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Discrete Mechanics—A General Treatment

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A new numerical method for use in the solution of classical equations of motion is described, accurate to third-order in the coordinates and second-order in the velocities. The method has the unique property of preserving the energy and total linear and angular momenta at their initial values in the computation. This "discrete mechanics" is derived from general symmetry properties of the equations of motion and is compared in several numerical examples with conventional predictor-corrector methods. The theory is applied to derive a general expression for the impulsive limit of motion due to a potential.

1. INTRODUCTION

The problem of finding the trajectory which describes the motion of a system of bodies under the influence of a potential ϕ and subject to the laws of classical mechanics is, once again, of broad, general interest. After fifty years of dormancy during the rise of the theories of relativity and quantum mechanics, the new complexity of problems accessible via the use of numerical techniques and digital computers has led to a reinstatement of classical mechanics as a useful tool in modern physics.

In celestial mechanics, the wealth of detail now available from orbiting satellites allows a very precise description of the motion of the planets, which cannot be obtained from analytical methods [1]. Similarly, the launching of manned spacecraft has made real-time calculations of complicated trajectories a necessity in astrodynamics [1–2].

In chemical kinetics, molecular scattering theory, and the theory of molecular potentials, the typical size of the systems involved has become so large that quantal methods are no longer feasible: classical mechanics, although approximate, is now being applied as the only recourse in such systems (see, e.g., [3–4] for reviews). In statistical mechanics and fluid dynamics, increasing use is being made of the

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fundamental model of a large system of interacting particles, solved via the equations of motion (see, e.g., [5–10]).

In any of the applications above, the typical problem of determining the motion of several bodies is solved in the following way: the initial conditions are determined from experimental data or from analysis of the theory involved, the potential ϕ of interaction is specified, and the classical equations of motion are solved numerically. This last step has been executed using very simple finite-difference formulas for the derivatives, predictor-corrector and Runge-Kutta type methods, Taylor-Series expansions, etc. What is desired in every case (and has sometimes been lost from view) is a calculated solution which corresponds as closely as possible to the exact, continuous trajectory of motion. One problem common to all the above mentioned methods, as well as to analytical perturbation expansions, is the unbounded deviation from the exact result as the time t increases. Besides ultimately destroying the value of the computations, this makes the discovery of long-term periodic motions extremely difficult. Thus, even with the aid of numerical solutions, the question of the stability of the solar system is still unsettled [1].

In the present work, a new numerical method, called "discrete mechanics," which was previously displayed for the special case of a potential composed of powers and inverse-powers of the interparticle distances [11–12], is derived for the general case in which ϕ can be represented by a separable expansion. This "discrete mechanics," now shown to be applicable to all physically reasonable systems, has the property of the conservation of the additive constants of motion in common with continuous mechanics. The generalized form of "discrete mechanics" will be obtained by requiring the difference equations of the method to have the same combinatorial and transformational invariances as the differential equations of motion.

2. Classical Equations of Motion

The system to be considered here is that of the general "many-body" problem, which, for completeness and for notational purposes, is summarized as follows: Let n particles, indexed by $i = 1, 2, \ldots, n$, of masses m_i, respectively, be interacting according to a potential ϕ, which is a function only of the coordinates of the n particles. At time t, particle i has position vector $\rho_i = \langle X_i, Y_i, Z_i \rangle$ with respect to an inertial reference frame $OXYZ$. Let the velocity of particle i be denoted by $\dot{\rho}_i = d\rho_i/dt$, which has, e.g., an X-component of $\dot{X}_i = dX_i/dt$. The vector distance ρ_{ij} from particle i to particle j is given by

$$\rho_{ij} = \rho_j - \rho_i . \tag{2.1}$$

Typically, the potential ϕ is a function only of the interparticle radii ρ_{ij}:

$$\rho_{ij} = |\, \boldsymbol{\rho}_{ij} \,| = \sqrt{(X_j - X_i)^2 + (Y_j - Y_i)^2 + (Z_j - Z_i)^2} \tag{2.2}$$

These coordinates are shown in Fig. 1.

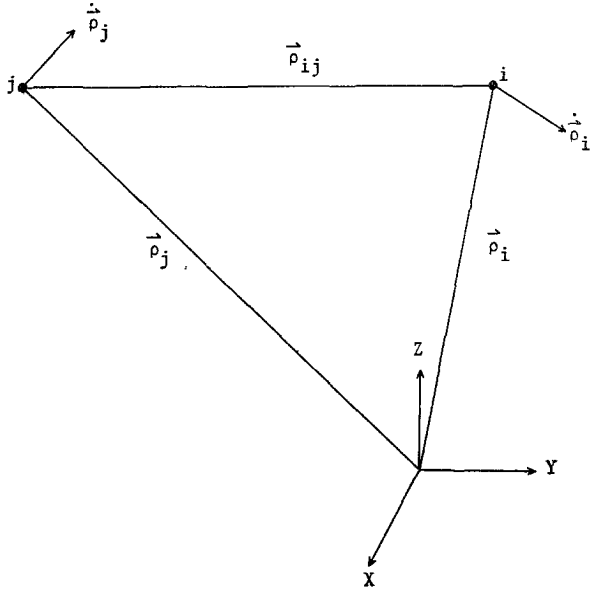

FIG. 1. Coordinates of particles i and j.

The kinetic energy T_i of particle i is defined by

$$T_i = \tfrac{1}{2} m_i(\dot{\boldsymbol{\rho}}_i \cdot \dot{\boldsymbol{\rho}}_i) = \tfrac{1}{2} m_i(\dot{X}_i^2 + \dot{Y}_i^2 + \dot{Z}_i^2) \tag{2.3}$$

and the total kinetic energy T of the system by

$$T = \sum_{i=1}^{n} T_i = \sum_{i=1}^{n} \tfrac{1}{2} m_i(\dot{X}_i^2 + \dot{Y}_i^2 + \dot{Z}_i^2) \tag{2.4}$$

Finally, the total energy E of the system is given by

$$E = T + \phi(\boldsymbol{\rho}_{12}, \boldsymbol{\rho}_{13}, \ldots, \boldsymbol{\rho}_{n-1,n}) \tag{2.5}$$

where ϕ is, in general, a function of the $N = n(n-1)/2$ interparticle radii $\boldsymbol{\rho}_{ij}$ $(i < j)$.

The problem to be solved is the following: given the position and velocity vectors $\boldsymbol{\rho}_i$ and $\dot{\boldsymbol{\rho}}_i$ $(i = 1, 2, \ldots, n)$ at some time t, find the position and velocity vectors $\boldsymbol{\rho}_i'$ and $\dot{\boldsymbol{\rho}}_i'$ at some later time $t' = t + \Delta t$. (In general primes will denote the

value at time t'). The exact solution is accomplished via Newton's equations of motion

$$m_i \ddot{\boldsymbol{\rho}}_i = \mathbf{F}_i \qquad (i = 1, 2, ..., n) \tag{2.6}$$

where $\ddot{\boldsymbol{\rho}}_i = d^2\boldsymbol{\rho}_i/dt^2$ is the acceleration of particle i, with, e.g., X-component $\ddot{X}_i = d^2X_i/dt^2$, and where $\mathbf{F}_i$ is the force on particle i. Here

$$\mathbf{F}_i = -\frac{\partial \phi}{\partial \boldsymbol{\rho}_i} \tag{2.7}$$

where $\partial/\partial\boldsymbol{\rho}_i$ denotes the gradient with respect to the coordinates X_i, Y_i, Z_i, i.e., $\partial/\partial\boldsymbol{\rho}_i = \langle \partial/\partial X_i, \partial/\partial Y_i, \partial/\partial Z_i \rangle$.

Newton's equations of motion (2.6), together with the initial conditions $\boldsymbol{\rho}_i$ and $\dot{\boldsymbol{\rho}}_i$ at time t, represent a system of second-order ordinary differential equations which can be solved in principle to find the $\boldsymbol{\rho}_i'$ and $\dot{\boldsymbol{\rho}}_i'$ at any time t'. In particular, for well behaved ϕ, Eq. (2.6) allow Taylor-Series expansions in Δt to be constructed, leading to

$$\boldsymbol{\rho}_i' = \boldsymbol{\rho}_i + \dot{\boldsymbol{\rho}}_i \Delta t + \ddot{\boldsymbol{\rho}}_i \frac{(\Delta t)^2}{2} + \cdots \tag{2.8a}$$

$$\dot{\boldsymbol{\rho}}_i' = \dot{\boldsymbol{\rho}}_i + \ddot{\boldsymbol{\rho}}_i \Delta t + \cdots \tag{2.8b}$$

where $\ddot{\boldsymbol{\rho}}_i$ is evaluated via Eq. (2.7), and the higher time-derivatives are obtained by the chain-rule and position derivatives of the forces, i.e.,

$$\frac{d}{dt} = \sum_{i=1}^{n} \dot{\boldsymbol{\rho}}_i \cdot \frac{\partial}{\partial \boldsymbol{\rho}_i} \tag{2.9a}$$

$$= \sum_{i=1}^{n} \left(\dot{X}_i \frac{\partial}{\partial X_i} + \dot{Y}_i \frac{\partial}{\partial Y_i} + \dot{Z}_i \frac{\partial}{\partial Z_i} \right) \tag{2.9b}$$

3. Conventional Numerical Solution

Typical methods for the numerical solution of the system of differential Eq. (2.6) involve finite-difference approximations for the derivatives (see, e.g., [6–9]), or the use of polynomial interpolation to give predictor-corrector or Runge-Kutta type methods (for review, see, e.g., [13]). This latter technique is illustrated by the following prototype, third-order Adams' corrector [14–15]:

$$\boldsymbol{\rho}_i' \simeq \boldsymbol{\rho}_i + \dot{\boldsymbol{\rho}}_i \Delta t + \ddot{\boldsymbol{\rho}}_i \left(\frac{\Delta t}{2}\right)^2 + \Delta\ddot{\boldsymbol{\rho}}_i \left(\frac{\Delta t}{6}\right)^2 \tag{3.1a}$$

$$\dot{\boldsymbol{\rho}}_i' \simeq \dot{\boldsymbol{\rho}}_i + \ddot{\boldsymbol{\rho}}_i \Delta t + \Delta\ddot{\boldsymbol{\rho}}_i \left(\frac{\Delta t}{2}\right) \tag{3.1b}$$

$$\ddot{\boldsymbol{\rho}}_i' = \ddot{\boldsymbol{\rho}}_i + \Delta\ddot{\boldsymbol{\rho}}_i \tag{3.1c}$$

Equation (3.1c) is used to define $\Delta\ddot{\rho}_i$. The use of Eqs. (3.1) leads to errors in the computed values of ρ_i' and $\dot{\rho}_i'$ which are proportional to $(\Delta t)^4$ and $(\Delta t)^3$, respectively; thus if Δt is small, Eqs. (3.1) give a good approximation to the exact solution. Since Eqs. (3.1) are implicit and nonlinear in ρ_i' via $\ddot{\rho}_i'$, they must be solved iteratively. Typically, "predicted" values for ρ_i' and $\dot{\rho}_i'$ are obtained via Eqs. (3.1) with $\Delta\ddot{\rho}_i$ set to zero. These first approximations are then refined via functional iteration of Eqs. (3.1) until suitable convergence is obtained.

Since the accuracy and convergence of Eqs. (3.1) depend upon the size of Δt, large time intervals are broken into smaller time increments, and the solution determined sequentially over these subintervals. Because of this, errors made in the early steps propagate through the later steps, leading to the problem of "stability" with respect to errors. The implicit nature of Eqs. (3.1) does much to alleviate this, but all methods of this type are subject to an amplification effect as the number of steps becomes large.

4. Constants of Motion and "Conservative" Numerical Methods

As is well-known [16], certain invariances of the classical equations of motion are reflected in the time-independence of certain functions of the positions and velocities. The stationary values of these functions are called the "constants of motion" of the system.

A. *Energy*

If the potential function ϕ does not depend explicitly upon the time t or the velocities $\dot{\rho}_i$, then the same trajectory occurs (but is traced out in reverse order) if t and t' are interchanged (i.e., $\Delta t \to -\Delta t$) and the $\dot{\rho}_i'$ replaced with $-\dot{\rho}_i'$. This effect is called the "principle of invariance with respect to time-reversal," and as a consequence the value of the Hamiltonian functional H

$$H = T + \phi \tag{4.1}$$

is "conserved," i.e., takes on a constant value (the total energy) which is independent of time. This "principle of conservation of energy" is summarized in the equations $H(t) = E$, or

$$\Delta H = H' - H = 0 \tag{4.2}$$

for all Δt.

B. *Linear Momentum*

If the potential ϕ is independent of the origin of the coordinate system, e.g., is a function of the ρ_{ij} only, then the equations of motion are independent of a translation of the coordinate system (Galilean invariance). Because of this, the total linear momentum **P**, defined by

$$\mathbf{P} = \sum_{i=1}^{n} m_i \dot{\boldsymbol{\rho}}_i \tag{4.3}$$

is a constant of the motion, i.e., $\mathbf{P}' = \mathbf{P}$ for all Δt.

If **R** is a position vector pointing to the center-of-mass of the system, i.e.,

$$M\mathbf{R} = \sum_{i=1}^{n} m_i \boldsymbol{\rho}_i \tag{4.4}$$

where M is the total mass

$$M = \sum_{i=1}^{n} m_i \tag{4.5}$$

then

$$\mathbf{P} = M\dot{\mathbf{R}} \tag{4.6}$$

and consequently the center-of-mass simply translates ($\dot{\mathbf{R}}$ constant) with time:

$$\mathbf{R}' = \mathbf{R} + \Delta t\, \mathbf{P}/M. \tag{4.7}$$

C. *Angular Momentum*

When the potential ϕ is independent of the orientation of the reference coordinate system, e.g., depends only upon scalars such as the ρ_{ij} or ρ_i, then the classical equations of motion are invariant with respect to a rotation of the coordinate frame. In this case, "space is isotropic," and the total angular momentum **L**, defined by

$$\mathbf{L} = \sum_{i=1}^{n} \mathbf{L}_i \tag{4.8}$$

where

$$\mathbf{L}_i = m_i \boldsymbol{\rho}_i \times \dot{\boldsymbol{\rho}}_i \qquad (i = 1, 2, \ldots, n) \tag{4.9}$$

is conserved, i.e.,

$$\Delta\mathbf{L} = \mathbf{L}' - \mathbf{L} = \mathbf{0} \tag{4.10}$$

Any numerical method of solution of the equations of motion which maintains the constants of motion at their initial values will be called "conservative." For example, in order to conserve energy $\Delta E = E' - E$ must be zero for each step, as calculated via Eq. (2.5). No other definition of "conservative" is consistent with that of classical mechanics. If a numerical method conserves energy, it is "better" in the sense of sharing a property with the exact, continuous solution. It is important to make a distinction between *exact* "conservation" as given here, and tautological definitions of "conservation" used by some authors [6–8] where, for example, ϕ is redefined to include the imbalance ΔE so that "conservation" occurs. This fallacy becomes most evident when a single time-step is considered.

It might be expected that any numerical method whose difference equations possess the same symmetries as the differential equations of motion would have the same invariant constants of motion. For example, any method which leads to the exact result for a constant acceleration will give zero acceleration of the center-of-mass **R**, thus preserving linear momentum and the center-of-mass motion of Eq. (4.7). Conservation of energy and angular momentum are, however, much more stringent requirements for a numerical method.

5. Discrete Mechanics

In conventional interpolatory numerical methods for solving the equations of motion, the differential Eqs. (2.6) and (2.7) specifying the accelerations are taken as defining the motion. In other words, conventional methods correspond to the approximate motion resulting from the use of *exact* forces. Since the constants of motion are *integral* properties of the differential equations, the functionals involved (i.e., H, **P**, **L**) are stationary only to the order of numerical approximation. The question of interest is how to design a numerical method whose difference equations (and their solution) have the same symmetries (and hence the same constants of motion) as the exact differential equations of motion (and their solution). With suitable restrictions, this question is answered by the method of "discrete mechanics" described below. Part of the results obtained for the special-case in which ϕ consists of pairwise-additive terms of the power or inverse-power type were presented previously ([11–12]) in an *ad hoc* way.

In what follows, the role of the Hamiltonian H is taken as paramount, since this functional contains all of the necessary information concerning the motion (via Hamilton's canonical equations). The lowest order problem is that of finding $\mathbf{a}_i^{(1)}$ and $\mathbf{a}_i^{(2)}$ such that the solution ($i = 1, 2, \ldots, n$)

$$\boldsymbol{\rho}_i' = \boldsymbol{\rho}_i + \dot{\boldsymbol{\rho}}_i \Delta t + \tfrac{1}{2}\mathbf{a}_i^{(1)}(\Delta t)^2 \tag{5.1a}$$

$$\dot{\boldsymbol{\rho}}_i' = \dot{\boldsymbol{\rho}}_i + \mathbf{a}_i^{(2)} \Delta t \tag{5.1b}$$

has the appropriate properties (i.e., satisfies conservation principles). For example, the method of Eqs. (3.1) is characterized by

$$\mathbf{a}_i^{(1)} = \tfrac{1}{3}(2\mathbf{a}_i + \mathbf{a}_i') \tag{5.2a}$$

$$\mathbf{a}_i^{(2)} = \tfrac{1}{2}(\mathbf{a}_i + \mathbf{a}_i') \tag{5.2b}$$

and has the property that the solution is of the highest order of exactness (error proportional to $(\Delta t)^4$ and $(\Delta t)^3$ in ρ_i' and $\dot{\rho}_i'$, respectively). Since energy conservation will be required, the Eqs. (5.1) must be symmetric with respect to time reversal. In "discrete mechanics" only the more basic problem where $\mathbf{a}_i^{(1)} = \mathbf{a}_i^{(2)} = \mathbf{a}_i{}^*$ will be considered:

$$\rho_i' = \rho_i + \dot{\rho}_i \Delta t + \mathbf{a}_i{}^* \frac{(\Delta t)^2}{2} \tag{5.3a}$$

$$\dot{\rho}_i' = \dot{\rho}_i + \mathbf{a}_i{}^* \Delta t \tag{5.3b}$$

For convenience in later formula manipulations, note that Eqs. (5.3) imply

$$\dot{\rho}_i' - \dot{\rho}_i = \mathbf{a}_i{}^* \Delta t$$

$$\frac{\dot{\rho}_i' + \dot{\rho}_i}{2} = \dot{\rho}_i + \frac{1}{2}\mathbf{a}_i{}^* \Delta t$$

$$\frac{\dot{\rho}_i' + \dot{\rho}_i}{2} = \frac{\rho_i' - \rho_i}{\Delta t}.$$

A. *One Particle Subject to a Central Force*

Suppose $n = 1$ and the single particle is moving under the influence of a central potential, i.e.,

$$\phi(\rho) = \phi(\rho) \tag{5.4}$$

Then, since ϕ is neither a function of t nor of the orientation of the coordinate system $OXYZ$, E and $\mathbf{L}$ are constants of the classical motion. However, ϕ is *not* independent of the origin O, so $\mathbf{P}$ is not conserved. The problem is to find $\mathbf{a}^*$ such that E and $\mathbf{L}$ are also constants of the discrete motion.

First consider conservation of the energy E. Now

$$\Delta E = \Delta T + \Delta\phi \tag{5.5}$$

where

$$\Delta T = \tfrac{1}{2}m[(\dot{\rho}' \cdot \dot{\rho}') - (\dot{\rho} \cdot \dot{\rho})] \tag{5.6a}$$

$$= \tfrac{1}{2}m[\dot{X}'^2 + \dot{Y}'^2 + \dot{Z}'^2 - \dot{X}^2 - \dot{Y}^2 - \dot{Z}^2] \tag{5.6b}$$

$$= \tfrac{1}{2}m[(\dot{X}'^2 - \dot{X}^2) + (\dot{Y}'^2 - \dot{Y}^2) + (\dot{Z}'^2 - \dot{Z}^2)] \tag{5.6c}$$

and

$$\Delta\phi = \phi(\rho') - \phi(\rho) \tag{5.7}$$

(For simplicity of notation, the dependence on ρ and ρ' will be denoted simply by $\phi' = \phi(\rho')$ and $\phi = \phi(\rho)$). The requirement is that $\Delta E = 0$ for an arbitrary time step Δt, i.e.,

$$\Delta T = -\Delta\phi \tag{5.8}$$

Noting that, from (5.3),

$$\Delta T = \tfrac{1}{2}m(\dot{\boldsymbol{\rho}}' - \dot{\boldsymbol{\rho}}) \cdot (\dot{\boldsymbol{\rho}}' + \dot{\boldsymbol{\rho}}) \tag{5.9a}$$

$$= m\mathbf{a}^* \cdot (\boldsymbol{\rho}' - \boldsymbol{\rho}) \tag{5.9b}$$

$$= \mathbf{F}^* \cdot \Delta\boldsymbol{\rho} \tag{5.9c}$$

where $\mathbf{F}^* = m\mathbf{a}^*$ and $\Delta\boldsymbol{\rho} = \boldsymbol{\rho}' - \boldsymbol{\rho}$, the energy equation becomes

$$\mathbf{F}^* \cdot \Delta\boldsymbol{\rho} = -\Delta\phi \tag{5.10}$$

This equation must be solved for $\mathbf{F}^*$ in such a way that: (1) $\mathbf{F}^*$ is symmetric (except for a change of sign) with respect to time-reversal (interchange of $\boldsymbol{\rho}'$ and $\boldsymbol{\rho}$); and (2) no coordinate X, Y, or Z is treated differently from the others (this condition is required by conservation of $\mathbf{L}$). A solution is considered to be given if an equation of the form

$$\mathbf{F}^* = \mathbf{G}(\mathbf{F}^*) \tag{5.11}$$

exists, from which $\mathbf{F}^*$ is solvable by iterative means.

Suppose

$$\mathbf{F}^* = F^*\hat{n} \tag{5.12}$$

where F^* is the signed magnitude of $\mathbf{F}^*$ and $\hat{n}$ is a unit vector in the direction of $\mathbf{F}^*$. Clearly equation (5.10) is sufficient to fix F^*, given $\hat{n}$:

$$F^* = -\frac{\Delta\phi}{\hat{n} \cdot \Delta\boldsymbol{\rho}} \tag{5.13}$$

(If $\hat{n} \cdot \Delta\boldsymbol{\rho} = 0$, any value of F^* conserves energy). What direction of $\hat{n}$ is appropriate? It is required that Eq. (5.10) hold for: (1) all initial conditions $\boldsymbol{\rho}$ and $\dot{\boldsymbol{\rho}}$; (2) all time steps Δt; (3) all ϕ satisfying equation (5.4). Under these constraints, the most general form for $\hat{n}$ is

$$\hat{n} = \alpha\boldsymbol{\rho}' + \beta\boldsymbol{\rho} \tag{5.14}$$

Otherwise one side of Eq. (5.10) would have explicit dependence on quantities such as $\dot{\boldsymbol{\rho}}$, which does not occur on the other side. Now

$$\hat{n} \cdot \Delta\boldsymbol{\rho} = \alpha\rho'^2 - (\alpha - \beta)\boldsymbol{\rho}' \cdot \boldsymbol{\rho} + \beta\rho^2 \tag{5.15}$$

and the right-hand side of equation (5.10) is $\Delta\phi$, which is independent of the term $\boldsymbol{\rho}' \cdot \boldsymbol{\rho}$ (which is anisotropic). Therefore $\alpha = \beta$ and, since $\hat{n}$ is a unit vector,

$$\hat{n} = \frac{\boldsymbol{\rho}' + \boldsymbol{\rho}}{|\boldsymbol{\rho}' + \boldsymbol{\rho}|} \tag{5.16}$$

Combining Eqs. (5.12), (5.13) and (5.16), the final form for $\mathbf{F}^*$ is

$$\mathbf{F}^* = -\frac{\Delta\phi}{\Delta\rho^2}(\boldsymbol{\rho}' + \boldsymbol{\rho}) \tag{5.17}$$

where $\Delta\rho^2 = \rho'^2 - \rho^2 = (\rho' - \rho)(\rho' + \rho) = (\boldsymbol{\rho}' - \boldsymbol{\rho}) \cdot (\boldsymbol{\rho}' + \boldsymbol{\rho})$.

The above expression (5.17) for $\mathbf{F}^*$ is, via (5.3), in the form of Eq. (5.11) with

$$\mathbf{G}(\mathbf{F}^*) = -\frac{\Delta\phi}{\Delta\rho^2}(\boldsymbol{\rho}' + \boldsymbol{\rho})$$

Since Eq. (5.17) may also be written

$$\mathbf{F}^* = -\frac{\Delta\phi}{\Delta\rho}\frac{\boldsymbol{\rho}' + \boldsymbol{\rho}}{\rho' + \rho}$$

then

$$\lim_{\Delta t \to 0} \mathbf{F}^* = -\frac{d\phi}{d\rho}\hat{\rho} = \mathbf{F}$$

where $\hat{\rho} = \boldsymbol{\rho}/\rho$ and $\mathbf{F}$ is the exact force given by Eq. (2.7). Therefore, the right-hand side of Eq. (5.17), i.e., $\mathbf{G}$, is to lowest-order in Δt independent of $\mathbf{F}^*$. Hence, for small enough Δt, Eq. (5.17) can always be solved by simple functional iteration.

The direction $\hat{n}$ of $\mathbf{F}^*$ may be obtained in a direct way from conservation of angular momentum. Now,

$$\Delta\mathbf{L} = \mathbf{L}' - \mathbf{L} \tag{5.18a}$$

$$= m[(\boldsymbol{\rho}' \times \dot{\boldsymbol{\rho}}') - (\boldsymbol{\rho} \times \dot{\boldsymbol{\rho}})] \tag{5.18b}$$

$$= \tfrac{1}{2}m[(\boldsymbol{\rho}' + \boldsymbol{\rho}) \times (\dot{\boldsymbol{\rho}}' - \dot{\boldsymbol{\rho}}) + (\boldsymbol{\rho}' - \boldsymbol{\rho}) \times (\dot{\boldsymbol{\rho}}' + \dot{\boldsymbol{\rho}})] \tag{5.18c}$$

Thus, from Eq. (5.3),

$$\Delta\mathbf{L} = m\left[\frac{\boldsymbol{\rho}' + \boldsymbol{\rho}}{2} \times \mathbf{a}^* \Delta t + (\boldsymbol{\rho}' - \boldsymbol{\rho}) \times \frac{\boldsymbol{\rho}' - \boldsymbol{\rho}}{\Delta t}\right] \tag{5.19}$$

Since, for all vectors **b**,

$$\mathbf{b} \times \mathbf{b} = \mathbf{0} \tag{5.20}$$

then

$$\Delta\mathbf{L} = m\,\Delta t\,\frac{\boldsymbol{\rho}' + \boldsymbol{\rho}}{2} \times \mathbf{a}^* \tag{5.21a}$$

$$= \Delta t\,\frac{\boldsymbol{\rho}' + \boldsymbol{\rho}}{2} \times \mathbf{F}^* \tag{5.21b}$$

By virtue of the constraints mentioned above that $\Delta\mathbf{L} = \mathbf{0}$ independently of the values given to Δt, $\boldsymbol{\rho}$, $\boldsymbol{\rho}'$ (via $\dot{\boldsymbol{\rho}}$), and $\phi(\rho)$, Eqs. (5.21) must vanish because the cross-product is identically zero, i.e., $\hat{n}$ lies along $\boldsymbol{\rho}' + \boldsymbol{\rho}$. This leads to the result given in Eq. (5.17), where the equivalent argument that $\hat{n}$ was independent of $\boldsymbol{\rho}' \cdot \boldsymbol{\rho}$ was used.

Thus, conservation of energy gives the *magnitude*, and conservation of angular momentum the *direction*, of the force expression for $\mathbf{F}^*$ which maintains E and $\mathbf{L}$ at their initial values for all values of Δt, $\boldsymbol{\rho}$, $\dot{\boldsymbol{\rho}}$, and $\phi(\rho)$. The solution to equations (5.17) and (5.3) agrees with the exact solution to terms of order $(\Delta t)^3$ and $(\Delta t)^2$ in $\boldsymbol{\rho}'$ and $\dot{\boldsymbol{\rho}}'$, respectively, and exactly conserves the energy and all components of the angular momentum. This is the type of solution which characterizes "discrete mechanics."

B. *System of Several Particles with Pairwise-Additive Forces*

Suppose there are n particles with coordinates as described in Section 2, and the potential ϕ is of the special form

$$\phi(\rho_{12}, \rho_{13}, \ldots, \rho_{n-1,n}) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \phi_{ij}(\rho_{ij}) \tag{5.22}$$

where, as before, $\rho_{ij} = |\,\boldsymbol{\rho}_{ij}\,| = |\,\boldsymbol{\rho}_j - \boldsymbol{\rho}_i\,|$. For convenience, set

$$\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} = \sum_{i<j} \tag{5.23}$$

and denote $\phi_{ij}(\rho'_{ij})$ by ϕ'_{ij}. Since ϕ is a function of the difference vectors $\boldsymbol{\rho}_{ij}$, total linear momentum $\mathbf{P}$ is conserved by the exact motion. Similarly, dependence only upon the magnitudes ρ_{ij} indicates $\mathbf{L}$ is to be conserved. The problem is to find the "discrete mechanics" forces $\mathbf{a}_i^*$ $(i = 1, 2, \ldots, n)$ which conserve these quantities, as well as energy.

For the case of several particles, the change ΔT in the kinetic energy over the time step Δt is given (via Eqs. (5.3)) by:

$$\Delta T = \sum_{i=1}^{n} \tfrac{1}{2} m_i [(\dot{\boldsymbol{\rho}}_i' \cdot \dot{\boldsymbol{\rho}}_i') - (\dot{\boldsymbol{\rho}}_i \cdot \dot{\boldsymbol{\rho}}_i)] \tag{5.24a}$$

$$= \sum_{i=1}^{n} \mathbf{F}_i^* \cdot \Delta \boldsymbol{\rho}_i \tag{5.24b}$$

where $\mathbf{F}_i^* = m_i \mathbf{a}_i^*$ and $\Delta \boldsymbol{\rho}_i = \boldsymbol{\rho}_i' - \boldsymbol{\rho}_i$.

1. *Linear Momentum*

The change $\Delta \mathbf{P}$ in total linear momentum over the time step is

$$\Delta \mathbf{P} = \sum_{i=1}^{n} m_i (\dot{\boldsymbol{\rho}}_i' - \dot{\boldsymbol{\rho}}_i) \tag{5.25a}$$

$$= \Delta t \sum_{i=1}^{n} \mathbf{F}_i^* \tag{5.25b}$$

If $\Delta \mathbf{P}$ is to be zero independently of Δt, the particular values of the coordinates $\boldsymbol{\rho}_i$, and a constant velocity of $OXYZ$, the sum of the forces $\mathbf{F}_i^*$ must be zero from general considerations. In continuous mechanics, because ϕ is pairwise-additive, so are the forces, i.e.

$$\mathbf{F}_i = -\sum_{j=i+1}^{n} \mathbf{F}_{ij} + \sum_{j=1}^{i-1} \mathbf{F}_{ji} \tag{5.26}$$

where

$$\mathbf{F}_{ij} = -\frac{\partial \phi_{ij}}{\partial \boldsymbol{\rho}_{ij}} \tag{5.27}$$

i.e., the gradient of ϕ_{ij} with respect to $X_{ij} = X_j - X_i$, etc. This follows from Eq. (2.7) and the chain-rule:

$$\frac{\partial}{\partial \boldsymbol{\rho}_i} = -\sum_{j=i+1}^{n} \frac{\partial}{\partial \boldsymbol{\rho}_{ij}} + \sum_{j=1}^{i-1} \frac{\partial}{\partial \boldsymbol{\rho}_{ji}} \tag{5.28}$$

Note that Eq. (5.26) must hold: (1) for the case of constant forces (i.e., to lowest-order in Δt); and (2) for all values of the ρ_{ij}, even as $\rho_{kl} \to \infty$ for all pairs $k_l \neq ij$ (i.e., arbitrary n). Therefore Eq. (5.26) is a general requirement, and

$$\mathbf{F}_i^* = -\sum_{j=i+1}^{n} \mathbf{F}_{ij}^* + \sum_{j=1}^{i-1} \mathbf{F}_{ji}^* \tag{5.29}$$

where the $\mathbf{F}_{ij}^*$ are now unknown. Subject to this condition,

$$\frac{\Delta \mathbf{P}}{\Delta t} = \sum_{i=1}^{n} \mathbf{F}_i^* \tag{5.30a}$$

$$= -\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \mathbf{F}_{ij}^* + \sum_{i=2}^{n} \sum_{j=1}^{i-1} \mathbf{F}_{ji}^* \tag{5.30b}$$

$$= -\sum_{i<j} \mathbf{F}_{ij}^* + \sum_{i<j} \mathbf{F}_{ij}^* \tag{5.30c}$$

$$= \mathbf{0} \tag{5.30d}$$

and thus $\mathbf{P}$ is conserved for any values of the $\mathbf{F}_{ij}^*$ $(i < j)$. This is consistent with the remark made at the end of Section 2 that any method accurate to $(\Delta t)^2$ (i.e., exact for constant forces) conserves linear momentum and the center-of-mass motion.

2. *Energy*

Using relation (5.29), ΔT may be rewritten as

$$\Delta T = \sum_{i=1}^{n} \mathbf{F}_i^* \cdot \Delta \boldsymbol{\rho}_i \tag{5.31a}$$

$$= \sum_{i=1}^{n} \left[-\sum_{j=i+1}^{n} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_i + \sum_{j=1}^{i-1} \mathbf{F}_{ji}^* \cdot \Delta \boldsymbol{\rho}_i \right] \tag{5.31b}$$

$$= -\sum_{i<j} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_i + \sum_{j=1}^{n-1} \sum_{i=j+1}^{n} \mathbf{F}_{ji}^* \cdot \Delta \boldsymbol{\rho}_i \tag{5.31c}$$

$$= -\sum_{i<j} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_i + \sum_{i<j} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_j \tag{5.31d}$$

$$= \sum_{i<j} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_{ij} \tag{5.31e}$$

In order to have $\Delta E = 0$, $\Delta T = -\Delta \phi$, or

$$\sum_{i<j} \mathbf{F}_{ij}^* \cdot \Delta \boldsymbol{\rho}_{ij} = -\Delta \phi \tag{5.32}$$

But, via Eq. (5.22),

$$\Delta \phi = \sum_{i<j} \Delta \phi_{ij} \tag{5.33}$$

where $\Delta\phi_{ij} = \phi'_{ij} - \phi_{ij}$, and letting $\Delta T_{ij} = \mathbf{F}^*_{ij} \cdot \Delta\boldsymbol{\rho}_{ij}$ yields

$$\sum_{i<j} \Delta T_{ij} = -\sum_{i<j} \Delta\phi_{ij} \tag{5.34}$$

or

$$\sum_{i<j} [\Delta T_{ij} + \Delta\phi_{ij}] = 0 \tag{5.35}$$

Now Eq. (5.35) must hold for all Δt, all initial conditions $\boldsymbol{\rho}_i$ and $\dot{\boldsymbol{\rho}}_i$, and all functions ϕ_{ij}. It is important to note that the distinguishability of the n particles is a consequence only of their different initial conditions $\boldsymbol{\rho}_i$ and $\dot{\boldsymbol{\rho}}_i$, and the interactions ϕ_{ij}. The invariance of Eq. (5.35) with respect to these quantities implies an invariance with respect to any reordering of the particles. Thus the principle of indistinguishability of particles requires *each* term in Eq. (5.35) vanish independently, i.e.,

$$\Delta T_{ij} + \Delta\phi_{ij} = 0 \qquad (i < j) \tag{5.36}$$

or

$$\mathbf{F}^*_{ij} \cdot \Delta\boldsymbol{\rho}^*_{ij} = -\Delta\phi_{ij} \qquad (i < j) \tag{5.37}$$

This fixes the *magnitude* of each $\mathbf{F}^*_{ij}$. Since ϕ_{ij} depends only upon the scalar ρ_{ij} ($\mathbf{L}$ conserved), the principle of isotropy of space fixes (as in Section 5.A) the *directions* of the $\mathbf{F}^*_{ij}$:

$$\mathbf{F}^*_{ij} = -\frac{\Delta\phi_{ij}}{\Delta\rho^2_{ij}} (\boldsymbol{\rho}'_{ij} + \boldsymbol{\rho}_{ij}) \qquad (i < j) \tag{5.38}$$

Equation (5.38) gives an implicit expression for $\mathbf{F}^*_{ij}$, which may be found by solving Eqs. (5.3), (5.29), and (5.38) iteratively, using, e.g., the starting values $\mathbf{F}^*_{ij} = 0$. Such a solution by functional iteration will always exist for small enough Δt.

3. *Angular Momentum*

By virtue of Eq. (4.8), $\Delta\mathbf{L}$ is given by the simple generalization of Eq. (5.21b):

$$\Delta\mathbf{L} = \Delta t \sum_{i=1}^{n} \frac{\boldsymbol{\rho}_i{}' + \boldsymbol{\rho}_i}{2} \times \mathbf{F}_i{}^* \tag{5.39}$$

By substitution of Eq. (5.29), and a procedure similar to that followed in Eq. (5.30),

$$\frac{\Delta\mathbf{L}}{\Delta t} = \sum_{i<j} \frac{\boldsymbol{\rho}'_{ij} + \boldsymbol{\rho}_{ij}}{2} \times \mathbf{F}^*_{ij} \tag{5.40}$$

As in the case of conservation of E and $\mathbf{P}$, if $\Delta\mathbf{L}$ is to be zero for all values of the ρ_{ij} and ρ'_{ij}, each term in Eq. (5.40) must be zero *separately*:

$$(\rho'_{ij} + \rho_{ij}) \times \mathbf{F}^*_{ij} = \mathbf{0} \qquad (i < j) \tag{5.41}$$

Equation (5.41) can hold only for all ρ_{ij} (arbitrary rotations of $OXYZ$) if $\mathbf{F}^*_{ij}$ lies along $\rho'_{ij} + \rho_{ij}$. This constraint, together with Eqs. (5.37), gives Eqs. (5.38).

It is interesting to note that, because of the identical forms of the pairs of Eqs. (5.31a) and (5.31b), and (5.39) and (5.40), a solution has also been found for the case of a potential ϕ of the form

$$\phi(\rho_1, \ldots, \rho_n) = \sum_{i=1}^{n} \phi_i(\rho_i) \tag{5.42}$$

Here Eq. (5.37) becomes

$$\mathbf{F}_i^* \cdot \Delta\rho_i = -\Delta\phi_i \qquad (i = 1, 2, \ldots, n) \tag{5.43}$$

which imply (via (5.39)).

$$\mathbf{F}_i^* = \frac{\Delta\phi_i}{\Delta\rho_i^2}(\rho_i' + \rho_i) \qquad (i = 1, 2, \ldots, n) \tag{5.44}$$

Equation (5.44) is a direct generalization of Eq. (5.17). Of course, since the ϕ of Eq. (5.42) is directly dependent on $OXYZ$ via the ρ_i, the total linear momentum $\mathbf{P}$ is no longer conserved.

C. *System of Several Particles with a General Separable Potential*

In this section, the results of the preceding sections will be used to obtain a "discrete mechanics" solution which conserves energy and both linear and angular momenta for the most general potential for which such a solution may be obtained.

Consider a potential ϕ which is a sum of terms $\phi^{(\ell)}$:

$$\phi = \sum_{\ell=1}^{\infty} \phi^{(\ell)}, \tag{5.45}$$

each of which is a separable product of $\phi_{ij}^{(\ell)}$:

$$\phi^{(\ell)}(\rho_{12}, \rho_{13}, \ldots, \rho_{n-1,n}) = \phi_{12}^{(\ell)}(\rho_{12})\, \phi_{13}^{(\ell)}(\rho_{13}) \times \cdots \times \phi_{n-1,n}^{(\ell)}(\rho_{n-1,n}) \tag{5.46a}$$

$$= \prod_{i<j} \phi_{ij}^{(\ell)}, \tag{5.46b}$$

where each $\phi_{ij}^{(\ell)}$ is arbitrary. This form for ϕ includes, in particular, Taylor and Laurent series expansions in terms of powers and inverse-powers of the ρ_{ij}'s, as well as Fourier expansions, etc.

In order for linear momentum $\mathbf{P}$, energy E, and angular momentum $\mathbb{L}$ to be conserved over the time step Δt, relations (5.29), (5.32), and (5.41) must hold for all $\boldsymbol{\rho}_{ij}$ and Δt. The problem, as before, is to find the $\mathbf{F}_{ij}^*$ which satisfy these conditions. Since each of these equations is linear in the $\mathbf{F}_{ij}^*$ and must hold for an arbitrary expansion (5.45), $\mathbf{F}_{ij}^*$ may be expanded correspondingly as

$$\mathbf{F}_{ij}^* = \sum_{\ell=1}^{\infty} \mathbf{F}_{ij}^{*(\ell)} \tag{5.47}$$

where

$$\sum_{i<j} \mathbf{F}_{ij}^{*(\ell)} \cdot \Delta\boldsymbol{\rho}_{ij} = -\Delta\phi^{(\ell)} \tag{5.48a}$$

$$(\boldsymbol{\rho}'_{ij} + \boldsymbol{\rho}^*_{ij}) \times \mathbf{F}_{ij}^{*(\ell)} = \mathbf{0} \tag{5.48b}$$

i.e., each term in the potential may be treated separately, and the results added. Therefore it suffices to consider a single term of the form

$$\phi = \prod_{i<j} \phi_{ij}(\rho_{ij}) \tag{5.49}$$

and the results for a general potential such as that of equation (5.45) composed via Eq. (5.47).

In order to solve

$$\sum_{i<j} \Delta T_{ij} = -\Delta\phi \tag{5.50}$$

where $\Delta T_{ij} = \mathbf{F}_{ij}^* \cdot \Delta\boldsymbol{\rho}_{ij}$ and

$$\Delta\phi = \prod_{i<j} \phi'_{ij} - \prod_{i<j} \phi_{ij}\,, \tag{5.51}$$

the nature of the solutions found in Sections 5.A and 5.B should be kept in mind. Because of the invariance with respect to time-reversal, ΔT_{ij} must be antisymmetric with respect to interchange of the $\boldsymbol{\rho}'_{k\ell}$ and $\boldsymbol{\rho}_{k\ell}$. The solution found for ΔT_{ij} must preserve the principle of indistinguishability of particles, and hold for arbitrary ρ_{ij}, ρ'_{ij}, and ϕ_{ij}. Because of the isotropy of space, no explicit dependence on coordinates can occur. This latter condition requires (since $\Delta T_{ij} = \mathbf{F}_{ij}^* \cdot \Delta\boldsymbol{\rho}_{ij}$) that $\mathbf{F}_{ij}^*$ lies along $\boldsymbol{\rho}'_{ij} + \boldsymbol{\rho}_{ij}$, which is also an immediate consequence of Eq. (5.48b). The magnitude of the $\mathbf{F}_{ij}^*$, or the ΔT_{ij}, must be obtained from conservation of energy via Eq. (5.50).

Since the right-hand side of Eq. (5.50) involves only products of the functions ϕ_{ij} and ϕ'_{ij}, and these are arbitrary, the most general form possible for the ΔT_{ij} is

$$\Delta T_{ij} = \sum_{\ell=0}^{N} \sum_{k=1}^{\binom{N}{\ell}} c_{\ell k}^{ij} \Phi_{\ell k} \qquad (i < j) \tag{5.52}$$

where $N = n(n-1)/2$ is the number of ρ_{ij},

$$\binom{N}{\ell} = \frac{N!}{\ell!\,(N-\ell)!} \tag{5.53}$$

the $c_{\ell k}^{ij}$ are arbitrary, and $\Phi_{\ell k}$ is a product of the N functions ϕ_{ij}, ℓ of which are evaluated at time $t + \Delta t$ (using ρ'_{ij}) and $N - \ell$ at time t (using ρ_{ij}). The subscript k runs over all possible combinations of ℓ of the ϕ'_{ij} from the total set N.

Thus, e.g.,

$$\Phi_{01} = \prod_{i<j} \phi_{ij} \tag{5.54a}$$

$$\Phi_{N1} = \prod_{i<j} \phi'_{ij} \tag{5.54b}$$

$$\Phi_{\ell k} = \underbrace{\left[\prod \phi'_{ij}\right]}_{\ell \text{ terms}} \times \underbrace{\left[\prod \phi_{ij}\right]}_{N-\ell \text{ terms}} \tag{5.54c}$$

Substitution of Eq. (5.52) into Eq. (5.50) gives

$$\sum_{i<j} \sum_{\ell=0}^{N} \sum_{k=1}^{\binom{N}{\ell}} c_{\ell k}^{ij} \Phi_{\ell k} = \Phi_{01} - \Phi_{N1} \tag{5.55}$$

Since Eq. (5.55) must hold for arbitrary ϕ_{ij}, ρ_{ij}, and ρ'_{ij}, the functions $\Phi_{\ell k}$ are independently variable. Therefore the coefficients of each $\Phi_{\ell k}$ on each side of equation (5.55) must coincide, which gives

$$\sum_{i<j} c_{01}^{ij} = 1 \tag{5.56a}$$

$$\sum_{i<j} c_{\ell k}^{ij} = 0 \qquad (\ell k \neq 01, N1) \tag{5.56b}$$

$$\sum_{i<j} c_{N1}^{ij} = -1 \tag{5.56c}$$

By the principle of indistinguishability of particles, the $c_{\ell k}^{ij}$ must be isotropic with respect to the ij, i.e., ρ_{ij} cannot be treated differently from ρ_{mn}. Further, once the interaction corresponding to the pair ij is singled out, the remaining particles

are indistinguishable. This latter condition implies the $c_{\ell k}^{ij}$ must be isotropic over all values of k which leave the status of ϕ_{ij} invariant. For ij and each l, there are $\binom{N-1}{\ell}$ functions $\Phi_{\ell k}$ containing the factor ϕ_{ij}' and $\binom{N-1}{\ell-1}$ functions $\Phi_{\ell k}$ containing the factor ϕ_{ij}'. The elements of each of these two sets must be indistinguishable from the values of the $c_{\ell k}^{ij}$:

$$c_{\ell k}^{ij} = \begin{cases} \hat{c}_\ell^{ij}, & \phi_{ij} \mid \Phi_{\ell k} \\ \tilde{c}_\ell^{ij}, & \phi_{ij}' \mid \Phi_{\ell k} \end{cases} \tag{5.57}$$

By the indistinguishability of particles, one cannot determine which pair ij was singled out. This gives the conditions

$$\hat{c}_\ell^{ij} = \hat{c}_\ell \qquad (i<j) \tag{5.58a}$$

$$\tilde{c}_\ell^{ij} = \tilde{c}_\ell \qquad (i<j) \tag{5.58b}$$

The above relations given in Eqs. (5.56), (5.57), and (5.58) are sufficient to fix all the $c_{\ell k}^{ij}$, with the solution given by ($\ell = 0, 1, \ldots, N$)

$$\hat{c}_\ell = \frac{1}{N}\frac{1}{\binom{N-1}{\ell}} \tag{5.59a}$$

$$\tilde{c}_\ell = -\frac{1}{N}\frac{1}{\binom{N-1}{\ell-1}} \tag{5.59b}$$

Thus $c_{\ell k}^{ij} = \hat{c}_\ell$ if $\Phi_{\ell k}$ contains the factor ϕ_{ij} or $c_{\ell k}^{ij} = \tilde{c}_\ell$ if $\Phi_{\ell k}$ contains the factor ϕ_{ij}':

$$c_{\ell k}^{ij} = \begin{cases} \dfrac{1}{N}\dfrac{1}{\binom{N-1}{\ell}}, & \phi_{ij} \mid \Phi_{\ell k} \\ -\dfrac{1}{N}\dfrac{1}{\binom{N-1}{\ell-1}}, & \phi_{ij}' \mid \Phi_{\ell k} \end{cases} \tag{5.60}$$

For example,

$$\sum_{i<j} c_{01}^{ij} = \sum_{i<j}\left[\frac{1}{N}\frac{1}{\binom{N-1}{0}}\right] \tag{5.61a}$$

$$= \sum_{i<j}\frac{1}{N} \tag{5.61b}$$

$$= 1 \tag{5.61c}$$

agreeing with Eq. (5.56a).

Using the $c_{\ell k}^{ij}$ given by Eq. (5.60) results, after substitution in Eq. (5.52), in the following expression for ΔT_{ij}:

$$\Delta T_{ij} = -\frac{1}{N}\sum_{\ell=0}^{N-1}\frac{1}{\binom{N-1}{\ell}}\left\{\sum_{1}^{\binom{N-1}{\ell}}\left(\prod_{s=1}^{\ell}\phi'_{i_s j_s}\right)\left(\prod_{s=\ell+1}^{N-1}\phi_{i_s j_s}\right)\right\}\Delta\phi_{ij} \tag{5.62}$$

where the inner sum is over the $\binom{N-1}{\ell}$ combinations of the $N-1$ possible index pairs $i_s j_s$, not including $i_s j_s = ij$, ℓ of which correspond to primed ϕ values. When expressed in this form, with the force $\mathbf{F}_{ij}^*$ being given by

$$\mathbf{F}_{ij}^* = -\Delta T_{ij}\frac{(\rho'_{ij}+\rho_{ij})}{\Delta\rho_{ij}^2} \tag{5.63a}$$

$$= -\frac{1}{N}\left\{\sum_{\ell=0}^{N-1}\frac{1}{\binom{N-1}{\ell}}\sum_{1}^{\binom{N-1}{\ell}}\left(\prod_{s=1}^{\ell}\phi'_{i_s j_s}\right)\left(\prod_{s=\ell+1}^{N-1}\phi_{i_s j_s}\right)\right\}$$
$$\times\frac{\Delta\phi_{ij}}{\Delta\rho_{ij}^2}(\rho'_{ij}+\rho_{ij}) \tag{5.63b}$$

Eq. (5.63) is seen to be a generalization of Eq. (5.38), with the part in braces being a totally symmetric representation of the other factors in the potential. Since the right-hand side of Eq. (5.63) is to lowest-order in Δt independent of any of the $\mathbf{F}_{ij}^*$, Eq. (5.63) can be solved for $\mathbf{F}_{ij}^*$ by functional iteration for small enough Δt.

The expression given in Eq. (5.63) is the "discrete mechanics" force which leads to a solution agreeing to order $(\Delta t)^3$ with the exact motion, and which conserves exactly the energy and total linear and angular momenta.

It is interesting to consider the possibility that some $\phi_{i_q j_q}$ is constant, e.g., $\phi_{i_q j_q} = 1$. Clearly if $i_q j_q = ij$, then $\Delta\phi_{ij} = 0$ and $\mathbf{F}_{ij}^* = 0$, in accord with continuous mechanics. If $i_q j_q \neq ij$, then the $\Phi_{\ell k}$ which differ only by the change $\phi_{i_q j_q} \leftrightarrow \phi'_{i_q j_q}$ become identical, and Eq. (5.63b) reduces to

$$\mathbf{F}_{ij}^* = -\frac{1}{N-1}\left\{\sum_{\ell=0}^{N-2}\frac{1}{\binom{N-2}{\ell}}\sum_{1}^{\binom{N-2}{\ell}}\left(\prod_{s=1}^{\ell}\phi'_{i_s j_s}\right)\left(\prod_{s=\ell+1}^{N-2}\phi_{i_s j_s}\right)\right\}$$
$$\times\frac{\Delta\phi_{ij}}{\Delta\rho_{ij}^2}(\rho'_{ij}+\rho_{ij}) \tag{5.64}$$

where the index pairs $i_s j_s$ now vary over those $N-2$ values for which $i_s j_s \neq ij$ or $i_q j_q$. Therefore if a $\phi_{i_q j_q} = 1$, i.e., $\rho_{i_q j_q}$ does not appear in the potential, the net effect is the same as setting up the original potential without including the $\phi_{i_q j_q}$

factor, and deleting the $i_q j_q$ term from ΔT. Thus $\rho_{i_q j_q}$ is an "ignorable coordinate" in "discrete mechanics" as well as in continuous mechanics. As a consequence, Eq. (5.63) holds even if N is not equal to the total number of possible radii ρ_{ij}, if the terms that are omitted do not occur in the potential ϕ.

For the case of $N = 1$, $\phi = \phi_{ij}$ and equation (5.63b) reduces to Eq. (5.38):

$$\mathbf{F}_{ij}^* = -\frac{\Delta\phi_{ij}}{\Delta\rho_{ij}^2}(\boldsymbol{\rho}'_{ij} + \boldsymbol{\rho}_{ij}) \tag{5.65}$$

If $N = 2$ and the two radii occurring in the potential are $\rho_{i_1 j_1}$ and $\rho_{i_2 j_2}$,

$$\phi = \phi_{i_1 j_1}\phi_{i_2 j_2} \tag{5.66}$$

then Eq. (5.63b) gives

$$\mathbf{F}_{i_1 j_1}^* = -\frac{1}{2}\{\phi'_{i_2 j_2} + \phi_{i_2 j_2}\}\frac{\Delta\phi_{i_1 j_1}}{\Delta\rho_{i_1 j_1}^2}(\boldsymbol{\rho}'_{i_1 j_1} + \boldsymbol{\rho}_{i_1 j_1}) \tag{5.67a}$$

$$\mathbf{F}_{i_2 j_2}^* = -\frac{1}{2}\{\phi'_{i_1 j_1} + \phi_{i_1 j_1}\}\frac{\Delta\phi_{i_2 j_2}}{\Delta\rho_{i_2 j_2}^2}(\boldsymbol{\rho}'_{i_2 j_2} + \boldsymbol{\rho}_{i_2 j_2}) \tag{5.67b}$$

For $N = 3$, with

$$\phi = \phi_{i_1 j_1}\phi_{i_2 j_2}\phi_{i_3 j_3} \tag{5.68}$$

the expression for, e.g., $\mathbf{F}_{i_1 j_1}^*$, is

$$\mathbf{F}_{i_1 j_1}^* = -\frac{1}{3}\left\{\phi'_{i_2 j_2}\phi'_{i_3 j_3} + \frac{1}{2}(\phi'_{i_2 j_2}\phi_{i_3 j_3} + \phi_{i_2 j_2}\phi'_{i_3 j_3}) + \phi_{i_2 j_2}\phi_{i_3 j_3}\right\} \times \frac{\Delta\phi_{i_1 j_1}}{\Delta\rho_{i_1 j_1}^2}(\boldsymbol{\rho}'_{i_1 j_1} + \boldsymbol{\rho}_{i_1 j_1}) \tag{5.69}$$

with similar formulas for $\mathbf{F}_{i_2 j_2}^*$ and $\mathbf{F}_{i_3 j_3}^*$ obtained by cyclic permutations of the subscripts 1, 2, 3.

Finally, it should be noted that, as in Section 5.6, if ϕ is a function of the ρ_i instead of the ρ_{ij}:

$$\phi = \prod_{i=1}^{n}\phi_i(\rho_i) \tag{5.70}$$

then the entire sequence of results except for conservation of linear momentum follow, leading to:

$$\mathbf{F}_i{}^* = -\frac{1}{n}\left\{\sum_{\ell'=0}^{n-1}\frac{1}{\binom{n-1}{\ell}}\sum_{1}^{\binom{n-1}{\ell}}\left(\prod_{s=1}^{\ell}\phi'_{i_s}\right)\left(\prod_{s=\ell+1}^{n-1}\phi_{i_s}\right)\right\} \times \frac{\Delta\phi_i}{\Delta\rho_i{}^2}(\boldsymbol{\rho}_i{}' + \boldsymbol{\rho}_i) \tag{5.71}$$

where the i_s vary over the $n - 1$ values not equal to i. Because of the property of "ignorable coordinates," n may be a number less than the total number of particles if the neglected radii do not occur in ϕ (for these $\mathbf{F}_i^* = \mathbf{0}$).

6. Impulsive Limit of Discrete Mechanics

In problems where collisions occur, extremely large forces of very short duration are typical at the height of the interaction. In this situation, "impulsive models" are a convenient approximate description and were investigated extensively in nineteenth-century physics (see, e.g., [17–19]). The impulsive limit is defined as the limit $\Delta t \to 0$ while $\Delta\phi$ is held fixed. Under these conditions $\mathbf{F}_{ij}\,\Delta t$ tends to a limit $\mathbf{I}_{ij}$, called the "impulse" transferred by the trajectory crossing the boundary over which the discontinuity $\Delta\phi$ occurs:

$$\mathbf{I}_{ij} = \lim_{\Delta t \to 0} (\mathbf{F}_{ij}\,\Delta t) \tag{6.1}$$

In the derivation of impulsive models, the limit $\Delta t \to 0$ is assumed, so that $\rho'_{ij} \simeq \rho_{ij}$, and the impulses $\mathbf{I}_{ij}$ which give the change in the momenta are obtained by requiring conservation of E, $\mathbf{P}$, and $\mathbf{L}$ during the collision. Since the limit follows from classical mechanics and the $\mathbf{F}_{ij}\,\Delta t$ at each point, the total change of the motion occurs in a direction $\hat{n}$ pointing towards the increase of ϕ. These conditions are sufficient to fix the impulses $\mathbf{I}_{ij}$ in simple cases: the collision of two rigid-bodies [17–19], and the motion of three particles on a discontinuous potential (see, e.g., [20]).

Since "discrete mechanics" obeys the same conservation principles as continuous mechanics, and differs from it only in terms of order $(\Delta t)^3$, it is expected that the impulsive limits of discrete and continuous mechanics will coincide. It is the purpose of this section to find the impulsive limit of "discrete mechanics," and thereby give the most general exposition of an impulsive model that has been presented to date.

It is conventional to consider the discontinuity $\Delta\phi$ to occur as the limit of a potential ϕ which becomes increasingly discontinuous as $\Delta t \to 0$. Of course, in practice there is a real, continuous potential ϕ whose interaction is being modeled by a discontinuous limit potential, rather than vice versa. Suppose for simplicity that, for fixed Δt, ϕ has the pairwise-additive form of Eq. (5.22). Then the "discrete mechanics" forces $\mathbf{F}_{ij}^*$ are given by Eq. (5.38). What are desired are the "discrete mechanics" impulses $\mathbf{I}_{ij}^*$ defined by the limits

$$\mathbf{I}_{ij}^* = \lim_{\Delta t \to 0} (\mathbf{F}_{ij}^*\,\Delta t) \qquad (i < j) \tag{6.2}$$

where the $\Delta\phi_{ij}$ tend to constant discontinuities simultaneously.

Clearly, from Eqs. (5.3),

$$\lim_{\Delta t \to 0} \rho'_{ij} = \rho_{ij} \tag{6.3}$$

and the only other term in equation (5.38) whose limit is unknown is $\Delta\rho^2_{ij}$. Note that

$$\Delta\rho^2_{ij} = (\rho'_{ij} + \rho_{ij}) \cdot (\rho'_{ij} - \rho_{ij}) \tag{6.4}$$

where

$$\rho'_{ij} - \rho_{ij} = \Delta\rho_j - \Delta\rho_i \tag{6.5}$$

Now, from Eq. (5.19a), Eq. (6.5) becomes

$$\Delta\rho_{ij} = \frac{\dot{\rho}_j' + \dot{\rho}_j}{2}\Delta t - \frac{\dot{\rho}_i' + \dot{\rho}_i}{2}\Delta t \tag{6.6a}$$

$$= \frac{\dot{\rho}'_{ij} + \dot{\rho}_{ij}}{2}\Delta t \tag{6.6b}$$

where

$$\dot{\rho}_{ij} = \dot{\rho}_j - \dot{\rho}_i \tag{6.7a}$$

$$\dot{\rho}'_{ij} = \dot{\rho}_j' - \dot{\rho}_i' \tag{6.7b}$$

Substitution of Eq. (5.29) into Eq. (6.6b) via Eq. (5.3) gives

$$\frac{\Delta\rho_{ij}}{\Delta t} = \frac{\dot{\rho}'_{ij} + \dot{\rho}_{ij}}{2} \tag{6.8a}$$

$$= \dot{\rho}_{ij} + \frac{\Delta t}{2}\sum_{k=1}^{n}\left(\frac{\mathbf{F}^*_{kj}}{m_j} - \frac{\mathbf{F}^*_{ki}}{m_i}\right) \tag{6.8b}$$

where the convention is that $\mathbf{F}^*_{kj} = -\mathbf{F}^*_{jk}$ for $k > j$ and $\mathbf{F}^*_{jj} = \mathbf{0}$ for all j. Thus Eq. (6.8b) may also be written

$$\frac{\Delta\rho_{ij}}{\Delta t} = \dot{\rho}_{ij} + \frac{\Delta t}{2}\left[\left(\frac{1}{m_j} + \frac{1}{m_i}\right)\mathbf{F}^*_{ij} + \frac{1}{m_j}\sum_{\substack{k<j \\ k\neq i}}\mathbf{F}^*_{kj} - \frac{1}{m_j}\sum_{k>j}\mathbf{F}^*_{jk} - \frac{1}{m_i}\sum_{k<i}\mathbf{F}^*_{ki} + \frac{1}{m_i}\sum_{\substack{k>i \\ k\neq j}}\mathbf{F}^*_{ik}\right], \qquad (i<j) \tag{6.9}$$

Finally,

$$\lim_{\Delta t\to 0}\frac{\Delta\rho_{ij}^2}{\Delta t}=\lim_{\Delta t\to 0}\frac{(\rho'_{ij}+\rho_{ij})\cdot\Delta\rho_{ij}}{\Delta t} \tag{6.10a}$$

$$=\rho_{ij}\cdot\lim_{\Delta t\to 0}\frac{\Delta\rho_{ij}}{\Delta t} \tag{6.10b}$$

$$=\rho_{ij}\cdot\left(\frac{\dot\rho'_{ij}+\dot\rho_{ij}}{2}\right) \tag{6.10c}$$

$$=\rho_{ij}\cdot\left[\dot\rho_{ij}+\frac{1}{2}\sum_{k=1}^{n}\left(\frac{\mathbf{I}_{kj}^*}{m_j}-\frac{\mathbf{I}_{ki}^*}{m_i}\right)\right] \tag{6.10d}$$

The expression for $\mathbf{I}_{ij}^*$ is thus

$$\mathbf{I}_{ij}^*=\lim_{\Delta t\to 0}(\mathbf{F}_{ij}^*\,\Delta t) \tag{6.11a}$$

$$=\lim_{\Delta t\to 0}\left\{-\frac{\Delta\phi_{ij}}{\Delta\rho_{ij}^2}(\rho'_{ij}+\rho_{ij})\right\} \tag{6.11b}$$

$$=-\frac{\Delta\phi_{ij}}{\rho_{ij}\cdot\left(\dfrac{\dot\rho'_{ij}+\dot\rho_{ij}}{2}\right)}\rho_{ij} \tag{6.11c}$$

$$\mathbf{I}_{ij}^*=-\frac{\Delta\phi_{ij}}{\hat\rho_{ij}\cdot\left(\dfrac{\dot\rho'_{ij}+\dot\rho_{ij}}{2}\right)}\hat\rho_{ij} \tag{6.11d}$$

where $\hat\rho_{ij}=\rho_{ij}/\rho_{ij}$ is a unit-vector in the ρ_{ij} direction, and this last expression is implicit in the other $\mathbf{I}_{k\ell}^*$ via Eq. (6.10). Equation (6.11d) gives the direction of $\mathbf{I}_{ij}^*$ as $\hat\rho_{ij}$. Denoting by $I_{k\ell}^*$ the signed magnitude of $\mathbf{I}_{k\ell}^*$, i.e.,

$$I_{k\ell}^*=-\frac{\Delta\phi_{k\ell}}{\hat\rho_{k\ell}\cdot\left(\dfrac{\dot\rho'_{k\ell}+\dot\rho_{k\ell}}{2}\right)} \tag{6.12}$$

then

$$\mathbf{I}_{k\ell}^*=I_{k\ell}^*\hat\rho_{k\ell} \tag{6.13}$$

(Note that $I_{k\ell}^*=I_{\ell k}^*$, since $\hat\rho_{k\ell}$ contains the change of sign.) Substitution of Eq. (6.13) into Eq. (6.11d) via Eq. (6.10d), with multiplication of both sides by the denominator of the right-hand side of Eq. (6.11d), gives

$$I_{ij}^*\dot\rho_{ij}+\frac{1}{2}\sum_{k=1}^{n}\left[\frac{I_{ij}^*I_{kj}^*}{m_j}(\hat\rho_{ij}\cdot\hat\rho_{kj})-\frac{I_{ij}^*I_{ki}^*}{m_i}(\hat\rho_{ij}\cdot\hat\rho_{ki})\right]+\Delta\phi_{ij}=0\qquad(i<j) \tag{6.14}$$

where

$$\dot{\rho}_{ij} = \hat{\rho}_{ij} \cdot \dot{\rho}_{ij} \tag{6.15}$$

is the radial-component of $\dot{\rho}_{ij}$. Equations (6.14) are a complete system of quadratic equations for the independent I_{ij}^*. Which set of roots of Eqs. (6.14) are chosen must be determined from considerations of the actual, physical motion (i.e., finite Δt).

Since the potential ϕ was given in the form of equations (5.22), the total potential shift $\Delta\phi$ is given by

$$\Delta\phi = \sum_{i<j} \Delta\phi_{ij} \tag{6.16}$$

in the impulsive limit. If constants β_{ij} are defined by

$$\Delta\phi_{ij} = \beta_{ij}\,\Delta\phi \tag{6.17}$$

then the β_{ij} are the direction cosines of a unit-vector $\hat{n}$ in the direction of the increase of ϕ in a plot against the ρ_{ij}. For finite Δt, $\hat{n}$ would be in the direction of the negative of the gradient of ϕ with respect to the magnitudes ρ_{ij}.

For a general potential of the form given in Eq. (5.45), Eqs. (6.13) and (6.14) for the impulses $\mathbf{I}_{ij}^*$ still hold, if the potential shift $\Delta\phi_{ij}$ is replaced by

$$\Delta\phi_{ij} = \sum_{\ell=0}^{\infty} \frac{1}{N} \left\{ \sum_{q=0}^{N-1} \frac{1}{\binom{N-1}{q}} \sum_{1}^{\binom{N-1}{q}} \left(\prod_{s=1}^{q} \phi_{i_s j_s}^{(\ell)'} \right) \left(\prod_{s=q+1}^{N-1} \phi_{i_s j_s}^{(\ell)} \right) \right\} \Delta\phi_{ij}^{(\ell)} \tag{6.18}$$

where now the $\phi_{i_s j_s}^{(\ell)'}$ and $\phi_{i_s j_s}^{(\ell)}$ are the values of the potential term $\phi_{i_s j_s}^{(\ell)}$ on the new and old sides of the discontinuity, respectively. The sum over ℓ is that of Eq. (5.45).

Since "discrete mechanics" obeys conservation of energy and total linear and angular momenta for each Δt, it also conserves these quantities in the impulsive limit. Thus the impulsive limit of "discrete mechanics" is the same as that of exact mechanics, i.e., $\mathbf{I}_{ij}^* = \mathbf{I}_{ij}$. The results obtained in Eqs. (6.13), (6.14) and (6.18) are the most general expression that has yet been given in the literature for the impulsive limit of motion due to a potential. Hence "discrete mechanics" obeys the fundamental conservation principles where the potential is both continuous and discontinuous. The impulse model can be considered as a special case of "discrete mechanics," or "discrete mechanics" viewed as a generalization of the impulsive model to finite Δt. "Discrete mechanics" is more than a numerical method: it is an approximate theoretical model for the classical motion.

7. Examples

Many numerical applications of "discrete mechanics" have been presented previously for the special case of forces of the pairwise-additive, inverse-powers form, i.e.,

$$\phi_{ij}(\rho_{ij}) = \frac{\alpha}{\rho_{ij}^{p}} + \frac{\beta}{\rho_{ij}^{q}} \tag{7.1}$$

where α and β are constants and p and q integers. These studies have included problems from astrodynamics, elastic oscillations of continuous media, heat transfer, etc. (for review, see [12]). These applications are extended here to include problems of molecular scattering.

The first example involves a potential of the inverse-power form of Eqs. (7.1) and serves to illustrate the coordinates and numerical methods involved. The second example is that of a three-body reactive interaction, and is taken from current research in this area [20].

Comparisons are made with the Adams' method of Eqs. (3.1), and a conventional method used on problems of this type, which has truncation errors of orders $(\Delta t)^8$ and $(\Delta t)^7$ in the ρ_i' and $\dot{\rho}_i'$. Programs implementing the "discrete mechanics" and Adams' formulas are given in Appendices I and II of [21].

A. *Two Particles Subject to a Lennard-Jones Potential*

Many of the properties of dilute gases can be well-approximated by the theory of structureless particles. One of the most common potential forms used in this connection is the Lennard-Jones form for the interaction of two particles 1 and 2:

$$\phi_{LJ}(\rho_{12}) = 4\epsilon \left[\left(\frac{\sigma}{\rho_{12}} \right)^{12} - \left(\frac{\sigma}{\rho_{12}} \right)^{6} \right] \tag{7.2}$$

where the parameter ϵ is the minimum value attained by ϕ_{LJ}, called the "well-depth" of the potential, and σ is the value of ρ_{12} for which $\phi_{LJ}(\rho_{12}) = 0$. The physical properties of many gases are summarized by giving values for ϵ and σ and have been tabulated for many systems. If the units of energy and length are chosen to be ϵ and σ, respectively, then ϕ_{LJ} assumes the dimensionless form

$$\phi_{LJ}(\rho_{12}) = 4 \left[\frac{1}{\rho_{12}^{12}} - \frac{1}{\rho_{12}^{6}} \right] \tag{7.3}$$

which will be used in the following discussion.

In the Adams' method of equations (3.1), the classical definition of force as the negative gradient of the potential is used, which gives

$$\mathbf{F}_{12} = -\frac{\partial \phi_{LJ}}{\partial \boldsymbol{\rho}_{12}} = -\hat{\rho}_{12}\frac{d\phi_{LJ}}{d\rho_{12}} \tag{7.4}$$

where $\hat{\rho}_{12} = \boldsymbol{\rho}_{12}/\rho_{12}$ is a unit-vector, and

$$\frac{d\phi_{LJ}}{d\rho_{12}} = 24\left[\frac{1}{\rho_{12}^{7}} - \frac{2}{\rho_{12}^{13}}\right], \tag{7.5}$$

directly from Eq. (7.3). In the case of the "discrete mechanics" solution, given by Eq. (5.17) or Eq. (5.38), the force $\mathbf{F}_{12}^{*}$ due to ϕ_{LJ} is given implicitly by

$$\mathbf{F}_{12}^{*} = -\frac{\phi_{LJ}(\rho_{12}') - \phi_{LJ}(\rho_{12})}{\rho_{12}'^{2} - \rho_{12}^{2}}(\boldsymbol{\rho}_{12}' + \boldsymbol{\rho}_{12}) \tag{7.6}$$

which is used in conjunction with Eqs. (5.3).

For the Adams' method, the equations which determine $\boldsymbol{\rho}_{12}'$ implicitly are

$$\boldsymbol{\rho}_{12}' = \boldsymbol{\rho}_{12} + \dot{\boldsymbol{\rho}}_{12}\,\Delta t + \ddot{\boldsymbol{\rho}}_{12}\frac{(\Delta t)^2}{2} + (\ddot{\boldsymbol{\rho}}_{12}' - \ddot{\boldsymbol{\rho}}_{12})\frac{(\Delta t)^2}{6} \tag{7.7a}$$

$$\dot{\boldsymbol{\rho}}_{12}' = \dot{\boldsymbol{\rho}}_{12} + \ddot{\boldsymbol{\rho}}_{12}\,\Delta t + (\ddot{\boldsymbol{\rho}}_{12}' - \ddot{\boldsymbol{\rho}}_{12})\frac{\Delta t}{2} \tag{7.7b}$$

where $\mu_{12}\ddot{\boldsymbol{\rho}}_{12} = \mathbf{F}_{12}$ and $\mu_{12}\ddot{\boldsymbol{\rho}}_{12}' = \mathbf{F}_{12}'$, with $\mathbf{F}_{12}$ and $\mathbf{F}_{12}'$ from Eqs. (7.4) using ρ_{12} and ρ_{12}', respectively, and μ_{12}, the "reduced mass," given by

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \tag{7.8}$$

For "discrete mechanics" the corresponding equations are

$$\boldsymbol{\rho}_{12}' = \boldsymbol{\rho}_{12} + \dot{\boldsymbol{\rho}}_{12}\,\Delta t + \ddot{\boldsymbol{\rho}}_{12}^{*}\frac{(\Delta t)^2}{2} \tag{7.9a}$$

$$\dot{\boldsymbol{\rho}}_{12}' = \dot{\boldsymbol{\rho}}_{12} + \ddot{\boldsymbol{\rho}}_{12}^{*}\,\Delta t \tag{7.9b}$$

where $\mu_{12}\ddot{\boldsymbol{\rho}}_{12}^{*} = \mathbf{F}_{12}^{*}$ with $\mathbf{F}_{12}^{*}$ given by Eq. (7.6). Equations (7.7) and (7.9) were solved by simple functional iteration (successive substitution of $\boldsymbol{\rho}_{12}'$ and redetermination of the forces $\mathbf{F}_{12}'$ and $\mathbf{F}_{12}^{*}$) until convergence was obtained in all components of $\boldsymbol{\rho}_{12}'$ to a relative tolerance of .00001. If this convergence could not be obtained in five iterations, the stepsize Δt was halved. In practice, only one or two iterations were required per step. Similar procedures were used to control the step-size Δt to bound the truncation error for both methods (for details, see the Appendices of [21]).

TABLE I[a]

Sample Trajectories Using ϕ_{LJ}

Quantity[b]	Method[c]	Case 1	Case 2	Case 3
b		1.0	1.0	2.0
E		1.0	10.0	1.0
χ	DM	0.996949	0.333310	−0.234471
	A	0.996957	0.333321	−0.234519
	HO	0.997050	0.333318	−0.234543
	Exact	0.996930	0.333309	−0.234487
E (final)[d]	DM	1.00004	10.00008	1.00000
	A	1.00000	10.00005	1.00000
	HO	1.00007	10.00008	1.00002
max ΔE[e]	DM	+.00004	+.00008	0.00000
	A	+.00004	+.00013	+.00002
	HO	+.00008	+.00008	+.00002
No. Steps	DM	1396	1006	335
	A	1530	1061	352
	HO	114	99	64
No. Function calls/step[f]	DM	2.8	2.7	3.2
	A	1.6	1.5	1.7
	HO	2.9	2.9	3.2.
Computing time (sec)[g]	DM	1.9	1.3	0.5
	A	1.9	1.3	0.5
	HO	0.4	0.3	0.2

[a] The implicit equations were, for methods DM and A, iterated until relative convergence in $\| \rho'_{12} \|$ was obtained to 10^{-5}; for method HO, two iterations were performed each step. Step-size was controlled to limit truncation error to about 10^{-3} (absolute) after 500 steps (100 for HO).

[b] See text for explanation of symbols.

[c] DM = Discrete Mechanics; A = Adams' method; HO = High-order method of [14]; "Exact" denotes exact answer.

[d] Calculated value of energy at last step.

[e] Maximum deviation of calculated energy at any step from initial energy. Error for DM is due solely to lack of convergence in the iteration.

[f] Total number of potential or force evaluations divided by number of steps. This includes all evaluations necessary for starting and step-size changes, as well as in the iteration.

[g] Univac 1108 (1.5 μs add time). Numbers are very crude ($\pm 20\%$).

The initial conditions at $t = 0$ for the trajectories calculated were of the following form:

$$\boldsymbol{\rho}_{12}^0 = \langle 0, b, Z_{12}^0 \rangle \tag{7.10a}$$

$$\dot{\boldsymbol{\rho}}_{12}^0 = \langle 0, 0, \sqrt{2E} \rangle \tag{7.10b}$$

where $Z_{12}^0 = -10$ (essentially infinite), and values of the impact parameter b and energy E used are listed with the results in Table I. In every case the reduced-mass μ_{12} was taken to be 1. The scattering was assumed to be ended at the time $t = t_f$ when again $\rho_{12}(t) > 10$ (i.e. $|\phi_{LJ}(\rho_{12})| < 10^{-5}E$). At this point, the value of the energy, and the value of the "angle of deflection" χ, defined by

$$\chi = \cos^{-1} \frac{\dot{\boldsymbol{\rho}}_{12}(t_f) \cdot \dot{\boldsymbol{\rho}}_{12}^0}{|\dot{\boldsymbol{\rho}}_{12}(t_f)| \, |\dot{\boldsymbol{\rho}}_{12}^0|} \tag{7.11}$$

were calculated, with the sign of χ taken to be that of the Y-component of $\dot{\boldsymbol{\rho}}_{12}(t_f)$. The calculated values of E and χ are compared to the correct values for several sample trajectories in Table I.

The results show the Adams' method and "discrete mechanics" give comparable computational accuracy from comparable computational effort (number of ϕ_{LJ} evaluations, or number of steps). Of course, the problem used as an example here is not a severe test of the Adams' method, since as $t \to \infty$, $\phi_{LJ}(\rho_{12}) \to 0$, and in this limit all methods are conservative.

B. *A Three-Particle Reactive System*

Another application of "discrete mechanics" to molecular interactions, this time requiring the formulas developed in the present work, is in the reactive scattering of potassium atoms from methyl iodide molecules, resulting in the products potassium iodide and a methyl radical. This system has been the subject recently of a study using a high-order Adams' method [20].

Let the potassium atom be denoted by the index 1, the iodine atom by 2, and the methyl group by a single particle with index 3. One of the potential forms used in [20] to model the interaction was the "modified Bunker-Blais" potential ϕ_{MBB} given by

$$\begin{aligned} \phi_{MBB}(\rho_{12}, \rho_{23}, \rho_{13}) = {} & D_{12}[e^{-\beta_{12}(\rho_{12}-\alpha_{12})} - 1]^2 \\ & + D_{23}[e^{-\beta_{23}(\rho_{23}-\alpha_{23})} - 1]^2 + D_{13}e^{-\beta_{13}(\rho_{13}-\alpha_{13})} \\ & + D_{23}e^{-\beta_{23}(\rho_{23}-\alpha_{23})}[1 - \tanh(\gamma\rho_{12} + \delta)] \end{aligned} \tag{7.12}$$

where values of the parameters D_{ij}, β_{ij}, α_{ij} ($ij = 12, 23, 13$), γ and δ are given in [20]. Also given in [20] are expressions for the forces $\mathbf{F}_{12}$, $\mathbf{F}_{23}$ and $\mathbf{F}_{12}$, resulting from the gradients of ϕ_{MBB}, to be used in the Adams' method of Eq. (3.1).

Now, the potential ϕ_{MBB} can be written in the form of equation (5.45):

$$\phi_{MBB} = \phi^{(1)} + \phi^{(2)} + \phi^{(3)} + \phi^{(4)} \tag{7.13}$$

where each $\phi^{(\ell)}$ ($\ell = 1, 2, 3, 4$) is of the form of Eq. (5.46)

$$\phi^{(\ell)}(\rho_{12}, \rho_{23}, \rho_{13}) = \phi_{12}^{(\ell)}(\rho_{12})\, \phi_{23}^{(\ell)}(\rho_{23})\, \phi_{13}^{(\ell)}(\rho_{13}) \tag{7.14}$$

TABLE II

Component Functions of ϕ_{MBB}

ℓ	$\phi_{12}^{(\ell)}$	$\phi_{23}^{(\ell)}$	$\phi_{13}^{(\ell)}$
1	$D_{12}[e^{-\beta_{12}(\rho_{12}-\alpha_{12})} - 1]^2$	1	1
2	1	$D_{23}[e^{-\beta_{23}(\rho_{23}-\alpha_{23})} - 1]^2$	1
3	1	1	$D_{13}e^{-\beta_{13}(\rho_{13}-\alpha_{13})}$
4	$1 - \tanh(\gamma\rho_{12} + \delta)$	$D_{23}e^{-\beta_{23}(\rho_{23}-\alpha_{23})}$	1

The $\phi_{ij}^{(\ell)}$ ($ij = 12, 23, 13$; $\ell = 1, 2, 3, 4$) are given in Table II. The "discrete mechanics" forces $\mathbf{F}_{ij}^{*}$ ($ij = 12, 23, 13$) have the corresponding expansions

$$\mathbf{F}_{ij}^{*} = \mathbf{F}_{ij}^{*(1)} + \mathbf{F}_{ij}^{*(2)} + \mathbf{F}_{ij}^{*(3)} + \mathbf{F}_{ij}^{*(4)} \tag{7.15}$$

where, e.g., for $ij = 12$, from Eq. (5.69),

$$\mathbf{F}_{12}^{*(\ell)} = -\frac{1}{3}\left\{\phi_{23}^{(\ell)'}\phi_{13}^{(\ell)'} + \frac{1}{2}[\phi_{23}^{(\ell)'}\phi_{13}^{(\ell)} + \phi_{23}^{(\ell)}\phi_{13}^{(\ell)'}] + \phi_{23}^{(\ell)}\phi_{13}^{(\ell)}\right\} \times \frac{\phi_{12}^{(\ell)'} - \phi_{12}^{(\ell)}}{\rho_{12}'^2 - \rho_{12}^2}(\boldsymbol{\rho}_{12}' + \boldsymbol{\rho}_{12}). \tag{7.16}$$

(Note that the factor $(\boldsymbol{\rho}_{12}' + \boldsymbol{\rho}_{12})/(\rho_{12}'^2 - \rho_{12}^2)$ may be extracted from each term of equation (7.15) for $\mathbf{F}_{12}^{*}$). The forces $\mathbf{F}_{23}^{*(\ell)}$ and $\mathbf{F}_{13}^{*(\ell)}$ may be obtained via cyclic permutation of the indices 12, 23, and 13 in Eq. (7.16).

A comparison of the results obtained using "discrete mechanics," the Adams' method of Eqs. (3.1), and the high-order method of [14] and [20] is given in Table III for two characteristic sample trajectories. The quantities calculated and

TABLE III[a]

Sample Three-body Trajectories Using ϕ_{MBB}

Quantity[b]	Method[c]	Case 1	Case 2
Total $E(10^{-14}$ erg)	—	384.431	587.286
Final Conditions[d]			
Configuration[e]	DM	1 + 23	12 + 3
	A	1 + 23	12 + 3
	HO	1 + 23	12 + 3
$E(10^{-14}$ erg)	DM	384.297	587.222
	A	384.252	587.107
	HO	384.397	587.141
$L(10^{-27}$ erg-sec)	DM	101.361	147.977
	A	101.355	147.971
	HO	101.380	147.973
χ[e] (rad.)	DM	17.167	114.769
	A	17.152	114.742
	HO	17.216	114.763
$J_{jk}(10^{-27}$ erg-sec)	DM	34.074	78.088
	A	34.066	78.085
$E_{jk}(10^{-14}$ erg)	DM	367.131	472.456
	A	367.101	472.365
	HO	367.181	472.414
Number of steps	DM	7700	5660
	A	8260	6120
	HO	380	285

[a,b,c] See Table I.

[d] At a final time t when all further interaction of the free particle i and bound pair jk was negligible.

[e] $i + jk$ denotes particle i free and particles j and k bound at the final state.

tabulated at the end of the trajectories were: the final total energy E; the magnitude of the total angular momentum L; the angle of deflection χ of the resultant free particle i with respect to the Z-axis; the final translational energy $E_{i,jk}$ of the free particle i with respect to the bound pair jk; and the magnitude of the rotational angular momentum J_{jk} and internal energy E_{jk} of the final bound pair. (Formulas for the calculation of these quantities from the ρ_i and $\dot{\rho}_i$ are given in [20].) The values of E and L are necessarily conserved by "discrete mechanics." (Since the calculations were carried out in the relative-internal center-of-mass cartesian coordinate system of [20], the conservation of the total linear momentum $\mathbf{P}$ was separated out ab initio).

In order to ease the comparison between "discrete mechanics" and the Adams' method, in both cases the implicit equations were iterated to convergence (10^{-5} relative error). Surprisingly enough, this convergence was usually attained in a single iteration. The net result of this procedure was that both methods were very stable for the examples shown, but the conservation principles of "discrete mechanics" served to enhance slightly the accuracy for the same number of steps. The high-order method of [14] and [20], because of the fewer ($\sim 1/10$) number of steps required, was of course the most efficient of the methods by a factor of about 5 in time.

8. Remarks

A. *Stability*

It is well-known in the theory of numerical methods for differential equations that the use of an implicit set of formulas (such as Eqs. (3.1)) is necessary to maintain "stability," i.e., retard the growth of accumulated error (see, e.g., [13] or [15]). Although this requires solution by an iterative method, in a "stable" system the error grows approximately proportional to the total number M of time steps (due to truncation error), rather than exponentially (due to feedback), as in an "unstable" method. Eventually, however, as time progresses, the error in the computed solution must grow unboundedly, and any method becomes inaccurate. For example, no matter which predictor-corrector system is used, the total energy of a system of particles becomes infinite with M.

In contrast, with "discrete mechanics" the total energy and momenta are *constrained* at their initial values, and the errors in the calculated motions are largely confined to errors in *phase* rather than *amplitudes*. Thus "discrete mechanics" is intrinsically more stable than any conventional numerical method.

B. *Periodic Orbits*

Bounded, periodic orbital motion can occur only if the total energy of a system of particles is below the "energy criterion" (see e.g., [2]). Since, in conventional numerical solutions of the equations of motion, the energy increases slowly, but surely, due to truncation error as time progresses, such solutions will never correspond to closed orbits. There are problems, such as the stability of the solar system or the semiclassical theory of stationary states of atoms and molecules, in which it is *only* the periodic orbits that are important. These problems are thus extremely difficult to solve by conventional methods.

"Discrete mechanics" therefore has a usuable advantage in the fact that for small Δt there is a one-to-one correspondence of periodic orbits with the exact

solution of the equations of motion. Initial conditions which lead to periodic orbits in "discrete mechanics" will correspond approximately to those which lead to such orbits in exact mechanics.

C. *Statistical Mechanics*

In the theory of statistical mechanics the equilibrium distribution of states of a dilute fluid is uniform over the manifold of constant E, $\mathbf{P}$, and $\mathbf{L}$ in phase-space [22]. Scattering due to a potential modifies this uniform distribution of initial conditions to a non-uniform distribution of final conditions, but still on the manifold of constant E, $\mathbf{P}$ and $\mathbf{L}$. Since "discrete mechanics" preserves this property of remaining on the constant E, $\mathbf{P}$, and $\mathbf{L}$ manifold, it gives rise to a complete corresponding theory of "discrete statistical mechanics," whose results differ from those of normal statistical mechanics by terms of the order of $(\Delta t)^3$. Thus "discrete mechanics" may be used for qualitative investigation of statistical-mechanical properties, such as correlation between collisions or the states of a large system of interacting particles, where conventional numerical methods have failed. The qualitative effects found will correspond to the exact solution, even though the quantitative results may only be approximate.

D. *Limitations of Discrete Mechanics*

Even as generalized in the present work, there still remain several disadvantages of "discrete mechanics" which may restrict its usefulness. Firstly, an obvious failing is the low order of accuracy in Δt. Traditional methods (Adams-Moulton, Runge-Kutta, etc.) as applied to dynamical motion have been of order $(\Delta t)^5$ or higher, and provide a solution with much less labor. Secondly, the potential ϕ must be given in the form of Eqs. (5.45) and (5.46), with the forces given by Eq. (5.63), which is more cumbersome and inefficient than the direct differentiation of a general form of ϕ. Thirdly, the conservation of energy follows only to the extent of the iteration to convergence of Eq. (5.3), while typical corrector equations of the form (3.1) are usually iterated only once or twice.

The first disadvantage has been partially alleviated by the discovery of higher-order energy conserving methods, which are currently under study. The second disadvantage may be insurmountable, since the conservation principles lead to a complete solution only when invariant with respect to an interchange of particles, which requires a separable potential form. Empirical results indicate the third "disadvantage" is in reality an advantage, improving the stability and reducing the accumulation of error, and typically requiring only one iteration (versus the two iterations necessary in usual implementations of predictor-corrector methods.)

REFERENCES

1. G. A. CHEBOTAREV, "Analytical and Numerical Methods of Celestial Mechanics," p. 18, American Elsevier Publ. Co., N. Y., 1967.
2. A. E. ROY, "Foundations of Astrodynamics," p. 158, MacMillan, N. Y., 1965.
3. D. L. BUNKER, Classical trajectory methods, "Methods of Computational Physics," Vol. 10, p. 287, Academic Press, N. Y., 1971.
4. D. SECREST, Theory of rotational and vibrational energy transfer in molecules, *Ann. Rev. Phys. Chem.* **24** (1974).
5. B. J. ALDER, Studies in molecular dynamics. III. A mixture of hard spheres, *J. Chem. Phys.* **40** (1964), 2724.
6. J. B. GIBSON, A. N. GOLAND, M. MILGRAM, AND G. H. VINEYARD, Dynamics of radiation damage, *Phys. Rev.* **120** (1960), 1229.
7. B. J. DALY, F. H. HARLOW, AND J. F. WELCH, Numerical Fluid Dynamics Using the Particle-and-Force Method, Report LA-3144, Los Alamos Scientific Laboratory, Los Alamos, N.M., 1964.
8. YU P. POPOV AND A. A. SAMARSKII, Completely conservative difference schemes, *Zh. vychisl. Mat. mat. Fiz.* **9**(1969), 4, 953. [*USSR Comput. Math. Math. Phys.* **9**(1970), 4, 296]. Completely Conservative Difference Schemes for the Equations of Gas Dynamics in Euler Variables, *Zh. vychisl. Mat. mat. Fiz.* **10** (1970), 3, 773. [*USSR Comput. Math. Math. Phys.* **10** (1970), 3, 265]. Completely Conservative Difference Schemes for Magneto-hydrodynamic Equations, *Zh. vychisl. Mat. mat. Fiz.* **10** (1970), 4, 990. [*USSR Comput. Math. Math. Phys.* **10** (1970), **4**, 233].
9. D. GREENSPAN, An Arithmetic, Particle Theory of Fluid Dynamics, Technical Report # 171, 1973, Computer Science Department, Univ. of Wisconsin, Madison.
10. A. K. MACPHERSON, The formulation of shock waves in a dense gas using a molecular dynamics type technique, *J. Fluid Mech.*, **45** (1971), 601.
11. D. GREENSPAN, Topics in the Computer Simulation of Discrete Physics, Technical Report # 130, 1971, Computer Science Department, Univ. of Wis., Madison. Discrete Newtonian Gravitation and the Three-Body Problem, Technical Report #133, 1971, Computer Science Department, Univ. of Wis., Madison, (to appear in Found. of Phys.). Discrete Bars, Conductive Heat Transfer, and Elasticity, Technical Report # 164, 1972, Computer Science Department, Univ. of Wis., Madison, (to appear on Computers and Structures). Discrete Newtonian gravitation and the *N*-body problem, *Utilitas Math.*, **2** (1972), 105. New forms of discrete mechanics, Kybernetes **1** (1972), 87. An algebraic, energy conserving formulation of classical molecular and Newtonian *n*-body interaction, *Bull. Amer. Math. Soc.* **79** (1973), 423.
12. D. GREENSPAN, "Discrete Models," Addison-Wesley, Reading, Mass., 1973.
13. F. CESCHINO AND J. KUNTZMANN, "Numerical Solution of Initial Value Problems," Prentice-Hall, Englewood Cliffs, N.J., 1966.
14. R. A. LABUDDE, Extension of Nordsieck's Method to the Numerical Integration of Higher-Order Ordinary Differential Equations, Univ. of Wis. Theoretical Chemistry Institute Report WIS-TCI-443 (1971).
15. C. W. GEAR, "Numerical Initial Value Problems in Ordinary Differential Equations", Section 9.2.5, Prentice-Hall, Englewood Cliffs, N.J., 1971.
16. E. J. SALETAN AND A. H. CROMER, "Theoretical Mechanics," Ch. 3, Wiley, N.Y., 1971.
17. W. THOMPSON AND P. G. TAIT, "Principles of Mechanics and Dynamics," Part I, Sections 168–198, 306–331, Dover, N.Y., 1960.

19. W. D. MacMillan, "Dynamics of Rigid Bodies," Chap. 9, Dover, N.Y., 1960.
20. R. A. LaBudde, Classical Mechanics of Molecular Collisions, Univ. of Wis. Theoretical Chemistry Institute Report WIS-TCI-414 (1973).
21. R. A. LaBudde and D. Greenspan, Discrete Mechanics, Technical Report # 192, 1973, Computer Science Department, Univ. of Wis., Madison.
22. L. D. Landau and E. M. Lifshitz, "Statistical Physics," 2nd Ed., Ch. 1, Addison-Wesley, Reading, Mass., 1969.