Interplay between GAD method and conjugate directions to locate transition states

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Abstract

An algorithm to locate transition states in a Potential Energy Surface is proposed and described. The technique is based in the gentlest ascent dynamics where the gradient of the Potential Energy Surface is projected in a given direction and perpendicular to it. In the present method the projection is not only applied in the gradient but in the Hessian matrix. The direction is updated according the gentlest ascent dynamics method. To ensure stability and to avoid high computational cost, a trust region technique is incorporated and the Hessian matrix is updated at each iteration. With some examples we discuss the performance of the algorithm.

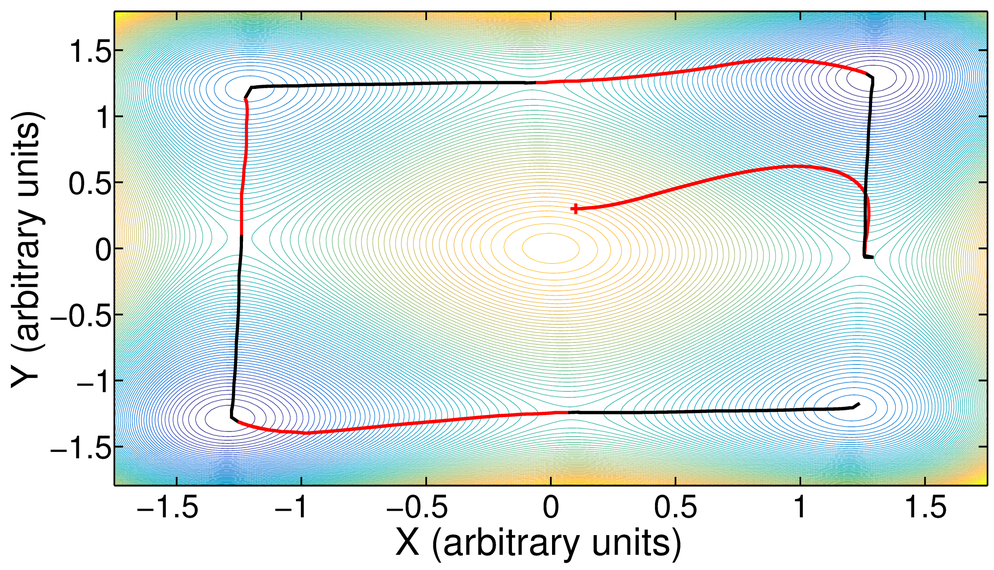
GAD + Newton dynamics

GAD + **Newton dynamics**

$$\frac{d\mathbf{x}}{dt} = -[\mathbf{I} - 2\mathbf{v}\mathbf{v}^T]\mathbf{g}(\mathbf{x})$$
$$\frac{d\mathbf{v}}{dt} = -[\mathbf{I} - \mathbf{v}\mathbf{v}^T]\mathbf{H}(\mathbf{x})\mathbf{v}$$

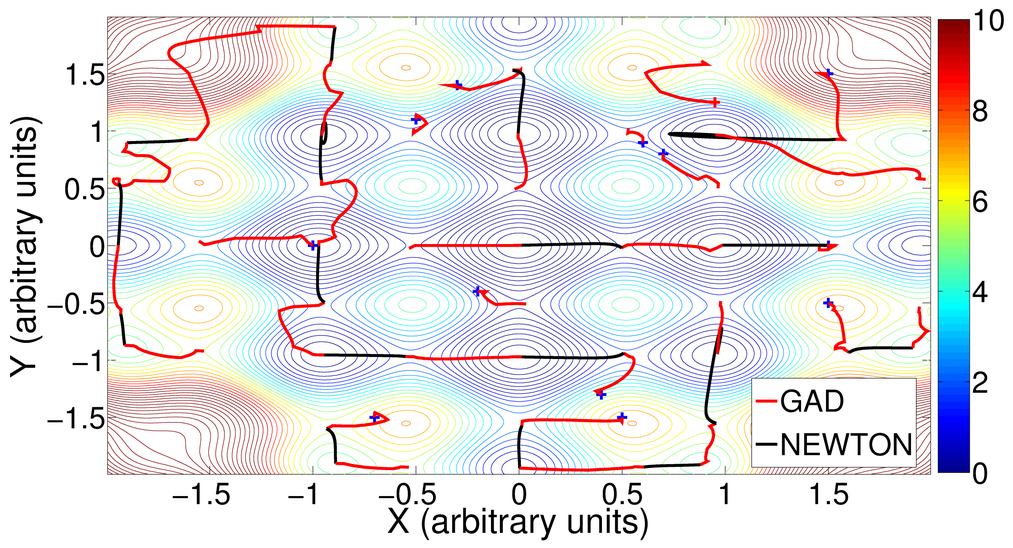
$$\frac{d^2\mathbf{x}}{dt^2} = -\mathbf{g}(\mathbf{x}) - \gamma\frac{d\mathbf{x}}{dt}$$

Porphine: $\epsilon(x,y) = \frac{U_0}{\Delta_0^4}\left[(x^2-\Delta_0^2)^2 + (x^2-\Delta_0^2)^2 - 4G\Delta_0^2 xy\right]$



A randomly initialized trajectory for the combined model GAD-Newtonian dynamics on the model porphine.

Rastrigin: $\epsilon(x,y) = AN + x^2 - Acos(2\pi x) + y^2 - Acos(2\pi y) + (xy)^2$



Due to the large number of possible reaction paths co-existing on the Rastrigin PES, the GAD-Newtonian trajectory is restarted as soon as an already known saddle point or minimum is reached.

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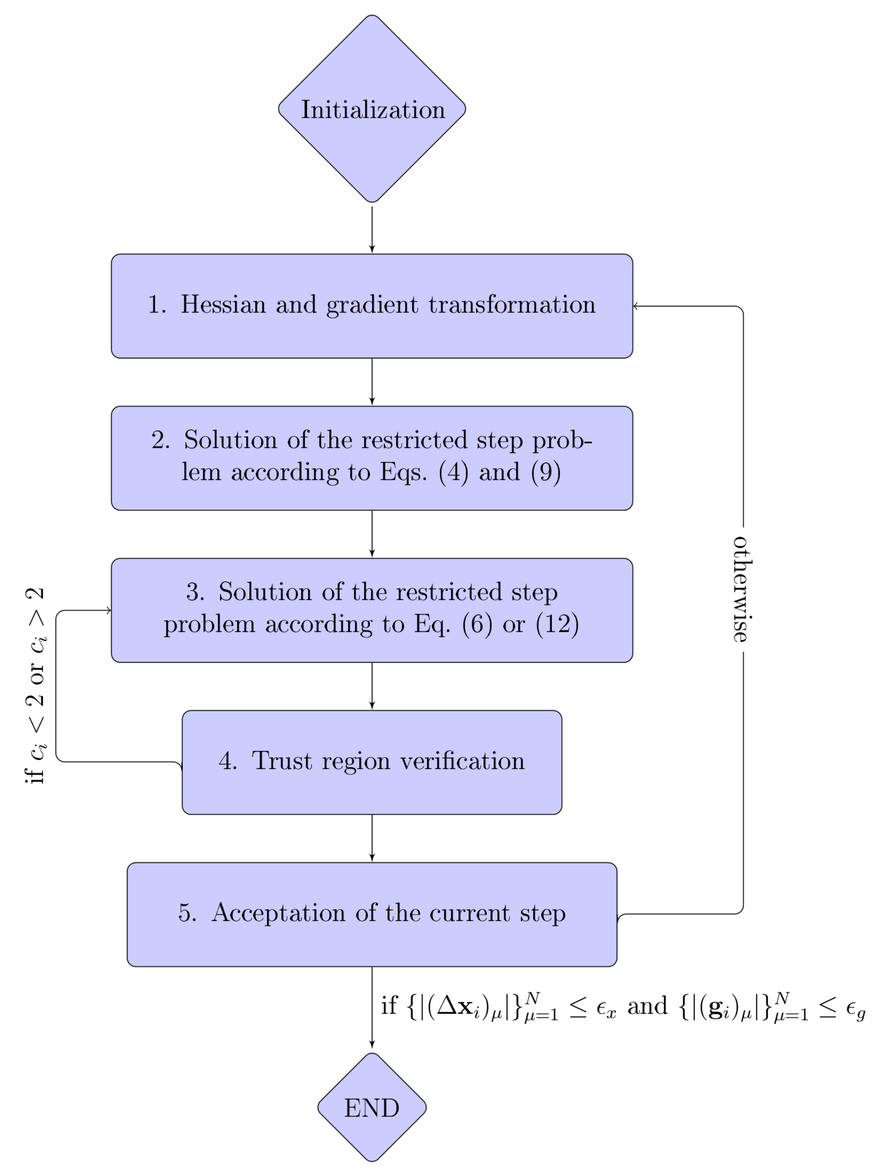
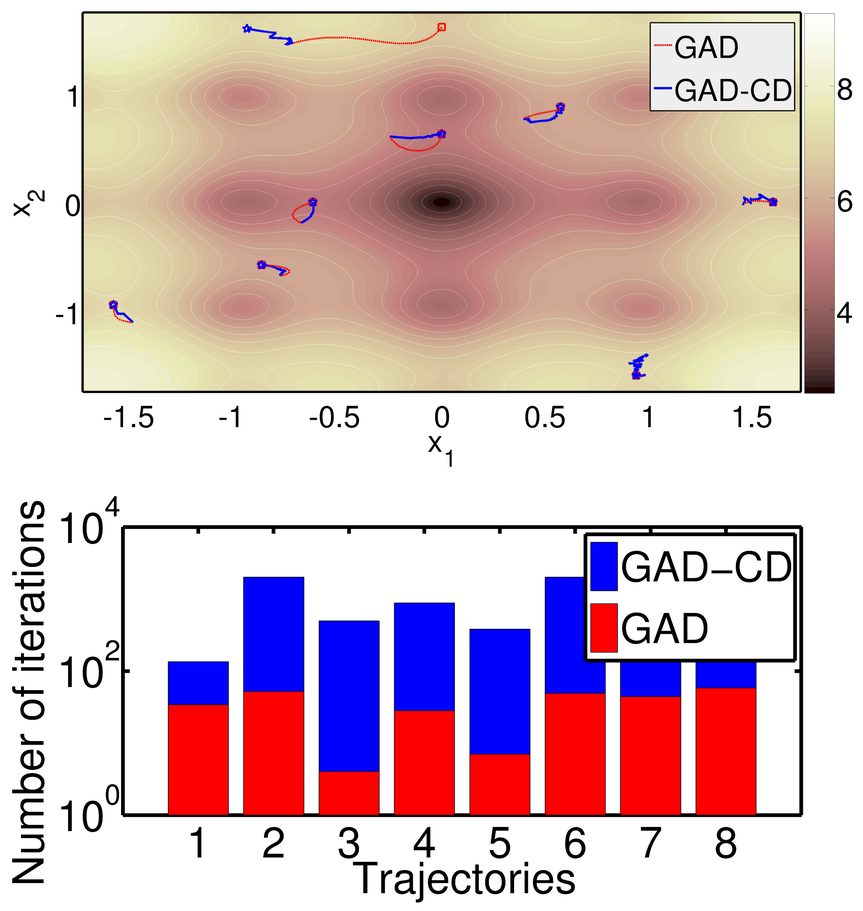
GAD + Conjugate directions

GAD-CD



Ackley: $\epsilon(x,y) = -ae^{-b\sqrt{(x^2+y^2)/2}} - e^{(\cos cx + \cos cy)/2}$



Performance of the GAD-CD method in comparison with the standard GAD technique. Top: evolution of eight randomly initialized trajectories for the GAD and the GAD-CD methods. Bottom: Number of iteration steps required for each of the above trajectories.

References

[1] W. E, X. Zhou, Nonlinearity, 24, 1831 (2011); [2] J. M. Bofill, W. Quapp, M. Caballero, Chem. Phys. Lett., 583, 203 (2013); [3] W. Quapp, J. M. Bofill, Theor. Chem. Acc., 133, 1510 (2014); [4] G. Albareda, JM Bofill, I de PR Moreira, W Quapp, J Rubio-Martínez, Theo. Chem. Acc. 137, 73 (2018); [5] G. Albareda et al., J. Chem. Phys. Lett. 6, 1529 (2015);