Reaction surface Hamiltonian for the dynamics of reactions in polyatomic systems

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The reaction path description of chemical reactions has difficulty if there are regions where the reaction path is sharply curved, as is typically the case, e.g., in light atom (e.g., H, D) transfer reactions. It is shown here how this can be overcome by introducing two reaction coordinate-like degrees of freedom, i.e., two coordinates, \( r_1 \) and \( r_2 \), that are allowed to undergo arbitrarily large amplitude motion (LAM). Rather than a reaction path and a reaction coordinate measuring distance along it, the picture is now that of a reaction surface with two reaction-like coordinates \( (r_1, r_2) \) which specify position on the surface. The reaction surface is defined by minimizing the potential energy of the polyatomic system for fixed values of \( r_1 \) and \( r_2 \), and an algorithm for using \textit{ab initio} quantum chemistry methods to do this is described. The remaining \((3N - 8)\) internal degrees of freedom are characterized as local harmonic motion orthogonal to the reaction surface; these local normal modes are defined by diagonalizing an appropriately projected force constant matrix. The classical (and quantum) reaction surface Hamiltonian is then derived, i.e., the Hamiltonian for which the dynamical variables are the two reaction-like coordinates \( (r_1, r_2) \) and the \((3N - 8)\) local normal mode coordinates (plus the usual three Euler angles for overall rotation), and their conjugate momenta. A zeroth order dynamical model is also described which has the form of a collinear-like atom--diatom reaction, i.e., a system with two degrees of freedom—in an effective 2D potential. This effective potential consists of the actual potential energy on the 2D reaction surface, the vibrationally adiabatic energy of the \((3N - 8)\) local normal modes, and the rotational energy of the complete polyatomic system, the latter two quantities being functions of the coordinates \( (r_1, r_2) \) on the reaction surface.

I. INTRODUCTION

Significant progress in understanding reaction dynamics in polyatomic molecular systems has been made by exploiting the notion of a reaction path.\textsuperscript{1,4} The first, and primary advantage of such an approach is that one does not require the entire potential energy surface of the \( N \)-atom system over its full \( 3N - 6 \) dimensional space. It is necessary only to determine it along a line, the reaction path, typically the steepest descent path is mass-weighted Cartesian coordinates (the "intrinsic" reaction path) through a transition state (i.e., a saddle point on the potential energy surface), and it is also necessary to calculate the force constant matrix along it. The overall picture is that of a harmonic valley (in \( 3N - 7 \) dimensions) about the reaction path. By utilizing the recent advances made by quantum chemists\textsuperscript{5} in evaluating gradients of potential energy surfaces efficiently, it is actually feasible to carry out \textit{ab initio} calculations to determine reaction paths and force constant matrices for polyatomic systems.

Given the reaction path approximation to the potential energy surface, it has been shown how a complete dynamical treatment can be based upon it; the reaction path Hamiltonian derived by Miller, Handy, and Adams\textsuperscript{6} takes the reaction coordinate (the distance along the reaction path) and the local normal mode coordinates for vibrations orthogonal to it, and their conjugate momenta, as the dynamical variables. The dynamics can be treated in various levels of approximation, e.g., ignoring the coupling between the reaction coordinate motion and the transverse vibrations, which leads to 1D motion along the reaction path in the vibrationally adiabatic potential, or taking it into account perturbatively, utilizing fully quantum mechanical treatments, or classical and semiclassical methods.\textsuperscript{3} In addition to applications carried out in our own group,\textsuperscript{7} Truhlar, Garrett, and co-workers,\textsuperscript{8} have also developed a number of useful models and applications based on the reaction path Hamiltonian.

In spite of these many desirable features, though, there are situations for which the reaction path picture has great difficulty. This typically arises when some regions of the reaction path have large curvature. There are practical difficulties with sharply curved reaction paths because the coupling between reaction coordinate motion and other degrees of freedom is proportional to the curvature\textsuperscript{8}; large curvature thus means large coupling, and then no simple dynamical approximation will be useful. There are even more fundamental problems, though, because the reaction path coordinates themselves become multivalued and thus not well defined at distances farther from the reaction path than the local radius of curvature.\textsuperscript{9} Large curvature (i.e., small radius of curvature) means that these multivalued regions are close to the reaction path and thus not in a region of configuration space that can be safely ignored.

An important example where these difficulties arise is hydrogen atom transfer reactions, for example the intramolecular H atom transfer in malonaldehyde\textsuperscript{7}
The situation is analogous to heavy + light–heavy collinear atom–diatom reactions, e.g., I + HI → IH + I, where the very small skew angle leads to a very sharply curved reaction path. Here it is well known that the reaction path picture is not useful, and in fact there is no way of describing these reactions well without dealing explicitly with the full two-dimensionality of the system.

The purpose of this paper is to present a model that we have developed for treating these more complex processes in general polyatomic systems. The key idea is that we introduce two degrees of freedom that can undergo arbitrarily large amplitude motion (LAM), i.e., two reaction coordinate-like degrees of freedom, rather than just one. For atom transfer reactions like Eq. (1.1) it is natural to take these two LAM coordinates as \( r_1 \) and \( r_2 \), the bond lengths of the bond being broken and the bond being formed, although the methodology we present is applicable for any choice of the two reaction parameters. The basic physical assumption is that once we have described the two important degrees of freedom correctly for arbitrarily large displacements, it should be a much better approximation to characterize the remaining degrees of freedom as small amplitude (i.e., harmonic) motion.

As for the reaction path Hamiltonian before, we develop the present methodology with the view to using ab initio quantum chemistry calculations as direct input, although it is of course not necessary that this always be done. Thus the first step of the approach, presented in Sec. II, is to give a prescription for determining the “reaction surface” (the generalization of the reaction path), i.e., an algorithm for determining the \( 3N \) nuclear cartesian coordinates \( \mathbf{a}(r_1, r_2) \) that minimize the potential energy of the complete polyatomic system for given values of \( r_1 \) and \( r_2 \). The equations given in Sec. II are the generalization of the gradient-following algorithm for determining the reaction path. For general nuclear geometries \( x \) the potential energy surface is then approximated by a quadratic expansion about the reaction surface

\[
V(x) = V(a) + \frac{1}{2}(x - a)\mathbf{K}(a)(x - a),
\]

where \( a = a(r_1, r_2) \) are the \( 3N \) nuclear coordinates of the reaction surface, and \( \mathbf{K}(a) \) is the force constant matrix evaluated on the reaction surface

\[
\mathbf{K}(a) = \left( \frac{\partial^2 V(x)}{\partial x_i \partial x_j} \right)_{x=a}.
\]

[The linear term in the Taylor series expansion, Eq. (1.2), is absent by virtue of the definition of the reaction surface; see Sec. III.]

The “reaction surface Hamiltonian” is then derived in Sec. III, the technology for doing this being a natural extension of that used before for the reaction path Hamiltonian. The two LAM coordinates \( r_1 \) and \( r_2 \), plus \( (3N - 8) \) local normal modes coordinates for motion orthogonal to the reaction surface, are the \( 3N - 6 \) internal coordinates of the system (the three rotations and three overall transitions are separated in the usual fashion), and the reaction surface Hamiltonian is expressed in terms of them and their conjugate momenta. The derivation is first presented for general nonlinear molecular geometries, and modifications that are necessary if the reaction surface geometry \( \mathbf{a}(r_1, r_2) \) corresponds to a linear molecule are also described.

Since two degrees of freedom are allowed to undergo arbitrarily large amplitude displacements in the present model, all dynamics that involve strong coupling between only two degrees of freedom can obviously be described exactly. Two degrees of freedom is, of course, equivalent to a collinear atom–diatom reaction, so that all dynamical phenomena that appear in collinear atom–diatom systems will be described correctly by the reaction surface Hamiltonian. The important case of atom transfer reactions, even H atom transfer like Eq. (1.1), typically involves only two degrees of freedom in an intimate way and should thus be described accurately by this approach.

Section IV discusses the simplest dynamical model that is suggested by the reaction surface Hamiltonian, namely a vibrationally adiabatic approximation to the \( (3N - 8) \) vibrational modes orthogonal to the reaction surface and the neglect of all rotation-vibration coupling. This is seen to lead to a collinear-like Hamiltonian, where the effective collinear potential is the sum of the actual potential energy on the reaction surface \( V[a(r_1, r_2)] = V_p(r_1, r_2) \), the adiabatic vibrational energy of the \( 3N - 8 \) modes normal to the reaction surface, and the rotational energy of a rigid (in general asymmetric) rotor, the latter two quantities evaluated for nuclear geometry \( a(r_1, r_2) \).

Finally, it should be noted that application of this reaction surface model will require more detailed input than is required by reaction path models. In the latter case one must evaluate the potential energy surface (and force constant matrix) only along a line, the reaction path, whereas the present reaction surface model requires that it be evaluated over a \( 2D \) grid of \( (r_1, r_2) \) values. This, of course, increases the number of \( ab \) initio quantum chemistry calculations that are required, but it should still be a feasible calculation for many interesting systems and is still considerably less demanding than having to determine the potential energy surface over a \( (3N - 6) \)-dimensional grid of values.

II. DEFINITION OF THE REACTION SURFACE

Let \( r_1 \) and \( r_2 \) be the two large amplitude motion, reaction coordinate-like variables. For atom transfer reactions such as Eq. (1.1) we envision that they will be chosen as indicated there, i.e., the length of the bond being broken and that of the bond being made, but any two molecular parameters can be chosen as the two reaction parameters.

The reaction surface is defined by minimizing the potential energy (i.e., the Born–Oppenheimer electronic ener-
gy) of the \( N \)-atom subject to the constraint of fixed values of \( r_1 \) and \( r_2 \). One thus minimizes the potential energy for a given initial pair of values \((r_1, r_2)\), changes (by a small increment, say) to another set of values \((r_1', r_2')\) and remini-
izes the potential energy, etc., over some 2D grid of \((r_1, r_2)\) values. \[ a(r_1, r_2) = a_{ij}(r_1, r_2), \]
where \( i = 1,...,N \), \( r, x, y, z \) denote the \( 3N \) Cartesian coordinates of the \( N \) atoms for these constrained minima, i.e., they are the coordinates of the atoms on the 2D \((r_1, r_2)\) reaction surface. As noted in the Introduction, it will also be necessary to have the force constant matrix on the reaction surface

\[
K(r_1, r_2) = \left( \frac{\partial^2 V}{\partial \alpha \partial \alpha} \right)_{x=x_0}, \tag{2.1a}
\]
where \( x = \{x_{ij}\}, i = 1,...,N; r, x, y, z \) denotes the \( 3N \) Cartesian coordinates, and of course the potential energy itself on the reaction surface

\[
V_0(r_1, r_2) = V(x). \tag{2.1b}
\]

Using the gradient methods of \( ab \) initio quantum chemistry it should be possible to carry out such a series of minimizations over, say, a 10\times10 grid of \((r_1, r_2)\) values with reasonable effort. If one increments systematically from one point on the 2D grid to another, then the minimizing geometry should change gradually, so that subsequent minimizations should be accomplished efficiently. An important practical note is that once the choice of the two reaction parameters \( r_1 \) and \( r_2 \) has been made, the resulting reaction surface is independent of what coordinates are used to carry out the constrained minimizations. Furthermore, provided the two reaction parameters do not involve the masses of any of the atoms—as is true for the bond coordinates we have suggested—the reaction surface (and the force constant matrix, inertia tensors, etc., on it) is invariant to isotopic substitution.

One can specify the above minimization procedure in a more elegant fashion by using a Lagrange multiplier technique. Thus let \( R_1(x) \) and \( R_2(x) \) be the two functions that express \( r_1 \) and \( r_2 \), respectively, as functions of the \( 3N \) Cartesian coordinates. We introduce two Lagrange multipliers \( \lambda_1 \) and \( \lambda_2 \), and the Lagrange function

\[
L(x, \lambda_1, \lambda_2) = V(x) + \lambda_1[r_1 - R_1(x)] + \lambda_2[r_2 - R_2(x)]. \tag{2.2}
\]

Setting derivatives of \( L \) with respect to \( x \), \( \lambda_1 \), and \( \lambda_2 \) equal to zero gives the following equations:

\[
\frac{d}{ds} a_{ij}(s) - \frac{\partial V}{\partial a_{ij}} \sqrt{m}, \tag{2.4}
\]

i.e., the gradient-following algorithm in mass-weighted Cartesian coordinates. We seek the generalization of Eq. (2.4) for the present case of two reaction parameters. Thus in Eq. (2.3) we set \( x = a(r_1, r_2) \) and consider \( \lambda_1, \lambda_2 \) also to be the functions of \( r_1 \) and \( r_2 \) defined by the equations, and differentiate implicitly, first with respect to \( r_1 \). This gives a set of three simultaneous linear equations for

\[
\frac{\partial a_{ij}(r_1, r_2)}{\partial r_1}, \quad \frac{\partial \lambda_1(r_1, r_2)}{\partial r_1}, \quad \text{and} \quad \frac{\partial \lambda_2(r_1, r_2)}{\partial r_1},
\]

the solution of which gives them as follows:

\[
\frac{\partial a_{ij}(r_1, r_2)}{\partial r_1} = \left( A^{-1} \frac{\partial R_1}{\partial a} \right) M_{ij} + \frac{\partial \lambda_1(r_1, r_2)}{\partial r_1}, \tag{2.5a}
\]

\[
\frac{\partial \lambda_1(r_1, r_2)}{\partial r_1} = -M_{ij}(M_{1j}M_{2i} - M_{ij}M_{2j}), \tag{2.5b}
\]

\[
\frac{\partial \lambda_2(r_1, r_2)}{\partial r_1} = M_{ij}(M_{1j}M_{2i} - M_{ij}M_{2j}), \tag{2.5c}
\]

where

\[
M_{i,j} = \frac{\partial R_i}{\partial a} - \frac{\partial R_j}{\partial a}, \quad i = 1,2, \tag{2.6a}
\]

\[
A = \lambda_1 \frac{\partial^2 R_1}{\partial a \partial a} + \lambda_2 \frac{\partial^2 R_2}{\partial a \partial a} - \frac{\partial V}{\partial a \partial a}. \tag{2.6b}
\]

The partial derivatives of \( a(r_1, r_2), \lambda_1(r_1, r_2), \lambda_2(r_1, r_2) \) with respect to \( r_2 \) are given by Eq. (2.5) with the interchange \( 1 \leftrightarrow 2 \).

Equations (2.5) (and the accompanying ones for derivatives with respect to \( r_2 \)) determine how the \( 3N \) Cartesian coordinates of the \( N \)-atom system change along the 2D \((r_1, r_2)\) reaction surface; these are the equations which generalize the gradient-following algorithm, Eq. (2.4), used to generate the reaction path. They must be integrated over a 2D grid in \((r_1, r_2)\) space to determine \( a(r_1, r_2) \) (and the Lagrange multipliers \( \lambda_1, \lambda_2 \) are determined simultaneously).

Clearly, determining the reaction surface—whether by successive minimization as described at the beginning of this section, or by integrating Eq. (2.5) over the 2D grid—will involve more quantum chemistry calculations than does the generation of a \((1D)\) reaction path by following the mass-weighted gradient. This is the price paid for a more accurate description of the reaction, and it is still considerably less demanding than determining the entire \( 3N \) - \( 6 \) dimensional potential energy surface. As noted above, one simplifying feature of the reaction surface, as we have defined it, is that it is invariant to isotopic substitution, unlike the "intrinsic" (i.e., mass-weighted gradient) reaction path.

III. THE REACTION SURFACE HAMILTONIAN

A. The general (nonlinear) case

The object here is to derive a classical (and later quantum) Hamiltonian in terms of the two LAM coordinates \( r_1 \) and \( r_2 \), and \((3N-8)\) local normal mode coordinates for vi-
brations orthogonal to the reaction surface, plus the usual three Euler angles for rotation of the \( N \)-atom system. (The three degrees of freedom for overall translation of the system can be ignored as usual.) The procedure is a straightforward extension of the derivation of the reaction path Hamiltonian,\(^{31}\) which itself used the approach of Hougen, Bunker, and Johnn\(^{9}\) to deal with a LAM coordinate. One should also note the recent work of Brand and Rao,\(^{10}\) Szalay,\(^{11}\) and Rusegger\(^{12}\) on the extension of the HBJ method to more than one LAM coordinate.

A slight difference in the present development of the reaction surface Hamiltonian is that here we do not use mass-weighted Cartesian coordinates. It was useful to do so before because the reaction path itself was most naturally defined using them, but it has already been noted that the reaction surface that we are presently using does not involve the mass; it is thus most convenient not to involve the mass in any unnecessary way in the coordinates. The mass is involved later, however, in the definition of normal coordinates for vibration.

Regarding notation, boldfaced vectors with no subscripts, e.g., \( \mathbf{x} , \mathbf{a} \), etc., denote \( 3N \)-dimensional vectors with components \( \{ x_i \} \), \( \{ a_i \} \), where \( i = 1 , \ldots , N \) denotes atoms and \( \gamma = x, y, z \). The boldface vectors with an atomic subscript, e.g., \( \mathbf{r}_i , \mathbf{a}_i \), denote three-dimensional vectors, whose components are \( \{ x_{i\gamma} \} \), \( \{ a_{i\gamma} \} \). Greek indices \( \alpha \) and \( \beta \), as well as \( \gamma \), refer to the three spatial directions \( x, y, \) or \( z \). The subscript \( K = 1, \ldots , 3N - 8 \) to appear below, denotes the various local normal mode vibrational coordinates for internal (i.e., nonrotational, translational) motion orthogonal to the reaction surface. Text is used to eliminate as much confusion as possible in the notation to indicate which boldface quantities are \( 2D \) vectors, \( 3D \) vectors, \( 3N - 8 \) vectors, and matrices.

Thus proceeding in parallel to earlier work,\(^{26,30,9}\) let \( \{ x_{i\gamma} \} , \{ x_i \} \) be the \( 3N \) Cartesian coordinates of the \( N \) atoms in a space-fixed system of axes and a molecule-fixed system of axes, respectively. The coordinates of the \( i \)th atom with respect to the molecule-fixed axis system and the space-fixed axis system are related by

\[
X_i = \mathbf{R}_{\text{COM}} + S(\chi, \theta, \phi)^{-1} x_i, \tag{3.1}
\]

where \( \mathbf{R}_{\text{COM}} \) is the \( 3D \) vector of the center of mass in the space-fixed axis system, and \( S(\chi, \theta, \phi) \) is the \( 3 \times 3 \) matrix of direction cosines which relate the orientation of the molecule- and space-fixed axis systems through the Euler angles \( (\chi, \theta, \phi) \). As before, the coordinates in the molecule-fixed system are expressed in terms of a “reference configuration” \( \mathbf{a}(r_1, r_2) \), i.e., a point on the reaction surface, and displacements \( \mathbf{d} \) from it,

\[
\mathbf{x}_i = \mathbf{a}(r_1, r_2) + \mathbf{d}_i. \tag{3.2}
\]

We also require that the molecule-fixed coordinates of the reaction surface have their origin at the center of mass, so that

\[
\sum_{i=1}^{N} m_i \mathbf{a}_i(r_1, r_2) = 0. \tag{3.3a}
\]

Furthermore, one can show that

\[
\sum_{i=1}^{N} \frac{m_i \mathbf{a}_i(r_1, r_2) \times \frac{\partial a_i(r_1, r_2)}{\partial r_i}}{r_i} = 0, \tag{3.3b}
\]

for \( n = 1, 2 \); this follows because the two LAM functions \( R_{ij}(x) \) and \( R_{ij}(x) \) of Sec. II will in general depend only as interatomic distances and is essentially the statement that displacements of the geometry along the reaction surface itself carry no angular momentum.

With Eq. (3.2) substituted into Eq. (31), there are \( 3N \) variables \( \{ X_i \} \) on the left-hand side and \( 3N + 8 \) variables—\( \{ \mathbf{d}_i \} , \{ r_1 , r_2 , \chi, \theta, \phi \} , \mathbf{R}_{\text{COM}} \)—on the right-hand side, so that eight equations between these latter variables must be introduced to make the transformation between the two sets one-to-one. These are the natural generalizations of those used before:

\[
\sum_{i=1}^{N} m_i \mathbf{d}_i = 0, \tag{3.4a}
\]

\[
\sum_{i=1}^{N} m_i \mathbf{a}_i(r_1, r_2) \times \mathbf{d}_i = 0, \tag{3.4b}
\]

\[
\sum_{i=1}^{N} m_i \frac{\partial a_i(r_1, r_2)}{\partial r_1} \cdot \mathbf{d}_i = 0, \tag{3.4c}
\]

\[
\sum_{i=1}^{N} m_i \frac{\partial a_i(r_1, r_2)}{\partial r_2} \cdot \mathbf{d}_i = 0. \tag{3.4d}
\]

Equation (3.4a) is the statement that the origin of the molecule-fixed axis system translates with the center of mass; Eq. (3.4b) is the usual Eckart condition and means that infinitesimal displacements away from the reference configuration do not contribute to the angular momentum. Equation (3.4c) and (3.4d) state that the mass-weighted displacement vectors \( \sqrt{m_i} \mathbf{d}_i \) must be orthogonal to the two vectors \( \sqrt{m_i} \times [\partial a_i(r_1, r_2)] / \partial r_n \), \( n = 1, 2 \); the latter two (linearly independent) vectors, however, are tangent to the reaction surface, so these two equations guarantee that the mass weighted displacement vectors \( \sqrt{m_i} \mathbf{d}_i \) are normal to the reaction surface.

Equations (3.4) are all satisfied by expressing the displacements \( \{ \mathbf{d}_i \} \) in terms of local normal coordinates which are defined to be orthogonal to the reaction surface and also to have no components corresponding to pure translation or rotation. This is accomplished by diagonalizing the projected, mass-weighted \( 3N \times 3N \) force constant matrix \( \mathbf{K}^{p}(r_1, r_2) = [\mathbf{K}_{ij}^{p}(r_1, r_2)] \), defined by

\[
\mathbf{K}^{p}(r_1, r_2) = [1 - \mathbf{P}(r_1, r_2)] \mathbf{K}^{*}(r_1, r_2) [1 - \mathbf{P}(r_1, r_2)], \tag{3.5a}
\]

where

\[
\mathbf{K}^{*}_{ij}(r_1, r_2) = \left( \frac{\partial^2 V(x)}{\partial x_i \partial x_j} / \sqrt{m_i m_j} \right)_{x = \mathbf{a}(r_1, r_2)}, \tag{3.5b}
\]

and where \( \mathbf{P}(r_1, r_2) \) is the \( 3N \times 3N \) matrix which projects onto the six \( 3N \) vectors corresponding to pure translation and rotation of the \( N \)-atom system and geometry \( \mathbf{a}(r_1, r_2) \), and also onto the two directions tangent to the reaction surface at \( \mathbf{a}(r_1, r_2) \). This projector is given by

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where $M$ is the total mass of all $N$ atoms, $I_{0}(r_{1}, r_{2})$ is the $3 \times 3$ inertia tensor at point $(r_{1}, r_{2})$ on the reaction surface

$$I_{0} = \sum_{i=1}^{N} m_{i} \left[ \mathbf{a}_{i} \mathbf{a}_{i}^{T} - a_{i} a_{i}^{T} \right].$$

(3.7)

$\epsilon_{ab}^{\gamma}$ is the usual totally antisymmetric Cartesian tensor, and $S(r_{1}, r_{2})$ is the $2 \times 2$ overlap matrix of the two vectors $\sqrt{m_{1}} \mathbf{a}_{1} / \partial r_{1}^{n}$, $n = 1, 2$,

$$S_{n,n'}(r_{1}, r_{2}) = \sum_{i=1}^{N} m_{i} \frac{\partial a_{n}(r_{1}, r_{2})}{\partial r_{n}} \cdot \frac{\partial a_{n'}(r_{1}, r_{2})}{\partial r_{n'}}.$$

(3.8)

The first term in Eq. (3.6) projects onto the three $3N$ vectors that are overall translations of the $N$-atom system, the second term projects onto the three vectors that are infinitesimal rotations of the $N$-atom system at geometry $a(r_{1}, r_{2})$, and the last projects onto the $2D$ plane tangent to the reaction surface at point $(r_{1}, r_{2})$.

The projected force constant matrix, Eq. (3.5), will have eight zero eigenvalues, corresponding to the eight vectors onto which $P$ projects, and $3N-8$ nonzero eigenvalues denoted by $\omega_{k}(r_{1}, r_{2})$, $k = 1, \ldots, 3N-8$. The corresponding eigenvectors are $L_{k}(r_{1}, r_{2}) = L_{k}(r_{1}, r_{2})$, $k = 1, \ldots, 3N-8$. (Note: $L_{k}$ is a $3N$ vector with components $L_{i,k}$; $L_{i,k}$ is a 3 vector with components $L_{i,k}$.) The statement of orthogonality for the eigenvectors $L_{i,k}(r_{1}, r_{2})$ is

$$L_{i}(r_{1}, r_{2}) \cdot L_{k}(r_{1}, r_{2}) = \delta_{i,k},$$

(3.9a)

and since $P(r_{1}, r_{2}) L_{i}(r_{1}, r_{2}) = 0$ one also has the following eight orthogonality relations:

$$\sum_{i=1}^{N} m_{i} L_{i,k}(r_{1}, r_{2}) = 0,$$

(3.9b)

$$\sum_{i=1}^{N} m_{i} a_{i}(r_{1}, r_{2}) \times L_{i,k}(r_{1}, r_{2}) = 0,$$

(3.9c)

$$\sum_{i=1}^{N} m_{i} \frac{\partial a_{i}(r_{1}, r_{2})}{\partial r_{n}} \cdot L_{i,k}(r_{1}, r_{2}) = 0,$$

(3.9d)

and the completeness relation is

$$P(r_{1}, r_{2}) + \sum_{k=1}^{3N-8} \mathbf{L}_{i,k}(r_{1}, r_{2}) \mathbf{L}_{i,k}(r_{1}, r_{2}) = 1.$$

(3.10)

In terms of the local normal mode vibrational coordinate $\{Q_{k}\}$, $k = 1, \ldots, 3N-8$, the atomic displacements $\mathbf{d}_{i}$ are given by

$$\mathbf{d}_{i} = m_{i}^{-1/2} \sum_{k=1}^{3N-8} L_{i,k}(r_{1}, r_{2}) Q_{k},$$

(3.11)

and it is easy to see [by using Eq. (3.9)] that Eqs. (3.4) are indeed satisfied. Finally, the atomic coordinates $\{x_{i}\}$ in the molecule-fixed coordinate system are given in terms of the $3N-6$ internal coordinates $r_{1}, r_{2}, \{Q_{k}\}$, by

$$\mathbf{x}_{i} = a_{i}(r_{1}, r_{2}) + m_{i}^{-1/2} \sum_{k=1}^{3N-8} L_{i,k}(r_{1}, r_{2}) Q_{k}.$$

(3.12)

In terms of the internal coordinates $r_{1}, r_{2}, \{Q_{k}\}$, the potential energy is given by [cf. Eqs. (1.2) and (3.12)]

$$V(r_{1}, r_{2}, \{Q_{k}\}) = V_{0}(r_{1}, r_{2}) + \sum_{k=1}^{3N-8} -\frac{1}{2} \omega_{k}(r_{1}, r_{2}) Q_{k}^{2},$$

(3.13)

where $\omega_{k}(r_{1}, r_{2})$ are the aforementioned eigenvalues of the projected force constant matrix. There is no linear term in the $Q_{k}$'s because the potential $V_{0}(r_{1}, r_{2})$ is, by construction, the minimum value of the potential for fixed values of $(r_{1}, r_{2})$.

The final task is to express the kinetic energy in terms of $r_{1}, r_{2}, \{Q_{k}\}$, their conjugate momenta, and the three components of total angular momentum $J$. This part of the development is essentially identical to that carried out before, except so we simply give the result. The kinetic energy $T$ is

$$T = \sum_{k=1}^{3N-8} -\frac{1}{2} P_{k}^{2} + T',$$

(3.14)

where $\{P_{k}\}$ are the momenta conjugate to $\{Q_{k}\}$, and

$$T' = \frac{1}{2}(J - \pi)(l_{0} + b)^{-1} l_{0}(l_{0} + b)^{-1}(J - \pi).$$

(3.15)

In Eq. (3.15) $J$ and $\pi$ are five-dimensional vectors and $l_{0}$ and $b$ $5 \times 5$ matrices, the first two components of each referring to the two coordinates $r_{1}$ and $r_{2}$, and the latter three components to the three spatial directions $x, y, z$. $J$ is a five-dimensional “angular momentum”

$$J = (P_{r_{1}}, P_{r_{2}}, J_{x}, J_{y}, J_{z}) \equiv (P_{J}, J).$$

(3.16)

where $J$ is the $3D$ total angular momentum vector and $P_{J}$ is the $2D$ vector $(P_{r_{1}}, P_{r_{2}})$ of momenta conjugate to $r_{1}$ and $r_{2}$, and $\pi$ is a five-dimensional “vibrational angular momentum” vector given by

$$\pi = \sum_{k=1}^{3N-8} B_{k,k}(r_{1}, r_{2}) Q_{k} P_{k},$$

(3.17a)

with

$$B_{k,k}(r_{1}, r_{2}) = \sum_{i=1}^{N} \frac{\partial L_{i,k}(r_{1}, r_{2})}{\partial r_{n}} \cdot L_{i,k}(r_{1}, r_{2}),$$

(3.17c)

and

$$B_{k,k}(r_{1}, r_{2}) = \sum_{i=1}^{N} L_{i,k}(r_{1}, r_{2}) \times L_{i,k}(r_{1}, r_{2}).$$

(3.17d)

and $I_{0}(r_{1}, r_{2})$ is a $5 \times 5$ “inertia tensor” which is block diagonal: the $2 \times 2$ block is the overlap matrix encountered above, Eq. (3.8), and the $3 \times 3$ block is the usual inertia tensor at the reference configuration $a(r_{1}, r_{2})$, given by Eq. (3.7); i.e.,

$$I_{0}(r_{1}, r_{2}) = \begin{pmatrix} S(r_{1}, r_{2}) & 0 \\ 0 & I_{0}(r_{1}, r_{2}) \end{pmatrix}.$$ 

(3.18)
And finally, \( b \) is a five-dimensional “centrifugal distortion” matrix, i.e., a linear correction to the inertia tensor

\[
 b = \sum_{k=1}^{3N-8} b_k(r_1, r_2) Q_k, \tag{3.19a}
\]

where it is also convenient to write the \( 5 \times 5 \) matrix \( b_k(r_1, r_2) \) in partitioned form:

\[
 b_k(r_1, r_2) = \begin{pmatrix}
 b_k^{(p,p)} & b_k^{(p,n)} \\
 b_k^{(n,p)} & b_k^{(n,n)}
\end{pmatrix}, \tag{3.19b}
\]

where the \( 2 \times 2 \) block is

\[
 b_k^{(p,p)}(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} \frac{\partial a_i(r_1, r_2)}{\partial r_n} \frac{\partial L_{i,k}(r_1, r_2)}{\partial r_n}, \tag{3.19c}
\]

the \( 3 \times 3 \) block is

\[
 b_k(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} \left[ \mathbf{1} L_{i,k}(r_1, r_2) a_i(r_1, r_2) - L_{i,k}(r_1, r_2) b_i(r_1, r_2) \right] \tag{3.19d}
\]

and the off-diagonal \( 2 \times 3 \) block is

\[
 b_k^{(p,n)}(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} L_{i,k}(r_1, r_2) \frac{\partial a_i(r_1, r_2)}{\partial r_n}. \tag{3.19e}
\]

If the usual action-angle variables \((J, M, K, \phi_J, \phi_M, \phi_K)\) are introduced, the components of angular momentum in the body-fixed coordinate system are

\[
 J_\phi = \sqrt{J^2 - K^2} \cos q_K, \tag{3.20}
\]

\[
 J_\tau = \sqrt{J^2 - K^2} \sin q_K, \tag{3.20}
\]

\[
 J_\nu = K. \tag{3.20}
\]

Finally, the classical Hamiltonian for total angular momentum \( J \) is given in terms of the coordinates \((r_1, r_2) \{ Q_k \}, \phi_K\) and conjugate momenta \((P_{r_1}, P_{r_2}, \{ P_k \}, K)\) by

\[
 H(r_1, r_2) = \sum_{k=1}^{3N-8} \frac{1}{2} \left[ P_k^2 + \omega_k(r_1, r_2)^2 Q_k^2 \right] + V_0(r_1, r_2) + T', \tag{3.21}
\]

with \( T' \) given by Eqs. (3.15)-(3.19).

\section*{B. Quantum mechanical Hamiltonian operator}

The quantum mechanical Hamiltonian corresponding to the classical Hamiltonian of Eq. (3.21) is obtained in the usual way:

\[
 P_n = \frac{\hbar}{i} \frac{\partial}{\partial r_n}, \quad n = 1, 2, \tag{3.22a}
\]

\[
 P_k = \frac{\hbar}{i} \frac{\partial}{\partial Q_k}, \quad k = 1, \ldots, 3N - 8. \tag{3.22b}
\]

If the volume element for normalization is

\[
 dr_1 dr_2 dQ_{1N-8} d\chi d\phi d\theta d\sin \theta, \tag{3.23}
\]

then the Hamiltonian operator is given by

\[
 H = \sum_{k=1}^{3N-8} \frac{1}{2} \left[ \mu^{1/4} \hat{P}_k \mu^{-1/2} \hat{P}_k \mu^{1/4} + \omega_k(r_1, r_2)^2 Q_k^2 \right] + \hat{V}_0(r_1, r_2) + \frac{1}{4} \mu^{1/4} \left( \hat{J} - \hat{\pi} \right) \mu^{-1/2} \times (l_0 + b)^{-1} l_0 (l_0 + b)^{-1} \left( \hat{J} - \hat{\pi} \right) \mu^{1/4}, \tag{3.24}
\]

where

\[
 \mu = \text{det}(l_0 + b)^{-1} l_0 (l_0 + b)^{-1}, \tag{3.25}
\]

and \( \hat{J}, \hat{\pi}, \hat{P}_k, \) and \( b \) are the operators indicated by Eq. (3.22).

\section*{C. Modifications for a linear reference geometry}

The reaction surface, or reference configuration \( a(r_1, r_2) \) may correspond to a linear geometry of the \( N \)-atom system. This is common, e.g., for the case of an atom–diatom reaction \( A + BC \rightarrow AB + C \): the \( A-B-C \) distances are the two LAM coordinates \( r_1 \) and \( r_2 \), and it often happens that the minimum geometry for fixed \( r_1 \) and \( r_2 \) is linear.

In such cases the development of the previous section needs modifications. These are essentially identical to the analogous modifications for the reaction path Hamiltonian,36 and so we simply quote the major results. There are only two rotational degrees of freedom in this case and \( 3N - 7 \) vibrational modes.

If the linear reference configuration \( a(r_1, r_2) \) is the \( z \) axis, i.e.,

\[
 a_{\nu}(r_1, r_2) = a_{\nu}(r_1, r_2) \delta_{\phi, z}, \tag{3.26}
\]

then Eqs. (3.14)-(3.19) are modified in that \( J \) and \( \pi \), etc., become four-dimensional vectors, and \( I_0 \) and \( b \), etc., \( 4 \times 4 \) matrices. The first two components still refer to \( r_1 \) and \( r_2 \), and the latter two components refer to \( x \) and \( y \); i.e., the modification is that the \( z \) components of the matrix expressions in Eq. (3.15) are deleted.

The rotational term in the projector \( P \), the second term in Eq. (3.6), is modified to be

\[
 \frac{\sqrt{m_i m_r}}{I_0(r_1, r_2)} \frac{a_{\nu}(r_1, r_2) \delta_{\phi, z}}{I_0(r_1, r_2)} (\delta_{\phi, z'} - \delta_{\phi, z} \delta_{\phi, z'}), \tag{3.27a}
\]

where

\[
 I_0(r_1, r_2) = \sum_{i=1}^{N} m_i a_{\nu}(r_1, r_2)^2. \tag{3.28a}
\]

The \( 2 \times 2 \) inertia tensor \( I_0(r_1, r_2) \) is

\[
 I_0(r_1, r_2) = I_0(r_1, r_2)(\hat{\chi} \hat{\chi} + \hat{\eta} \hat{\eta}), \tag{3.29a}
\]

and the \( 4 \times 4 \) “centrifugal distortion” matrix \( b \), Eq. (3.19), is given by

\[
 b_k(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} a_{\nu}(r_1, r_2) L_{i,k}(r_1, r_2), \tag{3.30a}
\]

and

\[
 b_k^{(p,n)}(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} a_{\nu}(r_1, r_2) L_{i,k}(r_1, r_2), \tag{3.30b}
\]

\[
 b_k^{(p,n)}(r_1, r_2) = \sum_{i=1}^{N} \sqrt{m_i} a_{\nu}(r_1, r_2) \left[ L_{i,k}(r_1, r_2) \hat{\chi} - L_{i,k}(r_1, r_2) \hat{\eta} \right]. \tag{3.30c}
\]
IV. ELEMENTARY DYNAMICAL CONSIDERATIONS

It is not our purpose in this paper to pursue in depth the various dynamical theories that can be based on the reaction surface Hamiltonian, but we do wish to point out the most obvious models which are suggested.

First, consider the "bare bones," zeroth order model, i.e., neglect of the generalized vibrational angular momentum vector \( \mathbf{r} \) and the generalized centrifugal distortion matrix \( b \). The term \( T' \) of Eq. (3.15) becomes

\[
T' = \frac{1}{2} \mathbf{P} \cdot \mathbf{S}(r_1r_2)^{-1} \mathbf{P} + \frac{1}{2} \mathbf{J} \mathbf{I}(r_1r_2)^{-1} \mathbf{J},
\]

where \( \mathbf{P} \) is the 2D vector of LAM momenta \( (P_r, P_r) \). The Hamiltonian then has the form

\[
H(r_1r_2; (Q_k, P_k); \omega_k, \omega_k^2) = H_{12}(r_1r_2; P_1P_2) + \sum_{k=1}^{N-8} \frac{1}{2} \left[ P_k^2 + \omega_k(r_1r_2) Q_k^2 \right] + H_{rot}(Q_k, \omega_k, P_1P_2),
\]

where

\[
H_{12}(r_1r_2; P_1P_2) = \frac{1}{2} \mathbf{P} \cdot \mathbf{S}(r_1r_2)^{-1} \mathbf{P} + V_0(r_1r_2),
\]

\[
H_{rot}(Q_k, \omega_k, P_1P_2) = \frac{1}{2} \mathbf{J} \mathbf{I}(r_1r_2)^{-1} \mathbf{J}.
\]

\( H_{12} \) is the Hamiltonian for the two LAM degrees of freedom on the 2D potential energy surface \( V_0(r_1r_2) \). [One recognizes that the inverse of the overlap matrix \( S(r_1r_2)^{-1} \) is Wilson's \( G \) matrix.] \( H_{rot} \) is the Hamiltonian for a rigid (in general asymmetric) rotor of molecular geometry \( \mathbf{r}(r_1r_2) \). If the frequencies \( \omega_k(r_1r_2) \) are sufficiently slowly varying functions of \( r_1 \) and \( r_2 \), it would be reasonable to proceed further and make a \textit{vibrationally adiabatic} approximation to the \( (3N-8) \) vibrational degrees of freedom. One replaces the canonical variables \( (Q_k, P_k) \) by the action angle variables \( (n_k, q_k) \),

\[
Q_k = \sqrt{2n_k + 1} \sin q_k,
\]

\[
P_k = \sqrt{2n_k + 1} \cos q_k,
\]

(units being used with \( \hbar = 1 \)), and if derivatives of \( \omega_k(r_1r_2) \) with respect to \( r_1 \) and \( r_2 \) are neglected, the Hamiltonian becomes

\[
H = \frac{1}{2} \mathbf{P} \cdot \mathbf{S}(r_1r_2)^{-1} \mathbf{P} + V_0(r_1r_2) + H_{rot},
\]

where \( V_0 \) is the vibrationally adiabatic effective potential

\[
V_0(r_1r_2) = V_0(r_1r_2) + \sum_{k=1}^{N-8} \frac{1}{2} \hbar \omega_k(r_1r_2)(n_k + \frac{1}{2}).
\]

If the geometry \( \mathbf{a}(r_1r_2) \) on the reaction surface is that of a symmetric top—or if one approximates an asymmetric top as a symmetric one in the usual way—then \( H_{rot} \) in Eq. (4.5) also becomes a potential energy-type term. For the general asymmetric top case, e.g., one has

\[
H_{rot} \approx E_{jk}(r_1r_2) = \frac{1}{2} \left[ A(r_1r_2) + B(r_1r_2) \right] (J(J + 1) - K^2) + C(r_1r_2) K^2,
\]

where \( A(r_1r_2), B(r_1r_2), \) and \( C(r_1r_2) \) are the three principle rotation constants for geometry \( \mathbf{a}(r_1r_2) \); \( C \) being the most distinct of the three. With this approximation—which is not an additional approximation if the geometry \( \mathbf{a}(r_1r_2) \) happens to be a symmetric top—Eq. (4.6) becomes a dynamical system of two degrees of freedom, equivalent to a collinear atom–diatom reaction with the effective collinear potential energy surface

\[
V_0(r_1r_2) + \sum_{k=1}^{N-8} \hbar \omega_k(r_1r_2)(n_k + \frac{1}{2}) + E_{jk}(r_1r_2).
\]

It is important to realize that all of the approximations that have been introduced above are approximations to the couplings between the LAM degrees of freedom and other degrees of freedom; there have been no approximations to the direct interactions between the two LAM degrees of freedom themselves. Equations (4.6)–(4.8) thus provide a zeroth order approach for retaining a fully exact treatment of the collinear-like dynamics of the two LAM degrees of freedom and incorporating effects of other vibrational modes and rotation in an approximate manner.

The "reduced dimensionality transition state" model of Bowman and the bending-corrected rotating linear model used recently by Walker and Hayes, which are ways for using collinear \( A + BC \rightarrow AB + C \) reactive scattering calculations to approximate the \( 3D \) \( A + BC \) process, are actually examples of the model described above. For the \( 3D \) \( H + H_2 \) reaction, e.g., with \( J = 0 \) the model suggests that for the ground vibrational state one should carry out collinear reactive scattering calculations on the effective collinear potential energy surface.

\[
V_0(r_1r_2) + \hbar \omega_k(r_1r_2),
\]

where \( \omega_k(r_1r_2) \) is the bending frequency at general collinear geometry \( \mathbf{a}(r_1r_2) \). This is essentially the calculation that Bowman has reported, and the results are in excellent agreement with the accurate values of full \( 3D \) scattering calculations, much better agreement than if one uses the adiabatic bending energy only along the minimum energy path, as is suggested by the corresponding zeroth order reaction \textit{path} model. Although this is a very elementary test, it is nevertheless an encouraging example of the increased accuracy that is possible with the reaction surface model, even in zeroth order, over that of a reaction \textit{path} description.

It is easy to see how one can improve on the above zeroth order approximation by using perturbation theory. Since the potential energy is described correctly only to second order in \( \{Q_k\} \), one is presumably only justified in keeping the various coupling terms through similar order in \( \{Q_k\} \) and \( \{P_k\} \). This corresponds to expanding \( T' \), Eq. (3.15), to first order in \( \pi \) and through second order in \( b \):

\[
T' = T'_0 + T'_1 + T'_2,
\]

where \( T'_0 \) is the zeroth order approximation given by Eq. (4.1), and

\[
T'_1 = -J[-l_0^{-1}\cdot b\cdot l_0^{-1}],
\]

\[
T'_2 = -J[-l_0^{-1}\cdot \pi + \hbar l_0^{-1}\cdot b\cdot l_0^{-1}],
\]

\( T'_1 \) and \( T'_2 \) can be treated as perturbations, e.g., ordinary Rayleigh–Schrödinger perturbation theory for eigenvalues, or distorted wave scattering theory if a scattering process is being described.
V. CONCLUSIONS

The principal goal of this paper has been to derive a Hamiltonian adapted to studying the dynamics of polyatomic systems with two strongly coupled nonharmonic degrees of freedom. The Hamiltonian has been derived in terms of the reaction surface variables \((r, \tau, \{Q_i\})\) (and their conjugate momenta) to facilitate approximation of the potential energy surface. The kinetic energy in terms of these variables is exact, and the potential energy is approximated by an expansion about the reaction surface. By allowing two degrees of freedom to undergo arbitrary large amplitude motion, we believe the present reaction surface Hamiltonian model will be able to provide an accurate description of a much wider class of dynamical phenomena in polyatomic systems than is possible with a reaction path model. H atom transfer reactions between two heavy molecular fragments where the reaction path typically has regions of large curvature, is the important example that has motivated our work but we have developed the approach more generally because we feel that it can have many useful applications.

It will be natural to base dynamical treatments of the reaction surface Hamiltonian on a "system-bath" notion, where the "system" consists of the two LAM degrees of freedom, and the "bath" the remaining harmonic ones. Treating the system accurately—whether one is looking for eigenvalues, or calculating reactive scattering S-matrices—is tantamount to dealing with a collinear atom–diatom system, something that can be dealt with quite accurately and efficiently using a variety of existing methods. The bath degrees of freedom will, of course, be dealt with more approximately, the simplest such possibility having been described in Sec. IV. It should be emphasized that basing the system-bath description on the reaction surface Hamiltonian is a major advance over the earlier work by Miller and Schwartz, where the 2D system itself was treated via a reaction path approximation, i.e., a reaction path plus one harmonic mode orthogonal to it.

Two-dimensional systems themselves, of course, already show many of the phenomena currently of interest in polyatomic reaction dynamics: (1) for bound 2D systems, questions of "regular" or "chaotic" spectra, and the general nature of highly vibrationally excited states has received considerable attention; (2) in unimolecularly decomposing systems, the relevant question has to do with mode specificity, i.e., is the unimolecular decay rate a function only of the total energy, or are there other "weak" quantum numbers by which one can characterize the decomposing states; and (3) for bimolecular reactions a 2D system can display resonances in the scattering, arising from both energy transfer (i.e., Feshbach resonances) and tunneling (potential resonances).

Since the reaction surface Hamiltonian describes the dynamics of 2D systems exactly, it is thus well suited to describe these phenomena in more general polyatomic systems and, e.g., to study how the additional degrees of freedom, i.e., the vibrational modes perpendicular to the reaction surface, modify the purely 2D results.

Finally, it should be clear how one could generalize the model developed in this paper to allow for three (or more) LAM reaction-like coordinates. Since this would require calculation of the potential energy surface over a 3D grid of values, however, the feasibility of applying such models diminishes greatly. Fortunately, many interesting dynamical phenomena arise even with two LAM degrees of freedom, and we look forward to investigating some of them.

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13 The projector onto a set of nonorthonormal vectors $|v_i\rangle$ is given by $\sum_i \langle v_i | \langle v_i | \langle \Sigma_i \rangle^{-1} \langle v_i | \langle v_i | \langle v_i |, where the matrix inverse denotes the $i-j$ element of the inverse of the overlap matrix $\langle v_i | v_j \rangle$.
15 See, for example, P. R. Bunker, Molecular Symmetry and Spectroscopy (Academic, New York, 1979), pp. 116–125.
16 Reference 14, pp. 61–62, and Appendix VII.
22 See, for example, W. H. Miller, Laser Chem. 2, 243 (1983).