Journal of Statistical Physics, Vol. 61, Nos. 5/6, 1990

Hamilton's Equations for Constrained Dynamical Systems

Simon W. de Leeuw,[1] John W. Perram,[2] and Henrik G. Petersen[2]

Received February 21, 1990; final July 12, 1990

We derive expressions for the conjugate momenta and the Hamiltonian for classical dynamical systems subject to holonomic constraints. We give an algorithm for correcting deviations of the constraints arising in numerical solution of the equations of motion. We obtain an explicit expression for the momentum integral for constrained systems.

KEY WORDS: Constraint dynamics; Hamiltonian; metric tensor.

1. INTRODUCTION

A general problem in classical mechanics can be formulated as follows. For a system of n particles at the points $\mathbf{r}_1(t),..., \mathbf{r}_n(t)$ at time t, subject to M holonomic constraints of the form

$$\begin{aligned} F_1(\mathbf{r}_1(t),..., \mathbf{r}_n(t)) &= 0 \\ &\vdots \\ F_M(\mathbf{r}_1(t),..., \mathbf{r}_n(t)) &= 0, \end{aligned} \tag{1.1}$$

moving with velocities $\dot{\mathbf{r}}_1(t),..., \dot{\mathbf{r}}_n(t)$ under the influence of forces derivable from a potential function $U(\mathbf{r}_1(t),..., \mathbf{r}_n(t)) = 0$, find and solve the Newtonian differential equations for which the initial values of the position and velocity vectors are specified. This problem is sufficiently general to cover all problems which arise in classical statistical mechanics.

[1] Laboratory for Physical Chemistry, University of Amsterdam, 1018 WS Amsterdam, The Netherlands.

[2] Department of Mathematics and Computer Science, Odense University, 5230 Odense M, Denmark.

0022-4715/90/1200-1203$06.00/0

The textbook approach to advanced classical mechanics stresses the use of *generalized coordinates.* In this approach, due to Lagrange, $K = 3n - M$ variables $q_1(t),..., q_K(t)$ are introduced, on the assumption that we can find n vector-valued functions $\mathbf{R}_1(q_1(t),..., q_K(t)),..., \mathbf{R}_n(q_1(t),..., q_K(t))$ of them for which the constraint equations (1.1) are identically satisfied, viz.,

$$\begin{aligned} f_1(q_1(t),..., q_K(t)) &= F_1(\mathbf{R}_1,..., \mathbf{R}_n) = 0 \\ &\vdots \\ f_M(q_1(t),..., q_K(t)) &= F_M(\mathbf{R}_1,..., R_n) = 0 \end{aligned} \tag{1.2}$$

The result is *analytical mechanics*, a theory of great power and beauty which can be approached at many levels of mathematical sophistication. At its most basic level, the original Cartesian coordinates $\mathbf{r}_i(t)$ and their time derivatives $\dot{\mathbf{r}}_i(t)$ are eliminated from the *Lagrangian function*

$$L = \tfrac{1}{2} \sum m_i \dot{\mathbf{r}}_i(t)^2 - U(\mathbf{r}_1(t),..., \mathbf{r}_n(t)) \tag{1.3}$$

in favor of the K generalized coordinates $q_i(t)$ and K generalized velocities $\dot{q}_i(t)$. In this case, we have formally

$$L = L(q_1(t),..., q_K(t), \dot{q}_1(t),..., \dot{q}_K(t)) \tag{1.4}$$

The equations of motion in terms of these quantities can then be derived either from D'Alembert's or Hamilton's principle, yielding the well-known *Euler–Lagrange equations*

$$\frac{d}{dt}\left\{\frac{\partial L}{\partial \dot{q}_i}\right\} - \frac{\partial L}{\partial q_i} = 0, \qquad i = 1,..., K \tag{1.5}$$

These are a set of K second-order differential equations whose solution can be regarded as providing, via the functions $\mathbf{R}_i(q_1(t),..., q_K(t))$, a *parametric representation* for the *trajectories* $\mathbf{r}_1(t),..., \mathbf{r}_n(t)$ moving *on the surface of a K-dimensional manifold in* $\mathbb{R}^{3n}$.

An alternative, and in many ways more powerful, approach to analytical mechanics is due to Hamilton. For each generalized coordinate $q_i(t)$, we define a *conjugate momentum* $p_i(t)$ by

$$p_i(t) = \frac{\partial L}{\partial \dot{q}_i} \tag{1.6}$$

and a *Hamiltonian function* $H(q_1(t),..., q_K(t), p_1(t),..., p_K(t))$ by

$$H = \sum p_i(t)\, \dot{q}_i(t) - L \tag{1.7}$$

The result is the differential equations of Hamilton

$$\dot{q}_i(t) = \frac{\partial H}{\partial p_i}$$
$$\dot{p}_i(t) = -\frac{\partial H}{\partial q_i} \tag{1.8}$$

The $2K$ first-order differential equations (1.8) are equivalent to the K second-order Euler–Lagrange equations (1.5).

In recent years, there has been a certain amount of interest in applying the method of *molecular dynamics* to systems containing complex molecules.[1–7] For such systems, the approach of analytical mechanics cannot be applied because of the impractibility of finding the generalized coordinates and the increasing complexity of the resulting equations. Moreover, some of the most popular parametrizations, *Euler angles*, for example, lead to singularities in the equations of motion which make their numerical solution impossible. This has led researchers in this field to make practical use of *constraint dynamics*. There are two theoretical approaches to this. The first is the realization that the *forces of constraint* must be normal to the *surfaces of constraint*, defined by Eqs. (1.1). When these forces of constraint are added, the Euler–Lagrange equations (1.5) become

$$\frac{d}{dt}\left\{\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right\} - \frac{\partial L}{\partial \mathbf{r}_i} = \sum_{\alpha=1}^{M} \mu_\alpha \frac{\partial F_\alpha}{\partial \mathbf{r}_i}, \qquad i = 1,\ldots, n \tag{1.9}$$

The physical interpretation of the μ_α here is as numbers proportional to the magnitude of the forces of constraint.

Another approach is to graft the theory of *isoperimetric problems*[8,9] (constrained variational methods) onto Hamilton's principle, expressed as extremizing the *action integral*

$$\int L(\mathbf{r}_1(t),\ldots, \mathbf{r}_n(t), \dot{\mathbf{r}}_1(t),\ldots, \dot{\mathbf{r}}_n(t))\, dt \tag{1.10}$$

with respect to the trajectories subject to the constraints (1.1). This problem is attacked using the method of *Lagrange multipliers*. Following the theory, one replaces the function L in the Euler–Lagrange equations by the function L^* defined by

$$L^* = L + \sum_{\alpha=1}^{M} \mu'_\alpha F_\alpha \tag{1.11}$$

where the μ'_α are Lagrange multipliers. The result is Eqs. (1.9) with the μ_α replaced by the multipliers μ'_α. The equivalence between the forces of constraint in the D'Alembertian formulation and the multipliers in the variational formulation appears to have been first noted by Lanczos.[8]

These equations can only be useful if some practical way can be found to calculate the forces of constraint (or multipliers). A formal method of doing this by eliminating accelerations from the second time derivative of the constraints

$$\frac{d^2F_\alpha}{dt^2} = \sum_i \left(\ddot{\mathbf{r}}_i \cdot \frac{\partial F_\alpha}{\partial \mathbf{r}_i} + \sum_j \dot{\mathbf{r}}_i \cdot \frac{\partial^2 F_\alpha}{\partial \mathbf{r}_i \, \partial \mathbf{r}_j} \cdot \dot{\mathbf{r}}_j \right) = 0, \qquad \alpha = 1,..., M \tag{1.12}$$

is given in the next section.[1,2,4,10] Taken with the Euler–Lagrange equations (1.9), Eqs. (1.12) enable us to find a set of nonsingular linear equations for the forces of constraint which can then be substituted back into the equations of motion.

Unfortunately, these differential equations are unstable with respect to errors, so that the first attempts to implement constraint dynamics were within the context of the *numerical algorithms* used to integrate the equations of motion, particularly the algorithm SHAKE[1,2] and its descendants.[3]

Edberg *et al.*[4] published a numerical technique for finding the forces of constraint based on Eqs. (1.12), using penalty functions to discourage constraint violation, although a better method is given in Section 6 of this paper.

However, a number of problems remain. One of these is the vexed question of what have come to be known as *metric tensor corrections*[3,11] to the statistical mechanics of complex molecules. The reason for this state of affairs is that although the *dynamics* can be obtained within the framework of the Lagrangian theory, all fundamental proofs in statistical mechanics are derived within the *Hamiltonian* formalism.[12] For example, this formalism is necessary to make the connection between *time averages* of dynamical variables and their corresponding averages over the *phase space* consisting of the coordinates and their conjugate momenta.

There is surprisingly very little in the literature on mechanics and statistical mechanics about this point. The point of view of most classical textbooks is that constraints are something to be got rid of as soon as possible,[8,10,13,14] and in any case, before starting the Hamiltonian theory. An exception is the book by Sudarshan and Mukunda,[15] which refers to the theory of Dirac[16,17] (unfortunately without giving the references). These and a related work by Anderson and Bergmann[18] attack the structure of constrained or *nonstandard* Lagrangians from the viewpoint of

gauge theories. They take the point of view that the Lagrangian equations are dependent and seek to construct conjugate momenta and a Hamiltonian.

In Section 2, we begin by generalizing the problem stated above in terms of Cartesian coordinates by (possibly) eliminating some of the constraints in favor of a set of *constrained generalized coordinates.* This generalization is important to cover situations which can occur in practice, especially for the study of models of large molecules with relatively few internal degrees of freedom.[7] The Lagrangian equations are then derived within this framework. This generalization also leads to a more convenient notation.

The next problem is how to define *momenta* $\mathbf{p}_i(t)$ conjugate to the coordinate vectors $\mathbf{r}_i(t)$ when there are constraints of the form (1.1) operating. In Section 3, we do this via an *ansatz* and derive a set of *Hamilton-like* equations based on a *pseudo-Hamiltonian* analogous to the constrained Lagrangian (1.4).

In Section 4, we address the problem of proving the equivalence between these equations and the Lagrangian equations in the presence of the constraint forces.

In Section 5, we address some of the consequences of these equations in respect to *conservation laws.* In particular, we use the formulation in terms of *Poisson brackets* to establish that not only the Hamiltonian, but also the *equations of constraint* are constants of the motion. This establishes that the constrained motion takes place on the (lower-dimensional) *manifold* determined by the equations of constraint.

In Section 6, we give a brief summary of correction algorithms to facilitate numerical implementation of the results of this paper. This makes use of the fact that the true velocities can have no components normal to the surface of constraint.

In Section 7 we address the problem of giving a meaning to as well as a practical means of computation of *phase space* integrals of the form

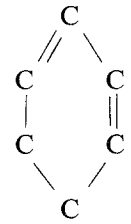
$$\int d\mathbf{p}_1 \cdots d\mathbf{p}_n \int d\mathbf{r}_1 \cdots d\mathbf{r}_n$$

over the manifold defined by the equations of constraint. This gives a practical solution to the problem, arising especially in Monte Carlo simulations, of computing the appropriate measure for integrals over the constrained configuration space.

2. LAGRANGIAN FORMULATION

The notation we developed in the introduction is in fact too restrictive. For example, although we may use the positions of the six carbon atoms

in a benzene molecule, shown below, as dynamical variables, if the molecule is assumed rigid, we may with advantage use the *principal axes vectors* as dynamical variables $\mathbf{u}_1(t),..., \mathbf{u}_3(t)$, as discussed elsewhere.[6,7]



To take account of this possibility, we consider a system described by N coordinates $q_1,..., q_N$ which are subject to M independent constraints of the form

$$f_\alpha(q_1,..., q_N) = 0, \qquad \alpha = 1,..., M \tag{2.1}$$

Differentiating the constraint equations (2.1) with respect to time yields

$$\frac{df_\alpha}{dt} = \sum_i \dot{q}_i \frac{\partial f_\alpha}{\partial q_i} = 0, \qquad \alpha = 1,..., M \tag{2.2a}$$

Differentiating once more, we find that the accelerations have to obey the equations

$$\frac{d^2 f_\alpha}{dt^2} = \sum_i \left(\ddot{q}_i \frac{\partial f_\alpha}{\partial q_i} + \sum_j \dot{q}_i \dot{q}_j \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \right) = 0, \qquad \alpha = 1,..., M \tag{2.2b}$$

The Lagrangian for the system can be written as

$$L(q_1,..., q_N, \dot{q}_1,..., \dot{q}_N) = \tfrac{1}{2} \sum_i m_i \dot{q}_i^2 - U(q_1,..., q_N) \tag{2.3}$$

where U is the potential energy. Because of the constraint equations (2.1) and (2.2), neither the coordinates q_i nor the velocities $\dot{q}_i$ are independent variables. Here we have assumed the mass tensor to be diagonal, which is adequate for most purposes. An extension to a more general form for the mass tensor is straightforward.

The classical method to integrate the equations of motion proceeds by eliminating the redundant variables from the Lagrangian using the constraint equations. Such a procedure is only feasible when the constraint equations can be inverted. However, such an inversion is usually not possible.

Alternatively, one can use Lagrange multipliers. Traditionally, one then starts from a constrained Lagrangian L' defined as

$$L' = L + \sum_{\alpha} \mu_\alpha f_\alpha(q_1, ..., q_N) \tag{2.4}$$

where the μ_α are the Lagrange multipliers. The Lagrangian equations of motion now contain the multipliers μ_α, which are eliminated using Eq. (2.2b).

For our purposes it turns out to be useful to incorporate the velocity constraints (2.2a) rather than the constraints themselves into the Lagrangian. Thus, we define the constrained Lagrangian L^* as

$$L^* = L + \sum_{\alpha} \kappa_\alpha \sum_j \dot{q}_j \frac{\partial f_\alpha}{\partial q_j} \tag{2.5}$$

The equations of motion are then derived in the usual manner from L^* as

$$\ddot{q}_i = m_i^{-1} \left(F_i - \sum_{\alpha} \dot{\kappa}_\alpha \frac{\partial f_\alpha}{\partial q_i} \right) \tag{2.6}$$

where F_i is the force $F_i = -\partial U/\partial q_i$. It is straightforward to show that these equations are identical to the equations of motion derived from (2.4) if one identifies $\dot{\kappa}_\alpha = \mu_\alpha$. To obtain an equation for the $\dot{\kappa}_\alpha$, we multiply (2.6) by $\partial f_\alpha/\partial q_i$ and sum over all i. Using Eq. (2.2b), we find

$$-\sum_i \sum_j \dot{q}_i \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \dot{q}_j = \sum_i m_i^{-1} F_i \frac{\partial f_\alpha}{\partial q_i} - \sum_i m_i^{-1} \sum_\beta \dot{\kappa}_\beta \frac{\partial f_\beta}{\partial q_i} \frac{\partial f_\alpha}{\partial q_i} \tag{2.7}$$

From this point on, we are going to make extensive use of matrix notation. We will distinguish between matrices of size M and those of size N by denoting the former by symbols $\underline{X}$ or $\underline{\underline{X}}$ and the latter by bold-faced symbols $\mathbf{X}$.

We now define a vector $\underline{T}$ with components

$$(\underline{T})_\alpha = \sum_i \sum_j \dot{q}_i \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \dot{q}_j \tag{2.8a}$$

a matrix $\underline{\underline{M}}$ with elements

$$(\underline{\underline{M}})_{\alpha\beta} = \sum_i m_i^{-1} \frac{\partial f_\beta}{\partial q_i} \frac{\partial f_\alpha}{\partial q_i} \tag{2.8b}$$

and vectors $\underline{F}$ and $\dot{\underline{K}}$ with components

$$(\underline{F})_\alpha = \sum_i m_i^{-1} F_i \frac{\partial f_\alpha}{\partial q_i} \tag{2.8c}$$

$$(\dot{\underline{K}})_\alpha = \dot{\kappa}_\alpha \tag{2.8d}$$

Equation (2.7) can be written as

$$\underline{\underline{M}}\dot{\underline{K}} = \underline{F} + \underline{T} \tag{2.9}$$

At this stage it is useful to consider some of the properties of the matrix $\underline{\underline{M}}$. It is obvious that $\underline{\underline{M}}$ is symmetric. We now show that $\underline{\underline{M}}$ is also positive definite.[10]

Consider a set of numbers c_α, $\alpha = 1,..., M$, not all equal to zero. Since the constraints f_α are independent, the vectors $(\partial f_\alpha/\partial q_1,..., \partial f_\alpha/\partial q_N) \equiv \mathbf{f}_\alpha$ are independent as well. Hence $\sum_\alpha c_\alpha \mathbf{f}_\alpha \neq \underline{0}$. Now consider the quadratic form

$$\sum_\alpha \sum_\beta c_\alpha (\underline{\underline{M}})_{\alpha\beta} c_\beta = \sum_\alpha \sum_\beta c_\alpha \sum_i m_i^{-1} \frac{\partial f_\alpha}{\partial q_i} \frac{\partial f_\beta}{\partial q_i} c_\beta$$

$$= \sum_i m_i^{-1} \left(\sum_\alpha c_\alpha \frac{\partial f_\alpha}{\partial q_i} \right)^2 > 0$$

which completes the proof. It follows that $\underline{\underline{M}}$ is nonsingular and its inverse $\underline{\underline{M}}^{-1}$ is also a positive-definite symmetric matrix.

We can now make contact with the Dirac theory[15–17] by inserting the explicit form of the multipliers given by Eq. (2.9) and using Eq. (2.2b) to eliminate the velocities to obtain

$$\sum_j (\mathbf{Q})_{ij} \ddot{q}_j = \sum_j (\mathbf{Q})_{ij} F_j \tag{2.10}$$

where $\mathbf{Q}$ is an $N \times N$ square matrix with elements given by

$$(\mathbf{Q})_{ij} = m_i^{-1} \delta_{ij} - m_i^{-1} \sum_\alpha \sum_\beta \frac{\partial f_\alpha}{\partial q_i} (\underline{\underline{M}}^{-1})_{\alpha\beta} \frac{\partial f_\beta}{\partial q_j} m_j^{-1} \tag{2.11}$$

This matrix has rank $N - M$, as we now show. Consider the M vectors $\mathbf{f}_\nu$ defined above with components

$$(\mathbf{f}_\nu)_j = \frac{\partial f_\nu}{\partial q_j} \tag{2.12}$$

Then

$$(\mathbf{Q}\mathbf{f}_\nu)_i = m_i^{-1} \frac{\partial f_\nu}{\partial q_i} - m_i^{-1} \sum_\alpha \sum_\beta \frac{\partial f_\alpha}{\partial q_i} (\underline{\underline{M}}^{-1})_{\alpha\beta} \sum_j m_j^{-1} \frac{\partial f_\beta}{\partial q_j} \frac{\partial f_\nu}{\partial q_j} \tag{2.13}$$

which is zero by the definition of the matrix $\underline{\underline{M}}$. Thus the M vectors $\mathbf{f}_\alpha$ are eigenvectors of the matrix $\mathbf{Q}$ with eigenvalues 0. Note that although these eigenvectors are independent, they are not necessarily orthonormal. However, it is a straightforward matter to construct a set of M vectors $\mathbf{v}_\alpha$ which form an orthonormal basis for the M-dimensional subspace of $\mathbb{R}^N$ spanned by the vectors $\mathbf{f}_\alpha$, for example, using the Gram–Schmidt method. Each of these is also an eigenvector of $\mathbf{Q}$ with eigenvector 0. Since $\mathbf{Q}$ is symmetric, its eigenvectors can always be chosen to form an orthonormal set.

Thus, only $N-M$ of the accelerations in Eq. (2.10) are independent. These considerations have a simple geometric interpretation. The motion [as described by the velocities $\dot{q}_i(t)$] takes place in an $(N-M)$-dimensional subspace of $\mathbb{R}^N$ orthogonal to the M-dimensional subspace spanned by the linearly independent vectors $\mathbf{f}_\alpha$. We can regard the matrix $\mathbf{Q}$ as a representation of an operator which projects any vector $\mathbf{v}$ onto that orthogonal subspace.

3. HAMILTONIAN FORMULATION

In this section we construct a Hamiltonian corresponding to the constrained Lagrangian L^* where all the coordinates q_i and generalized momenta p_i can be considered as independent variables.

Let us start from the Lagrangian

$$L^* = \frac{1}{2}\sum_i m_i \dot{q}_i^2 - U(q_1, \ldots, q_N) + \sum_\alpha \gamma_\alpha \sum_j \dot{q}_j \frac{\partial f_\alpha}{\partial q_j} \tag{3.1}$$

For clarity we have renamed the Lagrange multipliers γ_α, since at this stage it remains to be shown that they are identical to κ_α. We define momenta p_i in an obvious manner

$$p_i = \frac{\partial L^*}{\partial \dot{q}_i} = m_i \dot{q}_i + \sum_\alpha \gamma_\alpha \frac{\partial f_\alpha}{\partial q_i} \tag{3.2}$$

Inverting (3.2), we get for the velocity $\dot{q}_i$

$$\dot{q}_i = m_i^{-1}\left(p_i - \sum_\alpha \gamma_\alpha \frac{\partial f_\alpha}{\partial q_i}\right) \tag{3.3}$$

In terms of the generalized momenta p_i the velocity constraints become

$$0 = \sum_i \dot{q}_i \frac{\partial f_\alpha}{\partial q_i} = \sum_i m_i^{-1} p_i \frac{\partial f_\alpha}{\partial q_i} - \sum_i m_i^{-1} \sum_\beta \gamma_\beta \frac{\partial f_\beta}{\partial q_i}\frac{\partial f_\alpha}{\partial q_i} \tag{3.4}$$

or in matrix notation

$$\underline{P} = \underline{\underline{M}}\,\underline{\Gamma} \tag{3.5}$$

where we have defined a vector $\underline{P}$ with components

$$(\underline{P})_\alpha = \sum_i m_i^{-1} p_i \frac{\partial f_\alpha}{\partial q_i} \tag{3.6a}$$

and a vector $\underline{\Gamma}$ with components

$$(\underline{\Gamma})_\alpha = \gamma_\alpha \tag{3.6b}$$

Note that when $\underline{\Gamma}$ is obtained from Eq. (3.5) for a given set of p_i the velocity constraints are satisfied identically.

We now construct a Hamiltonian H as

$$H = \sum_i \dot{q}_i p_i - L = \sum_i \dot{q}_i p_i - \tfrac{1}{2} \sum_i m_i \dot{q}_i^2 + U(q_1, ..., q_N) \tag{3.7}$$

Because for any given set of p_i the velocity constraints are automatically satisfied, we use L rather than L^*. Eliminating the velocities in favor of the momenta, we get

$$H = \tfrac{1}{2} \sum_i m_i^{-1} p_i^2 - \tfrac{1}{2} \underline{\Gamma}^T \underline{\underline{M}}\,\underline{\Gamma} + U(q_1, ..., q_N) \tag{3.8}$$

Thus, we can obtain a Hamiltonian which is a function only of momenta and coordinates by eliminating $\underline{\Gamma}$ using Eq. (3.5),

$$H(q_1, ..., q_N, p_1, ..., p_N) = \tfrac{1}{2} \sum_i m_i^{-1} p_i^2 - \tfrac{1}{2} \underline{P}^T \underline{\underline{M}}^{-1} \underline{P} + U(q_1, ..., q_N) \tag{3.9}$$

We can now regard the Hamiltonian as a function of N *independent* coordinates q_i and N *independent* momenta p_i and derive the Hamiltonian equations of motion in the usual manner, i.e.,

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{3.10}$$

For the sake of completeness, we write these equations out in full: we find

$$\dot{q}_i = m_i^{-1} \left(p_i - \sum_\alpha \gamma_\alpha \frac{\partial f_\alpha}{\partial q_i} \right) \tag{3.10a}$$

and

$$\dot{p}_i = -\frac{\partial U}{\partial q_i} + \sum_\alpha \sum_j \gamma_\alpha \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \dot{q}_j \tag{3.10b}$$

We may view Eq. (3.10) in a different light by inserting in it the explicit forms for the multipliers given by Eqs. (3.5)–(3.6) to obtain

$$\dot{q}_i = \sum_j (\mathbf{Q})_{ij} p_j$$

showing that the velocities have no components perpendicular to the constraint surface.

In Section 5 we shall show that the constraint functions $f_\alpha(q_1, ..., q_N)$ are conserved quantities for the Hamiltonian H given in (3.9). Furthermore, as shown in the next section, the Hamiltonian equations of motion are entirely equivalent to the Lagrangian equations (2.5). The main advantage of using the Hamiltonian equations of motion is that if one starts with a set of coordinates which satisfy the constraints (2.1) at time $t = 0$, the motion of the system will automatically remain on the surface defined by the constraint equations (2.1) for all time. In other words, the solutions of Eq. (3.10) automatically satisfy the constraint equations if they satisfy Eq. (2.1) at some initial time t_0.

4. EQUIVALENCE OF THE HAMILTONIAN AND LAGRANGIAN EQUATIONS OF MOTION

To show the equivalence of the Hamiltonian and Lagrangian equations of motion, we first expand the Hamiltonian (3.9):

$$H = \tfrac{1}{2} \sum_i m_i^{-1} p_i^2 - \tfrac{1}{2} \sum_\alpha \sum_\beta P_\alpha (\underline{\underline{\mathbf{M}}}^{-1})_{\alpha\beta} P_\beta + U(q_1, ..., q_N) \tag{4.1}$$

Differentiating H with respect to p_i gives

$$\dot{q}_i = m_i^{-1} p_i - m_i^{-1} \sum_\alpha \frac{\partial f_\alpha}{\partial q_i} \sum_\beta (\underline{\underline{\mathbf{M}}}^{-1})_{\alpha\beta} P_\beta = m_i^{-1} p_i - m_i^{-1} \sum_\alpha \gamma_\alpha \frac{\partial f_\alpha}{\partial q_i} \tag{4.2}$$

which is the same as Eq. (3.3), as should be expected.

We now derive equations for $\ddot{q}_i$ from the Hamiltonian equations of motion. Differentiating Eq. (4.2) with respect to time yields

$$\ddot{q}_i = m_i^{-1} \left(\dot{p}_i - \sum_\alpha \dot{\gamma}_\alpha \frac{\partial f_\alpha}{\partial q_i} - \sum_\alpha \gamma_\alpha \sum_j \dot{q}_j \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \right) \tag{4.3a}$$

$$= m_i^{-1} \left[\dot{p}_i - \sum_\alpha \dot{\gamma}_\alpha \frac{\partial f_\alpha}{\partial q_i} - \sum_\alpha \gamma_\alpha \sum_j m_j^{-1} \left(p_j - \sum_\alpha \gamma_\alpha \frac{\partial f_\alpha}{\partial q_j} \right) \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \right] \tag{4.3b}$$

By substituting $\dot{p}_i$ from the Hamiltons equations (3.10), viz.

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} = F_i + \frac{1}{2}\frac{\partial}{\partial q_i}(\underline{\underline{P}}^T \underline{\underline{M}}^{-1} \underline{\underline{P}}) \tag{4.4}$$

we want to obtain equations for $\ddot{q}_i$ which have the same form as the Lagrangian equations of motion (2.5). This substitution gives

$$\ddot{q}_i = m_i^{-1}\left[F_i - \sum_\alpha \dot{\gamma}_\alpha \frac{\partial f_\alpha}{\partial q_i} + \frac{1}{2}\frac{\partial}{\partial q_i}(\underline{\underline{P}}^T \underline{\underline{M}}^{-1} \underline{\underline{P}}) - \sum_\alpha \gamma_\alpha \sum_j m_j^{-1}\left(p_j - \sum_\beta \gamma_\beta \frac{\partial f_\beta}{\partial q_j}\right)\frac{\partial^2 f_\alpha}{\partial q_i \partial q_j}\right] \tag{4.5}$$

This equation has the same form as (2.5) if the last two terms in (4.5) cancel. This is indeed the case, since

$$\begin{aligned}
&\sum_\alpha \gamma_\alpha \sum_j m_j^{-1}\left(p_j - \sum_\beta \gamma_\beta \frac{\partial f_\beta}{\partial q_j}\right)\frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \\
&\quad = \sum_\alpha \gamma_\alpha \frac{\partial}{\partial q_i}\left(\sum_i m_j^{-1} p_j \frac{\partial f_\alpha}{\partial q_j}\right) \\
&\qquad -\frac{1}{2}\sum_\alpha \sum_\beta \gamma_\alpha \gamma_\beta \frac{\partial}{\partial q_i}\left(\sum_j m_j^{-1}\frac{\partial f_\alpha}{\partial q_j}\frac{\partial f_\beta}{\partial q_j}\right) \\
&\quad = \underline{\underline{\Gamma}}^T \frac{\partial \underline{\underline{P}}}{\partial q_i} - \frac{1}{2}\underline{\underline{\Gamma}}^T \frac{\partial \underline{\underline{M}}}{\partial q_i}\underline{\underline{\Gamma}} = \frac{1}{2}\frac{\partial}{\partial q_i}(\underline{\underline{P}}^T \underline{\underline{M}}^{-1} \underline{\underline{P}})
\end{aligned}$$

Thus, Eq. (4.5) becomes

$$\ddot{q}_i = m_i^{-1}\left(F_i - \sum_\alpha \dot{\gamma}_\alpha \frac{\partial f_\alpha}{\partial q_i}\right) \tag{4.6}$$

which is the desired result.

Hence, Eq. (4.6) is equivalent to the Lagrangian equation of motion if we can identify the coefficients $\dot{\kappa}_\alpha$ obtained from Eq. (2.8) with the coefficients $\dot{\gamma}_\alpha$. Differentiating Eq. (3.5) gives

$$\underline{\dot{P}} = \underline{\underline{M}}\underline{\dot{\Gamma}} = -\underline{\dot{\underline{M}}}\underline{\Gamma} + \underline{\dot{P}} \tag{4.7}$$

so that the equivalence of the two equations is shown if

$$-\underline{\dot{\underline{M}}}\underline{\Gamma} + \underline{\dot{P}} = \underline{F} + \underline{T} \tag{4.8}$$

To establish this, consider the vector $\underline{T}$ defined in Eq. (2.8a), viz.

$$(\underline{T})_\alpha = \sum_i \sum_j \dot{q}_i \frac{\partial^2 f_\alpha}{\partial q_i \partial q_j} \dot{q}_j = \frac{d}{dt}\left(\sum_i \dot{q}_i \frac{\partial f_\alpha}{\partial q_i}\right) - \sum_i \ddot{q}_i \frac{\partial f_\alpha}{\partial q_i}$$

Substituting Eq. (3.3) for $\dot{q}_i$, we get

$$\begin{aligned}(\underline{T})_\alpha &= \frac{d}{dt}\left(\sum_i m_i^{-1} p_i \frac{\partial f_\alpha}{\partial q_i}\right) - \frac{d}{dt}\left(\sum_i m_i^{-1} \sum_\beta \frac{\partial f_\alpha}{\partial q_i}\frac{\partial f_\beta}{\partial q_i}\gamma_\beta\right) - \sum_i \ddot{q}_i \frac{\partial f_\alpha}{\partial q_i} \\ &= (\dot{\underline{P}})_\alpha - \frac{d}{dt}(\underline{\underline{M}}\underline{\Gamma})_\alpha - \sum_i m_i^{-1} F_i \frac{\partial f_\alpha}{\partial q_i} + \sum_i m_i^{-1} \sum_\beta \frac{\partial f_\alpha}{\partial q_i}\frac{\partial f_\beta}{\partial q_i}\dot{\gamma}_\beta\end{aligned}$$

where we have substituted Eq. (4.6) for the accelerations $\ddot{q}_i$. Then

$$(\underline{T})_\alpha = (\dot{\underline{P}})_\alpha - (\underline{F})_\alpha - \frac{d}{dt}(\underline{\underline{M}}\underline{\Gamma})_\alpha + (\underline{\underline{M}}\dot{\underline{\Gamma}})_\alpha = (\dot{\underline{P}})_\alpha - (\underline{F})_\alpha - (\dot{\underline{\underline{M}}}\underline{\Gamma})_\alpha$$

Hence $-\dot{\underline{\underline{M}}}\underline{\Gamma} + \dot{\underline{P}} = \underline{F} + \underline{T}$. Thus the $\dot{\gamma}_\alpha$ are the same as the $\dot{\kappa}_\alpha$, which completes the proof of the equivalence of the Lagrangian and Hamiltonian equations of motion.

5. CONSERVATION LAWS

Having established the equivalence of the Lagrangian and Hamiltonian formulations, we now show that the energy and (under certain assumptions) the total generalized momentum are conserved.

It is obvious that the Hamiltonian can be identified with the total energy E of the system. Energy conservation then follows because

$$\frac{dH}{dt} = \sum_i \left(\dot{q}_i \frac{\partial H}{\partial q_i} + \dot{p}_i \frac{\partial H}{\partial p_i}\right) = \sum_i \left(\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i}\right) = 0 \tag{5.1}$$

To ensure that the total generalized momentum is conserved, we must assume that the constraints are functions only of coordinate differences, i.e.,

$$f_\alpha(q_1, ..., q_N) = f_\alpha(q_1 - q_2, q_1 - q_3, ..., q_i - q_j, ..., q_{N-1} - q_N) \tag{5.2}$$

Then

$$\sum_i \frac{\partial f_\alpha}{\partial q_i} = 0 \tag{5.3}$$

We further assume that there is no external force field, i.e., that

$$\sum_i F_i = 0 \tag{5.4}$$

Almost all cases of interest where the total momentum should be conserved satisfy Eqs. (5.2)–(5.4).

Differentiating Eq. (3.2) and summing over all i gives

$$\sum_i \dot{p}_i = \sum_i m_i \ddot{q}_i + \sum_\alpha \dot{\gamma}_\alpha \sum_i \frac{\partial f_\alpha}{\partial q_i} + \sum_\alpha \gamma_\alpha \frac{d}{dt}\left(\sum_i \frac{\partial f_\alpha}{\partial q_i}\right)$$

$$= \sum_i F_i + \sum_\alpha \gamma_\alpha \frac{d}{dt}\left(\sum_i \frac{\partial f_\alpha}{\partial q_i}\right) = 0$$

Thus, under the assumptions (5.2)–(5.4) the total generalized momentum is a constant of the motion.

Finally, we prove that the functions f_α are constants of the motion prescribed by the Hamiltonian H. We define the Poisson bracket $[A, B]$ of two dynamical variables $A(p, q)$ and $B(p, q)$ in the usual way as

$$[A, B] = \sum_i \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i}\right) \tag{5.5}$$

It is immediately clear that a dynamical variable is a constant of the motion for H if

$$[H, A] = 0 \tag{5.6}$$

The Poisson bracket $[H, f_\alpha]$ is

$$[H, f_\alpha] = \sum_i \left(\frac{\partial H}{\partial q_i}\frac{\partial f_\alpha}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial f_\alpha}{\partial q_i}\right) = -\sum_i \dot{q}_i \frac{\partial f_\alpha}{\partial q_i} = 0 \tag{5.7}$$

Thus, the functions f_α, $\alpha = 1,..., M$, appearing in the equations of constraint are constants of the motion for the Hamiltonian H.

6. CORRECTION OF NUMERICALLY GENERATED TRAJECTORIES

These results are contained elsewhere, but are summarized here to enable the reader to implement the results of this paper numerically. Suppose we are solving the system of differential equations (3.10) numerically using a high-order DE solver algorithm. Then, although the constraint functions (2.1) are constants of the motion, the trajectories may be unstable with respect to small deviations from the constraint manifold. This is a widespread problem in constraint dynamics, and we do not expect it to disappear here. More precisely, suppose that a particular time step of the

solution generates a vector $\mathbf{q}^0(t)$ in the N-dimensional phase space, such that $f_\alpha(\mathbf{q}^0(t)) \neq 0$. If the constraints were satisfied at the previous integration step, then

$$\mathbf{f}_\alpha(\mathbf{q}^0) \sim O(h^k) \tag{6.1}$$

where h is the integration time step and k the order of the DE solver. Any correction to $\mathbf{q}^0$ can be written as

$$\mathbf{q} = \mathbf{q}^0 + \left(\sum_\beta \varepsilon_\beta \frac{\partial f_\beta(\mathbf{q})}{\partial \mathbf{q}} + \mathbf{w}_\perp \right) h^k \tag{6.2}$$

where the vector $\mathbf{w}_\perp$ is in the orthogonal subspace to the M-dimensional subspace spanned by the gradients of the constraint equations. For our purposes, it suffices to find the coefficients ε_α. We insert Eq. (6.2) into the constraint equations and apply Taylor's theorem to obtain

$$\begin{aligned} f_\alpha(\mathbf{q}) &= f_\alpha\left(\mathbf{q}^0 + \left(\sum_\beta \varepsilon_\beta \frac{\partial f_\beta(\mathbf{q})}{\partial \mathbf{q}} + \mathbf{w}_\perp \right) h^k \right) \\ &= f_\alpha(\mathbf{q}^0) + h^k \sum_\beta \varepsilon_\beta \frac{\partial f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}} \cdot \frac{\partial f_\beta(\mathbf{q})}{\partial \mathbf{q}} + h^k \mathbf{w}_\perp \cdot \frac{\partial f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}} + O(h^{2k}) \end{aligned} \tag{6.3}$$

We note that the right-hand side of Eq. (6.3) still contains the vector $\mathbf{q}$. A further application of Taylor's theorem gives

$$\frac{\partial f_\alpha(\mathbf{q})}{\partial \mathbf{q}} = \frac{\partial f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}} + h^k \frac{\partial^2 f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}\, \partial \mathbf{q}} \cdot \mathbf{w} \tag{6.4}$$

where

$$\mathbf{w} = \left(\sum_\beta \varepsilon_\beta \frac{\partial f_\beta(\mathbf{q})}{\partial \mathbf{q}} + \mathbf{w}_\perp \right)$$

Inserting Eq. (6.4) into Eq. (6.3) yields the result

$$f_\alpha(\mathbf{q}) = f_\alpha(\mathbf{q}^0) + h^k \sum_\beta \varepsilon_\beta \frac{\partial f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}} \cdot \frac{\partial f_\beta(\mathbf{q}^0)}{\partial \mathbf{q}} + O(h^{2k}) \tag{6.5}$$

Because of Eq. (6.1), the quadratic correction term in the last member of Eq. (6.3) is negligible. Then Eq. (6.5) leads to the nonsingular set of M linear equations

$$\sum_\beta \left[\frac{\partial f_\alpha(\mathbf{q}^0)}{\partial \mathbf{q}} \cdot \frac{\partial f_\beta(\mathbf{q}^0)}{\partial \mathbf{q}} \right] (h^k \varepsilon_\beta) = -f_\alpha(\mathbf{q}^0(t)) \tag{6.6}$$

for the M correction parameters $h^k\varepsilon_\beta$. No corrections are required for the velocity constraints, as these are automatically satisfied by construction of the p_i.

We have performed numerical tests of this correction algorithm by simulating rigid models of the molecules CCl_4 (tetrachloromethane) and PCl_3 (phosphorus trichloride) within the framework of the Lagrangian formalism. The equations of motion were solved using a fifth-order predictor-corrector algorithm. For these models, the bond length and bond angle constraints are all quadratic functions of relative atomic coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$ of the form

$$(\mathbf{r}_i - \mathbf{r}_j)^2 = d_{ij}^2$$

The correction algorithm was applied whenever

$$(\mathbf{r}_i - \mathbf{r}_j)^2/d_{ij}^2 - 1$$

exceeded 10^{-5}. With this tolerance, each molecule was corrected about every 20th integration step. Because of its nature, the correction algorithm does not affect motion on the constraint surface, and hence cannot do any violence to the dynamics. We believe that this algorithm represents the optimal solution to computational problems which have occurred in constraint dynamics.

7. PHASE SPACE INTEGRALS

The nature of the problem and a clue to its solution are best introduced by a simple example, which will also serve to illustrate many of the concepts in the preceding sections. The simplest case of a dynamic system for which these considerations should hold is the case of the rotation of an axially symmetrical body about its center of mass. Let $\mathbf{u}(t)$ denote the unit vector specifying the orientation of the rotation axis. Then the only constraint is

$$\mathbf{u}(t)^2 = 1 \tag{7.1}$$

and its differentiated form is

$$\mathbf{u}(t) \cdot \dot{\mathbf{u}}(t) = 0 \tag{7.2}$$

The considerations above suggest that the constrained Lagrangian is

$$L^* = \tfrac{1}{2}\lambda\dot{\mathbf{u}}(t)^2 + \gamma(t)\,\mathbf{u}(t) \cdot \dot{\mathbf{u}}(t) + U(\mathbf{u}(t)) \tag{7.3}$$

where λ is the (nonzero) eigenvalue of the inertia matrix. The momentum $\mathbf{p}(t)$ conjugate to $\mathbf{u}(t)$ is then

$$\mathbf{p}(t) = \lambda \dot{\mathbf{u}}(t) + \gamma(t)\, \mathbf{u}(t) \tag{7.4}$$

Taking the scalar product of this with the vector $\mathbf{u}(t)$ and using the constraint and its time-differentiated form, we find that

$$\gamma(t) = \mathbf{p}(t) \cdot \mathbf{u}(t) \tag{7.5}$$

so that

$$\dot{\mathbf{u}}(t) = \lambda^{-1}\{\mathbf{p}(t) - [\mathbf{p}(t) \cdot \mathbf{u}(t)]\, \mathbf{u}(t)\} \tag{7.6}$$

The Hamiltonian is then

$$H = \tfrac{1}{2}\lambda^{-1}\{\mathbf{p}(t) - [\mathbf{p}(t) \cdot \mathbf{u}(t)]\, \mathbf{u}(t)\}^2 + U(\mathbf{u}(t)) \tag{7.7}$$

$$= \tfrac{1}{2}\lambda^{-1}\{\mathbf{p}(t)^2 - [\mathbf{p}(t) \cdot \mathbf{u}(t)]^2\} + U(\mathbf{u}(t)) \tag{7.7a}$$

Note that this quantity is always nonnegative. We may now write down Hamilton's equations: the first is

$$\dot{\mathbf{u}}(t) = \lambda^{-1}\{\mathbf{p}(t) - [\mathbf{p}(t) \cdot \mathbf{u}(t)]\, \mathbf{u}(t)\} \tag{7.8}$$

and the second is

$$\dot{\mathbf{p}}(t) = \lambda^{-1}[\mathbf{p}(t) \cdot \mathbf{u}(t)]\, \mathbf{p}(t) - \frac{\partial U}{\partial \mathbf{u}} \tag{7.9}$$

These equations are equivalent to the corresponding constrained Lagrangian equations.

To illustrate the problems which arise in discussing statistical mechanics and, in particular, integrals over the momentum space, let us rewrite Eq. (7.7a) in the form

$$H = \tfrac{1}{2}\lambda^{-1}\mathbf{p}(t)^T\, (\mathbf{I} - \mathbf{u}(t)\, \mathbf{u}(t)^T)\, \mathbf{p}(t) + U(\mathbf{u}(t)) \tag{7.10}$$

The matrix $\mathbf{Q}$, given by

$$\mathbf{Q} = \mathbf{I} - \mathbf{u}(t)\, \mathbf{u}(t)^T \tag{7.11}$$

has rank 2, since it has an eigenvector $\mathbf{u}(t)$ with eigenvalue 0. Any attempt to compute the *momentum integral*

$$\int d\mathbf{p} \exp\{-\tfrac{1}{2}\beta\lambda^{-1}\mathbf{p}(t)^T\, [\mathbf{I} - \mathbf{u}(t)\, \mathbf{u}(t)^T]\, \mathbf{p}(t)\} \tag{7.12}$$

where $\beta = (k_B T)^{-1}$ in the *canonical ensemble* as an unrestricted integral over the three components of $\mathbf{p}$ will lead to a divergent result.

If $\mathbf{v}$ and $\mathbf{w}$ are any two orthonormal vectors spanning the subspace orthogonal to $\mathbf{u}$, then the unitary matrix $\mathbf{U}$ with columns consisting of $(\mathbf{u}, \mathbf{v}, \mathbf{w})$ diagonalizes the matrix $\mathbf{Q}$. If we denote by $\mathbf{p}'$ the vector $\mathbf{Up}$, then we may rewrite Eq. (7.10) as

$$H = \tfrac{1}{2}\lambda^{-1}\mathbf{p}'(t)^T\,(\mathrm{diag}(0, 1, 1))\,\mathbf{p}'(t) + \mathbf{U}(\mathbf{u}(t)) \tag{7.13}$$

In this representation the 1-component of the momentum is absent. As the integral in (7.12) is invariant under a unitary transformation, its correct value is given by the double integral

$$\iint dp_2'\,dp_3' \exp\{-\tfrac{1}{2}\beta\lambda^{-1}\mathbf{p}'(t)^T\,[\mathrm{diag}(0, 1, 1)]\,\mathbf{p}'(t)\} \tag{7.14}$$

leading to the well-known result for the momentum integral of the symmetric rotator.

Let us proceed to the general case and consider only the kinetic part T of the Hamiltonian.

$$T = \tfrac{1}{2}\sum_i m_i^{-1}p_i^2 - \tfrac{1}{2}\sum_\alpha\sum_\beta P_\alpha(\underline{\underline{\mathbf{M}}}^{-1})_{\alpha\beta}\,P_\beta$$

which, on inserting the explicit forms for the P_α, becomes

$$T = \frac{1}{2}\sum_i\sum_j p_i m_i^{-1}\delta_{ij}\,p_j - \frac{1}{2}\sum_i\sum_j p_i m_i^{-1}\sum_\alpha\sum_\beta \frac{\partial f_\alpha}{\partial q_i}(\underline{\underline{\mathbf{M}}}^{-1})_{\alpha\beta}\frac{\partial f_\beta}{\partial q_j}\,m_j^{-1}p_j \tag{7.15}$$

If we denote by $\mathbf{p}$ a vector in the momentum space whose N components are the momenta, then T may be written as

$$T = \tfrac{1}{2}\mathbf{p}^T\mathbf{Q}\mathbf{p} \tag{7.16}$$

where $\mathbf{Q}$ is the $N \times N$ square matrix with (ij) element defined in Eq. (2.11), given by

$$(\mathbf{Q})_{ij} = m_i^{-1}\delta_{ij} - m_i^{-1}\sum_\alpha\sum_\beta \frac{\partial f_\alpha}{\partial q_i}(\underline{\underline{\mathbf{M}}}^{-1})_{\alpha\beta}\frac{\partial f_\beta}{\partial q_j}\,m_j^{-1} \tag{7.17}$$

The rank of this matrix has been shown to be $N - M$ in Section 2, so that a result analogous to that obtained for the rigid rotator holds.

Let us now show that the matrix $\mathbf{Q}$ is nonnegative definite. Using Eq. (3.10a), we have

$$\frac{1}{2}\sum_i m_i^{-1}p_i^2 = \frac{1}{2}\sum_i m_i^{-1}\left(m_i\dot{q}_i + \sum_\alpha \gamma_\alpha\frac{\partial f_\alpha}{\partial q_i}\right)^2 \tag{7.18}$$

so that

$$\frac{1}{2}\sum_i m_i^{-1}p_i^2 - \frac{1}{2}\sum_\alpha\sum_\beta \gamma_\alpha \sum_i m_i^{-1}\frac{\partial f_\alpha}{\partial q_i}\frac{\partial f_\beta}{\partial q_i}\gamma_\beta = \frac{1}{2}\sum_i m_i \dot{q}_i^2 \tag{7.19}$$

which proves the nonnegativity of the kinetic energy.

To establish the general result analogous to Eq. (7.13), we need to find the $N-M$ positive eigenvalues $\lambda_{M+1},..., \lambda_N$ of the matrix $\mathbf{Q}$ and the corresponding (orthonormal) eigenvectors $\mathbf{v}_{M+1},..., \mathbf{v}_N$. Because of the symmetry of $\mathbf{Q}$, each of these is orthogonal to the vectors $\mathbf{v}_1,..., \mathbf{v}_M$. Thus, the $N \times N$ matrix $\mathbf{V}$ whose columns are the vectors $\mathbf{v}_\alpha$ is a unitary matrix which diagonalizes the matrix $\mathbf{Q}$. Thus, we have

$$T = \tfrac{1}{2}(\mathbf{Vp})^T \operatorname{diag}(0,..., 0, \lambda_{M+1},..., \lambda_N)(\mathbf{Vp}) \tag{7.20}$$

If we define $\mathbf{p}' = \mathbf{Vp}$, then the momentum integral for this Hamiltonian is

$$\int \cdots \int dp'_{M+1} \cdots dp'_N \exp\{-\tfrac{1}{2}\beta \mathbf{p}'(t)^T \operatorname{diag}(0,..., 0, \lambda_{M+1},..., \lambda_N)\, \mathbf{p}'(t)\}$$

The Gaussian integrals can now be performed to yield

$$\frac{(2\pi k_B T)^{(N-M)/2}}{(\lambda_{M+1} \cdots \lambda_N)^{1/2}} \tag{7.21}$$

for the momentum integral. This result is equivalent to that given elsewhere,[3,5,11] save that it is subject to direct calculation. The main advantage over previous treatments is that a set of generalized coordinates describing the motion of the system is not required.

REFERENCES

1. J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, Numerical integration of the Cartesian equations of motion of a system with constraints: Molecular dynamics of *n*-alkanes, *J. Comp. Phys.* **23**:327 (1977).
2. J. Orban and J. P. Ryckaert, unpublished (1974) [cited in ref. 1].
3. G. Ciccotti and J. P. Ryckaert, Molecular dynamics simulation of rigid molecules, *Comp. Phys. Rep.* **4**:345 (1986).
4. R. Edberg, D. J. Evans, and G. P. Morriss, Constrained molecular dynamics: Simulation of liquid alkanes with a new algorithm, *J. Chem. Phys.* **84**:6933 (1986).
5. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 1987).
6. J. W. Perram and H. G. Petersen, New rigid body equations of motion for molecular dynamics, *Mol. Simul.* **1**:239 (1988).
7. J. W. Perram and H. G. Petersen, Algorithms for computing the dynamical trajectories of flexible bodies, *Mol. Phys.* **65**:861 (1988).

8. C. Lanczos, *The Variational Principles of Mechanics* (University of Toronto Press, 1949).
9. R. Weinstock, *Calculus of Variations* (McGraw-Hill, 1952).
10. G. Gallivotti, *The Elements of Mechanics* (Springer-Verlag, 1983).
11. M. Fixman, Classical statistical mechanics of constraints: A theorem and application to polymers, *Proc. Natl. Acad. Sci. USA* **71**:3050 (1974).
12. C. J. Thompson, *Mathematical Statistical Mechanics* (Macmillan, 1972).
13. E. T. Whittaker, *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies* (Cambridge University Press, 1917).
14. H. Goldstein, *Classical Mechanics* (Addison-Wesley, 1950).
15. E. C. D. Sudarshan and N. Mukunda, *Classical Dynamics: A Modern Perspective* (Wiley, 1974).
16. P. A. M. Dirac, Generalized Hamiltonian dynamics, *Can. J. Math.* **2**:129 (1950).
17. P. A. M. Dirac, Generalized Hamiltonian dynamics, *Proc. R. Soc. A* **246**:326 (1958).
18. J. L. Anderson and P. G. Bergmann, Constraints in covariant field theories, *Phys. Rev.* **83**:1018 (1951).