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William H. Miller, Nicholas C. Handy, and John E. Adams



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Reaction path Hamiltonian for polyatomic molecules

William H. Miller,^{a)} Nicholas C. Handy,^{b)} and John E. Adams^{c)}

Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
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The reaction path on the potential energy surface of a polyatomic molecule is the steepest descent path (if mass-weighted Cartesian coordinates are used) connecting saddle points and minima. For an N -atom system in 3d space it is shown how the $3N-6$ internal coordinates can be chosen to be the reaction coordinate s , the arc length along the reaction path, plus $(3N-7)$ normal coordinates that describe vibrations orthogonal to the reaction path. The classical (and quantum) Hamiltonian is derived in terms of these coordinates and their conjugate momenta for the general case of an N atom system with a given nonzero value of the total angular momentum. One of the important facts that makes this analysis feasible (and therefore interesting) is that all the quantities necessary to construct this Hamiltonian, and thus permit dynamical studies, are obtainable from a relatively modest number of *ab initio* quantum chemistry calculations of the potential energy surface. As a simple example, it is shown how the effects of reaction path curvature can be incorporated in the vibrationally adiabatic approximation, and application to the collinear and 3d $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction shows that the tunneling probabilities given within this approximation are considerably improved when these curvature effects are included.

I. INTRODUCTION

Much progress has been made over the last 10–15 years in dynamically rigorous theoretical treatments of elementary processes in chemical dynamics. Within the realm of classical mechanical descriptions, for example, numerical trajectory calculations¹ of atom–diatom collision processes, e.g.,



are now essentially routine, and considerable progress is also being made in the quantum mechanical description² of such processes. Similar progress has also been made in describing intramolecular dynamics.³ Furthermore, a number of potential energy surfaces for triatomic systems have been calculated⁴ from first principles by the methods of quantum chemistry, so that the primitive beginnings of an “*ab initio* chemical dynamics” is becoming a reality.

Most of the systems treated to date, however, have been of the three-atom variety, and one of the reasons for this becomes apparent if one considers obtaining the potential energy surface (i.e., the Born–Oppenheimer electronic energy) by the methodology of *ab initio* quantum chemistry (e.g., Hartree–Fock, configuration interaction, etc.). Since the potential surface for an N -atom system depends on $3N-6$ coordinates and since one would need ~ 10 points on the surface for each coordinate in order to characterize it completely, this would require $\sim 10^{3N-6}$ *ab initio* quantum chemistry calculations. Indeed, the triatomic potential surfaces (e.g., $\text{F}-\text{H}-\text{H}$) that have been accurately determined⁴ this way have typically required $\sim 10^3$ calculations (if no allowance is made for symmetry). For $N > 3$ one immediately sees that the number of calculations required becomes out of

the question. For some applications, of course, one does not need to know the potential surface in all regions of the $(3N-6)$ -dimensional configuration space, and although this does indeed help the situation, for $N > 4$ or so matters nevertheless become essentially hopeless.

Quantum chemists are able, however, to make use of fully accurate *ab initio* calculations for many-atom systems, simply not the enormous number of such calculations required to determine the potential energy surface completely. Thus one of the questions which has motivated this paper is how one can best use a reasonable number (i.e., $\ll 10^{3N-6}$) of such calculations for purposes of studying the molecular dynamics, e.g., chemical reactions, of the molecular system. Karplus and co-workers⁵ have been concerned with this question and have implemented one version of a solution: in computing classical trajectories for a many-atom system, they calculate the force on the nuclei—i.e., the gradient of the potential energy surface—at each point as it is required along the classical trajectory. This still requires many calculations of the potential surface, however, and at present necessitates the use of relatively simple quantum chemistry methods.

This paper considers another response to this question of how a modest number of calculations of the potential energy surface of a many-atom ($N > 3$) system can best be used for dynamical purposes. The key idea that has led to progress is noting that it has become feasible in recent years for quantum chemists to compute the reaction path on a potential energy surface.⁶ This is the path of steepest descent (if mass-weight coordinates are used) from a saddle point on the potential surface to various minima, and it is relatively easy to perform such calculations because efficient algorithms have been developed⁷ to evaluate the gradient of the potential energy surface. It has also been reported⁸ that efficient algorithms have recently been developed and implemented which evaluate the second derivative matrix of the potential energy with respect to nuclear coordinates.

These reaction path calculations are usually performed

^{a)} Camille and Henry Dreyfus Teacher–Scholar.

^{b)} On sabbatical leave from the Department of Theoretical Chemistry, University of Cambridge, England.

^{c)} Present address: Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545.

using the full set of $3N$ Cartesian coordinates of the N atoms, so that the path of steepest descent, i.e., the reaction path, is obtained by starting at a saddle point and carrying out calculations at a sequence of nuclear positions determined by following the gradient vector (in mass-weighted coordinates),

$$v_{i\gamma} = -c \frac{\partial V}{\partial x_{i\gamma}}, \quad (1.2)$$

where c is a constant to normalize the $3N$ -dimensional vector $v_{i\gamma}$ to unity. Here $i=1, \dots, N$ labels the atoms and $\gamma=x, y, z$ the Cartesian components, $x_{i\gamma} = \sqrt{m_i} r_{i\gamma}$ are the mass-weighted Cartesian coordinates (i.e., \mathbf{r}_i is the position vector for atom i), m_i is the mass of atom i , and V is the Born-Oppenheimer electronic energy as a function of the atomic positions, i.e., the potential energy surface. At saddle points and minima of potential surfaces it is common to carry out normal mode analyses, i.e., to diagonalize the $3N \times 3N$ second derivative matrix \mathbf{K} whose matrix elements are

$$K_{i\gamma, i'\gamma'} = \frac{\partial^2 V}{\partial x_{i\gamma} \partial x_{i'\gamma'}}. \quad (1.3)$$

There are $3N-6$ nonzero eigenvalues of the matrix, $\{\omega_k^2\}$, $k=1, \dots, 3N-6$, and 6 zero eigenvalues corresponding to overall translation and overall rotation.

The only essentially new kind of quantum chemistry calculation needed to implement the approach described in this paper is a *normal mode analysis at a sequence of points along the reaction path*. Thus if the $3N$ -dimensional vector $\mathbf{a} \equiv \{a_{i\gamma}\}$ is a point on the reaction path, then for general points \mathbf{x} near \mathbf{a} one has

$$V(\mathbf{x}) = V(\mathbf{a}) + \frac{\partial V(\mathbf{a})}{\partial \mathbf{a}} \cdot \boldsymbol{\xi} + \frac{1}{2} \boldsymbol{\xi} \cdot \mathbf{K} \cdot \boldsymbol{\xi}, \quad (1.4)$$

where \mathbf{K} is the force constant matrix defined by Eq. (1.3) and $\boldsymbol{\xi}$ is the displacement vector

$$\boldsymbol{\xi} = \mathbf{x} - \mathbf{a}.$$

For displacements $\boldsymbol{\xi}$ that are *orthogonal* in the $3N$ -dimensional vector space to the gradient vector the linear term in Eq. (1.4) is absent and the potential is thus quadratic in the displacements. To define normal coordinates for vibrations orthogonal to the reaction path, however, it is also necessary to restrict the displacements $\boldsymbol{\xi}$ to be orthogonal to the six $3N$ -dimensional vectors which correspond to infinitesimal rotations and translations of the complete N -atom system. At each point \mathbf{a} on the reaction path one thus defines normal modes for vibration by diagonalizing the *projected force constant matrix* \mathbf{K}^P ,

$$\mathbf{K}^P = (\mathbf{1} - \mathbf{P}) \cdot \mathbf{K} \cdot (\mathbf{1} - \mathbf{P}), \quad (1.5a)$$

where \mathbf{K} is the $3N \times 3N$ matrix of Eq. (1.3) and \mathbf{P} the projector, a $3N \times 3N$ matrix, whose elements are

$$P_{i\gamma, i'\gamma'} = \sum_{k=3N-6}^{3N} L_{i\gamma, k} L_{i'\gamma', k}, \quad (1.5b)$$

where $\{L_{i\gamma, k}\}$, $k=3N-6, \dots, 3N-1$ are the six $3N$ -dimensional unit vectors that correspond to infinitesimal rotations and translations of the N -atom system, and $L_{i\gamma, 3N} \equiv v_{i\gamma}$ is the unit vector that points along the reac-

tion path. An explicit expression for this projector is given in Sec. IV. [In conventional rotational-vibrational analysis about the minimum of a potential energy surface, the eigenvectors for infinitesimal rotations, say, emerge automatically when the *unprojected* force constant matrix \mathbf{K} is diagonalized, but this is true only because \mathbf{K} is evaluated at a minimum on the potential surface (or at a saddle point). At a general point on the reaction path this will not be the case, so for the present analysis it is necessary to project out of \mathbf{K} not only the direction along the reaction path but also the directions corresponding to infinitesimal rotations and translations.] It is clear that \mathbf{K}^P will have seven zero eigenvalues corresponding to infinitesimal rotations, translations, and motion along the reaction coordinate, with eigenvectors $\{L_{i\gamma, k}\}$, $k=3N-6, \dots, 3N$. There will also be $3N-7$ nonzero eigenvalues, $\{\omega_k^2\}$, $k=1, \dots, 3N-7$, which give the frequencies for vibrations orthogonal to the reaction path, with eigenvectors $\{L_{i\gamma, k}\}$, $k=1, \dots, 3N-7$, in terms of which the normal coordinates for vibration are defined by

$$Q_k = \sum_{i\gamma} \xi_{i\gamma} L_{i\gamma, k}, \\ k=1, \dots, 3N-7.$$

The quantities provided by such quantum chemistry calculations would be $\{a_{i\gamma}(s)\}$, the mass-weighted Cartesian coordinates of the reaction path, $V_0(s)$, the potential energy on the reaction path, the $(3N-7)$ frequencies $\{\omega_k(s)\}$, and the eigenvalues $\{L_{i\gamma, k}(s)\}$ of the projected force constant matrix, all as a function of the reaction coordinate s , the arc length along the reaction path. This information provides the following approximation to the potential energy surface,

$$V(s, Q_1, \dots, Q_{3N-7}) = V_0(s) + \sum_{k=1}^{3N-7} \frac{1}{2} \omega_k(s)^2 Q_k^2, \quad (1.6)$$

in terms of the $3N-6$ internal coordinates s , $\{Q_k\}$, $k=1, \dots, 3N-7$, and has the form of a "harmonic valley" about the reaction path. For many purposes one expects this to be the relevant part of the potential energy surface. The remaining, more difficult task is to express the kinetic energy of the system in terms of these coordinates and their conjugate momenta, so as to obtain a complete Hamiltonian which will then permit dynamical studies. Most of this paper is concerned with this task of obtaining the kinetic energy in terms of the reaction path variables.

The reader will recognize that these variables are essentially an extension of the "natural collision coordinates" introduced by Marcus³ for A+BC collision systems (although these were not necessarily restricted to the steepest descent path). For the collinear A+BC system, for example, the classical Hamiltonian obtained by Marcus is (incorporating the harmonic approximations to the potential about the reaction path)

$$H(p_s, s, P, Q) = \frac{1}{2} p_s^2 / [1 + Q \kappa(s)]^2 + V_0(s) \\ + \frac{1}{2} P^2 + \frac{1}{2} \omega(s)^2 Q^2, \quad (1.7)$$

where $\kappa(s)$ is the curvature of the reaction path at position s , and (p_s, P) are the momenta conjugate to (s, Q) .

One of the goals of this paper is thus to obtain the classical Hamiltonian analogous to the above for the general case of an N -atom system in 3d space.

Having obtained the form of the classical Hamiltonian, one can carry out dynamical studies; classical trajectory calculations can be made, or one may consider the dynamics within various approximations. For example, the Hamiltonian has the form of one special, or "interesting" degree of freedom, i.e., the reaction coordinate s , coupled to a number of harmonic modes, suggesting models which formally eliminate the harmonic degrees of freedom and obtain a reduced equation of motion for only the s degree of freedom.¹⁰ Another standard approximation is that of vibrational adiabaticity,^{9,11} i.e., to assume that the $3N - 7$ harmonic degrees of freedom remain in the same adiabatic quantum state (or classically, conserve their action variables) along the reaction coordinate s . It will be seen in Sec. III, for example, that the vibrationally adiabatic approximation is actually a much better description of tunneling in the collinear $H + H_2$ reaction than had been previously believed, provided that the effects of curvature of the reaction path are properly taken into account.

The practical feature which makes this general approach feasible (and therefore interesting) for polyatomic systems is that it requires a relatively modest number of quantum chemistry calculations to obtain all the quantities necessary to construct the classical Hamiltonian. Suppose, for example, that one requires ~ 10 calculations along the reaction path to determine the functions $V_0(s)$, $\{\omega_k(s)\}$, $\{a_{i,r}(s)\}$, and $\{L_{i,r,k}(s)\}$. Estimates⁸ are that calculation of the gradient vector and force constant matrix of Eqs. (1.2) and (1.3) requires ~ 10 times the effort of a single quantum chemistry calculation, so that only the equivalent of ~ 100 quantum chemistry calculations would be required to determine all the necessary quantities, independent of the number of atoms N . Of course the larger the number of atoms, the larger the number of electrons, and the more difficult the quantum chemistry calculations. Nevertheless, a useful description of the dynamical system is achieved with a reasonably modest number of such calculations.

The structure of the paper is as follows: Section II first shows how the Hamiltonian is expressed in terms of reaction path coordinates and their conjugate momenta for a "generic Cartesian" system, i.e., one for which the complications of 3d space and the requisite conservation of total angular momentum are ignored. The result obtained actually does describe real molecular systems for the special case of zero total angular momentum and with the neglect of rotation-vibration coupling. Section III then briefly discusses the vibrationally adiabatic approximation, and for the example of tunneling in the collinear $H + H_2 \rightarrow H_2 + H$ reaction, shows that if curvature of the reaction path is taken into account, the approximation works considerably better than had been heretofore believed.

Section IV, the main body of the paper, then derives the classical Hamiltonian in terms of reaction path variables for the general case of an N -atom system in 3d space with nonzero total angular momentum. It is seen

how the simpler results of Sec. II are recovered if certain approximations are introduced, and the special case that the reaction path corresponds to a linear molecule is also treated. As a simple example, the vibrationally adiabatic approximation to this reaction path Hamiltonian is used to compute reaction probabilities for the $3d H + H_2 \rightarrow H_2 + H$ reaction, and the results are seen to be in reasonably good agreement with the correct quantum mechanical results. Finally, it is shown in Sec. V how the quantum mechanical Hamiltonian operator in these variables can be obtained from the expression for the classical Hamiltonian.

In concluding this Introduction it should be noted that this reaction path model for the Hamiltonian will not always be useful. For example, in the asymptotic region of the potential surface where the N -atom system fragments into two subsystems some of the $3N - 7$ vibrations become rotations, i.e., some of the frequencies go to zero, and the harmonic approximation to the potential about the reaction path thus fails. It should be quite useful, however, for describing intramolecular dynamics, e.g., unimolecular isomerizations, or in general in describing the dynamics in the saddle point region of the potential energy surface. It should thus be useful in any kind of generalized transition state theory which requires knowledge of the dynamics only in the saddle point region and, in particular, in calculating tunneling corrections to such theories. The quantum mechanical form of the Hamiltonian may also be of use in carrying out quantum scattering calculations in the saddle point region.

II. REACTION PATH HAMILTONIAN FOR GENERIC CARTESIAN SYSTEMS

A. General derivation

Before considering an actual molecular system, it is useful to treat a general F -dimensional Cartesian-like Hamiltonian without the complications of angular momentum considerations. Thus let $\{x_i\}$, $i = 1, \dots, F$ be mass-weighted Cartesian-like coordinates, and the Hamiltonian for the system be

$$H(\mathbf{p}, \mathbf{x}) = \sum_{i=1}^F \frac{1}{2} p_i^2 + V(x_1, \dots, x_F), \quad (2.1)$$

where V is the potential energy.

Suppose that the reaction path has been determined and the normal mode analysis carried out along it; this would be the "output" of an *ab initio* quantum chemistry calculation. One thus knows $\{a_i(s)\}$, $i = 1, \dots, F$, the Cartesian coordinates of the reaction path as a function of the reaction coordinate s , the arc length along the reaction path, the potential energy $V_0(s)$ along the reaction path, the normal mode frequencies $\{\omega_k(s)\}$, $k = 1, \dots, F - 1$, and the matrix of eigenvectors $\{L_{i,k}(s)\}$, $i, k = 1, \dots, F$ which result from diagonalizing the projected force constant matrix. (In this case the projector \mathbf{P} is the one-dimensional projector $\mathbf{P} = \mathbf{v}\mathbf{v}^\dagger$, i.e., its matrix elements are $P_{i,i'} = v_i v_{i'}$.) The potential energy is given, within a harmonic approximation about the reaction path, by

$$V(s, Q_1, \dots, Q_{F-1}) = V_0(s) + \sum_{k=1}^{F-1} \frac{1}{2} \omega_k(s)^2 Q_k^2, \quad (2.2)$$

where the term $k=F$ is absent from the sum because this is the zero eigenvalue corresponding to the direction along the reaction path; i.e., the F th eigenvector is the normalized gradient vector,

$$L_{i,F}(s) \equiv v_i(s) \propto - \left(\frac{\partial V(\mathbf{x})}{\partial x_i} \right)_{\mathbf{x}=\mathbf{q}}; \quad (2.3a)$$

we note also that

$$L_{i,F}(s) = a'_i(s), \quad (2.3b)$$

which follows by definition of arc length, i.e.,

$$ds^2 = \sum_{i=1}^F (dx_i)^2,$$

for displacements along the reaction path. The task is to determine the kinetic energy in terms of s , $\{Q_k\}$, and their conjugate momenta p_s , $\{P_k\}$.

One must thus carry out a canonical transformation¹² from the $2F$ "old" variables (x_i, p_i) , $i=1, \dots, F$, to the $2F$ "new" variables (s, p_s) , (Q_k, P_k) , $k=1, \dots, F-1$, where the old Cartesian coordinates $\{x_i\}$ are given in terms of the new reaction path coordinates $(s, \{Q_k\})$ by

$$x_i = a_i(s) + \sum_{k=1}^{F-1} L_{i,k}(s) Q_k \\ \equiv x_i(s, \{Q_k\}); \quad (2.4)$$

i.e., the Cartesian coordinates $\{x_i\}$ of a general point in configuration space are given by the Cartesian coordinates of a point on the reaction path, $\{a_i(s)\}$, plus $F-1$ displacements $\{Q_k\}$ orthogonal to the reaction path. Since the old coordinates are a function only of the new coordinates and not the new momenta, the canonical transformation is a point transformation and the F_3 -type generating function for it is given by¹²

$$F_3(s, \{Q_k\}; \{p_i\}) = - \sum_{i=1}^F p_i x_i(s, \{Q_k\}) \\ = - \sum_{i=1}^F p_i \left[a_i(s) + \sum_{k=1}^{F-1} L_{i,k}(s) Q_k \right]. \quad (2.5)$$

The transformation is defined in terms of the generating function by the following equations¹²:

$$x_i = -\partial F_3 / \partial p_i, \quad i=1, \dots, F, \quad (2.6a)$$

$$P_k = -\partial F_3 / \partial Q_k, \quad k=1, \dots, F-1, \quad (2.6b)$$

$$p_s = -\partial F_3 / \partial s. \quad (2.6c)$$

Equation (2.6a) is satisfied by construction, and Eqs. (2.6b) and (2.6c) give

$$P_k = \sum_{i=1}^F p_i L_{i,k}(s), \quad k=1, \dots, F-1, \quad (2.7a)$$

$$p_s = \sum_{i=1}^F p_i \left[a'_i(s) + \sum_{k=1}^{F-1} L'_{i,k}(s) Q_k \right]. \quad (2.7b)$$

Since the kinetic energy T is given in terms of the old momenta by

$$T = \sum_{i=1}^F \frac{1}{2} p_i^2, \quad (2.8)$$

the task is to solve Eq. (2.7) for the old momenta $\{p_i\}$ in terms of the new variables (s, p_s) , (Q_k, P_k) , and then Eq. (2.8) can be used to obtain the expression for the kinetic energy in terms of the new variables. In light of Eq. (2.3), Eq. (2.7b) can also be written as

$$p_s = \sum_{i=1}^F p_i \left[v_i + \sum_{k=1}^{F-1} L'_{i,k}(s) Q_k \right]. \quad (2.7b')$$

To solve Eq. (2.7) for $\{p_i\}$, one first multiplies Eq. (2.7a) by $L_{j,k}(s)$ and sums over k :

$$\sum_{k=1}^{F-1} L_{j,k}(s) P_k = \sum_{i=1}^F p_i \sum_{k=1}^{F-1} L_{j,k}(s) L_{i,k}(s). \quad (2.9)$$

But unitarity of $\{L_{i,k}\}$ implies that

$$\sum_{k=1}^{F-1} L_{j,k}(s) L_{i,k}(s) = \sum_{k=1}^F L_{j,k}(s) L_{i,k}(s) - L_{j,F}(s) L_{i,F}(s) \\ = \delta_{j,i} - v_j v_i,$$

so that Eq. (2.9) becomes

$$\sum_{k=1}^{F-1} L_{j,k}(s) P_k = p_j - v_j \sum_{i=1}^F p_i v_i. \quad (2.10)$$

Equation (2.10) shows that the old momenta $\{p_i\}$ are given by

$$p_i = \sum_{k=1}^{F-1} L_{i,k}(s) P_k + c v_i, \quad (2.11)$$

where c is unknown (because it depends on $\{p_i\}$). c is now determined by substituting Eq. (2.11) into Eq. (2.7b'):

$$p_s = \sum_{i=1}^F \left[\sum_{k=1}^{F-1} L_{i,k}(s) P_k + c v_i \right] \left[v_i + \sum_{k=1}^{F-1} L'_{i,k}(s) Q_k \right] \\ = c \left[\sum_{i=1}^F v_i^2 + \sum_{k=1}^{F-1} Q_k \left\{ \sum_{i=1}^{F-1} v_i L'_{i,k}(s) \right\} \right] + \sum_{i=1}^F P_i \sum_{k=1}^{F-1} v_i L_{i,k}(s) \\ + \sum_{k=1}^{F-1} Q_k P_i \sum_{i=1}^F L'_{i,k}(s) L_{i,i}(s). \quad (2.12)$$

Since

$$\sum_{i=1}^F v_i^2 = 1$$

and

$$\sum_{i=1}^F v_i L_{i,i}(s) = \sum_{i=1}^F L_{i,F}(s) L_{i,i}(s) = \delta_{i,F} = 0$$

for $l=1, \dots, F-1$, Eq. (2.12) gives c as

$$c = \frac{p_s - \sum_{k=1}^{F-1} Q_k P_i B_{k,i}(s)}{1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)}, \quad (2.13)$$

where

$$B_{k,i}(s) = \sum_{i=1}^F L'_{i,k}(s) L_{i,i}(s). \quad (2.14)$$

Using Eq. (2.13) in Eq. (2.11) gives the old momenta explicitly in terms of the new variables:

$$p_i = \sum_{k=1}^{F-1} L_{i,k}(s) P_k + L_{i,F}(s) \frac{[p_s - \sum_{k=1}^{F-1} Q_k P_i B_{k,i}(s)]}{[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)]}. \quad (2.15)$$

Using the unitarity of $\{L_{i,k}\}$ again, it is easy to obtain

from Eqs. (2.15) and (2.8) the following final result for the kinetic energy in terms of the new variables:

$$T = \sum_{k=1}^{F-1} \frac{1}{2} P_k^2 + \frac{1}{2} \frac{[p_s - \sum_{k=1}^{F-1} Q_k P_k B_{k,i}(s)]^2}{[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)]^2}. \quad (2.16)$$

Equation (2.16) is the desired result. Together with the potential energy, Eq. (2.2), it provides the classical Hamiltonian in terms of the reaction path coordinates and their conjugate momenta:

$$H(p_s, s, \{P_k, Q_k\}) = \sum_{k=1}^{F-1} (\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2) + V_0(s) + \frac{1}{2} \frac{[p_s - \sum_{k=1}^{F-1} Q_k P_k B_{k,i}(s)]^2}{[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)]^2}. \quad (2.17)$$

Central to the structure of this Hamiltonian are the coupling elements $B_{k,i}(s)$ which are defined by Eq. (2.14). If the eigenvectors of the projected force constant matrix are denoted in pseudo-Dirac notation by $|\psi_k\rangle$ and vector products by bra-kets, then one sees that

$$B_{k,i}(s) = \left\langle \frac{\partial \psi_k}{\partial s} \left| \psi_i \right. \right\rangle, \quad (2.18)$$

i.e., it has the same form as the nonadiabatic coupling elements in the Born-Oppenheimer approximation. The terms $k, l = 1, \dots, F-1$ in the numerator of the last term in Eq. (2.17) thus describe the coupling between the different $(F-1)$ vibrational modes induced by motion along the reaction coordinate, and the elements $B_{k,F}(s)$ in the denominator are the direct coupling between the reaction coordinate (the F th degree of freedom) and the various $F-1$ vibrational modes. We note that in general the matrix $\{B_{k,i}\}$ is skew symmetric,

$$B_{k,i}(s) = -B_{i,k}(s). \quad (2.19)$$

B. Simple examples

It is easy to show that Marcus' result for the collinear A + BC system, Eq. (1.7), is recovered in the limit $F = 2$. In this case the $(F-1) \times (F-1) = 1 \times 1$ matrix $\{B_{k,i}(s)\}$ in the numerator of the last term in the Hamiltonian of Eq. (2.17) is zero by virtue of Eq. (2.19), so that Eq. (2.17) becomes

$$H(p, s, P, Q) = \frac{1}{2} P^2 + \frac{1}{2} \omega(s)^2 Q^2 + V_0(s) + \frac{\frac{1}{2} p_s^2}{[1 + Q B_{1,2}(s)]^2}. \quad (2.20)$$

Furthermore, it is not hard to show that $B_{1,2}(s)$ is $\kappa(s)$, the curvature of the reaction path, so that Eq. (1.7) is obtained. In the general F -dimensional case one can show that the curvature of the reaction path, $\kappa(s)$, is given by

$$\kappa(s) = \left[\sum_{k=1}^{F-1} B_{k,F}(s)^2 \right]^{1/2}, \quad (2.21)$$

so one sees that the curvature is "partitioned" among the different vibrational modes in the general case.

To illustrate the nature of the coupling in the numerator of the last term in the Hamiltonian of Eq. (2.17), consider the three-dimensional case, $F=3$, where the reaction path is the z axis. (Here we denote the three Cartesian coordinates x_1, x_2 , and x_3 as x, y , and z .)

In this case there can be no effect of curvature because the reaction path is straight, but there is still the possibility of coupling because Q_1 and Q_2 can change with s . Q_1 and Q_2 are in general a linear combination of x and y , so that in this case the 3×3 unitary matrix $\{L_{i,k}\}$ has the form

$$L(s) = \begin{pmatrix} \cos \Omega & \sin \Omega & 0 \\ -\sin \Omega & \cos \Omega & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2.22)$$

where $\Omega = \Omega(s)$. It is then easy to show that the coupling matrix $B_{k,i}(s)$ is

$$B(s) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \Omega'(s). \quad (2.23)$$

The Hamiltonian of Eq. (2.17) then takes the form

$$H(p_s, s, P_1, Q_1, P_2, Q_2) = \sum_{k=1}^2 (\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2) + V_0(s) + \frac{1}{2} [p_s + \Omega'(s)(Q_1 P_2 - Q_2 P_1)]^2. \quad (2.24)$$

The term $(Q_1 P_2 - Q_2 P_1)$ may be interpreted as an angular momentum about the z axis, so that the coupling between the normal modes and motion along the reaction coordinate has the form of a Coriolis coupling due to the fact that the normal mode directions wind about the reaction path as the angle $\Omega(s)$ varies with s .

In general, therefore, the coupling elements $\{B_{k,i}\}$ in the numerator of Eq. (2.17) are Coriolis-like interactions, and the elements $\{B_{k,F}\}$ in the denominator of Eq. (2.17) describe the effects of reaction path curvature.

III. VIBRATIONAL ADIABATICITY; EFFECT OF INCLUDING REACTION PATH CURVATURE

For many purposes, e.g., to describe tunneling through the saddle point region of a potential energy surface, it is useful to approximate the motion of the system as one-dimensional motion along the s degree of freedom in an effective one-dimensional potential. The most obvious approximation of this type is to assume that the normal modes perpendicular to the reaction path are adiabatic, and this vibrationally adiabatic model was introduced by Marcus^{9,11} a number of years ago. Here we give a somewhat different treatment of it, showing how the effects of reaction path curvature and part of the effect of nonadiabaticity can be incorporated in a relatively simple manner. To keep the presentation clear, the collinear case ($F=2$) is treated explicitly first, and then generalized to the F -dimensional case.

A. Collinear case, $F=2$

The Hamiltonian for the $F=2$ case is given in terms of the reaction path variables by Eq. (1.7). To introduce the vibrationally adiabatic approximation one first makes a canonical transformation to replace the normal mode coordinate and momentum (Q, P) by the harmonic action-angle variables (n, q) . The F_2 generator¹² for the complete transformation is

$$F_2(s, Q; p'_s, n) = p'_s s + f_2(Q, n; s), \quad (3.1)$$

where the first term is the identity generator for the s degree of freedom, and

$$\begin{aligned} f_2(Q, n; s) &= \int_0^Q dQ' \sqrt{2[(n + \frac{1}{2})\omega(s) - \frac{1}{2}\omega(s)^2 Q'^2]} \\ &= (n + \frac{1}{2}) \sin^{-1} \left[\sqrt{\frac{\omega(s)}{2n+1}} Q \right] \\ &\quad + \frac{Q}{2} \sqrt{2[(n + \frac{1}{2})\omega(s) - \frac{1}{2}\omega(s)^2 Q^2]}. \end{aligned} \quad (3.2)$$

The classical action variable n has $\frac{1}{2}$ added to it for well-known semiclassical reasons, and units are used so that $\hbar = 1$; n is thus the classical counterpart to the vibrational quantum number. The canonical transformation from the old variables (p_s, s, P, Q) to the new variables (p'_s, s', n, q) is specified by the following equations:

$$P = \frac{\partial F_2}{\partial Q} = \sqrt{2[(n + \frac{1}{2})\omega(s) - \frac{1}{2}\omega(s)^2 Q^2]}, \quad (3.3a)$$

$$q = \frac{\partial F_2}{\partial n} = \sin^{-1} \left[\sqrt{\frac{\omega(s)}{2n+1}} Q \right], \quad (3.3b)$$

$$s' = \frac{\partial F_2}{\partial p'_s} = s, \quad (3.3c)$$

$$p_s = \frac{\partial F_2}{\partial s} = p'_s + \frac{\partial f_2(Q, n; s)}{\partial s}. \quad (3.3d)$$

Inverting these relations gives the old variables in terms of the new ones:

$$s = s', \quad (3.4a)$$

$$Q = \sqrt{\frac{2n+1}{\omega(s)}} \sin q, \quad (3.4b)$$

$$P = \sqrt{(2n+1)\omega(s)} \cos q, \quad (3.4c)$$

$$p_s = p'_s + (n + \frac{1}{2}) \frac{\omega'(s)}{\omega(s)} \sin q \cos q, \quad (3.4d)$$

so that the Hamiltonian of Eq. (1.7) is given in terms of the new variables by

$$\begin{aligned} H(p_s, s, n, q) &= \frac{\frac{1}{2}[p'_s + (n + \frac{1}{2})\frac{\omega'(s)}{\omega(s)} \sin q \cos q]^2}{[1 + \sqrt{(2n+1)\kappa(s)^2/\omega(s)} \sin q]^2} \\ &\quad + (n + \frac{1}{2})\omega(s) + V_0(s), \end{aligned} \quad (3.5)$$

where the prime has been dropped from p'_s and s' .

Equation (3.5) is still dynamically exact, and the idea of the vibrationally adiabatic approximation is to assume that the "quantum number" n is conserved, i.e., a constant of the motion. This will be a good approximation if the Q motion is fast compared to the s motion, i.e., this is a kind of Born-Oppenheimer approximation with the Q degree of freedom playing the role of the electrons. The effective potential for the s degree of freedom is obtained within this approximation by averaging the classical Hamiltonian, Eq. (3.5), over the angle variable q . This corresponds to a time average over the fast motion, and it has recently been used¹³ to derive classical pseudopotentials for electronic degrees of freedom. By averaging the Hamiltonian over q , one obtains a Hamiltonian which is independent of q and for which n is thus a constant of the motion.

The vibrationally adiabatic Hamiltonian for the s motion is thus given by

$$H_n(p_s, s) \equiv (2\pi)^{-1} \int_0^{2\pi} dq H(p_s, s, n, q). \quad (3.6)$$

The integrals are elementary, and one obtains

$$\begin{aligned} H_n(p_s, s) &= \frac{1}{2} p_s^2 [1 - \lambda(s)]^{3/2} \\ &\quad + \frac{(n + \frac{1}{2})^2 \omega'(s)^2}{2\omega(s)^2} f(\lambda) + (n + \frac{1}{2})\omega(s) + V_0(s), \end{aligned} \quad (3.7)$$

where

$$\lambda = \frac{(2n+1)\kappa(s)^2}{\omega(s)}, \quad (3.8a)$$

$$f(\lambda) = \left(\frac{\lambda}{2} - 3 + \frac{3-2\lambda}{\sqrt{1-\lambda}} \right) / \lambda^2. \quad (3.8b)$$

For small λ , i.e., small curvature, $f(\lambda) \rightarrow \frac{1}{8}$. Equation (3.7) gives the effective one-dimensional Hamiltonian for the most rigorous version of the vibrationally adiabatic approximation. The effective potential "seen" by the s degree of freedom is

$$V_{\text{eff}}(s) = V_0(s) + (n + \frac{1}{2})\omega(s) + \frac{(n + \frac{1}{2})^2 \omega'(s)^2}{2\omega(s)^2} f(\lambda), \quad (3.9)$$

of which the respective terms are identified as the actual potential along the reaction path, the adiabatic vibrational energy of the transverse oscillator, and the diagonal part of the nonadiabatic coupling. In most cases the nonadiabatic correction to the adiabatic potential is assumed to be small and thus discarded, giving

$$V_{\text{eff}}(s) = V_0(s) + (n + \frac{1}{2})\omega(s). \quad (3.9')$$

The curvature is also seen to affect the kinetic energy term in the Hamiltonian of Eq. (3.7) via the multiplicative factor

$$[1 - \lambda(s)]^{-3/2} > 1. \quad (3.10)$$

This may be thought of as lowering the effective mass for the s motion, so that it *increases the probability of tunneling* through the barrier. Specifically, the tunneling probability is given semiclassically (i.e., within the WKB approximation) by

$$P(E) = e^{-2\theta(E)}, \quad (3.11a)$$

where $\theta(E)$ is the imaginary action integral through the barrier:

$$\theta(E) = \int ds \operatorname{Im} p_s(s, E); \quad (3.11b)$$

$p_s(s, E)$ is determined by energy conservation,

$$H_n(p_s, s) = E,$$

yielding

$$\operatorname{Im} p_s(s, E) = [1 - \lambda(s)]^{3/4} \sqrt{2[V_{\text{eff}}(s) - E]}. \quad (3.11c)$$

Setting $\lambda(s) = 0$ in Eq. (3.11c) is the vibrationally adiabatic zero curvature approximation (VAZC), and one sees that $\lambda(s) > 0$ reduces the value of $\theta(E)$ and thus increases the tunneling probability.

Truhlar and Kuppermann¹⁴ carried out a fairly extensive test of the vibrationally adiabatic zero curvature

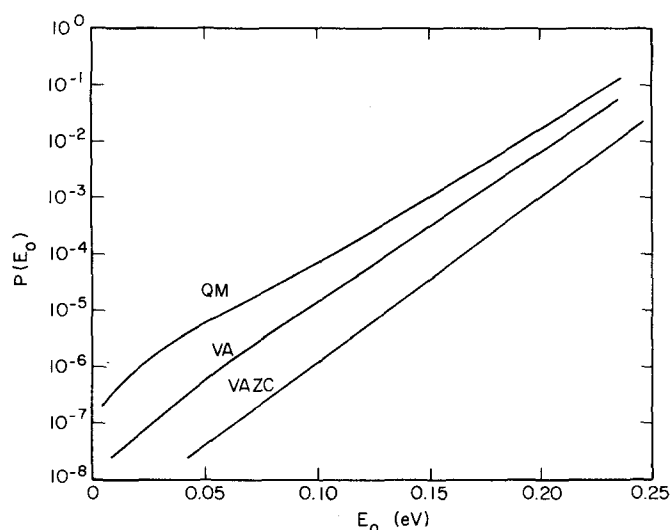


FIG. 1. Reaction probability for the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction as a function of initial translational energy. QM and VAZC are the correct quantum mechanical and vibrationally adiabatic zero curvature results of Ref. 14, and VA are the present results computed from Eq. (3.11).

(VAZC) approximation with regard to the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction and found it to be quite poor, giving reaction probabilities 1–2 orders of magnitude too small in the tunneling region. This is perhaps not too surprising since the transverse vibrational motion is actually not a great deal faster than motion along the reaction coordinate. It is nevertheless amusing to note that the vibrationally adiabatic (VA) model works considerably better for this example if the “zero curvature” part of the approximation is not made.

Figure 1 shows the exact quantum mechanical (QM) and vibrationally adiabatic zero curvature (VAZC) results obtained by Truhlar and Kuppermann,¹⁴ compared to the vibrationally adiabatic (VA) results obtained from the same potential energy surface if the zero curvature approximation is not made. [These latter results were obtained from Eqs. (3.9') and (3.11) with $n=0$. To check the reliability of the semiclassical approximation, calculations were also carried out this way but with $\lambda(s)=0$, and the VAZC results of Ref. 14 were reproduced to within 20%.] One sees that lifting the zero curvature part of the VAZC approximation goes more than half-way (in a logarithmic sense) to correcting the deficiencies of this model.

B. General case, $F > 2$

The approach of Sec. IIIA can also be applied to the Hamiltonian of Eq. (2.17) for the general F -dimensional case. To simplify matters, the diagonal parts of the nonadiabatic corrections will be omitted since they are usually ignored in applications. It is then easy to show that one obtains the following effective one-dimensional Hamiltonian for motion along the reaction coordinate,

$$H_n(p_s, s) = \frac{1}{2} p_s^2 A(s) + V_0(s) + \sum_{k=1}^{F-1} \frac{1}{2} \omega_k(s) (n_k + \frac{1}{2}), \quad (3.12)$$

where $\mathbf{n} \equiv \{n_k\}$, $k=1, \dots, F-1$ are the adiabatic vibra-

tional quantum numbers, and the correction factor $A(s)$ which multiplies the kinetic energy is

$$A(s) = \left\langle \left[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s) \right]^{-2} \right\rangle \\ = (2\pi)^{-(F-1)} \int_0^{2\pi} dq_1 \cdots \int_0^{2\pi} dq_{F-1} \left[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s) \right]^{-2}, \quad (3.13a)$$

where

$$Q_k = \left[\frac{(2n_k + 1)}{\omega_k(s)} \right]^{1/2} \sin q_k. \quad (3.13b)$$

It has not been possible to find a closed-form expression for $A(s)$, but a convergent series representation is

$$A(s) = \sum_{l_1=0}^{\infty} \cdots \sum_{l_{F-1}=0}^{\infty} \frac{(2l_1 + \cdots + 2l_{F-1} + 1)!}{(l_1! l_2! \cdots l_{F-1}!)^2} \\ \times \left\{ \prod_{k=1}^{F-1} \left[\frac{(2n_k + 1) B_{k,F}(s)^2}{4\omega_k(s)} \right]^{l_k} \right\}. \quad (3.13c)$$

IV. REACTION PATH HAMILTONIAN FOR POLYATOMIC SYSTEMS IN THREE DIMENSIONS

The reaction path Hamiltonian given by Eq. (2.17) of Sec. II is suggestive but not directly useable since it takes no account of the rotational symmetry of an N -atom system in 3d space and the resulting conservation of total angular momentum. The purpose of this section is to do this, i.e., to derive the reaction path Hamiltonian for an N -atom system in 3d space with a given non-zero value of the total angular momentum. As before, it is assumed that one knows all the quantities which would result from a quantum chemistry calculation of the reaction path: the nuclear coordinates of the reaction path, the potential energy along it, and the eigenvalues (i.e., frequencies) and eigenvectors that result from diagonalizing the projected force constant matrix.

To accomplish this we revert to the classic treatment of the general rotating-vibrating molecule given by Wilson, Decius, and Cross.¹⁵ The difference here is that the reaction coordinate is a special coordinate to be treated differently from the remaining normal coordinates. Unlike the latter, which have small changes, the reaction coordinate must be considered in a parallel fashion to the rotational coordinates (i.e., Euler angles) which can take on large values. A related problem has been treated by the theoretical vibration-rotation spectroscopists: typically one of the internal coordinates undergoes large amplitude motions and can therefore not be accurately described by the standard vibration-rotation theory.¹⁵ Simple examples are the bending coordinate in HCN, or the out of plane bending angle of CH_2 in excited states of HCHO. For such problems Hougen, Bunker, and Johns¹⁶ (HBJ) have derived a Hamiltonian which treats this bending coordinate apart from all the other internal coordinates. By considering this special coordinate to be the reaction coordinate, it is possible to borrow much of their analysis to achieve our present goal. The presentation below thus omits some of the details that are identical to that of HBJ, and to simplify matters we have also used mass-weighted Cartesian

coordinates and notation that coincides as closely as possible with that of Sec. II. Regarding notation, both three-dimensional and four-dimensional vectors and matrices appear below, and we switch between vector notation and component notation to use whichever seems to be clearest in the particular situation.

A. Derivation for the general case of a nonlinear reaction path

$\{\mathbf{X}_i\}$ and $\{\mathbf{x}_i\}$, $i=1, \dots, N$, are the mass-weighted Cartesian coordinate vectors of the N atoms in a space-fixed axis $OXYZ$ and molecule-fixed axis $0xyz$, respectively (i.e., if $\{\mathbf{R}_i\}$ and $\{\mathbf{r}_i\}$ are the actual Cartesian coordinates in these coordinate systems, then $\mathbf{X}_i = \sqrt{m_i} \mathbf{R}_i$ and $\mathbf{x}_i = \sqrt{m_i} \mathbf{r}_i$, where $\{m_i\}$ are the atomic masses). The Cartesian coordinates in these two different axis systems are related by

$$\mathbf{X}_i = \sqrt{m_i} \mathbf{R}_{c.m.} + \mathbf{S}^{-1}(\chi, \theta, \phi) \cdot \mathbf{x}_i, \quad (4.1)$$

where $\mathbf{R}_{c.m.}$ is the coordinate of the center of mass and is the origin of both coordinate systems, and $\mathbf{S}^{-1}(\chi, \theta, \phi)$ is the matrix of direction cosines relating the molecule-fixed axes to the space-fixed axes through the Euler angles χ , θ , and ϕ . It is convenient to express the coordinates in the molecule-fixed system as

$$\mathbf{x}_i = \mathbf{a}_i(s) + \xi_i, \quad (4.2)$$

where $\{\mathbf{a}_i(s)\}$ are the mass-weighted coordinates of the reaction path, which depend parametrically on the reaction coordinate s (the arc length along the reaction path), and where $\{\xi_i\}$ are the mass-weighted displacements away from the reaction path.

With Eq. (4.2) substituted into Eq. (4.1), there are $3N$ variables on the LHS, $\{\mathbf{X}_i\}$, and $(3N+7)$ variables on the RHS, $\mathbf{R}_{c.m.}$, χ , θ , ϕ , $\{\xi_i\}$, and s . Therefore seven relations must be specified between the $(3N+7)$ variables on the RHS to remove this inconsistency. One is at liberty to choose the relations in the computationally most convenient way, and these appear to be

$$\sum_{i=1}^N \sqrt{m_i} \xi_i = 0, \quad (4.3a)$$

$$\sum_{i=1}^N \mathbf{a}_i(s) \times \xi_i = 0, \quad (4.3b)$$

$$\sum_{i=1}^N \mathbf{a}'_i(s) \cdot \xi_i = 0. \quad (4.3c)$$

Relation (4.3a) is a center of mass condition; relation (4.3b) is commonly called the Eckart condition and assures that infinitesimal displacements do not contribute to the angular momentum. Since $\{\mathbf{a}'_i(s)\} \equiv \{v_i(s)\}$ is the $3N$ -dimensional unit vector v_i , which points along the reaction path, Relation (4.3c) states that the displacements $\{\xi_i\}$ are orthogonal to the reaction path. The relations (4.1)–(4.3) insure that a set of $\{\mathbf{X}_i\}$ will correspond uniquely to a set of $\mathbf{R}_{c.m.}$, χ , ϕ , θ , $\{\xi_i\}$, s , and *vice versa*.

In HBJ the reference positions $\{\mathbf{a}_i(s)\}$ are chosen such that

$$\sum_{i=1}^N \mathbf{a}_i(s) \times \mathbf{a}'_i(s) = 0, \quad (4.4)$$

and we show that this relation is automatically satisfied when s is the reaction coordinate. Since $\{\mathbf{a}'_i(s)\}$ is the $3N$ -dimensional unit vector which points along the reaction path, Eq. (1.2) implies that

$$\mathbf{a}'_i(s) = -c \frac{\partial V}{\partial \mathbf{x}_i} \bigg|_{\mathbf{x}=\mathbf{a}}, \quad (4.5)$$

where c is a constant. But the potential energy V is a function only of internuclear distances $x_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j|$, so that

$$\mathbf{a}'_i(s) = -c \sum_{j=1}^N \frac{a_i - a_j}{|\mathbf{a}_i - \mathbf{a}_j|} \frac{\partial V}{\partial x_{ij}} \bigg|_{\mathbf{x}=\mathbf{a}}. \quad (4.6)$$

It is then easy to see that Eq. (4.4) follows.

Normal coordinates $\{Q_k\}$ can be defined, for any fixed value of s , by diagonalizing the projected force constant matrix of Eq. (1.5). If $\{L_{i\gamma,k}(s)\} \equiv \{L_{i\gamma,k}(s)\}$, $\gamma = x, y, z$, $k = 1, \dots, 3N-7$, are the eigenvectors with the nonzero eigenvalues $\{\omega_k(s)^2\}$, then for a fixed value of s the $(3N-7)$ normal mode vibrational coordinates are defined in terms of the Cartesian displacements $\{\xi_i\}$ by

$$Q_k = \sum_{i,\gamma} \xi_{i\gamma} L_{i\gamma,k} = \sum_{i=1}^N \xi_i \cdot \mathbf{L}_{i,k}, \quad (4.7)$$

for $k = 1, \dots, 3N-7$. The coordinates for the seven "normal modes" which correspond to infinitesimal rotations, translations, and motion along the reaction coordinate are given by¹⁵

$$\mathbf{R} \equiv (Q_{3N-6}, Q_{3N-5}, Q_{3N-4}) = \mathbf{I}_0^{-1/2} \cdot \sum_{i=1}^N \mathbf{a}_i \times \xi_i, \quad (4.8a)$$

where the inertia tensor $\mathbf{I}_0(s)$ is defined below [Eq. (4.17b)];

$$\mathbf{T} \equiv (Q_{3N-3}, Q_{3N-2}, Q_{3N-1}) = \sum_{i=1}^N \sqrt{\frac{m_i}{M}} \xi_i, \quad (4.8b)$$

where

$$M = \sum_{i=1}^N m_i;$$

and

$$s \equiv Q_{3N} = \sum_{i=1}^N \mathbf{a}'_i(s) \cdot \xi_i. \quad (4.8c)$$

Because \mathbf{T} , \mathbf{R} , and s are associated with zero frequencies, their equations of motion for infinitesimal displacements have constants as solutions, so it is appropriate to set

$$\mathbf{T} = \mathbf{R} = 0, \quad s = 0. \quad (4.9)$$

In this way the relations in Eq. (4.3) are seen to be reasonable constraint equations.

Equations (4.8) are also equivalent to stating that the eigenvectors corresponding to infinitesimal rotations, translations, and motion along the reaction coordinate are given, respectively, by

$$L_{i\gamma,k}(s) = \sum_{\alpha,\beta} (\mathbf{I}_0(s)^{-1/2})_{\alpha\beta} a_{i\alpha}(s) a_{i\beta}(s), \quad (4.10a)$$

for $k=3N-6$, $3N-5$, $3N-4$, which correspond, respectively, to $\lambda=x, y, z$ ($\epsilon_{\alpha\beta\gamma}$ is the usual totally asymmetric Cartesian tensor);

$$L_{i\gamma,k}(s) = \sqrt{\frac{m_i}{M}} \delta_{\gamma,\lambda} \quad (4.10b)$$

for $k=3N-3$, $3N-2$, $3N-1$, which correspond, respectively, to $\lambda=x, y, z$; and

$$L_{i\gamma,3N}(s) = a'_{i\gamma}(s) \quad (4.10c)$$

It is then easy to show that the matrix elements of the projector in Eq. (1.5b) are given explicitly by

$$P_{i\gamma,i'\gamma'}(s) = a'_{i\gamma}(s)a'_{i'\gamma'}(s) + \frac{\sqrt{m_i m_{i'}}}{M} \delta_{\gamma,\gamma'} + \sum_{\alpha\beta} \epsilon_{\alpha\beta\gamma} a_{i\alpha}(s) \times (\mathbf{I}_0(s)^{-1})_{\alpha,\alpha'} \epsilon_{\alpha'\beta\gamma'} a_{i'\beta'}(s) \quad (4.11)$$

The orthogonality relations for the vibrational eigenvectors $\{L_{i\gamma,k}(s)\}$, $k=1, \dots, 3N-7$ may then be written concisely as

$$\sum_{i=1}^N \mathbf{L}_{i,k}(s) \cdot \mathbf{L}_{i,l}(s) = \delta_{k,l} \quad (4.12a)$$

$$\sum_{i=1}^N \sqrt{m_i} \mathbf{L}_{i,k}(s) = 0 \quad (4.12b)$$

$$\sum_{i=1}^N \mathbf{a}_i(s) \times \mathbf{L}_{i,k}(s) = 0 \quad (4.12c)$$

$$\sum_{i=1}^N \mathbf{a}'_i(s) \cdot \mathbf{L}_{i,k}(s) = 0 \quad (4.12d)$$

for $k, l=1, \dots, 3N-7$, and

$$\sum_{k=1}^{3N-7} L_{i\gamma,k}(s) L_{i'\gamma',k}(s) = \delta_{i,i'} \delta_{\gamma,\gamma'} - P_{i\gamma,i'\gamma'}(s) \quad (4.12e)$$

Furthermore, these orthogonality relations can be used with Eq. (4.9) to invert Eqs. (4.7) and express the Cartesian coordinates explicitly in terms of the reaction path coordinates:

$$\mathbf{x}_i = \mathbf{a}_i(s) + \sum_{k=1}^{3N-7} \mathbf{L}_{i,k}(s) Q_k \quad (4.13)$$

which is analogous to Eq. (2.4) of Sec. II A.

The theory has now reached the stage where it is identical in fashion to that of Moule and Ramachandra Rao,¹⁷ who introduced the more systematic notation into the work of HBJ,¹⁶ and we can derive the expression for the kinetic energy in terms of the canonical variables by following the procedure in Secs. 2-4 of Chap. 11 of Ref. 15 almost identically. The result one obtains for the kinetic energy T is

$$T = \sum_{k=1}^{3N-7} \frac{1}{2} P_k^2 + T_s \quad (4.14a)$$

with

$$T_s = \frac{1}{2} (\Pi - \pi) \cdot (\mathbf{I}_0 + \mathbf{b})^{-1} \cdot \mathbf{I}_0 \cdot (\mathbf{I}_0 + \mathbf{b})^{-1} \cdot (\Pi - \pi) \quad (4.14b)$$

where Π and π are four-dimensional vectors, and \mathbf{I}_0 and \mathbf{b} four-dimensional symmetric matrices, of which the first three elements are Cartesian components related to rotation in 3d space and the fourth a scalar component related to the reaction coordinate. These quantities are defined explicitly by Eqs. (4.15)–(4.18):

$$\Pi = (\mathbf{J}, p_s) = (J_x, J_y, J_z, p_s) \quad (4.15)$$

where \mathbf{J} is the total angular momentum vector of the N -atom system and p_s the momentum conjugate to the reaction coordinate s ;

$$\pi = (\pi, \pi_s) = \sum_{k=1}^{3N-7} Q_k P_k \mathbf{B}_{k,l}(s) \quad (4.16a)$$

with

$$\mathbf{B}_{k,l}(s) = (\mathbf{B}_{k,l}(s), B_{k,l}^s(s)) \quad (4.16b)$$

where

$$\mathbf{B}_{k,l}(s) = \sum_{i=1}^N \mathbf{L}_{i,k}(s) \times \mathbf{L}_{i,l}(s) \quad (4.16c)$$

$$B_{k,l}^s(s) = \sum_{i=1}^N \mathbf{L}'_{i,k}(s) \cdot \mathbf{L}_{i,l}(s) \quad (4.16d)$$

$$\mathbf{I}_0(s) = \begin{pmatrix} \mathbf{I}_0(s) & 0 \\ 0 & 1 \end{pmatrix} \quad (4.17a)$$

where $\mathbf{I}_0(s)$ is the inertia tensor on the reaction path,

$$\mathbf{I}_0(s) = \sum_{i=1}^N [1 \mathbf{a}_i(s) \cdot \mathbf{a}_i(s) - \cdot \mathbf{a}_i(s) \mathbf{a}_i(s) \cdot] \quad (4.17b)$$

$$\mathbf{b} = \begin{pmatrix} \mathbf{b} & \mathbf{b}_s \\ \mathbf{b}_s & b_{ss} \end{pmatrix} = \sum_{k=1}^{3N-7} Q_k \mathbf{b}_k \quad (4.18a)$$

with

$$\mathbf{b}_k = \begin{pmatrix} \mathbf{b}_k & \mathbf{b}_k^s \\ \mathbf{b}_k^s & b_{ks} \end{pmatrix} \quad (4.18b)$$

where

$$\mathbf{b}_k(s) = \sum_{i=1}^N [1 \mathbf{L}_{i,k}(s) \cdot \mathbf{a}_i(s) - \cdot \mathbf{L}_{i,k}(s) \mathbf{a}_i(s) \cdot] \quad (4.18c)$$

$$\mathbf{b}_k^s(s) = \sum_{i=1}^N \mathbf{L}_{i,k}(s) \times \mathbf{L}_{i,3N}(s) = \mathbf{B}_{k,3N}(s) \quad (4.18d)$$

$$b_{ks}^s(s) = \sum_{i=1}^N \mathbf{L}'_{i,k}(s) \cdot \mathbf{L}_{i,3N}(s) = B_{k,3N}^s(s) \quad (4.18e)$$

By differentiating Eq. (4.12c) with respect to s , one can show that \mathbf{b}_k^s of Eq. (4.18d) is also given by

$$\mathbf{b}_k^s(s) = \sum_{i=1}^N \mathbf{a}_i(s) \times \mathbf{L}'_{i,k}(s) \quad (4.18f)$$

Equation (4.14b) for T_s can be made more explicit by partitioning the 4×4 matrices and vectors into 3×3 and 1×1 components. This is reasonably straightforward, and one obtains the following result:

$$T_s = \frac{1}{2} (\mathbf{J} - \pi) \cdot \mathbf{I}'^{-1} \cdot (\mathbf{J} - \pi) + \frac{1}{2} (1 + \mathbf{b}_s \cdot \mathbf{I}'^{-1} \cdot \mathbf{b}_s) \phi_s^2 - \mathbf{b}_s \cdot \mathbf{I}'^{-1} \cdot (\mathbf{J} - \pi) \phi_s \quad (4.19a)$$

where

$$\mathbf{I}' = (\mathbf{I}_0 + \mathbf{b}) \cdot \mathbf{I}_0^{-1} \cdot (\mathbf{I}_0 + \mathbf{b}) \quad (4.19b)$$

$$\phi_s = \frac{p_s - \pi_s - \mathbf{b}_s \cdot (\mathbf{I}_0 + \mathbf{b})^{-1} \cdot (\mathbf{J} - \pi)}{1 + b_{ss} - \mathbf{b}_s \cdot (\mathbf{I}_0 + \mathbf{b})^{-1} \cdot \mathbf{b}_s} \quad (4.19c)$$

with \mathbf{I}_0 , \mathbf{b} , \mathbf{b}_s , b_{ss} , π , and π_s given by Eqs. (4.16)–(4.18).

To complete the specification of the classical Hamilto-

nian for an arbitrary value of the total angular momentum, one must express the three components of \mathbf{J} in terms of the canonical variables for rotation. These are most conveniently taken¹⁸ to be the action-angle variables (J, q_J) , (M, q_M) , and (K, q_K) , where J is the magnitude of \mathbf{J} , M is its projection onto the space-fixed Z axis, and K its projection onto the body-fixed z axis; q_J , q_M , and q_K are their conjugate angle variables. J and M are conserved quantities, so the Hamiltonian is not a function of q_J and q_M , and because of the isotropy of space, the Hamiltonian is also independent of M . The Hamiltonian does, however, depend on q_K , so that K is not conserved. For a given value of J , therefore, the Hamiltonian is a function of $3N - 5$ pairs of canonically conjugate variables: (s, p_s) , (Q_k, P_k) , $k = 1, \dots, 3N - 7$, and (K, q_K) . The three Cartesian components and \mathbf{J} are given in terms of K and q_K by¹⁹

$$J_x = \sqrt{J^2 - K^2} \cos q_K, \quad (4.20a)$$

$$J_y = \sqrt{J^2 - K^2} \sin q_K, \quad (4.20b)$$

$$J_z = K.$$

Taking into account the harmonic approximation to the potential energy about the reaction path, the final complete expression for the Hamiltonian in reaction path variables for total angular momentum J is

$$H_J(p_s, s, \{P_k, Q_k\}, K, q_K) = \sum_{k=1}^{3N-7} \left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right) + V_0(s) + T_s, \quad (4.21)$$

where T_s is given by Eq. (4.19).

We now consider several aspects of this result.

B. Simplified approximate expressions

Since the 3d vector $\pi = (\pi_x, \pi_y, \pi_z)$ of Eq. (4.16a) enters Eq. (4.19) as $(\mathbf{J} - \pi)$, where \mathbf{J} is the total angular momentum vector, it is often referred to as the "vibrational angular momentum."¹⁵ It is also often neglected, which we now do to obtain a simplified Hamiltonian.

If one first neglects all the terms in T_s which involve the vibrational coordinates $\{Q_k\}$, i.e., sets \mathbf{b} , \mathbf{b}_s , b_{ss} , and π_s also to zero, then Eq. (4.19) becomes

$$T_s = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_0(s)^{-1} \cdot \mathbf{J} + \frac{1}{2} p_s^2, \quad (4.22)$$

the two terms of which are recognized as the energy of a rigid asymmetric rotor with geometry $\{\mathbf{a}_i(s)\}$ and the kinetic energy for motion along the reaction coordinate, respectively. This is the usual model of separable rotation and internal motion.

Still neglecting π , a simple but more accurate approximation to T_s in Eq. (4.19) can be obtained for the case $\mathbf{J} = 0$ by retaining π_s and the \mathbf{b} dependence through quadratic terms:

$$T_s \approx \frac{\frac{1}{2}(p_s - \pi_s)^2(1 + \mathbf{b}_s \cdot \mathbf{I}_0^{-1} \cdot \mathbf{b}_s)}{(1 + b_{ss} - \mathbf{b}_s \cdot \mathbf{I}_0 \cdot \mathbf{b}_s)^2}. \quad (4.23a)$$

By using Eqs. (4.18f) and (4.10a), the following useful expression for the quadratic term can be obtained:

$$\mathbf{b}_s \cdot \mathbf{I}_0^{-1} \cdot \mathbf{b}_s = \sum_{k'=3N-6}^{3N-4} \left[\sum_{k=1}^{3N-7} Q_k B_{k,k'}(s) \right]^2. \quad (4.23b)$$

If this quadratic term is also neglected, then one obtains

$$T_s \approx \frac{\frac{1}{2}(p_s - \pi_s)^2}{(1 + b_{ss})^2}, \quad (4.23c)$$

and by making the following identifications with the notation of Sec. II,

$$3N - 6 \rightarrow F,$$

$$B_{k,i}^s(s) \leftrightarrow B_{k,i}(s),$$

$$b_k^{ss}(s) \leftrightarrow B_{k,F}(s),$$

one sees that the Hamiltonian obtained by using approximation (4.23c) in Eq. (4.21) is identical to that of the "generic Cartesian" system, Eq. (2.17), of Sec. II. All of the results and discussion of Sec. II thus apply to real molecular systems for the case of zero total angular momentum and within the approximation of Eq. (4.23c).

One can obtain more accurate approximate expressions for the rotating case, $\mathbf{J} \neq 0$, by expanding the various terms in Eq. (4.19) in powers of π , π_s , \mathbf{b} , \mathbf{b}_s , and b_{ss} . Since the π 's are quadratic in the vibrational variables, and the b 's linear, a consistent approximation would be to retain all terms that are linear in the π 's and linear or quadratic in the b 's.

C. Modifications for linear reaction paths (e.g., $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$)

The above expressions are not valid if the reaction path gives a linear geometry for the molecule, because one row and column of \mathbf{I}_0 will be zero and its inverse thus nonexistent. Watson²⁰ showed how to extend the ordinary vibration-rotation theory to linear molecules, but there has been no extension of this theory to cover the case when the large amplitude motion is associated with changes in linear geometry. The special considerations arise from the fact that

$$(\mathbf{a}_i)_r \equiv a_{ir} = a_{iz} \delta_{r,z}, \quad (4.24)$$

if the z axis is the linear molecule's axis. In this case the Eckart conditions (4.3b) become only two conditions,

$$\sum_{i=1}^N a_{iz} \xi_{ix} = \sum_{i=1}^N a_{iz} \xi_{iy} = 0. \quad (4.25)$$

The orientation of the x and y axes about the z axis is not specified, and thus only two Euler angles can be determined, the third being assigned an arbitrary value. There will thus be $3N - 6$ vibrational coordinates Q_k in this case.

The implications of Eq. (4.21) are that

$$\mathbf{I}_0(s) = \mathbf{I}_0(s)(1 - \hat{z}\hat{z}), \quad (4.26a)$$

where

$$\mathbf{I}_0(s) = \sum_{i=1}^N a_{iz}(s)^2, \quad (4.26b)$$

and furthermore that

$$\mathbf{b}_k(s) = (1 - \hat{z}\hat{z}) \sum_{i=1}^N a_{iz}(s) L_{iz,k}(s), \quad (4.27a)$$

$$b_k^{s,z}(s) = 0, \quad (4.27b)$$

$$b_k^{s,x}(s) = \sum_{i=1}^N L_{iy,k}(s) L_{iz,3N}(s), \quad (4.27c)$$

$$b_k^{s,y}(s) = -\sum_{i=1}^N L_{ix,k}(s) L_{iz,3N}(s), \quad (4.27d)$$

$$b_k^{s,z}(s) = \sum_{i=1}^N L'_{iz,k}(s) L_{iz,3N}(s). \quad (4.27e)$$

The projector $P_{i\gamma,i'\gamma'}$ of Eq. (4.11) becomes in this case

$$P_{i\gamma,i'\gamma'}(s) = \frac{\sqrt{m_i m_{i'}}}{M} \delta_{\gamma,\gamma'} + a'_{iz}(s) a'_{i'z}(s) \delta_{\gamma,z} \delta_{\gamma',z} \\ + \frac{a_{iz}(s) a_{i'z}(s)}{I_0(s)} (\delta_{\gamma,\gamma'} - \delta_{\gamma,z} \delta_{\gamma',z}), \quad (4.28)$$

and the orthogonality relations of Eq. (4.12) become

$$\sum_{i=1}^N a_{iz}(s) L_{ix,k}(s) = \sum_{i=1}^N a_{iz}(s) L_{iy,k}(s) = 0, \quad (4.29a)$$

$$\sum_{i=1}^N a'_{iz}(s) L_{ix,k}(s) = 0 \quad (4.29b)$$

for $k=1, \dots, 3N-6$, and

$$\sum_{k=1}^{3N-6} L_{i\gamma,k}(s) L_{i'\gamma',k}(s) = \delta_{i,i'} \delta_{\gamma,\gamma'} - P_{i\gamma,i'\gamma'}. \quad (4.29c)$$

Using the above relations and proceeding in a manner directly analogous to that in Sec. IV A, one obtains the following expression for the kinetic energy in terms of the canonical variables:

$$T = \sum_{k=1}^{3N-6} \frac{1}{2} P_k^2 + T_s, \quad (4.30)$$

where T_s is given still by Eq. (4.14b) except that here Π and π , and \mathbf{I}_0 and \mathbf{b} , are the three-dimensional vectors and matrices, respectively, in the indices (x, y, s) as defined above. As in Sec. IV A, this expression for T_s can be put in the form given by Eq. (4.19), where now \mathbf{J} , π , $\mathbf{I}_0(s)$, etc., are 2×2 matrices and vectors in the indices (x, y) . Since \mathbf{I}_0 and \mathbf{b} are both scalar quantities times the 2×2 unit matrix, Eq. (4.19) will have a considerably simpler structure in the linear case. Approximations essentially identical to those in Sec. IV B can also be developed for the linear case.

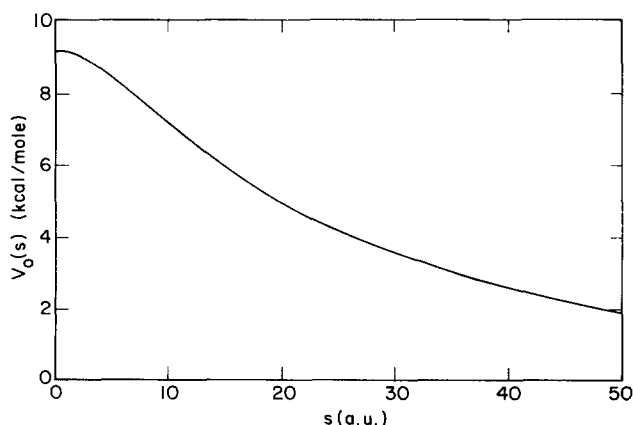


FIG. 2. The potential energy along the reaction path of the Porter-Karplus potential surface for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$, as a function of the mass-weighted reaction coordinate.

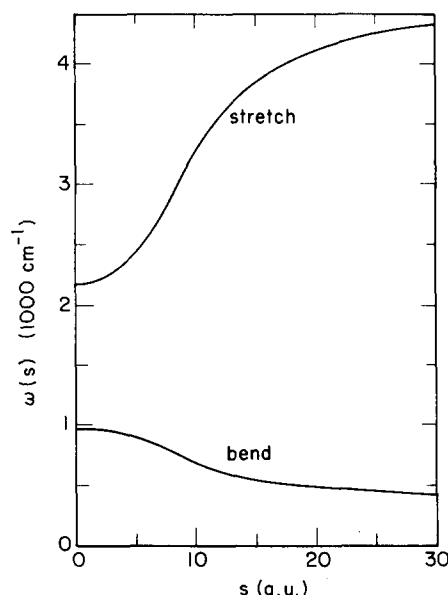


FIG. 3. The bending and stretch frequencies for vibrations orthogonal to the reaction path of the Porter-Karplus potential surface, as a function of the mass-weighted reaction coordinate.

D. Vibrationally adiabatic approximation for tunneling in $3d \text{ H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$

To test some aspects of the $3d$ reaction path Hamiltonian we have computed reaction probabilities in the tunneling region for the $3d \text{ H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction within the vibrationally adiabatic approximation. This is the $3d$ version of the calculation described in Sec. III, and for simplicity only the $J=0$ case has been treated.

We thus first carried out the reaction path calculation for the $\text{H} + \text{H}_2$ system using the Porter-Karplus²¹ potential energy surface. Figures 2 and 3 show the potential $V_0(s)$ along the reaction path and the "symmetric" stretch and bending frequencies, respectively, which result from diagonalizing the projected force constant matrix. (The symmetric stretch mode is only symmetric at the saddle point, $s=0$.) The coupling elements $B_{k,i}(s)$ were also computed. If $k=1$ denotes the stretch mode, $k=2$ and 3 the x and y bending modes (which are degenerate), respectively, and $k=4$ and 5 the x and y rotational modes, respectively, then for this linear reaction path with $N=3$ the only nonzero coupling elements are $B_{1,3N}(s)$ and $B_{2,4}(s) = B_{3,5}(s)$, and these are shown in Fig. 4.

Because $B_{k,3N}(s) \neq 0$ for only the one mode $k=1$, within the simplest approximation to the term T_s in the Hamiltonian, Eq. (4.23c), the vibrationally adiabatic Hamiltonian for the present $3d$ case is the same as that for the collinear case of Sec. III with

$$\kappa(s) \equiv B_{1,3N}(s), \quad (4.31a)$$

and with the effective potential modified to include the bending modes,

$$V_{\text{eff}}(s) = V_0(s) + (n_1 + \frac{1}{2})\omega_1(s) + (n_2 + n_3 + 1)\omega_2(s). \quad (4.31b)$$

With these modifications, Eq. (3.11) can then be used to compute the tunneling probability.

Figure 5 shows the semiclassical tunneling probability given by Eqs. (3.11) and (4.31), for $n_1 = n_2 = n_3 = 0$, compared to the correct quantum mechanical results of Schatz and Kuppermann.^{2a} The result of making the zero curvature approximation, i.e., setting $B_{1,3N}(s) \equiv 0$, is also shown to emphasize that including reaction path curvature makes a significant improvement to the vibrationally adiabatic approximation. The comparisons seen in Fig. 5 are quite similar to those in Fig. 1 for the collinear case, except that the vibrationally adiabatic approximation seems to work better in 3d than in 1d.

To assess the effect of rotation-vibration coupling, the more accurate approximation to T_s given by Eq. (4.23a) was also considered within the vibrationally adiabatic approximation. Using Eq. (4.23b), the vibrationally adiabatic approximation to Eq. (4.23a)—suitably modified for the current linear case—is thus

$$T_s \approx \frac{1}{2} \dot{p}_s^2 A(s), \quad (4.32)$$

where

$$A(s) = (2\pi)^{-3} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 \int_0^{2\pi} dq_3 [1 + B_{2,4}(s)^2 (Q_2^2 + Q_3^2)] \times [1 + Q_1 B_{1,3N}(s) - B_{2,4}(s)^2 (Q_2^2 + Q_3^2)]^{-2}, \quad (4.33a)$$

with

$$Q_k = \sqrt{\frac{2n_k + 1}{\omega_k(s)}} \sin q_k. \quad (4.33b)$$

Equation (3.11c) of Sec. III then reads

$$\text{Imp}_s(s, E) = \sqrt{2[V_{\text{eff}}(s) - E]/A(s)}. \quad (4.34)$$

If $B_{2,4}(s) \rightarrow 0$, it is clear that Eqs. (4.32)–(4.34) revert to the collinearlike formulas.

As seen in Fig. 4, however, for the present example

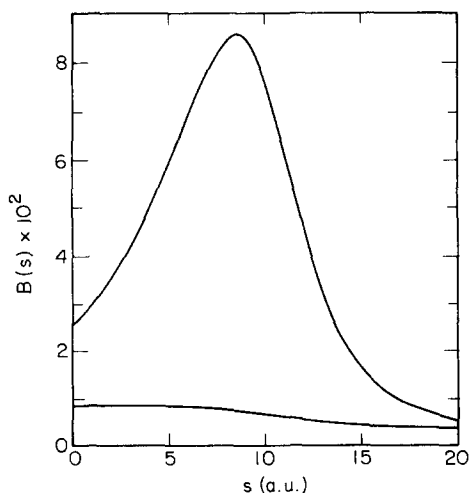


FIG. 4. Coupling elements $B_{k,1}(s)$ for the Porter-Karplus $\text{H} + \text{H}_2$ potential surface, as a function of the mass-weighted reaction coordinate. The larger of the two is $B_{1,3N}(s)$, the coupling between the symmetric stretch mode and the reaction coordinate, and the smaller is $B_{2,4}(s)$, the coupling between rotation and the bending vibration.

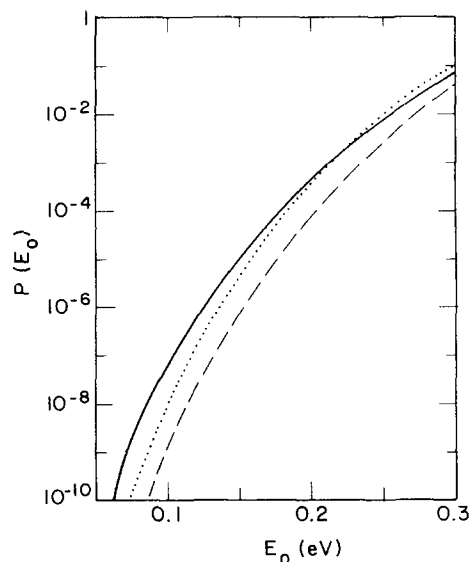


FIG. 5. Reaction probability for the 3d $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction for $J=0$, as a function of initial translational energy. The solid curve is the correct quantum mechanical result of Ref. 2(a) (Fig. 19, p. 4682), the dotted curve the vibrationally adiabatic result given by Eqs. (4.31) and (3.11), and the dashed curve the result of making the additional approximation of zero curvature, i.e., setting $B_{1,3N}(s)$ to zero.

the rotation-vibration coupling element $B_{2,4}(s)$ is much smaller than the direct coupling $B_{1,3N}(s)$ between the stretch mode and the reaction coordinate, and the tunneling probabilities calculated using Eqs. (4.32)–(4.34) are only slightly larger (32% at $E_0 = 0.1$ eV and 7% at $E_0 = 0.3$ eV) than if $B_{2,4}$ is completely neglected. Happily, therefore, it seems that rotation-vibration coupling is not a large effect in the present case.

V. QUANTUM MECHANICAL HAMILTONIAN

Once a classical Hamiltonian is given in terms of conjugate coordinates and momenta, it is a relatively straightforward matter to derive the corresponding quantum mechanical Hamiltonian operator. If the volume element for normalization is

$$dQ_1 dQ_2 \cdots dQ_{3N-7} ds d\theta \sin\theta d\phi d\chi \quad (5.1)$$

then, following Wilson, Decius, and Cross,¹⁵ HBJ show that the classical kinetic energy T of Eq. (4.14) becomes the operator \hat{T} given by

$$2\hat{T} = \mu^{1/4} (\hat{\Pi} - \hat{\pi}) \cdot \mu \cdot \mu^{-1/2} (\hat{\Pi} - \hat{\pi}) \mu^{1/4} + \sum_{k=1}^{3N-7} \mu^{1/4} \hat{P}_k \mu^{-1/2} \hat{P}_k \mu^{1/4}, \quad (5.2)$$

with

$$\mu = (\mathbf{l}_0 + \mathbf{b})^{-1} \cdot \mathbf{l}_0 \cdot (\mathbf{l}_0 + \mathbf{b})^{-1} \quad (5.3)$$

and

$$\mu = \det(\mu). \quad (5.4)$$

In Eq. (5.2), $\hat{\Pi} \equiv (\hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{p}_s)$, where \hat{J} are the usual angular momentum operators, and

$$\hat{p}_s = -i\hbar(\partial/\partial s), \quad \hat{P}_k = -i\hbar(\partial/\partial Q_k). \quad (5.5)$$

Equation (5.2) is an exact representation of the kinetic energy operator in these coordinates.

Equation (4.14b) may be used to simplify Eq. (5.2) somewhat:

$$\hat{T} = \frac{1}{2}\mu^{1/4}(\hat{\Pi} - \hat{\pi}) \cdot \mu \cdot \mu^{-1/2}(\hat{\Pi} - \hat{\pi})\mu^{1/4} - \frac{1}{8}\hbar^2(I'')^{-2} \times \sum_k \left(\frac{\partial I''}{\partial Q_k} \right)^2 + \frac{1}{4}\hbar^2(I'')^{-1} \sum_k \frac{\partial^2 I''}{\partial Q_k^2}, \quad (5.6)$$

where

$$I'' = \det(\mathbf{I}_0 + \mathbf{b}). \quad (5.7)$$

In the ordinary vibration-rotation problem with no reaction coordinate, Watson²² further simplified (5.6) using quadratic sum rules involving the b_k 's, obtaining

$$2\hat{T} = (\hat{J} - \hat{\pi}) \cdot \mu \cdot (\hat{J} - \hat{\pi}) + \sum_{k=1}^{3N-6} \hat{P}_k^2 - \frac{1}{8}\hbar^2 \sum_{\alpha} \mu_{\alpha\alpha}. \quad (5.8)$$

Some simplifications of Eq. (5.6) may likewise be possible using the quadratic sum rules derived by Moule and Ramachandra Rao,¹⁷ but it cannot be expected to take as tidy a form because of the dependence of μ on s .

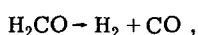
A useful approximation to Eq. (5.6) would be an expansion in Q_k through quadratic terms (the potential is only assumed to be known through quadratic terms). This can be achieved by the expansion of μ , μ , and I'' .

There are other quantum mechanical Hamiltonians in the literature which involve a reaction coordinate, notably those due to Marcus⁹ and Wyatt²³ for the $A + BC \rightarrow AB + C$ reactive collisions. For the special case of three atoms and to the extent that the potential surface is approximated as harmonic about the reaction path, these Hamiltonians should be equivalent.

VI. CONCLUDING REMARKS

The principal result of the paper is Eq. (4.21), the reaction path Hamiltonian for a general polyatomic molecule in 3d space with a given value of the total angular momentum. The kinetic energy part of the Hamiltonian is exact, and the potential energy is approximated as a harmonic valley about the reaction path. It has been emphasized that all the quantities necessary to construct this Hamiltonian are available from a relatively small number of calculations of the Born-Oppenheimer electronic energy of the N -atom system.

The classical dynamics of the molecular system may be determined exactly by computing trajectories with this Hamiltonian, or it may be desirable to treat the dynamics by simpler approximate models. Several aspects of the vibrationally adiabatic approximation have been considered, and in particular it was seen that the approximation is substantially better if the effect of reaction path curvature is included in the manner described. A more significant application of this nature would be to tunneling in the unimolecular decomposition of formaldehyde,



which has recently²⁴ been considered at a much more primitive level. As soon as the quantum chemistry information about the reaction path is available, the ap-

proach described in this paper should provide a more quantitatively reliable value for the unimolecular rate constant in the tunneling region.

ACKNOWLEDGMENTS

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conjugate momenta— (χ, p_χ) , (θ, p_θ) , (ϕ, p_ϕ) —to the action-angle variables (J, q_J) , (M, q_M) , (K, q_K) , is independent of any of the other degrees of freedom and thus proceeds just as for a rigid asymmetric rotor.

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