LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2001 issue.

COMMENTS

Comment on ''Critical points and reaction paths characterization on a potential energy hypersurface'' [J. Chem. Phys. 112, 4923 (2000)]

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In a recent paper,[1] Ramquet, Dive, and Dehareng (RDD) have discussed the coordinate dependence of reaction pathways and eigenvalues of the Hessian matrix. They say that the steepest descent depends of the coordinate system. The function of the surface $f(x,y)=-x(1+y^2)$ is given. There is the matrix of second derivatives

$$\begin{pmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} \end{pmatrix} = \begin{pmatrix} 0 & -2y \\ -2y & -2x \end{pmatrix}, \tag{1}$$

thus the point (0,0) is a valley-ridge-inflection point[2] of the surface.[1] RDD treat the nonlinear coordinate transformation $x(u,v)=u-v^2/2, y(u,v)=v$ giving the transformed function $f(x(u,v),y(u,v))=F(u,v)=(v^2/2-u)(1+v^2)$, and they use the matrix of second derivatives of this function at $u=v=0$ to show that the zero eigenvalues have changed under the transformation. This cannot be accepted without comment.

Reaction paths are a widely used concept in theoretical chemistry. It is evident that the invariance problem, which has been solved mathematically a long time ago (cf. the report[3]) again and again penetrates the discussions in this field.[4] The geometrical arrangement of the atoms of a molecule in the space $\mathcal{R}^3$ can be computed in a definite mathematical way and used to obtain the electronic energy of exactly this shape of the molecule. If we change the molecular structure, we will get another energy. Thus, the potential-energy surface (PES) emerges as the result of computations as a hypersurface over the configuration space of the molecule. The geometry of every molecular structure clearly corresponds to a particular molecular electronic energy, and these energies are independent of the kind of coordinates in the configuration space of the molecule. Analogic, we can go the next step: We define by a pure mathematical concept a ''pathway'' of changing the molecular structure from one special point of its configuration space to another point. A definite energy of the molecule belongs to any point along this hypothetical pathway of the molecular rearrangement in $\mathcal{R}^3$. From a mathematical point of view, it is clear that we can define this pathway as being independent of the choice of coordinates in the configuration space of the molecular system. Perhaps, the confusion concerning the invariance problem in Ref. 1 (and others, cf. Ref. 4) comes from the fact that the usual concepts for defining reaction paths use the properties of the PES in a concrete coordinate system. But a change in the coordinate system by means of a definite transformation formula can always be compensated for by changing the method for the computation of the reaction path by an inverse transformation formula. What is the original pathway? In general, this is, and remains, a question of convention. It depends on the purpose of the investigation. For instance, a mass-weighted Cartesian system is well suited, if we search for chemical reaction pathways. It is an isoinertial system, and it is useful for dynamic calculations as a natural continuation of the spectroscopic treatments of vibrations and force constants.

The (x,y) system may be a Cartesian system. The components of the gradient of $f(x,y)$ are $f_x=-1-y^2, f_y=-2xy$, and the incipient steepest descent equations are

$$x'=-f_x, \quad y'=-f_y. \tag{2}$$

To define the steepest descent in a coordinate invariant calculation, we start with the chain rule $f_x=F_u u_x+F_v v_x, f_y=F_u u_y+F_v v_y$, and use the transformed components $F_u=-1-v^2, F_v=v(1-2u+2v^2)$. They belong to the covariant gradient vector. We include these terms in Eq. (2) and we multiply Eq. (2) either (i) by u_x and u_y, correspondingly, and add both, or (ii) by v_x and v_y and add again both. There is

$$\begin{aligned} u' &= u_x x' + u_y y' = -F_u g^{11} - F_v g^{12} \quad \text{in case (i)}, \\ v' &= v_x x' + v_y y' = -F_u g^{21} - F_v g^{22} \quad \text{in case (ii)}, \end{aligned} \tag{3}$$

where we have used the symbols $g^{11}=u_x u_x+u_y u_y$, $g^{12}=g^{21}=u_x v_x+u_y v_y$, and $g^{22}=v_x v_x+v_y v_y$. We obtain the

components of the contravariant gradient vector, which is defined by

$$F^u = g^{11}F_u + g^{12}F_v$$

and

$$F^v = g^{21}F_u + g^{22}F_v . \tag{4}$$

The contravariant inverse metric tensor g^{ij} is

$$(g^{ij}) = \begin{pmatrix} 1+v^2 & v \\ v & 1 \end{pmatrix}. \tag{5}$$

We find

$$F^u = -1 + v^2(v^2 - 2u - 1)$$

and

$$F^v = v(-2u + v^2). \tag{6}$$

The contravariant gradient vector is the right-hand-side of a coordinate invariant steepest descent equation

$$\frac{du(s)}{ds} = -\frac{F^u}{|F^u|}, \quad \frac{dv(s)}{ds} = -\frac{F^v}{|F^v|}. \tag{7}$$

There is the same solution as in the original steepest descent equation in the Cartesian coordinates (x,y). The reason is that this gradient vector has tensor character.[3,5] The conclusion is: *The pathway of steepest descent is invariant from coordinate system* [if we calculate it in coordinate invariant form of Eq. (7)]. This cannot be said about the gradient used in Ref. 1.

In order to study the Hessian matrix, the next derivation of the gradient to u or v results in a two-dimensional field of combinations of second derivations. In general, co- or contravariant characteristic cannot be assigned to the only partial derivatives of this matrix under the coordinate transformation, because there are mixed terms coming out of the chain rule.[6] The invariance problem is trivial for stationary points because the gradient is zero at those points. Invariance problems arise from a nonvanishing gradient. The additional terms are connected with the new coordinate system and can be compressed in special symbols. The matrix becomes[6] in the case of the (u,v) system[1]

$$H_{11} = \frac{\partial^2 F}{\partial u \partial u} - \frac{\partial F}{\partial u}\Gamma^1_{11} - \frac{\partial F}{\partial v}\Gamma^2_{11},$$

$$H_{12} = H_{21} = \frac{\partial^2 F}{\partial u \partial v} - \frac{\partial F}{\partial u}\Gamma^1_{12} - \frac{\partial F}{\partial v}\Gamma^2_{12}, \tag{8}$$

$$H_{22} = \frac{\partial^2 F}{\partial v \partial v} - \frac{\partial F}{\partial u}\Gamma^1_{22} - \frac{\partial F}{\partial v}\Gamma^2_{22}.$$

This matrix (H_{ij}) shows the character of a twofold covariant tensor. In order to calculate the last term H_{22}, which emerges in Ref. 1 as a nonzero value at (0,0), we have to calculate the so-called Christoffel symbols[6–8]

$$\Gamma^1_{22} = \frac{1}{2}g^{11}\left(2\frac{\partial g_{21}}{\partial v} - \frac{\partial g_{22}}{\partial u}\right) + \frac{1}{2}g^{12}\frac{\partial g_{22}}{\partial v} = -1, \tag{9}$$

$$\Gamma^2_{22} = \frac{1}{2}g^{21}\left(2\frac{\partial g_{21}}{\partial v} - \frac{\partial g_{22}}{\partial u}\right) + \frac{1}{2}g^{22}\frac{\partial g_{22}}{\partial v} = 0. \tag{10}$$

It is also $\Gamma^1_{11} = \Gamma^2_{11} = \Gamma^1_{12} = \Gamma^2_{12} = 0$. Here, we have to use the covariant metric tensor g_{ij} which is the inverse of the g^{ij}. It is

$$(g_{ij}) = \begin{pmatrix} 1 & -v \\ -v & 1+v^2 \end{pmatrix}. \tag{11}$$

In noncurvilinear Cartesian coordinates, the metric elements g_{ij} are constant, the Christoffel symbols are zero, and (H_{ij}) reduces to the second partial derivatives of Eq. (1) only. For a general definition of the Hessian tensor in curvilinear coordinates we need Eq. (8).[6–8] For the example of Ref. 1 there is $H_{11} = 0$, $H_{12} = H_{21} = -2v$, and $H_{22} = 5v^2 - 2u$, and it is $H_{22} = 0$ for $u = v = 0$. The valley-ridge-inflection point has not moved in the invariantly defined Hessian. It comes out of the tensor character of this matrix that its zero attribute is invariant under coordinate transformations.

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