Locating Saddle Points of any Index on Potential Energy Surfaces by the Generalized Gentlest Ascent Dynamics

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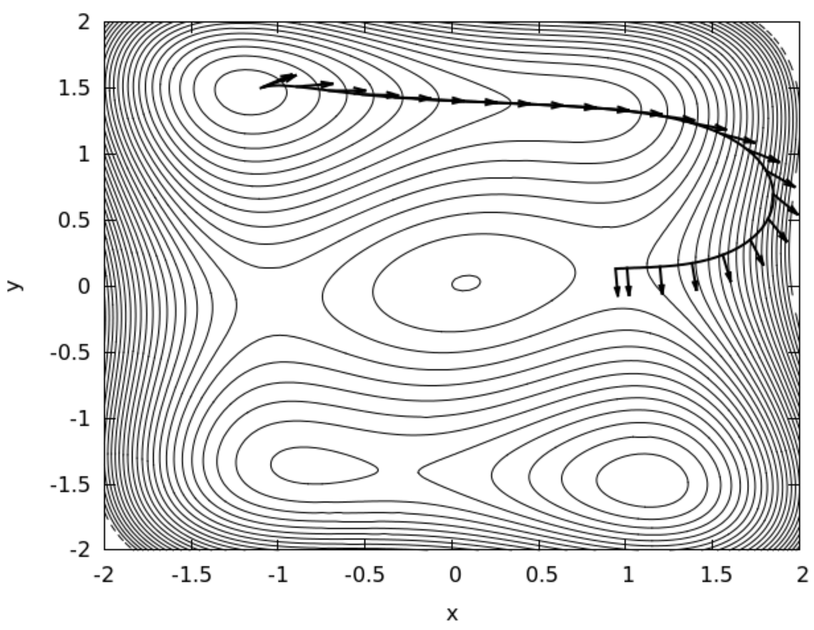
The basic equations of the Generalized Gentlest Ascent Dynamics (GGAD) for the location of a saddle point of index *n* in a *N*-dimensional Potential Energy Surface (PES) are

1.) $d\mathbf{q}/dt = -[\mathbf{I}-2\mathbf{V}\mathbf{V}^T]\mathbf{g}$ $\quad$ $\mathbf{q}^T=(q_1,\ldots,q_N)$: coordinates ; $\mathbf{g}$: PES gradient vector

2.) $d\mathbf{V}/dt = -[\mathbf{I}-\mathbf{V}\mathbf{V}^T]\mathbf{H}$ $\quad$ $\mathbf{H}$: PES Hessian matrix; $\mathbf{V}=[\mathbf{v}_1|\ldots|\mathbf{v}_n]$: matrix formed by *n*-orthonormalized vectors, $\mathbf{V}^T\mathbf{V} = \mathbf{I}$

Initial point, $(\mathbf{q}_0,\mathbf{g}_0,\mathbf{H}_0,\mathbf{V}_0)$, should be located near a minimum of the PES.

The GGAD curve $\mathbf{q}(t)$ moves along the *n*-orthogonal directions collected in the $\mathbf{V}$ matrix, minimize along the rest of *N-n* directions.
The stable fixed points of this dynamic are the stationary points of index *n* of the PES.

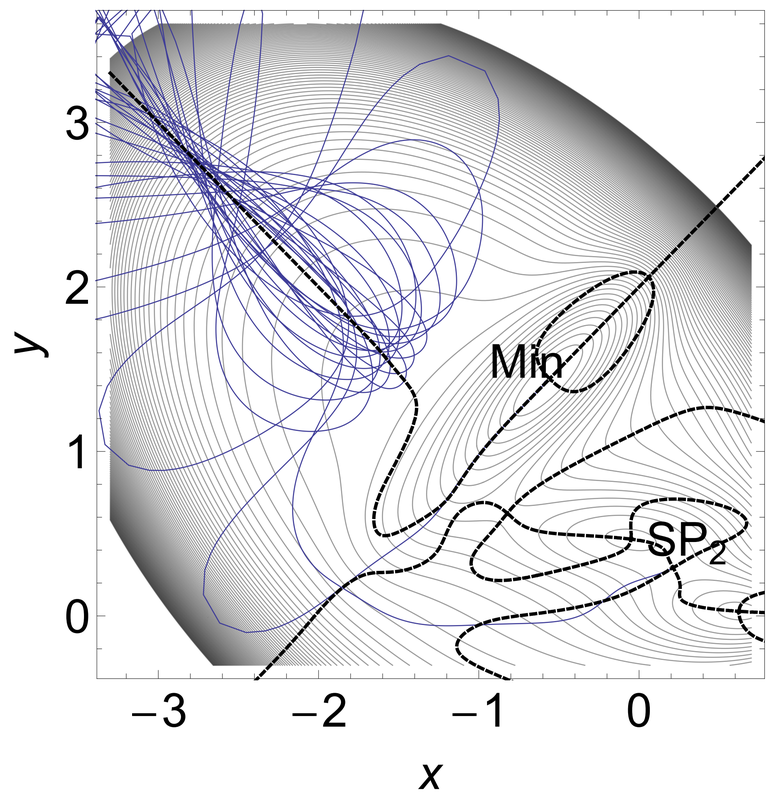


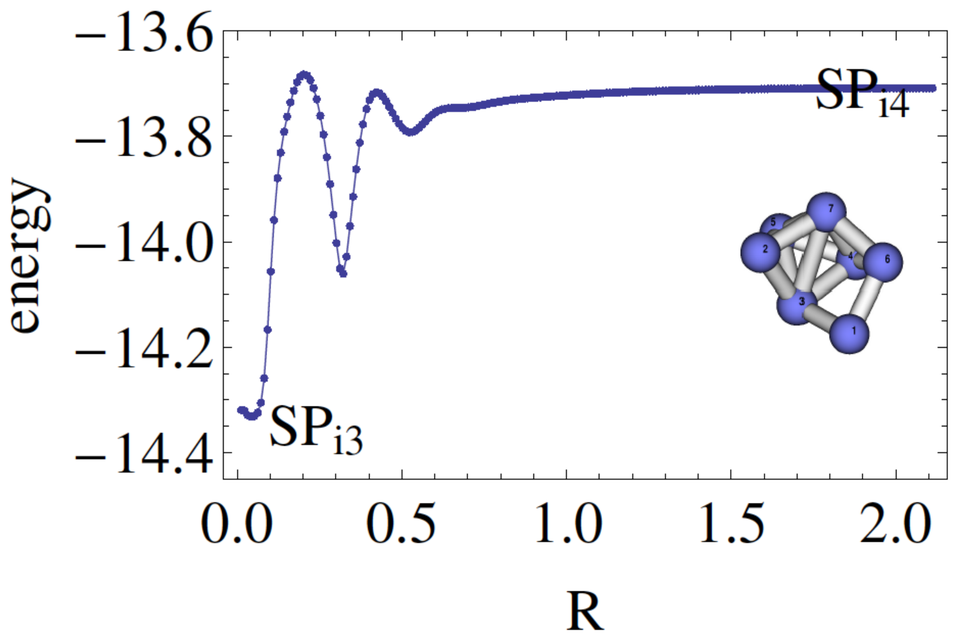
Behavior of the GGAD curve for $n = 1$ in the Wolfe-Quapp PES. The vectors are the $\mathbf{v}$-vector at each point of the curve. The curve is not gentlest ascent after the turning point.

The turning point condition for $n = 1$ occurs when the gradient and the $\mathbf{v}$-vector forms and angle of $\pi/4$.

For general *n* the turning point condition is: $\mathbf{g}^T\mathbf{V}\mathbf{V}^T\mathbf{g} / \mathbf{g}^T\mathbf{g} = ½$.

Müller-Brown PES. ‘Chaotic’ GAD trajectory, continuous lines, starting at point (-0.58, 1.427). The curve goes through the large side valley at the left hand side by repeated arcs. At last it leaves the valley at an accidental point and finds the TS labeled as SP2. At the upper, left hand side is no stationary point, so GAD cannot find any one. The region is a kind of a trap, a ‘dead’ valley. The fat, dashed lines are the Gradient-Extremal (GE) curves. The GE passes the region and leaves it to the mountains at the left hand side, but the GAD trajectory goes on and back, from one turning point to the next, and again back, and only by an accident, it later leaves the region. However, then it immediately leads to the TS2 of the Müller–Brown surface. It seems to be accidentally which TS is found. After the ‘chaotic’ evolution, the GAD trajectory finally catches a TS.





Energy profile over an index-4-GAD trajectory beginning at a LJ7-SP of index 3, to a LJ7-SP of index 4. R is an abstract 'reaction coordinate', the inlet is the shape of the SPi4. The search space of the Runge-Kutta method has the dimension $5*3N = 105$. The energy profile over the trajectory is shown. It enrolls the complicate search with some turning points of energy. The region of the SPi_4 is already touched at $R \approx 0.6$ units, but the remainder of the calculations, up to R = 6 units, is done for the exact convergence to the SP with a threshold of $|\mathbf{g}|_{max} < 2 *10^{-5}$. The full trajectory makes 3560 steps; note that the bullets in the figure are drawn at fixed R-steps. A conclusion of this test is: the GGAD can find SPs of any index of the PES. It is a determined, purposeful method. To search for an SP of index *n*, one should start near an SP of the lower index (*n* - 1). However, any other initial nodes are possible.

References.

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