}\phi_\alpha \middle| \phi_\beta \right\rangle \quad = B^*_{\beta\alpha} \tag{26}$$

$$\mathbf{B}^{A+}_{\alpha\beta} := \left\langle \frac{\partial}{\partial \mathbf{R}_A}\phi_\alpha \middle| \phi_\beta \right\rangle \quad = \mathbf{B}^{A*}_{\beta\alpha} \tag{27}$$

$$\mathbf{C}^{A+}_{\alpha\beta} := \left\langle \frac{\partial}{\partial \mathbf{R}_A}\phi_\alpha \middle| \frac{\mathrm{d}}{\mathrm{d}t}\phi_\beta \right\rangle = \mathbf{C}^{A*}_{\beta\alpha}. \tag{28}$$

With these definitions and the ansatz (17) the quantum mechanical action (12) can be written as

$$A_\mathrm{q} = \int_{t0}^{t1} F_\mathrm{q}(t)\mathrm{d}t - A_\mathrm{pot} \tag{29}$$

with

$$F_q(t) = \sum_{j=1}^{N_\mathrm{e}}\sum_{\alpha\beta} a^{j*}_\alpha \left[(\mathrm{i}B_{\alpha\beta} - T_{\alpha\beta})a^j_\beta + \mathrm{i}S_{\alpha\beta}\dot{a}^j_\beta\right]. \tag{30}$$

The final equations of motion are now obtained by independent variation of the total action with respect to $a^j_\alpha(t)$ and $\mathbf{R}_A(t)$. With

$$\frac{\delta A}{\delta a^{j*}_\alpha(t)} = \frac{\partial F_\mathrm{q}}{\partial a^{j*}_\alpha} - \int \mathrm{d}^3r \frac{\partial \rho}{\partial a^{j*}_\alpha}\frac{\delta A_\mathrm{pot}}{\delta \rho(\mathbf{r},t)} = 0 \tag{31}$$

this yields the Kohn-Sham-equations in basis representation

$$\dot{a}^j_\alpha = -\sum_{\beta\gamma} S^{-1}_{\alpha\beta}\left(\mathrm{i}H_{\beta\gamma} + B_{\beta\gamma}\right)a^j_\gamma \qquad j = 1,\ldots,N_\mathrm{e} \tag{32}$$

and using Euler's equations

$$\frac{\delta A}{\delta \mathbf{R}_A(t)} = \frac{\partial F_q}{\partial \mathbf{R}_A} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial F_q}{\partial \dot{\mathbf{R}}_A} - \frac{\delta A_\mathrm{pot}}{\delta \mathbf{R}_A(t)} + \frac{\delta A_\mathrm{c}}{\delta \mathbf{R}_A(t)} = 0 \tag{33}$$

one obtains after some algebra the classical equations of motion

$$M_A\ddot{\mathbf{R}}_A = -\frac{\partial U(\mathbf{R},t)}{\partial \mathbf{R}_A} + \sum_{j=1}^{N_\mathrm{e}}\sum_{\alpha\beta} a^{j*}_\alpha \left(-\frac{\partial H_{\alpha\beta}}{\partial \mathbf{R}_A} + \mathbf{D}^A_{\alpha\beta}\right)a^j_\beta$$
$$A = 1,\ldots,N_\mathrm{i} \tag{34}$$

with the matrix

$$\mathbf{D}^A_{\alpha\beta} = \left\langle \phi_\alpha \left| \frac{\partial}{\partial \mathbf{R}_A} (V_{\text{eff}} - V) \right| \phi_\beta \right\rangle + \sum_{\gamma\delta} \left(\mathbf{B}^{A+}_{\alpha\gamma} S^{-1}_{\gamma\delta} H_{\delta\beta} + H_{\alpha\gamma} S^{-1}_{\gamma\delta} \mathbf{B}^A_{\delta\beta} \right) + \mathrm{i} \left[\mathbf{C}^{A+}_{\alpha\beta} - \mathbf{C}^A_{\alpha\beta} + \sum_{\gamma\delta} \left(B^+_{\alpha\gamma} S^{-1}_{\gamma\delta} \mathbf{B}^A_{\delta\beta} - \mathbf{B}^{A+}_{\alpha\gamma} S^{-1}_{\gamma\delta} B_{\delta\beta} \right) \right]. \tag{35}$$

Equations (32, 34) represent the central result in the derivation of the general formalism of the NA-QMD.

Owing to the definition of $B_{\alpha\beta}$ (23) and $\mathbf{C}^A_{\alpha\beta}$ (25) the last term of (35) depends on the nuclear velocities. These contributions to the forces are essential for the correct momentum balance in the present basis set formalism (see Sect. 2.7). It is interesting to note that similar velocity dependent forces have been found recently also in a time-dependent tight binding approach [38]. Obviously, this term vanishes if the basis is complete, *i.e.* if

$$\sum_{\alpha\beta} |\phi_\alpha\rangle\, S^{-1}_{\alpha\beta}\, \langle\phi_\beta| = 1 \tag{36}$$

holds. It will be shown below, that in this case also the remaining terms of the electronic contribution to the forces in equations (34, 35) are drastically simplified. In any practical applications of the formalism, however, the completeness relation (36) can never be fulfilled, and thus, the full equations of motion (34) have to be considered.

2.5 Interpretation of the force corrections due to the finite basis set expansion

At first glance, the complicated structure of the forces in equations (34, 35) makes it difficult to give a transparent interpretation of the correction term resulting from the basis. From the theoretical point of view it is therefore very useful to present equations (34, 35) in an alternative (operator) form and rederive the KS-equations (32) from a *basis constrained* single particle Hamiltonian defined as

$$\hat{h}' = \hat{t} + V_{\text{eff}} + \hat{X} \tag{37}$$

with $\hat{h} = \hat{t} + V_{\text{eff}}$ the usual KS-Hamiltonian from equations (14, 16) and the additional operator

$$\hat{X} := \hat{P}\hat{h}\hat{P} - \hat{h} + \mathrm{i}\left(1 - \hat{P}\right)\hat{B} - \mathrm{i}\hat{B}^+\left(1 - \hat{P}\right) \tag{38}$$

defined with the projectors

$$\hat{P} := \sum_{\alpha\beta} |\phi_\alpha\rangle\, S^{-1}_{\alpha\beta}\, \langle\phi_\beta| \tag{39}$$

and

$$\hat{B} := \sum_{\alpha\beta} \left| \frac{\mathrm{d}}{\mathrm{d}t}\phi_\alpha \right\rangle S^{-1}_{\alpha\beta}\, \langle\phi_\beta|\,. \tag{40}$$

Obviously $\hat{X}$ vanishes for a complete basis (36).

With equations (38–40) the classical equations of motion (34) can now be rewritten as

$$M_A \ddot{\mathbf{R}}_A = -\frac{\partial U(\mathbf{R},t)}{\partial \mathbf{R}_A} - \sum_{j=1}^{N_{\mathrm{e}}} \sum_{\alpha\beta} a^{j*}_\alpha \left\langle \phi_\alpha \left| \frac{\partial}{\partial \mathbf{R}_A} V_{\text{int}}(\mathbf{r},\mathbf{R}) + \frac{\partial}{\partial \mathbf{R}_A} \hat{X} \right| \phi_\beta \right\rangle a^j_\beta \tag{41}$$

leading finally, with (17), to

$$M_A \ddot{\mathbf{R}}_A = -\frac{\partial U(\mathbf{R},t)}{\partial \mathbf{R}_A} - \sum_j \left\langle \Psi^j \left| \frac{\partial}{\partial \mathbf{R}_A} V_{\text{int}}(\mathbf{r},\mathbf{R}) + \frac{\partial}{\partial \mathbf{R}_A} \hat{X} \right| \Psi^j \right\rangle \cdot \tag{42}$$

In addition, the equations of motion (32) are equivalent to the standard form of the time-dependent KS-equations

$$\mathrm{i}\frac{\partial}{\partial t}\Psi^j = (\hat{t} + V_{\text{eff}}(\mathbf{r},\mathbf{R},t) + \hat{X})\Psi^j \tag{43}$$

however, with the additional single particle operator $\hat{X}$ (38). This can easily be seen by inserting the ansatz (17) into (43) which leads to

$$\sum_\alpha \left[\dot{a}^j_\alpha + \sum_{\beta\gamma} S^{-1}_{\alpha\beta} (\mathrm{i}H_{\beta\gamma} + B_{\beta\gamma}) a^j_\gamma \right] \phi_\alpha = 0 \tag{44}$$

and, therefore, finally to (32) because the basis $\{\phi_\alpha\}$ must be linearly independent.

The implicit equations of motion (42, 43) are thus completely equivalent to the explicit expressions (32, 34), used in practical calculations. They allow however a more transparent interpretation of the present theory: the use of a finite basis expansion has the same effect as the introduction of an additional operator in the Hamiltonian. This is similar to the introduction of constraining forces in classical mechanics, if the dynamics is investigated under boundary conditions. Further, one can now explicitly see that the "coupled channel" equations (32) and the "constrained" forces (34, 35) reduce to the standard KS-equations (14) and Newton-equations (15), respectively (10), if the basis is complete.

2.6 Energy balance

In order to derive the energy balance we define an exchange-correlation energy according to

$$A_{\text{xc}}[\rho] = \int_{t0}^{t1} E_{\text{xc}}[\rho](t)\mathrm{d}t \tag{45}$$

with the important property

$$\frac{\delta A_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r},t)} = \frac{\delta E_{\text{xc}}[\rho](t)}{\delta\rho(\mathbf{r})}\cdot \tag{46}$$

Note the different arguments in $\delta\rho$ on the left and right hand side of (46). With this, the potential energy of the quantum system can be written as

$$E_{\text{pot}}(t) = \int \rho(\mathbf{r},t)\left(V(\mathbf{r},\mathbf{R},t) + \frac{1}{2}\int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r'\right)\mathrm{d}^3r + E_{\text{xc}}[\rho](t). \quad (47)$$

The total time derivative of this functional is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}E_{\text{pot}}(t) = \int \mathrm{d}^3r\,\frac{\mathrm{d}}{\mathrm{d}t}\rho(\mathbf{r},t)V_{\text{eff}}(\mathbf{r},\mathbf{R},t) + \int \mathrm{d}^3r\,\rho(r,t)\frac{\mathrm{d}}{\mathrm{d}t}V(\mathbf{r},\mathbf{R},t) \quad (48)$$

with

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(\mathbf{r},t) = \frac{\partial}{\partial t}\rho(\mathbf{r},t) + \sum_{A=1}^{N_{\text{i}}}\dot{\mathbf{R}}_A\frac{\partial}{\partial\mathbf{R}_A}\rho(\mathbf{r},t) \quad (49)$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}V(\mathbf{r},\mathbf{R},t) = \frac{\partial V_{\text{L}}(\mathbf{r},t)}{\partial t} + \sum_{A=1}^{N_{\text{i}}}\dot{\mathbf{R}}_A\frac{\partial}{\partial\mathbf{R}_A}V_{\text{int}}(\mathbf{r},\mathbf{R}). \quad (50)$$

Now, the total energy of the system can be defined

$$E(t) = \sum_{A=1}^{N_{\text{i}}}\frac{M_A}{2}\dot{\mathbf{R}}_A^2 + U(\mathbf{R},t) + \sum_{j=1}^{N_{\text{e}}}\sum_{\alpha\beta}a_\alpha^{j*}T_{\alpha\beta}a_\beta^j + E_{\text{pot}}[\rho](t). \quad (51)$$

The total time derivative of this quantity is obtained after a longer calculation using equations (48–50) and the equations of motion (32) as

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \int \rho(\mathbf{r},t)\frac{\partial V_{\text{L}}(\mathbf{r},t)}{\partial t}\mathrm{d}^3r - \sum_{A=1}^{N_{\text{i}}}Z_A\frac{\partial V_{\text{L}}(\mathbf{R}_A,t)}{\partial t}\cdot \quad (52)$$

As expected, this quantity is conserved for vanishing or time-independent external fields.

A more transparent expression for the energy balance can be obtained in dipole approximation (*i.e.* $V_{\text{L}}(\mathbf{x},t) = -\mathbf{x}\cdot\mathbf{E}(t)$) leading to

$$\frac{\mathrm{d}}{\mathrm{d}t}E = -\mathbf{d}_{\text{e}}(t)\dot{\mathbf{E}}(t) + \mathbf{d}_{\text{i}}(t)\dot{\mathbf{E}}(t) \quad (53)$$

with the dipole moments of the electrons

$$\mathbf{d}_{\text{e}}(t) = \int \rho(\mathbf{r},t)\mathbf{r}\;\mathrm{d}^3r \quad (54)$$

and the ions

$$\mathbf{d}_{\text{i}}(t) = \sum_{A=1}^{N_{\text{i}}}Z_A\mathbf{R}_A(t). \quad (55)$$

From this expression it is clearly seen, that in a homonuclear system ($Z_A = Z = \text{const.}$) the ions will not be excited by the laser, because in the center of mass system the nuclear dipole moment vanishes, *i.e.*

$$\mathbf{d}_{\text{i}} = Z\sum_{A=1}^{N_{\text{i}}}\mathbf{R}_A = 0. \quad (56)$$

In order to obtain more insight into the electronic excitation (deexcitation) process, it is convenient to consider the total energy change

$$\Delta E_{\text{el}} = -\int_{-\infty}^{\infty}\mathbf{d}_{\text{e}}(t)\dot{\mathbf{E}}(t)\,\mathrm{d}t \quad (57)$$

together with the Fourier-transformed dipole moment

$$\mathbf{d}_{\text{e}}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{e}^{-\mathrm{i}\omega t}\mathbf{d}_{\text{e}}(t)\,\mathrm{d}t. \quad (58)$$

One now immediately realizes that in a *continuous wave field*

$$\mathbf{E} = \Re\left(\mathbf{E}_0\,\mathrm{e}^{-\mathrm{i}\omega_{\text{L}}t}\right) \quad (59)$$

the electronic system adsorbs (desorbs) energy only if the imaginary part of $\mathbf{d}_{\text{e}}(\omega)$ does not vanish at the laser frequency $\omega = \omega_{\text{L}}$, *i.e.*

$$\Delta E_{\text{el}} = \omega_{\text{L}}\,\Im(\mathbf{d}_{\text{e}}(\omega_{\text{L}})\cdot\mathbf{E}_0). \quad (60)$$

In the linear response region this is the case only if ω_{L} coincides with the excitation energy of an optical excited state.

In the other extreme case of *very short laser pulses*

$$\mathbf{E} = \mathbf{E}_0\,\delta(t) \quad (61)$$

all frequencies do contribute simultaneously to the excitation (deexcitation) process, *i.e.*

$$\Delta E_{\text{el}} = \int \mathrm{d}\omega\,\omega\,\Im(\mathbf{d}_{\text{e}}(\omega)\cdot\mathbf{E}_0). \quad (62)$$

For finite laser pulses, the total electronic energy change can be obtained by solving (57) numerically, together with the full equations of motion (32, 34) to calculate the dipole moment $\mathbf{d}_{\text{e}}(t)$.

We note also, that the present formalism can be favorably used to calculate optically excited states (*i.e.* Born-Oppenheimer surfaces) as well as optical excitation spectra in the linear response region from (58) by solving the KS-equations (32) for fixed nuclear position $\mathbf{R}$ and "numerically short" δ-pulses (61).

2.7 Momentum balance

In order to investigate the momentum balance we start with the total momentum

$$\mathbf{P} = \mathbf{P}_{\text{c}} + \mathbf{P}_{\text{q}} \quad (63)$$

as the sum of the classical part

$$\mathbf{P}_{\mathrm{c}} = \sum_{A=1}^{N_{\mathrm{i}}} M_A \dot{\mathbf{R}}_A \tag{64}$$

and the quantum-mechanical part

$$\mathbf{P}_{\mathrm{q}} = \sum_{j=1}^{N_{\mathrm{e}}} \left\langle \Psi^j \left| -\mathrm{i}\nabla \right| \Psi^j \right\rangle = -\mathrm{i} \sum_{j=1}^{N_{\mathrm{e}}} \sum_{\alpha\beta} a_\alpha^{j*} a_\beta^j \left\langle \phi_\alpha \left| \nabla \right| \phi_\beta \right\rangle \cdot \tag{65}$$

Using the identity

$$\begin{aligned}\frac{\partial}{\partial \mathbf{r}} \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) &= -\frac{\partial}{\partial \mathbf{R}_{A_\alpha}} \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \\ &\equiv -\sum_{A=1}^{N_{\mathrm{i}}} \frac{\partial}{\partial \mathbf{R}_A} \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha})\end{aligned} \tag{66}$$

the latter one can be transformed into

$$\mathbf{P}_{\mathrm{q}} = \mathrm{i} \sum_{j=1}^{N_{\mathrm{e}}} \sum_{\alpha\beta} a_\alpha^{j*} \sum_A \mathbf{B}_{\alpha\beta}^A a_\beta^j. \tag{67}$$

Now, the total derivative with respect to time can be obtained using equations (32, 34) leading after an extensive calculation to

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P} = &-\int \rho(\mathbf{r},t) \nabla (V_{\mathrm{L}}(\mathbf{r},t) + V_{\mathrm{xc}}(\mathbf{r},t)) \mathrm{d}^3 r \\ &+ \sum_A Z_A \nabla V_{\mathrm{L}}(\mathbf{R}_A, t).\end{aligned} \tag{68}$$

Besides the expected dependence on the laser field, this balance contains a term that depends on the exchange-correlation potential $V_{\mathrm{xc}} \equiv \delta A_{\mathrm{xc}}/\delta\rho(\mathbf{r},t)$. This one vanishes for the exact V_{xc}, which is a general property of TD-DFT [39]. Without this term one also immediately realizes, that in dipole approximation the total momentum balance vanishes for neutral systems, *i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P} = \left(-\int \rho(\mathbf{r},t) \mathrm{d}^3 r + \sum_{A=1}^{N_{\mathrm{i}}} Z_A \right) \mathbf{E}(t) = 0 \tag{69}$$

which is due to the classical, not quantized treatment of the laser field.

We note finally that the momentum balance (68) can be derived also (and much simpler) without basis expansion. The derivation, carried out here, therefore proofs nicely the validity and stresses the importance of the finite basis correction terms in the forces (34, 35) following from the variational principle.

3 Case study H_2^+

As a first application we will consider here the simplest possible case: the interaction of a laser with the H_2^+-molecule, which is aligned along the laser polarization axis $\mathbf{e}_z$.

For this one electron system the Coulomb potential and the exchange-correlation potential in (16) compensate each other and, thus the effective potential for the electron consists of the external potential (8b) only, *i.e.*

$$V_{\mathrm{eff}} \equiv V(\mathbf{r}, \mathbf{R}, t) = -\frac{1}{|\mathbf{R}_1 - \mathbf{r}|} - \frac{1}{|\mathbf{R}_2 - \mathbf{r}|} + V_{\mathrm{L}}(\mathbf{r}, t). \tag{70}$$

This simplifies the solution of the quantum mechanical problem (32) drastically. In addition, due to the alignment of the molecule with respect to $\mathbf{e}_z$, the classical equations of motion (34) reduce to a one dimensional problem by introducing the relative coordinate $R = |\mathbf{R}_1 - \mathbf{R}_2|$, *i.e.* $\mathbf{R}_1 = (R/2)\mathbf{e}_z$ and $\mathbf{R}_2 = -(R/2)\mathbf{e}_z$. Therefore, and together with (70), the first and the third term in (35) vanish, which simplifies the treatment of the classical problem (34), too. Next, for the basis expansion (17) we use a linear combination of atomic orbitals (LCAO) consisting of the $1s$ and $2s$ eigenstates of the H-atom, centered at each nucleus, *i.e.*

$$\begin{aligned}\phi_{1,2}(\mathbf{r}) &= \frac{1}{\sqrt{\pi}} \mathrm{e}^{-|\mathbf{r} - \mathbf{R}_{1,2}|} \\ \phi_{3,4}(\mathbf{r}) &= \frac{1}{2\sqrt{2\pi}} \left(1 - \frac{|\mathbf{r} - \mathbf{R}_{1,2}|}{2} \right) \mathrm{e}^{-|\mathbf{r} - \mathbf{R}_{1,2}|}.\end{aligned} \tag{71}$$

This allows us to calculate all matrix elements analytically. Finally, in order to compare the results with that obtained from full quantum mechanical calculations [12], the nuclei are assumed to be in their sixth vibronically excited state (see below) and the laser field is chosen to be identical that of [12], *i.e.*

$$V_{\mathrm{L}}(\mathbf{r}, t) = E_0(t)\, z\, \cos(\omega t)$$

with the envelop

$$E_0(t) = \begin{cases} 0 & \text{if } t < 0, \\ E_{\max}(t/t_0) & \text{if } 0 \le t < t_0, \\ E_{\max} & \text{if } t_0 \le t, \end{cases}$$

the frequency $\omega = 5.7$ eV, the ramp time $t_0 = 1$ fs and the field strength $E_{\max} = 0.032$ a.u., which corresponds to an intensity of 3.5×10^{13} W/cm^2.

At this relatively low intensity, the dissociation channel is known to be dominating against ionization [12]. We stress at this point, that ionization can generally not be described within the LCAO basis (71). However, it will be shown elsewhere [37], that a realistic description of the electronic continuum (ionization) dynamics in optical laser pulses can be achieved by joining a LCAO-basis together with corresponding continuum wave functions.

In Figure 1, the lowest three energy surfaces (electronic energy plus proton repulsion $1/R$) calculated within the basis (71) are shown. In addition, the ground state energy surface shifted by one and twice the photon energy $\omega = 5.7$ eV are plotted. A one- and a two-photon resonant transition to the first and the second excited state exist at distances of $R = 2.9$ a.u. and $R = 6$ a.u., respectively. The energy of the sixth vibronically excited state (calculated

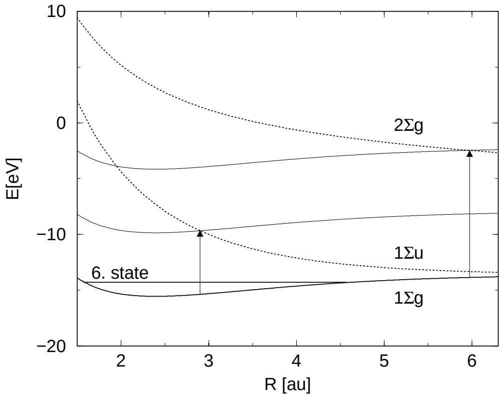

Fig. 1. Calculated energy levels for H_2^+. Shown are the ground state (straight line) and the first two excited states (dotted lines). The thin lines denote the ground state shifted by once and twice the photon energy. The resonant transitions at $R = 2.9$ a.u. and $R = 6$ a.u. are indicated by arrows.

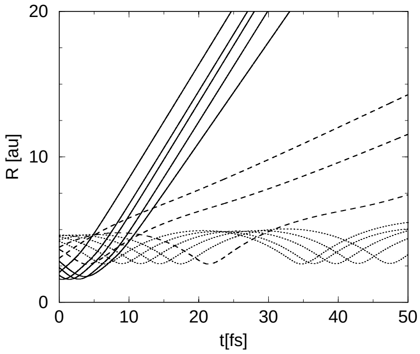

Fig. 2. Calculated trajectories obtained by using different initial conditions: direct fragmentation (solid lines), delayed fragmentation (dashed lines) and stable trajectories (dotted lines).

with the Bohr-Sommerfeld quantization method) is shown also. This energy determines the range of the nuclear initial conditions, *i.e.* 1.6 a.u. $\lesssim R \lesssim$ 4.6 a.u. for the classical equations of motion. These distances together with the corresponding initial velocities are chosen according to the classical probability distribution.

A very transparent and detailed physical picture from the occurring mechanisms, however, can be obtained already by discussing a few selected trajectories. In Figure 2, the nuclear distance $R(t)$ as function of time is shown for typical trajectories. As can be clearly seen, in strong dependence on the nuclear initial conditions $R(0)$, three different types of trajectories occur:

(i) direct fragmentation below the resonant region $R \lesssim$ 2.9 a.u. independent on the sign of $\dot{R}$ (upper bunch of trajectories shown in Fig. 2),

(ii) delayed fragmentation for intermediate distances around $R \gtrsim 3$ a.u. (middle bunch of trajectories in Fig. 2) and,

(iii) stable trajectories for the largest possible distances at $R \lesssim 4.6$ a.u. (bunch of oscillating trajectories in Fig. 2).

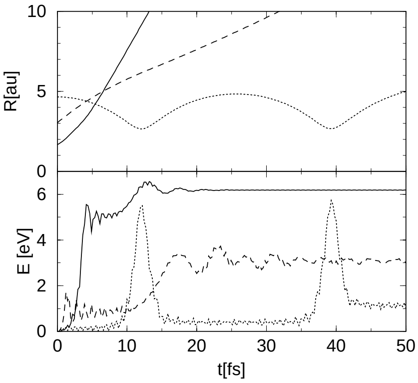

Fig. 3. Trajectories $R(t)$ and absorbed energy $E(t)$ as function of time for the three types of trajectories: direct fragmentation (solid lines), delayed fragmentation (dashed lines) and stabilization (dotted lines).

In a quantum mechanical language, these three types of trajectories characterize the evolution of different spatial parts of an initially excited vibrational wave packet of the molecule. The origin of this behavior can be understood by the present mixed classical-quantum approach. In Figure 3, for the three prototypes of trajectories the distance $R(t)$ as well as the absorbed energy $E(t)$ as function of time are shown. Both quantities should be discussed together with the energy surfaces and resonant transition regions shown in Figure 1. Direct fragmentation for initial distances below the resonant transition ($R < 2.9$ a.u.) occurs due to the immediate excitation when the molecule approaches $R \approx 2.9$ a.u. and, due to the further expansion, it absorbs energy again at the second resonant region at $R \approx 6$ a.u. (solid lines in Fig. 3). Delayed fragmentation for initial distances slightly above $R \approx 2.9$ a.u. occurs due to much less absorption of energy during the initial evolution, which, however, is large enough to expand the molecule up to distances around $R \approx 6$ a.u. where most of the energy is being absorbed, leading finally to fragmentation (dashed lines in Fig. 3). Stable trajectories, originating from the largest initial distances around $R \lesssim 4.6$ a.u., do absorb a remarkable amount of energy only if the distance $R(t)$ approaches the resonant region at $R \approx 2.9$ a.u., followed however by a direct deexcitation. Such a behavior, called *molecular stabilization*, is a theoretically well known mechanism and has been investigated using *dressed states* ([40] and references therein). Note, that in the present case the molecule can accumulate excitation energy, and, thus, in a cw-laser, one may expect finally fragmentation, too.

It is now of particular interest, how the results of this extremely simplified approach do compare with the exact, full quantum-mechanical ones, which are available for this system [12]. To this end, we have performed an ensemble average of about 1200 trajectories with different classical initial conditions. The probability distribution of the nuclear distances is obtained then by

$$P(R,t) = \frac{1}{N} \sum_{i=1}^{N} P^i(R,t) \qquad (72)$$

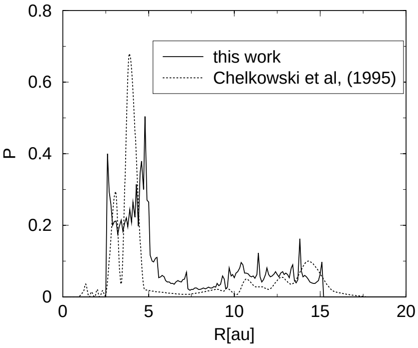

Fig. 4. Probability distribution $P(R,t)$ for the nuclear distance R at $t = 17.6$ fs. The quantum mechanical result [12] and the present classical-quantum result (solid line) are shown.

where N is the total number of trajectories and $P^i(R,t) = 1/\Delta R$ if the distance $R_i(t)$ for the event i lies within the range $R(t) - \Delta R/2 \leq R_i(t) < R(t) + \Delta R/2$ with the spatial bin distance $\Delta R = 0.1$ a.u. and $P^i(R,t) = 0$ otherwise. This quantity is being compared to the exact quantum mechanical probability distribution at $t = 17.6$ fs in Figure 4. Qualitatively both results are similar and show the expected features, molecular stabilization for small distances ($R \lesssim 5$ a.u.) and fragmentation for large values of R. Quantitatively, however, one can see expected differences, *e.g.* the classical turning points in bound state region are somewhat more extended as compared to the real quantum state. Integral quantities, however, like the total dissociation probability, defined as

$$P_{\mathrm{D}}(t) = \int_{R_0}^{\infty} P(R,t)\,\mathrm{d}R$$

with $R_0 = 9.5$ a.u. [12] are in satisfactory good agreement as shown in Figure 5.

4 summary and outlook

We have derived in a systematic way a general formalism of the NA-QMD which applies for finite atomic many-body systems in external fields. It is based on a mixed classical-quantum approach where the electronic system is described by TD-DFT in local basis expansion and the nuclear degrees of freedom are treated classically by molecular dynamics. Self-consistent equations of motion are derived from a general action principle.

We have presented here the general equations of motion. They have been solved without any further approximations for the one electron system H_2^+. The obtained results are in good agreement with that of full quantum mechanical calculations. For many-electron systems, approximate equations of motion, as derived *e.g.* in [27] on a tight-binding level, can be obtained from the general formalism as well. We intend however, to realize the numerical implementation of the whole formalism also on the *ab initio* level using the time-dependent optimized potential method [36] for the exchange correlation part in the action (13).

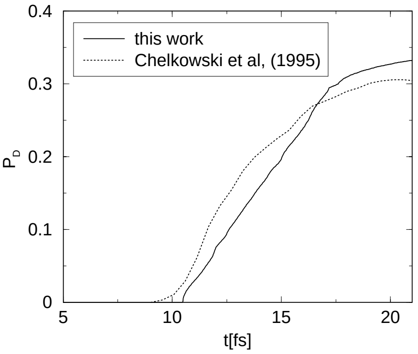

Fig. 5. Dissociation probabilities $P_{\mathrm{D}}(t)$ as function of time. The quantum mechanical result [12] and the present classical-quantum result (solid line) are shown.

A very interesting and fascinating field of application concerns the excitation, ionization and fragmentation mechanism of atomic clusters in intense laser fields [2–8]. Here an all electron treatment together with an appropriate description of the continuum in the ansatz (17) is required which, as discussed in the text, can be incorporated in the present formalism [37].

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