

Variational Monte Carlo (VMC) for AP3081 D

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Abstract

1 Introduction

In this report we will study simple quantum mechanical systems of particles which have bound states. The simplest such system is the quantum harmonic oscillator in one dimension, with which we start.

1.1 Monte Carlo

1.2 The variational Monte Carlo method

In mathematical physics variational Monte Carlo (VMC) is a quantum Monte Carlo method that applies the variational method to approximate the ground state of the system. In the VMC method we first construct a (many-particle) trial function $\Psi_{T,\alpha}$, which depends on a set of variational parameters $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_S)$. We want to find an efficient way to evaluate the expected value of the energy

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1)$$

where ψ depends on the combined position coordinate $R = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ of all the particles in the system. To approximate this integral we use a Metropolis algorithm in which we place N walkers in a random configuration and push into a natural position

1.3 Harmonic oscillator

1.4 Hydrogen atom

1.5 Helium atom

1.6 Hydrogen molecule H₂

2 Computer Simulation

3 Results

4 Conclusions

References

5 Appendix

5.1 Derivation of local energies

We will present the derivations for the atoms studied in this report To evaluate the local energy we must work out E_L in

$$\langle E \rangle = \frac{\int dR \Psi_T^2(R) E_L(R)}{\int dR \Psi_T^2(R)} \quad (2)$$

in which E_L is

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

$$\hat{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{e-b}(\mathbf{r}_i) \quad (4)$$

5.2 Hydrogen molecule H₂

$$\hat{H} = -\frac{\hbar}{2m} (\nabla_1^2 + \nabla_2^2) - \left[\frac{ke^2}{\left| \vec{r}_1 + \frac{s}{2} \hat{i} \right|} + \frac{ke^2}{\left| \vec{r}_1 - \frac{s}{2} \hat{i} \right|} + \frac{ke^2}{\left| \vec{r}_2 + \frac{s}{2} \hat{i} \right|} + \frac{ke^2}{\left| \vec{r}_2 - \frac{s}{2} \hat{i} \right|} \right] + \frac{ke^2}{|\vec{r}_1 + \vec{r}_2|} \quad (5)$$

in which the first term is the kinetic energy of the two electrons. The part in the square brackets is the attraction between the nucleus and the electrons and the last term is the Coulomb interaction between the electrons. Setting the

constants to unity, and setting $\vec{r}_{1L} = \vec{r}_1 + \frac{s}{2}\hat{i}$, $\vec{r}_{1R} = \vec{r}_1 - \frac{s}{2}\hat{i}$, $\vec{r}_{2L} = \vec{r}_2 + \frac{s}{2}\hat{i}$, $\vec{r}_{1R} = \vec{r}_2 - \frac{s}{2}\hat{i}$ and $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ we obtain

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left[\frac{1}{|\vec{r}_{1L}|} + \frac{1}{|\vec{r}_{1R}|} + \frac{1}{|\vec{r}_{2L}|} + \frac{1}{|\vec{r}_{2R}|} \right] + \frac{1}{|\vec{r}_{12}|} \quad (6)$$

In the light of the solvability of this Hamiltonian we split it up in two non-interacting Hamiltonians and a interaction term.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{ee} \quad (7)$$

in which $\hat{H}_1 = -\frac{1}{2}\nabla_1^2 - \frac{1}{|\vec{r}_{1L}|} - \frac{1}{|\vec{r}_{1R}|}$, $\hat{H}_2 = -\frac{1}{2}\nabla_2^2 - \frac{2}{|\vec{r}_{1L}|} - \frac{2}{|\vec{r}_{2R}|}$ and $\hat{H}_{ee} = \frac{1}{|\vec{r}_{12}|}$. We have chosen our trial variational wave function $\Psi_{T,\alpha}$ to be

$$\Psi_T(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\psi(\vec{r}_1, \vec{r}_2) \quad (8)$$

where $\psi(\vec{r}_1, \vec{r}_2)$ is the Jastrow function

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

and $\phi(\vec{r}_1)$ and $\phi(\vec{r}_2)$ are

$$\phi(\vec{r}_1) = e^{-|\vec{r}_{1L}|/a} + e^{-|\vec{r}_{1R}|/a} = \phi_1 = \phi_{1L} + \phi_{1R} \quad (10)$$

$$\phi(\vec{r}_2) = e^{-|\vec{r}_{2L}|/a} + e^{-|\vec{r}_{2R}|/a} = \phi_2 = \phi_{2L} + \phi_{2R} \quad (11)$$

$$E_L(R) = \frac{\hat{H}\Psi_T(R)}{\Psi_T(R)} = \frac{1}{\phi_1\phi_2\psi_{12}}\hat{H}\phi_1\phi_2\psi_{12} \quad (12)$$

We let the Hamiltonians only work on correct terms, which results in

$$\frac{1}{\phi_1\phi_2\psi_{12}}(\hat{H}_1 + \hat{H}_2 + \hat{H}_{ee})\phi_1\phi_2\psi_{12} = \frac{1}{\phi_1\psi_{12}}\hat{H}_1\phi_1\psi_{12} + \frac{1}{\phi_2\psi_{12}}\hat{H}_2\phi_2\psi_{12} + \frac{1}{|\vec{r}_{12}|} \quad (13)$$

Now we first consider

$$\frac{1}{\phi_1\psi_{12}}\hat{H}_1\phi_1\psi_{12} = -\frac{1}{\phi_1\psi_{12}}\frac{1}{2}\nabla_1^2(\phi_1\psi_{12}) - \frac{1}{|\vec{r}_{1L}|} - \frac{1}{|\vec{r}_{1R}|} \quad (14)$$

from which we first consider $\nabla_1^2(\phi_1\psi_{12})$, using the chain rule

$$\nabla_1^2(\phi_1\psi_{12}) = \psi_{12}\nabla_1^2\phi_1 + 2\nabla_1\phi_1 \cdot \nabla_1\psi_{12} + \phi_1\nabla_1^2\psi_{12} \quad (15)$$

where

$$\nabla_1\phi_1 = -\frac{1}{a}\left(e^{-|\vec{r}_{1L}|/a} + e^{-|\vec{r}_{1R}|/a}\right) = -\frac{1}{a}\left(e^{-|\vec{r}_{1L}|/a}\hat{r}_{1L} + e^{-|\vec{r}_{1R}|/a}\hat{r}_{1R}\right) \quad (16)$$

and ¹

¹from now on we will omit the vector signs when it's not ambiguous

$$\nabla_1^2 \phi_1 = \left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right] e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right] e^{-r_{1R}/a} \quad (17)$$

Similarly we find

$$\nabla_1 \psi_{12} = \nabla_1 \left(e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}} \right) = \frac{e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}}}{\alpha(\beta r_{12} + 1)^2} \hat{r}_{12} = \frac{\psi_{12}}{\alpha(\beta r_{12} + 1)^2} \hat{r}_{12} \quad (18)$$

and

$$\nabla_1^2 \psi_{12} = e^{\frac{r_{12}}{\alpha(1+\beta r_{12})}} \frac{2\alpha\beta r_{12} + 2\alpha + r_{12}}{r_{12}\alpha^2(\beta r_{12} + 1)^4} = \frac{(1 + 2\alpha\beta)r_{12} + 2\alpha}{r_{12}\alpha^2(\beta r_{12} + 1)^4} \psi_{12} \quad (19)$$

Now substituting equations 16, 17, 18 and 19 into 15.

$$\begin{aligned} \nabla_1^2(\phi_1 \psi_{12}) &= \psi_{12} \left(\left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right] e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right] e^{-r_{1R}/a} \right) + \\ &\quad \frac{2}{a} \left(e^{-r_{1L}/a} \hat{r}_{1L} + e^{-r_{1R}/a} \hat{r}_{1R} \right) \frac{\psi_{12}}{\alpha(\beta r_{12} + 1)^2} \hat{r}_{12} \\ &\quad + \left(e^{-|\vec{r}_{1L}|/a} + e^{-|\vec{r}_{1R}|/a} \right) \left(\frac{(1 + 2\alpha\beta)r_{12} + 2\alpha}{r_{12}\alpha^2(\beta r_{12} + 1)^4} \psi_{12} \right) \end{aligned} \quad (20)$$

shuffle to get

$$\begin{aligned} \frac{\nabla_1^2(\phi_1 \psi_{12})}{\phi_1 \psi_{12}} &= \frac{1}{\phi_1} \left(\left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right] e^{-r_{1L}/a} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right] e^{-r_{1R}/a} \right) + \\ &\quad \frac{1}{\phi_1} \left(e^{-r_{1L}/a} \hat{r}_{1L} + e^{-r_{1R}/a} \hat{r}_{1R} \right) \cdot \frac{2\hat{r}_{12}}{\alpha a(\beta r_{12} + 1)^2} + \frac{(1 + 2\alpha\beta)r_{12} + 2\alpha}{r_{12}\alpha^2(\beta r_{12} + 1)^4} \end{aligned} \quad (21)$$

replace the exponents for the corresponding ϕ to obtain

$$\begin{aligned} \frac{\nabla_1^2(\phi_1 \psi_{12})}{\phi_1 \psi_{12}} &= \left(\left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right] \frac{\phi_{1L}}{\phi_1} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right] \frac{\phi_{1R}}{\phi_1} \right) + \\ &\quad \left(\frac{\phi_{1L}}{\phi_1} \hat{r}_{1L} + \frac{\phi_{1R}}{\phi_1} \hat{r}_{1R} \right) \cdot \frac{2\hat{r}_{12}}{\alpha a(\beta r_{12} + 1)^2} + \frac{(1 + 2\alpha\beta)r_{12} + 2\alpha}{r_{12}\alpha^2(\beta r_{12} + 1)^4} \end{aligned} \quad (22)$$

in which

$$\begin{aligned} &\left[\frac{1}{a^2} - \frac{2}{ar_{1L}} \right] \frac{\phi_{1L}}{\phi_1} + \left[\frac{1}{a^2} - \frac{2}{ar_{1R}} \right] \frac{\phi_{1R}}{\phi_1} \\ &= \frac{1}{a^2} \left[\frac{\phi_{1L}}{\phi_1} + \frac{\phi_{1R}}{\phi_1} \right] - \frac{2}{a\phi_1} \left[\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right] \\ &= \frac{1}{a^2} - \frac{2}{a\phi_1} \left[\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right] \end{aligned} \quad (23)$$

Now adding the equations for the second electron, which are the same ² because of the symmetry of the problem, multiplying with 1/2 and adding the Coulomb interaction terms to get

$$\begin{aligned}
E_L = & -\frac{1}{a^2} + \frac{1}{a\phi_1} \left[\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right] + \frac{1}{a\phi_2} \left[\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right] + \\
& \left(\frac{\phi_{1L}}{\phi_1} \hat{r}_{1L} + \frac{\phi_{1R}}{\phi_1} \hat{r}_{1R} - \frac{\phi_{2L}}{\phi_2} \hat{r}_{2L} - \frac{\phi_{2R}}{\phi_2} \hat{r}_{2R} \right) \cdot \frac{\hat{r}_{12}}{\alpha a (\beta r_{12} + 1)^2} \\
& - \frac{(1 + 2\alpha\beta)r_{12} + 2\alpha}{r_{12}\alpha^2(\beta r_{12} + 1)^4} - \left[\frac{1}{|\vec{r}_{1L}|} + \frac{1}{|\vec{r}_{1R}|} + \frac{1}{|\vec{r}_{2L}|} + \frac{1}{|\vec{r}_{2R}|} \right] + \frac{1}{|\vec{r}_{12}|} \quad (24)
\end{aligned}$$

with $\alpha = 2$

$$\begin{aligned}
E_L = & -\frac{1}{a^2} + \frac{1}{a\phi_1} \left[\frac{\phi_{1L}}{r_{1L}} + \frac{\phi_{1R}}{r_{1R}} \right] + \frac{1}{a\phi_2} \left[\frac{\phi_{2L}}{r_{2L}} + \frac{\phi_{2R}}{r_{2R}} \right] + \\
& \left(\frac{\phi_{1L}\hat{r}_{1L} + \phi_{1R}\hat{r}_{1R}}{\phi_1} - \frac{\phi_{2L}\hat{r}_{2L} + \phi_{2R}\hat{r}_{2R}}{\phi_2} \right) \cdot \frac{\hat{r}_{12}}{2a(\beta r_{12} + 1)^2} \\
& - \frac{(1 + 4\beta)r_{12} + 4}{4r_{12}(\beta r_{12} + 1)^4} - \left[\frac{1}{|\vec{r}_{1L}|} + \frac{1}{|\vec{r}_{1R}|} + \frac{1}{|\vec{r}_{2L}|} + \frac{1}{|\vec{r}_{2R}|} \right] + \frac{1}{|\vec{r}_{12}|} \quad (25)
\end{aligned}$$

6 The use of my program

7 Data

²up to one minus sign