Non-adiabatic quantum molecular dynamics:
Generalized formalism including laser fields

Thomas Kunert and Rüdiger Schmidt

Institut für Theoretische Physik
Technische Universität Dresden,
01062 Dresden

Abstract

A generalized formalism of the so-called non-adiabatic quantum molecular dynamics is presented, which applies for atomic many-body systems in external laser fields. The theory treats the nuclear dynamics and electronic transitions simultaneously in a mixed classical-quantum approach. Exact, self-consistent equations of motion are derived from the action principle by combining time-dependent density functional theory in basis expansion with classical molecular dynamics. Structure and properties of the resulting equations of motion as well as the energy and momentum balance equations are discussed in detail. Future applications of the formalism are briefly outlined.
I. 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, 3, 4, 5, 6, 7, 8] have revealed a variety of fascinating new, typical non-adiabatic phenomena like the production of keV electrons [4], MeV ions [3] and intense x-rays [4]; the Coulomb explosion [3] 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, 14, 15, 16, 17, 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, 20, 21] or related semiclassical (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 \cite{25} (see \cite{26} for a review).

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 \cite{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 \cite{27} has been worked out for conservative systems, in particular to investigate adiabatic and non-adiabatic collisions involving molecules and atomic clusters. So the NA-QMD theory has been successfully applied so far for the description and interpretation of fragment correlations in collision-induced dissociation \cite{28}, charge transfer cross sections \cite{29,30,31}, as well as the excitation and fragmentation processes \cite{32,33} in collisions of atoms (ions) with small sodium clusters and systems as large as fullerenes.

In this work, we present a generalization of the NA-QMD formalism \cite{27} (hereafter refered to as I), suitable to describe also the interaction of large, but still finite atomic many-body systems with external laser fields. We derive and discuss the exact equations of motion in a systematic way, starting from a general mixed classical-quantum treatment. Energy and momentum balance equations are derived as well. Necessary approximations and possible simplifications to the exact equations of motion as well as future applications of the formalism are briefly summarized.

II. THEORY

A. General mixed classical-quantum treatment

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

$$ A = A_c + A_q $$

with

$$ A_c = \int_{t_0}^{t_1} \left\{ \sum_{A} \frac{M_A}{2} \dot{\mathbf{R}}_A^2 - U(\mathbf{R}, t) \right\} dt $$  \hspace{1cm} (2)

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

$$ A_q = \int_{t_0}^{t_1} \left\langle \Psi \left| i \frac{\partial}{\partial t} - \hat{H}(\mathbf{R}, t) \right| \Psi \right\rangle dt $$  \hspace{1cm} (3)

with $M_A$ the mass of the classical particles and the brackets $\langle \ldots \rangle$ denote integration over all coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}$. 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

$$ \frac{\delta A}{\delta (\Psi(t))} = 0 \Rightarrow i \frac{\partial}{\partial t} |\Psi\rangle = \hat{H}(\mathbf{R}, t) |\Psi\rangle $$  \hspace{1cm} (4)

$$ \frac{\delta A}{\delta \mathbf{R}_A(t)} = 0 \Rightarrow M_A \ddot{\mathbf{R}}_A = - \frac{\partial}{\partial \mathbf{R}_A} U(\mathbf{R}, t) - \left\langle \Psi \left| \frac{\partial}{\partial \mathbf{R}_A} \hat{H}(\mathbf{R}, t) \right| \Psi \right\rangle $$  \hspace{1cm} (5)

$$ A = 1, \ldots, N_i $$

Equations (4) and (5) have to be solved simultaneously. They represent the general equations of motion of the mixed classical-quantum system defined above. They are much more universal than those derived in I from energy conservation. Here they are obtained from a general action principle where both, the potential $U$ (defining the classical system) and the Hamiltonian $\hat{H}$ (defining the quantum system as well as the coupling to the classical one) may explicitly depend on time. There is no energy or momentum conservation, nevertheless classical motion $\mathbf{R}(t)$ and quantum dynamics $|\Psi(t)\rangle$ are coupled self-consistently owing to the action principle.

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

### B. Atomic many body system

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

$$U(R, t) = \sum_{A < B}^{N_i} \frac{Z_A Z_B}{|R_A - R_B|} - \sum_{A=1}^{N_i} Z_A V_L(R_A, t)$$

and the Hamiltonian becomes

$$\hat{H}(R, t) = \sum_{i=1}^{N_e} \hat{t}_i + \sum_{i=1}^{N_e} V(r_i, R, t) + \sum_{i<j} \frac{1}{|r_i - r_j|}$$

with the single particle kinetic energy operator $\hat{t} = -\frac{1}{2} \Delta^2$. The external single particle potential $V(r, R, t)$ contains the laser field $V_L(r, t)$ and the electron-ion interaction $V_{\text{int}}(r, R)$

$$V(r, R, t) = V_{\text{int}}(r, R) + V_L(r, t)$$

$$= -\sum_{A=1}^{N_i} \frac{Z_A}{|R_A - r|} + V_L(r, t) \quad . \quad (8a)$$

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

$$\rho(r, t) = N_e \cdot \int d^3r_2 \ldots d^3r_{N_e} \Psi^*(r, r_2, \ldots, r_{N_e}, t) \cdot \Psi(r, r_2, \ldots, r_{N_e}, t)$$

it becomes apparent that the general Newton-type equation (5) drastically simplifies with (4), (8), (9) leading to

$$M_A \ddot{R}_A = -\frac{\partial U(R, t)}{\partial R_A} - \int d^3r \rho(r, t) \frac{\partial V_{\text{int}}(r, R)}{\partial R_A} \quad A = 1, \ldots, N_i \quad . \quad (10)$$

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

C. TD-DFT coupled with MD

According to the basic theorems of TD-DFT [34] 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
\[ \rho(r, t) = \sum_{j=1}^{N_e} \Psi^j(r, t)\Psi^j(r, t) \] (11)

with \( \Psi^j(r, t) \) the time dependent Kohn Sham functions. The quantum mechanical part of the action (11) now reads
\[ A_q = \int_{t_0}^{t_1} \sum_{j=1}^{N_e} \left\langle \Psi^j \left| i \frac{\partial}{\partial t} - \hat{t} \right| \Psi^j \right\rangle dt - A_{pot} \] (12)

where the brackets \( \langle \ldots \rangle \equiv \int_V d^3r \) denote integration over the single particle coordinate. The potential part in (12)
\[ A_{pot} = \int_{t_0}^{t_1} \int \rho(r, t) \left( V(r, R, t) + \frac{1}{2} \int \frac{\rho(r', t)}{|r - r'|} d^3r' \right) d^3r dt + A_{xc}[\rho] \] (13)

is a functional of the density \( \rho(r, t) \) 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 [35]. In this paper we will not specify \( A_{xc} \) and, thus, are dealing with exact equations of motion.

In this sense, variation of (12), (13) with respect to the KS-orbitals leads to
\[ \frac{\delta A}{\delta \Psi^j(r, t)} = 0 \Rightarrow i \frac{\partial}{\partial t} \Psi^j = (\hat{t} + V_{\text{eff}}(r, R, t))\Psi^j, \quad j = 1, \ldots, N_e \] (14)

whereas, variation of (2), (12) and (13) with respect to the trajectories gives
\[ \frac{\delta A}{\delta R_A(t)} = 0 \Rightarrow M_A \frac{\dot{R}_A}{\partial R} U(R, t) - \sum_{j=1}^{N_e} \left\langle \Psi^j \left| \frac{\partial}{\partial R_A} V_{\text{int}}(r, R) \right| \Psi^j \right\rangle = \sum_{j=1}^{N_e} \left( \int \frac{\rho(r', t)}{|r - r'|} d^3r' \right) \frac{\delta A_{xc}[\rho]}{\delta \rho(r, t)} \] (15)

In (14), the effective single particle potential \( V_{\text{eff}}(r, R, t) \) is defined as
\[ V_{\text{eff}}(r, R, t) = \frac{\delta A_{pot}[\rho]}{\delta \rho(r, t)} \]
\[ = V(r, R, t) + \int \frac{\rho(r', t)}{|r - r'|} d^3r' + \frac{\delta A_{xc}[\rho]}{\delta \rho(r, t)} \] (16)
In (13), the interaction potential $V_{\text{int}}(\mathbf{r}, \mathbf{R})$, 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.

D. TD-DFT in basis expansion coupled with MD

In this section, we derive the final equations of motion of the general NA-QMD formalism and discuss their properties, in particular the resulting energy and momentum balance equations.

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

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

(17)

with the expansion coefficients $a^j_\alpha(t)$ and the symbol $A_\alpha$ denotes the atom to which the atomic orbital $\phi_\alpha$ 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 $\phi_\alpha$ are taken into account [36].

With the ansatz (17) the explicit expression of the density is given by
\[
\rho(\mathbf{r}, t) = \sum_{j=1}^{N_e} \sum_{\alpha\beta} a^j_\alpha(t) a^j_\beta(t) \phi^*_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \phi_\beta(\mathbf{r} - \mathbf{R}_{A_\beta}) .
\] (18)

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

\[
\frac{\partial}{\partial t} \Rightarrow \frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{A=1}^{N_i} \dot{\mathbf{R}}_A \frac{\partial}{\partial \mathbf{R}_A} .
\] (19)

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

the kinetic energy matrix

\[
T_{\alpha\beta} := \langle \phi_\alpha | \dot{\mathbf{i}} | \phi_\beta \rangle
\] ,

(20)

the hamilton matrix

\[
H_{\alpha\beta} := \langle \phi_\alpha | \dot{\mathbf{i}} + V_{\text{eff}} | \phi_\beta \rangle
\] containing the effective potential \( V_{\text{eff}} \) defined in (16), the overlap matrix

\[
S_{\alpha\beta} := \langle \phi_\alpha | \phi_\beta \rangle
\] ,

(22)

the non-adiabatic coupling matrices

\[
B_{\alpha\beta} := \langle \phi_\alpha | \frac{d}{dt} \phi_\beta \rangle
\] which due to (19) contains the vector matrices

\[
B^A_{\alpha\beta} := \langle \phi_\alpha | \frac{\partial}{\partial \mathbf{R}_A} \phi_\beta \rangle
\] ,

(24)

and finally, the double differential matrix

\[
C^A_{\alpha\beta} := \langle \frac{d}{dt} \phi_\alpha | \frac{\partial}{\partial \mathbf{R}_A} \phi_\beta \rangle
\] .

(25)

In addition, we define the transposed matrices

\[
B^+_{\alpha\beta} := \langle \frac{d}{dt} \phi_\alpha | \phi_\beta \rangle = B_{\beta\alpha}^*
\] (26)

\[
B^{A+}_{\alpha\beta} := \langle \frac{\partial}{\partial \mathbf{R}_A} \phi_\alpha | \phi_\beta \rangle = B^A_{\beta\alpha}^*
\] (27)

\[
C^{A+}_{\alpha\beta} := \langle \frac{\partial}{\partial \mathbf{R}_A} \phi_\alpha | \frac{d}{dt} \phi_\beta \rangle = C^A_{\beta\alpha}^*
\] .

(28)
With these definitions and the ansatz (17) the quantum mechanical action (12) can be written as

$$A_q = \int_{t_0}^{t_1} F_q(t) dt - A_{\text{pot}}$$

(29)

with

$$F_q(t) = \sum_{j=1}^{N_e} \sum_{\alpha\beta} a^*_\alpha \left[ (iB_{\alpha\beta} - T_{\alpha\beta}) a^j_{\beta} + iS_{\alpha\beta} \dot{a}_{\beta} \right].$$

(30)

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

$$\frac{\delta A}{\delta a^*_{\alpha}(t)} = \frac{\partial F_q}{\partial a^*_{\alpha}} - \int d^3r \frac{\partial \rho}{\partial a^*_{\alpha}} \delta A_{\text{pot}} = 0$$

(31)

this yields the Kohn-Sham equations in basis representation

$$\dot{a}^j_{\alpha} = - \sum_{\beta\gamma} S^{-1}_{\alpha\beta} (iH_{\beta\gamma} + B_{\beta\gamma}) a^j_{\gamma} \quad j = 1, \ldots, N_e$$

(32)

and using Euler’s equations

$$\frac{\delta A}{\delta R_A(t)} = \frac{\partial F_q}{\partial R_A} \frac{dt}{dt} \frac{\partial F_q}{\partial R_A} - \frac{\delta A_{\text{pot}}}{\delta R_A(t)} + \frac{\delta A_c}{\delta R_A(t)} = 0$$

(33)

one obtains after some algebra the classical equations of motion

$$M_A \ddot{R}_A = - \frac{\partial U(R, t)}{\partial R_A} + \sum_{j=1}^{N_e} \sum_{\alpha\beta} a^*_{\alpha} \left( - \frac{\partial H_{\alpha\beta}}{\partial R_A} + D^{A}_{\alpha\beta} \right) a^j_{\beta} \quad A = 1, \ldots, N_i$$

(34)

with the matrix

$$D^{A}_{\alpha\beta} = \left\langle \phi_{\alpha} \left| \frac{\partial}{\partial R_A} (V_{\text{eff}} - V) \right| \phi_{\beta} \right\rangle + \sum_{\gamma\delta} \left( B_{\alpha\gamma} S_{\gamma\delta}^{-1} H_{\delta\beta} + H_{\alpha\gamma} S_{\gamma\delta}^{-1} B_{\delta\beta}^{A} \right)$$

$$+ i \left[ C^{A+}_{\alpha\beta} - C^{A}_{\alpha\beta} + \sum_{\gamma\delta} (B_{\alpha\gamma} S_{\gamma\delta}^{-1} B_{\delta\beta}^{A} - B_{\alpha\gamma} S_{\gamma\delta}^{-1} B_{\delta\beta}) \right].$$

(35)

Equations (32) and (34) represent the central result in the derivation of the generalized formalism of the NA-QMD. The Kohn-Sham equations (32) are formally very similar to that derived in I, but now also contain the laser field which couples to the electronic system (see
definition $H_{\alpha\beta}$ \( (21) \), $V_{\text{eff}}$ \( (16) \), $V(8)$). The classical equations \( (34) \) include the laser field as well, which here acts on the nuclei (see definition of $U(R, t)$ \( (3) \)). Moreover, the quantum part of the forces in \( (34) \) differs appreciable from that derived in I obtained from energy conservation. In particular, the last term in \( (33) \) results from the variational principle. It represents an important contribution if the momentum balance is considered in the present basis set formalism (see below). Obviously, this term vanishes if the basis is complete, i.e. if

$$\sum_{\alpha\beta} |\phi_\alpha\rangle S_{\alpha\beta}^{-1} \langle \phi_\beta| = 1$$ \( (36) \)

holds. It will be shown below, that in this case also the remaining terms of the electronic contribution to the forces in \( (34) \), \( (35) \) 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.

At first glance, the complicated structure of the forces in \( (34) \), \( (35) \) 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 \( (34) \), \( (35) \) in an alternative (operator) form and rederive the KS-equations \( (32) \) from a basis constrained single particle hamiltonian defined as

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

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

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

defined with the projectors

$$\hat{P} := \sum_{\alpha\beta} |\phi_\alpha\rangle S_{\alpha\beta}^{-1} \langle \phi_\beta|$$ \( (39) \)

and

$$\hat{B} := \sum_{\alpha\beta} \left| \frac{d}{dt} \phi_\alpha \right| S_{\alpha\beta}^{-1} \langle \phi_\beta| .$$ \( (40) \)

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

With \( (38) \), \( (39) \), \( (40) \) the classical equations of motion \( (34) \) can now be rewritten as

$$M_A \ddot{R}_A = - \frac{\partial U(R, t)}{\partial R_A} - \sum_{j=1}^{N_e} \sum_{\alpha\beta} a^{j*}_\alpha \left( \phi_\alpha \right| \frac{\partial}{\partial R_A} V_{\text{int}}(r, R) + \frac{\partial}{\partial R_A} \hat{X} \phi_\beta \right) a^j_\beta$$ \( (41) \)
leading finally, with \((17)\), to

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

In addition, the equations of motion \((42)\) are equivalent to the standard form of the time-dependent KS-equations

\[
i \frac{\partial}{\partial t} \Psi^j = (\hat{t} + V_{\text{eff}}(r, R, t) + \hat{X}) \Psi^j
\]

however, with the additional single particle operator \(\hat{X} \) \((48)\). This can easily be seen by inserting the ansatz \((17)\) into \((43)\) which leads to

\[
\sum_\alpha \left[ \dot{a}^j_\alpha + \sum_{\beta\gamma} S^{-1}_{\alpha\beta}(iH_{\beta\gamma} + B_{\beta\gamma}) a^j_\gamma \right] \phi_\alpha = 0
\]

and, therefore, finally to \((42)\) because the basis \(\{\phi_\alpha\}\) must be linearly independent.

The implicit equations of motion \((42)\) and \((43)\) 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.

E. Energy and momentum balance

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

\[
A_{\text{xc}}[\rho] = \int_{t_0}^{t_1} E_{\text{xc}}[\rho](t) dt
\]

(45)

with the important property

\[
\frac{\delta A_{\text{xc}}[\rho]}{\delta \rho(r, t)} = \frac{\delta E_{\text{xc}}[\rho](t)}{\delta \rho(r)}
\]

(46)

11
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

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

The total time derivative of this functional is given by

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

with

$$\frac{d}{dt} \rho(r, t) = \frac{\partial}{\partial t} \rho(r, t) + \sum_{A=1}^{N_i} \dot{R}_A \frac{\partial}{\partial R_A} \rho(r, t) \quad (49)$$

and

$$\frac{d}{dt} V(r, R, t) = \frac{\partial V_L(r, t)}{\partial t} + \sum_{A=1}^{N_i} \dot{R}_A \frac{\partial}{\partial R_A} V_{\text{int}}(r, R). \quad (50)$$

Now, the total energy of the system can be defined

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

The total time derivative of this quantity is obtained after a longer calculation using (48), (49), (50) and the equations of motion (32) as

$$\frac{dE}{dt} = \int \rho(r, t) \frac{\partial V_L(r, t)}{\partial t} d^3r - \sum_{A=1}^{N_i} Z_A \frac{\partial V_L(R_A, t)}{\partial t}. \quad (52)$$

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. $V_L(x, t) = -x \cdot E(t)$) leading to

$$\frac{d}{dt} E = -d_e(t) \dot{E}(t) + d_i(t) \dot{E}(t) \quad (53)$$

with the dipole moments of the electrons

$$d_e(t) = \int \rho(r, t) r \ d^3r \quad (54)$$

and the ions

$$d_i(t) = \sum_{A=1}^{N_i} Z_A R_A(t). \quad (55)$$
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.

\[
d_i = Z \sum_{A=1}^{N_i} R_A = 0 \quad .
\] (56)

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

\[
\Delta E_{\text{el}} = - \int_{-\infty}^{\infty} d_e(t) \dot{E}(t) \, dt
\] (57)

together with the Fourier-transformed dipole moment

\[
d_e(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} d_e(t) \, dt \quad .
\] (58)

One now immediately realizes that in a continuous wave field

\[
E = \Re(E_0 e^{-i\omega_L t})
\] (59)

the electronic system adsorbs (desorbs) energy only if the imaginary part of \( d_e(\omega) \) does not vanish at the laser frequency \( \omega = \omega_L \), i.e.

\[
\Delta E_{\text{el}} = \omega_L \Im(d_e(\omega_L) \cdot E_0) \quad .
\] (60)

In the linear response region this is the case only if \( \omega_L \) coincides with the excitation energy of an optical excited state.

In the other extreme case of very short laser pulses

\[
E = E_0 \delta(t)
\] (61)

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

\[
\Delta E_{\text{el}} = \int d\omega \omega \Im(d_e(\omega) \cdot E_0) \quad .
\] (62)

For finite laser pulses, the total electronic energy change can be obtained by solving (57) numerically, together with the the full equations of motion (32), (34) to calculate the dipole moment \( d_e(t) \).

We note also, that the present formalism can be favourably used to calculate optically excited states (i.e. Born-Oppenheimer surfaces) as well as optical excitation spectra in the
linear response region from (38) by solving the KS-equations (32) for fixed nuclear position \( R \) and "numerically short" \( \delta \)-pulses (61). Details of this procedure will be discussed elsewhere [37].

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

\[
P = P_c + P_q
\]

as the sum of the classical part

\[
P_c = \sum_{A=1}^{N_i} M_A \dot{R}_A
\]

and the quantummechanical part

\[
P_q = \sum_{j=1}^{N_e} \langle \Psi| -i \nabla |\Psi \rangle = -i \sum_{j=1}^{N_e} \sum_{\alpha\beta} a_j^{\alpha*} a_j^{\beta} \langle \phi_\alpha | \nabla | \phi_\beta \rangle .
\]

Using the identity

\[
\frac{\partial}{\partial r} \phi_\alpha (r - R_{A\alpha}) = - \frac{\partial}{\partial R_{A\alpha}} \phi_\alpha (r - R_{A\alpha}) \equiv - \sum_{A=1}^{N_i} \frac{\partial}{\partial R_A} \phi_\alpha (r - R_{A\alpha})
\]

the latter one can be transformed into

\[
P_q = i \sum_{j=1}^{N_e} \sum_{\alpha\beta} a_j^{\alpha*} \sum_A B_{\alpha\beta}^A a_j^{\beta} .
\]

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

\[
\frac{d}{dt} P = - \int \rho (r, t) \nabla (V_L (r, t) + V_{xc} (r, t)) d^3r + \sum_A Z_A \nabla V_L (R_A, t) .
\]

Besides the expected dependence on the laser field, this balance contains a term that depends on the exchange-correlation potential \( V_{xc} \equiv \delta A_{xc}/\delta \rho (r, t) \). This one vanishes for the exact \( V_{xc} \), which is a general property of TD-DFT [38]. Without this term one also immediately realizes, that in dipole approximation the total momentum balance vanishes for neutral systems, i.e.

\[
\frac{d}{dt} P = \left( - \int \rho (r, t) d^3r + \sum_{A=1}^{N_i} Z_A \right) \mathbf{E} (t) = 0
\]
which is due to the classical, not quantized treatment of the laser field.

We note finally that the momentum balance (38) 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.

III. SUMMARY AND OUTLOOK

We have derived in a systematic way a generalized 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 exact equations of motion. They can be solved without further approximations for one electron systems, like H$_2^+$ or HD$^+$ [36] where the exact exchange-correlation term cancels the Hartree-term in the effective potential (16). For many-electron systems, approximate equations of motion, as derived e.g. in I 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 [35] for the exchange correlation part in the action (13). Preliminary results obtained within this method for organic molecules, like ethylene C$_2$H$_4$, show excellent agreement with CI-calculations [39] concerning the ground-state properties (i.e. bonding lengths, angles etc.) as well as optical excitation spectra [40]. As a first application of the whole time-dependent formalism we intend to investigate the cis-trans isomerization process of C$_2$H$_4$ in short laser pulses [40].

Another very interesting and fascinating field of application concerns the excitation, ionization and fragmentation mechanism of atomic clusters in intense laser fields [2, 3, 4, 5, 6, 7, 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].

This work was supported by the DFG through Forschergruppe “Nanostrukturierte Funk-
tionselemente in makroskopischen Systemen”.

[1] A. Bandrauk, ed., *Molecules in Laser Fields* (Marcel Dekker, New York, 1993).
[2] Y. L. Shao, T. Ditmire, J. W. G. Tisch, E. Springate, J. P. Marangos, and M. H. R. Hutchinson, Phys. Rev. Lett. **77**, 3343 (1996).
[3] T. Ditmire, J. W. G. Tisch, E. Springate, M. B. Mason, N. Hay, R. A. Smith, J. Marangos, and M. H. R. Hutchinson, Nature **386**, 54 (1997).
[4] A. McPherson, B. D. Thompson, A. B. Borisov, K. Boyer, and C. K. Rhodes, Nature **370**, 631 (1994).
[5] M. Lezius, S. Dobosz, D. Normand, and M. Schmidt, Phys. Rev. Lett. **80**, 261 (1998).
[6] T. Ditmire, J. Zweiback, V. P. Yanovsky, T. E. Cowan, G. Hays, and K. B. Wharton, Nature **398**, 489 (1999).
[7] R. Schlipper, R. Kusche, B. von Issendorff, and H. Haberland, Phys. Rev. Lett. **80**, 1194 (1998).
[8] L. Köller, M. Schumacher, J. Köhn, S. Teuber, J. Tiggesbäumker, and K. H. Meiwes-Broer, Phys. Rev. Lett. **82**, 3783 (1999).
[9] W. Domcke and G. Stock, Adv. Chem. Phys. **100**, 1 (1997).
[10] J. C. Brenot, H. Dunet, J. A. Fayeton, M. Barat, and M. Winter, Phys. Rev. Lett. **77**, 1246 (1996).
[11] J. Opitz, H. Lebius, S. Tomita, B. A. Huber, P. M. Capelle, D. B. Montesquieu, A. B. Montesquieu, A. Reinköster, U. Werner, H. O. Lutz, et al., Phys. Rev. A **62**, 022705 (2000).
[12] S. Chelkowski, T. Zuo, O. Atabek, and A. D. Bandrauk, Phys. Rev. A **52**, 2977 (1995).
[13] C. Rose-Petruck, K. J. Schafer, K. R. Wilson, and C. P. J. Barty, Phys. Rev. A **55**, 1182 (1997).
[14] I. Last and J. Jortner, Phys. Rev. A **60**, 2215 (1999).
[15] T. Ditmire, Phys. Rev. A **57**, R4094 (1998).
[16] K. Ishikawa and T. Blenski, Phys. Rev. A **62**, 063204 (2000).
[17] K. Boyer, B. D. Thompson, A. McPherson, and C. K. Rhodes, Journal of Physics B: Atomic, Molecular and Optical Physics **27**, 4373 (1994).
[18] C. Siedschlag and J. Rost, *submitted* (2001).
[19] M. Brewczyk, C. W. Clark, M. Lewenstein, and K. Rzazewski, Phys. Rev. Lett. **80**, 1857 (1998).

[20] M. Brewczyk and K. Rzazewski, Phys. Rev. A **60**, 2285 (1999).

[21] M. Rusek, H. Lagadec, and T. Blenski, Phys. Rev. A **63**, 013203 (2001), and refs. therein.

[22] K. J. LaGattuta, Eur. Phys. J. D **2**, 267 (1998).

[23] I. Grigorenko, K. H. Bennemann, and M. E. Garcia, submitted to Phys. Rev. Lett. (2001).

[24] F. Calvayrac, P. G. Reinhard, and E. Suraud, J. Phys. B **31**, 5023 (1998).

[25] E. Suraud and P. G. Reinhard, Phys. Rev. Lett **85**, 2296 (2000).

[26] F. Calvayrac, P.-G. Reinhard, E. Suraud, and C. Ullrich, Phys. Rep. **337**, 493 (2000).

[27] U. Saalmann and R. Schmidt, Z. Physik D **38**, 153 (1996).

[28] J. A. Fayeton, M. Barat, J. C. Brenot, H. Dunet, Y. J. Picard, U. Saalmann, and R. Schmidt, Phys. Rev. A **57**, 1058 (1998).

[29] O. Knospe, J. Jellinek, U. Saalmann, and R. Schmidt, Eur. Phys. J. D **5**, 1 (1999).

[30] O. Knospe, J. Jellinek, U. Saalmann, and R. Schmidt, Phys. Rev. A **61**, 022715 (1999).

[31] Z. Roller-Lutz, Y. Wang, H. O. Lutz, U. Saalmann, and R. Schmidt, Phys. Rev. A **59**, R2555 (1999).

[32] U. Saalmann and R. Schmidt, Phys. Rev. Lett. **80**, 3213 (1998).

[33] T. Kunert and R. Schmidt, Phys. Rev. Lett. **86**, 5258 (2001).

[34] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[35] T. Grabo, T. Kreibich, S. Kurth, and E. Gross, in *Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon & Breach, Tokyo, 1998).

[36] T. Kunert, M. Uhlmann, and R. Schmidt, to be published.

[37] T. Kunert and R. Schmidt, to be published.

[38] G. Vignale, Phys. Rev. Lett. **74**, 3233 (1995).

[39] M. Ben-Nun and T. J. Martinez, Chem. Phys. **259**, 237 (2000).

[40] T. Kunert, F. Großmann, and R. Schmidt, to be published.