Theoret. Chim. Acta (Berl.) 67, 115-136 (1985)

THEORETICA CHIMICA ACTA

The topology of energy hypersurfaces V. Potential-defying chemical species: a global analysis of vibrational stabilization and destabilization on potential energy hypersurfaces

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Local and global topological criteria for the existence or non-existence of "potential defying" chemical species are investigated. The number and type of chemical structures which are *not* indicated by the qualitative features of potential surfaces and which owe their existence to an interplay of vibrational stabilization and destabilization in various domains of potential surfaces are related to topological invariants of compact manifolds. The topological analysis implies that potential defying species (including both stable and transition structures) *never occur alone*, but several of them occur simultaneously. Conditions are given for the minimum number of potential defying species of various types.

Key words: Potential-defying chemical species—vibrational stabilization—potential surfaces—zero-point energy—tunneling

1. Introduction

In recent studies [1-3] an interesting new explanation has been proposed for the stability of the molecule IHI. Although no true minimum (besides degenerate minima at infinite nuclear separations) exists on the Born-Oppenheimer potential surface of IHI, the interplay of curvature variations and the resulting effects on the vibrational levels (most notably, on the zero-point energy) give rise to a bound state in the neighborhood of a saddle point of the potential surface.

On intuitive basis it appears evident that analogous effects of curvature variations are not restricted to the appearance of bound states near saddle points and in this note a simple topological model is proposed for the detection and analysis of such cases. In fact, peculiar curvature variations may result in a series of features that are unexpected according to the conventional interpretation of potential surfaces. On the one hand, a variety of stable structures as well as transition structures may emerge in domains where the semiclassical potential surface model does not indicate them, and on the other hand, some stable structures, as well as transition structures predicted by the semiclassical model do not necessarily appear in the more advanced model. We shall demonstrate the existence of the above unexpected features, using a topological technique based upon curvature properties, similar to the T_D topology originally devised to distinguish the chemically important "reactive domains" of potential surfaces from domains of lesser importance [4].

It has been recently shown that the Born–Oppenheimer potential energy hypersurface of a given electronic state of a system of N nuclei and k electrons gives rise to a variety of topologizations of the nuclear configuration space ^nR [4–9]. These topologies are useful for a global analysis of the network of all reactions possible for all molecules composed from N nuclei, within the constraints of the given electronic state [6]. For a local (e.g. vibrational) analysis of the neighborhoods of critical points (e.g. minima) of the hypersurface a differentiable manifold structure has been proposed [7].

Most (although not all) of the above topologies and topological manifolds are defined in terms of an intrinsic reaction coordinate [10–12], that corresponds to a hypothetical rotationless and vibrationless infinitely slow displacement of the nuclei in a mass-weighted reference frame. In the present study we shall show that for the development of a chemically useful and still fairly simple topologization of ^nR not all of the previously applied constraints and approximations are necessary. Analogous topologies and topological manifolds can be obtained within a model which incorporates certain vibrational information in the very definitions of these topologies. These topologies also lead, on the one hand, to the demonstration of the existence of unexpected chemical species, and on the other hand, to that of the non-existence of certain species, which could be expected on a purely intuitive basis.

The solution of the Schrödinger equation for the nuclear motions over a complicated multidimensional potential surface is an extremely difficult task. Rather than attempting such a solution, we propose an approximate model which incorporates an essential part of the vibrational energy and which also provides a basis for a chemically useful topology.

2. Motivation and topological preliminaries

The potential surface model of molecular systems, although only an approximation in the rigorous quantum mechanical sense, is a very successful tool in studying chemical problems. In the usual Born–Oppenheimer approximation this model is based on a formal separation of the nuclear kinetic energy from other energy terms. By considering formal trajectories of nuclear motions on the potential energy surface $E(\boldsymbol{r})$ over a nuclear configuration space ^nR, a semiclassical model of chemical reactions is obtained. One may, however, ask the following question: by analogy with the zero-point energy of harmonic oscillators in idealized parabolic potentials, is there an additional energy functional $\Delta E^0(\boldsymbol{r})$, defined over the *entire* nuclear configuration space ^nR, that represents (at least in some approximate sense) the *minimum amount* of kinetic energy, *intrinsic to the actual potential energy hypersurface*? Our aim is to find a continuous functional $E^0(\boldsymbol{r})$ over ^nR that contains, in addition to the potential energy, an "intrinsic part" of kinetic energy. We expect that this functional accounts for both "normal" and "potential defying" species in an intuitively simple way, in terms of its minima and saddle points, much like in the conventional interpretation of potential surfaces one expects minima and saddle points to represent chemical species (stable and transition structures, respectively).

As long as one focuses on a *single* (e.g. the lowest energy) bound state, the answer is rather straightforward. As a simple example, take a two-dimensional paraboloid as the potential surface. Evidently, in this case one can take $\Delta E^0(\boldsymbol{r}) = -E(\boldsymbol{r}) + E_0$ where E_0 is the (absolute) zero-point energy. Then the potential plus this intrinsic kinetic energy is constant,

$$E(\boldsymbol{r}) + \Delta E^0(\boldsymbol{r}) = E_0 \tag{1}$$

for the entire two-dimensional nuclear configuration space ^2R, as the lowest energy vibrational wavefunction is non-zero everywhere in ^2R, and it vanishes in the strict sense only at infinity.

On more realistic potential energy hypersurfaces, with many minima and saddle points, we do face, in principle, a similar situation. The wavefunction of the lowest vibrational state of the absolute minimum of $E(\boldsymbol{r})$, belonging to the lowest bound state, is not strictly localized. In principle, it extends over the entire nuclear configuration space ^nR: although it approaches zero rapidly far from the minimum, nonetheless, it is non-zero almost everywhere in ^nR. Hence, again, $\Delta E^0(\boldsymbol{r}) = -E(\boldsymbol{r}) + E_0$ is a possible choice. However, the above $\Delta E^0(\boldsymbol{r})$ is clearly unsatisfactory for our present purposes, since it treats every nuclear configuration $\boldsymbol{r} \in {}^nR$ as a (possibly severely distorted) geometry occurring during vibration about a single distinguished minimum in the lowest basin on the hypersurface. Instead, we may consider a functional $\Delta E^0(\boldsymbol{r})$ that for every $\boldsymbol{r} \in {}^nR$ refers to the zero-point energy of a minimum or saddle point in the *near vicinity* of $\boldsymbol{r}$. One can partition the entire nuclear configuration space ^nR into domains each containing one critical point (e.g. the catchment region partitioning, *vide infra*) and define $\Delta E^0(\boldsymbol{r})$ in each domain C in terms of the local zero-point energy $E_0(C)$ of the corresponding critical point: $\Delta E^0(\boldsymbol{r}) = -E(\boldsymbol{r}) + E_0(C)$. This $\Delta E^0(\boldsymbol{r})$, however, is discontinuous at the boundaries of the domains, that is contrary to our goal of a representation where minima and saddle points indicate both "normal" and "potential defying" species. A more important objection to the above construction is that the usual topological techniques for the enumeration of critical points are not applicable to the resulting functional $E^0(\boldsymbol{r})$. These techniques are applicable if $\Delta E^0(\boldsymbol{r})$ is at least continuous.

The intuitive concept of zero-point energy on a potential surface is based on a formal separation of the "slow", large amplitude motions of nuclei from the "fast" nuclear motions in the remaining degrees of freedom. The "slow" nuclear motions are often treated semiclassically using formal reaction paths, whereas the "fast" motions, giving rise to zero-point energy contributions, are treated quantum mechanically. This model is in fact an approximation that combines classical and quantum mechanical concepts. In the present study we shall explore a somewhat modified model. In one of the proposed approximations we shall treat all nuclear motions quantum mechanically, except those which occur along directions of *negative curvature* of the potential energy surface, which latter ones will be treated semiclassically, assuming that they do not contribute to the zero-point energy. Since the sign of various canonical curvatures may change from one domain of the potential energy hypersurface to another, at a point where such a sign change occurs the dimension of the formal subspace that is treated quantum mechanically, also changes. Neighborhoods of such points require special treatment in the model in order to ensure compatibility of the quantum mechanical and formal semiclassical components of nuclear motions.

If possible, we would like to construct a twice continuously differentiable functional $\Delta E^0(\boldsymbol{r})$ that is defined at every point $\boldsymbol{r} \in {}^nR$ in terms of some formal zero-point energy at the very point $\boldsymbol{r}$, irrespectively whether $\boldsymbol{r}$ is a critical point of $E(\boldsymbol{r})$ or not. The ideal $\Delta E^0(\boldsymbol{r})$ functional, when added to $E(\boldsymbol{r})$,

$$E^0(\boldsymbol{r}) = E(\boldsymbol{r}) + \Delta E^0(\boldsymbol{r}) \tag{2a}$$

converts it into a new hypersurface $E^0(\boldsymbol{r})$ that properly reproduce the local zero-point energy at nondegenerate critical points of $E(\boldsymbol{r})$ and does not introduce false critical points elsewhere. Hence the ideal hypersurface $E^0(\boldsymbol{r})$ has the intuitively appealing property that its minima and simplest saddle points indeed correspond to stable molecules and transition structures, resp., *after* the minimum kinetic energy, intrinsic to the original hypersurface $E(\boldsymbol{r})$ has been taken into account. In this study we shall propose various approximations to the postulated ideal functional $\Delta E^0(\boldsymbol{r})$ and we shall attempt to demonstrate their utility in studying potential defying species.

We expect our approximations to $\Delta E^0(\boldsymbol{r})$ to fulfill the following conditions:
(i) At every minimum m of potential energy $E(\boldsymbol{r})$ $\Delta E^0(\boldsymbol{r})$ should reproduce the *local* zero-point energy.
(ii) At every saddle point of transition structures $\Delta E^0(\boldsymbol{r})$ should contain the *local* zero-point energy contribution from all real vibrational frequencies.
(iii) In order to have $\Delta E^0(\boldsymbol{r})$ defined over the entire nuclear configuration space, $\Delta E^0(\boldsymbol{r})$ should continuously interpolate between ΔE^0 values at various minima and saddle points.
(iv) At non-critical points $\boldsymbol{r}$ of $E(\boldsymbol{r})$ the term $\Delta E^0(\boldsymbol{r})$ should contain a formal zero-point energy contribution from a *subspace* of ${}^nR$, within which subspace the actual point $\boldsymbol{r}$ is a minimum.

Note that the postulated $\Delta E^0(\boldsymbol{r})$ term is *not* an effective potential added upon $E(\boldsymbol{r})$. At minima and at various saddle points it represents a kinetic energy component, intrinsic to the potential energy hypersurface: the local zero-point energy. This energy component is *independent* of any actual trajectory considered and of the approach how these trajectories reach a neighborhood of a minimum. Consequently, there is no need for a separation of coordinate variables in the nuclear configuration space, to one along a specific trajectory and the rest of them which are orthogonal to it.

Since $\Delta E^0(\boldsymbol{r})$ describes the local zero-point energy at critical points of $E(\boldsymbol{r})$, we expect that the new functional defined as

$$E^0(\boldsymbol{r}) = E(\boldsymbol{r}) + \Delta E^0(\boldsymbol{r}) \tag{2}$$

will provide information on potential defying species which owe their existence to zero-point energy variations. Note, however, that due to the approximations in our model, the approach can guarantee a proper accounting only for one (although possibly the most important) type of potential defying species.

For our purposes it is useful to distinguish the following types of potential defying species:

Type A: those which occur at non-degenerate critical points of the original energy hypersurface $E(\boldsymbol{r})$, but are of different type than expected; e.g. a stable structure (minimum) appears where a transition structure (simplest saddle point) is expected. The example IHI, quoted above, belongs to this category.

Type B: those which occur at ordinary non-critical points of $E(\boldsymbol{r})$.

For completeness we shall also consider a third case (in certain sense the opposite of type B), when a species that is expected at a critical point of $E(\boldsymbol{r})$ does not exist on the hypersurface $E^0(\boldsymbol{r})$:

Type C: ("non-species") a critical point of $E(\boldsymbol{r})$ becomes an ordinary point of $E^0(\boldsymbol{r})$; i.e. an expected chemical species of $E(\boldsymbol{r})$ "disappears" on $E^0(\boldsymbol{r})$.

Although theoretically possible, the author is unaware of any actual chemical species that occurs at a degenerate critical point of a potential energy hypersurface where the redundant coordinates (e.g. those describing rigid translation of the molecule as a whole) are removed. However, for the unlikely case of a potential defying species occurring at a degenerate critical point of $E(\boldsymbol{r})$, a fourth category, Type A′, is introduced.

Chemical intuition places stable molecules at minima and transition structures at saddle points of $E(\boldsymbol{r})$. Hence, potential defying species of Type A are perhaps the most surprising and of greatest interest, since they involve not only the appearance of an unexpected chemical species, but also the disappearance of an expected species at the *same* point $\boldsymbol{r} \in {}^nR$. This implies, in fact, that $\Delta E^0(\boldsymbol{r})$ must also have a critical point at $\boldsymbol{r}$. Potential defying species of Type A are expected to be the most common, since any species *necessarily* belongs to Type A whenever the existence of the critical point is a consequence of the *symmetry* of the potential surface. The symmetry of the potential surface, in turn, is commonly implied by some three-space symmetry of the nuclear framework.

Potential defying species of Type B and "non-species" of Type C are of somewhat lesser surprise, since they do not involve the simultaneous disappearance and appearance of different types of chemical species in the same neighborhood.

In order to apply some general topological methods which can give *lower bounds for the number of potential defying species*, we shall require $\Delta E^0(\boldsymbol{r})$ to be a twice continuously differentiable functional, implying that condition (iii) must be strengthened: $\Delta E^0(\boldsymbol{r})$ must interpolate *smoothly* between local zero-point energies at critical points of $E(\boldsymbol{r})$. Whereas we shall study in detail only one actual construction for an approximate $\Delta E^0(\boldsymbol{r})$ functional, we shall also describe briefly two other possible models for $\Delta E^0(\boldsymbol{r})$ which may have some utility depending on the actual applications.

In the following we outline the basic geometrical and topological framework used throughout our study.

For sake of generality we assume that the Born-Oppenheimer energy hypersurface $E(\boldsymbol{r})$, $\boldsymbol{r} \in {}^nR$, is defined over a Riemannian nuclear configuration space ${}^nR$, where g_{ij} is the Riemannian metric. Whereas a general hypersurface $E(\boldsymbol{r})$ is not necessarily differentiable at every point $\boldsymbol{r} \in {}^nR$, we shall make this assumption (in Ref [8] a technique is described how to "make" $E(\boldsymbol{r})$ twice differentiable and a similar technique may be applied for higher order derivatives). In fact, we shall assume that $E(\boldsymbol{r})$ is at least fourfold continuously differentiable.

The second covariant derivative [13] of E, in tensorial form, is

$$H_{kl} = \frac{\partial^2 E}{\partial x^k \, \partial x^l} - \Gamma^i_{kl} \frac{\partial E}{\partial x^i} \tag{3}$$

where Γ^i_{kl} is the Christoffel symbol of the second kind,

$$\Gamma^i_{jk} = g^{il}[jk, l] \tag{4}$$

given in terms of the Christoffel symbol of the first kind,

$$[ij, k] = \frac{1}{2}\left(\frac{\partial g_{ik}}{\partial x^j} + \frac{\partial g_{jk}}{\partial x^i} - \frac{\partial g_{ij}}{\partial x^k}\right). \tag{5}$$

The second covariant derivative is the Hessian in the Riemannian space ${}^nR$ (also referred to as extended Hessian [11, 14]). $H_{ij}(\boldsymbol{r})$ at every point $\boldsymbol{r} \in {}^nR$ defines a bilinear form

$$H_{ij} x^i x^j. \tag{6}$$

A set $\{\boldsymbol{b}_{(k)}\}$ of unit vectors, called *local normal mode vectors* is defined by the condition

$$H_{ij} b^i_{(k)} b^j_{(k)} = \text{stationary}. \tag{7}$$

If the set $\{\boldsymbol{b}_{(k)}\}$ is chosen as the local basis at $\boldsymbol{r} \in {}^nR$ then the Hessian can be represented as a diagonal matrix, with eigenvalues

$$h_i = H_{ii}. \tag{8}$$

In order to make use of topological invariants [15-18] in enumerating potential defying species, we shall construct a topology $\boldsymbol{T}_C^0$ defined in terms of $E_0(\boldsymbol{r})$, which topology is analogous to the catchment region topology (Reaction Topology) $\boldsymbol{T}_C$ that has been defined [8, 9] in terms of $E(\boldsymbol{r})$. Various properties of the $\boldsymbol{T}_C$ topology has been discussed in some detail elsewhere [8, 9], and it is sufficient for our purposes to review only its definition.

A topology on the nuclear configuration space ${}^nR$ is defined if a consistent set of instructions is given specifying which subsets of ${}^nR$ are considered open sets. In a topological space *continuity of functions* is profoundly affected by this choice, since continuity is defined in terms of open sets. The catchment region topology $\boldsymbol{T}_C$ has been defined in terms of a generating subbase $\boldsymbol{C}$ [8, 9]. The elements of $\boldsymbol{C}$ are subsets of ${}^nR$, and each open set within the $\boldsymbol{T}_C$ topology can be generated as a union of finite intersections of sets from $\boldsymbol{C}$. Defining subbase $\boldsymbol{C}$ is the family of catchment regions $C^{(\lambda,i)}$ of $E(\boldsymbol{r})$ and their closures in the metric of ${}^nR$:

$$\boldsymbol{C} = \{C^{(\lambda,i)}\} \cup \{\bar{C}^{(\lambda,i)}\}. \tag{9}$$

Here each $C^{(\lambda,i)}$ catchment region is the set of origin points of all steepest descent paths which belong to an equivalence class of paths, defined in terms of a *common extremity* $\boldsymbol{r}^{(\lambda,i)}$ [8, 9]. Here λ is the number of negative eigenvalues of the Hessian matrix $\mathscr{H}(\boldsymbol{r})$ at extremity $\boldsymbol{r}^{(\lambda,i)}$ or is set equal to -1 if at the extremity $E(\boldsymbol{r})$ is not twice differentiable [15], and i is an index of ordering. From any point within a given catchment region an idealized vibrationless relaxation would lead to the *same extremity*, that is typically a critical point of $E(\boldsymbol{r})$. This generates an equivalence class partitioning of all nuclear geometries, and leads to the topological definition of *molecular structures* as catchment regions $C^{(\lambda,i)}$. In the topological model the concept of nuclear geometry, as a fundamental chemical concept, is replaced by an open set of geometries. Within the model of vibrationless nuclear displacements the catchment region $C^{(0,i)}$ of a minimum point $\boldsymbol{r}^{(0,i)}$ corresponds to a stable molecular structure, whereas the catchment region $C^{(1,j)}$ of a saddle point $\boldsymbol{r}^{(1,j)}$ (having precisely one negative canonical curvature, $\lambda = 1$) corresponds to a transition structure ("transition state") [8, 9]. With the aid of the above topological concept of molecular structure, several theorems have been proven on reaction networks and on computer-aided quantum chemical synthesis design [6].

3. The construction of approximate $\Delta E^0(\boldsymbol{r})$ functionals

Our aim is to develop a simple model for $\Delta E^0(\boldsymbol{r})$, that describes the inherently quadratic main contribution to zero-point energy in various domains of $E(\boldsymbol{r})$, and which model is defined in terms of curvature properties of $E(\boldsymbol{r})$. To some extent, the very desire for simplicity will lead to certain complications, however, many of the dominant topological features will be adequately described, and we shall be able to avoid the solution (even an approximate solution) of the Schrödinger equation for the nuclear motion.

It is useful to define a quantity $\widetilde{\Delta E}^0(\boldsymbol{r})$ for every $\boldsymbol{r} \in {}^nR$, as

$$\widetilde{\Delta E}^0(\boldsymbol{r}) = \tfrac{1}{2}\hbar \sum_{i=1}^{n} [h_i(\boldsymbol{r})]^{1/2}. \tag{10}$$

For a twice continuously differentiable $E(\boldsymbol{r})$ $\widetilde{\Delta E}^0(\boldsymbol{r})$ is a (generally complex valued) continuous functional over ${}^nR$. Taking the real part of $\widetilde{\Delta E}^0(\boldsymbol{r})$, and adding it to $E(\boldsymbol{r})$, a continuous real functional is obtained:

$$\tilde{E}^0(\boldsymbol{r}) = E(\boldsymbol{r}) + \operatorname{Re} \widetilde{\Delta E}^0(\boldsymbol{r}). \tag{11}$$

As follows from Eqs. (8) and (10), at every critical point $\boldsymbol{c} \in {}^nR$ of $E(\boldsymbol{r})$ the functional $\tilde{E}^0(\boldsymbol{r})$ incorporates the *locally defined* zero-point energy, in addition to the Born–Oppenheimer energy $E(\boldsymbol{r})$. Since the true zero-point energy is affected by curvature variations, Eq. (11) serves only as a local approximation. Nevertheless, for neighborhoods of critical points where $E(\boldsymbol{r})$ does not deviate severely from quadraticity the term Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ is by far the dominant component of the zero-point energy. At non-critical points $\boldsymbol{r} \in {}^nR$ of $E(\boldsymbol{r})$, functional $\tilde{E}^0(\boldsymbol{r})$ interpolates between values obtained at the critical points, using the locally defined *formal* zero-point energies at intermediate points, given in terms of local normal modes $\{\boldsymbol{b}_{(k)}\}$. Although in the strict sense a minimum (or a simple saddle point) of $E^0(\boldsymbol{r})$ does not necessarily imply a bound state (or a transition state, resp.) [19], nevertheless, Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ is the dominant correction to $E(\boldsymbol{r})$, influencing the occurrence of potential defying species. It is expected that the comparison of the topological properties of $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$ will result in some insight into the occurrence of such species.

It is easily seen that for any quadratic domain of $E(\boldsymbol{r})$ the effect of Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ is a constant shift of the energy hypersurface, and *all the topological features* of the hypersurface (in fact all metric properties as well) remain invariant within this domain. Quadraticity, however, is not a necessary condition for topological invariance, in spite of the fact that in non-quadratic domains of $E(\boldsymbol{r})$ various interesting and chemically significant topological changes can occur.

According to our assumptions $E(\boldsymbol{r})$ is at least fourfold continuously differentiable, implying that $\tilde{E}^0(\boldsymbol{r})$ is at least twice continuously differentiable in open neighborhoods of non-degenerate critical points of $E(\boldsymbol{r})$. Consequently, non-degenerate critical points of $\tilde{E}^0(\boldsymbol{r})$ can be characterized in terms of Hessians within the same open neighborhoods. In fact, functional Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ is twice continuously differentiable almost everywhere in ${}^nR$, with the exception of those points where any of the $h_i(\boldsymbol{r})$ eigenvalues passes through zero. At any such point Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ is not differentiable, since Re $(y^{1/2})$ is non-differentiable at $y = 0$. These points of non-differentiability may appear to limit the usefulness of Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ in studying potential defying species. However, they will not affect our conclusions regarding potential defying species of Type A, and by an arbitrarily small additive term these derivative discontinuities can be eliminated. Furthermore, if such a point of non-differentiability happens to be a critical point of $E(\boldsymbol{r})$ then it can be recognized easily since there the Hessian $\mathscr{H}$ of $E(\boldsymbol{r})$ must be singular.

Let us denote the set of all points of non-differentiability by D. With the exception of pathological surfaces having horizontal valley bottoms or flat plateaus [20], the measure of set D is zero in ${}^nR$. Furthermore, these points cannot occur in the immediate vicinity of non-degenerate critical points of $E(\boldsymbol{r})$, since there $|h_i(\boldsymbol{r})|>0$ for every i. Since potential defying species of Type A occur at such critical points, and all derivatives of Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ are continuous there, the enumeration problem of Type A species is not affected by derivative discontinuities. Furthermore, using a method analogous to the "smoothing technique", applied for the D_{excl} domains of $E(\boldsymbol{r})$ [8], one can eliminate the derivative discontinuities by adding an arbitrarily small term $f(\boldsymbol{r})$. By applying this technique we may construct our simplest model (model 1) for $\Delta E^0(\boldsymbol{r})$ as

$$\Delta E_1^0(\boldsymbol{r}) = \mathrm{Re}\,\widetilde{\Delta E}^0(\boldsymbol{r}) + f(\boldsymbol{r}) \tag{12}$$

where $f(\boldsymbol{r})$ is a continuous function that is zero everywhere in ${}^nR$ except in some arbitrarily small neighborhoods of points of D, where $f(\boldsymbol{r})$ is chosen such that that it makes $\Delta E_1^0(\boldsymbol{r})$ twice continuously differentiable.

Note that an actual evaluation of $f(\boldsymbol{r})$ is not required for the enumeration problem, and it suffices to establish that such $f(\boldsymbol{r})$ exists.

Functional $\Delta E_1^0(\boldsymbol{r})$ of model 1 fulfills all four conditions (i)-(iv) given for $\Delta E^0(\boldsymbol{r})$. It has the proper features at non-degenerate critical points of $E(\boldsymbol{r})$, it accounts for all potential defying species of Type A, and it is consistent with the usual local harmonic approximation, used in the conventional treatment of zero-point energy in single minimum potentials. In our case the local quadratic approximation refers to a hypersurface of many critical points: as long as the hypersurface can be approximated *locally* in small neighborhoods of any point $\boldsymbol{r}$ by quadratic functional, $\Delta E_1^0(\boldsymbol{r})$ is a good approximation. This underlines the privileged role of Type A potential defying species: as follows from the Morse lemma [20], at *every* non-degenerate critical point of an arbitrary hypersurface a local quadratic approximation is always sufficient, hence $\Delta E_1^0(\boldsymbol{r})$ describes properly the local neighborhoods of critical points of all potential defying species of Type A. Note that most hypersurfaces can be treated by local quadratic approximations in their various domains, even if they are very much non-quadratic globally. Degenerate critical points or analogous ordinary points where the surface is dominated by cubic or higher order terms, are required to render the local quadratic approximation inapplicable.

Due to the approximations involved in model 1, one may expect that $\Delta E_1^0(\boldsymbol{r})$ is inappropriate in all such special cases for which at any point $\boldsymbol{r}$ the cubic or higher order terms become large (dominant). However, such large cubic and higher order contributions to $E_1^0(\boldsymbol{r})$ which may cause the occurrence of false critical points, are not expected to be common. E.g. elementary calculus shows that along a repulsive segment of a one dimensional potential $E(r)$ the following condition must hold at some point r,

$$\frac{c}{2}\frac{E'''(r)}{(E''(r))^{1/2}} > |E'(r)| \tag{13}$$

in order to introduce a false minimum on the corresponding functional $E_1^0(r)$. Here constant c is the coefficient in the definition of $\widetilde{\Delta E}^0(\boldsymbol{r})$ (Eq. (10)):

$$c = \hbar/2.$$

Whereas the fulfillment of the above condition is not impossible, it implies a large relative value for the third derivative $E'''(r)$, i.e. a severe local non-quadraticity at point r. Whenever the local quadratic approximation fails to such an extent, then an approximate $\Delta E^0(\boldsymbol{r})$ is not applicable for the description of potential defying species of cases B and C. For these cases, if severe non-quadraticity occurs, then no simple approach seems to be viable, and one is ultimately facing the solution of the Schrödinger equation for the nuclear motions over $E(\boldsymbol{r})$. The important point, however, is that even if severe local non-quadraticities occur on $E(\boldsymbol{r})$, *potential defying species of Type A* are adequately accounted for by $\Delta E_1^0(\boldsymbol{r})$.

We note that raising the potential energy profile of barriers by the zero-point energy has been discussed by several authors [21-25], and there seems to exist some ambiguity as to the best approach [26]. Our choice of the functional $\Delta E_1^0(\boldsymbol{r})$ of model 1 in the local quadratic approximation is an attempt to account for most potential defying species by a simple approximate method.

The second approximate model discussed in this study can be regarded as an extension of model 1, that also includes a simple description of tunnel effects at the same level of local quadratic approximation. Several authors have noted the remarkable analogy between tunnel effect across parabolic barriers and the vibration problem in parabolic potential wells, obtained by simply inverting the barrier [27-31]. The above suggestions, which are based, at least in part, on intuition, appear to be consistent with a lowering of the barrier by a quantity analogous to Re $\widetilde{\Delta E}^0(\boldsymbol{r})$. We choose the approximate functional $\Delta E_2^0(\boldsymbol{r})$ of model 2 as

$$\Delta E_2^0(\boldsymbol{r}) = \mathrm{Re}\,\widetilde{\Delta E}^0(\boldsymbol{r}) - \mathrm{Im}\,\widetilde{\Delta E}^0(\boldsymbol{r}) + g(\boldsymbol{r}). \tag{15}$$

Note that the Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ − Im $\widetilde{\Delta E}^0(\boldsymbol{r})$ difference is smooth everywhere in ${}^nR$, since due to the properties of function $y^{1/2}$ at $y = 0$, −Im $\widetilde{\Delta E}^0(\boldsymbol{r})$ is the natural, smooth continuation of Re $\widetilde{\Delta E}^0(\boldsymbol{r})$ whenever any of the $h_i(\boldsymbol{r})$ eigenvalues changes its sign. Thus, there appears to be a (somewhat intuitive) justification for taking this difference as the basis of model 2. However, the derivatives of this difference are not everywhere bounded in ${}^nR$, and the role of functional $g(\boldsymbol{r})$ is to make the first and second derivatives of $\Delta E_2^0(\boldsymbol{r})$ finite. Functional $g(\boldsymbol{r})$ is defined analogously to $f(\boldsymbol{r})$ and it is zero everywhere in ${}^nR$ except in arbitrarily small neighborhoods of those points where any of the $h_i(\boldsymbol{r})$ eigenvalues of the local Hessian becomes zero.

In functional $\Delta E_2^0(\boldsymbol{r})$ the zero-point energy and tunneling are treated at the same level of local quadratic approximation. One may, however, address the tunneling problem differently, still within the framework of the local quadratic model. Considering an infinite parabolic barrier, and using the notations of Ref. [25], one may ask the following question: by what energy value E_T must one lower the parabolic barrier from V_0 to

$$V_0' = V_0 - E_T \tag{16}$$

in order to have a classical rate $J_c(V_0')$ of particle transfer for the new barrier that equals the quantum mechanical rate $J(V_0)$ for the original barrier? This problem can be solved exactly for the one-dimensional case and one obtains

$$E_T = kT(z^2/6 + z^4/180 + z^6/2835 + z^8/37800 + \cdots) \tag{17}$$

where

$$z = (\hbar/2kT)(-h_j)^{1/2} \tag{18}$$

and h_j is the curvature of negative value. (A derivation of the above result is given in the Appendix.)

Since this formula is strictly valid only for the one-dimensional case, on multidimensional potential surfaces it may serve only as an approximation at saddle points of transition structures or at analogous non-critical points of one negative canonical curvature in the local quadratic approximation. One may expect, however, some cancellation of errors in this model. On the one hand, one source of error is that cross sections of real potential hypersurfaces are not infinite parabolic barriers, hence, as compared to a more realistic truncated parabolic barrier, both J and E_T are overestimated by the model. On the other hand, tunneling contributions in the multidimensional case along directions intermediate between local canonical coordinate directions are not included, that tends to underestimate both J and E_T. These two features of the model result in a partial error cancellation.

Points with more than one negative local curvature are of lesser importance than those with one or none, and their significance in tunneling is less clear than that of simple saddle points [25], since such points can always be avoided on the surface by paths of lower energy. For the sake of a uniform treatment, at such points a sum of contributions from all negative local canonical curvature directions will be considered. We shall take $\Delta E_3^0(\boldsymbol{r})$ as

$$\Delta E_3^0(\boldsymbol{r}) = \mathrm{Re}\,\widetilde{\Delta E}^0(\boldsymbol{r}) - \sum_{\substack{j \\ (h_j<0)}} E_T(z_j) + f(r) \tag{19}$$

where $E_T(z_j)$ is defined by Eq. (17), and its argument is

$$z_j = (\hbar/2kT)(-h_j(r))^{1/2}. \tag{20}$$

All three models are based on a simple local quadratic approximation and in all three the dominant contribution to $\Delta E^0(\boldsymbol{r})$ comes from $\mathrm{Re}\,\widetilde{\Delta E}^0(\boldsymbol{r})$ in all those domains of the hypersurface where the positive local canonical curvatures outnumber the negative ones, that is valid for the chemically most important reactive domains D_μ of small μ indices [4]. We shall see later that all three models and possibly many other approximate models which satisfy certain constraints on their critical points and which can be defined on the same compact manifold, will lead to very similar topological constraints on potential defying species. In the following discussion many of the results will be equally applicable to all three approximations as well as to the postulated ideal functional $\Delta E^0(\boldsymbol{r})$. We shall in general refer to $\Delta E^0(\boldsymbol{r})$ and to the corresponding $E^0(\boldsymbol{r})$ functionals, and an actual approximate model will be specified only if its particular features give rise to special relations.

We define the new topology $\boldsymbol{T}_C^0$ by replacing $E(\boldsymbol{r})$ by $E^0(\boldsymbol{r})$ throughout the definition of $\boldsymbol{T}_C$.

The nuclear configuration space ${}^nR$, equipped with topology $\boldsymbol{T}_C$ or topology $\boldsymbol{T}_C^0$ becomes topological space $({}^nR, \boldsymbol{T}_C)$ or $({}^nR, \boldsymbol{T}_C^0)$, respectively. We shall show that these two topological spaces are not in general homeomorphic (topologically equivalent), that is, there does not necessarily exist a homeomorphism (continuous one-to-one and onto mapping) between them. The chemical implication of such a topological non-equivalence is that certain chemical structures that apparently exist according to the vibrationless approximation in $({}^nR, \boldsymbol{T}_C)$, become nonexistent in the local zero-point energy approximation of topological space $({}^nR, \boldsymbol{T}_C^0)$ or *vice versa*. Before reaching our conclusions on this topological non-equivalence, we shall investigate some local and global criteria for the occurrence of potential defying species.

4. Local geometric criteria

Take a critical point $\boldsymbol{r}^{(\lambda,i)} \in A \subset {}^nR$, where set A is a connected subset of ${}^nR$, open in the metric of ${}^nR$. Within set A the Hessian $\mathscr{H}(\boldsymbol{r})$, the local normal mode vectors $\boldsymbol{b}_{(k)}(\boldsymbol{r})$ and curvatures $h_k(\boldsymbol{r})$ are continuous in $\boldsymbol{r}$. We assume that the local normal mode vectors are *ordered* at every point, such that along any path from $\boldsymbol{r}$ to $\boldsymbol{r}^{(\lambda,i)}$ in A, $\boldsymbol{b}_{(k)}(\boldsymbol{r})$ converges smoothly to the k^{th} local normal mode vector $\boldsymbol{b}_{(k)}(\boldsymbol{r}^{(\lambda,i)})$ at critical point $\boldsymbol{r}^{(\lambda,i)}$. We assume that the curvatures are classified into four classes, (a), (b), (c) and (d):

(a) Within set A there are at least s "soft" local normal modes fulfilling

$$|h_i(\boldsymbol{r})| \le a, \qquad i = 1, \ldots, s \tag{21}$$

for every $r \in A$ and for some *small* positive number a.

(b) There are v local normal modes for which the curvatures $h_i(\boldsymbol{r})$ are positive and show *large* variations within A: for $i = s+1, \ldots, s+v$, and every $\boldsymbol{r} \in A$

$$h_i(\boldsymbol{r}) > 0, \tag{22}$$

$$\max_{\boldsymbol{r}\in A} h_i(\boldsymbol{r}) - \min_{\boldsymbol{r}\in A} h_i(\boldsymbol{r}) \ge b \tag{23}$$

where b is a large positive number,

$$b > a. \tag{24}$$

(c) There is one ($l = 1$) or none ($l = 0$) canonical curvature with a large negative value,

$$h_i(\boldsymbol{r}) < -a. \tag{25}$$

(d) For the remaining $n - s - v - l$ local normal modes the $h_i(\boldsymbol{r})$ curvature values are *positive* and show only *small* variations within A: for every $i = s + v + l + 1, \dots, n$, $\boldsymbol{r} \in A$

$$h_i(\boldsymbol{r}) > 0 \tag{26}$$

and

$$\max_{\boldsymbol{r} \in A} h_i(\boldsymbol{r}) - \min_{\boldsymbol{r} \in A} h_i(\boldsymbol{r}) < c \tag{27}$$

where c is a small positive number,

$$c \ll b. \tag{28}$$

The above classification of curvatures is possible within an appropriately chosen neighborhood A of any critical point $\boldsymbol{r}^{(\lambda,i)}$ that has at most one canonical curvature of large negative value, i.e. less than $-a$.

From the above conditions it follows that

$$\lambda \leq s + l. \tag{29}$$

The local subspace $\mathcal{S}(\boldsymbol{r})$, spanned by the "soft" local normal modes $\{\boldsymbol{b}_{(k)}(\boldsymbol{r})\}_{k=1}^{s}$ also converges smoothly to the local subspace $\mathcal{S}(\boldsymbol{r}^{(\lambda,i)})$, spanned by $\{\boldsymbol{b}_{(k)}(\boldsymbol{r}^{(\lambda,i)})\}_{k=1}^{s}$ at the critical point, as $\boldsymbol{r}$ converges to $\boldsymbol{r}^{(\lambda,i)}$. This latter subspace is of special importance. If $l = 0$, then for $\lambda = 1$, i.e. for a saddle point $\boldsymbol{r}^{(1,i)}$ of a transition structure, the minimum energy path passing through $\boldsymbol{r}^{(\lambda,i)}$ as its transition point, must have its tangent parallel to $\boldsymbol{b}_{(1)}(\boldsymbol{r}^{(1,i)})$ at the critical point, where the choice of indices k is such that

$$h_1(\boldsymbol{r}^{(1,i)}) = \min\{h_k(\boldsymbol{r}^{(1,i)})\}. \tag{30}$$

If $\lambda = 0$, i.e. if the critical point $[\boldsymbol{r}^{(0,i)}]$ is a minimum, then one can easily construct examples where a minimum energy path approaches $\boldsymbol{r}^{(0,i)}$ in the orthogonal complement of $\mathcal{S}(\boldsymbol{r})$. Nevertheless, in the set of *all* steepest descent paths approaching $\boldsymbol{r}^{(0,i)}$ such minimum energy paths form a subset of measure zero, that is, almost every steepest descent path has tangent at $\boldsymbol{r}^{(0,i)}$ that is within $\mathcal{S}(\boldsymbol{r}^{(0,i)})$. Furthermore, if $h_1(\boldsymbol{r}^{(0,i)})$ is a non-degenerate eigenvalue, then almost every tangent is parallel to $\boldsymbol{b}_{(1)}(\boldsymbol{r}^{(0,i)})$.

The differences between the $\boldsymbol{T}_C$ and $\boldsymbol{T}_C^0$ topologies, defined in terms of hypersurfaces $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$, respectively, are influenced mostly by the behavior of group (b) of the v variable curvatures, in the neighborhood A of $\boldsymbol{r}^{(\lambda,i)}$.

For simplicity, let us first consider a special case and assume that point $\boldsymbol{r}_c$ is a non-degenerate critical point of *both* $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$, having index λ and λ^0, respectively:

$$\boldsymbol{r}_c = \boldsymbol{r}^{(\lambda, i)} = \boldsymbol{r}^{(\lambda^0, i^0)}. \tag{31}$$

The above condition, although not necessarily valid, is often implied by symmetry of potential energy hypersurfaces. If this condition is valid, then *local* criteria can be given for the zero-point energy influenced existence of chemical species. Following the discussion of local criteria, we shall also discuss *global* criteria, applicable even if condition (31) is not valid.

We are interested mostly in those cases of potential defying species of Type A, where

$$\lambda \neq \lambda^0 \tag{32}$$

and either

$$\lambda \leq 1 \tag{33}$$

or

$$\lambda^0 \leq 1, \tag{34}$$

i.e. where the type of the critical point, hence that of the corresponding chemical structure *changes* upon inclusion of the local zero-point energy, and either on $E(\boldsymbol{r})$ or on $E^0(\boldsymbol{r})$ a formal stable molecule or a transition structure is involved.

Eq. (31) implies that $\boldsymbol{r}_C$ is a critical point of $\Delta E^0(\boldsymbol{r})$ as well, with an index λ^Δ:

$$\boldsymbol{r}_C = \boldsymbol{r}^{(\lambda^\Delta, i^\Delta)}. \tag{35}$$

The indices λ, λ^0 and λ^Δ of the respective critical points are not independent. Elementary considerations of the curvature properties, subject to conditions (32)-(34) on the chemically interesting cases, lead to the following relations:

$$\text{(i)} \quad \lambda = 0, \lambda^0 = 1 \quad \Rightarrow \quad \lambda^\Delta \geq 1 \tag{36}$$

$$\text{(ii)} \quad \lambda = 0, \lambda^0 \geq 2 \quad \Rightarrow \quad \lambda^\Delta \geq \lambda^0 \geq 2 \tag{37}$$

$$\text{(iii)} \quad \lambda = 1, \lambda^0 = 0 \quad \Rightarrow \quad \lambda^\Delta \leq n-1 \tag{38}$$

$$\text{(iv)} \quad \lambda = 1, \lambda^0 \geq 2 \quad \Rightarrow \quad \lambda^\Delta \geq 1 \tag{39}$$

$$\text{(v)} \quad \lambda \geq 2, \lambda^0 = 0 \quad \Rightarrow \quad \lambda^\Lambda \leq n-2 \tag{40}$$

$$\text{(vi)} \quad \lambda \geq 2, \lambda^0 = 1 \quad \Rightarrow \quad \lambda^\Delta \leq n-1. \tag{41}$$

For example, in case (i) the inclusion of zero-point energy converts a formal stable molecule of $E(\boldsymbol{r})$ into a transition structure of $E^0(\boldsymbol{r})$, implying that $\boldsymbol{r}_C$ cannot be a minimum point of $\Delta E^0(\boldsymbol{r})$. Case (iii) corresponds to the example IHI quoted above, implying that $\boldsymbol{r}_C$ cannot be a maximum of $\Delta E^0(\boldsymbol{r})$.

The converses of relations (36) $\cdots$ (41) are not in general valid; the listed inequalities for λ^Δ are only necessary but not sufficient conditions for the respective cases (i) $\cdots$ (vi). A more general necessary condition, applying also for the chemically unimportant cases of λ, $\lambda \geq 2$, can be written as

$$\lambda^0 - \lambda \leq \lambda^\Delta \leq n + \lambda^0 - \lambda. \tag{42}$$

Let us consider model 1 in which curvature properties are the most tractable.

In order to obtain sufficient conditions for cases (i) $\cdots$ (vi), we first observe that for any domain A where $E(\boldsymbol{r})$ is quadratic, the Hessian $\mathcal{H}^\Delta(\boldsymbol{r})$, associated with $\operatorname{Re} \widetilde{\Delta E}^0(\boldsymbol{r})$, is identically zero,

$$\mathcal{H}^\Delta(\boldsymbol{r}) = 0, \qquad \boldsymbol{r} \in A \tag{43}$$

hence at $\boldsymbol{r}_C \in A$ all eigenvalues of $\mathcal{H}^\Delta(\boldsymbol{r}_C)$ as well as λ^Δ are zero:

$$\lambda^\Delta = 0. \tag{44}$$

On the other hand, eigenvalues of large absolute values can occur for $\mathcal{H}^\Delta(\boldsymbol{r}_C)$ only if $E(\boldsymbol{r})$ shows severe deviations from quadraticity within A. Such severe deviations from quadraticity that may change the signs of curvatures along the "hard" local normal modes, are unlikely to occur in actual chemical problems. We may conclude that for a domain A within which $E(\boldsymbol{r})$ is moderately non-quadratic, the term $\operatorname{Re} \widetilde{\Delta E}^0(\boldsymbol{r})$ is likely to influence the signs of curvatures only within subspace $\mathcal{S}(\boldsymbol{r}_C)$ of the "soft" local modes. The deviations from quadraticity, on the other hand, are expected to originate mostly from variations of those "variable" curvatures which belong to a subspace $\mathcal{V}(\boldsymbol{r}_C)$, spanned by local normal mode vectors $\{\boldsymbol{b}_{(k)}(\boldsymbol{r}_C)\}_{k=s+1}^{s+v}$. Evidently, subspaces $\mathcal{S}(\boldsymbol{r}_C)$ and $\mathcal{V}(\boldsymbol{r}_C)$ are orthogonal to each other.

If all sign changes of curvatures occur within $\mathcal{S}(\boldsymbol{r}_C)$ then it is sufficient to consider the s-dimensional subset

$$A_s = A \cap \mathcal{S}(\boldsymbol{r}_C) \tag{45}$$

and the cross sections $E_s(\boldsymbol{r})$, $E_s^0(\boldsymbol{r})$ and $\operatorname{Re} \widetilde{\Delta E}_s^0(\boldsymbol{r})$ of $E(\boldsymbol{r})$, $E_1^0(\boldsymbol{r})$ and $\operatorname{Re} \widetilde{\Delta E}^0(\boldsymbol{r})$, respectively, within A_s. The corresponding Hessians $\mathcal{H}_s(\boldsymbol{r}_C)$, $\mathcal{H}_s^0(\boldsymbol{r}_C)$ and $\mathcal{H}_s^\Delta(\boldsymbol{r}_C)$, restricted to A_s, have the following critical point indices within A_s:

$$\lambda_s = \lambda - l \tag{46}$$

$$\lambda_s^0 = \lambda^0 - l \tag{47}$$

$$\lambda_s^\Delta = \lambda^0 - l. \tag{48}$$

On the basis of the $\{\boldsymbol{b}_{(k)}(\boldsymbol{r}_C)\}_{k=1}^{s}$ local normal modes the $(\mathcal{H}_s^\Delta)_{kk'}$ matrix element, where

$$1 \leq k, k' \leq s, \tag{49}$$

is obtained from Eq. (10) as

$$(\mathcal{H}_s^\Delta)_{kk'} = \tfrac{1}{4}\hbar \sum_{i:h_i>0} h_i^{-1/2} \left\{ \frac{\partial^2 h_i}{\partial x^k \partial x^{k'}} - \tfrac{1}{2} h_i^{-1} \frac{\partial h_i}{\partial x^k} \frac{\partial h_i}{\partial x^{k'}} \right\}. \tag{50}$$

Let us denote by $m(-a)$ the number of those h_k^{Δ} eigenvalues of $\mathcal{H}_s^{\Delta}(\boldsymbol{r}_C)$ for which

$$h_k^{\Delta} < -a, \tag{51}$$

and by $m(a)$ the number of those h_k^{Δ} eigenvalues for which

$$h_k^{\Delta} > a. \tag{52}$$

Then, in terms of $\mathcal{H}_s^{\Delta}(\boldsymbol{r}_C)$ *sufficient* local criteria can be given for cases (i) $\cdots$ (vi), as follows:

for cases (i) and (ii)

$$m(-a) = \lambda^0 \tag{53}$$

whereas for (iii) and (v)

$$m(a) = s - \lambda^0. \tag{54}$$

If $l = 0$, then for cases (iv) and (vi) a sufficient condition is that *both* (53) and (54) are fulfilled, whereas, if $l = 1$, then for case (iv)

$$m(-a) = \lambda^0 - l \tag{55}$$

and for case (vi)

$$m(a) = s - \lambda^0 + l \tag{56}$$

are sufficient conditions.

5. Global topological criteria

If condition (31), hence relation (35) are not satisfied, then local criteria, referring to a single point $\boldsymbol{r}_C \in {}^nR$, are insufficient to give indication for the existence or non-existence of "potential-defying" chemical species. In such cases, one may investigate the global topological properties of hypersurfaces $E(\boldsymbol{r})$, $E^0(\boldsymbol{r})$ and $\Delta E^0(\boldsymbol{r})$.

In particular, we shall investigate the necessity of simultaneous occurrence of *several* "potential defying" species, that is a consequence of the general topological properties of the hypersurfaces investigated. We shall conclude that if one potential defying species exists then others must also exist on the same surface, and there are topological invariants that restrict the number and type of such species.

Let us assume that we are interested in chemical structures within a connected open subset $A \subset {}^nR$. The relative topologies, T_{CA} and T_{CA}^0, restricted to A, are defined as

$$T_{CA} = \{G_A\colon G_A = A \cap G_C, G_C \in T_C\} \tag{57}$$

and

$$T_{CA}^0 = \{G_A^0\colon G_A^0 = A \cap G_C^0, G_C^0 \in T_C^0\} \tag{58}$$

respectively. In particular, chemical structures $C^{(\lambda,i)}$ and $C^{0(\lambda,i)}$ of topological spaces $({}^nR, T_C)$ and $({}^nR, T_C^0)$, respectively, for which

$$\boldsymbol{r}^{(\lambda,i)} \in A \tag{59}$$

and

$$\boldsymbol{r}^{0(\lambda,i)} \in A, \tag{60}$$

are represented in the relative topologies T_{CA} and T_{CA}^0 by

$$C_A^{(\lambda,i)} = A \cap C^{(\lambda,i)} \tag{61}$$

and

$$C_A^{0(\lambda,i)} = A \cap C^{0(\lambda,i)}, \tag{62}$$

respectively.

In order to investigate the global criteria, we shall map set A to a compact, orientable manifold, using a technique similar to the compactification and mappings described in Refs. [8, 15, 16].

We assume that the closure $\bar{A}$ of subset A is contained in a simply connected open set B,

$$\bar{A} \subset B \tag{63}$$

and within $B \backslash A$ both functions $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$ can be continuously and twice differentiably deformed into functions $\bar{E}(\boldsymbol{r})$ and $\bar{E}^0(\boldsymbol{r})$, respectively. These deformations are such that at the boundary of $\bar{B}$ the *new functions* take the constant values f and f^0, which are their respective maximum values within $\bar{B}$. Within set A there is no deformation,

$$\bar{E}(\boldsymbol{r}) = E(\boldsymbol{r}),\ \boldsymbol{r} \in A \tag{64}$$

$$\bar{E}^0(\boldsymbol{r}) = E^0(\boldsymbol{r}),\ \boldsymbol{r} \in A, \tag{65}$$

by definition. One may visualize these deformations as "pulling up" $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$ at the boundary of $\bar{B}$ to equal height, without changing the functions within set A. We shall also assume that these deformations are accomplished with the *minimum number* of critical points occurring in $B \backslash A$, and that these critical points are nondegenerate. Set $\bar{B}$, with functions $\bar{E}(\boldsymbol{r})$ and $\bar{E}^0(\boldsymbol{r})$ can then be mapped onto a compact manifold M', where the entire boundary of $\bar{B}$ can be identified with a single point $p \in M'$. For simply connected sets A and B manifold M' can be chosen as a topological sphere, point p being its "north pole", representing the absolute maximum of both $\bar{E}(\boldsymbol{r})$ and $\bar{E}^0(\boldsymbol{r})$ on M'.

In fact, it is sufficient to know that such deformations and transformations exist, and carrying out of an actual transformation is not required as long as the critical points in $B \backslash A$ are accounted for. We may illustrate this point using the example of the IHI system. One may choose A as a sufficiently large but bounded subset of ${}^3R$, containing a neighborhood of the saddle point $\boldsymbol{r}^{(1,1)}$ of $E(\boldsymbol{r})$. By taking a larger set B, containing A, and "pulling up" $E(\boldsymbol{r})$ at the rim of B, one introduces two new minima within $B \backslash A$, which in fact take the roles of the degenerate minima of the original function $E(\boldsymbol{r})$ at infinite nuclear separations. These *two* minima represent the *minimum* number of critical points that one can obtain within $B \backslash A$ by a continuous deformation of $E(\boldsymbol{r})$, subject to the condition that at the boundary of $\bar{B}$ $\bar{E}(\boldsymbol{r})$ is maximum. The interior of $\bar{B}$ is mapped onto a *punctured* topological sphere of dimension 3, from which the north pole $\boldsymbol{p}$ is removed, whereas the entire boundary of $\bar{B}$ is identified with the single point $\boldsymbol{p}$, completing the compact manifold. Function $\bar{E}(y)$ is re-defined on M', by taking the *same* function values at points of $M' \backslash \boldsymbol{p}$ and B that are assigned to each other, and by assigning the common function value f at the boundary of $\bar{B}$ to point $\boldsymbol{p} \in M'$. Function $\bar{E}^0(y)$ on M' is defined analogously.

The deformations in $B \backslash A$ can always be chosen such that the resulting functions $\bar{E}(y)$ and $\bar{E}^0(y)$ are twice differentiable at $\boldsymbol{p} \in M'$, at every other point $y \in M'$ this condition is assured by the definition of these functions, and by the application of the smoothing technique of Ref [8].

If neither function $\bar{E}(y)$ nor $\bar{E}^0(y)$ has degenerate critical points then the *number of various chemical structures* (catchment regions) defined by them is subject to a set of *common constraints*, governed by the *topological invariants* of manifold M'. That is, inclusion of the local zero-point energy, leading to function $\bar{E}^0(y)$, *cannot* cause arbitrary changes is the number and type of chemical structures appearing or disappearing, as compared to the simple potential surface approximation based on $\bar{E}(y)$. Whatever new "potential defying" chemical species occur on $\bar{E}^0(y)$, the total number of various species (stable molecules, transition structures, as well as unstable formal "species" represented by catchment regions of critical points of higher indices, $\lambda = 2, \ldots, n$, which are also required for a systematic partitioning of the hypersurface [8]) must fulfill the constraints set by the topological invariants of M', just as the catchment regions of the simple potential $\bar{E}(y)$ must satisfy these constraints. These topological invariants are the set $\{B_\lambda\}_{\lambda=0}^{n}$ of Betti numbers, that are lower bounds for the number m_λ of critical points of index λ,

$$m_\lambda \geq B_\lambda \qquad (\lambda = 0, \ldots, n) \tag{66}$$

and the Euler-Poincaré characteristic χ of M'. Critical point relations [17, 18], in particular the Morse relations

$$m_\lambda - m_{\lambda-1} + m_{\lambda-2} - \cdots \pm m_0 \geq B_\lambda - B_{\lambda-1} + B_{\lambda-2} - \cdots \pm B_0 \qquad (0 \leq \lambda < n) \tag{67}$$

and

$$\sum_{\lambda=0}^{n} (-1)^\lambda m_\lambda = \sum_{\lambda=0}^{n} (-1)^\lambda B_\lambda = \chi \tag{68}$$

constrain the possible combinations of the numbers m_λ of various chemical structures on M', hence in $B \subset {}^nR$.

As an illustration of the above constraints, take the example of the system IHI. $E(\boldsymbol{r})$ in set A has one saddle point of index $\lambda = 1$ and no other critical points.

Mapping of $\bar{B}$ onto M', that is, onto a topological three-sphere ${}^3\mathcal{S}$, certainly introduces one maximum of $\bar{E}(y)$ at $y = p$. The topological invariants of ${}^3\mathcal{S}$ are $B_1 = B_2 = \chi = 0$, $B_0 = B_3 = 1$. Consequently, Eq. (68) implies that $m_1 = 1$ and $m_3 = 1$ is possible only if

$$m_0 + m_2 = 2. \tag{69}$$

Inequality (66) for $\lambda = 0$ implies that

$$m_0 \geq 1 \tag{70}$$

and from symmetry it follows that

$$m_0 = 2 \tag{71}$$

$$m_2 = 0 \tag{72}$$

that is, we must have two minima in $B \backslash A$ for function $\bar{E}(\boldsymbol{r})$.

The effects of the inclusion of local zero-point energy for IHI are not restricted to the replacement of the saddle point with a minimum in $E^0(\boldsymbol{r})$ and $\bar{E}^0(y)$, since the constraints (66)-(68) apply to $\bar{E}^0(y)$ just as well as to $\bar{E}(y)$. Now we have at least one minimum and one maximum. In fact, the implied two chemical structures, one, the catchment region of the minimum, and one additional formal chemical structure, the single point "catchment region" at p, fulfill the topological constraints (66)-(68) with $m_0 = 1$, $m_1 = m_2 = 0$, $m_3 = 1$. One may expect, however, that on $E^0(\boldsymbol{r})$ the two degenerate minima at infinite nuclear separations (for $IH + I$ and $I + HI$, resp.) exist, consequently, for a large enough set A the function $\bar{E}^0(\boldsymbol{r})$ on B will have three minima. The numbers $m_0 = 3$ and $m_3 = 1$, however, are compatible with Eq. (68) only if

$$-m_1 + m_2 = -2. \tag{73}$$

The simplest solution to Eq. (73) is

$$m_1 = 2 \tag{74}$$

$$m_2 = 0 \tag{75}$$

that implies, two additional saddle points of transition structures. In this case, the inclusion of local zero-point energy caused the appearance not only of a "potential defying" stable molecule, as the catchment region of the new minimum, but also that of *two transition structures*, not present on $E(\boldsymbol{r})$. Whereas the above conclusions can be reached on an intuitive basis for chemical systems as simple as IHI, for more complicated multidimensional cases, intuition and attempts to visualize hypersurfaces may not be sufficient, and then the formal application of the topological constraints may well be the only available method.

Hypersurfaces $E(\boldsymbol{r})$ and $E^0(\boldsymbol{r})$ on A, as well as functions $\bar{E}(y)$ and $\bar{E}^0(y)$ on manifold M', can be continuously deformed into each other. Assuming that the local zero-point energy contribution is "switched on" in a continuous manner, one can define a (generally non-unique) homotopy $H(y, t)$ as

$$H(y, t): M' \otimes I \to {}^1R, \qquad y \in M', \qquad t \in I \tag{76}$$

$$H(y, 0) = \bar{E}(y) \tag{77}$$

$$H(y, 1) = \bar{E}^0(y) \tag{78}$$

$$H(y, t) = \bar{E}_{(t)}(y): M' \to {}^1R \tag{79}$$

where $I = [0, 1]$ is the unit interval, and $\bar{E}_{(t)}(y)$ is a twice continuously differentiable function on M'.

Any homotopy $H(y, t)$, fulfilling the above conditions, can be used for diagnosing the possibility of those cases where inclusion of local zero-point energy *changes* the character and/or the number of chemical structures. A simple necessary (although not in general sufficient) condition can be given as follows.

Whenever such a change occurs, then either
(i) the index λ of some critical points must change
or
(ii) there is a *simultaneous* change in several of the m_λ numbers, subject to constraints (66)-(68).

In case (i) the number of negative eigenvalues of the Hessian matrix *changes* at some critical point, consequently, there must exist some value t such that on the associated hypersurface $H(y, t) = \bar{E}_{(t)}(y)$ over manifold M' there is a critical point with a formal zero eigenvalue of its Hessian, i.e. a *degenerate critical point.* In case (ii) a simultaneous appearance or disappearance of several critical points implies that for certain t a *degenerate critical point,* e.g. one associated with a bifurcation of critical points of the corresponding hypersurface $H(y, t) = \bar{E}_{(t)}(y)$, must exist. Consequently, the existence of "potential defying" chemical species, as well as the non-existence of chemical species implied by the simple potential model of $E_\bullet(\mathbf{r})$, implies, for both cases (i) and (ii) that *any* homotopy satisfying conditions (76)-(79) must generate an $E_{(t)}(y)$ hypersurface with *degenerate critical points* for certain intermediate t value, $0 < t < 1$.

Acknowledgment. This study has been supported by a research grant of the Natural Sciences and Engineering Research Council of Canada.

Appendix

Following the notations of Ref. [25], the infinite parabolic potential barrier is given as

$$V(x) = -\tfrac{1}{2}Ax^2 \tag{A1}$$

where $A = -h_j > 0$ is the curvature of the parabola. J_c and J stand for the classical and quantum mechanical rates of particle transfer, respectively, where the latter includes tunneling. The permeability $G(W)$ of the barrier at energy W is given by

$$G(W)=\{1+\exp[(V_0-W)/\hbar\nu_{\neq}]\}^{-1} \tag{A2}$$

where the imaginary frequency $i\nu_{\neq}$ is given by

$$\nu_{\neq}=A^{1/2}/2\pi \tag{A3}$$

if mass-weighted coordinate x is used.

Our aim is to derive a formula for an effective lowering E_T of the potential, that produces a hypothetical classical potential with maximum

$$V_0'=V_0-E_T \tag{A4}$$

for which the classical rate is equal to the quantum mechanical rate of the original potential:

$$J_c(V')=J(V). \tag{A5}$$

Substitution of the classical and quantum mechanical expressions for the rates gives

$$\exp(-V_0'/kT)=1/kT\int_0^\infty \exp(-W/kT)/\{1+\exp[(V_0-W)/\hbar\nu_{\neq}]\}\,dW. \tag{A6}$$

Introducing the new variable $W'=W-V_0$ gives

$$\exp(E_T/kT)=1/kT\int_{-V_0}^\infty \exp(-W'/kT)/\{1+\exp[-W'/\hbar\nu_{\neq}]\}\,dW'. \tag{A7}$$

If $W=0$ corresponds to a sufficiently low energy value, then $-V_0$ can be replaced with $-\infty$ in the integration. Subject to the condition that

$$kT>\hbar\nu_{\neq} \tag{A8}$$

the above integral gives [32]

$$\exp(E_T/kT)=z\operatorname{cosec} z \tag{A9}$$

where

$$z=\pi\hbar\nu_{\neq}/(kT)=\hbar A^{1/2}/(2kT). \tag{A10}$$

Eq. (A9) can be rewritten as

$$-E_T/kT=\ln(\sin z/z)=\sum_{n=1}^{\infty}(-1)^n 2^{2n-1}/(n(2n)!)b_{2n}z^{2n} \tag{A11}$$

where b_n are the Bernoulli numbers [33]. Substitution up to the term of degree eight gives the final result as given in Eq. (17):

$$E_T=kT(z^2/6+z^4/180+z^6/2835+z^8/37800+\cdots). \tag{A12}$$

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Received January 2, 1984/August 1, 1984