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Explicit definition of the reaction coordinate for the Jackels–Gu–Truhlar projection technique to compute harmonic vibrational frequencies along the intrinsic reaction path

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Abstract. It is shown that the Jackels–Gu–Truhlar projection technique for computing harmonic frequencies along the intrinsic reaction path is equivalent to use of a new, enormously broad family of the so-called hyperplanar-vibrational-surface (HVS) reaction coordinates, namely, for any arbitrarily chosen set of internal variables σ, the appropriate HVS reaction coordinate, s^{σ}, is implicitly defined via the requirement that it remains constant on any so-called orthogonal-to-path hyperplane in the coordinate space spanned by variables σ. It is proven that s^{σ} defined in such a way satisfies the local Hofacker–Marcus conditions and therefore there is no linear term in a Taylor expansion of the potential in terms of vibrational coordinates Q^{σ}. Since the transformation from Q^{σ} and s^{σ} to σ is explicitly defined, one can use a standard technique to account for potential anharmonicities along the reaction path.

Keywords: Intrinsic reaction path – Reaction coordinate – Harmonic frequencies – Jackels–Gu–Truhlar projection technique

Introduction

One of main advantages of harmonic vibrational analysis in molecular spectroscopy is that the particular choice of vibrational coordinates in a Taylor series expansion of the molecular Hamiltonian has no effect on the values of the harmonic frequencies [1]. On the contrary, as initially pointed by the author [2] and explicitly demonstrated in Ref. [3], harmonic vibrational frequencies evaluated along a reaction path do depend on the choice of a reaction coordinate in the vicinity of the path.

A generally applicable method for computing harmonic vibrational frequencies along the gradient-following path in the space of mass-weighted Cartesian coordinates [4, 5, 6, 7] (often referred to as "intrinsic" reaction path [8]) was suggested in the broadly cited work of Miller et al. [9]. Since the method formally deals with a potential expansion in the space of mass-weighted Cartesian coordinates, it gives an impression that computation of harmonic vibrational frequencies is performed in a "universal fashion", with no need to specify the behavior of the reaction coordinate near the reaction path. It turns out that the choice of the reaction coordinate is implicitly embedded in the projection technique, which requires the nuclear displacements in space to satisfy the Eckart–Sayvetz constraints [10, 11].

As proven by the author [2], the Miller–Handy–Adams projection technique [9] is equivalent to using the so-called [2] least-squares reaction coordinate, s^{LS}, which maps each point in a space of rotating nuclear configurations to the closest point on the reaction path. (In the subspace of collinear triatomic configurations the least-squares set of variables coincides with Marcus' collision coordinates s and x [12].) As originally shown in Ref. [13], extremum conditions for the least-squares algorithm used in Ref. [2] to define the reaction coordinate s^{LS} are equivalent to the rectilinear Eckart–Sayvetz constraints [10, 11] on nuclear displacements measured relative to the body-fixed frame. Since a transformation to a body-fixed frame keeps the potential unchanged, an expansion of the potential as a Taylor series in terms of Miller–Handy–Adams generalized normal modes is equivalent to its expansion in terms of rectilinear vibrational coordinates, which are introduced via the Eckart–Sayvetz constraints [10, 11] in the body-fixed frame and therefore are internal variables by definition. Compared with the Miller–Handy–Adams approach [9] dealing with nuclear displacements in

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space, the accurate separation of internal motions from overall rotations leads to some additional kinematic coupling terms even at zero angular momentum. Contrary to the critical remarks made recently by Okuno et al. [14] (see Ref. [15] for a more detailed response), the author [2, 16] perfectly understood this deficiency of the Miller–Handy–Adams projection technique, but, as pointed out in Ref. [16], the resultant differences between the Miller–Handy–Adams [9] and Hougen–Bunker–Jones [17] Hamiltonians have only a small effect on practical computations of chemical reaction rates.

Note that a power expansion of an N-atom potential in terms of $3N{-}3$ Cartesian deviations from the reaction path in the center-of-mass system [18] would generally lead to $3N{-}3$ nonzero frequencies because infinitesimal rotations are eigenvectors of the quadratic potential form only in equilibrium configurations. As nuclei move away from a saddle point along the reaction path, some of three zero frequencies associated with infinitesimal rotations may become imaginary, whereas eigenvectors describing normal vibrations near the saddle point turn into superpositions of vibrations and infinitesimal rotations. By imposing the Eckart–Sayvetz constraints on nuclear motions in space, Miller et al. [9] managed to go around this problem.

To compute harmonic frequencies along a collinear reaction path for an atom–diatom exchange reaction, Garrett and Truhlar suggested a different, more specific recipe [19, 20], which was related by the author [21, 22] to a reaction coordinate of a special type. The latter was defined as a function of bond lengths only and was therefore referred to as the "bond-length" reaction coordinate, s^{BL}. A systematic comparison between bending vibrational frequencies associated with the two reaction coordinates, s^{LS} and s^{BL}, was performed in Ref. [3] for the collinear reactions $\mathrm{H}+\mathrm{H}_2 \rightarrow \mathrm{H}_2+\mathrm{H}$ and $\mathrm{O}+\mathrm{H}_2 \rightarrow \mathrm{OH}+\mathrm{H}$. Our analysis revealed significant deficiencies of the rectilinear approach. In particular, the bending frequency associated with the least-squares reaction coordinate rapidly vanished and even became imaginary over a wide fragment of the reaction path away from the vicinity of the saddle point. In contrast, the bending frequency computed at fixed values of bond lengths remained positive over the whole range of the reaction coordinate. Use of a similar bond-length reaction coordinate for the polyatomic reaction $\mathrm{CH}_3+\mathrm{H}_2 \rightarrow \mathrm{CH}_4+\mathrm{H}$ [3] again resulted in a much slower asymptotic change of harmonic frequencies for two of the four doubly degenerate symmetry-breaking modes, compared with the behavior of their counterparts computed using the Miller–Handy–Adams projection technique [9].

This analysis stimulated a search for a universal method, which would allow one to compute harmonic frequencies of nuclear vibrations associated with purely geometrical deformations of the molecular system in question. Such a method referred to here as the Jackels–Gu–Truhlar projection technique [23] was developed and thoroughly studied by Truhlar and collaborators in a series of the papers [23, 24, 25] covering a broad variety of chemical reactions. The purpose of this paper is to demonstrate that the Jackels–Gu–Truhlar projection technique is equivalent to the use of a new, enormously broad family of the so-called hyperplanar-vibrational-surface (HVS) reaction coordinates, s^{σ}, where the superscript σ is used to emphasize that the definition of the reaction coordinate depends on the choice of internal variables $\sigma \equiv \{\sigma^1,..., \sigma^F\}$; namely, by definition, s^{σ} remains constant on any hyperplane drawn in the space of variables σ under the constraint that it must be orthogonal to the reaction path at their crossing point. The appropriate vibrational coordinates $Q^{\sigma} \equiv \left\{Q_1^{\sigma}, \ldots, Q_\Gamma^{\sigma}\right\}$,, where $\Gamma = F{-}1$, are then introduced via simple linear relations, which visualize generalized normal modes in the Jackels–Gu–Truhlar projection technique. (It should be pointed out that the present analysis deals exclusively with $F = 3N{-}6$ independent internal variables and therefore does not cover an extension [26] of the cited projection technique [23, 24, 25] to redundant internal variables.)

By expressing the Hamiltonian in terms of Q^{σ} and s^{σ} and neglecting anharmonic terms, one can approximately separate harmonic vibrations from the large-amplitude motion along the reaction path. This justifies the use of the projection technique, which was formally introduced by Jackels et al. [23], to a large degree by analogy with the conventional Wilson GF matrix method [1] of the harmonic analysis near an equilibrium configuration. Knowing the exact transformation from $F = 3N{-}6$ independent internal variables σ to Q^{σ} and s^{σ} allows one to account for potential anharmonicities using the "independent-normal-mode" (INM) approximation [27, 28], for example.

Definition of the HVS reaction coordinate

Let $\sigma_0(s) \equiv \left\{\sigma_0^1, \ldots, \sigma_0^F\right\}$ be a reaction path in the coordinate space spanned by variables σ. (In the following we will refer to this space simply as σ space.) The so-called HVS for a point s of the path is defined via the following equation for a hyperplane in the σ space:

$$\sum_{\mu,\mu'} \left[\sigma^{\mu} - \sigma_0^{\mu}(s)\right] \boldsymbol{\Gamma}_{\mu\mu'}(s) \frac{\mathrm{d}\sigma_0^{\mu'}}{\mathrm{d}s} = 0. \tag{1}$$

It directly follows from Eq. (1) that the path crosses the hyperplane along the direction that is orthogonal to the hyperplane under the metric $\boldsymbol{\Gamma}_{\mu\mu'}$. The metric matrix $\boldsymbol{\Gamma}$ with elements $\boldsymbol{\Gamma}_{\mu\mu'}$ is chosen to be the inverse of the matrix $\mathbb{G}$ with elements

$$\mathbb{G}^{\mu\mu'} = \overline{\nabla}^{\mathrm{T}} \sigma^{\mu} \overline{\nabla} \sigma^{\mu'}, \tag{2}$$

where $\overline{\nabla}\sigma^{\mu}$ is the gradient of σ^{μ} with respect to mass-weighted Cartesian coordinates and the superscript T denotes a transported matrix (i.e., a row instead of a column in the given equation). To simplify the notation, we omit the argument σ in the definitions of matrix $\mathbb{G}$ and its inverse $\boldsymbol{\Gamma}$. Moreover, since we are only interested in values of their elements at points $\sigma = \sigma_0(s)$ lying on the reaction path, the latter are simply denoted in the following as $\mathbb{G}^{\mu\mu'}(s)$ and $\boldsymbol{\Gamma}_{\mu\mu'}(s)$, respectively, instead of $\mathbb{G}^{\mu\mu'}[\sigma_0(s)]$ and $\boldsymbol{\Gamma}_{\mu\mu'}[\sigma_0(s)]$. Since the metric $\boldsymbol{\Gamma}$ is non-Euclidean [2], the "orthogonal-to-path" hyperplane generally turns into a curved surface when transformed to another coordinate space; however, this surface is still orthogonal to the path at their crossing point (under the metric of our interest!).

Vibrational coordinates Q^σ and the reaction coordinate s^σ are then implicitly defined using the following quasi-linear relations:

$$\sigma^\mu = \sigma_0^\mu(s^\sigma) + \sum_{r=1}^{\Gamma} \boldsymbol{L}_r^\mu(s^\sigma) Q_r^\sigma \quad \text{for } \mu = 1,\dots, F, \tag{3}$$

where $\boldsymbol{L}_r^\mu(s)$ are components of Γ linear independent vectors $\boldsymbol{L}_r(s)$ orthogonal to the path at the point s, i.e.,

$$\sum_{\mu,\mu'} \boldsymbol{L}_r^\mu(\mathrm{s}) \boldsymbol{\Gamma}_{\mu\mu'}(\mathrm{s}) \frac{\mathrm{d}\sigma_0^{\mu'}}{\mathrm{d}s} = 0. \tag{4}$$

Since vibrational coordinates Q^σ describe small-amplitude oscillations near the reaction path $\sigma_0(s)$, there should be no linear term in a Taylor series expansion of V in terms of Q^σ at any point s of the path. In addition, to eliminate kinematic coupling between vibrations and large-amplitude internal motion along the reaction path [2], the reaction coordinate s^σ must satisfy [2] the so-called local Hofacker–Marcus conditions [5, 29]. As proven in Ref. [2], both requirements may be fulfilled [2] only along the so-called internal intrinsic reaction path [2, 30] governed by the equation [5]

$$\frac{\mathrm{d}\sigma_0^\mu}{\mathrm{d}s} = -\sum_{\mu'} \mathbb{G}^{\mu\mu'}(s)\, g_{\mu'}(s) / g(s) \quad \text{for} \mu = 1,\dots,F, \tag{5}$$

where $g_\mu(\mathrm{s})$ is the derivative of the potential V with respect to σ^μ at $\sigma = \sigma_0(s)$. It is worth pointing out that Eq. (5) describes a path in the space of $3N{-}6$ internal variables and therefore differs from reminiscent Eq. (9) in Marcus' pioneering paper [5] dealing with $3N$ curvilinear coordinates (including overall rotations and translational motions of the center of mass). Since matrix elements $\mathbb{G}^{\mu\mu'}$ and components of the contravariant metric tensor defined via Marcus' Eq. (4) coincide in the space of internal variables σ, whereas the potential function V is independent of external variables, our Eq. (5) is a subset of Marcus' Eq. (9). A more important difference between the two approaches, however, comes from the covariant metric tensor (see Eq. (2) in Ref. [5]), because its components associated with internal variables depend on the choice of the body-fixed frame and generally differ from matrix elements $\boldsymbol{\Gamma}_{\mu\mu'}$. As a result, to exclude external motions from Marcus' analysis [5], one needs to use matrix elements $\boldsymbol{\Gamma}_{\mu\mu'}$ instead of the appropriate components of the covariant metric tensor. If the variable s used to parameterize the path is chosen to satisfy the relation

$$\sum_{\mu,\mu'} \boldsymbol{\Gamma}_{\mu\mu'}(s) \frac{\mathrm{d}\sigma_0^\mu}{\mathrm{d}s} \frac{\mathrm{d}\sigma_0^{\mu'}}{\mathrm{d}s} \equiv 1, \tag{6}$$

then the function $g(s)$ coincides with the magnitude of the potential gradient, i.e.,

$$g(s) = \sqrt{\sum_{\mu,\mu'} \mathbb{G}^{\mu\mu'}(s)\, g_\mu(s)\, g_{\mu'}(s)}\,. \tag{7}$$

One can also represent Eqs. (5) and (7) in an equivalent form,

$$\frac{\mathrm{d}\sigma_0^\mu}{\mathrm{d}s} = -\left(\overline{\nabla}^{\mathrm{T}} \sigma^\mu \overline{\nabla} V\right)_{\bar{\mathbf{r}} = \bar{\mathbf{a}}(s)} \Big/ g(s) \quad \text{for } \mu = 1,\dots,F, \tag{8}$$

and

$$g(s) = \left.\sqrt{\overline{\nabla}^{\mathrm{T}} V \overline{\nabla} V}\right|_{\bar{\mathbf{r}} = \bar{\mathbf{a}}(s)}, \tag{9}$$

where $\bar{\mathbf{a}}(s)$ is the gradient-following path in the space of $3N$-dimensional vectors $\bar{\mathbf{r}}$ formed by mass-weighted Cartesian coordinates [4, 5, 6, 7, 8]. An analysis of Eq. (8) shows that the internal intrinsic reaction path defined via Eqs. (5) and (7) is nothing but a trace of $\bar{\mathbf{a}}(s)$ in the space of internal variables σ [2]. To eliminate the linear term in a Taylor series expansion of V, one also needs to require [2] that the reaction coordinate in question satisfies the "local" Hofacker–Marcus conditions:

$$\left(\overline{\nabla}^{\mathrm{T}} s^\sigma \overline{\nabla} Q_r^\sigma\right)_{\sigma = \sigma_0(s)} \equiv 0 \quad \text{for } r = 1,\dots,\Gamma. \tag{10}$$

In fact, representing the latter equations in an equivalent form,

$$\sum_{\mu,\mu'} \mathbb{G}^{\mu\mu'}(s) \left(\frac{\partial s^\sigma}{\partial \sigma^\mu} \frac{\partial Q_r^\sigma}{\partial \sigma^{\mu'}}\right)_{\sigma = \sigma_0(s)} \equiv 0 \quad \text{for } r = 1,\dots,\Gamma, \tag{11}$$

and combining these orthogonality conditions with the normalization condition given by Eq. (6), one finds

$$\left.\frac{\partial s^\sigma}{\partial \sigma^\mu}\right|_{\sigma = \sigma_0(s)} = \sum_{\mu'} \boldsymbol{\Gamma}_{\mu\mu'}(s) \frac{\mathrm{d}\sigma_0^{\mu'}}{\mathrm{d}s} \tag{12}$$

or, making use of Eq. (5),

$$\left.\frac{\partial s^{\sigma}}{\partial \sigma^{\mu}}\right|_{\sigma=\sigma_0(s)} = -g_{\mu}(s)/g(s). \tag{13}$$

Taking into account that

$$\left.\frac{\partial V}{\partial Q^{\sigma}}\right|_{s^{\sigma}=s,\ Q^{\sigma}=0} = \sum_{\mu} g_{\mu}(s) \left.\frac{\partial \sigma^{\mu}}{\partial Q^{\sigma}}\right|_{s^{\sigma}=s,\ Q^{\sigma}=0}, \tag{14}$$

one can immediately verify that

$$\left.\frac{\partial V}{\partial Q^{\sigma}}\right|_{s^{\sigma}=s,\ Q^{\sigma}=0} = 0, \tag{15}$$

as required.

To prove that the HVS reaction coordinate s^{σ} does satisfy Eq. (12), one simply needs to differentiate Eq. (3) with respect to σ^{μ}, put Q^{σ} equal to 0, and then substitute Eqs. (4) and (6) into the convolution of the resultant expression

$$\delta_{\mu}^{\mu'} = \frac{\mathrm{d}\sigma_0^{\mu'}}{\mathrm{d}s} \left.\frac{\partial s^{\sigma}}{\partial \sigma^{\mu}}\right|_{\sigma=\sigma_0(s)} + \sum_{r=1}^{\mathbb{\Gamma}} \boldsymbol{L}_r^{\mu'}(s) \left.\frac{\partial Q_r^{\sigma}}{\partial \sigma^{\mu}}\right|_{\sigma=\sigma_0(s)} \tag{16}$$

with the covariant vector in the right-hand side of Eq. (12). This completes the proof, since Hofacker–Marcus conditions (Eq. 11) are automatically fulfilled if a reaction coordinate satisfies Eq. (12).

Let us put

$$\boldsymbol{L}_F^{\mu}(s) \equiv \frac{\mathrm{d}\sigma_0^{\mu}}{\mathrm{d}s}, \tag{17}$$

so that the $\mathbf{F} \times \mathbf{F}$ matrix $\boldsymbol{L}(s)$ with elements $\boldsymbol{L}_j^{\mu}(s)$ is formed by first derivatives of σ^{μ} with respect to Q^{σ} and s^{σ} at $Q^{\sigma}=0$ and $s^{\sigma}=s$. By using the appropriate $\Gamma \times \Gamma$ s-dependent linear transformation, one can also choose the first $F-1$ columns of this matrix to be mutually orthogonal and normalized under the metric $\mathbb{\Gamma}_{\mu\mu'}(s)$ so that

$$\sum_{\mu,\mu'} \boldsymbol{L}_r^{\mu}(s) \mathbb{\Gamma}_{\mu\mu'}(s)\ \boldsymbol{L}_{r'}^{\mu'}(s) \equiv \delta_{rr'} \quad \text{for } r,r' = 1,\ldots,\Gamma. \tag{18}$$

By combining the latter relation with Eqs. (4) and (6), one finds

$$\boldsymbol{L}^{\mathrm{T}}(s)\mathbb{\Gamma}(s)\ \boldsymbol{L}(s) \equiv \mathbf{1}_{\mathrm{F}}, \tag{19}$$

where $\mathbf{1}_{\mathrm{F}}$ is the $F \times F$ identity matrix. An analysis of the inverse relation,

$$\boldsymbol{L}^{-1}(s)\ \mathbb{G}(s)\ \left[\boldsymbol{L}^{-1}(s)\right]^{\mathrm{T}} \equiv \mathbf{1}_{\mathrm{F}}, \tag{20}$$

shows that the $\Gamma \times \Gamma$ matrix $\mathbf{G}(s)$ with elements

$$G_{rr'}(s) \equiv \sum_{\mu,\mu'} \mathbb{G}^{\mu\mu'}(s) \left(\frac{\partial Q_r^{\sigma}}{\partial \sigma^{\mu}} \frac{\partial Q_{r'}^{\sigma}}{\partial \sigma^{\mu'}}\right)_{\sigma=\sigma_0(s)} \tag{21}$$

coincides with the identity matrix at each point of the reaction path, i.e.,

$$G_{rr'}(s) \equiv \delta_{rr'}. \tag{22}$$

For each values of s one can find a $\Gamma \times \Gamma$ orthogonal matrix, which (in following the conventional harmonic analysis of molecular systems [1]) diagonalizes the force matrix $\mathbf{F}(s)$ with elements

$$F_{rr'}(s) \equiv \left(\frac{\partial^2 V}{\partial Q_r^{\sigma} \partial Q_{r'}^{\sigma}}\right)_{s^{\sigma}=s,\ Q^{\sigma}=0}, \tag{23}$$

so that

$$F_{rr'}(s) = \Lambda_r(s)\delta_{rr'}. \tag{24}$$

We thus conclude that the coefficients $\boldsymbol{L}_r^{\mu}(s)$ in transformation in Eq. (3) can be always chosen to satisfy Eqs. (22) and (24), where the matrices $\mathbf{G}$(s) and $\mathbf{F}(s)$ are defined via Eqs. (21) and (23), respectively. Keeping in mind the erroneous [15] comments by Okuno et al. [14], it is worth pointing out once again [2, 3] that the matrix $\mathbf{G}(s)\mathbf{F}(s)$ undergoes an s-dependent similarity transformation under any linear transformation of vibrational coordinates at a fixed value of the reaction coordinate and therefore its eigenvalues must remain unchanged regardless of which set of vibrational coordinates is used to compute harmonic frequencies.

It will be shown in next section that diagonal elements of the matrix $\mathbf{F}(s)$ coincide with nonzero diagonal elements Λ_{rr} of the matrix Λ in the right-hand side of Eq. (22) in Ref. [23], which implies that the Jackels–Gu–Truhlar projection technique can be used as a useful practical tool for computing the harmonic vibrational frequencies

$$\omega_r^{\sigma}(s) = \Lambda_r^{1/2}(s) \tag{25}$$

associated with the reaction coordinate s^{σ}. (To be fully consistent, we should also mark the matrix $\mathbf{F}(s)$, its matrix elements $F_{rr'}(s)$ and its eigenvalues $\Lambda_r(s)$ by the superscript σ; however, for simplicity we will keep it only in the notation of harmonic frequencies $\omega_r^{\sigma}(s)$ to be able to distinguish between computations using different sets of internal variables.)

Numerical equivalence of the two algorithms for compuing harmonic frequencies along the intrinsic reaction path

Let us now prove that each column of the matrix $\boldsymbol{L}(s)$ is an eigenvector of the matrix

$$\mathbb{K}^{\mathrm{P}}(s) \equiv \mathbb{G}(s)\, \mathbb{F}^{\mathrm{P}}(s), \tag{26}$$

used in the Jackels–Gu–Truhlar projection technique [23] to compute harmonic vibrational frequencies along the reaction path. Here we put

$$\mathbb{F}^{\mathrm{P}}(s) \equiv \left[\mathbf{1}_{\mathrm{F}} - \mathbb{P}^{\mathrm{T}}(s)\right] \mathbb{F}(s)[\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)], \tag{27}$$

where $\mathbb{F}(s)$ is an $F \times F$ force constant matrix with elements

$$\mathbb{F}_{\mu\mu'}(s) = \left(\frac{\partial^2 V}{\partial\sigma^{\mu}\partial\sigma^{\mu'}}\right)_{\sigma=\sigma_0(s)} \tag{28}$$

and $\mathbb{P}(s)$ is the projection matrix with elements

$$\mathbb{P}^{\mu}_{\mu'}(s) = g_{\mu'}(s)\sum_{\mu''}\mathbb{G}^{\mu\mu''}(s)g_{\mu''}(s)/g^2(s) \tag{29a}$$

i.e., the matrix $\mathbf{h}^*(s)\mathbf{p}(\mathrm{s})$ in Eq. (21) of Jackels et al. [23]. Making use of Eqs. (5) and (13), one can also represent these matrix elements in an equivalent form:

$$\mathbb{P}^{\mu}_{\mu'}(s) = \frac{d\sigma_0^{\mu}}{ds}\frac{\partial s_{\sigma}}{\partial\sigma^{\mu'}}\bigg|_{\sigma=\sigma_0(s)}, \tag{29b}$$

and hence the last column of $\boldsymbol{L}(s)$ (see Eq. 17) is an eigenvector of matrix $\mathbb{K}^{\mathrm{P}}(s)$ associated with a zero eigenvalue.

It is a little more difficult to prove that other columns $\boldsymbol{L}_r(s)$ of $\boldsymbol{L}(s)$, with $r < F$, are eigenvectors of matrix $\mathbb{K}^{\mathrm{P}}(s)$ associated with its positive eigenvalues. To do it, let us first represent the latter matrix in a slightly different, but equivalent, form:

$$\mathbb{K}^{\mathrm{P}}(s) = [\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)]\ \mathbb{K}(s)[\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)], \tag{30}$$

which is reminiscent of Eq. (1.5a) of Miller et al. [9]. Here we put

$$\mathbb{K}(s) \equiv \mathbb{G}(s)\,\mathbb{F}(s) \tag{31}$$

and also took into account that, according to Eqs. (12) and (29b), $\mathbb{P}(s)\mathbb{G}(s)$ is a symmetric matrix. (Note that similar arguments were used in Ref. [15] to prove that Okuno's projected covariant Hessian matrix approach [31] is equivalent to the covariant Hessian matrix formalism suggested by the author [30].) Taking into account that

$$\left(\frac{\partial\sigma^{\mu}}{\partial Q^{\sigma}_{r}}\right)_{s^{\sigma}=s} = \boldsymbol{L}^{\mu}_{r}(s) \tag{32}$$

and making use of Eq. (29b), one finds that

$$[\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)]\boldsymbol{L}_{\mathrm{r}}(s) \equiv \boldsymbol{L}_{\mathrm{r}}(s)\ \text{ for } r = 1, 2, \ldots, \Gamma. \tag{33}$$

Since each column of the matrix $\boldsymbol{L}(s)$ is formed by derivatives of one of the variables σ with respect to Q^{σ}_{r} and s^{σ} (the first $F-1$ elements of the given column and its last element, respectively, with all derivatives computed at $Q^{\sigma}=0$ and $s^{\sigma}=s$), the rth row of the inverse matrix $\boldsymbol{L}^{-1}(s)$ is composed (for any $r < F$) by derivatives of Q^{σ}_{r} with respect to σ at $\sigma=\sigma_0(s)$ so that

$$\left\{\boldsymbol{L}^{-1}(s)[\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)]\right\}_{r\mu} = \left(\frac{\partial Q^{\sigma}_{r}}{\partial\sigma^{\mu}}\right)_{s^{\sigma}=s,\ Q^{\sigma}=0} \quad \text{for } r<F, \tag{34}$$

and hence, making use of Eqs. (11), (21), and (22),

$$\left\{\boldsymbol{L}^{-1}(s)[\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)]\ \mathbb{G}(s)\right\}^{\mu}_{r} = \boldsymbol{L}^{\mu}_{r}(s)\ \text{ for } r<F. \tag{35}$$

Taking into account that second derivatives of σ with respect to Q^{r}_{σ} are identically equal to zero, one can easily verify that

$$F_{rr'}(\mathrm{s}) \equiv \boldsymbol{L}^{\mathrm{T}}_{r}(\mathrm{s})\,\mathbb{F}(\mathrm{s})\boldsymbol{L}_{r'}(\mathrm{s}) \tag{36}$$

(contrary to a general expression, which also contains first derivatives of the potential in its right-hand side) and therefore Eq. (24) can be represented as

$$\boldsymbol{L}^{\mathrm{T}}_{r}(s)\,\mathbb{F}(s)\boldsymbol{L}_{r'}(s) = \Lambda_r(s)\delta_{rr'}. \tag{37}$$

By combining Eq. (35) with Eqs. (30) and (31) and making use of Eq. (37), one finds

$$\left\{\boldsymbol{L}^{-1}(s)\mathbb{K}^{\mathrm{P}}(s)\boldsymbol{L}(s)\right\}_{rr'} = \Lambda_r(s)\ \delta_{rr'} \quad \text{for } r,r'<F. \tag{38}$$

One can also verify that

$$\left\{\boldsymbol{L}^{-1}(s)\mathbb{K}^{\mathrm{P}}(s)\boldsymbol{L}(s)\right\}_{Fr'} \equiv 0 \quad \text{for } r'<F, \tag{39}$$

taking into account that the last row of the matrix $\boldsymbol{L}^{-1}(s)$ is formed by derivatives of s_{σ} with respect to σ^{μ} at $s^{\sigma}=s$ and $Q^{\sigma}=0$, and therefore

$$\left\{\boldsymbol{L}^{-1}(s)\ [\mathbf{1}_{\mathrm{F}} - \mathbb{P}(s)]\right\}^{\mu}_{F} \equiv 0. \tag{40}$$

This completes the proof that each column of $\boldsymbol{L}(s)$ is an eigenvector of the matrix $\mathbb{K}^{\mathrm{P}}(s)$ such that the appropriate eigenvalue coincides with a diagonal element of the matrix $\mathbf{F}(s)$ for the first $F-1$ columns and is equal to zero for the last one.

By representing Eq. (20) in an equivalent form,

$$\boldsymbol{L}(s)\boldsymbol{L}^{\mathrm{T}}(s) \equiv \mathbb{G}(s), \tag{41}$$

(similar to Eq. (23) in Ref. [23]), one finds that the normalization of eigenvectors is done here in exactly the same way as in Ref. [23], so that columns of the matrix $\boldsymbol{L}(s)$ must coincide with normalized eigenvectors describing generalized normal modes in the Jackels–Gu–Truhlar approach [23]. Assuming that the matrix $\mathbf{F}(s)$ has only nonzero eigenvalues and that all its eigenvalues are nondegenerate, we can use directly the normalized eigenvectors associated with nonzero eigenvalues in the Jackels–Gu–Truhlar projection technique [23] to define the transformation in Eq. (3). The Jackels–Gu–Truhlar algorithm can be thus viewed as an efficient utilization of a general approach to separate vibrations from a large-amplitude motion along the intrinsic reaction path [2], namely, the appropriate harmonic frequencies can be obtained by expressing the Hamiltonian in terms of internal variables Q^σ and s^σdefined via Eq. (3) and then neglecting both potential and kinematic vibrational anharmonicities in the neighborhood of the reaction path. It is worth pointing out again that there is no linear term in the expansion of a potential as a Taylor series of Q^σ, since the reaction coordinate s^σ satisfies the local Hofacker–Marcus conditions.

Incorporation of vibrational anharmonicities into computations of partition functions

The main advantage of the scheme dealing with approximate separation of motions (compared with projection techniques [9, 23]) is that neglected terms can be brought back using perturbation theory, for instance. It was Garrett and Truhlar [32] who emphasized the importance of incorporating bending anharmonicity in computations of transition-state rate constants of atom–diatom exchange reactions. It was explicitly demonstrated that correction of the bending partition function for quartic bending anharmonicity using energy levels of the harmonic-quartic oscillator [33] significantly improved the computation accuracy. This idea was later extended to polyatomic reactions within the INM approximation [27, 28] using energy levels of Morse and quadratic-quartic oscillators for stretching and bending modes, respectively.

As emphasized by Jackels, et al. [23], the use of deviations of bond lengths and bending angles from their values on the reaction path, instead of rectilinear vibrational coordinates, "reduces the importance of anharmonic bend–stretch interactions" [34, 35] (especially, if stretching and bending modes are separable in the harmonic approximation, as it happens for a collinear reactions path, for example).

If couplings between different modes are not negligible, they can be included using the Dunham formula for the quantized total energy [36]. As pointed out by Truhlar et al. [35], use of this formula allows one to "obtain reasonable simple analytical approximations to the vibrational partition functions and free-energy contributions by power-series methods and by definition of effective frequencies that take into account the leading anharmonic corrections under the assumption that anharmonic terms are small" (see Ref. [35] for the appropriate references). It is worth mentioning that computation of high-order derivatives of a potential with respect to Q^σ at a fixed value of the reaction coordinate s^σ is simplified by the fact that each *k*th-order derivative with respect to Q^σ is a superposition of only *k*th-order derivatives with respect to σ (contrary to a general transformation of derivatives from one set of coordinates to another, which also contains all lower-order derivatives).

Conclusions

It is proven that the Jackels–Gu–Truhlar projection technique is equivalent to choosing a reaction coordinate s^σ of a special type, which depends on the particular choice of internal variables σ. Since the reaction coordinate satisfies the local Hofacker–Marcus conditions, there is no linear term in a Taylor expansion of the potential in terms of vibrational coordinates Q^σ. Potential anharmonicities can be then taken into account either via the INM approximation [34, 35] or via the Dunham formula for the quantized total energy [36].

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References

1. Wilson EB Jr, Decius JC, Cross PC (1955) Molecular vibrations. McGraw-Hill, New York
2. Natanson GA (1982) Mol Phys 46: 481
3. Natanson GA, Garrett BC, Truong TN, Joseph T, Truhlar DG (1991) J Chem Phys 94: 7875
4. Shavitt I (1959) University of Wisconsin Theoretical Chemistry Laboratory Technical Report No WIS-AEC-23. University of Wisconsin, Madison, WI
5. Marcus RA (1964) J Chem Phys 41: 610
6. Shavitt I (1968) J Chem Phys 49: 4048
7. Truhlar DG, Kuppermann A (1971) J Am Chem Soc 93: 1840
8. Fukui K (1974) In: Daudel R, Pullman B (eds) The world of quantum chemistry. Reidel, Dordrecht, p 113
9. Miller WH, Handy NC, Adams JE (1980) J Chem Phys 72: 99
10. Eckart C (1935) Phys Rev 47: 552
11. Sayvetz A (1939) J Chem Phys 7: 383
12. Marcus RA (1966) J Chem Phys 45: 4493
13. Natanson GA, Adamov MN (1974) Vestn Leningr Univ 10: 24 (in Russian)
14. Okuno Y, Yokoyama S, Mashiko S (2000) J Chem Phys 113: 3136
15. Natanson GA (2002) J Chem Phys 117: 6378
16. Natanson GA (1992) Chem Phys Lett 190: 209
17. Hougen JT, Bunker PR, Johns JWC (1970) J Mol Spectrosc 34: 136
18. Garrett BC, Truhlar DG (1979) J Chem Phys 70: 1593
19. Garrett BC, Truhlar DG (1979) J Am Chem Soc 101: 4534
20. Garrett BC, Truhlar DG (1980) J Chem Phys 72: 3460
21. Natanson GA (1988) Chem Phys Lett 149: 551
22. Natanson GA (1991) J Chem Phys 94: 7875
23. Jackels CF, Gu Z, Truhlar DG (1995) J Chem Phys 102: 3188
24. Nguyen KA, Jackels CF, Truhlar DG (1996) J Chem Phys 104: 6491
25. Chuang Y-Y, Truhlar DG (1997) J Chem Phys 107: 83
26. Chuang Y-Y, Truhlar DG (1998) J Phys Chem 102: 242
27. Isaacson AD, Truhlar DG (1982) J Chem Phys 76: 1380
28. Truhlar DG, Isaacson AD, Garrett BC (1985) In: Baer M (ed) Theory of chemical reaction dynamics, vol 4. CRC, Boca Raton, FL, pp 65–137
29. Hofacker GL (1963) Z Naturforsch A 18: 607

30. Natanson GA (1991) Chem Phys Lett.178: 49
31. Okuno Y (2000) J Chem Phys 113: 3130
32. Garrett BC, Truhlar DG (1979) J Phys Chem 83: 1915
33. Truhlar DG (1971) J Mol Spectrosc 38: 415
34. Isaacson AD, Truhlar DG, Scanlon K, Overrend J (1981) J Chem Phys 75: 3017
35. Truhlar DG, Brown FB, Steckler R, Isaacson AD (1986) In: Clary DC (ed) Theory of chemical reaction dynamics. Reidel, Dordrecht, pp 285–329
36. Dunham JL (1932) Phys Rev 41: 721