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Time-dependent many-electron approach to slow ion-atom collisions: The coupling of electronic and nuclear motions

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We describe the coupling of electronic and nuclear motions in slow atomic collisions using a combination of the eikonal and time-dependent Hartree-Fock (TDHF) approximations. Starting with an eikonal representation of the total wave function, a wave function is constructed from classical trajectories in a way suitable for describing atomic collisions with velocities down to a fraction of an atomic unit. The TDHF formulation is developed in terms of its density operator. The differential equations coupling the density operator to the nuclear motions have been solved with a procedure developed to account for the coupling of fast (electronic) and slow (nuclear) degrees of freedom. This is based on a local-interaction picture and on a temporal linearization of the equations, allowing for the integration of the electronic density over large time intervals. Density-matrix equations are derived in a basis of traveling atomic orbitals, and numerical results are presented for $H^+ + H$ and $He^{2+} + H$. Good agreement is found with experimental results for $H^+ + H$, comparing integral electron transfer cross sections from 2 to 2000 eV. In addition, an analysis of the time dependence of atomic orbital populations provides insight on electronic rearrangement during collisions and shows that even very small contributions from the driving forces of the nuclei on the electrons have a cumulative effect on the density operator that can substantially change final populations.

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I. INTRODUCTION

Theoretical and experimental studies of slow ion-atom collisions provide valuable information on the nature of electronic rearrangement in molecular interactions. By concentrating attention on systems with only two nuclei, it is possible to gain insight on the collisional coupling of electronic and nuclear motions and the way electronic orbitals change over time. Our aims are to describe the *temporal rearrangement* of electrons in slow collisions (in addition to the final rearrangement) and to calculate collisional properties such as cross sections and polarization parameters.

Theoretical models can be developed in considerable detail for small diatomic systems to investigate their accuracy and to extend the range of kinematic conditions under which they are valid. The insight gained in these studies should be valuable in the interpretation of interactions between more complicated collision partners, such as molecules and solid surfaces, provided the same methods can be applied to larger systems, with more nuclear degrees of freedom. Our approach has therefore been chosen so that it can be applied to larger systems.

We mean by slow collisions that the nuclear velocities are small compared with electronic ones. Taking electronic velocities to be of the order of 1.0 a.u., and remembering that a proton with a kinetic energy of 1000 eV has a velocity of the order of 0.2 a.u., we find that a formulation for slow collisions should be applicable to a very wide range of collision energies, from several thousand eV to fractions of an eV. This contribution develops an approach that can be used for ion-atom collision partners with several electrons and for collision energies going from several thousand eV down to fractions of an eV, the region of interest in chemical phenomena.

The aim of most previous theoretical publications has been to provide cross sections for electronic excitation, electron transfer, and orbital polarization to compare with experimental measurements with ion beams. Much of the work concentrated on fundamental aspects of systems with only one electron, although more recent work has been done also on two-electron systems [1–5]. They have mostly covered collisional energies ranging from hundreds of eV to larger values, because these are the energies frequently available from experimental instruments. At the low energies of interest to us, theoretical descriptions have been based on both atomic and molecular orbital descriptions of the electrons and on classical trajectories for the nuclei. Quantal descriptions of the nuclear motions have also been recently done for very low collision energies [6,7].

Our approach has been developed so that applications to many-electron two-atom systems and to polyatomic systems would be practical. To these ends, we have introduced several innovations in the theory for small atomic velocities. We have carefully analyzed the short (de Broglie) wavelength, or eikonal approximation, to derive expressions valid at low velocities and to include quantum phase interference; this provides a link with the classical molecular dynamics of polyatomic systems. We have treated the many-electron system in terms of electron density operators to avoid having to specify the temporal occupation of molecular orbitals. The coupling of electronic density operators to nuclear trajectories involves very different time scales and their accompanying numerical difficulties; we have developed a solution to this problem based on temporal linearization of the coupled differential equations. Finally, we have introduced atomic orbital basis sets to expand molecular orbitals and to take advantage of the very extensive programming done in quantum chemistry to calculate one- and two-electron integrals.

Starting with the quantal equations for all the molecular particles, it is possible to introduce a variety of semiclassical limits for the nuclei to simplify the description of electronic transitions [8–14]. Along these lines, we have introduced an eikonal representation of the total wave function for a system at a given total energy, in a stationary collision process [15–19]. The limit of short de Broglie wavelengths can then be naturally taken to obtain an eikonal or semiclassical approximation, valid for many nuclear degrees of freedom, that contains as particular cases several of the expressions used in semiclassical treatments of ion-atom collisions. The description of many-electron interactions has been done within the time-dependent Hartree-Fock (TDHF) approximation insofar as this has been found sufficient to impose the initial conditions for many collision problems of interest [20–24]. Our work using the TDHF approximation started with an investigation of its limitations, comparing results of the TDHF approximation and of its variational improvements to exact calculations with a small basis set [25,26]. The variational improvement is based on TDHF trial functions from the initial and into the final states of the type described here. That variational treatment could therefore be used to go beyond TDHF calculations.

The combination of eikonal and TDHF approximations has been the subject of extensive testing in applications to several diatomic systems over a wide range of collision energies. Preliminary results and conclusions have been presented in several publications on different aspects of ion-atom [27,19,28,29] and ion-solid surface collisions [30–32]. In this contribution, we consider in greater detail the eikonal approximation for electronically diabatic collisions and look into the mathematical problems that arise in a time-dependent description of coupled nuclear and electronic motions due to the very different time scales on which electrons and nuclei evolve.

Our approach does not require the previous knowledge of potential-energy curves or their couplings. Instead, it generates the electronic information used to describe nuclear motions as needed during the atomic interactions. In this regard, it is an *ab initio* molecular dynamics, in the spirit of work found to be very useful in the description of ground electronic state properties of extended molecular systems [33,34]. In large systems, it has been possible to solve the problem of rapidly oscillating electronic densities by introducing an artificial electronic mass, leading to damping of electronic oscillations as the system moves towards its ground electronic state [35,36]. We have found that our approach provides an alternative useful also in the description of electronically excited states and electronic transitions.

A time-dependent description must deal with coupled differential equation solutions showing a short time scale for the fast electronic transitions and a long one for the slow nuclear motions. For example, for a proton colliding with a hydrogen atom the periods of electronic transitions are of the order of 1.0 a.u., or 2.42×10^{-17} sec, while collision times (for kinetic energies from 10 to 1000 eV and potential ranges of 10 a.u.) vary between 500 and 50 a.u. In our approach we do not introduce an artificial mass to dampen electronic oscillations, but instead separate the electronic density operator into a relaxation term at fixed nuclear conformations plus a density operator change due to moving nuclei. The procedure appears to be generally valid insofar as we have found it to applicable to both diatomic systems and to electron transfer at solid surfaces, a localized phenomenon. Solving the time-scale problem becomes more pressing as nuclear velocities are lowered and electrons have more time during interactions to jump back and forth between collision partners.

The electronic structure of molecules has been extensively investigated using carefully selected atomic basis sets. They have been chosen to simplify the calculation of one- and two-electron integrals and have been parametrized to optimize atomic energies [37–40]. The most computationally efficient basis sets are based on Gaussian functions, for which there are well tested programs [41]. Consequently, in our calculations we have chosen to express traveling atomic orbitals as combinations of Gaussian functions times electron translation factors [28]; this allows us to apply our approach to polyatomic systems and to use quite large basis sets.

Earlier work on ion-atom collisions demonstrated that physical insight can be gained by calculating the populations of diatomic orbitals over time [42–44]. In our work we have instead chosen to analyze the atomic populations over time with a procedure valid also for many-atom systems. Following our work on what we have termed a time-dependent molecular orbital description of molecular interactions, several publications have appeared using time-dependent descriptions of electrons in small systems, with driving forces calculated by means of available electronic structure packages [45,14]. These contributions point the way to a large variety of applications.

In what follows, Sec. II describes the coupling of electronic and nuclear motions in an eikonal-TDHF approximation and gives expressions for cross sections at two different levels of approximations. The more accurate description constructs a transition amplitude from an eikonal wave function in an expression valid for low collision velocities and many-electron systems. The time evolution of density operators and their decomposition is described in Sec. III, where a local interaction picture is introduced, followed by a local linearization procedure and by a discussion of the matrix equations which arise after expansion in a basis set of traveling atomic orbitals. Section IV gives details of the numerical procedure used here. Results are shown for the time-dependent electronic populations of nuclei in $H^{+}+H$ and $He^{2+}+H$ collisions to illustrate the need for a careful decomposition of the density matrix. We also show results for an angular distribution in slow $H^{+}+H$ collisions, clearly illustrating the importance of electronic-nuclear couplings at low velocities. Results of extensive calculations for systems with one and two active electrons have been collected in two other contributions [46,47] to better describe the calculations and their physical content for both time-dependent and asymptotic properties.

II. COUPLING OF ELECTRONIC AND NUCLEAR MOTIONS

We consider the collision of two atoms A and B; A contains a nucleus a and N_A electrons while B has a nucleus b and N_B electrons. The electronic variables for the $N=N_A+N_B$ position and spin coordinates $\mathbf{x}_j=(\vec{r}_j,\zeta_j)$ are $\mathbf{X}=(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ and the nuclear coordinates are $(\vec{R}_a,\vec{R}_b)$. In what follows we shall work in a reference frame with its origin at the center of mass of the nuclei, indicating with $\vec{R}=\vec{R}_b-\vec{R}_a$ the relative position of the nuclei. The total wave function Ψ, for all electrons and nuclei, is a solution of the Schrödinger equation for a given total energy E,

$$H\Psi(\mathbf{X},\vec{R})=E\Psi(\mathbf{X},\vec{R}) , \tag{1}$$

where the total molecular Hamiltonian is given by the sum of nuclear and electronic kinetic energy operators plus all Coulomb potentials,

$$\begin{aligned} H&=K_{\text{nu}}+K_{\text{el}}+V_{\text{Coul}}=K_{\text{nu}}+H_{\vec{R}} , \\ H_{\vec{R}}&=H_c^0+H_c' . \end{aligned} \tag{2}$$

In these expressions we have introduced the Hamiltonian $H_{\vec{R}}$ for fixed interatomic positions and decomposed it into two terms; the first one is the asymptotic Hamiltonian obtained when the electrons are in arrangement c as $R\rightarrow\infty$ and the second is the atom-atom interaction. The index c will designate a scattering channel.

The Schrödinger equation must be solved with boundary conditions for scattering. We introduce electronic states for fixed relative positions, satisfying the equation

$$H_c^0\Phi_I^0=E_I\Phi_I^0 , \tag{3}$$

where Φ_I^0 is an antisymmetrized product of atomic wave functions and E_I^0 is the sum of atomic energies, and also introduce free relative motion states

$$\psi^0_{\vec{k}_I}(\vec{R})=(2\pi\hbar)^{-3/2}\exp(i\vec{k}_I\cdot\vec{R}) \tag{4}$$

for the momentum $\vec{P}_I=\hbar\vec{k}_I$, giving the total energy

$$E=E_I+\hbar^2k_I^2/(2M_{AB}) , \tag{5}$$

where M_{AB} is the reduced mass for the atom pair. The relative position of the atoms is

$$\vec{R}_{BA}=\vec{R}_B-\vec{R}_A=\vec{R}+\vec{\rho}(\mathbf{X},\vec{R}) , \tag{6}$$

where

$$\begin{aligned} \vec{\rho}(\mathbf{X},\vec{R})=&\frac{N_Bm_e}{M_B}\left[\frac{1}{N_B}\sum_{j=1}^{N_B}\vec{r}_j-\vec{R}_b\right] \\ &-\frac{N_Am_e}{M_A}\left[\frac{1}{N_A}\sum_{i=1}^{N_A}\vec{r}_i-\vec{R}_a\right] \end{aligned} \tag{7}$$

arises from the difference between atomic and nuclear positions. When the relative distance becomes large in the solid angle direction Ω_{AB}, and choosing outgoing wave conditions, we have for a system with initial molecular quantum numbers $\alpha=(\vec{k}_I,I)$ the scattering state

$$\begin{aligned} \Psi_\alpha^{(+)}(\mathbf{X},\vec{R})\simeq(2\pi\hbar)^{-3/2}\Bigg[&\Phi_I^0(\mathbf{X};\vec{R})\exp(i\vec{k}_I\cdot\vec{R}_{AB}) \\ &+\sum_J\Phi_J^0(X;\vec{R})f_{JI}^{(+)}(\Omega_{AB}) \\ &\times\exp(ik_JR_{AB})R_{AB}^{-1}\Bigg] , \end{aligned} \tag{8}$$

where we have introduced the angular amplitudes $f_{JI}^{(+)}$.

In this expression, the exponential functions contain electronic coordinates, so that the electronic wave functions multiply electronic phase factors that can be important for large atomic momenta; their magnitude is not large for slow atomic collisions, but they are nevertheless essential to satisfy asymptotic conditions. Omitting them would lead to spurious intra-atomic couplings for moving nuclei [1–3]. These phase factors will later be included in the electronic wave functions by means of expansions in traveling atomic orbitals; consequently we introduce the new electronic states

$$\Phi_\alpha^0(\mathbf{X},\vec{R})=\Phi_I^0(\mathbf{X},\vec{R})\exp[i\vec{k}_I\cdot\vec{\rho}(\mathbf{X},\vec{R})] \tag{9}$$

in the expansion of the molecular states. Once the phase factors have been accounted for, we can neglect terms of order m_e/M and replace $\vec{R}_{AB}\approx\vec{R}$. In what follows we write

$$\begin{aligned} \Psi_\alpha^{(+)}(\mathbf{X},\vec{R})&=\sum_\beta\Phi_\beta^0(\mathbf{X};\vec{R})\psi_{\beta\alpha}^{(+)}(\vec{R}), \\ \psi_{\beta\alpha}^{(+)}(\vec{R})&\simeq(2\pi\hbar)^{-3/2}[\exp(i\vec{k}_I\cdot\vec{R})\delta_{JI} \\ &\qquad+f_{JI}^{(+)}(\Omega)\exp(ik_JR)R^{-1}] , \end{aligned} \tag{10}$$

where $\beta=(\vec{k}_J,J)$. Given the asymptotic solutions, cross sections follow as usual from

$$d\sigma_{JI}/d\Omega=(k_J/k_I)|f_{JI}^{(+)}(\Omega)|^2 . \tag{11}$$

A. The eikonal representation

It is well known that electrons must be treated quantum mechanically because of their small mass, but nuclei can be approximately treated with classical mechanics. In preparation for a treatment of electrons and nuclei that takes advantage of the difference in their masses, we introduce an exponential form for the molecular wave function

$$\Psi(\mathbf{X},\vec{R})=\chi(\mathbf{X},\vec{R})\exp[iS(\vec{R})/\hbar] , \tag{12}$$

where by choice the function S is real and χ is complex valued. This is an exact representation, which will be convenient to introduce an eikonal (or short de Broglie wavelength) approximation for the nuclear motions. In what follows we shall choose S for convenience to be an action integral approximating the quantal phase of the wave function; the phase of χ can compensate in principle for deviations from the correct phase.

The Hamiltonian of the atom pair can be written as

$$H=-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\vec{R}^2}+H_{\vec{R}}\left[\frac{\hbar}{i}\frac{\partial}{\partial\mathbf{X}},\mathbf{X}\right] . \tag{13}$$

Here M is the reduced mass of the nuclei and H_R is the Hamiltonian for fixed nuclear positions. For total energy E, we place the wave function in the time-independent Schrödinger equation to obtain

$$\left[\frac{1}{2M}\left[\frac{\hbar}{i}\frac{\partial}{\partial\vec{R}}+\frac{\partial S}{\partial\vec{R}}\right]^2+H_{\vec{R}}-E\right]|\chi(\vec{R})\rangle=0 , \tag{14}$$

which is valid for any S. Here we have used the angular bracket notation to describe states in the space of electronic functions; an angular bracket will indicate integration over electronic variables, but will remain a function of nuclear variables. An equation for S follows by projecting the above equation on χ and taking the real part of the result, which gives [15,18]

$$\frac{1}{2M}\left[\frac{\partial S}{\partial\vec{R}}\right]^2+V_{\mathrm{qu}}\left[\frac{\partial S}{\partial\vec{R}},\vec{R}\right]=E , \tag{15}$$

$$V_{\mathrm{qu}}=V+V'+V'',\quad V=\langle\chi|H_{\vec{R}}|\chi\rangle/\langle\chi|\chi\rangle , \tag{16}$$

$$\begin{aligned} V'&=\frac{i\hbar}{2M}\frac{\partial S}{\partial\vec{R}}\cdot\left[\left\langle\frac{\partial\chi}{\partial\vec{R}}\middle|\chi\right\rangle-\left\langle\chi\middle|\frac{\partial\chi}{\partial\vec{R}}\right\rangle\right]\Big/\langle\chi|\chi\rangle ,\\ V''&=-\frac{\hbar^2}{2M}\frac{1}{2}\left[\left\langle\frac{\partial^2\chi}{\partial\vec{R}^2}\middle|\chi\right\rangle+\left\langle\chi\middle|\frac{\partial^2\chi}{\partial\vec{R}^2}\right\rangle\right]\Big/\langle\chi|\chi\rangle , \end{aligned} \tag{17}$$

where the first term can be identified as the Ehrenfest potential for the nuclear motions while the second and third terms give quantal corrections.

The function S satisfies a time-independent Hamilton-Jacobi equation [48], which can be solved introducing trajectories. Defining the momentum

$$\vec{P}=\partial S/\partial\vec{R} , \tag{18}$$

it follows that trajectories of nuclei can be obtained for a fixed energy E by introducing position and momentum functions of the time t, satisfying the Hamiltonian equations

$$\begin{aligned} &H_{\mathrm{qu}}(\vec{P},\vec{R})=\vec{P}\cdot\vec{P}/(2M)+V_{\mathrm{qu}}(\vec{P},\vec{R}) ,\\ &d\vec{R}/dt=\partial H_{\mathrm{qu}}/\partial\vec{P} ,\\ &d\vec{P}/dt=-\partial H_{\mathrm{qu}}/\partial\vec{R} \end{aligned} \tag{19}$$

for initial $(\vec{P}_i,\vec{R}_i)$ at the time t_i. The trajectories give

$$S(\vec{R})=S(\vec{R}_i)+\int_{\vec{R}_i}^{\vec{R}}d\vec{R}\cdot\vec{P} . \tag{20}$$

Cross sections may be extracted from these wave functions using their asymptotic form or the transition integral of scattering theory. The asymptotic form is easier to calculate, but as we shall show it neglects certain phase interference during collisions. We give both expressions for future reference.

We first notice that in the absence of interactions the molecular wave function is

$$\Psi_\alpha^0=\chi_\alpha^0\exp(iS_\alpha^0/\hbar),\quad \chi_\alpha^0=(2\pi\hbar)^{-3/2}\Phi_\alpha^0,\quad S_\alpha^0=\hbar\vec{k}_I\cdot\vec{R} . \tag{21}$$

In the presence of interactions, we instead have

$$S_\alpha(\vec{R})=S_\alpha^0(\vec{R})+\int d\vec{R}\cdot(\vec{P}-\hbar\vec{k}_I) \tag{22}$$

and the asymptotic form at $R\rightarrow\infty$,

$$\tilde{\Psi}_\alpha^{(+)}=\tilde{\chi}_\alpha^{(+)}\exp(i\tilde{S}_\alpha/\hbar) . \tag{23}$$

Projecting on the final electronic state along the scattering direction, we find

$$f_{JI}^{(+)}(\Omega)=(2\pi\hbar)^{3/2}R\,\langle\Phi_\beta^0|\tilde{\chi}_\alpha^{(+)}\rangle\exp[i\tilde{S}_\alpha(\vec{R})/\hbar-ik_JR\,] \tag{24}$$

from which the cross section readily follows.

An alternative and more accurate expression can be constructed from the values of the wave function over all space, calculating the scattering integral [49]

$$\begin{aligned} T_{\beta\alpha}&=\int d^3R\,\langle\Psi_\beta^0|(H_{\vec{R}}-H_f^0)|\Psi_\alpha^{(+)}\rangle\\ &=\int d^3R\,\langle\chi_\beta^0|H_f'|\chi_\alpha^{(+)}\rangle\exp[i(S_\alpha-S_\beta^0)/\hbar] , \end{aligned} \tag{25}$$

where H_f' is the atom-atom coupling in the final arrangement channel $c=f$; the cross section follows then from

$$f_{JI}^{(+)}(\Omega)=-(2\pi)^2\hbar MT_{\beta\alpha} . \tag{26}$$

B. The eikonal-TDHF approximation

We next introduce two simplifying assumptions: we assume that the de Broglie wavelengths for the nuclear degrees of freedom are very short, so that gradients of wave functions change little over a wavelength; we also assume that the electronic states may be accurately described by Hartree-Fock wave functions, implying that asymptotic states can also be described by them, in the limit of large interatomic distances.

1. The eikonal approximation

We introduce the approximation of short de Broglie wavelengths $\lambda=h/P$, or eikonal approximation, whereby

$$\left|\left\langle\chi_\alpha\middle|\frac{\partial\chi_\alpha}{\partial\vec{R}}\right\rangle\right|\Big/|\langle\chi_\alpha|\chi_\alpha\rangle|\ll\lambda^{-1} \tag{27}$$

and

$$\left|\left\langle\chi_\alpha\middle|\frac{\partial^2\chi_\alpha}{\partial\vec{R}^2}\right\rangle\right|\Big/\left|\left\langle\chi_\alpha\middle|\frac{\partial\chi_\alpha}{\partial\vec{R}}\right\rangle\right|\ll\lambda^{-1} . \tag{28}$$

This allows us to neglect V' and V'' so that the trajectories of the nuclear variables are now determined by the effective (momentum independent) potential

$$V_\alpha(\vec{R})=\langle\chi_\alpha(\vec{R})|H_{\vec{R}}|\chi_\alpha(\vec{R})\rangle/\langle\chi_\alpha(\vec{R})|\chi_\alpha(\vec{R})\rangle \tag{29}$$

and the trajectory momentum is $\vec{P}=Md\vec{R}/dt$.

In addition, it is sometimes useful (but not necessary) to define an average effective potential (AEP)

$$\mathcal{V}(\vec{R})=\sum_I w_I V_\alpha(\vec{R}) \tag{30}$$

with chosen fractional weights w_I, adding over energetically accessible states I. The flexibility provided by these weights can be used to develop an approach satisfying state-to-state time reversibility [18].

Using the eikonal inequalities, Eq. (14) is approximated by the differential equation

$$\begin{gathered}\left[\frac{\vec{P}}{M}\cdot\frac{\hbar}{i}\frac{\partial}{\partial\vec{R}}+H_{\vec{R}}-W_\alpha(\vec{R})\right]|\chi_\alpha(\vec{R})\rangle=0\ ,\\ W_\alpha(\vec{R})=V_\alpha(\vec{R})+i\frac{\hbar}{2M}\frac{\partial}{\partial\vec{R}}\cdot\vec{P}\ .\end{gathered} \tag{31}$$

We therefore find a complex potential with an imaginary part describing the divergence of streamlines. As the collision ends, this divergence is positive and the magnitude of χ decreases; it is, however, compensated by the increasing factor R in Eq. (23) to give a finite cross section. The divergence effect can be extracted from χ introducing the solution a_α of the differential equation

$$\frac{\vec{P}}{M}\cdot\frac{\partial}{\partial\vec{R}}a_\alpha=\frac{1}{2M}\left(\frac{\partial}{\partial\vec{R}}\cdot\vec{P}\right)a_\alpha \tag{32}$$

and writing

$$|\chi_\alpha(\vec{R})\rangle=(2\pi\hbar)^{-3/2}a_\alpha(\vec{R})|\Phi_\alpha(\vec{R})\rangle\ . \tag{33}$$

The new equation for Φ may be simplified transforming variables from the Cartesian components of the relative position vector to trajectory coordinates for given initial conditions. Using initially cylindrical coordinates (b,ϕ,Z_i), where b is an impact parameter and ϕ the azimuthal angle of the initial collision plane, we have that $\vec{R}=\vec{R}(t;b,\phi)$ for fixed t_i and Z_i. We work with the new variables (t,b,ϕ) and use

$$\frac{\vec{P}}{M}\cdot\frac{\partial}{\partial\vec{R}}=\left(\frac{\partial}{\partial t}\right)_{b,\phi}\ . \tag{34}$$

Defining time-dependent electronic states η_α by means of

$$|\phi_\alpha[\vec{R}(t)]\rangle=|\eta_\alpha(t)\rangle\exp\left[\frac{i}{\hbar}\int_{t_i}^{t}dt'V_\alpha[\vec{R}(t')]\right] \tag{35}$$

and replacing in Eq. (30) we find the equation and boundary conditions

$$\begin{gathered}\left[\frac{\hbar}{i}\frac{\partial}{\partial t}+H_{\vec{R}}\right]|\eta_\alpha(t)\rangle=0\ ,\\ |\eta_\alpha(t)\rangle\simeq|\Phi_\alpha^0\rangle\exp\left[-\frac{i}{\hbar}E_I^0(t-t_i)\right]\quad\text{for } t\to t_i\ .\end{gathered} \tag{36}$$

The exponential factor containing the divergence of streamlines is given by

$$a_\alpha=\exp\left[-\frac{1}{2}\int_{t_i}^{t}dt'\frac{1}{M}\left(\frac{\partial}{\partial\vec{R}}\cdot\vec{P}\right)\right] \tag{37}$$

and can be obtained transforming the divergence differentials from the Cartesian coordinates (X,Y,Z) to (t,b,ϕ) by means of the Jacobian determinant

$$J(t,b,\phi)=\frac{\partial(X,Y,Z)}{\partial(t,b,\phi)} \tag{38}$$

to find [17,50]

$$\frac{1}{M}\frac{\partial}{\partial\vec{R}}\cdot\vec{P}=\frac{\partial(\ln J)}{\partial t},\quad a_\alpha=(J/J_i)^{-1/2} \tag{39}$$

as the factor giving amplitude changes due to divergence of streamlines; here J_i is the initial value of J. In the absence of interaction, the time-dependent free states are given by

$$|\eta_\beta^0(t)\rangle=|\Phi_\beta^0\rangle\exp\left[-\frac{i}{\hbar}E_J^0(t-t_i)\right] \tag{40}$$

and satisfy the differential equation

$$\left[\frac{\hbar}{i}\frac{\partial}{\partial t}+H_c^0\right]|\eta_\beta^0(t)\rangle=0\ . \tag{41}$$

Equations (36) must be solved simultaneously with the trajectory equations

$$\begin{gathered}d\vec{P}/dt=-dV_\alpha/dR\ ,\\ V_\alpha(\vec{R})=\langle\Phi_\alpha|H_{\vec{R}}|\Phi_\alpha\rangle/\langle\Phi_\alpha|\Phi_\alpha\rangle\end{gathered} \tag{42}$$

in a procedure we have called the *self-consistent eikonal method* [15]. The gradient of the potential is calculated along the trajectories rewriting the potential as a function of t, b, and ϕ, and calculating its gradient components by the chain rule, using the Jacobian determinant and its minors.

Cross sections for electronic transitions $I\to J$ follow from $f_{JI}^{(+)}$ in the eikonal approximation, noting that $|R\cdot a|^2$ is proportional to the elastic differential cross section obtained from classical trajectories in the potential V_I. Therefore

$$\left(\frac{d\sigma}{d\Omega}\right)_{JI}=\left(\frac{d\sigma}{d\Omega}\right)_{I}|\langle\eta_\beta^0(t_f)|\eta_\alpha(t_f)\rangle|^2\ , \tag{43}$$

where the first factor is the elastic differential cross section and the angular bracket is a transition probability obtained projecting the evolved electronic state at the final time t_f on the noninteracting final state. The scattering solid angle results from a trajectory with a specific choice of initial impact parameter and azimuthal angle; if more than one set of initial conditions leads to the same scattering solid angle, then one must add the cross sections over all such trajectories. The trajectories must be generated for each initial state. Using the AEP one can alternatively calculate trajectories and elastic differential cross sections independent of the initial quantum state.

A more generally applicable and more accurate result can usually be obtained from the transition integral, which incorporates information about the final state and potential coupling. To obtain the cross section from the transition integral in the eikonal approximation, we start with

$$T_{\beta\alpha}=(2\pi\hbar)^{-3}\int d^3R\, a_\alpha(\vec{R})\langle\Phi_\beta^0|H_f'|\Phi_\alpha\rangle \times\exp\left[\frac{i}{\hbar}\int_{t_i}^{t}dt'V_\alpha(\vec{R})\right] \times\exp[i(S_\alpha-S_\beta^0)/\hbar] \tag{44}$$

and we again transform integration variables from space coordinates to trajectory coordinates by means of the Jacobian J, using the previous expression (39) for the divergence of streamlines.

Introducing the energy relations $E_J^0=E-\hbar^2k_J^2/(2M)$ and $V_\alpha=E-\vec{P}_\alpha^2/(2M)$ we obtain

$$\begin{aligned} T_{\beta\alpha}&=\int_0^\infty db\, b\int_0^{2\pi}d\phi\int_{t_i}^{t_f}dt\langle\eta_\beta^0|H_f'|\eta_\alpha\rangle g_{\beta\alpha}\ ,\\ g_{\beta\alpha}&=(2\pi\hbar)^{-3}(JJ_i)^{1/2}\exp(-i\Delta_{\beta\alpha}/\hbar)\ , \\ \Delta_{\beta\alpha}&=S_\beta^0-\frac{\hbar^2k_J^2}{2M}(t-t_i)-\left[S_\alpha-\int_{t_i}^{t}dt'\left[\frac{\vec{P}_\alpha^2}{2M}\right]_{t'}\right]\ . \end{aligned} \tag{45}$$

The factor g contains the Jacobians and a difference of action integrals and can be calculated from trajectory bundles [17]. The angular bracket is an integral over all the electronic coordinates that can be simplified as follows. Replace there $H_f'=H_{\vec{R}}-H_f^0$, operate with the first term on the electronic state to the right and with the second term to the left, and use

$$\frac{\partial}{\partial t}\langle\eta_\beta^0|\eta_\alpha\rangle=\left\langle\frac{\partial}{\partial t}\eta_\beta^0\middle|\eta_\alpha\right\rangle+\left\langle\eta_\beta^0\middle|\frac{\partial}{\partial t}\eta_\alpha\right\rangle \tag{46}$$

to obtain

$$T_{\beta\alpha}=\int db\, b\int d\phi\int dt\left[-\frac{\hbar}{i}\frac{\partial}{\partial t}\langle\eta_\beta^0|\eta_\alpha\rangle\right]g_{\beta\alpha}(t)\ . \tag{47}$$

This is a compact expression that can be used in calculations. For each chosen initial impact parameter and azimuthal angle, the integral over time may be done along a trajectory, and then one can add over initial conditions.

When the trajectory is approximated, e.g., by a constant velocity trajectory, the factor g is simplified and it is possible to do an integration by parts in the time integral. This is in fact the procedure frequently followed to calculate cross sections for fast collisions [51,52]. The present derivation applies also to slow collisions. The integrals over impact parameter and azimuthal angle may also be evaluated by stationary phase approximations, in which case the transition amplitude becomes a sum of complex terms approximately describing phase interference when several trajectories lead to the same state-to-state transitions [53,54].

2. The TDHF approximation

Choose next for η_α the approximate form

$$\eta_\alpha(\mathbf{X},t)\approx D_\alpha(\mathbf{X},t)\ , \tag{48}$$

where D_α is a time-dependent determinantal function constructed from molecular orbitals (MO's) for an initial electronic state I, which includes the translational phase factor. For a chosen state I and a given trajectory $\vec{R}(t)$, the determinant is written as

$$\begin{aligned} D_\alpha(\mathbf{X},t)&=(N!)^{1/2}\mathcal{A}\prod_{i=1}^{N}\psi_i(\mathbf{x}_i,t)\ ,\\ \psi_i(\mathbf{x}_i,t)&=\psi_i^\gamma(\vec{r}_i,t)\gamma(\zeta_i)\ ,\\ \langle\psi_i^\gamma|\psi_j^\gamma\rangle&=\delta_{ij}\ , \end{aligned} \tag{49}$$

where N is the number of electrons, $\mathcal{A}$ is the antisymmetrizing projection operator, and the ψ_i^γ are time-dependent (TD) MO's for electron spin $\gamma=\alpha,\beta$. These MO's must be constructed including electron translation factors (ETF's) to account for the motion of nuclei; they therefore depend on nuclear positions and velocities. The differential equations for the TD MO's may be derived from a time-dependent variational functional in a well-known procedure [55]. The result is the set of equations

$$F^\gamma\psi_i^\gamma+\sum_j\psi_j^\gamma\epsilon_{ji}^\gamma=i\hbar\partial\psi_i^\gamma/\partial t \tag{50}$$

with the Lagrange multipliers ϵ forming a Hermitian matrix. Here

$$F^\gamma=H^{(1)}+G^\gamma[\rho^\alpha,\rho^\beta] \tag{51}$$

is the Fock operator written as a sum of a one-electron term $H^{(1)}$ plus the Hartree-Fock (HF) self-consistent potential energy operator G^γ.

The initial conditions come from the implied assumption that the free electronic states are also determinantal wave functions agreeing asymptotically with D_α at the initial time. From the HF state and energy of noninteracting atoms,

$$\begin{aligned} \Phi_\alpha^0(\mathbf{X},\vec{R})&=(N!)^{1/2}\mathcal{A}\prod_{i=1}^{N}\varphi_i^0(\mathbf{x}_i,\vec{R})\ ,\\ E_I^0(HF)&=\sum_i u_i^0\ ,\\ u_i^0&=\frac{1}{2}\frac{\langle\varphi_i^0|(H^{(1)}+F)|\varphi_i^0\rangle}{\langle\varphi_i^0|\varphi_i^0\rangle}\ , \end{aligned} \tag{52}$$

it follows that the initial conditions for the TD MO's are

$$\psi_i(t)\simeq\varphi_i^0\exp\left[-\frac{i}{\hbar}\int_{t_i}^{t}dt'u_i^0(t')\right]\quad\text{for } t\to t_i\ . \tag{53}$$

Instead of working with the differential equation for the MO's, it is computationally convenient to introduce the electronic density operator

$$\rho^\gamma(t)=\sum_{\text{occ } i}|\psi_i^\gamma(t)\rangle\langle\psi_i^\gamma(t)|\ , \tag{54}$$

satisfying the TDHF equation

$$F^\gamma\rho^\gamma-\rho^\gamma F^\gamma=i\hbar\partial\rho^\gamma/\partial t\ . \tag{55}$$

This provides a direct way for calculating single-particle properties. To calculate detailed transition amplitudes or other matrix elements, the MO's may be recovered as the eigenstates of the density operator.

In the present notation, the effective potential is given by

$$V_\alpha^{(\mathrm{HF})} \approx V_I^{(\mathrm{HF})} = V_{cc} + \sum_\gamma \mathrm{tr}[\rho_I^\gamma (H+F^\gamma)]/2 \ , \tag{56}$$

where the first term is the atom-core–atom-core interaction potential and we have neglected terms of order $k_I m_e/M$ (coming from the phase factors) compared to electronic momenta. The average effective potential is now

$$\begin{aligned} \mathcal{V}^{(\mathrm{HF})} &= V_{cc} + \sum_\gamma \mathrm{tr}[\bar{\rho}^\gamma (H+F^\gamma)]/2 \ , \\ \rho^\gamma &= \sum_I w_I \rho_I^\gamma \ . \end{aligned} \tag{57}$$

The TDHF states are usually acceptable to describe short-time events and to calculate expectation values of single-electron properties. Improved treatments of the electronic states could be based on superpositions of electronic configurations, leading to time-dependent multiconfigurational HF states, or on time-dependent coupled cluster states. A simpler variational improvement of TDHF transition amplitudes can also be carried out by analogy with work done on ion-atom collisions [26]. Here TDHF functions of the type just introduced are chosen as trial functions, developing forward in time from state I and backward in time from state J. That variational procedure has been found to be accurate for one- and two-electron transfer in two-electron system and holds promise for many-electron systems.

The combined eikonal and TDHF approximation provides the required cross sections. From the asymptotic form

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{JI} &= \left(\frac{d\sigma}{d\Omega}\right)_I |\langle D_\beta^0(t_f)|D_\alpha(t_f)\rangle|^2 \\ &= \left(\frac{d\sigma}{d\Omega}\right)_I |[\det[\langle \psi_j^0(t_f)|\psi_i(t_f)\rangle]|^2 \ , \end{aligned} \tag{58}$$

where we have used the fact that the brackets of two determinants are the determinants of the matrix formed by their MO brackets [56]. Similarly, the transition integral may be obtained integrating along trajectories in accordance with

$$\begin{aligned} T_{\beta\alpha} = \int db\, b \int d\phi \int dt\, g_{\beta\alpha}(t) \\ \times \left(-\frac{\hbar}{i}\right) \frac{\partial}{\partial t}\{\det[\langle \psi_j^0(t)|\psi_i(t)\rangle]\} \ . \end{aligned} \tag{59}$$

For fast collisions the g factor simplifies and one can integrate by parts over time to obtain the results in the literature for the special case of TDHF states. The present derivation is valid also for slow collisions.

III. TIME EVOLUTION OF THE DENSITY OPERATOR

The MO's contributing to the density operator may be classified into orbitals describing the atomic cores and orbitals describing valence electrons shared by the atoms. The valence orbitals may further be classified as undergoing electronically adiabatic or diabatic evolution. The diabatic valence orbitals may be said to describe the active electrons in the collision. In what follows we briefly discuss the decomposition of the density operator corresponding to the above classifications. We show how the valence contributions may be calculated over time and introduce basis sets leading to matrix equations convenient for numerical calculations.

A. Decomposition of the density operator

We identify the core orbitals as the ones that do not change during interactions, so that they are time independent. The core and valence terms in the density operator satisfy

$$\begin{aligned} \rho &= \rho_c + \rho_v \ , \\ \rho_c &= \sum_{\mathrm{core}\, j} |\psi_j\rangle\langle\psi_j| \ , \\ \rho_v &= \sum_{\mathrm{val}\, j} |\psi_j\rangle\langle\psi_j| \ , \\ \rho_c\rho_v &= 0 \ . \end{aligned} \tag{60}$$

Since the self-consistent electron-electron interaction potential in the Fock operator is linear with ρ, we can regroup its terms to define a core Hamiltonian, which can be treated as a one-electron operator,

$$F = H^{(1)} + G[\rho_c + \rho_v] = H_c^{(1)} + G[\rho_v] \ . \tag{61}$$

In what follows we concentrate on the valence density and drop the subscript v.

We assume that the evolution of the system at large distances is electronically adiabatic and the density operator changes smoothly with time only to the extent that it takes new values at each given nuclear conformation. This is assumed here to occur between incoming trajectory times t_i and t_a and outgoing trajectory times t_b and t_f. Within these time intervals the charge density may nevertheless get polarized or may relax as time and the conformation changes. The initial density operator to be used starting at t_i, $\rho(t_i) = \rho_i(\vec{R}_i)$, is generated solving for the static HF equations at time t_i. The adiabatic density operator may be constructed from the knowledge of the Fock operator at each position $\vec{R}(t)$ in the adiabatic time intervals.

We construct the solution between times t_0 and t_1, assuming that the density and Fock operators ρ_0 and F_0 are known at time t_0, for which the position is $\vec{R}_0$. Then the differential equation for the density, to zeroth order in the local velocity, is

$$\frac{\partial \rho^0}{\partial t} = (i\hbar)^{-1}(F_0\rho^0 - \rho^0 F_0) \ , \tag{62}$$

where F_0 is evaluated at $\vec{R}_0$ and the initial condition is $\rho^0(t_0) = \rho_0$. The solution to this operator equation is given in terms of a time-evolution operator by

$$\begin{aligned} \rho^0(t) &= \exp[-iF_0(t-t_0)/\hbar]\rho^0(t_0)\exp[iF_0(t-t_0)/\hbar] \\ &= U_0(t,t_0)\rho_0[U_0(t,t_0)]^\dagger \ , \end{aligned} \tag{63}$$

where the last equality defines the time-evolution operator. This operator describes electronic relaxation for fixed nuclei.

A criterion must be given to identify the beginning of the diabatic regime; indicating with $\Delta\rho$ the change of the density over a time step, the diabatic regime is started when the norm $\|\Delta\rho\|$ is larger than a prescribed value. In the diabatic regime, electronic rearrangement leads to rapid relaxation (smooth or oscillatory) of the charge density. Usually, one must describe electronic oscillations over time scales much shorter than those for nuclear motions. To accomplish this we separate two terms in ρ,

$$\rho(t)=\rho^0(t)+\sigma(t)\ . \tag{64}$$

The first term describes *electronic relaxation for fixed nuclei,* as before, and the second term the density operator *change due to the driving forces of nuclear motions.* Here the second term accounts for diabatic contributions from finite nuclear velocities and can be monitored at early times, comparing its magnitude to that of the first term. The diabatic regime is assumed to start when its value becomes larger than a prescribed amount. We construct the solution for the driving term also between times t_0 and t_1, from the knowledge of the same density and Fock operators ρ_0 and F_0.

B. The driven term in the local interaction picture

It is further advantageous to work in a local interaction picture generated by the local Fock operator. For *moving nuclei,* with the Fock operator change $\Delta F(t) = F(t)-F_0$ giving their driving energy, we define the *local-interaction picture* of an operator A by means of

$$A_L(t)=[U_0(t,t_0)]^\dagger A(t)U_0(t,t_0) \tag{65}$$

and in particular introduce the density terms

$$\rho_L^0(t)=\rho_0,\quad \sigma_L(t)=\rho_L(t)-\rho_0\ , \tag{66}$$

with the latter satisfying the differential equations

$$\begin{aligned} i\hbar\dot\sigma_L(t)&=D_L(t)+\Gamma_L(t)\ ,\\ D_L(t)&=\Delta F_L(t)\rho_0-\rho_0\Delta F_L(t)\ ,\\ \Gamma_L(t)&=\Delta F_L(t)\sigma_L(t)-\sigma_L(t)\Delta F_L(t)\ , \end{aligned} \tag{67}$$

where D_L is the term driving the density, found to be linearly dependent on the nuclear displacements, and Γ_L is of higher order; this must be solved with the initial condition

$$\sigma_L(t_0)=\rho_0-\rho_0^0=0\ . \tag{68}$$

Alternatively, the solution can be obtained from the integral equations

$$\begin{aligned} \sigma_L(t)&=\sigma_L^D(t)+(i\hbar)^{-1}\int_{t_0}^{t}dt'[\Delta F_L(t'),\sigma_L(t')]\ ,\\ \sigma_L^D(t)&=(i\hbar)^{-1}\int_{t_0}^{t}dt'D_L(t')\ , \end{aligned} \tag{69}$$

which give, when solved by iteration, between times t_0 and t_1,

$$\sigma_L(t_1)=\sigma_L^D(t)+(i\hbar)^{-1}\int_{t_0}^{t_1}dt'[\Delta F_L(t'),\sigma_L^D(t')]+\dots\ . \tag{70}$$

Calculations at short distances must include both ρ^0 and σ. To integrate the differential equation for the density operator at short distances, we propagate the solution by small time intervals t_1-t_0, within which the solution for σ can be constructed accurately to first order in the local nuclear velocity.

Insofar as both $\Delta F_L(t)$ and $\sigma_L(t)$ go to zero linearly with vanishing nuclear displacements, we find that retaining only the driving term $D_L(t)$ leads to a local linearization in time, or a *temporal linearization,* of the differential equation for $\sigma_L(t)$, with a solution given by the first term in Eq. (70). Transforming to the original representation, we obtain for the full density operator

$$\begin{aligned} \rho(t)&=\rho^0(t)+(i\hbar)^{-1}\int_{t_0}^{t}dt'U_0(t,t')D(t')[U_0(t,t')]^\dagger\ ,\\ D(t)&=\Delta F(t)\rho^0(t)-\rho^0(t)\Delta F(t)\ . \end{aligned} \tag{71}$$

This expression may be evaluated at time t_1, and the procedure may be repeated to advance the time again. This is done for $t_a\le t\le t_b$, after which the system evolves again adiabatically.

The procedure described here, with a relaxing density operator taken as the zeroth order in an expansion, turns out to have better convergence properties than a straightforward expansion with ρ_0 as the zeroth order. In the latter case the driven term could be sizable, forcing a choice of very small intervals and possibly leading to numerical inaccuracy. Furthermore our procedure includes the driving factor ΔF, which is slowly varying, into a quadrature which may be reduced to simple integrals. This, as we shall see next, provides a solution to the problems created by coupled functions with very different time scales.

C. TDHF in a basis set

The MO's can be expanded as combinations of atomic or localized orbitals. If, however, these MO's were expanded, as usual in quantum chemistry, in a basis of static atomic orbitals $\{\chi_\mu\}$ and then replaced in the TDHF equation, we would find spurious asymptotic couplings appearing in the form of $\langle\chi_\mu|\partial\chi_{\mu'}/\partial t\rangle$ terms, where the two atomic orbitals (AO's) are located at the same nucleus. To avoid this problem, MO's will instead be expanded at large distances as linear combinations of traveling atomic orbitals (TAO's) ξ_μ, which will eliminate the spurious couplings and will account for translational phase factors. We next introduce a general basis set of electronic orbitals $\{\phi_p\}$, with overlap integrals $\langle\phi_p|\phi_q\rangle = \Delta_{pq}$ and expand MO's in this basis to obtain

$$\psi_i^\gamma(\vec r,t)=\sum_p \phi_p(\vec r,t)c_{ip}^\gamma(t)\ , \tag{72}$$

where the coefficients are complex valued.

The density operator in this basis is

$$\rho^\gamma(t)=\sum_{pq}|\phi_p\rangle P_{pq}^\gamma(t)\langle\phi_q|\ , \tag{73}$$

where P_{pq} is the (pq) element of the density matrix $\mathbf{P}^{\gamma}$. In matrix notation

$$\rho^{\gamma}=|\phi\rangle\mathbf{P}^{\gamma}\langle\phi| \ , \tag{74}$$

where $|\phi\rangle$ and $\langle\phi|$ are row and column matrices of ϕ_p orbitals, respectively. The matrix elements of $\mathbf{P}$ are

$$P^{\gamma}_{pq}(t)=\sum_{\text{occ } i} c^{\gamma}_{pi}(t)[c^{\gamma}_{qi}(t)]^{*} \ . \tag{75}$$

The Fock matrix $\mathbf{F}^{\gamma}$ is defined as

$$\mathbf{F}^{\gamma}=\langle\phi|F|\phi\rangle \ . \tag{76}$$

Inserting Eq. (61) into the above definition we have

$$\mathbf{F}^{\gamma}=\mathbf{H}+\mathbf{G}^{\gamma}(\mathbf{P}^{\gamma},\mathbf{P}^{\gamma'}) \ , \tag{77}$$

where

$$\mathbf{H}=\mathbf{K}+\mathbf{V}_{A}+\mathbf{V}_{B} \tag{78}$$

is the core Hamiltonian matrix, $\mathbf{G}^{\gamma}$ the Hartree-Fock electron-electron interaction matrix, $\mathbf{K}$ the electron kinetic energy matrix, and $\mathbf{V}_{A}$ the electron-(atom A) potential matrix.

To derive the TDHF equation for the density matrix, let us define a matrix

$$\mathbf{\Omega}=\left\langle\phi\left|\frac{\partial}{\partial t}\phi\right.\right\rangle \tag{79}$$

and multiply the differential equation for ρ by $\langle\phi|$ from the left and by $|\phi\rangle$ from the right. We then have from Eq. (55)

$$i\dot{\mathbf{P}}^{\gamma}=\mathbf{S}^{-1}(\mathbf{F}^{\gamma}-i\mathbf{\Omega})\mathbf{P}^{\gamma}-\mathbf{P}^{\gamma}(\mathbf{F}^{\gamma}-i\mathbf{\Omega})^{\dagger}\mathbf{S}^{-1} \ , \tag{80}$$

where $\mathbf{S}=\langle\phi|\phi\rangle$ is the overlap matrix. Here and in what follows $\hbar=1$.

D. Matrix equations and solutions

The density matrix can be decomposed as done for the density operator, working now with the basis-set expansions. The operators $\rho^{0}(t)$ and $\sigma_{L}(t)$ have matrix representations $\mathbf{P}^{0}(t)$ and $\mathbf{Q}_{L}(t)$ in that basis. For fixed nuclei (and fixed spin γ) the density matrix $\mathbf{P}^{0}(t)$ satisfies

$$i\dot{\mathbf{P}}^{0}(t)=\mathbf{W}_{0}\mathbf{P}^{0}(t)-\mathbf{P}^{0}(t)\mathbf{W}_{0}^{\dagger} \ , \tag{81}$$

where $\mathbf{W}=\mathbf{S}^{-1}(\mathbf{F}-i\mathbf{\Omega})$ and $\mathbf{W}_{0}=\mathbf{W}(t_{0})$, or equivalently

$$\begin{aligned}&\mathbf{P}^{0}(t)=\mathbf{U}_{0}(t,t_{0})\mathbf{P}_{0}[\mathbf{U}_{0}(t,t_{0})]^{\dagger} \ ,\\ &\mathbf{U}_{0}(t,t_{0})=\exp[-i\mathbf{W}_{0}(t-t_{0})] \ .\end{aligned} \tag{82}$$

The equation for the density-matrix change in the linearized approximation is then simply

$$i\dot{\mathbf{Q}}_{L}(t)=\mathbf{D}_{L}(t) \ . \tag{83}$$

The original change in the density matrix is given by

$$\begin{aligned}\mathbf{Q}(t)&=\mathbf{U}_{0}(t,t_{0})\mathbf{Q}_{L}(t)[\mathbf{U}_{0}(t,t_{0})]^{\dagger}\\ &=\int_{t_0}^{t}dt\,\mathbf{U}_{0}(t,t')\mathbf{D}(t)[\mathbf{U}_{0}(t,t')]^{\dagger} \ ,\\ \mathbf{D}&=\Delta\mathbf{W}\,\mathbf{P}^{0}-\mathbf{P}^{0}\Delta\mathbf{W}^{\dagger} \ ,\end{aligned} \tag{84}$$

where $\Delta\mathbf{W}=\mathbf{W}-\mathbf{W}_{0}$. The density change can be explicitly constructed at time t_1 from the integrals

$$\Gamma_{k\nu\rho l}(t_1,t_0)=\int_{t_0}^{t_1}\exp[-i(w_k-w_l^{*})(t_1-t')]D_{\nu\rho}(t')dt' \ , \tag{85}$$

where the w_k are eigenvalues of the $\mathbf{W}_0$ matrix. Therefore, one may integrate the equations step by step from beginning to end *without encountering numerical problems due to rapid variations* in the density matrix, because $\mathbf{Q}(t)$ is constructed from quadratures within each time interval.

E. Matrix equations in the TAO basis

As a special case we can choose a basis set of TAO's; MO's are then expanded as linear combinations of traveling atomic orbitals ξ_{μ},

$$\begin{aligned}&\psi^{\gamma}_{i}(\vec{r},t)=\sum_{\mu}\xi_{\mu}(\vec{r},t)c^{\gamma}_{\mu i}(t) \ ,\\ &\xi_{\mu}(\vec{r},t)=\chi_{\mu}(\vec{r})T_{m}(\vec{r},t) \ ,\end{aligned} \tag{86}$$

where χ_{μ} is an AO centered at nuclear position $\vec{R}_{m}(t)$ and

$$T_{m}(\vec{r},t)=\exp\left[im_{e}\left[\vec{v}_{m}(t)\cdot\vec{r}-\int_{t_a}^{t}dt'v_{m}^{2}(t')/2\right]\right] \tag{87}$$

is an electron translation factor, a function of the velocity vector of nucleus m. It may also be considered an eigenvalue of the translation (or boost) multiplicative operator T_m, which gives $|\xi_{\mu}\rangle=T_{m}|\chi_{\mu}\rangle$. Reconstructing the determinantal state from the MO's in Eq. (87), one can verify that the phases in Eq. (8) containing electron coordinates are correctly reproduced. The density operator in this basis is given now in matrix notation by

$$\rho^{\gamma}=|\xi\rangle\mathbf{P}^{\gamma}\langle\xi| \tag{88}$$

and the Fock matrix $\mathbf{F}^{\gamma}$ is defined as

$$\mathbf{F}^{\gamma}=\langle\xi|F^{\gamma}|\xi\rangle \ . \tag{89}$$

Calculating matrix elements of Ω and of the electron kinetic energy operator in the basis of TAO's and canceling terms, Eq. (81) becomes

$$i\dot{\mathbf{P}}^{\gamma}=\mathbf{S}^{-1}\mathbf{F}^{\gamma}_{T}\mathbf{P}^{\gamma}-\mathbf{P}^{\gamma}(\mathbf{F}^{\gamma}_{T})^{\dagger}\mathbf{S}^{-1} \ , \tag{90}$$

where $\mathbf{S}=\langle\xi|\xi\rangle$ is the new overlap matrix and we have introduced a modified Fock-like matrix

$$\mathbf{F}^{\gamma}_{T}=\mathbf{H}_{T}+\mathbf{G}^{\gamma} \ , \tag{91}$$

where

$$\mathbf{H}_{T}=\mathbf{K}_{T}+\mathbf{V}_{A}+\mathbf{V}_{M}+\boldsymbol{L}_{T} \ , \tag{92}$$

$$\begin{aligned}(\mathbf{K}_{T})_{\mu\nu}&=\langle\xi_{\mu}|K_{T}|\xi_{\nu}\rangle\\ &=\int d^{3}r[\xi_{\mu}(\vec{r},t)]^{*}T_{n}(\vec{r},t)\hat{K}[T_{n}(\vec{r},t)]^{*}\xi_{\nu}(\vec{r},t) \ ,\end{aligned} \tag{93}$$

$$\begin{aligned}(\mathbf{L}_{T})_{\mu\nu}=-m_{e}\vec{a}_{n}\cdot\int d^{3}r[\xi_{\mu}(\vec{r},t)]^{*}T_{n}(\vec{r},t)\\ \times\vec{r}[T_{n}(\vec{r},t)]^{*}\xi_{\nu}(\vec{r},t) \ ,\end{aligned} \tag{94}$$

and $\vec{a}_n = d\vec{v}_n/dt$ is the acceleration of nucleus n. Equation (94) gives the work done by the dragging force of the nucleus on the electron; since it involves the nuclear acceleration it is found to vanish asymptotically, where the nuclear velocities are constant. Therefore, no spurious couplings remain at large distances when using TAO's. At short distances the acceleration term is present and must in principle be calculated; from bounds to its magnitude it is, however, usually found that its magnitude at short distance is small compared to other Hamiltonian terms.

A calculation for all times may now be done with the TAO basis at large distances and a convenient basis at short distances [5]. The transformation bases is done using the overlap integrals between the two bases. Omitting for the moment the spin index γ and introducing a superscript to distinguish the ϕ and ξ bases, we can write

$$\rho = |\phi\rangle \mathbf{P}^{(\phi)} \langle \phi| = |\xi\rangle \mathbf{P}^{(\xi)} \langle \xi| \tag{95}$$

and find

$$\mathbf{P}^{(\phi)} = \langle \phi|\xi\rangle \mathbf{P}^{(\xi)} \langle \xi|\phi\rangle \ , \tag{96}$$

providing the starting density matrix in the new basis. One must simultaneously switch to the new basis in the calculation of the potential for the trajectory. When the bases are sufficiently large, this can be done without introducing artificial potential or density-matrix jumps. An alternative is to use the same basis for all times, that of TAO's, to avoid matching problems. This is the procedure followed in our calculations here.

IV. NUMERICAL ASPECTS

The implementation of the above formulation in a basis of TAO's requires the calculation of the overlap matrix $\mathbf{S}$ and the Fock-like matrix $\mathbf{F}_T$. Other authors have chosen to calculate these matrix elements by numerical integration [57,5]. In our calculation, these matrix elements are calculated starting with hydrogenic atomic orbitals and reexpressing them as segmented contracted sets of Gaussian basis functions [58]. The matrix elements, including the ETF's, may be calculated analytically in this basis, which adds to the speed of the evaluation of the elements at each nuclear conformation [28].

Within the eikonal-TDHF approximation, the time propagation of a collisional state is obtained by solving Eq. (42) for the nuclear trajectories and Eqs. (83) and (85) for the reference density matrix and density-matrix change. In a basis of TAO's, the matrix $\mathbf{W}$ takes the form

$$\mathbf{W} = \mathbf{S}^{-1}\mathbf{F}_T \tag{97}$$

and its elements are calculated as discussed above. The equations for the time propagation of the nuclei and the electronic densities must be propagated together.

A. Criteria for integration of the differential equations

The propagation of the above differential equations in time requires the choice of a time step. Criteria have been developed that allow for their efficient integration using an appropriate time step with particular consideration given to the change in the electronic density matrix. The time step $\Delta t = t_1 - t_0$ is chosen so that the condition

$$\epsilon_{\text{lower}} \le \frac{\|\mathbf{Q}\|}{\|\mathbf{P}\|} \le \epsilon_{\text{higher}} \tag{98}$$

is satisfied. Here the tolerance lower bound ϵ_{lower} allows for larger time steps in the adiabatic region where the evolution of the density matrix is nearly equal to the evolution of the reference density. The tolerance higher bound ϵ_{higher} restricts the procedure to smaller time steps in the diabatic region where the change in the density matrix is relatively large. Hence this method is able to automatically adjust the time step size in order to efficiently and accurately integrate the equation for the electronic density matrix.

The trajectory equations may be integrated over the time step determined above with the use of any of a number of numerical integration routines. The present method uses the fourth-order Runge-Kutta (RK) algorithm because it is a self-starting procedure. This property allows for the selection of the time step from the above criteria without any deleterious effects on the integration of the nuclear trajectories. In addition, we have found that the quadratures (quadr) required for $\mathbf{Q}$ are more accurate if the integrands are expanded around $t_{1/2} = t_0 + \frac{1}{2}\Delta t$. The order in which the integrations are performed is portrayed schematically in the following way:

$$(\vec{\mathbf{R}},\vec{\mathbf{P}},\mathbf{P},\mathbf{W},V)_{t_0} \xrightarrow{\text{RK}} (\vec{\mathbf{R}},\vec{\mathbf{P}})_{t_{1/2}} \xrightarrow{\text{UT}} (\mathbf{P}^{(0)},\mathbf{W},V)_{t_{1/2}} \xrightarrow{\text{quadr}} (\mathbf{Q})_{t_1} \xrightarrow{\text{RK}} (\vec{\mathbf{R}},\vec{\mathbf{P}})_{t_1} \xrightarrow{\text{UT}} (\mathbf{P}=\mathbf{P}^{(0)}+\mathbf{Q},\mathbf{W},V)_{t_1} \ . \tag{99}$$

Therefore, first the time is advanced by one-half of the total time step. As we know the full electronic density matrix at time t_0, we may calculate the potential which depends on the density matrix at time t_0. From the positions and momenta of the nuclei and the potential due to the electronic densities at time t_0, as well as their values at earlier times, we are able to move the nuclei to their positions and momenta at time $t_{1/2}$ using the RK algorithm. We are also able to calculate the reference density at time $t_{1/2}$ using the unitary transformation (UT) from Eq. (82). After the nuclear coordinates have been calculated at time $t_{1/2}$, and with this new reference density, we are now ready to complete the time step. The matrix $\mathbf{D}$ is calculated at $t_{1/2}$ and the integral in Eq. (85) is done analytically assuming $\mathbf{D} = \mathbf{D}(t_{1/2})$ for $t_0 \le t \le t_1$; this gives the density-matrix change at t_1. Completing the time step requires the calculation of the electronic potential at time $t_{1/2}$, which is done using the new reference density. Next the nuclear coordinates are propagated to the end of the time step t_1. Having the nuclear positions and momenta at time t_1 we are able to again use Eq. (82) to calculate the reference density matrix at time t_1. Finally, $\mathbf{W}_1$ and V_1 are calculated at t_1 to start the propagation to time t_2.

B. Electronic basis sets and population analyses

Atomic populations provide insight on the time evolution of the interacting atoms even though they cannot be defined in a unique way. Two useful definitions [39] are based on the Mulliken and Lowdin decompositions of density functions. In the Mulliken decomposition we write the density operator as the sum

$$\rho(t)=\sum_a \rho_a^M(t) ,$$

$$\rho_a^M(t)=\sum_{\mu\in a}\sum_{\nu}[|\xi_\mu\rangle P_{\mu\nu}(t)\langle\xi_\nu|+\text{H.c.}]/2 , \qquad (100)$$

$$n_a^M=\sum_{\mu\in a}\sum_{\nu}[P_{\mu\nu}(t)S_{\nu\mu}+\text{c.c.}]/2 ,$$

where n_a is the occupation number of center a, and H.c. and c.c. mean the Hermitian and complex conjugate, respectively, of the preceding term.

Alternatively we can introduce the orthonormal (traveling) Lowdin orbitals

$$|\eta_\lambda\rangle=\sum_{\mu}|\xi_\mu\rangle(\mathbf{S}^{-1/2})_{\mu\lambda} \qquad (101)$$

and the Lowdin populations

$$n_a^L=\sum_{\lambda\in a}\sum_{\mu,\nu}[(\mathbf{S}^{1/2})_{\lambda\mu}P_{\mu\nu}(\mathbf{S}^{1/2})_{\nu\lambda}+\text{c.c.}]/2 . \qquad (102)$$

The two definitions lead to qualitatively similar populations, but can be numerically different. We have found in our work that the Lowdin populations stay positive, as populations should, but Mulliken values can become negative at some times. In what follows we have calculated Lowdin populations.

C. Comparison of asymptotic values with other work

Various experimentally measurable quantities may be calculated with our procedure. We have calculated integral state-to-state cross sections, elastic and inelastic differential cross sections, and polarization parameters for systems with one and two active electrons [28], but we defer most of these results to two following papers [46,47] where we explain in detail the implementation of our methods and the physical significance of the results. However, we do present here the integral charge-transfer cross section for the collision of a proton projectile with a target ground-state hydrogen atom to illustrate the scope and accuracy of our approach. Figure 1 shows the integral charge-transfer cross section over a projectile energy range from 2 eV to 2 keV. The calculated cross sections show good agreement with experimental values [59,60] over the entire range of projectile energies. The calculations were done in a basis of TAO's written as linear combinations of Gaussians, including five orbitals (the 1s, 2s, and 2p orbitals) on each center.

Calculations were done with the effective potential of Eq. (56) and also with the average effective potential of Eq. (57); they lead to similar results. The AEP was used to more accurately maintain state-to-state time reversibility, because it does not depend on the initial state. A numerical study of AEP's further showed [28] that averaging over 2s and 2p channels did not have a noticeable effect; consequently the present calculations were done with equal weights of $\frac{1}{2}$ for the 1s orbital of each center; we refer to this potential as the screened Coulomb potential (SCP) because it allows for dynamical screening of the nuclei during the collision.

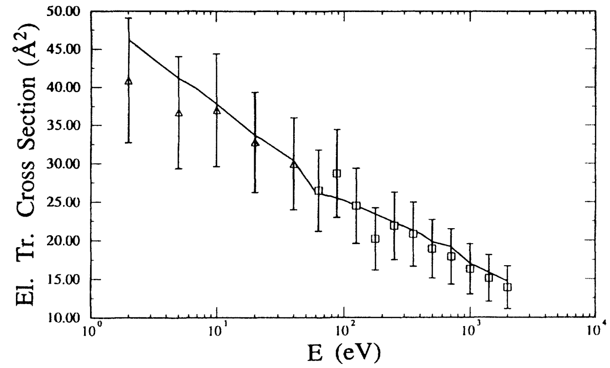

FIG. 1. Comparison of integral electron transfer cross sections versus projectile kinetic energy for $H^+ + H$ collisions. The full line was calculated as explained in the text; the experimental results are shown by triangles and squares with their experimental errors.

D. Results for $H^+ + H$ and $He^{2+} + H$

It is instructive to analyze the temporal change of atomic orbital populations, to learn about the nature of electronic rearrangement, and to gain an understanding of what terms must be accounted for in the calculation of the density matrix. An analysis of the separation of the electronic density into the reference density ρ^0 and the density change σ is revealing. Figure 2 presents the target population in the 1s orbital of the reference density and the change in the density as a function of time for a projectile proton of energy 10 eV colliding with a target

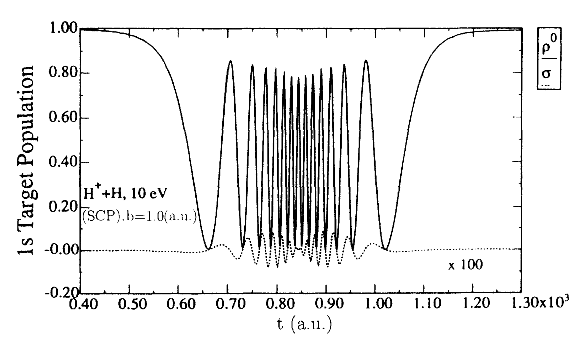

FIG. 2. Target H 1s-orbital population in collisions with H^+, at a laboratory projectile kinetic energy $E=10$ eV and impact parameter $b=1.0$. a.u. versus time, in a.u., during a collision. The full line is from the reference density ρ^0 and the dashed line from the density change σ. Notice that the latter is multiplied by a factor of 100. The trajectory was calculated with the screened Coulomb potential (SCP), including dynamical screening.

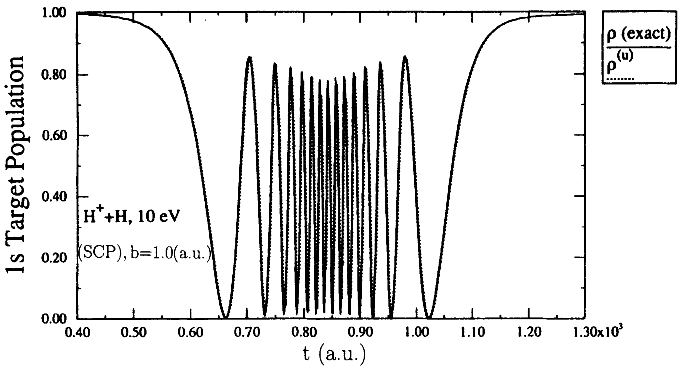

FIG. 3. Cumulative effect of adding the density change σ to the reference density. The full line is the population from the "exact" procedure including the density change σ over time. The dashed line is the population from the uncorrect density $\rho^{(u)}$ (without σ) for the conditions of Fig. 2.

ground-state hydrogen atom. The impact parameter is 1.0 a.u. and the SCP is used for the propagation of the nuclei. Notice that the density change is small throughout the collision.

To ascertain the cumulative effect of adding σ at each time interval, we now define the uncorrected density $\rho^{(u)}$, which is the density that results when the reference density is propagated without the addition of the density change σ at each time step, and compare it to the exact density. One might expect that the uncorrected density would always be close to the exact density because the criteria in Eq. (98) for the integration of Eqs. (81) and (83) require that the density change be kept below a small tolerance bound. Figure 3 compares the uncorrected density to the exact density, which is the sum of the reference density and the density change. In this case the static and exact densities are comparable as the inward and outward portions of the nuclear trajectories are similar, and the effect of adding σ in the way in is compensated by its effect going out. A different situation may be expected for electronic excitation or heteronuclear systems.

Indeed, if we consider a higher collision energy, the situation is quite different. Figure 4 shows the target population in the $2p_x$ orbital of the reference density and the change in the density as a function of time for a 1-keV proton projectile. The collision is taken to be in the x-z plane with the z axis pointing in the direction of the initial projectile velocity. Here we see that the density change is appreciable for a short time in the midst of the collision. Figure 5 demonstrates that this slight change in the density creates a large difference between the exact and uncorrected densities by the end of the propagation. This large difference between the exact and uncorrected densities may be attributed to the fact that adding σ

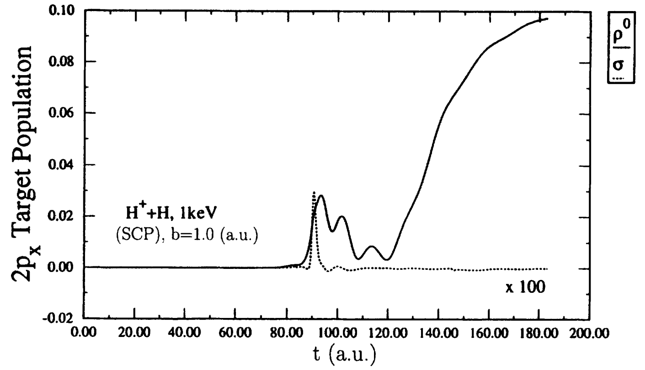

FIG. 4. Reference density and density change contributions to the population of the H $2px$ orbital during electronic excitation, as in Fig. 2, but for $E = 1.0$ keV.

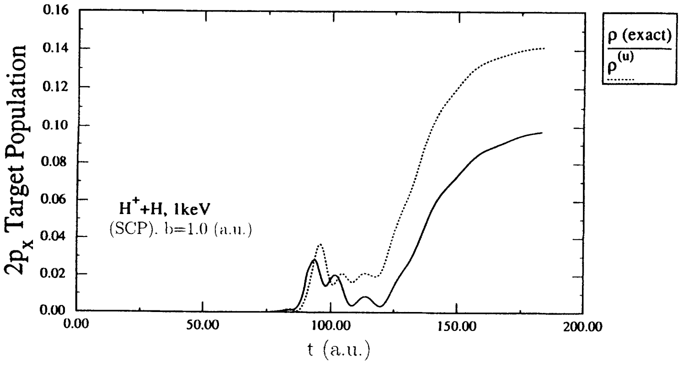

FIG. 5. The exact and uncorrelated density contributions to the $2px$ population of H, from Fig. 4.

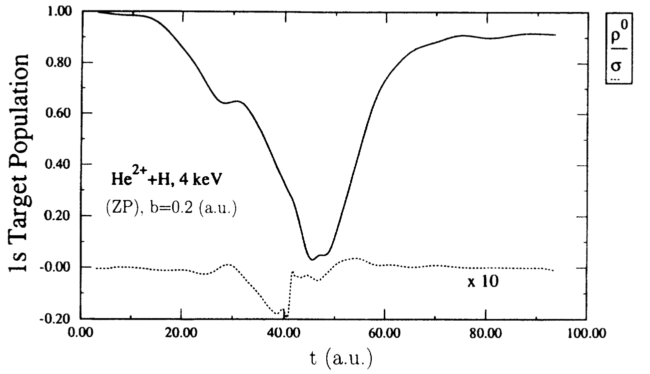

FIG. 6. Target H 1s-orbital population in collisions with He^{2+}, at a laboratory projectile kinetic energy $E=4.0$ keV and impact parameter $b=0.2$ a.u. versus time, in a.u., during a collision. The full line is from the reference density ρ^0 and the dashed line from the density change σ. Notice that the latter is multiplied by a factor of 10. The trajectory was calculated with a constant velocity, for a negligible potential (ZP).

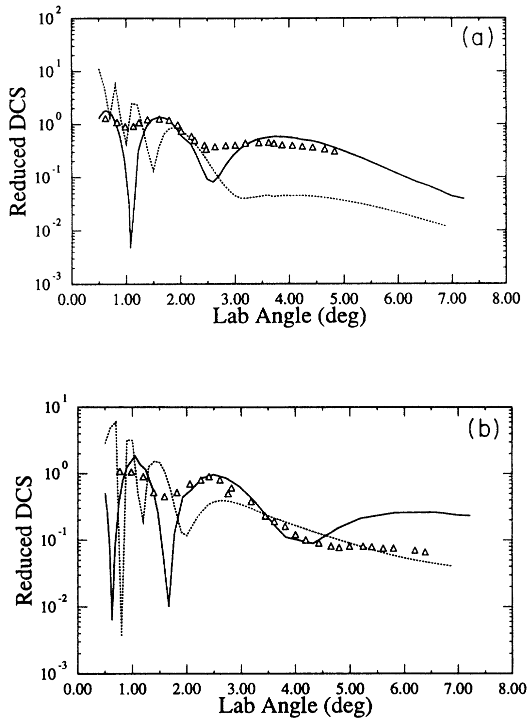

FIG. 8. (a) Reduced elastic differential cross section (in degrees × a.u.) vs the laboratory angle for a proton incident at 410 eV on a hydrogen atom target. Full line, SCP calculation; dotted line, CP; triangles, measurements from Houver, Fayeton, and Barat. (b) Same as (a), but for the electron transfer reduced differential cross section.

changes both populations and phases of the density-matrix elements and that these changes accumulate as time advances. Unlike the previous example, a small error in the uncorrected density is not canceled over a large number of fluctuations.

A similar calculation has been performed for the heteronuclear collision of a projectile He^{2+} ion with a target ground-state hydrogen atom. The projectile energy is 4 keV, the impact parameter is 0.2 a.u., and the nuclei move along straight lines at constant velocity, i.e., the effective potential has been set to zero. This is accurate for the present collision energy. Again, a basis of TAO's has been used including five orbitals per center (the 1s, 2s, and 2p orbitals). Figure 6 shows the target population in the 1s orbital of the reference density and the change in the density as a function of time. As in the previous example, we see that the change in the density is appreciable for only a short time. Figure 7 shows that this slight change in the density again creates a large difference between the exact and static densities by the end of the propagation.

Finally, we present a result which clearly shows the importance of coupling of electronic and nuclear degrees of freedom even in a simple case such as H$^+$+H. Figures 8(a) and 8(b) present results for the elastic and electron transfer reduced differential cross sections $\theta_L \sin(\theta_L)(d\sigma/d\Omega)_L$, respectively, versus laboratory angle θ_L at an incident energy of 410 eV. Theoretical results obtained with the screened Coulomb potential between nuclei and a simple Coulomb repulsion potential (CP) show marked differences at low angles. Compared with experimental results [61], 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 [46].

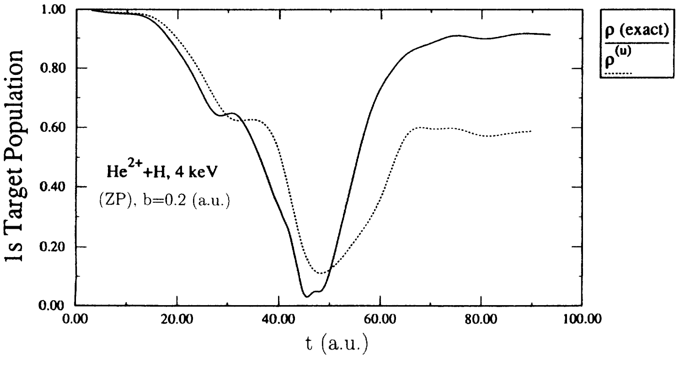

FIG. 7. The exact and uncorrelated density contributions to the 1s population of H, from Fig. 6.

V. CONCLUSION

Combining the eikonal and time-dependent Hartree-Fock approximations, it has been possible to derive compact expressions for cross sections and transition amplitudes, given by Eqs. (58) and (59), that can be used to do calculations at the low velocities of present interest. The first expression is simpler in that it contains only the asymptotic values of TD MO's and has been used for the cross sections presented here. The second expression requires knowledge of the time evolution of a system over the duration of the collision and should have a wider range of applications.

We have shown how it is possible to generate the detailed time dependence while allowing for the coupling of electronic and nuclear motions with different time scales. This has been achieved decomposing the density operator into terms corresponding to relaxation and driven effects, as given by Eq. (71). The procedure combines unitary transformations and quadratures to allow large time steps in the advancement of nuclear positions and velocities.

Calculated atomic populations are found to change extensively over time, acquiring values which can be very different from the final ones, and showing in some cases, for low collision energies, extensive oscillations. The results in Figs. 2–7 illustrate the unique perspective, provided by the use of time-dependent molecular orbitals and density matrices, for electronic rearrangement.

An analysis of populations during collisions, based on Figs. 2–6, shows how sensitive the results are to the accuracy of the intermediate density matrices. Even small changes in their matrix elements during the collisions may lead to large final differences in state populations because of the amplification of collisional dephasing. The results presented here for integral cross sections of electron transfer are in agreement with experiment and other calculations over a wide range of collision velocities. Several other cross-section results obtained with our approach, for $H^+ + H$, $He^{2+} + H$, $H + H$, and $He^+ + H$, are also in good agreement with other works [28]. This indicates that the proposed procedure for calculations of temporal properties are reliable for phenomena where the TDHF approximation is applicable, as in the mentioned systems.

The figures show that populations can rapidly oscillate during collisions and provide insight on the nature of these collisions. It is clear that any sensible population analysis would lead to oscillating atomic populations. Here we chose to work with the Lowdin populations of Eq. (102) because these were found to stay positive during collisions.

The most time consuming stage of computations in our approach involve the generation of the one- and two-electron integrals which make up the Fock matrix. This time increases with the number of atomic basis functions. Therefore, for a given basis set of, e.g., *s*, *p*, and *d* orbitals, the same approach can readily be applied to pairs of atoms with many electrons. Going from two atoms to more than two would involve the additional calculation of three- and four-center electron integrals, for which computer packages are available [41]. On the other hand, the resulting increase in the number of degrees of freedom for the nuclei does not present a serious problem. Methods of molecular dynamics can be used for this purpose [62], which include well understood algorithms for propagation of positions and velocities, and for sampling of initial conditions.

Results presented in this paper were obtained using three different computer architectures. A Sun Sparc ELC station was sufficient for single trajectory calculations and for computer code development work. An IBM 3090 was used for production runs involving about 100 trajectories per collision energy. Here the CPU times varied from less than 1 min to about 2 min per trajectory, depending on the initial conditions. Finally, since these calculations are well adapted to parallel architectures because of the independence of initial conditions, we also used a Kendall Square Research KSR1 computer with 96 processors to calculate as many as 50 trajectories simultaneously, reaching a nearly linear speedup with the number of processors. More detailed computing times will be included in following papers [46,47]. Therefore, the computing times required for our calculations, with our algorithms and computing facilities, allow for extensive investigations of phenomena with one and two active electrons.

ACKNOWLEDGMENTS

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