Nonadiabatic nuclear dynamics of atomic collisions based on branching classical trajectories

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The branching classical trajectory method for inelastic atomic collision processes is proposed. The approach is based on two features: (i) branching of a classical trajectory in a nonadiabatic region and (ii) the nonadiabatic transition probability formulas particularly adapted for a classical trajectory treatment. In addition to transition probabilities and inelastic cross sections, the proposed approach allows one to calculate incoming and outgoing currents. The method is applied to inelastic Na + H collisions providing the results in reasonable agreement with full quantum calculations.

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Inelastic collision cross sections are in permanent demand in many fields of physics and chemistry, e.g., it is generally recognized that inelastic collisional processes in the stellar atmospheres are of fundamental importance in modern astrophysics [1]. Cross sections are predominantly obtained from theoretical treatments, which are mainly performed within the standard adiabatic approach. It results in electronic structure calculations followed by nuclear dynamical studies. While quantum dynamical calculations possess high accuracy, they require complete quantum-chemical data and are rather costly when many channels are taken into account. The use of models continues to be an important alternative because of their lower computational costs and the physical insight they provide into the dynamics of a process. Inelastic cross sections are required for a wide variety of atomic collision processes, but accurate quantum calculations are rather seldom. For lack of a better alternative, the Drawin formula is often used in astrophysical applications. It has recently been reviewed and has been pointed out [2] that the Drawin formula overestimates cross sections by up to 8 orders of magnitude for optically allowed transitions, underestimates cross sections by several orders of magnitude for optically forbidden transitions, and provides no data for charge-exchange processes. It is concluded [2] that, in order to provide estimates for a wide range of elements, simplified models, based on the physical understanding, are required. This is the goal of the present Brief Report: to propose an approach that provides estimates for atomic collision inelastic cross sections, based only on adiabatic potential data (when nonadiabatic couplings are not available) and on evidence of the existence of avoided crossings (e.g., ionic-covalent crossings).

The nonadiabatic models, e.g., the Landau-Zener (LZ) model [3], are formulated as two-state problems in a diabatic representation for an isolated nonadiabatic region and encounter the following problems in practical applications: (i) A collision usually involves many channels with a variety of nonadiabatic regions; (ii) quantum-chemical data are usually provided in an adiabatic representation, and often, only adiabatic potentials are known. In practice, it is a challenge to extract diabatic parameters in order to apply an analytical model, even the most widely used LZ model, in its simplest form. More rigorous solutions of the LZ problem [4–6] lead to more complicated formulas, which makes its applications even more difficult. Reference [7] points out that many states contribute to dynamics, and unless all these channels are included in the theory, an accurate description of dynamics and, hence, determination of cross sections is not possible, as well as this makes theoretical calculation very heavy and time consuming. In model treatments, to account for several channels, the multichannel models have been proposed [8,9] in which nonadiabatic regions are passed in a particular order, that is, a single diabatic term crosses several noninteracting diabatic terms. In practical applications, however, incoming and outgoing currents are distributed among many channels after traversing many nonadiabatic regions without any particular order.

In this Brief Report, these problems are solved by means of the branching classical trajectory approach applied to atomic collisions. The simplicity of classical trajectory surface-hopping methods, developed by Tully and others [10–13], renders them attractive for the study of high-dimensional quantum systems. The present approach has some similarities to that used in polyatomic nonadiabatic dynamics [11–13] and can be applied to multidimensional systems as well; a multidimensional study is beyond the scope of this Brief Report and will be published elsewhere [14]. Within the proposed method, all nonadiabatic regions are accounted for by classical trajectories in any order that they appear during a collision. The basis of the method is twofold: branching of a classical trajectory and the formulas for LZ nonadiabatic transition probabilities adapted for classical trajectories. A classical trajectory simulation of nonadiabatic dynamics involves the following steps: (i) sampling of the initial condition, (ii) performing classical trajectory propagation, (iii) accounting for nonadiabatic effects, and (iv) evaluation of the observables of interest from the ensemble of trajectories. The branching classical trajectory method for atomic collisions performs these tasks as follows.

(i) *Sampling of initial conditions*. Since an atomic collision treatment is reduced to a one-dimensional problem of a radial nuclear motion, there is no need for an initial condition sampling distribution. A given collision energy E and a given total angular momentum quantum number J generate the only initial trajectory in a chosen initial adiabatic state with a unit weight. At the initial moment, an initial internuclear distance

R is taken to be larger than a distance for an outermost nonadiabatic region. An initial velocity at this distance is readily determined from the energy conservation law.

(ii) *Classical trajectory propagation*. Between nonadiabatic regions, a classical trajectory is propagated along a corresponding effective adiabatic potential. The propagation is straightforward. In a one-dimensional case, the energy conservation law can also be used for calculating a trajectory. After each traverse of a nonadiabatic region, each classical trajectory branches into two trajectories (adjusting momentum); each of them carries a weight that is determined by the old weight and the nonadiabatic transition probability. This approach is similar to the splitting of quantum incoming and outgoing probability currents taking place in rigorous quantum treatments of inelastic atomic collisions [15,16]; see also Refs. [11–13]. If a weight for a new trajectory is smaller than a critical weight, a new trajectory is not created; if a remaining weight after a nonadiabatic region is smaller than the critical weight, the old trajectory is stopped, and the remaining weight is transported into a new trajectory.

(iii) *Nonadiabatic transitions*. The important feature of a surface-hopping approach is a way of calculating nonadiabatic transition probabilities, which distinguishes different surface-hopping methods. In the branching classical trajectory method, transition probabilities are calculated within the LZ model by two formulas that do not require a diabatization procedure and are particularly adapted for classical trajectories without *a priori* analysis, see below. Within the LZ model, the center of a nonadiabatic region corresponds to a minimum of an adiabatic splitting $Z_{jk} = |U_j - U_k|$, $U_{j,k}(R)$ being adiabatic potentials for states j and k. The code calculates splitting Z_{jk} between adjacent adiabatic potentials along a trajectory. If the function $Z_{jk}(t)$ attains a local minimum (except for classical turning points), a branch occurs. The main assumption of the approach, the applicability of LZ estimates, is valid when there is physical evidence for avoided crossings, such as ionic-covalent crossings or a clear structure of adiabatic potentials.

(iv) *Observables*. The computed observables are the time- and distance-dependent adiabatic-state populations, which are calculated as sums over all corresponding trajectories with proper weights. This readily allows one to extract incoming and outgoing currents as well as final nonadiabatic transition probabilities. Calculations of inelastic cross sections are straightforward.

Nonadiabatic transition probability formulas. The way of incorporating nonadiabatic transitions is crucial. The most widely used nonadiabatic model is the LZ one [3]. Within this model, the probability p_{if}^{LZ} for the nonadiabatic transition $i \to f$ after a single traverse of a nonadiabatic region is expressed by the conventional analytical formula in a diabatic representation,

$$p_{if}^{\mathrm{LZ}} = \exp\left(-\frac{2\pi H_{if}^2}{\hbar|H'_{ii} - H'_{ff}|v}\right), \qquad (1)$$

where H_{if} is a constant off-diagonal matrix element, H_{ii} and H_{ff} are linear R-dependent diagonal matrix elements, and $v = \dot{R}$ is a radial velocity of colliding atoms. All values are evaluated at the center of the nonadiabatic region R_c, where diabatic potentials cross. Primed quantities are referred to as derivatives with respect to the distance R, while a dot stands for a time derivative.

The diabatic representation allows one to calculate adiabatic potentials $U_i(R)$ and $U_f(R)$ as well as the splitting Z_{if}. Within the LZ model, this leads to $H_{if} = Z_{if}(R_c)/2$ and, hence, to a relation between $|H_{ii} - H_{ff}|$ and Z_{if}, which gives a slope difference derived via the splitting $|H'_{ii} - H'_{ff}| = \sqrt{Z_{if}\ddot{Z}_{if}}$ at R_c. It turns out that the nonadiabatic transition probability within the LZ model is written by means of the following formula:

$$p_{if} = \exp\left(-\frac{\pi}{2\hbar v}\sqrt{\frac{Z_{if}^3}{Z''_{if}}}\right) = \exp\left(-\frac{\pi}{2\hbar}\sqrt{\frac{Z_{if}^3}{\ddot{Z}_{if}}}\right), \qquad (2)$$

which expresses the transition probability only in terms of the adiabatic splitting Z_{if} and its second time (or distance) derivative at R_c. Equation (2) can be called the adiabatic-potential-based transition probability formula. This formula (the right-hand side) is particularly adapted for classical trajectories.

The formula (2) is derived from the conventional LZ formula (1) without any approximation, so the results of applications of both formulas must coincide if the LZ model prerequisites are fulfilled. We have performed test calculations for a model case (fixed H'_{ii}, H'_{ff}, v; varying H_{if}) and found perfect agreement of trajectory results based on Eq. (2) with the LZ formula (1) over a wide range of the LZ parameter $s = \frac{2\pi H_{if}^2}{\hbar|H'_{ii} - H'_{ff}|v}$, see Fig. 1(g). As discussed above, practical applications of the conventional LZ formula (1) are often troublesome, as diabatic LZ parameters are usually unknown and their determination can give substantial uncertainties, see, e.g., Refs. [17,18]. The formula (2) is easy implemented in practice.

It is worth mentioning that one version of the Zhu-Nakamura formula [6] for the LZ model nonadiabatic

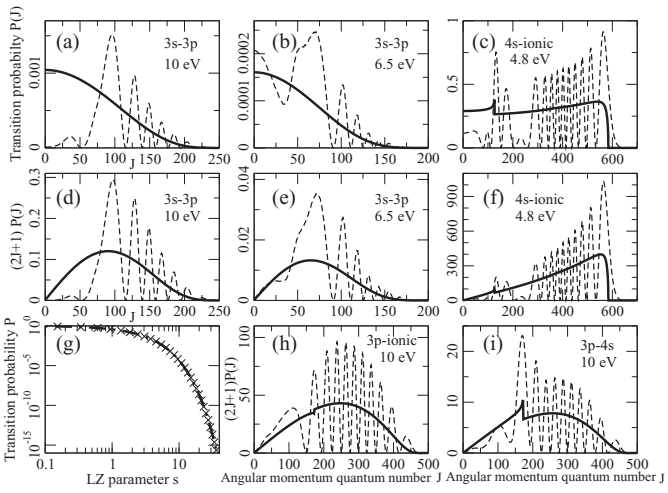

FIG. 1. The transition probabilities (a)–(c) $P(J)$ and the products (d)–(f), (h), (i) $(2J+1)P(J)$ as a function of J for different transitions and energies in Na + H collisions as well as (g) $P(s)$ as a function of the LZ parameter s obtained by Eq. (1) (dot-dashed line) and by the present method based on Eq. (2) (crosses). The solid lines, the branching classical trajectory calculations; the dashed curves, the quantum results [18].

transition probability is obtained in terms of several parameters expressed via adiabatic potentials. Those parameters are different from $Z_{if}(R_c)$ and $\ddot{Z}_{if}|_{R=R_c}$ used in the present Brief Report, and hence, the adiabatic-potential-based formula (2) is different from the Zhu-Nakamura formula. In Refs. [12,19], transition probabilities were also calculated within the LZ model based on adiabatic potentials along a trajectory. In those works, the conventional LZ formula (1) was used, and diabatic LZ parameters were calculated numerically from adiabatic potentials in a nonadiabatic region.

A nonadiabatic transition probability within the LZ model can also be written in terms of parameters in an adiabatic representation when complete information also includes a nonadiabatic radial coupling $\langle i|\partial/\partial R|f\rangle$. In this case, the LZ transition probability is given as follows [17]: $p_{if}^{\mathrm{LZ}} = \exp(-\frac{\pi Z_{if}}{4\hbar D_R v})$, where $D_R = \max|\langle i|\partial/\partial R|f\rangle|$. The product of velocity v and matrix element $\langle i|\partial/\partial R|f\rangle$ gives a matrix element of a derivative with respect to time t, $\langle i|\partial/\partial t|f\rangle$, see also Ref. [20]. Taking this into account, the nonadiabatic transition probability within the LZ model reads

$$p_{if} = \exp\left(-\frac{\pi Z_{if}}{4\hbar D_t}\right), \tag{3}$$

where $D_t = |\langle i|\partial/\partial t|f\rangle|$ is taken at the center of a nonadiabatic region R_c. This formula allows one to calculate a transition probability via the adiabatic splitting Z_{if} and the time-derivative nonadiabatic coupling $\langle i|\partial/\partial t|f\rangle$ at R_c. Let us call Eq. (3) as the time-derivative-based transition probability formula. If a Hamiltonian matrix is known in a diabatic representation, a time-derivative nonadiabatic coupling is readily evaluated numerically.

It should be pointed out that the value similar (but not identical) to $\langle i|\partial/\partial t|f\rangle$ was used in Ref. [21]. In that paper, the value similar to $\langle i|\partial/\partial t|f\rangle$ represented the nonadiabatic coupling over a time period, was evaluated via the nonadiabatic coupling vector in the coordinate space, and was used for a switching between two adiabatic surfaces.

In a pure LZ case, all the formulas (1)–(3) give identical results. In practice, however, results of using different formulas may deviate substantially, see, e.g., Ref. [17].

Thus, the formulas (2) and (3) derived in the present Brief Report provide a nonadiabatic transition probability within the LZ model based either on the adiabatic splitting Z_{if} and its second time derivative $\ddot{Z}_{if}$ at the center of a nonadiabatic region Eq. (2) or on both Z_{if} and the time-derivative nonadiabatic coupling $\langle i|\partial/\partial t|f\rangle$ at the same distance Eq. (3). Equation (2) gives a probability when only adiabatic potentials are known and a nonadiabatic coupling is unknown, while Eq. (3) is applicable when both adiabatic potentials and a coupling are available.

Na + H application. In this Brief Report, the branching classical trajectory method based on Eq. (2) is applied to inelastic Na + H collision processes. The available quantum-chemical data for the NaH molecule are discussed in detail in Ref. [18]. The present treatment is performed on the potentials from the pseudopotential calculation [22]. We consider the five $^1\Sigma^+$ state potentials: the four lowest $^1\Sigma^+$ adiabatic potentials and the hybrid $^1\Sigma^+$ potential, which corresponds to the fifth $^1\Sigma^+$ adiabatic potential at short distances ($R < 40$ a.u.) and to the ionic $^1\Sigma^+$ diabatic potential otherwise; see Ref. [18]. The ionic potential is taken into account because the ion-pair production processes are especially important in astrophysics [23] and have the largest cross sections [18]. The potentials are shown in Fig. 2 by dots; a number of avoided crossings is clearly seen.

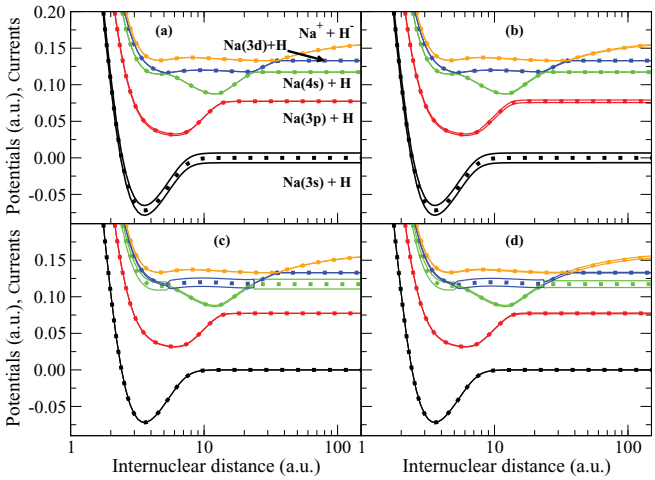

FIG. 2. (Color online) The NaH adiabatic potentials (dotted lines) as well as the (a) and (c) incoming and (b) and (d) outgoing currents for (a) and (b) Na(3s) + H and (c) and (d) Na(4s) + H collisions; $E = 10$ eV and $J = 0$. The currents are depicted by widths between solid curves along the corresponding potentials.

The incoming and outgoing probability currents calculated by means of the present approach are shown in Fig. 2 by widths between solid curves along corresponding potentials for Na(3s) + H and Na(4s) + H collisions at the collision energy $E = 10$ eV and $J = 0$. The physical mechanisms of the processes are clearly seen from the figure and correspond to the avoided crossings.

The results of the branching classical trajectory calculations are compared with the accurate quantum dynamical calculations [18]. Figure 1 shows the probabilities $P(J)$ and the products $(2J+1)P(J)$ for several transitions calculated by the present approach and by the quantum method. The products are important for cross sections. The results agree reasonably well, apart from the fact that the classical trajectories do not reproduce quantum interference effects, in particular, the Stückelberg oscillations [4]. Marked interference effects at small J are washed out for the products, see Figs. 1(d)–1(f), 1(h), and 1(i) [cf. Figs. 1(a)–1(c)].

Figure 3 compares the cross sections for the excitation and the ion-pair production processes in collisions Na(nl) + H calculated by the present method and by the full quantum approach. Satisfactory agreement is obtained. Again, the classical trajectory calculations do not provide the Stückelberg oscillations, which are substantially washed out for cross sections and deviate in the near-threshold Na($3s \to 3p$) + H excitation region. The point is that the LZ prerequisites are not entirely fulfilled in the broad nonadiabatic region around 7.7 a.u., where the $3s \to 3p$ transition mainly occurs [16–18]. As usual, the LZ model works better for other narrow nonadiabatic regions. Moreover, the near-threshold Na($3s \to 3p$) + H excitation quantum cross section is very

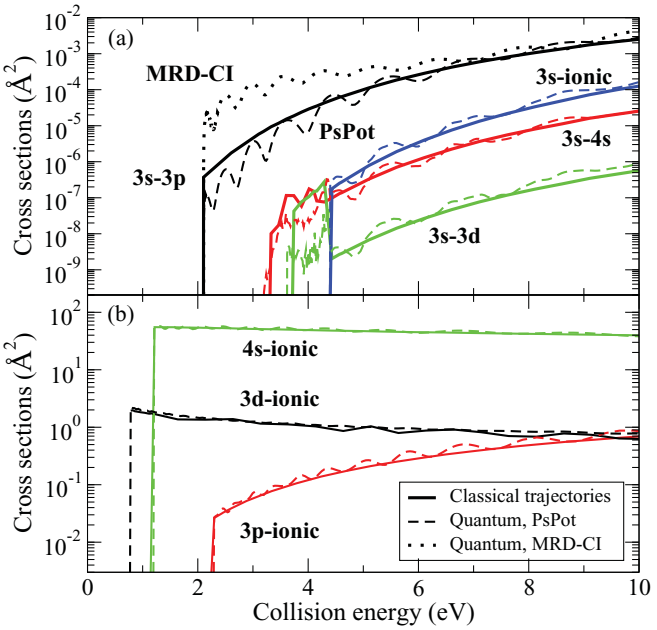

FIG. 3. (Color online) The cross sections for the excitation $Na(3s) + H \rightarrow Na(nl) + H$ and the ion-pair production $Na(nl) + H \rightarrow Na^+ + H^-$ processes. The solid lines, branching classical trajectories; the dashed curves, the quantum calculations [18] based on the pseudopotential data; the dotted curve, the quantum calculation based on the multireference single- and double-excitation configuration-interaction (MRD-CI) data [16].

sensitive to the nonadiabatic coupling [18,24]. Using the MRD-CI data increases the quantum $Na(3s \rightarrow 3p) + H$ cross section up to 2 orders of magnitude [16,18], see Fig. 3. Thus, the branching classical trajectory method provides reasonable estimates even for the low-energy cross sections, although as stated in Ref. [10]: As with any mixed quantal-classical dynamics approach, a method cannot succeed in all situations, e.g., in cases of quantum interference.

In astrophysics, the ion-pair production processes are of particular importance [23]. For this reason, Fig. 3(b) compares the ion-pair production cross sections obtained by the present method and by the quantum approach [18]. Except for the oscillations, the classical trajectory approach reproduces the quantum results well, in particular, for the $Na(4s) + H \rightarrow Na^+ + H^-$ process with the largest cross section in Na + H collisions [18].

Thus, it has been demonstrated that the branching classical trajectory method applied to atomic Na + H collisions provides reliable nonadiabatic transition probabilities and inelastic cross sections that agree reasonably well with the results of the accurate quantum calculations. The proposed method is essentially based on two features: (i) branching of a classical trajectory after a traverse of a nonadiabatic region with proper weights according to a nonadiabatic transition probability and (ii) the adiabatic-potential-based formula (2) derived in the framework of the LZ model for calculations of transition probabilities along classical trajectories. The alternative is the time-derivative-based formula (3) also obtained in the present Brief Report. The test calculations show that applications of these two formulas to Na + H collisions give close results. The adiabatic-potential-based formula (2) has the advantage that it requires information only about a splitting between adjacent adiabatic potentials along a trajectory, so it provides estimates when a nonadiabatic coupling is unknown but there is avoided-crossing evidence. In addition, the proposed method allows one to calculate incoming and outgoing currents and to determine a mechanism for a process.

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