J Math Chem (2015) 53:1725–1732
DOI 10.1007/s10910-015-0514-6

ORIGINAL PAPER

Electrostatic potentials at the nucleus for isoelectronic series of light atomic ions using the QMC method in relation to DFT

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Received: 4 February 2015 / Accepted: 10 May 2015 / Published online: 19 May 2015

Abstract The electrostatic potential at the nucleus is here calculated using the quantum Monte Carlo method. Both variational and diffusion-type data are presented for four different isoelectronic series of atomic ions, namely He, Li, Be and B. These results are then utilized to evaluate the ground-state energies of such atomic ions.

Keywords Quantum Monte Carlo · Electrostatic potential at nuclei · He, Li, Be and B ionic series

1 Introduction

Early work of Foldy [1] was important in emphasizing an intimate correlation between the ground-state energy of neutral atoms of nuclear charge Ze, namely $E(Z)$, and the electrostatic potential created by the electrons, denoted as V_0 below, evaluated at the assumed point nucleus. Before Foldy's study, such a correlation could be extracted analytically from the Thomas–Fermi (TF) semi-classical theory, beginning with the ground-state energy $E(Z)$ of neutral atoms having nuclear charge Ze derived by Milne [2]. His result was explicitly

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$$E(Z) = -0.7687 Z^{7/3} \frac{e^2}{a_0}, \quad a_0 = \frac{\hbar^2}{me^2}. \tag{1}$$

The electron–nuclear potential energy U_{en} in the TF model is also known (see, for example [3]) to be given by

$$U_{en}(Z) = \frac{7}{3} E(Z). \tag{2}$$

But on physical grounds, $U_{en}(Z)$ is simply the interaction energy of the charge Ze sitting in a potential V_0, ie

$$U_{en}(Z) = ZeV_0. \tag{3}$$

Hence, using Eq. (3) in Eq. (2), the desired correlation is expressed by

$$V_0(Z) = \frac{7}{3} \frac{E(Z)}{Ze} = -1.79 Z^{4/3} \frac{e}{a_0} \tag{4}$$

which is the precise semi-classical (non-relativistic) prediction for neutral atoms. Unfortunately, the self-consistent TF ground-state density $n_{TF}(r)$ has two truly major difficulties: (1) it is infinite at the assumed point nucleus, being singular as $r^{-3/2}$, and (2) the decay at large r is not exponential but has the much longer ranged r^{-6} form.

Politzer and Parr [4] proposed a generalization of Eq. (4) to read (see also Politzer chapter in Ref. [3] and Politzer et al. [5])

$$E(Z, N) = \int_0^Z V_0(Z')dZ'. \tag{5}$$

However, it is now known that as Z' is varied through an isoelectronic series of atomic ions with N electrons, there is a critical (non-integral) atomic number, say $Z_c(N)$, at which, on further infinitesimal reduction, one electron ionizes, sometimes referred to, somewhat loosely, as a 'phase transition'. Hence, we shall rewrite Eq. (5) in our present study as

$$E(Z, N) = E(Z_c, N) + \int_{Z_c}^Z V_0(Z')dZ'. \tag{6}$$

Obviously V_0 to be inserted in Eq. (6) is the central tool of the present work and this is naturally to be determined from the ground-state electron density $n(Z, N; \mathbf{r})$ through the isoelectronic series of atomic ions with N electrons.

It is relevant at this point to emphasize that, at least in principle, $E(Z, N)$ is determined solely by the ground-state electron density $n(Z, N; \mathbf{r})$, through the Hohenberg–Kohn theorem [6]. Unfortunately, the functional $E[n(\mathbf{r})]$ remains unknown, and we bypass this fact here by invoking quantum Monte Carlo (QMC) calculations for the appropriate range of Z' to very accurately evaluate numerically the integral appearing in Eq. (6).

With this as background, we turn immediately to present the QMC results to insert into Eq. (6).

2 Computational details

As the variational Monte Carlo (VMC) wave function for the atomic ions, we employed a spin-free Slater–Jastrow form of the type

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots) J(r_1, r_2, \ldots, r_{12}, \ldots). \tag{7}$$

The determinantal component is given by

$$\Phi = \sum_k D_k^{\uparrow} D_k^{\downarrow} d_k \tag{8}$$

where $D_k^{\uparrow}$ and $D_k^{\downarrow}$ are the Slater determinants written in terms of occupied orbitals of spin-up and spin-down electrons, respectively, and d_k are the mixing coefficients. The Jastrow correlation factor is the exponential of the sum of three contributions which are functions of electron–nuclear (e–n), electron–electron (e–e), and pure three-body mixed e–e and e–n distances [7]. In all cases, we used a many determinant wave function with a flexible Slater-type basis set. We optimized all parameters at the VMC level in energy minimization and we performed the diffusion Monte Carlo (DMC) calculation with a time step of 0.05 a.u.

3 Discussion of results

We record in Tables 1, 2, 3 and 4 results for the ground-state energy E and for V_0 from QMC calculations. Both VMC and DMC are here utilized, for $N = 2$–5 (He- to B-like isoelectronic series of atomic ions). V_0 values for the neutral atoms from VMC and DMC are in pretty good agreement. In particular for the B neutral atom V_0 values are $-11.41(1)$ and $-11.39(1)$ Hartree for VMC and DMC, respectively. The electron–nuclear potential energies U_{en} corresponding to these values follow from Eq. (3) for the neutral B atom as -57.07 and -56.95 Hartree. $U_{en}/E = 2.316$ and 2.310, these ratios being somewhat smaller than the TF prediction of 7/3 in Eq. (2). In the customary language of DFT, the ground-state energy E and the universal density functional F, on the minimum, are related by

$$E = F + U_{en}. \tag{9}$$

Hence for VMC, for neutral B, $F = 32.43$ Hartree compared with $F = 32.30$ Hartree for DMC. We anticipate that the DMC value for F will be somewhat more accurate than that from the variational approach. If T denotes the total kinetic energy including correlation kinetic energy, then the virial theorem would give as a useful approximation $T = -E$, in each case.

Table 1 Quantum Monte Carlo results for the electrostatic potential at the nucleus for the He-like series of atomic ions for some thirty values (mostly non-integral) of nuclear charge Ze

Z	E (*VMC*)	err	V_0 (*VMC*)	err	E (*DMC*)	err	ZV_0 (*DMC*)	err
0.88	−0.38517	0.00001	−0.8925	0.001	−0.38548	0.00001	−0.7867	0.002
0.89	−0.39398	0.00001	−0.9056	0.001	−0.39452	0.00001	−0.7991	0.002
0.90	−0.40306	0.00001	−0.9146	0.001	−0.40347	0.00001	−0.8213	0.002
0.905	−0.40784	0.00001	−0.9178	0.001	−0.40800	0.00001	−0.8270	0.002
0.907	−0.41029	0.00001	−1.1545	0.002	−0.41042	0.00002	−1.0189	0.002
0.91	−0.41378	0.00001	−1.1563	0.002	−0.41380	0.00002	−1.0349	0.002
0.911	−0.41495	0.00001	−1.1579	0.002	−0.41494	0.00002	−1.0427	0.002
0.9113	−0.41528	0.00001	−1.1589	0.001	−0.41524	0.00002	−1.0533	0.002
0.9115	−0.41559	0.00001	−1.1553	0.001	−0.41550	0.00002	−1.0452	0.002
0.912	−0.41598	0.00001	−1.1609	0.001	−0.41611	0.00002	−1.0614	0.002
0.915	−0.41957	0.00001	−1.1667	0.001	−0.41963	0.00002	−1.0756	0.002
0.92	−0.42547	0.00001	−1.1853	0.001	−0.42550	0.00002	−1.0845	0.002
0.93	−0.43743	0.00001	−1.2097	0.001	−0.43744	0.00002	−1.1244	0.002
0.96	−0.47479	0.00001	−1.2827	0.001	−0.47478	0.00002	−1.2307	0.002
1.00	−0.52773	0.00001	−1.3602	0.001	−0.52771	0.00002	−1.3655	0.002
1.10	−0.67475	0.00001	−1.5713	0.001	−0.67476	0.00002	−1.7379	0.002
1.30	−1.02980	0.00001	−1.9737	0.001	−1.02989	0.00002	−2.5669	0.003
1.50	−1.46519	0.00001	−2.3765	0.002	−1.46534	0.00002	−3.5699	0.004
1.70	−1.98061	0.00001	−2.7767	0.002	−1.98074	0.00002	−4.7168	0.005
1.95	−2.73736	0.00001	−3.2749	0.003	−2.73742	0.00002	−6.4033	0.006
1.98	−2.83657	0.00001	−3.3334	0.003	−2.83657	0.00002	−6.6097	0.007
2.00	−2.90364	0.00001	−3.3776	0.003	−2.90373	0.00004	−6.7484	0.007
2.01	−2.93757	0.00001	−3.4024	0.003	−2.93757	0.00003	−6.8330	0.007
2.03	−3.00590	0.00001	−3.4328	0.003	−3.00588	0.00003	−6.9968	0.007
2.05	−3.07503	0.00001	−3.4745	0.003	−3.07509	0.00003	−7.1379	0.007
2.10	−3.25133	0.00001	−3.5759	0.003	−3.25133	0.00004	−7.5318	0.008
2.30	−4.00664	0.00002	−3.9701	0.003	−4.00674	0.00003	−9.1471	0.008
2.65	−5.52082	0.00002	−4.6765	0.003	−5.52087	0.00003	−12.3791	0.009
3.00	−7.27989	0.00001	−5.3803	0.004	−7.27990	0.00003	−16.1282	0.0010
3.50	−10.21775	0.00001	−6.3776	0.005	−10.21780	0.00004	−22.3467	0.0017
4.00	−13.65555	0.00002	−7.3775	0.006	−13.65562	0.00005	−29.5164	0.0020
5.00	−22.03087	0.00003	−9.3803	0.007	−22.03134	0.00010	−46.8642	0.0027

As to the ground-state density at the nucleus, n_0 say, this is not an easy quantity to calculate accurately from QMC, though it is, in essence, an observable via the Mössbauer effect. However, Fig. 1 shows our rough estimates for n_0 from QMC. Apart from statistical error, our values are in agreement with literature data for neutral atoms [8–11].

Table 2 QMC results for Li-like isoelectronic series of atomic ions for about 20 values of fractional nuclear charge Ze

Z	E (VMC)	err	V_0 (VMC)	err	E (DMC)	err	ZV_0 (DMC)	err
1.95	−2.73407	0.00001	−3.3204	0.002	−2.73597	0.00001	−6.4446	0.002
2.01	−2.93414	0.00004	−3.4207	0.002	−2.93757	0.00001	−6.8702	0.002
2.05	−3.07421	0.00003	−3.5127	0.002	−3.07612	0.00001	−7.2125	0.002
2.10	−3.25455	0.00002	−3.6534	0.002	−3.25508	0.00001	−7.6669	0.002
2.30	−4.03046	0.00004	−4.1283	0.003	−4.03236	0.00006	−9.5009	0.003
2.50	−4.90202	0.00003	−4.5836	0.003	−4.90269	0.00003	−11.4711	0.002
2.70	−5.86398	0.00003	−5.0385	0.003	−5.86469	0.00002	−13.6113	0.002
2.81	−6.43108	0.00004	−5.2894	0.004	−6.43253	0.00002	−14.8618	0.002
2.84	−6.59192	0.00002	−5.3555	0.004	−6.59216	0.00002	−15.2186	0.002
2.845	−6.61868	0.00002	−5.3647	0.004	−6.61900	0.00002	−15.2732	0.002
2.85	−6.64559	0.00002	−5.3799	0.004	−6.64584	0.00002	−15.3327	0.002
2.855	−6.67250	0.00002	−5.3917	0.004	−6.67276	0.00002	−15.3879	0.002
2.86	−6.69947	0.00002	−5.3918	0.004	−6.69974	0.00002	−15.4451	0.002
3.00	−7.47779	0.00002	−5.7200	0.004	−7.47810	0.00002	−17.1661	0.003
3.50	−10.61908	0.00002	−6.8491	0.005	−10.61971	0.00003	−23.9474	0.004
4.00	−14.32433	0.00004	−7.9774	0.005	−14.32527	0.00010	−31.8723	0.0015
5.00	−23.42402	0.00006	−10.2136	0.007	−23.42581	0.00016	−51.1051	0.0020

Table 3 QMC results for Be-like isoelectronic series of atomic ions for some fifteen values of fractional nuclear charge Ze

Z	E (VMC)	err	V_0 (VMC)	err	E (DMC)	err	ZV_0 (DMC)	err
2.81	−6.42351	0.00003	−5.3520	0.004	−6.42963	0.00007	−14.9583	0.005
2.84	−6.58742	0.00002	−5.4496	0.004	−6.59033	0.00006	−15.5090	0.005
2.845	−6.61478	0.00003	−5.4832	0.006	−6.61785	0.00006	−15.5917	0.005
2.85	−6.64236	0.00004	−5.5108	0.004	−6.64480	0.00005	−15.7154	0.005
2.855	−6.67001	0.00003	−5.5267	0.004	−6.67227	0.00005	−15.7704	0.005
2.86	−6.69905	0.00003	−5.5644	0.004	−6.70082	0.00006	−15.8568	0.005
2.90	−6.91779	0.00005	−5.6429	0.004	−6.92404	0.00008	−16.3710	0.005
3.00	−7.49685	0.00004	−5.9034	0.004	−7.50053	0.00007	−17.6939	0.006
3.50	−10.76575	0.00005	−7.1637	0.005	−10.76827	0.00008	−25.0570	0.007
3.95	−14.24689	0.00006	−8.3000	0.006	−14.25006	0.00011	−32.7569	0.009
4.00	−14.66461	0.00007	−8.4101	0.006	−14.66791	0.00011	−33.6570	0.009
4.05	−15.08962	0.00007	−8.5547	0.006	−15.09286	0.00011	−34.5678	0.009
4.10	−15.52029	0.00007	−8.6760	0.006	−15.52382	0.00012	−35.5470	0.010
4.30	−17.30648	0.00008	−9.1839	0.006	−17.30963	0.00012	−39.4211	0.010
4.50	−19.19290	0.00008	−9.6728	0.006	−19.19638	0.00012	−43.5149	0.011
4.70	−21.17892	0.00009	−10.1850	0.007	−21.18294	0.00013	−47.8008	0.012
5.00	−24.34664	0.00007	−10.9277	0.007	−24.35036	0.00013	−54.6127	0.014

Table 4 QMC results for B-like isoelectronic series of atomic ions for seven values of fractional nuclear charge Ze

Z	E (*VMC*)	err	V_0 (*VMC*)	err	E (*DMC*)	err	ZV_0 (*DMC*)	err
3.90	−13.83248	0.00006	−8.1922	0.005	−13.83736	0.00009	−31.8800	0.007
3.95	−14.24454	0.00006	−8.3012	0.005	−14.24887	0.00008	−32.7797	0.007
4.05	−15.08983	0.00008	−8.5864	0.006	−15.09302	0.00008	−34.7415	0.010
4.10	−15.52244	0.00006	−8.6979	0.006	−15.52767	0.00017	−36.1269	0.010
4.30	−17.34745	0.00007	−9.4313	0.006	−17.35668	0.00015	−40.5444	0.010
4.70	−21.34813	0.00008	−10.566	0.007	−21.35827	0.00018	−49.5728	0.012
5.00	−24.64189	0.00008	−11.414	0.007	−24.65164	0.00018	−56.9498	0.013

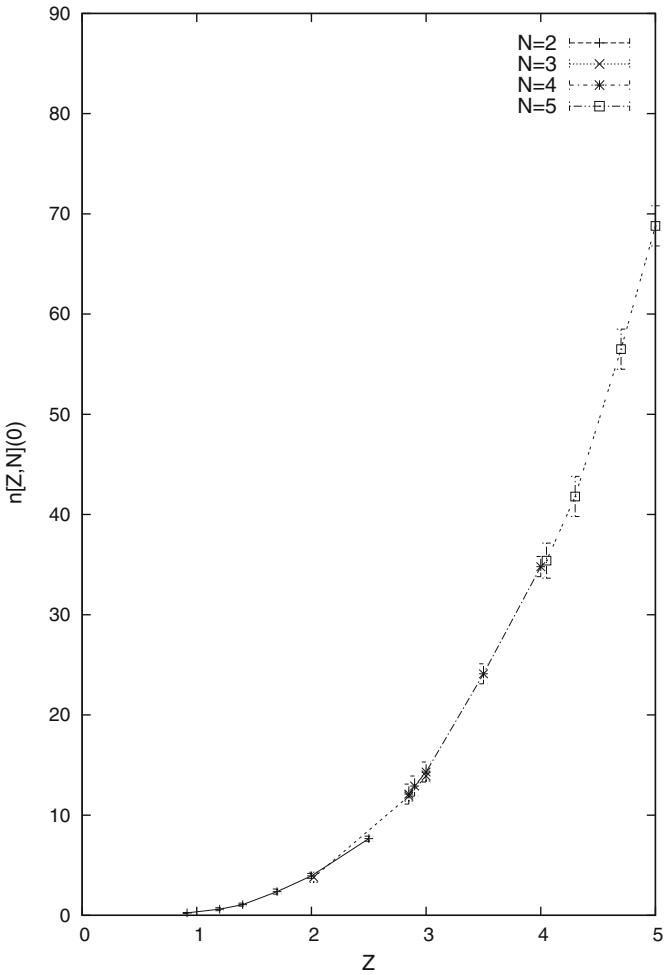

Fig. 1 Plot of the electron density at the nucleus $n_0[Z, N]$ as a function of the fractional nuclear charge Z for the four series of atomic ions considered in this work. Neutral atoms correspond to the case $N = Z$. These are the only observables

Table 5 Displays magnitudes of the two terms on the RHS of Eq. (6)

$Z = N$	Z_c	$E_c(Z_c, N)$	$\int V_0$	$E(Z, Z)$	$E(DMC)$	Ratio
2	0.911	−0.41494(2)	−2.4890	−2.9039	−2.90372	0.1667
3	2.000	−2.90372(4)	−4.5801	−7.4838	−7.47810	0.6340
4	2.856	−6.68112(5)	−7.9819	−14.6630	−14.66791	0.8370
5	4.000	−14.6679(10)	−9.9727	−24.6406	−24.65164	1.4708

In Table 5 we show, for comparison, the separate magnitudes of the two terms on the right-hand-side (RHS) of Eq. (6) together with the total energy $E(Z, Z)$ for neutral atoms. It is important here to make contact with the fairly recent work of Politzer et al. [5]. These authors, however, did not integrate $V_0(Z', N)$ from the critical value $Z_c(N)$ to Z, but from a chosen value of Z', namely $N - 1$. It was the existence of Z_c, at which V_0 is continuous, but non-analytic, which prompted us to separate into the form of Eq. (6). Politzer et al. analyzed a larger interval of nuclear charges. For the four neutral atoms of the present study, their results show an energy which is about 0.2 Hartree lower then the exact one. In our case, as shown in Table 5, the discrepancy is much lower, ranging from 0.0002 Hartree for He to 0.01 Hartree for B. It should be noted that they used the B3PW91 functional to compute V_0 while here we use QMC.

It is worthy of note then that one could view Eq. (6) as a formally exact summation of the $1/Z$ expansion [12] to all orders for the difference energy $E(Z, N) - E(Z_c, N)$. Unfortunately, so far no known exact analytic formula exists for $Z_c(N)$, though Cordero et al. [13] give an empirical fit over a restricted range of N. Also the inequality (see, for example [14])

$$N - 1 \geq Z_c(N) \geq N - 2 \tag{10}$$

is well established.

In summary, the main achievement of the present work is to exhibit extensive QMC calculations for four isoelectronic series of light elements. These are finally utilized to determine the ground-state energies $E(Z, N)$ of such ions from Eq. (6).

Acknowledgments C.A. wishes to acknowledge partial support from MIUR (PRIN 2009). N.H.M. began his contribution to the present study during a visit to the Chemistry Department of the University of Pisa. Thanks are due to Prof. C. Amovilli for generous hospitality. The work of N.H.M. on the final form was brought to fruition during a subsequent visit to Abdus Salam ICTP, Trieste. Thanks are due to Prof. V. E. Kravtsov, for much stimulation and encouragement. Finally, N.H.M. is grateful to Profs. D. Lamoen and C. Van Alsenoy for making his continuing affiliation with the University of Antwerp possible.

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