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COLLINEAR COLLISION CHEMISTRY. II. ENERGY DISPOSITION IN REACTIVE COLLISIONS

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# COLLINEAR COLLISION CHEMISTRY.
## II. ENERGY DISPOSITION IN REACTIVE COLLISIONS

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# Collinear Collision Chemistry. II.

## Energy Disposition in Reactive Collisions

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In part I of this series (1), I outlined the mechanics of collinear atom-diatom collisions, and showed how the vibrational energy imparted to a diatom BC as a result of its collinear collision with the atom A depends on the masses of the atoms and certain basic features of primitive potential energy surfaces. In this article, I wish to extend the collinear model to reactive collisions, and show how the mass distribution and potential energy surface features affect the disposition of the product energy between the translational and internal vibrational modes.

## Mechanics of Collinear Collisions

To review briefly the method by which these problems are approached, we note that the dynamics of a collinear atom-diatom encounter is most simply discussed in terms of a coordinate system for which the kinetic energy is a constant times a sum of squares of velocities (2). Such a coordinate system can be expressed in terms of the respective A-B and B-C bond distances $r_1$ and $r_2$ by the equations

$$x = r_1 + \frac{C}{B+C} r_2$$

$$y = \frac{r_2}{a}, \quad a^2 = \frac{A(B+C)}{BCM}$$

where the letters stand for the masses of the various atoms, and M is the total mass of the system. The total relative kinetic energy is then

$$T = \frac{1}{2} \frac{A(B+C)}{M} (\dot{x}^2 + \dot{y}^2). \tag{1}$$

When lines of constant $r_1$ and $r_2$ are plotted on the Cartesian x-y system, they intersect at an internal angle β, which is given implicity by

$$\tan^2 \beta = \frac{BM}{AC}.$$

Since the relative kinetic energy of the system in terms of $\dot{x}$ and $\dot{y}$ has the very simple form given by eqn. 1, if x and y are used as Cartesian coordinates and the potential energy $V(x, y)$ is represented in the third dimension, a single particle of mass $A(B+C)/M$ sliding frictionless on the resulting potential energy surface will carry out an x-y motion which exactly represents the behavior of the real three particle system.

### Thermoneutral Reactions without Activation Energy

The simplest form for the potential energy surface for the reaction

$$A + BC \rightarrow AB + C$$

results if BC and AB are assumed to be bound by identical square-well potentials. The representation of this potential surface in the x-y coordinate system is shown in Figure 1. In regions of small x or y, the potential energy is infinite because of the hardsphere repulsion between A and B or B and C. In the region where x and y are simultaneously large, the system consists of free atoms, and has the constant potential energy $D_o$, the dissociation energy of the B-C or A-B bond. The system passes from reactants to products by traveling in the trough of zero potential energy which represents bound BC or AB molecules. A number of authors have discussed reaction dynamics on such potential surfaces, using both quantum and classical mechanics (3-12).

The "square trough" type of potential energy surface is of course very primitive, and in general will be a poor representation of the actual potential surfaces which govern chemical reaction dynamics. However, under certain circumstances the square trough surface and some of its variants can lead to qualitatively correct analyses of collision phenomena. For example, if the initial relative kinetic energy is large, the small variations in potential energy which occur along most of the trajectory on a realistic surface can influence the results of a collision only to a slight degree. It is when rapidly moving atoms come into close contact, and their mutual potential energy changes rapidly, that the outcome of the trajectory is influenced most profoundly. Fortunately, the square trough type of potential is a fairly reasonable approximation to the true potential in these critical "turning point" regions. Consequently, we can expect conclusions based on the primitive surface to apply best to high energy collision phenomena which occur in certain ion and molecular beam experiments (13) and in nuclear recoil and photochemical hot atom systems (14). This optimism should be tempered with the realization that even with a satisfactory potential energy surface, a collinear collision model can faithfully represent only a small fraction of the many reactive collisions which occur in three dimensional space.

Let us examine the types of trajectories that can occur on this simple flat bottomed trough potential energy surface. Figure 2 shows some of these for the case where $\beta = 60^\circ$, which corresponds to equal masses for atoms A, B, and C, or to A:B:C = 1:2:6, and to many other mass combinations. A large number of different initial conditions for the trajectories may be chosen. In Figure 2a the total kinetic energy of the reactants is present as relative translation, and so the initial leg of a trajectory is parallel to the x-axis. Because the trough is flat bottomed, it is possible to have similar trajectories with starting points displaced along the y-axis. Figure 2a shows that when the widths of the product and reactant channels are the same, all trajectories with zero initial vibrational energy lead into the product channel, and the final vibrational energy of the products is also zero. These results apply to the $\beta = 60^\circ$ case, of course, and other kinematic angles lead to different divisions of the product energy between vibration and translation.

Let us examine the effects of initial vibrational energy of the reactants on the energy disposition. The vibrational energy of the reactants can be specified by giving the value of the angle $\theta$, which is defined by

$$\tan \theta = \dot{y}/\dot{x}$$

where $\dot{y}$ and $\dot{x}$ are measured at a standard reference line perpendicular to the x axis, as shown in Figure 2b. Thus the translational energy $E_t$ and vibrational energy of the reactants can be expressed in as

$$E_t = E \cos^2\theta, \; E_v = E \sin^2\theta$$

where E is the total kinetic energy of the system. As the magnitude of $\theta$ is increased from zero to $30^\circ$ for the $\beta = 60^\circ$ case, an increasing fraction of all possible trajectories is reflected back into the reactant channel. Those trajectories which have $\theta$ positive and large values of $y$ at the reference line are lost first from the product channel. For example, when $|\theta| = 15^\circ$, no trajectories with $\theta = +15^\circ$ can enter the product channel, while all those with $\theta = -15^\circ$ can. When $|\theta| = 30^\circ$, which corresponds to 25% of the total energy in initial vibration, no trajectories reach the product channel. This is illustrated in Figure 2b.

Figure 2c shows how to find the angle $\theta'$ in terms of $\theta$ and $\beta$. Merely by making use of the fact that the sum of the angles of a triangle is $\pi$ radians, we find

$$|\theta'| = \pi - 2\beta - \beta', \; |\theta| = \beta - \beta'$$

$$|\theta'| = \pi - 3\beta - |\theta|.$$

For the special case that $\beta = 60^\circ$, $|\theta'| = |\theta|$. Thus as $|\theta|$ increases in the range $0^\circ \leq |\theta| < 30^\circ$, the number of trajectories which reach the product channel decreases, but the vibrational energy of the products increases and is the same as that of the reactants.

When the initial vibrational energy is increased still more so that $30^\circ < |\theta| < 60^\circ$, the fraction of trajectories that reach the product channel increases, and for $|\theta| \geq 60^\circ$, all trajectories lead to products. This behavior is illustrated in Figure 2d. In the interval $30^\circ < |\theta| < 90^\circ$, the magnitude of the angle of the trajectory with respect to the product channel axis is readily found to be

$$|\theta'| = \pi - \beta - |\theta|.$$

Thus as $|\theta|$ increases from $30^\circ$ to $90^\circ$, the transmission to products increases, but the vibrational energy of the products decreases. We see that the overall effects of changing the partitioning of the initial energy of the reactants on the dynamics of the reaction are not particularly simple, even for this very primitive potential energy surface.

## Exoergic and Endoergic Reactions

The simplest way to represent the potential energy surface for an exoergic reaction is to introduce a single step in the bottom of the square trough that we have just studied. The location and orientation of this potential energy step is at our disposal, and it is of interest to see how various choices affect the transmission of particles to the product channel, and the partitioning of energy among vibration and translation of the products. To simplify matters, we will consider only those trajectories in which there is no initial vibrational energy of the reactants.

Figure 3 illustrates the effects of variation of the location of the potential energy step. In Figure 3a, a step is located in the reactant channel perpendicular to the x-axis, which corresponds to an attraction between the atom A and the center-of-mass of BC. If the initial leg of the trajectory is parallel to the x-axis, the representative particle crosses the step and has its kinetic energy changed to $E - \phi$, where $\phi$ is the minimum potential energy of the products relative to that of the reactants. Since the trajectory is perpendicular to the step, there is no deflection of the representative particle. Thus the trajectory intercepts the reflecting wall at the end of the reactant channel with the angle $\beta$, when A hits B. Then B hits C, and finally the representative particle proceeds toward the product channel. After the B-C encounter, the angle which the trajectory makes with the x-axis is $\pi - 2\beta$, and as a result, the angle with respect to the product channel axis is

$$\theta' = \pi - 3\beta.$$

Consequently, the final vibrational energy is

$$E_V' = (E-\phi) \sin^2 (\pi-3\beta) = (E-\phi) \sin^2 (3\beta) \qquad (2)$$

if the representative particle does indeed enter the product channel. We see that the total kinetic energy $E - \phi$ is partitioned according to a simple function of the kinematic angle $\beta$. In other words, of the exoergicity $-\phi$, only a fraction $\sin^2(3\beta)$ appears as product vibrational energy when the step is in the reactant channel, perpendicular to the reactant channel axis.

If the step is in the product channel, perpendicular to the channel axis, as shown in Figure 3b, the exoergicity of the reaction is released entirely as repulsion between the centers-of-mass of the products. As shown in Figure 3b, the trajectory makes an angle $\pi-2\beta$ with the x-axis after the A-B and B-C repulsive interactions. To find the energy disposition after the trajectory crosses the step, we simply partition the energy of the representative particle before it crosses the step into contributions associated with motion parallel and perpendicular to the product channel axis. Thus

$$E_{\parallel} = E\cos^2(\pi-3\beta)$$

$$E_{\perp} = E\sin^2(\pi-3\beta).$$

As the particle crosses the step, the kinetic energy parallel to the axis is increased by $-\phi$, and that perpendicular to the axis is unchanged. Therefore

$$E_t' = E\cos^2(3\beta) - \phi \tag{3}$$

$$E_v' = E\sin^2(3\beta). \tag{4}$$

Thus the exoergicity of the reaction appears entirely as translational energy of the products in this case.

So far, our discussion of the effects of potential energy steps has been concerned with reactions proceeding in the exoergic direction. However, the examples can serve equally well for reactions run in the endoergic direction. Equations (2) and (4) still give the vibrational energy in the products, provided

$\phi$ is taken to be positive instead of negative. Note, however, that when there is a positive potential energy step in the reactant channel, the condition for crossing this barrier is just

$$E = E_t > \phi.$$

That is, the translational energy of the reactants must be greater than the step height. In contrast, if the step is in the product channel, the condition for reaction is that the final translational energy must be greater than zero. From eqn. (3) we get

$$0 < E_t' = E \cos^2 (3\beta) - \phi$$

$$E \cos^2 (3\beta) > \phi.$$

Thus in this case, when the trajectories have no initial vibrational energy, the threshold kinetic energy at which reaction is possible is greater than the potential energy step height $\phi$.

In situations such as the one just described, the reaction probability or rate constant is very sensitive to increases in the vibrational energy of the reactants. The best documented (15) reaction of this type is

$$H_2^+ + He \rightarrow HeH^+ + H \qquad \Delta H = 0.8 \text{ eV}$$

where it has been very convincingly demonstrated that near the threshold for reaction, a given amount of energy in vibration of $H_2^+$ is orders of magnitude more effective in promoting reaction than is the same amount of energy present as relative translation of reactants. An accurate <u>ab initio</u> calculation (16) of the potential energy surface does show that the 0.8 eV potential energy step lies almost entirely in the product channel.

Another simple modification can be made to our potential energy surface which makes it more representative of realistic surfaces. As atom A approaches BC, we can expect that a weakening of the BC bond occurs, and consequently a repulsion develops between atoms B and C. This is represented in Figure 4 by a new reflecting wall which makes an angle $\alpha$ with respect to the x-axis. In effect, the mutual hard sphere radii of B and C increase as A approaches B. The effect of this modification can be substantial. Consider the case shown in Figure 4a, where $\beta = 45^\circ$ and $\alpha = 157.5^\circ$. The trajectory is such that the A-B repulsive wall is encountered first, then as the BC molecule is compressed, the modified BC repulsive wall is reached. After this final reflection the trajectory is directed exactly along the product channel axis. Without the modified BC repulsion, the trajectory would have led back to the reactant channel.

The sequence in which the two repulsive walls are encountered is important, as Figure 4b shows. Now the surface and the trajectory are such that the BC repulsion starts to act before the AB repulsion occurs. As a result, the representative particle is reflected back into the reactant channel. This example shows how important the internuclear separation or phase of the BC oscillator can be in determining whether a trajectory leads to reaction.

It is a simple matter to find the angle that the final leg of the trajectory of the representative particle makes with the product channel axis for the two types of trajectories shown in Figure 4. When the AB repulsive wall is encountered first, as in Figure 4a, summation of the reflection angles gives

$$|\theta'| = \pi + 3\beta - 2\alpha \tag{5}$$

and therefore the product vibrational energy is

$$E_V' = E \sin^2 (3\beta - 2\alpha) \tag{6}$$

if the trajectory does in fact enter the product channel. Similarly, when the BC repulsion acts before the AB repulsive wall is reached, as in Figure 4b, summation of the angles gives

$$|\theta'| = \pi + \beta - 2\alpha \tag{7}$$

and consequently the product vibrational energy is

$$E_V' = E \sin^2 (\beta - 2\alpha) \tag{8}$$

if products are formed.

## Surfaces with Wells and Barriers

We can combine the potential steps and reflecting walls studied so far to give a surface which has a potential energy well when the three atoms are close to each other. The result is shown in Figure 5. As atom A approaches BC, there is an attraction between the centers-of-mass of the reactants which is represented by the step of depth $\phi_2$ oriented perpendicular to the x-axis. In the region of small x and y, the BC repulsive wall makes an angle $\alpha$ with respect to the x-axis. In the exit channel, there is a potential step perpendicular to the channel axis, such that the potential energy in the product channel (and the $\Delta H_o^o$ of the reaction) is $\phi_2$.

The trajectory we have chosen is such that A hits B, B hits C, then the products AB and C separate. To find the energy disposition in the reaction, it is simplest to calculate the translational energy at three points along the trajectory. After the step in the reactant channel is crossed, the kinetic energy of the representative particle changes to $E - \phi_1$. After the A-B and B-C reflections, the angle of the trajectory with respect to the channel axis is given by eqn. 5, so the translational energy of AB relative to C at this stage is simply $(E-\phi_1) \cos^2 (3\beta-2\alpha)$; that is, the energy of the representative particle associated with motion in the direction of the product channel. Finally, the representative particle must cross the potential step in the product channel. To do this, the kinetic energy in the direction of the channel must be greater than the height of the potential step $\phi_2 - \phi_1$. Thus we must have

$$(E-\phi_1) \cos^2 (3\beta-2\alpha) > \phi_2 - \phi_1 \qquad (9)$$

if the particle is to be able to enter the product channel on its first try. If this condition is not met, the system may return to the reactants or be temporarily trapped as the sticky collision complex ABC. If the representative particle does cross the product step on its first try, it loses translational energy $\phi_2 - \phi_1$, and therefore the final product translational energy is

$$E_t' = (E-\phi_1)\cos^2(3\beta-2\alpha) - (\phi_2-\phi_1). \qquad (10)$$

Note that if $\phi_1$ is zero, eqn. 10 is equivalent to eqn. 6, and if in addition $\alpha$ is zero, eqn. 10 reduces to eqn. 3.

Equation 10 also gives the final relative translational energy of the products of a reaction in which a potential energy barrier appears in place of the potential energy well in the region of small x and y. It is merely necessary to assume that $\phi_1$ is a positive number less than $D_o$, the dissociation energy of BC. Also, the energy condition that must be met for reaction to occur is now $E > \phi_1$, and the inequality (9) no longer applies.

In the analysis of experimental molecular beam scattering data, it is customary to compute the quantity Q, the difference between the final and initial relative kinetic energies. The model we have just discussed gives for Q the expression

$$Q = E_t' - E = (\phi_1-E)\sin^2(3\beta-2\alpha) - \phi_2.$$

Thus the value of Q is determined in this model by the initial translational energy and four parameters: the mass distribution factor $\beta$, the BC repulsion induced by the approach of A represented by the angle $\alpha$, and the potential steps $\phi_1$ and $\phi_2$. In addition, there are the three implicit assumptions that the potential steps are oriented perpendicular to the channel axes, and that the vibrational energy of the reactant BC is zero. This is a convincing demonstration that even for a system which has a very simple potential surface, there are a large number of factors which affect the distribution of energy among the internal and external modes of the products. Thus the problem of determining a true potential surface from experimental data is a very difficult one, even for the simplest systems. It is no surprise that such a determination has not yet been made.

## Summary

The collinear collision model combined with the square trough potential energy surface is an extreme simplification of the practical problem of three atoms in three dimensional space interacting by a realistic potential energy function. However, the simple model does have the advantage that it can be solved entirely by elementary geometric or trigonometric methods, and it does provide a clear indication of the effects that such factors as the mass distribution and potential energy barriers and wells have on the reaction probability and on the distribution of energy among the modes of motion of the products. The model illuminates many of the results (17) of very extensive exact trajectory calculations in which realistic surfaces have been used, and makes clear just how difficult it will be to determine a true potential energy surface for a chemical reaction from experimental data like that provided by molecular beam scattering and infrared chemiluminescence. Perhaps the greatest value of the model is that it allows a rational approach to the problem of the mechanics of reactive collisions without requiring any substantial calculational effort.

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## FIGURE CAPTIONS

1. A square trough potential energy surface for the thermoneutral chemical reaction A(BC, C) AB.

2. Effects of initial vibrational energy and phase on produce formation and energy distribution for a surface with $\beta = 60^\circ$. (a) Trajectories with no initial vibrational energy. (b) Trajectories with $\theta = 30^\circ$, $E_v = 0.25$ E. (c) Construction for deducing $\theta'$ for a collision sequence in which A hits B, then B hits C. (d) Construction for finding $\theta'$ when the collision sequence is B hits C, A hits B.

3. The effects of the position of a potential energy step for an exoergic reaction. (a) Step in the entrance channel. (b) Step in the exit channel. In this case, if $\phi$ had been chosen to be positive, the refraction of the trajectory at the potential step would have been in the opposite sense from that shown.

4. The effects of a modified B-C repulsion and vibrational phase on trajectories. (a) A collision sequence in which A hits B, then B hits C, and products are formed.

5. A trajectory on a surface with a potential energy well and a modified B-C repulsive wall. Here $\phi_1$ and $\phi_2$ are negative, with $\phi_1 < \phi_2$. If $\phi_1$ were assumed positive and $\phi_1 > \phi_2$, only the direction and magnitude of the refraction of the trajectory at the final step would be changed.

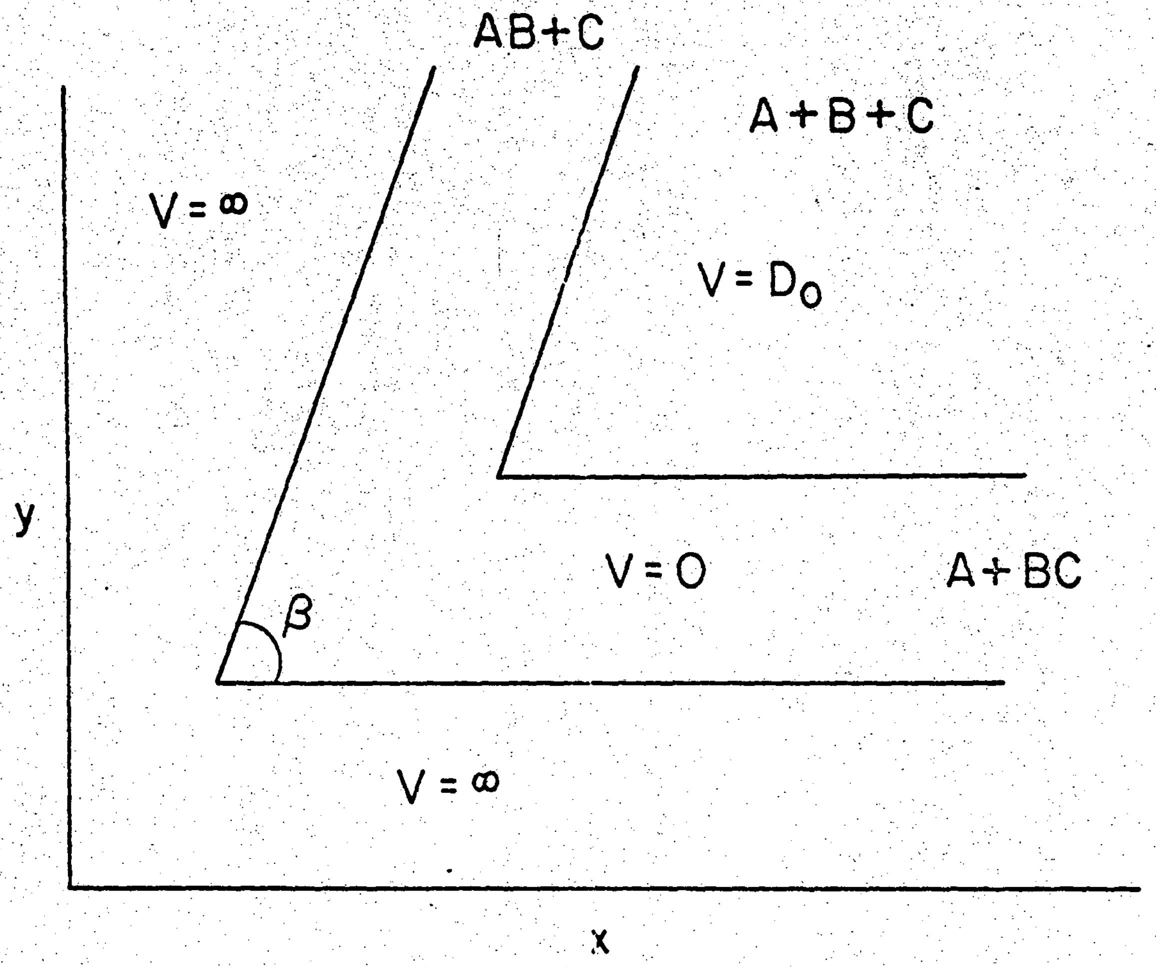


Fig. 1

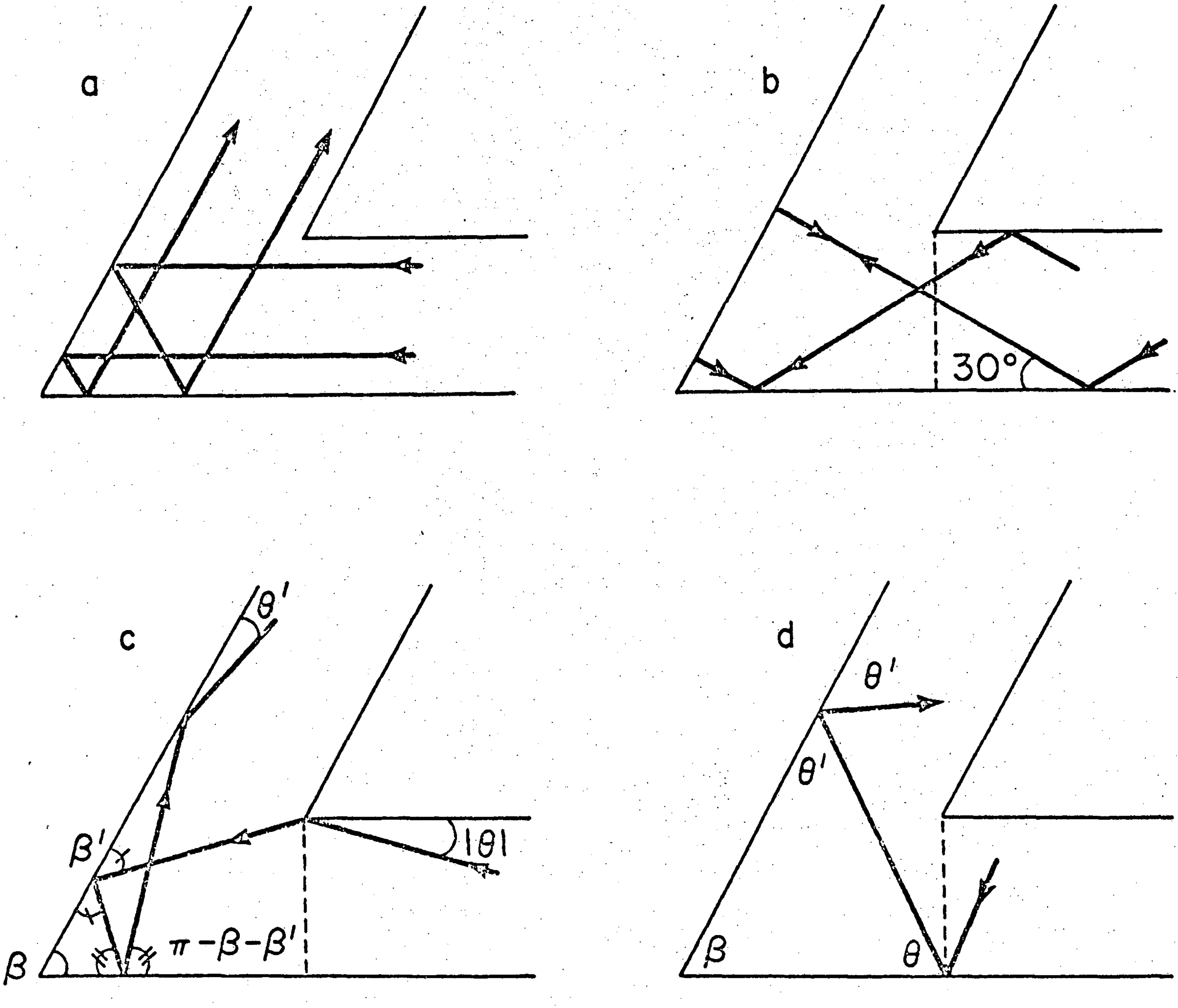
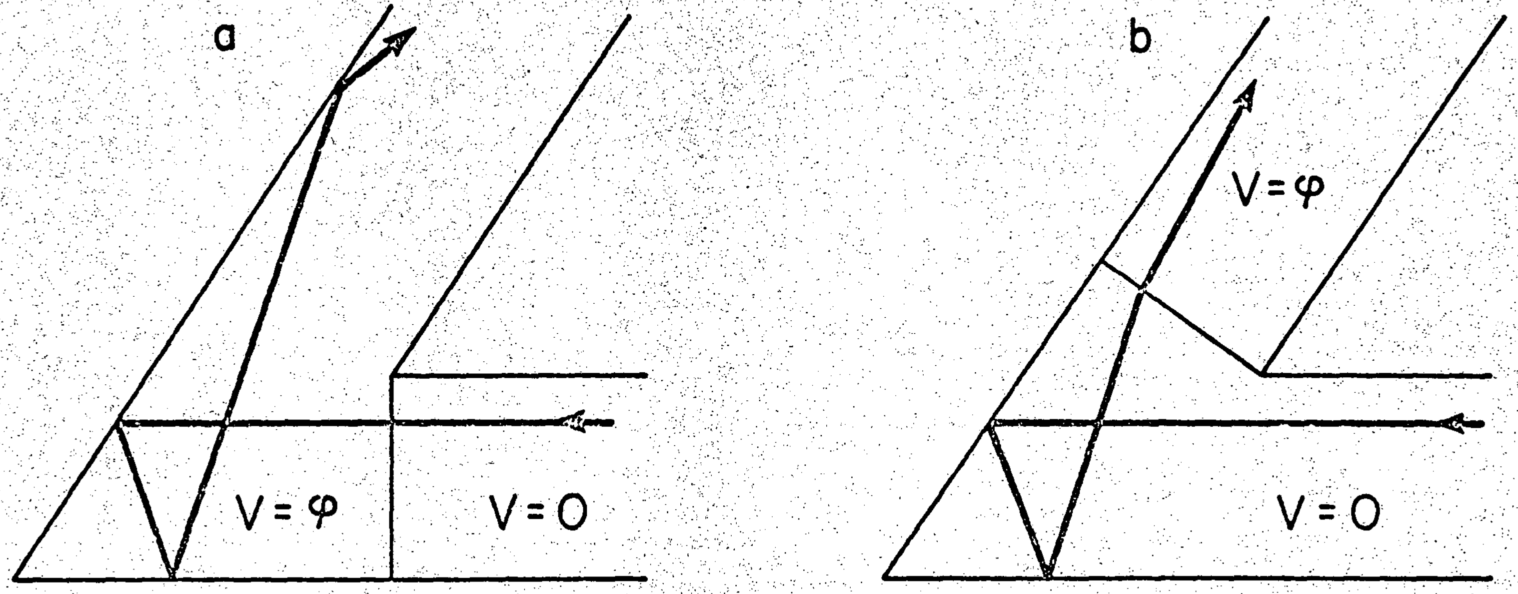


Fig. 2



$E_v' = (E-\varphi)\sin^2(3\beta)$

$E_v' = E\sin^2(3\beta)$

Fig. 3

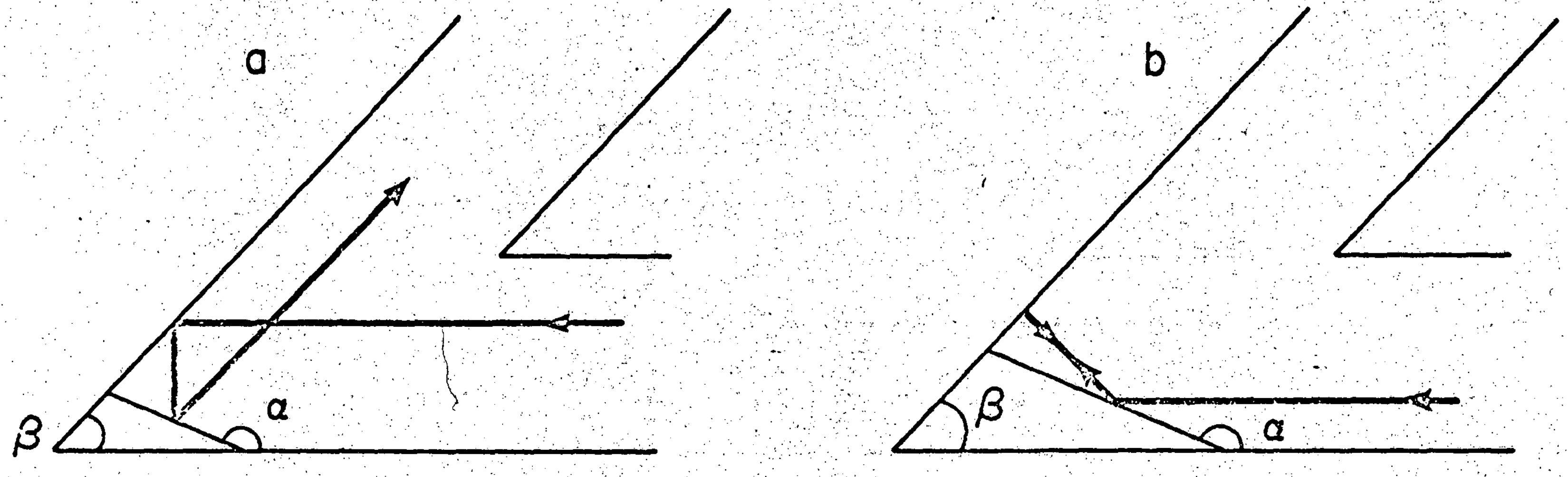


Fig. 4

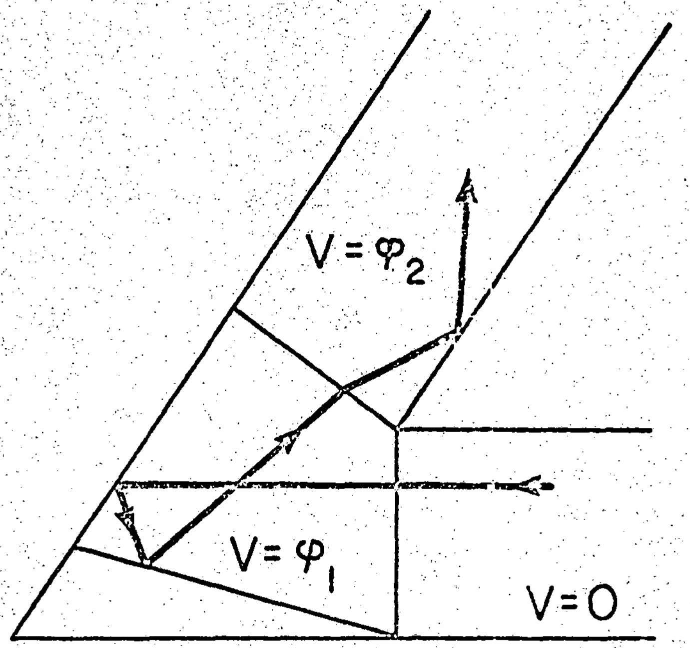


Fig. 5

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