

# Calculation of the Ground State Energy of Hydrogen using Quantum Monte Carlo Methods

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In this paper the ground state energy of a hydrogen molecule is estimated in the Born-Oppenheimer approximation using variational quantum Monte Carlo and diffusion quantum Monte Carlo methods. The first method leads to a binding energy the hydrogen molecule of  $(3.917 \pm 0.004)$  eV, while the second method leads to a binding energy of  $(4.518 \pm 0.002)$  eV, which is very close to the experimental value. This shows that the diffusion Monte Carlo method leads to an accurate estimate for the ground state energy for this particular physical system.

## I. INTRODUCTION

In quantum mechanics, the time evolution of the state of a system is completely described by the Schrödinger equation. The hydrogen atom has always served as a test case for quantum theory, since it is a simple physical system containing interaction potentials between different particles. It consists of one positively charged proton and one negatively charged electron, interacting via the Coulomb potential. The Schrödinger equation admits an analytical solution for this simple case, which leads to predictions of the energy-levels of the hydrogen atom, which resemble experimental results closely.

One might think that since the Schrödinger equation correctly describes the evolution of every (non-relativistic) system, we can easily find the ground state energies and wave functions of every physical system we can imagine. This is definitely not the case. In fact, the hydrogen atom is one of the very few systems which can be solved analytically. In this project we consider a hydrogen molecule, a system which consists of two protons and two electrons, interacting via the Coulomb potential. This system is already too complex to solve the Schrödinger equation analytically. It is therefore that we need the aid of a computer to get insight into properties of the system, such as the ground state energy.

In this paper, we approximate the ground state energy of the hydrogen molecule using two quantum Monte Carlo methods: the Variational Monte Carlo method and the Diffusion Monte Carlo method. Monte Carlo methods are a broad class of computational techniques which invoke any form of random sampling. In section II, we give a description of the physical system and the two Monte Carlo methods. In section III we give the results to which these computational methods lead and compare them with experimental values.

## II. THEORY & METHOD

### A. Hydrogen Molecule

In this paper the ground state energy  $E_g$  of the hydrogen molecule is estimated in the Born-Oppenheimer (BO) approximation. In this approximation the wave function of the molecule is separated in its electronic and nuclear components. Therefore we can estimate the electronic ground state energy for a fixed nuclear separation  $s$ . This is justified by the fact that the timescale for nuclear processes is much longer than for electronic processes. The electronic configuration will rapidly adapt to a given nuclear separation. For this reason we examine the Hamiltonian of the system for a fixed  $s$ , which is in natural units given by

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

where  $r_{1L}$  ( $r_{1R}$ ) is the distance between the first electron and the left (right) nucleus and  $r_{2L}$  ( $r_{2R}$ ) is the distance between the second electron and the left (right) nucleus.  $r_{12}$  is the distance between the electrons. This Hamiltonian contains four attractive Coulomb interactions, between the electrons and the nuclei, and two repulsive Coulomb interactions, between the pair of electrons and the pair of protons. In the BO approximation this Hamiltonian does not contain the kinetic energy of the nuclei, which is justified by the fact that the proton mass is much larger than the electron mass.

In the natural units used in Eq. 1, lengths are measured in units of Bohr radius  $a_0 = \hbar^2/(m_e k e^2) = 0.529 \text{ \AA}$ , where  $k$  is Coulomb's constant. The natural unit of energy (atomic units a.u) is given by  $(k e^2)^2/a_0 = 27.2 \text{ eV}$ .

Two approaches are used to determine the smallest eigenvalue of this Hamiltonian: Variational

Monte Carlo (VMC, Section IIB) and Diffusion Monte Carlo (DMC, Section IIC). In VMC, a trial wave function is used to estimate  $E_g$ . Consequently, using DMC, we allow the system to vary from the optimal trial wave function which is established using VMC. The result of this simulation can be used to determine the quality of the VMC result.

## B. Variational Monte Carlo

The first method that is considered is the VMC method. It is based on the variational method for finding the ground state energy  $E_g$  of a system whose evolution is governed by the Hamiltonian  $\hat{H}$ . The idea of the variational method is as follows: Use a trial wavefunction  $\Psi_\alpha$  with a certain set of parameters  $\alpha$  as a guess for the true ground state wave function of the system. Since

$$\langle E \rangle = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \geq E_g \quad (2)$$

is valid for every  $\Psi_\alpha$ , we find an upper bound for the ground state energy of the system [1]. By minimizing the expectation value over the parameters  $\alpha$ , we try to find the lowest upper bound possible.

For an arbitrary (real) trial function  $\psi_T(R)$ , where  $R$  is a certain configuration of the system, we can define the local energy

$$E_L(R) = \frac{\hat{H}\psi_T(R)}{\psi_T(R)}. \quad (3)$$

Note that if  $\psi_T$  is an eigenstate of the Hamiltonian, then  $E_L$  is constant and equal to the energy of this state.

Rewriting Eq. 2 using the local energy gives

$$\begin{aligned} \langle E \rangle &= \frac{\int dR \psi_T(R) \hat{H} \psi_T(R)}{\int dR \psi_T^2(R)} \\ &= \int dR \rho(R) E_L(R). \end{aligned} \quad (4)$$

We now see that we can use the Metropolis method with sampling distribution

$$\rho(R) = \frac{\psi_T^2(R)}{\int dR' \psi_T^2(R')},$$

to approximate this integral. The combination of the variational method with the Metropolis method is called VMC. For the Metropolis method the stepsize  $d = 0.6$  has been chosen, such that approximately half of the steps are accepted. The complete algorithm is given in Algorithm 1.

### 1. Trial Wave Function

It is clear that the choice of the trial wave function is important for the upper bound which is obtained. It requires physical insight to guess good trial wave functions. For the hydrogen molecule, the Hamiltonian is given by Eq. 1. The variational wavefunction is chosen to be

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (5)$$

where

$$\begin{aligned} \phi(\mathbf{r}_1) &= e^{-r_{1L}/a} + e^{-r_{1R}/a} = \phi_{1L} + \phi_{1R} \\ \phi(\mathbf{r}_2) &= e^{-r_{2L}/a} + e^{-r_{2R}/a} = \phi_{2L} + \phi_{2R} \\ \psi(\mathbf{r}_1, \mathbf{r}_2) &= \exp \left[ \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{\alpha(1 + \beta|\mathbf{r}_1 - \mathbf{r}_2|)} \right] \end{aligned}$$

and  $\mathbf{r}_1$  ( $\mathbf{r}_2$ ) is the position of the first (second) electron.

Since we are looking at a system with two fixed protons, the function  $\phi$  is the sum of two wavefunctions which resemble the ground state wavefunction of hydrogen atom and contain a parameter  $a$ . For the two electrons in the system, we take the product of these functions  $\phi$ . The interaction of the two electrons is captured in the function  $\psi$ , the Jastrow function, which depends on the distance  $r_{12}$  between the electrons and the free parameters  $\alpha$  and  $\beta$ . By using this trial wavefunction, a singlet spin configuration is anticipated, as Eq. 5 is symmetric under the exchange of the two electrons.

The local energy (Eq. 3) for this trial wavefunction is given in Appendix A. It depends on the four parameters  $s, a, \alpha$  and  $\beta$ . It turns out that we can remove two of these four parameters by imposing the so-called Coulomb cusp conditions. These conditions make sure that the local energy  $E_L$  does not diverge as two electrons approach each other, or as one of the electrons approaches a proton. The calculations (Appendix A) lead to the conditions

$$\begin{aligned} a(1 + e^{-s/a}) &= 1 \\ \alpha &= 2. \end{aligned} \quad (6)$$

### 2. Optimizing over $\beta$

The previous subsection leaves us with two free parameters in the trial wavefunction. The parameter  $\beta$  is varied for fixed  $s$  such that the lowest expectation value of the energy as a function of separation can be determined.  $\beta$  is optimized using a damped steepest descent method:

$$\beta_{new} = \beta_{old} + \gamma \left( \frac{dE}{d\beta} \right)_{old} \quad (7)$$

In this project, the value  $\gamma = 5$  was chosen.  $dE/d\beta$  is estimated using [2]

$$\left\langle \frac{dE}{d\beta} \right\rangle = 2 \left( \left\langle E_L \frac{d \ln \psi_T}{d\beta} \right\rangle - E \left\langle \frac{d \ln \psi_T}{d\beta} \right\rangle \right). \quad (8)$$

The minimization procedure is stopped after several iterations. We summarize the algorithm used for the Variational Monte Carlo method [3]:

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**Algorithm 1** Variational Monte Carlo

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1:  $\beta = \beta_0$ 
2: repeat
3:   Put N walkers at random positions
4:   for each step do
5:     for each walker do
6:       Shift walker to new position  $R'$  in
         configuration space by taking
         random steps with maximum
         stepsize  $d$ 
7:       Calculate  $p = \psi_T^2(R')/\psi_T^2(R)$ ,
         where  $R$  is the old position.
8:       if  $p < 1$  then
9:         Accept position with probability  $p$ 
10:      else
11:        Accept position
12:      end if
13:    end for
14:    Calculate energy based on local energy and
      the position of the walkers (Eq. 4)
15:  end for
16:  Update  $\beta = \beta + \gamma \left( \frac{dE}{d\beta} \right)_{old}$ 
17: until finished

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### C. Diffusion Monte Carlo

When comparing the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (9)$$

with the Fokker-Planck equation for a diffusion process of a density  $\rho$  with a diffusion constant  $D$

$$\frac{\partial \rho}{\partial t} = D \nabla \cdot (\rho \nabla V + \nabla \rho), \quad (10)$$

it can be noted that these two equations are equivalent if a Wick rotation is performed ( $\tau = it$ ) and  $\Psi = \rho \exp(V/2)$  is substituted [4]. This similarity is exploited in the DMC, where a diffusion process is simulated to determine  $E_g$  for the system governed by Eq. 9. The basic procedure is explained in [3] and an overview will be given below.

The kinetic energy contribution of the Hamiltonian is incorporated by displacing the walkers from a position  $R$  to a new position  $R'$  with a random number drawn from a normal distribution with  $\sigma = \sqrt{dt}$ . We note that for each walker,  $R$  is a six-dimensional vector as it contains the position of two electrons.

Subsequently, the potential energy  $V(R')$  at the new position is calculated. We then evaluate the parameter  $t = \exp(-dt[V(R') - E_T]) + U[0, 1]$ , where  $E_T$  is our best estimate of the ground state energy and  $U[0, 1]$  is a number drawn from a uniform distribution between 0 and 1. The potential energy of the Hamiltonian is taken into account by the annihilation or creation of walkers at the position  $R'$  based on the integer part of  $t$ : if  $[t] = 0$  the walker is deleted, else  $[t]$  walkers are created.

In the next iteration  $E_T$  is updated using

$$E_T = E_0 + \alpha \ln \left( \frac{\tilde{N}}{N} \right), \quad (11)$$

where  $\tilde{N}$  is the desired number of walkers,  $N$  is the actual number of walkers and  $\alpha$  is a small parameter. After many iterations  $E_T$  should converge to the ground state energy. In a first simulation,  $\alpha = 0.1$  is used to get a rough estimate of  $E_g$ . Based on this estimate the results shown in section III were obtained with  $\alpha = 0.01$  and  $dt = 0.05$ .

#### 1. Guide function

Guide functions can be used in DMC for two reasons. First, the use of a guide function can solve problems caused by the divergence of the potential function. Furthermore, a well chosen guide function can decrease the convergence time of the algorithm.

In the DMC simulations the optimal trial wave functions (Eq. 5 for the optimal  $\beta$  found with VMC) were used as guide function. The use of a guide function can be incorporated in the protocol by changing the potential  $V$  in the local energy (Eq. 3). If a suitable guide function is used, then the local energy is much flatter then the original potential and the divergences are removed.

Compared with the DMC method without guide functions, the displacement of the walkers has to be changed. In addition to the displacement according to the normal distribution, the walkers are displaced over a distance  $\mathbf{F}dt/2$ , with  $\mathbf{F} = 2\nabla \Psi_T(R)/\Psi_T(R)$ . For the guide wave function, the six-dimensional force is given by:

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{bmatrix} \quad (12)$$

$$\mathbf{F}_1 = -\frac{2}{a\phi_1} [e^{\frac{-r_{1L}}{a}} \hat{r}_{1L} + e^{\frac{-r_{1R}}{a}} \hat{r}_{1R}] + \frac{\hat{r}_{12}}{(1 + \beta r_{12})^2}$$

$$\mathbf{F}_2 = -\frac{2}{a\phi_2} [e^{\frac{-r_{2L}}{a}} \hat{r}_{2L} + e^{\frac{-r_{2R}}{a}} \hat{r}_{2R}] - \frac{\hat{r}_{12}}{(1 + \beta r_{12})^2}$$

### 2. Correct for time step error

In the DMC calculations, time step errors were corrected by a Metropolis procedure. This is done by accepting the displacement with a probability[3]

$$p = \min \left( 1, \frac{T_{dt}(R' \rightarrow R) \Psi_T(R')^2}{T_{dt}(R \rightarrow R') \Psi_T(R)^2} \right), \quad (13)$$

where

$$T_{dt}(R \rightarrow R') = \frac{1}{\sqrt{2\pi dt}} e^{-[R' - R - \mathbf{F}(R)dt/2]^2 / (2dt)}$$

We summarize the algorithm used for the Diffusion Monte Carlo Approach [3]:

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#### Algorithm 2 Diffusion Monte Carlo

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- 1: Put N walkers at random positions
  - 2: **for** each step **do**
  - 3:   **for** each walker **do**
  - 4:     Calculate force and local energy at the old position R.
  - 5:     Calculate new walker position  $R'$  by taking random steps according to a  $N(0, \sqrt{dt})$  distribution and by moving over a distance  $\mathbf{F}dt/2$ .
  - 6:     Calculate force and local energy at the new position  $R'$
  - 7:     Accept according to Eq. 13
  - 8:     **if** Accept **then**
  - 9:       Evaluate  $[t]$
  - 10:      **if**  $[t] = 0$  **then**
  - 11:       Delete walker
  - 12:      **else**
  - 13:       Create  $[t]$  walkers at  $R'$
  - 14:      **end if**
  - 15:    **end if**
  - 16:   **end for**
  - 17:   Update  $E_T$  according to Eq. 11
  - 18: **end for**
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### III. RESULTS

To obtain the VMC results, an optimization over  $\beta$  was performed. This is illustrated in Fig.

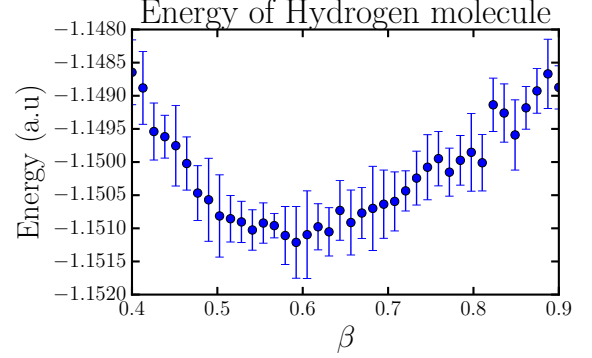


FIG. 1: Energy as a function of  $\beta$  for fixed  $s = 1.4a_0$ . 1000 walkers were simulated for 40000 timesteps after 1000 initialization steps. Errorbars were obtained from datablocking with blocksize 4000.

1, where the energy is plotted against  $\beta$  for fixed separation.

In Fig. 2 the ground state energy found using both the VMC and DMC method are plotted as a function of the proton separation  $s$ . For both methods, the optimal separation is found to be  $s \approx 1.41 a_0 = 0.75 \text{ \AA}$ , which matches well the experimental value of  $0.74 \text{ \AA}$  very well. [5].

For each value of  $s$  the ground state energy obtained using DMC is lower than found using VMC. This can be explained by the fact that in DMC the wavefunction can vary from the guide wave-

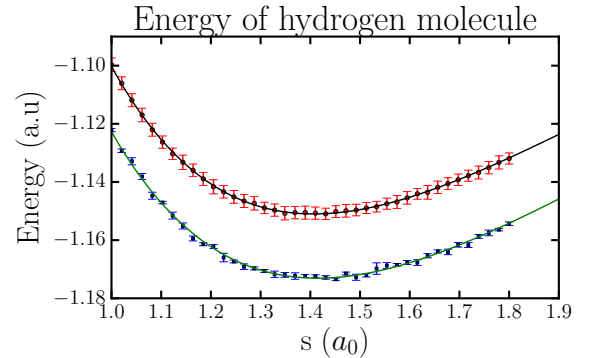


FIG. 2: Ground state energy found using VMC method for optimal  $\beta$  (red) and DMC method (blue). Errorbars depict the variance found using datablocking [3]. For VMC, 400 walkers were first initialized for 1000 timesteps. Then 40000 steps were simulated and divided into blocks of size 400 for datablocking. For DMC, 1000 walkers and 10 blocks of 1000 steps were used after 1000 initialization steps. The solid line indicates a fit to the Morse potential (Eq. 14). The fit parameters are listed in Table I.

TABLE I: Table with fit parameters for Fig. 2.

	VMC	DMC
$D_e$ (a.u.)	$0.151 \pm 6 \cdot 10^{-5}$	$0.173 \pm 1 \cdot 10^{-4}$
$s_e$ ( $a_0$ )	$1.41 \pm 6.6 \cdot 10^{-4}$	$1.41 \pm 1.6 \cdot 10^{-3}$
$a$ ( $a_0^{-1}$ )	$1.12 \pm 2.6 \cdot 10^{-3}$	$1.04 \pm 6 \cdot 10^{-3}$

function, and by doing so it can lower its energy, whereas in VMC the energy corresponding to a fixed trial wave function is determined.

So far the vibrational energy of the nuclei has not been taken into account. However, we should add the vibrational zero-point energy to the obtained result to find the dissociation energy  $D_0$ . This can be taken into account by fitting the Morse potential to acquired results

$$V(s) = D_e((1 - e^{-a(s-s_e)})^2 - 1) - 1, \quad (14)$$

where  $D_e$  is the well depth,  $s_e$  is the equilibrium distance and  $a$  defines the width of the potential [6]. The constant offset  $-1$  makes sure that the energy goes to  $-1$  for  $s$  large, which corresponds to the energy of two isolated, non-interacting hydrogen atoms. The spectrum of the Morse potential can be solved exactly. Based on the fit in Fig. 2 the vibrational zero-point energy can be calculated, which results in  $E_{vibr,0} \approx 0.0071$  a.u. = 0.19 eV for both cases

The dissociation energy can be calculated by subtracting this contribution from the fit parameter  $D_e$ . For VMC this results in  $(0.144 \pm 6 \cdot 10^{-6})$  a.u. =  $(3.917 \pm 0.004)$  eV, whereas for DMC

$(0.166 \pm 1 \cdot 10^{-4})$  a.u. =  $(4.518 \pm 0.002)$  eV is found. The DMC result is very close to the experimental value of 0.165 a.u. = 4.47 eV. [7].

The final total energy of the system calculated using VMC, is higher than the true ground state energy, as anticipated. The ground state energy found using the DMC simulation is much more accurate than the value found using VMC.

#### IV. CONCLUSION

In this paper the ground state energy of the hydrogen molecule has been approximated using Diffusion Quantum Monte Carlo and Variational Quantum Monte Carlo methods. Using both methods the equilibrium separation  $s \approx 1.41 a_0 \approx 0.75 \text{ \AA}$  was found, which is close to the experimental value of 0.74  $\text{\AA}$ .

By varying the value of  $\beta$  in the trial wave function for every separation an estimate of the energy could be found which deviates from both experimental values and other results. The optimal trial wavefunction is however very important for the DMC simulations, where it serves as guide wavefunction.

The ground state energy found using DMC is always lower than the value found using VMC, since in DMC the wavefunction is allowed to deviate from the guide wavefunction. If the zero-point vibrational energy of the nuclei is taken into account, then a dissociation energy of  $(0.166 \pm 1 \cdot 10^{-4})$  a.u. =  $(4.518 \pm 0.002)$  eV is found, which is very close to the experimental value of 0.165 a.u. = 4.47 eV.

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## Appendix A LOCAL ENERGY AND COULOMB CUSP CONDITION

In this section we would like to determine the local energy (Eq. 3) for the trial wavefunction given by equation 5 and the Hamiltonian given by equation ???. The local energy can be written as as

$$\begin{aligned} E_L(R) &= \frac{1}{\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2)} \hat{\mathcal{H}} \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{1}{\phi(\mathbf{r}_1)\psi(\mathbf{r}_1, \mathbf{r}_2)} \hat{\mathcal{H}}_1 \phi(\mathbf{r}_1)\psi(\mathbf{r}_1, \mathbf{r}_2) + \frac{1}{\phi(\mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2)} \hat{\mathcal{H}}_2 \phi(\mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2) + \frac{1}{r_{12}} + \frac{1}{s}, \end{aligned}$$

where  $\hat{\mathcal{H}}_1 = \nabla_1^2/2 + 1/r_{1L} + 1/r_{1R}$  and likewise for  $\hat{\mathcal{H}}_2$ . Using that

$$\begin{aligned} \frac{1}{\phi(\mathbf{r}_1)\psi(\mathbf{r}_1, \mathbf{r}_2)} \hat{\mathcal{H}}_1 \phi(\mathbf{r}_1)\psi(\mathbf{r}_1, \mathbf{r}_2) &= \\ - \frac{1}{2\phi(\mathbf{r}_1)\psi(\mathbf{r}_1, \mathbf{r}_2)} (\phi(\mathbf{r}_1)\nabla_1^2\psi(\mathbf{r}_1, \mathbf{r}_2) + 2\nabla_1\phi(\mathbf{r}_1) \cdot \nabla_1\psi(\mathbf{r}_1, \mathbf{r}_2) + \psi(\mathbf{r}_1, \mathbf{r}_2)\nabla_1^2\phi(\mathbf{r}_1)) &- \frac{1}{r_{1L}} - \frac{1}{r_{1R}}, \end{aligned}$$

and likewise for  $\hat{\mathcal{H}}_2$ , it can be shown that the local energy is given by

$$\begin{aligned} E_L(R) &= -\frac{1}{a^2} + \frac{1}{a\phi(\mathbf{r}_1)} \left( \frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right) + \frac{1}{a\phi(\mathbf{r}_2)} \left( \frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right) - \frac{1}{r_{1L}} - \frac{1}{r_{1R}} - \frac{1}{r_{2L}} - \frac{1}{r_{2R}} + \frac{1}{r_{12}} + \frac{1}{s} \\ &+ \left( \frac{\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}}{\phi(\mathbf{r}_1)} - \frac{\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}}{\phi(\mathbf{r}_2)} \right) \cdot \frac{\hat{r}_{12}}{\alpha a(1 + \beta r_{12})^2} - \frac{(2\alpha\beta + 1)r_{12} + 2\alpha}{\alpha^2(1 + \beta r_{12})^4 r_{12}}. \end{aligned} \quad (\text{A.1})$$

The potential energy diverges when the two electrons approach each other and when an electron approaches a proton. Therefore the conditions on the parameters in the trial wave function are determined such that the local energy does not diverge. These conditions are called the Coulomb cusp conditions.

Let us for example investigate what happens when  $r_{1L} \rightarrow 0$ . In that case, two contributions in the local energy diverge. Those two contributions cancel if  $a(1 + \exp(-s/a)) = 1$ . This is the first Coulomb cusp condition.

In addition it is necessary to look at what happens if  $r_{12} \rightarrow 0$ . In that case the last term in Eq. A.1 should cancel against the  $1/r_{12}$  contribution. This happens if  $\alpha = 2$ , which gives the second condition.