Automatic potential energy surface sampling based on Voronoi Tessellations

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Introduction

The concept of potential energy surface (PES) is central in Chemistry as PESs are effective potential functions for molecular motion governing molecular structure and dynamics.[1] In order to build an adequate representation of the PES, one has to: 1) sample a large number of configurations, typically of the order of 10^{3N-6} for a system with N atoms (N>2); 2) calculate the electronic energy at each configuration; 3) fit the results to a suitable analytical form. The unfavorable scaling of this problem with respect to the number of atoms requires the development of novel schemes that can make this first principles approach to PESs manageable for large polyatomic systems.

Results and Discussion

In this study, an algorithm to generate an optimal set of configurations to be used to fit *ab initio* PESs is proposed. The central idea is to partition the configuration space using centroidal Voronoi tessellations. In computational geometry, the determination of a Voronoi tessellation consists in, given a set of points, finding the regions of space that are closer to a specific point than to any other point in the set. This technique is a very popular method in the scientific computing community to generate quality meshes to solve complex numerical problems.[2,3]

The sampling approach was used to generate grids of ten points that were then used to calculated the spectroscopic constants of the ground state of HCl. The grids were generated using an uniform and a triangular random distribution of internuclear distances in the range [0.786,2.620] Å. A comparison between the random distributions and the converged distributions resulting from the proposed algorithm is displayed in Figure 1. The calculated harmonic vibrational constants using the converged grids are 3037.45 and 3031.72 cm^{-1} for the uniform and triangular distributions, respectively. These results should be compared to the value of 3105.98 cm^{-1}, obtained using an equally spaced grid in the same range. The experimental value is 2990.95 cm^{-1}.

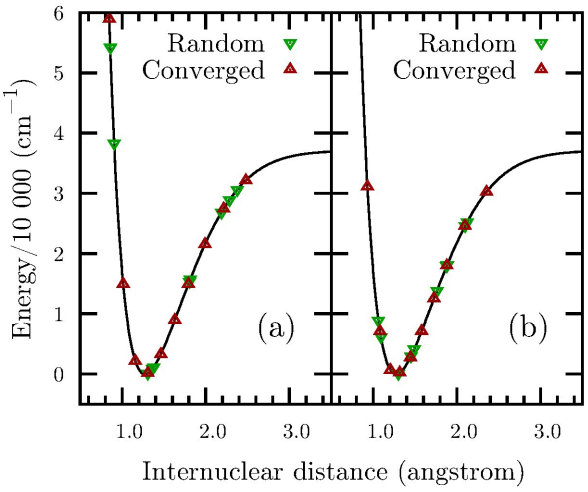

Figure 1. Random and converged samplings of ten distances for HCl using uniform (a) and triangular (b) random distributions.

Conclusion

The use of a triangular distribution for internuclear distances yields slightly better spectroscopic constants than an uniform distribution. Both random distributions perform much better than an equally spaced grid. The preliminary results show that the automated sampling based on Voronoi tessellations is a viable approach to improve the quality of fitted PESs.

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