ness of the wall increases as $\ln g$, due to thermal fluctuations. A similar effect was noted by Buff, Lovett, and Stillinger[7] in computing the surface diffuseness of a classical liquid in a tub, as the force of gravity was assumed to approach zero. Had these authors considered the effects of exchange of surface waves on the properties of their systems, they would clearly have had the same troublesome divergences as we. Presumably, the renormalization procedure to be used in their case is similar to ours as well.

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[1]P. J. Feibelman, Ann. Phys. (N.Y.) 48, 369 (1968).

[2]This is probably a stronger assumption than is necessary. Nevertheless, it is the simplest way to obtain the formal expressions we need.

[3]The question of the analyticity of the kernel at $q=0$, $\omega=0$ is treated in Sec. IV.

[4]S. Engelsberg and P. M. Platzman, Phys. Rev. 148, 103 (1966).

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Binary Collisions in the Nonrelativistic Three-Particle Problem

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A method is provided whereby all the possible results of sequences of three-particle binary collisions may be calculated, given the initial velocities of the three particles. All the one-dimensional bounds on the number of collisions given by Doolen are confirmed. It is further found that only sequences of certain types are possible, the longest of which arises when the lightest particle rebounds between the two heavier particles. If in this instance, we let θ be the angle between the relative velocity of the first and second pairs of colliding particles and remove the one-dimensional restriction, we find that an upper bound on the maximum number of collisions n_c is given by

$$\frac{\pi_c}{n_c-1} > \cos^{-1}\left[\left(\frac{m_B m_C}{(m_A+m_B)(m_A+m_C)}\right)^{1/2}\cos\theta\right],$$

where n_c is the largest integer which satisfies the inequality and m_A is the mass of the lightest particle.

I. INTRODUCTION

Sugar, Rubin, and Tiktopoulos have demonstrated in Ref. 1 that one can anticipate a class of singularities in the nonrelativistic three-particle scattering amplitude. These singularities occur where the incoming and outgoing states are connected by a sequence of two-particle processes which satisfy the following rules: (i) Each two-particle process in the sequence conserves both energy and momentum. (ii) Each sequence of collisions would be kinematically possible for classical point particles.

Doolen[2] has shown that the maximum number of collisions satisfying these conditions occurs when all three particles scatter along a line and the lightest of the three particles scatters between the heavier particles. In this paper, we will provide a means for visualizing the results of sequences of collisions where the binary collisions do not necessarily occur along a line.

II. TWO-PARTICLE COLLISION

In making an analysis of two-particle collision it is most helpful to have a geometrical view of two-particle kinematics. The corresponding algebraic view contains the same information but leads to algebraic entanglements which are avoided geometrically. To produce this geometrical view, we will first give a construction which allows one to visualize all the possible results of the nonrelativistic collision of two particles. We are not aware of any reference in which the appropriate construction is given; even though many textbooks give constructions which are sufficiently close to the appropriate construction, we feel that we should not merely state the result and leave the demonstration to the skeptical reader.[3]

Consider two particles of masses m_1 and m_2 with velocities $\vec{v}_1$ and $\vec{v}_2$, respectively. If the two particles collide they will produce two new velocities $\vec{v}_1' \cdot \vec{v}_2'$. The possible results of this collision are shown in Fig. 1. The velocity $\vec{v}_1'$ can lie anywhere on the sphere S_1 and the velocity $\vec{v}_2'$ must lie at the opposite point on sphere S_2. We will assume that any scattering angle is possible in every collision.

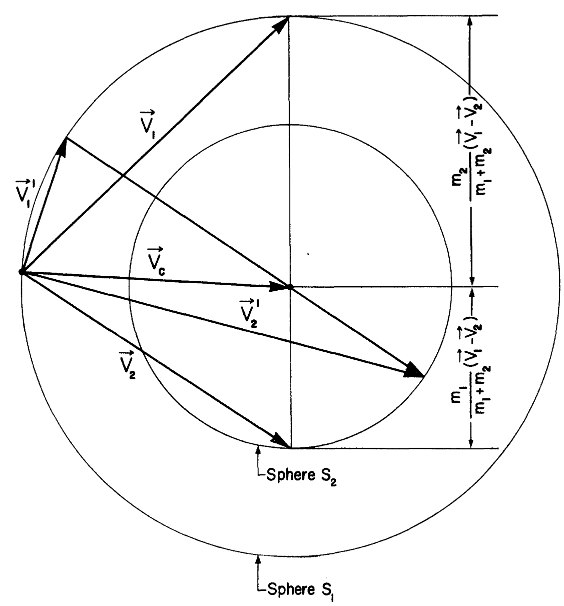

FIG. 1. Geometrical construction for two-particle scattering.

III. SEQUENCES OF BINARY COLLISIONS IN THE THREE-PARTICLE PROBLEM

We now extend our construction of Sec. II to three particles that collide two at a time. In a collision of three particles, there are three velocity vectors involved. Consider the plane found by the terminal points of those three vectors. This plane is the plane of the paper in Fig. 2. The triangle thus formed has sides which are of length $|\vec{v}_1 - \vec{v}_2|$, $|\vec{v}_2 - \vec{v}_3|$, and $|\vec{v}_1 - \vec{v}_3|$. In a collision between two particles, one velocity will remain fixed (the velocity of the particle not involved in the collision), and one relative velocity will remain fixed in magnitude (the relative velocity of the pair of particles which collide). This triangle may be deformed in accordance with the rule of Sec. II, which allows the interacting pair to retain the same magnitude of relative velocity while keeping the velocity of the c.m. fixed. The remaining vertex of the triangle is determined by the velocity of the particle not involved in the collision.

It is not difficult to establish some properties of the triangle. For example: (i) If the sides of the triangle are divided according to the rules of Sec. II, the lines joining the vertices and the division point of the opposite side intersect at a point in the interior of the triangle. This point is the terminus of the vector velocity of the c.m. of all three particles. (ii) Any allowed two-particle deformation of the triangle keeps the three-particle c.m. velocity fixed.

IV. KINEMATICALLY POSSIBLE SEQUENCES

Thus far we have succeeded in establishing a geometrical construct which allows us to visualize the result of any two-particle collision. We now proceed to consider what sort of two-particle deformations are kinematically possible, that is, which sequences are allowed, recognizing that in order to collide the particles must be in the same place at the same time.

We first note that any sequence of collisions has an arbitrary beginning. Any pair of particles may collide first, and either of the two particles involved in the first collision may collide with the third particle. Let us call the particles involved in the first collision particles A and B, and let us assert that A and C will collide next. After the collision between A and B, we will have some velocity triangle, for example, the triangle in Fig. 3. In the collision between A and C, the point B is fixed and the line AC is free to rotate through any angle about the fixed point at the velocity of the c.m. of the AC system. There are two possibilities for the third collision, either A collides with B or C collides with B. Viewed in the c.m. of the AB system, particles A and B have left their common collision point in opposite directions. Their distances away from this common collision point are proportional to their velocities relative to the c.m. of the AB system. One of the particles (in

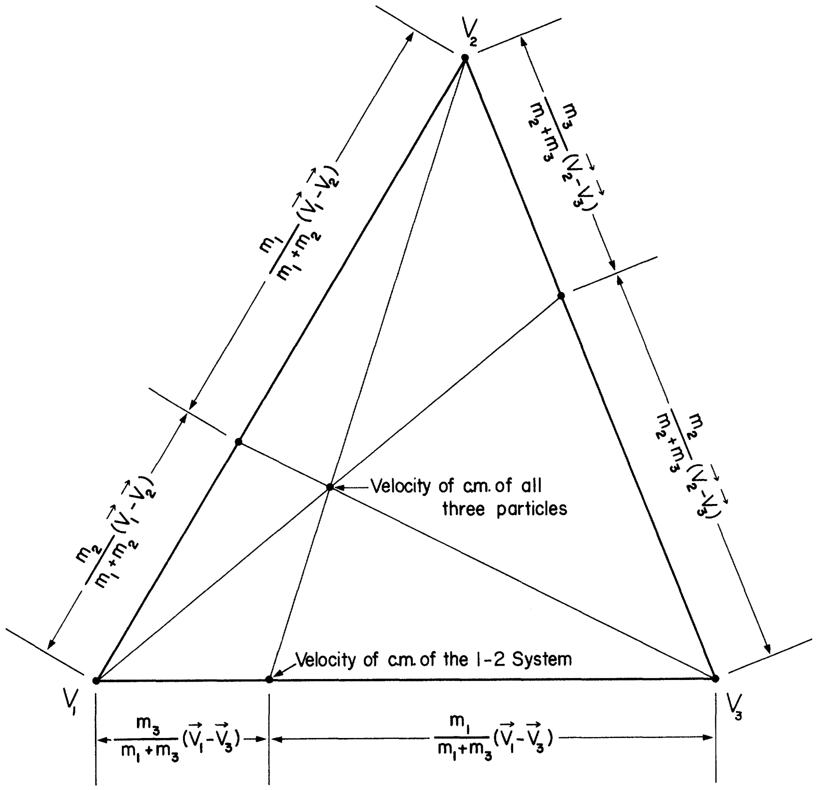

FIG. 2. Three-particle velocity triangle.

this case particle A) is to undergo a second collision, this time with particle C. We seek circumstances which allow one of the products of this collision to subsequently collide with particle B. This third collision can occur only if the velocity of one of the products of the AC collision after the AC collision is collinear with the velocity of particle B after the AB collision, and if the velocity of the particle which leaves the AC collision is sufficient to lead to a collision with particle B at some later time.

Again the geometrical interpretation is fairly simple. Figure 3 is a sketch of a typical velocity triangle of the type discussed above. The point B is the velocity of particle B after the AB collision. This velocity is, of course, unaffected by the AC collision. The AC collision as depicted has produced a new velocity for particle A, and this velocity is represented by the line OA'. The situation represented by Fig. 3 will lead to a second collision, between A and B because particle A is now headed in the right direction to catch particle B, and its velocity in that direction exceeds that of particle B.

Again, as depicted in Fig. 3, no collision between B and C is possible because the point C is too far removed from the line AB to allow C' to lie on that line, much less to supply the velocity required for particle C to catch particle B.

The process outlined above may be continued. We now have a situation where A and C have just collided and we want to ask whether a collision between B and C or A and C is possible after the collision between A and B. The question is answered in the same way. Any particle which is to collide with C must be directed in the same direction as the point C' in the AC c. m. system, and must have sufficient velocity to catch particle C. Therefore, the geometrical question is, can either arc $O'A'$ or $O'B'$ intersect the line $A'C'$ so that the intersection lies outside the vertex of the triangle at C'? As depicted, the answer is certainly no.

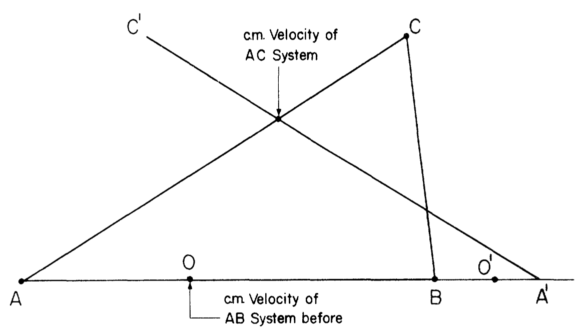

FIG. 3. Geometrical construction for a kinematically possible sequence of collisions.

V. 3-SEQUENCES

We now wish to develop an algebraic technique based on the preceding geometrical observations. We begin by noting that any sequence of collisions may be viewed as a nested combination of sequences of three collisions at a time. For example, the sequence *AB, AC, BC, AB, AC* could be thought of as the nested sequence *AB, AC, BC; AC, BC, AB; BC, AB, AC*. The advantage of this somewhat contrived point of view will become apparent below. We call these nested sequences 3-sequences.

We now note that all 3-sequences are generated by a relabeling of two types of 3-sequences.

By a type-I 3-sequence, we will mean a 3-sequence such as *AB, AC, AB* where the first and the third colliding pair are the same, or alternatively where one particle (in this case, particle *A*) is involved in all three collisions. A type-II 3-sequence will be a sequence such as *AB, AC, BC*, where all three possible two-particle collisions take place.

Now consider the type-I 3-sequence *AB, AC, AB*. The situation in velocity space is characterized by some velocity triangle after the collision *AB*. According to the 3-sequence the collision *AC* takes place in such a way to cause the collision *AB* to take place later. According to the ideas of Sec. IV, we can completely characterize the parameters of the velocity triangle prior to the second *AB* collision, given the situation after the first *AB* collision. The appropriate geometrical construction is given in Fig. 4. If we let ρ_2 be the magnitude of the velocity difference between the pair of particles which collide second (in this case, the distance *AC*), and ρ_1 be the magnitude of the velocity difference of the pair which collided first (in this case, the distance *AB*), and θ be the angle between these two velocities, we see geometrically from Fig. 4 that we have

$$\rho_3 = [2m_C \cos\theta/(m_A + m_C)]\rho_2 - \rho_1 \,.$$

The angle between ρ_3 and ρ_2 is the same as the angle between ρ_2 and ρ_1.

A similar construction may be used for the type-II 3-sequence. Figure 5 gives this construction for the 3-sequence *AB, AC, BC*. Again if we let ρ_1 be the magnitude of the velocity difference between particles *A* and *B* before the collision *AC*, ρ_2 be the magnitude of the velocity difference between particles *A* and *C*, and ρ_3 be the velocity difference between particles *B* and *C* after the *AC* collision, we have

$$\rho_3 = \left(\frac{m_C}{m_A + m_C}\cos\theta + \frac{m_A}{m_A + m_C}\cos\psi\right)\rho_2 - \rho_1 \,,$$

where θ is the angle between ρ_1 and ρ_2, ψ is the angle between ρ_2 and ρ_3; θ and ψ are related by $\sin\psi = (m_C/m_A)\sin\theta$.

VI. TERMINAL SEQUENCES

As we shall see, a sequence of kinematically possible collisions will always terminate. We shall now examine certain classes of kinematically possible sequences and their termination.

A basic rule of all allowed sequences is that the same pair of particles cannot collide twice in succession.

A second basic rule is that any allowed sequence can terminate at any point in that sequence by simply scattering out of the plane defined by the termination of the three velocity vectors. Any scattering out of the plane will certainly not allow the condition of Sec. IV to be met.

Now let us make explicit the types of the 3-sequences which make up a collision sequence. The sequence

AB, AC, AB, BC, AC, AB, AC

we will label

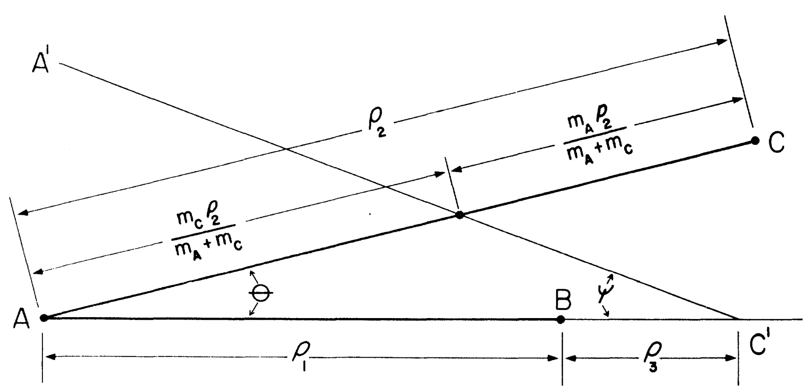

FIG. 4. Geometrical construction for a type-I 3-sequence.

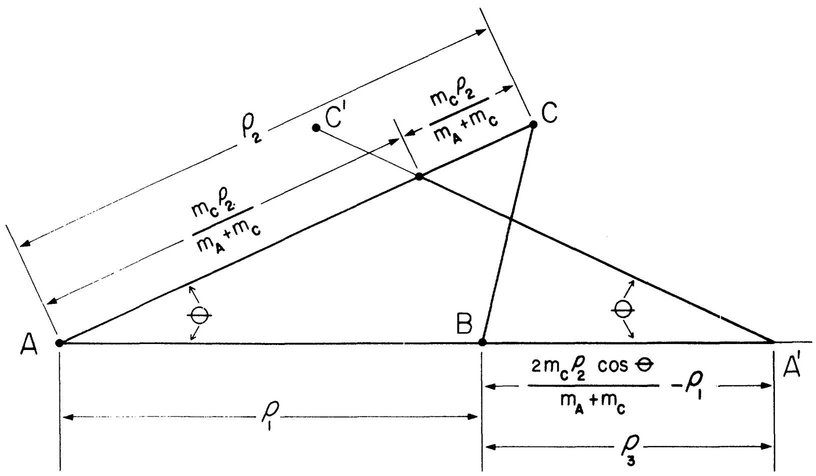

FIG. 5. Geometrical construction for a type-II 3-sequence.

$$AB(AC)_{\rm I}(AB)_{\rm II}(BC)_{\rm II}(AC)_{\rm II}(AB)_{\rm I}AC \ .$$

The notation needs further explanation. The letters inside the parenthesis indicate that the collision is the central member of a 3-sequence. The left-hand letter denotes the particle involved in the collision which preceded the collision in parenthesis. The subscript denotes the collision type, and hence implies a connection formula. From Sec. V, we see that the connection formulas are

(a) For $(AC)_{\rm I}$ the nth collision:

$$\rho_{n+1} = [2m_C \cos\psi/(m_A + m_C)]\rho_n - \rho_{n-1} \ .$$

(b) For $(AC)_{\rm II}$ the nth collision:

$$\rho_{n+1} = \left(\frac{m_C \cos\theta}{m_n + m_C} + \frac{m_n \cos\psi}{m_A + m_C}\right)\rho_n - \rho_{n-1} \ ,$$

where $\sin\psi = (m_A/m_C)\sin\theta$.

We will now demonstrate that a type-II 3-sequence can fall only at the beginning or the end of a sequence.

Consider the sequence of 3-sequences

$$(AC)_{\rm I}(AB)_{\rm II}(AC)_{\rm I} \ .$$

This sequence leads to the connection formulas:

$$\rho_{n+1} = [2m_c \cos\theta/(m_A + m_C)]\rho_n - \rho_{n-1} \ ,$$

$$\rho_{n+2} = \left(\frac{m_B \cos\theta + m_A \cos\psi}{m_A + m_B}\right)\rho_{n+1} - \rho_n \ ,$$

$$\sin\psi = (m_B/m_A)\sin\theta \ ,$$

$$\rho_{n+3} = [2m_c \cos\psi/(m_B + m_C)]\rho_{n+2} - \rho_{n+1} \ ,$$

which, after some algebra, yields

$$\rho_{n+3} = \left[\frac{2m_C \cos\psi}{m_B + m_C}\left(\frac{m_B(\cos\theta - 1) + m_A(\cos\psi - 1)}{m_A + m_B}\right) - \frac{2m_C \cos\theta}{m_A + m_C}\right]\rho_n$$
$$- \left(\frac{2m_C \cos\psi}{m_B + m_C}\,\frac{m_B \cos\theta + m_A \cos\psi}{m_A + m_B} - 1\right)\rho_{n-1} \ .$$

That both the coefficient of ρ_n and the coefficient of ρ_{n-1} are negative implies that

$$\rho_{n+3} < 0 \ ,$$

and hence the sequence is impossible. This result is independent of any particle masses or triangle parameters; thus, this is a demonstration that a type-II sequence may not occur between the two type-I sequences, and hence must occur either at the beginning or the end of a sequence.

We now demonstrate that a type-II 3-sequence may not occur at both the beginning and the end of a sequence.

Consider the sequence

$$AB, (AC)_{II}, (CB)_I, (CA)_I, (CB)_I, \dots ,$$

where the first 3-sequence is type II, and all remaining 3-sequences are type I. The connection formulas implied by this sequence are

$$\rho_3 = \left(\frac{m_C \cos\theta + m_A \cos\psi}{m_A + m_C}\right)\rho_2 - \rho_1 ,$$

$$\times \sin\psi = (m_C/m_A) \sin\theta ,$$

$$\rho_4 = [2m_B \cos\psi/(m_B + m_C)]\rho_3 - \rho_2 ,$$

$$\rho_5 = [2m_A \cos\psi/(m_B + m_C)]\rho_4 - \rho_3 .$$

The necessary condition for the third collision to be possible is

$$\rho_3 > 0 ,$$

which implies

$$\rho_2 > \rho_1 ,$$

since the factor

$$(m_C \cos\theta + m_A \cos\psi)/(m_A + m_C) \leq 1$$

for all θ, ψ. From this, it also follows that

$$\rho_2 > \rho_3 .$$

Examining the remaining type-I connection formulas, we observe that

$$\rho_{n+1} = \lambda_n \rho_n - \rho_{n-1} ,$$

$$\lambda_n \leq 2 .$$

Thus, $\rho_{n+1} - \rho_n = (\lambda_n - 1)\rho_n - \rho_{n-1}$,

and $\rho_n - \rho_{n-1} > \rho_{n+1} - \rho_n$.

Since we have demonstrated that

$$0 > \rho_3 - \rho_2 ,$$

we find that

$$0 > \rho_{n+1} - \rho_n .$$

Thus, the ρ_n decrease monotonically after a type-II 3-sequence. A second type-II 3-sequence would be possible only if, for some n

$$\rho_n > \rho_{n+1} .$$

Since we have shown that this does not happen if the sequence begins with a type-II 3-sequence, we have demonstrated that a sequence containing a type-II 3-sequence may only begin or end with that 3-sequence, but not with both.

Because of time-reversal invariance, a sequence which terminates in a type-II 3-sequence must be preceded by a type-I 3-sequence which leads to ρ_n's which are monotonically increasing in n.

VII. SEQUENCES WITH NO TYPE-II 3-SEQUENCES

An interesting class of sequence is that which contains no type-II sequences. We shall later demonstrate that this class of sequences contains the longest sequences possible, i.e., those with the greatest number of collisions. Consider the sequence

$$AB, AC, AB, AC, \dots ;$$

in our present notation this sequence is relabeled

$$(AC)_I (AB)_I (AC)_I \cdots .$$

This sequence implies the connection formulas

$$\rho_3 = x\rho_2 - \rho_1 , \quad \rho_4 = y\rho_3 - \rho_2 , \quad \rho_5 = x\rho_4 - \rho_3 ,$$

where $x = 2m_C \cos\theta/(m_A + m_C)$,

$$y = 2m_B \cos\theta/(m_A + m_B) .$$

The set of equations above may be converted into an ordinary second difference equation by the change of variable:

$$P_n = x^{1/2}\rho_n, \qquad n \text{ even}$$

$$P_n = y^{1/2}\rho_n, \qquad n \text{ odd} .$$

With this change of variable the equations read

$$P_{n+1} = (xy)^{1/2} P_n - P_{n-1} .$$

The solution to this equation is

$$P_n = A \cos n\phi + B \sin n\phi ,$$

where

$$\cos\phi = \tfrac{1}{2}(xy)^{1/2} = \left(\frac{m_B m_C}{(m_A+m_C)(m_A+m_C)}\right)^{1/2} \cos\theta \ .$$

The coefficients A and B may be evaluated by using our knowledge of the initial triangle parameters

$$A = \sin^{-1}\phi[y^{1/2}\rho_1 \sin 2\phi - x^{1/2}\rho_2 \sin\phi] \ ,$$

$$B = \sin^{-1}\phi[x^{1/2}\rho_2 \cos\phi - x^{1/2}\rho_1 \cos 2\phi] \ .$$

As we have indicated before, the nth collision is impossible if $\rho_n < 0$. The solution given above shows that ρ_n varies trigonometrically with n. The longest sequence of collisions of this type occurs when $\rho_1 = 0$ (the limit where first collision takes place between a pair of particles with 0 relative velocity). In this case,

$$P_n = P_2 \sin(n-1)\phi/\sin\phi \ ,$$

P_n, and hence ρ_n, will change from positive to negative when n is large enough. The maximum number of collisions is given by choosing an integer n_c to be largest integer such that

$$(n_c - 1)\phi < \pi \ .$$

The number n_c is maximized by making as small as possible which is achieved when θ is zero. This implies that the maximum number of collisions occurs when the first collision scattering angle is such that all of the resulting velocities are collinear. This is always possible for three particles. This bound on the number of collisions is

$$\frac{\pi}{n_c - 1} > \cos^{-1}\left(\frac{m_B m_C}{(m_A+m_B)(m_A+m_C)}\right)^{1/2} ,$$

where n_c is chosen to be the largest integer which satisfies the inequality.

The largest n_c will be obtained when particle A is the lightest particle. The sequence of collisions thus defined is the sequence where the lightest particle bounces back and forth between the two more massive particles.

If the three particles are of equal mass this inequality is met by a sequence of three collisions. The fourth collision is just barely impossible. Any departure from equality of masses will allow a fourth collision. This conclusion has been demonstrated previously by several authors.[1,2,4]

If the three particles do not have their velocities collinear, the maximum number of collisions is given by

$$\frac{\pi}{n_c - 1} > \cos^{-1}\left[\left(\frac{m_B m_C}{(m_A+m_C)(m_A+m_B)}\right)^{1/2} \cos\theta\right],$$

where n_c is the largest integer which satisfies the inequality.

In this case, the angle θ is the angle between the relative velocity of the first pair and second pair of particles which collide. This angle is a measure of the collinearity of the velocities after the first collision. It is thus demonstrated that the one-dimensional result does give an upper bound to the number of collisions, but that upper bound may be attained even though the particle velocities are not all aligned. As θ increases, the number of collisions decreases discontinuously to three at $\theta = \frac{1}{2}\pi$. If ρ_1 is nonzero, the third collision will not be possible at $\theta = \frac{1}{2}\pi$.

By applying the results of Sec. VI, we see that the sequences which contain no type-II 3-sequences are the longest. We showed in Sec. VI that a type-II 3-sequence may only begin or end a sequence. If we consider the case where the central member of a type-II 3-sequence is the nth collision, we know that the necessary condition for the $n+1$ (and last) collision is

$$\rho_{n-1} > \rho_n \ .$$

As we see from this section, this condition is met in the most favorable circumstance only for about half the length of the sequence of collisions ($n\phi \approx \frac{1}{2}\pi$), thus the type-II 3-sequence will terminate the square more rapidly than a continuation of type-I 3-sequences. A similar conclusion is reached if we consider a sequence which begins with a type-II 3-sequence.

Of course, sequences which begin with type-II 3-sequences lead to the same conclusion because of time-reversal invariance.

VIII. CONCLUSIONS

We have demonstrated that it is possible to form a geometrical construct which allows one to visualize the result of a succession of binary collisions. This construct allows one to follow a sequence of collisions to the point where no further collisions are possible among these particles when each collision individually conserves energy and momentum.

We confirm the result that every sequence of collisions terminates and that the longest sequence is defined by the lightest particle rebounding between the heavier pair of particles.

We find that the number of binary sequences which may occur is limited compared to what one might at first anticipate. We need only consider those sequences which consist of one particle rebounding between the other two, or sequences which begin or end with a 3-sequence in which all three pairs of particles are involved.

In the c.m. system the binary collisions of three particles will all lie in a plane determined by the velocity vector of the three particles. In addition, binary collisions are favored in a situation where the first collision causes the particle velocities to lie on a line. Binary collisions will occur, however, even if the collinear condition is not met. A useful condition for setting the upper bound to the number of collisions which may occur in a noncollinear situation is

$$\frac{\pi}{n_c - 1} > \cos^{-1}\left[\left(\frac{m_B m_C}{(m_A+m_B)(m_A+m_C)}\right)^{1/2} \cos\theta\right],$$

where n_c is the number of collisions and the largest integer which satisfies the inequality; m_A is the mass of the lightest particle; and θ is the angle between the relative velocity of the first and second pair of colliding particles.

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PHYSICAL REVIEW A VOLUME 1, NUMBER 2 FEBRUARY 1970

Spin-Projected Hartree-Fock Calculations on the He-Like Ions Using General Spin Orbitals*

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Spin-projected Hartree-Fock (PHF) wave functions are obtained for the isoelectronic series H^-, He, Li^+, and Be^{++}, using different orbitals for different spins and general spin-orbitals (GSO), in both cases of pure s character. The GSO energy for He is -2.87887 a.u., accounting for 99.1% of the radial correlation energy. A natural orbital analysis of the GSO function shows that it corresponds to a configuration interaction function with three s^2 configurations. The one-electron energies obtained from the PHF equations are given an interpretation as ionization energies. In the GSO case, the one-electron energies are not unique, but an upper limit is obtained.

I. INTRODUCTION

In the projected Hartree-Fock (PHF) method[1] the total wave function for a system of n electrons is written

$$\Psi = \mathcal{O}\Phi \quad, \tag{1}$$

where Φ is a Slater determinant built from n spin orbitals $[\psi_i(\vec{x}_j)]$,

$$\Phi = (n!)^{-1/2} |\psi_1(\vec{x}_1)\psi_2(\vec{x}_2), \ldots, \psi_n(\vec{x}_n)| , \tag{2}$$

and $\mathcal{O}$ is a projection operator[2] appropriate to the symmetry of the state considered. The total energy associated with the wave function (1) is

$$E_{av} = \langle \mathcal{O}\Phi | H | \mathcal{O}\Phi \rangle / \langle \mathcal{O}\Phi | \mathcal{O}\Phi \rangle$$
$$= \langle \Phi | \mathcal{O}H | \Phi \rangle / \langle \Phi | \mathcal{O} | \Phi \rangle \equiv \langle \mathcal{O}H \rangle / \langle \mathcal{O} \rangle \quad, \tag{3}$$

where H is the total Hamiltonian for the system. The second equality sign follows from the properties of the projection operator.[2] The best wave function of the form (1) is obtained by varying the spin orbitals in (2) in order to minimize the total energy

$$\delta \frac{\langle \mathcal{O}H \rangle}{\langle \mathcal{O} \rangle} = \frac{\langle \mathcal{O} \rangle \delta \langle \mathcal{O}H \rangle - \langle \mathcal{O}H \rangle \delta \langle \mathcal{O} \rangle}{\langle \mathcal{O} \rangle^2}$$