JCTC Journal of Chemical Theory and Computation
Article
pubs.acs.org/JCTC

A Relation Between the Eikonal Equation Associated to a Potential Energy Surface and a Hyperbolic Wave Equation

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ABSTRACT: The potential energy surface (PES) of a molecule can be decomposed into equipotential hypersurfaces. We show in this article that the hypersurfaces are the wave fronts of a certain hyperbolic partial differential equation, a wave equation. It is connected with the gradient lines, or the steepest descent, or the steepest ascent lines of the PES. The energy seen as a reaction coordinate plays the central role in this treatment.

1. INTRODUCTION

The potential energy surface (PES)[1−3] is the basic element of the chemical reaction path and of theories of chemical dynamics. The PES is a continuous function with respect to the coordinates of the nuclei, having also continuous derivatives up to a certain order not specified here, but required by the operations which are to be carried out. The PES can be seen as formally divided in catchments associated with local minimums.[1] The minimums are associated with chemical reactants and products. The first order saddle points or transition states (TSs) are located at the deepest points of the boundary of the basins. According to these definitions, both points, TS and minimums, correspond to stationary points of the PES, but they differ in the structure of the Hessian matrix. Two minimums of the PES can be connected through a TS via a continuous curve in the N-dimensional coordinate space, describing the coordinates of the nuclei. The curve characterizes a reaction path (RP). One can define many types of curves satisfying the above requirement. This is the reason for the variety of RP models. One of the most used RP models is the steepest descent (SD) from the TS to the reactant or product. The SD reaction path in mass weighted coordinates is normally called the intrinsic reaction coordinate (IRC).[4−6] The discussion of a coordinate independent definition of SD curves was already given.[7]

The SD curves and in particular the IRC path are in fact orthogonal trajectories to the contour hypersurfaces, $V(\mathbf{q}) = \nu = constant$, if the corresponding metric relations are used, see ref 7. In this paper, we will assume N orthogonal and equidistant coordinates, $\mathbf{q}$, thus Cartesians of the n atoms with $N = 3n$, for simplicity only. Then the metric matrix reduces to the unity matrix. In the determination of the SD curves, the relation between the gradient field and the associated orthogonal trajectories is relevant. At this point it is important to remember that the Hamilton−Jacobi equation or eikonal equation describes a relation between the contour of a surface and curves.[8] In addition the difference between two contour hypersurfaces is related to a functional depending on some arguments that characterize the SD curves. The connection between the field of SD curves of a PES and the picture of the Hamilton−Jacobi theory was discussed by Bofill and Crehuet.[8] From a theoretical point of view (however not numerically) the SD curves and the inverse ones, the steepest ascent (SA) curves, are equivalent. (Intensive numerical treatments of IRC following procedures are known.[9]) The SA curves emerging from a minimum of the PES can be seen as traveling in an orthogonal manner through the contour hypersurfaces of this PES. In addition, it should be noted that the construction of the contour hypersurface, $V(\mathbf{q}) = \nu = constant$, such that all points satisfying this equation possess the same equipotential difference with respect to another contour hypersurface and specifically with the value of the PES in the minimum, is similar to the construction of the Fermat−Huygens of propagation of the cone rays. Notice that the construction of the Fermat−Huygens of propagation of rays and Hamilton−Jacobi theory are strongly connected.[10] Using this analogy, we will develop a wave equation theory for contour hypersurfaces of the PES.

2. THE EIKONAL EQUATION

The eikonal equation of SD curves in a PES domain is[8,11,12]

$$\nabla_{\mathbf{q}}^{T} V(\mathbf{q}) \nabla_{\mathbf{q}} V(\mathbf{q}) = G(\mathbf{q}) \tag{1}$$

where $\nabla_{\mathbf{q}}^{T} = (\partial/\partial q_1,\ldots,\partial/\partial q_N)$ and $G(\mathbf{q})$ is the square of the gradient norm at the point $\mathbf{q}$. The equation means that, if a function $G(\mathbf{q})$ is given, then we search for a potential $V(\mathbf{q})$ fulfilling this eikonal condition. In eq 1 the PES function $V(\mathbf{q})$ represents the minimal total geodetic distance, and $G(\mathbf{q})$ is the geodetic distance function at each point $\mathbf{q}$ of the PES domain. This geodetic distance function is defined at the beginning of the problem, and the solution $V(\mathbf{q})$ to the above problem represents the total geodetic distance, which is the smallest obtainable integral of $G(\mathbf{q})$, considered over all possible curves throughout the computational domain from a start point to a

Special Issue: Berny Schlegel Festschrift

Received: June 23, 2012

   dx.doi.org/10.1021/ct300654f | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

final point. The integral of $G(\mathbf{q})$ on the SA curve joining these two points is[8,11−14]

$$V(\mathbf{q}) = {}_{\mathrm{SA}}\int_{t_0}^{t_f} \sqrt{G(\mathbf{q})\ (d\mathbf{q}/dt)^T (d\mathbf{q}/dt)}\ \mathrm{d}t \tag{2}$$

where t is the parameter that characterizes the SA curve and $\mathbf{q} = \mathbf{q}_{\mathrm{SA}}(t)$. From a practical point of view, first order nonlinear partial differential eq 1 is solved for this total geodetic distance function $V(\mathbf{q})$ first, and the actual stationary or cheapest path from $\mathbf{q}_{\mathrm{SD}}(t_f)$ to $\mathbf{q}_{\mathrm{SD}}(t_0)$ is obtained by starting at the final point and integrating a trajectory backward along the gradient field $\nabla_{\mathbf{q}}V(\mathbf{q})$. Eikonal eq 1 is an example of the general static Hamilton−Jacobi equation. In other words, eikonal eq 1 tells us that as the parameter t evolves, the coordinates $\mathbf{q} = \mathbf{q}_{\mathrm{SA}}(t)$ evolve, and the contour hypersurface with constant potential energy $V(\mathbf{q}) = \nu$ changes, through the coordinates $\mathbf{q}$. A point of this contour hypersurface is linked to a point of the neighborhood contour hypersurface. This set of points defines a SD curve that makes the integral functional, eq 2, extreme. One can establish some analogies between the propagation of light through a medium having a variable index of refraction and the present problem. Just as the light rays are given as extremal paths of least time, now the SD curves are extremal paths of the PES.

3. AN ANSATZ OF A WAVE EQUATION

The SA curves starting at a minimum are a set of curves traveling in an orthogonal manner through the contour hypersurfaces of the PES. Notice the important fact that each SA curve cuts each member of the family of contour hypersurfaces in one and only one point. Additionally, the SA curves are strictly monotonic in ν between stationary points. Thus, we can establish a one-to-one relation between a point of the curve and the energy value of the member of the family of contour hypersurfaces. In other words the SA curve, $\mathbf{q}(t)$, can be expressed as $\mathbf{q}(\nu)$ being ν the energy of the contour hypersurface at the point $\mathbf{q}(t)$.[13] The family of contour hypersurfaces is geodesically equidistant. In the present understanding the distance is the energy difference. It is known that a family of energy equidistant contour hypersurfaces is the solution of eikonal eq 1.[10] But the construction of a solution of eikonal eq 1 as a contour hypersurface with constant potential energy is similar to the Fermat−Huygens principle for the construction of wave fronts.[8,11,15] The aim of this paper is to find the equation that governs the propagation of the "wave" associated with the SA curves. The unique possibility is a second order partial differential equation such that its associated characteristic equation is eikonal eq 1, which is related with the PES. Furthermore, characteristic curve solutions of eq 1 are just the SA curves.[8] Consequently, let us consider a wave equation in $N + 1$ dimensions, $q_1,...,q_N$, and ν

$$\nabla_{\mathbf{q}}^2\psi(\mathbf{q}, \nu) - G(\mathbf{q})\frac{\partial^2}{\partial^2\nu}\psi(\mathbf{q}, \nu) = 0 \tag{3}$$

where $\nabla_{\mathbf{q}}{}^2 = \nabla_{\mathbf{q}}^T\nabla_{\mathbf{q}} = \partial^2/\partial q_1{}^2 + ...+ \partial^2/\partial q_N{}^2$. Note that we treat ν as an independent variable. $\psi(q,\nu)$ is, for the time being, an abstract field in any medium with slowness $1/G(\mathbf{q})^{1/2}$, which also emerges in eq 1. Equation 3 looks like a wave equation where the time variable, t, is replaced by the variable ν and where the factor $1/G(\mathbf{q})^{1/2}$ plays the role of the velocity of the corresponding wave solution. The concept of "medium" is used here by comparison with the propagation of waves associated with rays of light that propagate in a (maybe inhomogeneous) medium.

Of course, eq 3 is of hyperbolic type by signature ++...+− since $G(\mathbf{q}) > 0$, thus outside of stationary points. Note that the factor, $G(\mathbf{q})$, changes the character of eq 3 into a differential equation with variable coefficients. The solution of such equations is usually assumed to be more difficult than that of equations with constant coefficients. However, in this case, a particular solution will become easier, see section 4.

First, we look for the characteristic manifold of eq 3, see ref 10, part II, chapter VI, paragraph 2. The solutions of hyperbolic equations are "wave-like". If a disturbance is done in the initial data of a hyperbolic differential equation, then not every point of space feels the disturbance at once. Relative to the fixed "energy" coordinate, ν, the disturbances have a finite propagation speed. They travel along the so-called characteristics of the equation. The method of characteristics is a technique to solve this type of partial differential equation. Though it is usually applied to first order equations, the method of characteristics is valid also for our second order hyperbolic equation. The idea is to reduce a partial differential equation to a family of ordinary differential equations along which the solution can be integrated from some initial data given on a suitable hypersurface. To find here the characteristics, we have to treat the quadratic form, which is connected with eq 3

$$\sum_{i=1}^{N}\varphi_{q_i}^2 - G(\mathbf{q})\varphi_\nu^2 = 0 \tag{4}$$

where φ_{q_i} means the derivation to q_i of the characteristic function φ, and the last derivation to energy, ν, with number $(N + 1)$ is symbolized by the index ν. We note that the factor $G(\mathbf{q})$ creates problems since it becomes zero at stationary points. The shapes of the solution of eq 4, the characteristics, are N-dimensional hypersurfaces. They are conoids in regions outside of a stationary point of the PES. The global behavior is distorted by the zero of the gradient at a stationary point. On the other hand, the characteristic equation of eq 3 has an associated characteristic plane

$$((\mathbf{q} - \mathbf{q}_0)^T, (\nu - \nu_0))\begin{pmatrix} \nabla_{\mathbf{q}}\varphi|_{\mathbf{q}=\mathbf{q}_0} \\ \partial\varphi/\partial\nu|_{\mathbf{q}=\mathbf{q}_0}\end{pmatrix} = 0 \tag{5}$$

We call the vector $\mathbf{r}$ the resulting vector of the normalization of the vector $(\nabla_{\mathbf{q}}^T\varphi,\partial\varphi/\partial\nu)$. An element of the $\mathbf{r}$ vector, say r_i, is the cosine of the angle between the normal vector to the characteristic plane and the q_i axis. Because the characteristic equation, eq 4, is homogeneous with respect to the vector $(\nabla_{\mathbf{q}}^T\varphi,\partial\varphi/\partial\nu)$, we can replace it by the normalized vector $\mathbf{r}$ and get in eq 4

$$\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}} - G(\mathbf{q})r_\nu^2 = \underbrace{[(\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}})^{1/2} - G(\mathbf{q})^{1/2}r_\nu]}_{\textit{forward conoid}}\ \underbrace{[(\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}})^{1/2} + G(\mathbf{q})^{1/2}r_\nu]}_{\textit{backward conoid}} = 0 \tag{6}$$

Using the normalization condition of the $\mathbf{r}$ vector, the left-hand side of the equation can be transformed in the following manner

$$\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}} - G(\mathbf{q})r_\nu{}^2 = 1 - (1 + G(\mathbf{q}))r_\nu{}^2 = 0 \tag{7}$$

From this, we find

$$r_\nu = \frac{1}{(1 + G(\mathbf{q}))^{1/2}} \tag{8}$$

which is the cosine of the angle between the ν axis and the normal vector to the characteristic plane. Using the forward conoid expression, we obtain the radius of the "circle" of the conoid, for an intersection hyperplane to a fixed ν,

$$(\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}})^{1/2} = \frac{G^{1/2}(\mathbf{q})}{(1+G(\mathbf{q}))^{1/2}} \tag{9}$$

A schematic view to a straightforward cone with apex $\mathbf{q}_o$ is given in Figure 1.

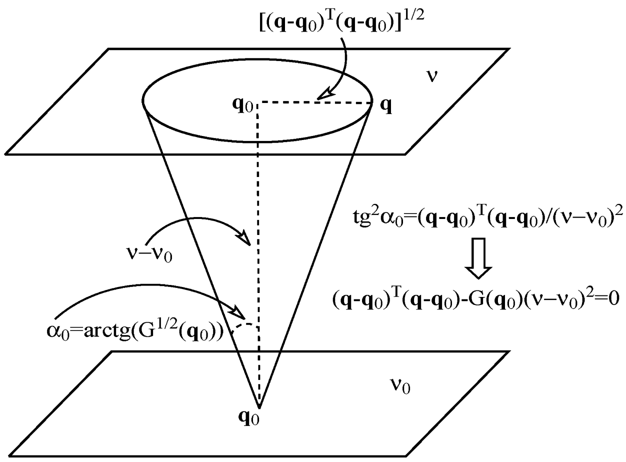

Figure 1. Schematic forward cone in three dimensions, if $G(\mathbf{q}) = 1$ is used for simplicity.

A surface $\varphi(\mathbf{q},\nu) = 0$, such that at every point $(\mathbf{q},\nu)$ the gradient vector $(\nabla_{\mathbf{q}}^T\varphi,\partial\varphi/\partial\nu)$ has the same direction as the $\mathbf{r}$ vector, is a characteristic surface. The Cauchy−Kowalewsky theorem breaks down at such points.

A trivial conclusion is the following. If $d\mathbf{q}/dt$ is the tangent of a steepest ascent (descent) curve, then the two relations hold

$$r_\nu = 1/(1 + (d\mathbf{q}/dt)^T(d\mathbf{q}/dt))^{1/2} \tag{10}$$

$$(\mathbf{r}_{\mathbf{q}}^T\mathbf{r}_{\mathbf{q}})^{1/2} = [(d\mathbf{q}/dt)^T(d\mathbf{q}/dt)/(1 + (d\mathbf{q}/dt)^T(d\mathbf{q}/dt))]^{1/2} \tag{11}$$

which determine the direction of the tangential hyperplane of a characteristic surface, $\varphi(\mathbf{q},\nu)$, through the curve.

We develop a one-dimensional example ($N = 1$), and we use $x = q_1$ for the coordinate. The test function is a double well potential

$$V(x) = (x^2 - 1)^2 \tag{12}$$

The gradient of the function is $\nabla_x V(x) = 4x(x^2 - 1)$, and $G(x)$ is the square of the gradient. The stationary points of the surface are located at $x = 0$ and ±1, point 0 being a first order saddle point with $V(0) = 1$. The two other points are the minimums with $V(\pm1) = 0$. We have

$$r_\nu = 1/(16x^2(x^2 - 1)^2 + 1)^{1/2} \tag{13}$$

So, for both $x = 0$ (saddle point) and $x = 1$ (minimum), it is $r_\nu = 1$ and $r_x = 0$. For the coordinate x, we have the following relation on the (0,1) interval

$$r_x = 4x(x^2 - 1)/(16x^2(x^2 - 1)^2 + 1)^{1/2} \tag{14}$$

The development of the vector (r_x,r_ν) is shown in Figure 2.

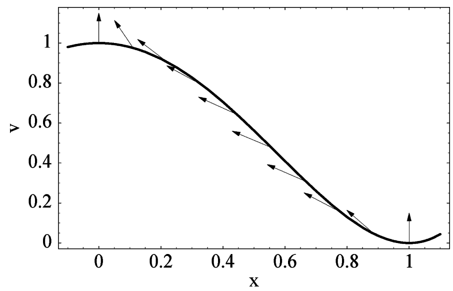

Figure 2. Function $V(x)$ and vectors of the characteristic direction (r_x,r_ν) along the profile.

The opening angle of the conoid changes along the profile. At the stationary points, the cone apex is a pure vector head. Its opening angle is zero. The vector is "energy-like" along the energy axis, ν. The vector is orthogonal to the gradient, which is zero. It is obvious that only nonstationary points with $G(\mathbf{q}) > 0$ are useful points for any treatments. In analogy, if the profile is a minimum energy path (MEP) in a higher dimensional example, say for $V(x,y) = (x^2 - 1)^2 + y^2$, and we move a tiny step away from the SP, then we can calculate the steepest descent from SP to a minimum, as well as have the steepest ascent, and vice versa. Note, at values $x_1 = 0.27$ and $x_2 = 0.84$, the characteristic direction crosses the gradient. The gradient has an "energy-like" direction inside the interval (x_1,x_2). (One could speculate that along "energy-like" gradients a steepest descent method works well; however, if the gradient is "space-like," then such a method can tend to zig-zag.)

To solve eq 4, we try a function $\varphi(\mathbf{q},\nu)$ in the form[16]

$$\varphi(\mathbf{q}, \nu) = e^{i[\nu - V(\mathbf{q})]} - 1 \tag{15}$$

Its substitution into eq 4 fulfills this equation, because the derivations of φ lead directly to eikonal eq 1. If we put φ = *constant* = 0, we can obtain the solution for the variable ν, with $\nu = V(\mathbf{q})$, which is exactly its definition; thus it is correct. The wavefront of eq 3 develops along its characteristic manifold along a curve in the $(N + 1)$ space, which is described by a SA curve with $V(\mathbf{q}) = \nu$ for the current t value. We can say that the progression of wave eq 3, which is a hyperbolic partial differential equation, is regulated by eikonal eq 1, a first order partial differential equation. A general rigorous proof of this result is based on the theory of characteristics of partial differential equations.[10,17,18]

4. A MORE REFINED WAVE EQUATION

The function $\varphi(\mathbf{q},\nu)$ from eq 15 does not fulfill the first ansatz of wave eq 3 because of the chain rule. There emerges an additional term besides the eikonal terms of eq 1. However, we can attempt an extension of eq 3 via a "friction" term

$$\left(\nabla_{\mathbf{q}}^2 - G(\mathbf{q})\frac{\partial^2}{\partial^2\nu} + \mathit{Trace}\ \mathbf{H}\frac{\partial}{\partial\nu}\right)\psi(\mathbf{q}, \nu) = 0 \tag{16}$$

$\mathbf{H}$ is the Hessian of the PES at the current point $\mathbf{q}$; thus $\mathbf{H} = \nabla_{\mathbf{q}}\mathbf{g}^T$ with the gradient of the PES, $\mathbf{g}$. If F is any function of one real variable, $F(x)$, with first and second continuous derivations, then

$$\Psi(\mathbf{q}, \nu) = F(\nu - V(\mathbf{q})) \tag{17}$$

is a solution of extended wave eq 16. The proof is straightforward. The solution is a kind of generalized plane wave with the fixed phase function, $Z(\mathbf{q},\nu) = \nu - V(\mathbf{q})$, and the waveform function F, see ref 10, part II, chapter VI, paragraph 18. Note that the solution, eq 17, is simpler than some spherical wave solutions for wave equations with constant coefficients,[19] and ref 10 part II, chapter VI, paragraph 13, section 4, because we can drop the so-called "distortion" factor. The principal part of eq 16 is the same as in eq 3; thus the characteristic manifold here is also the same. Since the friction term is of low order, eikonal eq 1 is not affected. Note that the plus sign in the "friction" term with the *Trace* **H** coefficient is somewhat "unphysical" if *Trace* **H** > 0.

The solution, eq 17, of the refined wave equation allows the application of deep conclusions concerning the Huygens principle, see section 7 below.

In the general theory of hyperbolic differential equations, one uses the normal form of the wave equation. We will now derive it. The part of second order in eq 3, or eq 16, is

$$\nabla^2_{\mathbf{q}}\psi(\mathbf{q},\nu) - G(\mathbf{q})\frac{\partial^2}{\partial^2\nu}\psi(\mathbf{q},\nu) \tag{18}$$

Note that the factor $G(\mathbf{q})$ depends only on the space variables, $\mathbf{q}$, but not on the potential variable, ν. The so-called metric matrix in eq 18 is

$$(g^{i,j})_{i,j=1,...,N+1} = \begin{pmatrix} \mathbf{E} & \mathbf{0} \\ \mathbf{0}^T & -G(\mathbf{q}) \end{pmatrix} \tag{19}$$

E is the N-dimensional unit matrix, and **0** is the N-dimensional zero vector. Because the metric matrix here is only a diagonal matrix, its inverse matrix is simply

$$(g_{i,j})_{i,j=1,...,N+1} = \begin{pmatrix} \mathbf{E} & \mathbf{0} \\ \mathbf{0}^T & -1/G(\mathbf{q}) \end{pmatrix} \tag{20}$$

(Compare a remark in the Introduction: the metric matrix in $\mathbf{q}$ space is a simplification.) The absolute value of the determinant of the inverse matrix is $\gamma = 1/G(\mathbf{q})$.

Now, we can write the ν part of eq 18:

$$\begin{aligned} &G(\mathbf{q})^{1/2}\frac{\partial}{\partial\nu}\left(G(\mathbf{q})^{-1/2}G(\mathbf{q})\frac{\partial}{\partial\nu}\right)\psi(\mathbf{q},\nu) \\ &= \frac{1}{\sqrt{\gamma}}\frac{\partial}{\partial\nu}\left(\sqrt{\gamma}g^{N+1,N+1}\frac{\partial}{\partial\nu}\right)\psi(\mathbf{q},\nu) \end{aligned} \tag{21}$$

For the space variables, $\mathbf{q}$, we have

$$G(\mathbf{q}) = \sum_{i=1}^{N}\left(\frac{\partial}{\partial q_i}V(\mathbf{q})\right)^2, \text{ thus } \frac{\partial}{\partial q_k}G(\mathbf{q}) = 2\sum_{i=1}^{N}V_{q_i}V_{q_i q_k} \tag{22}$$

Because it holds for the coefficients $g^{i,j} = \delta^{i,j}$, for $i,j = 1,...,N$, we can try an ansatz

$$\frac{1}{\sqrt{\gamma}}\frac{\partial}{\partial q_i}\left(\sqrt{\gamma}\frac{\partial}{\partial q_i}\right)\psi(\mathbf{q},\nu) \tag{23}$$

If we differentiate the factor $\sqrt{\gamma}$ inside the formula, with the product rule we get

$$\frac{\partial^2}{\partial q_k^2}\psi(\mathbf{q},\nu) + G(\mathbf{q})^{1/2}\left(-\frac{1}{2}\right)\frac{1}{G(\mathbf{q})^{3/2}}2\sum_{i=1}^{N}V_{q_i}V_{q_i q_k}\frac{\partial}{\partial q_k}\psi(\mathbf{q},\nu) \tag{24}$$

Consequently, we get for the second order part of eq 18

$$\begin{aligned} &\nabla^2_{\mathbf{q}}\psi(\mathbf{q},\nu) - G(\mathbf{q})\frac{\partial^2}{\partial^2\nu}\psi(\mathbf{q},\nu) \\ &= \frac{1}{\sqrt{\gamma}}\frac{\partial}{\partial q_i}\left(\sqrt{\gamma}g^{i,j}\frac{\partial}{\partial q_j}\right)\psi(\mathbf{q},\nu) - \frac{1}{\sqrt{\gamma}}\frac{\partial}{\partial\nu} \\ &\left(\sqrt{\gamma}g^{N+1,N+1}\frac{\partial}{\partial\nu}\right)\psi(\mathbf{q},\nu) + \frac{1}{G(\mathbf{q})}\sum_{i=1}^{N}((\nabla^T_{\mathbf{q}}V)\mathbf{H}_i) \\ &\frac{\partial}{\partial q_i}\psi(\mathbf{q},\nu) \end{aligned} \tag{25}$$

where $\mathbf{H}_i$ means the ith column of $\mathbf{H}$. The first two parts of the right-hand side build the normal form of a second order wave equation with $(N + 1)$ variables and with variable coefficients. For such a normal form, we have an integration theory which guarantees the existence of exactly one forward (and one backward) fundamental solution.[20] But we stop here and look for other properties of the phase function $V(\mathbf{q}) = \nu$.

5. A CHARACTERISTIC INITIAL VALUE PROBLEM

No stationary point should emerge between a $\mathbf{q}(t_0)$ on a hypersurface for ν_0 and the corresponding $\mathbf{q}(t_f)$ on an upper hypersurface at energy ν_f. A wave equation with a second order part like eq 18 allows a characteristic initial value problem posed for the characteristic surface in section 3. If we put the value $\nu = V(\mathbf{q})$ into solution, eq 17, we get

$$\psi(\mathbf{q},\nu)|_{\nu=V(\mathbf{q})} = F(\nu - V(\mathbf{q})) = F(0) \tag{26}$$

everywhere on the characteristic surface, because for $\nu = V(\mathbf{q})$ we are also on the characteristic surface $\varphi(\mathbf{q},\nu) = 0$ with eq 15. Without a loss of generality, we can assume $F(0) = 0$. We treat a double-conoid (DC) between two points $P_o = (\mathbf{q}(t_0),\nu_0)$ and $P_f = (\mathbf{q}(t_f),\nu_f)$, see Figure 3, compare Figure 56 in ref 10, chapter VI, paragraph 6, section 1. The corresponding defining formula is eq 4. We can multiply eq 18 by $(-2\psi_\nu)$ everywhere in the DC, and we have

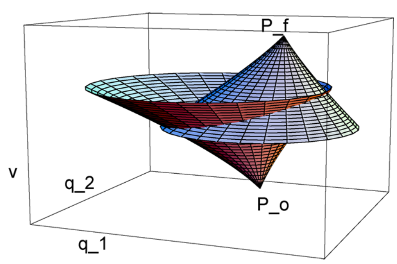

Figure 3. Three-dimensional schematic representation of two intersecting conoids, one forward conoid with the apex in P_o and one backward conoid with the apex in P_f. They form by their curve of intersection a double conoid: all points in the interior of both conoids between P_o and P_f.

$$2\psi_\nu\left(G(\mathbf{q})\psi_{\nu\nu} - \sum_{i=1}^{N}\psi_{q_i q_i}\right) = 0 \tag{27}$$

where the indices mean the corresponding derivation. It is equal to

$$(G(\mathbf{q})\psi_\nu^2)_\nu - 2\sum_{i=1}^{N}(\psi_{q_i}\psi_\nu)_{q_i} + \sum_{i=1}^{N}(\psi_{q_i}^2)_\nu = 0 \tag{28}$$

which is proved by a straightforward calculation. The expression of eq 28 is a divergence; its integration over the full region of the double conoid and application of Gauss' integral theorem results in a surface integral over the borders of the double conoid with

$$\iint_{\mathrm{DC}} \{G(\mathbf{q})\psi_\nu^2 r_\nu - 2\sum_{i=1}^{N} \psi_{q_i}\psi_\nu r_{q_i} + \sum_{i=1}^{N} \psi_{q_i}^2 r_\nu\}\, \mathrm{d}S = 0 \tag{29}$$

It is equivalent to the integral[10]

$$\iint_{\mathrm{DC}} \left\{\frac{1}{r_\nu}\sum_{i=1}^{N} (\psi_{q_i} r_\nu - \psi_\nu r_{q_i})^2\right\} \mathrm{d}S = 0 \tag{30}$$

which again is examined by a straightforward calculation where the relation of eq 7 still is taken into account, at least. The integral delivers the proof of the uniqueness for the characteristic initial value problem:

We suppose that the initial values of a solution vanish on the characteristic forward conoid and integrate the expression eq 28 over the double conoid DC. Since the integral vanishes, therefore, the integrand likewise vanishes because it is the sum of quadrates. The integral over the lower conoid vanishes, since in the integrand only interior derivatives appear, and they, by hypothesis, are all zero. Hence, the interior derivatives of the brackets in the integral eq 30 likewise vanish on the upper conoid. In other words, on the surface of the upper conoid, ψ is constant and therefore zero, since ψ vanishes on the intersection of the surfaces of the two conoids.

6. BACK TO THE SA EQUATION

In the present problem, we recall that we should find a solution $\psi(\mathbf{q},\nu)$ for eq 16, having prescribed the data on a hypersurface S given by the zero function $Z(\mathbf{q},\nu) = \nu - V(\mathbf{q}) = 0$. The function $\psi(\mathbf{q},\nu)$ has to have second continuous derivatives, and the surface is automatically regular in the sense that $(\nabla_{\mathbf{q}}^T Z, \partial Z/\partial\nu) \neq \mathbf{0}^T$, where $\mathbf{0}$ is the zero vector of dimension $(N + 1)$. It holds because it is allways $\partial Z/\partial\nu = 1$. The data on S for the second-order equation eq 3, or eq 16, consist of $\psi(\mathbf{q},\nu)$ and of the set of the first derivatives of $\psi(\mathbf{q},\nu)$ with respect to $\mathbf{q}$ and ν. We will find a solution $\psi(\mathbf{q},\nu)$ near S which has these data on S. We say that S is noncharacteristic if we can obtain all first and second derivatives of $\psi(\mathbf{q},\nu)$ with respect to $\mathbf{q}$ and ν on S from a linear algebraic system of equations building the compatibility conditions of the data and the partial differential eq 3, or eq 16, taken on S. We call S characteristic if at each point $(\mathbf{q},\nu)$ the hypersurface S is not noncharacteristic. If we set $G(\mathbf{q})$ to be any given function of the space variables, $q_1,...,q_N$, then eikonal eq 1 can be used with a function

$$Q(\nabla_{\mathbf{q}} V, \mathbf{q}) = \nabla_{\mathbf{q}}^T V(\mathbf{q}) \nabla_{\mathbf{q}} V(\mathbf{q}) - G(\mathbf{q}) \tag{31}$$

$Q(\nabla_{\mathbf{q}}V,\mathbf{q}) = 0$ is satisfied on S with the values of $V(\mathbf{q})$ and $\nabla_{\mathbf{q}}V(\mathbf{q})$ given by the data. Equation 31 is the characteristic condition resulting in a partial differential equation. We remember that eq 1 is the Hamilton–Jacobi equation of steepest-ascent curves.[8] An important consequence is that the second order partial differential eq 3, or eq 16, is an interior differential operator in the following sense. If along the characteristic hypersurface S the values of $V(\mathbf{q})$ and $\nabla_{\mathbf{q}}V(\mathbf{q})$ are given, then the second order parts of eq 18 are known.

Taking into account the theory of first order partial differential equations, each member of the family of solutions, $\nu = V(\mathbf{q})$, is generated by a family of bicharacteristic curves or rays being linked with the second order partial differential eq 3, or eq 16. We understand the function $Q(\nabla_{\mathbf{q}}V,\mathbf{q})$ to be the Hamiltonian of a certain problem. Then, the generating strips should be obtained by a Hamilton–Jacobi system of $2N$ ordinary differential equations and characterized by a suitable parameter t,

$$\frac{d\mathbf{q}}{dt} = \frac{1}{2}\nabla_{(\nabla_{\mathbf{q}} V)} Q(\nabla_{\mathbf{q}} V, \mathbf{q}) = \nabla_{\mathbf{q}} V(\mathbf{q}) = \mathbf{g}(t) \tag{32}$$

where we have $\mathrm{grad}(V(\mathbf{q})) = \mathbf{g}(\mathbf{q}) = \nabla_{\mathbf{q}}V(\mathbf{q})$, and then the bicharacteristic strip is (theoretically) given by $\mathbf{q}(t)$ and $\mathbf{g}(t)$ with

$$\begin{aligned}\frac{d\mathbf{g}}{dt} &= -\frac{1}{2}\nabla_{\mathbf{q}} Q(\nabla_{\mathbf{q}} V, \mathbf{q})\\ &= \frac{1}{2}\nabla_{\mathbf{q}} G(\mathbf{q})\\ &= \mathbf{H}(t)\mathbf{g}(t)\\ &= \mathbf{H}(t)\frac{d\mathbf{q}}{dt}\end{aligned} \tag{33}$$

Note that eq 32 is nothing but the differential equation that characterizes the SA curve of a PES. But eq 33 is nothing but its next derivation,[8] thus $d^2\mathbf{q}/dt^2$. It means that the second equation, eq 33, is not a new condition; thus the system of eqs 32 and 33 reduces to only N differential equations in the SA system of eq 32. The system of eq 32 yields to all possible characteristic curves for the solution $\psi(\mathbf{q},\nu)$. We emphasize that the integral curves of the system of eq 32 of the first order partial differential equation $Q(\nabla_{\mathbf{q}}V,\mathbf{q}) = 0$ are the characteristic "rays" of the given second order partial differential eq 3, or eq 16; they generate all members of the family of hypersurfaces $\nu = V(\mathbf{q})$. The characteristic hypersurfaces of eq 31 play a role as "wave fronts", compare also section 7. The "wave fronts" occur as frontiers beyond which there is currently no excitation at potential ν. We remark that ν is interpreted as the potential, and ψ is a function in the N-dimensional $\mathbf{q}$ space with the potential ν as an additional dimension. Then, we deal with a solution $\psi(\mathbf{q},\nu)$ of eq 16 with a hypersurface, where all points are a map of points of the lower surface $V(\mathbf{q}) = \nu_0$, by a point to point map. (For every SA, we have to use the corresponding t_f to finish at the hypersurface with energy value ν_f. The values t_f can be different from one SA curve to any other SA curve.) For wave eq 16, we see the propagation of the initial "wave front" $V(\mathbf{q}) = \nu_0$, a hyperplane in the configuration space, to the parallel "wave fronts" $V(\mathbf{q}) = \nu$ for any ν. (However, the map works only before the next stationary point, which itself will cause a "caustic" of the level hypersurfaces.)

The map looks indeed like a wavefront. Note that $V(\mathbf{q}(t_f))$ does not depend on a full backward conoid; from this point of view, it only depends on the point $V(\mathbf{q}(t_0))$, along the SA curve. The reason is that differential eq 32 now defines the curve in a local way. So to say, the backward conoid of the solution of a usual hyperbolic differential equation[10,17,18] contracts to a curve on the conoid, $V(\mathbf{q}(t)) = \nu(t)$. Every parallel equipotential hypersurface is the result of a map from a former one, as well as it also being the initial surface for the step to a next one. So to say, the propagation of the equipotential hypersurfaces goes along the **Huygens principle** of propagation of wave fronts. Note that here the dimension of the configuration space can be even or odd. It contrasts with the Cauchy initial value problem for a general wave equation where the decision criterion of the dimension plays an important role.[20,21] Already the solution of the wave equation in two- or three-dimensional spaces is different. A pointwise perturbation at an initial source produces a spherical wave in $\boldsymbol{R}^3$, while in $\boldsymbol{R}^2$ the full region inside a circle will be disturbed. In the first case, the Huygens principle holds in a strong sense, in the second case the wave diffuses.

7. THE HUYGENS PRINCIPLE

In 1678, the Dutch physicist Christian Huygens (1629–1695) wrote a treatise called Traité de la Lumière (on the wave theory of light).[22] In the work, he stated that the wavefront of a propagating wave of light at any instant conforms to the envelope of spherical wavelets emanating from every point on the wavefront at the prior instant, with the understanding that the wavelets have the same speed as the overall wave.

Though the action of the family of SA curves, to map a hypersurface of fixed energy, is another action of a wavefront by an envelope, we may assume that also the equipotential hypersurfaces are "fronts" of the ascending energy, especially because they fulfill a hyperbolic wave equation.

The above explanation of the Huygens principle can be described as a syllogism due to Hadamard.[23] The first premise, which is the major premise of this syllogism adapted to the problem under consideration, is the following. A steepest ascent curve arrives at a point located on the equipotential hypersurface $\nu = \nu_0$ and achieves a highest equipotential hypersurface $\nu = \nu_f$ via a mediation of every intermediate equipotential hypersurface, say, $\nu = \nu'$ assuming that $\nu_0 < \nu' < \nu_f$. In order to elucidate how the steepest ascent curve takes places at $\nu = \nu_f$, we can deduce from the position at $\nu = \nu_0$ the position at $\nu = \nu'$ and, from the latter, the required position at $\nu = \nu_f$. The second premise, which is the minor premise, is enunciated in the following manner. If we produce a "disturbance" at point $\mathbf{q}_0$, where the steepest ascent is localized in the equipotential hypersurface $\nu = \nu_0$, the effect of it will be, for $\nu = \nu'$, localized in the immediate neighborhood of the surface of the sphere with center $\mathbf{q}_0$ and radius $\Delta\nu = \nu' - \nu_0$; that is, it will be localized in a thin spherical shell with center $\mathbf{q}_0$, including the afore-mentioned sphere. The conclusion of this syllogism based on these two premises is that the effect of the initial "disturbance" produced at $\mathbf{q}_0$ at $\nu = \nu_0$ may be replaced by a proper system of disturbances taking place at $\nu = \nu'$ and distributed over the surface of the sphere with center $\mathbf{q}_0$ and radius $\nu' - \nu_0$. An illustration of this idea, now known as the Huygens principle, is shown in Figure 4.

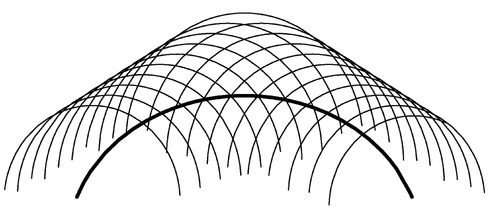

Figure 4. Model for the action of the Huygens principle. Wavelets of different "speeds", $1/G(\mathbf{q})^{1/2}$, start from a lower level line (the bold curve). They build an envelope. It is the new wavefront, that is, the new level line.

8. CONCLUSION

The present work still does not claim to lead to results in experimental research. The authors ask that it be considered as a contribution to the theory of SD/SA curves and their orthogonal equipotential hypersurfaces. One can formulate wave equations with the energy of the molecular PES as an $(N + 1)$st variable, see eq 3 or eq 16. The characteristic manifold of the wave equations is given by long known eikonal eq 1. We report a particular solution of eq 16 using eq 17, it being very simple, and we report some properties of the solution and its connection to the SD/SA problem. Note that eq 16 has an unphysical "friction" term with false sign, if *Trace* $\mathbf{H} > 0$. We do not develop in this paper the general solution of wave eq 16, but a normal form is prepared, which is a first step. For the type of wave eq 3 with "variable speed", there exist special solutions, in the here uninteresting case of $N = 1$, depending on the "speed" $1/\sqrt{G}$.[24,25] In the case of a general $N > 1$, there already exists a mathematical treatment of a solution with a certain behavior of the geometrical optics.[26] Of course, the full-fledged, theoretical possibilities of the second order wave eq 16 cannot be adapted to the first order system of SA equations, eq 32. However, we state that wave eq 16 allows a particular phase function solution with argument $\nu - V(\mathbf{q})$, which itself behaves with the Huygens principle. The wave "fronts" are the phases of the equipotential hypersurfaces, $\nu = V(\mathbf{q})$.

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Notes

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■ ACKNOWLEDGMENTS

Financial support from the Spanish Ministerio de Ciencia e Innovación, DGI project CTQ2011-22505 and, in part, from the Generalitat de Catalunya projects 2009SGR-1472 is fully acknowledged. M.C. gratefully thanks the Ministerio de Economía y Competitividad for a predoctoral fellowship. We thank a reviewer for suggestions and comments.

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