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13. ABSTRACT (Maximum 200 words) Electronic rearrangement in atomic interactions involve two very different time scales, for nuclear (slow) and electronic (fast) motions. This requires special care when one calculates solutions to the corresponding coupled differential equations. A method has been developed to treat the coupling of very different time scales, based on density operators in Liouville space. Its implementation in terms of density matrices, within an eikonal/TDHF formulation, has allowed us to follow the time-evolution of atomic populations in ion-atom and ion-surface interactions.			
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1. Introduction.

Electronic rearrangement is a common occurrence in interactions of an atom with other atoms or with solid surfaces, and in molecular photodissociation by visible and UV light. Theoretical treatments have mostly focused on the comparison of calculated cross sections or reaction rates with experimental measurements. In this contribution, the emphasis is on the way properties change over time, as a system progresses from its initial to its final state. This aspect of molecular phenomena provides new insight on the nature of molecular interactions and molecular dynamics. By slow collisions, we mean that the nuclear velocities are small compared with electronic ones. Taking electronic velocities to be of the order of 1.0 au, and remembering that a proton with a kinetic energy of 1.000eV has a velocity of the order of 0.2 au, 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.

We review some of our recent work describing electronic rearrangement in terms of coupled differential equations for electronic orbitals and nuclear degrees of freedom. We also present a new compact formulation in terms of operators in Liouville space, for both small and extended molecular systems, and illustrate the method with selected results.

We have developed a theoretical approach applicable to systems with many atoms, and therefore many degrees of freedom. It starts with an exponential expression for the total wavefunction, an eikonal representation, suitable for describing mixtures of quantal and classical degrees of freedom. It then introduces two main assumptions. The nuclear degrees of freedom are described by wavefunctions in the limit of short de Broglie wavelengths, the so called eikonal limit, while the electronic states are described in the time dependent Hartree Fock approximation. Their combination provides an approximation, called here the eikonal/TDHF approximation, of wide usefulness.

The eikonal approximation may be considered an extension of the WKB approximation to many degrees of freedom, that was introduced in the theory of many-body collisions quite a while ago [1]. Related approaches based on propagators [2] and scattering wavefunctions [3] have been applied to atomic and molecular collisions. Our work is based on a paper we wrote on the eikonal method for electronically diabatic phenomena, [4] where we showed how a wavefunction can be constructed from trajectories and then included in a transition integral to calculate quantal state-to-state cross sections, allowing for the coupling of electronic and nuclear motions. It requires the solutions of initial value problems and appears to have wide applicability [5]. We have used it in the description of electronic rearrangement in ion-diatomic reactions, [6] in the theory of photodissociation, [7] and in model studies of atom-atom collisions. [8] A number of alternative approaches to collision induced electronic excitation have been published, differing on the way they describe the coupling of electronic and nuclear motions. [9]

In a different aspect of our work, relating to the description of atomic collisions in terms of atomic and molecular orbitals, [10] we have introduced time-dependent molecular orbitals and the time-dependent Hartree-Fock approximation, as well as some extensions, to describe electronic energy and charge transfer in atomic collisions. [11] Our more recent work has combined these two aspects in a theory that allows for the simultaneous description of molecular orbitals and nuclear motions [12]. This work develops an ab initio molecular dynamics insofar it does not require the previous knowledge of potential energy surfaces and their couplings, to do the molecular dynamics of collisions or spectra, nor does it require previous knowledge of transition dipoles to describe the dynamics of photodissociation. It has been done in the spirit of recent work on the ab initio molecular dynamics of the equilibrium properties of solids, [13] but is different in that its emphasis is on electronic excitation. This requires that electronic transition are described realistically, so that no artificial electronic masses have been used in our work to dampen electronic fluctuations as done for equilibrium studies. Several other publications have

appeared with calculations combining electronic and nuclear dynamics, in most cases making use of already available electronic structure packages which provide atomic force fields. [14]

Our approach has dealt with ways to overcome the difficulties associated with the coupling of differential equation solutions showing two very different time scales: a short one 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 au , or $2.42 \times 10^{-17} \text{ sec}$, while collision times (for kinetic energies from 10 eV to $1,000 \text{ eV}$ and potential ranges of 10 au) vary between 500 au and 50 au . This has lead us to develop a new approach to the calculation of the time-dependence of the electronic density operator as nuclei move, based on decomposing the solution of the TDHF equation into two terms, with a relaxation density as the leading term and a correction term given by an expansion in powers of a driving force [15]. Solving the time scales problem becomes more pressing as nuclear velocities are lowered, and electrons have more time during interactions to jump back and forth between collision partners. This is the problem we focus on here.

The complications due to coupled time scales are compensated by the advantages of an *ab initio* time dependent approach: the correct initial conditions for nonstationary phenomena appear naturally, which simplifies calculations; there is no need for a previous knowledge of potentials and their couplings or transition dipoles, and the approach is suitable for many degrees of freedom insofar there is no need to parameterize potentials.

In what follows, we introduce the *ekonal* representation of the total wavefunction, and describe the *ekonal*/TDHF approximation. The solution of the TDHF equation for the density operator is developed by means of a local interaction picture in Section 3. Here we also present a general formulation in terms of superoperators in Liouville space, that can readily be applied to expanded systems by a partitioning technique. The result is a quantal generalized Langevin equation showing the role of fluctuation and dissipation forces.

Section 4 briefly describes the procedure we have followed to do calculations with matrix equations, after introducing suitable basis sets. Results of our approach have been compared for several systems with other theoretical and experimental results for cross sections, with good agreement. Our detailed calculations may be found in work recently published [12] to appear, [16] and to be published [17]. Here, selected results are instead presented to show how atomic populations change over time, and to analyze their physical significance.

2. The *ekonal*/TDHF approximation

To simplify the following, we assume here that our system is made up of only two collision partners A and B (two atoms or an atom and a solid surface), with their relative position in a center of mass reference system given by the position vector \vec{R} . The wavefunction for the total system of electrons and nuclei is a function of all the electron variables, \mathbf{X} , and of the nuclear variables.

The total wavefunction Ψ , for all electrons and nuclei, is a solution of the Schroedinger equation for a given total energy E :

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

where the total molecular Hamiltonian is given by the sum of nuclear and electronic kinetic energy operators plus all Coulomb potentials. The Schroedinger equation must be solved with boundary conditions for scattering. In the absence of interactions between A and B, we introduce electronic states for fixed relative positions, satisfying the equation

$$H_e^0 \phi_f^0 = E_f \phi_f^0 \quad (2)$$

where ϕ_f^0 is an antisymmetrized electronic wavefunction and E_f^0 is its energy, the sum of internal fragment energies; we also define free relative motion states

$$\psi_{\vec{k}_f}^0(\vec{R}) = (2\pi\hbar)^{-3/2} \exp(i\vec{k}_f \cdot \vec{R}) \quad (3)$$

or the momentum $\vec{P} = \hbar \vec{k}_J$, giving the total energy

$$E = E_J + \hbar^2 k_J^2 / (2M) \quad (4)$$

where M is the reduced mass of the colliding pair.

The total wavefunction for a collision state can be written as

$$\begin{aligned} \psi_{\beta\alpha}^{(+)}(\mathbf{X}, \vec{R}) &= \sum_{\mathbf{J}} \phi_{\mathbf{J}}^{(+)}(\mathbf{X}, \vec{R}) \psi_{\beta\alpha}^{(+)}(\vec{R}) \\ \psi_{\beta\alpha}^{(+)}(\vec{R}) &\approx (2\pi\hbar)^{-3/2} |\exp(i\vec{k}_J \cdot \vec{R}) \delta_{\mathbf{J}\mathbf{I}} \\ &\quad + f_{\mathbf{J}\mathbf{I}}^{(+)}(\Omega) \exp(i\vec{k}_J \cdot \vec{R}) R^{-1} | \end{aligned} \quad (5)$$

where $\alpha = (\vec{k}_I, I)$ and $\beta = (\vec{k}_J, J)$ and we have introduced the usual scattering amplitudes for scattering solid angle Ω .

Given the asymptotic solutions, cross sections follow as usual from

$$d\sigma_{\mathbf{J}\mathbf{I}}/d\Omega = (k_J/k_I) |f_{\mathbf{J}\mathbf{I}}^{(+)}(\Omega)|^2 \quad (6)$$

In what follows we shall assume that the nuclear motions are almost classical. In anticipation of the eikonal approximation, we generally represent the total wavefunction in an exponential form.

$$\psi(\mathbf{X}, \vec{R}) = \chi(\mathbf{X}, \vec{R}) \exp(iS(\vec{R})/\hbar) \quad (7)$$

where by choice the function S is real, while 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 (or convenience to be an action integral approximating the quantal phase of the wavefunction; the phase of χ can compensate in principle for deviations from the correct phase. We refer to this as the *eikonal representation*.

The hamiltonian of the atom pair can be written as

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + H_A \left(\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{X}}, \mathbf{X} \right) \quad (8)$$

Here H_A is the Hamiltonian for fixed nuclear positions. For total energy E , we place the wavefunction in the time-independent Schrödinger equation to obtain

$$\left[\frac{1}{2M} \left(\frac{\partial}{\partial R} \right)^2 + H_A - E \right] \chi(\vec{R}) = 0 \quad (9)$$

which is valid for any S . Here we have used the bracket notation to describe states in the space of electronic functions; a 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 $\langle \chi |$, and taking the real part of the result, which gives [4, 8]

$$\frac{1}{2M} \left(\frac{\partial S}{\partial \vec{R}} \right)^2 + V_{\text{en}} \left(\frac{\partial S}{\partial \vec{R}}, \vec{R} \right) = E \quad (10)$$

$$V_{\text{en}} = V + V' + V''$$

$$(11)$$

$$V = \langle \chi | H_A | \chi \rangle / \langle \chi | \chi \rangle$$

$$V' = -\frac{\hbar}{2M} \frac{\partial S}{\partial R} \left[\left(\frac{\partial \chi}{\partial R} \right) / \chi - \left(\chi \left| \frac{\partial \chi}{\partial R} \right. \right) / \langle \chi | \chi \rangle \right]$$

$$(12)$$

$$V'' = -\frac{\hbar^2}{2M} \frac{1}{2} \left[\frac{\partial^2 \chi}{\partial R^2} / \chi + \left(\chi \left| \frac{\partial^2 \chi}{\partial R^2} \right. \right) / \langle \chi | \chi \rangle \right]$$

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 [18], which can be solved introducing trajectories. Defining the momentum

$$\vec{P} = \partial S / \partial \vec{R} \quad (13)$$

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

$$H_{\text{en}}(\vec{P}, \vec{R}) = \vec{P} \cdot \vec{P} / (2M) + V_{\text{en}}(\vec{P}, \vec{R})$$

$$d\vec{R}/dt = \partial H_{\text{en}} / \partial \vec{P} \quad (14)$$

$$d\vec{P}/dt = -\partial H_{\text{en}} / \partial \vec{R}$$

for initial (\vec{R}_i, \vec{P}_i) . The trajectories give

$$S(\vec{R}) = S(\vec{R}_i) + \int_{\vec{R}_i}^{\vec{R}} d\vec{R} \cdot \vec{P} \quad (15)$$

Cross sections may be extracted from these wavefunctions using their asymptotic form or the transition integral of scattering theory [19]. The asymptotic form is easier to calculate, but it neglects certain phase interference during collisions. We give both expression for future reference.

We first notice that in the absence of interactions the molecular wavefunction for an initial state α is

$$\begin{aligned} \psi_{\alpha}^0 &= \chi_{\alpha}^0 \exp(iS_{\alpha}^0/\hbar) \\ \chi_{\alpha}^0 &= (2\pi\hbar)^{-3/2} \phi_{\alpha}^0 \\ S_{\alpha}^0 &= \hbar \vec{k}_{\alpha} \cdot \vec{R} \end{aligned} \quad (16)$$

where S_{α}^0 is the action for free motion. In the presence of interactions, we instead have

$$S_{\alpha}(\vec{R}) = S_{\alpha}^0(\vec{R}) + \int d\vec{R} (\vec{P} - \hbar \vec{k}_{\alpha}) \quad (17)$$

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

$$\psi_{\alpha}^{(+)} = \chi_{\alpha}^{(+)} \exp(i\tilde{S}_{\alpha}/\hbar) \quad (18)$$

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

$$f_{j\beta}^{(+)}(\Omega) \simeq (2\pi\hbar)^{3/2} R \langle \Phi_{\beta}^0 | \chi_{\alpha}^{(+)} \rangle \exp(i\tilde{S}_{\alpha}(\vec{R})/\hbar - ik_{\beta}R) \quad (19)$$

from which the cross section readily follows.

An alternative and more accurate expression can be constructed from the values of the wavefunction over all space, calculating the scattering integral [19]

$$\begin{aligned} T_{\beta\alpha} &= \int d^3R \langle \Phi_{\beta}^0 | (H_{\beta} - H_{\alpha}^0) | \psi_{\alpha}^{(+)} \rangle \\ &= \int d^3R \langle \chi_{\beta}^0 | H_{\beta}^{(+)} | \chi_{\alpha}^{(+)} \rangle \exp(i(S_{\alpha} - S_{\beta}^0)/\hbar) \end{aligned} \quad (20)$$

where H_{β} is the A - B coupling in the final arrangement channel $c = \beta$, the cross section follows then from

$$f_{j\beta}^{(+)}(\Omega) = -(2\pi)^{-2} \hbar M T_{\beta\alpha} \quad (21)$$

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 wavefunctions change little over a wavelength; we also assume that the electronic states may be accurately described by Hartree-Fock wavefunctions, implying that asymptotic states can also be described by them, in the limit of large interatomic distances

The eikonal approximation

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

$$\left| \langle \chi_{\alpha}^0 | \frac{\partial \chi_{\alpha}^0}{\partial R} \rangle \right| / |\langle \chi_{\alpha}^0 | \chi_{\alpha}^0 \rangle| \ll \lambda^{-1} \quad (22)$$

and

$$\left| \langle \chi_{\alpha}^0 | \frac{\partial^2 \chi_{\alpha}^0}{\partial R^2} \rangle \right| / |\langle \chi_{\alpha}^0 | \chi_{\alpha}^0 \rangle| \left| \langle \chi_{\alpha}^0 | \frac{\partial \chi_{\alpha}^0}{\partial R} \rangle \right| \ll \lambda^{-1} \quad (23)$$

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

$$V_0(\vec{R}) = \langle \chi_0(\vec{R}) | H_B | \chi_0(\vec{R}) \rangle / \langle \chi_0(\vec{R}) | \chi_0(\vec{R}) \rangle \quad (24)$$

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

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

$$V(\vec{R}) = \sum_j w_j V_0(\vec{R}) \quad (25)$$

with chosen fractional weights w_j , adding over energetically accessible states j . The flexibility provided by these weights can be used to develop an approach satisfying state-to-state time reversibility [8].

Using the eikonal inequalities, Eq. (9) is approximated by the differential equation

$$\left[\frac{\vec{P}}{M} \cdot \frac{\hbar}{i} \frac{\partial}{\partial \vec{R}} + H_B - W_0(\vec{R}) \right] \chi_0(\vec{R}) = 0 \quad (26)$$

$$W_0(\vec{R}) = V_0(\vec{R}) + \frac{\hbar}{2M} \frac{\partial^2 \vec{P}}{\partial \vec{R}}$$

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. (19), to give a finite cross section.

The equation for χ may be simplified transforming variables from the cartesian components of the relative position vector to trajectory coordinates for given initial conditions, noting that $\vec{R} = \vec{R}(t, \rho, \phi)$ (or fixed t_i and Z_i). We work with the new variables (t, ρ, ϕ) and use that

$$\frac{\vec{P}}{M} \cdot \frac{\partial}{\partial \vec{R}} = \left(\frac{\partial}{\partial t} \right)_{\rho, \phi} \quad (27)$$

Defining time-dependent electronic states η_0 by means of

$$|\chi_0(\vec{R}(t))\rangle = (2\pi\hbar)^{-3/2} |\eta_0(t)\rangle \exp\left(\frac{i}{\hbar} \int_{t_i}^t dt' W_0(\vec{R}(t'))\right) \quad (28)$$

and replacing in Eq (26) we find the equation and boundary conditions

$$\left(\frac{\hbar}{i} \frac{\partial}{\partial t} + H_B \right) |\eta_0(t)\rangle = 0 \quad (29)$$

$$|\eta_0(t)\rangle \approx |\phi_0^0\rangle \exp\left(-\frac{i}{\hbar} E_0^0(t-t_i)\right) \quad \text{for } t \rightarrow t_i$$

Equations (29) must be solved simultaneously with the trajectory equations

$$d\vec{P}/dt = -dV_0/d\vec{R} \quad (30)$$

so that the electronic state adapts to the nuclear trajectories and reciprocally, in a procedure we have called the *self-consistent eikonal method*.

Cross sections for electronic transitions $I \rightarrow J$ follow from $f_{JI}^{(I)}$ in the eikonal approximation, noting that the divergence of streamlines is related to the elastic differential cross section obtained from classical trajectories in the potential V_I . Therefore

$$\left(\frac{d\sigma}{d\Omega} \right)_{JI} = \left(\frac{d\sigma}{d\Omega} \right) | \langle \eta_0^J(t_f) | \eta_0^I(t_f) \rangle |^2 \quad (31)$$

where the first factor is the elastic differential cross section, and the bracket is a transition probability obtained projecting the evolved electronic state at the final time t_f , on the non-interacting 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. Using the AEP one can alternatively calculate trajectories and elastic differential cross sections independent of the initial quantum state. The above expression should be accurate provided the effective potential changes over time to properly include electronic transitions.

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

This may be calculated from [17a]

$$T_{\beta\alpha} = \int_0^{\infty} d\alpha \rho_\alpha \int_0^{2\pi} d\phi \int_{\mathcal{L}} dt (\eta_\beta^\dagger | H_I | \eta_\alpha) g_{\beta\alpha} \quad (12)$$

$$g_{\beta\alpha} = (2\pi\hbar)^{-3} (\Delta\Delta_\alpha)^{1/2} \exp(-iA_{\beta\alpha}/\hbar)$$

$$A_{\beta\alpha} = S_\beta^0 - \frac{\hbar^2 k^2}{2M} (t - t_\alpha) - |S_\alpha - \int_{t_\alpha}^{t_\beta} dt' \left(\frac{\partial^2}{\partial M}\right) r|$$

The factor g contains the Jacobian determinants Δ and a difference of action integrals, and can be calculated from trajectory bundles [7b]. 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.

The TDHF approximation.

Choose next for η_0 the approximate form

$$\eta_0(\mathbf{X}, t) \approx D_0(\mathbf{X}, t) \quad (13)$$

where D_0 is a time-dependent determinantal function constructed from MO's, for an initial electronic state I , and with the correct asymptotic behaviour for large R .

For a chosen state I , and a given trajectory $\tilde{\mathbf{R}}(t)$, the determinant is written as

$$D_0(\mathbf{X}, t) = (N!)^{1/2} \mathcal{A} \prod_{i=1}^N \psi_i(\mathbf{x}_i, t) \quad (14)$$

$$\psi_i(\mathbf{x}_i, t) = \psi_i^0(\tilde{\mathbf{r}}_i, t) \gamma_i(\mathbf{G}_i)$$

$$(\psi_i^0 | \psi_j^0) = \delta_{ij}$$

where N is the number of electrons. \mathcal{A} the antisymmetrizing projection operator, and the ψ_i^0 are time dependent (TI) 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 depend on nuclear positions and velocities [10a]. The differential equations for the TI MO's may be derived from a time dependent variational functional in a well known procedure [20]. The result

s the set of equations

$$F^\gamma \psi_i^\gamma + \sum_j \psi_j^\gamma c_{ij} = i\hbar \partial_t \psi_i^\gamma / \partial t \quad (15)$$

with the Lagrange multipliers c forming a hermitian matrix. Here,

$$F^\gamma = \hat{H}^{(1)} + \hat{G}^\gamma(\hat{p}^\alpha, \hat{p}^\beta) \quad (16)$$

s the Fock operator written as a sum of a one-electron term $F^{(1)}$, plus the HF self-consistent potential energy operator G^γ . The initial conditions come from the implied assumption that the free electronic states are also determinantal wavefunctions agreeing asymptotically with D_0 at the initial time.

Instead of working with the differential equation for the MO's, it is more convenient in treatments of time dependent phenomena, to introduce the electronic density operator

$$\hat{\rho}^\gamma(t) = \sum_{\text{occ } i} |\psi_i^\gamma(t)\rangle \langle \psi_i^\gamma(t)| \quad (17)$$

satisfying the TDHF equation

$$F^\gamma \hat{\rho}^\gamma - \hat{\rho}^\gamma F^\gamma = i\hbar \partial_t \hat{\rho}^\gamma / \partial t \quad (18)$$

This operator may be generated without a preliminary knowledge of which orbitals are the occupied ones. In addition, it 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

$$V_0^{(HF)} \approx V_I^{(HF)} = V_{Ic} + \sum_j \text{tr}[\hat{\rho}_j^0 (H + F^\gamma)] / 2 \quad (19)$$

where the first term is the (A core) - (B core) interaction potential.

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 multi-configurational HF states, or on time-dependent coupled cluster states. A variational improvement of TDHF transition amplitudes can also be carried out by analogy with work done on ion-atom collisions [11]

The combined eikonal and TDHF (Eik/TDHF) approximation provides the required cross sections. From the asymptotic form of the electronic wavefunction,

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{TJ} &= \left(\frac{d\sigma}{d\Omega}\right)_{TJ} |D_{\alpha}^0(t_f)| |D_{\alpha}^0(t_f)|^2 \\ &= \left(\frac{d\sigma}{d\Omega}\right)_{TJ} |\det\{\langle \psi_j^0(t_f) | \phi_i(t_f) \rangle\}|^2 \end{aligned} \quad (40)$$

where we have used that the bracket of two determinants is the determinant of the matrix formed by their MO brackets [21]. Similarly, the transition integral may be obtained integrating along trajectories in accordance with [17a]

$$T_{\beta\alpha} = \int d\theta_{\beta} \int d\phi_{\beta} \int dt g_{\beta\alpha}(t) \left(-\frac{\hbar}{i}\right) \frac{\partial}{\partial t} \{\det\{\langle \psi_j^0(t) | \psi_i(t) \rangle\}\} \quad (41)$$

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 expression is valid also for slow collisions

3. Liouville-space formulation for finite and extended systems.

It is convenient to calculate the density operator breaking up the whole time interval into subintervals corresponding to electronic adiabatic or diabatic regions. At large distances, the evolution of the system is electronically adiabatic and the density operator changes with time only to the extent that the density relaxes at each given nuclear conformation. This is assumed here to occur between incoming trajectory times t_i and t_o , and outgoing trajectory times t_s and t_f . Solving for the adiabatic density operator between incoming trajectory times t_i and t_o , we obtain the initial conditions for the electronically diabatic interval between times t_s and t_o

We develop a convenient computational procedure for the density operator by decomposing it into two contributions. The first term describes electronic relaxation for fixed nuclei, and the second term the density operator change due to the driving forces of nuclear motions. We write the full density operator as

$$\rho(t) = \rho^0(t) + \sigma(t) \quad (42)$$

and construct solutions for the two terms 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 first term, the density to zeroth order in the local velocity, is

$$\frac{\partial \rho^0}{\partial t} = (i\hbar)^{-1} (F_0 \rho^0 - \rho^0 F_0) = (i\hbar)^{-1} \mathcal{F}_0 \rho^0(t) \quad (43)$$

where ρ^0 is evaluated at \vec{R}_0 , and the initial condition is $\rho^0(t_0) = \rho_0$. We use here a notation where script symbols signify superoperators in Liouville space, to present compact expressions; the last equality introduces the Liouville superoperator corresponding to the Fock operator. The solution to this operator equation is given by

$$\rho^0(t) = U_0(t, t_0) \rho^0(t_0) U_0^\dagger(t, t_0) \quad (44)$$

$$U_0(t, t_0) = \exp[-i(t - t_0) \mathcal{F}_0 / \hbar]$$

or alternatively in terms of a time-evolution superoperator in Liouville space, by

$$\rho^0(t) = \exp[-i \mathcal{F}_0(t - t_0) / \hbar] \rho^0(t_0) = U_0(t, t_0) \rho^0(t_0) \quad (45)$$

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

In actual calculations 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

$$A_L(t) = U_0(t, t_0)^\dagger A(t) U_0(t, t_0) \quad (46)$$

This expression may be evaluated at time t_1 , and the procedure may be repeated to advance the time again. This is done for $t_0 \leq t \leq t_1$, after which the system evolves again adiabatically.

For extended systems it is more convenient, instead of finding the solution for the whole density operator, to concentrate on the part of the density that changes over time. We consider here an atom colliding with an extended system such as a solid surface, the target. The mathematical way to do that relies on the introduction of projection operators on the primary and secondary regions of the whole system. The first projector includes the projectile and the impact zone of the target, while the second one includes the outer regions of the target, which changes little over the duration of the collision. We indicate the corresponding orthogonal projectors by O_p and O_s , satisfying $O_p + O_s = I$ and $O_p O_s = 0$.

We define the diagonal and non-diagonal parts of the density operator by means of

$$\rho_D(t) = O_p \rho O_p + O_s \rho O_s \quad (51)$$

$$\rho_N(t) = O_p \rho O_s + O_s \rho O_p$$

so that

$$\rho(t) = \rho_D(t) + \rho_N(t) \quad (52)$$

The same partition applies to the relaxation and the driven terms of the density operator.

Next we derive a reduced differential equation for the diagonal part. The derivation is

simplified using the relations

$$(AB)_D = A_D B_D + A_N B_N \quad (53)$$

$$(AB)_N = A_D B_N + A_N B_D$$

for two operators A and B . The equations take a simpler form when the projectors are time-independent, we treat this case in detail and give the more general results later on. For time-independent projectors we have for either D or N parts,

$$\left(\frac{\partial \rho}{\partial t}\right)_{D,N} = -\left(\frac{\partial \rho_{D,N}}{\partial t}\right) \quad (54)$$

and in particular introduce the density terms

$$\rho_L^0(t) = \rho_0 \quad (47)$$

$$\sigma_L(t) = \rho_L(t) - \rho_0$$

with the latter satisfying the differential equation

$$i\hbar \sigma_L(t) = D_L(t) + \Delta F_L(t) \sigma_L(t) - \sigma_L(t) \Delta F_L(t) \quad (48)$$

$$D_L(t) = \Delta F_L(t) \rho_0 - \rho_0 \Delta F_L(t) = \Delta \mathcal{F}_L(t) / \rho_0$$

where D_L is the term driving the diabatic density, found to be linearly dependent on the adiabatic density; given the initial condition $\sigma_L(t_0) = \rho_L(t_0) - \rho_0^0 = 0$, the formal solution is

$$\sigma_L(t) = (i\hbar)^{-1} \int_{t_0}^t dt' [D_L(t') + \Delta \mathcal{F}_L(t') \sigma_L(t')] \quad (49)$$

which can be solved by iteration, between times t_0 and t_1 .

At large distances the difference between the Fock operator at times t and t_0 is very small because the time dependence comes from the Coulomb interactions and its changes are inversely proportional to the distance between the collision partners. Therefore if σ is small to begin with, it can be neglected at all times corresponding to large distances.

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 within 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

Insular 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 $D_L(t)$ in Eq. (48) leads to a local linearization in time (or a temporal linearization) of $\sigma_L(t)$, which gives the full density operator as

$$\rho(t) = \rho^0(t) + (i\hbar)^{-1} U_0(t, t_0) \int_{t_0}^t dt' D_L(t') \quad (50)$$

$$\rho^0(t) + (i\hbar) \int_{t_0}^t dt' U_0(t, t') D(t') U_0(t', t_0) \rho^0(t_0)$$

This gives, taking diagonal and non-diagonal parts of the differential equation for the density operator,

$$i\hbar \dot{\rho}_D = \mathcal{F}_{DD} \rho_D + \mathcal{F}_{DN} \rho_N \quad (55)$$

$$i\hbar \dot{\rho}_N = \mathcal{F}_{DN} \rho_D + \mathcal{F}_{NN} \rho_N$$

Solving for the nondiagonal part of ρ ,

$$\begin{aligned} \rho_N(t) &= \rho_N(t_0) + (i\hbar)^{-1} \int_{t_0}^t dt' U_D(t, t') \mathcal{F}_{DN}(t') \rho_D(t') \\ U_D(t, t') &= \exp[-i \int_{t'}^t dt'' \mathcal{F}_{DD}(t'') / \hbar] \end{aligned} \quad (56)$$

where we have introduced the (time-ordered) time evolution operator in Liouville space generated by the diagonal part of the time-dependent Fock operator. This may be introduced in the differential equation for ρ_D to obtain the reduced differential equation

$$\begin{aligned} i\hbar \dot{\rho}_D &= \mathcal{F}_{DD} \rho_D + \int_{t_0}^t dt' M_D(t, t') \rho_D(t') + w_D(t) \\ M_D(t, t') &= (i\hbar)^{-1} \mathcal{F}_{DN}(t) U_D(t, t') \mathcal{F}_{ND}(t') \\ w_D(t) &= \mathcal{F}_{NN}(t) \rho_N(t_0) \end{aligned} \quad (57)$$

As expected in a partitioning procedure, it contains a memory (or dissipation) term and a fluctuation term with the physical meaning of an energy density fluctuation [22]. This is a quantum generalized Langevin equation for the THF density operator

This general procedure can now be specialized to the relaxation and driven terms in the density operator. For the first term, the equation simplifies because the Fock operator here is time independent, calculated at a fixed nuclear position. This equation may be solved by Laplace transform methods. For our present purposes, we only need to write it in terms of an effective Hamiltonian with a new term describing transitions from the primary region to the secondary

region and back,

$$i\hbar \dot{\rho}_D^0 = (\mathcal{F}_{DD} + V_D) \rho_D^0(t) + w_{0,D} \quad (58)$$

$$V_D = \mathcal{F}_{0,N} \mathcal{G}_{0,D} \mathcal{F}_{0,N}$$

$$w_{0,D} = \mathcal{F}_{0,N} \rho_N(t_0)$$

For the driven term we can readily write the diagonal and nondiagonal parts to lowest order, as

$$\begin{aligned} \sigma_{L,D}(t) &= (i\hbar)^{-1} \int_{t_0}^t dt' D_{L,D}(t') \\ \sigma_{L,N}(t) &= (i\hbar)^{-1} \int_{t_0}^t dt' D_{L,N}(t') \end{aligned} \quad (59)$$

When the projectors depend on time, it may yet be possible to assume they are temporarily constant in the $t_0 \leq t \leq t_1$ interval, taking them equal e.g. to $O_p(t_0)$ and $O_s(t_0)$ there.

A more rigorous procedure recognizes that their time derivatives are opposite and non-diagonal so that

$$\dot{O}_p = O_p \dot{\Omega} O_s + O_s \dot{\Omega} O_p = -\dot{O}_s \quad (60)$$

where the operator Ω must be constructed in each application. Replacing these derivatives into

$$\frac{\partial \rho_D}{\partial t} = \left(\frac{\partial \rho}{\partial t} \right)_D + \dot{O}_p \rho O_p + O_p \dot{\rho} O_p + \dot{O}_s \rho O_s + O_s \dot{\rho} O_s \quad (61)$$

and the similar equation for the non-diagonal part, a pair of differential equations result for ρ_D and ρ_N with a modified Fock operator containing Ω . Instead of continuing along these lines, we show next how calculations may be done with a given basis set. Other choices for the projectors are suggested by work with time-independent density operators introduced to describe localized electronic structure [21]

4. The calculation of time-dependent properties.

The MO's can be expanded in basis sets of orbitals for the atom pair, and these in turn 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 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) $\{\phi_\mu\}$, 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

$$\psi_i^j(\vec{r}, t) = \sum_p \phi_p(\vec{r}, t) c_{pi}^j(t) \quad (62)$$

where the coefficients are complex valued.

The density operator in this basis is

$$\rho^j(t) = \sum_{pq} |\phi_p\rangle P_{pq}^j(t) \langle \phi_q| \quad (63)$$

where P_{pq} is the (pq) -element of the density matrix \mathbb{P}^j . In matrix notation,

$$\hat{\rho}^j = |\phi\rangle \mathbb{P}^j \langle \phi| \quad (64)$$

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

$$P_{pq}^j(t) = \sum_{\mu\nu} c_{p\mu}^j(t) c_{q\nu}^j(t)^* \quad (65)$$

The Fock matrix \mathbb{F}^j is defined as

$$\mathbb{F}^j = \langle \phi | \hat{F} | \phi \rangle \quad (66)$$

Inserting Eq. (36) into the above definition we have

$$\mathbb{F}^j = \mathbb{H} + \mathbb{G}^j(\mathbb{P}^j, \mathbb{P}^j) \quad (67)$$

where

$$\mathbb{H} = \mathbb{K} + \mathbb{V}_A + \mathbb{V}_B \quad (68)$$

is the core Hamiltonian matrix, \mathbb{G}^j the Hartree-Fock electron-electron interaction matrix, \mathbb{K} the electron kinetic energy matrix, and \mathbb{V}_A the electron-(atom A) potential matrix.

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

$$\Omega = \langle \phi | \frac{\partial}{\partial t} | \phi \rangle \quad (69)$$

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. (12)

$$i\dot{\rho}^j = S^{-1}(\mathbb{F}^j - i\Omega)\mathbb{P}^j - \mathbb{P}^j(\mathbb{F}^j - i\Omega)S^{-1} \quad (70)$$

where $S = \langle \phi | \phi \rangle$ is the overlap matrix.

Working in a basis of travelling AO's, we have for the MO's

$$\psi_i^j(\vec{r}, t) = \sum_p \xi_p(\vec{r}, t) c_{pi}^j(t) \quad (71)$$

$$\xi_p(\vec{r}, t) = \chi_p(\vec{r}) T_{pm}(\vec{r}, t)$$

where χ_p is an AO centered at nuclear position $\vec{R}_{pm}(t)$, and

$$T_{pm}(\vec{r}, t) = \exp(im_e [v_{pm}^2(t) \vec{r} - \int dt v_{pm}^2(t')/2]) \quad (72)$$

is an electron translation factor. The density operator in this basis is (omitting the spin index)

$$\rho(t) = \sum_{\mu\nu} f_{\mu\nu}(t) F_{\mu\nu}^j(t) \quad (73)$$

where $F_{\mu\nu}$ is the $\mu\nu$ element of the density matrix \mathbb{F}^j . In matrix notation,

$$\hat{\rho} = |\xi\rangle \mathbb{F}^j \langle \xi| \quad (74)$$

where $W = S^{-1}F_T$ and $W_0 = W(t_0)$, and is given by

$$\begin{aligned} P^0(t) &= U_0(t, t_0) P_0 U_0^\dagger(t, t_0) \\ U_0(t, t_0) &= \exp[-iW_0(t - t_0)] \end{aligned} \quad (79)$$

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

$$i\dot{Q}_L(t) = D_L(t) \quad (80)$$

The original change in the density matrix is given by

$$\begin{aligned} Q(t) &= U_0(t, t_0) Q_L(t) U_0^\dagger(t, t_0) = \int_{t_0}^t dt U_0(t, t) D(t) U_0^\dagger(t, t) \\ D &= \Delta W P^0 - P^0 \Delta W \end{aligned} \quad (81)$$

with $\Delta W = W(t) - W_0$, and can be explicitly constructed at time t_1 by quadratures.

For an extended system, a partitioning can be done by analogy with the described operator procedure. Working now with matrices, one can instead introduce basis sets for primary and secondary regions, and the density matrix can then be partitioned in blocks. We consider here again an atom colliding with an extended system such as a solid surface, the target.

In the adiabatic regime, during the incoming and outgoing time intervals, we use a basis of travelling AOs (ζ_μ) and delocalized target orbitals (ϕ_ν), which we can assume are orthogonal sets because the distances are large. These two sets constitute the primary and secondary sets to be used in the partition.

During the electron transfer interval, a basis of travelling AOs (ζ_μ) and another of localized target orbitals (ζ_ν) are introduced, taking into account that they are non-orthogonal at short distances. The primary set includes now the atomic orbitals and the localized orbitals in the target region that undergoes diabatic transitions. The secondary basis set is the remaining set

where $\{\zeta\}$ and $\{\zeta\}$ are row and column matrices of ζ_μ orbitals, respectively. Similarly, the matrix elements needed to construct the Fock matrix and the overlap matrix must be calculated in this basis. We use this basis in what follows, and omit the superscripts. An advantage of using this basis is that $F-i\Omega$ is replaced in the matrix differential equations by a matrix F_T (involving translation factors) which goes asymptotically to F at low velocities.[12]

Once the density matrices have been obtained over time, it is possible to calculate temporal properties such as atomic populations, and orbital alignment or orientation versus time. Atomic populations provide insight on the time evolution of the interacting atoms even though they can not be defined in a unique way. Two useful definitions are based on the Mulliken and Lowdin decompositions of density functions. In the Mulliken decomposition we write the density operator as the sum

$$\begin{aligned} \rho(t) &= \sum_a \rho_a^M(t) \\ \rho_a^M(t) &= \sum_{\mu, \nu} |\zeta_\mu\rangle P_{\mu\nu}(t) \langle \zeta_\nu| + h.c. / 2 \end{aligned} \quad (75)$$

$$n_a^M = \sum_{\mu, \nu} |P_{\mu\nu}(t) S_{\mu\nu} + c.c. / 2|$$

where n_a is the occupation number of center a .

Alternatively we can introduce the orthonormal (travelling) Lowdin orbitals

$$|\eta_\lambda\rangle = \sum_{\mu} |\zeta_\mu\rangle (S^{-1/2})_{\mu\lambda} \quad (76)$$

and the Lowdin populations

$$n_a^L = \sum_{\lambda, \mu} (S^{1/2})_{\lambda\mu} P_{\mu\nu} (S^{1/2})_{\nu\lambda} + c.c. / 2 \quad (77)$$

The operators $\rho^0(t)$ and $\sigma_L(t)$ have matrix representations $P^0(t)$ and $Q_L(t)$ in the basis of TAO's. For fixed nuclei (and fixed spin γ) the density matrix $P^0(t)$ satisfies

$$i\dot{P}^0(t) = W_0 P^0(t) - P^0(t) W_0^\dagger \quad (78)$$

of localized solid orbitals. Although these two sets are not orthogonal, the blocking of matrix equations can be done as before, provided physical properties are reconstructed with the proper overlap matrix elements

We correspondingly partition the density matrix in both regimes, into (pp), (ps), (sp), and

(ss) blocks. The matrix P^0 is written as

$$P^0 = \begin{pmatrix} P_{pp}^0 & P_{ps}^0 \\ P_{sp}^0 & P_{ss}^0 \end{pmatrix} \quad (82)$$

and other matrices are partitioned in a similar way. Equation (78) (or P^0) is then split into four equations for $P_{pp}^0(t)$, $P_{ps}^0(t)$, $P_{sp}^0(t)$, $P_{ss}^0(t)$, and similarly four equations appear for $Q_{pp}(t)$, $Q_{ps}(t)$, $Q_{sp}(t)$ and $Q_{ss}(t)$. Details of calculations can be found in ref. [16]

We illustrate our formalism with some results for atomic populations in the collisions $H^+ + H$ [24] and $Na^+ + W(011)$ [16]. Figures (1a) and (1b) show the population of a proton projectile colliding at 10 eV kinetic energy with a hydrogen atom target, as a function of time for two impact parameters, $b = 1.0$ au and 1.2 au respectively. The calculations were done with a basis set of travelling hydrogenic orbitals of 1s, 2s and 2p type, with an average effective potential (a screened Coulomb potential), obtained as explained in Section 2, from Eqs. (24) and (25). Two features are remarkable in the results. Firstly, the electron repeatedly jumps between the two nuclei, and secondly, a small change in the impact parameter (only 0.2 au) leads to a large change in the final result, although the incoming portions of the trajectories are almost indistinguishable. Both effects are related to strong quantum phase interference. The first comes mostly from the MO oscillations due to interference of the $1\sigma_g$ and $1\sigma_u$ orbitals in the standard time-independent nomenclature, although there are also transient contributions from molecular orbitals deriving from 2s and 2p atomic orbitals. The change in the outward portion of the trajectory is the result of accumulated phase shifts, all with similar dephasing angle, adding up to a large final difference

Figure 2 shows the total Mulliken population of the Na^+ projectile as it interacts with the metal surface $W(011)$ in a collision with velocity perpendicular to the surface and a kinetic energy of 1.0 au (or 27.2 eV). The potential here was an exponentially repulsive function of the distance to the surface with parameters appropriate for the Na^+ core interacting with a rigid solid slab; this is a simplification adopted after numerically verifying that at these high collision energies the effective potential does not change with the population of Na. The calculation of the density matrix was done with a basis of 3s and 3p orbitals in a Na^+ pseudopotential, and generalized Wannier functions (localized and showing the effect of the surface) at a lattice of points in a metal slab. Fluctuation and dissipation effects were modelled to include image charges and localization of electrons at the point of impact.[25, 12b, 16] The calculated population, initially equal to zero, increases rapidly with time when the electronic charge distributions start to overlap; it then oscillates rapidly, reflecting phase interference between localized and atom orbitals, and finally settles at a constant value. The observation here is that a lot more happens than one would assume by analyzing only the asymptotic values of the population probability, because of the temporary appearance of electronically excited states.

5. Conclusion.

Studies of temporal rearrangements in the interaction of electronic and nuclear motions provide new insight on the transient events taking place in atomic and molecular interactions.

Starting with a general decomposition of the total molecular wavefunction in an eikonal representation, it is possible to develop approximations where nuclear motions are described in a classical language while electrons are described quantum mechanically. In the eikonal approximation, results from classical trajectories of the nuclei can be used to reconstruct the wavefunction and from it to calculate state-to-state transition probabilities. The electronic states can be described in the time-dependent Hartree-Fock approximation, which is usually sufficient

to incorporate the initial conditions. It can be used in many problems provided there is no electronic state averaging due to long lasting phenomena or strongly coupled events (such as in transfer of two electrons). This case can instead be treated with time-dependent configuration interaction methods, or with a variational procedure as we have shown some time ago [11]

Here we have concentrated on the theory needed to overcome the problems arising from the coupling of different time scales for electrons and nuclei. We have found that there is a solution based on the decomposition of the density operator into two terms, one describing its relaxation for a fixed conformation, and the other adding the effect of driving forces from the moving nuclei. The formulation in terms of density operators in a local interaction picture was put in a general framework with the introduction of superoperators in Liouville space.

The superoperator formalism was helpful in the treatment of extended systems, after introducing projection operators on primary and secondary regions. This led to quantal generalized Langevin equations, which can be solved in matrix form using a basis set of localized orbitals.

We illustrated the formalism with two selected examples. These show that electronic density oscillations can be very pronounced during interactions due to phase interference and temporary excitations. They provide insight on the quantal molecular dynamics of electronic energy and charge transfer, insofar they illustrate behaviour that should be frequently present in these phenomena.

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FIGURE CAPTIONS

Fig. 1. Population of a proton projectile colliding at 10 eV kinetic energy with a hydrogen atom target, as a function of time for two impact parameters: (a) $b = 1.0$ au and (b) 1.2 au respectively.

Fig. 2. Total Mulliken population of the N_{1s} projectile as it interacts with the metal surface $W(011)$ in a collision with velocity perpendicular to the surface and a kinetic energy of 1.0 au (or 27.2 eV).

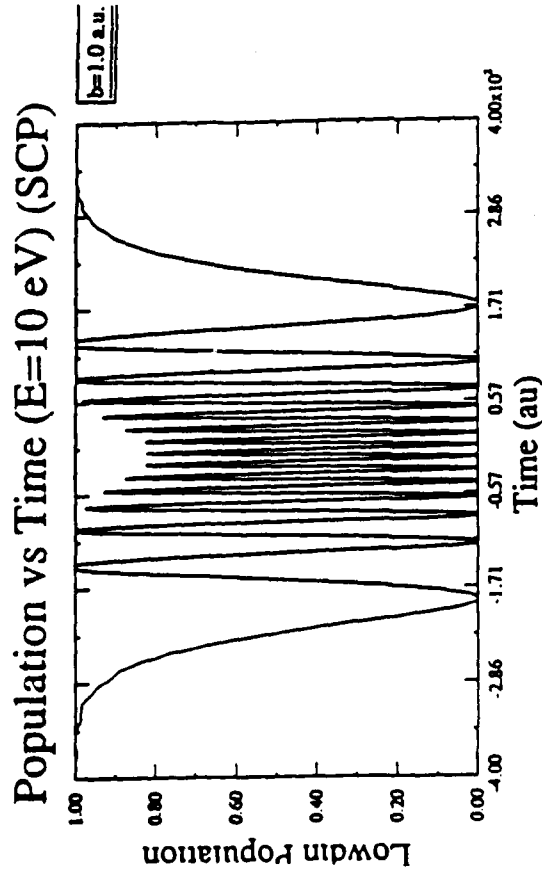


Figure 1a

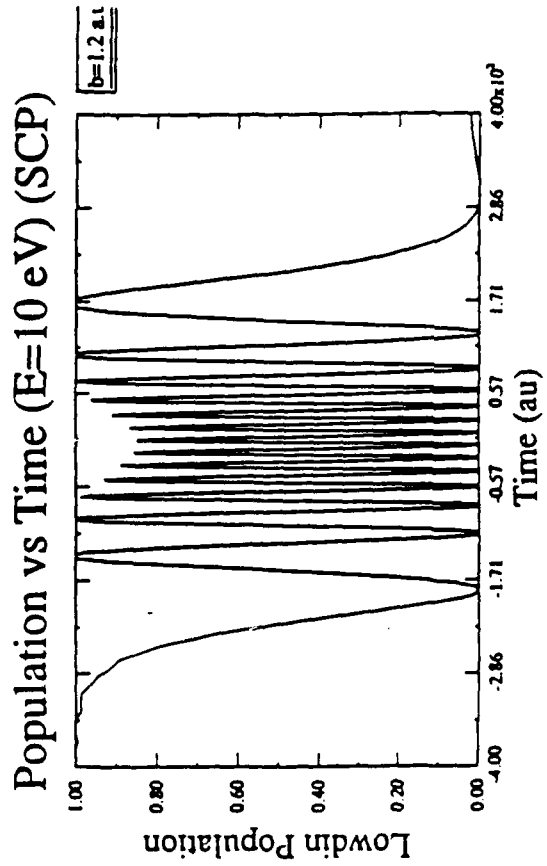


Figure 1b

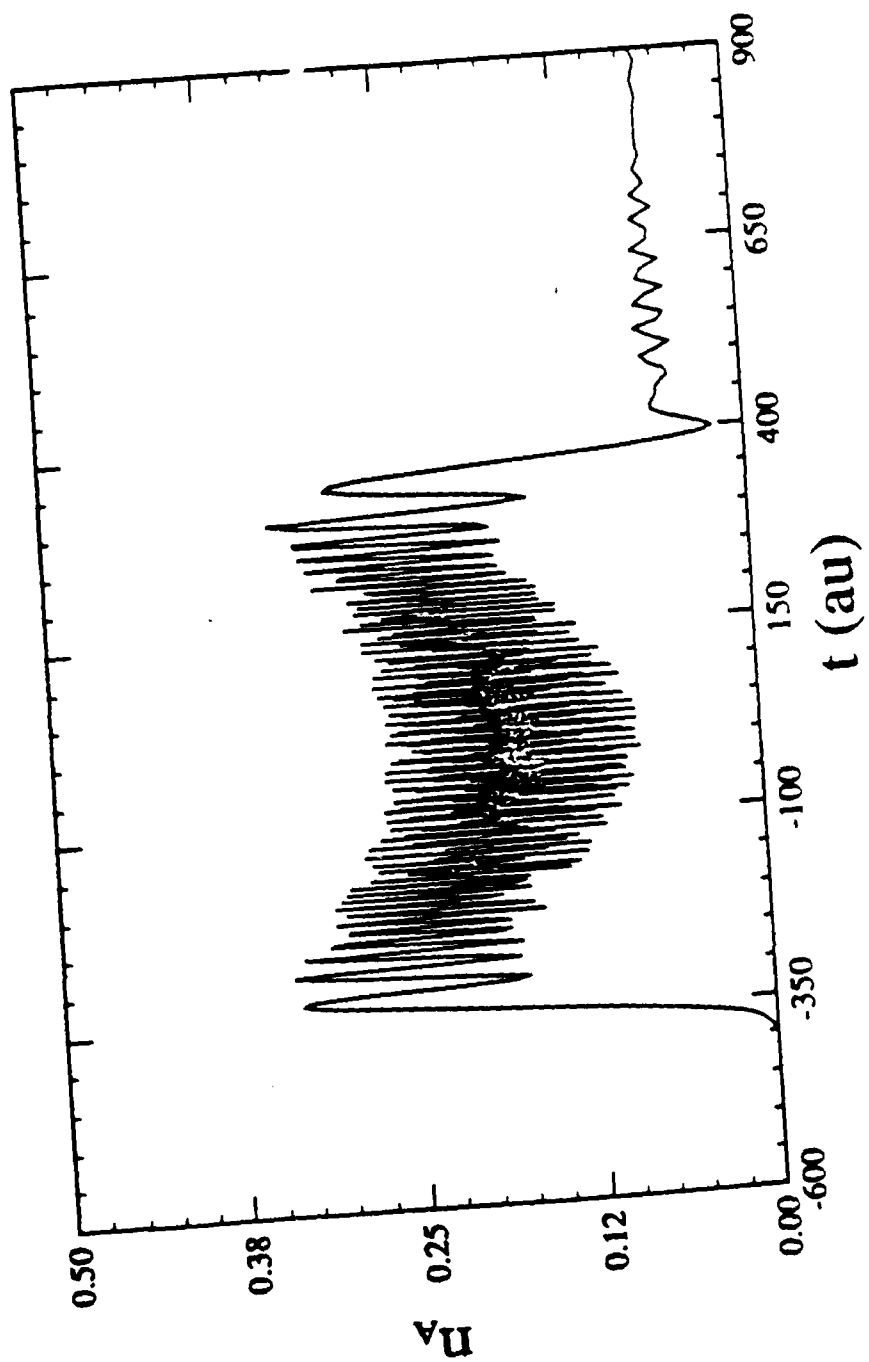


Figure 2