Kinetic Equations in Hamiltonian Treatments

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Chemical kinetic equations are easily cast in a Hamiltonian form, making them amenable to a wealth of established techniques. The formalism allows for canonical transformations to simplify the rate equations, enables application of standard perturbation methods, and provides an approach for finding system invariants. Each of these features is illustrated for nontrivial systems.

Introduction

Hamiltonian theory is a beautiful and powerful tool in classical and quantum dynamics. Symmetry analyses, conservation laws, applications of statistical mechanics, and approximation methods are most readily treated with Hamiltonian formulations. Here we are interested in developing chemical kinetic equations in a Hamiltonian form so various established techniques become available for solutions or analyses.

The basic idea is to construct a Hamiltonian using chemical concentrations as generalized coordinates with the reaction rates expressed by Hamilton's equations. A quantum mechanical version of this formulation was developed to examine energy relations for a set of interaction chemicals.[1] This note develops a classical counterpart and explores its use in analyzing rate equations.

E. H. Kerner introduced Hamiltonian analyses for Lotka−Volterra rate equations.[2−4] He applied the formalism to a statistical-mechanical analysis of interacting biological species and arrived at an analogue of temperature for biosystems.[5] B. Goodwin followed a similar tack to model ensembles of genetic control mechanisms based on a Hamiltonian for a set of rate equations modeling end product repression.[6,7] These pioneering treatments illustrate some of the interesting and clever applications made possible with a Hamiltonian formulation. The Kerner and Goodwin Hamiltonians have specialized forms, whereas the formalism described here applies to general reactions. The cost of this generality is a doubling of independent variables to include conjugate "momenta" for the coordinates. Fortunately, the result is an extremely simple degenerate form that is shown here to have significant utility.

Three features of the Hamiltonian treatment seem especially useful. In particular, canonical transformations are introduced to simplify the kinetic equations, perturbation theory is applied for approximate solutions, and invariants are shown to extract information without requiring a full solution.

The Hamiltonian

Let q_j represent the concentration of the jth chemical species. The time development of these concentrations is governed by a set of m rate equations,

$$\dot{q}_j = f_j(q_1...q_m) \qquad (1)$$

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where the time derivative is denoted by a dot and j runs from 1 to m. We now construct a Hamiltonian H from which eq 1 is recovered using the q's as generalized coordinates. This requires that we introduce a conjugate variable p_j for each q_j. Doubling the number of state variables may seem an excessive complication, but the higher dimensionality is compensated largely by greater flexibility in transformations and methodology.

We begin the construction with Hamilton's equations

$$\dot{q}_j = \frac{\partial H}{\partial p_j} \qquad (2)$$

and

$$-\dot{p}_j = \frac{\partial H}{\partial q_j} \qquad (3)$$

Substitute f_j from eq 1 in the left-hand side of eq 2 and impose the property of exact differentials, $\partial^2 H/\partial p_j\partial q_i = \partial^2 H/\partial q_i\partial p_j$, so that eqs 2 and 3 give

$$-\frac{\partial \dot{p}_i}{\partial p_j} = \frac{\partial f_j}{\partial q_i}$$

The general solution for the latter expression is

$$-\dot{p}_j = \sum_j \frac{\partial f_j}{\partial q_i} p_j + \epsilon_i$$

where ϵ_i is a constant of integration and the sum is over all j. Substituting for the left-hand side from eq 3 and integrating with respect to q_i gives the Hamiltonian up to an arbitrary additive constant,

$$H = \sum_j f_j p_j + \sum_j \epsilon_j q_j \qquad (4)$$

We can choose $\epsilon_j = 0$ as these are arbitrary and cannot affect the rate relations. The resulting form used here is[8]

$$H = \sum_j f_j p_j \qquad (5)$$

H is a degenerate Hamiltonian that cannot be converted to a Lagrangian by a Legendre transform. Despite its simplistic form, eq 5 will be shown to have robust applicability.

There is no particular need to ascribe a physical interpretation to the conjugate momenta for our present purposes since we are ultimately concerned only with relations for the concentration coordinates q. We treat p's as formal entities and leave any interpretation in abeyance, as they do not impact our narrow focus on rate equations.

Canonical Transformations

The Hamiltonian formalism is nicely illustrated with the Lotka−Volterra equations,

$$dq_1/dt = k_1q_1 - kq_1q_2$$
$$dq_2/dt = kq_1q_2 - k_2q_2 \qquad (6)$$

This system is well studied and has interesting properties. In particular, it has oscillatory solutions in neighborhoods around the steady state. It was introduced[9] in 1920, and only recently have analytic solutions been developed.[10,11] Nothing fundamental can be learned by analyzing this fully solved system. It does, however, provide a good test case and our treatment highlights the relative contributions of amplitude and phase in perturbations near the steady state.

The Hamiltonian is simply

$$H = (k_1q_1 - kq_1q_2)p_1 + (kq_1q_2 - k_2q_2)p_2 \qquad (7)$$

This can be changed to a more tractable form by transforming to a coordinate system appropriate to small oscillations around the steady-state values of the q's. A necessary and sufficient condition for the transformation to new coordinates (r,θ) and conjugate momenta (p_r,p_θ) to be canonical is that the Poisson brackets with respect to the new variables satisfy[12]

$$[q_i, p_j] = \delta_{ij} \qquad (8)$$

The chosen transformation is

$$q_1 = \sqrt{k_2}r\cos\theta + k_2/k$$
$$q_2 = \sqrt{k_1}r\sin\theta = k_1/k$$
$$p_1 = (p_r\cos\theta - p_\theta\sin\theta/r)k_2^{-1/2}$$
$$p_2 = (p_r\sin\theta - p_\theta\cos\theta/r)k_1^{-1/2} \qquad (9)$$

The new Hamiltonian becomes

$$H = \omega p_\theta + h_1r + h_2r^2 \qquad (10)$$

where $\omega = (k_1k_2)^{1/2}$ and h_1 and h_2 are given by

$$h_1 = kp_\theta\sin\theta\cos\theta(\sqrt{k_1}\sin\theta + \sqrt{k_2}\cos\theta)$$
$$h_2 = kp_r\sin\theta\cos\theta(\sqrt{k_2}\sin\theta - \sqrt{k_1}\cos\theta) \qquad (11)$$

The canonical transformation produces a particularly revealing Hamiltonian in eq 10. Coordinate r is essentially the amplitude of displacement from the steady state, so a gross approximation for small displacements can neglect the last two terms and Hamilton's equations immediately determine

$$\theta = \omega t + \theta_0$$
$$p_\theta = L$$
$$r = R$$
$$p_r = P_R \qquad (12)$$

where θ_0, L, R, and P_R are constants. Substituting into q_1 and q_2 of eq 9 gives the system's oscillatory behavior in this approximation. Higher order approximations can be achieved with perturbation theory, the topic of the next section.

Perturbation Theory

A Hamiltonian formulation is the basis for time-dependent perturbation theory in classical dynamics.[13] The Hamiltonian H for the full problem is separated into a solvable unperturbed portion H_0, and a small perturbation H_1,

$$H = H_0 + H_1 \qquad (13)$$

A transformation to new conjugate variables Q and P is then sought so that the unperturbed Hamiltonian vanishes and the transformed Hamiltonian equals only the perturbation H_1. Hamilton's equations for the new variables are then

$$dQ/dt = \partial H_1/\partial P \qquad dP/dt = -\partial H_1/\partial P \qquad (14)$$

It follows from $H_0 = 0$ that the new variables are constants for the unperturbed case. These are substituted in the right-hand sides of eqs 14, which can be integrated in successive approximations.

The transformation to Q and P is found by first solving the unperturbed Hamilton−Jacobi equation for the principal function $S(q,P,t)$,

$$H_0(q,\partial S/\partial q) + \partial S/\partial t = 0 \qquad (15)$$

The P's are integration constants (or equivalently, separation constants) of the partial differential equation. The transformation equations linking the new coordinates to the originals are then obtained from the relations

$$Q = \partial S/\partial P \qquad p = \partial S/\partial q \qquad (16)$$

Clearly, the entire procedure can be adopted without alteration to the chemical case.

Applying eq 15 to the Lotka−Volterra system returns the results of eq 12, where the Q set is $\{\theta_0,R\}$ with the corresponding conjugate P set $\{L,P_R\}$. These new variables are substituted for the originals into the Hamiltonian, which reduces to

$$H_1 = h_1R + h_2R^2$$

with the h coefficients now expressed in the new coordinates.

First-order corrections for our model case were easily found by integrating eqs 14. The results are in excellent agreement with numerical solutions in the region $R \ll \omega/k$. Detailed outcomes are of little concern here, but we note that the phase is more sensitive than the amplitude to small perturbations because the first-order corrections are proportional to R and R^2, respectively.

The value of the method is not limited to perturbations around a steady state. We considered the reactions

$$A + A \xrightarrow{k_1} \text{products}$$
$$A + B \xrightarrow{k_2} \text{products}$$
$$B + B \xrightarrow{k_3} \text{products} \qquad (17)$$
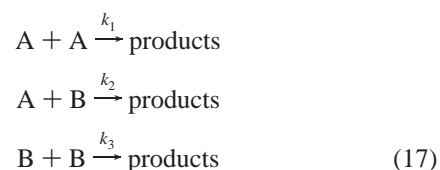
No general solution to the corresponding rate equations is known, but Hagemann and Schwarz[14] proposed special restrictions on the rate constants for which the system can be solved

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and which gave a satisfactory description of their experimental results,

$$k_2 = 2k_1 = 2k_3 \tag{18}$$

We relaxed these restrictions by adding arbitrary increments to k_1 and k_3 and treating the alteration as a perturbation.

Denoting the concentrations in an obvious notation, the first-order perturbation produces a result

$$(A + B)^{-1} = (A_0 + B_0)^{-1} + k_2(1 - \alpha)t \tag{19}$$

where A_0 and B_0 are the initial concentrations and α is the correction due to the perturbation,

$$\alpha = \frac{k_1 + k_3 - k_2}{2k_2}\left(1 + \frac{A_0 - B_0}{A_0 + B_0}\right)^2$$

Hagemann and Schwarz found that their data for $(A + B)^{-1}$ was well described as a linear function of time. Here we see that their finding is validated for a wide domain of rate coefficients including the special case $\alpha = 0$ they solved exactly.

Invariant Quantities

The rate of change of any function of generalized coordinates, G, is given by the Poisson bracket relation,

$$[G, H] = dG/dt \tag{20}$$

G is an invariant when the bracket vanishes,

$$[G, H] = 0 \tag{21}$$

and thereby provides information about the system without requiring a full solution. Moreover, such invariants can be used to simplify the original rate equations. As in classical dynamics, the time-independent Hamiltonian is constant. Another useful, though less ubiquitous, application occurs when G is found to generate a constant α,

$$[G, H] = \alpha \tag{22}$$

It follows that time dependence is introduced from $G = \alpha t + \phi$, where ϕ is a constant of integration.

Consider, for example, a second-order reaction $A + B \rightarrow C$. Equation 21 is satisfied by G's that are arbitrary functions of $A + C$ or $A - B$, the expected invariant quantities. It is amusing to solve the rate equations algebraically by choosing $G = \ln[B^2(p_C - p_A - p_B)]$ giving

$$[G, H] = k(A - B) = k(A_0 - B_0)$$

so that $G = k(A_0 - B_0)t + \phi$. The full solution then follows by substituting G into $H = $ constant.

Restricting G in eq 21 to be solely a function of coordinates q gives a time-independent partial differential equation,

$$\sum_j f_i \partial G/\partial q_j = 0 \tag{23}$$

Solutions to this expression are "constants of the motion" that provide information about the system without benefit of a full solution. Moreover, such invariants can be used to simplify the original rate equations. Applying eq 23 to the Lotka−Volterra equations reveals a known invariant quantity,

$$G = k_2 \ln(A) + k_1 \ln(B) - k(A + B)$$

This is an exact result that gives the system trajectories for an arbitrary initial condition even without knowing time-dependent solutions.

Equation 23 merely expresses that the function G has a vanishing time derivative. Nevertheless, it is particularly useful in Hamiltonian treatments because of the flexibility afforded by canonical transformations. The following case illustrates this point and produces a heretofore unknown invariant for the Hagemann−Schwarz system.

We were unable to solve eq 23 directly for the full system (17) when it was expressed in the original concentrations A and B. It became tractable with standard methods, however, after performing a canonical transformation,

$$A = (q_1 + q_2)/2 \qquad p_A = p_1 + p_2$$
$$B = (q_1 - q_2)/2 \qquad p_B = p_1 - p_2$$

Transforming the solution $G(q_1, q_2)$ back to the original variables produces the invariant,

$$G =$$
$$2k_2k_3 \ln A + 2k_1k_2 \ln B - k_2^2 \ln u - 4k_1k_3(\ln AB - \ln u)$$

where

$$u = (2k_1 - k_2)A + (k_2 - 2k_3)B$$

This expression determines the system trajectories although the full time-dependent solutions are unknown.

Concluding Remarks

Our Hamiltonian has a completely transparent form that likely was obvious to investigators previously. The primary contribution of this note was to demonstrate that the formalism is effective despite a doubling of state variables and a degenerate form for H. Indeed, highly nontrivial systems were effectively treated with canonical transformations, perturbation theory, and analyses of invariants, and some new results were generated in the process.

References and Notes

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(8) Readers will notice that the Hamiltonian formalism is not restricted to rate equations originating from chemical kinetics. Thus, any set of rate equations may be treated as a chemical kinetic analogue.

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