THE MASS WEIGHTING PROBLEM OF POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS: DISSOCIATION AND ISOMERISATION PATHWAYS OF HCN

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(Received 25 April 1989)

ABSTRACT

The mass-weighting problem is discussed in the context of the reaction pathways of a chemical rearrangement. Some simple differential geometrical relations are used to connect different co-ordinate systems and achieve an independent definition of a reaction path from the coordinate system. In order to describe the procedure in more detail, it is applied to the molecule hydrogen cyanide (HCN) and its different reaction paths. The action of mass weighting on these paths is illustrated.

INTRODUCTION

One of the fundamental problems in chemistry is the understanding of the stability of molecules, as well as the possibility of their alteration by a chemical reaction. An important theoretical tool is the computation of a potential-energy surface of a defined electronic state, where the atoms can move and the change in their potential energy can be observed by tracing a trajectory on the potential-energy surface. Stable arrangements (reactants, products and intermediates) are minima on the potential-energy surface, and transition structures in a chemical reaction correspond to saddle points of first order. A suitable definition of a continuous line connecting reactants and products via a saddle point has been subject to extensive investigation and has been at the forefront of theoretical chemistry research to date. It is the aim of the definition to obtain a one-dimensional section of the high-dimensional potential-energy surface. One of the mathematical problems in this field is the question of the dependence of a reaction-coordinate definition on the choice of coordinate system [1], and a sub-problem is the mass weighting of the displacement

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coordinates [2]. Mass weighting arose from the spectroscopy of small stable vibrations of a molecule [3] and it was a milestone in the understanding of molecular spectra. Its influence on the understanding of a reaction coordinate is the subject of this paper. The problem is discussed by using the examples of the diatom CH and the triatomic molecule HCN, because we wanted to avoid as far as possible the dimension problem of $(3N-6)$ internal degrees of freedom of an N-atomic molecule. Secondly, the seemingly simple molecule HCN shows a unimolecular reaction to CNH which is well adapted to theoretical reaction-coordinate treatment and, of course, it can dissociate, thereby giving another reaction channel.

THE IRC CONCEPT AND MASS-WEIGHTING

A theoretical analysis of the mass-weighting problem of a reaction coordinate has been reported previously [1,2]. There is the possibility of an alternative definition of a static valley floor path using pure geometric coordinates the addition to reaction-path calculations which are now generally provided by workers in this area. The reason is simply that the pure geometry of atoms only gives the value of the potential-energy surface. In addition, the different mass of isotopic atoms does not alter the potential-energy surface, giving occasion to search a valley path which is independent of the mass.

We start here with the diatomic potential of CH [4] which has an equilibrium distance of 1.0823 Å, and atomic weights of 12 a.u. (C) and 1 a.u. (H). The laboratory frame zero was assumed for the equilibrium structure, with the x axis being used for displacements of the C atom and the y axis for displacements of the H atom along a line without any rotation. At equilibrium there is a zero level of the potential energy. Any distortion (shortening or lengthening of the CH distance) produces a reactive force. A change in the position of the molecule as a whole, against the laboratory frame, does not change the potential of CH. Thus, equipotential lines are obtained for constant CH distances. The straight lines $y - x = $ constant are also the equipotential levels. If a distorted geometry is assumed for CH, then the force of the potential energy acts as a push on both nuclei of exactly the same amount $|F_x| = |F_y|$ [1]. Figure 1 shows the resulting force vector along the direction $y = -x$ orthogonal to the equipotential lines. Of course, the steepest descent in the cartesian (x,y) coordinates proceeds along this direction orthogonal to the equipotential lines. However, it is known from Newton that force=mass×acceleration, and thus the accelerations of the atoms C and H are very different and act to preserve the centre of mass of the diatom. In Fig. 1 the resulting direction $y = -12x$ is the geometric location of the possible movements due to the vibration of CH under preserving of the centre of mass. In the two-dimensional configuration space (x,y) of the diatom CH the gradient points in a very different direction
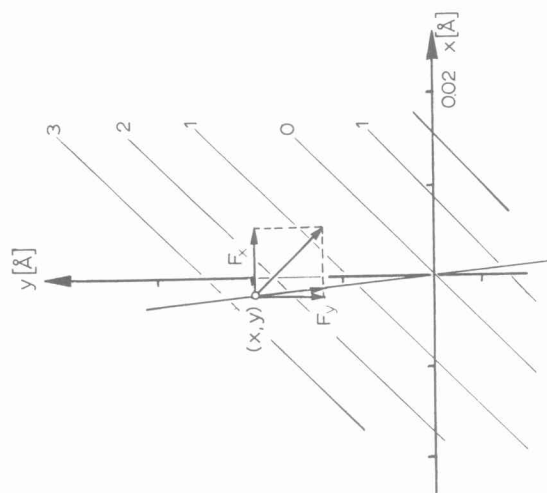

Fig. 1. The potential-energy "surface" for CH. Coordinate x is the distortion of C and y is the distortion of H against a laboratory frame. The equipotential lines 0 to 3 in 1000-cm^{-1} steps are the lines $y = x + $ constant, the gradient is the orthogonal direction $y = -x$, but CH vibrates along the $y = -12x$ line.

energy are coupled by very different masses. The key idea of an intrinsic reaction coordinate (IRC) [5] is to transform the (x,y) coordinate system by mass weighting, such that the gradient direction coincides with the real distortion with conservation of the centre of mass. If it is assumed that a reaction coordinate may only follow the global direction of a valley of the genuine potential-energy surface $U = U(x)$ downhill from the saddle point, and if the dynamical arguments are disregarded, the course of this path $x(t)$ can be obtained by a gradient ansatz starting infinitesimally near to the saddle point and proceeding downhill (independently of the valley floor)

$$\frac{dx^i}{dt} = -\frac{\partial U[x(t)]}{\partial x^i}, \quad i = 1, 2, \ldots, 3N \qquad (1)$$

where t is a curve length parameter [6–8]. Here x^i are the pure cartesian coordinates of the nuclei. In matrix formulation $\dot{x} = \partial U/\partial x$, but in the form of eqn. (1) the defined gradient path depends on the choice of the coordinate system. This can be illustrated by means of a simple example [9]. We assume the potential energy $U(x,y) = 1/2(x^2+y^2)$; the gradient paths are shown in Fig. 2(a) by the arrows (x,y), they are straight lines. The potential energy is transformed to a weighted system by putting $p = mx, q = y$ with a constant $m > 1$. The new potential energy is $V(p,q) = 1/2(p^2/m^2 + q^2)$, the equipotential lines become ellipses and, if we start at any point $\tilde{p}$, the gradient $-(p/m^2, q)$ is
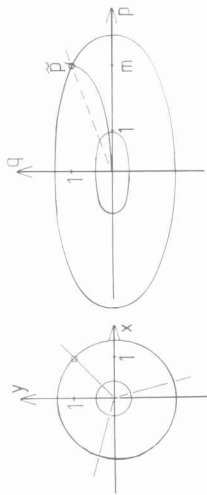
Fig. 2. Change of gradient paths by a mass-weighting procedure. In the (x,y) system gradients are depicted as straight lines. In the (p,q) system the gradient path starting at the point $\hat{p}=(m,1)$ is depicted. The dashed line is the transformation of the old path.

different from a formal transformation of $-(x,y)$ to $-(p,q)$. For any n curvilinear or mass-weighted coordinates $q=q(x)$, we get $\dot{q}=B\dot{x}$, $A\dot{q}=-B^T\partial U/\partial x$, and with $BA=$ unit and $BB^T=G$ eqn. (1) is analogous to that modified by a metric tensor $G=(g^{ij})$, (see refs. 1 and 3)

$$\dot{q}=-G\frac{\partial V}{\partial q}$$

or

$$\frac{dq^i}{dt}=-\sum_{j=1}^n g^{ij}\frac{\partial V}{\partial q^j}, \quad i=1,2,\ldots,n \qquad (2)$$

where the potential-energy surface, U, in eqn. (1) becomes

$$U(x)=V[q(x)]$$

and

$$g^{ij}=\sum_{k=1}^n \frac{\partial q^i}{\partial x^k}\frac{\partial q^j}{\partial x^k}$$

The steepest descent path of definition (1) is orthogonal to the equipotential levels of the potential-energy surface, where this path must be described by gradient (1) in the same coordinate system as the potential-energy surface itself. The aim of the definition of the genuine steepest descent on the potential-energy surface thus implicates the requirement to use well-adapted coordinates of the genuine potential-energy surface. Any coordinate transformation may distort the map of the potential-energy surface. Then the tensor g^{ij} in eqns. (2) provides a mathematical device for compensating for this distortion and for conserving the direction of the original gradient. Thus, with the full gradient in eqns. (2) we have a geometric feature which is independent of the actual coordinate system.

For the simple example shown in Fig. 2

$$g^{11}=m^2, \ g^{22}=1, \ g^{12}=g^{21}=0$$

and so the equation

$$\frac{dx}{dt}=-\frac{\partial U}{\partial x}=-x$$

becomes

$$\frac{dp}{dt}=-g^{11}\frac{\partial V}{\partial p}=-m^2 p/m^2=-p$$

thus the two gradient eqns. (1) and (2) are analogous. These equations give, in the two different coordinate systems, similar straight paths.

It is a question of logic to comprehend that the mathematical gradient (2) in a transformed and distorted potential-energy surface $V(q)$ does not orthogonally cross the equipotential levels, because the orthogonal direction is only $-\partial V/\partial q^i$, but even this formal orthogonal vector includes the distortion by the coordinate transformation in question. Continuing the treatment, it is observed that the so-called minimum-energy path (MEP) or valley floor, changes its bed with a coordinate change. This may be visualised by taking a single convex piece of an equipotential line crossing the floor line. The coordinate transformation generally changes different directions in different ways. Hence, the points $x(s)$ (s being the contour line parameter) are changed in different distance steps and so the curvature of $x(s)$ may be changed to another curvature of $q(s)$. Therefore, there may be a change in the point $q(\text{MEP})$, i.e. the point of maximal curvature. Therefore, the transformation is $q=q(x)$, but, in general, $q_{\text{MEP}}\neq q(x_{\text{MEP}})$.

It is for the above reason that care must be taken with respect to the genuine potential-energy surface which defines the reference coordinates and the genuine gradient (1) which is an approximation of the minimum-energy path. Any further tensor g^{ij} will give in eqns. (2) another approximation of the minimum-energy path, which may be worse or not. The tensor g^{ij} must be developed mathematically from the first selection, which is a question of physics and not of mathematics.

AN EXAMPLE OF MASS WEIGHTING OF REACTION PATHS

The enormous influence of mass weighting can be illustrated by considering the two linear stretching modes v_1 and v_3 of the HCN molecule. The HCN molecule has the linear equilibrium structure $r_{\text{CH}}=1.065$ Å, $r_{\text{CN}}=1.153$ Å and $y_i=z_i=0$ ($i=$H, C or N) for centre-of-mass distances on the x axis ($x_{\text{H}}=1.622$ Å, $x_{\text{C}}=0.557$ Å, $x_{\text{N}}=-0.594$ Å) which can be joined to one point in the three-dimensional subspace $(x_{\text{N}}, x_{\text{C}}, x_{\text{H}})$ of all nine cartesian coordinates (see the left-hand part of Fig. 3). Only the possible co-linear movement of the atoms H, C and N is treated, but the centre of mass (the zero point in Fig. 3) is not
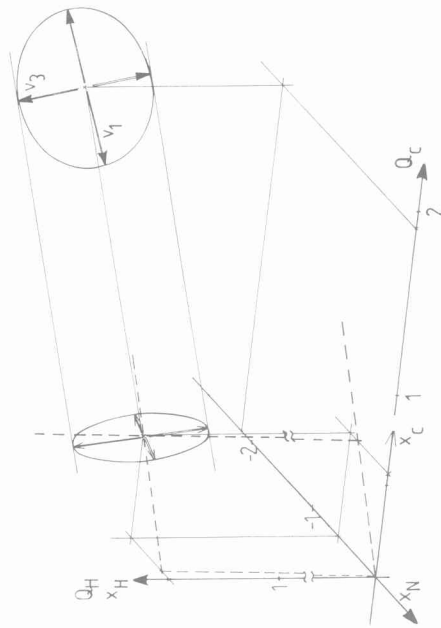
allowed to change. Therefore, the three-dimensional problem is constrained to two degrees of freedom. A two-dimensional plane of the possible movements of the system point (x_N, x_C, x_H) in three-dimensional space is obtained from the linear centre-of-mass equation

$$m_H x_H + m_C x_C + m_N x_N = 0 \qquad (3)$$

The corresponding plane is depicted in Fig. 3 by the dashed lines

$$x_N = -0.857 \, x_C$$

and

$$x_N = -0.071 \, x_H$$

Fig. 3. Change of an equipotential ellipse of linear HCN stretchings by mass weighting. For further details see text.

Now, if the distances r_{CH} or r_{CN} are perturbed from their equilibrium values, different retrograde force constants are obtained, i.e. $F_{33} = 6.25 \times 10^{-18}$ and $F_{11} = 18.73 \times 10^{-18}$ J Å^{-2}, cf. ref. 10. By searching for all distortions of the linear structure under the same change of potential energy an equipotential line in the two-dimensional co-linear configuration plane of HCN is obtained which, at the harmonic level of approximation, is an ellipse with half axes of a ratio of nearly 1:3 from the force constants. Such an ellipse is depicted on the left-hand part of Fig. 3. The thick arrows in Fig. 3 are the pure CH or CN stretches. Because of eqn. (3), in a pure diatomic stretch the third coordinate is also changed, and the system point remains on the plane of the dashed lines.

Now, the usual mass-weighting procedure (cf. ref. 1), a simple linear transformation of the cartesian coordinates, is done

$$Q_i = m_i^{1/2} x_i, \qquad i = H, C \text{ or } N \qquad (4)$$

with the atomic masses $m_H = 1.008$, $m_C = 12.0$ and $m_N = 14.003$. The transformation of the equilibrium point gives $Q_H^\circ = 1.628$, $Q_C^\circ = 1.929$ and $Q_N^\circ = -2.223$. Thus, the Q_H values are obtained by parallel transport of x_H at the same level, and the ratio between the x_C and x_N values is slightly turned in the direction of $(-x_N)$ for Q_C and Q_N. The right-hand part of Fig. 3 shows the transformation of the single depicted equipotential ellipse from x_i coordinates to Q_i coordinates. In the special case of H (with unit mass) there is no distortion of the vertical x_H direction, but there is a large stretching of the two directions in the x_N, x_C plane. The result is a quite different equipotential ellipse in the Q_i coordinates, where the half axes have changed their order: the ν_3 vibration of CH is now stronger (3311 cm^{-1}) than the ν_1 vibration of CN (2097 cm^{-1}), as in the case of HCN. In the (x_N, x_C, x_H) coordinates, a minimum-energy path would point in the direction of a CH change, of course in the direction of the clearly lower force constant. However, in the (Q_N, Q_C, Q_H) coordinate system the minimum-energy path points to a CN stretch with a lower eigenfrequency that the CH mode. Thus, the two-dimensional model gives a change in the direction of the minimum-energy path of the PES as a result of mass weighting. (Note that the third degree of freedom, the bending mode, which here really is the lowest mode, the true minimum-energy path, has been ignored; see below.)

Figure 4 shows another example of a two-dimensional section of a mass-weighted potential-energy surface fit of HCN (cf. ref. 10) in the internal dimensionless coordinates (q_i) of the normal modes including the coupling by cubic and quartic anharmonic coefficients. Figure 4 clearly shows the general exchange of the slopes of the CN and CH directions in the potential-energy surface. However, because the force constant, F_{33}, of the CH bond is only one-third of F_{11}, and the potential-energy
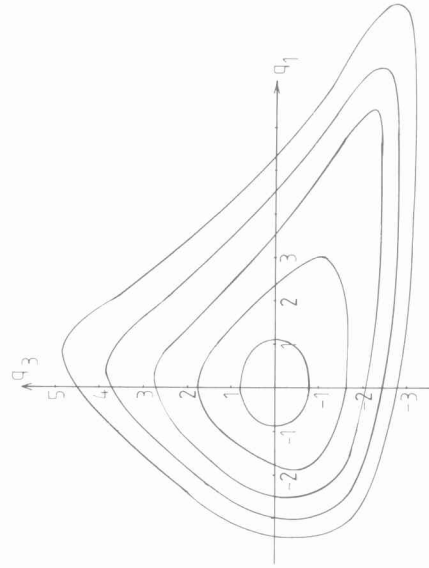

Fig. 4. The potential-energy surface for anharmonic HCN [10] showing the section of the two normal stretching modes q_1 (CN) and q_3 (CH) with equipotential lines at 1000 and 5000 cm^{-1} in steps of 5000 cm^{-1} uphill.

curve of the diatomic CH bond is anharmonically stronger than those of the CN bond, the dissociation HCN → H + CN is found to be much lower in energy (5.65 eV ≈ 45 500 cm^{-1}) than that of the dissociation HCN → HC + N (9.69 eV ≈ 80 000 cm^{-1}) [11]. Despite the effect of the mass weighting of the potential-energy surface, or to be more exact, despite its dependence, the reaction coordinate for the dissociation HCN → H + CN should proceed almost along the normal mode direction (v_3) of the vibration of the CH bond. In the mass-weighted potential-energy surface this direction is that of the strongest mode q_3. Hence, its starting direction in the potential-energy-surface well cannot be the minimum-energy path; at least it becomes weaker than the CN valley beyond an energy level of 30 000 cm^{-1} over the zero state where the two dissociation channels are already clearly separated, (cf Fig. 168 in ref. 11).

Altogether, and because stationary points are not changed by the mass weighting, in both cases (with or without mass weighting) the global existence of the two exit valleys of the HCN potential well is obtained. In general, the valley structure of the genuine potential-energy surface and the direction of the periodic orbits of the molecular overtones and combination modes would be different from one another. The discussion given below is restricted to the former problem, i.e. the valley path of the genuine potential-energy surface without mass weighting, and only the change of path under mass weighting is determined.

STEEPEST DESCENT PATHS, ONCE MORE

In all systems of gradient equations it is necessary to start near the saddle point when using eqns. (1) or (2) because to start in x_{SP} itself is impossible. In x_{SP} there are the displacements dx^i/d$t = 0$, and so the definition of the descent must be completed by a first step along the negative curvature of the barrier. If eqn. (1) is expanded using the norm of the gradient [12]

$$\frac{dx^i}{d\tau} = -\frac{1}{C}\frac{\partial U[x(\tau)]}{\partial x^i}, \quad i = 1, \ldots, 3N$$

with

$$C = \left\{ \sum_{i=1}^{3N} \left(\frac{\partial U}{\partial x^i}\right)^2 \right\}^{1/2}$$

the same solution curves $x(\tau)$ are obtained in the configuration space for τ as those obtained with the parametrisation t. Here τ is the arc length, and the limit $x \to x_{SP}$ gives, by the l'Hospital rule, the eigenvector of the negative eigenvalue for the direction $x(\tau)$ in x_{SP}. However, we can choose for a start in eqn. (1) this eigenvector of the negative eigenvalue of the Hessian of the potential-energy surface in x_{SP} [8]; but the direction is in general different from the so-

called "decomposition mode of the vibrating molecule" in the saddle-point configuration [2], because the latter represents an eigenvector of the mass-weighted potential-energy surface. The difference between the main axes of the potential-energy surface (being eigenvectors of the Hessian matrix) and the normal modes of a molecule in a stationary point of the potential-energy surface is an essential part of the Wilson FG formulation [3]. Of course, with respect to the real decomposition mode of a reaction, the reaction path over a saddle-point starting in the decomposition mode direction can be defined, which is an eigenvector of FG (cf. ref. 13 and references therein), and a mass-weighted gradient can be traced downhill, as was used by Fukui [5]. However, it has been shown (see [1,14]) that a dynamic proof of a gradient equation of the type of eqns. (1) or (2) is not possible. At first sight it seems that a mass-weighted gradient path is well adapted to a good definition of the reaction coordinate of the system. One could also hope to describe vibrations of the molecule orthogonal to and along a reactive development in these coordinates. However, this is only an illusion.

The steepest descent path on the genuine potential-energy surface is described by the pure geometric gradient (1) and all other paths go somewhere else down the slope. It does not help much to know that mass-weighted displacements can be used along such a path both for a tracing of the path itself and for a definition of "fictive" vibrational frequencies somewhere on the slope. On the contrary, there is "no dynamical significance" to a path of steepest descent [15]. The reason for selecting the mass-weighted variant of a descent path in the literature seems to lie in the feeling that a dynamic trajectory can be defined independently by classical mechanics in any coordinate system. This is true, but the classical equations of motion also involve the use of a tensor G^{ij} and Christoffel symbols Γ_{ij}^k to reach such an independence of the trajectory from the coordinate choice [1] where, in the definition of G^{ij}, the geometric influence of the coordinate transformation and of mass weighting have been combined. This definition is a roundabout way of obtaining a simple descent path and is more complicated and obscures the basic properties of the potential-energy surface. Likewise, the normal modes of a mass determined vibration of the molecule do not meet the directions of the eigenvectors of the pure force-constant matrix, and a curvilinear valley floor path of the potential cannot therefore be the exact stream bed of the molecule's dynamic behaviour of its periodic orbits. At least this direction can be an approximated mean value of the reaction path [16].

The system of gradient equations (2) is a mathematical toy which is quite versatile. Starting with the geometric potential-energy surface and definition (1) the same path is obtained after any transformation in other regular coordinates by use of the corresponding g^{ij} tensor in eqn. (2). If we start, in another way, with a "dynamic" definition of a mass-weighted path by tracing it in correspondence to a classical particle sliding down with "infinitesimal" velocity

(cf. ref. 13), we get another path; but these other paths may be computed in any coordinate system [1]. In general, the two paths must be slightly distinct from each other because a mass-weighted displacement vector has in its components different mass factors for a molecule containing different atoms.

We believe that the definition of these two different paths may be understandable. However, a real source of problems may emerge by a kind of mathematical variety, a trifle: the mass-weighted path can be formulated in pure cartesian coordinates [1]

$$m_i \frac{dx^i}{dt} = -\frac{\partial U}{\partial x^i}, \quad i = 1, \ldots, 3N \quad (5)$$

or, secondly, a little more absurdly, the pure geometric path can be formulated in mass-weighted cartesian coordinates [eqn. (4)].

$$Q^i = m_i^{1/2} x^i$$

by

$$\frac{dQ^i}{dt} = -m_i \frac{\partial V}{\partial Q^i}, \quad i = 1, \ldots, 3N$$

The reader should not be confused by these possibilities which must exist because a well-defined gradient path can be expressed in any coordinate system. However, it should be remembered that any gradient path is only an approximation of the valley floor of the minimum-energy path of a general potential-energy surface.

METRIC TENSORS AND COMPUTATION

A simple example of a system having slightly different reaction pathways in two different coordinates is given here using an analytic potential-energy surface of HCN [4] in the range of the isomerisation energy up to 20 000 cm^{-1}. The model potential-energy surface [4] was chosen and not the newer one [10], because the new anharmonic fit only corresponds to a lower region of the HCN potential bowl where the molecule is linear and does not really reach the saddle-point region of the HCN–CNH isomerisation path. (A further paper is in progress to connect the mass-weighted fit [10] and the isomerisation path.)

In ansatz [4], the triple bond C≡N is only slightly changed, but the hydrogen moves in a large amplitude around the CN kernel. The reaction coordinate may be shown in two-dimensional configuration subspace by drawing the hydrogen walk alone against CN fixed in direction and in distance (see Fig. 3.7 in ref. 17). The reaction coordinate has a moderate slope along the valley floor, but has considerably strong valley walls orthogonal to it. The main active H atom has unit weight. Therefore, problems are not expected in tracing the global course of the valley, and it is possible to look for the exact differences between

the two paths with or without mass weighting along the two different gradient paths.

The model potential-energy surface of HCN [4] has three curvilinear coordinates, the distances of the triatomic molecule

$$r^1 = r_{CH}, \quad r^2 = r_{CN}, \quad r^3 = r_{NH},$$

with

$$r^1 = [(x^4-x^1)^2 + (x^5-x^2)^2 + (x^6-x^3)^2]^{1/2}$$
$$r^2 = [(x^4-x^7)^2 + (x^5-x^8)^2 + (x^6-x^9)^2]^{1/2} \quad (5)$$
$$r^3 = [(x^1-x^7)^2 + (x^2-x^8)^2 + (x^3-x^9)^2]^{1/2}$$

We do not start with potential $U(x)$ in cartesian coordinates, but directly with a potential-energy surface $V(r)$, although we indirectly assume the genuine reaction coordinate exists on the potential-energy surface $U(x)$ of HCN. It is necessary to take formulae (2) with the symmetric contravariant metric tensor components g^{ij}, from $B B^T$ (cf. [1,3,18,19]) following directly from eqns. (5)

$$g^{ii} = -2$$

$$g^{ij} = -[(r^i)^2 + (r^j)^2 - (r^k)^2]/(2r^i r^j) \quad (6)$$

with $i \neq j$ and $k \neq i,j$ and $i,j,k = 1,2,3$, which relates the curvilinear coordinates r^i and pure cartesian coordinates x^i.

The tensor can also be derived by dynamic treatment [3] with the s vector method, but its geometrical kernel is independent of the masses and the pure metric tensor g^{ij} is obtained from a mass weighted G^{ij} by setting $m_k = 1$ for $k = H, C$ or N. [This also simplifies the "cliffs" assumed in ref. 1, p. 257 for eqn. (8a).] To obtain tensor G^{ij} for a mass-weighted formulation the internal distances r^i in eqns. (5) are reformulated by setting for all x^i the terms $m_i^{-1/2} Q^i$ of eqn. (4). Then $G = B M^{-1} B^T$ and the tensor components are

$$G^{ii} = -(1/M_j + 1/M_k)$$

$$G^{ij} = g^{ij}/M_k \text{ for } i \neq j, k \neq i,j \text{ and } i,j,k = 1,2,3 \quad (7)$$

where the numeration $M_1 = m_N$, $M_2 = m_H$, and $M_3 = m_C$ have been used the other way round. The tensor G^{ij} relates the same pure geometric coordinates r^i to mass-weighted cartesian coordinates Q^i. If we set $M_k = 1$ we actually obtain the tensor g^{ij}. The accidental singularity of the g^{ij} matrix for r^i coordinates in the final linear structure of HCN does not influence the computation of the steepest descent path from a bent structure.

The path $r(t) = [r^1(t), r^2(t), r^3(t)]$ is computed following the ansatz (2) by a Runge–Kutta code in the modification of Gill. With a very small, but variable, step size of nearly 0.001 Å a zig-zagging of the procedure is avoided (cf. [16,20]). First, two alternatives are used, eqn. (2) with tensor g^{ij} and eqn.

(6) for the MEP, and secondly, eqn. (2) with the mass-weighted tensor G^{ij} [eqn. (7)] giving step-by-step mass-weighted displacements of dr^i/dt. The concept also seems to underly all the reaction-coordinate treatments in the literature. The potential-energy surface is considered, in an abstract way, as a fixed hypersurface over cartesian x or, more comprehensibly, over $(3N-6)$ internal coordinates r like distances or angles. It is sometimes open to discussion that such an abstractly fixed potential-energy surface needs a physical foundation. It is given, for example, in quantum-chemistry programs which calculate the total energy and its derivatives, by the use of $3N$ space fixed cartesian coordinates for all N atomic positions of the molecule; this choice leads to system (1).

RESULTS OF A NUMERICAL TEST

Note that, for simplicity, the calculation is started with 0.005 Å greater $r^1 = r_{CH}$ and $r^2 = r_{CN}$ distances, of a nearby saddle-point configuration in both cases, which are thus near the saddle point on the potential-energy surface, but without a distinction of the directions of both paths in the saddle point. The result of the computation is shown in Fig. 5. Two distances, r_{CN} and r_{CH}, are depicted on the left- and on the right-hand sides against the angle of HCN going-down from the near-saddle-point geometry (left and right) to the minimum (MIN) of the potential-energy surface. The term r_{CN} varies little with change in sign, but the r_{CH} distance is influenced greatly by the mass weighting (just as in the qualitative figure in ref. 2). As expected, it is observed that the valley floor approaches the weighted, but not too greatly distorted, gradient path. Therefore, there is a distinction between mass-weighted and non-mass-weighted displacements, but, at least in the HCN isomerisation on the Murrell PES [4], it is more of academic than of numerical interest. So far, if an addi-
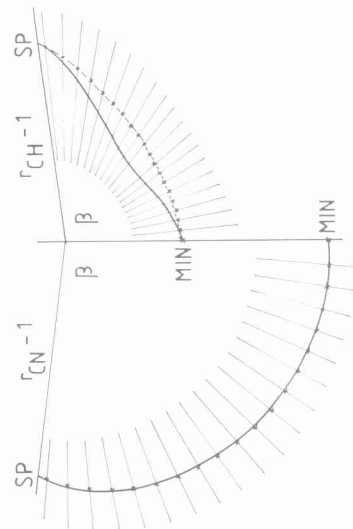
Fig. 5. Computed gradient paths of the HCN isomerisation with (+) and without (—) including the masses on an analytic potential-energy surface [4]. The distances $(r_{CH}-1)$ and $(r_{CN}-1)$ are given in 0.1 Å units.

tional correction step is used in tracing the descent path [21,22], this distinction loses its meaning.

DISCUSSION

We give here a summary of some of the paths which are used to connect the minimum and the saddle point of a potential-energy surface. The steepest descent path [see eqn. (1)] gives the genuine line corresponding to a potential-energy surface in cartesian coordinates. To compute it the initial saddle point must be known. The definition of the term reaction coordinate, or reaction path, is still open to individual use. The intrinsic reaction coordinate (4) is Fukui's SDP defined by eqn. (2) in mass-weighted coordinates. It preserves the centre of mass of the molecule which is an important property. The minimum-energy path is a nebulous, indistinct definition. If it is associated with the minimum energy necessary to surmount the saddle point, we may go uphill to the saddle point on different paths. Hence, for more local treatment it should be replaced by the valley floor path which is defined by the property of a maximal curvature of contour levels [23] or, equally, by the incidence of the gradient and an eigenvector of the Hessian [24]. The valley floor path is a gradient extrema [25,26], and to compute it the Hessian matrix, which may be expansive, must be known.

The SDP or another weighted descent must not be equal to the valley floor path, as can be seen from previously reported examples [1,13]. But, tracing the valley floor path uphill from a minimum is in general a successful way of reaching a saddle point [23–28]. The stabilizing action of a valley floor path on to a point gradient occurs if a point configuration lying near the valley floor is lying on the convex piece of the contour level of the potential-energy surface which connects this point and the valley floor path of similar energy level (see
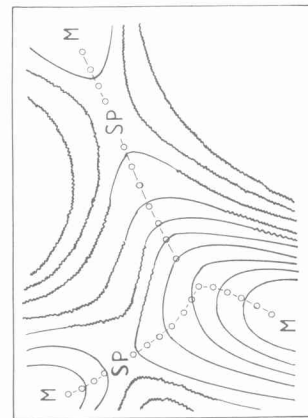
Fig. 6. Qualitative influence of the concave (wavy lines) and convex (full lines) regions of a potential-energy surface. Depicted are three minima M, the ten equipotential levels and the two valley floor paths (– ∘ – ∘ –) connecting M via two saddle points (cf. [26]). The existence of concave regions results in a loss of the unique valley pattern.

Fig. 6, and the problematic wavy lines illustrating this). This may be understood as a definition of the stability property of a valley floor path [29]. The emergence of a ridge [30–33] will indicate the existence of another valley and the division of regions of influence on a gradient direction will become a new problem (see the discussion of catchment regions [7,34]).

CONCLUSIONS

The course of a proper reaction coordinate can be given by geometric features of the potential-energy surface. Considerable care should be taken not to attribute too much chemical meaning to it. The case of HCN shows that the valley structure of the isomerisation potential-energy surface is obtained as the main result in both descent formulations (2) with g^{ij} or G^{ij}. The global valley structure of the potential-energy surface is a convenient way of measuring the possible progress of a molecule in a reaction. The global curvature of the valley in question, the onset of bifurcations [25,26,30] and the emergence of potential ridges are other important features which can determine the reactive properties or the internal redistribution of vibrational energy in the molecule [32,33], which are only understandable if we additionally include dynamic arguments to the definition of a reaction coordinate.

The question of defining a unique SDP is solved [1]. We may define it on the genuine potential-energy surface by use of the g^{ij} tensor in eqn. (2) in internal coordinates r^i. Conversely, the so-called intrinsic reaction coordinate can be uniquely defined [13] by going step by step along mass-weighted displacements by the use of the G^{ij} tensor in internal coordinates. Of course, the two paths are not identical, but may be similar. In order to choose the former as the genuine SDP, mathematical means are not required, but, instead, a physical argument is used.

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