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## Gradient extremals and valley floor bifurcations on potential energy surfaces

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Gradient extremals are curves in configuration space defined by the condition that the gradient of the potential energy is an eigenvector of the Hessian matrix. Solutions of a corresponding equation go along a valley floor or along a crest of a ridge, if the norm of the gradient is a minimum, and along a cirque or a cliff or a flank of one of the two if the gradient norm is a maximum. Properties of gradient extremals are discussed for simple 2D model surfaces including the problem of valley bifurcations.

**Key words:** Potential energy surfaces — Reaction paths — Saddle points  
Bifurcation problems — HCN

### 1. Introduction

In the adiabatic approach, the reactive rearrangement of a chemical system is described by a motion of the system point on the potential energy surfaces (PES) from one minimum over a saddlepoint (SP) to another minimum. Once the stationary points have been determined, the next issue of interest is the characterization of possible reaction channels by valleys of the PES and hence, the definition of PES valleys by a formula of their valley floor. This is done in [1] by gradient extremals (GE) (cf also former papers cited there).

The next question is the problem of valley bifurcations. In 1984 we published a paper dealing with the steepest descent path [2], and a further aspect of this matter was discussed in a recent note [3]. A steepest descent does not, however, indicate a bifurcation [2], so here we tackle this problem by tracing the valleys of the PES. We continue the treatment of [1] and use an example of Hoffman,