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Classical irregular scattering and fluctuation of quantum transition probability

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Abstract

S-matrix of a collision system exhibiting classical irregular scattering is analyzed on the basis of the classical S-matrix theory. The S-matrix is represented as an infinite series, each term of which possesses a random phase factor. Each S-matrix element, in consequence, performs random walk on the complex plane when one varies the final state. Probability distribution of the S-matrix elements is derived theoretically.

1. Introduction

The statistical theory of chemical reaction, such as the phase space theory of Light [1], has successfully been utilized in many studies. The theory is based on 'the principle of equal weight': All the final states energetically accessible are produced in equal probability [1,2]. Such 'statistical behavior' has been believed to originate from the chaotic behavior of underlying classical dynamics.

The advance of the state-to-state chemistry, however, has revealed that the final states sometimes exhibit strong state-selectivity. The systems which are believed to exhibit the statistical behavior are found to give rise to complicated state-selectivity. In such cases, the state-selectivity is so complicated that it is useful to interpret the final state distribution as random. Recently, a novel interpretation of the statistical behavior has been proposed: The statistical behavior means a 'fluctuation' of transition probability, decay rate, and spectral intensity [3–9]. It does not indicate that all the final states have exactly equal transition probabilities, but rather indicates that the transition probabilities are 'randomly' distributed. In the previous studies [3–9], however, fluctuation is analyzed in a phenomenological manner by assuming that the basic matrix elements such as those of coupling matrix, Franck–Condon matrix and S-matrix, obey a normal (Gaussian) distribution. The origin of the fluctuation and the reason why the matrix elements obey a normal distribution are left unclear. In the present study, the fluctuation of transition probability is derived on the basis of the classical S-matrix theory applied to irregular scattering, which is a manifestation of classical chaos in collision processes.

The classical S-matrix theory was presented by Miller [10–12]. In the case of vibrationally inelastic collisions and collinear chemical reactions, the S-matrix element is represented as

$$S_{i\to f}(E) = \sum_n r_n \mathrm{e}^{\mathrm{i}\theta_n}, \tag{1}$$

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where θ_n is the action integral, r_n originates from the Van Vleck determinant, and the summation is taken over the classical trajectories having initial vibrational action J_i, final action J_f and total energy E. The trajectories satisfying such boundary conditions can be detected in an 'excitation profile', which is the graph of J_f plotted against ϕ_i (initial vibrational angle variable) for given J_i and E. A typical excitation profile is shown in Fig. 1. The intersections between the horizontal line, $J_f = \text{const.}$, and the curve, $J_f(\phi_i)$, corresponds to the trajectories satisfying the boundary condition. The values of J_i and J_f should be restricted to half odd integers if one discusses the transition probability between quantized initial and final states. In the primitive semiclassical approximation, r_n is given by $(\partial J_f/\partial\phi_i)^{-1/2}$ at the intersection. The smaller slope of the tangent $\partial J_f/\partial\phi_i$ at the intersection gives rise to a large contribution to the S-matrix element.

The above formalism has been applied to $H + Cl_2$ reaction by Rankin and Miller [13]. The excitation profile was found to consist of a smooth curve and a fractalic part (irregular part). This can be interpreted as a manifestation of classical chaos. Due to the fractalic property the contribution

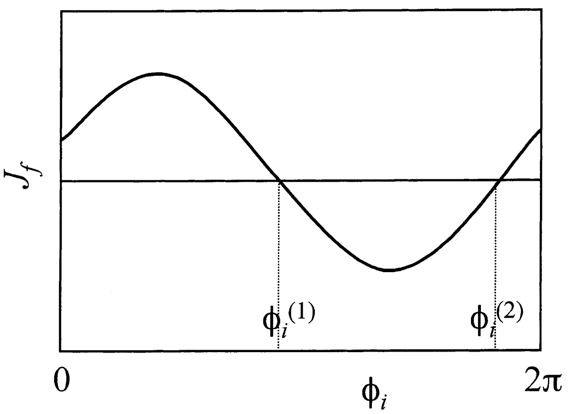


Fig. 1. A schematic drawing of excitation profile of the regular case. The final vibrational action J_f is plotted against the initial vibrational phase angle ϕ_i with fixed initial vibrational action and collision energy. For a given value of J_f (indicated by the horizontal line) there are two trajectories (corresponding to the intersections at $\phi_i = \phi_i^{(1)}$ and $\phi_i^{(2)}$) satisfying the boundary condition. The two intersection points contribute to the classical S-matrix.

from the irregular part consists of an infinite number of terms (an infinite number of trajectories).

Rankin and Miller proposed a 'random phase approximation', in which one assumes that the contribution from the irregular part is negligible due to cancellation of many terms having random phase factors, i.e.,

$$S_{i\to f}(E) = \sum_{\text{regular}} r_n \mathrm{e}^{\mathrm{i}\theta_n} + \sum_{\text{irregular}} r_{n'} \mathrm{e}^{\mathrm{i}\theta_{n'}} \simeq \sum_{\text{regular}} r_n \mathrm{e}^{\mathrm{i}\theta_n}. \quad (2)$$

The random phase, however, does not mean that the contribution from the irregular part exactly vanishes. A certain correction term should remain. In the present study, attention is focused on this correction term, and the fluctuation of S-matrix elements is shown to originate from it.

2. Summation prescription

The structure of fractalic part of an excitation profile has been investigated closely and found to consist of an infinite number of graphs having the shape of an icicle [14–16]. A typical example of excitation profile in the irregular case is shown in Fig. 2. When the fractalic part is magnified, an iciclic structure appears. A classical mechanical analysis has shown that the iciclic structure originates from temporary trapping of classical trajectories. Narrower icicles correspond to the trajectories trapped for a longer time. It is shown that the residence time of the trapped trajectory has no upper bound, and there exist an infinite number of icicles having an infinitely narrow width.

Since the classical S-matrix is represented by an infinite series in the case of irregular scattering, convergence problem arises. As mentioned in the preceding section, a large $\partial J_f/\partial\phi_i$ at the intersection between the icicle and the line $J_f = \text{const.}$ gives rise to a small contribution to the S-matrix element. The narrower icicle, consequently, has a tendency to have a small contribution. With increasing residence time of trapped trajectory, the

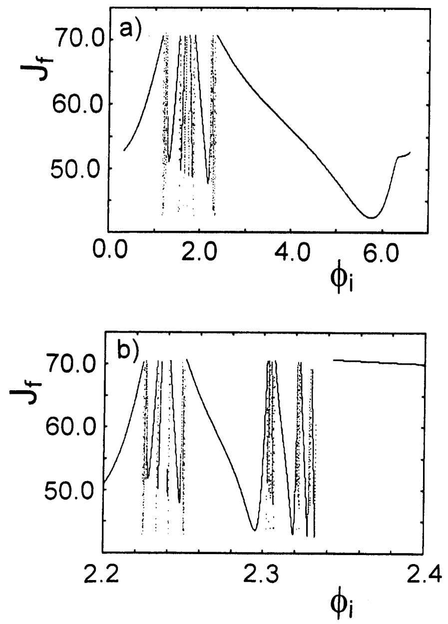


Fig. 2. (a) A typical example of excitation profile of the irregular case calculated based on the model system described in Section 3. The parameters are as follows: collision energy $E_{\rm coll} = 4.83 \times 10^{-4}$ (in a.u.), initial vibrational action $J_i = 70.5\hbar$. (b) A magnification of the indicated portion of panel (a). The unit of the vertical axis is $\hbar$. The iciclic structures are seen.

corresponding icicle becomes narrower, and thus the contribution from each icicle to the S-matrix element decreases. The number of icicles, however, is known to increase with the residence time. It is thus not trivial whether the infinite series converges or not. It has been shown that the series is not always absolutely convergent [17]. A summation prescription with a robust physical meaning is needed.

In the present study we adopt the following summation prescription: The S-matrix series is summed in the order of increasing residence time of trajectory. This prescription is believed to give a physically meaningful result because a truncated sum up to a residence time T gives an estimation of transition probability having a finite energy resolution $\Delta E \simeq h/T$. how is this true, if the sum is divergent?

The primitive semiclassical version of the classical S-matrix theory is apt to break down because of the divergence of $(\partial J_f/\partial \phi_i)^{-1/2}$ at the bottom of the icicle. We adopted the remedy based on the uniform approximation which has also been proposed by Miller [10]. When icicles possess a simple shape without branching, each icicle has a pair of intersection points, i.e., two trajectories contribute to the S-matrix from each icicle. The S-matrix can be expressed as a sum of these pairs over icicles as

$$S_{i\to f}(E) = \sum_{\rm icicle} \left(r_a e^{i\theta_a} + r_b e^{i\theta_b}\right). \qquad (3)$$

When this pair of intersections are located near the bottom of icicle, two intersections come close to each other, and the primitive semiclassical approximation breaks down. In the uniformized version [10], the S-matrix can be written as

$$S_{i\to f}(E) = \sum_{\rm icicle} r e^{i\theta}, \qquad (4)$$

where r is expressed by using the Airy function. Details of the expression of r are omitted here because they are not essential to the discussion below. It should be noted that uniformization among different icicles is unnecessary because the trajectories which belong to different icicles have action integrals very different from each other even when they are located close to each other in the graph of excitation profile.

3. Numerical calculation

We adopt a model mimicking $Xe + I_2$. This collision system $Xe + I_2$ is fixed in the collinear configuration, and two degrees of freedom, i.e., the collision coordinate of $Xe + I_2$ and the vibrational coordinate of I_2, are taken into consideration. The potential energy functions are composed of a Morse potential for the I_2 vibration and a Lennard-Jones potential for the Xe–I interaction. The values of parameters follow those of Noid et al. [15] for I_2 and those of Benjamin and Wilson [18] for the Xe–I interaction.

Propagating classical trajectories numerically, we obtain the excitation profile. The classical S-matrix is calculated on the basis of the uniformized version described in the preceding section. Behavior of truncated sums on the complex plane is examined and shown in Fig. 3a, b, where the values of parameters are as follows: collision

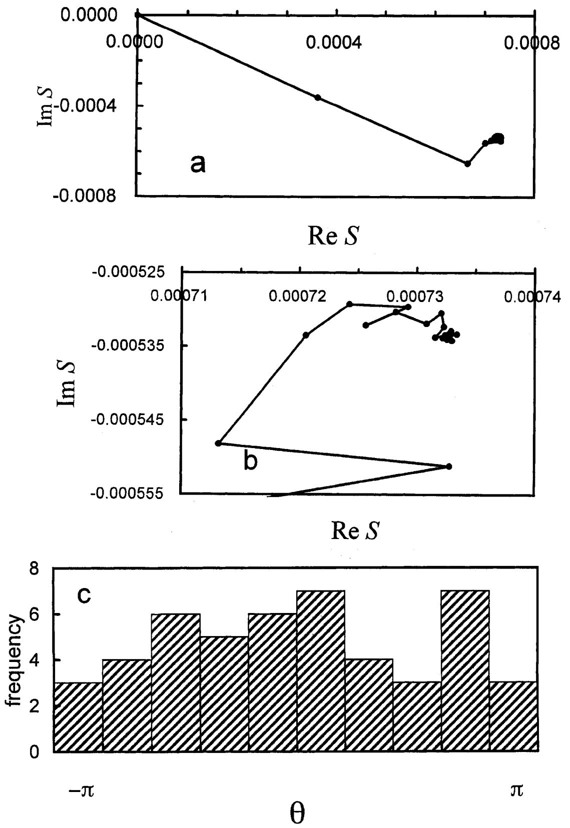


Fig. 3. (a) An illustration of summation process to construct the classical S-matrix on the complex plane. Each arm represents $r_n e^{i\theta_n}$. The data are the results of numerical calculation of the model $Xe + I_2$ system. The parameters E_{coll} and J_i are the same as in Fig. 2, and $J_f = 64.5\hbar$. (b) A magnification of a portion of panel (a). The whole diagram resembles a trajectory of random walk. This implies that the S-matrix element performs a kind of random walk on the complex plane. (c) Histogram representing the statistical distribution of the phase angle $\{\theta_n\}$. The graph indicates the uniformity of distribution.

energy $E_{coll} = 4.83 \times 10^{-4}$ (a.u.), $J_i = 70.5\hbar$ and $J_f = 64.5\hbar$. Each arm of the zigzag graph in Fig. 3a, b represents the complex value $r_n e^{i\theta_n}$, and the arms are connected in the order of decreasing arm length, r_n, to form the whole zigzag graph. Each pivot of the graph indicates the value of the truncated sum on the complex plane. Figs. 3a, b imply that the truncated sum performs a kind of random walk on the complex plane.

The random walk is believed to originate from the randomness of the phase factor θ_n of each arm. We estimate the statistical distribution of θ_n and r_n. The distribution of $\{\theta_n\}$ is found to be uniform as shown in Fig. 3c. In the next section, we derive the distribution function of the S-matrix elements on the basis of the distributions of $\{\theta_n\}$ and $\{r_n\}$.

4. Probability distribution of S-matrix elements

4.1. Outline of formalism

We define a set of small intervals $I_v \equiv [r_{v+1}, r_v]$ ($v = 1, 2, 3, \ldots$) on the r-axis. The width of I_v is sufficiently small so that the icicles contained within I_v are assumed to have the same value of r, i.e., $r = r_v$. We define ΔN_v as the number of icicles having $r_n \in I_v$. In the first step we calculate the probability distribution of

can this assumption be made, strictly?

$$\bar{r}_v \equiv \sum_{n \in I_v} r_v e^{i\theta_n} = r_v \sum_{n=1}^{\Delta N_v} e^{i\theta_n}, \tag{5}$$

and in the second step we calculate the probability distribution of

$$S_{i\to f} = \sum_{v=1}^{\infty} \bar{r}_v. \tag{6}$$

4.2. Probability distribution of $\bar{r}_v$

We define (u_n, v_n) as $r_v e^{i\theta_n} \equiv u_n + i v_n$. As discussed in Section 3, $\{\theta_n\}$ possesses the uniform distribution in the interval $[0, 2\pi]$. The distribution function of (u, v) can be written as

$$P(u, v)\,du\,dv = \frac{1}{2\pi}\delta(r - r_v)\,dr\,d\theta. \tag{7}$$

The characteristic function of $P(u, v)$ is given by

$$\Phi(\xi, \eta) = \frac{1}{2\pi}\int du\,dv\,e^{i(\xi u + \eta v)} P(u, v). \tag{8}$$

The variable transformation $\xi = \rho\cos\phi$ and $\eta = \rho\sin\phi$ enables us to carry out the integral, and we obtain

$$\begin{aligned}\Phi(\xi, \eta) &= \frac{1}{2\pi}\int_0^{\infty} dr \int_0^{2\pi} d\theta\,\delta(r - r_v)\,e^{ir\rho\cos(\theta-\phi)} \\ &= J_0(r_v\rho),\end{aligned} \tag{9}$$

where J_0 represents the Bessel function of order 0. In order to derive the distribution function of $\bar{r}_v$, we introduce the variable $(\bar{u}, \bar{v})$ as

$$\bar{u} + \mathrm{i}\,\bar{v} \equiv \frac{1}{(\Delta N_v)^{1/2}} \sum_{n=1}^{\Delta N_v} (u_n + \mathrm{i}\,v_n). \tag{10}$$

The distribution function $P(\bar{u}, \bar{v})$ can be derived based on the central limit theorem. The characteristic function of $P(\bar{u}, \bar{v})$ is given by

$$\begin{aligned}\bar{\Phi}(\bar{\xi}, \bar{\eta}) &= \left\{ \Phi\left(\frac{\bar{\xi}}{(\Delta N_v)^{1/2}}, \frac{\bar{\eta}}{(\Delta N_v)^{1/2}} \right) \right\}^{\Delta N_v} \\ &= \left\{ J_0\left(r_v \left(\frac{\bar{\xi}^2 + \bar{\eta}^2}{\Delta N_v} \right)^{1/2} \right) \right\}^{\Delta N_v}. \end{aligned} \tag{11}$$

In the first equality we used the fact that (u_n, v_n) with different n's are independent probabilistic variables. We consider the case of $\Delta N_v \gg 1$. In the limit of $\Delta N_v \to \infty$, the characteristic function is reduced as

$$\begin{aligned}\bar{\Phi}(\bar{\xi}, \bar{\eta}) &= \left[1 - \frac{r_v^2}{4} \frac{\bar{\xi}^2 + \bar{\eta}^2}{\Delta N_v} + \mathrm{o}\left(\left(r_v^2 \frac{\bar{\xi}^2 + \bar{\eta}^2}{\Delta N_v} \right)^2 \right) \right]^{\Delta N_v} \\ &\simeq \exp\left[-\frac{r_v^2}{4} \left(\bar{\xi}^2 + \bar{\eta}^2 \right) \right]. \end{aligned} \tag{12}$$

The distribution function $P(\bar{u}, \bar{v})$ can be obtained by the Fourier transform of $\bar{\Phi}(\bar{\xi}, \bar{\eta})$ as

$$P(\bar{u}, \bar{v}) = \frac{1}{2\sigma_v^2 \pi} \exp\left[-\frac{1}{2} \left(\frac{\bar{u}^2}{\sigma_v^2} + \frac{\bar{v}^2}{\sigma_v^2} \right) \right]. \tag{13}$$

This represents a 2-dimensional isotropic normal distribution with variance $\sigma_v^2 \equiv r_v^2/2$. What is sought next is the distribution function of $(\tilde{u}, \tilde{v})$ which is defined as

$$\tilde{u} + \mathrm{i}\,\tilde{v} \equiv \sum_{n=1}^{\Delta N_v} r_v\, \mathrm{e}^{\mathrm{i}\theta_n} = (\Delta N_v)^{1/2} (\bar{u} + \mathrm{i}\,\bar{v}). \tag{14}$$

By a simple scaling of variables, the distribution function of $(\tilde{u}, \tilde{v})$ is obtained as

$$P(\tilde{u}, \tilde{v}) = \frac{1}{2\tilde{\sigma}_v^2 \pi} \exp\left[-\frac{1}{2} \left(\frac{\tilde{u}^2}{\tilde{\sigma}_v^2} + \frac{\tilde{v}^2}{\tilde{\sigma}_v^2} \right) \right], \tag{15}$$

where $\tilde{\sigma}_v^2 = \Delta N_v \sigma_v^2 = r_v^2 \Delta N_v / 2$.

4.3. Probability distribution of S-matrix element

The S-matrix is expressed as

$$S = \sum_{v=1}^{\infty} (\tilde{u}_v + \mathrm{i}\,\tilde{v}_v). \tag{16}$$

Since $(\tilde{u}_v, \tilde{v}_v)$ obeys a normal distribution, the probability distribution of $(\mathrm{Re}S, \mathrm{Im}S)$ is also a normal distribution and its variance is given by the sum of $\tilde{\sigma}_v^2$. The distribution function is represented as

$$P(\mathrm{Re}S, \mathrm{Im}S) = \frac{1}{2\pi\Sigma^2} \exp\left[-\frac{1}{2} \frac{(\mathrm{Re}S)^2 + (\mathrm{Im}S)^2}{\Sigma^2} \right], \tag{17}$$

where

$$\Sigma^2 = \sum_{v=1}^{\infty} \tilde{\sigma}_v^2 = \frac{1}{2} \sum_{v=1}^{\infty} \Delta N_v r_v^2. \tag{18}$$

By using the distribution function of $\{r_n\}$, $P(r)$, the value of ΔN_v can be obtained as $\Delta N_v = P(r)\,\mathrm{d}r$. Substituting this expression in Eq. (18) and replacing the summation by integral, we obtain

$$\Sigma^2 = \frac{1}{2} \int_0^{r_{\max}} P(r) r^2 \,\mathrm{d}r, \tag{19}$$

where $r_{\max}$ is the largest value of $\{r_n\}$. A numerical analysis of the model system described in Section 3 shows that the distribution of the arm-length $\{r_n\}$ can be represented as

$$P(r) \overset{r\to 0}{\sim} \mathrm{const.} \times r^{-0.38}. \tag{20}$$

This certifies the convergence of the integral in Eq. (19). In summary, (ReS, ImS) obeys the 2-dimensional isotropic normal distribution, Eq. (17). Its variance is given by Eq. (19).

5. Discussion

5.1. Probability prediction of S-matrix elements

From a practical point of view, the random walk of S-matrix element on the complex plane enables a probability-prediction of S-matrix element. We can predict a probability for the value of S-matrix element to fall in a given interval. The S-matrix is divided into two parts, the deterministic part $S^{(\mathrm{D})}_{i\to f}$ and fluctuating part $S^{(\mathrm{F})}_{i\to f}$, i.e.,

$$S_{i\to f} = S^{(\mathrm{D})}_{i\to f} + S^{(\mathrm{F})}_{i\to f}, \tag{21}$$

where

$$S^{(\mathrm{D})}_{i\to f} \equiv \sum_{r_n > R} r_n\, \mathrm{e}^{\mathrm{i}\theta_n} \tag{22}$$

and

$$S^{(\mathrm{F})}_{i\to f} \equiv \sum_{r_n \le R} r_n\, \mathrm{e}^{\mathrm{i}\theta_n}. \tag{23}$$

This division is identical with Rankin and Miller's division (Eq. (2)), and the deterministic and fluctuating parts correspond to their regular and irregular parts, respectively. The regular part and the irregular part of the excitation profile can be classified by use of the threshold R. The regular part consists of a finite number of big icicles, and the irregular part of an infinite number of small icicles. The deterministic part is given by a finite sum free from the convergence problem. The fluctuating part can be estimated according to the formulae presented in the preceding section, and the probability of finding the value of $S^{(\mathrm{F})}_{i\to f}$ in a given area in the complex plane is given by the distribution function Eq. (17). In short, we can estimate the magnitude of the correction term to be added to the random phase approximation of Rankin and Miller.

5.2. Fluctuation of transition probability as a function of final state

The fluctuation of transition probability as a function of final state mentioned in Section 1 can be derived from the random walk of S-matrix elements. Based on the numerical calculation we find the fact that when we sweep J_f, r_n changes slowly, but θ_n changes rapidly. The reason for the slow change of r_n is that the slope of tangent to an icicle changes slowly except at the bottom. In the uniform approximation, r_n mildly changes even at the bottom of icicle. On the other hand, θ_n diverges at the root (the top part) of each icicle, and therefore the phase angle of $\mathrm{e}^{\mathrm{i}\theta_n}$ rotates quickly when J_f sweeps. Consequently, we can assume that when J_f changes from J_f to $J_f + \Delta J_f$, the sequence $\{r_n\}_{J_f+\Delta J_f}$ is approximately identical with $\{r_n\}_{J_f}$, but the set $\{\theta_n\}_{J_f+\Delta J_f}$ is totally different from $\{\theta_n\}_{J_f}$. We can regard $\{\theta_n\}$ as random numbers in the interval $[0, 2\pi]$. This gives rise to irregular behavior or fluctuation of $S^{(\mathrm{F})}_{i\to f}$ as a function of J_f. Thus the S-matrix elements exhibit random walk due to the randomness of the phase factors $\{\theta_n\}$. The distribution function of 'fluctuating' $S^{(\mathrm{F})}_{i\to f}$ is exactly given by the distribution function Eq. (17).

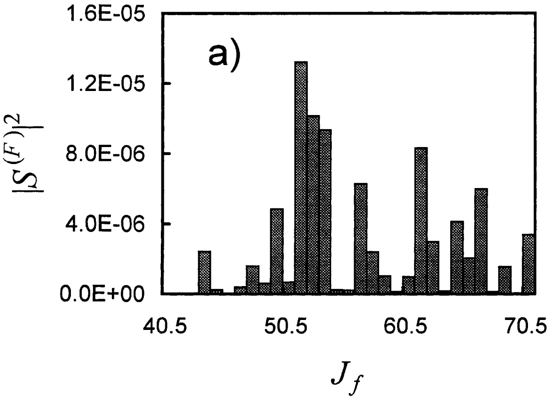
5.3. Numerical confirmation of the theory

Numerical calculation is carried out to confirm the argument given in preceding subsection. The contributions from two largest icicles are regarded as the deterministic part $S^{(\mathrm{D})}_{i\to f}$ defined in Eq. (22). The fluctuating part $S^{(\mathrm{F})}_{i\to f}$ (Eq. (23)) is calculated as a function of final state and plotted in Fig. 4. It exhibits a kind of random walk on the complex plane. The magnitude of $|S^{(\mathrm{F})}_{i\to f}|^2$, however, is found to be approximately one-hundredth of that of $|S^{(\mathrm{D})}_{i\to f}|^2$, and it would probably be difficult to detect this kind of fluctuation from the experimental point of view.

The distribution of $|S^{(\mathrm{F})}_{i\to f}|^2$ is analyzed to confirm the formal theory described in Section 4. The distribution of $\{r_n\}$ is estimated numerically to obtain $P(r)$ in Eq. (19), and it leads to the value $\Sigma^2 = 3.0 \times 10^{-6}$. According to Eq. (17), the distribution function of $|S^{(\mathrm{F})}_{i\to f}|^2$ is predicted to be

$$P(x)\,\mathrm{d}x = \frac{1}{2\Sigma^2} \exp\left(-\frac{x}{2\Sigma^2}\right) \mathrm{d}x, \tag{24}$$

where x represents $|S^{(\mathrm{F})}_{i\to f}|^2$. On the other hand, the distribution of $|S^{(\mathrm{F})}_{i\to f}|^2$ is numerically estimated by constructing a histogram and shown in Fig. 5 as well as the theoretical curve (Eq. (24)) with the predicted value $\Sigma^2 = 3.0 \times 10^{-6}$. The distribution



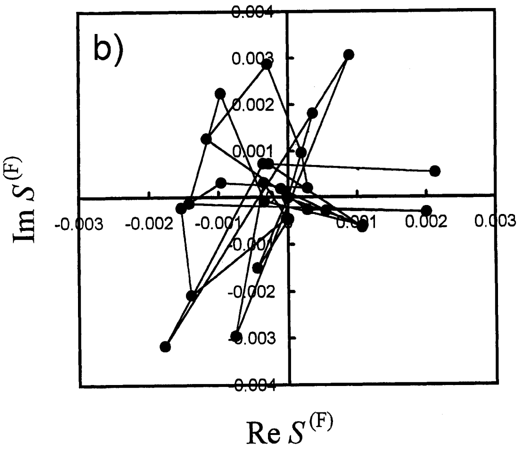


Fig. 4. The fluctuating part of the S-matrix element $S^{(F)}_{i\to f}$ of the inelastic collision Xe + I_2. (a) $|S^{(F)}|^2$ as a function of J_f at quantized values. (b) $S^{(F)}$ is plotted on the complex plane. The value of J_i is $70.5\hbar$ and the value of J_f is swept from 40.5 to $70.5\hbar$ by $\hbar$.

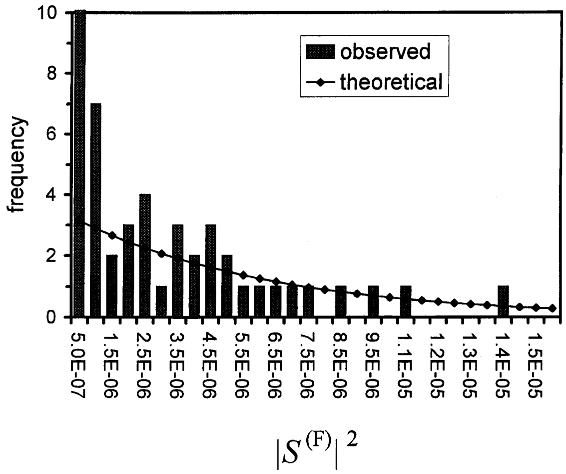


Fig. 5. Distribution of $|S^{(F)}_{i\to f}|^2$. The curve is the theoretical prediction discussed in Section 5.3.

agrees well with the theoretical prediction. The formal theory based on the central limit theorem is numerically verified.

5.4. Connection with quantum mechanical resonance scattering

Classical irregular scattering originates from trapping of classical trajectories. From a quantum mechanical point of view, the trapping gives rise to resonance scattering, which causes certain anomalous peaks and dips in transition probability as a function of collision energy and final state. In the classical limit, i.e., when the vibrational action involved in the collision process is sufficiently large, the semiclassical treatment discussed in the present study and a quantum mechanical treatment should coincide with each other.

In a quantum mechanical picture, level spacing between adjacent resonance states becomes narrower in the classical limit. The resonances begin to overlap with each other, and the resonance peaks and dips of transition probability become congested. The transition probability thus exhibits extremely complicated dependence on the collision energy and final state. The fluctuation of transition probability is believed to originate from such circumstances from the purely quantum mechanical point of view.

6. Summary

A kind of random walk of S-matrix elements on the complex plane is discussed. The random walk is shown to originate from the classical irregular scattering on the basis of the semiclassical treatment. The randomness is ascribable to the interference among infinitely many different classical paths contributing to the same S-matrix element. In this sense, the randomness is a result of the quantum effect.

A probability distribution function of S-matrix elements is derived. The central limit theorem applies to the present issue. Accumulation of many small causes leads to the result obeying a normal (Gaussian) probability distribution. The random walk of S-matrix element thus obeys a two-dimensional normal distribution on the complex plane.

The random walk of S-matrix element gives rise to fluctuation of the transition probability as a function of final state. A numerical analysis of a model $Xe + I_2$ collision system confirms the existence of the fluctuation and validity of the formal theory.

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