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Multiple impacts and energy transfer in a three-body system for noncollinear collisions

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Summary. Within the impulsive framework, the energy transfer processes in collisions of atoms with diatomic molecules are considered. In the case of noncollinear collisions involving multiple impacts between the particles, analytic expressions for the amount of the collision energy transferred to the internal degrees of freedom of the molecule have been derived. The limiting cases of these expressions are the well-known Mahan (a single impact) and Mahan–Shin (collinear collisions) formulas. The efficiency of energy transfer in collisions of cesium halide molecules with xenon atoms has been computed as an example; the results obtained agree well with the data of accurate trajectory calculations.

Key words: Energy transfer – Atom–diatom collisions – Impulsive model – Multiple impacts – Noncollinear configurations

1 Introduction

Conversion of the translational energy of atomic and molecular collisions into the internal energy of the partners plays a major role in the reagent activation mechanisms in bimolecular processes [1]. The T–V, R exchange is of great importance also in relaxation phenomena. The role of energy transfer has been thoroughly described for collision-induced dissociation of molecules into atoms and ions [2–5]. As has been shown by several authors [3–9], the efficiency of fragmentation of alkali halide molecules via collisions with chemically inert particles strongly depends upon the collision partner orientation, the masses of atoms involved, and the attack location, which is due to the fact that the process endothermicity to be compensated requires a high degree of conversion of the collision energy into the internal energy of the molecule.

By now, side by side with the experimental technique [10–14], diverse theoretical methods [15–20] have been developed which allow one to calculate, more or less accurately, the vibrational and rotational excitation of a diatomic molecule colliding with an atom for various collision configurations and energies, or to determine the effect of the excitation of a given degree of freedom of the molecule on the reaction cross section (an ample bibliography on the T–V, R, E exchange is compiled in Ref. [1]). Nevertheless, a rigorous quantum mechanical solution of the problem is still almost inaccessible. Quasiclassical trajectory simulation requires a detailed information on the potential energy surface and is also not always applicable. A description of energy transfer processes which qualitatively (and sometimes even quantitatively) agrees with the experimental data can often be presented by the *impulsive model* [5, 21–24] that treats particles as hard balls exchanging energies and momenta according to the elastic impact laws. The impulsive approximation is especially useful if one studies reactions involving atoms heavy enough to neglect a lot of quantal effects.

Within the impulsive approximation framework, the amount of energy transferred to the internal degrees of freedom of a diatomic molecule in its collision with an atom can be sometimes computed analytically. By now, in the case where the initial internal energy of the molecule is zero, two expressions for the amount of energy transfer have been known, namely, the Mahan formula [25, 26] and the Mahan–Shin formula [27, 28].

Let an atom A collide with the atom (or ion) B of a diatomic molecule BC which was at rest (i.e., with zero internal energy) before the encounter. We shall treat the particles A, B, C as elastic balls. At the moment of impact, the ball B is tangent to the balls A and C (Fig. 1a). Denote by Φ the angle between the AB and BC axes and by ψ the angle between the AB axis and the incident direction of A in the BC center-of-mass frame (Fig. 1a). The hypothesis that at the moment of impact the balls B and C touch is inessential for the collinear motion ($\Phi = \psi = 0$) but is rather restrictive in analyzing noncollinear collisions. Also let m_1, m_2, and m_3 be the masses of the particles A, B, and C respectively, E_{col} the collision energy and E_{BC} the final relative kinetic energy of the balls B and C. If the second A–B strike does not occur (i.e., the collision consists of a single hit A–B or two sequential hits A–B and B–C only), simple calculations based on mechanics of encounters of elastic balls give the Mahan formula [3, 4, 23, 25, 26]:

$$\delta = \frac{E_{\mathrm{BC}}}{E_{\mathrm{col}}} = K\cos^2\psi, \quad K = \frac{4m_1m_2m_3(m_1+m_2+m_3)}{(m_1+m_2)^2(m_2+m_3)^2} = \sin^2(2\beta), \tag{1}$$

where β is the Eyring–Polanyi skewing angle [29] which characterizes the strength of coupling between translational and vibrational motions:

$$0 < \beta < \pi/2, \quad \cos^2\beta = \frac{m_1m_3}{(m_1+m_2)(m_2+m_3)}. \tag{2}$$

The smaller is m_2 compared with m_1 and m_3, the smaller is the angle β. Equation (1) implies that in the absence of the second A–B strike the quantity E_{BC} is independent of the angle Φ, i.e., of the orientation of the molecule BC at the instant of impact.

The Mahan formula (1) is widely exploited in investigations of dynamics of inelastic scattering as well as chemical reactions [3, 4, 20, 22, 23, 30]. However, when m_2 is smaller than m_1 and m_3 (to be more precise, when $m_2(m_1+m_2+m_3) < 3m_1m_3$, i.e., $\beta < \pi/3$ [31, 32]), *multiple* (or *repeated*) encounters in the A + BC system become possible in which A strikes B, then B strikes C, then B strikes A again, and so on. For small m_2, such multiple impacts considerably change the process dynamics [28, 31]. On the other hand, the inequality $\beta < \pi/3 = 1.047$ ensuring the possibility of repeated encounters holds for many systems A + BC; e.g., in the case of cesium salt dissociation, for the collisions of the Xe atom with the halogen ion X^- of the salt molecule CsX, the angle β is 0.5069, 0.6626, 0.8981, 1.036 for X = F, Cl, Br, I respectively. In the presence of multiple impacts, Eq. (1) is not valid.

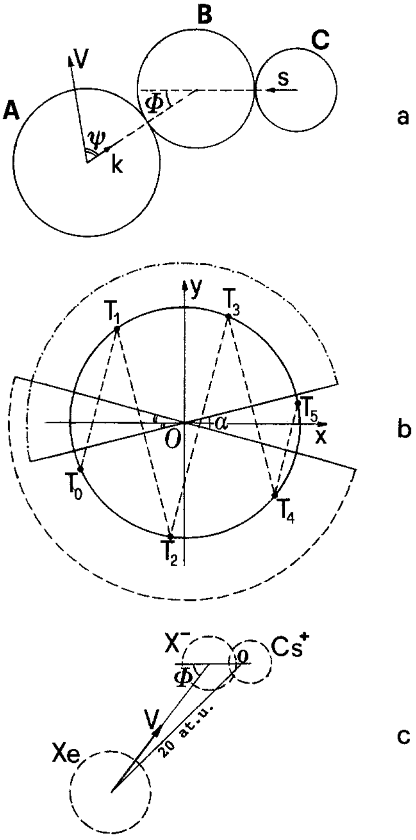

Fig. 1. (**a**) Particles at the moment of impact. (**b**) The collision kinematics in terms of the natural coordinates (x, y). The *dashed* and *dashed-dotted hemicircles* mark the halfplanes (10) and (11), respectively. (**c**) The initial conditions for the trajectory calculations. The center-of-mass of the salt molecule is marked as O

Via the so-called method of images introduced by Jepsen and Hirschfelder in Ref. [33], or the kaleidoscope method, Shin [28] derived an expression for the amount of energy transfer for any number of A–B impacts in *collinear* collisions A + BC ($\Phi = \psi = 0$):

$$\delta = \frac{E_{\mathrm{BC}}}{E_{\mathrm{col}}} = \sin^2(2n\beta). \tag{3}$$

Here n is the number of A–B encounters which is equal to

$$n = \Xi\left(\frac{\pi - \beta}{2\beta}\right)$$

(see Ref. [28]), where $\Xi(t)$ denotes the smallest integer subject to the inequality $\Xi(t) \geqslant t$ (e.g., $\Xi(4.2) = \Xi(4.7) = \Xi(5) = 5$). Equation (3) was first pointed out by Mahan [27], however, Ref. [27] contained neither proof nor indication what the number n is equal to. As in the Mahan formula (1), one assumes in the Mahan–Shin formula (3) that the BC molecule had zero internal energy before the collision. Analytic expressions for the amount of energy transfer in the case of nonzero initial vibrational excitation of the molecule BC are also obtained in Ref. [28]. Of other papers containing formulas for the amount of energy transfer in impulsive collisions of an atom A with an excited molecule BC, we mention here Refs. [5, 23, 31, 32, 34]. In papers [25, 35], impulsive energy exchange is specifically treated as the *limiting case* of energy transfer processes when the collision duration becomes negligible compared with the vibrational period of the diatomic molecule.

Equation (3) confirms the well known thesis that the dynamics of collinear collisions is controlled to a great extent by the Eyring–Polanyi angle (2) [36, 37]. As we will see in the sequel, for noncollinear collisions (in the configuration shown in Fig. 1a) the role of the angle β is played by the angle α defined as:

$$\beta \leqslant \alpha \leqslant \pi - \beta, \quad \cos\alpha = \cos\beta \cos\Phi \tag{4}$$

($\alpha = \beta$ for $\Phi = 0$ and $\alpha = \pi/2$ for $\Phi = \pi/2$).

Equations (1) and (3) refer to two diametrically opposite extreme situations: A + BC collisions with *an arbitrary configuration* which involve *a single encounter* A–B, and *collinear* collisions A + BC with *an arbitrary number* of A–B *hits*. On the other hand, it is in the case of multiple impacts where it is of great importance to take into account the whole variety of collision configurations, not only collinear collisions, since for repeated impacts the energy E_{BC} exhibits a strong dependence on the angle Φ. Besides, for many processes (in particular, for collision-induced dissociation $A + MX \rightarrow A + M^+ + X^-$ where A, M, and X denote a rare gas or mercury atom, an alkali metal atom, and a halogen atom respectively) the sideways collisions turn out to be the most effective [4–9].

In the present paper, we obtain an analytic expression for the amount of energy transfer in the impulsive limit for arbitrary masses m_1, m_2, m_3 (and, hence, for an arbitrary number of impacts during a single collision) and an arbitrary value of the angle Φ (i.e., an arbitrary collision configuration). The derivation of this expression is briefly presented in Sect. 2, while some calculation details are given in Appendix A. Our expression should be considered as a generalization of the Mahan formula (1) to the case of multiple encounters and at the same time as a generalization of the Mahan–Shin formula (3) to the case of noncollinear collisions. In Sect. 3, we compare, for various angles Φ, the efficiency of translational-internal energy exchange predicted by the impulsive model with the results of accurate trajectory calculations for four systems Xe + XCs with X = F, Cl, Br, I.

These systems were chosen for comparison of impulsive and trajectory results due to the following reasons. Firstly, the impulsive approximation predicts the values of the differential and total cross sections for dissociation and molecular-ion formation in Xe + XCs collisions which are in a qualitative agreement with the experimental data [5, 21–23]. Secondly, there is a direct evidence for the impulsive nature of the Xe + XCs interactions. Namely, the duration of the Xe + BrCs collision calculated in Ref. [38] turned out to be much shorter than the characteristic rotation periods of CsBr. Thirdly, the Xe + BrCs collision configuration most favourable for dissociation is a hit of the xenon atom on the bromine anion with the incident Xe velocity orthogonal to the salt molecule axis [4–7, 9] which indicates importance of the orientation effects in the systems under consideration.

Finally, in Appendix B we present a formula for the scattering angle of the projectile A within the impulsive framework.

2 Energy transfer in the impulsive approximation

In this section, we obtain a general formula for the amount of energy transfer in the impulsive limit (some technical details are presented in Appendix A). Since the kaleidoscope method exploited in Refs. [28, 31] to analyze multiple impacts in a collinear system of three elastic balls with a piecewise constant interaction potential seems to be of low efficiency when applied to noncollinear configurations, we propose another construction where to each encounter, there will correspond the reflection with respect to a certain straight line in a special coordinate frame on the plane.

Consider a system of three perfectly elastic balls A, B, C with masses m_1, m_2, m_3 in which the ball B is tangent to the balls A and C, the angle between the AB and BC axes being Φ (Fig. 1a). In such a system, a sequence of impacts A–B, B–C, A–B, . . . taking an infinitesimal time interval can occur (one may imagine a system of three balls A, B, C where the distance between A and B and that between B and C are very small and equal to ε, and then examine the limiting behaviour of this system as $\varepsilon \to 0$). The angle Φ is left fixed during the whole series of encounters whereas the velocities $\mathbf{V}_1, \mathbf{V}_2, \mathbf{V}_3$ of the balls vary. We shall study the general case where $\mathbf{V}_1$, $\mathbf{V}_2$, and $\mathbf{V}_3$ are arbitrary before the collision (and not necessarily $\mathbf{V}_2 = \mathbf{V}_3 = 0$).

Denote by $\mathbf{k}$ and $\mathbf{s}$ the unit vectors along the axes AB and BC respectively directed at B (see Fig. 1a) and set:

$$\mathbf{W} = m_1(\mathbf{V}_1, \mathbf{k})\mathbf{k} + m_2\mathbf{V}_2 + m_3(\mathbf{V}_3, \mathbf{s})\mathbf{s}$$

where (,) is the standard inner product. It is not hard to verify that each impact leaves the vector $\mathbf{W}$ invariant and that the equation:

$$m_1(\mathbf{a}, \mathbf{k})\mathbf{k} + m_2\mathbf{a} + m_3(\mathbf{a}, \mathbf{s})\mathbf{s} = \mathbf{W}$$

with respect to $\mathbf{a}$ has a unique solution:

$$\mathbf{a} = \frac{1}{m_2}\left(\mathbf{W} - \frac{m_1\xi\mathbf{k} + m_3\eta\mathbf{s}}{(m_1 + m_2)(m_2 + m_3)\sin^2\alpha}\right),$$

where

$$\xi = (m_2 + m_3)(\mathbf{W}, \mathbf{k}) + m_3(\mathbf{W}, \mathbf{s})\cos\Phi,$$

$$\eta = (m_1 + m_2)(\mathbf{W}, \mathbf{s}) + m_1(\mathbf{W}, \mathbf{k})\cos\Phi,$$

and α is defined by Eq. (4). In the new coordinate frame moving with the velocity $\mathbf{a}$ with respect to the initial frame, the velocities $\mathbf{V}_1 - \mathbf{a}$, $\mathbf{V}_2 - \mathbf{a}$, $\mathbf{V}_3 - \mathbf{a}$ of the balls A, B, C become:

$$u\mathbf{k} + \mathbf{u}_1, \quad -(m_1u\mathbf{k} + m_3v\mathbf{s})/m_2, \quad v\mathbf{s} + \mathbf{v}_1 \tag{5}$$

respectively, with $\mathbf{u}_1$ orthogonal to the AB axis and $\mathbf{v}_1$ orthogonal to the BC axis. The vectors $\mathbf{u}_1$ and $\mathbf{v}_1$ are left fixed during the collision. The kinematic relations for encounters of elastic balls [5, 23] imply that the impacts A–B and B–C act on the (u, v)-plane as linear operators:

$$u' = -u + \frac{2m_3v}{m_1 + m_2}\cos\Phi, \quad v' = v$$

and

$$u' = u, \quad v' = -v + \frac{2m_1u}{m_2 + m_3}\cos\Phi$$

respectively (u, v being the values of the coordinates defined by Eq. (5) before an encounter and u', v', after the encounter). Introduce new coordinates:

$$x = -\frac{1}{m_2^{1/2}}[u(m_1(m_1+m_2))^{1/2} + v(m_3(m_2+m_3))^{1/2}]\sin\frac{\alpha}{2},$$

$$y = -\frac{1}{m_2^{1/2}}[u(m_1(m_1+m_2))^{1/2} - v(m_3(m_2+m_3))^{1/2}]\cos\frac{\alpha}{2}. \tag{6}$$

The inverse transformation is:

$$u = -\left(\frac{m_2}{m_1(m_1+m_2)}\right)^{1/2}\frac{1}{\sin\alpha}\left(x\cos\frac{\alpha}{2} + y\sin\frac{\alpha}{2}\right),$$

$$v = -\left(\frac{m_2}{m_3(m_2+m_3)}\right)^{1/2}\frac{1}{\sin\alpha}\left(x\cos\frac{\alpha}{2} - y\sin\frac{\alpha}{2}\right). \tag{7}$$

In terms of the coordinates (x, y) the operators of impacts A–B and B–C take the form:

$$x' = x\cos\alpha - y\sin\alpha, \quad y' = -x\sin\alpha - y\cos\alpha$$

and

$$x' = x\cos\alpha + y\sin\alpha, \quad y' = x\sin\alpha - y\cos\alpha$$

respectively, i.e., they become reflections with respect to the straight lines:

$$y = -x\tan\frac{\alpha}{2} \tag{8}$$

and

$$y = x\tan\frac{\alpha}{2} \tag{9}$$

respectively (Fig. 1b). The angle between these straight lines is equal to α. An A–B encounter is possible only if $(\mathbf{V}_1 - \mathbf{V}_2, \mathbf{k}) > 0$ just before it, which, as one can verify, is equivalent to:

$$y < -x\tan\frac{\alpha}{2}, \tag{10}$$

while a B–C encounter is possible only if $(\mathbf{V}_3 - \mathbf{V}_2, \mathbf{s}) > 0$ just before it, which is equivalent to:

$$y > x\tan\frac{\alpha}{2}. \tag{11}$$

The collision kinematics on the (x, y)-plane looks as follows. The point $T_0(x_0, y_0)$ corresponding to the initial state of the system (before the first impact A–B) lies in the halfplane (10). The initial values x_0 and y_0 of the coordinates x and y can be easily computed by the initial values of $\mathbf{V}_1$, $\mathbf{V}_2$, $\mathbf{V}_3$. In the most important particular case where an atom A collides with a "cold" molecule BC (i.e., initially

$\mathbf{V}_2 = \mathbf{V}_3 = 0$) and the angle between the incident vector $\mathbf{V}_1 = \mathbf{V}$ and the axis AB is ψ (Fig. 1a):

$$x_0 = -\left(\frac{m_1 m_2}{m_1 + m_2}\right)^{1/2} \frac{V\cos\psi}{\sin\alpha}\cos\frac{\alpha}{2},$$

$$y_0 = -\left(\frac{m_1 m_2}{m_1 + m_2}\right)^{1/2} \frac{V\cos\psi}{\sin\alpha}\sin\frac{\alpha}{2}$$

(note that in this case T_0 lies on the straight line (9)). The subsequent states of the ball system (after the A–B encounter, the B–C encounter, the second A–B encounter, . . .) are described by points $T_1, T_2, T_3, \ldots$ where each T_i ($i \geqslant 1$) is the image of T_{i-1} under the reflection with respect to the straight line (8) for i odd or line (9) for i even (Fig. 1b). All the points T_i are at the same distance R from the origin 0. If the initial point T_0 has the coordinates:

$$T_0 = (R\cos\varphi,\ -R\sin\varphi)$$

with $\alpha/2 < \varphi < \pi + \alpha/2$ then the coordinates of the point T_i ($i \geqslant 0$) are:

$$T_i = (R\cos(\varphi - i\alpha), (-1)^{i+1} R\sin(\varphi - i\alpha)).$$

The impacts halt (i.e., the balls start flying apart) as soon as a point $T_i = T_{M_*}$ finds itself outside the halfplane (10) for i even or outside the halfplane (11) for i odd (see Fig. 1b), whence it is not hard to obtain that the total number M_* of encounters is:

$$M_* = M_*(\varphi) = \Xi\left(\frac{2\varphi - \alpha}{2\alpha}\right), \tag{12}$$

where $\Xi(t)$ denotes the smallest integer subject to the inequality $\Xi(t) \geqslant t$. The number of A–B encounters is therefore:

$$M = M(\varphi) = \Xi\left(\frac{M_*}{2}\right) = \Xi\left(\frac{2\varphi - \alpha}{4\alpha}\right). \tag{13}$$

For the collision of an atom A with a "cold" molecule BC one has $\varphi = \pi - \alpha/2$ whence in this case the total number of impacts is:

$$n_* = M_*\left(\pi - \frac{\alpha}{2}\right) = \Xi\left(\frac{\pi}{\alpha}\right) - 1 \tag{14}$$

and the number of A–B impacts is:

$$n = M\left(\pi - \frac{\alpha}{2}\right) = \Xi\left(\frac{\pi - \alpha}{2\alpha}\right). \tag{15}$$

The maximum total number of impacts which can occur in our system (for arbitrary initial velocities $\mathbf{V}_1, \mathbf{V}_2, \mathbf{V}_3$) is:

$$N_* = M_*\left(\pi + \frac{\alpha}{2}\right) = \Xi\left(\frac{\pi}{\alpha}\right) = n_* + 1 \tag{16}$$

and the maximum number of A–B impacts is:

$$N = M\left(\pi + \frac{\alpha}{2}\right) = \Xi\left(\frac{\pi}{2\alpha}\right). \tag{17}$$

For $\Phi = 0$ Eq. (16) (with α replaced by β) was obtained in Refs. [39–41] (see also Refs. [42, 43]) and Eq. (17) in Ref. [28] (see also Ref. [32]) via the kaleidoscope method.

One can compute the final values of the coordinates (u, v) (after the last encounter) from the final values of the coordinates (x, y) by Eq. (7). Having found the vectors $\mathbf{u}_1$, $\mathbf{v}_1$ (5) and the final values of the coordinates (u, v), one then easily obtains the final relative kinetic energy E_{BC} of the balls B and C. Postponing the calculation details to Appendix A, we shall give the result for the collision of an atom A with a "cold" molecule BC. In this case the ratio of the energy E_{BC} transferred to the molecule BC to the collision energy E_{col} is:

$$\begin{aligned}\delta = \frac{E_{\mathrm{BC}}}{E_{\mathrm{col}}} &= K\frac{\sin^2(n\alpha)}{\sin^4\alpha}\left\{\sin^2(n\alpha) - \frac{1}{\cos^2\beta}\sin[(n+1)\alpha]\sin[(n-1)\alpha]\right\}\cos^2\psi \\ &= \frac{\sin^2\beta}{\sin^2\alpha}\left[\sin^2(2n\alpha) + \frac{4\sin^4(n\alpha)}{\sin^2\alpha}\sin(\alpha+\beta)\sin(\alpha-\beta)\right]\cos^2\psi. \end{aligned} \tag{18}$$

Having in view various possible applications, we have presented two equivalent expressions for δ. Equation (18) was first derived in preprint [44] and announced in Ref. [45]. Recall that β is defined by Eq. (2), K by (1), α by (4) and n by Eq. (15). For $\Phi = 0$ (a collinear configuration) we obtain the Mahan–Shin formula with additional factor $\cos^2\psi$:

$$\delta = \frac{E_{\mathrm{BC}}}{E_{\mathrm{col}}} = \sin^2(2n\beta)\cos^2\psi$$

(cf. Eq. (3)). For $n = 1$, Eq. (18) reduces to $\delta = K\cos^2\psi$ (the Mahan formula (1)), and for $n = 2$, it takes the form:

$$\delta = 4K\cos^2\Phi(1 - K\cos^2\Phi)\cos^2\psi. \tag{19}$$

Note that δ is independent of E_{col}.

If, for instance, $\pi/3 \leqslant \beta < \pi/2$ then $n = 1$ for all Φ [31, 32], and $\delta = K\cos^2\psi$. In other words, for $\beta \geqslant \pi/3$ more than a single A–B impact cannot occur for any collision configuration, and the Mahan formula (1) always holds. If $\pi/5 \leqslant \beta < \pi/3$ then $n = 1$ (a single A–B hit) for $\Phi \geqslant \Phi_0$ (and then $\delta = K\cos^2\psi$) and $n = 2$ (two A–B hits) for $\Phi < \Phi_0$ (and then δ is to be calculated by the formula (19)). Here Φ_0 is determined by the condition $\alpha = \pi/3$, i.e., $\cos\Phi_0 = (2\cos\beta)^{-1}$. If $\beta < \pi/5$ then $n \geqslant 3$ for small Φ (to be more precise, for $\cos\Phi > \cos(\pi/5)/\cos\beta$).

For the collision of an atom A with a "cold" molecule BC, it is also possible to calculate how the energy E_{BC} transferred to the molecule is distributed among vibrational and rotational degrees of freedom. To be more precise, set:

$$E_{\mathrm{BC}}^{\mathrm{vib}} = \frac{m_2 m_3}{2(m_2 + m_3)}(\mathbf{V}_{2f} - \mathbf{V}_{3f}, \mathbf{s})^2, \quad E_{\mathrm{BC}}^{\mathrm{rot}} = \frac{m_2 m_3}{2(m_2 + m_3)}[\mathbf{V}_{2f} - \mathbf{V}_{3f}, \mathbf{s}]^2,$$

where [,] is the standard vector product while $\mathbf{V}_{2f}$ and $\mathbf{V}_{3f}$ are the final velocities of the balls B and C. The quantities $E_{\mathrm{BC}}^{\mathrm{vib}}$ and $E_{\mathrm{BC}}^{\mathrm{rot}}$ model the amount of energy transferred to vibrations and rotations respectively of the molecule BC, and we show in Appendix A that:

$$\delta^{\mathrm{vib}} = \frac{E_{\mathrm{BC}}^{\mathrm{vib}}}{E_{\mathrm{col}}} = \sin^2\beta \frac{\sin^2(2n\alpha)}{\sin^2\alpha}\cos^2\psi,$$

$$\delta^{\mathrm{rot}} = \frac{E_{\mathrm{BC}}^{\mathrm{rot}}}{E_{\mathrm{col}}} = 4\sin^2\beta\frac{\sin^4(n\alpha)}{\sin^4\alpha}\sin(\alpha+\beta)\sin(\alpha-\beta)\cos^2\psi. \tag{20}$$

These formulas were announced in Ref. [46]. Of course, $\delta^{\mathrm{vib}} + \delta^{\mathrm{rot}} = \delta$. For $\Phi = 0$ (a collinear configuration) one has $\delta^{\mathrm{rot}} = 0$, whereas for $\Phi = \pi/2$ (an orthogonal configuration) $\delta^{\mathrm{vib}} = 0$.

We conclude this section with the following remarks. It is well known that when the number of impacts is very large (or, in the case of motions in a realistic potential, when the collision duration greatly exceeds the characteristic vibrational period), translational-internal energy exchange is, as a rule, inefficient [28, 31, 32, 34, 47, 48]. Equation (20) for the amount δ^{vib} of energy transfer to the *vibrational* degree of freedom confirms this thesis. Indeed, one obtains from Eq. (15) that:

$$\frac{\pi}{2n+1} \leqslant \alpha < \frac{\pi}{2n-1} \quad \text{and} \quad |2n\alpha - \pi| \leqslant \alpha < \frac{\pi}{2n-1},$$

n being the number of A–B encounters. Consequently, for $n \geqslant 2$:

$$\delta^{\mathrm{vib}} = \sin^2\beta\frac{\sin^2(2n\alpha)}{\sin^2\alpha}\cos^2\psi \leqslant \sin^2(2n\alpha)\cos^2\psi < \sin^2\left(\frac{\pi}{2n-1}\right)\cos^2\psi$$

(we have used the fact that $\beta \leqslant \alpha \leqslant \pi - \beta$ and therefore $\sin\alpha \geqslant \sin\beta$). Thus, as $n \to \infty$, the quantity δ^{vib} decreases with asymptotics n^{-2}.

In collinear collisions $\delta = \delta^{\mathrm{vib}}$, and δ approaches zero with asymptotics n^{-2}as $n \to \infty$. On the other hand, in *noncollinear* collisions the amount δ of energy transfer can be considerable (and, moreover, *arbitrarily close* to 1) for an *arbitrarily large* number of impacts, due to a special choice of β and Φ! For instance, let β be sufficiently small and $\alpha = \sqrt{c}\beta$ with c being an arbitrary constant greater than 1, i.e.:

$$\cos\Phi = \cos\Phi_{\mathrm{c}} = \frac{\cos(\sqrt{c}\,\beta)}{\cos\beta} \tag{21}$$

(as we will see in the sequel, it is indeed more convenient to write $\alpha = \sqrt{c}\,\beta$ instead of $\alpha = c\beta$). Then as $\beta \to 0$, the number n of A–B encounters tends to infinity, but, as is not hard to see from Eq. (18):

$$\delta = \frac{4(c-1)}{c^2}\left(1 + \frac{c-2}{3}\beta^2 + \frac{2-c}{c-1}\gamma^2\right)\cos^2\psi + O(\beta^4)$$

where $\gamma = (\pi/2) - n\alpha$ (note that $|\gamma| \leqslant \alpha/2 = \sqrt{c}\beta/2$ according to Eq. (15)). Thus, in this case δ is bounded from below by a positive constant (provided that ψ is fixed).

One should emphasize that this effect is entirely due to the energy transfer to *rotations*, since δ^{vib} in our example tends to zero as $\beta \to 0$:

$$\delta^{\mathrm{vib}} = \frac{4\gamma^2}{c}\cos^2\psi + O(\beta^4)$$

according to Eq. (20).

Table 1. The amount δ of energy transfer for $m_1 = m_{\mathrm{Xe}}$, $m_3 = m_{\mathrm{Cs}}$ and various m_2. The angle Φ_2 is defined by Eq. (21)

m_2	β in rad	n for $\Phi = 0$	δ for $\Phi = 0$	Φ_2 in deg	n for $\Phi = \Phi_2$	$1 - \delta$ for $\Phi = \Phi_2$
m_{F}	0.50690	3	1.00×10^{-2}	30.424	2	5.12×10^{-3}
m_{H}	0.12314	13	3.59×10^{-3}	7.0732	9	2.56×10^{-5}
m_{Mu}	0.041527	38	2.09×10^{-4}	2.3800	27	1.25×10^{-7}
m_{Ps}	0.0040757	385	1.08×10^{-5}	0.23323	273	4.39×10^{-12}

The maximum of the function $4(c-1)c^{-2}$ is attained at $c = 2$ and is equal to 1. If $c = 2$ then Eq. (18) implies that:

$$\delta = \left[1 - \left(\frac{\beta^2}{3} - \gamma^2\right)^2\right]\cos^2\psi + O(\beta^6).$$

We can conclude the following. Let the Eyring–Polanyi skewing angle β and the angle Φ determining the collision geometry vary in such a manner that Eq. (21) with $c = 2$ remains valid. Suppose that the collision is head-on ($\psi = 0$). Then as $\beta \to 0$, the number of A–B impacts during a single collision tends to infinity whereas the amount of energy transfer to rotations tends to unity.

This conclusion is illustrated by Table 1 which presents some features of head-on collisions A + BC for fixed masses $m_1 = m_{\mathrm{Xe}}$, $m_3 = m_{\mathrm{Cs}}$ and a varying mass m_2 of the "middle" particle B. The computations have been performed for four m_2 values equal to m_{F}, m_{H}, m_{Mu} and m_{Ps} (Mu $= \mu^+e^-$ being muonium and Ps $= e^+e^-$, positronium). Of course, one should not expect that the impulsive model can describe adequately the behaviour of real systems involving muonium or positronium, but we are interested here in a theoretical possibility of impulsive interactions with a large number of impacts and the amount of energy transfer close to 1. For each of four masses m_2, the value of β as well as the number n of A–B encounters and the amount δ of energy transfer are pointed out for two angles Φ, namely, angle $\Phi = 0$ and angle $\Phi_2 = \Phi_2(\beta)$ defined by Eq. (21) in which the value of c is set to be 2. One sees in Table 1 that n increases as $\beta \to 0$ for both angles. Nevertheless, for $\Phi = 0$ the efficiency of energy transfer decreases rapidly, whereas for $\Phi = \Phi_2$ the amount of energy transfer tends to unity *even more rapidly* (although the angle $\Phi_2(\beta)$ itself vanishes as $\beta \to 0$).

Note finally that from the viewpoint of the general theory of collisions of elastic balls moving in space [40–42, 49], our model describes a degenerate situation where at some moment one of the balls is tangent to two other balls simultaneously. In generic systems of balls, there occur only double collisions.

3 Comparison with quasiclassical trajectory model

It is useful to compare the efficiency of energy transfer predicted by the impulsive model with the results of accurate trajectory calculations. We have fulfilled in-plane trajectory simulation of inelastic scattering:

$$\mathrm{Xe} + \mathrm{XCs} \to \mathrm{Xe} + \mathrm{XCs}^*$$

of Xe atoms by CsX molecules, where X = F, Cl, Br, I. Since our purpose is to determine the amount of energy transfer as a function of the angle Φ between the AB and BC axes (A = Xe, B = X^-, C = Cs^+, see Figs. 1a, c) in head-on collisions with the fixed collision energy, two-dimensional calculations are sufficient.

For the systems Xe + CsX, we used the potential energy surface of the following form (similar to that exploited in Refs. [3–9, 21, 38, 44, 50, 51]):

$$\begin{aligned} U(R_1,R_2,R_3) = {} & A_2\exp(-R_2/\rho_2) - \frac{1}{R_2} - \frac{\alpha_+ + \alpha_-}{2R_2^4} - \frac{C_2}{R_2^6} \\ & + A_1\exp(-R_1/\rho_1) + A_3\exp(-R_3/\rho_3) - \frac{C_1}{R_1^6} - \frac{C_3}{R_3^6} \\ & - \frac{\alpha_0}{2}\left(\frac{1}{R_1^4} + \frac{1}{R_3^4} + \frac{R_2^2 - R_1^2 - R_3^2}{R_1^3R_3^3}\right)\left(1 - \frac{\alpha_+ + \alpha_-}{R_2^3}\right)^2 \end{aligned}$$

(we have presented the formula for U in atomic units). Here R_1, R_2, R_3 are the internuclear distances Xe–Cs^+, Cs^+–X^-, Xe–X^- respectively while α_0, α_+, α_- denote the polarizabilities of a xenon atom, cesium cation and halogen anion respectively. This surface includes a T-Rittner potential for the salt molecule [52] plus similar potentials, but without the Coulomb term $-1/R$, for interactions Xe–Cs^+ and Xe–X^- plus a summand responsible for the polarization interaction of the Xe atom in the presence of the Cs^+–X^- dipolar field. The parameters A_j and ρ_j of the Born–Mayer walls $A_j\exp(-R_j/\rho_j)$ and the dispersion constants C_j in the pair potentials were determined via fitting the corresponding analytic curves to the interaction potentials extracted from the experimental data. The details of the calculation are to be found in Ref. [50] (see also Ref. [21]), while the resulting values of the parameters are presented in Ref. [44].

In our studies, both ions of the salt molecule CsX were assumed to be at rest and at the equilibrium distance before the collision, whereas the initial position and velocity of the projectile atom Xe were chosen as shown in Fig. 1c. The calculations were performed for $0 \leqslant \Phi \leqslant 90^\circ$ and $1\ \mathrm{eV} \leqslant E_{\mathrm{col}} \leqslant E_{\mathrm{max}}$ where E_{col} denotes the collision energy and E_{max} was equal to 5 eV for X = F and 4 eV for X = Cl, Br, I. For collision energies $E_{\mathrm{col}} = E_{\mathrm{max}} + 1$ eV, we observed dissociation of the salt molecule and formation of complexes $XeCs^+$ for some values of the angle Φ (for the Xe + ICs system, dissociation without complex formation only).

The results obtained are shown in Figs. 2–5. The plots of δ as a function of the angle Φ with the collision energy E_{col} fixed are presented in Figs. 2a–5a, δ being the ratio of the energy transferred to the salt molecule in the collision to the collision energy. In Figs. 2b–5b, δ is plotted vs the collision energy E_{col} with the angle Φ fixed. The values of E_{col} (in eV) in Figs. 2a–5a and those of Φ (in deg) in Figs. 2b–5b are given by numbers near the corresponding curves. The boldfaced lines indicate the relative energy transfer δ in the impulsive limit calculated by Eq. (18).

Note that similar trajectory studies were carried out in Ref. [4] but Parks et al. [4] fixed the collision energy and the impact parameter with respect to the center-of-mass of the salt molecule, whereas in the present paper we set the initial velocity of the projectile atom Xe to be directed precisely at the halogen ion (Fig. 1c), i.e., the impact parameter with respect to the center-of-mass of the CsX molecule depended on the angle Φ and was equal to $r\sin\Phi$ where r is the distance between the nucleus of the X^- ion and the CsX center-of-mass.

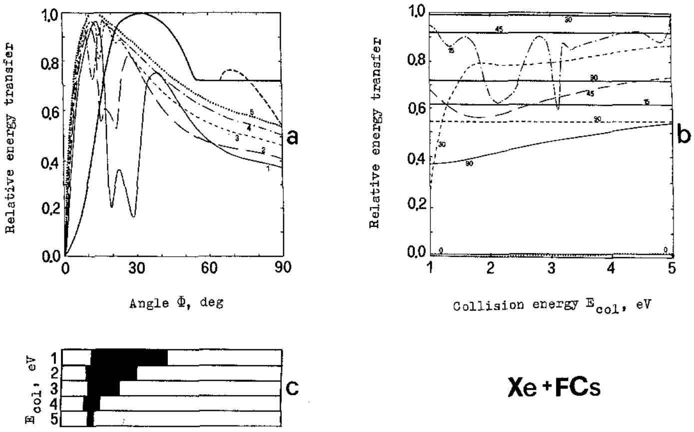

Fig. 2. Energy transfer δ in inelastic scattering of Xe by CsF. *Non-boldfaced lines* indicate trajectory results. In panel (**a**), the value of the collision energy E_{col} is fixed and shown (in eV) near the corresponding curve $\delta(\Phi)$. The *boldfaced line* presents the impulsive energy transfer. In panel (**b**), the value of the configuration angle Φ is fixed and shown (in deg) near the corresponding *non-boldfaced line* $\delta(E_{col})$ and *boldfaced* one (the latter pertains to the impulsive approximation). The *boldfaced dashed lines* in both panels refer to the refined impulsive model (discussed at the end of Sect. 3) that takes into account the motion of the particles after the main collision. Panel (**c**) points out, for various values of E_{col}, the ranges of Φ where the inequality (22) is satisfied

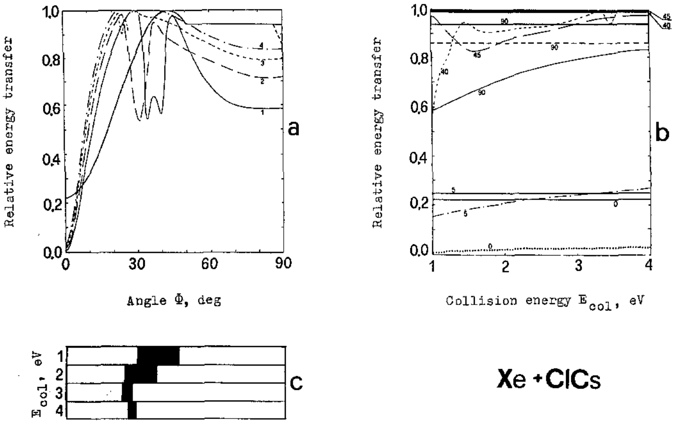

Fig. 3. Same as Fig. 2 but for inelastic scattering of Xe by CsCl

Note also that the ample experimental data available for the Xe + XCs collisions [3–7, 9, 22, 38] pertain mainly to dissociation of the salt molecule (with possible formation of molecular ions) rather than to inelastic scattering, and are not selected in the location and angle of attack. So, the comparison of these data with the impulsive predictions for the amount of energy transfer is hardly possible.

Within the impulsive framework, in all the four systems in question *multiple impacts* take place for sufficiently small angles Φ. E.g., for $\Phi = 0$ (collinear collisions)

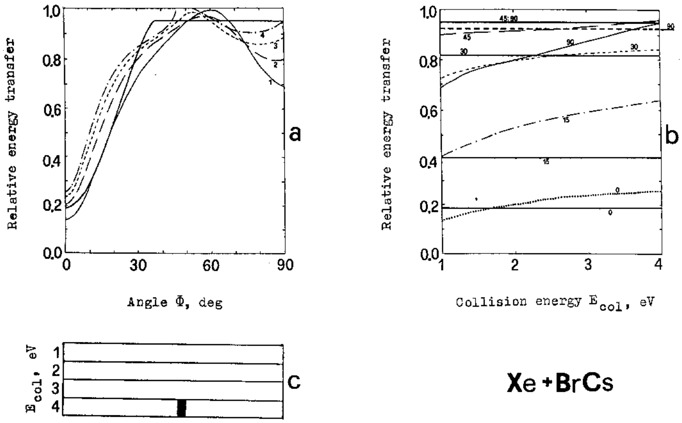

Fig. 4. Same as Fig. 2 but for inelastic scattering of Xe by CsBr

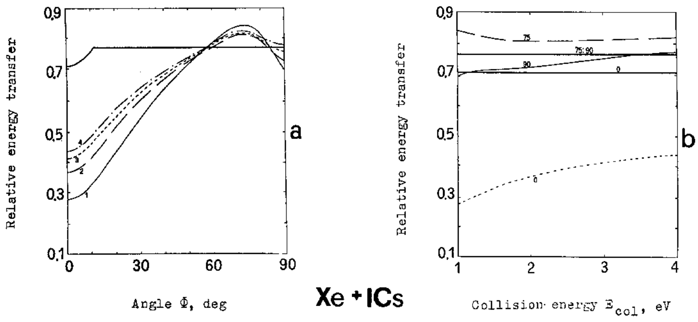

Fig. 5. Same as Fig. 2 but for inelastic scattering of Xe by CsI. The inequality (22) fails for any Φ and E_{col}

in the systems Xe + XCs with X = I, Br there occur 3 encounters (two Xe–X^- hits and a single X^-–Cs^+ hit), in the system Xe + ClCs, 4 encounters (two Xe–Cl^- hits and two Cl^-–Cs^+ hits), and in the system Xe + FCs, 6 encounters (three Xe–F^- hits and three F^-–Cs^+ hits).

For the Xe + FCs and Xe + ClCs systems (Figs. 2a and 3a respectively) the most obvious feature of the dependencies of δ on the angle Φ with the collision energy E_{col} fixed is the existence of a range of the Φ values over which the amount of energy transfer is very low compared with both the calculation results outside this range and the impulsive predictions. Moreover, for fixed angles Φ in that range, δ turns out to be extremely sensitive to E_{col} (Figs. 2b and 3b). This behaviour of the amount of energy transfer as a function of Φ and E_{col} is a consequence of *repeated approaches* of the Xe atom to the X^- ion during the collision. At the beginning of a trajectory, the xenon atom quickly closes in on the halogen anion (at a short distance R_0) which causes excitation of the salt molecule. In the further motion, the Xe atom may draw near to the same X^- ion some more times (at distances R_1, R_2, . . . , R_l), and if R_1, R_2, . . . , R_l are sufficiently small then rotational excitation (and in some cases vibrational excitation) of the salt molecule can reduce considerably which leads to a diminished net δ value (cf. Ref. [4]). This effect seems to defy interpretation within the framework of an impulsive model. In Figs. 2c–4c for various E_{col}, the ranges of the angle Φ values are shown over which:

$$\min(R_1, R_2, \cdots, R_l) < 8 \text{ at.u.} \tag{22}$$

One sees that these ranges coincide precisely with those ranges of the Φ values where the ratio δ is abnormally small. For the Xe + ICs system, the inequality (22) is not satisfied for any Φ and E_{col}.

The breaks in the curves $\delta = \delta(\Phi)$ for the Xe + FCs system at $E_{col} = 5$ eV (Fig. 2a), for the Xe + ClCs system at $E_{col} = 3$ eV, 4 eV (Fig. 3a), and for the Xe + BrCs system at $E_{col} = 4$ eV (Fig. 4a), as well as that in the curve $\delta = \delta(E_{col})$ for the Xe + ClCs system at $\Phi = 40°$ (Fig. 3b) indicate the trajectories leading to formation of a quasistable three-particle $\mathrm{XeCs^+X^-}$ complex which lives more than 5×10^{-12} s (but finally breaks up, and the $\mathrm{Cs^+}$ ion returns to the $\mathrm{X^-}$ ion). The break in the curve $\delta = \delta(\Phi)$ for the Xe + ClCs system at $E_{col} = 1$ eV (Fig. 3a) is due to prolonged rotation of the Xe atom around the CsCl molecule. In both cases the amount of energy transfer as a function of Φ or E_{col} exhibits very frequent oscillations which cannot be shown in the scale of our figures.

If we now would forget these peculiarities of the curves $\delta = \delta(\Phi)$ for the Xe + FCs and Xe + ClCs systems, we would conclude from Figs. 2a–5a that the most characteristic feature of the dependency of δ on the angle Φ for all the four systems is its "*bell-like*" shape (cf. Ref. [4]): as Φ increases from 0 to 90°, the amount of energy transfer steeply grows at first, and then begins decreasing. This behaviour of the function $\delta(\Phi)$ may be explained by the following two reasons.

1) For Φ not very large, for all the four systems in the impulsive limit, multiple impacts of the $\mathrm{X^-}$ ion with the Xe atom and the $\mathrm{Cs^+}$ ion occur which leads to strong lowering in the efficiency of energy transfer.

2) If Φ is very close neither to 0 nor to 90°, the incoming projectile Xe atom after its encounter with the $\mathrm{X^-}$ ion can push appreciably the $\mathrm{Cs^+}$ ion and therefore augment vibrational excitation of the salt molecule and increase the final δ value.

The first effect is of completely impulsive nature. We have tried to perform an impulsive simulation for the second effect. Namely, for the model considered in Sect. 2, we have examined whether an impact of the balls A and C can occur after the series of encounters of the ball B with the balls A and C is over and the configuration has disintegrated. This investigation requires specification of the radii of the balls, and we set the radii of the Xe atom and the $\mathrm{Cs^+}$, $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$ ions to be 2.09 Å and 1.67 Å, 1.33 Å, 1.81 Å, 1.96 Å, 2.19 Å, respectively [4, 53]. The calculations have confirmed that in the Xe + FCs, Xe + ClCs, and Xe + BrCs systems an additional A–C (i.e., Xe–$\mathrm{Cs^+}$) impact indeed occurs, but for the angles Φ close to 90°, which leads, as a rule, to *reduction* in the amount of energy transfer due to partial rotational relaxation of the CsX molecule (the calculation results are shown in Figs. 2–4 by boldfaced dashed lines). It seems that the second effect cannot be described by an impulsive model.

Comparing the impulsive and trajectory data, one concludes that over a wide range of the Φ and E_{col} values, there is a certain agreement between predictions of the impulsive model and results of the accurate trajectory calculations which *for multiple encounters is not poorer than for a single impact.* This is perhaps partially due to a simple topography of the potential energy surface of the systems in question [5]. For Xe + BrCs collisions, the agreement between the dependency $\delta = \delta(\Phi)$ obtained in the impulsive approximation and the functions calculated from trajectories is excellent (Fig. 4a).

As was mentioned above, the number of approaches of the projectile Xe atom to the halogen X^- ion in our trajectory simulation (i.e., the number of minima of the function $R(t)$ where R denotes the distance between Xe and X^- while t is the time) bears no relation, generally speaking, to the number of Xe–X^- impacts in the impulsive approximation. We saw that the number of minima of $R(t)$ may exceed the number of impulsive encounters (which is sometimes accompanied by a slump in the efficiency of energy transfer in the trajectory studies). The opposite situation is also possible. For small values of the angle Φ, in all the systems except Xe + ClCs a single approach of Xe to X^- occurs in the trajectory calculations (cf. Ref. [4]). At the same time, the amount of energy transfer for those Φ values has been found to be close to the quantity predicted by the impulsive model, several Xe–X^- impacts occurring in the latter. Apparently, as one gradually changes the rigid sphere potential into a realistic interaction potential, these impulsive encounters spread out in time, start to overlap, and finally merge to form a single minimum of the trajectory function $R(t)$. During this process, the efficiency of energy transfer varies only slightly.

4 Conclusion

The results of the present paper suggest that multiple impacts in noncollinear impulsive A + BC collisions are amenable to analysis (as well as in the case of collinear collisions) and can be described analytically. Our Eq. (18) for the amount of energy transfer in a collision of an A atom with a "cold" BC molecule is not, from our viewpoint, much more complicated than its simplest particular cases, namely, the Mahan formula (1) valid for a single A–B encounter only, and the Mahan–Shin formula (3) suitable for collinear collisions only. An application of Eq. (18) as well as Eq. (20) takes no computer time.

Comparison of the data of trajectory calculations for the Xe + XCs systems with X = F, Cl, Br, I and calculations in the impulsive approximation shows that at least for some systems our model can estimate the amount of energy transferred by the projectile atom to the "cold" target molecule with a satisfactory accuracy in a wide range of energies and collision configurations. This model provides a much more visual collision picture than forcing trajectories and promotes deeper comprehension of dynamics of endothermic reactions, such as collision-induced dissociation.

The model proposed may be successfully used for a rough but very fast estimate of the amount of energy transfer in various systems and various collision geometries as well as to distinguish orientation effects of the impulsive nature from effects which are due to another factors (such as peculiarities of topography of the potential energy surface). Nikitin [20] points out that analytic expressions for the impulsive limit of the efficiency of energy transfer in multiple impacts are of importance for approximately calculating the probabilities of transitions between various vibrational and rotational molecular states.

One of the promising ways to develop our model further is to generalize it to A + BC collisions where the B and C particles are not assumed to touch at the moment that the atom A hits the atom or ion B. Although such collisions seem to be much more difficult to study than those considered in the present paper (where the particle B is tangent to the particles A and C at the moment of collision), one may expect that the improved model will represent the results of trajectory calculations for noncollinear configurations more accurately.

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Appendix A

Some intermediate calculations

In this Appendix we derive Eqs. (18) and (20) via the construction presented in Sect. 2. First of all, it is easy to verify that for the collision of an atom A with a "cold" molecule BC the vector $\mathbf{v}_1$ (5) is equal to:

$$\mathbf{v}_1 = -\frac{m_1 V \cos\psi}{(m_1 + m_2)\sin^2\alpha}(\mathbf{k} + \mathbf{s}\cos\Phi)$$

(see Fig. 1a for the notations) and its length is equal to:

$$v_1 = \frac{m_1 V \sin\Phi \cos\psi}{(m_1 + m_2)\sin^2\alpha}. \tag{A1}$$

Now one should calculate the final values of the coordinates (x, y). The total number n_* of impacts in the system under consideration is given by Eq. (14) and equal to either $2n - 1$ or $2n$. In the latter case, the last $(2n)$th impact is an encounter between the balls B and C which affects neither $(\mathbf{V}_2 - \mathbf{V}_3, \mathbf{s})^2$ nor $[\mathbf{V}_2 - \mathbf{V}_3, \mathbf{s}]^2$. We can therefore ignore this impact. The values of the coordinates (x, y) just after the $(2n - 1)$th encounter are:

$$x_f = -\left(\frac{m_1 m_2}{m_1 + m_2}\right)^{1/2} \frac{V\cos\psi}{\sin\alpha}\cos\frac{(4n-1)\alpha}{2},$$

$$y_f = \left(\frac{m_1 m_2}{m_1 + m_2}\right)^{1/2} \frac{V\cos\psi}{\sin\alpha}\sin\frac{(4n-1)\alpha}{2},$$

whence the final values of the coordinates (u, v) are:

$$u_f = \frac{m_2 V\cos\psi}{(m_1 + m_2)\sin^2\alpha}\cos(2n\alpha),$$

$$v_f = m_2\left(\frac{m_1}{m_3(m_1 + m_2)(m_2 + m_3)}\right)^{1/2} \frac{V\cos\psi}{\sin^2\alpha}\cos[(2n-1)\alpha] \tag{A2}$$

according to Eq. (7).

It is clear in view of Eq. (5) that the energies $E_{\mathrm{BC}}^{\mathrm{vib}}$ and $E_{\mathrm{BC}}^{\mathrm{rot}}$ are equal to:

$$E_{\mathrm{BC}}^{\mathrm{vib}} = \frac{m_3}{2m_2(m_2+m_3)}(m_1 u_f \cos \Phi - (m_2+m_3)v_f)^2,$$

$$E_{\mathrm{BC}}^{\mathrm{rot}} = \frac{m_3}{2m_2(m_2+m_3)}(m_1 u_f \sin \Phi - m_2 v_1)^2. \tag{A3}$$

Substituting the expressions (A1) and (A2) for v_1, u_f, v_f into Eq. (A3) and taking into account that:

$$E_{\mathrm{col}} = \frac{m_1(m_2+m_3)}{2(m_1+m_2+m_3)}V^2$$

we arrive, after some straightforward algebra, at the expressions (20) for δ^{vib} and δ^{rot}. The sum of these expressions is the second of Eqs. (18) for δ. The first of Eqs. (18) for δ can now be obtained via simple trigonometrical relations.

Appendix B

The scattering angle of the projectile

Within the framework of the impulsive model for A + BC collisions developed in Sect. 2, it is also possible to derive an analytic expression for the scattering angle ϑ of the projectile A in the A–BC center-of-mass frame for the collision of A with a "cold" target BC (ϑ being the angle between the initial velocity of A and the final velocity). Namely, one can easily verify that:

$$\cos\vartheta = \frac{(\lambda+1)+(\lambda-1)\cos 2\psi}{\{2[(\lambda^2+1)+(\lambda^2-1)\cos 2\psi]\}^{1/2}},$$

where

$$\lambda = 1 - 2\frac{\sin^2(n\alpha)}{\sin^2\alpha}\sin^2\beta.$$

For head-on collisions ($\psi = 0$) one has $\vartheta = 0$ (if $\lambda > 0$) or $\vartheta = \pi$ (if $\lambda < 0$). The inverse formula expressing ψ in terms of ϑ has the form:

$$\cos^2\psi = \frac{1}{2}[1 + \Lambda\sin^2\vartheta \pm (1-\Lambda^2\sin^2\vartheta)^{1/2}\cos\vartheta],$$

where $\Lambda = (1+\lambda)/(1-\lambda)$.

For the case $n = 1$ similar formulas were presented in Ref. [26], their applications to scattering problems being exemplified by Ref. [54].

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Note added in proof

After this paper had been submitted the important papers

> Skrebkov OV, Smirnov AL (1985) Teor Eksper Khim 21:129 [in Russian]; (1990) Sov J Chem Phys 5:705

came to our attention. In these papers, the Mahan–Shin formula (3) was reobtained (independently of Mahan and Shin) and analytic expressions for the impulsive amount of energy transfer in collinear collisions of an atom A with an excited molecule BC were derived as well. Moreover, Skrebkov and Smirnov proposed also a more complicated analytic formula for the amount of energy transfer in collinear A + BC collisions which takes into account the interaction potential of the particles involved. This formula turns to the purely impulsive Mahan–Shin formula (3) as the collision energy tends to infinity.