

Variational QMC

Variational QMC for the Hydrogen molecule

Quantum problems provide an added complexity for Monte Carlo methods and many approaches have been developed. Here we use the variational method where we use a wavefunction form that is inspired by the physics and minimize the energy with respect to the parameters in the wavefunction. This approach requires good physical insight to find a good variational form for the wavefunction. This is possible for the Hydrogen molecule (and many other molecules) where we know the basic structure of the electronic orbitals.

The mathematical form seems simple: we write a variational wavefunction Ψ and we find the energy

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad \text{where } E \geq E_G \quad (1)$$

where E_G is the ground state energy of the molecule. Of course we get equality if we find the exact ground state. All other wavefunctions give higher energy - this is the variational principle.

The Hamiltonian of the Hydrogen molecule, in the Born-Oppenheimer approximation where we assume that the nuclear motion is negligible, includes the kinetic and potential energies of the two electrons as well as their interaction. The positions of the two atomic nuclei are assumed to be symmetrically located and on the x-axis at positions $-s/2, s/2$. The nuclei are thus a distance s apart. The positions of the two electrons are \vec{r}_1 and \vec{r}_2 . The Hamiltonian is then

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \left[\frac{ke^2}{|\vec{r}_1 + \frac{s}{2}\hat{i}|} + \frac{ke^2}{|\vec{r}_1 - \frac{s}{2}\hat{i}|} + \frac{ke^2}{|\vec{r}_2 + \frac{s}{2}\hat{i}|} + \frac{ke^2}{|\vec{r}_2 - \frac{s}{2}\hat{i}|} \right] + \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \quad (2)$$

where the first part is the kinetic energy of the two electrons, the second part (square brackets) is the four attraction terms between the two electrons and the two nuclei and the last term is the Coulomb repulsion between the two electrons. It is useful to introduce atomic units where lengths are in units of the Bohr radius,

$$a_0 = \frac{\hbar^2}{m_e k e^2} = 0.529 \text{ \AA} \quad (3)$$

The unit of energy is twice the ionization energy of the Hydrogen atom,

$$E = \frac{(ke^2)^2}{a_0} = 27.2eV \quad (4)$$

With these units the Hamiltonian is

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left[\frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}} \right] + \frac{1}{|r_{12}|} \quad (5)$$

where

$$\vec{r}_{1L} = \vec{r}_1 + \frac{s}{2}\hat{i}; \quad \vec{r}_{1R} = \vec{r}_1 - \frac{s}{2}\hat{i}, \quad (6)$$

$$\vec{r}_{2L} = \vec{r}_2 + \frac{s}{2}\hat{i}; \quad \vec{r}_{2R} = \vec{r}_2 - \frac{s}{2}\hat{i}, \quad (7)$$

and

$$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2 \quad (8)$$

It is useful to break the Hamiltonian up into two non-interacting Hamiltonians plus the interaction term,

$$H = H_1 + H_2 + H_{ee} \quad (9)$$

where,

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1L}} - \frac{1}{r_{1R}}; \quad H_2 = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2L}} - \frac{1}{r_{2R}}; \quad H_{ee} = \frac{1}{r_{12}} \quad (10)$$

The variational wavefunction is chosen to be,

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2) \quad (11)$$

where

$$\phi(\vec{r}_1) = e^{-r_{1L}/a} + e^{-r_{1R}/a} = \phi_{1L} + \phi_{1R} \quad (12)$$

and

$$\phi(\vec{r}_2) = e^{-r_{2L}/a} + e^{-r_{2R}/a} = \phi_{2L} + \phi_{2R}. \quad (13)$$

The key new thing here is the assumption of a form for the interaction term ψ . A form that is very useful is (see Jos Thijssen's book, Equation 12.9 of the first edition), the Jastrow function,

$$\psi(\vec{r}_1, \vec{r}_2) = \exp\left[\frac{|\vec{r}_1 - \vec{r}_2|}{\alpha(1 + \beta|\vec{r}_1 - \vec{r}_2|)}\right] \quad (14)$$

The first step is to find convenient expressions for the energy E given above using the variational wavefunction and Hamiltonian above. This is quite laborious but interesting exercise. The resulting expressions are six dimensional integrals in the electron co-ordinates \vec{r}_1 and \vec{r}_2 . The MC part of the project is to use a diffusion method to approximate these integrals.

The method should be carried out to find the energy E as a function of the interatomic separation s to find the ground state size of the hydrogen molecule. The electron density minus the electron density of the non-interacting H atoms at the same separation should also be plotted to illustrate the effect of the e-e Coulomb repulsion on the electronic configuration and compare with [1] below.

It is convenient to introduce the weight,

$$\omega(\vec{r}_1, \vec{r}_2, s) = \frac{\Psi^2(\vec{r}_1, \vec{r}_2, s)}{\langle \Psi | \Psi \rangle} \quad (15)$$

and the local energy,

$$\epsilon(\vec{r}_1, \vec{r}_2, s) = \frac{H\Psi(\vec{r}_1, \vec{r}_2, s)}{\Psi(\vec{r}_1, \vec{r}_2, s)} \quad (16)$$

so that,

$$E = \int d^3r_1 \int d^3r_2 \omega(\vec{r}_1, \vec{r}_2, s) \epsilon(\vec{r}_1, \vec{r}_2, s) \quad (17)$$

There are at this point four parameters in the variational problem: s, a, α, β . We can remove one of two of them by using the so-called Coulomb cusp conditions. These are required to ensure that there is no singularity in the energy when either electron approaches either proton, or when the two electrons are at the same position. The four cases of an electron approaching a proton lead to the same condition $a(1 + e^{-s/a}) = 1$, while the case of two electrons approaching each other lead to the condition $\alpha = 2$ (See Appendix A).

We use a Monte Carlo method that does not require the normalization $\langle \Psi | \Psi \rangle$, however we need an expression for $\epsilon(\vec{r}_1, \vec{r}_2, s)$. This is a bit tedious and leads to (see the Appendix B)

$$\begin{aligned} \epsilon = & -\frac{1}{a^2} + \frac{1}{a\phi_1} \left(\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right) + \frac{1}{a\phi_2} \left(\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right) - \left[\frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}} \right] + \frac{1}{|r_{12}|} \\ & + \left(\frac{\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}}{\phi_1} - \frac{\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}}{\phi_2} \right) \cdot \frac{\hat{r}_{12}}{2a(1 + \beta r_{12})^2} - \frac{(4\beta + 1)r_{12} + 4}{4(1 + \beta r_{12})^4 r_{12}} \end{aligned} \quad (18)$$

The algorithm

The algorithm consists of starting with random positions of the electrons \vec{r}_1, \vec{r}_2 with their associated value for $\Psi^2(\vec{r}_1, \vec{r}_2, s)$. Then,

1. Randomly move the two positions to locations \vec{r}'_1, \vec{r}'_2 .
2. If $\frac{\Psi'^2}{\Psi^2} > \text{Random Number}$ accept the move

3. Return to 1. Warm up for around 10000 steps and average the energy ϵ for millions of steps.

Note that there are two parameters remaining in the variational calculation, β and s . You need to calculate for a range of values of these parameters and find the minimum - that is the estimate of the energy of the Hydrogen molecule. If you subtract the energy of the two separated Hydrogen atoms from it (energy -1 in our normalized units), you get the binding energy of the Hydrogen molecule. Compare that and the bond length at the lowest energy state with the literature values. In your report you need to provide the details of the Coulomb Cusp and energy (ϵ) calculations.

[1] L. Wolniewicz. Nonadiabatic energies of the ground state of the hydrogen molecule J. Chem. Phys. 103, 1792 (1995).

A. Coulomb cusp conditions

(i) *Electron approaching a proton*

There are four cases to consider, but each of them leads to the same condition so we will only consider one case. Electron 1 approaching the left proton. In that case we consider the limits $r_{1L} \rightarrow 0$, $r_{1R} \rightarrow s$. The Coulomb interaction blows up due to the term $1/r_{1L}$ however we can cure the problem by choose the variational parameters so that in this limit,

$$H\phi_1 = \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1L}}\right]\phi_1 = 0; \quad \text{or} \quad -\frac{1}{2\phi_1}\nabla_1^2\phi_1 = \frac{1}{r_{1L}} \quad (19)$$

We have,

$$\frac{1}{2\phi_1}\nabla_1^2\phi_1 = \frac{1}{\phi_1}\left(\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}}\right) - \frac{1}{a^2} \quad (20)$$

We keep only the singular term and write,

$$\frac{1}{\phi_1}\left(\frac{\phi_{1L}}{r_{1L}}\right) = \frac{e^{-r_{1L}/a}}{e^{-r_{1L}/a} + e^{-r_{1R}/a}} \frac{1}{r_{1L}} \quad (21)$$

Taking the limit $r_{1L} \rightarrow 0$ and comparing to equation (19) we find the condition $a(1 + e^{-s/a}) = 1$ is required to remove the singularity.

(ii) *Two electrons approaching each other*

We take the limit $r_{12} \rightarrow 0$ where the term $1/r_{12}$ is singular. This singularity case be cured by choosing the variational parameters so that in this limit,

$$Hf = \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{r_{12}}\right]f = 0; \quad \text{or} \quad \frac{1}{f}\nabla_1^2 f = \frac{1}{r_{12}} \quad (22)$$

Note that the singular part of the kinetic energy operator for electrons one and two is the same, so

we can consider just twice one of them. This leads to,

$$\frac{1}{f} \nabla_1^2 f = \frac{2\alpha + r_{12}(2\alpha\beta + 1)}{\alpha^2(1 + \beta r_{12})^4 r_{12}} \quad (23)$$

In the limit $r_{12} \rightarrow 0$, this reduces to $\frac{2}{\alpha r_{12}}$. Comparing to Eq. () we thus choose $\alpha = 2$ to ensure that the singularity is removed.

B. Derivation of $\epsilon(\vec{r}_1, \vec{r}_2, s)$

We have to evaluate $H\Psi/\Psi$ using Eqs. (10) and (11). We have,

$$\frac{1}{\phi_1 \phi_2 f} (H_1 + H_2 + H_{ee})(\phi_1 \phi_2 f) = \frac{1}{\phi_1 f} H_1 \phi_1 f + \frac{1}{\phi_2 f} H_2 \phi_2 f + \frac{1}{r_{12}} \quad (24)$$

First consider,

$$\frac{1}{\phi_1 f} H_1[\phi_1 f] = \left(-\frac{1}{2\phi_1 f} \nabla_1^2[\phi_1 f]\right) - \frac{1}{r_{1L}} - \frac{1}{r_{1R}} \quad (25)$$

The complicated part is the first term on the right hand side. We expand this as,

$$\frac{1}{2\phi_1 f} \nabla_1^2 \phi_1 f = \frac{1}{2\phi_1 f} (\phi_1 \nabla_1^2 f + 2\nabla_1 \phi_1 \cdot \nabla_1 f + f \nabla_1^2 \phi_1) \quad (26)$$

Carrying out the derivatives we find as follows.

$$\nabla_1 \phi_1 = \frac{-1}{a} [e^{-r_{1L}/a} \nabla_1 r_{1L} + e^{-r_{1R}/a} \nabla_1 r_{1R}] = \frac{-1}{a} [e^{-r_{1L}/a} \hat{r}_{1L} + e^{-r_{1R}/a} \hat{r}_{1R}]. \quad (27)$$

To evaluate $\nabla_1^2 \phi_1$ you can use Cartesian co-ordinates and evaluate one term. The others can be deduced from the structure of the result. Using the chain rule this leads to,

$$\nabla_1^2 \phi_1 = \left[\frac{1}{a^2} - \frac{2}{ar_{1L}}\right] e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}}\right] e^{-r_{1R}/a} \quad (28)$$

Similarly we find (using $r_{12}^2 = ((x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2)$),

$$\nabla_1 f = \frac{f}{\alpha r_{12}(1 + \beta r_{12})} \left[1 - \frac{\beta r_{12}}{1 + \beta r_{12}}\right] = \frac{f}{\alpha r_{12}(1 + \beta r_{12})^2} = \frac{f \hat{r}_{12}}{\alpha(1 + \beta r_{12})^2} \quad (29)$$

This $\nabla_1^2 f$ may be treating one of the derivatives and then deducing the rest. Perhaps a more elegant method is to use the identity $\nabla_1 \cdot (a\vec{F}) = \nabla_1 a \cdot \vec{F} + a \nabla_1 \cdot \vec{F}$, with $a = (f/(\alpha(1 + \beta r_{12})^2))$ and $\vec{F} = \hat{r}_{12}$, so that (using $\nabla_1 \cdot \hat{r}_{12} = 2/r_{12}$ and $\nabla_1 r_{12} = \hat{r}_{12}$) yields,

$$\begin{aligned} \nabla_1^2 f &= \nabla_1 \cdot \nabla_1 f = \frac{f}{\alpha(1 + \beta r_{12})^2} \nabla_1 \cdot \hat{r}_{12} + \hat{r}_{12} \cdot \nabla_1 \left(\frac{f}{\alpha(1 + \beta r_{12})^2} \right) \\ &= \frac{2f}{\alpha r_{12}(1 + \beta r_{12})^2} - \frac{2\beta f}{\alpha(1 + \beta r_{12})^3} + \frac{f}{\alpha^2(1 + \beta r_{12})^4} = \frac{2\alpha + r_{12}(1 + 2\alpha\beta)}{\alpha^2 r_{12}(1 + \beta r_{12})^4} \end{aligned} \quad (30)$$

Using the Eq. (1), (2), (3) and (4) yields,

$$\frac{\nabla_1^2(\phi_1 f)}{\phi_1 f} = \frac{2\alpha + r_{12}(1 + 2\alpha\beta)}{\alpha^2 r_{12}(1 + \beta r_{12})^4} + \frac{2\hat{r}_{12}}{a\alpha(1 + \beta r_{12})^2} \cdot \left(\frac{\phi_{1L}}{\phi_1} \hat{r}_{1L} + \frac{\phi_{1R}}{\phi_1} \hat{r}_{1R} \right) + \frac{1}{a^2} - \frac{2}{a\phi_1} \left(\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right) \quad (31)$$

It is then evident that

$$\frac{\nabla_2^2(\phi_2 f)}{\phi_2 f} = \frac{2\alpha + r_{12}(1 + 2\alpha\beta)}{\alpha^2 r_{12}(1 + \beta r_{12})^4} - \frac{2\hat{r}_{12}}{a\alpha(1 + \beta r_{12})^2} \cdot \left(\frac{\phi_{2L}}{\phi_2} \hat{r}_{2L} + \frac{\phi_{2R}}{\phi_2} \hat{r}_{2R} \right) + \frac{1}{a^2} - \frac{2}{a\phi_2} \left(\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right) \quad (32)$$

Adding these terms and multiplying by $-1/2$, and adding the Coulomb interaction terms, yields Eq. (18) of the text.