Profile Contour Plots: Alternative Projections of 3D Free Energy Surfaces

Kyle Wm. Hall* University of Calgary
Peter G. Kusalik† University of Calgary
Sheelagh Carpendale‡ University of Calgary

Abstract

We present profile contour plots as a technique for representing the 3D energy surfaces encountered in computational chemistry. Profile contour plots are alternative projections of 3D energy surfaces. We explain and illustrate the profile contour plot technique using the 3D free energy surface resulting from a simulation of two hydroxyl radicals in a solvent. Our chemistry collaborator now primarily uses a profile contour plot to discuss this free energy surface instead of other alternative representations.

Keywords: Free energy surfaces, projections, contour plots

1 Introduction

The visualization challenge that we address is how to represent the 3D free energy surface describing the interactions of two hydroxyl radicals in a solvent so as to facilitate comparisons between minima and paths on this surface. A hydroxyl radical is an oxygen atom bonded to a hydrogen atom, and can be indicated as OH*. The interactions between two OH*'s in a solvent are of interest to our collaborator. The contribution of this work is the introduction of profile contour plots, which solve the aforementioned visualization challenge when used in conjunction with traditional contour plots. We use the results of a metadynamics simulation of two OH*'s in a solvent to illustrate the profile contour plot technique.

2 Description of Challenge

When trying to understand chemical processes, free energy differences are of fundamental importance since they control both kinetics, e.g. rates of reactions, and thermodynamics, e.g. the stability of chemical species. A given chemical system moves along a multidimensional free energy surface that dictates which processes will occur. More specifically, it is the minima and saddle points on the surface that determine which chemical processes will occur.

In the case of two OH*'s in a solvent, our collaborator determined the free energy surface for their interactions using metadynamics. Metadynamics determines the free energy of a system as a function of collective variables, i.e. user-specified metrics that describe the processes taking place in the system. For the two HO*'s in a solvent, two collective variables were used to monitor their interactions yielding a 3D free energy surface. Consequently, our specific challenge was how to represent a 3D free energy surface to facilitate comparisons of minima and saddle points.

3 Related Work

Fig. 1 shows a 3D free energy surface represented in a style currently used in publications. The contour plot attempts to indicate the variation in the free energy with respect to the collective variables, angle and distance. However, the ambiguous color scheme of the contours makes it difficult to understand the order of the minima and the shape of the surface. The overlaid surface attempts to ameliorate this, but the overlaid surface is also problematic. In Fig. 1, the right most minimum appears to be the global minimum when in fact the central minimum is the global minimum.

Given these difficulties, chemists have attempted to improve figures like Fig. 1 in one of two ways. First, chemists will attempt to improve the contour plot of the free energy surface by using color ramps in conjunction with contour lines to indicate free energies, and omit the 3D surface entirely, e.g. as in [6]. Such contour plots do allow one to determine the locations of minima and saddle points in terms of collective variables, but the free energy values and thence order of minima can remain ambiguous. As a second alternative, chemists will split the contour plot and 3D surface into two separate figures, and then view the surface from an alternative angle while coloring the 3D surface according to free energies, e.g. as in [5]. The latter approach can remove some of the ambiguity with respect to the free energy values of the minima, but the viewer still has to deal with the challenges associated with 3D compared to 2D, e.g. information is retrieved significantly more slowly in 3D compared to 2D [2].

In the visualization community, graphs based on Morse complexes have also been used to represent energy minima and saddle-points on energy surfaces [1]. This approach does not visually represent differences in the free energies of the minima, so the global minimum is unclear unless one compares the labeled free energy values of every minima. In this approach, it is also unclear what relation the edges of the graph, i.e. the pathways connecting the free energy minima, have to the collective variables describing the system [1]. Consequently, while several different approaches have attempted to represent 3D energy surfaces, it still remains an open challenge to represent 3D free energy surfaces to facilitate comparisons of minima and saddle points in terms of free energies and collective variables.

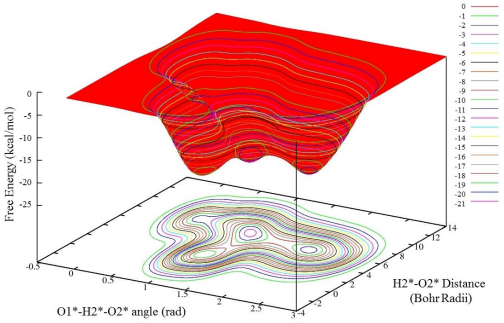

Figure 1: The 3D free energy surface for the interactions of two OH*'s in a solvent as calculated using the Vreco_CPMD program by Dr. N. Nair, which is provided by CPMD [3].

4 The Solution: Profile Contour Plots

Using contour plots is a well-established means of considering 3D surfaces. In cartographic examples, one is looking down on a landscape from an aerial view and the contours indicate elevation. More generally, let us define an aerial contour plot to be the plot resulting from creating contours with respect to z-values for a function

*e-mail: hallkw@ucalgary.ca
†e-mail: pkusalik@ucalgary.ca
‡e-mail: sheelagh@ucalgary.ca

z=f(x,y) and viewing the resulting contours parallel to the z-axis. The contour plots used to represent energy surfaces in chemistry, e.g. [5, 6], correspond to aerial contour plots. Such contour plots enable one to locate minima and saddle points in terms of collective variables, but not necessarily free energies. Therefore, we chose to retain an altered form of aerial contour plots as shown in Fig. 2, and to create a supplementary view of the surface that would graphically reveal free energy values more explicitly. In particular, our goal was to provide a 2D supplementary view that would leverage the chemistry community's familiarity with contour plots in the context of free energy surfaces.

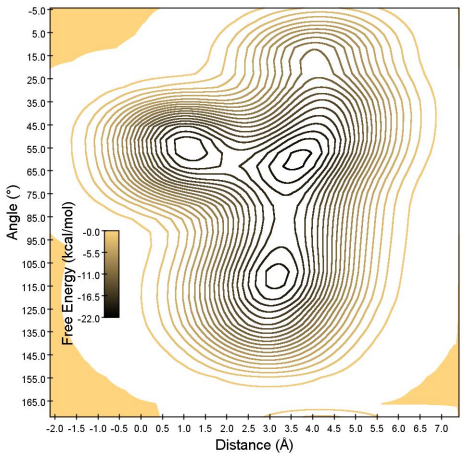

Figure 2: An aerial contour plot of the free energy surface represented in Fig. 1 describing the interactions of two OH*'s in a solvent. The regions that correspond uniformly to the value of a contour are filled to accentuate that the free energy surface is flat in these areas.

In engineering, an alternative formulation of contour plots has been widely used where contours are drawn with respect to independent variables while the dependent variable is indicated using an axis. Psychrometric charts are an example of this where the relationships between six variables are plotted using a single 2D plot such that numerical readings of all six variables are possible. Psychrometric charts have been used for over a hundred years by the engineering community [4]. Using psychrometric charts as inspiration, one can create a contour plot for the function z=f(x,y) such that contours are drawn with respect to one independent variable, i.e. x or y, and then viewed parallel to the axis of that variable. This allows the dependent variable to be indicated using an axis. Let us refer to this alternative type of contour plot as a profile contour plot.

In this spirit, we created a free energy surface profile contour plot as shown in Fig. 3 for the free energy surface of two OH*'s interacting in a solvent. This view shows the topography of the free energy surface spatially in terms of free energy values and one independent variable. The other independent variable is encoded using contours in conjunction with a linear hue ramp at constant saturation and value. This view helps to reveal certain features that are obscured in the corresponding aerial contour plot in Fig. 2, e.g. the free energy difference between the two blue minima is $\sim$1.5 kcal/mol. Unlike traditional aerial contour plots like Fig. 2, Fig. 3 spatially represents free energy while still providing information about both independent variables, angle and distance. In terms of free energies, the readability of Fig. 3 for our collaborator is significantly greater than that of corresponding aerial contour plots. In fact, our collaborator now primarily uses a profile contour plot like Fig. 3 to analyze and discuss the two OH*'s free energy surface with colleagues, and alternative representations rarely appear.

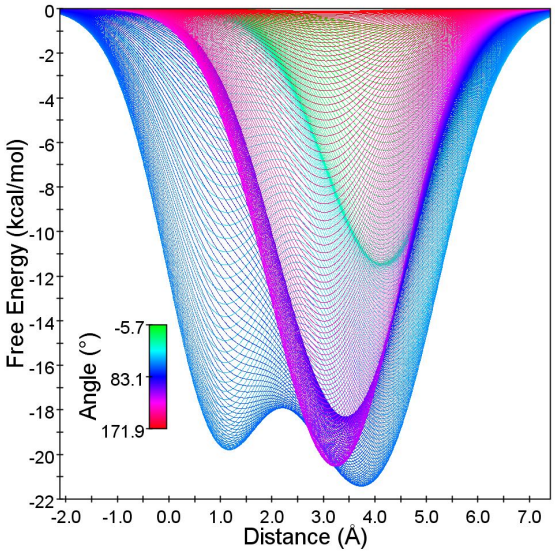

Figure 3: A profile contour plot for the free energy surface describing the interactions of two OH*'s in a solvent. This is the same free energy surface as is shown in Fig. 1 and 2.

5 Conclusion

We have presented profile contour plots as alternative projections of 3D free energy surfaces that explicitly represent free energies spatially. For our collaborator, profile contour plots provide a greater graphical description of free energies than traditional aerial contour plots. Given that our collaborator has fully adopted and now primarily uses profile contour plots, profile contour plots may be useful to other fields attempting to represent multidimensional surfaces statically, and warrant further investigation.

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