Exploring Potential Energy Surfaces of Complex Molecular Systems using Zermelo's Navigation Variational Model

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1. Abstract.

We propose an <u>*optimal navigation*</u> in a Potential Energy Surface, $V(\mathbf{x})$ (PES), of fixed gradient-field, where the objective is to find the fastest path between an initial Minimum point of this PES and a final Transition State (TS). The optimal navigation problem is based in the <u>*Zermelo's problem*</u> due to Ernst Zermelo, who first studied optimal navigation of airships in wind-fields, using <u>*variational principles*</u> [1,2]. In the present problem the wind-field is the gradient field.

2. Method.

We *employed Pontryagin's celebrated maximum principle* [3] to characterize the optimal paths in the gradient PES flow.

Consider the system described by the differential equation:

$$d\mathbf{x}/dt = -\left(\mathbf{I} - \mathbf{w}(t)\mathbf{w}(t)^T\right)\mathbf{g}(\mathbf{x}(t)) + \phi'\mathbf{w}(t)\mathbf{w}(t)^T\mathbf{g}(\mathbf{x}(t))$$
$$= -\mathbf{g}(\mathbf{x}(t)) + \phi\left(\mathbf{w}(t)^T\mathbf{g}(\mathbf{x}(t))\right)\mathbf{w}(t) = -\mathbf{g}(\mathbf{x}(t)) + f\left(\phi, \mathbf{x}(t), \mathbf{w}(t)\right)\mathbf{w}(t)$$

where $\mathbf{g}(\mathbf{x})$ is the gradient vector, $\mathbf{x}(t)$ is the position vector, $\mathbf{w}(t)$ is the control vector such that $\mathbf{w}(t)^T\mathbf{w}(t)=1$ and ϕ is a number $\phi \geq 1.1$. The initial conditions are given by $\mathbf{x}(0) = \mathbf{x}_M$ (minimum of the PES) and $\mathbf{w}(0)$ is an eigenvector of the Hessian matrix computed at $\mathbf{x}_0$. The position vectors are required to lie in a set of circles. At the final t, t_f, the circle degenerates in a point locates in the equipotential curve level, $V(\mathbf{x}(t_f)) - \nu = 0$. The curve level $V(\mathbf{x}(t_f)) - \nu = 0$ contains the transition state being the point $\mathbf{x}(t_f) = \mathbf{x}_{TS}$. We seek a control evolution, $\mathbf{w}^*(t)$, a corresponding position evolution, $\mathbf{x}^*(t)$, and a final t_f such that

1. The pair $\mathbf{x}^*(t)$, $\mathbf{w}^*(t)$ satisfies the above system of differential equations.
2. $\mathbf{x}^*(t_f)$ is the point such that $V(\mathbf{x}_{TS}) - \nu = 0$.
3. The integral $J = \int_0^{t_f} dt = t_f$ is minimized.

The variational Hamiltonian is, $2H(\mathbf{x},\mathbf{y},\mathbf{w}) = f^2\mathbf{y}^T\mathbf{y} - (1+\mathbf{y}^T\mathbf{g}(\mathbf{x}))^2 = f^2\mathbf{y}^T\mathbf{y} - \omega^2 = 0$, where $\mathbf{y}(t)$ is a variable differentiable vector function of t referred as a *conjugate vector* to the position vector $\mathbf{x}(t)$. We drop the dependence of f. For fixed values of $\mathbf{x}$ and $\mathbf{y}$, the continuous function H becomes a function of the control vector $\mathbf{w}$. We implicitly assumes that the maximum of H with respect to $\mathbf{w}$ is attained.

Along the optimal path the conjugate vector $\mathbf{y}$ satisfy the differential equation,

$$d\mathbf{y}/dt = -\nabla_{\mathbf{x}}H\big|_{\mathbf{x}^*,\mathbf{w}^*} = -\left(\mathbf{y}^T\mathbf{y}f\nabla_{\mathbf{x}}f - \omega\mathbf{H}(\mathbf{x})\mathbf{y}\right)$$

where $\mathbf{H}(\mathbf{x})$ is the Hessian matrix of the PES. Through the transversality condition we can transform the $d\mathbf{y}\,/\,dt$ equation by one that only involves the control vector, $\mathbf{w}$. The resulting equation is

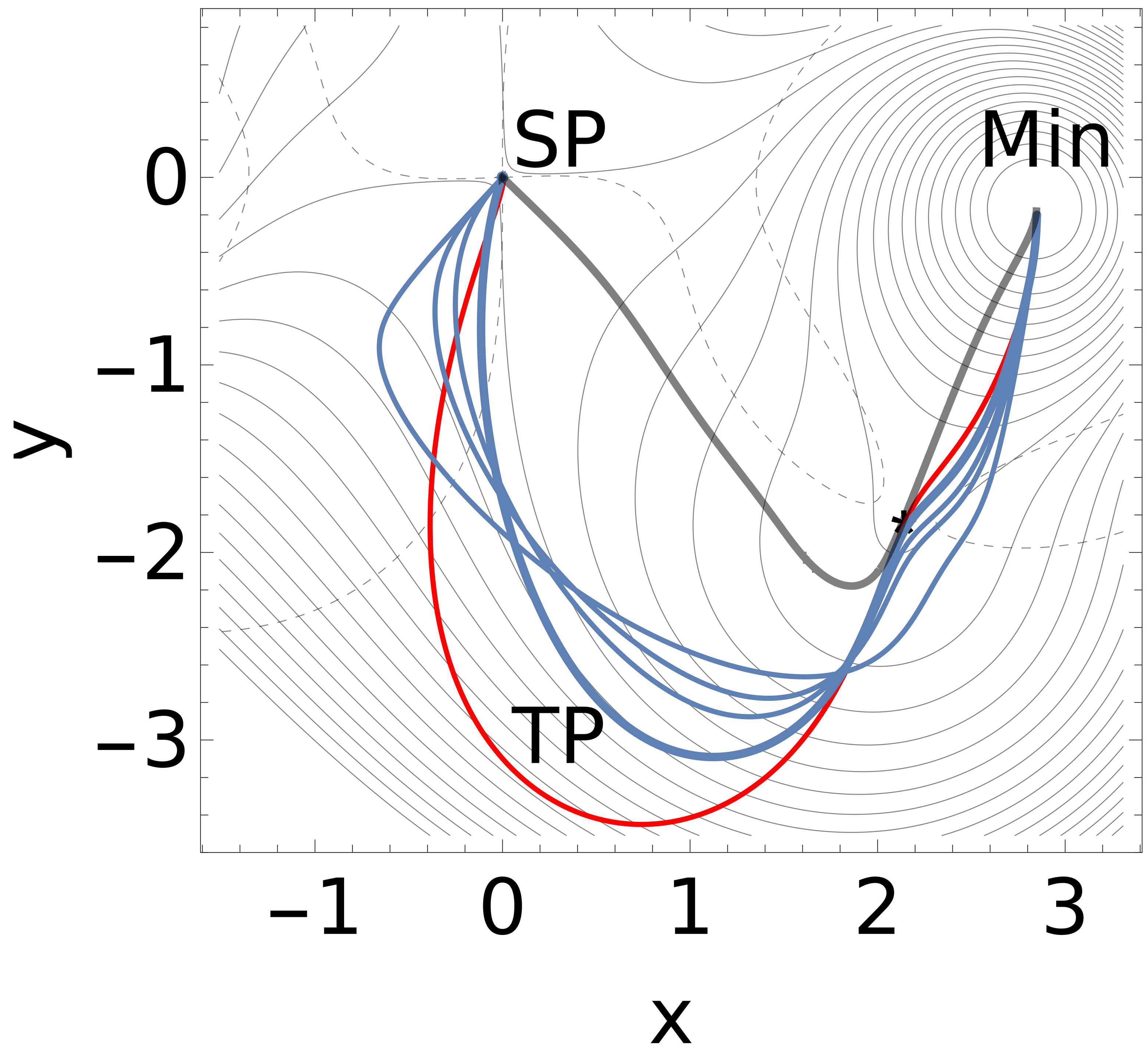
$$d\mathbf{w}/dt = -\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\left(\nabla_{\mathbf{x}}f - \mathbf{H}\mathbf{w}\right)$$

<u>This equation forms with the equation for $d\mathbf{x}/dt$ a system of coupled first order ordinary differential equations which permits all the extremals to be found if the initial values are given,</u> $(\mathbf{x}(0), \mathbf{w}(0))$.

By comparing integrals, J and J^*, using the Weierstrass error function, the pair solution $(\mathbf{x}^*(t), \mathbf{w}^*(t))$ that satisfies the system of differential equations, $d\mathbf{x}/dt$, makes $J > J^*$ for any other pair [4].

3. Example.

In this Figure, the curves (blue with $\phi \geq 2$, red with $\phi = (2)^{1/2}$) to the above Equation $d\mathbf{x}/dt$ for with $f(\phi,\mathbf{x},\mathbf{w}) = \mathbf{g}(\mathbf{x})^T\mathbf{w}(t)$. Start is at minimum. The bold curve is the Gentlest Ascent Dynamics curve with $\phi = 2$, the other blue curves are to $\phi = 3$, 4, and 10. The control vector is calculated by Equation for $d\mathbf{w}/dt$. The surface is a modified NFK case [5,6]. The * marks a quasi-shoulder, and the thin dashes mark the borderline between valleys and ridges. For comparison the Gradient Extremal is given (thick black curve) which is here the valley floor pathway between SP and Min.



4. Conclusion.

An <u>*optimal navigation*</u> method is proposed to explore Potential Energy Surfaces, $V(\mathbf{x})$ (PES), of fixed gradient-field, to locate TS and Reaction Paths from a Minimum point of the PES. This method provides a robust and automatic algorithm to locate TS points using a minimum information on the PES, describing a curve that can be a Reaction Path.

<u>**References.**</u>

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