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Non-adiabatic quantum molecular dynamics: basic formalism and case study

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Abstract. A general formalism is presented that treats self-consistently and simultaneously classical atomic motion and quantum electronic excitations in dynamical processes of atomic many-body systems (non-adiabatic quantum molecular dynamics). On the basis of time-dependent density functional theory, coupled highly non-linear equations of motion are derived for arbitrary basis sets for the time-dependent Kohn-Sham orbitals. Possible approximations to make the approach practical for large atomic cluster systems are discussed. As a first application of the still exact equations of motion, non-adiabatic effects in the scattering of H^++H, as a case study, are investigated.

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1 Introduction

Great progress has been made in the study of atomic clusters during the last decade [1, 2]. Metal clusters especially, which show remarkable analogies to atomic nuclei [3], as well as fullerenes have been studied extensively. Recently, dynamical processes with and within atomic clusters have become a very attractive field of cluster research.

In particular, it is now possible to study even cluster-cluster collisions (CCC) [4], as well as molecule-cluster collisions (MCC) [5], and atom-cluster collisions (ACC) [6–10], experimentally. Further, so called "half collisions", i. e. fragmentation of (charged and especially highly charged) clusters are studied in detail in novel experiments [10–15].

In contrast to this fascinating experimental progress, the theory and, therefore, the (microscopic) physical understanding of these processes is still modest. So far, most of the theoretical studies have been performed with the help of molecular dynamics (MD) calculations [16–24], in which the interatomic forces are calculated phenomenologically by two- or three-body interactions [16] or within tight-binding approximations [17–19]. Fully microscopic calculations – restricted to small systems – are based on classical MD combined with Hartree-Fock (HF) theory [20, 21], density functional theory (DFT) [12, 22] or approximate DFT [23, 24] – applicable also to larger systems – for the quantum electronic system. Methods like [20–24] are hereafter referred to as adiabatic quantum molecular dynamics, or simply as QMD.

However, in *all* these MD or QMD calculations the atomic dynamics is governed by forces resulting from the electronic ground-state configuration (adiabatic dynamics on the Born-Oppenheimer (BO) ground-state surface). Although one may obtain some microscopic insight into the reaction mechanism, the adiabatic approximation is by no means justified if clusters collide or dissociate. Moreover, in ion-cluster collisions electronic charge transfer as well as electronic excitations or ionization processes [6, 9, 10, 25] are just the phenomena of interest. Therefore, the development of non-adiabatic methods to include electronic transitions in cluster dynamics is one of the great challenges for theory in the coming years.

In the field of chemical reaction theory (with typical kinetic energies of eV and below) the treatment of non-adiabatic processes has a long tradition [26–28]. However, "surface-hopping" models [27] or combinations [29] of "surface-hopping" and the Pechukas theory [26] are generally not suited to describe dynamical processes in clusters, because the large number of classical degrees of freedom prevents one from defining BO surfaces prior to considering the dynamics. Therefore any non-adiabatic approach to clusters must be formulated without the use of BO surfaces.

In the traditional field of ion-atom scattering, where one deals with typical kinetic energies of keV, electronic excitations have been considered in time-dependent (td) mean-field approximations [30–32]. In this case, the classical trajectory of the ion is usually predefined (e. g. by a "straight line" or Coulomb trajectory).

For low-energy collisions there are also attempts to treat the classical ionic motion self-consistently with electronic excitations by the use of time-dependent HF theory [31–34]. All these studies are restricted to few-electron problems (one or two "active" electrons) whereas in clusters one encounters a real many-body situation. (E. g., in a C_{60}^{+}+C_{60} collision [4] there are 479 "active" and correlated electrons.)

Recently, an MD approach combined with a time-dependent treatment of the electronic many-body problem has been proposed in solid state physics [35] on the basis of td DFT

[36–38]. The td Kohn-Sham (KS) equations are solved by a plane-wave expansion. In collisions, however, an adequate treatment of electronic transitions requires the accurate description of the asymptotic form of the density (or wavefunction) and so, as in ion-atom scattering, local basis sets have to be used (see discussion below).

Very recently, an interesting non-adiabatic MD approach (based on an extended Tully-type coupling [27] and taking into account quantum effects on the atomic motion) has been developed and applied to the photo-excitation dynamics of Ba(Ar)$_N$ ($N = 10, 20$) clusters [39].

In this paper, the basic formalism of a non-adiabatic QMD is presented. First we discuss general equations of motion and related problems in Sect. 2. Using td DFT, self-consistent equations for the classical atomic motion and the electronic dynamics are derived in Sect. 3. Possible approximations to make the approach practical for large systems are presented. As a case study and first application of the still exact equations, the scattering of H+H$^+$ is considered over a wide range of incident energies (10 eV. . . 10 keV) within a transparent model where all matrix elements can be calculated analytically (Sect. 4). It is found that non-adiabatic effects become important above ~20 eV and below ~100 eV bombarding energy.

2 General equations of motion

In order to formulate the general problem as well as to discuss relationships with other fields, we derive in this section general equations of motion for a mixed system consisting of N_i classical ions (nuclei) and N_e electrons treated within quantum mechanics. The hamilton operator for the whole system can be divided into three parts

$$\hat{H} = H_\mathrm{coll}(\mathbf{R},\mathbf{P}) + \hat{H}_0(\hat{\mathbf{r}},\hat{\mathbf{p}}) + \hat{H}_\mathrm{int}(\hat{\mathbf{r}},\mathbf{R})\,. \tag{1}$$

Here $\mathbf{R} \equiv \{\mathbf{R}_1,\ldots,\mathbf{R}_{N_\mathrm{i}}\}$ and $\mathbf{P} \equiv \{\mathbf{P}_1,\ldots,\mathbf{P}_{N_\mathrm{i}}\}$ are the sets of classical positions and momenta of the ions, while $\hat{\mathbf{r}} \equiv \{\hat{\mathbf{r}}_1,\ldots,\hat{\mathbf{r}}_{N_\mathrm{e}}\}$ and $\hat{\mathbf{p}} \equiv \{\hat{\mathbf{p}}_1,\ldots,\hat{\mathbf{p}}_{N_\mathrm{e}}\}$ are the position and momentum operators of the electrons. The single terms of the hamilton operator (1) are defined as

$$H_\mathrm{coll} = \sum_A^{N_\mathrm{i}} \frac{\mathbf{P}_A^2}{2M_A} + \frac{1}{2}\sum_A^{N_\mathrm{i}}\sum_B^{N_\mathrm{i}}{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \tag{2a}$$

$$\hat{H}_0 = \sum_a^{N_\mathrm{e}} \frac{\hat{\mathbf{p}}_a^2}{2} + \frac{1}{2}\sum_a^{N_\mathrm{e}}\sum_b^{N_\mathrm{e}}{}' \frac{1}{|\hat{\mathbf{r}}_a - \hat{\mathbf{r}}_b|} \tag{2b}$$

$$\hat{H}_\mathrm{int} = \sum_a^{N_\mathrm{e}}\sum_A^{N_\mathrm{i}} \frac{-Z_A}{|\hat{\mathbf{r}}_a - \mathbf{R}_A|} \equiv \sum_a^{N_\mathrm{e}} V(\mathbf{r}_a,\mathbf{R}) \tag{2c}$$

where H_coll describes the “free” dynamics of classical ions, $\hat{H}_0$ depends only on the quantum electronic degrees of freedom including the electron-electron interaction and $\hat{H}_\mathrm{int}$ is the coupling between nuclei and electrons mediated by the single-particle potential $V(\mathbf{r},\mathbf{R})$. In Eq. (2), M_A and Z_A stand for the mass and the charge of nucleus A, respectively. The prime at the sum excludes the divergent terms. Atomic units ($\hbar$=e=m_e=$1/4\pi\varepsilon_0$=1) are used.

The ad hoc splitting of a hamiltonian into classical and quantum mechanical degrees of freedom, as done e. g. in Eq. (1), has been already suggested by Mott [41] as early as 1931. It has been used and applied in different fields of physics (e. g. nuclear heavy-ion collisions [42], ion-atom scattering [43, 44], molecular processes [27], etc.). We adopt this approximation here also from the very beginning. One should note, however, that the hybrid description is justified only as long as the *individual* quantum transition does not change considerably the *collective* dynamics of the system described classically. Otherwise, a fully quantum treatment of the whole system is necessary which is beyond the scope of this paper (for a discussion of this point and a derivation of Eq. (1) see e. g. [27, b]).

The time evolution of the electronic many-body state is given by the time-dependent Schrödinger equation

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\Psi(\mathbf{r},t) = \left\{\hat{H}_0(\hat{\mathbf{r}},\hat{\mathbf{p}}) + \hat{H}_\mathrm{int}(\hat{\mathbf{r}},\mathbf{R})\right\}\Psi(\mathbf{r},t) \tag{3}$$

with $\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \dot{\mathbf{R}}\frac{\partial}{\partial \mathbf{R}} := \frac{\partial}{\partial t} + \sum_A \dot{\mathbf{R}}_A \frac{\partial}{\partial \mathbf{R}_A}$. This abbreviation for the scalar product of the ionic velocities and the gradients of all ions will be used in the following.

The equations of motion for the classical system can be derived from the conservation of the total energy

$$E = H_\mathrm{coll} + \left\langle \Psi \left| \hat{H}_0 + \hat{H}_\mathrm{int} \right| \Psi \right\rangle = \mathrm{const} \tag{4}$$

because the total hamiltonian (1) does not depend explicitly on time. In Eq. (4) as elsewhere in the paper, the brackets $\langle \ldots \rangle$ denote integration over all electronic coordinates. The total time derivative of energy (4) vanishes

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}E = &\sum_A^{N_\mathrm{i}} \dot{\mathbf{P}}_A \frac{\mathbf{P}_A}{M_A} + \sum_A^{N_\mathrm{i}} \dot{\mathbf{R}}_A \left(\frac{\partial}{\partial \mathbf{R}_A} \sum_B{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \right) \\ &+ \dot{\mathbf{R}} \left\langle \Psi \left| \frac{\partial}{\partial \mathbf{R}} \hat{H}_\mathrm{int} \right| \Psi \right\rangle \\ &+ \left\langle \frac{\mathrm{d}}{\mathrm{d}t}\Psi \left| \hat{H}_0 + \hat{H}_\mathrm{int} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{H}_0 + \hat{H}_\mathrm{int} \right| \frac{\mathrm{d}}{\mathrm{d}t}\Psi \right\rangle \\ &\overset{!}{=} 0\end{aligned} \tag{5}$$

which is equivalent to the equations ($A = 1, \ldots, N_\mathrm{i}$)

$$\dot{\mathbf{R}}_A = \mathbf{P}_A / M_A\,, \tag{6}$$

$$\dot{\mathbf{P}}_A = -\frac{\partial}{\partial \mathbf{R}_A} \sum_B^{N_\mathrm{i}}{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \left\langle \Psi(t) \left| \frac{\partial}{\partial \mathbf{R}_A} \hat{H}_\mathrm{int} \right| \Psi(t) \right\rangle \tag{7}$$

and

$$\left\langle \frac{\mathrm{d}}{\mathrm{d}t}\Psi \left| \hat{H}_0 + \hat{H}_\mathrm{int} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{H}_0 + \hat{H}_\mathrm{int} \right| \frac{\mathrm{d}}{\mathrm{d}t}\Psi \right\rangle = 0\,. \tag{8}$$

Equation (8) is fulfilled automatically if Ψ represents the exact solution of the Schrödinger equation (3). Equations (6) and (7), which must be solved simultaneously with Eq. (3), have a transparent interpretation. They represent classical Hamilton equations of motion for the ions, which move within an explicit time-dependent potential. Thus, in contrast to adiabatic QMD where the second term in Eq. (7) does not depend explicitly on time, energy can be transferred from the classical subsystem to the quantum-mechanical one and vice versa. Equations (3), (6) and (7) are self-consistent in the sense that the classical motion $\mathbf{R}(t)$ determines the quantum dynamics (3) and the quantum state $\Psi(t)$ governs the classical dynamics (6), (7).

The quantum force in (7) has been derived in different ways starting from a fully quantum mechanical treatment [26, 45, 46]. Firstly, Pechukas [26] has applied the stationary-phase approximation within a path-integral formulation. Kwong [45] used an eikonal approximation for the derivation and Diestler [46] applied the narrow-wave-packet approximation to the ions.

It is interesting to note, that the same general form of Eqs. (6) and (7), has been derived and used also in the theory of nuclear heavy-ion collisions [42]. In this case, H_{coll} describes the classical "free" motion of two nuclei (including the conservative part of the nuclear interaction), $\hat{H}_0$ is the internal hamiltonian, i. e. that of the nucleons and $\hat{H}_{\text{int}}$ the interaction between relative motion and intrinsic system approximated by two (static) HF-fields of the individual nuclei moving along classical trajectories [42]. In [42], the retardation effects contained in forces like (7) on the classical motion (note that Eq. (7) is actually an integro-differential equation and the force depends on the whole history of the trajectory) have been studied in detail too. Owing to the short-range nuclear interaction the asymptotic range of the HF (single-particle) wave functions is not decisive in heavy-ion reactions and crude model assumptions may give a realistic description of nuclear collisions.

In striking contrast, in atomic collisions, and particularly while describing charge transfer, it is important to properly describe the exponential tails of the wave functions. A plane-wave expansion, often used in solid state physics (e. g. [35]), or the standard linear combination of Gaussian orbitals used in quantum chemistry [47], are generally not suited to describe atomic collisions. (For a detailed discussion of this important point see e.g. [32a].) On the other hand, any use of (realistic and adequate) local basis sets complicates the force calculations (in the static case or in adiabatic QMD simulations well known as Pulay forces [48]). In the td case, the force corrections resulting from local, finite basis sets can be obtained from Eq. (8).

This will be shown in the following by expanding the many-body wave function

$$\Psi(\mathbf{r},t) = \sum_{\alpha} \Psi_\alpha(\mathbf{r};\mathbf{R})\, a_\alpha(t) \tag{9}$$

where $\{\Psi_\alpha\}$ is a many-particle basis *parametrically* depending on the ionic positions $\mathbf{R}$. Although the basis is not specified, one can assume without loss of generality $\langle \Psi_\alpha | \Psi_\beta \rangle = \delta_{\alpha\beta}$ to simplify the following equations. With this ansatz, the Schrödinger equation (3) can be rewritten in terms of coupled-channel equations for the expansion coefficients $a_\alpha(t)$

$$\begin{aligned}\dot{a}_\alpha(t) = -\mathrm{i}\sum_{\beta} \Big\{ &\left\langle \Psi_\alpha \middle| \hat{H}_{\text{el}} \middle| \Psi_\beta \right\rangle \\ &+ \dot{\mathbf{R}} \left\langle \Psi_\alpha \middle| \frac{\partial}{\partial \mathbf{R}} \Psi_\beta \right\rangle \Big\}\, a_\beta(t)\end{aligned} \tag{10}$$

where the abbreviation $\hat{H}_{\text{el}} := \hat{H}_0 + \hat{H}_{\text{int}}$ is used. These coupled equations describe electronic transitions by non-diagonal matrix elements $\langle \Psi_\alpha | \hat{H}_{\text{el}} | \Psi_\beta \rangle$ and by the velocity-dependent term $\dot{\mathbf{R}} \langle \Psi_\alpha | \frac{\partial}{\partial \mathbf{R}} \Psi_\beta \rangle$.

With Eq. (10), the expression on the l. h. s. of (8) reads

$$\begin{aligned}&\mathrm{i} \sum_{\alpha\beta\gamma} a_\alpha^* \langle \Psi_\alpha | \hat{H}_{\text{el}} | \Psi_\beta \rangle \langle \Psi_\beta | \hat{H}_{\text{el}} | \Psi_\gamma \rangle\, a_\gamma \\ &-\mathrm{i} \sum_{\gamma\alpha\beta} a_\gamma^* \langle \Psi_\gamma | \hat{H}_{\text{el}} | \Psi_\alpha \rangle \langle \Psi_\alpha | \hat{H}_{\text{el}} | \Psi_\beta \rangle\, a_\beta \\ &-\dot{\mathbf{R}} \Big\{ \sum_{\alpha\beta\gamma} a_\alpha^* \langle \tfrac{\partial}{\partial \mathbf{R}} \Psi_\alpha | \Psi_\beta \rangle \langle \Psi_\beta | \hat{H}_{\text{el}} | \Psi_\gamma \rangle\, a_\gamma \\ &\qquad - \sum_{\alpha\gamma} a_\alpha^* \langle \tfrac{\partial}{\partial \mathbf{R}} \Psi_\alpha | \hat{H}_{\text{el}} | \Psi_\gamma \rangle\, a_\gamma \\ &\qquad + \sum_{\gamma\alpha\beta} a_\gamma^* \langle \Psi_\gamma | \hat{H}_{\text{el}} | \Psi_\alpha \rangle \langle \Psi_\alpha | \tfrac{\partial}{\partial \mathbf{R}} \Psi_\beta \rangle\, a_\beta \\ &\qquad - \sum_{\gamma\alpha} a_\gamma^* \langle \Psi_\gamma | \hat{H}_{\text{el}} | \tfrac{\partial}{\partial \mathbf{R}} \Psi_\beta \rangle\, a_\beta \Big\}\end{aligned}$$

and does not vanishes in general. Whereas the first two terms cancel each other in any basis, the term $\{\ldots\}$ vanishes only if the basis does not depend parametrically on $\mathbf{R}$, i.e. $\frac{\partial}{\partial \mathbf{R}} \Psi_\alpha \equiv 0$, *or* if the basis is complete, i.e. $\sum_\alpha \Psi_\alpha(\mathbf{r};\mathbf{R})\, \Psi_\alpha(\mathbf{r}';\mathbf{R}) = \delta(\mathbf{r}-\mathbf{r}')$ for any $\mathbf{R}$. In practical calculations the second condition cannot be realized, and so the term $\{\ldots\}$ proportional to velocity gives rise to additional corrections to the force (7). Analogous corrections have to be taken into account if the electronic system is treated within td density functional theory (next section).

3 Molecular dynamics combined with time-dependent density functional theory

3.1 General

The basic theorem of Runge and Gross [36] states that the many-body state $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}, t)$ and thus any observable of the system are uniquely defined by the td single-particle density $\varrho(\mathbf{r},t)$. (From now on, $\mathbf{r}$ denotes the single-particle coordinate.) As in the ground-state DFT, one can introduce in the td case a non-interacting reference system with the same density as the interacting system

$$\varrho(\mathbf{r},t) = \sum_{j}^{N_e} \left| \psi^j(\mathbf{r},t) \right|^2 \tag{11}$$

with td single-particle functions $\psi^j(\mathbf{r},t)$ determined by an effective potential V_{eff} still to be defined. The time evolution of the system is determined by the action

$$\begin{aligned}A[\psi^j] = \int_{t_0}^{t_1} \mathrm{d}t' \Bigg\{ &\sum_{j}^{N_e} \left\langle \psi^j \middle| \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t'} - \hat{t} \middle| \psi^j \right\rangle \\ &- \int \mathrm{d}^3 r\, \varrho(\mathbf{r},t') \Big[V(\mathbf{r},\mathbf{R}) \\ &\qquad + \frac{1}{2} \int \mathrm{d}^3 r'\, \frac{\varrho(\mathbf{r}',t')}{|\mathbf{r}-\mathbf{r}'|} \Big] \Bigg\} - A_{\text{xc}}[\varrho]\end{aligned} \tag{12}$$

with $\hat{t}$ the kinetic energy operator. The last term A_{xc} accounts, in principle, for *all* exchange and correlation effects of the interacting electrons. The solutions of the td Kohn-Sham equations [36, 38]

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\psi^j(\mathbf{r},t) = \left\{\hat{t} + V_{\mathrm{eff}}(\mathbf{r},t)\right\}\psi^j(\mathbf{r},t) \tag{13}$$

with the effective potential

$$V_{\mathrm{eff}}(\mathbf{r},t) = V(\mathbf{r},\mathbf{R}) + \int \mathrm{d}^3r'\,\frac{\varrho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + V_{\mathrm{xc}}[\varrho](\mathbf{r},t) \tag{14}$$

and

$$V_{\mathrm{xc}}[\varrho](\mathbf{r},t) = \frac{\delta A_{\mathrm{xc}}[\varrho]}{\delta\varrho(\mathbf{r},t)} \tag{15}$$

make the action (12) stationary. The exchange-correlation potential V_{xc} must be derived from an approximated A_{xc} because an exact form is not available. In the following, the simplest approximation for the exchange-correlation part, the so called adiabatic (or time-dependent) local-density approximation (LDA) [38]

$$A_{\mathrm{xc}}[\varrho] = \int_{t_0}^{t_1}\mathrm{d}t'\int \mathrm{d}^3r\,\varrho(\mathbf{r},t')\epsilon_{\mathrm{xc}}[\varrho](\mathbf{r},t') \tag{16}$$

is used. Obviously, the ansatz (16) should be a good approximation for slow time-dependent processes. This can be expected to be realized for any situations where the time-dependence of the electronic density is governed only by the slow atomic motion. In addition, Eq. (16) guarantees that the non-adiabatic QMD formalism includes and describes automatically adiabatic situations (see below).

As A_{xc} is local in space *and* time one has an explicit expression for $V_{\mathrm{xc}} = \epsilon_{\mathrm{xc}} + \varrho\,\delta\epsilon_{\mathrm{xc}}/\delta\varrho$. Thus one can obtain the electronic energy as

$$E_{\mathrm{el}}[\psi^j](t) = \sum_j^{N_{\mathrm{e}}}\left\langle\psi^j\,\middle|\,\hat{t}\,\middle|\,\psi^j\right\rangle + \int \mathrm{d}^3r\,\varrho(\mathbf{r},t)\Bigg[V(\mathbf{r},\mathbf{R}) + \frac{1}{2}\int \mathrm{d}^3r'\,\frac{\varrho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \epsilon_{\mathrm{xc}}[\varrho](\mathbf{r},t)\Bigg]\,. \tag{17}$$

This energy depends on time and corresponds to the expectation value with the many-body wave function in Eq. (4). The total time derivative of this energy is

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}E_{\mathrm{el}}[\psi^j](t) &= \dot{\mathbf{R}}\int \mathrm{d}^3r\,\varrho(\mathbf{r},t)\frac{\partial}{\partial\mathbf{R}}V(\mathbf{r},\mathbf{R}) \\ &\quad + \sum_j^{N_{\mathrm{e}}}\left\{\int \mathrm{d}^3r'\,\frac{\mathrm{d}\psi^{*j}(\mathbf{r}',t)}{\mathrm{d}t}\,\frac{\delta E_{\mathrm{el}}[\psi^j]}{\delta\psi^{*j}(\mathbf{r}',t)} + \int \mathrm{d}^3r'\,\frac{\mathrm{d}\psi^j(\mathbf{r}',t)}{\mathrm{d}t}\,\frac{\delta E_{\mathrm{el}}[\psi^j]}{\delta\psi^j(\mathbf{r}',t)}\right\} \\ &= \dot{\mathbf{R}}\int \mathrm{d}^3r\,\varrho(\mathbf{r},t)\frac{\partial}{\partial\mathbf{R}}V(\mathbf{r},\mathbf{R}) \\ &\quad + \sum_j^{N_{\mathrm{e}}}\left\{\left\langle\frac{\mathrm{d}\psi^j}{\mathrm{d}t}\middle|\hat{t} + V_{\mathrm{eff}}\middle|\psi^j\right\rangle + \left\langle\psi^j\middle|\hat{t} + V_{\mathrm{eff}}\middle|\frac{\mathrm{d}\psi^j}{\mathrm{d}t}\right\rangle\right\}\,.\end{aligned} \tag{18}$$

The first term leads to the force for ion A

$$-\int \mathrm{d}^3r\,\varrho(\mathbf{r},t)\frac{\partial}{\partial\mathbf{R}_A}V(\mathbf{r},\mathbf{R})$$

which is equivalent to the explicit time-dependent force of Eq. (7). This can easily be seen if one integrates (7) over all but one electronic variables. The last term in Eq. (18) has to be discussed in detail if the td single-particle functions ψ^j are represented in a basis.

3.2 Basis representation and equations of motion

Assume now that the td single-particle functions are expanded within an *arbitrary* single-particle basis $\{\phi_\alpha\}$

$$\psi^j(\mathbf{r},t) = \sum_\alpha \phi_\alpha(\mathbf{r};\mathbf{R})a^j_\alpha(t) \tag{19}$$

which depends parametrically on $\mathbf{R}$. Then the td Kohn-Sham equations (13) read ($j = 1,\ldots,N_{\mathrm{e}}$)

$$\dot{a}^j_\alpha(t) = -\sum_{\beta\gamma}\left(S^{-1}\right)_{\alpha\beta}\left\{\mathrm{i}H_{\beta\gamma} + \sum_A^{N_{\mathrm{i}}}\dot{\mathbf{R}}_A\mathbf{R}^A_{\beta\gamma}\right\}a^j_\gamma(t) \tag{20}$$

with the following definition of matrices

$$S_{\alpha\beta} := \left\langle\phi_\alpha\,|\phi_\beta\right\rangle \tag{21a}$$

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

$$\mathbf{R}^A_{\alpha\beta} := \left\langle\phi_\alpha\,\middle|\frac{\partial}{\partial\mathbf{R}_A}\phi_\beta\right\rangle\,. \tag{21c}$$

Using Eq. (20) one can express $\frac{\mathrm{d}}{\mathrm{d}t}\psi^j$ explicitly and the time derivative of the total energy $E = H_{\mathrm{coll}} + E_{\mathrm{el}}$ becomes

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}E = \sum_A^{N_{\mathrm{i}}}\Bigg\{&\dot{\mathbf{P}}_A\frac{\mathbf{P}_A}{M_A} + \dot{\mathbf{R}}_A\left(\frac{\partial}{\partial\mathbf{R}_A}\sum_B^{N_{\mathrm{i}}}{}'\,\frac{Z_AZ_B}{|\mathbf{R}_A-\mathbf{R}_B|}\right) \\ &+ \dot{\mathbf{R}}_A\int \mathrm{d}^3r\,\varrho(\mathbf{r},t)\frac{\partial}{\partial\mathbf{R}_A}V(\mathbf{r},\mathbf{R}) \\ &- \dot{\mathbf{R}}_A\sum_j^{N_{\mathrm{e}}}\Bigg[\sum_{\alpha\beta\gamma\delta}{a^*}^j_\alpha H_{\alpha\beta}\left(S^{-1}\right)_{\beta\gamma}\mathbf{R}^A_{\gamma\delta}a^j_\delta \\ &\quad + \sum_{\alpha\beta\gamma\delta}{a^*}^j_\alpha\left(\mathbf{R}^{\mathrm{T}}\right)^A_{\alpha\beta}\left(S^{-1}\right)_{\beta\gamma}H_{\gamma\delta}a^j_\delta \\ &\quad - \sum_{\alpha\beta}{a^*}^j_\alpha\left\langle\phi_\alpha\middle|\hat{t} + V_{\mathrm{eff}}\middle|\frac{\partial}{\partial\mathbf{R}_A}\phi_\beta\right\rangle a^j_\beta \\ &\quad - \sum_{\alpha\beta}{a^*}^j_\alpha\left\langle\frac{\partial}{\partial\mathbf{R}_A}\phi_\alpha\middle|\hat{t} + V_{\mathrm{eff}}\middle|\phi_\beta\right\rangle a^j_\beta\Bigg]\Bigg\}\,.\end{aligned} \tag{22}$$

In the transposed matrix $\left(\mathbf{R}^{\mathrm{T}}\right)^A_{\alpha\beta}$ the derivation with respect to $\mathbf{R}_A$ acts to the left. It is obvious that the term [...] in (22) vanish only if the underlying basis is complete, i. e. if $\sum_{\beta\gamma}\phi_\beta(\mathbf{r};\mathbf{R})(S^{-1})_{\beta\gamma}\phi_\gamma(\mathbf{r}';\mathbf{R}) = \delta(\mathbf{r}-\mathbf{r}')$, or the basis does not depend on $\mathbf{R}$. Rearranging some terms one can deduce from Eq. (22) the following equations of motion ($A = 1,\ldots,N_{\mathrm{i}}$)

$$\dot{\mathbf{R}}_A = \mathbf{P}_A / M_A \tag{23a}$$

$$\begin{aligned}\dot{\mathbf{P}}_A = &-\frac{\partial}{\partial \mathbf{R}_A} {\sum_{B}^{N_\mathrm{i}}}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \\ &-\sum_j^{N_\mathrm{e}} \Bigg\{ \sum_{\alpha\beta} a^{*j}_{\alpha} \left(\frac{\partial}{\partial \mathbf{R}_A} H_{\alpha\beta} \right) a^j_\beta \\ &\quad - \sum_{\alpha\beta} a^{*j}_{\alpha} \left\langle \phi_\alpha \left| \frac{\partial}{\partial \mathbf{R}_A} (V_\mathrm{eff} - V) \right| \phi_\beta \right\rangle a^j_\beta \\ &\quad - \sum_{\alpha\beta\gamma\delta} \Big[a^{*j}_{\alpha} H_{\alpha\beta} \left(S^{-1}\right)_{\beta\gamma} \mathbf{R}^A_{\gamma\delta} a^j_\delta \\ &\qquad + a^{*j}_{\alpha} \left(\mathbf{R}^\mathrm{T}\right)^A_{\alpha\beta} \left(S^{-1}\right)_{\beta\gamma} H_{\gamma\delta} a^j_\delta \Big] \Bigg\} \, .\end{aligned} \tag{23b}$$

The td Kohn-Sham equations (20) and the Hamilton equations (23) represent the basic equations of motion of the non-adiabatic QMD. They are *exact* in the sense of the time-dependent LDA (16) and they are valid for *any* basis. They describe self-consistently and simultaneously the *dynamics* of N_i classical ions and N_e quantum electrons including their excitations. For completeness we show in the appendix that the non-adiabatic Eqs. (20), (23) reduce to (or include) the corresponding equations of motion of an adiabatic QMD for situations where electronic excitations do not occur.

An exact numerical solution of the highly non-linear Eq. (20) and the Eq. (23) with local basis sets is rather difficult to obtain (if not impossible at all for realistic cluster dynamics). These equations still contain all electrons including the "non-active" core electrons. In the next section we propose and derive successive approximations for the solution of the coupled Eqs. (20) and (23).

3.3 *Approximate equations of motion*

For the following discussion it is convenient to start with an LCAO (linear combination of atomic orbitals) representation of the td Kohn-Sham orbitals ($j = 1, \ldots, N_\mathrm{val}$)

$$\psi^j(\mathbf{r}, t) = \sum_\alpha \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha})\, a^j_\alpha(t) \, . \tag{24}$$

Here A_α stands for the atom on which the atomic orbital ϕ_α is centered. We treat at the very beginning valence electrons N_val only. Then the collective part of the total energy $E = H_\mathrm{coll} + E_\mathrm{el}$ becomes

$$H_\mathrm{coll} = \sum_A^{N_\mathrm{i}} \frac{\mathbf{P}_A^2}{2M_A} + \frac{1}{2} \sum_A^{N_\mathrm{i}} {\sum_B^{N_\mathrm{i}}}' \frac{Z^0_A Z^0_B}{|\mathbf{R}_A - \mathbf{R}_B|} \tag{25}$$

with Z^0_A the valence charge of the ion A. The electronic part E_el is obtained from (17) by rearranging some terms using (21b) with (14) and the density

$\varrho(\mathbf{r}, \mathbf{R}, t) = \sum_j^{N_\mathrm{val}} \sum_{\alpha\beta} a^{*j}_{\alpha}\, \phi_\alpha \phi_\beta\, a^j_\beta$

from (24) as

$$\begin{aligned}E_\mathrm{el}\left(\mathbf{R}, a^j_\alpha(t)\right) = &\sum_j^{N_\mathrm{val}} \sum_{\alpha\beta} a^{*j}_{\alpha}(t)\, H_{\alpha\beta}\, a^j_\beta(t) \\ &-\frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{\varrho(\mathbf{r}, \mathbf{R}, t) \varrho(\mathbf{r}', \mathbf{R}, t)}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \int \mathrm{d}^3 r \, \varrho(\mathbf{r}, \mathbf{R}, t) \Big(\epsilon_\mathrm{xc}[\varrho] - V_\mathrm{xc}[\varrho] \Big)\end{aligned} \tag{26}$$

where the external potential $V(\mathbf{r}, \mathbf{R})$ in (14) has now to be understood as the sum of atomic pseudopotentials $V(\mathbf{r}, \mathbf{R}) = \sum_A^{N_\mathrm{i}} V_\mathrm{ps}(\mathbf{r} - \mathbf{R}_A)$. The energy (26) is still considered on the ab-initio level. It is the aim of the following considerations to simplify these expressions and then to derive appropriate approximate coupled equations of motion.

To do this we divide the density ϱ into two parts

$$\varrho(\mathbf{r}, \mathbf{R}(t), t) = \varrho^0(\mathbf{r}, \mathbf{R}(t)) + \Delta\varrho(\mathbf{r}, \mathbf{R}(t), t) \tag{27}$$

where $\varrho^0(\mathbf{r}, \mathbf{R}(t))$ depends smoothly on time via the coordinates $\mathbf{R}(t)$ and $\Delta\varrho(\mathbf{r}, \mathbf{R}(t), t)$ contains the explicit time dependence of the density. Independent on the total charge of the actual system under consideration we define $\varrho^0(\mathbf{r}, \mathbf{R})$ as the adiabatic density of the neutral reference system. This definition allows to treat charge and polarization effects with the help of $\Delta\varrho$ explicitly, including that in neutral systems (see below). One may now simplify the Coulomb- as well as the exchange-correlation integrals contained in (26) leading to an approximate expression of the total energy which will have a transparent interpretation.

The ansatz (27) splits the two Coulomb terms in (26) into three terms of the structure $\varrho^0\, \varrho^0$, $(\varrho^0 + \Delta\varrho)\, \varrho^0$, and $\Delta\varrho\, \Delta\varrho$. Whereas the first two (and large) terms are taken into account exactly, the last one (in general a small correction) is treated in point charge approximation, i. e. with

$$\Delta\varrho(\mathbf{r}, \mathbf{R}, t) := -\sum_A^{N_\mathrm{i}} Q_A(\mathbf{R}, t)\, \delta(\mathbf{r} - \mathbf{R}_A) \tag{28}$$

where $Q_A(\mathbf{R}, t)$ is the net charge located on the centre A. Consistent with the definition of $\varrho^0(\mathbf{r}, \mathbf{R})$ the point charges Q_A can be obtained with help of the Löwdin population analysis [47]

$$Q_A(\mathbf{R}, t) = Z^0_A - \sum_j^{N_\mathrm{val}} \sum_{\alpha\beta} a^{*j}_{\alpha}(t)\, S^A_{\alpha\beta}(\mathbf{R})\, a^j_\beta(t) \tag{29}$$

where the symmetric matrix $S^A_{\alpha\beta}$ is defined with the square root of the overlap matrix (21a) as

$$S^A_{\alpha\beta}(\mathbf{R}) := \sum_{\gamma_A} \left(S^{1/2}\right)_{\alpha\gamma_A} \left(S^{1/2}\right)_{\gamma_A\beta} \, . \tag{30}$$

In Eq. (30) the sum has to be taken over all atomic orbitals belonging to the centre A.

Any practical application of (or approximation to) DFT is connected with an approximate treatment of the exchange-correlation effects. As a first approximation of a non-adiabatic QMD (and enlighting arguments given below) we replace the td density $\varrho(\mathbf{r}, \mathbf{R}, t)$ in the last term of Eq. (26) as well as in the exchange-correlation potential V_xc, contained in $H_{\alpha\beta}$, by the adiabatic density $\varrho^0(\mathbf{r}, \mathbf{R})$. Together with (28) this leads after some algebra to an approximate total energy of the form

$$E = \sum_{A}^{N_\mathrm{i}} \frac{\mathbf{P}_A^2}{2M_A} + U(\mathbf{R}) + E_\mathrm{coul}\left(\mathbf{R}, a_\alpha^j(t)\right) + \sum_{j}^{N_\mathrm{val}} \sum_{\alpha\beta} {a^*}_\alpha^j(t)\, H_{\alpha\beta}^0\, a_\beta^j(t) \tag{31}$$

with the conservative potential

$$\begin{aligned} U(\mathbf{R}) = & \frac{1}{2} \sum_{A}^{N_\mathrm{i}} {\sum_{B}^{N_\mathrm{i}}}' \frac{Z_A^0 Z_B^0}{|\mathbf{R}_A - \mathbf{R}_B|} \\ & -\frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{\varrho^0(\mathbf{r},\mathbf{R})\varrho^0(\mathbf{r}',\mathbf{R})}{|\mathbf{r}-\mathbf{r}'|} \\ & - \int \mathrm{d}^3 r \, \left[\varrho^0(\mathbf{r},\mathbf{R},t)\right]^2 \frac{\delta\epsilon_\mathrm{xc}[\varrho^0]}{\delta\varrho^0(\mathbf{r},\mathbf{R})} , \end{aligned} \tag{32}$$

and the Coulomb correction

$$E_\mathrm{coul}\left(\mathbf{R}, a_\alpha^j(t)\right) = \frac{1}{2} \sum_{A}^{N_\mathrm{i}} {\sum_{B}^{N_\mathrm{i}}}' \frac{Q_A(\mathbf{R},t) Q_B(\mathbf{R},t)}{|\mathbf{R}_A - \mathbf{R}_B|} . \tag{33}$$

The last term in Eq. (31) still contains the full density but is obtained now with the Hamilton matrix

$$H_{\alpha\beta}^0 = \left\langle \phi_\alpha \left| \hat{t} + V_\mathrm{eff}^0 \right| \phi \right\rangle \tag{34}$$

which does not depend explicitly on time due to the effective potential

$$V_\mathrm{eff}^0(\mathbf{r},\mathbf{R}) = V(\mathbf{r},\mathbf{R}) + \int \mathrm{d}^3 r' \, \frac{\varrho^0(\mathbf{r}',\mathbf{R})}{|\mathbf{r}-\mathbf{r}'|} + V_\mathrm{xc}[\varrho^0](\mathbf{r},\mathbf{R}) . \tag{35}$$

The sense of the upper made approximations becomes now apparent. In the adiabatic limit (automatically contained in the present formalism) the approximate energy (31) has formally the same structure as that used in the tight-binding approximation [49]. Here, however, one has explicit time-dependent coefficients $a_\alpha^j(t)$. In addition, and in striking contrast to the tight-binding method, the matrix elements $H_{\alpha\beta}^0$ and the potential $U(\mathbf{R})$ (in general short range and repulsive, see the structure of (32)) do not contain any free parameter. Owing to the inclusion of the Coulomb term E_coul in (31), charged systems (still a delicate problem in the tight-binding method) can be treated self-consistently as well (see below). In any case, the approximate energy (31) provides a direct link between the (in principle exact) MD combined with DFT and molecular dynamics combined with the tight-binding theory. This is especially so because the lower given equations of motion (37), (38) remain valid (and therefore are consistent with (31)) *independent* of the assumptions or approximations made in calculating the matrix elements $H_{\alpha\beta}^0$ and the potential $U(\mathbf{R})$.

It is worth to note that (31) is still the exact energy for neutral systems in the adiabatic limit.

Two longer calculations lead to the final equations of motion. First, the variation of the action

$$A\left[a_\alpha^j\right] = \int_{t_0}^{t_1} \mathrm{d}t' \left\{ \sum_{j}^{N_\mathrm{val}} \sum_{\alpha\beta} {a^*}_\alpha^j(t') \left\langle \phi_\alpha \left| \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t'} \right| \phi_\beta \right\rangle a_\beta^j(t') - E\left(\mathbf{R}, a_\alpha^j(t')\right) \right\} \tag{36}$$

with respect to ${a^*}_\alpha^j$, i. e. $\delta A/\delta {a^*}_\alpha^j(t) \overset{!}{=} 0$, provides the Kohn-Sham equations ($j = 1, \ldots, N_\mathrm{val}$)

$$\dot{a}_\alpha^j(t) = -\sum_{\beta\gamma} \left(S^{-1}\right)_{\alpha\beta} \left\{ \mathrm{i}\overline{H}_{\beta\gamma} + \sum_{A}^{N_\mathrm{i}} \dot{\mathbf{R}}_A \mathbf{R}_{\beta\gamma}^A \right\} a_\gamma^j(t) . \tag{37}$$

Second, the time derivative of the total energy, i.e. $\mathrm{d}E/\mathrm{d}t \overset{!}{=} 0$, results in the Newton equations

$$\begin{aligned} M_A \ddot{\mathbf{R}}_A = & -\frac{\partial}{\partial \mathbf{R}_A} \left[U(\mathbf{R}) + E_\mathrm{coul}\left(\mathbf{R}, a_\alpha^j(t)\right) \right] \\ & - \sum_{j}^{N_\mathrm{val}} \left\{ \sum_{\alpha\beta} {a^*}_\alpha^j \left(\frac{\partial}{\partial \mathbf{R}_A} H_{\alpha\beta}^0 \right) a_\beta^j \right. \\ & - \sum_{\alpha\beta\gamma\delta} \left[{a^*}_\alpha^j \overline{H}_{\alpha\beta} \left(S^{-1}\right)_{\beta\gamma} \mathbf{R}_{\gamma\delta}^A a_\delta^j \right. \\ & \left. \left. + {a^*}_\alpha^j \left(\mathbf{R}^\mathrm{T}\right)_{\alpha\beta}^A \left(S^{-1}\right)_{\beta\gamma} \overline{H}_{\gamma\delta} a_\delta^j \right] \right\} . \end{aligned} \tag{38}$$

In Eqs. (37) and (38) we have introduced the abbreviation

$$\overline{H}_{\alpha\beta} := H_{\alpha\beta}^0 - \sum_{B}^{N_\mathrm{i}} \Phi_B(\mathbf{R},t)\, S_{\alpha\beta}^B \tag{39}$$

with the potential

$$\Phi_B(\mathbf{R},t) := {\sum_{C}^{N_\mathrm{i}}}' \frac{Q_C(\mathbf{R},t)}{|\mathbf{R}_B - \mathbf{R}_C|} . \tag{40}$$

Owing to the Q_A dependence of $\overline{H}_{\alpha\beta}$ the Kohn-Sham equations (37) are still non-linear. However, in neutral (or slightly charged) systems with delocalized electronic states and therefore negligible charge localization effects (like metal clusters or fullerenes) one may linearize (and therefore extremly simplify the numerical solution of) the Kohn-Sham equations (37) because the assumption $Q_A \equiv 0$ and hence $\overline{H}_{\alpha\beta} \equiv H_{\alpha\beta}^0$ is expected to be a good approximation. This, however, must be checked carefully. For charged (and especially highly charged) systems one is confronted in any case with the non-linear Kohn-Sham problem (37).

A numerical implementation of the equations of motion (37), (38) and first non-adiabatic studies of cluster fragmentation and collisions with clusters will be presented elsewhere [40].

In the next section we study non-adiabatic effects for a model system using the exact Eqs. (20), (23).

4 Case study: one-particle model

In order to obtain a first insight into the non-adiabatic interplay between classical motion and electronic excitations, we study here the simplest case – the collision of a proton with a hydrogen atom H^++H. To make the approach as transparent as possible only central collisions are considered and a minimal basis set that allows for non-adiabatic transitions is used.

The (trivial) case of a one-electron system can be treated with the exact equations of motion (20), (23) by omitting the Hartree and exchange-correlation terms in the “effective” potential (14). In that case the single-particle “Kohn-Sham orbital” (19) corresponds to the one-particle wavefunction $\psi(\mathbf{r}, t)$. Assuming the nuclei to be located on the z–axis at the relative distance R, one has

$$V_{\text{eff}}(\mathbf{r}, t) \equiv V(\mathbf{r}, R) = \frac{-1}{|\mathbf{r} + \mathbf{e}_z R/2|} + \frac{-1}{|\mathbf{r} - \mathbf{e}_z R/2|} \,. \tag{41}$$

Instead of an LCAO-ansatz (24) we use here the molecular or adiabatic basis $\{\psi_n(\mathbf{r}, R)\}$ for the representation of $\psi(\mathbf{r}, t)$ with the ansatz

$$\psi(\mathbf{r}, t) = \sum_{n=1}^{4} \psi_n(\mathbf{r}, R)\, \mathrm{e}^{-\mathrm{i} \int^t \mathrm{d}t' \varepsilon_n(R)}\, a_n(t) \,. \tag{42}$$

The basis functions $\psi_n(\mathbf{r}, R)$ as well as the energy levels $\varepsilon_n(R)$ are obtained from the solution of (A10) using intentionally the smallest possible (symmetric) set of atomic hydrogen orbits ϕ_α in (A9) that may lead to excitations, i. e., the 1s- and 2s-functions centered on both nuclei. The coefficients a_1 and a_3 belong to the gerade states whereas a_2 and a_4 are the coefficients of the ungerade states. This choice provides a very transparent correlation diagram with one avoided crossing between the two ungerade states $n = 2$ and $n = 4$ at a distance of about $R_0 \approx 0.65$ a.u. (see Fig. 1). Therefore electronic excitations are expected to be important at centre-of-mass incident energies E_{cm} larger than about $E_{\text{cm}} \gtrsim 1/R_0 + \frac{1}{2}\left(\varepsilon_1(R_0) - \varepsilon_1(\infty) + \varepsilon_2(R_0) - \varepsilon_2(\infty)\right) \approx 32\,\text{eV}$ which corresponds to the BO energy at $R = R_0$ of the model system with half-filled states ε_1 and ε_2 (see below). The real crossing between the gerade ($n = 3$) and ungerade state ($n = 2$) does not contribute to excitations owing to the different symmetry.

With the adiabatic basis (42) the matrices (21) simplify to

$$S_{nm} = \delta_{nm} \tag{43a}$$

$$H_{nm} = \varepsilon_n \delta_{nm} \tag{43b}$$

$$R_{nm} = \left\langle \psi_n \left| \frac{\partial}{\partial R} \psi_m \right. \right\rangle = -\left(R^{\mathrm{T}}\right)_{nm} \tag{43c}$$

and the equations of motion (20), (23) become

$$\dot{a}_n = -\dot{R} \sum_m R_{nm} \mathrm{e}^{-\mathrm{i} \int \mathrm{d}t' (\varepsilon_m - \varepsilon_n)}\, a_m \tag{44}$$

$$\mu \ddot{R} = 1/R^2 - \sum_n a_n^* \left(\frac{\partial}{\partial R} \varepsilon_n \right) a_n + \sum_{nm} a_n^* (\varepsilon_n - \varepsilon_m) R_{nm} a_m \mathrm{e}^{-\mathrm{i} \int \mathrm{d}t' (\varepsilon_m - \varepsilon_n)} \,. \tag{45}$$

with $\mu = 918$ a.u. the reduced mass of the system. They are solved with the initial conditions $a_1{}^2(t_0) = a_2{}^2(t_0) = 1/2$ and $a_3{}^2(t_0) = a_4{}^2(t_0) = 0$, which ensure that the electron is initially located at one proton in its ground state.

The results following from the self-consistent solution of (44) and (45) are compared with those of two other extreme cases:

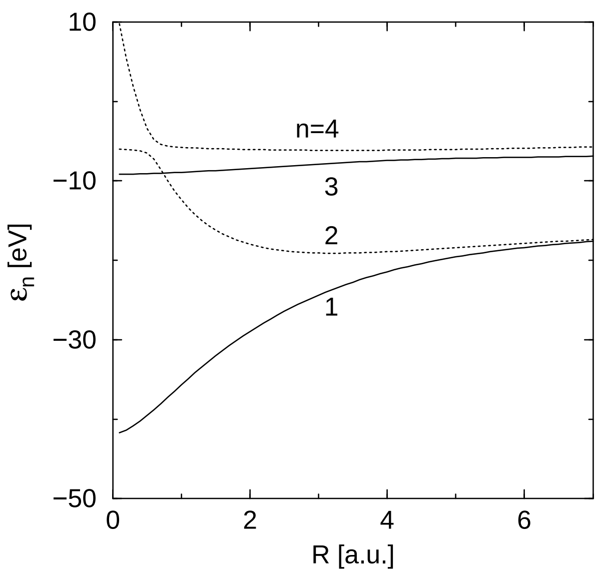

Fig. 1. Correlation diagram of the model system H$^+$+H. The adiabatic single-particle energies ε_n ($n = 1, \ldots, 4$) are plotted as a function of the distance between the nuclei R. The molecular states with an ungerade (*gerade*) symmetry are drawn by dotted (*solid*) lines. Note the avoided crossing at $R_0 \approx 0.65$ a.u. between the ungerade states

i) Equation (45) is solved with fixed coefficients

$$\dot{a}_n \equiv 0, \qquad a_n(t) \equiv a_n(t_0) \,. \tag{46}$$

This provides a classical trajectory $R(t)$ on the BO ground-state surface, i. e., that of an adiabatic QMD. The comparison with the self-consistent trajectory allows us then to study the influence of the non-adiabatic effects on the classical motion.

ii) Equation (44) is solved with a classical Coulomb trajectory

$$\mu \ddot{R} = 1/R^2 \,. \tag{47}$$

This corresponds to the classical-trajectory approximation (or “impact-parameter method”) of the ion-atom scattering theory [44]. The comparison of the electronic excitation energies calculated self-consistently and within the approximation (47) reveals the importance of the self-consistent coupling between the trajectory and the dynamics of the quantum system.

In Fig. 2, the classical trajectories $R(t)$ and the corresponding kinetic energies of the relative motion $E_{\text{kin}} = \frac{\mu}{2}\dot{R}^2$ are plotted as a function of time for all three cases (non-adiabatic QMD, adiabatic QMD, and Coulomb trajectory). The chosen bombarding energy is $E_{\text{cm}} = 45$ eV. The classical trajectories $R(t)$ are very similiar in all three types of calculation. The Coulomb trajectory, however, has a somewhat smaller stiffness and, more importantly, a slightly larger distance of closest approach (located at $t = 0$ in Fig. 3) as compared to the two QMD trajectories. It is just this effect which may induce large differences in the calculated electronic excitation energies if different trajectories are used to follow the quantum system by Eq. (44) (see discussion for Fig. 4).

The different classical dynamics for the three cases considered becomes more apparent in the behavior of the ki-

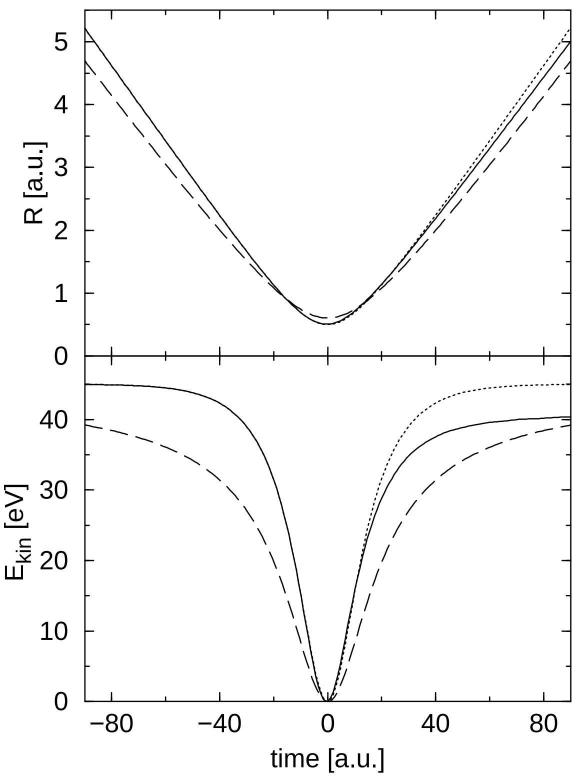

Fig. 2. Computed relative distance between the ions $R(t)$ and the corresponding kinetic energy of the relative motion $E_{\rm kin} = \frac{\mu}{2}\dot{R}^2$ as a function of time for three different calculations: non-adiabatic QMD (*solid line*), adiabatic QMD (*dotted*), and Coulomb trajectory (*dashed*). In all cases the bombarding energy is $E_{\rm cm}$ = 45 eV and the impact parameter is b=0

netic energies $E_{\rm kin}(t)$. While the classical motion in the adiabatic QMD and for the Coulomb scattering is strongly conservative (manifested by completely symmetric curves with respect to the point of closest approach) the non-adiabatic QMD leads to a mean energy loss of about $\Delta E_{\rm kin}/E_{\rm cm} \approx$ 10% (lower part of Fig. 2). This energy is stored into electronic excitations.

A more detailed insight into the classical dynamics can be obtained from the calculated forces (Fig. 3). In the upper part of Fig. 3 the forces originating only from the electron-ion coupling $F_{\rm ion-el}$, i. e. that without the Coulomb term $1/R^2$ in Eq. (45), for the two QMD cases are presented while in the lower part the total forces (45) are plotted as a function of time for all three cases. Because of the simplicity of the chosen model system, all details of the different behavior of the forces can be physically understood in connection with with the correlation diagram of Fig. 1 and the trajectories of Fig. 2.

Note first that initially the states n = 1, 2 are filled with one-half probability. In the adiabatic QMD this occupation remains unchanged for all times and the system moves on the BO surface $1/R + \frac{1}{2}\big(\varepsilon_1(R) - \varepsilon_1(\infty) + \varepsilon_2(R) - \varepsilon_2(\infty)\big)$ of the model system. In the non-adiabatic QMD remarkable changes in the occupation can be expected where the system passes through the avoided crossing at R_0 = 0.65 a.u. During the approach phase the forces $F_{\rm ion-el}$ of the adiabatic and non-adiabatic QMD are identical and attractive. This results

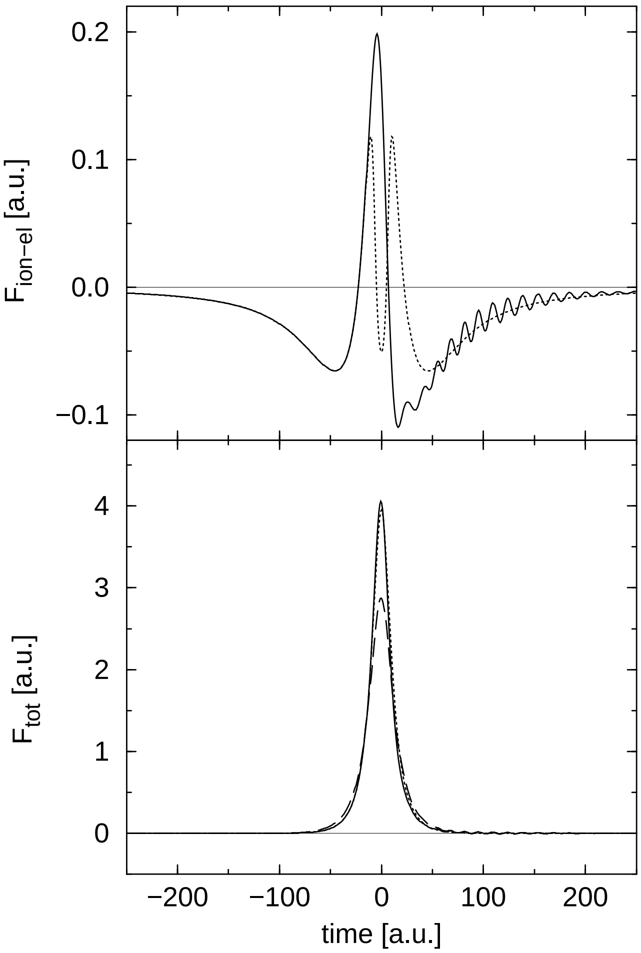

Fig. 3. Calculated forces mediated by the ion-electron coupling $F_{\rm ion-el}(t)$, i. e. that without the $1/R^2$ term in Eq. (45) (*upper part*), and total forces $F_{\rm tot}$ (*lower part*) for the same trajectories as shown in Fig. 2: *solid lines:* non-adiabatic QMD, *dotted lines:* adiabatic QMD, *dashed line:* Coulomb trajectory

from the larger decrease of ε_1 as compared to the repulsive ε_2–state (Fig. 1). As the systems approach closer, the repulsive component resulting from ε_2 dominates leading to repulsive forces in both cases. The forces begin to differ in the region around the classical turning point. The adiabatic one (which must be completely symmetric with respect to t = 0) becomes attractive (and again repulsive) around $t \approx 0$ because of the decreasing slope of ε_2 around R_0. The non-adiabatic force continue to act repulsively, which is clearly due to the electronic transitions from n = 2 to n = 4 around this point (note the repulsive behaviour of ε_4 in Fig. 1). On the way "back" it becomes attractive again, with typical oscillations resulting from the energy differences between the ε_2 and ε_4 states and mediated by the last term in Eq. (45). These oscillations are damped out owing to the vanishing coupling matrix R_{mn} (for increasing R) contained in this term.

Although there is a large difference in the time behavior of the ion-electron forces $F_{\rm ion-el}$ in the two QMD cases, the total forces are strongly dominated by the Coulomb term $1/R^2$ in Eq. (45). This can be seen in the lower part of Fig. 3

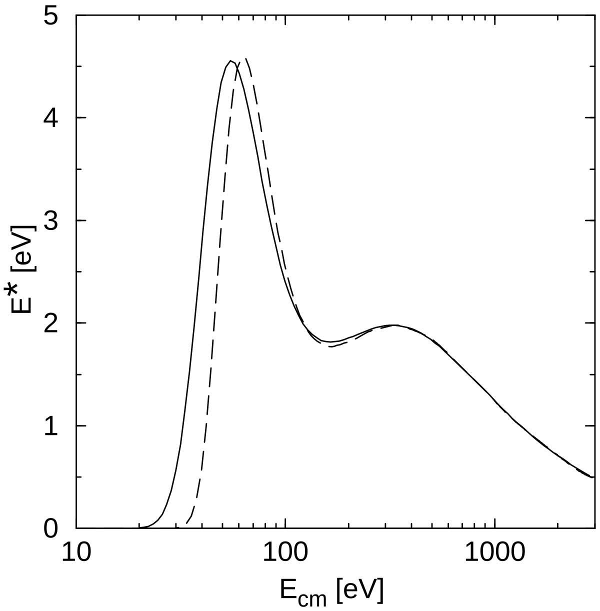

Fig. 4. Calculated mean electronic excitation energies $E^\star$ as function of the bombarding energy E_{cm} for the model system H^++H (*b*=0). The *solid line* corresponds to the self-consistent non-adiabatic QMD calculation, whereas the *dashed line* is obtained with a Coulomb trajectory

where for all three types of calculation the total forces F_{tot} are drawn as a function of time. Whereas the two QMD forces are practically equal, the pure Coulomb force is somewhat less repulsive around $t = 0$ and therefore leads to a slightly different trajectory (cf. discussion for Fig. 2). The quantum system, however, reacts very sensitively to fine differences in the classical trajectories.

This is demonstrated in Fig. 4 where the calculated electronic excitation energies $E^\star$ as a function of the bombarding energy E_{cm} are plotted for a self-consistent non-adiabatic calculation and for the solution of (44) with a pure Coulomb trajectory (47). Obviously, in the region between $E_{\mathrm{cm}} \approx 20 \ldots 100\,\mathrm{eV}$ there are large differences in the calculated values $E^\star$ for both cases demonstrating the importance of a self-consistent trajectory for the dynamics of the quantum system. For energies $E_{\mathrm{cm}} \gtrsim 100\,\mathrm{eV}$ the trajectories are dominated by the Coulomb repulsion only and (as expected) the results coincidence. Finally, we remark that the double-humped behavior of $E^\star$ as a function of E_{cm} is due to the interference between both electronic transitions during the approach and the recoil phases of the relative motion. Owing to the simplicity of our model, with only one avoided crossing, this can be understood qualitatively within the Landau-Zener-Stückelberg theory [44] too.

5 Summary and outlook

The basic formalism of a non-adiabatic QMD is presented. Based on td DFT, exact equations of motion are derived which describe self-consistently and simultaneously classical atomic motion and quantum electronic *dynamics*. They are valid for any basis for the representation of the td Kohn-Sham orbitals.

In the framework of an LCAO ansatz approximate equations of motion are derived. In the adiabatic limit they lead to well known tight-binding-like equations, but are basically different from the tight-binding theory because the microscopic part of these equations is still based on the ab-initio level and does not contain free parameters or parameterized matrix elements. In addition, the consistent treatment of charged systems causes no problems.

As a case study, non-adiabatic effects are studied in collisions between a proton and a hydrogen atom using (in that case) an adiabatic minimal basis which makes the equations of motion simple and the interpretation of the results transparent. For the chosen model system, non-adiabatic effects are found to be important in the bombarding energy range between about 20 eV and 100 eV. As a possible outlook for future studies in this field, the non-adiabatic QMD can be a good candidate to study ion-atom collisions for real many-electron systems (e. g., C^++C with 7 active and correlated electrons [51]) where the present status of ion-atom scattering theory fails [44, 52].

As the main field of applications of the non-adiabatic QMD formalism, however, we intend to investigate dynamical processes with atomic clusters, namely, fragmentation of (highly charged) clusters as well as collisions of ions (atoms) with clusters (cluster-ions) and cluster-cluster collisions [40, 51].

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Appendix

The coupled Eqs. (20) and (23) of the non-adiabatic QMD should contain as limit the adiabatic QMD if electronic transitions are unlikely or unimportant. To demonstrate this, we first derive the corresponding coupled equations for an *adiabatic* QMD combined with static DFT using local basis sets for the KS orbitals $\psi_n(\mathbf{r};\mathbf{R})$. The index n numerates the static single-particle levels.

The starting point is the density $\varrho(\mathbf{r})$ which can be represented in the formulation of Kohn-Sham [50] by

$$\varrho(\mathbf{r}) = \sum_{n}^{N_e} |\psi_n(\mathbf{r};\mathbf{R})|^2 \ . \tag{A1}$$

The total energy of the system including the classical part is given by

$$E = H_{\mathrm{coll}} + E_{\mathrm{el}}[\psi_n](\mathbf{R}) \tag{A2}$$

with H_{coll} according to (2a) and the electronic part

$$E_{\mathrm{el}}[\psi_n](\mathbf{R}) = \sum_{n}^{\mathrm{occ}} \left\langle \psi_n \,\middle|\, \hat{t} \,\middle|\, \psi_n \right\rangle + \int \mathrm{d}^3r\, \varrho(\mathbf{r}) \left[V(\mathbf{r},\mathbf{R}) + \frac{1}{2} \int \mathrm{d}^3r'\, \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right] + E_{\mathrm{xc}}[\varrho] \tag{A3}$$

which determines the Born-Oppenheimer surface of the electronic ground state. Minimization of the functional (A3) with respect to $\psi_n^*(\mathbf{r};\mathbf{R})$ leads to the Kohn-Sham equations

$$\left\{\hat{t} + V_{\mathrm{eff}}(\mathbf{r},\mathbf{R})\right\} \psi_n(\mathbf{r};\mathbf{R}) = \varepsilon_n(\mathbf{R})\, \psi_n(\mathbf{r};\mathbf{R}) \tag{A4}$$

with the effective potential

$$V_{\mathrm{eff}}(\mathbf{r},\mathbf{R}) = V(\mathbf{r},\mathbf{R}) + \int \mathrm{d}^3 r' \, \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{\mathrm{xc}}[\varrho](\mathbf{r}) \tag{A5}$$

including the exchange-correlation part

$$V_{\mathrm{xc}}[\varrho](\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[\varrho]}{\delta \varrho(\mathbf{r})} \,. \tag{A6}$$

In the adiabatic theory the forces acting on the ions can be derived straightforwardly by differentiation of (A2) with (A3) with respect to $\mathbf{R}_A$ leading to the equations of motion ($A = 1, \ldots, N_i$)

$$\begin{aligned} M_A \ddot{\mathbf{R}}_A = &-\frac{\partial}{\partial \mathbf{R}_A} \sum_B{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \\ &- \int \mathrm{d}^3 r \, \varrho(\mathbf{r}) \frac{\partial}{\partial \mathbf{R}_A} V(\mathbf{r},\mathbf{R}) + \mathbf{F}_A \end{aligned} \tag{A7}$$

where the second term is the usual Hellman-Feynman force and the third term is formally given by

$$\begin{aligned} \mathbf{F}_A = &-\sum_n \left\{ \int \mathrm{d}^3 r' \, \frac{\partial \psi_n^*(\mathbf{r}';\mathbf{R})}{\partial \mathbf{R}_A} \frac{\delta E_{\mathrm{el}}[\psi_n]}{\delta \psi_n^*(\mathbf{r}';\mathbf{R})} \right. \\ &\left. + \int \mathrm{d}^3 r' \, \frac{\partial \psi_n(\mathbf{r}';\mathbf{R})}{\partial \mathbf{R}_A} \frac{\delta E_{\mathrm{el}}[\psi_n]}{\delta \psi_n(\mathbf{r}';\mathbf{R})} \right\} \\ = &-\sum_n \left\{ \left\langle \frac{\partial \psi_n}{\partial \mathbf{R}_A} \middle| \hat{t} + V_{\mathrm{eff}} \middle| \psi_n \right\rangle \right. \\ &\left. + \left\langle \psi_n \middle| \hat{t} + V_{\mathrm{eff}} \middle| \frac{\partial \psi_n}{\partial \mathbf{R}_A} \right\rangle \right\} \,. \end{aligned} \tag{A8}$$

This force vanishes for the *exact* solutions of (A4) only. If the Kohn-Sham functions are expanded in a local basis $\{\phi_\alpha\}$

$$\psi_n(\mathbf{r};\mathbf{R}) = \sum_\alpha \phi_\alpha(\mathbf{r};\mathbf{R})\, C_{\alpha n}(\mathbf{R}) \tag{A9}$$

the KS equations (A4) reduce to algebraic equations

$$\sum_\beta \left\{ H_{\alpha\beta} - \varepsilon_n S_{\alpha\beta} \right\} C_{\beta n} = 0 \,. \tag{A10}$$

Without loss of generality one can assume real expansion coefficients $C_{\alpha n}$. The matrices $H_{\alpha\beta}$ and $S_{\alpha\beta}$ are defined as in (21). Using the ansatz (A9), the force (A8) alters to

$$\begin{aligned} \mathbf{F}_A = -\sum_n \sum_{\alpha\beta} \Bigg\{ & C_{n\alpha} \left\langle \frac{\partial}{\partial \mathbf{R}_A} \phi_\alpha \middle| \hat{t} + V_{\mathrm{eff}} \middle| \phi_\beta \right\rangle C_{\beta n} \\ & + C_{n\alpha} \left\langle \phi_\alpha \middle| \hat{t} + V_{\mathrm{eff}} \middle| \frac{\partial}{\partial \mathbf{R}_A} \phi_\beta \right\rangle C_{\beta n} \\ & + \left(\frac{\partial}{\partial \mathbf{R}_A} C_{n\alpha} \right) H_{\alpha\beta} C_{\beta n} \\ & + C_{n\alpha} H_{\alpha\beta} \left(\frac{\partial}{\partial \mathbf{R}_A} C_{\beta n} \right) \Bigg\} \,. \end{aligned} \tag{A11}$$

With the normalization condition for the KS functions

$$\langle \psi_n | \psi_n \rangle = \textstyle\sum_{\alpha\beta} C_{n\alpha} S_{\alpha\beta} C_{\beta n} \overset{!}{=} 1$$

and rearranging some terms in (A7) and (A11) one obtains finally

$$\begin{aligned} M_A \ddot{\mathbf{R}}_A = &-\frac{\partial}{\partial \mathbf{R}_A} \sum_B{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \\ &- \sum_n \sum_{\alpha\beta} \Bigg\{ C_{n\alpha} \left(\frac{\partial}{\partial \mathbf{R}_A} H_{\alpha\beta} \right) C_{\beta n} \\ &\quad - C_{n\alpha} \left\langle \phi_\alpha \middle| \frac{\partial}{\partial \mathbf{R}_A} (V_{\mathrm{eff}} - V) \middle| \phi_\beta \right\rangle C_{\beta n} \\ &\quad - C_{n\alpha} \varepsilon_n \left(\frac{\partial}{\partial \mathbf{R}_A} S_{\alpha\beta} \right) C_{\beta n} \Bigg\} \end{aligned} \tag{A12}$$

the equations of motion for the adiabatic QMD. They have to be solved simultaneously with Eq. (A10) and provide the classical dynamics of the ions on the Born-Oppenheimer ground state surface.

It remains to show that the non-adiabatic equations of motion (20) and (23) reduce to the adiabatic ones if electronic transitions are neglected. In this case the initial conditions for the amplitudes $a_\alpha^j(t{=}0)$ must be given by the adiabatic coefficients $C_{n\alpha}$ with $n \equiv j$ ($n = 1, \ldots, N_e$) and their time dependence is the trivial one of a stationary single-particle state

$$a_\alpha^n(t) = \exp\left(-\mathrm{i}\, \varepsilon_n(\mathbf{R})\, t\right)\, C_{\alpha n}(\mathbf{R}) \,. \tag{A13}$$

Note that for the solution of the time-dependent KS equations (20) $\mathbf{R}$ has to be considered time-independent which is valid only if the second term on the r. h. s. of (20) remains small as compared to the first one, or in other words, if the time scales of the classical motion and that of the quantum system are completely separated. Under these circumstances Eq. (20) reduces together with (A13) to the secular equation (A10). Using this secular equation (and the corresponding transposed one) multiplied by the inverse of the overlap matrix $\left(S^{-1}\right)_{\alpha\beta}$ from the left (and the right) one obtains for the non-adiabatic force (23b)

$$\begin{aligned} M_A \ddot{\mathbf{R}}_A = &-\frac{\partial}{\partial \mathbf{R}_A} \sum_B{}' \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \\ &- \sum_n^{\mathrm{occ}} \sum_{\alpha\beta} \Bigg\{ C_{n\alpha} \left(\frac{\partial}{\partial \mathbf{R}_A} H_{\alpha\beta} \right) C_{\beta n} \\ &\quad - C_{n\alpha} \left\langle \phi_\alpha \middle| \frac{\partial}{\partial \mathbf{R}_A} (V_{\mathrm{eff}} - V) \middle| \phi_\beta \right\rangle C_{\beta n} \\ &\quad - \left[C_{n\alpha} \varepsilon_n \mathbf{R}_{\alpha\beta}^A C_{\beta n} + C_{n\alpha} \left(\mathbf{R}^{\mathrm{T}}\right)_{\alpha\beta}^A \varepsilon_n C_{\beta n} \right] \Bigg\} \end{aligned} \tag{A14}$$

which is equivalent to (A12) because $\mathbf{R}_{\alpha\beta}^A + \left(\mathbf{R}^{\mathrm{T}}\right)_{\alpha\beta}^A = \frac{\partial}{\partial \mathbf{R}_A} S_{\alpha\beta}$.

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