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Extended Hessian Matrix Along the Reaction Coordinate

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We shall prove by the coordinate-free covariant treatment that the vibrational frequency along the reaction coordinate is exactly given by the extended Hessian matrix in a rigged configuration space where the reaction coordinate is identified with a "straight line". The diagonalization of the extended Hessian matrix is straightforward with no recourse to the prescribed procedure of eliminating the coupling matrix elements between the promoting mode of chemical reaction and the vibrational modes.

Key words: Extended Hessian matrix – Vibration theory – Rigged Riemannian space – Intrinsic reaction coordinate (IRC) approach.

1. Introduction

In the study of chemical reaction dynamics, the notion of reaction coordinate [1] has played an important role for the reduction of complicated phenomena of reaction dynamics. Especially, the IRC (intrinsic reaction coordinate) presented by Fukui [2] has been useful in this direction of research [3]; the covariant nature of the IRC equation guarantees the coordinate-free character of the notion of the reaction coordinate [4]. The reaction dynamics along the reaction coordinate has been studied in terms of the intrinsic dynamism, and the introduction of the "extended" Hessian matrix plays an important role in order to analyze the vibrational degrees of freedom along the reaction coordinate [4, 5]. An intrinsic principle of least action has been proposed for the intrinsic dynamism, and as the stationary trajectory, the IRC draws a particular geodesic curve in a rigged configuration space [6]. The minimum character of the variational principles of the IRC-approach to chemical reaction has also been investigated [7].

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The progress of chemical reaction is conveniently described by the variation of the adiabatic potential energy U which is a function of n generalized coordinates: $U = U(q^1, \ldots, q^n)$ (n is $3N-6$, N being the number of nuclei). Note that the configuration space of the adiabatic potential is Riemannian and it is not always possible to find out the appropriate orthogonal coordinate system [4]. In the n-dim Riemannian configuration space R_n, the reaction coordinate cannot be identified with the path of minimum distance between a pair of termini of chemical reaction. But, in a special configuration space, namely the rigged Riemannian configuration space R_n^* [6], the reaction coordinate is provided with the special character of the path of minimum distance, i.e. the "straight line" between a pair of termini of chemical reaction [6, 7].

On the other hand, the vibrational modes along the reaction coordinate have been analyzed only in R_n [4–6]. Then, it has been pointed out that the vibrational modes are not obtained by the straightforward diagonalization of the extended Hessian matrix; this is because the direction of the reaction coordinate is not necessarily parallel to one of the eigenvectors of this matrix. So, we should trace the following process: (1) find out the direction of the reaction coordinate, (2) neglect the off-diagonal matrix elements which couple the motion along the reaction coordinate and the other vibrational motions perpendicular to the reaction coordinate, and (3) diagonalize the "reduced" Hessian matrix to obtain the normal vibrational modes along the reaction coordinate. In this process, it should be noted that the matrix to be diagonalized is not the full one but the "reduced" one.

In the present paper, we shall show that in the rigged Riemannian configuration space R_n^*, the reduction process (1)–(3) is not necessary and the straightforward diagonalization of the extended Hessian matrix exactly gives the normal vibrational modes along the reaction coordinate.

2. Theory

In the n-dim Riemannian configuration space, the extended Hessian matrix is defined by [4]

$$H_{ij} = \partial^2 U/\partial q^i \partial q^j - \Gamma_{ij}^k \partial U/\partial q^k \qquad (i, j = 1, \ldots, n), \tag{2.1}$$

and, in the operator form [6], this is represented by

$$|\boldsymbol{e}^i > H_{ij} < \boldsymbol{e}^j|. \tag{2.2}$$

Γ_{ij}^k is the Christoffel symbol of second kind and $\boldsymbol{e}^i$ is the basis vector. Note that the extended Hessian matrix is a covariant tensor of second kind [4]; if the transformation of coordinates $q^1, \ldots, q^n \to q'^1, \ldots, q'^n$ is performed, then the new covariant component is given by

$$H'_{ij} = H_{rs}(\partial q^r/\partial q'^i)(\partial q^s/\partial q'^j). \tag{2.3}$$

We shall examine the geometrical property of this matrix in two kinds of configuration spaces, R_n and R_n^*; the metric tensor of R_n is described by a_{ij}', and that of R_n^* by g_{ij} [6].

2.1. *Extended Hessian Matrix in R_n*

In the study of reaction dynamics along the reaction coordinate, the reduced Hessian matrix plays an important role. This matrix is constructed by eliminating the off-diagonal matrix elements of the extended Hessian matrix between the reaction coordinate and the other coordinates perpendicular to the reaction coordinate. In the operator form, this is represented by

$$|e'^{i}(a)>\bar{H}'_{ij}(a)<e'^{j}(a)| \tag{2.4}$$

(hereafter in the present paper, the geometrical quantities related to the particular metric tensors a_{ij} or g_{ij} are emphasized by a or g, respectively, in parentheses), where

$$\begin{aligned} \bar{H}'_{ij}(a) &\equiv H'_{ij}(a) \qquad (i, j = 1, \ldots, n-1), \\ &\equiv 0 \qquad \text{(otherwise).} \end{aligned} \tag{2.5}$$

The primed coordinate system is particularly chosen so that the reaction coordinate is the nth coordinate. If we diagonalize the reduced Hessian matrix, then we have $n-1$ eigenvalues corresponding to the vibrational modes (reduced) along the reaction coordinate [4]:

$$\bar{\mu}_1(a), \ldots, \bar{\mu}_{n-1}(a). \tag{2.6}$$

It should be noted here that if we add an operator

$$-|e'^{n}(a)>H'_{nn}(a)<e'^{n}(a)|$$

to (2.4), the spectra (2.6) of the reduced Hessian operator are invariant (hereafter in the present paper, n is not the dummy index to be summed over); so, the matrix of the amended operator may also be called the reduced Hessian again. This amendment is adopted so as to obtain the most simplifized form of the coordinate-free covariant representation of the reduced Hessian matrix in R_n (see Appendix); after the amendment, we have

$$|e^{i}(a)>\bar{H}_{ij}(a)<e^{j}(a)| \equiv |e'^{i}(a)>\bar{H}'_{ij}(a)<e'^{j}(a)| - |e'^{n}(a)>H'_{nn}(a)<e'^{n}(a)|. \tag{2.7}$$

Here, $\bar{H}_{ij}(a)$ is the coordinate-free covariant representation of the reduced Hessian matrix:

$$\bar{H}_{ij}(a) = \partial^2 U/\partial q^i\,\partial q^j - \{1/\Delta_1 U(a)\}u_{ij} - \Gamma^k_{ij}(a)\,\partial U/\partial q^k + \{1/\Delta_1 U(a)\}\gamma_{ij}, \tag{2.8a}$$

where

$$\begin{aligned} u_{ij} = {} & (\partial^2 U/\partial q^i\,\partial q^r)(a^{rs}\,\partial U/\partial q^s)(\partial U/\partial q^j) \\ & + (\partial U/\partial q^i)(a^{rs}\,\partial U/\partial q^s)(\partial^2 U/\partial q^r\,\partial q^j), \end{aligned} \tag{2.8b}$$

$$\begin{aligned}\gamma_{ij} = {} & \Gamma^k_{ir}(a)(\partial U/\partial q^k)(a^{rs}\,\partial U/\partial q^s)(\partial U/\partial q^j) \\ & +(\partial U/\partial q^i)(a^{rs}\,\partial U/\partial q^s)\Gamma^k_{rj}(a)(\partial U/\partial q^k),\end{aligned} \tag{2.8c}$$

$\Delta_1 U(a)$ being Beltrami's differential parameter of first kind with respect to the adiabatic potential:

$$\Delta_1 U(a) = a^{ij}(\partial U/\partial q^i)(\partial U/\partial q^j). \tag{2.8d}$$

The number of eigenvalues of this matrix now becomes n, $n-1$ of them being the same as in (2.6):

$$\bar{\mu}_1(a), \ldots, \bar{\mu}_{n-1}(a), -\bar{\mu}_n(a)(=-H'_{nn}(a)). \tag{2.9}$$

Note that the reduced Hessian matrix $\bar{H}_{ij}(a)$ obtained in (2.8) is also a covariant tensor of second order and this representation is valid for any coordinate system employed to describe the chemical reaction process.

2.2. *Extended Hessian Matrix in R_n^**

Now, let us obtain the extended Hessian matrix in R_n^*. Since the eigenvalues themselves do not depend on the particular representation of the matrix, we shall represent the extended Hessian matrix in terms of the basis vectors in R_n for the sake of simplicity. Then, the matrix element has the form of (2.1) apart from the Christoffel symbol of second kind: $\Gamma^k_{ij}(g)$ in R_n^* is not identical to that $\Gamma^k_{ij}(a)$ in R_n but is given by

$$\Gamma^k_{ij}(g) = \Gamma^k_{ij}(a) + \{1/\Delta_1 U(a)\}\Delta^k_{ij}, \tag{2.10a}$$

where

$$\begin{aligned}\Delta^k_{ij} = {} & (\partial^2 U/\partial q^i \partial q^r)(a^{rs}\partial U/\partial q^s)\delta^k_j + \delta^k_i(\partial^2 U/\partial q^j \partial q^r)(a^{rs}\partial U/\partial q^s) \\ & -a_{ij}(a^{kr}\partial^2 U/\partial q^r \partial q^s)(a^{st}\partial U/\partial q^t) - \Gamma^r_{is}(a)(\partial U/\partial q^r)(a^{st}\partial U/\partial q^t)\delta^k_j \\ & -\delta^k_i \Gamma^r_{js}(a)(\partial U/\partial q^r)(a^{st}\partial U/\partial q^t) + a_{ij}a^{kr}\Gamma^s_{rt}(a)(\partial U/\partial q^s)(a^{tu}\partial U/\partial q^u).\end{aligned} \tag{2.10b}$$

Using (2.1), (2.10), and (2.8), it is found that the extended Hessian matrix in R_n^* is nothing but the reduced Hessian matrix in R_n apart from a constant matrix ca_{ij}:

$$H_{ij}(g) = \bar{H}_{ij}(a) + ca_{ij}, \tag{2.11a}$$

where the constant c is given by

$$\begin{aligned}c = {} & \{1/\Delta_1 U(a)\}[(a^{kr}\partial^2 U/\partial q^r \partial q^s)(a^{st}\partial U/\partial q^t)(\partial U/\partial q^k) \\ & -a^{kr}\Gamma^s_{rt}(a)(\partial U/\partial q^s)(a^{tu}\partial U/\partial q^u)(\partial U/\partial q^k)].\end{aligned} \tag{2.11b}$$

This demonstrates the following theorem:

Theorem. The vibrational frequency along the reaction coordinate is given by diagonalizing the extended Hessian matrix in R_n^*.

The eigenvalues of the extended Hessian matrix in R_n^* differ from those of the reduced Hessian matrix in R_n by the *constant* c:

$$\mu_i(g) = \bar{\bar{\mu}}_i(a) + c \qquad (i = 1, \ldots, n), \tag{2.12}$$

where $\bar{\bar{\mu}}_i(a)$ is the ith eigenvalue of the reduced Hessian matrix in R_n. Since the constant c is nothing but the $\bar{\mu}_n(a)$ in (2.9),

$$c = \bar{\mu}_n(a), \tag{2.13}$$

the eigenvalues of the extended Hessian matrix in R_n^* are related to those in (2.9) as follows:

$$\bar{\mu}_1(a) + c, \ldots, \bar{\mu}_{n-1}(a) + c, 0. \tag{2.14}$$

3. Example

Here we shall elucidate the present theory by a simple model potential using a 2-dim orthogonal coordinate system $\{x, y\}$. The analytical form of the potential is as follows [4]:

$$U(x, y) = (1/a^2)x^2(x-1)^2 + (1/b^2)y^2. \tag{3.1}$$

The metric tensor g_{ij} of R_2^* is given by

$$g_{ij} = \Delta_1 U(a)\delta_{ij}, \tag{3.2a}$$

with

$$\Delta_1 U(a) = (4/a^4)x^2(x-1)^2(2x-1)^2 + (4/b^4)y^2. \tag{3.2b}$$

The extended Hessian matrix in R_2^* is then given by using (2.1) and (2.10) as follows:

$$H_{ij}(g) = \{1/\Delta_1 U(a)\}\{a^2 + 6b^2(x-\alpha_+)(x-\alpha_-)\}(8/a^6b^6)h_{ij}, \tag{3.3a}$$

where

$$h_{11} = a^4y^2, \qquad h_{22} = b^4x^2(x-1)^2(2x-1)^2,$$

$$h_{12} = h_{21} = -a^2b^2x(x-1)(2x-1)y, \tag{3.3b}$$

and

$$\alpha_\pm = (3 \pm \sqrt{3})/6. \tag{3.3c}$$

Thus, the eigenvalues of this matrix are obtained as

$$\mu_1(g) = (2/b^2) + (12/a^2)(x-\alpha_+)(x-\alpha_-), \qquad \mu_2(g) = 0. \tag{3.4}$$

Note that the constant c is now given by using (A.1d) as

$$c = \{1/\Delta_1 U(a)\}[(48/a^6)x^2(x-1)^2(2x-1)^2(x-\alpha_+)(x-\alpha_-) + (8/b^6)y^2]. \tag{3.5}$$

Accordingly, using (2.14), (3.4), and (3.5), the force constant $\bar{\mu}_1(a)$ of the normal vibration along the reaction coordinate should be

$$\bar{\mu}_1(a) = \{(12/a^2)(x-\alpha_+)(x-\alpha_-)\bar{f}^2 + (2/b^2)\bar{g}^2\}/(\bar{f}^2 + \bar{g}^2), \tag{3.6a}$$

with

$$\begin{aligned} \bar{f} &= (2/b^2)/(2/a^2)x(x-1)(2x-1), \\ \bar{g} &= 1/y, \end{aligned} \tag{3.6b}$$

which is identical to the previously obtained result of $\bar{\mu}_1(a)$: see (6.3)–(6.5) of [5].

Table 1. Meta-IRC and the normal modes along the reaction coordinate for the system H_2O which belongs to the point group C_{2v}

$\Delta\tau$[a]	$\Delta q^{1,2}$[b]	Δq^3[c]	Eigenvalues[d] and eigenvectors[e]					
0.0	0.0	5.0	$\bar{\mu}_1$	3955.485	$\bar{\mu}_2$	3391.715	$\bar{\mu}_3$	2046.284
			v^1	0.733370		0.698154		0.171783
			v^2	−0.733370		0.698154		0.171783
			v^3	0.0		−0.448677		1.465164
−1.0	−0.00016	4.92011		3955.281		3431.901		2016.299
				0.733342		0.701363		0.158302
				−0.733342		0.701363		0.158302
				0.0		−0.420452		1.473713
−2.0	−0.00030	4.84148		3955.080		3468.168		1987.057
				0.733315		0.704148		0.145551
				−0.733315		0.704148		0.145551
				0.0		−0.393716		1.481255
−3.0	−0.00043	4.76410		3954.881		3500.890		1958.689
				0.733288		0.706558		0.133513
				−0.733288		0.706558		0.133513
				0.0		−0.368443		1.487895
−4.0	−0.00054	4.68794		3954.685		3530.411		1931.298
				0.733261		0.708636		0.122166
				−0.733261		0.708636		0.122166
				0.0		−0.344594		1.493729
−5.0	−0.00064	4.61298		3954.492		3557.042		1904.965
				0.733235		0.710421		0.111486
				−0.733235		0.710421		0.111486
				0.0		−0.322124		1.498847
	0.0	0.0		3942.204		3831.998		1648.313
				0.731591		0.719627		−0.040902
				−0.731591		0.719627		−0.040902
				0.000000		−0.000975		1.528605

[a] Accumulation time of reaction: see (3.18) of [5] (in $\mathrm{sec}^2\mathrm{amu/kg} = 1.66057 \times 10^{-27}\ \mathrm{sec}^2$).

[b] Deviation of the OH distance from its equilibrium value: $\Delta q^{1,2} = q^{1,2} - q^{1,2}_{\mathrm{eq}}$ (in Å).

[c] Deviation of the angle ∡HOH from its equilibrium value: $\Delta q^3 = q^3 - q^3_{\mathrm{eq}}$ (in deg).

[d] Vibrational frequency along the reaction coordinate (in cm^{-1}).

[e] The eigenvectors are normalized in R_3, not in R_3^*.

Another example is the general case of non-orthogonal internal coordinates for the system H_2O which belongs to the point group C_{2v}. The internal coordinates of the present problem are given by $q^1 = q^2$ (OH distance) and q^3 ($\measuredangle$HOH). The adiabatic potential energy is approximately given by Wilson's F-matrix treatment [8, 9]: the geometrical parameters used in the present paper are $q_{\text{eq}}^{1,2} = 0.9572$ Å, $q_{\text{eq}}^3 = 104°32'$, $f_{11} = = 8.454$ md/Å, $f_{13} = 0.224$ md, $f_{33} = 0.6971$ md Å and $f_{12} = -0.100$ md/Å. In Table 1, we shall show 1) the solution of the reaction coordinate, which is designated as meta-IRC [4], and 2) the eigenvalues and eigenvectors of the extended Hessian matrix along the reaction coordinate. At the bottom of Table 1, the results of the usual Hessian-matrix theory at the stable equilibrium configuration are shown. As the reaction coordinate approaches the stable equilibrium configuration, the normal modes of the extended Hessian matrix in R_3^* smoothly converge to those of the usual Hessian matrix in R_3. In particular, the reaction coordinate, which is the third normal mode of the extended Hessian matrix in R_3^*, converges to the weakest normal mode at the stable equilibrium configuration: this assures the *Stable Limit Theorem* [5].

4. Discussion

We have presented the coordinate-free covariant theory of the extended Hessian matrix along the reaction coordinate. This enables us to obtain the vibrational modes of chemical reaction along the reaction coordinate at any non-equilibrium structure of the reaction system.

It should be noted that, at the equilibrium structure of molecule, (1) the extended Hessian matrix becomes identical to the usual Hessian matrix [4], and (2) the normal vibrational modes of a molecule are obtained by diagonalizing the usual Hessian matrix. Therefore, the present result obtained above is considered to be the extension of the Hessian-matrix theory of equilibrium molecule to the non-equilibrium process of chemical reaction dynamics.

The inclusion of the translational and the rotational degrees of freedom to the present treatment is trivial; since the rotational coordinates are not orthogonal to the internal coordinates, the final form of the extended Hessian matrix is *not* the extended Hessian matrix in the enlarged coordinate system *but* the embedded one of the extended Hessian matrix which is defined in the internal coordinate system, whose embedding process is of course not performed by the orthogonal transformation at all.

In conclusion, the present theory unifies (1) the theory of the reaction coordinate (the promoting mode of chemical reaction), and (2) the theory of the extended Hessian matrix (the reduced normal vibrational modes along the reaction coordinate): in the rigged Riemannian space R_n^* in the ultimately natural manner.

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Appendix

If an orthogonal coordinate system is available, the representation of the extended Hessian matrix is more simplified. Let the particular orthogonal coordinate system be written as $\{x^1, \ldots, x^n\}$, then the extended Hessian matrix in R_n^* can be represented in the form of (2.11) as follows:

$$H_{ij}(g) = \partial^2 U/\partial x^i \, \partial x^j - \{1/\Delta_1 U(a)\} u_{ij} + c\delta_{ij}, \tag{A.1a}$$

where

$$\begin{aligned} u_{ij} = {} & (\partial^2 U/\partial x^i \partial x^r)(\delta^{rs} \partial U/\partial x^s)(\partial U/\partial x^j) \\ & + (\partial U/\partial x^i)(\delta^{rs} \, \partial U/\partial x^s)(\partial^2 U/\partial x^r \, \partial x^j), \end{aligned} \tag{A.1b}$$

$$\Delta_1 U(a) = \delta^{ij}(\partial U/\partial x^i)(\partial U/\partial x^j), \tag{A.1c}$$

$$c = \{1/\Delta_1 U(a)\}(\delta^{kr} \, \partial^2 U/\partial x^r \, \partial x^s)(\delta^{st} \, \partial U/\partial x^t)(\partial U/\partial x^k). \tag{A.1d}$$

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