Local Approximation of Potential-Energy Surfaces by Surfaces Permitting Separation of Variables*

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In the immediate vicinity of a potential-energy minimum or of a saddle point, it is shown that major topographical features of a "nonseparable" potential-energy surface can be imitated by those of a surface permitting separation of variables. For each extremal path of descent or ascent to the cited critical point of the surface, there is an exact match of the tangent, the first curvature vector in configuration space, and the force constant along that path provided that the known curvature vector satisfies an equation containing the metric tensor of the selected coordinate system and known force constants. Because of the wide choice of coordinate systems available for selection, it is anticipated that this relation may be fulfilled for each extremal path, partly by choice of the coordinate system and partly by subsequent choice of the curvilinear coordinates of the critical point.

There are several possible applications of this local approximation, including those to problems involving anharmonic coupling of normal modes and those involving n-dimensional tunneling and other calculations in reaction-rate theory. Use will be made of the formalism to extend the activated complex theory in chemical kinetics. As a preliminary test of the local-approximation concept, literature data on n- and one-dimensional tunneling rates are compared. They are found to be fairly similar when proper cognizance is taken of zero-point energies.

INTRODUCTION

A SEPARATION of variables can be made in the Schrödinger equation and in its classical counterpart, the Hamilton–Jacobi equation, for certain conditions on the potential-energy function and on the metric tensor.[1-3] In the present paper it will be shown that in the immediate vicinity of a potential-energy minimum or saddle-point, major topographical features of a ("nonseparable") potential-energy surface can be matched by those of ones permitting separation of variables. These features involve (a) the direction of the tangent, and the direction and magnitude of the principal normal (the "first curvature vector") in mass-weighted configuration space of some or all extremal paths[4] of ascent or descent to the cited critical point,[5]

and (b) the force constants (positive or negative) for such paths at the critical point.

The usual harmonic approximation for vibrational potential-energy functions in the vicinity of a critical point corresponds, in fact, to paths which have zero curvature in mass-weighted configuration space. Anharmonic coupling between normal modes then causes a curvature. There is a variety of problems where this anharmonic coupling plays a major role and where there is potential application for the present results. Another application lies in n-dimensional tunneling and other rate calculations in reaction-rate theory[6] and in the generalization of activated-complex theory.[7]

There is now available an increasing number of numerical studies, made with high-speed computers, of intramolecular energy transfer,[8,9] unimolecular[9] and bimolecular[10] reaction rates, and nuclear tunneling.[10a] Comparison of the results obtained from such studies with those obtainable by the local-approximation technique should serve to test the useful range of the.

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[1] (a) P. G. Stäckel, Habilitationsschrift, Halle, Germany (1891); (b) Ann. Mat. Pura Appl., Ser. 2A, **25**, 55 (1897).

[2] (a) H. P. Robertson, Math. Ann. **98**, 749 (1927); (b) L. P. Eisenhart, Ann. Math. **35**, 284 (1934).

[3] R. A. Marcus, J. Chem. Phys. **41**, 603 (1964).

[4] By definition, each such path passes through the critical point[5] and has a tangent vector * (in mass-weighted configuration space) codirectional with the gradient of the potential-energy function. (Hence, this path is normal to every potential-energy contour that it crosses.) When there are two extremal paths and when the critical point is a saddle point, one path is the path of steepest ascent to the point, and the other is the path of steepest ascent from it. When the critical point is a minimum instead, one extremal path is again the path of steepest ascent from it, and the other is that of least steep ascent.

[5] Since the critical point of a surface f $(q^1, \cdots q^n)$ plotted vs $(q^1, \cdots, q^n)$ is any point where ∇f vanishes, critical points include local maxima of f also. The present derivation applies equally well to such points, but they do not appear to be of physical interest.

[6] J. Lane and R. A. Marcus (unpublished results for $n=2$).

[7] R. A. Marcus (to be published).

[8] E. Fermi, J. Pasta, and S. Ulam, Los Alamos Scientific Lab. Rept. LA-1940 (1955); J. Ford, J. Math Phys. **2**, 387 (1961); E. A. Jackson, *ibid.*, **4**, 551, 686 (1963); J. Ford and J. Waters, *ibid.* p. 1293.

[9] D. L. Bunker, J. Chem. Phys. **40**, 1946 (1964); D. L. Bunker, *ibid.* **37**, 393 (1962); N. C. Hung and D. J. Wilson, *ibid.* **38**, 828 (1963), and references cited therein. Comparison would be restricted initially to relatively low amplitudes of vibration and to intramolecular energy transfer.

[10] (a) E. M. Mortensen and K. S. Pitzer, Chem. Soc. (London) Spec. Publ. **16**, 57 (1962). (b) F. T. Wall, L. A. Hiller, Jr., and J. Mazur, J. Chem. Phys. **29**, 255 (1958); **35**, 1284 (1961). (c) N. C. Blais and D. L. Bunker *ibid.* **39**, 315 (1963). Comparison would be restricted, initially at least, to reactions which have an activation energy (or, more precisely, to those for which a saddle point is well-defined).

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latter. The limitations will arise from its local nature.[11] At the same time, the comparison could provide further physical insight into the numerical results in terms of topographical features of the potential-energy surface and in terms of approximate constants of the motion.

In the derivation, we characterize the geometry of the extremal[4] paths of ascent and descent to a critical point[5] of the potential-energy surface, obtaining Eq. (14). The properties of the associated curvilinear coordinate system which permits separation of variables are then given by Eq. (19). A method of application to some problems is then outlined in subsequent sections. The usual definitions, techniques, and symbols in tensor calculus will be employed,[12,13] including absolute differentiation, first curvature, tangent, principal normal, and Christoffel symbols.

PRELIMINARY REMARKS

We let x^{3r}, x^{3r+1}, x^{3r+2} denote the three Cartesian coordinates of an atom r of mass m_r and let q^i denote the i'th generalized coordinate. Let there be n' coordinates in all. The line element ds in a mass-weighted space is given by

$$ds^2 = \sum_{i,j=1}^{n'} g_{ij} dq^i dq^j, \qquad (1)$$

where

$$g_{ij} = \sum_{r=1}^{n'} m_r \frac{\partial x^r}{\partial q^i} \frac{\partial x^r}{\partial q^j}. \qquad (2)$$

The metric tensor g_{ij} can be a function of all coordinates. (Accordingly, if the q^i are Cartesian coordinates, x^i, g_{ij} equals $\delta_{ij} m_i$. If they are mass-weighted Cartesians, i.e., if $q^i = m_i^{\frac{1}{2}} x^i$, g_{ij} equals δ_{ij}, etc.)

The tensor conjugate to g_{ij} is denoted by g^{ij}

$$\sum_{j=1}^{n'} g^{ij} g_{jk} = \delta_k{}^i, \qquad (3)$$

$$g^{ij} = \sum_{r=1}^{n'} \frac{1}{m_r} \frac{\partial q^i}{\partial x^r} \frac{\partial q^j}{\partial x^r}. \qquad (4)$$

The g_{ij} and g^{ij} are both symmetric in i and j, of course. The former varies covariantly and the latter contravariantly in any coordinate transformation.[12,13]

The arc length along any curve will be denoted by s. The tangent vector $\mathbf{t}$ along any curve has contravariant components dq^i/ds. The ith contravariant component of the principal normal $\mathbf{p}$, p^i, is $\delta t^i/\delta s$. The latter is the ith component of $\delta \mathbf{t}/\delta s$, the intrinsic derivative of $\mathbf{t}$

with respect to the arc length[14a]

$$p^i = \frac{\delta t^i}{\delta s} = \frac{dt^i}{ds} + \sum_{k,m} \{_k{}^i{}_m\} t^k t^m, \qquad (5)$$

where $\{_k{}^i{}_m\}$ is a Christoffel symbol of the second kind.[14b] The first curvature κ of any curve is a scalar and is given by

$$\kappa = \left(\sum_{i,j} g_{ij} p^i p^j\right)^{\frac{1}{2}}. \qquad (6)$$

HAMILTONIAN

The total kinetic energy of the system is $\frac{1}{2}(ds/dt)^2$. Using (1), this becomes

$$\frac{1}{2} \sum_{i,j=1}^{n'} g_{ij} \dot{q}^i \dot{q}^j.$$

In terms of the conjugate momenta P_i, it is[15a]

$$\frac{1}{2} \sum_{i,j=1}^{n'} g^{ij} P_i P_j.$$

The n' coordinates can be those of a single molecule in the case of a unimolecular gas reaction, a pair of molecules in a bimolecular reaction, and so forth. Translational, rotational, and vibrational coordinates may be introduced, the g_{ij} being given by (2). Initially, nonrotating molecules will be considered, the approximate inclusion of rotation being given in a subsequent section.

When the vibrational angular momentum[15a] is neglected, the kinetic energy becomes the sum of three terms: translational, rotational, and vibrational.[15b] When the angular momentum is zero, the kinetic energy is given by (7), aside from the irrelevant translational term. The vibrational space is Euclidean, because the Eckart conditions used to select the n vibrational coordinates are linear.[15,] Since this subspace is Euclidean, curvilinear coordinate systems exist in it which permit the kinetic energy to be written in the diagonal form ($g^{ij} = 0$ for $i \neq j$), as in Eq. (7).

$$T = \frac{1}{2} \sum_{i=1}^{n} g^{ii} P_i{}^2 = \frac{1}{2} \sum_{i=1}^{n} g_{ii} \dot{q}^i{}^2. \qquad (7)$$

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[11] No attempt is made here to match properties which only affect the higher-order terms in Eq. (15). (For further detail, see Ref. 28.)

[12] For example, C. E. Weatherburn, *Riemannian Geometry and Tensor Calculus* (Cambridge University Press, London, 1957).

[13] E.g., A. J. McConnell, *Applications of Tensor Calculus* (Dover Publications Inc., New York, 1957).

[14] Reference 12: (a) p. 72 (cf. p. 95 for the notation $\delta t^i/\delta s$). (b) See p. 55. (c) See p. 43.

[15] (a) See, for example, Wilson, Decius, and Cross (Ref. 29, Chap. 11). (b) *Ibid.* p. 278, Eq. (5). The rotational term contains vibrational coordinates in the coefficients of angular momenta and angular velocities, i.e., in the $\mu_{\alpha\beta}$ of the cited equation and in the $I_{\alpha\beta}$ of Eq. 14, p. 278. The rotational term thereby gives rise to a centrifugal potential, which vanishes for the nonrotating molecule. (c) The vibrational coordinates are chosen so as to satisfy the Eckart conditions (Ref. 29). These conditions can be used to eliminate all but the first n of the dx^i's appearing in the line element ds in mass-weighted space:

$$ds^2 = \sum_{i=1}^{n'} m_i dx^i{}^2.$$

Since the Eckart conditions are linear, the coefficient of each $dx^i dx^j$ ($i, j = 1$ to n) in this subspace is a constant. Hence, the n-dimensional subspace is Euclidean.

When the kinetic energy is diagonal, the results of Stäckel[1] and Robertson and Eisenhart[2] can be applied.[16] For separation of variables, the metric tensor g_{ij} must satisfy certain conditions described by Stäckel[1] for the Hamilton–Jacobi equation and by Robertson[2] for the Schrödinger equation. Robertson obtained one condition in addition to those found by Stäckel. The geometric significance of this extra condition has been discussed by Eisenhart.[2] It is automatically satisfied for Euclidean (i.e. flat) spaces and for those with constant curvature.[2]

One of the necessary and sufficient conditions for separation of variables in the diagonalized T system is that V be of the form[16]

$$V = \sum_{i=1}^{n} g^{ii} X_i(q^i), \qquad (8)$$

where $X_i(q^i)$ is a function of q^i alone.

In the neighborhood of any point, the space having the fundamental form of (1) with n instead of n', can be described in terms of local Cartesian coordinates[17] (constant g_{ij}, and $g_{ij}=0$ if $i\neq j$). Almost invariably, the physical systems considered are those for which the expansion of the potential energy in local Cartesians about the critical point has leading quadratic terms rather than leading cubic or higher ones.[18] In the present paper, we limit our considerations to such systems.

In such an expansion in local Cartesians, these normal coordinates diagonalize the potential and kinetic energy. They define orthogonal directions at the critical point when they are nondegenerate. When there is degeneracy, normal coordinates which are orthogonal can be defined. We wish to introduce orthogonal curvilinear coordinates ($g^{ij}=0$ for $i\neq j$) whose curves are tangential to these orthogonal normal coordinates at the critical point and which have other properties given by Eq. (19) below. The n extremal paths of descent or ascent (n, because the leading terms were quadratic) are cotangential with these normal

coordinate curves at the critical point, and hence, with the n curvilinear coordinate curves there.

EQUATIONS OF EXTREMAL PATHS OF ASCENT OR DESCENT

The plot of V is considered in the vicinity of a critical point of the potential-energy surface or, more specifically, in the vicinity of a saddle-point or a minimum. Recalling the definition of the extremal paths[4] passing through the critical point,[5] these paths satisfy the equations

$$\frac{dq^1}{ds} \bigg/ \sum_{j=1}^{n} g^{1j}\frac{\partial V}{\partial q^j} = \frac{dq^2}{ds} \bigg/ \sum_{j=1}^{n} g^{2j}\frac{\partial V}{\partial q^j} = \cdots = \frac{dq^n}{ds} \bigg/ \sum_{j=1}^{n} g^{nj}\frac{\partial V}{\partial q^j},$$

$$(9)$$

since $\mathbf{t}$ has contravariant components $t^i (= dq^i/ds)$, and since ∇V has contravariant components,[14c]

$$\sum_{j=1}^{n} g^{ij}\frac{\partial V}{\partial q^i}.$$

We note that for the selected coordinate systems, g^{ij} equals 0 if $i\neq j$. The n extremal paths of ascent (descent) are denoted by $C_{(1)}, \cdots, C_{(n)}$, the displacements by Δq^i, and the critical point $(q_P{}^1, \cdots, q_P{}^n)$ by P: $\Delta q^i = q^i - q_P{}^i$. By means of a coordinate transformation, it will be supposed that one can avoid singularities and zeros in the metric tensor at the critical point.[19] We may expand the displacements Δq^i in powers of the arc length along $C_{(N)}$ for sufficiently smooth curves[20]; dq^i/ds for curve $C_{(N)}$ at P equals that for the q^N-coordinate curve at P, since the two curves are cotangential there. It is therefore zero for $i\neq N$ and is $1/(g_{NN})^{\frac{1}{2}}$ for $i=N$.[21] We thus write Eq. (10), where g_{NN} is evaluated at P and

$$\left.\begin{array}{l} \Delta q^N = g_{NN}{}^{-\frac{1}{2}}s + O(s^2) \\[2mm] \Delta q^i = O(s^2)\ (i\neq N) \end{array}\right\} \text{ along } \quad C_{(N)}, \qquad (10)$$

where O denotes "order of". From Eq. (10), Δq^i is seen to be of the order of $(\Delta q^N)^2$ near P for $i\neq N$.

We choose the zero of the $X_i(q^i)$ so as to occur at the critical point P. It then follows from the fact that $\partial V/\partial q^i$ vanishes there, that dX_i/dq^i also vanishes at P.[22] Expanding each $\partial V/\partial q^i$ in (9) about its value at P

[16] Somewhat weaker conditions than diagonal g_{ij} for all i, j and weaker than Condition (8) suffice when only separation into sets of variables is required [cf. Refs. 1(b) and 3].

[17] J. L. Synge and A. Schild, *Tensor Calculus* (University of Toronto Press, Toronto, Canada, 1962), p. 58. Since the vibrational space was seen to be Euclidean,[15c] the term "local" can be omitted. It is included, however, in case the Eckart conditions[29] are ever replaced by nonlinear conditions, in which case the vibrational space need not be Euclidean.

[18] When the leading terms are cubic and the critical point is a saddle point, one obtains a "monkey saddle" [cf. E. Kreysig, *Differential Geometry* (University of Toronto Press, Toronto, 1959), pp. 137–138]. Monkey saddles have apparently not been considered in the literature of activated-complex theory. One case where they would occur is in the reaction $A+A_2\rightarrow A_2+A$ if the activated complex were triangular: Considering the two-dimensional subspace formed by the two antisymmetrical stretching modes, leading to dissociation, there are three paths of steepest descent corresponding to three modes of dissociation. That is, the saddle point in this subspace is a monkey saddle. Higher saddle points can also occur (see reference cited above). However, most saddle points are the conventional ones, namely those for which the leading terms in the potential-energy expansion are quadratic.

[19] For example, in the case of circular cylinder coordinates, the metric tensor for the coordinate system (q^1, q^2, q^3) equal to $(r, \cos\phi, z)$ is singular at $\phi=0$, and g^{22} then vanishes there. However, for the coordinate system (r, ϕ, z) none of the diagonal elements of the metric tensor is singular or zero.

[20] For validity of the Taylor's expansion in (10), it suffices to have continuity of the q^i's and of their first derivatives with respect to s, together with the existence of the second derivative; cf. A. E. Taylor, *Advanced Calculus* (Ginn and Company, New York, 1955), p. 112.

[21] Along the q^N-coordinate curve all dq^i vanish, except for $i=N$. $ds^2 = g_{NN}dq^{N2}$ on it. Hence, $dq^i/ds=0$ for $i\neq N$. $dq^N/ds=1/(g_{NN})^{\frac{1}{2}}$.

[22] $\partial V/\partial q^i$ equals $\Sigma X_j \partial g^{jj}/\partial q^i + g^{ii}dX_i/dq^i$. By suitable choice of the coordinate system (no singularity or zero in the g_{ii}'s at the critical point), g^{ii} does not vanish at P, and $\partial g^{ii}/\partial q^i$ does not become infinite. Since X_j vanishes at P, $\partial V/\partial q^i$ then equals $g^{ii}dX_i/dq^i$ there. Since all $\partial V/\partial q^i$ vanish at P, so do all dX_i/dq^i.

and retaining only leading terms of the same order of magnitude, one finds

$$dq^N \Big/ \frac{X_N{''}\Delta q^N}{(g_{NN})^2} = dq^i \Big/ \frac{X_i{''}\Delta q^i}{(g_{ii})^2} + \frac{1}{2}\frac{X_N{''}(\Delta q^N)^2}{g_{ii}}\frac{\partial}{\partial q^i}\frac{1}{g_{NN}}$$

$$\text{on } C_{(N)}(i\neq N), \quad (11)$$

where $X_i{''}$ denotes $d^2X_i(q^i)/dq^{i2}$ evaluated at P and where the g_{ii}, g_{NN}, and $\partial g_{NN}/\partial q^i$ are also evaluated there.

It can be shown that the force constant k_i along path $C_{(i)}$ at the critical point is[23]

$$k_i = X_i{''}/(g_{ii})^2. \quad (12)$$

On multiplying numerator and denominator of the left-hand side of (11) by Δq^N, so that it becomes $\frac{1}{2}d(\Delta q^i)^2/k_N(\Delta q^N)^2$, and introducing (12), a linear equation is obtained:

$$\frac{2d(\Delta q^i)}{dy} = \frac{k_i\Delta q^i}{k_N y} - \frac{1}{2g_{ii}}\frac{\partial g_{NN}}{\partial q^i}, \quad (13)$$

where y equals $(\Delta q^N)^2$ and where g_{ii} and $\partial g_{NN}/\partial q^i$ are again evaluated at P. On solving (13), using the fact that the desired curve is the one passing through P, Eq. (14) is obtained,[24] except when $k_i = 2k_N$.

$$\Delta q^i = \frac{\{N^iN\}}{[2-(k_i/k_N)]}(\Delta q^N)^2 + O[(\Delta q^N)^\alpha]$$

$$\text{on } C_{(N)}, \ (i\neq N), \alpha > 2. \quad (14)$$

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[23] Along any curve, the second derivative of V with respect to arc length is:

$$\frac{d^2V}{ds^2} = \sum_{i,i=1}^{n} \frac{\partial^2 V}{\partial q^i\partial q^j}t^it^j + \sum_{i=1}^{n}\frac{\partial V}{\partial q^i}\frac{dt^i}{ds}.$$

The second sum vanishes at P since $\partial V/\partial q^i$ vanishes. There being no singularity in the metric tensor at P in the present case, the only nonzero contributions to $\partial^2 V/\partial q^i\partial q^j$ are those which do not contain any X_i or dX_i/dq^i for both these vanish[22] at P. In fact the only nonzero term occurs when $i=j$. It is $g^{ii}X''$. Using the value of t^i for Curve C_N at P,[21] it then follows that at P on Curve C_N, d^2V/ds^2 equals $X_N{''}/g_{NN}{}^2$.

[24] When $k_i\neq 2k_N$, the solution of (13) is of the form $x = by(1-a)^{-1}+cy^a$, where x is Δq^i, a is $k_i/2k_N$, b is $-(4g_{ii})^{-1}\partial g_{NN}/\partial q^i$, and c is an arbitrary constant. When a is greater than one, the y^a term can be ignored, since only leading terms are being considered here. When a is less than one, c must be set equal to zero in order that the curve pass through P. Emphasizing the fact that only leading terms are considered, as in (10), the term $O[(\Delta q^N)^\alpha]$ is included in (14). When $k_i = 2k_N$, the solution of (13) is of the form $x = y(b\ln y + c) \cong yb\ln y$, since $\ln y$ dominates c at small y. Since y equals Δq^{N2}, and since $\Delta q^N \ln q^N$ vanishes as Δq^N tends to zero, the point $(x=0, \Delta q^N=0)$ lies on this curve, i.e., the curve passes through P. However, we have not explored the possible implications of the logarithmic dependence and its behavior when higher order terms are included in Eq. (13). Therefore, we simply shall omit the case $k_i = 2k_N$ in the present paper. When this cited function Δq^i of Δq^N is expressed as a function of s, it can be shown that although d^2q^i/ds^2 does not exist, and so one cannot write $\Delta q^i = O(s^2)$ as in Eq. (10), the first derivative of Δq^i in the cited function does satisfy a Lipschitz condition: $\Delta q^i = O(s^{1+\alpha})$, $0 < \alpha < 1$.

Using (10), we can rewrite Eq. (14) as

$$\left.\begin{array}{r}\Delta q^i = \frac{\{N^iN\}}{[2-(k_i/k_N)]}\frac{s^2}{g_{NN}} + O(s^{1+\gamma}) \\[2mm] i\neq N, \gamma > 1 \\[2mm] \Delta q^N = s/(g_{NN})^{\frac{1}{2}} + O(s^\gamma) \qquad \gamma > 1.\end{array}\right\} \text{on } C_{(N)} \quad (15)$$

When k_i equals $2k_N$, it can be shown that d^2q^i/ds^2 does not exist[25]; the curve is still well-defined, with s^2 in Eq. (10) replaced by $s^\beta(1 < \beta < 2)$, but the fitting of the separable and nonseparable surfaces must be performed via the equation relating Δq^i to Δq^N rather than via the curvature properties in Eq. (19) below.

In (14) the Christoffel symbol $\{N^iN\}$ reduces to (16) for the case that $i\neq N$ and that the g_{ij}'s are diagonal:

$$\{N^iN\} = -\frac{1}{2g_{ii}}\frac{\partial g_{NN}}{\partial q^i} \quad (i\neq N; \text{ diagonal } g_{ij}). \quad (16)$$

The properties of the path $C_{(N)}$, e.g., $\mathbf{p}_{(N)}$ and $\kappa_{(N)}$, are indicated below by a subscript (N). The component $p_{(N)}{}^N$ vanishes at P.[26] The remaining $p_{(N)}{}^i$ follow from (14)[26]

$$\left.\begin{array}{r}(i\neq N), \ p_{(N)}{}^i = \{N^iN\}g^{NN}\dfrac{4-(k_i/k_N)}{2-(k_i/k_N)} \\[3mm] p_{(N)}{}^N = 0\end{array}\right\} \text{ on } C_{(N)}. \quad (17)$$

These equations hold for each $C_{(N)}$, $N=1$ to n.

The properties of the q^N-coordinate curve $C_{(N)}{}^0$, cotangential to $C_{(N)}$ at P, are denoted by a superscript 0. Equation (18) follows from (5), since dt^i/ds and t^i vanish everywhere on this curve for $i\neq N$:

$$\left.\begin{array}{r}(i\neq N), \ p_{(N)}{}^{0i} = \{N^iN\}g^{NN} \\[2mm] p_{(N)}{}^{0N} = 0\end{array}\right\} \text{ on } C_{(N)}{}^0. \quad (18)$$

(If, in a reaction, the extremal path leading from reactants to the saddle-point is denoted by $C_{(r)}$, the "reaction coordinate" will be $C_{(r)}{}^0$ near P.)

Using (17) and (18), one finds that $p_{(N)}{}^0$, the first curvature vector of $C_{(N)}{}^0$ at P, is related to the first

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[25] Substitution of the formal series $\Delta q^k = a_{k1}s + a_{k2}s^2 + \cdots$ into Eq. (9), expansion of the g^{ii} and the V in powers of the Δq^k's and, thence, in powers of s, and the equating of coefficients of each power of s shows that a_{i2} becomes infinite on C_N when $k_i = 2k_N$; $2a_{i2}$ is d^2q^i/ds^2.

[26] Noting that $\Sigma g_{ij}t^i\delta t^j/\delta s$ vanishes (cf. p. 157, Ref. 13, observing that $\mathbf{t}$ is a unit vector λ), that for $i\neq N$ each t^i vanishes on path C_N at P since C_N is cotangential to the q^N-coordinate curve there, and that g_{ij} vanishes for $i\neq j$, it follows that $\delta t^N/\delta s = 0$, i.e., $p^N = 0$.

To obtain p^i along C_N for $i\neq N$, one notes that dt^i/ds is obtained by twice differentiating Eq. (15) and that at P, $t^i = 0$ for $i\neq N$. These results are then introduced into Eq. (5).

curvature vector for $C_{(N)}$ at P by

$$p_{(N)}^{0i} = p_{(N)}^{i}(2 - k_i/k_N)/(4 - k_i/k_N) \quad \text{(for all } j\text{)}, \quad (19a)$$

$$\kappa_{(N)}^{0} = \left(\sum_{i,j=1}^{n} g_{ij} p_{(N)}^{0i} p_{(N)}^{0j} \right)^{\frac{1}{2}}; \qquad \kappa_N = \left(\sum_{i,j=1}^{n} g_{ij} p_{(N)}^{i} p_{(N)}^{j} \right)^{\frac{1}{2}}.$$

$$(19b)$$

Two dimensions only:

$$\kappa_{(N)}^{0} = \kappa_{(N)}(2 - k_i/k_N)/(4 - k_i/k_N). \quad (20)$$

Equation (19) holds for each extremal path of ascent (descent), $C_{(N)}$, $N = 1, \cdots, n$. The quantities $\mathbf{p}_{(N)}$, $\kappa_{(N)}$, k_i, and k_N are all known topographical properties of the potential-energy surface. The second derivative of the potential-energy function along each of these coordinate curves at the critical point, d^2V/ds^2, can be shown[27] to be equal to that of the cotangential path $C_{(N)}$ at P.

From the measured $p_{(N)}^{i}$'s, k_i's, and k_N, Eq. (19a) prescribes the value of each $p_{(N)}^{0i}$ for the coordinate curves of the system permitting separation of variables. Noting Eqs. (16) and (18), the metric tensor must be such as to satisfy this value of $p_{(N)}^{0i}$. Since the condition $p_{(N)}^{0N} = 0$ is satisfied automatically, there are $n - 1$ conditions to be fulfilled for each $C_{(N)}$, and hence, $n(n-1)$ conditions in all. Since the g_{jj} vary with position, the process of attempting to satisfy these conditions involves selecting the (curvilinear) coordinates of the critical point, as well as selecting the coordinate system. Because of the wide latitude in choice of systems permitting separation of variables [see, for example, Eq. (3.14) of Ref. 2(a) for the g^{ii} and the tabulation of the functions g^{ii} for the various coordinate systems], there is ample opportunity, we assume, for fulfilling most or all of these $n(n-1)$ conditions. When applicable, symmetry considerations simplify this choice of the coordinate system. Our applications, thus far, have been confined to systems of very few dimensions (see post), where no difficulty has been encountered in satisfying Eq. (19). It may also be possible to match higher curvatures of $C_{(N)}$ than the first, but we shall not attempt this matching here.[28]

[27] Along C_N^0, the expression for the value of d^2V/ds^2 in Ref. 23 reduces at P to the first sum, since $\partial V/\partial q^i$ vanishes. Since the tangent of the curve C_N^0 equals that of C_N at P, the value of d^2V/ds^2 also equals that of C_N at P. For the same reason, d^2V/ds^2 equals the value for the cotangential Cartesian coordinate (the normal coordinate) curve in this vibrational space at P.

[28] No match was made of the torsions of C_N (i.e., the second and higher curvatures) or of the derivatives of any curvatures or of the terms in the expansion of V in powers of s higher than the second. These properties would influence the higher order terms in Eq. (15), listed as $O(s^{1+\gamma})$ and $O(s^{\gamma})$. To attempt such a matching, formal-series expansions of the Δq^i in powers of s could be introduced into Eq. (9), and further terms could be included in the expansion of V and the g^{ii}'s in powers of the Δq^i's, and thence, in powers of s. Equating the coefficients of similar powers leads to the evaluation of additional terms in the series Eq. (15), where they exist. The torsions could then be calculated. [See, e.g., Ref. 12, p. 96 and J. C. H. Gerretsen, *Lectures on Tensor Calculus and Differential Geometry* (P. Noordhoff, Ltd., Groningen, The Netherlands, 1962), pp. 74–77.] One could then see if a system of coordinate curves C_N^0 exists which permits separation of variables and which permits the torsions, the first curvature, and the appropriate powers in a potential-energy-function expansion to be matched. It may be recalled that torsions do not occur for $n = 2$ (the major application thus far[6]) or for plane curves.

For purposes of atom-tunneling calculations for which the tunneling energy is so low that the quadratic expansion of V along the reaction coordinate curve $C_{(r)}^0$ is inadequate, a somewhat-improved answer might be obtained by choosing $X_r(q^r)$ along $C_{(r)}^0$ so that X_r'' at P satisfies (12), and so that the potential energy (8) along $C_{(r)}^0$ equals the actual potential energy. Similar modifications could be made in each $X_N(q^N)$, so that the potential energy (8) equals the actual potential energy along all $C_{(N)}^0$'s.

ROTATING SYSTEMS

When the molecule is rotating, a choice of internal coordinates to satisfy the Eckart condition minimizes the importance of the vibrational angular momentum.[29] When the residual, vibrational angular momentum is then ignored, the remaining effect of the rotations on the vibrational motion is to introduce a centrifugal potential. In that approximation, the results described in the preceding section apply if V is the effective potential energy, the sum of the original potential energy and of the centrifugal terms. All the properties of the surface, including the position of the saddle point, now depend on the rotational state of the molecule. The normal coordinates mentioned earlier are now replaced by those for this new effective Hamiltonian for the vibrational motion.

Application to the Three-Center Reaction Problem

A chemical reaction which has received much theoretical and experimental attention is the three-center one, $A + BC \rightarrow AB + C$. Often, in the specific examples considered in the literature, the reaction is assumed to proceed via a linear collision-complex. In that case, the course of reaction is determined by two coordinates in the activated complex region, r_{ab} and r_{bc}. The potential-energy surface is often plotted in mass-weighted coordinates as a function of the two distances, and the tunneling rate and other aspects of the reaction are computed. In a typical approximation, the potential energy is assumed to be such as to permit separation of this pair of variables from the remaining ones. Rotation–vibration interactions are also neglected.

In the local approximation described in this paper, the reaction rate due to nonrotating linear complexes in this nonseparable problem would be computed as follows. Along the two paths of steepest ascent (descent) to the saddle-point, one computes the two force constants (one positive, one negative), as well as the curvature of these paths in mass-weighted configuration space. An orthogonal, curvilinear coordinate system which permits separation of variables is then introduced. Two-dimensional circular, elliptic, and parabolic sys-

[29] C. Eckart, Phys. Rev. **47**, 552 (1935); A. Sayvetz, J. Chem. Phys. **7**, 383 (1939); S. M. Ferigle and A. Weber, Am. J. Phys. **21**, 102 (1957); E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 11.

tems are available.[30] The origin (or foci) of the coordinate system is selected in such a way that there exists a pair of curvilinear coordinate curves intersecting at the saddle point, cotangential with the two corresponding paths of steepest ascent (descent) at the saddle point and having curvatures related to the latter paths by Eqs. (19) and (20). The separated equations are then solved, and the results inserted into a statistical expression for the reaction rate. The usual expression in the literature was not designed for curvilinear reaction paths, but a recent generalization and modification of it takes the curvilinear aspects into account.[7]

A comparison of such a calculation can be made with the usual reaction-rate calculations and with some recent computer calculations involving a numerical solution of the two-dimensional nonseparable Schrödinger equation.[10a] Some work on this problem is in progress at present, and only a few preliminary remarks are made here.[6]

Since one of the force constants in (20) is negative, the curvature of the (separable) curvilinear reaction coordinate is seen to be less than that of the path of steepest ascent. That is, in classical mechanics a dynamical trajectory which passes through the saddle point does not follow the path of steepest ascent but rather follows one which proceeds along the sides of the valley. Physically, this behavior is readily understood. Because of path curvature there is a centrifugal force which flings the particle outwards—the more so the greater its velocity along the trajectory. Since this velocity is least at the saddle point (most of the energy is now potential energy), the centrifugal force is least there.

A centrifugal effect occurs also in quantum mechanics, only now phrased in terms of probabilities, as one may see from the behavior of the wavefunction of the separated system. The effect is similar to the classical one for energies sufficient to make the system surmount the potential-energy barrier. Preliminary calculations suggest that a nonclassical centrifugal effect, negative in nature, appears to occur under tunneling conditions.[6,7]

When the negative force constant along the reaction coordinate curve $C_{(r)}{}^0$ vanishes, the curvature of the corresponding extremal path $C_{(r)}$ equals that of $C_{(r)}{}^0$, as one may see from Eq. (20). Because of the centrifugal-force argument just mentioned, this behavior is understandable on physical grounds also.

In a calculation of atom-tunneling rates, Weston computed the potential-energy function along the path of steepest descent from the saddle point and neglected the effect of path curvature in the formalism[31]—i.e., he used the activated complex rate equation that had been derived for rectilinear paths. The present study reveals two additional effects whose importance is under current investigation.[6]

(1) The activated-complex rate equation for curvilinear coordinates differs from that for rectilinear coordinates (but reduces to it, of course, when path curvatures vanish), because of a coupling of the separated degrees of freedom via constants of the motion. This coupling occurs, at least in part, in the form of the centrifugal potential arising from path curvature.

(2) Although the second derivative of the potential energy along $C_{(r)}$ equals that along $C_{(r)}{}^0$, the potential barrier along $C_{(r)}{}^0$ is "thicker" because of the higher-order of terms. (The barrier is "thinnest" along the path of steepest ascent.) In solving the separated wave equation for this coordinate, an effect of these higher-order terms can be estimated by including them in the separated equation.

Some preliminary evidence in support of a local approximation is given later. It is shown there that the numerical tunneling rates for one- and n-dimensional calculations are fairly similar, at low energies at least, when proper cognizance is taken of zero-point energies.

In the three-center reaction $A+BC\rightarrow AB+C$, there is also dynamical coupling not only between the two degrees of freedom mentioned above but also with the other motions. The effects are presumed to be small for linear complexes. However, the effects of such coupling on path curvature for the various extremal paths can be included by using equations for as many i's and N's as are involved. To obtain the separated wave equations, one must know the Stäckel coefficients which appear in them. Eisenhart has given these explicitly for a Euclidean space of three dimensions.[30] He has also described the coordinate systems permitting separation of variables in n dimensions, and one can derive the Stäckel coefficients from the metric tensor for these coordinate systems.[32] The situation is simplified appreciably where only a few of the extremal paths have appreciable curvature. Symmetry considerations play a role here, of course.[33]

OTHER PROBLEMS

In some problems there are "hidden" approximate constants of the motion. With each variable separated, a new constant of the motion appears. Numerical calculations may help reveal them.

Upon examination of the results of some recent quantum-mechanical computer calculations[10a] on the three-center reaction-rate problem, for example, one may note (with caution since very few results were available) that in the case of elementary processes with a fairly large probability, there was some tendency to

[30] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 655.

[31] Compare R. E. Weston, Jr., J. Chem. Phys. **31**, 892 (1959).

[32] For example, from the metric tensor, Eq. (1.8) in Ref. 2(b) may be solved for a quantity P_i and, with the aid of (2.1), one thereupon obtains $\phi^{i\alpha}/\phi$. The determinant of the latter is $1/\phi^{n+1}$, and so $\phi^{i\alpha}$ may be obtained. Inversion yields the Stäckel coefficients $\phi_{i\alpha}$. However, a much more direct method of obtaining them may be available.

[33] For example, in a symmetrical reaction $A+BA\rightarrow AB+A$, the vibrational motion of the linear activated complex is Cartesian.

TABLE I. Calculated tunneling probabilities κ for
$H+H_2$ reaction.

$\epsilon-v_0$ (kcal mole^{-1})	One-dimensional		
	(Bell κ)	(Eckart κ)	n-dimensional
-4.33	0.0069	0.0035	0.0059
-1.83	0.11	0.13$_5$	0.14
-0.83	0.28	0.36	0.65
-0.33	0.41	0.51	0.90
0	0.50	0.60	

preserve the vibrational quantum state.[34] These processes include reflection from or passage through the saddel-point region. For such processes, the vibrational motion would be approximately adiabatic and, presumably, a separation of variables would be appropriate as a first approximation. However, any detailed conclusions should await further numerical results.

Another problem which has been the subject of recent attention has been the problem of intramolecular energy transfer among vibrational modes in a linear chain of atoms, coupled by harmonic plus certain anharmonic terms.[8] At least in certain cases, a pronounced type of nonergodicity was observed when one "normal" vibrational mode was excited, the energy transferring into the other modes and then, surprisingly, reaccumulating almost entirely in the first mode followed by a repetition of the cycle. It would be interesting to explore the possible implications of this nonergodicity in terms of the local approximation described in the present study.

APPENDIX I. COMPARISON OF ONE- AND n-DIMENSIONAL TRANSMISSION COEFFICIENTS

In the reaction $H+H_2\rightarrow H_2+H$, the vibrations used for the activated complex were[10a,31] 2108, 877, 877, and 1918 i cm^{-1}; that used for H_2 was 4405 cm^{-1}. Let E denote the total energy in the n-dimensional system, ϵ some "equivalent" total energy in a one-dimensional calculation, and ΔU the potential energy of the n-dimensional activated complex minus that of the reactants. Let E_0 and E_0^+ denote the zero-point energy of H_2 and of the activated complex, respectively.

[34] From the rows of Table I of Ref. 10(a) for $E=20$, one sees that a particle initially in a vibrational state $v=2$ (the first excited state) has a probability of reflection of 0.42 into $v=2$ and of 0.07 into $v=1$. (The transmission probabilities were 0.36 and 0.15, respectively.) For a particle initially in the ground vibrational state $(v=1)$, the transmission probability was 0.76 for no change in v and only 0.15 for forming a state with a higher v $(v=2)$. No such approximate conservation of v may be found in the reflection probabilities, which are so low (0.01, 0.07) as to represent unimportant processes.

In the spirit of the local-approximation method, and indeed of activated-complex theory, a comparison of one- and n-dimensional calculations should be made at equivalent values of the energy at the saddle point, i.e., at equal values of the total energy minus the potential and zero-point energy at that point. This energy difference is $E-(\Delta U+E_0^+)$ for the n-dimensional computation. If v_0 is the saddle-point value of the potential energy in the one-dimensional model, then the above energy difference in the one-dimensional case is $\epsilon-v_0$, a common quantity in WKB[35] calculations. One thus has:

$$\epsilon-v_0=E-(\Delta U+E_0^+),$$

ΔU was taken[10a] to be 8.81 kcal/mole^{-1}, i.e., the activation energy at 0°K, 8.03, plus the difference of zero-point energies of activated complex and reactants. Two cases may be distinguished in the n-dimensional calculations of Mortensen and Pitzer: (a) bending vibrations included, E_0^+ being 5.52 kcal/mole^{-1}, (b) bending vibrations neglected, E_0^+ being 3.02 kcal mole^{-1}. Values of E of 10 and 15 kcal mole^{-1} in Case (a) and of 10 and 11 in Case (b) correspond to values of $\epsilon-v_0$ equal to -4.33, -0.33, -1.83, and -0.83 kcal mole^{-1}, respectively. The corresponding values[10a] of κ are given in Table I. The corresponding one-dimensional κ's calculated from Bell's tunneling formula[36] for a parabolic barrier of imaginary frequency $\nu=1918$ cm^{-1} depend only on $\epsilon-v_0$ and on ν. They are given in Table I. The one-dimensional κ's calculated from Eckart's formula,[37] for which the top of the barrier is fitted to the above imaginary frequency and for which the height is 8.03 kcal mole^{-1}, are also given in Table I.

The one- and n-dimensional values for the larger $|\epsilon-v_0|$'s agree well with each other, though those for the smaller $|\epsilon-v_0|$'s are surprisingly high in the n-dimensional case. Indeed, the latter would be nearer to those obtainable from the usual WBK tunneling formula[35] that does not take account of the proximity of the two transition points near the top of the barrier (0.0069, 0.12, 0.39, 0.69, and 1.0). Perhaps a closer examination of the assumptions made in the numerical n-dimensional calculation for energies near the top of the barrier is in order.

The conclusions drawn here differ somewhat from those in Ref. 10(a), where the incident energies of the one- and n-dimensional systems were made equivalent (rather than those at the saddle point).

[35] R. P. Bell, Proc. Roy. Soc. (London) A148, 241 (1935).
[36] R. P. Bell, Trans. Faraday Soc. 55, 1 (1959).
[37] C. E. Eckart, Phys. Rev. 35, 1303 (1930).