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VQMC Study of Three Atoms under a New Jastrow Factor

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Abstract:
This paper is to report the ground state energy of few light weight atoms like He, Li, Be using variational monte carlo method. A trial wave function as the product of Slater determinants of spin-up and spin-down single particle orbitals with a Jastrow factor have been taken for optimization. A new Polynomial Padé Jastrow factor is taken with only one variational parameter. The wave function is optimized and the ground state energy is obtained. the performance of the new Jastrow factor is satisfactory. More than 95% of correlation energy is recovered using the new Jastrow factor for He and Li but for Be this is 57%.

Keywords: *Variational Monte Carlo, Local Energy, Jastrow factor, Dynamic correlation, Cusp condition, Variance minimization.*

1. Introduction

An accurate knowledge of non-relativistic ground state energy of an atom is of great importance in computational chemistry. This can be obtained if one can solve the Schrödinger equation for many electron systems. Quantum monte carlo methods can produce very accurate results for the ground state energy of atoms, molecules and solids. Although many works have been reported using supercomputers and high-performance computing machines, but this is an independent attempt to construct a program which can run on an ordinary desktop or laptop machine having sufficiently fast processing speed. In QMC method it is possible to construct a compact and accurate wave function if its functional form incorporates the analytical features of the true wave function. Choice of trial wave function is quite flexible in QMC. The simplest and possibly most commonly used wave function of this sort consists of a single determinant multiplied by a simple Jastrow factor that is a product over electron pair contributions. The Jastrow factor is a function of the interelectron distances so that it directly correlates electrons with one another. Despite the freedom available in the construction of the Jastrow factor, a very simple form has been used in this work unlike SMBH [1]. Incorporating a generalized Jastrow factor that also includes electron-electron-nucleus correlation term is a future plan for the development of the program. Jastrow factor takes care of so-called dynamic correlation. The other component of the wave function is the determinant part. Although a single determinant wave function has often been employed, but a modified choice also works well which takes care of the non-dynamic correlation. The statistical error, the computational time and the difficulty in obtaining good trial wave functions increase with atomic number.

2. VMC

Two of many flavors of QMC are VMC and DMC. The VMC method is based on a combination of two ideas, namely the variational principal and Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm. It is used to compute quantum expectation values of an operator. In particular, if the operator is the Hamiltonian, its expectation value is the variational energy,

$$E_{VMC} = \frac{\int \Psi_T^*(R)\hat{H}\Psi_T(R)dR}{\int \Psi_T^*(R)\Psi_T(R)dR}$$

where Ψ_T is a trial wave function and R is the 3N-dimensional vector of the electron coordinates. According to the variational principle, a trial wave function for a given state must produce an energy which is above the exact value of that state; i.e. $E_{VMC} \geq E_{exact}$. To evaluate the integrals, we first construct a trial wave function, $\Psi_T^b(R)$, depending on variational parameter b and then vary the parameter to obtain minimum energy. Variational Monte Carlo calculations determine E_{VMC} by writing it as

$$E_{VMC} = \int P(R)E_L(R)dR$$

where $P(R) = \dfrac{\left|\Psi_T(R)\right|^2}{\int \left|\Psi_T(R)\right|^2 dR}$ is positive everywhere and interpreted as a probability distribution and $E_L = \dfrac{\hat{H}\Psi_T(R)}{\Psi_T(R)}$ is the local energy function.

The value of E_L is evaluated using a series of points R_1, R_2, R_3, ... sampled from the probability density $P(R)$. At each of these points the weighted average

$\left\langle E_L \right\rangle = \dfrac{\int \Psi_T{}^2(R) E_L dR}{\int \Psi_T{}^2(R) dR}$ is evaluated. After a sufficient number of evaluations, the VMC estimate of E_{VMC} will be

$$E_{VMC} = \left\langle E_L \right\rangle = \lim_{N \to \infty} \sum_{i=1}^{N} E_L(R_i)$$

N is the number of samples chosen according to the Metropolis algorithm.

3. Functional Form of the Wave Function

The trial wave function used in VMC calculation is usually chosen to be the product of Slater determinants of spin-up and spin-down single particle orbitals with a Jastrow factor.

$$\Psi_T = D^{\uparrow} D^{\downarrow} e^{J}$$

This form is anti-symmetric with respect to electron interchange of same spin but non anti-symmetric on exchange of opposite spins but its convenient to use and also increases computational efficiency. The expectation value of spin independent operator such as Hamiltonian does not alter due to such modification. Single particle orbitals are of Slater type.

$$\phi(r_i) = \sum_{k} c_k N_k e^{\zeta_k - 1} Y_{l_k m_k}$$

where $N_k = (2n_k)^{-1/2}(2\zeta_k)^{n_k - 1/2}$ is the normalization constant. The Jastrow factor is a symmetric term. In this work a Polynomial Padé Jastrow factor is used.

$$J = \sum_{i=1}^{n} \sum_{j>i}^{n} \dfrac{ar_{ij}}{1+br_{ij}} + \dfrac{ar_{ij}}{(1+br_{ij})^2}$$

b is the variational parameter. The value of a is fixed by the electron-electron cusp condition

$$\left. \dfrac{1}{J}\dfrac{\partial J}{\partial r_{ij}} \right|_{r_{ij} \to 0} = \dfrac{1}{2} \; or \; \dfrac{1}{4}$$

for opposite or same spin respectively. Defining $\beta = \sqrt{(a/b)}$ the variational parameter is transformed. The results are also compared with Padé function of the form

$$J = \sum_{i=1}^{n} \sum_{j>i}^{n} \dfrac{ar_{ij}}{1+br_{ij}}$$

Local energy can be calculated by evaluating

$$E_L = \dfrac{\hat{H}\Psi_T(R)}{\Psi_T(R)} = -\dfrac{1}{2}\sum_{i=1}^{n} \dfrac{\nabla_i^2 \Psi_T(R)}{\Psi_T(R)} + V$$

V is the potential energy which is a function of R and r_{ij}. To calculate the kinetic energy part, the following form is used

$$KE = \sum_{i=1}^{n} -\dfrac{1}{2}\left[\nabla_i^2 \ln \Psi_T(R) + (\nabla_i \ln \Psi_T(R))^2 \right]$$

where [2]

$$\nabla_i \ln \Psi_T(R) = \dfrac{\nabla_i D^{\uparrow}}{D^{\uparrow}} + \dfrac{\nabla_i D^{\downarrow}}{D^{\downarrow}} + \nabla_i J$$

$$\nabla_i^2 \ln \Psi_T(R) = \left(\dfrac{\nabla_i D^{\uparrow}}{D^{\uparrow}} \right)^2 + \dfrac{\nabla_i^2 D^{\uparrow}}{D^{\uparrow}} + \left(\dfrac{\nabla_i D^{\downarrow}}{D^{\downarrow}} \right)^2 + \dfrac{\nabla_i^2 D^{\downarrow}}{D^{\downarrow}} + \nabla_i^2 J$$

4. Results and Discussion

A. Ground state of He, Li, Be

It took around 8Hrs, 12Hrs, 29Hrs to optimize He, Li, Be wave function respectively. 3×10^5 steps are used on each run and 1.5×10^5 steps are used for equilibration. Ground state energy for the atoms are tabulated with respect to variance minimization and energy minimization in Table 1 and 2 respectively. All energies are in atomic unit. It appears that energy minimization recovers a significant amount of correlation energy in all the three cases. A steady decrease in correlation energy recovered is observed as the nuclear charge increases. Polynomial Padé Jastrow factor performed better than the simple Padé Jastrow factor. Its performance is comparable to the 9-parameter correlation function by Schmidt.

Also the statistical error which can be calculated as square root of (variance/step) increases with atomic number. This seems to indicate that some electron-nuclear correlation has not been taken care off. The nature of this correlation needs to be studied. Charge density of Li is shown in Fig 1.
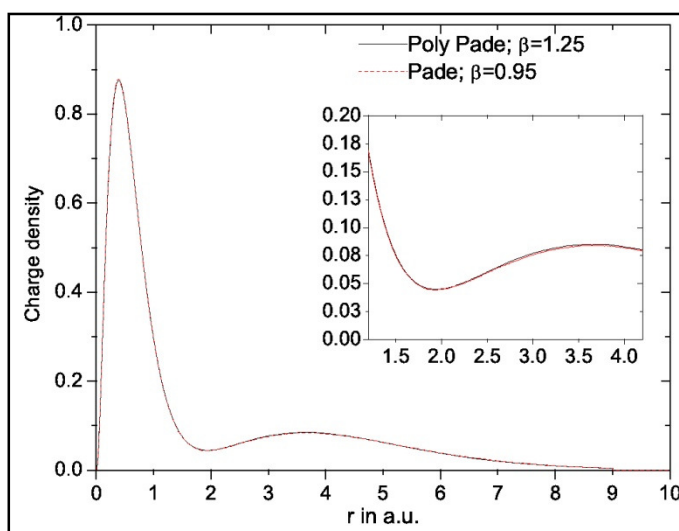

Figure 1: The graph shows the charge density for Li atom for the two Jastrow factors.

Atom	$E^{VMC}_{padé}$	E^{VMC}_{pp}	Variance	beta	$\%CE^{VMC}_{pp}$
He	-2.89872847	-2.90216837	0.13465983	1.45	96.30
Li	-7.47447565	-7.47457179	0.37992084	1.25	92.09
Be	-14.62184183	-14.6215439	0.82906343	1.05	51.43

Table 1: The VMC energy of this work using variance minimization

Atom	$E^{VMC}_{padé}$	E^{VMC}_{pp}	Variance	beta	$\%CE^{VMC}_{pp}$
He	-2.90213277	-2.90233716	0.1370618	1.25	96.70
Li	-7.47723937	-7.4788497	0.40320385	1.00	101.74
Be	-14.62697166	-14.6268758	0.88598948	0.85	57.09

Table 2: The VMC energy of this work using energy minimization

Atom	E_{HF}	E_{Exact}	E^{VMC} Others	E^{VMC} This work	Ref
He	-2.8616799	-2.90372437	-2.903722[13]	-2.90216837	[6] Flad *et al.* 1995
			-2.9037[12]		[3] Huang *et al.* 1997
			-2.89810[11]		[4]** Brown *et al.* 2007
			-2.9029[10]		[10]* Schmidt *et al.* 1990
Li	-7.432727	-7.47806032	-7.47310[6]	-7.47457179	[11] Doma *et al.* 2010
			-7.47427[3]		[12]† Hylleraas 1929
			-7.47683[4]		[13] Kinoshita 1959
			-7.4731[10]		
Be	-14.573023	-14.66736	-14.6311[6]	-14.621544	
			-14.66088[3]		
			-14.6311[4]		
			-14.6332[10]		

Table 3: Comparison chart
* using 9-parameter correlation function.

** Ref [5}.
† With 38-parameters.

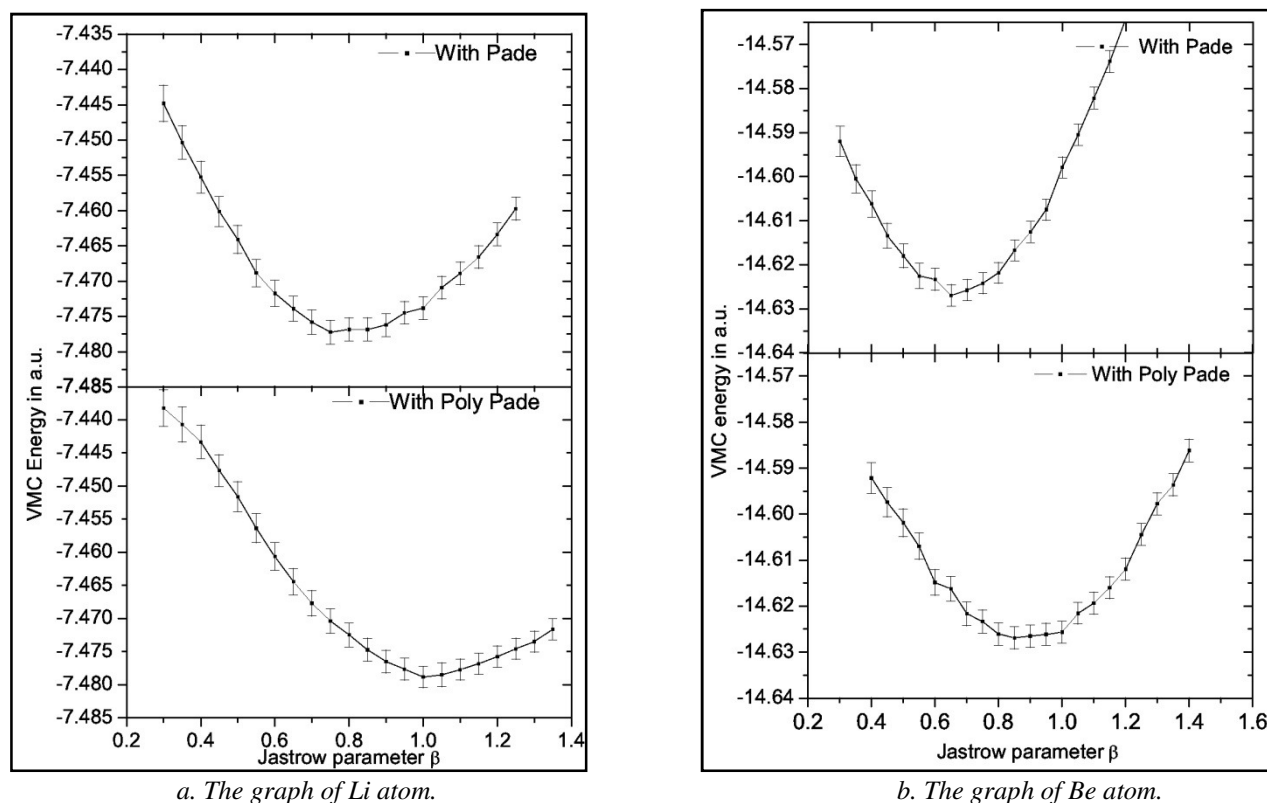*a. The graph of Li atom.*   *b. The graph of Be atom.*
Figure 2: The graphs show the variation of E_{VMC} of Li and Be atoms with the Jastrow parameter β for the two Jastrow factors.

It is now interesting to compare the correlation energies obtained for our ansatz with those obtained for other forms of Jastrow factors reported in the literature. Of special interest are the Jastrow factors of Schmidt and Moskowitz [10] due to their partitioning of different contributions to electron correlation. Table 3 shows this comparison. This table shows that with such simple Jastrow factor and with little computational resource this is a significant achievement. This seems to indicate that a substantial portion of the correlation energy has been recovered.

5. Acknowledgements

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