Bosonized DFT potential estimated from QMC calculations of the ground-state density for the inhomogeneous electron liquid in Be

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Abstract

To avoid solution of numerous Kohn-Sham one-body potential equations for wave functions in DFT, various groups independently proposed the use of Pauli potential to bosonize the customary one-body potential theory. Here, we utilize our recent QMC calculations of the ground-state electron density of the Be atom to estimate the bosonized one-body potential $V_B(r)$ and hence extract the Pauli potential for this atom.

Keywords:Inhomogeneous electron liquids. Pauli potential. Be atom.

1 Introduction

As reviewed in [1] and [2], various research groups throughout the world independently proposed the use of the so-called Pauli potential $V_P(r)$ [3] to bosonize the ground-state electron density calculation in density functional theory (DFT). However, while $V_P(r)$ has been extracted for some simple model potentials (e.g. the bare Coulomb potential $-Ze^2/r$), by March et al [4]), its form is not well understood even for the ground-state of closed shell atoms with spherical density $n(r)$.

Therefore, in the present work, we study the bosonized DFT potential $V_B(r)$. Then the usual chemical potential of DFT reads (see, for example, [5])

$$\mu = \frac{\delta T_s}{\delta n(r)} + V(r) \tag{1}$$

where $T_s[n]$ is the (as yet unknown) single-particle kinetic energy functional, while

$$V(r) = V_{ext}(r) + \int \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' + V_{xc}(r) \tag{2}$$

is the Kohn-Sham potential which includes the exchange-correlation potential $V_{xc}(r)$.

As one of us pointed out [3], the bosonized potential $V_B(r)$ then has the merit, since

$$\frac{\delta T_s}{\delta n(r)} - \frac{\delta T_W}{\delta n(r)} = V_B(r)\ , \tag{3}$$

that Eq.(1) becomes

$$\mu = \frac{\delta T_W}{\delta n(r)} + V_P(r) + V(r)\ . \tag{4}$$

The considerable merit of Eq.(4) is that the von Weizsäcker kinetic energy $T_W[n]$ is explicitly known as[6]

$$T_W[n] = \frac{\hbar^2}{8m} \int \frac{|\nabla n|^2}{n}\, d\mathbf{r}\ . \tag{5}$$

If we define therefore the bosonized (B) DFT potential from Eq.(4) as

$$V_B(r) = V(r) + V_P(r) \tag{6}$$

Eq.(4) is readily rewritten, in atomic units, as

$$\mu = \frac{1}{8}\frac{|\nabla n|^2}{n^2} - \frac{1}{4}\frac{\nabla^2 n}{n} + V_B(r) \; . \tag{7}$$

2 Quantum Monte Carlo results

Fairly recently, we calculated by diffusion quantum Monte Carlo (DMC) the ground-state electron density for the Be atom[7] and we take this as starting point to extract an estimate of the bosonized potential $V_B(r)$. In our previous work, we used such ground-state density to get an accurate estimate of the exchange-correlation potential of DFT for this atom. Here, to reconstruct the density in a form that can be easily differentiated, we expand the Be Kohn-Sham (KS) orbitals, namely ϕ_{1s} and ϕ_{2s}, in terms of Slater-type atomic orbitals and solve the Kohn-Sham equation (in atomic units)

$$\left[-\frac{1}{2}\nabla^2 - \frac{4}{r} + \int \frac{n(r')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + V_{xc}(r)\right]\phi_j(r) = \epsilon_j \phi_j(r) \tag{8}$$

where

$$\phi_j(r) = \sum_k c_{kj} r^{a_k} e^{-\zeta_k r} \; . \tag{9}$$

in which the basis set parameters are chosen in a way to satisfy the Kato cusp condition at the nucleus, the correct asymptotic behaviour and to reproduce properly the shape of the density at all distances from the nucleus. c_{kj} are computed by diagonalizing the Kohn-Sham operator above in the subspace spanned by the atomic basis set. $V_{xc}(r)$, in local form, is taken from our previous work[7]. In Table 1, we show our final results. The smallest exponent has been set to $\sqrt{2I}$ where I is the experimental ionization potential. Here, for I, we take the value of 0.3426 Hartree that we have already used in a previous work on Be-like series of atomic ions [8]. The ground-state electron density for Be atom is then rewritten as

$$n(r) = 2\phi_{1s}^2(r) + 2\phi_{2s}^2(r) = 2\sum_{j=1}^{2}\sum_{kl} c_{kj}c_{lj} r^{a_k+a_l} e^{-(\zeta_k+\zeta_l)r} \tag{10}$$

The plots of the density $n(r)$ and of the radial density $4\pi r^2 n(r)$ are shown, respectively, in Figures 1 and 2. In these Figures, we plot also for comparison, the computed DMC corresponding values. Figure 3, therefore, shows $V_B(r)$

extracted from Eqs (4) and(6) by insertion of the QMC density $n(r)$ for the Be atom reconstructed from Eq.(10). The shape is seen to be rather simple.

Finally, we computed the Pauli potential $V_P(r)$ by means of Eq.(6) taking the accurate exchange-correlation potential $V_{xc}(r)$ from our previous work on Be [7]. The resulting plot, as a function of r, is shown in Figure 4 in the range of distances from the nucleus between approximately zero to 5 a_0. $V_P(r)$ from this plot is finite at all distances, it is flat at the origin in agreement with the recent study of Levämäki et al [9] and has a maximum at about 0.89 a_0 reflecting the shell structure of the electron density of Be. To complete this analysis, we report in Table 2 also a set of properties which have been computed through the solution of the Kohn-Sham equation (8) and that are directly related to $n(r)$, $V_B(r)$ and $V_P(r)$.

In summary, the main results of the present article are summarized in Figures 3 and 4. The former shows $V_B(r)$ as a function of r which derived solely by the QMC electron density shown in Eq.(10). The latter shows, instead, the Pauli potential $V_P(r)$ derived from Eq.(6). However, Figure 4 needs information on the exchange-correlation contribution to the one-body DFT potential which we have taken from Amovilli and March [7].

Acknowledgments

NHM wishes to acknowledge that his contribution to this work was carried out mainly during a visit to the University of Pisa. Professors D. Lamoen and C. Van Alsenoy are thanked for making possible the continuing affiliation of NHM with the University of Antwerp (B).

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a_k	ζ_k	$c_{k,1s}$	$c_{k,2s}$
0	8.000	-1.8634664	3.6312290
0	5.154	13.3496637	31.8219522
0	4.000	-8.0781624	-36.4529063
0	2.000	0.8396784	-1.7626738
0	1.000	-0.1322915	1.9315786
1	6.746	-4.9896492	10.8643272
1	4.519	11.8198807	39.9820628
1	2.012	-0.2652587	-1.1289335
1	1.3065	0.1019443	-0.7916701
1	0.827768	0.0020884	0.0522140

Table 1: Parameters entering the Kohn-Sham orbitals defined in Eq.(9)

property	value	property	value
T_W	13.612	n_0	35.25
T_s	14.573	n_0'	282.0
E_{xc}	–2.769	n_0''	2330.8
E	–14.667	$V_e(0)$	8.42
ϵ_{1s}	–4.1271	$V_{xc}(0)$	–2.94
ϵ_{2s}	–0.3485	$V_P(0)$	3.6

Table 2: Some DFT properties calculated in this work: von Weizsäcker kinetic energy (T_W), single particle kinetic energy (T_s), exchange-correlation energy (E_{xc}), total energy from DMC (E), KS orbital energies (ϵ_j), values at the origin of electron density and derivatives (n_0, n_0', n_0''), electronic electrostatic potential ($V_e(0)$), exchange-correlation potential ($V_{xc}(0)$), Pauli potential ($V_P(0)$). All data are in atomic units.

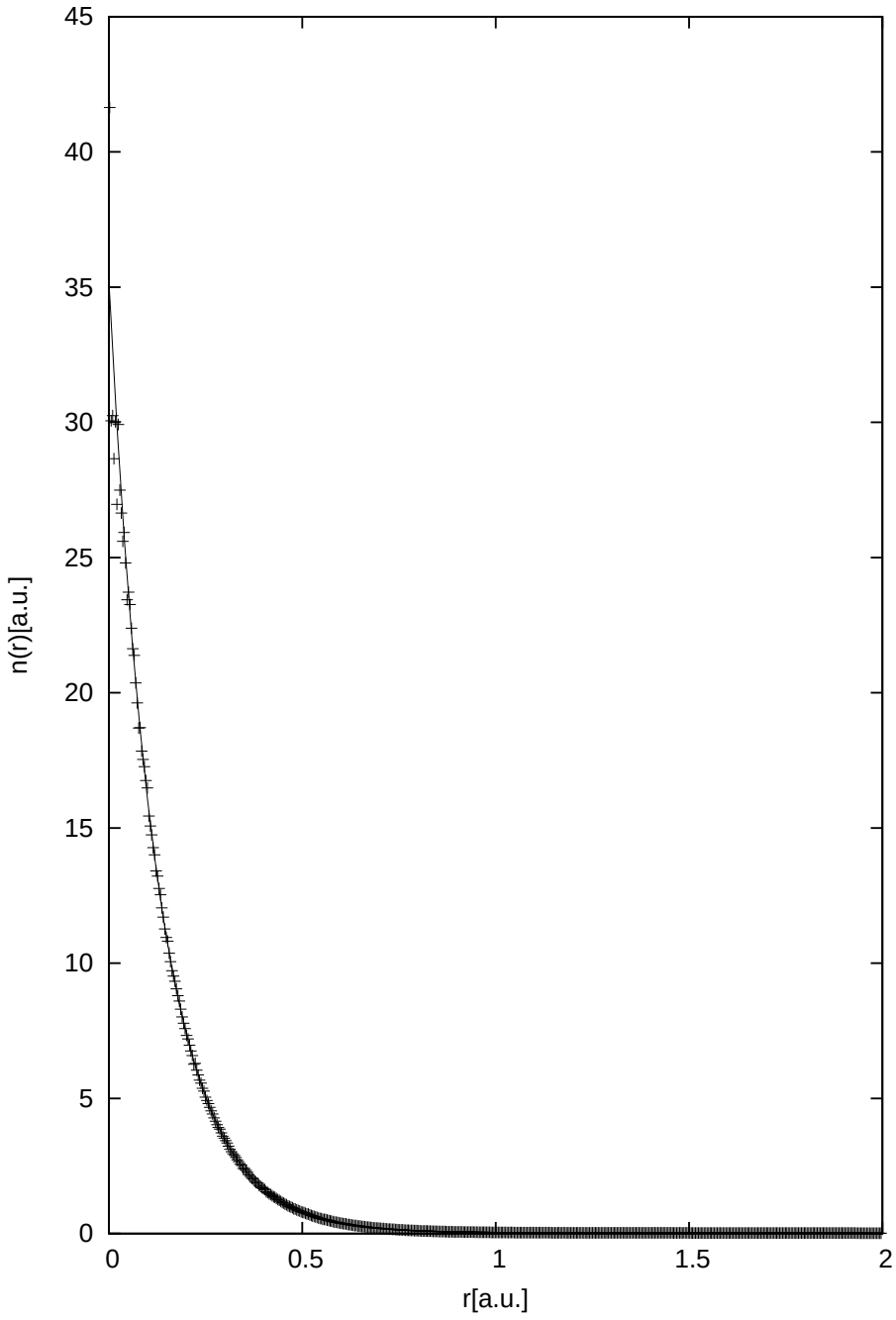

Figure 1: Displays ground-state density $n(r)$ for the Be atom, as calculated by QMC.

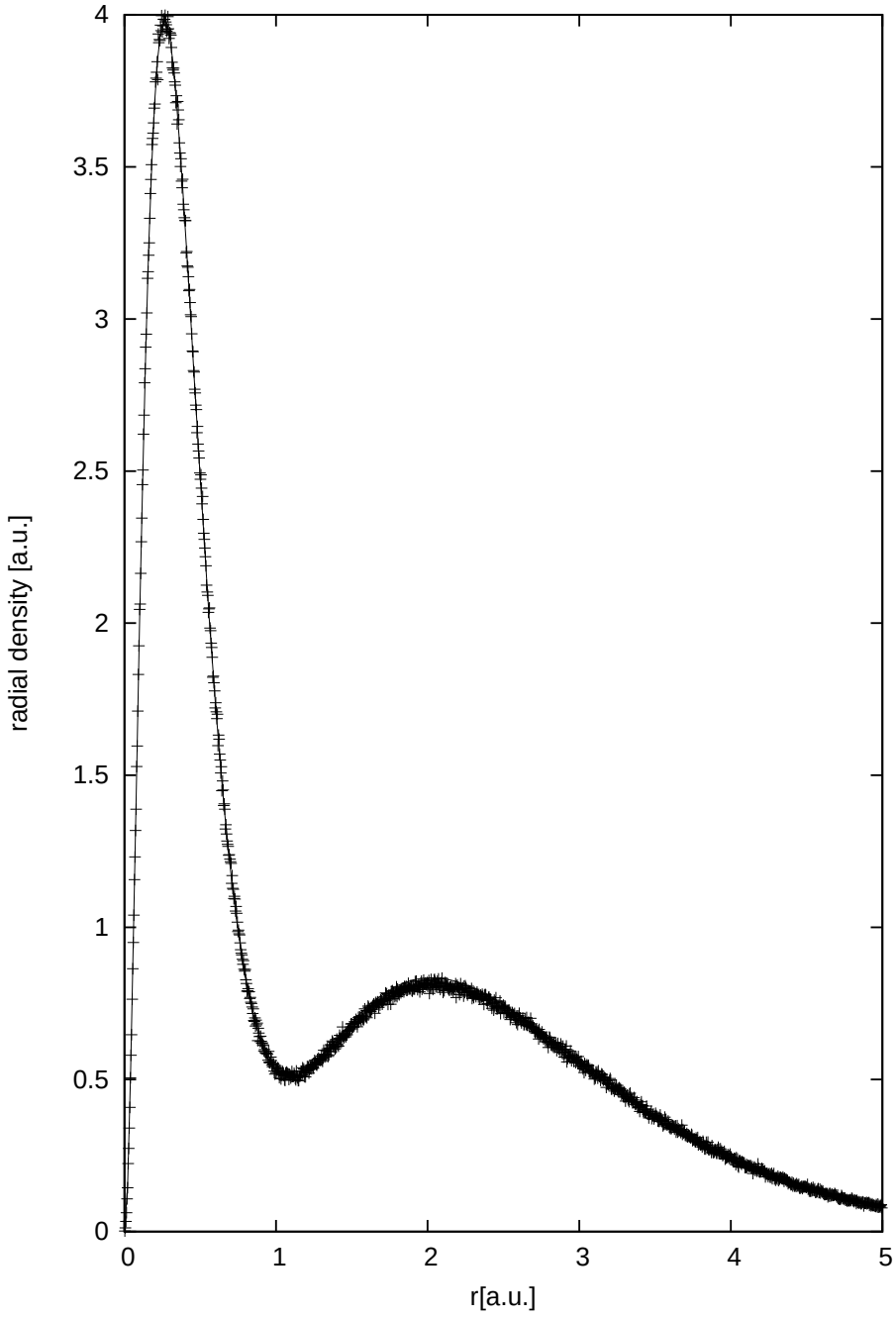

Figure 2: Radial form $4\pi r^2 n(r)$ versus r in a.u. for ground-state of the Be atom, using QMC density in Figure 1.

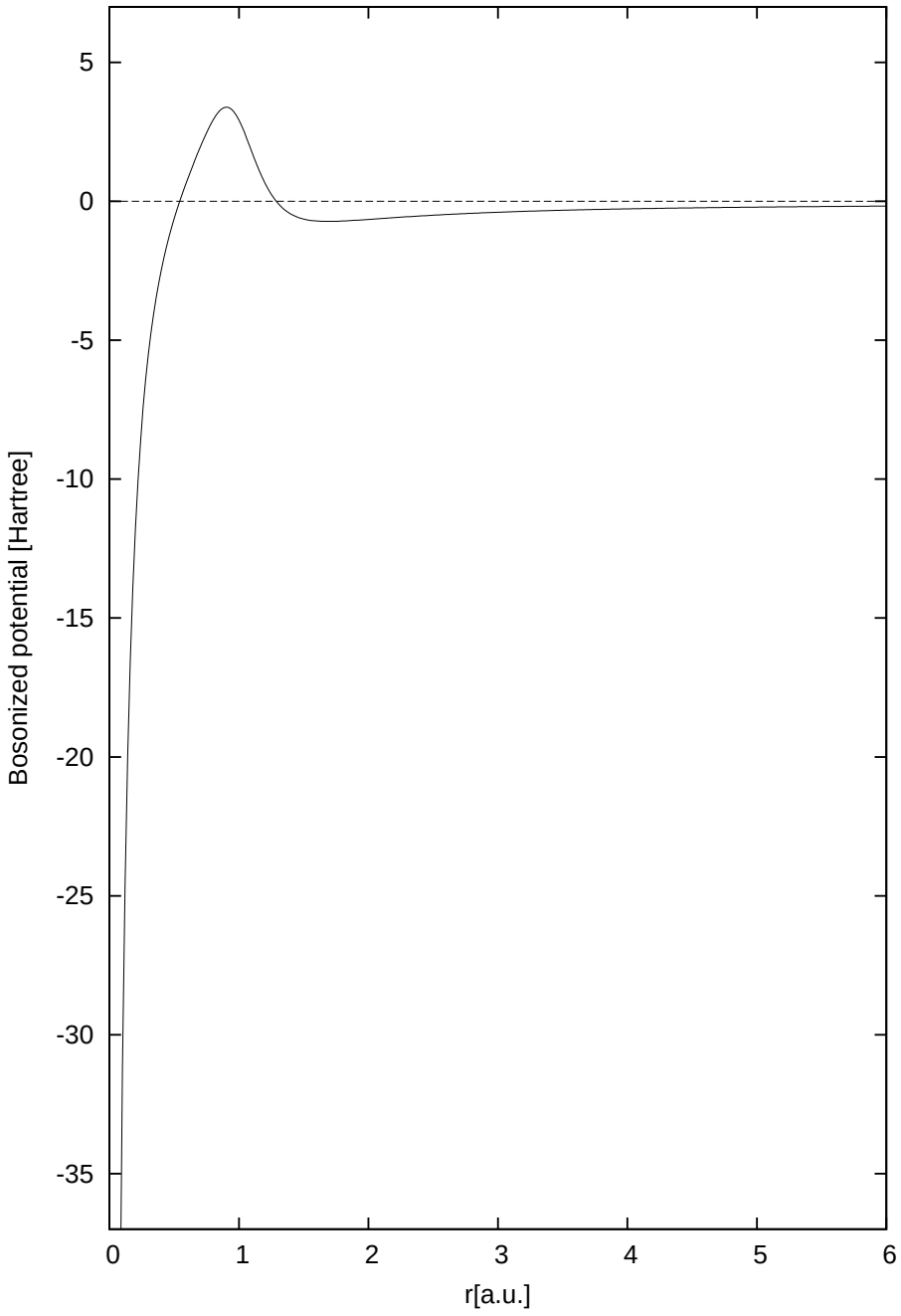

Figure 3: Displays bosonized potential $V_B(r)$ obtained from QMC ground-state density in Figure 1.

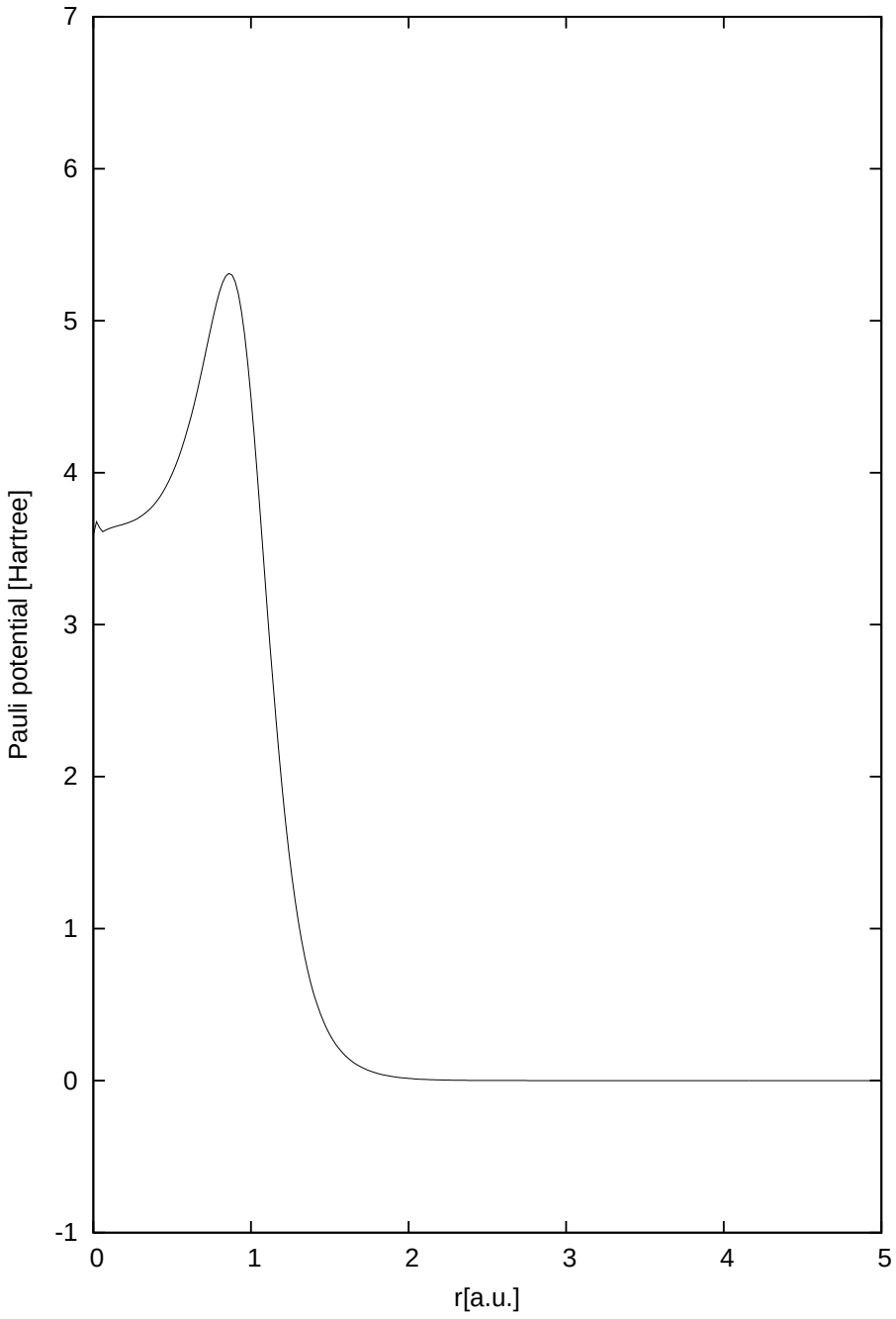

Figure 4: Displays estimate of Pauli potential $V_P(r)$ for ground-state of the Be atom.