Atom-atom momentum-transfer cross section in the presence of resonances

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(Received 4 February 1982; revised manuscript received 9 March 1983)

The atom-atom momentum-transfer cross section is analyzed for low-energy collisions in which resonances may be present. It is shown that their contribution to this cross section can be substantial, and this is confirmed in the calculation on H^+-He system.

I. INTRODUCTION

The central place in the theory of the transport properties of gases is played by the integral[1,2]

$$\sigma_D = 2\pi \int_0^\pi (1-\cos\theta)\sigma(\theta)\sin\theta\, d\theta \ , \tag{1.1}$$

where $\sigma(\theta)$ is the differential cross section for the scattering of the atoms of the diluted gas on the atoms of the parent gas. The integral has acquired different names: momentum-transfer cross section,[3] transport cross section,[1] etc. We will refer to it as the momentum-transfer cross section. The momentum-transfer cross section has been studied on various occasions,[2–5] mostly as an integral part of the diffusion coefficient. The theory has also been applied to the inversion problem.[6–9] It has been shown that very good values of the atom-atom (ion-atom) potential can be obtained by a suitable parametrized inversion procedure of the experimental data for the diffusion coefficient. This finding is quite surprising, knowing that there are many steps from the potential to the diffusion coefficient, and in each one of them part of the information is lost about the structure of the collision process.[10] Therefore, it was not surprising when it was found that the quantum effects in diffusion are small compared with the classical ones. Nevertheless, it would be of interest to study the momentum-transfer cross section in more detail to unravel how various processes in collision contribute to this quantity. In particular, we would be interested in finding out what effect the resonance processes in collision have on (1.1).

Such an analysis has been done[11] but the purpose of it was to estimate the order of magnitude of the lifetime of the resonances formed in atom-atom collisions. It is argued that if such a lifetime is much longer than the average rate of atom-atom collisions in the gases, then the diffusion coefficient will change due to the presence of these metastable molecules. However, our aim is not in this direction. Instead we will analyze whether the formation of resonances in atom-atom collision has any direct effect on σ_D and what its order of magnitude is.

Very conveniently, this can be done with the use of the complex angular momentum formalism. The formalism was initially developed for use in nuclear physics,[12] and later was adapted for use in atom-atom collisions.[13] It was shown to be very useful for analysis of the resonance and orbiting effects in the differential cross section[14] and total cross section.[15] One particularly advantageous feature of this formalism is that the various contributions of the collision process are parametrized in a simple way, specifically, the contribution of resonances.

An alternative to using such an approach is the formalism based on complex energy.[16–18] Although the latter approach is very useful for description of decaying states (i.e., states prepared with a well defined angular momentum) it is less convenient in description of a scattering process (where many angular momenta contribute). The two approaches are, therefore, complementary in description of resonances: Where one is inconvenient the other must be used. Since we are dealing with the second case, the use of complex-energy formalism can produce misleading results.

II. THE THEORY

The momentum-transfer cross section is an integral of the form

$$\sigma_D = 2\pi \int_0^\pi (1-\cos\theta)\sin\theta\sigma(\theta)d\theta \tag{2.1}$$

and resembles very much the total cross section, in which the factor $1-\cos\theta$ is missing. The quantity $\sigma(\theta)$ in (2.1) is the differential cross section. Therefore, we expect that (2.1) can be replaced by a relationship analogous to the optical theorem for the total cross section,[19] i.e., we can write

$$\sigma_D = \frac{4\pi}{k}\mathrm{Im}[f_D(0)] \ , \tag{2.2}$$

where f_D is a quantity which we will call the "momentum-transfer amplitude" in the forward direction. It is simple to show that

$$f_D(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(l+1)(S_l S_{l+1}^{-1}-1)P_l(\cos\theta) \tag{2.3}$$

satisfies (2.2), hence it plays the same role as the scattering amplitude in the optical theorem for the total cross section. We can prove (2.2) by replacing $f_D(0)$ with (2.3), in which case we obtain

$$\begin{aligned}\sigma_D &= \frac{2\pi}{k^2}\sum_{l=0}^{\infty}(l+1)[1-\mathrm{Re}(S_l S_{l+1}^{-1})] \\ &= \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_l-\delta_{l+1})\end{aligned} \tag{2.4}$$

and this is exactly equal to (2.1).[3] The advantage of using (2.3) for analyzing σ_D is that we can now apply the complex angular momentum theory developed for the scattering amplitude,[13] with additional care that S_{l+1}^{-1} is present in (2.3).

As the first step we replace the sum in (2.3) by a set of integrals in the continuous angular momentum variable.

This is done with the use of the Poisson sum formula[20]

$$2ikf_D(0)=\sum_{m=-\infty}^{\infty}(-1)^m\int_0^{\infty}d\lambda(\lambda+\tfrac{1}{2})(S_\lambda S_{\lambda+1}^{-1}-1)\times e^{2im\pi\lambda}, \tag{2.5}$$

where we have set θ to zero. The sum over m can be split into three parts: the sum involving only negative m, the sum over the positive m, and the term with $m=0$. Since the integrand in (2.5) is not singular in a small vicinity of the real λ axis, which follows from the properties of the S matrix,[21] the sum over the negative m can be written as

$$2ikf_D^{m<0}=-\int_{0-}^{\infty}d\lambda(\lambda+\tfrac{1}{2})(S_\lambda S_{\lambda+1}^{-1}-1)\frac{e^{-2i\pi\lambda}}{1+e^{-2i\pi\lambda}}, \tag{2.6}$$

where the minus sign of the lower limit in the integral means that the integration path is slightly shifted from the real λ axis into the lower part of the complex λ plane. In what follows we will assume that the potential has a hard core[22] in which case the S matrix has poles in the first and the third quadrant of the λ plane.[13] Likewise, the zeros of the S matrix are in the second and fourth quadrant of the λ plane. This is simply proved from the unitarity of the S matrix

$$S_\lambda^{-1}=S_{\lambda^*}^* \tag{2.7}$$

meaning that if λ_n is a pole of S_λ then λ_n^* is its zero. Therefore, the integrand in (2.6) is singular in the fourth quadrant at the points λ_n^*-1.

We can now replace the integration path in (2.6) by the one along the negative imaginary axis, provided two conditions are fulfilled: the contribution of the poles of the integrand are properly taken into account and that on any ray originating at $\lambda=0$ and going into the fourth quadrant, including the imaginary axis, the integrand goes to zero sufficiently fast. It has been shown that for potentials with a hard core, the S matrix is exponentially increasing in the lower half of the λ plane as $\exp(\pi\,|\,\mathrm{Im}\lambda\,|\,)$,[13] therefore the integrand in (2.6) indeed goes to zero as $\exp(-2\pi\,|\,\mathrm{Im}\lambda\,|\,)$. Because of this the integration path can be shifted to the negative imaginary axis, in which case (2.6) becomes

$$2kf_D^{m<0}=\pi\sum_n(\lambda_n^*-\tfrac{1}{2})(S_{\lambda_n^*-1}^*)^{-1}\beta_n^*\frac{e^{-i\pi\lambda_n^*}}{\cos(\pi\lambda_n^*)}+\int_0^{\infty}d\lambda(-i\lambda+\tfrac{1}{2})(S_{-i\lambda}S_{-i\lambda+1}^{-1}-1)\frac{e^{-2\pi\lambda}}{1+e^{-2\pi\lambda}}, \tag{2.8}$$

where we have used the unitarity property of S_λ.

Similarly, we can evaluate the sum over the positive m in (2.5), but the integration path is shifted to the positive imaginary axis. When we do this, the momentum-transfer amplitude is finally

$$2ikf_D(0)=\int_0^{\infty}d\lambda(\lambda+\tfrac{1}{2})(S_\lambda S_{\lambda+1}^{-1}-1)+\int_0^{\infty}d\lambda[(\lambda-\tfrac{1}{2}i)S_{i\lambda}S_{i\lambda+1}^{-1}+(\lambda+\tfrac{1}{2}i)S_{-i\lambda}S_{-i\lambda+1}^{-1}-2\lambda]\frac{e^{-2\pi\lambda}}{1+e^{-2\pi\lambda}}$$
$$-\pi i\sum_n(\lambda_n+\tfrac{1}{2})S_{\lambda_n+1}^{-1}\beta_n\frac{e^{i\pi\lambda_n}}{\cos(\pi\lambda_m)}+\pi i\sum_n(\lambda_n^*-\tfrac{1}{2})(S_{\lambda_n^*-1}^*)^{-1}\beta_n^*\frac{e^{-i\pi\lambda_n^*}}{\cos(\pi\lambda_n^*)}. \tag{2.9}$$

In the last expression we notice two distinct contributions in the amplitude f_D: one coming from the poles of the S matrix, the so-called Regge poles, and the other coming from the integrals in the variable λ. The former is the contribution of the resonances and the latter is the so-called background contribution. In the background contribution some terms can be neglected, as will be shown in Sec. III.

III. ESTIMATE OF BACKGROUND CONTRIBUTION

Essential for the analysis of the background term is the estimate of the ratio

$$S'_\lambda=S_\lambda S_{\lambda+1}^{-1} \tag{3.1}$$

and in terms of the phase shifts this is

$$S'_\lambda=e^{2i(\delta_\lambda-\delta_{\lambda+1})}. \tag{3.2}$$

In atomic collisions, where many partial waves contribute in the scattering amplitude, we can safely assume the approximation

$$\delta_\lambda-\delta_{\lambda+1}\sim-\frac{\partial\delta_{\lambda+1/2}}{\partial\lambda}\sim-\delta'_\lambda. \tag{3.3}$$

The approximation works very well for all real λ except in the vicinity of those Regge poles which have a small imaginary part. In such a case we must use another estimate for (3.1).

For an imaginary argument of the S-matrix, i.e., $S_{i\lambda}$, the phase shift is

$$\delta_{i\lambda}=i\frac{\pi}{2}\lambda+\eta_{i\lambda}, \tag{3.4}$$

where λ is real. It can be shown that η_x is an even function of x, therefore, $\eta_{i\lambda}$ is real. $\eta_{i\lambda}$ is also a smoothly varying function of λ,[23] therefore, the approximation (3.3) is valid for all λ, and we can write

$$S_{i\lambda}S_{i\lambda+1}^{-1}\sim-e^{-2i\eta'_{i\lambda}}. \tag{3.5}$$

And since $\eta_{i\lambda}$ is an even function of λ we have

$$\eta'_{i\lambda}\sim\lambda\eta''_0, \tag{3.6}$$

where η''_0 is the second derivative of η with respect to λ evaluated for $\lambda=0$. η''_0 is also a small quantity so that we can write

$$S_{i\lambda}S_{i\lambda+1}^{-1}-S_{-i\lambda}S_{-i\lambda+1}^{-1}\sim4i\lambda\eta''_0 \tag{3.7}$$

and the second integral in (2.8) is

$$2\int_0^{\infty}\lambda\,d\lambda(\eta''_0-2)\frac{e^{-2\pi\lambda}}{1+e^{-2\pi\lambda}}\sim O(\hbar^0) \tag{3.8}$$

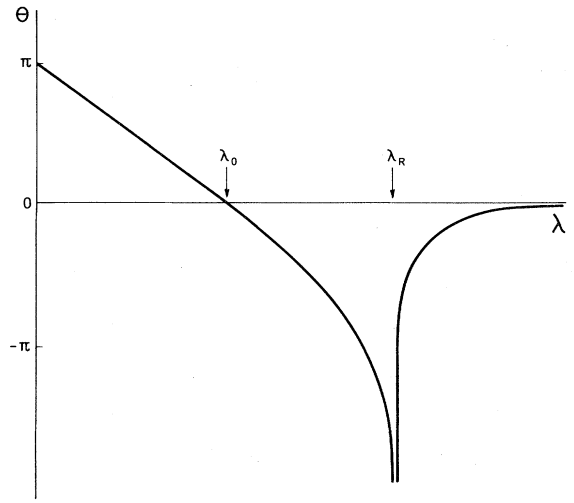

FIG. 1. Typical deflection function for atom-atom (ion-atom) system when orbiting is present.

meaning that when σ_D is calculated from (2.2) the contribution of this integral is of the order $\hbar^2$, and therefore small in the semiclassical limit.

Let us now estimate the first integral in (2.9):

$$I=\int_0^\infty d\lambda(\lambda+\tfrac{1}{2})(S_\lambda S_{\lambda+1}^{-1}-1)\ . \tag{3.9}$$

The analysis of (3.9) is further simplified if we notice that in the "optical theorem" for σ_D only the imaginary part of f_D is required, hence we only have to estimate the real part of I, which is

$$\mathrm{Re}(I)\sim -2\int_0^\infty d\lambda\,\lambda\sin^2(\tfrac{1}{2}\theta_\lambda)\ , \tag{3.10}$$

where we have neglected $\frac{1}{2}$ and used the definition of the deflection function

$$\theta_\lambda=2\delta_\lambda'\ . \tag{3.11}$$

The integral (3.10) is very well known from the analysis of momentum-transfer cross sections.[1,10] It has been shown that its value is finite and gives the classical contribution to σ_D.[24,25] Evaluation of this integral has been discussed on various occasions and nowadays this is a routine procedure.[26–29] Therefore, we can say that this part of the problem in the analysis of the background term has been solved. However, very often one needs an approximate value of this integral. One way to estimate it is by using the random-phase method,[10] in which the central role is played by an effective impact parameter. Such approximation is sufficient for many purposes, but here we will briefly outline an alternative way to estimate (3.10).

In Fig. 1 we show a typical deflection function with orbiting singularity. In the deflection function we distinguish three regions: between 0 and λ_0, which corresponds to direct reflection; then $\lambda_0<\lambda<\lambda_R$, which corresponds to the orbiting region; and $\lambda>\lambda_R$, which corresponds to the diffraction region. In the first two regions the deflection function can be approximated by a straight line. For direct reflection the straight line connects the points $\theta=\pi$ for $\lambda=0$ and $\theta=0$ for $\lambda=\lambda_0$, while in the orbiting region the straight line connects the points $\theta=0$ for $\lambda=\lambda_0$ and $\theta=-\pi$ for $\lambda=\lambda_R$. In these two cases it is not difficult to evaluate (3.10) analytically. It can be also shown that the contribution of the diffraction region in (3.10) is negligible, therefore, σ_D^B is

$$\sigma_D^B=\frac{2\pi\lambda_R}{k^2}\left[\lambda_R\left[\frac{1}{2}+\frac{2}{\pi^2}\right]-\frac{4\lambda_0}{\pi^2}\right]\ . \tag{3.12}$$

IV. CONTRIBUTION OF RESONANCES

Let us now turn our attention to the sum in (2.9) over the poles of the S matrix. The sum is

$$2ikf_D^R=-\pi i\sum_n\left[(\lambda_n+\tfrac{1}{2})S_{\lambda_n+1}^{-1}\beta_n\frac{e^{i\pi\lambda_n}}{\cos(\pi\lambda_n)}-(\lambda_n^*-\tfrac{1}{2})(S_{\lambda_n^*-1}^*)^{-1}\beta_n^*\frac{e^{-i\pi\lambda_n^*}}{\cos(\pi\lambda_n^*)}\right] \tag{4.1}$$

and the momentum-transfer cross section is proportional to the real part of f_D^R. The contribution of each pole in σ_D is additive, i.e., there is no interference term in the contribution of different poles, such as in the case of the differential cross section.[14] Therefore, we can analyze the contribution of a single pole in (4.1) knowing that the overall value of f_D^R is the algebraic sum of the individual contributions, which we designate by $f_D^{R,n}$.

Each term in the sum (4.1) is a function of λ_n and β_n (residues of the S matrix at $\lambda=\lambda_n$) and the value of the S matrix for $\lambda=\lambda_n\pm1$. The properties of the Regge poles and the residues for the atom-atom potentials have been very well studied,[13,30–32] however, it is worth repeating some of their main features. The poles λ_n are found only in the first and third quadrant of the λ plane, but only those from the first quadrant, i.e., those with $\mathrm{Im}\lambda_n>0$ and $\mathrm{Re}\lambda_n>0$, enter the sum (4.1). Among these poles we distinguish those with the small imaginary part ($\mathrm{Im}\lambda_n<0.1$), and those with the large imaginary part, i.e., $\mathrm{Im}\lambda_n>0.1$. For atom-atom potentials there are a finite number of poles with the small imaginary part, but there is an infinite number of those with $\mathrm{Im}\lambda_n\gg1$. Furthermore, if the potential does not have a barrier then the lower value for the real part of λ_n, for the poles with small $\mathrm{Im}\lambda_n$, is approximately λ_R (see Fig. 1).

The residues β_n have also some general properties. For the poles with a small imaginary part the corresponding residues have the modulus which is of the same order of magnitude as $\mathrm{Im}\lambda_n$.[13] As the imaginary part of λ_n increases the modulus of β_n also increases, with an estimate of

$$|\beta_n|\sim O(e^{\pi\,\mathrm{Im}\lambda_n})\ . \tag{4.2}$$

However, when the index n reaches a certain value, corresponding to a pole with some large value of the imaginary part, the trend (4.2) is reversed and the modulus of β_n is a decreasing function of the index n, with the limiting value $|\beta_n|\to0$ for $n\to\infty$.[13] Therefore, we are sure that the series (4.1) is convergent.

The properties of $S_{\lambda_n\pm1}$ follow, more or less, the trend of the residues, because in their neighborhood we have approximately

$$S_\lambda \sim \frac{\beta_n}{\lambda-\lambda_n} \ . \tag{4.3}$$

The exception is for the poles with a small imaginary part, when a good estimate of the S matrix is $|S_\lambda| \sim 1$.

With this short review of the properties of λ_n, β_n, and S_λ we can discuss individual terms in (4.1). Let us start by assuming that $\mathrm{Im}\lambda_n \gg 1$. In such a case the estimate for $f_D^{R,n}$ is

$$f_D^{R,n} \sim O(e^{-2\pi \mathrm{Im}\lambda_n}) \tag{4.4}$$

meaning that the terms in (4.1), corresponding to the poles with large imaginary part, are negligible. Therefore, only the poles with a small imaginary part have any significant contribution in (4.1).

Let us, therefore, assume that the imaginary part of λ_n is small. In such a case the modulus of S_{λ_n+1} and S_{λ_n-1} is of the order of unity, and the modulus of β_n is of the order $\mathrm{Im}\lambda_n$, therefore an estimate for $f_D^{R,n}$ gives

$$f_D^{R,n} \sim O(\mathrm{Im}\lambda_n) \tag{4.5}$$

which is small. The estimate (4.5) was obtained under the assumption that $\mathrm{Re}\lambda_n$ is not half-integral. When this is the case, i.e., when

$$\mathrm{Re}\lambda_n = m + \tfrac{1}{2} \ , \tag{4.6}$$

where m is an integer, $\cos(\pi\lambda_n)$ in (4.1) is nearly zero, and $f_D^{R,n}$ is approximately

$$2kf_D^{R,n} = -\frac{m}{\epsilon}[\beta_n^*(S_{\lambda_n-1}^*)^{-1} - \beta_n S_{\lambda_n+1}^{-1}] \ , \tag{4.7}$$

where we have neglected $\frac{1}{2}$ and $\epsilon = \mathrm{Im}\lambda_n$ compared to $\mathrm{Re}\lambda_n$. The resonance momentum-transfer cross section, as we will call this contribution in σ_D, is proportional to the imaginary part of $f_D^{R,n}$, hence from (4.7) we obtain approximately

$$\sigma_D^{R,n} \sim 2\pi \frac{m}{\epsilon k^2} |\beta_n| [\sin(\alpha-\delta_+) + \sin(\alpha-\delta_-)] \ , \tag{4.8}$$

where

$$\alpha = \arg \beta_n, \quad \delta_+ = \arg S_{\lambda_n+1}, \quad \delta_- = \arg S_{\lambda_n-1} \ . \tag{4.9}$$

We have also assumed $|S_\lambda| \sim 1$. It is apparent that the resonance momentum-transfer cross section can have two signs. In some cases it can be even zero, depending on the value of the phases $\alpha - \delta_\pm$. However, in the maximum possible case, (4.8) has the value

$$\sigma_D^{R,n} \sim \frac{4m}{k^2} \tag{4.10}$$

which is much larger than (4.5), when the value of $\mathrm{Re}\lambda_n$ is not half-integral.

The cross section σ_D^R will, therefore, display a typical resonance phenomena behavior when analyzed as a function of the collision energy. In a small neighborhood of the collision energy, for which $\mathrm{Re}\lambda_n$ is half-integral, the momentum-transfer cross section undergoes a rapid change, usually rising from a small value outside this interval to a comparatively large value at the value of (4.6). However, this may not always be the case, depending on the value of the phases in (4.8).

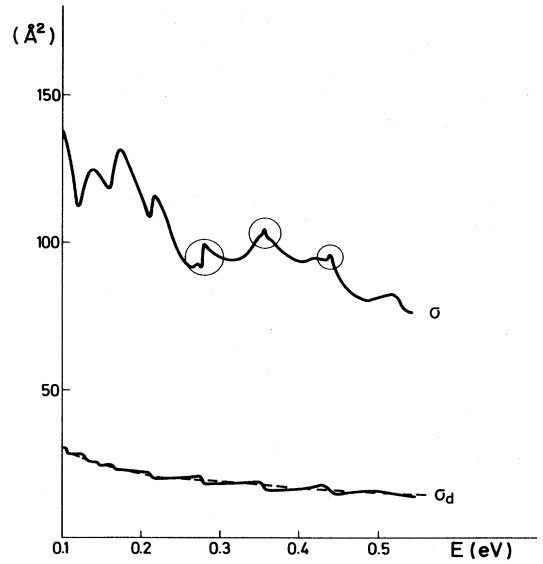

FIG. 2. Momentum-transfer cross section (σ_D) and the total cross section (σ) for the system H^+-He. Circles show the presence of the resonance contribution in σ, which appear more prominent in σ_D. Broken line shows the value of the background contribution σ_D^B.

Although, for the poles with a small imaginary part, the cross section σ_D^R may have an appreciable value, the width of the energy interval in which this happens is so narrow that for all practical purposes the contribution of resonances in σ_D is negligible. Therefore, we expect the contribution of resonances to be appreciable only when $\mathrm{Im}\lambda_n$ is in the transition region between the large and small values, around $\mathrm{Im}\lambda_n \sim 0.1$. In such a case the width of the contribution in σ_D is relatively wide but is not yet small, as estimated by (4.4). Physically this is just when the centrifugal barrier, corresponding to $\mathrm{Re}\lambda_n$ of this pole, equals the collision energy k^2. In the notation of Sec. III, the real part of λ_n is equal to λ_R, hence (4.10) is

$$\sigma_D^R \sim \frac{4\lambda_R}{k^2} \tag{4.11}$$

and if we compare (4.11) with (3.12) we obtain

$$\left|\frac{\sigma_D^R}{\sigma_D^B}\right| \sim \frac{2}{\lambda_R\left[\frac{1}{2}+\frac{2}{\pi^2}\right]-\frac{4\lambda_0}{\pi^2}} \ . \tag{4.12}$$

As an example we have calculated the momentum-transfer cross section for the H^+-He system in the energy range $E = 0.1$–0.5 eV. The points of the potential were taken from those numerically calculated by Kolos *et al.*,[33] and were fitted to a ten-parameter analytic form.[34] The dominant poles were calculated numerically[35] for several points from the interval. In Fig. 2 we show results of the calculation of σ_D.

In the same figure we also show the total cross section σ so that we can compare the relative contribution of resonances in both quantities. The solid line σ_D represents the

exact calculation of the momentum-transfer cross section, from the formula (2.4). The background term σ_D^B, given by (3.27), is shown by the broken line, and it appears as an average of σ_D in most of the energy interval. Deviation of σ_D^B from σ_D is the most prominent in the vicinity of the resonances, which appear as the "steps" in the momentum-transfer cross section. When σ_D^R is calculated, taking only one pole contribution in (4.1) for one resonance in Fig. 2, the lines σ_D and $\sigma_D^B+\sigma_D^R$ cannot be distinguished.

We also notice a large difference in the relative contribution of the resonance cross section in σ_D and σ. This difference is due to the fact that the main contribution in the total cross section comes from the diffraction scattering, which in the case of σ_D is very small. Therefore, the low-energy resonances, which appear relatively prominent in σ_D, are hardly visible in σ and hence they are not shown. Only the resonances for $E>0.2$ eV are more prominent in σ and, therefore, they are shown encircled.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation Grant No. NSF-F6F006-Y.

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