

# A VQMC simulation for the hydrogen molecule

Xukun Xiang Misha Klein

## Abstract

In this report, the Variational Quantum Monte Carlo method (VMC) has been used to simulate and calculate the potential energy of the Hydrogen molecule as a function of internuclear distance. By fitting the data with the Morse potential, the dissociation energy ( $D_e=0.1512\pm0.0005\text{Hartree}$ ), equilibrium binding distance ( $s_e=1.405\pm0.003a_0$ ) and vibrational frequency ( $\omega_{vib}\approx4510\text{ cm}^{-1}$ ) were obtained. In addition, by tracking the positions of the electrons throughout simulation the electron orbits can be made visible.

## 1 Introduction

Variational Monte Carlo (VMC) combines the variational method for solving the Schrödinger equation and Monte Carlo integration. In the variational method, one chooses a parameterized wavefunction. The resulting energy is minimized within the subspace of parameterized wavefunctions to obtain the ground state energy. Monte Carlo integration is a numerical method for dealing with high dimensional integrals in which random numbers are generated (which makes it a Monte Carlo method) to sample the integrant. In this report, the results of a VMC calculation for the Hydrogen molecule ( $\text{H}_2$ ) are presented. The chosen trial wavefunction contains multiple parameters. One of them being the distance between the two nuclei. By imposing appropriate (cusp) conditions and leaving one parameter to be varied, the potential energy as a function of the distance between the two H nuclei is determined. In addition, the electron orbits are made visible by tracking the positions of the electrons throughout simulation for the ground state.

## 2 Description of variational Monte Carlo for $\text{H}_2$ molecule

### 2.1 Setup Variational method

The system at hand consists of two electrons and two nuclei. The goal of our experiment is to find the potential energy felt by the two electrons, due to the nuclei, as a function of the distance between the nuclei. By considering both the kinetic contribution and the coulomb interaction between any set of two particles, one obtains the following Hamiltonian:

$$H_n = -\frac{1}{2}\nabla_{\vec{R}_L}^2 - \frac{1}{2}\nabla_{\vec{R}_R}^2 + V_n(\vec{R}_L, \vec{R}_R) \quad \text{with:} \quad (1a)$$

$$V_n(\vec{R}_L, \vec{R}_R) = \frac{1}{|\vec{R}_L - \vec{R}_R|} + \frac{\int d^3\vec{r}_1 d^3\vec{r}_2 \Psi_e^* H_e \Psi_e}{\int d^3\vec{r}_1 d^3\vec{r}_2 |\Psi_e|^2} \quad (1b)$$

The coördinates of the "left" and "right" nucleus are denoted by  $\vec{R}_L$  and  $\vec{R}_R$  respectively. The above Hamiltonian is what can be identified as the Hamiltonian for the nuclei. The electron Hamiltonian,  $H_e$ , contains all terms involving the coördinates of the electrons:

$$H_e = -\frac{1}{2}\nabla_{\vec{r}_1}^2 - \frac{1}{2}\nabla_{\vec{r}_2}^2 + \frac{1}{|\vec{r}_1 - \vec{r}_2|} - \frac{1}{|\vec{r}_1 - \vec{R}_R|} - \frac{1}{|\vec{r}_1 - \vec{R}_L|} - \frac{1}{|\vec{r}_2 - \vec{R}_R|} - \frac{1}{|\vec{r}_2 - \vec{R}_L|} \quad (2)$$

The system's minimal potential energy,  $V_n$ , is found by using variational calculus. Since the coulomb interaction between the nuclei is a fixed function of the distance between the nuclei,  $V_n$  is minimized by minimizing the integral term. For the variational method, one chooses a parameterized trial wavefunction and minimizes the resulting energy within the subspace to which all such trial wavefunctions belong. The integral term in equation (1b) is rewritten, by defining a local energy function:

$$\frac{\int d^3\vec{r}_1 d^3\vec{r}_2 \Psi_e^* H_e \Psi_e}{\int d^3\vec{r}_1 d^3\vec{r}_2 |\Psi_e|^2} \equiv \int d^3\vec{r}_1 d^3\vec{r}_2 \mu(\vec{r}_1, \vec{r}_2) E_L(\vec{r}_1, \vec{r}_2, \vec{R}_L, \vec{R}_R) \quad (3)$$

where the local energy,  $E_L$ , and normalized probability density,  $\mu$  are defined by:

$$\mu(\vec{r}_1, \vec{r}_2) = \frac{|\Psi_e|^2}{\int d^3\vec{r}_1 d^3\vec{r}_2 |\Psi_e|^2} \quad (4a)$$

$$E_L(\vec{r}_1, \vec{r}_2, \vec{R}_L, \vec{R}_R) = \frac{H_e \Psi_e}{\Psi_e} \quad (4b)$$

The chosen trial wavefunction takes on the following form:

$$\Psi_e = \psi(\vec{r}_1) \psi(\vec{r}_2) f(|\vec{r}_1 - \vec{r}_2|) \quad (5a)$$

$$\psi(\vec{r}) = e^{-|\vec{r} - \vec{R}_L|/a} + e^{-|\vec{r} - \vec{R}_R|/a} \quad (5b)$$

$$f(r) = e^{\frac{r}{a(1+\beta r)}} \quad (5c)$$

Since it is known that in the ground state of  $H_2$  the electrons spins are in the (assymmetric) singlet state, a symmetric spatial wavefunction is constructed. The electron orbits,  $\psi$ 's, are accompanied by the so called Jastrow factor,  $f(r)$ . The Jastrow factor ensures that the two electrons will obey the Pauli principle, making it impossible to place them at the same point in space.

In the limit that an electron gets close to a nucleus, the corresponding coulomb interaction term in the potential blows up. The same can be said for bringing the two electrons close to each other. To prevent the potential energy from becoming infinitely large we require the wavefunction to satisfy appropriate cusp conditions. These fix two of the three parameters in the wavefunction:

$$\alpha = 2 \quad (6a)$$

$$a = \frac{1}{1 + e^{-|\vec{R}_L - \vec{R}_R|/a}} \quad (6b)$$

The second of these equations can be solved numerically (using the Newton-Raphson method) for a given internuclear distance. After having determined the local energy function, the integral of equation (3) is evaluated by carrying out Monte Carlo integration. Importance sampling, with probability distribution  $\mu$ , is performed by using the Metropolis algorithm.

## 2.2 Local energy function

Combining equations (5), (4b) and (2) results the following expression for the local energy:

$$\begin{aligned} E_L = & \frac{1}{r_{1L}} \left[ \left( 1 + \frac{\vec{r}_{1L} \cdot \hat{r}_{12}}{\alpha \gamma^2} \right) \frac{e^{-\frac{r_{1L}}{a}}}{a \psi(\vec{r}_1)} - 1 \right] \\ & + \frac{1}{r_{1R}} \left[ \left( 1 + \frac{\vec{r}_{1R} \cdot \hat{r}_{12}}{\alpha \gamma^2} \right) \frac{e^{-\frac{r_{1R}}{a}}}{a \psi(\vec{r}_1)} - 1 \right] \\ & + \frac{1}{r_{2L}} \left[ \left( 1 - \frac{\vec{r}_{2L} \cdot \hat{r}_{12}}{\alpha \gamma^2} \right) \frac{e^{-\frac{r_{2L}}{a}}}{a \psi(\vec{r}_2)} - 1 \right] \\ & + \frac{1}{r_{2R}} \left[ \left( 1 - \frac{\vec{r}_{2R} \cdot \hat{r}_{12}}{\alpha \gamma^2} \right) \frac{e^{-\frac{r_{2R}}{a}}}{a \psi(\vec{r}_2)} - 1 \right] \\ & + \frac{1}{r_{12}} \left( 1 - \frac{2\alpha\gamma + r_{12}}{\alpha^2 \gamma^4} \right) \\ & - \frac{1}{a^2} \end{aligned} \quad (7)$$

Here,  $r_{ij}$  denotes the length of the vector  $\vec{r}_{ij} \equiv |\vec{r}_i - \vec{r}_j|$  and  $\gamma = 1 + \beta r_{12}$ . The restrictions that follow from the cusp conditions can be (re)derived from the expression for the local energy. Consider the limiting case of bringing the two electrons towards the same point ( $r_{12} \rightarrow 0$ ). The fourth term in equation (7)

now becomes dominant. The constraints on the parameters are such that the limit  $\text{Lim}_{r_{12} \rightarrow 0} E_L$  exists.

$$\begin{aligned} \frac{1}{r_{12}} \left(1 - \frac{2\alpha\gamma + r_{12}}{\alpha^2\gamma^4}\right) &\rightarrow \\ \frac{1}{r_{12}} \left(1 - \frac{2\alpha\gamma}{\alpha^2\gamma^4}\right) &\rightarrow \\ \frac{1}{r_{12}} \left(1 - \frac{2\alpha}{\alpha^2}\right) \end{aligned}$$

where  $\text{Lim}_{r_{12} \rightarrow 0} \gamma = 1$  has been used in the third line. To prevent  $E_L$  from becoming infinitely large we require:

$$\left(1 - \frac{2\alpha}{\alpha^2}\right) = 0$$

from which equation (6a) follows. The constraint on  $a$  is such that  $\text{Lim}_{\vec{r} \rightarrow \vec{R}} E_L$  exists, for all combinations of electron and nuclei coordinates. Consider, for example, the limit in which the first electron gets placed on top of the leftmost nucleus ( $r_{1L} \rightarrow 0$ ). The first term in equation (7) becomes dominant.

$$\begin{aligned} \frac{1}{r_{1L}} \left[ \left(1 + \frac{\vec{r}_{1L} \cdot \hat{\vec{r}}_{12}}{\alpha\gamma^2}\right) \frac{e^{-\frac{r_{1L}}{a}}}{a\psi(\vec{r}_1)} - 1 \right] &\rightarrow \\ \frac{1}{r_{1L}} \left[ \frac{1}{a\psi(\vec{r}_1)} - 1 \right] &\rightarrow \\ \frac{1}{r_{1L}} \left[ \frac{1}{a(1 + e^{-\frac{|\vec{R}_L - \vec{R}_R|}{a}})} - 1 \right] \end{aligned}$$

From equation (5b) it follows that  $\text{Lim}_{r_{1L} \rightarrow 0} \psi(\vec{r}_1) = 1 + e^{-\frac{|\vec{R}_L - \vec{R}_R|}{a}}$ . The local energy does not become infinitely large if we require:

$$\left[ \frac{1}{a(1 + e^{-\frac{|\vec{R}_L - \vec{R}_R|}{a}})} - 1 \right] = 0$$

from which equation (6b) follows. In a similar fashion this same constraint can be derived by bringing the first electron close to the rightmost nucleus or bringing the second electron close to any one of the nuclei.

It is insightful to consider the limiting behavior of the local energy as a function of the internuclear distance. When the two nuclei are brought together ("fused"), the system becomes equivalent to that of a helium atom.

$$\begin{aligned} \text{Lim}_{\vec{R}_L \rightarrow \vec{R}_R} E_L &= \text{Lim}_{\vec{R}_L \rightarrow \vec{R}_R} \left( \frac{2}{r_{1L}} \left[ \left(1 + \frac{\vec{r}_{1L} \cdot \hat{\vec{r}}_{12}}{2\gamma^2}\right) \frac{1}{2a} - 1 \right] \right. \\ &\quad + \frac{2}{r_{2L}} \left[ \left(1 - \frac{\vec{r}_{2L} \cdot \hat{\vec{r}}_{12}}{2\gamma^2}\right) \frac{1}{2a} - 1 \right] \\ &\quad + \frac{1}{r_{12}} - \frac{1}{r_{12}\gamma^3} - \frac{1}{4r_{12}\gamma^4} - \frac{1}{a^2} \\ &= \frac{(\vec{r}_1 - \vec{r}_2) \cdot \hat{\vec{r}}_{12}}{2ar_{12}\gamma^2} + \frac{1}{r_{12}} - \frac{1}{r_{12}\gamma^3} - \frac{1}{4r_{12}\gamma^4} - \frac{1}{a^2} \end{aligned}$$

In this limit it holds that  $r_{iL} = r_{iR}$ . To arrive at the final line both the constraint  $\alpha=2$  and the fact that  $(\vec{r}_{1L} - \vec{r}_{2R}) \cdot \hat{\vec{r}}_{12} = (\vec{r}_1 - \vec{r}_2) \cdot \hat{\vec{r}}_{12}$  have been used. It can be verified that this expression is precisely the local energy for the helium atom when using similar trial wavefunctions (see reference (1)).

In the opposite limit of separating the two sets of nuclei + electron, the local energy expression reduces to that of two separate hydrogen atoms. To see this, one must take the following four limits of equation

(7) simultaneously:

$$\begin{array}{l} |\vec{R}_L - \vec{R}_R| \rightarrow \infty \\ r_{1R} \rightarrow \infty \\ r_{2L} \rightarrow \infty \\ r_{12} \rightarrow \infty \end{array}$$

Using the constraint on  $\alpha$  and that  $\gamma \rightarrow \infty$  in the above limits results in:

$$E_L \rightarrow -\frac{1}{r_{1L}} - \frac{1}{2a} \left( \frac{1}{a} - \frac{2}{r_{1L}} \right) - \frac{1}{r_{2R}} - \frac{1}{2a} \left( \frac{1}{a} - \frac{2}{r_{2R}} \right)$$

This is precisely twice the local energy for a H-atom (see reference (1)).

### 3 Results and discussion

During MC simulation, 400 independent pairs of walkers were used. For every walker 4000 initialization steps and 26000 simulations steps were used. During initialization, the size of the spatial step the walkers take is adjusted such that the average acceptance rate (in the Metropolis algorithm) gets close to 50%. All energies are given in Hartree and all distances in Bohr radii ( $a_0$ ).

#### 3.1 Potential energy

As described above, the potential energy as a function of internuclear distance is obtained by means of combining MC integration and variational calculus with parameter  $\beta$ . The data is fitted with the Morse potential:

$$V_{Morse} = D_e(e^{-2a(s-s_e)} - 2e^{-a(s-s_e)}) - C \quad (8)$$

Here,  $s = |\vec{R}_L - \vec{R}_R|$ ,  $C = -1$  indicates a constant shift and  $s_e$  is the equilibrium (binding) distance. The Morse potential is a convenient model for the potential energy of a diatomic molecule. It is a better approximation than the quantum harmonic oscillator or the Lennard-Jones potential, because it explicitly includes the effects of bond breaking. Using a Taylor series approximation, an expression for the (estimated) vibrational frequency is obtained:

$$\omega_{vib} = a \sqrt{\frac{2D_e}{m_{reduced}}} \quad (9)$$

where  $m_{reduced} = 918m_e$  is the reduced mass of a  $H_2$  molecule in atomic units. Figure 1 shows the obtained potential energy curve.

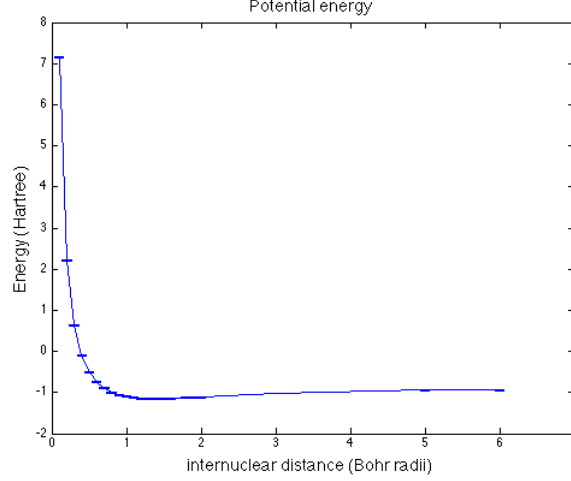


Figure 1: Potential energy as a function of internuclear distance. Errorbars indicate 95% confidence intervals. Simulation for 400 sets of walkers, 4000 initialization steps and 26 000 simulation steps.

The shape of the curve is what one would expect based on physical grounds. There is a minimum (ground state) energy, indicating that a bond between the two H atoms should form. At large distances, the potential energy tends towards -1Hartree, precisely the ground state energy of two separate H-atoms. At small distances, the energy diverges due to the coulomb interaction between the two nuclei. Figure 2 shows a fit of equation (8) to a part of the obtained energy curve. For this plot the data in the range of  $s \in [1.1, 1.7]$  is used to obtain a more accurate estimate of the ground state energy.

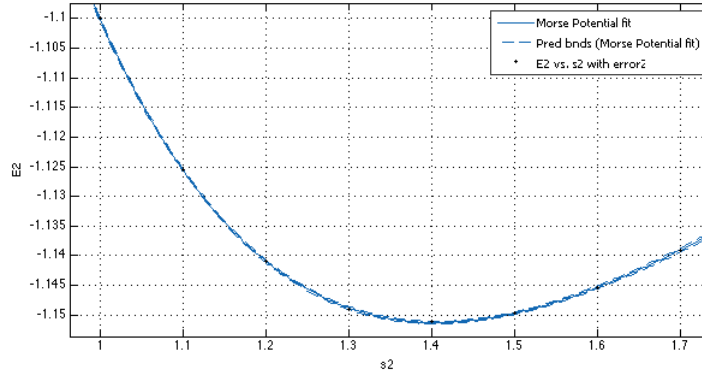


Figure 2: Potential energy fitted with Morse potential. Black dots are data points. Solid line represents best fit of equation (8) to the data. Dashed lines indicate 95% confidence interval. Best fit values for fitting parameters are  $D=0.1512 \pm 0.0005 \text{ Hartree}$ ,  $s_e=1.405 \pm 0.003 a_0$  and  $a=1.133 \pm 0.020 a_0^{-1}$ . Simulation for 400 sets of walkers, 4000 initialization steps and 26 000 simulation steps.

The minimum value of the Energy is obtained at  $s_e=1.405 \pm 0.003 a_0$ . The corresponding dissociation energy is  $D=0.1512 \text{ Hartree}$ , with a 95% confidence interval of  $[0.151, 0.1515]$ . The best fit value for the parameter  $a$  is  $a=1.133 \pm 0.020 a_0^{-1}$ . This results in an estimate of the vibrational frequency of  $\omega_{vib} \approx 4510 \text{ cm}^{-1}$ .

According to literature (see reference (2) and (3)), the equilibrium distance is  $s_e = 1.401 a_0$  (see(2)) and the dissociation energy is  $D_e \approx 0.1646 \pm 10^{-5} \text{ Hartree}$  (see(3)). Our value for the dissociation energy, is within 8% of the literature value. The obtained equilibrium distance is within 0.3% of the literature value. The experimental value for the vibrational frequency is  $4401 \text{ cm}^{-1}$ , a 2.5% difference. The main reason for deviation with experimental values is due to systematic errors of the VMC method. The exact

solution for the ground state wavefunction of a  $H_2$ , does not belong to the class of chosen parameterized wavefunctions (Equations 5). This induces a systematic error in the (local) energy that can not be reduced by extending the simulation. This also explains why all errors are of the same order (within a few %). Diffusion Monte Carlo methods (DMC) or Green's function Monte Carlo methods (GFMC), as used in reference (3), have less systematic errors. Our value is lower than the DMC value, as expected. Energy values are higher than in DMC or GFMC, the minimum is found less accurately in VMC.

### 3.2 Electronic orbits

For the ground state ( $s=1.405a_0$  and  $\beta=0.6$ ) the final position of all 400 pairs of walkers (800 electron positions in total) are plotted. In this manner the electronic orbits are made visible. The result is displayed in figure 3.

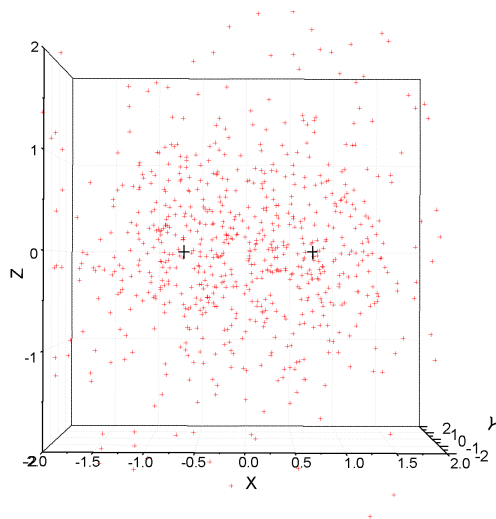


Figure 3: "Electron Cloud" around the nuclei,  $s = 1.405a_0$  and  $\beta = 0.6$ . The simulation is done for 400 pairs of electrons, 4000 initialization steps and 26 000 simulation steps. The plot shows the distribution of walkers after the final Monte Carlo step (26000th).

As is known for the Hydrogen molecule, the two atoms form a covalent bond. Therefore, the probability of finding an electron in between the two nuclei should be relatively high when compared to finding either one of them elsewhere. In figure 3 this is reflected by the relatively high density of points (red crosses) in between the two nuclei (black crosses).

## 4 Conclusion

In this report, we have presented the results of a computational VMC experiment. The potential energy for the  $H_2$  molecule is found. Before doing so, an analytic expression for the local energy was found. Appropriate cusp conditions exclude non-physical behavior. The potential energy curve from experiment is fitted with the Morse potential. The resulting dissociation energy is  $D_e=0.1512$ Hartree, with a 95% confidence interval of [0.151, 0.1515]. The equilibrium distance and vibrational frequency are  $s_e=1.405\pm0.003a_0$  and  $\omega_{vib}\approx4510\text{ cm}^{-1}$  respectively. These values are in good agreement with literature values (within few %).

A plot of the electron positions in the ground state after simulation reveals the electron orbits. The covalent bond is clearly reflected by the resulting plot.

## 5 References

- 1) J.M.Thijssen, Computational Physics, second edition, Cambridge university press

- 2) CRC Handbook of Chemistry and physics, 93rd edition 2012-2013
- 3)J.Chem.Phys. 94(5), 1 March 1991