which is also seen near the SP's). From point (0.685, 0.920) downhill to (0, 0) the GE_3 traces the maximal cirque region of the flank of valley v_1, and uphill to (2, 2) the GE_3 traces the maximal cliff region of the flank of r_1. So, over three contour lines the CCI belt substitutes for the CCI point as in Examples 2 and 3. The model surface in Fig. 9 consists of three valleys and three ridges meeting in an asymmetric central region. An intuitive concept of a valley v_1 bifurcating uphill to SP_1 and SP_2, and of a ridge r_1 also bifurcating downhill to SP_1 and SP_2 is not supported by the GE result. The valley floor from SP_1 downhill ends in (0, 0), analogously the crest to the right from SP_2 uphill on r_1 in northwest direction ends in (2, 2) (cf an analogous result on another simple model surface in [10]). The end of a valley floor downhill is the mathematical result of a lacerated bifurcation point and of a new connected arc to a cirque ascending GE branch. It is characterized by Basilevsky's double point [8] which in mathematical terms is a turning point [9].

Of course, from any point of the final floor we can draw a steepest descent line and thus get a connection, or a bridge, over the region behind (0, 0), i.e. over the lacerated bifurcation region. The numerical result of a GE test in this region gives $GE(x, y) \neq 0$, but the deviation from zero is only small. We call such a bridged region a quasivalley from inspection of the 2D, Fig. 9. The former bifurcation point of GE's in Fig. 8 for the case $\mu = 1.08$ now changes in a flat SP region of a GE surface surrounded by zero contour lines. These zero equipotential lines are the GE's of the model surface.

3. Discussion

On PES's we do not generally find a coincidence of SP's CCI points and BP's. With clear definitions of these points on the GE curves, we now have a well suited instrument for characterizing PES's.

First of all, a first order SP gives the globally minimal energy required to drive a reaction of a chemical configuration over the corresponding transition structure. It should be noted that SP's of higher order are also of some chemical interest [11]. From a first order SP we can trace a steepest descent trajectory starting in an eigenvector direction of the Hessian. This gives Fukui's IRC, the intrinsic reaction coordinate [12]. Using the terms of a very old paper this path is the watercourse [13], because the actual acceleration of a water drop is tangential to the negative gradient. In the general case, however, we have no local criterion for a steepest descent trajectory being the IRC [2, 3]; i.e. there is no way to tell if a point is or is not on this IRC path by looking at the PES only in the neighbourhood of a point.

This deficiency is surmounted by the GE definition if we additionally test whether we get a valley or a ridge for a GE [1]. The price is more computation for both the Hessian elements and the curve tracing of a corresponding GE from any stationary point to another [4]. In general, the latter is complicated [9] and only theoretically possible. If we use crude curve tracing algorithms then sometimes we may hop over bifurcation regions and bridge different branches of GE's with

diagonal turning points. In summary GE's are a tool to reach an SP on a 1D path in an "unknown" landscape.

The steepest descent path and GE are curves defined on the static PES: they are only a frame for the real dynamics of a molecular transition in a chemical reaction. We have seen in Example 3 how imperceptibly a side valley can emerge. Thus, a molecular vibration, a mode, will not feel a BP but will be stable in the region around the BP of a GE, as long as the contour lines are still convex. The situation changes dramatically behind the CCI point. Then the contour lines become concave, from the point of view of the mode, and the molecular vibration bouncing on the cliff shows a propensity to vibrational redistribution. We assume two possible kinds of qualitative behaviour.

(i) If we have a flat cliff which quickly goes over into a ridge and which is accompanied by two closely neighbouring valleys, then the mode bounces on a double minimum section of the PES. Such a vibration is quantum mechanically possible and the spectroscopic category of quasilinear molecules gives an example, cf [14] for a review. The angle of a corresponding valley floor with the vibration direction should not be greater than 25°–35° in the molecular geometry [14], Table XIII. Figure 13 in [14] is the commonly used representation of the quasilinearity problem. It shows different 1D potential energy curves of double minimum shape for different quasilinear states of the same mode, i.e. in a 2D view a ridge and two ascenting neighbouring valleys. The slightly strange character of a quasilinear mode is due to the fact that a stretch mode goes along the crest of a ridge.

(ii) If we have a broad and precipitous cliff then the mode cannot be stabilized and suffers a vibrational redistribution. Recently, we have assumed this to be the case in HCN [15] since even in its fundamental transition the ν_1 mode, which is mainly the CN stretch, reaches a concave contour line in its compression phase. As a result, the quantum state (100) of HCN exist, but is expected to be quite unstable. We could assign the redistribution process to two effects, (i) the anomalous infrared excitation of single rotational lines of ν_1 itself connected with a sudden redistribution to $3\nu_2^1$ [15], and (ii) the known HCN gas laser [16].

Hence, CCI points or belts are very important for real molecular vibrations. Any CCI point lies on a GE and if we trace a GE to reach an SP we also get the CCI points [1, 6]. If the region around the CCI point is asymmetric it will be a factor which influences the direction of an excited vibration, i.e. a factor in the selection of possible reactions as we can imagine from Figs. 7–9.

Cautionary remark. The definition of a valley floor, and in general of a GE, is a metric dependent concept and one needs to consider explicitly what is the physically relevant metric in every instance, cf the discussion in [2, 3]. This is because of the metric dependence of the Hessian matrix [17]. An invariant formulation of GE's is given in [18, 19], cf also the textbook [20].

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