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.

Introduction

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.

Modeling

The Model

The DMC model is not novel. It[1] was first introduced over 40 years ago and has been refined since. At a high level, the model takes an array of walkers, each representing a possible state

of the system, and propagates the atoms in each walker. After propagation, the potential energy of each system is calculated. Systems with potential energy that is too high are deleted, while systems with reasonable potential energy are replicated. Given the pseudo-randomness leveraged in code-based implementations of the DMC algorithm, this serves to approximate every possible configuration of the system, within the bounds that it would normally exist in nature.

Over time, the rolling average the potential energy of all systems that are valid converge to the zero point energy, or the ground state energy of the system. This produces an approximate solution of the Schrodinger equation, which is what the DMC algorithm is modelling.

Implementation

In our implementation of DMC, we write a script-based implementation in Python, relying heavily on the NumPy library, which provides vectorization for fast operations on large matrices. The most important variable in the code is a 4D array which stores the positions of each atom in each molecule in each walker. As we move through the simulation loop of the algorithm, we operate on the walker array to delete and replicate walkers as required by the algorithm.

Notably, the function that calculates potential energy is drastically different from molecular system to molecular system, so the main simulation loop uses calls to the potential energy fucntion for the purpose of extendability. From system to system, the only other varying part of our code is how we propagate each walker. This could potentially change with each system, although we hope to find a data structure that allows our code to remain effiicient without needing to change how the walkers are propagated at each step. Otherwise, the entire model is controlled by the initial variables of the simulation.

Through the simulation loop, rely heavily on the broadcasting features of NumPy to different array dimensions to figure out which walkers are to be deleted or replicated. We

like to think that this is done quite cleanly, and do it in a mere 11 lines of code after the walkers are propagated. This efficiency is appealing and has been why we are hesitant to walkk away from the 4D array based implementation that we provide.

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.

Simulations

Discussion

When creating a piece of code in the field of Computational Science, its worth is often based on how extendable it is to other projects of interest. In the case of our work, we provide a fast, script based implementation of the DMC algorithm by leveraging the vectorization provided in the NumPy library. Currently, our work relies on the assumption that the molecules in the modeled system are homogeneous. Clearly, this is not a particularly extendable piece of code, as there are many other interesting systems made up of hetereogeneous molecules.

This begs us to consider how to create generalizable code that can be used in a variety of circumstances without sacrificing efficiency. Observe that NumPy works well when dealing with arrays of many dimensions. As soon as we change the sizes of the molecules in a walker, the dimensions of our array are no longer even, and so NumPy cannot cleanly vectorize the solution in the 4D data structure that we have presented up to this point. From a programming point of view, it would not be particularly difficult to represent each walker on a singular array dimesion. However, this also reduces the extendablility of our code as it makes the potential energy function extraordinarily difficult to calculate, given that each molecule and atom corresponds to a particular index on the same array dimesion.

We hope that the users of our code are domain experts, and want to create a scientific instrument that is easy and intuitive for them to use. As such, we continue to try and refine our ideas to create an implementation of DMC that balances both efficiency and ease of use.

Conclusion

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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.