Potential Energy Surfaces for Quantum Dynamics

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When solving the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\sum_{i=1}^{d}\frac{\hbar^2}{2m_i}\frac{\partial^2\Psi}{\partial x_i^2} + V\Psi \tag{1}$$

for the nuclei of a molecule under the Born-Oppenheimer approximation, the interaction with the electrons is described by a potential energy surface (PES) V.

To calculate just one point on the potential energy surface using ab initio quantum chemistry calculations is time consuming, and the fewer points that need to be calculated the better. That is, many methods have been developed to interpolate this surface to high enough accuracy while using a minimal number of points. One example is the adaptive radial basis function (RBF) method developed and implemented in [1]. An example of cross sections of a three-dimensional potential interpolated using our method is shown in Figure **??**.

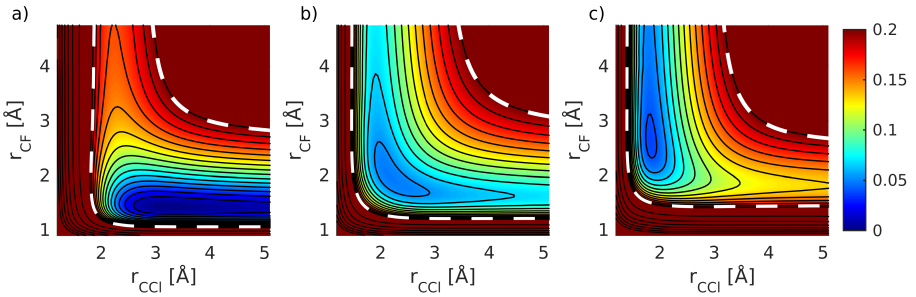

Figure 1: 2D slices through the interpolated PES of the nucleophilic substitution reaction $Cl^- + CH_3F \rightarrow ClCH_3 + F^-$ for different values of θ: (a) 71.5°, (b) 95°, and (c) 108°. The color scale is truncated above 0.2 Hartree (5.44 eV) (indicated by the white dashed line). The spacing between the black, solid contour lines is 0.11 Hartree for energie values > 0.2 and 0.013 Hartree for energie values < 0.2 Hartree.

In this work, we did not use any particular information about the shape of the surface. However, at a recent Quantum Dynamics, we were asked if we can

improve the cost to accuracy ratio of the method if we know where the extreme points of the surface are located and we use not only the function value, but also the gradient and Hessian of the potential at these points. In [2], knowledge of the optima is used to select method parameters.

In this project, your task would be to investigate if there are advantages with knowing the locations of the optima, and the derivatives at these points compared with not having any information available. For simplicity it would be good to start with a one-dimensional potential to investigate cost versus accuracy with different amounts of knowledge. Then it would be interesting to test if the results carry over to the two-dimensional case. Some of the practical tasks would include to

- Modify an existing MATLAB code for the one-dimensional model problem to include information about optima and derivatives.
- Perform numerical experiments to evaluate the accuracy and cost when using different amounts of information.
- Formulate a hypothesis for which is the most efficient approach.
- Test this hypothesis for the two-dimensional problem. For this part, there can be different levels of how many aspects are included in the implementation. As it can become quite technical.

References

[1] M. Kowalewski, E. Larsson, and A. Heryudono, *An adaptive interpolation scheme for molecular potential energy surfaces*, J. Chem. Phys., 145, 084104 (2016), 10 pp.

[2] Z. Majdisova, V. Skala, and M. Smolik, *Near optimal placement of reference points and choice of an appropriate variable shape parameter for RBF approximation*, Integrated Computer-Aided Engineering, to appear. `http://afrodita.zcu.cz/~skala/publications.htm`