Variational Quantum Monte Carlo Ground State of Lithium on a Slater orbital basis

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Abstract

The ground state of bulk lithium at zero temperature is simulated by the variational quantum Monte Carlo algorithm. The total energy and its constituents are determined for two parametrized sets of trial wave functions. Including correlation by a Jastrow factor the one-determinant ansatz consists of either plane waves or a linear combination of Slater orbitals for the Li $2s$ states. The latter yields results near those of the diffusion Monte Carlo algorithm.

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I. INTRODUCTION

Increasing computer power actually renders the numerical simulation of quantum mechanical systems more feasible. The early application to such a system dates back to the work of McMillan [1] on ^{4}He utilizing the Metropolis Monte Carlo algorithm [2] combined with energy minimization. Recently, this scheme has been used to simulate the ground state of metallic lithium within an all-electron calculation [3] and the ground state of some semiconductors within a pseudopotential approach [4]. This kind of calculation is motivated by the fact that the local density approximation (LDA), though being extremely successful, relies on an *a posteriori* quantity, the exchange correlation functional. The adequacy of a chosen functional type is proved by the results and not by first principles. Furthermore, some of its deficiencies, as the self-interaction [5] and the self-energy correction [6] are topics of current research.

Within the stochastic procedure the correlation is included by a Jastrow-ansatz, a choice which clearly is not unique. However, different from LDA, the energy functional is known here, and the adequate choice of an ansatz is safely guided by a variational principle. The limiting property of this method is the magnitude of the system, which is bounded by computer capacity. Thus, the number of atoms in the simulation cell and the number of electrons per atom should be small, which restricts all-electron calculations to the light elements of the periodic table.

In a substantial and very detailed investigation Sugiyama et al. [3] treat the ground state of lithium on the footing of two stochastic schemes, the variational (VQMC) and the diffusion (DQMC) quantum Monte Carlo procedure. The DQMC bases on the VQMC result and improves the obtained wave function by relaxation according to the imaginary time Schrödinger equation at the expense of an enhanced consumption of CPU time. The system was studied in various density regions using Gaussian type orbitals for the $1s$ electrons and several trial wave functions for the delocalized $2s$-$2p$ electrons.

We closely rely on that paper and report here about variational MC calculations performed at low pressure and zero-temperature on an extended set of parameters using Slater type orbitals for the localized $1s$ atomic state. The minimization has been carried through with regard to the atomic parameters as well as to the correlation parameters in the wave function ansatz for a large set of values. It shows that the variational procedure yields results of a quality attaining that of the diffusion method.

The computational details are described in the next section. It is followed by the discussion of the results in Section III.

II. METHOD

The Metropolis algorithm calculates expectation values of the form

$$< f > = \frac{\int f(x)p(x)dx}{\int p(x)dx}. \tag{1}$$

It is automatically normalized. The expectation value is calculated as a statistical mean over points distributed according to the probability density p. Any statistical property as the variance or the autocorrelation function can be controlled during the calculation. The error of the calculation is of purely statistical nature and depends on the variance of the function f, on the number of simulation points M, and on the autocorrelation function. The quantum mechanical expectation value of an observable B is obtained by setting

$$p = |\psi|^2 \quad , \quad f = (B\psi)/\psi. \tag{2}$$

The result is exact within the statistical error, that vanishes, if the function f is constant, i.e. if the wave function is an eigen function of the operator B.

In the present approach we simulate N electrons in a supercell containing a limited number of crystal unit cells. Periodic boundary conditions are assumed to model the infinite solid. Three electrons per lithium atom are simulated with an hamiltonian representing the exact many particle system by the potential energy

$$V = \tfrac{1}{2}\tfrac{N}{3}V_{n-n} + \sum_{i=1}^{N} V_{e-n}(\mathbf{r}_i) + \tfrac{1}{2}\sum_{i\neq j}^{N} V_{e-e}(\mathbf{r}_i - \mathbf{r}_j). \tag{3}$$

V_{n-n} is the coulomb interaction of one nucleon with all others, $V_{e-n}(\mathbf{r}_i)$ that of electron i with all nucleons, and $V_{e-e}(\mathbf{r}_i - \mathbf{r}_j)$ is the coulomb interaction between electron i and all electrons that are periodically equivalent with electron j. Only the sum of the three terms in eq. (3) converges for neutral crystals. They are calculated in Ewald summation technique and thus are exactly periodic with respect to the supercell.

For the many particle wave function the Jastrow-Slater ansatz is used, i.e. an anti-symmetric Slater determinant with a symmetric Jastrow factor. With D^σ denoting the determinant for all electrons of spin σ, the singlet state is expressed as

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = exp(-\sum_{i<j} u(r_{ij}))D^{\uparrow}(\mathbf{r}_1,\ldots,\mathbf{r}_{N/2})D^{\downarrow}(\mathbf{r}_{N/2+1},\ldots,\mathbf{r}_N), \tag{4}$$

$$\phi(r) = \sum_i c_i r^{n_i} \exp(-\frac{\alpha_i}{\zeta} r), \tag{5}$$

$$u(r) = \frac{A}{r}(1 - e^{-r/F}), \tag{6}$$

where $D^{\uparrow}, D^{\downarrow}$ consist of Slater type orbitals of the form $\phi(r)$ with c_i, α_i, and n_i taken from Clementi and Roetti [7]. The varied Slater parameters are ζ_{1s} and ζ_{2s} for the corresponding single particle states. For a value smaller than 1 they represent a compression of the wave function towards the nuclei, which usually is introduced by the one particle part of the Jastrow factor. A is the Jastrow parameter to be varied. The parameter F is fixed by the cusp condition to remove the coulomb singularity.

The calculation of the probability after a change of the coordinates of one electron is done via the ratio $\Psi_{\text{new}}/\Psi_{\text{old}}$ with the help of the inverse matrices and the Sherman-Morrison-Woodbury formula [8]. These inverse matrices are conveniently used to obtain the kinetic energy by the derivatives of the single particle wave functions constituting the Slater determinant. The periodic boundary conditions for the wave functions are not exactly fulfilled but controlled by an observable which checks Green's relation $-\int \Psi\Delta\Psi = \int(\nabla\Psi)^2$.

The number of simulation steps for the calculation of the total energy of one parameter set was chosen between 800,000 and 2,500,000 depending on the variance of the total energy and its autocorrelation function. Such a point of the minimization took approximately 4 CPU hours on a SIEMENS H90-D or 2 CPU hours on a Sparc 10-51.

III. RESULTS

At first, a minimization for the ground state energy of the lithium atom has been carried through. It yields -203.37 ± 0.005 eV per atom, which includes 1.12 eV of correlation energy. The Slater parameters equal to 0.96, i.e. compression of the $1s$ and $2s$ atomic orbitals is observed. The difference to the experimental value is approximately 0.11 eV. This total energy is the reference for the calculation of binding energies.

For the ground state of bulk lithium two approaches have been used, a plane wave and a LCAO ansatz with $2s$ Slater orbitals. The $1s$ state was taken as a pure atomic state. The supercell contains 16 primitive bcc unit cells like in Ref. [3]. Fig. 1 shows the contour plot of the total energy where we took the lattice constant of 6.9 a.u. from the minimization result in that paper. The plane coordinates are the Jastrow parameter A and the Slater parameter ζ_{1s} for the $1s$ wave function. A minimization with respect to the parameter ζ_{2s} of the $2s$ funtion has been included in each data point of the plane. The mesh in the displayed frame comprises 244 points. The asterisk shows the global minimum in the plot. According to our minimization the range of various parameters arises as a result. A compression of the $1s$ state by a scale factor of $0.94-0.96$, a stretching of the $2s$ state by $1.04-1.06$ and a Jastrow parameter of $0.25-0.6$ a.u. are reliable values. To check the finite size effects the calculation has been repeated for some points of this plot. This has been done with a system containing 54 primitive unit cells, which increased the amount of computation time by a factor of 6. No statistically significant differences are observed, so that finite size scaling corrections need not to be considered. Special values are given in Table I for the point at the minimum. They are also typical for other points in the parameter plane.

The total energy, minimized with respect to all wave function parameters, is displayed in Fig. 2 as a function of the lattice constant. The plotted curve is obtained with a quadratic function from a gaussian fit of the data points. Plane waves used as extended $2s$ states show to be significantly inferior to LCAO wave functions. Compared with the VQMC calculations of Ref. [3], see Table II, we obtain a distinctly lower value for the total energy, which we attribute to the use of Slater orbitals here instead of gaussian orbitals there. Both lattice constants agree within the error bar and also reasonably with the experimental value. Our minimal total energy is by 0.09 eV higher than that obtained from the DQMC calculations of [3]. However, in that calculation the lattice constant is at variance with the experimental value. This is maybe due to a different point density of the parameter mesh used. The value of the bulk modulus is derived from the quadratic fit displayed in Fig. 2. The plane wave ansatz for the $2s$ state yields 164.9 kbar and the LCAO ansatz yields 159.8 kbar, both approaches being not far from the experimental value of 120.0 kbar [9].

In Table III the results for a Hartree-Fock (HF) simulation, i.e. the Jastrow parameter A is set to zero, are compared with those which include the correlation by $A \neq 0$. For this comparison the lowest energy data point of Fig. 2 was chosen. The introduction of the Jastrow factor lowers the total energy by an amount of -1.723 eV which represents 0.8% compared with the HF result. The energy gain in the electron-electron interaction is about the same magnitude as the increase in the electron-nucleon interaction. The latter would arise as even higher, if the $1s$ orbital was not contracted. This contraction partially compensates the delocalization forced by the Jastrow factor as being obvious from the lowering of the kinetic energy. The stretching of the $2s$ orbital in the extended state does not produce such significant changes. The pair correlation functions show very little differences, less than 3%, when the extended state is changed. The magnitude of the variance of the total energy usually indicates the quality of the wave function ansatz. It rapidly converges to a constant value during the simulation. In this example we obtain 8.25 eV^2 for the HF calculations and, including correlation, 4.15 eV^2 for the plane waves and 3.66 eV^2 for the LCAO wave functions as extended states. This shows once more that the LCAO state is superior to a plane wave ansatz.

IV. CONCLUSION

Slater orbitals have been shown to be useful in the variational quantum Monte Carlo method for bulk lithium. Compared to DQMC this rather simple stochastic procedure yields the total energy of the ground state, the lattice constant, and the bulk modulus quite near to the experimental values. The difference between plane waves and LCAO wave functions used as the extended states is statistically significant in the low pressure region.

TABLES

N	a_0 a.u.	ζ_{1s}	ζ_{2s}	Jastrow A a.u.	E_{tot} eV/atom	σ_E eV/atom
48	6.6	0.96	1.04	0.32	−204.53	0.05
162	6.6	0.96	1.04	0.32	−204.50	0.06

TABLE I. Test of the dependence on the system size; the 3rd and 4th column denote the values of the Slater parameters ζ_{1s} and ζ_{2s}, see Eq.(5), the 5th column that of the Jastrow parameter A, see Eq.(6)

	a_0 Bohr	E_{tot} eV/atom	E_{atom} eV	E_{bind} eV/atom
Experiment	6.58	−205.04	−203.48	−1.66
VQMC [3]	6.62	−202.86		
DQMC [3]	6.9	−204.57		−1.09
VQMC L	6.64	−204.48	−203.37	−1.11
VQMC P	6.68	−204.24	−203.37	−0.87

TABLE II. Comparison of ground state energy and lattice constant of bulk lithium for different stochastic computation schemes and the experiment [9], L denoting the LCAO, P the plane wave ansatz. The total energy is the minimum of the quadratic fit.

	Hartree-Fock	with Jastrow factor
E_{tot}	-202.804 eV/atom ± 0.041	-204.527 eV/atom ± 0.046
E_{kin}	203.843 eV/atom ± 0.343	201.640 eV/atom ± 0.489
$E_{\text{pot}}^{\text{e-n}}$	-484.655 eV/atom ± 0.357	-480.643 eV/atom ± 0.504
$E_{\text{pot}}^{\text{e-e}}$	78.009 eV/atom ± 0.046	74.476 eV/atom ± 0.192
E_{corr}		-1.723 eV/atom ± 0.087

TABLE III. Total energy and its constituents for $2s$ LCAO wave functions near the energy minimum with lattice constant 6.6 a.u.; 1st column, Hartree-Fock ($A = 0$) result with Slater parameters $\zeta_{1s} = 1.0$, $\zeta_{2s} = 1.0$ and 50000 steps per electron; 2nd column, correlation included with Jastrow factor ($A = 0.32$ a.u.) and modified Slater parameters $\zeta_{1s} = 0.96$, $\zeta_{2s} = 1.04$ and 20000 steps per electron, see lowest data point (diamond) in Fig. 2.

FIGURES

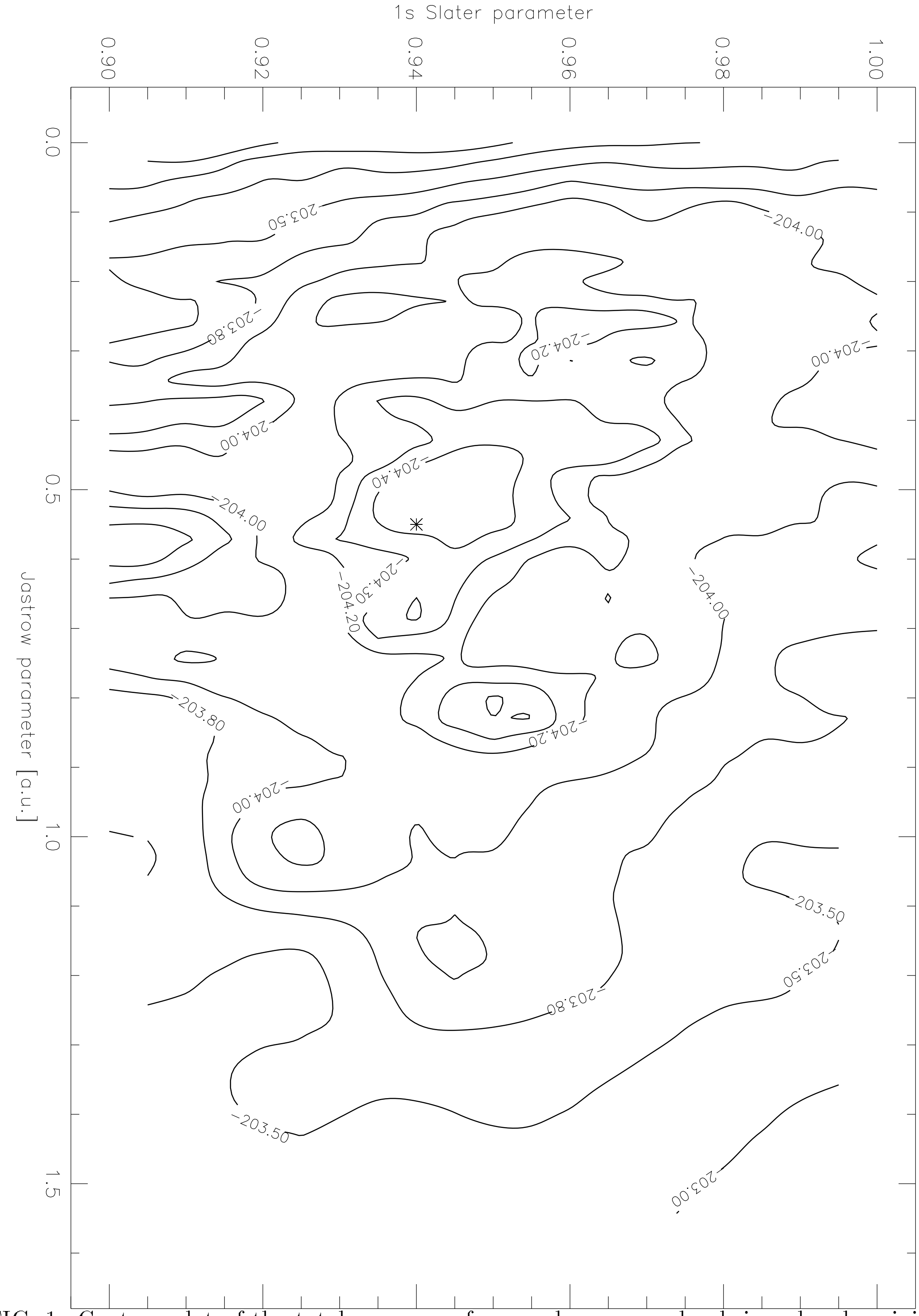

FIG. 1. Contour plot of the total energy surface, each energy value being already minimized with respect to the Slater parameter ζ_{2s}.

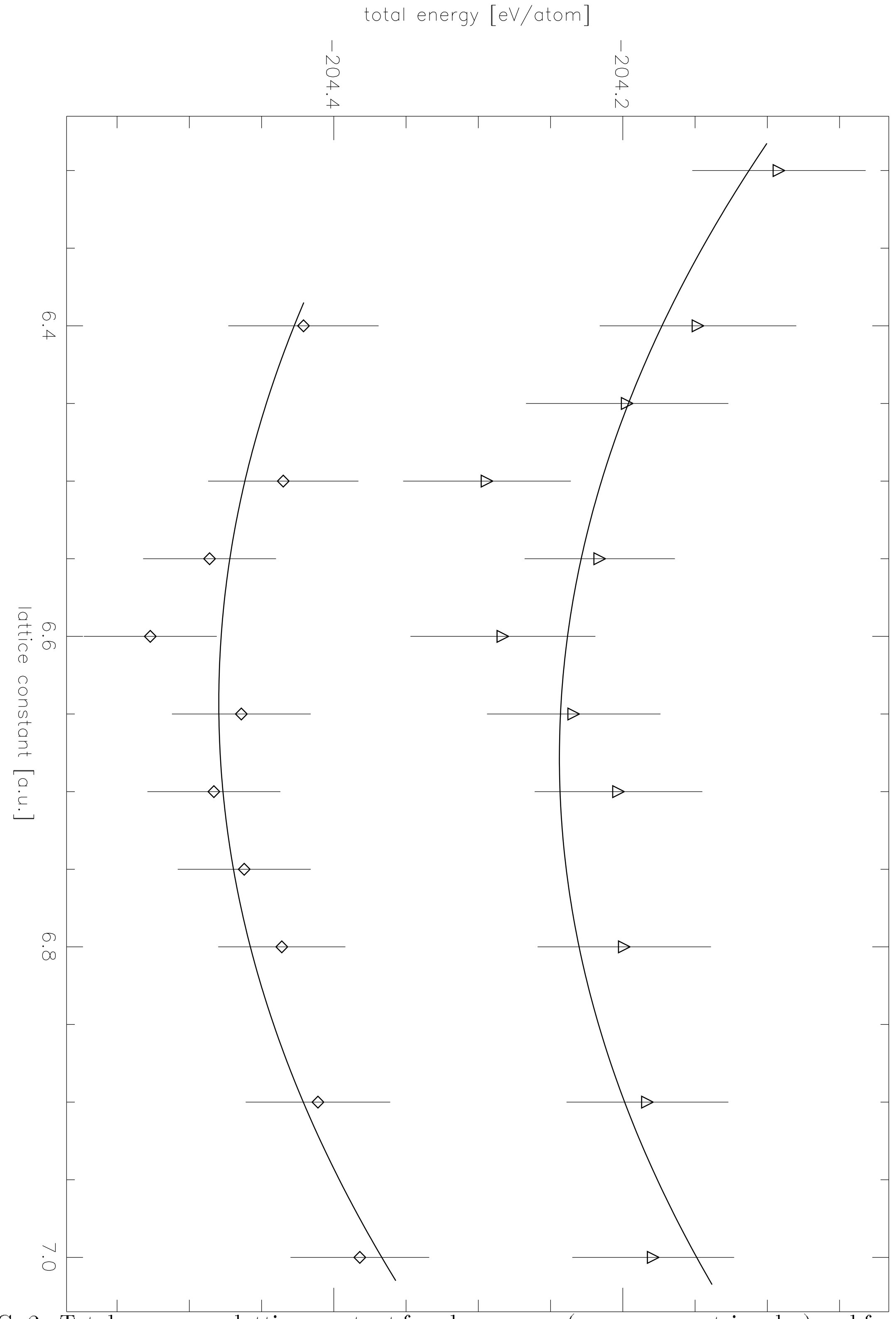

FIG. 2. Total energy vs. lattice constant for plane waves (upper curve, triangles) and for LCAO wave functions (lower curve, diamonds) being used as extended $2s$ states. The curves represent quadratic functions obtained from a gaussian fit.

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