Quantum Monte Carlo

QMC-project

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1 Abstract

This report is submitted as part of the coursework for the Winter School on Lessons & Tutorials in Theoretical Chemistry held in Aspet, France, from January 15_{th} to 26_{th}, 2024. As a second year Master's student in Theoretical Chemistry and Computational Modeling at the University of Perugia, I engaged in this task under the supervision of Professor Anthony Scemama. The assignment required the development of a Quantum Monte Carlo algorithm with the implementation of both variational and pure diffusion methods to compute the energies of polyelectronic systems containing hydrogen and helium atoms (e.g. H, H_2^+, H_2, He, H_3^+).

The document discusses the foundational principles of the Monte Carlo method, providing an in-depth analysis of the variational and pure diffusion techniques. It further explores the theoretical framework supporting the algorithm, including wave function description, and potential and kinetic energy calculations. Finally, the results of these simulations are analyzed and discussed, highlighting the effectiveness and insights provided by the Quantum Monte Carlo approach in theoretical chemistry.

2 Introduction to Quantum Monte Carlo Methods

Quantum Monte Carlo (QMC) represents a class of computational techniques used to study quantum systems, particularly focusing on the calculation of electronic structures and inter-particle interactions within a quantum framework. The method is distinguished by its use of stochastic processes to solve quantum mechanical problems that are otherwise intractable with traditional deterministic methods [1].

Indeed, QMC tackles the many-body problem through statistical sampling, estimating the properties of quantum systems more effectively as the number of samples increases.

The primary goal of the QMC method is to solve the Schrödinger equation, which is the fundamental formula for describing the behavior of quantum systems [2]. The time-independent form of the Schrödinger equation is expressed as:

$$\hat{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}) \tag{1}$$

where $\hat{H}$ is the Hamiltonian operator of the system; $\psi_n(\mathbf{r})$ is the wave function describing the n_{th} quantum state and E_n is the corresponding energy; $\mathbf{r}$ is the vector representing the 3N coordinates of N particles (electrons and nuclei).

In the absence of electric or magnetic fields, the Hamiltonian simplifies to the form:

$$\hat{H} = \hat{T} + \hat{V} \tag{2}$$

where $\hat{T}$ is the kinetic energy operator, and $\hat{V}$ is the potential energy operator, often described as the Coulomb potential between charged particles:

$$\hat{T} = -\frac{1}{2}\nabla_{\mathbf{r}}^2 \tag{3}$$

$$\hat{V} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} \tag{4}$$

The first proposal for a Monte Carlo solution to the Schrödinger equation dates back to Enrico Fermi, who indicated that a solution to the stationary equation

$$-\frac{1}{2}\nabla_{\mathbf{r}}^2\psi(\mathbf{r}) = E\psi(\mathbf{r}) - V(\mathbf{r})\psi(\mathbf{r}) \tag{5}$$

could be obtained by introducing a wave function in the form: $\psi(\mathbf{r},\tau) = \psi(\mathbf{r})e^{-E\tau}$. This yields the equation:

$$\frac{\partial \psi(\mathbf{r},\tau)}{\partial \tau} = \frac{1}{2}\nabla_{\mathbf{r}}^2\psi(\mathbf{r},\tau) - V(\mathbf{r})\psi(\mathbf{r},\tau) \tag{6}$$

where τ is the imaginary time.

Analyzing equation 6 and taking τ to the limit as it approaches infinity ($\tau \to \infty$), we retrieve the form of equation 5. If we ignore the second term on the right side of equation 6, it transforms into a diffusion equation that can be simulated through a random walk, a method that models the stochastic movement of particles.

Alternatively, ignoring the first term reduces the equation to a first-order kinetic equation, where a position-dependent velocity constant, described by $V(\mathbf{r})$, modulates the survival rate of particles. This behavior can be interpreted as a stochastic survival probability, where random walkers move through space, proliferating in areas of low potential and vanishing in regions of high potential. This process leads to a stationary distribution that is proportional to the wave function $\psi(\mathbf{r})$, thus facilitating the calculation of expectation values.

From the late 1940s to the early 1960s, Monte Carlo methods and related techniques gained considerable interest. QMC methods are especially advantageous due to their ability to scale effectively with system size, the simplicity of the algorithms employed, and the versatility of trial wave functions, which are crucial for importance sampling.

2.1 Variational Quantum Monte Carlo

Variational Monte Carlo (VMC) is a quantum Monte Carlo method that utilizes a variational approach to approximate the ground state of a system. The expectation value can be expressed in terms of a representative formula in the toal space as follows:

$$\frac{\langle\psi(\mathbf{r},a)|\hat{H}|\psi(\mathbf{r},a)\rangle}{\langle\psi(\mathbf{r},a)|\psi(\mathbf{r},a)\rangle} = \frac{\int |\psi(\mathbf{r},a)|^2 \frac{\hat{H}\psi(\mathbf{r},a)}{\psi(\mathbf{r},a)}\,d\mathbf{r}}{\int |\psi(\mathbf{r},a)|^2\,d\mathbf{r}} \tag{7}$$

Following the application of the Monte Carlo method for the evaluation of integrals, the ratio

$$\frac{|\psi(\mathbf{r},a)|^2}{\int \psi(\mathbf{r},a)\,d\mathbf{r}} \tag{8}$$

can be assumed as a probability distribution function, where the expectation value of the energy $E(a)$ is evaluated as the average from the local function $\frac{\hat{H}\psi(\mathbf{r},a)}{\psi(\mathbf{r},a)}$, and the system proceeds to minimize $E(a)$.

VMC is fundamentally similar to any classic variational method, with the exception that while multidimensional integrals are numerically evaluated in VMC, only the wave function value needs to be calculated. This confers great flexibility to the method.

2.2 Pure Diffusion Quantum Monte Carlo

The Pure Diffusion Monte Carlo (PDMC) method is an advanced computational technique used to simulate quantum systems more accurately by approximating their ground state energy. PDMC builds on the principles of Diffusion Monte Carlo (DMC) but introduces a unique approach by treating the potential energy as a cumulative product of weights, allowing for continuous adjustment based on the energy landscape of the system.

The method operates by simulating the quantum system over an imaginary time τ, using a series of systematic steps to evolve the system's wave function towards its ground state. The fundamental equation governing this process is the time-dependent Schrödinger equation:

$$i\frac{\partial \psi(\mathbf{r},t)}{\partial t} = (\hat{H} - E_{ref})\psi(\mathbf{r},t) \tag{9}$$

where $\psi(\mathbf{r},t)$ is the wave function of the system at position $\mathbf{r}$ and time t; $\hat{H}$ is the Hamiltonian operator that includes kinetic and potential energy terms and E_{ref} is a reference energy used to stabilize the simulation.

The evolution of the system is tracked by calculating weights that reflect the potential energy differences from E_{ref}. These weights are defined as:

$$W(\mathbf{r}_n,\tau) = \prod_{i=1}^{n} \exp\left(-\delta\tau(E_L(\mathbf{r}_i) - E_{ref})\right) \tag{10}$$

The weights $W(\mathbf{r}_n,\tau)$ help in modulating the wave function's probability density, focusing it more on regions with lower potential energy, consistent with the ground state.

This method allows for a detailed exploration of the system's energy landscape by tracking how modifications in the potential energy influence the statistical weights of particle configurations over imaginary time. This approach helps in refining the accuracy of ground state energy calculations.

3 Implementation of the QMC algorithm

In the preceding chapter, we delved into the theoretical underpinnings of Quantum Monte Carlo (QMC) methods, focusing particularly on the Variational Monte Carlo (VMC) and Pure Diffusion Monte Carlo (PDMC) approaches. Building on that foundation, this chapter aims to elucidate the practical implementation of these methods in calculating the total energy of simple atomic systems, containing hydrogen and helium, using a Fortran90 computational framework.

The architecture of the QMC methods develops across three Fortran90 files: `QMC_main.F90`, `QMC_energy.F90` and `QMC_utilities.F90`.

In `QMC_main.F90`, the simulation parameters and the system under study are specified by the user through an input file. This module coordinates the execution of the VMC and PDMC algorithms, leveraging routines and functions defined across the suite to compute local energies and manage electron positions within the system's probabilistic landscape.

The `QMC_energy.F90` file is focused on calculating local energy, encompassing both kinetic and potential components. Moreover, it implements the calculation of the drift vector and defines the trial wave function that guides the stochastic trajectories of the electrons.

Lastly, `QMC_utilities.F90` contains utility subroutines that significantly aid in initializing the electrons' positions randomly within a Gaussian distribution, calculating mean values and error margins (particularly for the mean energy and acceptance rates), and writing the results to the screen and to output files.

3.1 Trial Wave Function

In the development of Quantum Monte Carlo simulations, a critical component is the choice of the trial wave function. For systems comprising N nuclei and n_{el} electrons, a wave function characterized by the following form has been adopted:

$$\psi(\mathbf{r}) = \prod_{i=1}^{n_{el}} \sum_{j=1}^{N} e^{-ar_{ij}} \tag{11}$$

where r_{ij} is the Euclidean distance between the i_{th} electron and the j_{th} nucleus, and a is a parameter that must be optimized. This parameter is crucial in shaping the wave function to accurately reflect the physical characteristics of the system being studied.

3.2 Drift Vector

In Quantum Monte Carlo simulations, the drift vector is a critical component designed to enhance the efficiency and accuracy of the particle sampling process. For each electron in the system, the drift vector is a three-dimensional array, corresponding to the spatial coordinates x, y and z. This renders the drift vector as a matrix of dimensions $n_{el} \times 3$, where n_{el} represents the number of electrons. The computation of the drift vector is carried out by taking the first derivative of the wave function with respect to each spatial coordinate. This derivative is then divided by the total wave function:

$$b = \frac{\nabla \psi(\mathbf{r})}{\psi(\mathbf{r})} \tag{12}$$

thus forming a vector field that points in the direction of increasing probability density.

In our specific case, given the wave function defined in equation 11, the first derivative of the wave function with respect to the x coordinate for the k_{th} electron is expressed as follows:

$$\frac{\partial \psi_k(\mathbf{r})}{\partial x} = \left(\prod_{\substack{i=1 \\ i \neq k}}^{n_{el}} \sum_{j=1}^{N} e^{-ar_{ij}} \right) \times \left(\sum_{j=1}^{N} -ae^{-ar_{kj}} \left(\frac{x_k - x_j}{r_{kj}} \right) \right) \tag{13}$$

This formulation must also be applied to the y and z coordinates, and the calculation should be performed for each electron. Moreover, each derivative must be divided by the total wave function to determine the components of the total drift vector matrix. This vectors effectively guides each electron through the configuration space, steering them toward regions of lower energy and higher probability density, which are critical for the accurate representation of the quantum system.

3.3 Energy

For a given system with Hamiltonian $\hat{H}$ and wave function ψ, we define the local energy as

$$E_L(\mathbf{r}) = \frac{\hat{H}\psi(\mathbf{r})}{\psi(\mathbf{r})} \tag{14}$$

where $\mathbf{r}$ denotes the 3N-dimensional electronic coordinates.

We can compute the electronic energy of a system, E, as the expected value of the local energy with respect to a probability density $P(\mathbf{r})$ defined in 3N dimensions:

$$E = \int_{-\infty}^{+\infty} E_L(\mathbf{r})P(\mathbf{r})d\mathbf{r} \equiv \langle E_L \rangle_P \tag{15}$$

where the probability density is given by the square of the wave function:

$$P(\mathbf{r}) = \frac{|\psi(\mathbf{r})|^2}{\int |\psi(\mathbf{r})|^2 \, d\mathbf{r}} \tag{16}$$

If we can sample N_{MC} configurations $\{\mathbf{r}\}$ distributed as P, we can estimate E as the average of the local energy computed over these configurations:

$$E \approx \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} E_L(\mathbf{r_i}) \tag{17}$$

The local energy for the generic configuration $\mathbf{r_i}$ is computed by summing both kinetic (T) and potential (V) energy contributions:

$$E_L(\mathbf{r_i}) = T(\mathbf{r_i}) + V(\mathbf{r_i}) \tag{18}$$

Kinetic Energy

The local kinetic energy is defined as

$$T(\mathbf{r}) = -\frac{1}{2}\frac{\Delta\psi(\mathbf{r})}{\psi(\mathbf{r})} \tag{19}$$

where $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator, which acts on the wave function ψ defined in equation 11.

After completing all the mathematical calculations and summing the second partial derivatives of the wave function with respect to x, y and z, for the k_{th} electron, the following expression is obtained:

$$\Delta\psi_k(\mathbf{r}) = \left(\prod_{\substack{i=1 \\ i \neq k}}^{n_{el}} \sum_{j=1}^{N} e^{-ar_{ij}} \right) \times \left(\sum_{j=1}^{N} e^{-ar_{kj}} \left(a^2 - \frac{2a}{r_{kj}} \right) \right) \tag{20}$$

To compute the local kinetic energy, it is necessary to sum the contributions from each electron and substitute the value of $\Delta\psi$ into expression 19.

Potential Energy

The local potential energy was calculated by considering the contributions from nucleus-nucleus, electron-electron, and electron-nucleus interactions

$$V(\mathbf{r}) = V_{NN} + V_{eN} + V_{ee} \tag{21}$$

where the potential for a generic pair of particles i and j is given by:

$$V_{ij} = \frac{q_i q_j}{r_{ij}} \tag{22}$$

4   Results and Conclusions

Quantum Monte Carlo simulations were conducted on simple systems comprising hydrogen and helium. Both Variational and Pure Diffusion Monte Carlo methods were implemented for each system. Table 1 displays the calculated energy values, the reference energy of the system, and the simulation parameters.

System	N_{MC}	N_{step}	dt	a	τ	E_{VMC}	E_{PDMC}	E_{REF}
H	50	100000	0.05	1.2	100	-0.480	-0.500	-0.500
H_2^+	50	100000	0.10	1.2	100	-0.518	-0.557	-0.557
H_2	50	100000	0.05	1.2	100	-1.128	-1.171	-1.171
H_3^+	50	100000	0.10	1.2	100	-1.230	-1.341	-1.342
He	50	100000	0.03	1.8	100	-2.835	-2.904	-2.903

Table 1: Quantum Monte Carlo simulation results. The table lists the simulation parameters: the number of independent samples (N_{MC}), indicating unique system states; iterations (N_{step}), showing how each state evolves; the time step (dt), which controls temporal precision; wave function coefficient (a), tailoring the model to the system; projection time (tau), for long-term behavior analysis; and reference energy (E_{REF}), used for benchmarking each studied system.

As demonstrated in the table, besides the coefficient a which varies depending on the system being studied, the only parameter that has been adjusted across different simulations is the time step dt. For each case, the ideal time step was meticulously determined to minimize the discrepancy between the energy calculated using the Pure Diffusion method and the reference energy.

The results indicate that the variational method overestimates the energy of the system. On the other hand, the Pure Diffusion Monte Carlo method demonstrates remarkable accuracy, with precision extending to the third decimal place.

Figure 1 illustrates the energy estimations across 50 configurations for each system, highlighting a slight overestimation using the variational approach. In contrast, Figure 2 reveals that the reference energy falls within the error bars derived from the pure diffusion Monte Carlo calculations. This comparison underscores the superior accuracy and precision of the Pure Diffusion method in energy estimation.
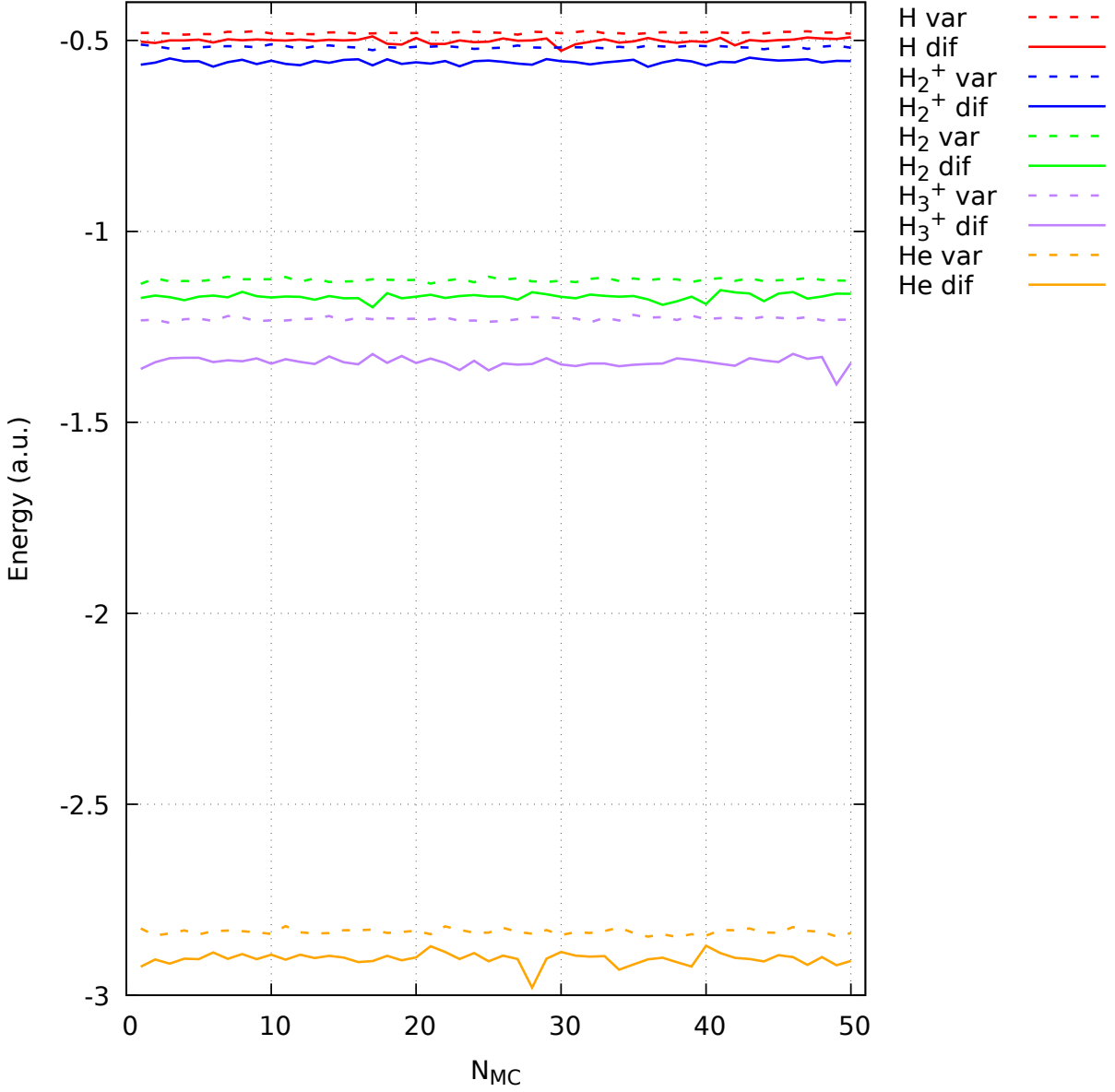
Figure 1: The graph presents the energy values for each system derived using the Quantum Monte Carlo approach, employing both Variational and Pure Diffusion methodologies. Energy calculations were performed across 50 distinct configurations for each system. Each system is represented by a unique color to facilitate differentiation. Dashed lines in the graph denote the energies computed using the Variational method, whereas solid lines represent those calculated via the Pure Diffusion approach. This visualization aids in comparing the performance and accuracy of the two methods across different systems
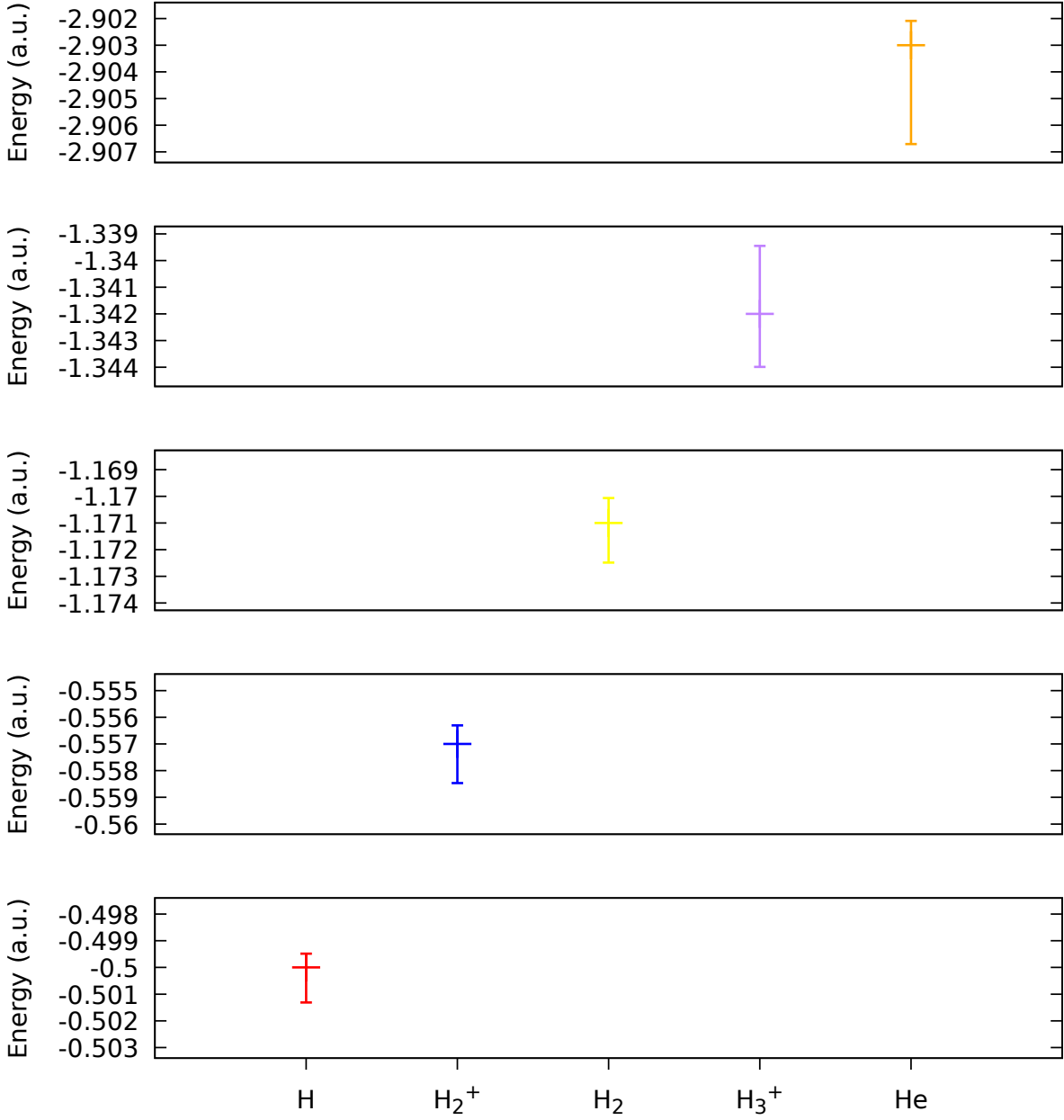
Figure 2: The graph provides a detailed comparison for each system studied, showcasing the reference energy values alongside the error bars obtained through the Pure Diffusion method of Quantum Monte Carlo simulations. This visualization emphasizes the precision and reliability of the Pure Diffusion method in estimating the energy states.

References

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