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Probability currents in inelastic atomic collision studies

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Abstract. The rigorous probability current method within the quantum collision theory is tested in detail on the Tully A and B models for a single traverse of nonadiabatic regions during atomic collisions. Calculations are performed in a diabatic representation by numerical integration of the coupled channel equations for nuclear radial wave functions. The results of precise quantum calculations are compared with those predicted by the Landau–Zener model for the same electronic structures. It is established that the probability current method is an efficient tool for investigations of inelastic atomic collision processes.

Keywords: atomic collisions, probability current, Tully models, transition probability, Landau–Zener model, diabatic representation

Introduction

Inelastic processes in low-energy atomic collisions are important for modelling plasma and gas medium, for example, stellar photospheres. Experimental studies are difficult to conduct in order to obtain the information needed, and therefore, theoretical calculations become the main source of data. For this reason, theoretical methods used should be reliable and efficient for practical implementation. The present study tests different theoretical approaches to investigations of inelastic transitions in atomic collisions, in particular the probability current method and the Landau–Zener model.

There are different theoretical methods for studying atomic collisions, for example, the approach based on the Faddeev equations (Faddeev 1961) and the hyperspherical adiabatic approach (Lin 1995), to mention a few. Nevertheless, the most widely used approach is the Born–Oppenheimer one (Born, Oppenheimer 1927), which implies the separation of electronic and nuclear motions. Electronic structure calculations provide molecular potentials and non-adiabatic couplings. This information enters the coupled channel equations for nuclear dynamics. The present paper deals with the nuclear dynamics part. It should be mentioned that in addition to strict quantum studies, model approaches are widely used as well, for example, the Landau–Zener model (Landau 1932; Zener 1932). In this paper we test the rigorous probability current method for different cases of non-adiabatic regions and compare its results to the Landau–Zener model ones.

Atomic units (a. u.) are used throughout the paper unless stated otherwise.

Collision theory in brief

The rigorous quantum atomic collision theory is usually based on the stationary Schrödinger equation for a molecular system of colliding atoms:

$$\left(\hat{H}_e + \hat{T}_n\right)\Psi^{tot} = \mathrm{E}\Psi^{tot}, \tag{1}$$

where $\hat{H}_e$ stands for the fixed-nuclei electronic Hamiltonian which consists of the electron kinetic energy operator and the operators of the following interactions: electron–nucleus, electron–electron and nucleus–nucleus. $\hat{T}_n$ is the kinetic energy operator for the nuclei. The total wave function of the system (quasi-molecule) is taken as a superposition of partial waves:

$$\Psi^{tot} = \sum_{J,M} \Psi_{J,M}\,, \tag{2}$$

where J is a quantum number of the total molecular angular momentum, and M is a quantum number of its projection. Each partial wave is a solution of equation (1). The first step of the Born–Oppenheimer approach consists of calculations of the eigenfunctions and eigenvalues of the fixed-nuclei electronic Hamiltonian. The non-adiabatic nuclear dynamics is treated during the second step by different methods, strict or model ones, based on the information obtained in the first step.

Strict quantum approach

In strict quantum approaches, accurate eigenfunctions and eigenvalues of the electronic Hamiltonian ϕ_j and $U_j(R)$ are usually calculated by means of *ab initio* methods for each partial wave providing adiabatic potential energies and a number of non-adiabatic couplings for a set of molecular states. Every total (electronic and nuclear) partial wave function is then expanded on the electronic wave functions ϕ_j as follows:

$$\Psi_{J,M}(\boldsymbol{r},\boldsymbol{R}) = \phi_j(\boldsymbol{r},\boldsymbol{R})Y_{J0}\frac{F_j(R)}{R}, \tag{3}$$

where j is an index that enumerates the electronic molecular state, $F_j(R)$ is a radial and Y_{j0}, an angular nuclear wave function. The sigma molecular states are treated here as an example. In the adiabatic representation, the radial wave functions obey the coupled channel equations:

$$\left(-\frac{1}{2\mu}\frac{d^2}{dR^2} + U_j^{eff}(R) - E^{tot}\right)F_j(R) = \frac{1}{\mu}\sum_{k,k\neq j}\left\langle\phi_j\left|\frac{\partial}{\partial R}\right|\phi_k\right\rangle\frac{dF_k}{dR} + \frac{1}{2\mu}\sum_{k,k\neq j}\left\langle\phi_j\left|\frac{\partial^2}{\partial R^2}\right|\phi_k\right\rangle\frac{dF_k}{dR}, \tag{4}$$

E^{tot} being the total collision energy, μ — the reduced mass of the quasi-molecule, U_j^{eff} — the effective potential energy of the channel j and $\left\langle\phi_i\left|\frac{\partial}{\partial R}\right|\phi_k\right\rangle$ — radial non-adiabatic couplings. It is worth noting that equations (4) and (5) are justified only for channels belonging to the same symmetry.

The set of coupled channel equations in a diabatic representation reads:

$$\left(-\frac{1}{2\mu}\frac{d^2}{dR^2} + V_{jj}^{eff}(R) - E^{tot}\right)F_j(R) = \sum_{k,k\neq j} V_{jk}F_k\,, \tag{5}$$

V being a matrix of the electronic Hamiltonian in a diabatic representation.

In order to solve the set of coupled equations, one needs to put boundary conditions. Generally, boundary conditions for nuclear dynamics are set at $R \to 0$:

$$\Psi_j \to 0. \tag{6}$$

In the asymptotic region, at $R \to \infty$:

$$\Psi_j = k_j^{-\frac{1}{2}}\left(a_j^- \exp\left(-ik_jR\right) + a_j^+ \exp\left(ik_jR\right)\right), \tag{7}$$

where k_j is a wave number of a corresponding state, and $a_j^{\pm}$ — the incoming and outgoing amplitudes. When the radial functions are computed, one needs to calculate transition probabilities. This can be done using the S-matrix method (Grosser et al. 1999) or the probability current method (Belyaev, Grosser 1996). Both methods are rigorous and based on the same wave functions, but the S-matrix method yields only inelastic state-to-state transition probabilities after a collision, while the probability current method provides probabilities during the collision for the whole interval of the internuclear distance treated.

To calculate the probability currents from the radial functions, one can use the following equations (Belyaev, Grosser 1996):

$$F_j^{\pm} = \sqrt{k_j}F_j \mp \frac{i}{\sqrt{k_j}}\frac{dF_j}{dR}, \tag{8}$$

$$\tau_j^{\pm} = \left|F_j^{\pm}\right|^2; \tag{9}$$

the $\tau_j^{\pm}$ physical implications are ambiguous in this case, but the difference $\tau_j^+ - \tau_j^-$ gives exactly the total current in the channel j

$$P_j = \tau_j^+ - \tau_j^-. \tag{10}$$

Approaches based on the Landau–Zener model

Let us assume that the electronic structure is computed and all data needed for studying nuclear dynamics are known. One can then estimate transition probabilities using the surface hopping or branching probability current models (Belyaev 2013).

In the asymptotic region, when the internuclear distance R goes to infinity, the probability currents are defined as follows:

$$\tau_j^{\pm} = \left|a_j^{\pm}\right|^2. \tag{11}$$

The currents are a function of the internuclear distance R. The incoming current $\tau^-(R)$ starts in the initial channel i $\left(\tau_j^- = \begin{cases}1, j = i\\ 0, j \neq i\end{cases}\right)$ and proceeds elastically till the nearest non-adiabatic region, where it can hop to another molecular state or splits into two parts according to the non-adiabatic transition probability. It keeps moving to the next non-adiabatic region and so on until it reaches a classical turning point. Then it changes the direction to the opposite and propagates as outgoing current $\tau_j^+(R)$ until it goes away into the asymptotic region. Current evolution can be approached deterministically or stochastically.

In either approaches the Landau–Zener transition probability determines the current in the non-adiabatic region. The Landau–Zener original formula is determined in the diabatic representation as follows:

$$P_{ij} = \exp\left(-\frac{2\pi V_{ij}^2}{\left|\frac{dV_{ii}}{dx} - \frac{dV_{jj}}{dx}\right|\dot{x}}\right), \tag{12}$$

$$\dot{x} = \sqrt{\frac{2(E^{tot} - V_{jj})}{\mu}}. \tag{12.1}$$

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The Landau–Zener formula can be modified for the adiabatic representation (Belyaev, Lebedev 2011):

$$P_{ij} = \exp\left(-\frac{\xi_{\mathrm{LZ}}}{v}\right);\ \xi_{LZ} = \frac{\pi}{2}\sqrt{\frac{Z^3}{Z''}}\ (\text{at } R = R_c), \tag{13}$$

at the local minimum of the adiabatic splitting $Z = U_i - U_j$.

Branching probability currents

An initial current in a non-adiabatic region is split into two currents according to the Landau–Zener transition probability:

$$\tau_i \to \tau_j' + \tau_i', \tag{14.1}$$

$$\tau_j' = P_{ij}^{LZ}, \tau_i' = 1 - P_{ij}^{LZ}. \tag{14.2}$$

Every split current evolves in its molecular state until reaching the next non-adiabatic region and splits again. After all currents return to the asymptotic region, the sum of currents corresponding to the same channel results in the final transition probability.

Hopping probability currents

Another possible propagation of the probability current is treated by the hopping probability method. In this case the current reaches a non-adiabatic region, and a random number between zero and unity is generated. If the generated number is greater than the Landau–Zener transition probability, then the current remains in the initial molecular state, otherwise it hops into another state. A reasonable number (N) of initial currents populates the same channel. After the simulation, a certain number (N_f) of currents populates each of the studied channels. The resulting transition probability is determined as such:

$$P_{if} = \frac{N_f}{N}. \tag{15}$$

Models

In this paper we use the model problems proposed by Tully (Tully 1990) for testing the probability current method. The two aforementioned model problems defined by Tully in a diabatic representation (names and corresponding letters from (Tully 1990) were carried over as well to avoid confusion) are used in the present work:

Model A 'Simple avoided crossing':

$$\begin{cases} V_{11} = -V_{22} = \begin{matrix} A\,(1 - \exp(-Bx)), x > 0 \\ -A\,(1 - \exp(Bx)), x < 0 \end{matrix} \\ V_{12} = V_{21} = C\exp(-Dx^2)\,. \end{cases} \tag{16}$$

Model B 'Dual avoided crossing':

$$\begin{cases} V_{11} = 0 \\ V_{22} = -A\,exp(-Bx^2) + E_0 \\ V_{12} = V_{21} = C\exp(-Dx^2)\,. \end{cases} \tag{17}$$

Since there is no potential barrier like in real molecules, these models allow us to see how probabilities behave when passing the non-adiabatic region once. Thus, boundary conditions should be slightly adapted for this case $x \to \pm\infty$:

$$\Psi_j = k_j^{-\frac{1}{2}}\left(a_j^- \exp\left(-ik_j x\right) + a_j^+ \exp\left(ik_j x\right)\right). \tag{18}$$

Since the incoming current does not change the direction, only one of these terms, τ^+ and τ^-, in equation (8) is non-zero and completely defines the probability. Thus, one of the amplitudes a_j^+ or a_j^- is equal to zero, and the probability current is determined by the single term in equation (18).

Results

Model A. Simple avoided crossing

In the present work the following parameters were used for the model A: $A = 0.011$, $B = 1.6$, $C = 0.005$ and $D = 1.0$. The diabatic potential energies and off-diagonal matrix elements are depicted in Fig. 1 by solid lines and a dashed line, respectively. The blue solid line is the potential of the first diabatic channel which is the initial channel. The green solid line is the potential of the second diabatic channel. The crossing of the diabatic potentials is clearly seen. The examples of the calculated wave functions are shown in Fig. 2 for the collision energy equals 0.38 *eV* for the transition from state 1 to state 2. It is seen that the wave functions are highly oscillating functions with different amplitudes before and after a collision, which makes the transition mechanism obscure.

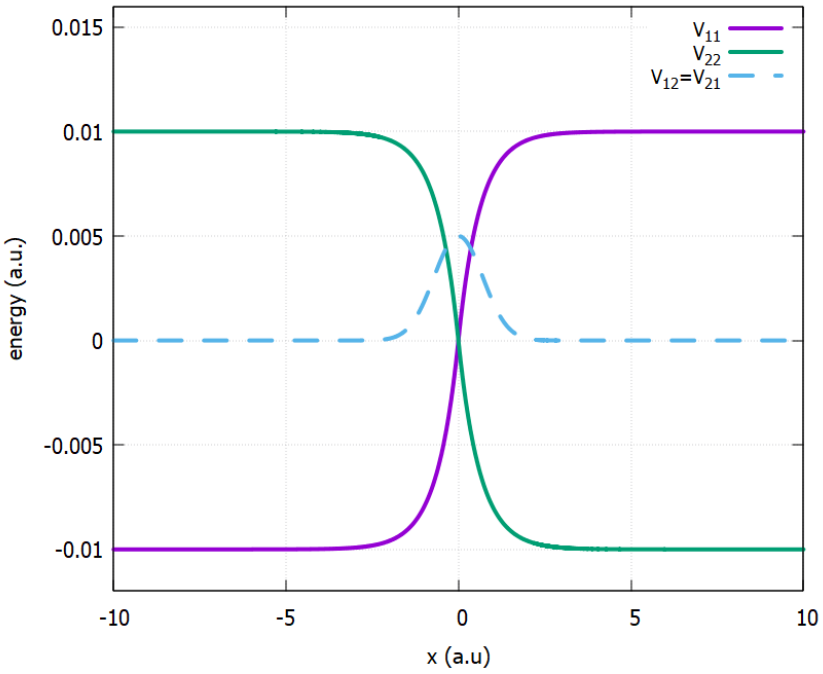

Fig. 1. Tully model 'A', parameter values: $A = 0.011$, $B = 1.6$, $C = 0.005$ and $D = 1.0$

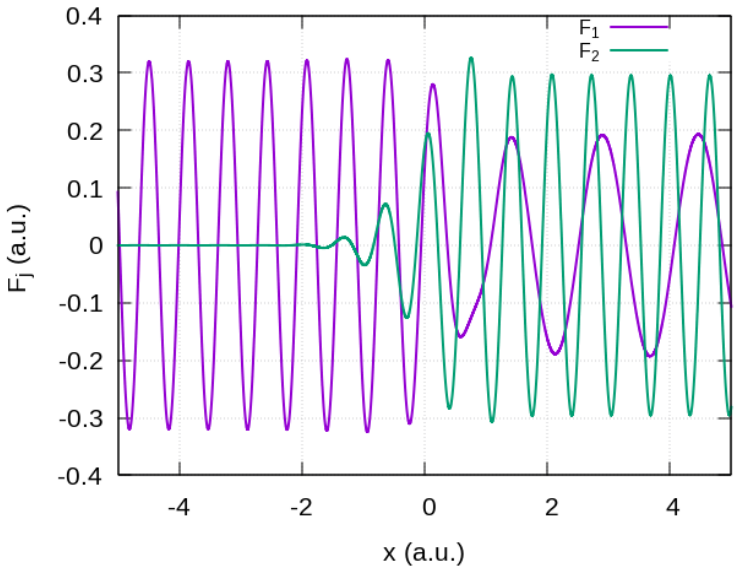

Fig. 2. Computed wave functions for potentials depicted in Fig. 1, total collision energy $E^{tot} = 0.014$ a.u.

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Fig. 3 shows the probability currents as a function of the position x measured from the center of the non-adiabatic region. It is clearly seen where the transition occurs and what the transition probability values are. Note that in a diabatic representation, the calculated probabilities correspond to the ones in the initial state, so the probabilities of a transit from one adiabatic molecular state into another state are presented by the differences $\boldsymbol{P_{if}^{ad} = 1 - P_{if}^{di}}$.

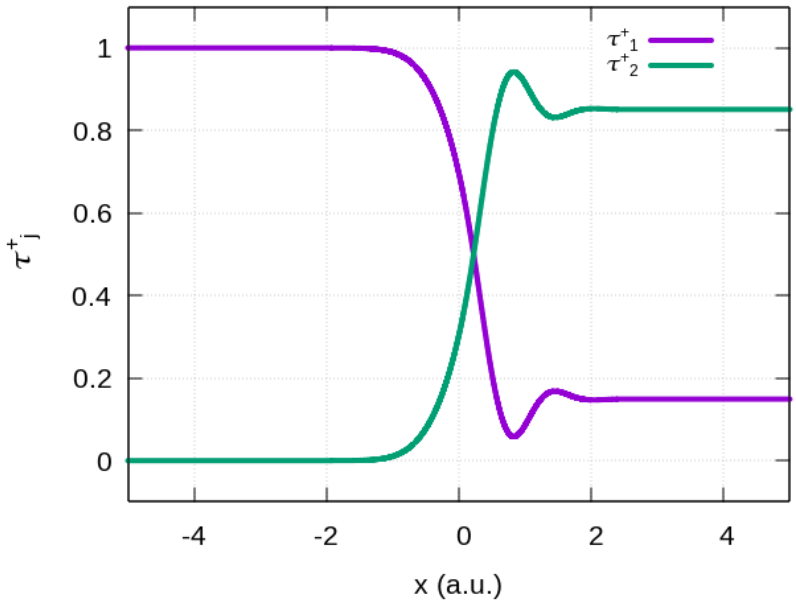

Fig. 3. Probability currents extracted from the wave functions depicted in Fig. 2

Model B. Dual avoided crossing

For the second model B, the following parameters are taken: A = 0.1, B = 0.28, C = 0.015, D = 0.06 and E_0 = 0.05. In this case the diabatic potentials and off-diagonal matrix elements have the form plotted in Fig. 4. The potential energy of the initial channel is again represented by a blue solid line in Fig. 4. This model presents the case of two overlapping non-adiabatic regions.

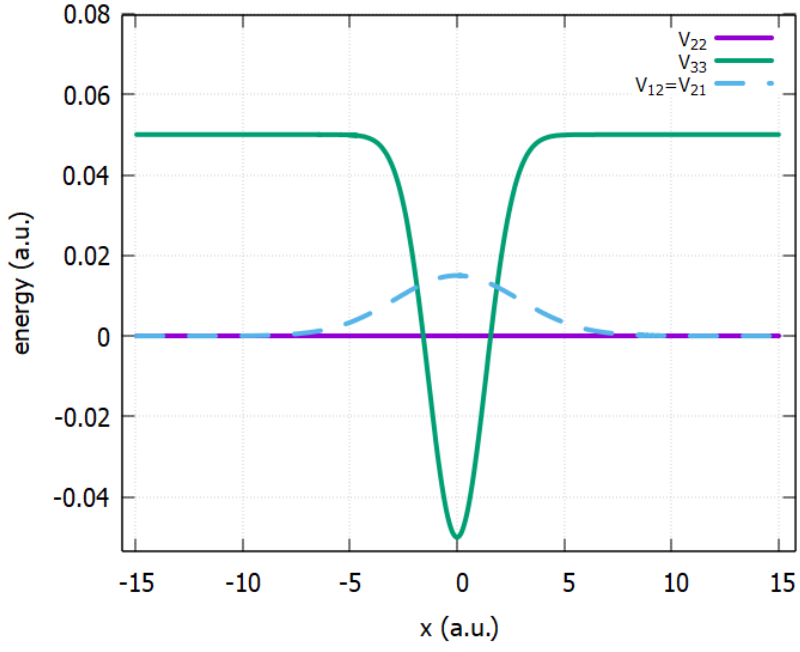

Fig. 4. Tully model 'B', parameter values: A = 0.1, B = 0.28, C = 0.015, D = 0.06 and E_0 = 0.05

Examples of the calculated wave functions are shown in Fig. 5. It shows that the wave functions are more complicated than for model A, and it is not quite clear how transitions occur in this case. The transition mechanism can be better understood if one calculates the probability currents, see Fig. 6. It is clear that the incoming probability current populates the upper molecular state; then the main part of the current transfers into another molecular state, and finally the current passes the second non-adiabatic region and splits between two molecular states exhibiting interference and convergence.

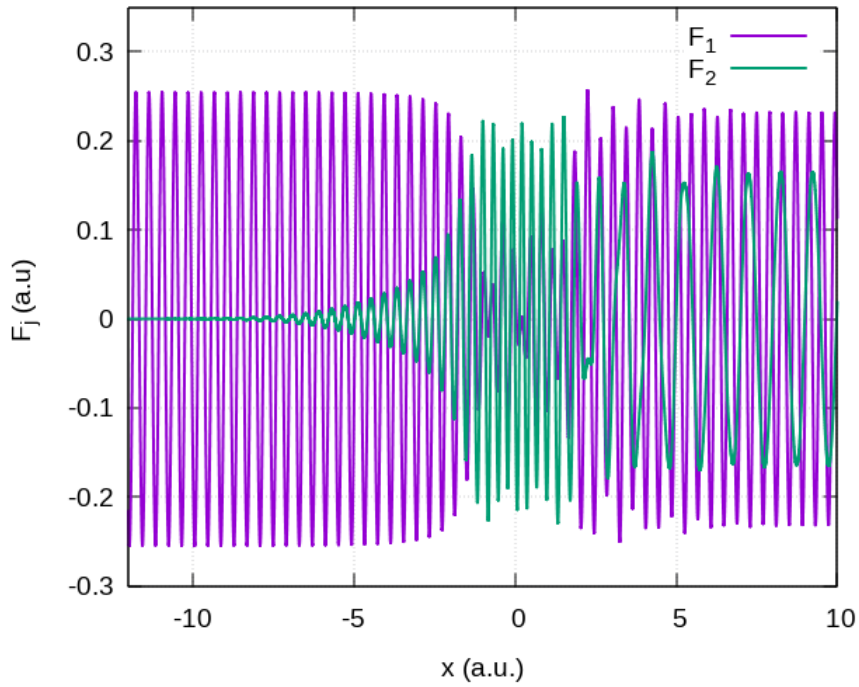

Fig. 5. Computed wave functions for potentials depicted in Fig. 4, total collision energy E^{tot} = 0.06 a.u.

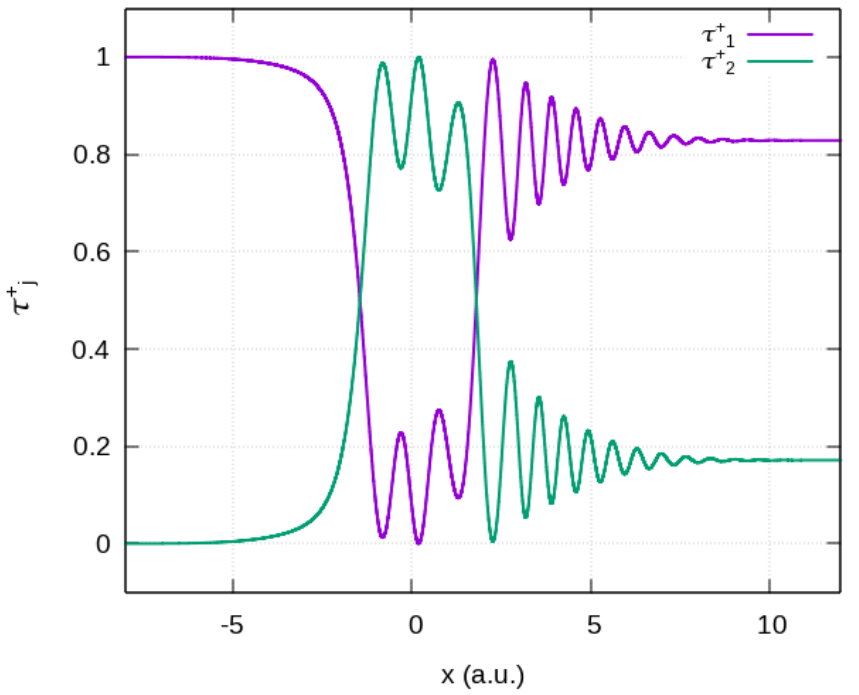

Fig. 6. Probability currents extracted from wave functions depicted in Fig. 5

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The results of calculating the probability currents can be compared with the Landau–Zener estimates. Equations (12) and (13) indicate that the usual Landau–Zener formulas do not include phases, while the currents take phases into account automatically, so the transition probability method provides more information than the Landau–Zener model. Fig. 7 shows the transition probabilities obtained by the two methods as a function of the total energy. It is seen that the Landau–Zener model does not reproduce oscillations, while the probability currents method does. It is seen that the Landau–Zener model provides transition probabilities in reasonable agreement with the results of the strict calculation by the transition current method.

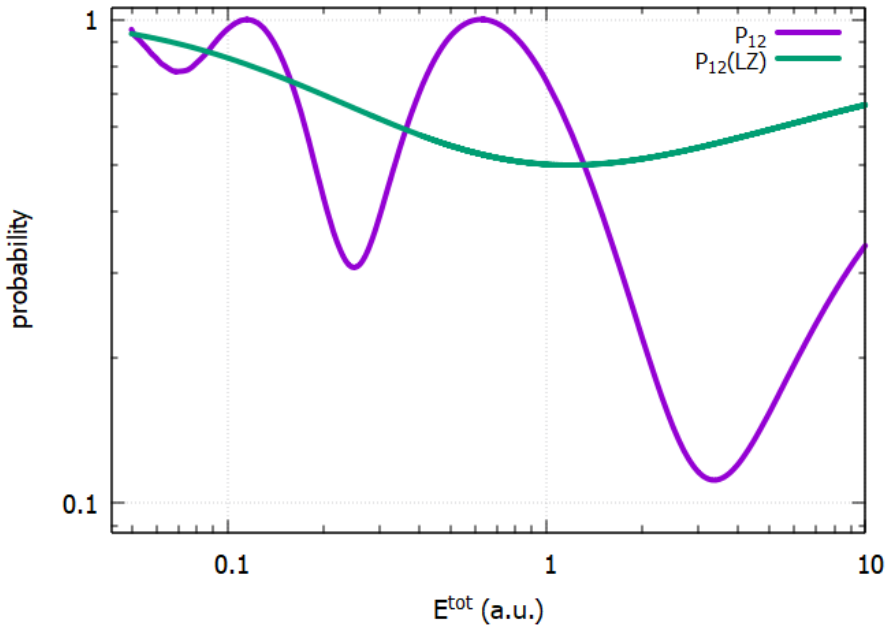

Fig. 7. Transition probability as a function of the total energy (Tully model B)

Conclusions

A computer program is derived in the present work in order to study inelastic atomic collisions using the probability current method based on accurate quantum coupled channel equation solutions. It is found that the probability current method allows one to calculate the transition probabilities with the same accuracy as the S-matrix method, but the former gives insight on the mechanism of the process, while the latter provides only final transition probabilities. Thus, the transition probability method is an effective tool in studying inelastic state-to-state transitions.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

The authors have made an equal contribution to the paper.

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