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First Ionization Potential of Li atom from VQMC Calculation

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Abstract:

The total non-relativistic energies of the Lithium atom and its positive ion are calculated using the fixed-node VQMC method. Over 90% of the correlation energy is obtained for both the neutral atom and the cation. Subtracting these energies yields the ionization potential of 5.345 electron volts, in excellent agreement with the recommended experimental value 5.39 electron volt. Calculations were performed using Slater-Jastrow type trial wave function with Polynomial Pade Jastrow factor having one variational parameter.

Keywords: Variational Monte Carlo, Local Energy, Jastrow factor, Cusp condition, Variance minimization

1. Introduction

The variational quantum Monte Carlo method is one of the most valuable tools of quantum chemistry because a wide variety of wave function forms for which analytical integration would be impossible can be used allowing one to incorporate terms that explicitly describe interelectronic distances into a wave function. These interelectronic terms have proven to describe dynamic correlation effects very well. The computational cost of this method is much less than other schemes such as the configuration interaction and coupled cluster methods. Explicitly correlated wave functions have the advantage of being compact compared to large multideterminant wave functions, and thus lend themselves more readily to physical interpretation.

Typical VMC trial wave functions are constructed by multiplying Slater determinants of spin up and spin down electrons, using single particle orbital obtained from the Roothan-Hartree-Fock equations, with a Jastrow factor. Two common forms of Jastrow functions are Pade-Jastrow and Schmidt-Moskowitz Jastrow [1] function. These interelectronic correlation terms are functions of the distance between all distinct electron pair and are responsible for describing electron correlation effects. The Jastrow function is positive everywhere and so the nodes of the Slater determinant remain unaltered. This property is essential to optimize Jastrow parameter without changing the nodal structure of the complete wave function.

In this study a new Jastrow function is tested for its performance. The results are also compared with Pade-Jastrow results.

2. Computational Details

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 [2]. 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. To evaluate the integrals, we first construct a trial wave function, $\phi_T^b(R)$, 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 $E_{VMC} = \int P(R)E_L dR$

Where $P(R) = \frac{|\phi_T(R)|^2}{\int |\phi_T(R)|^2 dR}$ is positive everywhere and interpreted as a probability distribution and $E_L = \frac{\hat{H}\phi_T(R)}{\phi_T(R)}$ is the local

energy function. The value of E_L is evaluated using a series of points $R_1, R_2, R_3 \dots$ sampled from the probability density $P(R)$. At

each of these points the weighted average $\langle E_L \rangle = \frac{\int \phi_T^2(R)E_L dR}{\int \phi_T^2(R)dR}$ is evaluated. After a sufficient number of evaluations, the VMC

estimate of E_{VMC} will be $E_{VMC} = \langle E_L \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N E_L(R_i)$; Where N is the number of samples chosen according to the Metropolis algorithm.

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 orbital and a Jastrow factor.

$$\phi_T = D^\uparrow D^\downarrow e^J$$

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

$$J = \sum_{i=1}^n \sum_{j>i}^n \frac{\alpha r_{ij}}{1 + b r_{ij}} + \frac{\alpha r_{ij}}{(1 + b r_{ij})^2}$$

b is the variational parameter. The value of α is fixed by the electron-electron cusp condition. Defining $\beta = \sqrt{\alpha/b}$ the variational parameter is transformed. The results are also compared with Pade function. Local energy can be calculated by evaluating

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

V is the potential energy which is a function of R and r_{ij} . The kinetic energy is calculated using the following form.

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

3. Results and Discussions

Correlated wave function of Li and Li+ are optimized under both variance minimization and energy minimization approach in the light of a new two-body Jastrow factor with one variational parameter. The ground state energy for Li and Li+ are estimated. The charge densities are also estimated and presented in Fig 3. A significant amount of correlation energy is recovered and results are very close to exact ground state energy. The ionization potential of Li is also determined which is found to be 5.345eV under variance minimization. 3×10^5 steps are used on each run and 1.5×10^5 steps are used for equilibration. Ground state energies 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.

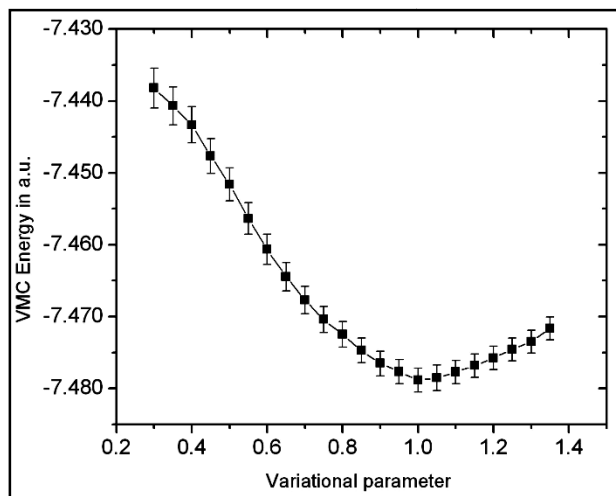


Figure 1: Optimization of VMC energy of Li.

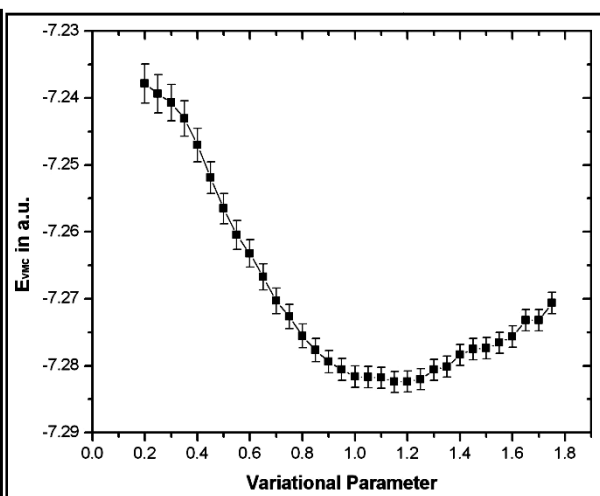


Figure 2: Optimization of VMC energy of Li+.

Atom	E_{Exact}	$E_{\text{Pade}}^{\text{VMC}}$	$E_{\text{PP}}^{\text{VMC}}$	Variance	β	$\%CE_{\text{PP}}^{\text{VMC}}$
Li+	-7.27991341	-7.280025	-7.2823861	0.3657875	1.2	105.68
Li	-7.47806032	-7.47447565	-7.47457179	0.37992084	1.25	92.30
Ionization Potential					0.19218569 Ha	5.2294 eV

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

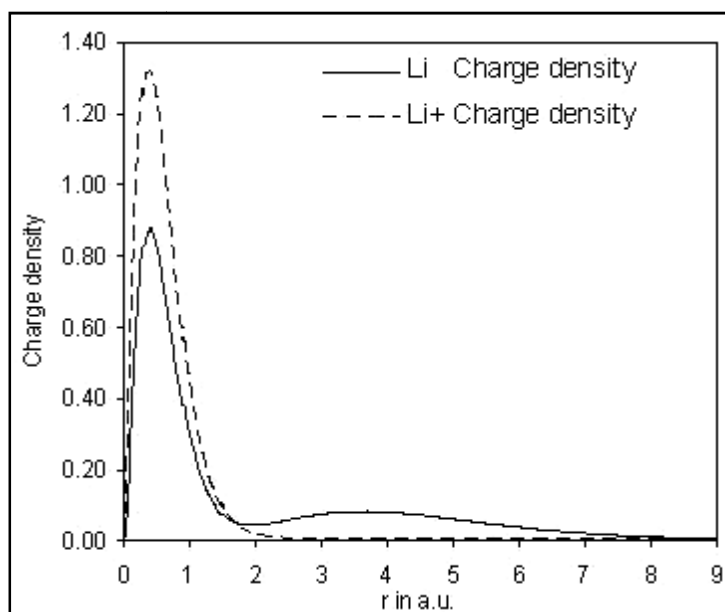


Figure 3: Plot of charge densities of Li and Li+

Atom	E_{Exact}	$E_{\text{Pade}}^{\text{VMC}}$	$E_{\text{PP}}^{\text{VMC}}$	Variance	β	$\%CE_{\text{PP}}^{\text{VMC}}$
Li+	-7.27991341	-7.2822156	-7.28241086	0.37250687	1.15	105.74
Li	-7.47806032	-7.47723937	-7.4788497	0.40320385	1.00	101.74
Ionization Potential					0.19643884 Ha	5.3451 eV

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

The experimental value of the Ionization Potential is 5.391 eV [3]

4. Acknowledgements

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5. References

- i. K. E. Schmidt, J. W. Moskowitz, J. Chem. Phys., Vol. 93, No. 6, (1990)
- ii. N. Metropolis and S. Ulam, J. Am. Stat. Assoc. 44, 335 (1949)
- iii. M Anwar-ul-Haq, S Mahmood, M Riaz, R Ali and M A Baig, J. Phys B, Vol. 38, No. 2, (2005)