Small Assignment 10/7 - Code Validation

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Abstract

We[1] give an overview of the Diffusion Monte Carlo (DMC) algorithm and its applications into finding solutions to the Schrodinger Equation when no analytical solution is available. An implementation of the DMC algorithm is presented with a specific focus on understanding the behaviour of Clathrate Hydrates, a complex, multi-atomic structure often made up of water molecules and a greenhouse gas. Given the many ways of representing such a system, we present conditions for which different representations produce the computationally efficient results. We show how Importance Sampling can be used to reduce some of the computational inefficiency that abounds when working in high dimensional data sets with results that mirror those of a straightforward DMC implementation. Finally, we provide an analysis of the above algorithm when implemented in a Object Oriented versus script-based format to conclude that script-based programming is more computationally efficient in this scope.

Related Work

This semester, we code a python based implementation of the Diffusion Monte Carlo algorithm originally presented in Anderson 1975. Our implementation of the DMC algorithm

can be directly attributed to Anderson's work, as he was one of the first to propose such a method. At the time, other methods were seen as more computationally efficient for a given level of accuracy. We take Anderson's algorithm and refine it in the scope of being efficient for computing the ground level energy and bond strength of Clathrate Hydrates. While Anderson was initially only concerned with the calculation of the ground energy of H3, his simplifying approach to the 1D and 6D systems greatly influenced our approach in initial versions of our implementation. We improve on his work by designing a more efficient, vector-based implementation using the numpy library provided by python. We hope to extend this approach to the task of modelling more complicated Clathrate Hydrates which require an increased computational load. As Anderson points out, the Schrodinger Equation is only analytically solvable for certain, small systems. His DMC algorithm provides such a way to approximate solutions to complex systems. The best solution to modelling Clathrate Hydrates, given the lack of an analytical solution, is an open question. We hope to build off of Anderson's work to provide a computationally efficient method for the solution of this problem.

Discussion

Code Validation

In any implementation of an algorithm, rigorous testing is required to ensure that the code is producing accurate results. Ideally, data generated from a simulation would be corroborated with data collected experimentally. However, due to the nature of the study of particles, outside of the simplest systems, it is difficult to accurately calculate the ground state energy. As such, results generated from the DMC algorithm cannot be verified against real world data.

Instead, we turn to manual validation of the code. An outline of the process is as follows: a set of walkers is generated. The validator calculates the potential energy and the

reference energy. Using a randomly generated set of thresholds, the validator determines which walkers should be deleted and replicated, and then compares the final array to the final array produced by the algorithm. To be sure of correctness, this process was repeated multiple times with sets of ten walkers over five time steps. These groups of calculations should be comprehensive enough to validate the correctness of the algorithm due to the stochastic nature of the simulation, and generalize well to larger groups of walkers.

As a final measure, the implementaion of the DMC algorithm was tested to model the carbon monoxide bond, given that the Zero-Point energy of the CO bond is well known. When tested over multiple simulations, the 1,000 step rolling average varied on the order of $1 \cdot 10^{-4}$, with a variance on the order of $1 \cdot 10^{-3}$. Based on prior DMC implementations, this amount of inaccuracy is normal.

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References

(1) Anderson, J. B. A random-walk simulation of the Schrödinger equation: H+3. *The Journal of Chemical Physics* **1975**, *63*, 1499–1503.