

1 Hydrogen molecule

This document describes how to calculate the ground-state energy of a hydrogen molecule using the Variational Monte Carlo (VMC) method.¹ The best known experimental value for the dissociation energy is $36118.1 \pm 0.2 \text{ cm}^{-1}$.² This corresponds to a total energy of $1.164566 \pm 0.000001 \text{ a.u.}$

1.1 Born-Oppenheimer approximation

In atomic units, the Hamiltonian of a system consisting of n electrons and N nuclei with mass M_i and charge Z_i is given by

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i=1}^n \sum_{j=1; j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_{\mathbf{R}_i}^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j=1; j \neq i}^N \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{i=1}^n \sum_{j=1}^N \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}.$$

We now make the Born-Oppenheimer approximation, where we separate the electronic and nuclear degrees of freedom:

$$\Psi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}) \Psi_n(\{\mathbf{R}\}).$$

$\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})$ is the electronic wavefunction, which is governed by the electronic Hamiltonian:

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^n \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i=1}^n \sum_{j=1; j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^n \sum_{j=1}^N \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}.$$

The nuclear wavefunction $\Psi_n(\{\mathbf{R}\})$ is governed by the nuclear Hamiltonian

$$\hat{H}_n = -\frac{1}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_{\mathbf{R}_i}^2 + V_n(\{\mathbf{R}\}).$$

$V_n(\{\mathbf{R}\})$ is the effective potential of the nuclei, containing their Coulomb interaction and the average potential due to the electrons:

$$V_n(\{\mathbf{R}\}) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1; j \neq i}^N \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + E_e(\{\mathbf{R}\}),$$

where

$$E_e(\{\mathbf{R}\}) = \langle \hat{H}_e \rangle(\{\mathbf{R}\}) \equiv \frac{\int d\{\mathbf{r}\} \Psi_e^*(\{\mathbf{r}\}, \{\mathbf{R}\}) \hat{H}_e \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})}{\int d\{\mathbf{r}\} |\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})|^2}.$$

This is the integral we will calculate with VMC.

1.2 Nuclei

In the case of a hydrogen molecule, we have two nuclei, both with $Z = 1$. In this case the nuclear Hamiltonian is a single-particle Hamiltonian which only depends on the distance between the nuclei:

$$\hat{H}_n = -\frac{1}{M} \nabla_{\mathbf{R}_1 - \mathbf{R}_2}^2 + V_n(\mathbf{R}_1 - \mathbf{R}_2),$$

with

$$V_n(\mathbf{R}_1 - \mathbf{R}_2) = \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|} + E_e(\mathbf{R}_1 - \mathbf{R}_2).$$

The extra factor of two in the kinetic energy is due to the fact that the reduced mass of two hydrogen nuclei is half that of a single nucleus. The nuclear potential has a minimum at the equilibrium distance

of the nuclei. Around this minimum, the potential can be approximated by a harmonic oscillator. However, the Morse potential³ will give a better fit:

$$V_n(R) = D \left(1 - e^{-a(R-R_0)}\right)^2, \quad (1)$$

where $R = |\mathbf{R}_1 - \mathbf{R}_2|$, R_0 is the equilibrium distance, D is the dissociation energy and $a = \sqrt{K/(2D)}$ with K the spring constant. The spectrum of the Morse potential can be calculated analytically and is given by

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) \left(1 - \frac{\hbar\omega \left(n + \frac{1}{2}\right)}{4D}\right),$$

where $\omega = \sqrt{K/M}$. The dissociation energy is the total energy difference between a hydrogen molecule and two hydrogen atoms infinitely far away; in atomic units $D = 1 - E$.

1.3 Electrons

The electronic Hamiltonian of the hydrogen molecule is given by

$$\hat{H}_e = -\frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|}.$$

There is no known analytical solution for the electronic wavefunction, so we will resort to VMC. In order to get an accurate answer, we need to find a trial wavefunction that matches the real wavefunction as closely as possible. Particularly in the limits where the potential blows up, *i.e.*, when $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ or $\mathbf{r}_1 \rightarrow \mathbf{R}_1$ *etc.*, it needs to have the right form.

We know that the ground state of a hydrogen atom has the form

$$\psi(\mathbf{r}) = e^{-\frac{|\mathbf{r}-\mathbf{R}|}{a}}.$$

Our initial guess for the single-particle electronic wavefunction of the hydrogen molecule is therefore simply a linear combination of the wavefunctions of the individual atoms:

$$\psi(\mathbf{r}) = e^{-\frac{|\mathbf{r}-\mathbf{R}_1|}{a}} + e^{-\frac{|\mathbf{r}-\mathbf{R}_2|}{a}}.$$

This is known as the LCAO (Linear Combination of Atomic Orbitals) approximation. The two-particle wavefunction is simply the product of two single-particle wavefunctions, modified by a correlation factor:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)f(\mathbf{r}_1, \mathbf{r}_2).$$

The correlation function $f(\mathbf{r}_1, \mathbf{r}_2)$, known as the Jastrow factor, must satisfy the so-called cusp conditions. Note that this wavefunction does not obey Fermi-Dirac statistics. However, the ground-state of a hydrogen molecule is a singlet, which means that the required antisymmetry is incorporated in the spin wavefunction:

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

For excited states, or systems with more than two electrons, we need to incorporate the antisymmetry into the spatial part of the wavefunction (using Slater determinants).

1.4 Cusp conditions

In general, when two particles approach each other, whether electrons, nuclei, or one of both, the terms in the Hamiltonian depending on their mutual distance r dominate. In that case we can write the two-particle Schrödinger equation as a single-particle radial Schrödinger equation with a reduced mass m :

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{2} \frac{l(l+1)}{r^2} + V(r) \right] R(r) = ER(r).$$

By defining $u(r) = rR(r)$, this simplifies to

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial r^2} + \frac{1}{2} \frac{l(l+1)}{r^2} + V(r) \right] u(r) = Eu(r).$$

When an electron i approaches nucleus j , $m \approx 1$, and the Schrödinger is

$$-\frac{1}{2} \frac{\partial^2 u(r)}{\partial r^2} + \left[\frac{1}{2} \frac{l(l+1)}{r^2} - \frac{Z_j}{r} \right] u(r) = 0,$$

where we have defined $r \equiv |\mathbf{r}_i - \mathbf{R}_j|$. In the limit of $r \rightarrow 0$, this equation is satisfied by

$$u(r) = r^{l+1} e^{-\frac{Z_j}{l+1} r},$$

hence

$$R(r) = r^l e^{-\frac{Z_j}{l+1} r},$$

and we obtain the limit

$$\lim_{r_i \rightarrow \mathbf{R}_j} \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}) \sim |\mathbf{r}_i - \mathbf{R}_j|^l e^{-\frac{Z_j}{l+1} |\mathbf{r}_i - \mathbf{R}_j|}.$$

Similarly, when electron i approaches electron j , the radial Schrödinger equation is

$$-\frac{\partial^2 u(r)}{\partial r^2} + \left[\frac{1}{2} \frac{l(l+1)}{r^2} + \frac{1}{r} \right] u(r) = 0,$$

with $r \equiv |\mathbf{r}_i - \mathbf{r}_j|$ (note the opposite sign in the Coulomb potential!). The extra factor 2 in the kinetic energy is caused by the fact that the reduced mass of a two-electron system is half that of a single electron. In the limit of $r \rightarrow 0$, we obtain

$$u(r) = r^{l+1} e^{\frac{1}{2(l+1)} r},$$

hence

$$R(r) = r^l e^{\frac{1}{2(l+1)} r},$$

and we have

$$\lim_{r_i \rightarrow \mathbf{r}_j} \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}) \sim |\mathbf{r}_i - \mathbf{r}_j|^l e^{\frac{1}{2(l+1)} |\mathbf{r}_i - \mathbf{r}_j|}.$$

To satisfy the electron-nucleus cusp condition in the ground state ($l = 0$) of hydrogen, we have:

$$\lim_{r \rightarrow \mathbf{R}_1} e^{-\frac{|r - \mathbf{R}_1|}{a}} + e^{-\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a}} = A e^{-|\mathbf{r} - \mathbf{R}_1|}.$$

Differentiating with respect to \mathbf{r} yields $A = 1/a$ at $\mathbf{r} = \mathbf{R}_1$, hence

$$a = \frac{1}{1 + e^{-\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a}}}. \quad (2)$$

This has to be solved numerically. When $|\mathbf{R}_1 - \mathbf{R}_2|$, $a = 1$ and we recover the case of separate hydrogen atoms. In the opposite case, where $|\mathbf{R}_1 - \mathbf{R}_2| = 0$, we get $a = \frac{1}{2}$, which means the electrons are on average much closer to the nuclei. This is to be expected, since this corresponds to a helium atom.

The Jastrow factor should ensure that the trial wavefunction satisfies the cusp conditions in limit where $\mathbf{r}_1 \rightarrow \mathbf{r}_2$. Additionally, when $r = |\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$, the two electrons are uncorrelated and the Jastrow factor should be constant. These conditions are satisfied by

$$f(r) = e^{\frac{r}{\alpha(1+\beta r)}}. \quad (3)$$

The electron-electron cusp condition demands that $\alpha = 2(l + 1) = 2$ for the ground state ($l = 0$). β is a free parameter.

1.5 Local energy

The local energy is made up of the kinetic of both particles and potential energy. The latter is simply

$$U = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|}.$$

The kinetic energy is harder to calculate. For electron 1:

$$T_1 \equiv -\frac{1}{2} \frac{\nabla_{\mathbf{r}_1}^2 \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})}{\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})} = -\frac{1}{2} \frac{\nabla_{\mathbf{r}_1}^2 \psi(\mathbf{r}_1)}{\psi(\mathbf{r}_1)} - \frac{(\nabla_{\mathbf{r}_1} \psi(\mathbf{r}_1)) \cdot (\nabla_{\mathbf{r}_1} f(\mathbf{r}_1, \mathbf{r}_2))}{\psi(\mathbf{r}_1) f(\mathbf{r}_1, \mathbf{r}_2)} - \frac{1}{2} \frac{\nabla_{\mathbf{r}_1}^2 f(\mathbf{r}_1, \mathbf{r}_2)}{f(\mathbf{r}_1, \mathbf{r}_2)},$$

and similarly for T_2 . To calculate the gradient, we use the fact that

$$\nabla_{\mathbf{r}} f(r') = (\nabla_{\mathbf{r}} r') \frac{\partial f(r')}{\partial r'} = \frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|} \frac{\partial f(r')}{\partial r'},$$

where $r' = |\mathbf{r} - \mathbf{r}_0|$. Additionally,

$$\nabla_{\mathbf{r}} \cdot \frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|} = \frac{2}{|\mathbf{r} - \mathbf{r}_0|}.$$

Combining the two gives

$$\nabla_{\mathbf{r}}^2 f(r') = \frac{2}{|\mathbf{r} - \mathbf{r}_0|} \frac{\partial f(r')}{\partial r'} + \frac{\partial^2 f(r')}{\partial r'^2}.$$

For the atomic wavefunction we have

$$\nabla_{\mathbf{r}} \psi(\mathbf{r}) = -\frac{1}{a} \frac{\mathbf{r} - \mathbf{R}_1}{|\mathbf{r} - \mathbf{R}_1|} e^{-\frac{|\mathbf{r} - \mathbf{R}_1|}{a}} - \frac{1}{a} \frac{\mathbf{r} - \mathbf{R}_2}{|\mathbf{r} - \mathbf{R}_2|} e^{-\frac{|\mathbf{r} - \mathbf{R}_2|}{a}},$$

hence the contribution to the kinetic energy is

$$\nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) = \frac{1}{a^2} \psi(\mathbf{r}) - \frac{1}{a} \frac{2}{|\mathbf{r} - \mathbf{R}_1|} e^{-\frac{|\mathbf{r} - \mathbf{R}_1|}{a}} - \frac{1}{a} \frac{2}{|\mathbf{r} - \mathbf{R}_2|} e^{-\frac{|\mathbf{r} - \mathbf{R}_2|}{a}}.$$

For the Jastrow factor we get

$$\nabla_{\mathbf{r}_1} f(\mathbf{r}_1, \mathbf{r}_2) = -\nabla_{\mathbf{r}_2} f(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\alpha \gamma^2} \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} f(\mathbf{r}_1, \mathbf{r}_2),$$

where $\gamma = 1 + \beta |\mathbf{r}_1 - \mathbf{r}_2|$. This yields for the contribution to the kinetic energy:

$$\nabla_{\mathbf{r}_1}^2 f(\mathbf{r}_1, \mathbf{r}_2) = \left[\frac{1}{\alpha \gamma^2} \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{\alpha^2 \gamma^4} - \frac{2\beta}{\alpha \gamma^3} \right] f(\mathbf{r}_1, \mathbf{r}_2) = \frac{2\alpha \gamma + |\mathbf{r}_1 - \mathbf{r}_2|}{\alpha^2 \gamma^4 |\mathbf{r}_1 - \mathbf{r}_2|} f(\mathbf{r}_1, \mathbf{r}_2).$$

Finally,

$$\begin{aligned} (\nabla_{\mathbf{r}_1} \psi(\mathbf{r}_1)) \cdot (\nabla_{\mathbf{r}_1} f(\mathbf{r}_1, \mathbf{r}_2)) &= -\frac{1}{a} \frac{1}{\alpha \gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{R}_1| |\mathbf{r}_1 - \mathbf{r}_2|} e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_1|}{a}} f(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad - \frac{1}{a} \frac{1}{\alpha \gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{R}_2| |\mathbf{r}_1 - \mathbf{r}_2|} e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_2|}{a}} f(\mathbf{r}_1, \mathbf{r}_2). \end{aligned}$$

Combining the terms yields for the kinetic energy of electron 1:

$$\begin{aligned} T_1 &= -\frac{1}{2a^2} - \frac{2\alpha\gamma + |\mathbf{r}_1 - \mathbf{r}_2|}{2\alpha^2\gamma^4 |\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad + \frac{1}{a} \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} \left(1 + \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_1|}{a}}}{\psi(\mathbf{r}_1)} \\ &\quad + \frac{1}{a} \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} \left(1 + \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_2|}{a}}}{\psi(\mathbf{r}_1)}, \end{aligned}$$

and similarly for electron 2. The local energy now becomes

$$\begin{aligned} E_L = T_1 + T_2 + U &= -\frac{1}{a^2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \left[1 - \frac{2\alpha\gamma + |\mathbf{r}_1 - \mathbf{r}_2|}{\alpha^2\gamma^4} \right] \\ &\quad + \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} \left[\left(1 + \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{1}{a} \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_1|}{a}}}{\psi(\mathbf{r}_1)} - 1 \right] \\ &\quad + \frac{1}{|\mathbf{r}_1 - \mathbf{R}_2|} \left[\left(1 + \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_1 - \mathbf{R}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{1}{a} \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_2|}{a}}}{\psi(\mathbf{r}_1)} - 1 \right] \\ &\quad + \frac{1}{|\mathbf{r}_2 - \mathbf{R}_1|} \left[\left(1 - \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_2 - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{1}{a} \frac{e^{-\frac{|\mathbf{r}_2 - \mathbf{R}_1|}{a}}}{\psi(\mathbf{r}_2)} - 1 \right] \\ &\quad + \frac{1}{|\mathbf{r}_2 - \mathbf{R}_2|} \left[\left(1 - \frac{1}{\alpha\gamma^2} \frac{(\mathbf{r}_2 - \mathbf{R}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \frac{1}{a} \frac{e^{-\frac{|\mathbf{r}_2 - \mathbf{R}_2|}{a}}}{\psi(\mathbf{r}_2)} - 1 \right]. \end{aligned}$$

The first term in brackets should go to zero when $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow 0$, because there its prefactor explodes. In this case $\gamma \rightarrow 1$ and we are left with

$$1 - \frac{2\alpha}{\alpha^2} = 0,$$

hence $\alpha = 2$. This is exactly the electron-electron cusp condition derived above. Similarly, the second term in brackets should go to zero when $|\mathbf{r}_1 - \mathbf{R}_1| \rightarrow 0$. In that case the term in brackets reduces to

$$\frac{1}{a \left(1 + e^{-\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a}} \right)} - 1 = 0.$$

Solving for a yields

$$a = \frac{1}{1 + e^{-\frac{|\mathbf{R}_1 - \mathbf{R}_2|}{a}}},$$

which is again the electron-nucleus cusp condition (Eq. 2). It is easily checked that this condition also prevents singularities in the remaining terms. Also, when the nuclei are far apart, *i.e.*, $|\mathbf{R}_1 - \mathbf{R}_2| \rightarrow \infty$ (and similarly for $|\mathbf{r}_1 - \mathbf{R}_2|$, $|\mathbf{r}_2 - \mathbf{R}_1|$ and $|\mathbf{r}_1 - \mathbf{r}_2|$), the local energy reduces to

$$E_L = -\frac{1}{a^2} = -1,$$

which is twice the energy of a hydrogen atom, as expected.

Finally, when $\mathbf{R}_1 \rightarrow \mathbf{R}_2$ we are essentially modeling a Helium atom. The potential energy reduces to

$$U = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|},$$

and the total kinetic energy to

$$T = -\frac{1}{a^2} + \frac{1}{a} \frac{1}{|\mathbf{r}_1|} + \frac{1}{a} \frac{1}{|\mathbf{r}_2|} + \frac{1}{a\alpha\gamma^2} \left(\frac{\mathbf{r}_1}{|\mathbf{r}_1|} - \frac{\mathbf{r}_2}{|\mathbf{r}_2|} \right) \cdot \left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) - \frac{1}{\alpha\gamma^3} \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{\alpha^2\gamma^4}.$$

Since $\alpha = 2$ and $a = \frac{1}{2}$ (see above), the local energy becomes

$$E_L = -4 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{\gamma^2} \left(\frac{\mathbf{r}_1}{|\mathbf{r}_1|} - \frac{\mathbf{r}_2}{|\mathbf{r}_2|} \right) \cdot \left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) - \frac{1}{\gamma^3} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{4\gamma^4},$$

which is indeed the expected result for Helium.¹

1.6 Parameters

The trial wavefunction has three parameters: a , α , and β . For the ground state, $\alpha = 2$ (see above), while a is given by Eq. 2. This equation can be solved with the Newton-Raphson method, using

$$f(a) = \frac{1}{1 + e^{-\frac{s}{a}}} - a, \quad f'(a) = \frac{-se^{-\frac{s}{a}}}{\left(ae^{-\frac{s}{a}} \right)^2} - 1,$$

where $s = |\mathbf{R}_1 - \mathbf{R}_2|$. We start with the initial guess $a = \frac{1}{2}$, corresponding to $s = 0$, and for each iteration update a according to $a \rightarrow a - da$, with $da = f(a)/f'(a)$. We continue the iteration until $|da|$ is smaller than some convergence criterion.

The only free parameter in the system is β . We can try finding the optimum value by minimizing the energy of many VMC calculations as a function of β , but there is a faster way.^{4,5} After a m MC iterations, we update β with a damped steepest decent method according to

$$\beta \rightarrow \beta - \gamma \frac{dE}{d\beta},$$

where γ is a scaling factor (not to be confused with the γ defined above), and

$$\frac{dE}{d\beta} = 2 \left(\left\langle E_L \frac{d \ln(\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}))}{d\beta} \right\rangle + \langle E_L \rangle \left\langle \frac{d \ln(\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}))}{d\beta} \right\rangle \right).$$

The average is taken over the m configurations. In our trial wavefunction, only the Jastrow factor (Eq. 3) depends on β , and we have (with $r = |\mathbf{r}_1 - \mathbf{r}_2|$)

$$\frac{d \ln(\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\}))}{d\beta} = \frac{1}{f(r)} \frac{df(r)}{d\beta} = -\frac{r^2}{\alpha(1 + \beta r)^2}.$$

1.7 Results

The simulations are performed with 1000 random walkers. The first 20000 iterations are used to find equilibrium, and every 200 iterations both the random step size and β are optimized. The former by scaling the step size such that the average acceptance rate is 50%, the latter using the damped

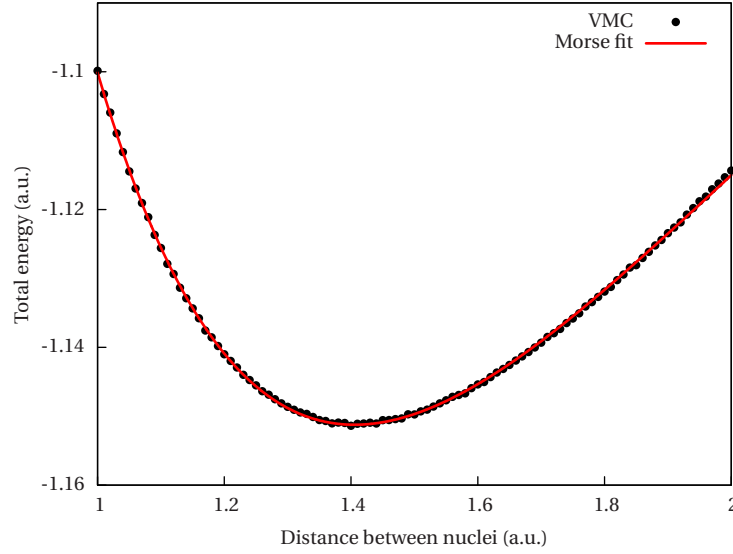


Figure 1: Total energy of the hydrogen molecule calculated with VMC (black dots). The red line is a fit to the Morse potential (Eq. 1). The parameters resulting from the fit are $D = 0.15123(3)$ a.u. ($33192(8)$ cm⁻¹), $R_0 = 1.4054(2)$ a.u. ($0.74371(1)$ Å), and $\hbar\omega = 0.02044(2)$ a.u. ($4486(5)$ cm⁻¹).

steepest descent method described above. Once the parameters have been optimized, 40000 steps are used to gather statistics. The resulting energy as a function of nuclear separation, and a fit to the Morse potential (Eq. 1), are shown in Fig. 1.

For the total energy we need to subtract the ground-state energy ($n = 0$) of the Morse potential from the dissociation energy, yielding a final value of $D = 0.14119(4)$ a.u. ($30987(10)$ cm⁻¹), which is 14% lower than the experimental value.² The vibrational frequency is closer to the experimental value⁶ of 4401.21 cm⁻¹, *i.e.*, within 2%, and R_0 is even better: 0.74144 Å in literature,⁶ giving an error of 0.3%.

2 Diffusion Monte Carlo

The ‘force’ on electron 1 is given by

$$\mathbf{F}(\mathbf{r}_1) \equiv \frac{2\nabla_{\mathbf{r}_1} \Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})}{\Psi_e(\{\mathbf{r}\}, \{\mathbf{R}\})} = -\frac{\mathbf{r}_1 - \mathbf{R}_1}{|\mathbf{r}_1 - \mathbf{R}_1|} \frac{2}{a} \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_1|}{a}}}{\psi(\mathbf{r}_1)} - \frac{\mathbf{r}_1 - \mathbf{R}_2}{|\mathbf{r}_1 - \mathbf{R}_2|} \frac{2}{a} \frac{e^{-\frac{|\mathbf{r}_1 - \mathbf{R}_2|}{a}}}{\psi(\mathbf{r}_1)} + \frac{2}{\alpha\gamma^2} \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

and similarly for $\mathbf{F}(\mathbf{r}_2)$.

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