Simulation of the Hydrogen molecule ground state using Monte Carlo methods

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Abstract

This paper presents the simulation of the ground energy and wave function of a Hydrogen molecule by using two types of Monte Carlo methods: VMC and DMC. The simulations have been performed for varying internuclear distances for which the limits were compared to simulations of the ground states of a Hydrogen and Helium atom which were well in correspondence. For intermediate internuclear distance the ground state of the molecule was found including its vibrational spectrum which showed exceptionally good similarities with experimental values. Lastly, the molecular bonding energy of the formed σ bond was obtained which was close to the experimental value.

I. Introduction

As quantum mechanical systems increase in number of particles they rapidly become rather difficult or impossible to solve analytically. There exist numerous methods to obtain the (ground) state energy and wave functions of quantum mechanical systems, such as density functional theory (DFT) or Hartree-Fock (HF). Moreover, Monte Carlo methods provide another technique for solving systems with many coupled degrees of freedom. Because the exact Hamiltonian of many-body systems are in principle known, the Quantum Monte Carlo method allows a direct treatment of complex many-body effects encoded in the wave function. Previous research has already extensively researched small quantum mechanical systems using various Monte Carlo methods [1][2]. This paper discusses the results using both Variational and Diffusion Monte Carlo to obtain ground state properties of the Hydrogen and Helium atom and the Hydrogen Molecule.

It will therefore firstly discuss the different Monte Carlo methods that are used and give the description of the atoms and molecule that are studied in section II. Thereafter, in section III, the results of the simulations are discussed, for the atoms and for the Hydrogen Molecule in particular the potential landscape, its vibrational spectrum and the probability distribution of the electrons are considered. The closing section IV will give a conclusion and recommendations for improvement and future research.

II. Methods

The principle of using a Monte Carlo method is rather simple, the configurational space is sampled by random, so called, walkers which on average represent a physical quantity. The trick of implementing a usefull MC method is to place the walkers within the configurational space such that it is most representable of the sampled quantity. Here, two types of implementations are used, variational and diffusion MC.

Variational Monte Carlo (VMC) The variational method approximates the ground state energy of particles by using a trial wave function Ψ_T that is expected to be close to the real wave function. The walkers are moved in each step to a new position R' with a certain probability $(\Psi_T(R')/\Psi_T(R))^2$. After performing sufficient steps the average local energy of the ensemble of walkers represents an estimate for the energy of the system. The local energy of a walker is given by

$$E_L = \frac{H\Psi_T}{\Psi_T} \tag{1}$$

where H is the Hamiltonian of the system. Since the trial wave function is in principle dependent of a set of variational parameters $(c_1,...,c_N)$ the energy that is found is dependent of those parameters. To find the ground state energy, the parameters have to be varied in order to to find the minimum. For this a minimization algorithm is needed, for example a

simple steepest decent method:

$$c_{i,new} = c_{i,old} - \gamma \left(\frac{dE}{dc_i} \right)_{old} \qquad (2)$$

with $\frac{dE}{dc_i}$ the derivative sample over the ensemble of walkers:

$$\frac{dE}{dc_i} = 2 \left(\left\langle E_L \frac{d \ln \Psi_T}{dc_i} \right\rangle - E \left\langle \frac{d \ln \Psi_T}{dc_i} \right\rangle \right) \qquad (3)$$

Since the trial wave function in general only represents a fraction of the Hilbert space the variational Monte Carlo method will systematically overestimate the ground state energy.

Diffusion Monte Carlo (DMC) This restriction is resolved by using the DMC method in which the entire Hilbert space is in general sampled. The used DMC here is the special implementation of DMC guided by a function which resolves singularity problems.

The implementation consists of two steps within each iteration, the diffusion and branching steps. In the **diffusion** step the walkers are shifted by the force acting on them, given by

$$F = \frac{2\nabla_R \Psi_T(R)}{\Psi_T(R)} \qquad (4)$$

and thereafter diffused to a new position with probability

$$\min \left(1, \frac{T_{\Delta\tau}(R' \to R)\rho(R')}{T_{\Delta\tau}(R \to R')\rho(R)} \right) \qquad (5)$$

with

$$T_\tau(R_n \to R_{n+1}) = \frac{1}{\sqrt{2\pi\tau}} e^{-\frac{\left[R_{n+1} - R_n - \frac{1}{2}F(R_n)\tau\right]^2}{2\tau}} \qquad (6)$$

where τ is the imaginary time step and $\rho(R)$ simply Ψ_T^2. To enhance the probability of finding a walker at a representable location a **branching** step is introduced where $[s] + 1$ walkers are created at a position with probability $s - [s]$ or $[s]$ walkers with the complementary probability where s is given by

$$s = e^{-\tau \left[\frac{E_L(R) + E_L(R')}{2} - E_T \right]} + r \qquad (7)$$

with r begin a uniform random variable between 0 and 1 and E_T the estimate for the ground state energy. This estimate is updated after every imaginary time step by $E_T = E_0 + \alpha \ln \left(\frac{\tilde{M}}{M} \right)$ where E_0

is the initial estimate for the energy, $\tilde{M}$ the target number of walkers and M the actual number of walkers.

Since the walkers in DMC are forced to move to positions in configuration space that are representative for sampling the ground state energy, the ensemble of walker are a representation of the ground state wave function. Therefore, DMC can also be used to provide information about the wave function on top of the ground state energy.

To facilitate the rapid convergence of the DMC estimate to the ground state energy, the guide function and initial estimate for the energy should be close to those of the ground state. This can be accomplished by firstly performing VMC including optimization of the variational parameters and using these as input for DMC.

The Hamiltonian and trial wave function for a system are the only things that are needed for both described Monte Carlo methods, the other required quantities such as the local energy, equation 1, and force, equation 4, can be derived from these. The other quantities are completely independent of the system. Therefore, in the following paragraphs it suffices to define the systems only by their Hamiltonians and trial wave functions. This is done for the Hydrogen and Helium atom and the Hydrogen molecule. All derived quantities are included in Appendix A

To reduce the complexity of the Hamiltonians atomic units are introduced in which energy is given in Hartree ($\frac{(ke^2)^2}{a_0} = 27.2eV$) and distance in Bohr ($\frac{\hbar^2}{m_e ke^2} = 0.529A$).

Hydrogen Atom The Hamiltonian of the Hydrogen atom, a proton with one electron, is given by

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} \qquad (8)$$

and the trial wave function by

$$\Psi_T = e^{-\alpha r} \qquad (9)$$

Helium Atom The Helium atom consists of a nucleus with two protons with two electrons. The Hamiltonian of the electrons is

$$H = -\frac{1}{2}\left[\nabla_1^2 + \nabla_2^2\right] - \left[\frac{2}{r_1} + \frac{2}{r_1} - \frac{1}{r_{12}}\right] \qquad (10)$$

where the indices represent both electrons. The trial wave function is given by

$$\Psi_T = e^{-2r_1}e^{-2r_2}e^{\frac{r_{12}}{2(1+\alpha r_{12})}} \qquad (11)$$

The interacting part of the two electrons is modeled in this trial wave function by the so called Jastrow function.

Hydrogen Molecule A Hydrogen molecule is described by two protons, with a certain internuclear distance, with two electron. The Hamiltonian of Hydrogen molecule is approximated by the Born-Oppenheimer Hamiltonian which neglects the nuclear motion of the protons. The Hamiltonian for both electrons is

$$H = \sum_{n \in 1,2}\left[-\frac{1}{2}\nabla_n^2 - \frac{1}{r_{nL}} - \frac{1}{r_{nR}}\right] + \frac{1}{r_{12}} \qquad (12)$$

Where r_{nL}, r_{nR} are the relative distance between the left and right nuclei and the electron. The first part of the Hamiltonian is the non-interacting part consisting of the kinetic energy of the electrons and the attraction term between the electron and the nuclei and the last part is the interacting term. The trial wave function for the hydrogen molecule is given by

$$\Psi_T(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2) \qquad (13)$$

where

$$\phi(\vec{r}_n) = e^{-r_{nL}/a} + e^{-r_{nR}/a} = \phi_{nL} + \phi_{nR} \qquad (14)$$

$$\psi(\vec{r}_1, \vec{r}_2) = e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}} \qquad (15)$$

This trial wave function is in principle dependent on four parameters, the internuclear distance, a, α and β. However, removing singularities caused by coulomb interaction, the so called cusp conditions, reduce the number of free parameters to the internuclear distance and β. The cusp conditions are derived in appendix A.3.

III. Results

Hydrogen and Helium Atoms The energies of the ground states for the atoms are shown in table 1, the energy for the Hydrogen atom is very well in correspondence with the experimental value. For Helium the energy is -2.8779 ± 0.0003 and -2.8486 ± 0.0071 for VMC and DMC respectively compared to the experimental ionization value of -2.9034. The overestimation of the energy for the VMC method is expected due to the restricted Hilbert space. However, the DMC is expected to do better, but on the contrary it gives an overestimate that is twice as much. The origin for this overestimation was not found.

Table 1: *The ground state energy for the Hydrogen Atom, the Helium Atom and the Hydrogen molecule using Variational and Diffusion Monte Carlo methods. In the case of the Hydrogen molecule the ground and the first excited states are given for the harmonic and Morse potential, where the excited vibrational states are given with respect to the ground vibrational state. The frequency and the position of the well are given for VMC and DMC. The data is simulated with the following parameters: for optimization a threshold of 0.001 and damping factor of 0.7 is used. For VMC 400 walkers perform 30.000 steps and data is collected after 4000 steps and the walkers are shifted within a cube of size 0.1. For DMC 6000 walkers perform 4000 time steps of length 0.01 and data is collected after 400 steps, the damping factor is 0.5. All data is given in a.u.*

		VMC		DMC		Experimental [5] [4]
Hydrogen Atom ($\alpha = 1$)		-0.5000 $\pm$ 0.0000		-0.5000$\pm$0.0001		-0.4997
Helium Atom ($\alpha = 0.144$)		-2.8779 $\pm$ 0.0003		-2.8486$\pm$0.0071		-2.9034
		Harmonic	Morse	Harmonic	Morse	
	s_0	1.487$\pm$0.005	1.445$\pm$0.012	1.450$\pm$0.007	1.381$\pm$0.003	1.4015
	ω (10^{-3})	13.66$\pm$0.26	18.63$\pm$0.57	12.96$\pm$0.32	21.11$\pm$0.19	14.19
	ν=0	-1.1440$\pm$0.0007	-1.1397$\pm$0.0081	-1.1749$\pm$.0009	-1.1733$\pm$0.0016	-1.1660
	ν=1	13.7$\pm$0.7	18.0$\pm$8.2	13.0$\pm$0.9	19.9$\pm$1.6	18.0
	ν=2	27.3$\pm$0.7	35.3$\pm$8.3	25.9$\pm$0.9	38.7$\pm$1.6	36.8
	ν=3	41.0$\pm$0.8	51.9$\pm$8.4	38.9$\pm$0.9	56.3$\pm$1.7	53.7
	ν=4	54.6$\pm$0.8	67.9$\pm$8.6	51.9$\pm$80.9	72.6$\pm$1.8	69.5
	ν=5	68.3$\pm$0.8	83.3$\pm$8.8	64.8$\pm$0.9	87.9$\pm$1.9	84.2

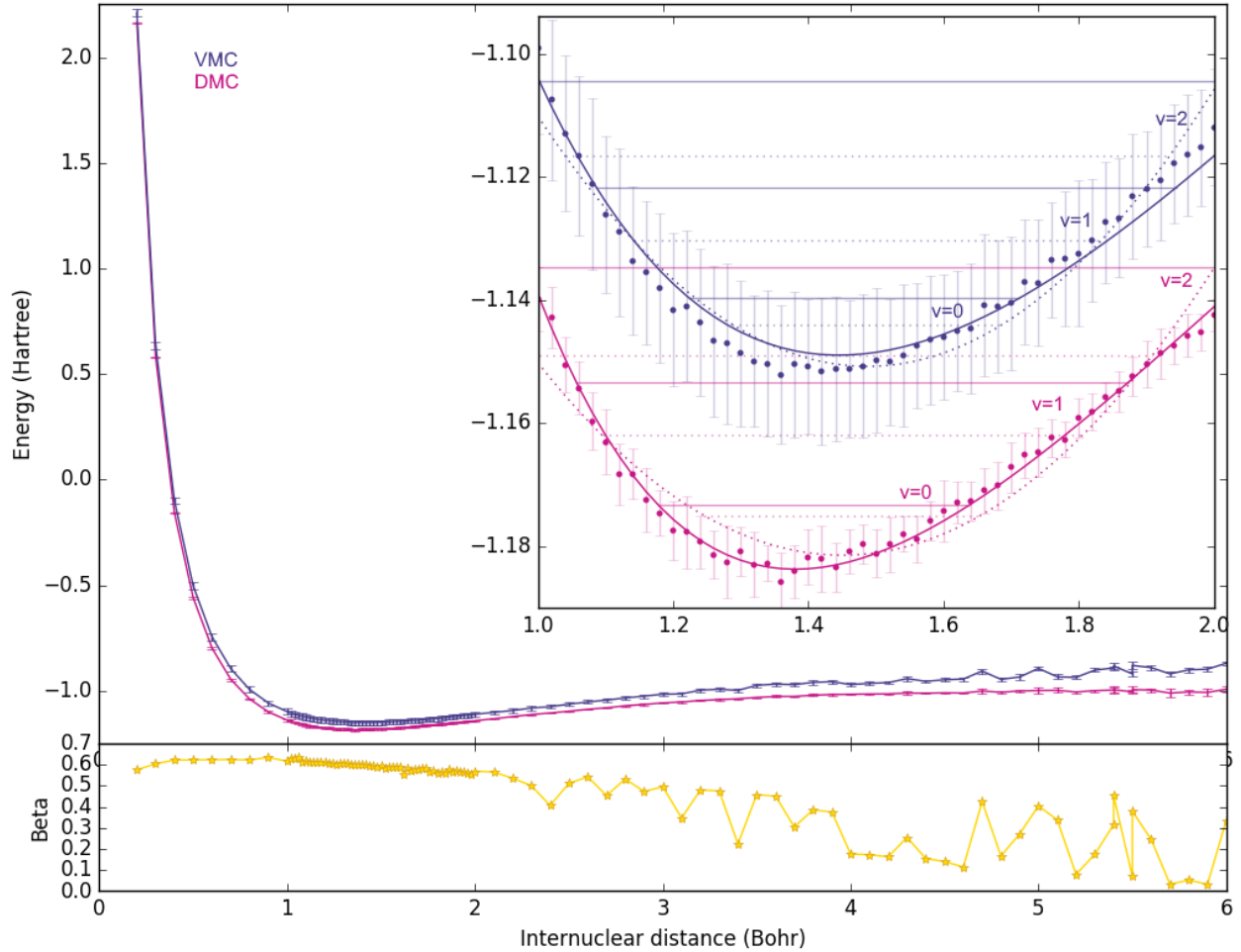*Hydrogen Molecule — Vibrational Spectrum*

Figure 1: Energy diagram for different internuclear distance. The purple data points give the VMC method and the pink ones the DMC method. The yellow data points represent the value of β at at which an optimum was found. In the inset the data is fitted to a harmonic (dotted line) and Morse (solid line) potential for which their respective quantized energy levels are shown.

Hydrogen Molecule Figure 1 shows the results for simulations of the Hydrogen molecule with different internuclear separations for both the VMC and DMC method. As can be seen, the potential has a clear minimum that represents the ground state of the diatomic molecule. The internuclear distance of the ground state is, depending on whether a harmonic or Morse potential is assumed (which are introduced in the next paragraph), 1.487 ± 0.005 or 1.445 ± 0.012 for VMC and 1.450 ± 0.007 or 1.381 ± 0.003. These values are close to the experimental value of 1.4015 [5] especially for the DMC fitted to a Morse potential.

Vibrational modes Around the ground state energy the potential as a function of the internuclear distance is approximately harmonic. Therefore, the two protons can be seen as two masses connected by an imaginary spring, thus the protons can start to vibrate with respect to the center of mass. The frequency of this motion is determined by the form of the potential. In the inset of figure 1 the potential around the ground state is shown and the data is fitted to a harmonic potential

$$E(s) = E_0 + \kappa(s - s_0)^2 \qquad (16)$$

where E_0 is the depth of the well, s_0 the center and κ the spring constant. The corresponding frequency is easily related by $\omega = \sqrt{\kappa/m}$ where $m = 918$ is

the reduced mass of the protons. The frequencies are shown in table 1 and are well in correspondence with the experimental value of 14.19. Because of the size of the system the vibrational energy levels are quantized and thus the effective ground state energy is higher than the minimum of the potential well. The vibrational energy level spectrum is formed by $E(v) = E_0 + 2\pi\omega(\frac{1}{2} + v)$. These levels are shown in the inset of figure 1 and table 1. The values for the vibrational spectrum are systematically too low in comparison to experimental values for both VMC and DMC. The reason for this dissimilitude is the asymmetry of the potential well. A better approximation for this form is the Morse potential

$$E(s) = E_0 + D_e \left(e^{-2a(s-s_0)} - 2e^{-a(s-s_0)} \right) \quad (17)$$

where D_e is the dissociation energy and a a control variable for the well width. Fitting the data to this function results in a frequency, that is obtained via $\omega = a\sqrt{2D_e/m}$, of 18.63 ± 0.57 and 21.11 ± 0.19 for VMC and DMC respectively. These values are a lot higher than the experimental value, which can be explained by non-optimal fitting. Looking at the vibrational spectrum the energy level spacing is obtained by

$$E(v) = (E_0 - D_e) + 2\pi\omega(\frac{1}{2} + v) + \frac{\omega^2}{D_e}(\frac{1}{2} + v)^2 \quad (18)$$

The spectrum for both VMC and DMC are shown in table 1 and are in outstanding correspondence with the experimental level spacing due to the vibrational states.

Molecular bonding Varying the internuclear distance between the two protons results in two familiar cases in both limits. For the distance approaching zero the protons effectively form one nucleus with two orbiting electrons, which is known as the Helium atom. Looking at the energy of this state and neglecting the proton-proton energy, which becomes infinitely large, the electron energy is found to be $E = -2.8261 \pm 0.0120$ [1]. Comparing this to the results of the Helium atom of $E = -2.8486 \pm 0.0071$ there is a slight difference, even though the trial wave functions are equal for $s = 0.0$. Looking at the wave functions, depicted in figure 2a and figures 2b and 2c, the resemblance is evident.

[1] All of these values are found by DMC
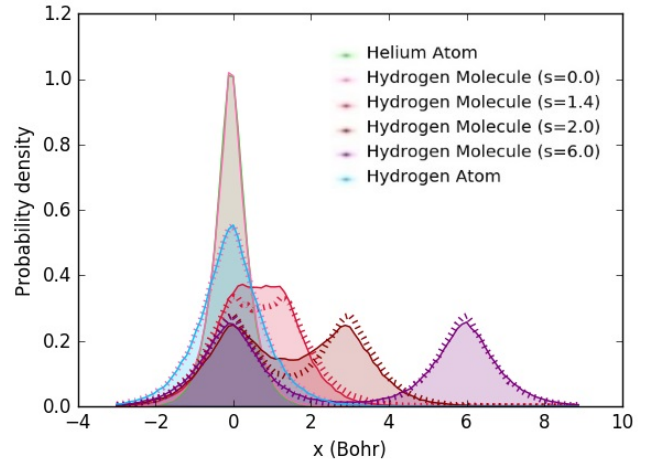
(a) Probability distribution of the electrons with respect to the x-coordinate including the expected value for the case of individual Hydrogen atoms (dotted)

(b) Wave function of hydrogen molecule at s=0.0
$E = -2.8261 \pm 0.0120$

(c) Wave function of Helium atom.
$E = -2.8486 \pm 0.0071$

(d) Wave function of Hydrogen molecule at s=1.4
$E = -1.1832 \pm 0.0027$

(e) Wave function of Hydrogen molecule at s=3.0
$E = -1.0591 \pm 0.0016$

(f) Wave function of Hydrogen molecule at s=6.0
$E = -0.9942 \pm 0.0122$

(g) Wave function of Hydrogen atom.
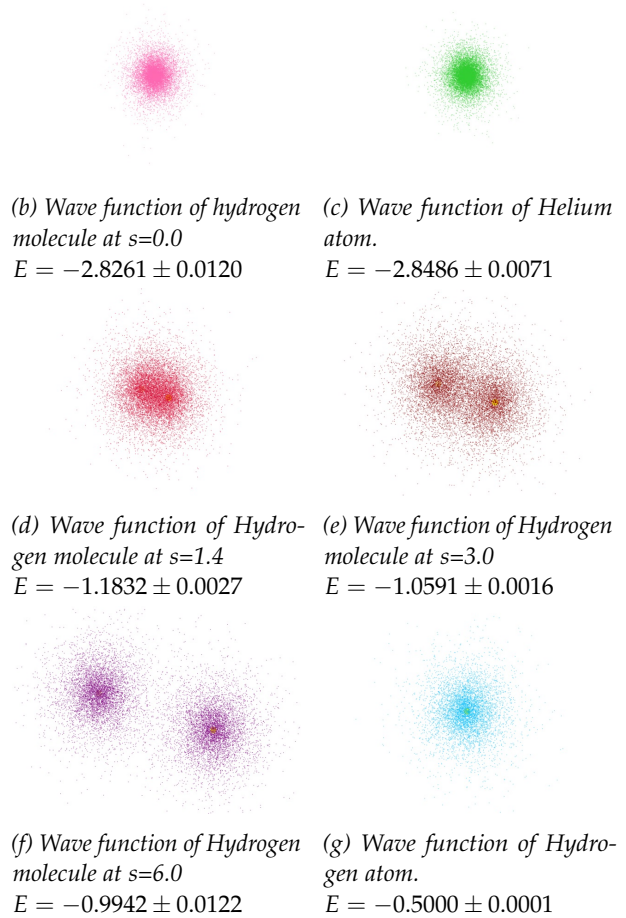$E = -0.5000 \pm 0.0001$

Figure 2: Probability distribution and 3D wave function for the Hydrogen and Helium atom and for the Hydrogen molecule for different internuclear separations obtained by DMC

In the other limit, where the internuclear distance is large, the two protons and electrons form two individual hydrogen atoms. The energy of an individual Hydrogen atom is $E = -0.5000 \pm 0.0001$, whereas the combined energy of the Hydrogen molecule at large internuclear separation is $E = -0.9942 \pm 0.0122$ which is as expected approximately twice the energy of individual atoms, which is again confirmed by the form of the wave function as shown in figure 2a and figures 2f and 2g.

The more interesting part is formed by the intermediate internuclear distance where the electrons of both hydrogen atoms start to interact and form molecular orbitals for close enough distances. As can be seen in figure 2a the electron probability already starts to shift at a distance of 3.0 compared to the expected probability distribution for two individual hydrogen atoms. The wave function of the electron is increased in between the protons, whereas it is reduced at the outer parts of the formed molecule. Because of this enhanced probability of finding an electron in the center the protons are effectively attracted to each other which is known as the bonding state σ. The bonding energy can be found by comparing the energy of the molecule to the energy of two hydrogen atoms. This bonding energy is found to be -0.1832 ± 0.0028 or -0.1733 ± 0.0017 if the vibrational quantization is taken into account. This is slightly higher than the expected experimental value of 0.1660 [5].

IV. Conclusion

This report has discussed the use of two Monte Carlo methods, variational (VMC) and diffusion (DMC), to obtain the ground state energy and wave function of Hydrogen and Helium atoms and the Hydrogen molecule. The ground state energy of the Hydrogen atom was found in excellent correspondence to the experimental value whereas the energy for Helium was overestimated by both methods.

The potential landscape for the ground state as a function of the nuclear distance was determined and a fit to a harmonic and Morse potential were made in order to obtain the vibrational spectrum. The values for the frequency, particularly for the harmonic potential, were in good correspondence with experimental data whereas the Morse potential resulted in a frequency estimate that was contradictory to the experimental value of 14.19. On the other hand, the vibrational spectrum was impressively accurately reproduced by using a Morse potential fit and diffusive Monte Carlo method. Lastly the molecular bond formed between the two hydrogen atoms forming the molecule was studied. The formed bonding state (σ) was seen by an increased electron probability in between the protons and the molecular bonding energy was found to be 0.1733 ± 0.0017 compared to the experimental value of 0.1660.

The used models can in principle be used to study even larger systems, however the used walkers can only represent positive values for the wave function, so the phase of the wave function is not incorporated. This becomes problematic for DMC when larger systems are studied, but this problem can be resolved by dividing the configuration space in hypervolumes where the wave function is considered to be restrictively positive or negative. This method is called 'fixed-node' and can be implemented in the used model to obtain ground state energies, wave functions, vibrational spectra, molecular bonding energies and so on for more complicated atoms and molecules such as Lithium and Beryllium atoms and the corresponding diatomic molecules or even mixtures of diatomic molecules.

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A. Appendix

The Monte Carlo methods are fully determined by the Hamiltonian and the wave function of the system. The derived system dependent quantities such as the local energy, equation 1, log-derivative needed for equation 3 and force, equation 4 are given here for the Hydrogen Atom, Helium Atom and the Hydrogen Molecule.

A.1   Hydrogen

The local energy of the Hydrogen Atom is given by

$$E_L(\vec{r}) = -\frac{1}{r} - \frac{1}{2}\alpha\left(\alpha - \frac{2}{r}\right) \tag{19}$$

The log-derivative of the trial wave function is

$$\frac{\partial \ln \Psi_T}{\partial \alpha} = -r \tag{20}$$

and the force

$$F = -2\alpha \tag{21}$$

A.2   Helium

The local energy of the Helium Atom is given by

$$E_L(\vec{r}_1, \vec{r}_2) = -4 + (\hat{r}_1 - \hat{r}_2)\cdot(\vec{r}_1 - \vec{r}_2)\frac{1}{r_{12}(1+\alpha r_{12})^2} - \frac{1}{r_{12}(1+\alpha r_{12})^3} - \frac{1}{4(1+\alpha r_{12})^4} + \frac{1}{r_{12}} \tag{22}$$

The log-derivative of the trial wave function is

$$\frac{\partial \ln \Psi_T}{\partial \alpha} = \frac{-r_{12}^2}{2(1+\alpha r_{12})^2} \tag{23}$$

and the force

$$F = -2\begin{bmatrix}\vec{r}_1\\\vec{r}_2\end{bmatrix} + \frac{\alpha(2+r_{12})}{(1+\alpha r_{12})^2}\begin{bmatrix}\hat{r}_{12}\\-\hat{r}_{12}\end{bmatrix} \tag{24}$$

A.3   Hydrogen Molecule

The local energy of the Hydrogen Molecule is given by

$$\begin{aligned}
E_L(\vec{r}_1, \vec{r}_2) = &-\frac{1}{a^2} + \frac{1}{a\phi_1}\left(\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}}\right) + \frac{1}{a\phi_2}\left(\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}}\right) - \left[\frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}}\right] + \frac{1}{|r_{12}|}\\
&+ \left(\frac{\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}}{\phi_1} - \frac{\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}}{\phi_2}\right)\cdot\frac{\hat{r}_{12}}{2a(1+\beta r_{12})^2} - \frac{(4\beta+1)r_{12}+4}{4(1+\beta r_{12})^4 r_{12}}
\end{aligned} \tag{25}$$

The log-derivative of the trial wave function is

$$\frac{\partial \ln \Psi_T}{\partial \beta} = \frac{-\alpha r_{12}^2}{2(1+\beta r_{12})^2} \tag{26}$$

and the force

$$F = \frac{2\nabla\Psi_T(\vec{r}_1, \vec{r}_2)}{\Psi_T(\vec{r}_1, \vec{r}_2)} = \frac{\nabla_1\phi_1}{\phi_1} + \frac{\nabla_1\Psi_T(\vec{r}_1, \vec{r}_2)}{\Psi_T(\vec{r}_1, \vec{r}_2)} + \frac{\nabla_2\phi_2}{\phi_2} + \frac{\nabla_2\Psi_T(\vec{r}_1, \vec{r}_2)}{\Psi_T(\vec{r}_1, \vec{r}_2)} \tag{27}$$

Where

$$\frac{\nabla_1 \phi_1}{\phi_1} + \frac{\nabla_1 \Psi_T(\vec{r}_1, \vec{r}_2)}{\Psi_T(\vec{r}_1, \vec{r}_2)} = \frac{-1}{a} \frac{\left[e^{-r_{1L}/a} \hat{r}_{1L} + e^{-r_{1R}/a} \hat{r}_{1R}\right]}{e^{-r_{1L}/a} + e^{-r_{1R}/a}} + \frac{\hat{r}_{12}}{\alpha(1 + \beta r_{12})^2} \tag{28}$$

As already mentioned, the number of free parameters can be used by introduction of the cusp conditions. These conditions prevent the occurrence of singularities, which occur when a proton and electron or both electrons approach each other. The first condition leads to the condition:

$$\frac{1}{\phi_n} \frac{\phi_{n_L}}{r_{1L}} = \frac{e^{-r_{1L}/a}}{e^{-r_{1L}/a} + e^{-r_{1R}/a}} \frac{1}{r_{1L}} \tag{29}$$

Taking the limit $r_{1L} \to 0$ leads to the condition $a(1 + e^{-s/a}) = 1$ For the second case, both electrons approaching each other, the following holds

$$\frac{1}{\psi} \nabla_1^2 \psi = \frac{2\alpha + r_{12}(2\alpha\beta + 1)}{\alpha^2 (1 + \beta r_{12})^4 r_{12}} \tag{30}$$

which leads to the condition $\alpha = 2$, when taking the limit $r_{12} \to 0$.