https://ntrs.nasa.gov/search.jsp?R=19720013445 2018-07-24T14:56:06+00:00Z

THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

EVALUATION OF JACOBIAN DETERMINANTS BY MONTE CARLO METHODS: APPLICATION TO THE QUASICLASSICAL APPROXIMATION IN MOLECULAR SCATTERING

Robert A. La Budde

(NASA-CR-125978) EVALUATION OF JACOBIAN DETERMINANTS BY MONTE CARLO METHODS: APPLICATION TO THE QUASICLASSICAL APPROXIMATION IN R.A. LaBudde (Wisconsin Univ.) 29 Nov. 1971 12 p CSCL 07B G3/06

N72-21095

Unclas 15257

WIS-TCI-462

MADISON, WISCONSIN 29 November 1971

CAT. 06

EVALUATION OF JACOBIAN DETERMINANTS BY MONTE CARLO METHODS: APPLICATION TO THE QUASICLASSICAL APPROXIMATION IN MOLECULAR SCATTERING *

by

Robert A. La Budde

Theoretical Chemistry Institute

and

Department of Chemistry

University of Wisconsin, Madison, Wisconsin 53706

ABSTRACT

Sampling techniques have been used previously to evaluate Jacobian determinants that occur in classical mechanical descriptions of molecular scattering. These determinants also occur in the quasiclassical approximation. A new technique is described which can be used to evaluate Jacobian determinants which occur in either description. This method is expected to be valuable in the study of reactive scattering using the quasiclassical approximation.

- - - - - - - - - - - - - - - - - - -

*Supported by National Science Foundation Grant GP-26014 and National Aeronautics and Space Administration Grant NGL 50-002-001.

INTRODUCTION

The essence of molecular scattering is the transformation of an initial distribution of states into a final distribution of states, by means of a scattering process. The formal description of the scattering in either of the classical or the quasiclassical frameworks frequently invokes Jacobian determinants of the transformations. These determinants are difficult to evaluate in systems with several degrees of freedom, since they involve many partial derivatives. It will be shown below how these transformations may be carried out by sampling methods, and how the related Jacobians may be obtained from the sample distributions.

APPLICATION TO TRANSFORMATIONS

Suppose $X = (X_1, X_2, \ldots, X_N)$ and $Y = (Y_1, Y_2, \ldots, Y_N)$ are random vectors defined on a probability space. Let $\rho_X(X)$ denote the probability density function (p.d.f.) of X, and suppose X and Y are functionally related, i.e. $Y = F(X)$. Then ρ_X and F induce a p.d.f. $\rho_Y(Y)$,

$$\rho_Y(Y) = \lim_{\mu(V)\to 0} \frac{\int_{F^{-1}(V)} \rho_X(X)\, d\tau_X}{\mu(V)} \tag{1}$$

where $d\tau_X$ is the volume element in the X representation, V is a measurable set containing the point Y, and $\mu(V)$ is the measure of V. Suppose F and ρ_X are continuous. Then

$$\rho_Y(Y) = \sum_{F(X)=Y} \frac{\rho_X(X)}{\frac{d\tau_Y}{d\tau_X}} \tag{2}$$

where the sum is over all values of X such that $F(X) = Y$,

and

$$\frac{d\tau_Y}{d\tau_X} = \lim_{\mu(V)\to 0} \frac{\int_{F(V)} d\tau_Y}{\mu(V)} \tag{3}$$

If F is regular at each value of X for which $F(X)=Y$, then $d\tau_Y/d\tau_X = J$, where J is the Jacobian determinant

$$J = \frac{\partial(Y_1, Y_2, \ldots, Y_N)}{\partial(X_1, X_2, \ldots, X_N)} = \det\left\{\frac{\partial Y_i}{\partial X_j}\right\} \tag{4}$$

<u>i.e</u>. (2) may be written

$$\rho_Y(Y) = \sum_{F(X)=Y} \frac{\rho_X(X)}{J} \tag{5}$$

The quantity $d\tau_Y/d\tau_X$ defined by (3) is much more amenable to computation than J defined by (4), since the latter quantity involves N^2 partial derivatives. The method usually followed in classical mechanical studies (see, e.g., [1]) is to find $\rho_Y(Y)$ directly from (1). Suppose $\{{}^k X\}_{k=1}^{M}$ is a set of uniformly distributed random vectors* X . For small fixed V ,

---

*To avoid confusion with the k-th component of the vector X , the set index k is written as a left superscript.

$$\rho_Y(Y) \simeq \frac{\sum_{F({}^kX)\in V} \rho_X({}^kX)}{M\mu(V)} \tag{6}$$

For example, if V is the rectangle $\{\hat{Y} : Y_i - \frac{\Delta Y_i}{2} \leq \hat{Y}_i \leq Y_i + \frac{\Delta Y_i}{2}, 1 \leq i \leq N\}$, then $\mu(V) = \prod_{i=1}^{N} \Delta Y_i$

and

$$\rho_Y(Y) \simeq \frac{\sum \rho_X({}^kX)}{M \prod_{i=1}^{N} \Delta Y_i} \tag{7}$$

where the sum is over those values of k for which $Y_i - \frac{\Delta Y_i}{2} \leq {}^kY_i \leq Y_i + \Delta Y_i/2$, $1 \leq i \leq N$. Thus there is no need to evaluate J itself in order to determine $\rho_Y(Y)$.

In the quasiclassical approximation (to be described below) it is necessary to obtain J explicitly. The following method may be used to estimate J directly. For the same sample $\{{}^kX\}_{k=1}^{M}$, which is now assumed ordered so that ${}^{k-1}X_i \leq {}^kX_i$ for $2 \leq k \leq M$ and $1 \leq i \leq N$, but using (3),

$$J_k = \frac{d\tau_Y}{d\tau_X}({}^kX) \simeq M\Delta^kY \tag{8}$$

where $\Delta^kY = \prod_{i=1}^{N} |{}^kY_i - {}^{k-1}Y_i|$ for $k > 1$ and** $\Delta^1Y = \Delta^2Y$. If desired, $\rho_Y(Y)$ may be then

---

**Depending upon how the sample is chosen, it may be more accurate to estimate Δ^kX by $\prod_{i=1}^{N} |{}^kX_i - {}^{k-1}X_i|$ instead of by 1/M as in (7) and (8).

---

found from (5). Equation (8) is seen to be essentially a finite difference approximation to the measure derivative $d\tau_Y / d\tau_X$.

In the case of molecular scattering, X is a vector of initial conditions, and Y is a vector of final conditions.

EXAMPLE

An example of the use of (7) and (8) which isolates their difference might be the approximation of the differential scattering cross section $d\sigma/d\Omega$ for the case of scattering by a spherically symmetric potential:

$$\frac{d\sigma}{d\Omega}(\chi) = \sum_i \frac{b_i}{\left|\sin\chi \frac{d\chi}{db_i}\right|} \tag{9}$$

where the sum is over regions of the impact parameter b which contribute to the differential cross section at the angle of deflection χ (i.e. usually over one or three "branches" of the deflection function $\chi(b)$). Suppose a set of M values of b are chosen equally spaced, and $b_{k-1} < b_k$ for $2 \leq k \leq M$. Applying (7),

$$\frac{d\sigma}{d\Omega}(\chi) \simeq \frac{1}{M\Delta\chi} \sum \frac{b_k}{|\sin\chi_k|} \tag{10}$$

where the sum is over the values of k such that $\chi - \Delta\chi/2 \leq \chi_k \leq \chi + \Delta\chi/2$. Note that the Jacobian $d\chi/db$ occurs implicitly by affecting the number of values of k for which $\chi - \Delta\chi/2 \leq \chi_k \leq \chi + \Delta\chi/2$. On the other hand, applying (8),

$$\frac{d\chi}{db}(b_k) \simeq \frac{\Delta\chi_k}{\Delta b} \tag{11}$$

where $\Delta\chi_k = \chi_k - \chi_{k-1}$ for $k > 1$ and $\Delta\chi_1 = \Delta\chi_2$, and $\Delta b = b_k - b_{k-1}$ is a constant, proportional to 1/M.***

***Note for the case of one dimension, (3) and (4) are identical.

QUASICLASSICAL APPROXIMATION

The technique of sampling distributions of initial conditions, computing the classical trajectories which link them to the final states, and constructing the final state distributions (by (7) above), has been used extensively in the past in classical calculations (see, e.g., [1]). The suggestion is now made that this technique can be applied to the quasiclassical formalism for molecular scattering, which is emerging through the work of Miller [2-6], Marcus [7-9], Levine [10-11], and coworkers.

Briefly, the quasiclassical approximation is obtained as follows: let

$$\Psi_E(q,t) = A(q)\, e^{\frac{i}{\hbar}\phi(q,t)} \tag{12}$$

where Ψ_E is solution to the time-dependent Schrödinger equation for energy E, $q = (q_1, q_2, \cdots, q_N)$ is the generalized coordinate vector, and A and ϕ are real-valued. Substitution of (12) into the time-dependent Schrödinger equation yields [12]

$$\frac{\partial \phi}{\partial t} + \frac{1}{2m}(\nabla\phi)^2 + V(q) = \nabla^2 A / A \tag{13a}$$

$$2\,\nabla A \cdot \nabla\phi + A\nabla^2\phi = 0 \tag{13b}$$

where $V(q)$ is the interaction potential, and m is the mass appropriate to each coordinate.† The quasiclassical approximation

---

† For example, in cartesian coordinates,

$$\frac{1}{2m}(\nabla\phi)^2 = \sum \frac{1}{2m_i}\left[\left(\frac{\partial\phi}{\partial x_i}\right)^2 + \left(\frac{\partial\phi}{\partial y_i}\right)^2 + \left(\frac{\partial\phi}{\partial z_i}\right)^2\right]$$

where the sum is over particles.

---

results when the right-hand side of (13a) is neglected. Equations (13) may then be written

$$\frac{\partial \phi}{\partial t} + \frac{1}{2m}(\nabla\phi)^2 + V = 0 \tag{14a}$$

$$\nabla \cdot (A^2 \nabla\phi) = 0 \tag{14b}$$

Equation (14a) is recognized as the Hamilton-Jacobi equation with solution

$$\phi(q,t) = \int_0^t 2T\,dt' - Et + p^\circ \cdot q^\circ \tag{15}$$

where T is the kinetic energy $E - V$. Equation (14b) is the equation of continuity of the trajectory determined by ϕ, with

solution A^2 the p.d.f. of $\underline{q}$ [13]. Thus

$$A^2(\underline{q}) = A^2(\underline{q}^\circ)\,\frac{\partial(q_1, q_2, \ldots, q_N)}{\partial(q_1^\circ, q_2^\circ, \ldots, q_N^\circ)} \tag{16}$$

where $\underline{q}^\circ = \underline{q}(0)$ is the coordinate vector of the system at $t = 0$, which is assumed to correspond to a time for which $V(\underline{q}) \simeq 0$. The boundary conditions of (14a) are that $\nabla\phi(\underline{q}^\circ, 0) = \underline{p}^\circ = \underline{p}(0)$, where $\underline{p}^\circ$ is the initial momentum vector.

Thus in the quasiclassical approximation, the same Jacobian determinants that occur in classical mechanics occur to the one-half power via $A(\underline{q})$. It is suggested that these Jacobians may be evaluated by the procedure illustrated by equation (8).[††]

[††]The difficulty with the use of (7) is that the square-root present in the quasiclassical approximation means that the sum over "branches" and the sum over trajectories corresponding to these branches no longer commute. That is, the Jacobian occurs implicitly in (7), but its square-root is needed to obtain $A(\underline{q})$.

To consider an example, W. H. Miller [3, eq. (29)] gives the following expression for the S matrix element for the transition from $n = n_1$ to $n = n_2$ for the collinear collision of an atom with a diatomic oscillator:

$$S_{n_2 n_1} = \frac{1}{2\pi\hbar}\int_0^{2\pi} d\bar{q}_1 \left[\frac{\partial \bar{q}_2(\bar{q}_1, n_1)}{\partial \bar{q}_1}\right]^{1/2} e^{\frac{i}{\hbar}\hat{\phi}} \tag{17}$$

where $\hat{\phi}$ is a phase similar to ϕ, $\bar{q}$ is a reduced phase of vibration, and $t = t_1$ and $t = t_2$ correspond to the initial and final states. To evaluate $S_{n_2 n_1}$ equation (8) may be used, giving

$$S_{n_2 n_1} \simeq \left[\frac{M}{2\pi\hbar^2}\right]^{1/2} \sum_{k=1}^{M} \left[\Delta\bar{q}_{2,k}\right]^{1/2} e^{\frac{i}{\hbar}\hat{\phi}_k} \tag{18}$$

where the sum is over the results of M trajectories with initial conditions chosen uniformly in $\bar{q}_1$, and $\Delta\bar{q}_{2,k} = |\bar{q}_{2,k} - \bar{q}_{2,k-1}|$ for $k > 1$ and $\Delta\bar{q}_{2,1} = \Delta\bar{q}_{2,2}$.†††

---

†††Note that the integration over $\bar{q}_1$ and the estimation of $\partial\bar{q}_2 / \partial\bar{q}_1$ are performed simultaneously.

CONCLUSION

It has been shown how sampling techniques may be used to evaluate Jacobian determinants and to transform distributions, with particular application to the classical and quasiclassical descriptions of molecular scattering. A method of obtaining the Jacobian of the scattering transformation directly by sampling was described, which allows application of the quasiclassical approximation to the sampled classical results in a natural way. It should be noted that with the use of the method illustrated by equation (8), all that is required to extend the classical results to quasiclassical is the additional information of the phase ϕ associated with each

trajectory. This method should be valuable in the case of reactive scattering, where (thus far) analytical techniques have failed (see [6]).

ACHNOWLEDGEMENTS

The author wishes to express his thanks to Professors R. D. Levine, W. H. Miller, and R. B. Bernstein for the benefit of several enlightening discussions. The continual encouragement of R. B. Bernstein is appreciated.

REFERENCES

[1.] R. A. La Budde and R. B. Bernstein, J. Chem. Phys. 55, (1971), in press, and references 8-10 therein.

[2.] W. H. Miller, J. Chem. Phys. 53, (1970) 1949.

[3.] W. H. Miller, J. Chem. Phys. 53, (1970) 3578.

[4.] W. H. Miller, Chem. Phys. Lett. 7, (1970) 431.

[5.] W. H. Miller, J. Chem. Phys. 54, (1970) 5386.

[6.] C. C. Rankin and W. H. Miller, J. Chem. Phys. 55, (1971) 3150.

[7.] R. A. Marcus, Chem. Phys. Lett. 7, (1970) 525.

[8.] R. A. Marcus, J. Chem. Phys. 54, (1971) 3965.

[9.] R. A. Marcus, J. Chem. Phys., to be published.

[10.] R. D. Levine and B. R. Johnson, Chem. Phys. Lett. 7, (1970) 404.

[11.] R. D. Levine and B. R. Johnson, Chem. Phys. Lett. 8, (1971) 501.

[12.] A. Messiah, Quantum Mechanics, (Wiley, New York, 1966), Vol. I, p.222f.

[13.] J. H. Van Vleck, Proc. Nat. Acad. Soc. (U.S.), 14, (1928) 178.