Determining the Bond-Dissociation Energy of H_2 using the Variational Quantum Monte Carlo Method

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https://github.com/rubenb1993/quantum_monte_carlo

Abstract

The Variational Quantum Monte Carlo (VQMC) method is used to find approximate forms of the ground state wave function of the hydrogen atom and the hydrogen molecule by minimizing their energies. This is done by applying a steepest decent method with respect to the variational parameters. Subsequently the expectation values of the energy of the hydrogen molecule at different interatomic distances are calculated. As a final result the bond-dissociation energy of H_2 is determined at an interatomic distance of $s = 1.4011\ r_b$; this value is computed as $-0.15110 \pm 1.3 \cdot 10^{-5}$ Hartree. The calculated values show good coherence with the literature values.

1 Introduction

In chemistry, the bond-dissociation energy can be used in order to determine the total energy released by a chemical reaction. This is of importance when designing large scale reactions, especially when they are exothermic.

In order to find the bond-dissociation energy, the sum of energies of the separate atoms can be subtracted from the energy of the molecule itself. These energies can be found when the Schrödinger wave function is known for the atoms and the molecule. This wave function, however, is usually not known analytically. A good approximation can be made by guessing a 'trial' wave function, with adjustable parameters. By varying these parameters, the energy of the trial wave function can be minimized.

The expectation value of the energy of a quantum mechanical system is determined by integrating over the degrees of freedom of the system. In simple systems this can be done numerically in a deterministic way, but in high-dimensional, many-body systems a quantum Monte Carlo approach is much more efficient [1]. In this paper the variational quantum Monte Carlo (VQMC) method is used. This is a useful approach that can be extended to very complicated systems.

The most basic example of the calculation of the bond-dissociation energy, that of diatomic hydrogen, is given here. This is done by finding the values of $\langle E \rangle$ for the hydrogen atom and the hydrogen molecule. From these quantities the bond-dissociation energy can be calculated.

2 Theory

2.1 Variational Quantum Monte Carlo

The goal of the variational quantum Monte Carlo method is to find the wave function $\Psi(\vec{r})$ of a (many-body) problem by using a trial wave function. This function is an estimate of the actual wave function $\Psi(\vec{r})$ and is still dependent on one or more parameters.

The variational method prescribes that, when the trial wave function is in a suitable form, the expectation value of the energy, for any set of parameters, can never be lower than the ground state energy of the system [1]. It is therefore possible to look for the global minimum in energy as a function

1

of the parameters without fear that a non-feasible state with an energy lower than the ground state is reached. The set of parameters that produce the lowest energy, also create the wave function closest to the ground state. The minimum in energy is found per set of parameters by using the Metropolis algorithm [1].

In the Metropolis algorithm the minimum of the energy is found by letting a number of walkers take a predetermined number of displacements in position. The size of these displacements are drawn from a $U(-d/2, d/2)$ distribution, where d is a certain step size. The trajectory that these walkers take is determined by a stochastic variable constructed from the squared wave function. This makes sure that the walkers end up at positions such that the energy averaged over the walkers and the displacements approaches the value of the global energy minimum.

The parameter set $\vec{\alpha}$ for which $\langle E \rangle$ is minimized can be found by either trial and error or by implementing a minimization algorithm. In this report, both options are utilized.

3   Simulation

3.1   Units

In this simulation natural units are used to simplify the calculations. The units are chosen in such a way that the following holds for the kinetic energy operator:

$$-\frac{\hbar^2}{2m}\nabla^2 \equiv -\frac{1}{2}\nabla^2 \qquad (1)$$

This means that $\hbar = 1$ $[\hbar]$ and $m = 1$ $[m_e]$, where m_e is the electron mass. All distances are expressed in the Bohr radius $r = [r_b] = [0.529 \text{ Å}]$. From these units and the kinetic energy operator, it follows that energy has the unit of

$$E = \frac{[\hbar]^2}{[m_e][r_b]^2} = [27.2 \ eV] = 1 \,[\text{Hartree}]. \qquad (2)$$

All electric charges are furthermore expressed in units of the elementary charge; $Q = [e] = [1.6 \cdot 10^{-19} \ C]$.

3.2   Hydrogen Atom

In order to find the bond-dissociation energy of the hydrogen molecule, the energy of two separate hy-drogen atoms is needed. The Hamiltonian for the hydrogen atom in the Born-Oppenheimer approximation can be expressed in reduced units as

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}, \qquad (3)$$

where r is the distance between the nucleus at the origin and the electron.

The trial wave function chosen for the electron is

$$\Psi(\vec{r}) = e^{-\alpha r}, \qquad (4)$$

where α is the parameter that can be varied in order to find the minimum energy.

The local energy is then given by [1]

$$\varepsilon = \frac{\hat{H}\Psi(\vec{R})}{\Psi(\vec{R})} = -\frac{1}{r} - \frac{\alpha}{2}\left(\alpha - \frac{2}{r}\right). \qquad (5)$$

3.3   Hydrogen Molecule

The calculation of the wave function of the hydrogen molecule is done similarly to the hydrogen atom. The hydrogen molecule is modelled by two hydrogen nuclei on the $x-$axis, around the origin, separated by a distance s. The system has two electrons with positions $\vec{r}_1$ and $\vec{r}_2$.

In this model, the Hamiltonian of a hydrogen molecule is defined as [2]

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_1^2) + \frac{1}{s} + \frac{1}{|r_{12}|}$$
$$- \left[\frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}}\right] \qquad (6)$$

where $\vec{r}_{iL} = \vec{r}_i + \frac{s}{2}\hat{x}$ and $\vec{r}_{iR} = \vec{r}_i - \frac{s}{2}\hat{x}$ for $i = 1, 2$ and $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$.

An appropriate trial wave function for a hydrogen molecule is [1]

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2), \qquad (7)$$

with

$$\phi(\vec{r}_i) = e^{-r_{iL}/a} + e^{-r_{iR}/a} = \phi_{iL} + \phi_{iR}, \qquad (8)$$

for $i = 1, 2$ and the Jastrow function

$$\psi(\vec{r}_1, \vec{r}_2) = e^{\frac{|\vec{r}_{12}|}{\alpha(1+\beta|\vec{r}_{12}|)}}. \qquad (9)$$

Using this trial wave function, the expression for the local energy is derived (Appendix A) to be

$$
\begin{aligned}
\varepsilon = & -\frac{1}{a^2} - \frac{2\alpha + r_{12}(1 + 2\alpha\beta)}{\alpha^2 r_{12}(1 + \beta r_{12})^4} \\
& + \sum_{\substack{i \in \{1,2\} \\ j \in \{L,R\}}} \left(\frac{\phi_{ij}}{a\phi_i r_{ij}} - \frac{1}{r_{ij}} \right) + \frac{1}{r_{12}} + \frac{1}{s} \\
& + \frac{\hat{r}_{12}}{\alpha a(1 + \beta r_{12})^2} \cdot \sum_{j \in \{L,R\}} \left(\frac{\phi_{1j}\hat{r}_{1j}}{\phi_1} - \frac{\phi_{2j}\hat{r}_{2j}}{\phi_2} \right),
\end{aligned}
\tag{10}
$$

where the interatomic distance s, and the parameters α, β, and a determine the wave function.

3.3.1 Cusp conditions

There are three singularities that are encountered when determining the energy; when an electron approaches a proton, when two electrons approach each other and when the two nuclei approach each other. [3] The last singularity is removed by never setting s to 0. By removing the other two singularities, two parameters are fixed as

$$
a\left(1 + e^{-s/a}\right) = 1,
\tag{11}
$$

and

$$
\alpha = 2.
\tag{12}
$$

The full derivation can be found in Appendix B. This leaves only β and s to be varied in order to find the minimum energy.

3.4 Minimizer

It is assumed that the trial wave function defined by [1] has an optimal value for β, given an internuclear distance s, where the energy is minimized due to the fact that the trial wave function should describe a physical system. In order to find this optimum value for β, a steepest descent method is used.

In the following discussion α is the parameter to be minimized. The parameter is updated according to

$$
\alpha_{\text{new}} = \alpha_{\text{old}} - \gamma \left(\frac{dE}{d\alpha} \right)_{\text{old}},
\tag{13}
$$

where the factor γ can be chosen such that α converges. In this paper values of γ of 0.3 and 0.5 are

used for the minimization of the energy of the hydrogen atom and hydrogen molecule respectively. The derivative of the energy is calculated as such [1]:

$$
\frac{dE}{d\alpha} = 2 \left(\left\langle \varepsilon \frac{d\ln\Psi}{d\alpha} \right\rangle - E \left\langle \frac{d\ln\Psi}{d\alpha} \right\rangle \right),
\tag{14}
$$

where the quantities are averaged over all the walkers and an amount of displacements in the order of thousand times smaller than the displacements required for the energy calculation. This is order to be less sensitive to the local minima in the energy [4].

4 Results

4.1 Hydrogen Atom

The minimum of the local energy of the hydrogen atom can be calculated analytically. The optimal value of $\alpha = 1$ results in $\langle E \rangle = -1/2$ Hartree. In order to verify this, the VQMC simulation is done for five instances of α. This is done by using 400 walkers and 30 000 displacements. During the first 4000 displacements the system is not yet in equilibrium; the measured values during this period are not used in the calculation of $\langle E \rangle$. In order to determine the error the measured series of displacements is divided into 5 data blocks.

Tab. 1: VQMC energy of the hydrogen atom, using 400 walkers and 30 000 displacements; 4000 displacements are discarded in order to obtain equilibrium.

α	$\langle E \rangle$ [Hartree]	Error [Hartree]
0.8	-0.48084	$3.7\cdot10^{-4}$
0.9	-0.49496	$1.6\cdot10^{-4}$
1.0	-0.5	0
1.1	-0.49488	$1.3\cdot10^{-4}$
1.2	-0.47951	$3.8\cdot10^{-4}$

When the minimizer is used the value $\alpha = 0.99998$ is reached with energy $\langle E \rangle = -0.49999999 \pm 3.8 \cdot 10^{-8}$ Hartree. This shows a good convergence to the analytical values of $\alpha = 1$ and $\langle E \rangle = -1/2$ Hartree.
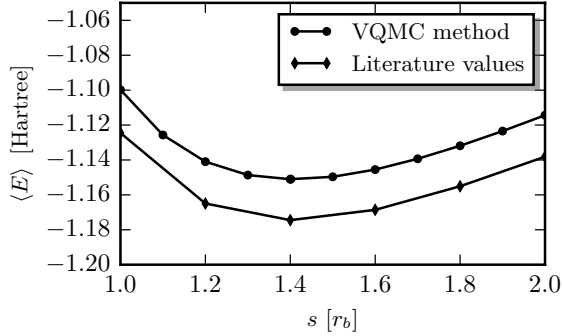
Fig. 1: The dependence of the energy $\langle E \rangle$ of the hydrogen molecule on the interatomic distance s with optimized β. Literature values adapted from [5]
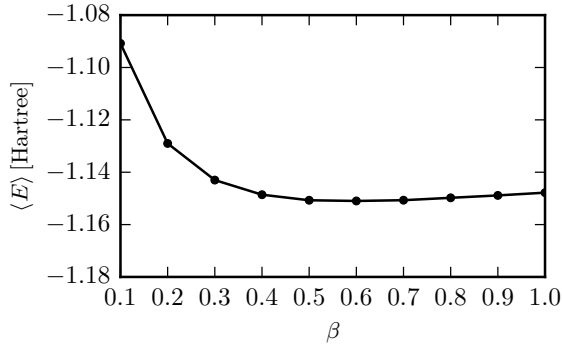

Fig. 2: A graph of the dependence of $\langle E \rangle$ of the hydrogen molecule on the parameter β with a fixed interatomic distance $s = 1.4011 \, r_b$.

4.2 Hydrogen Molecule

The energy, $\langle E \rangle$, of the hydrogen molecule is calculated over a certain range of s. Per value of s the optimal value of β is calculated using the minimization technique described in subsection 3.4. The energy is calculated with 400 walkers over 800 000 displacements. Of these displacements, the system uses the first 20 000 to reach equilibrium; measurements from these displacements are discarded. The remaining displacements are divided into 39 data blocks in order to determine the error of the measurement. The relation between the energy and the interatomic distance s is shown in Figure 1, and Table 2.

Tab. 2: VQMC energy of the hydrogen molecule, using 400 walkers and 800 000 displacements. 20000 displacements were discarded in order to obtain equilibrium

$s \; [r_b]$	$\langle E \rangle$ [Hartree]	Error [Hartree]
1.0	-1.09981	$1.2 \cdot 10^{-5}$
1.1	-1.12569	$1.2 \cdot 10^{-5}$
1.2	-1.14098	$1.4 \cdot 10^{-5}$
1.3	-1.14866	$9.0 \cdot 10^{-6}$
1.4	-1.15104	$1.3 \cdot 10^{-5}$
1.4011	-1.15110	$1.3 \cdot 10^{-5}$
1.5	-1.14965	$8.3 \cdot 10^{-6}$
1.6	-1.14550	$9.9 \cdot 10^{-6}$
1.7	-1.13933	$9.3 \cdot 10^{-6}$
1.8	-1.13187	$8.2 \cdot 10^{-6}$
1.9	-1.12346	$6.7 \cdot 10^{-6}$
2.0	-1.11438	$9.3 \cdot 10^{-6}$

From Figure 1 it can be seen that $s \simeq 1.4 \, r_b$ is the optimal value; in the literature the value of $s = 1.4011 \, r_b$ with a binding energy of -0.174475 Hartree is found with the use of computational physics [5], while an experimental value of $s = 1.3989 \, r_b$ with bond-dissociation energy -0.1645 Hartree is found in experimental data [6]. The literature values in Figure 1 are of the same shape but lower, due to the fact that vibrational energy is taken into account in [5]. Due to the Born-Oppenheimer approximation, the current research does not take the vibrational energy into account.

Even though the trial wave function was an approximation, the calculations show that it adequately matches reality. The total energy of the hydrogen molecule is found to be $\langle E \rangle = -1.15110 \pm 1.3 \cdot 10^{-5}$ Hartree. To derive the bond-dissociation energy, one has to subtract the energy of two hydrogen atoms $\langle E \rangle = -1$ Hartree (subsection 4.1) from the energy of the hydrogen molecule. The bond-dissociation energy is found to be $-0.15110 \pm 1.3 \cdot 10^{-5}$ Hartree.

To visualize the dependence of the energy of the hydrogen molecule on β at a fixed value of $s = 1.4011 \, r_b$ a plot can be seen in Figure 2. This shows that the found value of $\beta = 0.57903$ at $s = 1.4011 \, r_b$ is a good approximation of the minimum.

This figure has been produced by only discarding

the first 7000 displacements and dividing the data in 10 blocks. Due to this, the error was in the order of $1 \cdot 10^{-5}$.

5   Conclusion

In this report the bond-dissociation energy of a hydrogen molecule is determined using the variational quantum Monte Carlo method. The value of this energy is found to be $-0.15110 \pm 1.3 \cdot 10^{-5}$ Hartree. It was minimized for $\beta = 0.57903$ and $s = 1.4011 \quad r_b$. The calculated values for the bond-dissociation energy at $s = 1.4011 \, r_b$ and $\langle E \rangle = -1.15110$ Hartree are comparable to values found in the literature, i.e. $s = 1.3989 \, r_b$ and a bond-dissociation energy of -0.1645 Hartree [6]. The difference between the found value and literature value can be explained due to the fact that the wave function was approximated by a relatively simple Jastrow function.

References

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Appendices

A   Local Energy derivation

For variational Monte Carlo it is necessary to define the local energy. This section will discuss the derivation of the local energy

$$\varepsilon = \frac{\hat{H}\Psi}{\Psi}, \tag{15}$$

where Ψ is approximated for the hydrogen molecule as a product of two separate electron wave functions

$$\phi(\vec{r}) = e^{-|\vec{r} - s\hat{x}/2|/a} + e^{-|\vec{r} + s\hat{x}/2|/a}, \tag{16}$$

and a Jastrow function

$$\psi(r_{12}) = e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}}, \tag{17}$$

where $r_{12} = |\vec{r_1} - \vec{r_2}|$, and the interatomic distance s, α, β and a are variational parameters.

In the Born-Oppenheimer approximation the Hamiltonian of the system is defined as a sum of the potential and kinetic energy of the two electrons, and the interaction between the two electrons, and the two protons. The Hamiltonian therefore becomes

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{\text{ee}} + \hat{H}_{\text{pp}}, \tag{18}$$

where the separate Hamiltonians (in reduced units) are defined as

$$\begin{aligned}
\hat{H}_1 &= -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1L}} - \frac{1}{r_{1R}}, \\
\hat{H}_2 &= -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2L}} - \frac{1}{r_{2R}}, \\
\hat{H}_{\text{ee}} &= \frac{1}{r_{12}}, \\
\hat{H}_{\text{pp}} &= \frac{1}{s}.
\end{aligned} \tag{19}$$

Here r_{1L} is the notation of the position of electron 1 with respect to the left proton. The notations r_{2L}, r_{1R} and r_{2R} are analogous.

Combining this, the expression for the local energy can be written as

$$\varepsilon = \frac{\hat{H}\phi(\vec{r}_1)\phi_2(\vec{r}_2)\psi(r_{12})}{\phi(\vec{r}_1)\phi(\vec{r}_2)\psi(r_{12})}. \tag{20}$$

To evaluate this expression, first $\hat{H}_1\phi(\vec{r}_1)\phi(\vec{r}_2)\psi(r_{12})$ will be considered. Using the fact that $\phi(\vec{r}_2)$ does not depend on $\vec{r}_1$, the expression can be simplified to

$$\frac{\hat{H}_1\phi(\vec{r}_1)\phi_2(\vec{r}_2)\psi(r_{12})}{\phi(\vec{r}_1)\phi(\vec{r}_2)\psi(r_{12})} = \frac{\hat{H}_1\phi(\vec{r}_1)\psi(r_{12})}{\phi(\vec{r}_1)\psi(r_{12})}. \tag{21}$$

Only the kinetic energy part of $\hat{H}_1$ needs expansion, and using the product rule this becomes

$$\nabla_1^2[\phi_1\psi] = \phi_1\nabla_1^2\psi + 2\nabla_1\phi_1 \cdot \nabla_1\psi + \psi\nabla_1^2\phi_1, \tag{22}$$

with $\phi_1 = \phi(\vec{r}_1)$ and $\psi = \psi(r_{12})$. The derivation of the terms of Equation 22 will be done for one of the three dimensions, from which the other dimensions and final expression can be deduced. This results in the following derivations:

$$\begin{aligned}
\frac{\partial \phi_1}{\partial x_1} &= \frac{\partial}{\partial x_1}\left\{ e^{-r_{1L}/a} + e^{-r_{1R}/a} \right\} \\
&= \frac{-1}{a}\left\{ \frac{x_1 + s/2}{r_{1L}}e^{-r_{1L}/a} + \frac{x_1 - s/2}{r_{1R}}e^{-r_{1R}/a} \right\} \\
\nabla_1 \phi_1 &= \frac{-1}{a}\left\{ e^{-r_{1L}/a}\hat{r}_{1L} + e^{-r_{1R}/a}\hat{r}_{1R} \right\},
\end{aligned} \tag{23}$$

$$\begin{aligned}
\frac{\partial^2 \phi_1}{\partial x_1^2} &= \frac{\partial}{\partial x_1}\frac{-1}{a}\left\{ \frac{x_1 + s/2}{r_{1L}}e^{-r_{1L}/a} + \frac{x_1 - s/2}{r_{1R}}e^{-r_{1R}/a} \right\} \\
&= \frac{1}{a^2}\left\{ \frac{x_1 + s/2}{r_{1L}^2}e^{-r_{1L}/a} + \frac{x_1 - s/2}{r_{1R}^2}e^{-r_{1R}/a} \right\} - \\
&\qquad \frac{1}{a}\left\{ \frac{y_1^2 + z_1^2}{r_{1L}|r_{1L}|^2}e^{-r_{1L}/a} + \frac{y_1^2 + z_1^2}{r_{1R}|r_{1R}|^2}e^{-r_{1R}/a} \right\} \\
\nabla_1^2 \phi_1 &= \left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right]e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right]e^{-r_{1R}/a},
\end{aligned} \tag{24}$$

$$\begin{aligned}
\frac{\partial \psi}{\partial x_1} &= \frac{\partial}{\partial x_1}\left\{ e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}} \right\} \\
&= \frac{\psi(x_1 - x_2)}{\alpha r_{12}(1 + \beta r_{12})^2} \\
\nabla_1 \psi &= \frac{\psi \hat{r}_{12}}{\alpha(1 + \beta r_{12})^2},
\end{aligned} \tag{25}$$

$$\begin{aligned}
\nabla_1^2 \psi &= \nabla_1 \cdot \frac{\psi \hat{r}_{12}}{\alpha(1 + \beta r_{12})^2} \\
&= \nabla_1 \frac{\psi}{\alpha(1 + \beta r_{12})^2} \cdot \hat{r}_{12} + \frac{\psi \nabla_1 \cdot \hat{r}_{12}}{\alpha(1 + \beta r_{12})^2} \\
\frac{\partial}{\partial x_1}\left[\frac{\psi}{\alpha(1 + \beta r_{12})^2} \right] &= \frac{\frac{\partial \psi}{\partial x_1}\alpha(1 + \beta r_{12})^2 - \psi\frac{\partial}{\partial x_1}(\alpha(1 + \beta r_{12})^2)}{\alpha^2(1 + \beta r_{12})^4} \\
&= \frac{\psi(x_1 - x_2)(1 - 2\alpha\beta(1 + \beta r_{12}))}{r_{12}\alpha^2(1 + \beta r_{12})^4} \\
\nabla_1\left[\frac{\psi}{\alpha(1 + \beta r_{12})^2} \right] &= \frac{\psi(1 - 2\alpha\beta(1 + \beta r_{12}))\hat{r}_{12}}{r_{12}\alpha^2(1 + \beta r_{12})^4} \\
\nabla_1^2 \psi &= \frac{\psi(1 - 2\alpha\beta(1 + \beta r_{12}))}{r_{12}\alpha^2(1 + \beta r_{12})^4} + \frac{2\psi}{r_{12}\alpha(1 + \beta r_{12})^2} \\
&= \frac{\psi(2\alpha + r_{12}(1 + 2\alpha\beta))}{r_{12}\alpha^2(1 + \beta r_{12})^4}.
\end{aligned} \tag{26}$$

Combining these results and working out the dot product between $\nabla_1 \psi$ and $\nabla_1 \phi_1$ results in

$$\begin{aligned}
\nabla_1^2[\phi_1 \psi] &= \phi_1 \frac{\psi(2\alpha + r_{12}(1 + 2\alpha\beta))}{r_{12}\alpha^2(1 + \beta r_{12})^4} - \frac{2\psi \hat{r}_{12}}{a\alpha(1 + \beta r_{12})^2} \cdot [\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}] \\
&\quad + \psi\left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right]e^{-r_{1L}/a} + \psi\left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right]e^{-r_{1R}/a}.
\end{aligned} \tag{27}$$

Similarly,

$$\nabla_2^2[\phi_2\psi] = \phi_1 \frac{\psi(2\alpha + r_{12}(1+2\alpha\beta))}{r_{12}\alpha^2(1+\beta r_{12})^4} + \frac{2\psi\hat{r}_{12}}{a\alpha(1+\beta r_{12})^2} \cdot [\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}]$$
$$+ \psi\left[\frac{1}{a^2} - \frac{2}{ar_{2L}}\right]e^{-r_{2L}/a} + \psi\left[\frac{1}{a^2} - \frac{2}{ar_{2R}}\right]e^{-r_{2R}/a}. \tag{28}$$

Combining Equations 19 to 28 results in an expression for the local energy

$$\varepsilon = -\frac{1}{a^2} - \frac{2\alpha + r_{12}(1+2\alpha\beta)}{\alpha^2 r_{12}(1+\beta r_{12})^4} + \frac{\hat{r}_{12}}{\alpha a(1+\beta r_{12})^2} \cdot \left\{\frac{\phi_{1L}}{\phi_1}\hat{r}_{1L} + \frac{\phi_{1R}}{\phi_1}\hat{r}_{1R} - \frac{\phi_{2L}}{\phi_2}\hat{r}_{2L} - \frac{\phi_{2R}}{\phi_2}\hat{r}_{2R}\right\}$$
$$+ \frac{1}{a\phi_1}\left(\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}}\right) + \frac{1}{a\phi_2}\left(\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}}\right) - \left\{\frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}}\right\} + \frac{1}{r_{12}} + \frac{1}{s}, \tag{29}$$

and in more compact notation

$$\varepsilon = -\frac{1}{a^2} - \frac{2\alpha + r_{12}(1+2\alpha\beta)}{\alpha^2 r_{12}(1+\beta r_{12})^4} + \sum_{\substack{i\in\{1,2\}\\j\in\{L,R\}}}\left(\frac{\phi_{ij}}{a\phi_i r_{ij}} - \frac{1}{r_{ij}}\right)$$
$$+ \frac{1}{r_{12}} + \frac{1}{s} + \frac{\hat{r}_{12}}{\alpha a(1+\beta r_{12})^2} \cdot \sum_{j\in\{L,R\}}\left(\frac{\phi_{1j}\hat{r}_{1j}}{\phi_1} - \frac{\phi_{2j}\hat{r}_{2j}}{\phi_2}\right). \tag{30}$$

B   Cusp conditions

From Equation 29 it can be seen that the local energy diverges when one of the electrons goes near a proton, when the two electrons approach each other, or when the two protons approach each other. In order to counteract this, parameters are chosen in such a way that in these limits, the total energy converges to 0. For parameter s it is simple; s is not chosen to be 0 when varying s. For the other limits, the energy is set to 0.

B.1   Electron approaches a proton

The first case discussed is when electron 1 approaches the left proton. It can be easily shown that the other cases will give the same constraints for the parameters.

$$\lim_{r_{1L}\to 0}\hat{H}\phi_1 = 0 \tag{31}$$

The relevant parts of the Hamiltonian for this limit are addressed and the following constraints are found:

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1L}}\right]\phi_1 = 0$$
$$\frac{-1}{2}\left\{\left[\frac{1}{a^2} - \frac{2}{ar_{1L}}\right]e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}}\right]e^{-r_{1R}/a}\right\} - \frac{\phi_1}{r_{1L}} = 0. \tag{32}$$

In this limit, the ϕ_1/r_{1L} term has to be cancelled by the rest of the equation. This leads to

$$\frac{e^{-r_{1L}/a}}{ar_{1L}} = \frac{\phi_1}{r_{1L}} \tag{33}$$

in this limit. Now, a can be chosen in such a way that this equality always holds. This corresponds to the following equation

$$
\begin{aligned}
a &= \lim_{r_{1L} \to 0} \frac{e^{-r_{1L}/a}}{\phi_1} \\
&= \frac{1}{1 + e^{-s/a}}.
\end{aligned}
\tag{34}
$$

B.2   Electron approaches electron

The case when an electron approaches an electron can be solved by setting the Hamiltonian to 0 when r_{12} approaches 0. This means that

$$
\begin{aligned}
\lim_{r_{12} \to 0} \hat{H}\psi &= 0 \\
\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_1^2 + \frac{1}{r_{12}} \right] \psi &= 0
\end{aligned}
\tag{35}
$$

It can be shown that the kinetic energy for electron 1 and 2, due to the Jastrow factor, are the same and equal to

$$
-\frac{1}{2}\nabla_1^2 \psi = -\frac{1}{2}\nabla_2^2 \psi = -\frac{1}{2} \frac{2\alpha + r_{12}(1 + 2\alpha\beta)\psi}{\alpha^2 r_{12}(1 + \beta r_{12})^4}
\tag{36}
$$

Enforcing the equality of Equation 35 in the limit of $r_{12} \to 0$ leads to

$$
\begin{aligned}
\lim_{r_{12} \to 0} -\nabla_1^2 \psi + \frac{\psi}{r_{12}} &= 0 \\
\lim_{r_{12} \to 0} \frac{1}{r_{12}} &= \frac{\nabla_1^2 \psi}{\psi} \\
&= \frac{2\alpha + r_{12}(1 + 2\alpha\beta)\psi}{\alpha^2 r_{12}(1 + \beta r_{12})^4} \\
&= \frac{2\alpha}{\alpha^2 r_{12}}
\end{aligned}
\tag{37}
$$

This leads to the Coulomb cusp condition

$$
\alpha = 2
\tag{38}
$$