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Variational quantum Monte Carlo for the harmonium system

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Abstract

Relatively good accuracy (< 2%) for intermediate and strong regime for the ground state energy of the harmonium system (Hook's atom) was obtained by variational Monte-Carlo (VMC) calculations. Our study focus on the variation of the ground state energy with respect to the oscillation frequency ω and the balance between the three different part of the energy (kinetic, coulomb and harmonic). Results were compared with several exactly known values of ground state energy for a series of discreet but limited values of the oscillation frequency.

Keywords: Harmonium, VMC, MC integration, Gradient Descent.

1 Introduction

The harmonium quantum system, also called hook's atom, is a model of 2 electrons confined in spherical harmonic potential. Introduced in the 1960s and further developed by Kestner [1] and Kais [2][3], it is an exactly solvable model but only for a certain values of the oscillator frequency ω (Taut [4], Cioslowski [5][6]). It is a benchmark for approximations like

DFT and configuration interaction and serves as a paradigmatic system for studying electron correlation effects in few-body physics. The aim of this paper is to apply VMC calculation to this model and compare with exact results.

2 Method

Schrödinger equation: In atomic units ($\hbar = m_e = ke^2 = 1$), the kinetic energy for the two electrons in the system is given by $T = -\Delta_1/2 - \Delta_2/2$, the harmonic potential energy operator is $V_{HO} = \omega r_1^2/2 + \omega r_2^2/2$, and the Coulomb interaction energy operator between the 2 electrons is $V_{ee} = 1/r_{12}$. The Schrödinger equation then reads:

$$\left(-\frac{1}{2}(\Delta_1 + \Delta_2) + \frac{1}{2}\omega(r_1^2 + r_2^2) + \frac{1}{r_{12}}\right)\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2) \qquad (1)$$

The exact ground state solution is only known for a certain number of discrete frequencies ω_n (representing the roots of polynomials of degree [n/2]) [4]. These ground states are singlet states in witch the antisymmetry of the wave function is captured by the spin part.

Variational calculation: The computation of the ground state involves the minimization of the expectation value of the Hamiltonian:

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi \mid \psi \rangle} = \langle T \rangle + \langle V_{HO} \rangle + \langle V_{ee} \rangle \qquad (2)$$

We use Gaussian trial wave functions with 2 parameters α_1, α_2 derived from the independent electrons model (where e-e interaction is neglected): $\psi_{\alpha_1}(r_1) = c_1 e^{-\alpha_1 r_1^2}, \psi_{\alpha_1}(r_2) = c_2 e^{-\alpha_2 r_2^2}$. Spin functions are not considered (they factor out and reduce to unity by normalization). The normalized wave function is :

$$\psi_{\alpha_1,\alpha_2}(r_1, r_2) = \left(\frac{4\alpha_1\alpha_2}{\pi^2}\right)^{3/4} e^{-(\alpha_1 r_1^2 + \alpha_2 r_2^2)} \qquad (3)$$

This leads to 6-d spatial integrals, some of which, arising from 1-body terms, are calculated exactly, while others, stemming from the 2-body Coulomb term, are computed numerically with MC integration. Due to these 2-body integrals, the minimization of $\langle H \rangle$ leads to non-explicit equations for (α_1, α_2). We then use the gradient descent method for our optimization.

Monte Carlo Integration: The integrals arising from the e-e interaction term are difficult to evaluate exactly. They are numerically evaluated using

Monte Carlo integration with a probability density function $\rho(\vec{r}_1,\vec{r}_2) = \left|\psi_{\alpha_1,\alpha_2}(\vec{r}_1,\vec{r}_2)\right|^2$. The formula for the expectation value for a sample size of N points allows us to write:

$$\int_D \rho(\vec{r}_1,\vec{r}_2) f(\vec{r}_1,\vec{r}_2) dv_1 dv_2 \simeq \frac{1}{N}\sum_{i=1}^{N} f(\vec{r}_1,\vec{r}_2) \qquad (4)$$

Gradient Descent: This optimization method allows us to calculate the minimum of a function $F(\alpha_1,\alpha_2)$ by following the opposite direction of the local gradient. The calculation of the points $\vec{R}_k(\alpha_{1k},\alpha_{2k})$ uses the iterative formula with step δ_k :

$$\vec{R}_{k+1} = \vec{R}_k - \delta_k \vec{\nabla} F(\alpha_{1k},\alpha_{2k}) \qquad (5)$$

3 Calculations

The exact calculation of the expectation values of the kinetic and harmonic potential energies gives:

$$\langle T\rangle(\alpha_1,\alpha_2) = \frac{3}{2}(\alpha_1+\alpha_2), \qquad \langle V_{Ho}\rangle(\alpha_1,\alpha_2) = \frac{3}{8}\omega^2\left(\frac{1}{\alpha_1}+\frac{1}{\alpha_2}\right) \qquad (6)$$

For the coulomb e-e interaction energy, we obtain the following 6-d integral:

$$\langle V_{ee}\rangle = I(\alpha_1,\alpha_2) = \int_{6d} \left(\frac{4\alpha_1\alpha_2}{\pi^2}\right)^{3/2} \frac{e^{-2(\alpha_1 r_1^2+\alpha_2 r_2^2)}}{|\vec{r}_1-\vec{r}_2|} dv_1 dv_2 \qquad (7)$$

Witch gives:

$$\langle H\rangle = E(\alpha_1,\alpha_2) = \frac{3}{2}(\alpha_1+\alpha_2) + \frac{3}{8}\omega^2\left(\frac{1}{\alpha_1}+\frac{1}{\alpha_2}\right) + I(\alpha_1,\alpha_2) \qquad (8)$$

Then the gradient descent method leads to the iterative equations:

$$\left\{\begin{aligned}
\alpha_{1,k+1} &= \alpha_{1,k} - \delta_k\left(\frac{3}{2} - \frac{3}{8}\frac{\omega^2}{\alpha_{1,k}^2} + \frac{3}{2\alpha_{1,k}} I(\alpha_{1,k},\alpha_{2,k}) - I_1(\alpha_{1,k},\alpha_{2,k})\right) && (9)\\
\alpha_{2,k+1} &= \alpha_{2,k} - \delta_k\left(\frac{3}{2} - \frac{3}{8}\frac{\omega^2}{\alpha_{2,k}^2} + \frac{3}{2\alpha_{2,k}} I(\alpha_{1,k},\alpha_{2,k}) - I_2(\alpha_{1,k},\alpha_{2,k})\right) && (10)\\
&\text{with}: I_{1,2}(\alpha_1,\alpha_2) = \int_{6d}\left(\frac{4\alpha_1\alpha_2}{\pi^2}\right)^{3/2} 2r_{1,2}^2 \frac{e^{-2(\alpha_1 r_1^2+\alpha_2 r_2^2)}}{|\vec{r}_1-\vec{r}_2|} dv_1 dv_2 && (11)
\end{aligned}\right.$$

4 Results

In the iterative equations (9, 10), the integrals I, I_1, I_2 are evaluated at each step δ_k using Monte Carlo with sufficient precision (sample size $= 10^8$). The convergence of (α_1, α_2) and the optimal energies is achieved after a certain number of steps. This calculation was carried out for a wide range of frequencies ω. The result is shown in the table and figures below.

ω	$\langle T \rangle$	$\langle V_{HO} \rangle$	$\langle V_{ee} \rangle$	$\langle H \rangle$	E (exact [4]	$\Delta E/E$
0.00140	0.00054	0.00817	0.01522	0.02394	0.01831	0.307
0.00189	0.00081	0.00999	0.01854	0.02934	0.02275	0.289
0.00263	0.00125	0.01249	0.02306	0.03681	0.02901	0.268
0.00382	0.00199	0.01647	0.02911	0.04758	0.03823	0.244
0.00584	0.00341	0.02249	0.03807	0.06397	0.05257	0.216
0.00957	0.00637	0.03236	0.05202	0.09076	0.07662	0.184
0.01734	0.01331	0.05084	0.07517	0.13933	0.12142	0.147
0.03653	0.03274	0.09172	0.11791	0.24238	0.21922	0.105
0.1	0.10574	0.21278	0.21179	0.53031	0.5	0.060
0.5	0.63945	0.87965	0.52096	2.04007	2	0.020
1	1.323	1.70068	0.74946	3.77314		:
2	2.93470	3.06674	1.11638	7.11783		:
4	5.625	6.4000	1.54548	13.5704		:
8	11.8952	12.1056	2.24652	26.2474		< 0.02
16	23.9109	24.0893	3.18544	51.1857		:
32	47.6876	48.3144	4.49665	100.498		:
64	95.9655	96.0344	6.38215	198.382		:
128	191.873	192.126	9.02678	393.026		:

Table 1: Optimal values (for the ground state) of the kinetic, coulomb, harmonic, and total energy $\langle H \rangle$ (in Hartree) as a function of the frequency ω. The first ten values correspond to the first ten frequencies for which the exact solution is known.

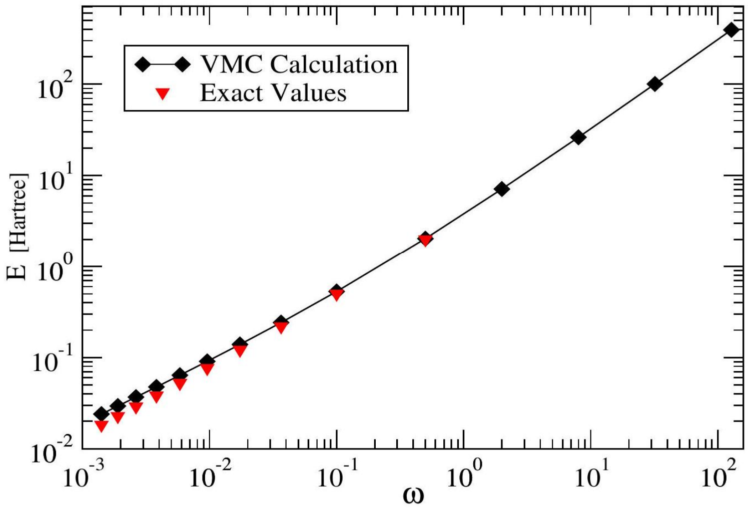

Figure 1: Energy of the ground state of the harmonium system vs frequency ω

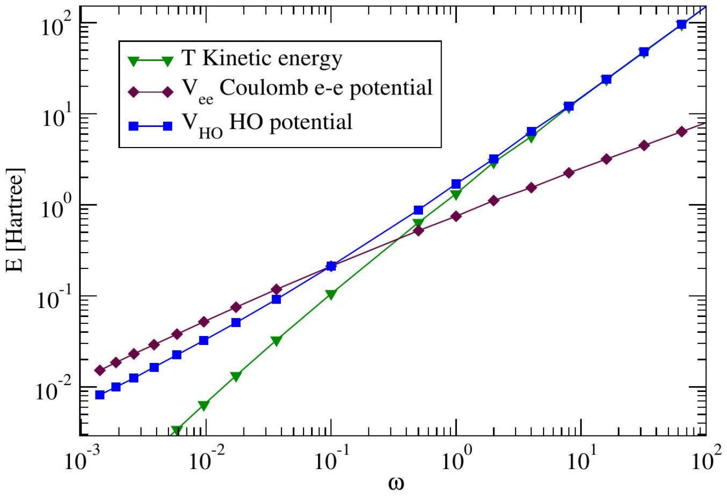

Figure 2: Kinetic, coulomb and harmonic energies for the ground state

5 Discussion

The results of our calculations of the ground state energy of the harmonium (table 1 and figure 1) shows a good accuracy for the variational Monte Carlo method with gradient descent minimization, particularly for the medium and high frequency regime ($\Delta E/E \leq 0.02$ for $\omega \geq 0.5$ a.u. $= 4.13 \cdot 10^{16}\ \mathrm{s}^{-1}$) despite the use of a simple two parameters Gaussian trial wave function. Indeed, for $\omega = 0.5$ a.u. we obtained $\langle H \rangle = 2.04 E_H$

compared to the exact value $E = 2E_H$. The accuracy then follows an upward trend for high frequencies. It is important to note that at high frequencies, the harmonic and kinetic energies are dominant compared to the Coulomb energy, as shown in figure 2, thus the influence of the latter remains minimal. Around the value $\omega = 0.5$ a.u. the three energies show the same order of magnitude, then the Coulomb interaction between electrons becomes dominant at low frequency (< 0.5 a.u.) where the precision begins to degrade. We can confidently assert that the source of errors primarily stems from the choice of the trial wave function and not from the Monte Carlo integration, which is more than sufficient for this calculation.

6 Conclusion

In this work, we tried to test the accuracy of the Variational Monte Carlo method with gradient descent optimization for the 2-electrons harmonium quantum system and compare the results with exact calculation. Our calculations make use of a two-parameter Gaussian trial wave function and the results showed that the method converges well and yields good results. The accuracy can be improved by choosing a better trial function with more parameters.

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