

# Variational Quantum Monte Carlo calculations of molecular Hydrogen

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## Abstract

The variational quantum Monte Carlo method is used to evaluate the ground state energy of the hydrogen molecule. Using a 'trial' function – dependent on the to be varied parameters – posing as the wavefunction, 400 randomly placed walkers are perform a random walk through the 6 dimensional space, where at each position the local energy  $\frac{H\Psi_T}{\Psi_T}$  is calculated. The variance in energy should be low for the ground state. The found dissociation energy using this method is -0.1510(1), which considering the error due to non-exact trial function resembles the value from the literature of -0.16450(2)[3].

## 1 Introduction

The variational method is a method for finding the ground state and the first few excited states of a quantum Hamiltonian. This is done by taking a parametrised trial wave function, and then finding the minimum of the expectation value of the energy in the space of parameters occurring in the chosen parametrised trial wave function. Calculating the expectation value of the energy involves solving integrals over the degrees of freedom of the collection of particles. Because directly solving higher dimensional integrals with reasonable accuracy is a computationally expensive task, we will use Monte Carlo methods. This is called the variational quantum Monte Carlo (VQMC) approach.

## 2 Theoretical model

In realistic many-body systems the wave function assumes very small values in large parts of configuration space. Therefore a Metropolis algorithm in which a collection of random walkers is pushed towards those regions of configuration space where the value of the wave function is significant. This is done by shifting the coordinates of each walker to a new position within a cube with a chosen side  $d$ . Next the value of  $p = [\psi_T(R')/\psi_T(R)]^2$  is calculated where  $\psi_T$  is the trial wave function,  $R'$  is the new and  $R$  is the old configuration. If  $p$  is larger than 1 the new config-

uration is accepted and if  $p$  is smaller than 1 it is accepted with probability  $p$ . After this the local energy of the resulting configuration is calculated and stored. The local energy is defined as:

$$E_L(R) = \frac{H\psi_T(R)}{\psi_T(R)} \quad (1)$$

where  $H$  is the Hamiltonian of the system. The more closely the shape of the trial wave function approaches that of the exact wave function, the less strongly will  $E_L$  vary with  $R$ . The expectation value of the local energy is calculated as the average of the samples generated in this procedure, excluding a number of steps at the beginning, necessary to reach equilibrium. With this method, we estimate the energy of the ground state of a hydrogen molecule.

The Hamiltonian of the Hydrogen molecule includes the kinetic and potential energies of the two electrons as well as their interaction. The positions of the atomic nuclei are assumed to be fixed on the x-axis at positions  $-s/2$ ,  $s/2$ , which means they are separated with a distance  $s$ . The positions of the electrons are  $\vec{r}_1$  and  $\vec{r}_2$ . The Hamiltonian in atomic units is:

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left( \frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}} \right) + \frac{1}{r_{12}} \quad (2)$$

where  $r$  is the distance between two particles. The number in the subscripts denotes the electron and the letter in the subscripts denotes the atom.

We use the trial function:

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2) \quad (3)$$

where

$$\phi_1(\vec{r}_1) = e^{-r_{1L}/a} + e^{-r_{1R}/a} = \phi_{1L} + \phi_{1R} \quad (4)$$

and

$$\phi_2(\vec{r}_2) = e^{-r_{2L}/a} + e^{-r_{2R}/a} = \phi_{2L} + \phi_{2R} \quad (5)$$

For the form of the interaction term we use the Jastrow function:

$$\psi(\vec{r}_1, \vec{r}_2) = \exp\left(\frac{r_{12}}{\alpha(1 + \beta r_{12})}\right) \quad (6)$$

At this point there are four parameters:  $s$ ,  $a$ ,  $\alpha$ ,  $\beta$ . We can remove two of them using the Coulomb cusp conditions. These remove the singularity in the energy when either electron approaches either proton, or when the two electrons approach each other. The four cases of an electron approaching a proton lead to the same condition:  $a(1 + e^{-s/a}) = 1$ . The case of two electron approaching each other lead to the condition:  $\alpha = 2$ .

The trial function leads to the following expression of the local energy:

$$\begin{aligned} E_L = & -\frac{1}{a^2} + \frac{1}{a\phi_1} \left( \frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right) \\ & + \frac{1}{a\phi_2} \left( \frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right) \\ & - \left( \frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}} \right) + \frac{1}{r_{12}} \\ & + \left( \frac{\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}}{\phi_1} - \frac{\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}}{\phi_2} \right) \\ & \cdot \frac{\hat{r}_{12}}{2a(1 + \beta r_{12})^2} \\ & - \frac{(4\beta + 1)r_{12} + 4}{4(1 + \beta r_{12})^4 r_{12}} \end{aligned} \quad (7)$$

Using these expressions, we can estimate the energy of the ground state of a hydrogen molecule. To find the dissociation energy of the bond, we have to subtract the energy of the two separated hydrogen atoms, which is together  $-1$ , and add the energy of the nucleus- nucleus interaction, which is  $1/s$ .

### 3 Results

Three different limits are evaluated; negligible distance between the nuclei, the distance corresponding

to that of molecular hydrogen, and long distance between the nuclei. The first case should show close resemblance to the Helium atom, the latter should resemble two separated hydrogen atoms.

In the helium atom limit –  $s = 0$  – the values found for the mean energy and its variance among the walkers are respectively  $-2.8739(10)$  and  $0.0885(3)$ . This is in agreement with the value found for the helium model as described in section 12.2.2 of Thijssen's book[1]. This is of no surprise as in this limit the expressions 3 and 7 literally reduce to their helium counterparts.

In the separated hydrogen atoms limit ( $s = 100$ ) We find the walkers to reside at energy  $-1.001(1)$  with very little variance namely  $0.0007(2)$ . This is twice the bonding energy of a single hydrogen atom, which is what we expect.

In order to find the distance between the two nuclei and the electrons' associated dissociation energy of molecular hydrogen, a variational approach is taken by minimizing the binding energy of the electrons. In figure 3 the minimum binding energy occurs at  $s = 1.4$ , and  $\beta = 0.6125$ , namely  $\langle E_b \rangle = -0.1510(1)$  and  $\text{Var}(E) = 0.05260(3)$ . The bond length we found is in agreement with the literature value of  $s=1.4$ [2]. The dissociation/bonding energy respectably close with  $E = 0.16450(2)$ [3]. This is due to the fact that the test function 3 is not the exact ground state wave function.

Curiously, the minimum of the variance for  $s = 1.4$  occurs at  $\beta = 0.475$ . This means that in the spectral decomposition of the test function 3 with respect to the Hamiltonian's eigenstates, the shift in weights towards the ground state is accompanied by a contraction of the distribution for higher eigenstates (Analogously:  $\langle [0, 1, 2, 3] \rangle = \langle [0, 0, 3, 3] \rangle$ , but  $\text{Var}([0, 1, 2, 3]) < \text{Var}([0, 0, 3, 3])$ ).

### 4 Conclusion

In this paper, the variational quantum Monte Carlo method was used to evaluate the ground state energy of the hydrogen molecule. The obtained results for the various energies were in accordance what was to be expected with respect to the theory. Although the obtained results were quite reasonable, the error due to the non-exact trial function persists. One may solve this issue by using the diffusion Monte Carlo method as described by Thijssen[1]. Although computation time was very manageable, opportunities exist for additional speedup. In particular, as all walk-

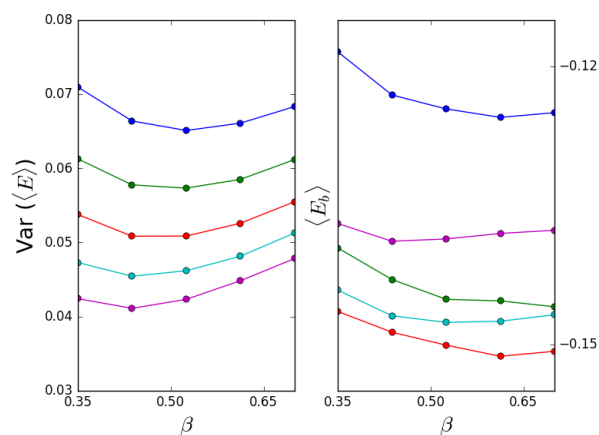


Figure 1: Mean variance of local energy(left) and mean local energy(right) as a function of variational parameter  $\beta$  for different internuclear distance  $s$  : (purple = 1.1 , light blue = 1.25, red = 1.4, green = 1.55, blue = 1.7). The simulations were evaluated for 400 walkers with 20000 iterations, not including the initial 10000 to allow the system to equilibrate (thus 30000 in total).

ers are independent of each other, calculations may be performed in parallel with respect to the walkers. Additionally, the method of steepest descent was attempted but did not yield better results, so it was decided not to use it.

## References

- [1] Thijssen, J.M., *Computational Physics*, (2007)
- [2] DeKock, R.L. and Gray, H.B. *Chemical Structure and Bonding*, (1989)
- [3] Darwent, B.B. *Bond dissociation energies in simple molecules*, (1970)