Analysis of the Valley-Ridge Inflection Points through the Partitioning Technique of the Hessian Eigenvalue Equation.

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Abstract: The Valley-Ridge Inflection (VRI) points are related to the branching of a reaction valley or reaction channel. These points are a special class of points of the Potential Energy Surface (PES). They are also special points of the Valley-Ridge borderline of the PES. The nature of the VRI points and their differences with respect to the other points of the Valley-Ridge borderline is analyzed using the Löwdin's partitioning technique applied to the eigenvalue equation of the Hessian matrix. Eigenvalues and eigenvectors of the Hessian are better imaginable than the former used adjoint matrix.

Keywords: Valley-Ridge Inflection Point; Bifurcation of Reaction Path; L**ö**wdin Partitioning Technique; Potential Energy Surface.

Introduction.

The analysis of PESs remain an important basis for classifying and understanding the grounds of the mechanisms of chemical reactions as well as their dynamics. It is associated to the concept of the reaction path (RP) or to the definition of the minimum energy path on a PES. This is an important theoretical tool in the reaction theory with a high intuitive power for chemists [1]. The RP is roughly defined [2] as the curve, which connects two minima by passing through a first order saddle point (SP), or transition state (TS) between them. The chemical reaction may be composed by a number of elementary processes characterizing the mechanism of the reaction. RP bifurcations are omnipresent on PESs; they happen at VRI points already on the PES of very small molecules like H_2O [3], H_2S, H_2Se, H_2CO [4], HCN [5,6], the ethyl cation [7], H_3CO, C_2H_5F [8], and many others. The importance of VRI points for the chemical reactivity is described in the reviews of Ess et al. [9], Bakken et al. [10] and references [11,12].

The type of an RP widely used is a mass-weighted steepest descent (SD) curve from the SP, the intrinsic reaction coordinate (IRC) [13,14,15,16,17]. However, in "skew", non-symmetric cases the IRC usually does not meet a VRI point being nearby. There is a variety of other types of curves that can be used as RP models, and which

meet VRIs. The curves following a constant gradient direction (Newton trajectories (NT), a former ansatz was coordinate driving) can be used in many cases to characterize the RP [18,19]. Sometimes the gradient extremals (GEs) curves [20,21,22,23,24,25] also appear to form a suitable ansatz for such purposes. Certain Newton trajectories describe the valley or cirque structures of a PES, as well as their complements of ridges or cliffs (for the definition of such structures see reference [26]). The structures are related to important chemical properties of the PES of the reaction under study [11,12]. The use of NTs opens the possibility to find and to study VRI points and, in succession, bifurcation or branching points of reaction channels, because the reaction channel-branching is related to the existence of a special class of points of the PES, the VRI points [27,28]. A VRI point is that point in the configuration space where, orthogonally to the gradient, at least one main curvature of the PES becomes zero [29]. This definition implies that the gradient vector is orthogonal to an eigenvector of the Hessian matrix where its eigenvalue is zero. Usually, VRI points represent nonstationary points of the PES. Note that the VRI points are independent of the RP curve model used. They are related to the nature of the PES topography. Normally the VRI points are not related to the branching point of the RP curve except for NT curves [19, 28]. So to say, a geometrical indicator of a VRI point is the bifurcation of a singular NT.

However, a more general concept emerges. For it we go back to the IRC curve as an RP model. This curve is defined by an autonomous system of differential equations for the tangent vector describing its evolution [30]. Its solution is unique; due to this fact no bifurcations can occur before reaching the next stationary point after the SP. No branching of PES valleys will be truly described or located by using the IRC curve as an RP type model [29,31]. It orthogonally traverses the family of levels, the equipotential energy surfaces [30]. Hirsch and Quapp [32] gave an example of a two-

dimensional PES where the IRC is going over a skew ridge, however, it does not find the valley ground nearby, which is here characterized by a GE. The IRC or any other SD curve do not take into account the curvature of the traversed contours in their evolution, in other words it does not give information on the valley floor or ridge character of its pathway. After a change of levels from convex to concave form the IRC curve ceases to be a valley pathway and is actually a merely RP. An early visualization of such an instable minimum energy path was given by Mezey in reference [33], page 112, Figure II.13, see also [34]. As explained, the IRC curve traverses in its evolution a family of equipotential energy surfaces. At any point of a SD curve we can define a tangential plane to the equipotential energy surface orthogonally traversed by the SD curve at the point, and the normal of the tangential plane is the gradient vector of the point. All direction vectors contained in the tangential plane are orthogonal to the gradient vector. If at least one of these direction vectors is connected with the curvature zero then we say that the SD curve crosses a **valley-ridge transition** (**VRT**) point. The curve leaves a valley and enters a ridge region of the PES or vice-versa. The VRT points are the border between valley- and ridge-regions. The concept of a VRT point is much more general than the VRI point concept. In fact a VRI point is a special case of a VRT point. In the general VRT situation, the gradient vector is not orthogonal to the set of eigenvectors of the Hessian matrix. This is the most general behavior. The zero curvature of the PES along the level line or equipotential energy surface at the VRT point comes from a suitable linear combination of the eigenvectors with their eigenvalues of the Hessian matrix. In fact a manifold of points with these features exist on a PES. They are border points between quasi-convex valley regions and ridges. NTs there have a turning point. So to say, a turning point of an NT is the geometrical indicator of a VRT point, see [35]. The VRI points are special VRT points.

In this article we analyze the relations between VRT and VRI points using the Löwdin's partitioning technique applied to the Hessian eigenvalue equation [36]. This partitioning technique was used to analyze the behavior of the Newton-Raphson procedure during the optimization of the Multi-Configurational Wave Function [37] and the location of minima and SPs on a PES [38,39,40]. The connection with previous formulations based on the adjoint matrix is also reported. The use of the Hessian itself is better imaginable, in contrast to the use of its adjoint matrix in former calculations.

The Matrix Partitioning Theory applied to the Hessian at the VRI point.

Previous Remarks.

In the treatment of the theory of the VRI and VRT points we use the gradient vector of the PES, **g**, and a set of *N-1* linear independent direction vectors, $\{\mathbf{s}_i\}_{i=1,N-1}$, orthogonal to the gradient vector. *N* is the dimension of the PES. Without loss of generality we take the set of *N-1* linear independent direction vectors as a set of orthonormalized vectors, and we collect them using the rectangular matrix $\mathbf{S} = [\mathbf{s}_1 \mid ... \mid \mathbf{s}_{N-1}]$. The **S** matrix has the property, $\mathbf{S}^T\mathbf{S} = \mathbf{I}_{N-1}$, where $\mathbf{I}_{N-1}$ is the unit matrix of dimension *N-1*. The superscript *T* means transpose. Initially the Hessian matrix at any point of the PES, **H**, is expressed in the set of coordinates where the PES function is defined. Now we assume that **g** is not the zero vector. We transform the Hessian

matrix into the base formed by the normalized gradient vector and the subset of *N-1* linear independent direction vectors, collected in the **S** matrix,

$$\mathbf{T}^T\mathbf{H}\mathbf{T} = \left[\mathbf{r}\middle|\mathbf{S}\right]^T \mathbf{H}\left[\mathbf{r}\middle|\mathbf{S}\right] = \begin{bmatrix} H_{rr} & \mathbf{H}_{rS} \\ \mathbf{H}_{Sr} & \mathbf{H}_{SS} \end{bmatrix} = \begin{bmatrix} \mathbf{r}^T\mathbf{H}\mathbf{r} & \mathbf{r}^T\mathbf{H}\mathbf{s}_1 & \cdots & \mathbf{r}^T\mathbf{H}\mathbf{s}_{N-1} \\ \mathbf{s}_1^T\mathbf{H}\mathbf{r} & \mathbf{s}_1^T\mathbf{H}\mathbf{s}_1 & \cdots & \mathbf{s}_1^T\mathbf{H}\mathbf{s}_{N-1} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{s}_{N-1}^T\mathbf{H}\mathbf{r} & \mathbf{s}_{N-1}^T\mathbf{H}\mathbf{s}_1 & \cdots & \mathbf{s}_{N-1}^T\mathbf{H}\mathbf{s}_{N-1} \end{bmatrix} \qquad (1)$$

where **r** is the normalized gradient vector, $\mathbf{r} = \mathbf{g} / (\mathbf{g}^T\mathbf{g})^{1/2}$, and $H_{rr} = \mathbf{r}^T\mathbf{H}\mathbf{r}$, $\mathbf{H}_{Sr} = \mathbf{S}^T\mathbf{H}\mathbf{r}$, $\mathbf{H}_{rS} = \mathbf{r}^T\mathbf{H}\mathbf{S}$, $\mathbf{H}_{SS} = \mathbf{S}^T\mathbf{H}\mathbf{S}$. The matrix transformation **T** has the property that $\mathbf{T}^T\mathbf{T} = \mathbf{I}$ being **I** the unit matrix of dimension *N*. Note that H_{rr} is a matrix block of dimension one while $\mathbf{H}_{Sr}$ and $\mathbf{H}_{rS}$ are two vectors of dimension *N-1*. Finally, $\mathbf{H}_{SS}$ is a matrix block of dimension *(N-1)*x*(N-1)*. The H_{rr} block matrix is in fact an element of the full Hessian matrix $\mathbf{T}^T\mathbf{H}\mathbf{T}$, in other words, $(\mathbf{T}^T\mathbf{H}\mathbf{T})_{11} = H_{rr}$. A deeper inspection of the vector $\mathbf{H}_{Sr} = \mathbf{S}^T\mathbf{H}\mathbf{r}$ reveals its entries. If **r** is an eigenvector of **H**, then $\mathbf{H}\ \mathbf{r} = h_r\ \mathbf{r}$, h_r being its eigenvalue, and we have $\mathbf{S}^T\mathbf{H}\mathbf{r} = h_r\ \mathbf{S}^T\mathbf{r} = \mathbf{0}_{N\text{-}1}$, the zero vector of dimension *N-1*, because the **S** matrix is formed by *N-1* vectors orthogonal to **r** per construction. If **r** is not an eigenvector, only then the vector $\mathbf{H}_{Sr}$ can have non-zero entries, at all. Of course, the same holds for $\mathbf{H}_{rS}^T$.

The eigenvalue equation of the Hessian matrix in the original coordinates, $\mathbf{H}\ \mathbf{a}_I = h_I\ \mathbf{a}_I$, $I = 1,N$ where the set, $\{h_I,\ \mathbf{a}_I\}_{I=1,N}$, are the corresponding eigenpairs, can be transformed into the new base vectors, taking the form,

$$\begin{bmatrix} H_{rr} & \mathbf{H}_{rS} \\ \mathbf{H}_{Sr} & \mathbf{H}_{SS} \end{bmatrix} \begin{pmatrix} c_I^r \\ \mathbf{c}_I^S \end{pmatrix} = h_I \begin{pmatrix} c_I^r \\ \mathbf{c}_I^S \end{pmatrix} \qquad I = 1,N \qquad (2)$$

where $\mathbf{c}_I = \mathbf{T}^T\mathbf{a}_I$, and its components are $c^r_I = \mathbf{r}^T\mathbf{c}_I$ and $\mathbf{c}^S_I = \mathbf{S}^T\mathbf{c}_I$. At a VRI point the Hessian matrix has at least an eigenpair, say J, such that, $h_J = 0$ and the corresponding eigenvector has the structure $(\mathbf{T}^T\mathbf{a}_J)^T = (\mathbf{c}_J)^T = (c^r_J, (\mathbf{c}^S_J)^T) = (0, (\mathbf{c}^S_J)^T)$. This condition of a VRI point implies that $det(\mathbf{H}) = det(\mathbf{T}^T\mathbf{H}\mathbf{T}) = 0$ while in a VRT point $det(\mathbf{H}_{SS}) = 0$ is required only. In this case we will have that one column (or one row) of the $\mathbf{H}_{SS}$ matrix is linearly dependent from the others. There is an $\mathbf{s}_I$ and there are N-2 $\mathbf{s}_J$ vectors with

$$\mathbf{S}^T\mathbf{H}\mathbf{s}_I = \sum_{J\neq I}^{N-2} \lambda_J \mathbf{S}^T\mathbf{H}\mathbf{s}_J \tag{3}$$

with any real numbers λ_J. The λ_J are not all equal zero because that would be the case of a zero eigenvalue of $\mathbf{H}$, thus it would correspond to a VRI point. Multiplication of equation (3) from the left hand side with $\mathbf{S}$ gives,

$$\mathbf{H}\mathbf{s}_I = \sum_{J\neq I}^{N-2} \lambda_J \mathbf{H}\mathbf{s}_J \,. \tag{4}$$

Because the set $\{\mathbf{s}_K\}_{K=1,N\text{-}1}$ is an orthonormal system of vectors, they cannot be eigenvectors of $\mathbf{H}$, if equation (4) is fullfiled. In the contrary case, it would be $h_I\ \mathbf{s}_I = \Sigma_{J\neq I}^{N\text{-}2}\ \lambda_J\ h_J\ \mathbf{s}_J$, which is a contradiction, if h_I and at least one h_J are not zero. So, equation (4) cannot be fulfilled for eigenvectors of $\mathbf{H}$. Because $\mathbf{H}$ is a symmetric

matrix, it has N orthogonal eigenvectors. Since $\mathbf{H}$ has not zero eigenvalues, its determinant is not zero.

From the algebraic point of view, we note that $det(\mathbf{H}_{SS}) = 0$ does also not imply $det(\mathbf{H}) = 0$. The proof is the following. We assume that we are in a point where $H_{rr} \neq 0$. First we take the Schur factorization [41] on the $\mathbf{T}^T\mathbf{HT}$ matrix,

$$\begin{bmatrix} H_{rr} & \mathbf{H}_{rS} \\ \mathbf{H}_{Sr} & \mathbf{H}_{SS} \end{bmatrix} = \begin{bmatrix} 1 & \mathbf{0}_{N-1}^T \\ \mathbf{H}_{Sr}H_{rr}^{-1} & \mathbf{I}_{N-1} \end{bmatrix} \begin{bmatrix} H_{rr} & \mathbf{0}_{N-1}^T \\ \mathbf{0}_{N-1} & \mathbf{H}_{SS} - \mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS} \end{bmatrix} \begin{bmatrix} 1 & H_{rr}^{-1}\mathbf{H}_{rS} \\ \mathbf{0}_{N-1} & \mathbf{I}_{N-1} \end{bmatrix} \quad (5)$$

where $\mathbf{0}_{N-1}$ is the zero vector of dimension $N-1$, and $H_{rr}^{-1} = 1 / H_{rr}$. Second we apply the determinant theory to the above equality (5), obtaining, $det(\mathbf{H}) = det(\mathbf{T}^T\mathbf{HT}) = H_{rr}\, det(\mathbf{H}_{SS}-\mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS})$. Now we assume that we are in a VRT point, however, not in a VRI point. The H_{rr} is a matrix element different from zero and $det(\mathbf{H}_{SS}) = 0$. For a dyadic product of two vectors, $\mathbf{p}$ and $\mathbf{f}$, we have the relation $det(\mathbf{I} - \mathbf{pf}^T) = 1 - \mathbf{f}^T\mathbf{p}$, and for a non-singular quadratic matrix $\mathbf{B}$ we can extend this to $det(\mathbf{B} - \mathbf{pf}^T) = det(\mathbf{B})(1 - \mathbf{f}^T\mathbf{B}^{-1}\mathbf{p})$ [42]. If we use for the inverse matrix the adjoint matrix, $\mathbf{A}$, divided through the determinant, $\mathbf{B}^{-1} = \mathbf{A} / det(\mathbf{B})$, we can shorten the *det*-factor and we get,

$$\det\left(\mathbf{B} - \mathbf{pf}^T\right) = \det\left(\mathbf{B}\right) - \mathbf{f}^T\mathbf{Ap}. \quad (6)$$

Now let be $\mathbf{B} = \mathbf{H}_{SS}$ and $\mathbf{A} = \mathbf{A}_{SS}$ its adjoint matrix. We treat the limes case that $det(\mathbf{B}) \rightarrow 0$. Then also equation (6) holds. In equation (6) we have to test $\mathbf{p} = \mathbf{S}^T\mathbf{Hr}$ and $\mathbf{f} = \mathbf{p}H_{rr}^{-1}$. Let $\{\mathbf{w}_i\}_{i=1,N-1}$ the set of eigenvectors of $\mathbf{H}_{SS}$. Without lost of generality let $\mathbf{w}_1$

the eigenvector with null eigenvalue. Notice that at least an eigenvalue should be zero because $det\,(\mathbf{H}_{SS}) = 0$. The $\mathbf{A}_{SS}$ has the same eigenvectors, but its eigenvalues are $\rho_1 \neq 0$ and $\rho_i = 0$ for $i = 2,N\text{-}1$. Now we put the vector $\mathbf{p} = \mathbf{S}^T\mathbf{H}\mathbf{r} = \mathbf{H}_{Sr}$ as a function of the eigenvectors of $\mathbf{H}_{SS}$,

$$\mathbf{p} = \mathbf{I}_{N-1}\mathbf{p} = \left(\sum_{i=1}^{N-1} \mathbf{w}_i \mathbf{w}_i^T\right)\mathbf{p} = \sum_{i=1}^{N-1} \chi_i \mathbf{w}_i \tag{7}$$

where $\chi_i = \mathbf{w}_i^T\mathbf{p}$. We multiply both sides of equation (7) from the left by $\mathbf{A}_{SS}$ and we get,

$$\mathbf{A}_{SS}\mathbf{p} = \sum_{i=1}^{N-1} \chi_i \mathbf{A}_{SS}\mathbf{w}_i = \chi_1\rho_1\mathbf{w}_1 \tag{8}$$

because the eigenvalues ρ_i for $i=2,N\text{-}1$ are zero. With the result we have $\mathbf{f}^T\mathbf{A}_{SS}\mathbf{p} = \mathbf{p}^T\mathbf{A}_{SS}\mathbf{p}\ H_{rr}^{-1} = \chi_1^2\rho_1 H_{rr}^{-1}$, and the determinant expression (6) becomes, $det\,(\mathbf{H}_{SS} - \mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS}) = -\chi_1^2\rho_1 H_{rr}^{-1}$. If $\chi_1 \neq 0$, the determinant of the matrix $(\mathbf{H}_{SS} - \mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS})$ is also not zero, and $det\,(\mathbf{H}) = det\,(\mathbf{T}^T\mathbf{H}\mathbf{T}) \neq 0$. In summary in a VRT point $det\,(\mathbf{H}_{SS}) = 0$ but $det\,(\mathbf{H}) = det\,(\mathbf{T}^T\mathbf{H}\mathbf{T}) = H_{rr}\ det\,(\mathbf{H}_{SS} - \mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS}) = -\chi_1^2\rho_1 \neq 0$.

In contrast, at a VRI point in addition to $det\,(\mathbf{H}_{SS}) = 0$ at least an element of the $\mathbf{H}_{Sr}$ vector and by symmetry the corresponding element of the $\mathbf{H}_{rS}$ vector should be zero obtaining the condition $det\,(\mathbf{H}) = det\,(\mathbf{T}^T\mathbf{H}\mathbf{T}) = H_{rr}\ det\,(\mathbf{H}_{SS} - \mathbf{H}_{Sr}H_{rr}^{-1}\mathbf{H}_{rS}) = 0$, as required in this type of points. These are the reasons why the condition of a point of the PES to be a VRI is much stronger than that to be a VRT point. Before entering into a

more detailed analysis we transform the above eigenvalue equation (2) using the unitary transformation,

$$\mathbf{U} = \begin{bmatrix} 1 & \mathbf{0}_{N-1}^T \\ \mathbf{0}_{N-1} & \mathbf{W}_{SS} \end{bmatrix} \tag{9}$$

where $\mathbf{W}_{SS} = [\mathbf{w}_1| \ ... \ |\mathbf{w}_{N-1}]$ is the matrix formed by the set of eigenvectors that diagonalize the block matrix $\mathbf{H}_{SS}$. The product is $\mathbf{U}^T\mathbf{U} = \mathbf{I}$ because $\mathbf{W}_{SS}{}^T\mathbf{W}_{SS} = \mathbf{I}_{N-1}$. The set of eigenvectors, which we collected in the matrix $\mathbf{W}_{SS}$, is defined by the base of the $N-1$ linear independent directions **S** being orthogonal to the gradient vector. Now we transform the eigenpair equation (2) using the unitary matrix **U**, that is $\mathbf{U}^T(\mathbf{T}^T\mathbf{H}\mathbf{T})\mathbf{U}\mathbf{U}^T\mathbf{c}_I = h_I\mathbf{U}^T\mathbf{c}_I$. The structure of the resulting eigenpair equation is

$$\begin{bmatrix} H_{rr} & \mathbf{z}_{rS}^T \\ \mathbf{z}_{Sr} & \mathbf{Z}_{SS} \end{bmatrix} \begin{pmatrix} c_I^r \\ \mathbf{d}_I^S \end{pmatrix} = h_I \begin{pmatrix} c_I^r \\ \mathbf{d}_I^S \end{pmatrix} \qquad I = 1, N \tag{10}$$

where $\mathbf{z}_{Sr} = \mathbf{W}_{SS}{}^T\,\mathbf{H}_{Sr}$, $\mathbf{d}^S{}_I = \mathbf{W}_{SS}{}^T\,\mathbf{c}^S{}_I$ and $\mathbf{Z}_{SS} = \mathbf{W}_{SS}{}^T\,\mathbf{H}_{SS}\,\mathbf{W}_{SS} = \{z_i\ \delta_{ij}\}_{i,j=1,N-1}$ being z_i the eigenvalues of the $\mathbf{H}_{SS}$ block matrix. At a VRT point $det\ (\mathbf{H}_{SS}) = det\ (\mathbf{Z}_{SS}) = 0$ which means that at least one eigenvector exists there, say $\mathbf{w}_j$, whose eigenvalue $z_j = 0$. This eigenvector is orthogonal to the gradient vector but is not an eigenvector of the full Hessian matrix **H**. As explained in the Introduction section, the latter implies that the equipotential energy surface has a direction, $\mathbf{w}_j$, of zero curvature, $z_j = 0$, but this direction does not coincide with an eigenvector, $\mathbf{c}_I$, of the full Hessian matrix [29, 31].

The Theory of the Partition Technique applied to the eigenpair equation (10) at the VRI point.

We consider the eigenpair equation (10), where the set of eigenvalues of the $\mathbf{H}_{SS}$ block matrix are in increasing order, $z_1 \leq z_2 \leq \ldots \leq z_{N-1}$. This eigenpair equation can be written as a system of two coupled equations,

$$H_{rr} c_I^r + \mathbf{z}_{rS}^T \mathbf{d}_I^S = h_I c_I^r \qquad (11.a)$$

$$\mathbf{z}_{Sr} c_I^r + \mathbf{Z}_{SS} \mathbf{d}_I^S = h_I \mathbf{d}_I^S \,. \qquad (11.b)$$

For any h_I for which the $\mathbf{d}^S{}_I$ components of the eigenvector I are nonvanishing, we can write the component $c^r{}_I$ as a function of $\mathbf{d}^S{}_I$,

$$c_I^r = -\left(H_{rr} - h_I\right)^{-1} \mathbf{z}_{rS}^T \mathbf{d}_I^S \qquad \text{for } \forall I = 1,N \text{ such that } \mathbf{d}^S{}_I \neq \mathbf{0}_{N\text{-}1}. \qquad (12)$$

Substituting in equation (11.b) we obtain the next expression

$$\left[\mathbf{Z}_{SS} - \mathbf{z}_{Sr}\left(H_{rr} - h_I\right)^{-1} \mathbf{z}_{rS}^T\right] \mathbf{d}_I^S = h_I \mathbf{d}_I^S \qquad \text{for } \forall I = 1,N \text{ such that } \mathbf{d}_I^S \neq \mathbf{0}_{N-1}. \qquad (13)$$

The eigenpair solutions of equation (10) or equation (2) are equivalent to the solutions of the above partitioned equation (13). We define the vectorial function or multivalued function $\mathbf{l}(h)$ as the vector whose elements are the eigenvalues of the matrix $\mathbf{L}(h) = [\mathbf{Z}_{SS} - \mathbf{z}_{Sr}(H_{rr} - h)^{-1} \mathbf{z}_{rS}{}^T]$, and the single valued function $R(h) = h$. The set of eigenpairs of the $\mathbf{L}(h)$ matrix is $\{\mathbf{l}(h)_i,\ \mathbf{v}(h)_i\}_{i=1,N\text{-}1}$, for simplicity in the future we omit the h

dependence of $\mathbf{v}_i$. At each h the eigenvalues of $\mathbf{L}(h)$ matrix are in increasing order, $\mathbf{l}(h)_1 \leq \mathbf{l}(h)_2 \leq \ldots \leq \mathbf{l}(h)_{N-1}$. The eigenvalues of the eigenpair equation (10) or equation (2) are given by the set of h_I for which exists a $\mathbf{l}(h_I)_i = R(h_I) = h_I$, $i = 1,N-1$. The $\mathbf{v}_i$ eigenvector associated to this eigenvalue $\mathbf{l}(h_I)_i = h_I$ is the normalized form of the $\mathbf{d}^S{}_I$ vector. Substituting it in equation (12) we get the whole un-normalized $(\mathbf{U}^T\mathbf{T}^T\mathbf{a}_I)^T = (c^r{}_I, (\mathbf{d}^S{}_I)^T)$ eigenvector. The graph of each branch of $\mathbf{l}(h)$ as a function of h is given in Figure 1 and explained in the next subsection. The horizontal asymptotes of these branches are the eigenvalues z_i of the block diagonal matrix $\mathbf{Z}_{SS}$ with,

$$\lim_{h\to\pm\infty}\mathbf{l}(h) = \lim_{h\to\pm\infty}\begin{pmatrix} \mathbf{l}(h)_1 \\ \vdots \\ \mathbf{l}(h)_{N-1} \end{pmatrix} = \begin{pmatrix} z_1 \\ \vdots \\ z_{N-1} \end{pmatrix}. \tag{14}$$

In the same way the corresponding set of eigenvectors of $\mathbf{L}(h)$ tends to the set of eigenvectors of the block matrix $\mathbf{H}_{SS}$,

$$\lim_{h\to\pm\infty}\begin{bmatrix} \mathbf{v}_1 & \cdots & \mathbf{v}_{N-1} \end{bmatrix} = \begin{bmatrix} \mathbf{w}_1 & \cdots & \mathbf{w}_{N-1} \end{bmatrix}. \tag{15}$$

The vertical asymptote is located at the h value that corresponds to the value of H_{rr}. Each branch of $\mathbf{l}(h)$ is a nonincreasing function of h and satisfies a noncrossing rule with the other branches. The shape of each branch say, $\mathbf{l}(h)_i$, is governed by the block coupling matrix, $\mathbf{z}_{Sr}$, or the equivalent one, $\mathbf{z}_{rS}{}^T$, and the corresponding eigenvector, $\mathbf{v}_i$. As h approaches to the vertical asymptote H_{rr}, due to the noncrossing rule, only the lowest branch of $\mathbf{l}(h)$ namely, $\mathbf{l}(h)_1$, becomes singular and has the principal part

$$\mathbf{l}(h)_1 = \mathbf{v}_1^T \mathbf{L}(h) \mathbf{v}_1 \approx -(H_{rr} - h)^{-1} \mathbf{v}_1^T \mathbf{z}_{Sr} \mathbf{z}_{rS}^T \mathbf{v}_1 = -(H_{rr} - h)^{-1} (\mathbf{v}_1^T \mathbf{z}_{Sr})^2 \quad (16)$$

where the last equality holds due to the fact that $\mathbf{z}_{rS}{}^T = \mathbf{z}_{Sr}$. At these values of h the eigenvector $\mathbf{v}_1$ becomes proportional to the vector $\mathbf{z}_{Sr}$ and because the eigenvectors are orthonormalized, the remainder of the set of eigenvectors does not interact with the principal part. Due to this fact, $\mathbf{l}(h)_i = \mathbf{v}_i{}^T \mathbf{L}(h) \mathbf{v}_i \approx \mathbf{v}_i{}^T \mathbf{Z}_{SS} \mathbf{v}_i$, for $i = 2, N-1$.

At the VRI point at least one eigenvalue of the Hessian matrix is zero, there must be at least a branch, say $\mathbf{l}(h)_i$, such that at $h = 0$, $\mathbf{l}(0)_i = R(0) = 0 = \mathbf{v}_i{}^T \mathbf{Z}_{SS} \mathbf{v}_i - H_{rr}^{-1} (\mathbf{v}_i{}^T \mathbf{z}_{Sr})^2$. At the VRI point as well at least a diagonal element, say j, has the value zero, $(\mathbf{Z}_{SS})_{jj} = z_j = 0$, implying that the branch $\mathbf{l}(h)_j$ tends to zero as h tends to $-\infty$ and $\mathbf{l}(h)_{j+1}$ tends to zero as h tends to $+\infty$. This behavior is due to both the nonincreasing rule of the branches and the existence of a vertical asymptote. In addition the substitution of the corresponding $\mathbf{v}_i$ eigenvector as a normalized $\mathbf{d}^S_1$ vector in equation (12) the resulting c^r_1 component should be equal zero, which is the second condition at the VRI point as explained in the previous subsection. These two conditions are satisfied by the $\mathbf{v}_i$ eigenvector if it is, at $h = 0$, orthogonal to $\mathbf{z}_{Sr}$ vector since $\mathbf{v}_i \neq \mathbf{0}_{N-1}$ and from its structure should be a vector such that the j component is equal one, $\mathbf{v}_i{}^T = (0_1, \ldots, 1_j, \ldots, 0_{N-1})$. The latest satisfies that $R(0) = \mathbf{l}(0)_i = \mathbf{v}_i{}^T \mathbf{Z}_{SS}{}^D \mathbf{v}_i = z_j = 0$, as required. Notice that the subscript i of $\mathbf{l}(0)_i$ can be j or $j+1$ depending if H_{rr} is positive or negative, respectively. Finally, the component j of the vectors $\mathbf{z}_{Sr}$ and $\mathbf{z}_{rS}{}^T$ should be equal zero since in this manner $\mathbf{v}_i{}^T \mathbf{z}_{Sr} = 0$, as required too. This ends the general analysis of the Hessian matrix at the VRI point using the theory of Löwdin's Partitioning Technique [36].

Finally, from this analysis based on the structure of the Hessian matrix, we can say that the sufficient condition that a point of the PES is a VRT point is that the determinant of

$\mathbf{H}_{SS}$ is zero. The $\mathbf{H}_{SS}$ comes from the Hessian matrix of this point projected in the subspace spanned by the set of *N-1* linear independent directions orthogonal to the gradient vector. On the other hand this condition is necessary but it is not sufficient for a VRI point. The sufficient condition for a VRI point is that in addition to the condition that the $\mathbf{H}_{SS}$ matrix has at least a null eigenvalue, this null eigenvalue which is an element of the $\mathbf{Z}_{SS}$ matrix must be decoupled with respect to the H_{rr} diagonal element.

The features of the plot of ***l****(h) of a Hessian matrix at the VRI point.*

We assume a VRI point on a five-dimensional surface as a generic example. In Figure 1 is shown the **l***(h)* plot as a function of *h* of the Hessian matrix in this point. At the VRI point holds that at least a horizontal asymptote of the graph coincides with the *h* axis. This asymptote corresponds to the eigenvalue or eigenvalues of the block Hessian matrix, $\mathbf{H}_{SS}$, with the value zero. A branch should cross the point, $h = 0$, $l(h) = 0$, and because the straight line $R(h) = h$ also crosses this point, then, according to the explanation given in the previous subsection, this implies that the full matrix has at least an eigenpair with null eigenvalue. The shape of each branch is a function of the factor $(\mathbf{v}_i^T \mathbf{z}_{Sr})^2$ being $\mathbf{v}_i$ the eigenvector associated to the considered branch. The graph also has a unique vertical asymptote at $h = H_{rr}$, where H_{rr} is the element of the one-dimensional block matrix $\mathbf{H}_{rr}$. A general graph is pictured in Figure 1 for the case of a negative H_{rr}. The block Hessian matrix $\mathbf{H}_{SS}$ has a negative eigenvalue, z_1, the eigenvalue zero, labeled as z_2, and two positive eigenvalues, z_3 and z_4. The resulting full Hessian has two negative eigenvalues, h_1 and h_2, two positive eigenvalues, h_4 and h_5, and the null eigenvalue, h_3. These values are located where the branches cut the straight

line $R(h) = h$. The branch $l(h)_2$ as h tends to $-\infty$ asymptotically approaches to the level of the eigenvalue $z_2 = 0$. However in its evolution as h tends to $+\infty$ asymptotically approaches to the level of the eigenvalue z_1. This decreasing effect starts before the branch reaches the point $h = 0$, $l(h) = 0$. Paying attention to the branch $l(h)_3$, as h tends to $-\infty$ this branch asymptotically approaches to the level of the eigenvalue z_3 but it asymptotically approaches to the level of the eigenvalue z_2 when h tends to $+\infty$. During this evolution the branch $l(h)_3$ crosses the point, $h = 0$, $l(h) = 0$, which is also a point of the straight line, $R(h) = h$. Due to this fact this branch is responsible for the full Hessian matrix having a null eigenvalue, labeled as h_3. The associated eigenvector of the branch $l(h)_3$ at the point, $h = 0$, $l(h) = 0$, has the structure, $(\mathbf{v}_3)^T = (0, 1, 0, 0)$, which is orthogonal at this point to the vector, $\mathbf{z}_{Sr}$, the block of matrix coupling elements. This orthogonality is the reason why the eigenvector with null eigenvalue of the full Hessian matrix is orthogonal to the gradient vector.

At the value $h = H_{rr}$, the eigenvector of the branch $l(h)_1$, $\mathbf{v}_1$, is parallel to the block coupling vector, $\mathbf{z}_{Sr}$. The value of $l(h)_1$ goes to $-\infty$ as h approaches to H_{rr} from the left. In this interval the branch crosses the straight line $R(h) = h$ at the value $h = h_1$. Note that $h_1 < H_{rr}$. For the remainder of the branches at $h \approx H_{rr}$ holds, their eigenvectors are orthogonal to the $\mathbf{z}_{Sr}$ coupling vector, that their values are given by $\mathbf{v}_i^T \mathbf{Z}_{SS} \mathbf{v}_i$ for $i = 2, 3, 4$. The values of $\mathbf{v}_i^T \mathbf{Z}_{SS} \mathbf{v}_i$ for $i = 2, 3, 4$ are between z_1 and z_4, in other words, $z_1 \leq \mathbf{v}_i^T \mathbf{Z}_{SS} \mathbf{v}_i \leq z_4$ thanks to the MiniMax Eigenvalue theorem [43].

In the h interval that goes from H_{rr} to $+\infty$ a new branch appears just at $h \approx H_{rr}$ on the right hand side part. This new branch is labeled as $l(h)_5$ and its values decrease asymptotically from $+\infty$ to the value of the eigenvalue z_4 as h tends to $+\infty$. In this interval this branch crosses the straight line $R(h) = h$ at the value of $h = h_5$ which is the highest eigenvalue of the full Hessian matrix.

Connection with previous expressions used to characterize the VRT and VRI points.

So far the basic element used in the present analysis is the Hessian matrix. We derive its structure at the VRT and VRI points. From these results the necessary and sufficient conditions for a point to be VRT or VRI point have been discussed. However, these conditions were derived and analyzed some time ago using the adjoint matrix of the Hessian matrix rather than the Hessian itself. Now we expose the equivalence between both views in this subsection. From the matrix theory and the determinant theory it is known that a matrix multiplied by its adjoint matrix is equal to the unit matrix times the determinant value of the matrix. We apply this formula to the $\mathbf{T}^T\mathbf{HT}$ matrix,

$$\mathbf{T}^T\mathbf{A}\mathbf{T}\mathbf{T}^T\mathbf{H}\mathbf{T} = \mathbf{T}^T\mathbf{T}\det(\mathbf{H}) = \begin{bmatrix} A_{rr} & \mathbf{A}_{rS} \\ \mathbf{A}_{Sr} & \mathbf{A}_{SS} \end{bmatrix}\begin{bmatrix} H_{rr} & \mathbf{H}_{rS} \\ \mathbf{H}_{Sr} & \mathbf{H}_{SS} \end{bmatrix} = \begin{bmatrix} 1 & \mathbf{0}_{N-1}^T \\ \mathbf{0}_{N-1} & \mathbf{I}_{N-1} \end{bmatrix}\det(\mathbf{H}) \quad (17)$$

where we applied that $\mathbf{T}^T\mathbf{T} = \mathbf{I}$, the unit matrix of dimension N. The adjoint matrix $\mathbf{A}$ is defined as $\mathbf{A}_{ji} = [(-1)^{i+j}\, m_{ij}]^T$, where m_{ij} is the minor of $\mathbf{H}$ obtained by the deletion of the ith row and the jth column from $\mathbf{H}$, and taking the determinant. Note that j and i are interchanged in $\mathbf{A}_{ji}$. In the $\mathbf{T}^T\mathbf{A}\mathbf{T}$ matrix we have the element $A_{rr} = \mathbf{r}^T\mathbf{A}\mathbf{r}$. $\mathbf{A}_{rS} = \mathbf{r}^T\mathbf{A}\mathbf{S}$ and $\mathbf{A}_{Sr} = \mathbf{S}^T\mathbf{A}\mathbf{r}$ are vectors of dimension $N-1$, where due to the symmetry $(\mathbf{A}_{Sr})^T = \mathbf{A}_{rS}$ and $\mathbf{A}_{SS} = \mathbf{S}^T\mathbf{A}\mathbf{S}$ is a block matrix of dimension $(N-1)$x$(N-1)$. As noted above, if a point is a VRT point then the sufficient condition is $det\,(\mathbf{H}_{SS}) = 0$. Using the definition of the

adjoint matrix we have, $A_{rr} = \mathbf{r}^T\mathbf{A}\mathbf{r} = det\,(\mathbf{H}_{SS}) = 0$, now since $\mathbf{r} = \mathbf{g} / (\mathbf{g}^T\mathbf{g})^{1/2}$ we finally obtain

$$\mathbf{r}^T\mathbf{A}\mathbf{r} = \frac{\mathbf{g}^T\mathbf{A}\mathbf{g}}{\mathbf{g}^T\mathbf{g}} = 0\,. \tag{18}$$

Equation (18) was found by Hirsch [31], so it will be labeled as the Hirsch equation. It gives the sufficient condition of a VRT point. The connection to the previous analysis based on the Hessian matrix is now well established. However, this is a necessary condition but not a sufficient one for a point to be a VRI point given in terms of the **A** matrix. In terms of the adjoint matrix **A** the sufficient condition of a VRI point can be derived as follows. Using the structure of the Hessian matrix, $\mathbf{T}^T\mathbf{H}\mathbf{T}$ at the VRI point and the definition of the adjoint matrix, at the VRI point the $\mathbf{T}^T\mathbf{A}\mathbf{T}$ matrix has the form

$$\begin{bmatrix} A_{rr} & \mathbf{A}_{rS} \\ \mathbf{A}_{Sr} & \mathbf{A}_{SS} \end{bmatrix} = \begin{bmatrix} 0 & \mathbf{0}_{N-1}^T \\ \mathbf{0}_{N-1} & \mathbf{A}_{SS} \end{bmatrix}. \tag{19}$$

The reason of this result is due to the decoupling between the diagonal element H_{rr} and the null element of the diagonal $\mathbf{Z}_{SS}$ matrix. According to these results all elements of the first column and the first row of the $\mathbf{T}^T\mathbf{A}\mathbf{T}$ matrix are zero. Due to this fact we can write the first column or due to the symmetry the first row of this adjoint matrix as $(A_{rr}\ \mathbf{A}_{rS}) = (\mathbf{r}^T\mathbf{A}\mathbf{r}\ \ \mathbf{r}^T\mathbf{A}\mathbf{S}) = \mathbf{r}^T\mathbf{A}[\mathbf{r} \mid \mathbf{S}] = \mathbf{r}^T\mathbf{A}\mathbf{T} = \mathbf{0}^T$. Since the **T** matrix is built by a set of N linear independent vectors and using the definition of the **r** vector we obtain,

$$\mathbf{A}\mathbf{r} = \mathbf{A}\mathbf{g}\left(\mathbf{g}^T\mathbf{g}\right)^{-1/2} = \mathbf{0}\,. \tag{20}$$

Equation (20) gives the necessary and sufficient condition for a point of the PES to be a VRI point using the adjoint matrix of the Hessian as a basic element [5]. We conclude that it is equivalent for a VRT point to say $det(\mathbf{H}_{SS}) = 0$ means that $\mathbf{r}^T\mathbf{Ar} = 0$, and for a VRI point it is equivalent to say that the null or null elements of $\mathbf{Z}_{SS}$ matrix are decoupled with respect to the diagonal element of H_{rr} which means that $\mathbf{Ar} = \mathbf{0}$.

Some Numerical Examples.

A Two-Dimensional Case.

This is the trivial case but it helps to clarify the above conclusions. The PES is given in Cartesian coordinates, $V(\mathbf{x})$, where $\mathbf{x}^T = (x_1, x_2)$. The normalized gradient vector is $\mathbf{r}^T = (r_1, r_2)$ and its orthogonal normalized direction vector, $\mathbf{s}^T = (s_1, s_2)$. These two vectors define the **T** matrix transformation $\mathbf{T} = [\mathbf{r} \mid \mathbf{s}]$. Let us assume that the current point is a VRT point, then the transformed Hessian matrix to the **r** and **s** base vectors is

$$\mathbf{T}^T\mathbf{HT} = \begin{bmatrix} \mathbf{r} & \mathbf{s} \end{bmatrix}^T \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} \mathbf{r} & \mathbf{s} \end{bmatrix} = \begin{bmatrix} \mathbf{r}^T\mathbf{Hr} & \mathbf{r}^T\mathbf{Hs} \\ \mathbf{s}^T\mathbf{Hr} & \mathbf{s}^T\mathbf{Hs} \end{bmatrix} = \begin{bmatrix} H_{rr} & H_{rs} \\ H_{sr} & 0 \end{bmatrix} . \quad (21)$$

Due to the symmetry of the Hessian matrix $H_{rs} = H_{sr}$ and from this $det\,(\mathbf{H}) = -H_{rs}^2$. If the point is a VRI then $H_{rs} = H_{sr} = 0$ and $det\,(\mathbf{H}) = 0$. In these conditions the eigenpair with the eigenvalue, $h = 0$, of the Hessian matrix given in equation (21) is $\mathbf{c}^T = (0, 1)$. Transforming the eigenvector back to Cartesian coordinates we obtain $\mathbf{a}^T = \mathbf{c}^T \mathbf{T}^T = \mathbf{s}^T$. This eigenvector coincides with the normalized direction vector orthogonal to the gradient vector. In this way the eigenvector with null eigenvalue is tangent to the equipotential energy curve at the VRI point.

A numerical example of a two-dimensional PES is that proposed by Quapp and coworkers [31]. The PES is characterized by the following expression

$$V(\mathbf{x}) = 1/2\left(x_1 x_2^2 - x_2 x_1^2 - 7/4\, x_1 + 2 x_2\right) + 1/30\left(x_1^4 + x_2^4\right) \qquad (22)$$

This PES is pictured in Figure 2. The values are given in arbitrary units. At the point $\mathbf{x}^T = (0, 0)$ the normalized gradient vector is $\mathbf{r}^T = (-7, 8)(113)^{-1/2}$ and the orthogonal direction vector is $\mathbf{s}^T = (8, 7)(113)^{-1/2}$. All the elements of the Hessian matrix take the value zero, $H_{11} = H_{22} = H_{21} = H_{12} = 0$. Clearly the $det\,(\mathbf{H}) = 0$ implying that the point $(0, 0)$ is a VRI point of this PES. Taking into account the previous discussion means that the **s** vector is just the eigenvector of null eigenvalue orthogonal to the gradient vector. Furthermore, in this case the normalized gradient vector **r** is also an eigenvector of null eigenvalue. For the reason this point is a point belonging to a GE curve [20, 21, 22, 23, 24, 25] of this PES.

Now we take the point $\mathbf{x}^T = (0.44, -0.80)$ located on the valley ridge borderline indicated as a thin dashed line in Figure 2. The normalized gradient vector is $\mathbf{r}^T = (-0.37, 0.93)$ and the orthogonal direction vector is $\mathbf{s}^T = (0.93, 0.37)$. In the [**r** | **s**] base representation the elements of the Hessian matrix take the values, $H_{rr} = 1.57$, $H_{rs} = H_{sr}$

$= -0.96$ and $H_{ss} = 0.0$. Due to this Hessian structure this point is a VRT point and the **s** direction vector has null curvature. The **s** direction is tangent to the equipotential curve at this point. The equipotential curve has null curvature at this point. The eigenvectors of the Hessian matrix in the Cartesian coordinates are $\mathbf{a}^T_1 = (0.68, 0.73)$ and $\mathbf{a}^T_2 = (-0.73, 0.68)$ and their eigenvalues are $h_1 = -0.46$ and $h_2 = 2.03$ respectively. Note that $det(\mathbf{H}) \neq 0$ and no eigenvector coincides with the **s** vector, the direction vector of null curvature. Clearly the point $\mathbf{x}^T = (0.44, -0.80)$ is a VRT point of the PES given in equation (22). This point is also a point that belongs to the IRC curve joining the SP with the minimum. For the reason this IRC is an RP but achieves the category of minimum energy path. In its evolution from the first order saddle point it leaves a valley and enters a ridge and finally again enters the valley of the minimum. In Figure 2 this IRC curve is the dotted line. Note, the crossing of the IRC with the border line between valley and ridge, the dashed curve of VRT points, does not indicate where a possible RP bifurcation can take place on the PES. Additionally, there is such a border line through every SP where no bifurcation takes place.

A Three-Dimensional Chemical Example.

As a chemical example we report the three dimensional system HCN. For simplicity only, we approximate the coordinates as Cartesians: uncoupled, orthogonal coordinates. The PES function is given in internal coordinates defined by the two bond distances, namely, CH and CN, and the bond angle, HCN, labeled by α. In this case equation (1) takes the form,

$$\mathbf{T}^T\mathbf{H}\mathbf{T} = \left[\mathbf{r}\ \mathbf{s}_1\ \mathbf{s}_2\right]^T \begin{bmatrix} H_{CH,CH} & H_{CH,CN} & H_{CH,\alpha} \\ H_{CN,CH} & H_{CN,CN} & H_{CN,\alpha} \\ H_{\alpha,CH} & H_{\alpha,CN} & H_{\alpha,\alpha} \end{bmatrix} \left[\mathbf{r}\ \mathbf{s}_1\ \mathbf{s}_2\right] = \begin{bmatrix} \mathbf{r}^T\mathbf{H}\mathbf{r} & \mathbf{r}^T\mathbf{H}\mathbf{s}_1 & \mathbf{r}^T\mathbf{H}\mathbf{s}_2 \\ \mathbf{s}_1^T\mathbf{H}\mathbf{r} & \mathbf{s}_1^T\mathbf{H}\mathbf{s}_1 & \mathbf{s}_1^T\mathbf{H}\mathbf{s}_2 \\ \mathbf{s}_2^T\mathbf{H}\mathbf{r} & \mathbf{s}_2^T\mathbf{H}\mathbf{s}_1 & \mathbf{s}_2^T\mathbf{H}\mathbf{s}_2 \end{bmatrix}. \tag{23}$$

Both matrices are symmetric. Figure 3 shows a schematic section of some VRT points on the PES of HCN obtained at the level RHF/6-31G* using the GAMESS code [44]. They are approximated by the dashed line. The picture is a projection into the plane CH = *1.125 Å*, and for the level lines, all energies are optimized to the corresponding raster of the two coordinates CN, and angle α. There is a VRI point of the dissociation of the N-atom from the SP of the isomerization. The VRI is at the cross of the four branches *a*, *b*, *c*, and *d* of the singular NT through the point. Further dotted curves are regular NTs, like the curve *e*. At their turning points are cross-symbols: these are the VRT points. There is the border between the branches *a*, and *b*, however, not between *a,* and *d*, because the VRI point is of a mixed character. It is not a usual "pitchfork" bifurcation. The branches *b* and *c* are valley pathways, however, *a*, and *d* are on the ridge. The "southern" NTs increase in energy from the SP and lead anywhere into the PES mountains to an SP of index two. They do not have a turning point. Branches *b* and *c*, (or, not shown, NTs on the right hand side, and over them) may serve as an RP model of the dissociation of the N-atom from the HCN minimum.

At each point of the NT depicted by *e* we compute the eigenvalues and the eigenvectors of the corresponding Hessian matrix to find a VRT point. The VRT is at the point $\mathbf{q}^T$ = $(q_{CH}, q_{CN}, q_\alpha) = (1.297, 1.090, 94.7)$. The bond distances are given in *Å* and the bond angle in degrees. At this point the Hessian matrix in internal coordinates is $H_{CH,CH}$ = *0.11193*, $H_{CH,CN}$ = *-0.01487*, $H_{CN,CN}$ = *2.04173*, $H_{CH,\alpha}$ = *0.07521*, $H_{CN,\alpha}$ = *0.07936*, $H_{\alpha,\alpha}$

$= -0.03748$. The units are given in Hartree / bohr^2, Hartree / (bohr radian) and Hartree / radian^2. The eigenpairs of this Hessian matrix are $h_1 = -0.07$, $\mathbf{a}_1^T = (-0.037, -0.381, 0.924)$; $h_2 = 0.14$, $\mathbf{a}_2^T = (-0.009, 0.924, 0.381)$; $h_3 = 2.04$, $\mathbf{a}_3^T = (-0.999, 0.006, -0.038)$. The main component of the first eigenvector is the bond angle α, while for the second and the third eigenvectors the main components are the bond distances CN and CH, respectively. Note that $det(\mathbf{H}) \neq 0$ indicating that this point is not a VRI point. The gradient vector at this point in Hartree / bohr and Hartree / radian is, $\mathbf{g}^T = (-0.230, 0.078, -0.044)$. Using this gradient vector a $\mathbf{T}$ matrix transformation is computed by a Gram-Schmidt orthogonalization using the gradient for the first vector. Their components are, $\mathbf{r}^T = (-0.933, 0.315, -0.176)$, $\mathbf{s}_1^T = (0.213, 0.875, 0.434)$, $\mathbf{s}_2^T = (-0.291, -0.367, 0.884)$. The components of the resulting $\mathbf{T}^T\mathbf{H}\mathbf{T}$ symmetric matrix are, $\mathbf{r}^T\mathbf{H}\mathbf{r} = 1.812$, $\mathbf{s}_1^T\mathbf{H}\mathbf{r} = -0.398$, $\mathbf{s}_1^T\mathbf{H}\mathbf{s}_1 = 0.238$, $\mathbf{s}_2^T\mathbf{H}\mathbf{r} = 0.508$, $\mathbf{s}_2^T\mathbf{H}\mathbf{s}_1 = -0.121$, $\mathbf{s}_2^T\mathbf{H}\mathbf{s}_2 = 0.066$. The block matrix $\mathbf{H}_{SS}$ is characterized by the elements of the $\mathbf{T}^T\mathbf{H}\mathbf{T}$ matrix, $\mathbf{s}_1^T\mathbf{H}\mathbf{s}_1$, $\mathbf{s}_2^T\mathbf{H}\mathbf{s}_1$, $\mathbf{s}_2^T\mathbf{H}\mathbf{s}_2$ and due to the symmetry $\mathbf{s}_2^T\mathbf{H}\mathbf{s}_1 = \mathbf{s}_1^T\mathbf{H}\mathbf{s}_2$. The eigenpairs of this $\mathbf{H}_{SS}$ matrix are, $z_1 = 0.00$, $\mathbf{w}_1^T = (0.458, 0.889)$; $z_2 = 0.30$, $\mathbf{w}_2^T = (0.889, -0.458)$. From these results we see that $det(\mathbf{H}_{SS}) = 0$. The coupling vector between $\mathbf{r}^T\mathbf{H}\mathbf{r}$ and $\mathbf{Z}_{SS} = \mathbf{W}^T\mathbf{H}_{SS}\mathbf{W}$, namely, $\mathbf{z}_{rS}^T = (\mathbf{s}_1^T\mathbf{H}\mathbf{r}\ \mathbf{s}_2^T\mathbf{H}\mathbf{r})\ \mathbf{W} = (\mathbf{s}_1^T\mathbf{H}\mathbf{r}\ \mathbf{s}_2^T\mathbf{H}\mathbf{r})\ [\mathbf{w}_1 \mid \mathbf{w}_2] = (0.269, -0.586) \neq \mathbf{0}_2^T$. Because $det(\mathbf{H}_{SS}) = 0$ and $\mathbf{z}_{rS} \neq \mathbf{0}_2$ or that it is equal $det(\mathbf{H}) \neq 0$ and $det(\mathbf{H}_{SS}) = 0$ we conclude that this point is a VRT point.

Figure 4 shows the same VRI region like Figure 3 in the full three-dimensional configuration space of all internal coordinates. Note that this VRI point is part of a one-dimensional VRI manifold on the two-dimensional ridge of the PES, a curve, thus a manifold of dimension *N-2*, see [6]. The VRT points form a two-dimensional surface in the full space.

Conclusions and Final Remarks.

The purpose of this paper is to show the mathematical features of VRI- and VRT points and their subtle differences. Based on the application of Löwdin's Partitioning Technique [36] on the Hessian eigenpair equation at the VRT and VRI points we derive the structure of this matrix at these special points of the PES. This analysis was carried out in the space spanned by the gradient and the complete subset of linear independent directions orthogonal to the gradient vector. The change of coordinates permits to study the curvature of the proper directions contained in the equipotential energy surface in a better way. The nature of this curvature is related to the existence of VRT and VRI points. The Hessian matrix in this new set of coordinates can be divided into two diagonal blocks. A block corresponds to the Hessian projection into the gradient subspace and the other one of the resulting projection of this Hessian into the subset of directions tangent to the equipotential energy surface. The coupling block of these two diagonal block matrices should also be taken into account. The L**ö**wdin's Partitioning Technique enables us to use the structure of these blocks to conclude if the point is a VRT or a VRI point. If the diagonal form of the block Hessian matrix has at least a null eigenvalue and this element is decoupled with respect to the block of Hessian projected into the gradient subspace then we are in a VRI point. If the blocks are coupled then we are in a VRT point. In the latter case the eigenvector of null eigenvalue of this block matrix is not an eigenvector of the full Hessian matrix, since this eigenvector is defined in the subspace of directions tangent to the equipotential energy surface. It does not

make the decoupling between the null eigenvalue and the block Hessian projected into the gradient subspace. In the former case the eigenvector of null eigenvalue due to the decoupling with the block Hessian projected into the gradient subspace is an actual eigenvector of the full Hessian matrix of this point.

Note that the eigenvalues of the Hessian may depend from the used coordinate system. Fortunately, the sign or the zero value are independent. Thus, the location of the VRI points does not depend from the coordinate system [2,45,46]. We can use any convenient linear transformation to highlight VRI points.

Finally we report the connection with a former alternative way to characterize these points by the adjoint Hessian matrix. However, the adjoint matrix is more abstract and not well imaginable. The Hirsch equation for a VRT point, equation (18), and their counterpart for the VRI points, equation (20), are the equivalent form using the adjoint matrix to that just explained using the Hessian as a basic element.

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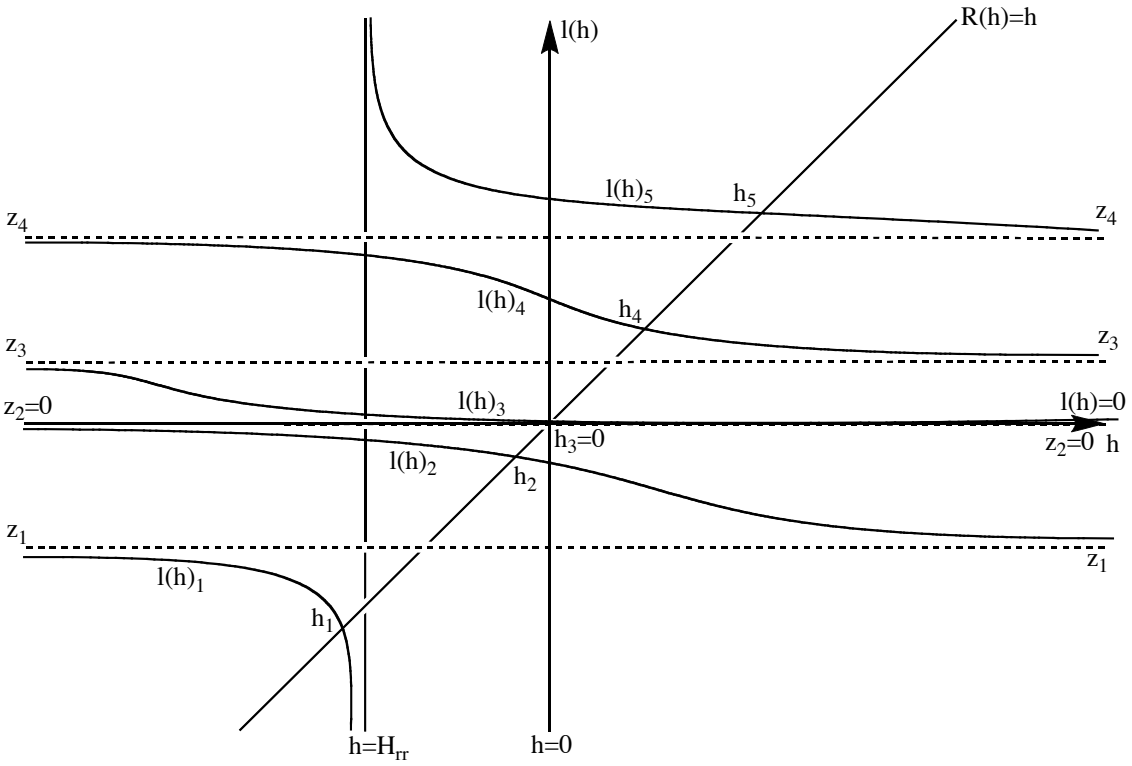
Figure 1.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z4
z4
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h4
z3
z3
z2=0
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l(h)=0
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z1
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h=0

Figure 2.

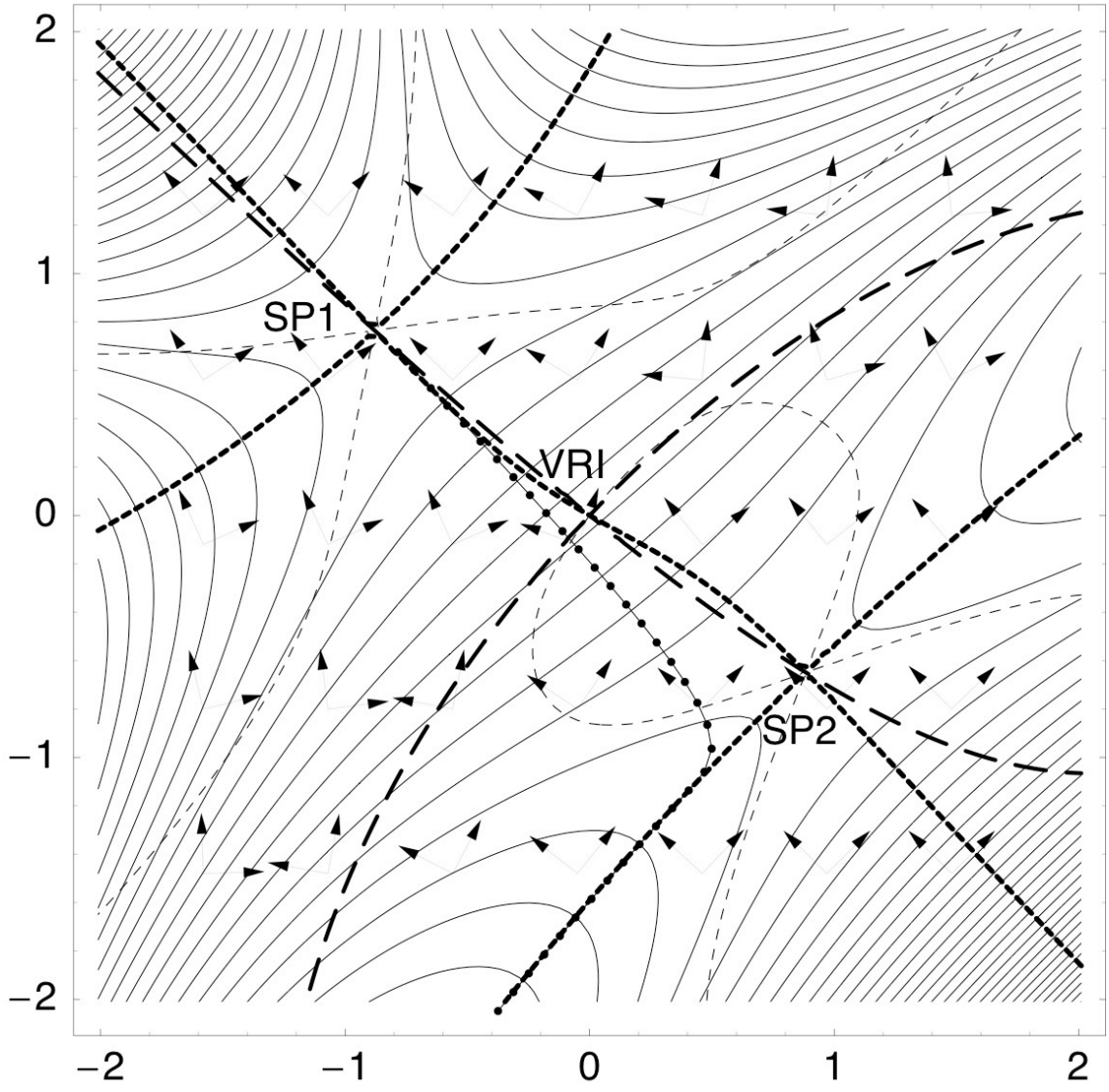
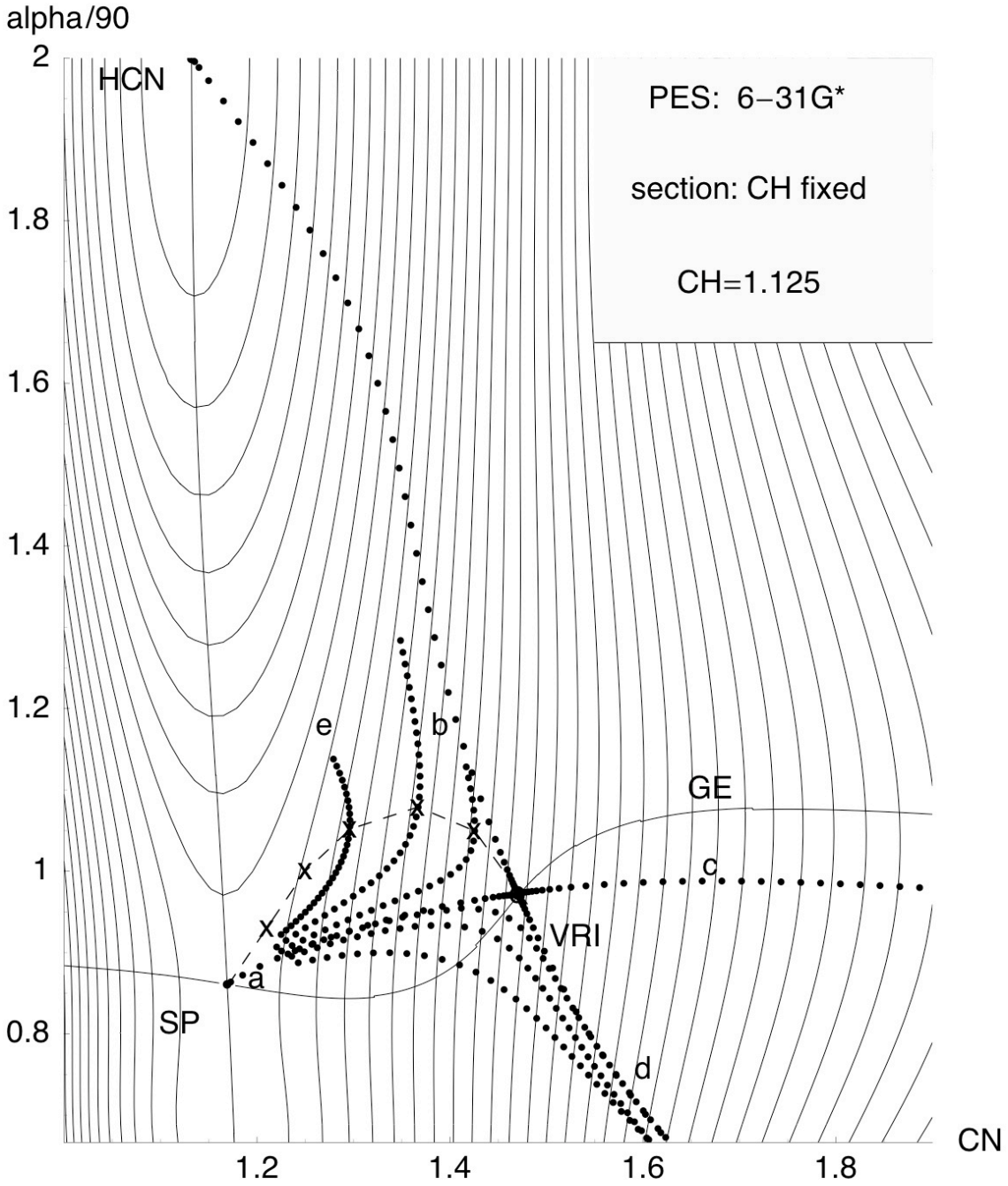


Figure 3.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1.4
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Figure 4.

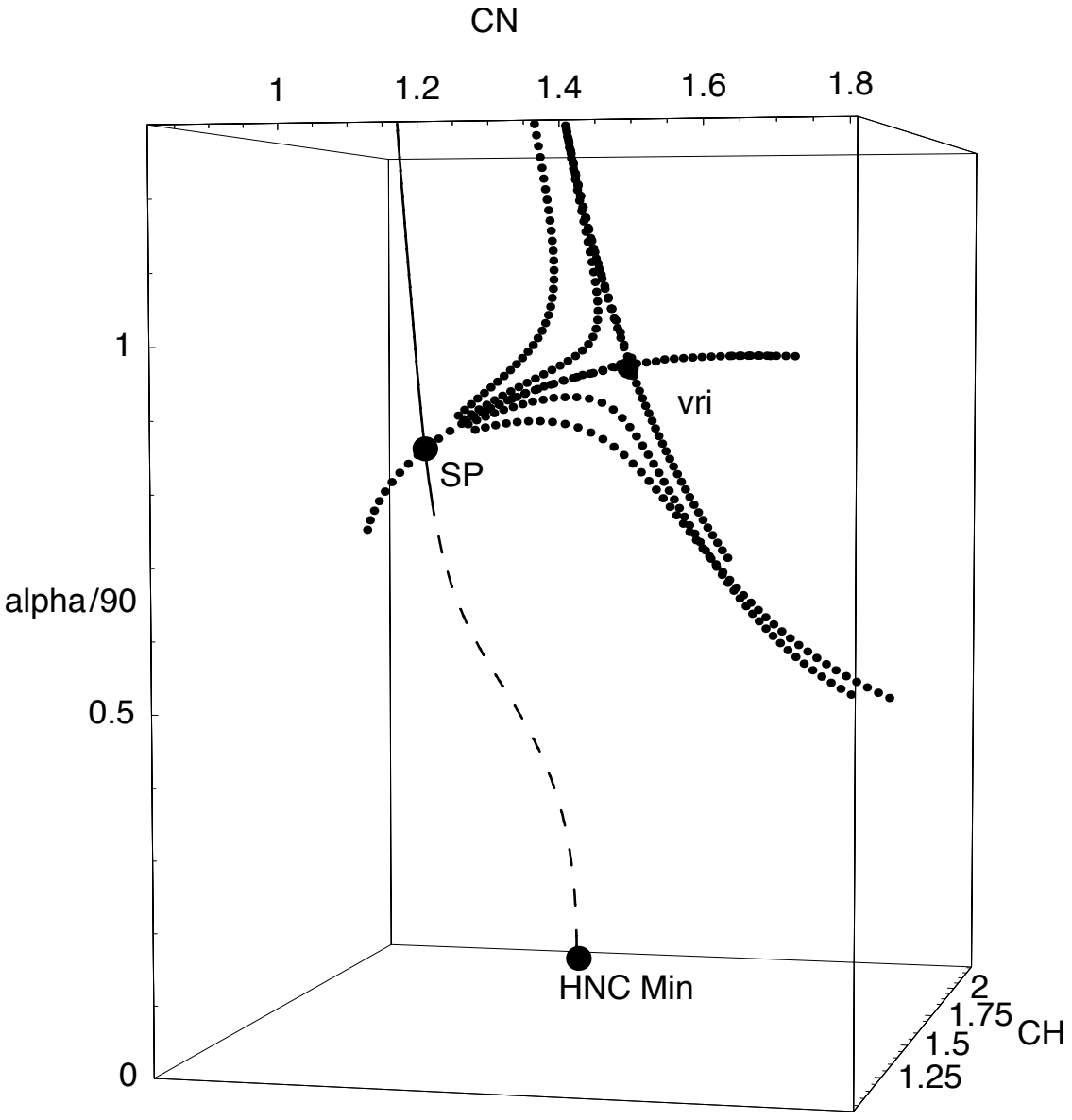

Figure Captions.

Figure 1. Plot of the vectorial function or multivalued function $\mathbf{l}(h)$ as function of h. The elements of this vectorial function represent the eigenvalues of the matrix $\mathbf{L}(h) = [\mathbf{Z}_{SS}-\mathbf{z}_{Sr}(H_{rr}-h)^{-1}\mathbf{z}_{rS}^{T}]$, and the eigenvalues of the Hessian matrix are represented by the intersections of these branches with the line $R(h) = h$. The Hessian matrix corresponds to a VRI point of a generic five dimensional surface. The H_{rr} element is taken negative. We show the case where the block Hessian matrix $\mathbf{H}_{SS}$ has in addition to the eigenvalue zero (z_2) a negative eigenvalue, z_1, and two positive eigenvalues, z_3 and z_4. The resulting full Hessian has two negative eigenvalues, h_1 and h_2, two positive eigenvalues h_4 and h_5 and the null eigenvalue, h_3. These values are located where the branches cut the straight line $R(h) = h$. The asymptote of the branch $l(h)_3$ at negative values of h takes the value of z_3 whereas at positive values takes the value of z_2 and across the point $h = 0$, $l(h) = 0$. This branch is responsible for the fact that the full Hessian matrix has a null eigenvalue. At the value $h = H_{rr}$, the eigenvector of the branch $l(h)_1$, $\mathbf{v}_1$, is parallel to the block coupling matrix which is a vector, $\mathbf{z}_{Sr}$. For the remainder of the branches their eigenvectors are orthogonal to this coupling vector. The branch $l(h)_3$ at the point $h = 0$, $l(h) = 0$ the associated eigenvector has the structure, $(\mathbf{v}_3)^T = (0, 1, 0, 0)$, being orthogonal to the $\mathbf{z}_{Sr}$ vector. This is the reason way the eigenvector of the null eigenvalue of the full Hessian is orthogonal to the gradient vector. For this reason this Hessian belongs to a point of the PES that is a VRI point. See text for more details.

Figure 2. Equipotential curves of the two-dimensional PES model given in equation (22). The IRC curve from the SP1 to the minimum is the dotted line. GEs are the thick

dotted curves, branches of a singular NT are the bold dashes. Pairs of eigenvectors of the Hessian are shown at a grid of points. The thin dashed lines are the border between the valley and the ridge of the PES. Each point of this border is a VRT point and satisfies the Hirsch equation (18).

Figure 3. Two-dimensional contour diagram of the HCN PES section for CH = *1.125 Å* fixed [31]. The fixed value is the CH distance of the VRI point. The NTs are projected from their three-dimensional space into this plane. The dotted branches *a*, *b*, *c*, *d* are the singular NT through the VRI point, where other dotted curves are regular NTs. The NTs between branches *a*, and *b* have TPs depicted by crosses. They are VRT points. There is the border between the bowl of the HCN minimum, and the ridge through the SP. Further properties of the VRT point of curve *e* are given in the text. There is also a GE (thin line) which connects the SP and the VRI point. It does not bifurcate at the VRI point.

Figure 4. Singular NT (dots) which meets the VRI point of an N-dissociation from HCN saddle in the full three-dimensional configuration space of internal coordinates. The singular NT connects SP and VRI point, as well as the HCN minimum and the VRI point. There are regular NTs (dots also) turning off the VRI region. The full and dashed line (left and below) is the valley line of the isomerization [5].

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