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FEATURE ARTICLE

Time-Dependent Many-Electron Treatment of Electronic Energy and Charge Transfer in Atomic Collisions

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Electronic energy and charge transfer in atomic collisions are described within a first principles molecular dynamics including an explicit treatment of electronic motions, in terms of time-dependent many-electron wavefunctions. Following an overview of treatments in the literature based on expansions in sets of adiabatic and diabatic electronic states, this article emphazises the use of time-dependent molecular orbitals and time-dependent Hartree−Fock states. Three fundamental problems are identified in a first principles dynamics, relating to the calculation of state-to-state transition probabilities and expectation values, to the translational motion of electrons moving with nuclei, and to the coupling of fast electronic transitions and slow nuclear motions. Solutions to these problems are described on the basis of an eikonal representation of wavefunctions and sums over initial conditions, of the use of traveling atomic functions to expand molecular orbitals, and of a relax-and-drive propagation procedure for electrons and nuclei. Examples are presented of applications in ion−atom and ion−surface collisions, relating to electronic excitation and charge transfer, orbital polarization, and light emission during collisions.

1. Introduction

The purpose of this feature article is to present our treatment of the first principles molecular dynamics of systems undergoing electronic rearrangement and excitation, including an explicit description of electronic motions. A time-dependent description is appealing on conceptual grounds because it provides new insight on the nature of electronic motions during molecular interactions and on their interaction with light and supplements the more usual studies of transitions between stationary states of reactants and products. It can also serve in the interpretation and prediction of new experiments where light pulses are used to investigate femtosecond dynamics and spectra.[1−5] This article gives an overview of related work in the past ten years, but it does not attempt to review the field. This is very active, and involves contributions from several areas of chemistry and physics, relating to molecular spectra and dynamics, atomic collisions of interest in accelerators and plasmas, planetary atmospheres and interstellar media, molecular dynamics in solution and surfaces, etc. The present article further does not cover the first principles molecular dynamics of extended systems, which involve dissipative phenomena and where similar methods can be applied.

Our aims for a first principles quantum molecular dynamics approach are

- To gain insight on what electrons do during interactions, going beyond the calculation of state-to-state transition probabilities to describe the time evolution of electrons. This includes the calculation of auxiliary quantities, such as atomic populations, and of observables, such as intensities of light emission, as they evolve during interactions.
- To develop a treatment of the nuclear motions that incorporates from the outset couplings to electronic transitions so that the molecular dynamics can be generated with similar methods for systems with few or many atoms, and for systems with small or large total energy.
- To develop a treatment of electronic rearrangement in molecular interactions that can be directly applied to series of compounds and systems with several active electrons, instead of solving first for potential energy functions and couplings for each particular system.

The emphasis in this work is on the time dependence of electronic states induced by nuclear motions, as described by many-electron theories. It is therefore closely related to areas of quantum chemistry as well as quantum molecular dynamics. The time-dependence of many-electron states may be described by means of the Born−Oppenheimer states derived by first fixing nuclei,[6−10] or at a deeper level by constructing time-dependent molecular orbitals. The advantage of the second approach is that it provides new insight on the dynamics of electrons, not apparent when the Born−Oppenheimer states are introduced.

Recent quantum chemical approaches to electronic structure have been very successful. They have emphasized the development of general computer programs that can be applied to a wide range of molecular species and their interactions and have been systematically improved until they can now provide useful and accurate results that compete with experimental data. The standard approach to molecular dynamics is to divide the problem into two stages, relating firstly to electronic structure and secondly to the nuclear dynamics.[11−15] This involves the

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calculation of electronic states $\Phi_I(q;Q)$, where q and Q are the collections of electronic and nuclear (or atomic core) variables, of potential energy surfaces (PESs) $E_I(Q)$, of their couplings $\langle \Phi_I/\partial\Phi_J/\partial Q\rangle$ due to the displacement of nuclei (the Born–Oppenheimer momentum couplings), and of the structural dependence of properties such as electric transition dipoles $D_{IJ}(Q)$.[16–20] This approach succeeds on two accounts. It can be applied to many different species, and it can be made accurate enough to provide relevant PESs properties such as locations of minima and saddle points, curvatures at minima, and transition energy barriers for ground electronic states. Similar generality and accuracy have not been available in dynamics studies involving electronically excited systems. Here the PESs and couplings have been parametrized as needed in each special case, and then the dynamics involving coupled PESs have been described with a variety of methods from purely quantal to classical ones, chosen for their feasibility. This approach becomes progressively more difficult and less insightful as the number of nuclear degrees of freedom increases, and PESs must be pictured in many dimensions.

Extensive work has been done in recent years combining quantum chemical and molecular dynamics methods for ground electronic states, to achieve some of the generality missing in the past. The Car–Parrinello method[21,22] introduced a variational procedure with a Lagrangian density based on Hamiltonian density functionals and an electronic amplitude evolving with an artificial mass chosen to dampen electronic oscillations induced by the moving nuclei, to generate a dynamic simulated annealing of electronic motions. This leads to an efficient procedure to describe the dynamics of systems in their electronic ground state. Another successful approach for systems remaining in single electronic states has been the so-called Born–Oppenheimer molecular dynamics approximation, which simultaneously solves for the motion of nuclei and a single electronic state using a variety of many-electron descriptions. These have been based on density functional as well as methods going beyond the Hartree–Fock approximation, such as the generalized valence bond approximation, to provide useful PESs during the molecular motions.[23–30] Here the electronic wavefunction is obtained at each nuclear configuration from a quantum chemical calculation that does not depend on the nuclear velocities. In our notation, known positions $Q(t)$ and electron densities $\rho(t)$ are advanced to time $t + \Delta t$ by using the classical equations for accelerations $\ddot{Q}$,

$$M\ddot{Q} = -\partial V_{ii}/\partial Q - \int \mathrm{d}q\, [\rho(q;Q)\, \partial V_{ei}(q;Q)/\partial Q]_{Q(t)} \quad (1)$$

where V_{ii} and V_{ei} are the ion–ion and electron–ion Coulomb interactions, and by numerically calculating the electronic state, and therefore ρ, at the new conformation.

Extensions of molecular dynamics to incorporate electronic transitions by explicitly calculating the electronic states during interactions, in a first principles molecular dynamics, have only recently been developed, aided by the increasing power of computers and the development of efficient algorithms for electronic structure calculations. The time-dependent molecular wavefunction is given by an expansion in electronic states,

$$\Psi(q,Q,t) = \sum_I \Phi_I(q;Q)\, F_I(Q,t) \quad (2)$$

with coefficient functions F_I describing the quantal nuclear motion over time. The electronic states may be chosen for convenience to be the adiabatic Born–Oppenheimer states or some diabatic states obtained by transformations that simplify the dynamics.[31–34] The computational effort can be very large when a system has many atoms or if one needs for example a very accurate electronic description of transition states. Therefore, great care is needed to select the combination of electronic structure and molecular dynamics methods to be used.

A brief discussion of the computational choices for the nuclear dynamics indicates their advantages and disadvantages. A general approach for stationary states, which can be made as accurate as it is affordable, is the coupled-channels expansion method where a stationary molecular wavefunction starting in scattering state $\alpha = (\vec{k}_I, I)$ is expanded in electronic states, $\Psi_\alpha^{(+)}(q,Q) = \sum \Phi_I(q;Q)\, F_\alpha^{(+)}(Q)$, and the coefficient functions describe a nuclear scattering state with outgoing waves.[11,15,17,35–40] This appears to be the most accurate method but is limited by its large computational cost, which increases geometrically with the number of coupled channels and is not practical for many degrees of freedom (many-atom systems require the calculation of electronic states for all relevant nuclear conformations, i.e., over the range of $F^{(+)}$) or for high total energies of the systems (i.e., many electronic excited states). The alternative has been to introduce time-dependent treatments[41–44] and to describe the nuclear motions with wavepackets, or in in some classical or semiclassical approximation, so that electronic states are needed only along nuclear trajectories specified by position and conjugated momentum variables $\bar{Q}(t)$ and $\bar{P}(t)$. One such approach is the surface hopping approximation for many-atom systems and its extensions.[45–52] This provides a prescription for making transitions between potential energy surfaces at crossings or avoided crossings in such a way that there is no need to know in advance where the transitions would occur and gives a stochastic picture correct on the average for the electronic transition probabilities, obtained by adding over a discrete set of initial conditions. Treatments based on semiclassical or WKB wavefunctions in each electronic state and on wavefunction matching near crossings or avoided crossings have been developed by several groups to account for quantal phase interference, although they generally require preliminary insight about the regions of the nuclear motion phase space where electronic transitions may occur and have therefore been applied mostly to few-atom systems.[14,15,53,54] Turning to methods applicable to many- as well as few-atom systems, the best candidates so far have relied on expansions in localized wavepackets,[44,55–62] path integral methods,[28,30,41,63–65] discrete variable representations,[66,67] and short-wavelength or eikonal methods for electronically diabatic phenomena.[34,68–70,71–73] Expansion and grid methods lead to electronic probability amplitudes that depend only on time, for example, expanding the time-dependent nuclear wavefunctions on the basis of localized functions (e.g., Gaussians $g_j(Q,t)$) as in $F_I(Q,t) = \sum g_j(Q,t)\, C_{jI}(t)$ or discretizing the nuclear coordinates over a grid $\{Q_j\}$ to work with functions $A_{jI}(t) = F_I(Q_j,t)$.[74,75]

The combination of semiclassical methods with electronic structure calculations require some sort of integration over initial values of nuclear positions and momenta, or initial phase space. This relates to the early work on semiclassical molecular dynamics[76,77] and the eikonal treatment of scattering amplitudes[15,34,69,78] and has been reactivated in recent years with developments of cellular dynamics[59,79,80] and a variety of other initial value methods[56,69,77,81–85] that appear quite promising for first principles treatments of molecular dynamics. Another common aspect of semiclassical treatments is the need for simultaneous propagation of electronic amplitudes and nuclear trajectories $\bar{Q}(t)$. This can be done numerically by solving the coupled time-dependent Schroedinger and Hamiltonian equations or using a purely Hamiltonian formulation where real and imaginary parts of the complex electronic amplitudes $C_{jI}(t)$ play the role of position-like and momentum-like variables.[86−88] This Hamiltonian (or symplectic) treatment can be generalized in a mathematically elegant way in terms of coherent states[89−92] and has been applied to molecular dynamics.[72,93] Path integral methods have been implemented to do calculations of molecular dynamics, using centroid approximations, and numerical techniques for the integration of rapidly oscillating exponentials.[65,94−96]

The combination of electronic structure and dynamics introduces new aspects into the molecular orbital and many-electron treatments of molecular interactions. One of them is that the molecular orbitals must be allowed to take complex values to satisfy the time-dependent Schroedinger equation for electronic states with nonstationary initial conditions. Another more subtle aspect is that the atomic orbitals must move with the nuclei on which they are located. In effect, the momentum couplings between electronic states turn into integrals of the form $\langle\Phi_I|\partial\Phi_J/\partial t\rangle$ when trajectories are used. Given molecular orbitals as combinations of atomic orbitals χ_ν, it follows that the coupling derivative leads to one-electron integrals $\langle\chi_\nu|\partial\chi_{\nu'}|\partial t\rangle$, where ν and ν' refer to the same nucleus n. Such integrals do not vanish as nucleus n is removed to large distances with velocity $\vec{v}_n$, and ignoring this leads to spurious intra-atomic orbital couplings at large distances. The problem is present at both high and low collision energies and must be considered when looking into collision-induced excitation or deexcitation of species and into state-to-state transition probabilities. This was first identified as a problem and given a solution in terms of electron translation factors $T(\vec{r},t;\vec{v}_n)$ and expansions in traveling atomic functions $\xi_\nu(\vec{r},t) = \chi_\nu(\vec{r})\ T(\vec{r},t)$ in pioneering work relating to fast atomic collisions[97,98] and has been investigated and applied to collision-induced charge rearrangement within molecular orbital and atomic orbital descriptions.[15,99−103]

To complete this brief overview, it is worth mentioning that extensions of the wave mechanical treatments of molecular dynamics are possible using density functions $\Gamma(q,Q,q',Q',t)$,[104,105] which appear suitable for treatments of coherence (or decoherence in large systems) and also allow for semiclassical approximations.

Our interest in time-dependent many-electron treatments of molecular interactions derived from a study of ion−atom collisions using a time-dependent variational principle we introduced for state-to-state transitions.[106−108] It considered the applicability of the time-dependent Hartree−Fock (TDHF) approximation and its limitations for collisions involving more than one electron transfer (i.e., several final charge states), and it provided an extension of TDHF in terms of forward and backward evolving TDHF states.

In our treatment of molecular dynamics from first principles, we have introduced time-dependent molecular orbitals and TDHF as well as multiconfiguration (MC) TDHF many-electron states.[109−113] By analogy with time-independent MC-HF methods,[114−116] we have developed the equations and computational aspects required to couple the electronic rearrangements to the motion of nuclei, while allowing for the quantal nature of electronic transitions and quantal features of nuclear motions such as wavefunction phase interference within an eikonal representation.

We have done this using the methodology already developed in quantum chemistry: molecular orbitals formed from combinations of atomic functions, determinantal states, the available algorithms for calculation of one- and two-electrons integrals, etc. We have also incorporated aspects absent in quantum chemistry and relating to moving nuclei: electron translation factors, traveling atomic basis functions, and velocity-dependent Hamiltonian operators. The implementation of a treatment along the lines we have described involves three fundamental problems:

- Calculating state-to-state transition probabilities and expectation values of properties for systems with complicated sequences of electronic rearrangements along nuclear paths, from our knowledge of eikonal wavefunctions constructed from those paths.
- Accounting for the translational motion of electrons moving with the nuclei, to avoid spurious couplings of atomic states, in many-atom systems. This requires a rethinking of atomic function expansions and of methods for calculating one- and two-electron integrals for the electronic structure.
- Solving the coupled differential equations for the time-dependent interactions of fast electronic and slow nuclear motions while avoiding numerical difficulties (accumulation of computer roundoff errors) associated with the simultaneous propagation of functions with very different time scales.

The way we have dealt with these problems is briefly described in the coming sections. Our solution to the first problem has been based on an *eikonal representation* of the molecular wavefunction,[69,78] combined with a procedure to calculate transition probabilities and expectation values of properties in collisions. This is done in section 2, for both stationary and nonstationary states, using in the latter case a time-dependent variational approach to derive the relevant equations.[110,111,113] The way the eikonal treatment has been combined with many-electron states and implemented for ion collisions with atoms and surfaces is described in section 3, where the eikonal/TDHF (Eik/TDHF) and other approximations are considered. The second problem is dealt with in terms of *linear combinations of traveling atomic functions* (LCTAFs) and switching between basis sets.[110,112,117,118] The coupling of fast electronic and slow nuclear motions over time, the third problem, is considered in section 4, within a procedure we have termed the *relax-and-drive* propagation method. This was introduced in our early work on collision-induced electron transfer in ion−atom and ion−surface interactions[109,111,119,120] and appears to be generally applicable to problems involving different time scales. In this respect it seems to provide an alternative to recent popular multiple-time-scales propagation methods.[30,121−123]

Our choices of applications to physical systems have been dictated by the need to check the validity and accuracy of our calculations. This has been done by comparing our results with other calculations based on different approaches or with experimental results. Diatomic systems are a good starting point because in many cases atom−atom interactions show axial symmetry and the relevant nuclear variables reduce to only one, the interatomic distance. Its motion can be coupled to electronic rearrangement, and this may be done first for systems with only one active electron outside closed shells, and then followed by systems with several active electrons. In the first case one is dealing with a time-dependent molecular orbital (TDMO) theory, while for several electrons the simplest meaningful approach is that of the TDHF approximation. Polyatomic systems add more nuclear degrees of freedom and new demands on the treatment of the nuclear dynamics, which must be developed to construct bound states such as diatomic vibrational-rotational states in atom−diatom collisions. Here again studies can be done for one or several active electrons. There are few studies of the many-electron dynamics of polyatomic systems because of the expense of doing calculations for many trajectory steps, and also because the incorporation of traveling atomic orbitals is more difficult here, and requires modifications of the computer programs available from quantum chemistry for one- and two-electron integrals. Calculations have, however, been done with ab initio potentials and couplings,[70,73,100] and also with TDHF states constructed from static AFs, which is acceptable if state-to-state probabilities are not needed.[124]

Other phenomena of interest to us have been atomic ions interacting with solid surfaces. Electronic rearrangement is then a localized event leading for example to electron transfer, which neutralizes projectile ions. For that reason it is possible to describe surface phenomena in a way analogous to molecular phenomena, by using localized electronic orbitals for the surfaces.[120,125] The additional challenges here are to account for electronic excitations in the solid and to include lattice vibrations.

In addition, a very broad area of applications deals with molecular interactions in electromagnetic fields, including collision-induced light emission and absorption. This has been well studied for phenomena where a product species from a collision is formed in excited states and emits light while perturbed as it leaves the collision region, but it also occurs for complexes formed during electronic interactions at short distances. In this case it is necessary to describe not only the coupling of electronic and nuclear motions but also their coupling to the present or created radiation field. We have considered collision-induced light emission by a molecular complex assuming that the radiation is classical, by working with the time-dependent dipoles of the interacting system.[126]

We have applied our approach to the time dependence of collision-induced electronic energy and electron transfer[110,112] and orbital polarization[127] in $H^+ + H(1s)$ and isotopic variations, and in $He^{2+} + H(1s)$; we have also obtained some of the first results on light emission by the complex formed in $H^+ + H(1s)$ interactions.[126] Although these systems contain only one electron, they are challenging three-body systems undergoing quantal dynamics and excellent tests for theoretical methods. They also hold some surprises, such as the brief duration (and possible detectability) of the light emission. We have also considered systems with several electrons, in particular $H^+ + Li(1s^22s)$ (with an active atomic core) and $He^+(1s) + D(1s)$ (an active electron at each center).[128] Our earlier work dealt with 1- and 2-electron transfer in $He^{2+} + He(1s^2)$, and spin rearrangement in $H(1s\gamma) + H(1s\gamma')$, where $\gamma = \alpha$ or β spins.[106,108] Studies of collisional electron transfer have also been done for the ion−surface system $Na^+ + W(011)$ using electronic orbitals localized at the surface.[119,120] Some of these applications will be presented in section 5.[119,120]

2. Expectation Values and State-to-State Transition Probabilities

Our solution to the first problem, accounting for the dynamics of complex electronic rearrangements, has been based on an *eikonal representation* of the molecular wavefunction.[69,78] In this representation, wavefunctions are written in the form $\chi(q,Q,t)\exp[iS(Q,t)/\hbar]$, with a factorized exponential function of classical-like variables Q, with S meaning a classical-like mechanical action; this representation is formally exact and can be used to derive equations of motion of the Q variables, before making approximations. It provides an approach that can be generally applied without detailed preliminary knowledge of sequences of electronic rearrangements. The usual eikonal approximation is obtained in the limit of short deBroglie wavelengths $\lambda_{dB} = P/h \ll a_B$, the Bohr radius. The procedure provides a straighforward derivation of integrals and expectation values expressed as sums over initial values of trajectories and can be described as an initial value method. This eikonal treatment derives from our work on collision-induced state-to-state transitions using stationary scattering states, and given potentials and couplings for electronic states. It was applied to $H^+ + H_2$ collisions[88] and to the photodissociation of CH_3I,[129] with diabatic electronic potentials and couplings, to a model system of two coupled electronic states in both adiabatic and diabatic representations,[34] and to angular distributions in hyperthermal atom−atom collisions,[130] with very good results. It was adapted to the treatment of coupled electronic and nuclear motions,[109−112] where it leads to time-dependent electronic states driven by the time evolution of the classical-like variables, and more recently it has been developed for nonstationary solutions of the time-dependent Schroedinger equation.[113] We give in what follows an overview of the treatment and refer to the original papers for the derivations. Taking the nuclear coordinates Q to be classical-like, the eikonal representation gives the wavefunction $\Psi(q,Q,t)$ for an initial electronic state I as a superposition of functions, of the form

$$\Psi_I(q,Q,t) = \int d\Lambda\, a(\Lambda)\, \chi_I(q,Q,t;\Lambda)\, \exp[iS(Q,t;\Lambda)/\hbar] \quad (3)$$

with parameters Λ (such as initial values of momenta and coordinates) and combination coefficients $a(\Lambda)$ chosen to construct the initial state, $\Psi^{(in)}(q,Q)$ from $\chi^{(in)}(q,Q;\Lambda)$ and $S^{(in)}(Q;\Lambda)$. Here the variables q refer to electronic coordinates and spin, but more generally they could also include the coordinates of protons if they must be treated as quantum variables, for example in studies of proton transfer requiring phase interference and tuneling. The function $S(Q,t)$ is chosen to be real. The preexponential factor $\chi(q,Q,t)$ is, however, complex and has its own phase, dependent on the electronic state. Differential equations satisfied by these two functions can be obtained quite generally[113] from the Dirac−Frenkel time-dependent variational principle (TDVP).[131,132] The equation for S is, for given I,

$$\frac{1}{2M}\left(\frac{\partial S}{\partial Q}\right)^2 + V_{qu}\left(Q,\frac{\partial S}{\partial Q},t\right) + \frac{\partial S}{\partial t} = 0 \quad (4)$$

and the one for χ is

$$\left[\frac{1}{2M}\left(\frac{\hbar}{i}\frac{\partial}{\partial Q} + \frac{\partial S}{\partial Q}\right)^2 + \hat{H}_Q - \left(i\hbar\frac{\partial}{\partial t} - \frac{\partial S}{\partial t}\right)\right]\chi(q,Q,t) = 0 \quad (5)$$

where $\hat{H}_Q$ is the electronic Hamiltonian operator obtained fixing nuclear coordinates Q. It follows from the first equality that S is a solution of a Hamilton−Jacobi equation and can be interpreted as a mechanical action governed by a quantum potential V_{qu} while χ satisfies a time-dependent Schroedinger equation with shifted momenta and energy. The quantal potential is given, for a system starting initially in state I, by $V_{qu,I} = V_I + V'_I + V''_I$,[34,69] with

$$V_I = \langle\chi_I|H_Q|\chi_I\rangle/\langle\chi_I/\chi_I\rangle$$

$$V'_I = \frac{i\hbar}{2M}\frac{\partial S}{\partial Q}\left[\left\langle\frac{\partial\chi_I}{\partial Q}\middle|\chi_I\right\rangle - \left\langle\chi_I\middle|\frac{\partial\chi_I}{\partial Q}\right\rangle\right]/\langle\chi_I|\chi_I\rangle$$

$$V''_I = -\frac{\hbar^2}{2M}\frac{1}{2}\left[\left\langle\frac{\partial^2\chi_I}{\partial Q^2}\middle|\chi_I\right\rangle + \left\langle\chi_I\middle|\frac{\partial^2\chi_I}{\partial Q^2}\right\rangle\right]/\langle\chi_I|\chi_I\rangle \quad (6)$$

where the first term is identified as the Ehrenfest potential with its meaning of a classical effective potential, and the following terms are quantal corrections. The bracket notation here and in what follows signifies an integration only over electronic variables, so that the brackets are yet functions of nuclear variables. The quantal corrections are small in regions where the function χ varies slowly over distances of the order of the deBroglie wavelength of the nuclear momenta. These equations are formally exact. In practice, the quantal corrections are neglected or included only as corrections for short de Broglie wavelengths, in improved eikonal approximations. The effective potential is then $V_{\mathrm{qu}} = V_{\mathrm{I}}$ or, if an average is taken over several initial states I with weights w_{I}, it is $\bar{V}_{\mathrm{qu}} = \sum w_{\mathrm{I}} V_{\mathrm{I}}$. The solution to the Hamilton−Jacobi equation can be written as the integral of a Lagrangian L,[133]

$$S(Q,t) = S_{\mathrm{in}}(Q) + \int_{t_{\mathrm{in}}}^{t} \mathrm{d}t'\, L(\bar{Q},\dot{\bar{Q}},t') \tag{7}$$

with $L(Q,\dot{Q},t) = M\dot{\bar{Q}}^2/2 - V_{\mathrm{qu}}$, and where M is the mass of (scaled) coordinates Q. This action can alternatively be constructed introducing the momenta $P = \partial S/\partial Q$, from solutions to the Hamiltonian equations with the same potential,

$$\partial P/\partial t = -\partial H_{\mathrm{qu}}/\partial Q, \qquad \partial Q/\partial t = \partial H_{\mathrm{qu}}/\partial P \tag{8}$$

$$H_{\mathrm{qu}} = P^2/(2M) + V_{\mathrm{qu}}(Q,P,t) \tag{9}$$

where now P and Q can be interpreted as the position and momentum variables of trajectories originating at initial values P_{in} and Q_{in} and evolving as $P(t;P_{\mathrm{in}},Q_{\mathrm{in}})$ and $Q(t;P_{\mathrm{in}},Q_{\mathrm{in}})$. Some initial values of generalized momenta may be fixed by initial conserved quantities such as energy and angular momentum, while the others are available to combine the elementary solutions in eq 5 and construct the initial states, so that one can write that $a(\Lambda) = a(P_{\mathrm{in}},Q_{\mathrm{in}})$ and integrate over the available P_{in}. This leaves a dependence of the states Ψ on the Q_{in}, which can be used to calculate expectation values as follows. The expectation values of properties $\hat{A} = \hat{A}(Q,Q',t)$, written here as operators on the electronic states and functions of the nuclear coordinates, are given by integrals $\langle A(t)\rangle = \int \mathrm{d}Q \int \mathrm{d}Q' \langle\Psi(Q,t)|\hat{A}(Q,Q',t)|\Psi(Q',t)\rangle$, which can be transformed by making a change of variables from the space coordinates Q to the initial values Q_{in} to obtain the initial value expressions

$$\begin{aligned} \langle A(t)\rangle = \int \mathrm{d}P_{\mathrm{in}} \int \mathrm{d}Q_{\mathrm{in}} \int \mathrm{d}P'_{\mathrm{in}} \int \mathrm{d}Q'_{\mathrm{in}} \times \\ J(t;Q_{\mathrm{in}},P_{\mathrm{in}})\, J'(t;Q'_{\mathrm{in}},P'_{\mathrm{in}})\, F_{\mathrm{A}}(P_{\mathrm{in}},Q_{\mathrm{in}},P'_{\mathrm{in}},Q'_{\mathrm{in}},t) \\ F_{\mathrm{A}} = a(P'_{\mathrm{in}},Q'_{\mathrm{in}})^*\langle\chi(Q',t)|\hat{A}|\chi(Q,t)\rangle a(P_{\mathrm{in}},Q_{\mathrm{in}}) \times \\ \exp\{\mathrm{i}[S(Q,t) - S(Q',t)]/\hbar\} \end{aligned} \tag{10}$$

written in terms of the Jacobians $J = \partial(Q)/\partial(Q_{\mathrm{in}})$ of the transformations. This expression suggests a computational approach based on the discretization of the initial phase space of the classical variables, followed by integration over time of the coupled equations for the P, Q, and χ originating at each discrete set of values.

It would appear as if the choice of a single phase factor S in the eikonal representation would prevent the wavefunction from evolving differently when the system changes between electronic states (i.e., jumps between potentials energy surfaces). But such changes are allowed through the phases of the complex χ function. The equation for S, or instead the Hamiltonian equations, solved for an initial grid in phase space, provide a time evolving grid adapted to the physical situation, covering only the relevant range of phase space over time. This avoids the calculation of electronic wavefunctions over physically irrelevant regions of Q values. The electronic wavefunction χ is generated on this grid by solving its equation, which allows for potential jumps. Furthermore, the time-evolving grid is governed by the potential V_{qu}, which is not an average of PESs but really an effective potential showing sharp transitions among PESs, so that it can change, for example, from a repulsive to an attractive potential. See, e.g., refs 34 and 88.

Our original introduction of the eikonal representation was done for the time-independent Schroedinger equation for total energy E and scattering states $\chi^{(+)}$ as they appear in collisions or photodissociation. This can be recovered with the choice $S(Q,t) = S_0(Q) + Et$ and $\chi(q,Q,t) = \chi^{(+)}(q,Q) \exp[-\mathrm{i}f(t)/\hbar]$.[110,113] The function $S_0(Q)$ satisfies the time-independent Hamilton−Jacobi equation and this leads again to $Q(t)$ and $P(t)$ functions of initial values. Collision-induced state-to-state transition probabilities $\alpha = (\vec{k}_{\mathrm{I}},\mathrm{I}) \rightarrow \beta = (\vec{k}_{\mathrm{J}},J)$ between states in arrangement channels c = i, f can then be obtained from the scattering integrals[34,69,110]

$$\begin{aligned} T_{\beta\alpha} &= \int \mathrm{d}Q\, \langle\chi^0_\beta(Q)|\hat{H}'_{\mathrm{f}}|\chi^{(+)}_\alpha(Q)\rangle \exp[-\mathrm{i}(S_\alpha - S^0_\beta)/\hbar] \\ &= \int \mathrm{d}t \int \mathrm{d}\bar{Q}_{\mathrm{in}}\, \bar{J}(t;\bar{Q}_{\mathrm{in}})\, F_{\mathrm{T}}(t;\bar{Q}_{\mathrm{in}}) \end{aligned} \tag{11}$$

where now the integration variables were changed first from Q to $Q_{\mathrm{in}} = (Q_1^{\mathrm{in}}, Q_2^{\mathrm{in}}, ..., Q_{\mathrm{f}}^{\mathrm{in}})$ and then to the time t and the set $\bar{Q}_{\mathrm{in}} = (Q_2^{\mathrm{in}}, ..., Q_{\mathrm{f}}^{\mathrm{in}})$ of all except one initial coordinate. The eliminated coordinate is any convenient one varying linearly with time. This integral can be calculated by starting with a set of initial coordinates and advancing time and adding over all initial sets of coordinates. The operator $\hat{H}'_{\mathrm{f}}$ is the coupling potential in the final channel. Cross sections follow from these integrals or, in the stationary phase approximation of the integral, from

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{JI}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{I}} P_{\beta\alpha} \tag{12}$$

where the first factor to the right is a differential cross section generated by the effective potential and the second factor is a probability of transition that can be obtained from the many-electron wavefunctions.

The shape of the effective potential $V_{\mathrm{qu,I}}(Q)$ depends on the electronic state I specified by the initial conditions. This leads to transition probabilities $P_{\beta\alpha}$, which would not exactly satisfy microscopic reversibility conditions. The related numerical error in $P_{\beta\alpha}$ is expected to be small when the collision energies are appreciably larger than electronic excitation energies, as indeed found in many applications. However, the errors related to nonreversibility would increase for low collision energies or for interactions leading to long-lived complexes. This problem has been addressed by us in two ways. In our early work[108] using a variational functional for transition amplitudes, we showed how to construct time-reversible probability amplitudes using two trial states, $\Psi_{\mathrm{I}}^{(+)}(t)$ and $\Psi_{\mathrm{J}}^{(-)}(t)$, with specified initial and final conditions and running forward and backward in time, respectively. It was shown there that excellent agreement with exact results could then be obtained for low-energy atom−atom collisions. The second way we have avoided biasing the effective potential by the initial conditions,[34] has been to instead use the average effective potential $\bar{V}_{\mathrm{qu}}$, obtained from the weighted sum of the $V_{\mathrm{qu,I}}(Q)$ for all the involved states I. It was shown, by comparison with exact results for atom−atom collisions at low energies, that this gives accurate results satisfying microscopic reversibility.

3. Eikonal/TDHF Approximation and Extensions

The advantage of using an eikonal description is that the electronic wavefunctions are needed only along nuclear trajectories. In the eikonal limit of short deBroglie wavelengths, the potential energies in the second and third lines of eq 6 can be ignored, and eq 5 simplifies to

$$\left[\frac{\hbar}{\mathrm{i}}\frac{P}{M}\frac{\partial}{\partial Q} + \hat{H}_Q - W(P,Q,t) - \mathrm{i}\hbar\left(\frac{\partial}{\partial t}\right)_{q,Q}\right]\chi(q,Q,t) = 0 \quad (13)$$

with $W(P,Q,t) = V_{\mathrm{qu}}(Q,P,t) + \mathrm{i}\hbar(\partial P/\partial Q)/(2M)$. Letting P and Q change with time along trajectories, with $P = M\dot{Q}$ and $\dot{Q}\partial/\partial Q + (\partial/\partial t)_{q,Q} = (\partial/\partial t)_q$, the replacement

$$\chi_{\mathrm{I}}[q,Q(t),t] = \eta_{\mathrm{I}}(q,t)\exp[\mathrm{i}\int_{t_{\mathrm{in}}}^{t}\mathrm{d}t'\, W(t')/\hbar] \quad (14)$$

leads to the usual time-dependent Schroedinger equation for the electronic wavefunction,

$$\left[\hat{H}_{Q(t)} - \mathrm{i}\hbar\left(\frac{\partial}{\partial t}\right)_q\right]\eta_{\mathrm{I}}(q,t) = 0 \quad (15)$$

In a general case, the trial function for N electrons is a combination of Slater determinants $D_{\mathrm{I}}(1,2,...,N,t) = (N!)^{-1/2}\det[\psi_{i_m}(n,t)]$, constructed from N time-dependent molecular spin-orbitals (MSOs), $\{\psi_i(\vec{r},\zeta,t)\}$, and where n in the arguments is a short hand for all the coordinates (position and spin) of electron n and $m = 1-N$. In the simplest choice, useful in many applications, the trial function is a single determinant and the variational procedure leads to the TDHF approximation. The MSOs can be chosen at the initial time so that electrons are localized at a given nucleus, unlike the situation when the MSOs are time-independent and delocalized. Furthermore, the TDHF approximation includes some electron correlation.[7]

Instead of working with MSOs, it is more convenient to introduce the TDHF density formed from occupied MSOs,

$$\hat{\rho}_{\mathrm{I}}(t) = \sum_{\mathrm{occ}\ i}|\psi_i\rangle\langle\psi_i| \quad (16)$$

because this provides a compact description and does not require specification of occupied and unoccupied orbitals, which would change in a time evolution. It satisfies the equation

$$\hat{F}\hat{\rho}_{\mathrm{I}} - \hat{\rho}_{\mathrm{I}}\hat{F} = \mathrm{i}\hbar\partial\hat{\rho}_{\mathrm{I}}/\partial t \quad (17)$$

where $\hat{F} = \hat{H}^{(1)} + \hat{G}[\hat{\rho}_{\mathrm{I}}]$ is the Fock operator written as a sum of a one-electron term $\hat{H}^{(1)}$, plus the HF self-consistent potential energy operator $\hat{G}[\hat{\rho}_{\mathrm{I}}]$.

The average effective potential needed in the Hamiltonian equations is now

$$V_{\mathrm{qu}}^{(\mathrm{HF})} = V_{\mathrm{cc}} + \sum_I w_{\mathrm{I}}\,\mathrm{tr}[\hat{\rho}_{\mathrm{I}}(\hat{H}^{(1)} + \hat{F})]/2 \quad (18)$$

where the first term is the core−core interaction potential and the second term is a sum over all initially populated states. The TDHF equations for each $\hat{\rho}_{\mathrm{I}}$ and the classical Hamiltonian equations must be solved simultaneously and entail a combination of the eikonal approximation for the nuclear motions and the TDHF approximation for the electrons or, in our notation, the Eik/TDHF approximation.

State-to-state cross sections follow from

$$\begin{aligned}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{JI}} &= \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{I}}|\langle D_{\mathrm{J}}^{0}(t_{\mathrm{f}})|D_{\mathrm{I}}(t_{\mathrm{f}})\rangle|^2 \\ &= \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{I}}|\det[\langle\psi_{\mathrm{j}}^{0}(t_{\mathrm{f}})|\psi_{\mathrm{i}}(t_{\mathrm{f}})\rangle]|^2 \\ &= \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{I}}\det[\langle\psi_{\mathrm{j}}^{0}(t_{\mathrm{f}})|\hat{\rho}_{\mathrm{I}}(t_{\mathrm{f}})|\psi_{\mathrm{j'}}^{0}(t_{\mathrm{f}})\rangle]\end{aligned} \quad (19)$$

where we have used that the overlap of determinants is a determinant of overlaps and that the product of determinants of matrices is the determinant of the matrix product, to find a compact expression in terms of the propagated density operator.

The driving effect of nuclear displacements on electronic states is large, and the TDHF equations cannot be solved using perturbation theory. A nonperturbative treatment can, however, be done for each initial state I introducing basis sets and solving matrix TDHF equations. Given a general basis set of one-electron orbitals $\{\phi_p(t)\}$, with overlap integrals $\langle\phi_p|\phi_q\rangle = S_{pq}$, and expanding MSO's with spin state $\gamma(\zeta)$ in that basis,

$$\psi_i^{\gamma}(\vec{r},t) = \sum_p \phi_p(\vec{r},t)\, c_{pi}^{\gamma}(t) \quad (20)$$

where the coefficients are complex valued. The density operator in the basis is

$$\hat{\rho}(t) = \sum_{pq}|\phi_p\rangle P_{pq}^{\gamma}(t)\langle\phi_q| \quad (21)$$

with P_{pq}^{γ} the (pq)-element of the one-electron density matrix $\mathbf{P}^{\gamma}$. The TDHF equation for the density matrix is then

$$\mathrm{i}\hbar\dot{\mathbf{P}}^{\gamma} = \mathbf{S}^{-1}(\mathbf{F}^{\gamma} - \mathrm{i}\hbar\mathbf{\Omega})\mathbf{P}^{\gamma} - \mathbf{P}^{\gamma}(\mathbf{F}^{\gamma} - \mathrm{i}\hbar\mathbf{\Omega})^{\dagger}\mathbf{S}^{-1} \quad (22)$$

where $\mathbf{S} = \langle\phi|\phi\rangle$ is the overlap matrix and $\mathbf{\Omega} = \langle\phi|\partial\phi/\partial t\rangle$ is an orbital coupling due to the motion of the nuclei, both given in a matrix notation where $|\phi\rangle$ is a $1 \times N_{\mathrm{B}}$ row matrix of basis functions. The $\mathbf{\Omega}$ matrix is the one that contains spurious couplings of atomic states at large distances, but it can be eliminated with a transformation to a basis of traveling atomic functions (TAFs) ξ_{μ}; MO's are then expanded as linear combinations of TAF's, or LCTAFs,

$$\psi_i^{\gamma}(\vec{r},t) = \sum_{\mu}\xi_{\mu}(\vec{r},t)\, c_{\mu\mathrm{i}}^{\gamma}(t) \quad (23)$$

where $\xi_{\mu}(\vec{r},t) = \chi_{\mu}(\vec{r})\, T_m(\vec{r},t)$; here χ_{μ} is an AF centered at nuclear position $\vec{R}_m(t)$, and

$$T_m(\vec{r},t) = \exp\{\mathrm{i}m_{\mathrm{e}}[\vec{v}_m(t)\cdot\vec{r} - \int_{t_{\mathrm{in}}}^{t}\mathrm{d}t'\, v_m{}^2(t')/2)]/\hbar\} \quad (24)$$

is an electron translation factor, a function of the velocity vector of nucleus m. In this TAF basis, the TDHF equation becomes[110]

$$\mathrm{i}\dot{\mathbf{P}}^{\gamma} = \mathbf{S}^{-1}\mathbf{F}_{\mathrm{T}}^{\gamma}\,\mathbf{P}^{\gamma} - \mathbf{P}^{\gamma}(\mathbf{F}_{\mathrm{T}}^{\gamma})^{\dagger}\mathbf{S}^{-1} \quad (25)$$

which does not contain spurious coupling terms. The modified Fock-like matrix appearing here is given by $(\mathbf{F}_{\mathrm{T}}^{\gamma})_{\mu\nu} = \langle\xi_{\mu}|T_n\hat{F}^{\gamma}T_n^{-1}|\xi_{\nu}\rangle$.

It is convenient to evaluate one- and two-electron Coulomb integrals in the basis of static AFs and then transform to the TAFs. For a general matrix $\mathbf{O}^{(\phi)}$ expressed in a ϕ basis, we have $\mathbf{O}^{(\xi)} = \mathbf{B}^{\dagger}\mathbf{O}^{(\chi)}\mathbf{B}$, where we have used the transformation matrix with elements

$$B_{\mu\nu} = \sum_{\kappa} [(\mathbf{S}^{(\chi)})^{-1}]_{\mu\kappa} [\mathbf{S}^{(\chi\xi)}]_{\kappa\nu} \tag{26}$$

where $[\mathbf{S}^{(\chi)}]_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ and $[\mathbf{S}^{(\chi\xi)}]_{\mu\nu} = \langle \chi_\mu | \xi_\nu \rangle$. We solve the TDHF matrix equation (for given spin γ) with the sequence of transformations $\mathbf{P}^{(\xi)} \rightarrow \mathbf{P}^{(\chi)} \rightarrow \mathbf{F}^{(\chi)} \rightarrow \mathbf{F}^{(\xi)}$ that use

$$P^{(\chi)}_{\mu\nu} = \sum_{\mu'\nu'} B_{\mu\mu'} P^{(\xi)}_{\mu'\nu'} (\mathbf{B}^\dagger)_{\nu'\nu} \tag{27}$$

and

$$G^{(\xi)}_{\mu\nu} = \sum_{\mu'\nu'} (\mathbf{B}^\dagger)_{\mu\mu'} G^{(\chi)}_{\mu'\nu'} B_{\nu'\nu} \tag{28}$$

which avoid the calculation of the inverse of **B** and of 4-index transformations of the 2-electron integrals, and therefore considerably increase the efficiency of the computation. Details of computational aspects with these basis sets can be found in refs 110, 112, and 128.

A multiconfiguration extension of TDHF, or MCTDHF, can be developed also starting from Slater determinants $D_K(1,2,...,N,t)$, where $K = (k_1,...,k_m,...,k_N)$ is an ordered set among $N_B > N$ MSOs that can be combined into configuration spin functions (CSFs) $\Phi_K(1,2,...,N,t)$, which are eigenstates of the spin operators. The multiconfiguration function

$$\eta_I(1,2,...,N,t) = \sum_{K=1}^{N_C} \Phi_K(1,2,...,N,t) C_{KI}(t) \tag{29}$$

depends parametrically on the expansion coefficients C_{KI}, and on the LCTAFs parameters within the MSOs. It is a sum over a selected subset of N_C configurations, usually smaller than the total number of configurations that can be constructed from the complete active space of MSOs. Placing this trial function into the TDVP, a variation of the expansion coefficients gives the set of coupled equations for the C_{KI} coefficients. Details of the derivation may be found in ref 113.

4. Propagation of Coupled Electronic and Nuclear Motions

For thermal energies or hyperthermal energies up to about 10 000 eV, nuclear velocities are small compared with electronic ones, and oscillations of electronic states are much faster than changes of the nuclear variables. Since these degrees of freedom are interacting, it is not efficient to solve their coupled differential equations by straightforward time-step methods. We have instead developed a propagation procedure suitable for coupled equations with very different time scales: short for electronic states and long for nuclear motions. The procedure introduces a local interaction picture with a unitary transformation at each time interval. The equations in the Eik/TDHF approximation are eqs 8 coupled to

$$\mathbf{WP} - \mathbf{PW}^\dagger = i\hbar\, d\mathbf{P}/dt \tag{30}$$

with $\mathbf{W}(t) = \mathbf{S}^{-1}\mathbf{F}_T$ and must be solved for the initial conditions at $t = t_{in}$: $Q_{in} = Q(t_{in})$, $P_{in} = P(t_{in})$, and $\mathbf{P}_{in} = \mathbf{P}(t_{in})$. The matrices and trajectory variables are assumed known at a time t_0; the density matrix is first obtained as it relaxes over the interval $t_0 \leq t \leq t_0 + \Delta t = t_1$, while the nuclear variables remain fixed. Its matrix elements are the solutions of the equations

$$\mathbf{W}_0 \mathbf{P}^0(t) - \mathbf{P}^0(t) \mathbf{W}_0^\dagger = i\hbar\, d\mathbf{P}^0/dt \tag{31}$$

where $\mathbf{W}(t_0) = \mathbf{W}_0$, which show that the density matrix elements change with time as they relax from their (nonstationary) values at t_0, where $\mathbf{P}(t_0) = \mathbf{P}_0$. Since the $\mathbf{W}_0$ matrix is constant in time, these coupled equations are simple first-order differential equations with constant coefficients and can be integrated by diagonalizing the $\mathbf{W}_0$ matrix. The results are sums of rapidly oscillating functions in time, reflecting the rapid electronic motions. Relaxation occurs by rearrangements of the molecular orbitals. The nuclear motions introduce a driving effect within the interval $t_0 \leq t \leq t_1$. Choosing this interval to be short in the time scale of nuclear motions (although long compared to periods of electronic oscillations), one can assume that the driving effect will only introduce small corrections to the relaxing densities; this can be verified by shortening the time interval and repeating the calculations. The corrected densities are obtained by writing

$$\mathbf{P}(t) = \mathbf{P}^0(t) + \mathbf{U}^0(t)\, \mathbf{P}'(t)\, \mathbf{U}^0(t)^\dagger$$
$$\mathbf{U}^0(t) = \exp\left[-\frac{i}{\hbar}\mathbf{W}_0(t - t_0)\right] \tag{32}$$

for the density matrix, where $\mathbf{U}^0$ defines a unitary transformation to a local interaction picture at each time t_0. With the displacement energy matrix $\mathbf{V}(t) = \mathbf{U}^0(t)[\mathbf{W}(t) - \mathbf{W}^0]\mathbf{U}^0(t)^\dagger$, the solution for the density matrix correction is

$$\mathbf{P}'(t) = \mathbf{\Delta}'(t) + (i\hbar)^{-1} \int_{t_0}^{t} dt'\, [\mathbf{V}(t'),\mathbf{P}'(t')]$$
$$\mathbf{\Delta}'(t) = (i\hbar)^{-1} \int_{t_0}^{t} dt'\, [\mathbf{V}(t'),\mathbf{P}_0] \tag{33}$$

where the driving term $\mathbf{\Delta}'$ can be obtained from a quadrature and the second term in $\mathbf{P}'$ can be neglected for a small time interval. With the new density matrices known up to time t_1, it is possible to advance the nuclear positions and momenta by integrating their Hamiltonian equations. This completes a cycle that can be repeated to advance to a later time t_2. This sequence, based on relaxing the density matrix for fixed nuclei and then correcting it with a quadrature to account for the driving effect of nuclear motions, has been called by us the *relax-and-drive procedure* and has been numerically implemented in several applications.[109,110,112,119,120,126−128]

5. Some Applications to Collisional Transfer of Electronic Energy and Charge and Light Emission

Results in this section have been obtained with TAFs and the linear combinations of Gaussians,

$$\chi_{nl\kappa}(\vec{r}) = \sum_{k=1}^{K} d_{nl,k}\, g_{l\kappa}(\vec{r};\alpha_{nl,k}) \tag{34}$$

with orbital quantum numbers $l = 0, 1, 2$ and where the $\alpha_{nl,k}$ are exponential coefficients that scale with the square of the effective nuclear charge. The number K in our studies is either 6 or 12. Differential cross sections for electronic transitions I → J have been obtained from $(d\sigma/d\Omega)_{JI} = (d\sigma/d\Omega)P_{\beta\alpha}(t_f)$ as previously described. The time steps in the propagation of trajectories and the density matrix have been determined, so the ratio of the magnitudes of the density matrix change **Q** to the full density matrix **P** always satisfies $\epsilon_{lower} \leq ||\mathbf{Q}||/||\mathbf{P}|| \leq \epsilon_{higher}$, where ϵ_{lower} and ϵ_{higher} are lower and higher tolerances.[110]

The applications we have chosen relate to phenomena where nuclear velocities are small compared to electronic velocities, the situation typical in chemical interactions, and for which our

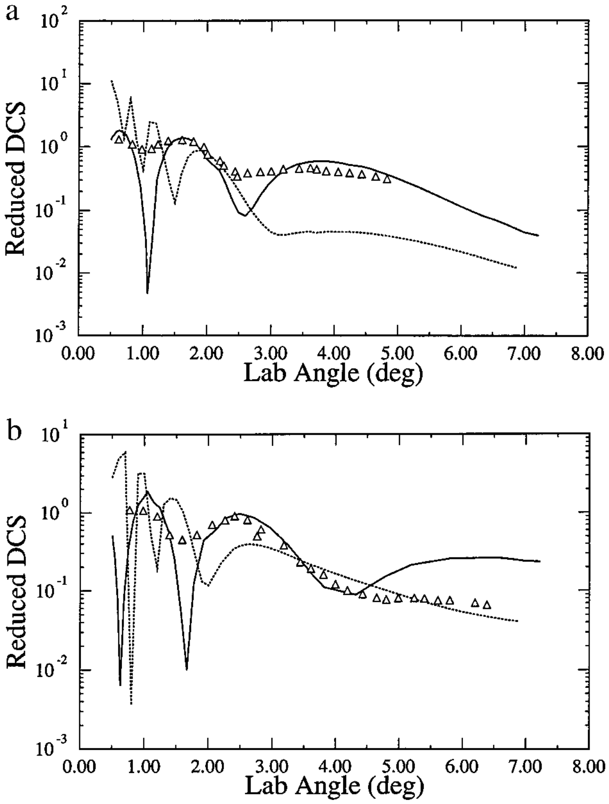

Figure 1. (a) Elastic differential cross section (in degrees × au's) vs lab angle for a proton incident at 410 eV on a hydrogen atom target: (full line) SCP calculation; (dotted line) CP; (triangles) measurements from Houver et al., 1974. (b) Same as (a) for the electron transfer differential cross section. From Micha and Runge: *Phys. Rev.* **1994**, *A50*, 322. Reproduced with permission from the American Physical Society. Copyright 1994.

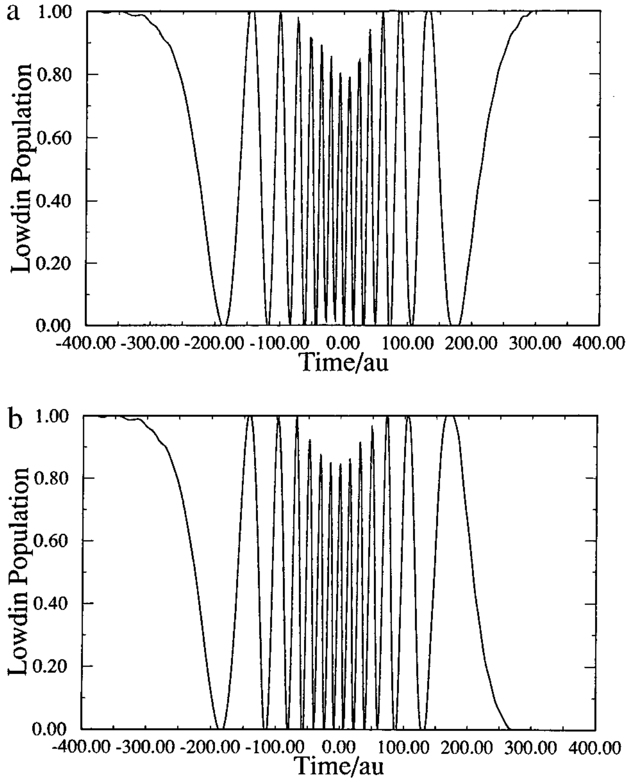

Figure 2. (a) Löwdin population of the target 1s state vs time in au in a 10 eV proton−hydrogen atom collision, at $b = 1.0$ au. (b) Löwdin population of the target 1s state vs time in au in a 10 eV proton−hydrogen atom collision, at $b = 1.2$ au. From Runge and Micha: *Phys. Rev.* **1996**, *A53*, 1388. Reproduced with permission from the American Physical Society. Copyright 1994.

methods have been developed. Therefore, although some collision energies (of several keV) in the following examples seem beyond chemical values, they in fact correspond to low velocities and provide valid tests of our methodology. The system $H^+ + H(1s)$, although simple in chemical terms, is very illustrative of the challenges and issues arising in a first principles dynamics. In addition, there are several theoretical and experimental results for cross sections available in the literature for comparisons. In our work, we have reproduced these measurable quantities, and in addition have shown how electronic populations and trajectories change over time during collisions. Parts a and b of Figure 1 present results for reduced differential cross sections $\theta_L \sin(\theta_L)(d\sigma/d\Omega)^{(L)}_{ji}$ of elastic and electron transfer processes, respectively, vs laboratory angle θ_L at an incident energy of 410 eV. Theoretical results obtained with the screened Coulomb potential between nuclei (SCP) and a simple nuclear Coulomb repulsion potential (CP) show marked differences at low angles. Compared with experimental results,[134] the bare CP shows artificial oscillations at low angles while the agreement is clearly better for the SCP, which includes the dynamical screening arising from electronic rearrangement during the collision. Here the experimental values for the angle have considerable errors and have been shifted by a constant value to superimpose the second maximum with the theoretical value. Similar agreement is found for other incident energies.[135]

In addition to asymptotic properties such as cross sections, we can obtain time-dependent populations as shown in Figure 2a,b, in which the time evolution of the target H(1s) populations are given for a 10 eV proton projectile in collisions for impact parameters of 1.0 and 1.2 au, respectively. Here we see multiple oscillations in the target atom population as a function of time over an interval of 600.0 au (time), or about 15 fs; the period of the oscillations is about 20 au's, longer than at higher collision energies. We also notice that a small change in the impact parameter causes a large change in the result of the collision; in this case a change of 0.2 au in the impact parameter makes the difference between complete retention of the electron by the target and complete transfer to the projectile, after collision. The populations are very similar in the incoming portions of the trajectories but diverge as the effects of coupling of the electron and nuclei add up at close distances.

Pronounced population oscillations could be expected for identical nuclei, but they also appear for heteronuclear systems, such as $He^{2+} + H(1s)$ undergoing excitation to $He^{2+} + H(n = 2, 3)$, and electron transfer to $He^{+}(n = 2, 3) + H^{+}$. Figure 3 presents a comparison of our results for charge transfer integral cross sections with various experimental and theoretical results. Our results are seen to be in very good agreement with the available experimental data at the higher energies. At lower energies our method is in good agreement with other theoretical results for this system.[136−141] Time-dependent phenomena of interest for this system include the orbital alignment of the projectile and the changes of electronic population of the target 1s state and the projectile 2s, $2p_x$, and $2p_z$ states. Figure 4 shows the Löwdin populations of the target and projectile states, obtained from the formula

$$n_{\mathrm{a}}^{\mathrm{L}} = \sum_{\lambda\in \mathrm{a}} \sum_{\mu,\nu} [(\mathbf{S}^{1/2})_{\lambda\mu} P_{\mu\nu} (\mathbf{S}^{1/2})_{\nu\lambda} + \mathrm{cc}]/2 \qquad (35)$$

for the population at nucleus a. The variation in time of the alignment parameter for the projectile orbitals of H is shown

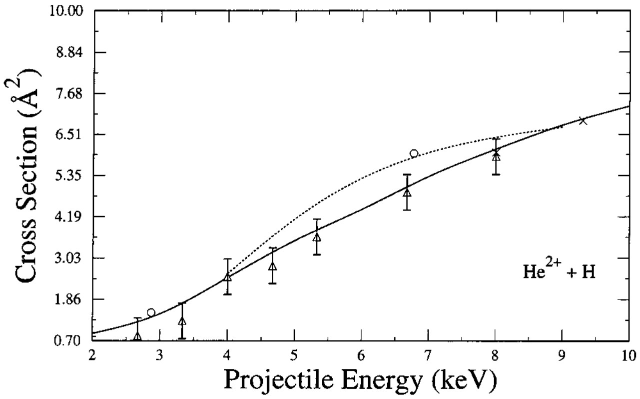

Figure 3. Charge transfer integral cross section vs projectile energy for He^{2+}−H collision: (full line) Eik/TDHF; (dotted line) Errea *et al.*;[18] (circles) Hatton *et al.*;[17] (crosses) experiment.[34] From Runge and Micha: *Phys. Rev.* **1996**, *A53*, 1388. Reproduced with permission from the American Physical Society. Copyright 1996.

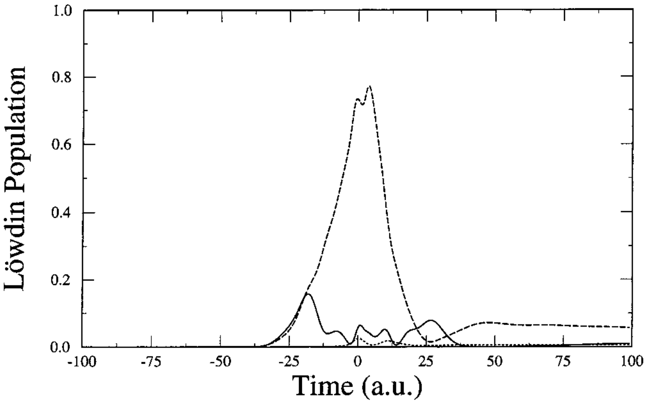

Figure 4. Löwdin population of the projectile atom vs time in au in a 4 keV He^{2+}−H collision at $b = 0.2$ au: (full line) 2s; (dotted line) 2p$_x$; (dashed line) 2p$_z$. From Runge and Micha: *Phys. Rev.* **1996**, *A53*, 1388. Reproduced with permission from the American Physical Society. Copyright 1996.

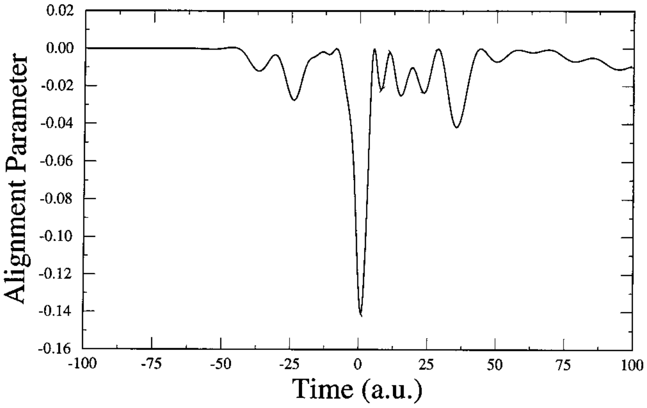

Figure 5. Alignment parameter vs time in au in a 4 keV He^{2+}−H collision at $b = 0.2$ au. From Runge and Micha: *Phys. Rev.* **1996**, *A53*, 1388. Reproduced with permission from the American Physical Society. Copyright 1996.

in Figure 5, from $A_0^{(2)}(t) = n^{\mathrm{M}}_{2\mathrm{p}_x}(t) - 2n^{\mathrm{M}}_{2\mathrm{p}_z}(t)$.[142] It is clear that significant oscillations are present during collisions also in this case.

In addition to the previous one-electron systems, we have done calculations for systems with several active electrons. Issues of interest are whether the Eik/TDHF approximation correctly accounts for electron correlation during collisions, and whether atomic cores can be assumed to be inactive during the course of the collision. We show in Tables 1 and 2 (from ref 128) results for He$^+$(1s) + D(1s), with one electron at each nucleus, at a collision energy of 10 keV (at which other theoretical[143−145] and experimental values are available for comparison[146−148]) for integral electron exchange and excitation cross sections respectively, corresponding to He$^+$(1s) + D(1s) → He(1s2s, 1s2p) + D$^+$ and → He$^+$(1s) + D(2s, 2p). Our results are in excellent agreement with the previously known total transfer cross sections and, in addition, show the breakup between transfer to 1s2s and 1s2p states of He. For excitation, the present work agrees well with both theoretical and experimental results, available for both D(2s) and D(2p) excitation. Results for differential cross sections (to be published[117]), which are more demanding on model accuracy, similarly show very good agreement with experiments at 1.5 keV.

TABLE 1: Comparison of Our Results with Other Calculations and Experiments for the He$^+$(1s) + D(1s) Integral Cross Sections for Charge Transfer into He(1s2s) and He(1s2p), at a Projectile Ion Kinetic Energy of 10 keV[a]

	theory				
state	present work	EMR	EJSW	KCL	experiment OSPM
2s	0.02	<0.1	<0.1	NA	NA
2p	0.74	0.72	0.72	NA	NA
total	0.76	0.72	0.72	0.75	0.8 ± 0.1

[a] Values are in units of 10^{-16} cm^3. Here EMR, EJSW, and KCL stand for refs 143−145 and OSPM for ref 146. From Runge and Micha: *Chem. Phys. Lett.* **1999**, *303*, 15. Reproduced with permission of Elsevier Science. Copyright 1999.

TABLE 2: Similar to Table 1 but for Integral Cross Sections for Excitation of *D*[a]

	theory				experiment	
state	present work	EMR	EJSW	KCL	MSGG	GDHHG
2s	0.06	<0.1	<0.1	0.02	0.04 ± 0.04	NA
2p	0.39	0.49	0.48	0.39	0.42 ± 0.04	0.48 ± 0.03
total	0.45	0.49	0.48	0.41	0.46	NA

[a] Here MSGG and GDHHG stand for refs 147 and 148. From Runge and Micha: *Chem. Phys. Lett.* **1999**, *303*, 15. Reproduced with permission of Elsevier Science. Copyright 1999.

TABLE 3: Comparison of Our Results with Other Calculations and Experiments for the H$^+$ + Li(1s^{2}2s) Integral Cross Sections for Charge Transfer into H(1s), H(2s), and H(2p$_x$,2p$_z$), at a projectile Ion Kinetic Energy of 2 keV, with Trajectories on the *xz*-plane[a]

	theory					experiment		
state	present work	SK	ADM	E	FL	GSKM	AFW	VWC @ 1943 eV
1s	0.6	NA	NA	0.8	NA	NA	NA	Na
2s	14.3	NA	NA	15.0	14.8	NA	NA	NA
2p$_x$	11.4	NA	NA	NA	NA	NA	NA	NA
2p$_z$	16.1	NA	NA	NA	NA	NA	NA	NA
2p	27.5	NA	NA	22.1	18.8	NA	23 ± 8	NA
total	42.4	∼23	15−58	37.9	33.6	32−70	NA	25.0 ± 3.5

[a] Here SK, ADM, E, and FL stand for refs 149−152 and GSKM, AFW, and VWC for refs 153−156. From Runge and Micha: *Chem. Phys. Lett.* **1999**, *303*, 15. Reproduced with permission of Elsevier Science. Copyright 1999.

Some results on integral cross sections for H$^+$ + Li(1s^{2}2s), a system with an active atomic core, are shown in Tables 3 and 4 (from ref 128) at a projectile energy of 2 keV. We included here atomic orbitals for both core and valence electrons. Values of integral cross sections are presented in Tables 3 and 4 for charge transfer and excitation, H(1s,2s,2p) + Li$^+$(1s^2) →

TABLE 4: Similar to Table 3 for Excitation to Li(1s^{2}2p$_x$,2p$_z$)^a

state	theory: present work	theory: E	experiment AFW
2p$_x$	7.4	NA	NA
2p$_z$	6.6	NA	NA
2p	14.0	20.6	23 ± 5

[a] From Runge and Micha: *Chem. Phys. Lett.* **1999**, *303*, 15. Reproduced with permission of Elsevier Science. Copyright 1999.

$H^+ + Li(1s^22s)$ and → $H^+ + Li(1s^22p)$, respectively. Our results for total transfer to H are in very good agreement with four other calculations,[149−152] and also agree with values for transfer into 1s, 2s, and 2p orbitals of H available in two of them.[151,152] We have also obtained the breakup into 2p$_x$ and 2p$_z$ components (for trajectories in the *xz*-plane) from which polarization parameters can be obtained. There is also good agreement with three experimental results for total transfer, the last one of them at a slightly smaller collision energy.[153−156] The experimental values are somewhat smaller than the detailed calculations but reasonably close. Much less has been available on the excitation cross sections. Here we find excitation only to H(2p) but none to H(1s) or H(2s), as others have found from theory[151] and experiment,[155] although our value is smaller that the others. We have also obtained time-dependent populations for this collision process (to be published[118]) that indeed show some amount of 1s Li core transient excitation at this collision energy.

An appealing aspect of a first principles molecular dynamics is that the electronic density matrices allow calculations of properties during collisions, such as the total electrical dipole for a collision complex, $\mathbf{D} = \mathbf{D}_{\text{nucl}} + \mathbf{D}_{\text{el}} = \mathbf{D}(t;b,v_P)$, where $\mathbf{D}_{\text{el}}(t) = \text{tr}(\hat{\rho}_I\hat{\mathbf{D}}_{\text{el}})$. We have described light emission from the complex formed during $H^+ + H(1s)$ collisions that arises from electronic charge transfer and the related oscillatory dipole of the complex. Calculations were done[126] with a basis set of traveling atomic functions, for collision energies of 100, 250, and 1000 eV, to obtain the energy emitted per solid angle versus both time and the light frequency in terms of the emission energy cross section

$$\frac{d^2Q_k}{dt\, d\Omega_{\text{LD}}} = \int_0^\infty db\, b \int_0^{2\pi} d\Phi \left(\frac{d^2E_k}{dt\, d\Omega_{\text{LD}}}\right)_{b,\Phi} \tag{36}$$

where Ω_{LD} is the solid angle subtended by the light detector and E_k is the light energy with polarization $k = x, z$, for trajectories starting at (b, Φ). Results are presented for the intensity components of the light emitted parallel (along z) and perpendicular (along x) to the incoming projectile H^+ velocity, in Figure 6a,b. Light emission is found to last several femtoseconds and to be distributed over ultraviolet frequencies, and the intensity of light emitted by the complex H_2^+ is found to increase as collision energies are lowered. Figure 7 compares our results for the cross section $d\sigma_L/d\omega = (\hbar\omega)^{-1}\, dQ/d\omega$ after integration over the solid angles of emission with those in ref 157 for their $4\pi\, d\sigma/d\omega$. The general features of the two results are similar, although we find additional structure due to our use of a larger basis set. We find the atomic emission peak at the frequency of 0.375 au (wavelength of 121.5 nm); to its left there is a small peak at 0.326 au (139.7 nm) corresponding to the $3d\sigma_g \rightarrow 2p\sigma_u$ transition of H_2^+, and another one at 0.367 au (124.1 nm) for $2p\pi_u \rightarrow 1s\sigma_g$ hidden by the atomic emission. To its right we find peaks at 0.411 au (110.8 nm) and 0.465 au (97.9 nm) for the transitions $2s\sigma_g \rightarrow 2p\sigma_u$ and $3d\pi_g \rightarrow 2p\sigma_u$, respectively, and smaller peaks at larger frequencies. The results also show a broad intensity distribution underneath the spectral peaks, a feature of the emission by the collision complex which might be important in studies of light emission in planetary and stellar atmospheres.

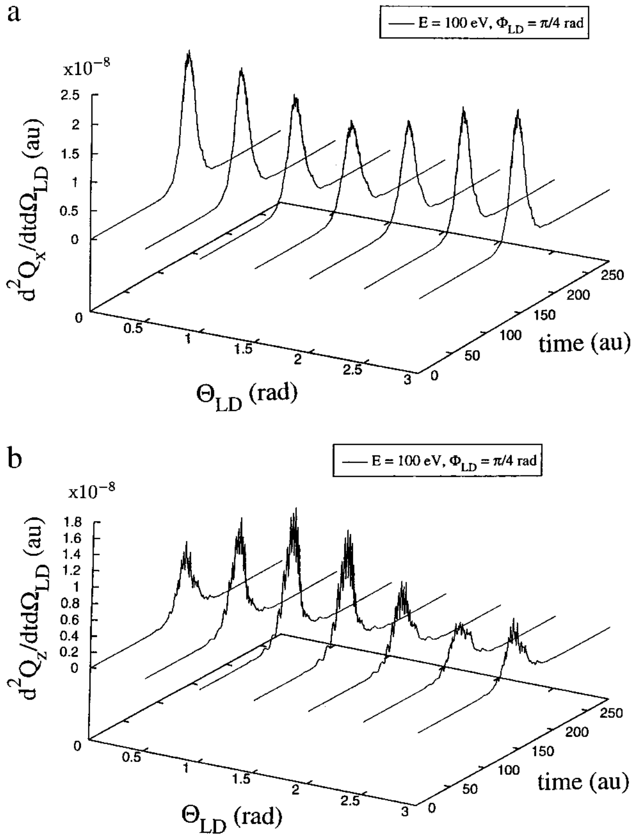

Figure 6. Energy cross section radiated per unit solid angle and time vs time and vs light detector angle Θ_{LD} (Φ_{LD} is kept fixed at $\pi/4$ rad). The collision energy is 100 eV. (a) Component of the cross section (indicated here as the x-component) perpendicular to the incoming projectile direction. (b) z-component along the projectile direction. From DaCosta, Micha, and Runge: *J. Chem. Phys.* **1997**, *107*, 9018. Reproduced with permission from the American Physical Society. Copyright 1997.

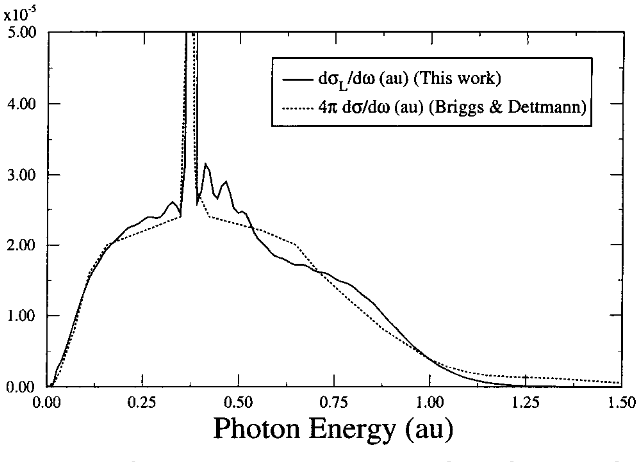

Figure 7. Light emission cross section integrated over detector angles versus photon energy from the power spectrum derived from our time-dependent calculations, compared with ref 157. From DaCosta, Micha, and Runge: *J. Chem. Phys.* **1997**, *107*, 9018. Reproduced with permission from the American Physical Society. Copyright 1997.

Finally, oscillatory electronic charges may be expected to appear in condensed matter phenomena such as in collisions of ions with metal surfaces. We have some time ago developed a model for electron transfer in ion−metal surface collisions based

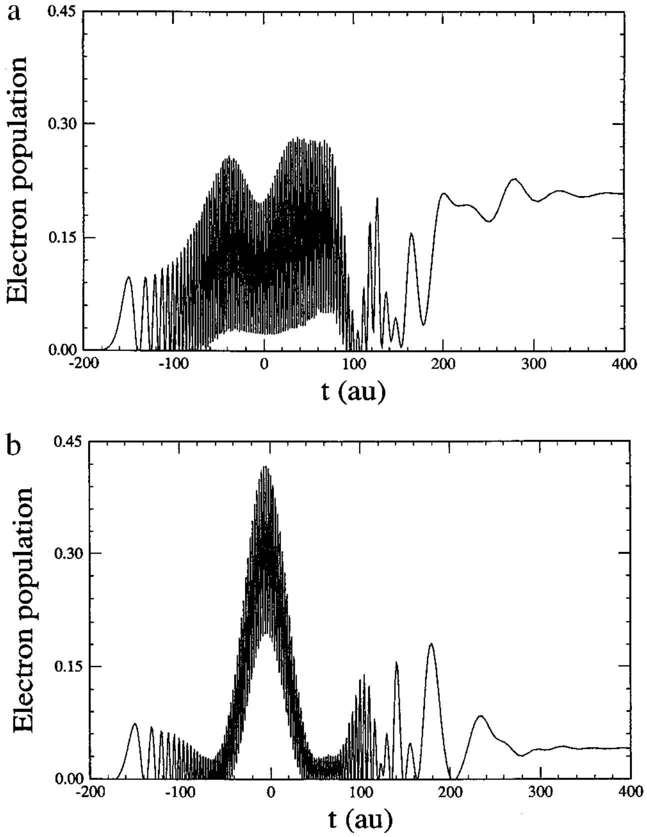

Figure 8. Time evolution of the electronic populations of the 3s and $3p_z$ orbitals of Na^+ colliding with the W(110) surface (parts a and b, respectively), for a collision energy of 10.0 au. Reproduced from Feng, Micha, and Runge: *Int. J. Quantum Chem.* **1991**, *40*, 545.

on partitioning of the density matrix and its equation, classifying orbitals into a primary set that includes atomic orbitals and localized metal orbitals at the impact area and a secondary set with the other localized metal orbitals. Calculations were done for the probability of neutralization in collisions of Na^+ with the W(011) metal surface, at collision energies between 1.0 and 100.0 au, for which some experimental results were available.[119,120] The localized states were constructed from generalized Wannier states written as linear combinations of Gaussians, and the projectile orbitals were TAFs similar to the ones used for ion−atom collisions. Figure 8 shows the time evolution of the electronic populations of the 3s and $3p_z$ orbitals of Na^+ colliding with the W(110) surface (parts a and b, respectively), for a collision energy of 10.0 au. Rapid population oscillations are found to occur near the impact region for trajectories perpendicular to the surface. At long times after collision the populations settle into constant values from which neutralization probabilities are obtained. These oscillations are present also at the other collision energies and suggest that light emission during electron transfer should also be present here as it is the case for $H^+ + H$.

6. Conclusion

We have provided answers to three fundamental problems identified in a first principles molecular dynamics that explicitly describe electronic rearrangements. The calculation of probabilities and expectation values has been based on the eikonal representation and its approximations, combined with sums over initial conditions. The problem of accounting for the translational motion of electrons moving with nuclei has been dealt with via traveling atomic orbitals. Finally, the solution of coupled differential equations for fast electronic transitions and slow nuclear motions was solved with a relax-and-drive propagation method.

These solutions have provided a theoretical framework of general applicability and have given good results in applications chosen to test our approach. We have established that extensive electronic rearrangement occurs during collisions even when final results change smoothly with kinematic parameters such as collision velocities and deflection angles. We can therefore expect new femtosecond phenomena developing during collision dynamics, particularly in connection with light emission. Similar challenging and conceptually enlightening subjects could be explored for systems with more electrons and more atoms.

There are issues that should be addressed in further studies. Trajectories generated from effective potentials seem to give good answers but they could possibly be limited to relatively large collision energies, an aspect that needs additional testing. The TDHF wavefunctions appear to contain a relevant description of electron correlation, but they are known to fail in some cases, such as we found in our early work on two-electron transfer.[108] Ways to improve electron correlation in molecular dynamics may require a new look into many-electron theories, to develop time-dependent versions with the desired accuracy and computational efficiency, as we have outlined for multiconfiguration TDHF.

Our present applications have pointed out some directions for future research. Areas of research within reach of present computational methods are first principles dynamics of the optical spectra of atoms and diatomics in clusters and solvents and at surfaces, provided electronic rearrangements are localized. Density matrix methods should be especially valuable to describe large systems, including coherence and relaxation phenomena. Some intriguing fundamental problems could also be studied at a deeper level. One of them is the extent to which nuclear motions remain regular instead of becoming chaotic, while being coupled to rapid electronic oscillations. This is also closely related to the calculation of physical properties from sums over initial conditions for the nuclear variables.

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