Cumulative Reaction Probability without Absorbing Potentials

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Cumulative reaction probability, introduced in the collision theory by W. H. Miller [J. Chem. Phys. **62**, 1899 (1975)], characterizes a net efficiency of a rearrangement process as a function of the total energy of the collision system. We derive a formula that expresses this quantity in terms of the outgoing wave Green function. Our formula is free from the ambiguities of previous formulations; in particular, no absorbing potentials are required for its implementation. The formula has a potentially wide range of applications in atomic and molecular collision physics. As an illustration, we consider the rearrangement processes in the $dt\mu$ system for the energies up to the $n = 6$ threshold. [S0031-9007(97)04887-4]

Collisions resulting in rearrangement of particles constituting the colliding fragments play an important role in many phenomena, providing a basic mechanism of mutual transformations between different physical species. Numerous examples of rearrangement collisions (we use this term interchangeably with "reactions") are given by a variety of electron transfer processes, chemical reactions, and nuclear reactions. Their most detailed description is contained in the block $\mathbf{S}_{ab}(E)$ of the scattering matrix off-diagonal with respect to the indices a and b specifying arrangements. The matrix elements $S_{n_a n_b}(E)$ of this block, where n_a and n_b label different asymptotic states in the arrangements a and b, respectively, determine all the state-to-state reaction probabilities between a and b. However, in many situations it would suffice to know a net efficiency of the reaction as a function of the total energy E of the collision system. This feature is characterized by the *cumulative reaction probability,*

$$N_{ab}(E) = \text{Tr}[\mathbf{S}_{ab}(E)\mathbf{S}_{ab}^{\dagger}(E)] = \sum_{n_a n_b} |S_{n_a n_b}(E)|^2, \quad (1)$$

introduced in the collision theory by Miller [1]. An excellent account on the physical meaning of this quantity can be found in [2]. We just note that $N_{ab}(E)$ enables one to determine the reaction rate constant, which is often the only characteristic required for applications. This alone warrants the need for developing methods capable of evaluating $N_{ab}(E)$ *directly,* i.e., without first calculating the matrix $\mathbf{S}_{ab}(E)$. Besides, there is a deeper argument in support of focusing on $N_{ab}(E)$ rather than on $\mathbf{S}_{ab}(E)$. As can be seen from (1), $N_{ab}(E)$ is invariant under the unitary transformations mixing the asymptotic states separately in each arrangement. The interactions causing the rearrangement decay exponentially with the increase of the distances between initial and/or final fragments of the reaction, while the interactions governing the dynamics within the same arrangement may have a much longer range. Thus a direct calculation of $N_{ab}(E)$ may present an easier computational task due to a reduction of the size of the region to be considered. Moreover,

the asymptotic states, hence the matrix $\mathbf{S}_{ab}(E)$, may be defined poorly (collisions between metastable states), or even not defined at all (collisions in external fields), while the notion of arrangements and the cumulative reaction probability $N_{ab}(E)$ may still have a physical meaning.

Recently, Seideman and Miller [3] derived an alternative representation for $N_{ab}(E)$,

$$N_{ab}(E) = 4\,\text{Tr}[G_\varepsilon^*(E)\varepsilon_a G_\varepsilon(E)\varepsilon_b], \quad (2)$$

which has opened the first avenue towards the direct evaluation of this quantity. Here $G_\varepsilon(E) = (H - E - i\varepsilon)^{-1}$ is the outgoing wave Green function of the collision system, and $\varepsilon = \varepsilon_a + \varepsilon_b$. Formula (2) is ambiguous, for in the limit $\varepsilon \to +0$ assumed by the quantum mechanics it leads to the uncertainty $0 \times \infty$. Instead of resolving this uncertainty, the authors of [3] resorted to regarding the infinitesimal positive constant ε as an absorbing potential [4] which is zero in the region important for the rearrangement dynamics and turned on smoothly outside to assure the outgoing wave boundary conditions, with ε_a and ε_b being the parts of ε introduced in the arrangements a and b, respectively. This approach has been successfully demonstrated by several examples (see [2], and references therein) and justly attracted much interest. Yet the intrinsic ambiguity of Eq. (2) remains unresolved which sets the grounds for the following criticisms. First, use of the absorbing potentials, though this might seem to be appealing as a means to avoid explicit imposing the outgoing wave boundary conditions for constructing the Green function (see, e.g., [5]), introduces arbitrariness and makes the results dependent on one's choice of a "good" absorbing potential for a particular problem. Second, even a good absorbing potential essentially modifies the dynamics in the region where it differs from zero and leads to appearance of unphysical diverging states localized there [6], that is, precisely where $N_{ab}(E)$ accumulates its value as according to Eq. (2). These problems question the consistency of the approach based on Eq. (2). Meanwhile, the whole idea would benefit only if the limit $\varepsilon \to +0$ in Eq. (2) is taken properly.

In this paper we derive a new formula for $N_{ab}(E)$ which is free from the ambiguity discussed above. First we briefly outline the derivation, and then consider an illustrative example.

Our basic idea stems from the observation that the initial and final states of the system undergoing a reaction are localized in different potential valleys in multidimensional configuration space, so the reaction can be treated as a passage from one of these valleys a to another b through a "reaction zone" I; see Fig. 1. The reaction zone I is a region adjacent to the potential ridge separating the valleys. The rearrangement flux goes across the ridge through an energetically accessible window in the vicinity of the saddle point of the potential energy (SP in Fig. 1), also known as the *transition state* or *activated complex* [7], and a wider part of the ridge becomes operative when the energy of the system grows. The concept of the ridge is well familiar from the Wannier theory of the threshold electron impact ionization of atoms and the theory of the saddle-point electron production in ion-atom collisions; its role in fragmentation processes was discussed by Fano [8], and its importance in chemical reaction dynamics was emphasized by Nakamura [9]. Treating a reaction as a passage between two regions in configuration space is a standard viewpoint in the theory of chemical rate processes [7]. In atomic collision physics, similar ideas were used in the formulation given by Gerjuoy [10] and, within the impact parameter approach, in the method proposed by Demkov and Ostrovsky [11]. Such an approach would be in the spirit of the hyperspherical methodology outlined by Fano [8], though it is not used by many more conventional theoretical methods.

For concreteness of the derivation we adopt the framework of the hyperspherical method [8,12]. The configuration space is parametrized by $\mathbf{R} = (R, \Omega)$, where R is the hyperradius and Ω is a collective notation for a set of angular variables. The Schrödinger equation reads

$$[H(\mathbf{R}) - E]\psi(\mathbf{R}) = 0, \qquad (3)$$

where

$$H(\mathbf{R}) = -\frac{1}{2}\frac{\partial^2}{\partial R^2} + \frac{H_{\mathrm{ad}}(\Omega;R) + \frac{1}{8}(d-1)(d-3)}{R^2}.$$

Here d is the dimension of the configuration space [$d = 3(N-1)$ for the N-body system], and the Jacobian factor $R^{(d-1)/2}$ is separated out. Let $U_\nu(R)$ and $\Phi_\nu(\Omega;R)$ be the eigenvalues and eigenfunctions of the adiabatic Hamiltonian $H_{\mathrm{ad}}(\Omega;R)$, and let ν_a (ν_b) label different
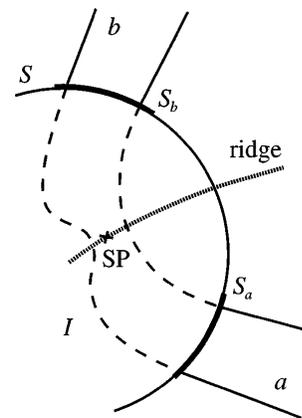
FIG. 1. Sketch of the part of the configuration space important for the rearrangement dynamics (see text).

open channels in the arrangement a (b) for the given total energy E. Apart from a possible degeneracy, ν_a (ν_b) coincides with the index n_a (n_b) in Eq. (1). Let S be a hypersphere of radius R_{m} (matching surface), and let S_a (S_b) be the segment where the functions $\Phi_{\nu_a}(\Omega;R_{\mathrm{m}})$ $[\Phi_{\nu_b}(\Omega;R_{\mathrm{m}})]$ are localized. We assume that S_a and S_b do not overlap (see Fig. 1), which is always possible to achieve by increasing R_{m}. Recalling the discussion of the previous paragraph, the cumulative reaction probability can be defined by

$$N_{ab}(E) = \sum_{\nu_a}\int_{S_b} d\Omega\, j_{\nu_a}(\mathbf{R}), \qquad (4)$$

where

$$j_{\nu_a}(\mathbf{R}) = \frac{1}{2i}\left(\frac{\partial \psi_{\nu_a}(\mathbf{R})}{\partial R}\psi^*_{\nu_a}(\mathbf{R}) - \psi_{\nu_a}(\mathbf{R})\frac{\partial \psi^*_{\nu_a}(\mathbf{R})}{\partial R}\right).$$

Here $\psi_{\nu_a}(\mathbf{R})$ is an exact solution of Eq. (3) such that at $R \to \infty$ it has an incoming wave of unit flux in the channel ν_a and only outgoing waves in all other channels, and $j_{\nu_a}(\mathbf{R})$ is the radial component of the flux associated with $\psi_{\nu_a}(\mathbf{R})$. The radius R_{m} is assumed to be sufficiently large, so that the flux that passes through S_b does not return back. Similarly, one can define $\psi_{\nu_b}(\mathbf{R})$ and $j_{\nu_b}(\mathbf{R})$ and rewrite the right-hand side of Eq. (4) with a and b interchanged. Note that at this stage Eq. (4) appears to be nonsymmetric with respect to these indices, although the final formula is symmetric as will be seen shortly.

An important step made in Eq. (4) is replacement of the summation over n_b in Eq. (1) by the integration over $\Omega \in S_b$. To make a similar step for the arrangement a, we use the Green formula,

$$\psi(\mathbf{R}) = \frac{1}{2}\int_S d\Omega'\left(G(\mathbf{R}, \mathbf{R}';E)\frac{\partial \psi(\mathbf{R}')}{\partial R'} - \frac{\partial G(\mathbf{R}, \mathbf{R}';E)}{\partial R'}\psi(\mathbf{R}')\right), \qquad (5)$$

where $G(\mathbf{R}, \mathbf{R}';E)$ is the kernel of the outgoing wave Green function $G_\varepsilon(E)$ [the same as in Eq. (2)] taken at $\varepsilon \to +0$. This formula holds for any solution of Eq. (3). For $\psi_{\nu_a}(\mathbf{R})$ substituted in Eq. (5), the region of integration can be reduced to S_a because both $\psi_{\nu_a}(\mathbf{R}')$ and $G(\mathbf{R}, \mathbf{R}';E)$ have only outgoing waves in the valley b. The same is true with a and b interchanged. Using these relations, from Eq. (4) we obtain

$$N_{ab}(E) = \frac{1}{4} \int_{S_a} d\Omega \int_{S_b} d\Omega' \left(\frac{\partial G(\mathbf{R}, \mathbf{R}'; E)}{\partial R} \frac{\partial G^*(\mathbf{R}, \mathbf{R}'; E)}{\partial R'} + \frac{\partial G^*(\mathbf{R}, \mathbf{R}'; E)}{\partial R} \frac{\partial G(\mathbf{R}, \mathbf{R}'; E)}{\partial R'} \right.$$
$$\left. - G(\mathbf{R}, \mathbf{R}'; E) \frac{\partial^2 G^*(\mathbf{R}, \mathbf{R}'; E)}{\partial R \partial R'} - G^*(\mathbf{R}, \mathbf{R}'; E) \frac{\partial^2 G(\mathbf{R}, \mathbf{R}'; E)}{\partial R \partial R'} \right). \tag{6}$$

This formula is the main result of this paper. It is apparently more general than the derivation presented. In particular, it remains valid if the surface S is modified arbitrarily, with $\partial/\partial R$ replaced by the normal derivative to S. Besides, though the asymptotic states were explicitly referred to in the derivation, Eq. (6) is free from such a reference and can be applied even if the asymptotic states are not defined. The only important physical conditions assumed in Eq. (6) are (i) S_a and S_b do not overlap, i.e., the arrangements are well separated outside S, and (ii) $G(\mathbf{R}, \mathbf{R}'; E)$ with $\mathbf{R}$ and $\mathbf{R}'$ lying in different valleys has only outgoing waves outside S. As is illustrated below, these conditions are much easier to meet by increasing R_m than to reach the region where the functions $\psi_{\nu_a}(\mathbf{R})$ and $\psi_{\nu_b}(\mathbf{R})$ assume their asymptotic form.

To implement Eq. (6) one has to construct the Green function $G(\mathbf{R}, \mathbf{R}'; E)$. This can be done by different methods, even absorbing potentials [3–5] now can be used safely, provided that they are introduced outside S. More elegantly, $G(\mathbf{R}, \mathbf{R}'; E)$ can be expanded in terms of Siegert states. The possibility to use such expansion reveals an important advantage of Eq. (6) over the formula derived in [13]; see Ref. [14]. Recently, we have proposed an efficient method for calculating the Siegert states [15] and eventually we hope to apply it for implementing Eq. (6). Here, we use an approach which falls most naturally in the framework of the hyperspherical method. For $\mathbf{R} \in S_a$ and $\mathbf{R}' \in S_b$ we have

$$G(\mathbf{R}, \mathbf{R}'; E) = \sum_{\nu_a \nu_b} G_{\nu_a \nu_b} \Phi_{\nu_a}(\Omega; R_m) \Phi_{\nu_b}(\Omega'; R_m). \tag{7}$$

Using Eq. (5), the matrix $G_{\nu_a \nu_b}$ can be expressed in terms of the $\mathcal{R}$ matrix defined with respect to the same basis,

$$\mathbf{G} = 2(\mathbf{I} - i\mathbf{k}\mathcal{R})^{-1}\mathcal{R}, \tag{8}$$

where $i\mathbf{k}$ is the logarithmic derivative matrix for the outgoing wave solutions of Eq. (3). Methods of calculating the $\mathcal{R}$ matrix are well developed. The matrix $\mathbf{k}$ can be obtained by an appropriate matching procedure. For $R_m \rightarrow \infty$ it becomes diagonal, $\mathbf{k} = \mathrm{diag}[k_\nu]$, where k_ν are the asymptotic values of the channel momenta. Wishing to disentangle the implementation of Eq. (6) from any reference to the asymptotic states, we substitute k_ν by the local values $k_\nu(R_m)$ at the surface S. In this approximation, Eq. (6) takes the remarkably simple form

$$N_{ab}(E) = \sum_{\nu_a \nu_b} k_{\nu_a}(R_m) k_{\nu_b}(R_m) |G_{\nu_a \nu_b}|^2. \tag{9}$$

Equations (8) and (9) provide a practical recipe to implement our approach.

As an illustration, we consider the reaction

$$t + \mu d(nl) \leftrightarrow t\mu(n'l') + d \tag{10}$$
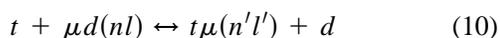
for zero total angular momentum. The $dt\mu$ system lies on the border between the realms of atomic physics and chemical reactions. Indeed, the process (10) resembles the electron transfer in ion-atom collisions, yet in terms of the mass ratios for the particles involved it is closer to the light atom transfer reactions. Another peculiarity of $dt\mu$ which dictates its choice here is the presence of the strong dipole coupling between the states of excited manifolds [16]. This feature mimics a situation where the asymptotic states are defined poorly.

Our computational scheme is based on the hyperspherical elliptic coordinates [17], the slow/smooth variable discretization (SVD) method [18], and the $\mathcal{R}$-matrix propagation technique of Ref. [19]. This yields the $\mathcal{R}$ matrix at the surface S as a function of the energy E and the matching radius R_m. Then we can extract the complete scattering matrix by applying a two-dimensional matching procedure similar to that used in [20] and calculate the cumulative probability $N(E)$ for the reaction (10) using Eq. (1). Alternatively, we can obtain $N(E)$ directly from Eqs. (8) and (9). We use the muonic atomic units. Figure 2 shows adiabatic potentials for $dt\mu$. The dashed line represents the potential ridge. For the Coulomb systems, this is defined by C_{SP}/R, where $C_{SP} \approx -9.792$ for $dt\mu$. Let $R_r(E)$ be the radius where the ridge crosses the given energy E, i.e., $R_r(E) = C_{SP}/E$. For $R > R_r(E)$ different arrangements are separated by a potential barrier whose height and width grow with the increase of R. Thus one can expect that $R_r(E)$ estimates the size of
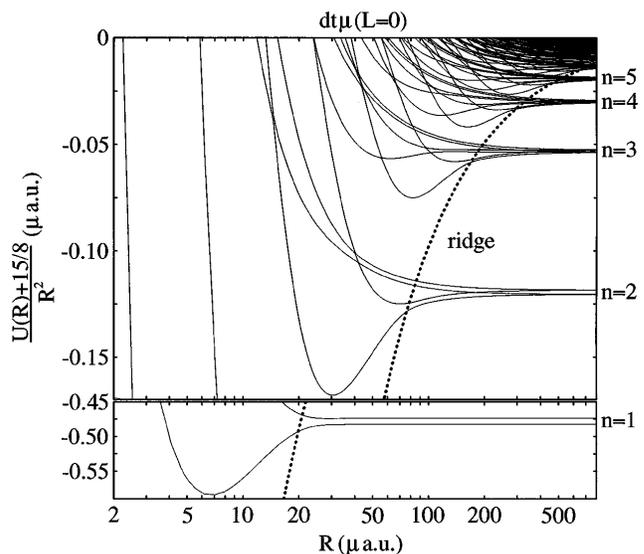
FIG. 2. The hyperspherical adiabatic potentials for $dt\mu$. The ridge position is defined by $-9.792/R$ in μ a.u.
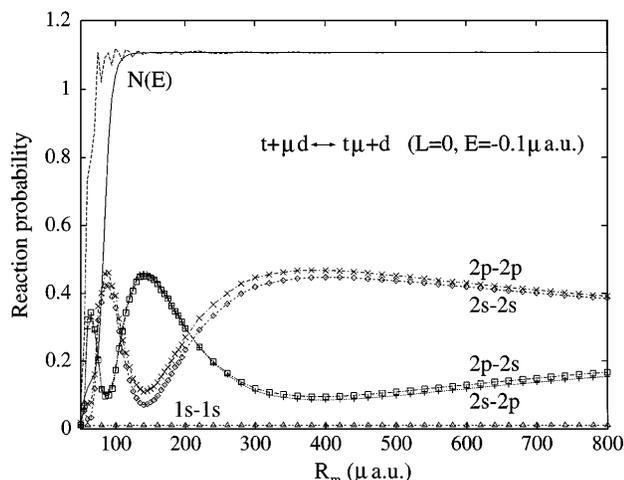
FIG. 3. State-to-state (lines with symbols labeled as $nl - n'l'$) and cumulative (solid and dashed lines) probabilities for the reaction (10) as functions of the matching radius R_m for $E = -0.1 \ \mu$ a.u. For $n \neq n'$, the probabilities are too small to be seen in the figure. The dashed line is the sum of all the state-to-state contributions according to Eq. (1). The solid line is the result obtained from Eq. (9).

the region essential for calculating $N(E)$. This feature is illustrated in Fig. 3. The probabilities of the $2l \leftrightarrow 2l'$ reactive transitions as functions of the matching radius R_m calculated at $E = -0.1$ oscillate wildly at small R_m and keep varying appreciably even up to the largest $R_m = 800$ considered here. However, the cumulative reaction probability $N(E)$ obtained either from Eq. (1) or from Eq. (9) rapidly stabilizes beyond $R_m = R_r(-0.1) \approx 100$. [One should not be surprised that the "probability" $N(E)$ exceeds unity, mind the definition (1).] This value is much smaller than $R_m = 20\,000$ required to reproduce the Gailitis-Damburg oscillations in the same energy range [16]. The behavior shown in Fig. 3 is typical for all energies, except very narrow intervals around the reaction thresholds. For chemical reactions, similar behavior was indicated in [21]. Finally, Fig. 4 shows our results for
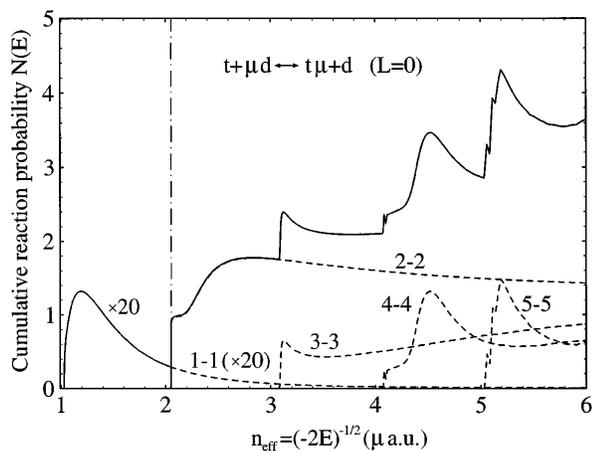
FIG. 4. Solid curve—cumulative probability for the reaction (10); dashed curves—$n - n'$ contributions. Note the break in scale shown by the vertical line.

$N(E)$ calculated for E up to the $n = 6$ threshold, which is the highest energy we can treat with $R_m = 800$. Qualitative discussion of these results in terms of the mechanisms of the reaction (10) as well as more challenging applications to chemical reactions will be reported elsewhere.

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