

Comment on “Compact wave functions for four-electron atomic systems”

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This communication comments on the work of A.M. Frolov and D.M. Wardlaw in *Phys. Rev. A* **78**, 042506 (2008), and specifically on its treatment of the expansion of the total nonrelativistic energies of small atomic systems in inverse powers of the nuclear charge.

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The paper by Frolov and Wardlaw [1] that motivated this Comment (“the PRA paper”) is one of a series of contributions [1–4] taking the viewpoint that their electronic-energy computations on small atomic systems provide a basis for study of the so-called $1/Z$ expansion, i.e., an expansion that describes the nonrelativistic energies (in Hartree units) of the members of an atomic isoelectronic series with nuclear charges Z :

$$E(Z) = a_2 Z^2 + a_1 Z + a_0 + b_1 Z^{-1} + b_2 Z^{-2} + \dots \quad (1)$$

In fact, the $1/Z$ expansion is the only application presented in the PRA paper.

Unfortunately, the PRA paper is flawed because it does not base its computations on the wealth of knowledge about this expansion that has accumulated since it was first studied in the 1930s. Work in the area prior to 1981 was summarized in a paper by Silverman [5], who made a detailed study of the expansion for systems with two through 10 electrons. An important later paper was that in 1990 by Baker, Freund, Hill, and Morgan [6], who studied the expansion for the Helium series in detail and also provided many references. It is clear that Frolov and Wardlaw did not make use of this relevant information, as they recently wrote (Ref. [2], page 10): “Note that the Z^{-1} expansions have never been applied in earlier studies to three- and four-electron atomic systems with the exception of our recent work.”

The early literature, and particularly a 1960 paper by Linderberg and Shull [7], show that the leading terms of the $1/Z$ expansion have readily calculable known values for arbitrary numbers of electrons. The leading (a_2) coefficient is a simple sum of hydrogenic orbital energies, and in the absence of degeneracy in the zero-order wave function (i.e., for the He and Li series) the coefficient a_1 is simply a weighted sum of atomic electron-repulsion integrals. For systems with four to 10 electrons, degenerate-state perturbation theory can be applied to obtain a_1 as an exact, closed form. Frolov and Wardlaw do not understand this, as they wrote (Ref. [2], page 10): “... the approximate (sic) values of the first two coefficients ... are ≈ -1.125 and ≈ 1.0225 for three-electron systems, and ≈ -1.250 and ≈ 1.55 for four-electron atoms and ions.” In addition, from *inter alia* the work of Baker *et al.* [6], some more recent work by Yan, Tambasco, and Drake [8], and older work by Chisholm and Dalgarno [9], it is known how to relate values of the constant term a_0 in the $1/Z$ expansion for different numbers of electrons.

The known or calculable values of a_2 , a_1 , and a_0 should have been used by Frolov and Wardlaw when fitting their calculated data to the expansion; their failure to do so causes the expansions they reported in the PRA paper to have incorrect asymptotic behavior and to be unsuited to the use for which the expansions are intended. Moreover, even if Frolov and Wardlaw had chosen not to make a highly accurate computation of the coefficient a_0 , they could have used the moderately accurate values of a_0 that were reported in 1969 by Knight [10] for systems with three to 10 electrons.

There is no archival value to the tabulations presented by Frolov and Wardlaw of the $1/Z$ expansion coefficients. The basic issue is that the determination of the expansion from a relatively small number of atomic energies is notoriously ill-conditioned. The problem can be illustrated using Frolov and Wardlaw’s data for the Beryllium ground-state series, for which they provided two different sets of data in Refs. [1] and [2], as shown in Table I. It is not clear why these data sets differ, as both were in press at the same time, but (as shown in the top half of Table II), the small differences produce large changes in the expansion coefficients. It is also the case that improvements in the accuracy of the least-squares curve-fitting process (requiring computation at very high precision) cause slight reductions in the mean square fitting error but major changes in the coefficients. Compare, for example, the fit in the third column of the FW section of Table II with the present author’s recomputation at higher precision (third column in the FEH section). A similar comparison is made between FW’s fit and the FEH recomputation in column 6.

TABLE I. Calculated ground-state energies of the Be isoelectronic series (for infinite nuclear mass), as reported by Frolov and Wardlaw.

	Reference [1]	Reference [2]
Li ⁻	-7.5005825	-7.5007729
Be	-14.6672858	-14.6673557
B ⁺	-24.3487629	-24.3488833
C ²⁺	-36.5346987	-36.5348500
N ³⁺	-51.2224986	-51.2227085
O ⁴⁺	-68.4112548	-68.4115355
F ⁵⁺	-88.1005581	-88.1009190
Ne ⁶⁺	-110.290464	-110.2906497
Na ⁷⁺	-134.980025	-134.9802311
Mg ¹⁰⁺	-162.170163	-162.1703565

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TABLE II. Coefficients in $1/Z$ expansion for the ground states of the Be isoelectronic series, as reported by Frolov and Wardlaw (FW) and as recalculated for the present communication (FEH). The coefficients are defined in Eq. (1). Different columns within the same heading describe expansions with different numbers of terms.

\FW	Reference [1]			Reference [2]		
a_2	-1.24916893	-1.25023612	-1.24960246	-1.2491393959	-1.2502544251	-1.2498153630
a_1	+1.53995665	+1.56666629	+1.54629748	+1.5393980568	+1.5673049547	+1.5531914987
a_0	-0.72961516	-0.96119275	-0.71363865	-0.7265622393	-0.9685202159	-0.7969911757
b_1	-0.44483674	+0.38132362	-1.04034589	-0.4503325704	+0.4128601372	-0.5722078051
b_2	-1.02933292	+2.83411527	-1.0754723965	+1.6014921969
b_3	-3.98341752	-2.7600907695
$\Sigma(\text{Error})^2$			2.52×10^{-7}			4.24×10^{-8}
\FEH	With Ref. [1] data ^a		↓	With Ref. [2] data ^a		↓
a_2	-1.25000000	-1.25000000	-1.24986342	-1.2500000000	-1.2500000000	-1.2499051782
a_1	+1.559274208	+1.559274208	+1.55454855	+1.559274208	+1.559274208	+1.5561648542
a_0	-0.873146415	-0.874513830	-0.81131376	-0.872740769	-0.872607498	-0.8342259862
b_1	-0.114382271	-0.080158653	-0.49503886	-0.127078264	-0.130664051	-0.3521873862
b_2	+0.290560898	-0.006164206	+1.39063876	+0.367318958	+0.39840840	+0.9881113715
b_3	-1.334053575	-0.27547741	-2.52844052	-1.46602806	-1.57694063	-2.1137776360
b_4	-1.31890530	+0.13818861
$\Sigma(\text{Error})^2$			5.31×10^{-8}			3.76×10^{-8}

^aThe columns below the up-down arrows are recalculations at higher accuracy of the corresponding FW least-squares fits above the arrows. The other columns in the FEH section are fits with a_2 and a_1 set to their known values.

Also shown in columns 1, 2, 4, and 5 of the FEH section of Table II are the results obtained when the coefficients a_2 and a_1 are set to their known exact values. Setting these coefficients to accurate values causes major changes in the remaining coefficients, and the instability of the coefficient determination indicates that the calculated energies (though probably rather accurate) are for the Beryllium series far too imprecise for the derived $1/Z$ expansion to have any value.

It is generally the case that a useful $1/Z$ expansion cannot be obtained from modest numbers of computations for small Z . For example, Frolov and Wardlaw examined the calculated energies of a three-electron system (the Li ground-state series), for nuclear charges Z from 3 (Li) through 12 (Mg^{9+}) in Ref. [2] (published in 2008) and in JETP [3] (published in 2009). These two data sets are presented to seven decimal places, but most corresponding entries differ in the sixth or seventh place. These two data sets yield very different $1/Z$ expansion coefficients, showing that neither set of data is accurate enough to yield meaningful expansion coefficients.

Energies for the Lithium series (through $Z = 20$) had already been studied in 1998 by Yan, Tambasco, and Drake [8]; those authors reported ground-state energies to 12 decimals and a set of $1/Z$ expansion coefficients derived therefrom. In addition, they gave similar data for the lowest 2P state. This range of Z and the 12-digit accuracy were barely sufficient to determine useful $1/Z$ expansions; these facts document the

futility of an attempt to fit the expansion with fewer and less precise data.

For the two-electron (Helium) ground-state series, the situation is quite different. The work by Baker *et al.* presents explicit calculation of the first 402 $1/Z$ expansion coefficients to 10 decimal places, which completely obviates any need for Frolov and Wardlaw to deduce the coefficients from calculated energies. Baker *et al.*'s work also shows that direct, explicit calculation of the $1/Z$ series coefficients is practical, producing results not accessible by the indirect procedure used by Frolov and Wardlaw. Moreover, Baker *et al.* also call attention to another opportunity, namely to use the expansion to check energies obtained by direct computation. They summed the 402 coefficients to obtain an energy of H^- that is now known to be correct to nine decimals.

Calculated energies for the He ground-state series were given by Frolov and Wardlaw in Ref. [2] and by Frolov and Smith in Ref. [4]. The two sources differ slightly and produce poor $1/Z$ expansion coefficients, but the energies are in full agreement with energy computations based on Baker *et al.*'s $1/Z$ expansion to within the precision of the expansion computation (about 10^{-13} Hartree).

Baker *et al.* also provide the first 27 coefficients for the $1/Z$ expansion of the lowest singlet excited state of the He series. These data are far superior to the coefficients developed by Frolov and Wardlaw, and reproduce the excited singlet energies (in Ref. [2]) to within the precision of the expansion.

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