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The Thomas–Fermi–Scott–Schwinger expansion and the Schrödinger ground state energy of complex neutral atoms

V. C. Aguilera-Navarro,[a] M. de Llano, and O. Rojo[b]

Instituto de Física, UNAM, Apdo. Postal 20-364, 01000 México, D. F.

S. L. L. Verardi

Instituto de Física Teórica, São Paulo, Brasil

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The large Z Thomas–Fermi–Scott–Schwinger expansion for the total nonrelativistic binding energy of a neutral atom is used, together with the Bohr energy formula valid at $Z = 1$, to construct various Padé approximants among which the two-point [3//3] approximant gives an overall improved representation for the energy for Z from 1 to 290, and very especially for the closed shell values $Z = 10, 18, 36, 54, 86, 118, 168$, and 290. The presence of oscillatory terms for open shells in the large Z expansion is also confirmed.

I. INTRODUCTION

The old Thomas–Fermi (TF) theory[1] for the total binding energy of neutral atoms has recently acquired great importance since Lieb and Simon[2] proved it to coincide exactly with the (nonrelativistic) Schrödinger ground state energy of Z electrons in the field of a point nucleus of charge Z, in the limit of $Z \to \infty$. The TF energy (in a.u.) $E_{TF} = C_1 Z^{7/3}$, $C_1 = -0.768\,745\ldots$ due to the *bulk* electrons in the spherical cloud, has been corrected by a term $C_2 Z^{6/3}$, $C_2 = 1/2$, by Scott[3] who conjectures this to come from the *innermost* electrons. Schwinger[4] recently supported this result and subsequently[5] determined a second correction to the TF result of the form $C_3 Z^{5/3}$, $C_3 = -0.2699$, as due to exchange and other quantum effects.

The widely believed notion that the Schrödinger ground state energy E may be the (perhaps asymptotic) series in descending powers of $Z^{1/3}$, which we call the TFSS expansion

$$E = C_1 Z^{7/3} + C_2 Z^{6/3} + C_3 Z^{5/3} + C_4 Z^{4/3} + \cdots \quad (Z \to \infty) \tag{1}$$

has been critically examined by Spruch and collaborators[6] in terms of three distinct soluble models. They conclude that although the series (1) may be correct for *closed* shells ($Z = 2, 10, 18, \ldots$), for *open* shells corrections following the $Z^{5/3}$ term are in the nature *not* of a smooth function of Z but rather of a function with a discontinuity in its value or its first derivative.

Schwinger[4] has pointed out that (1) (with $C_4 = 0$) already gives the energy to within 8% of the Schrödinger value. Figure 1 shows a comparison of Eq. (1), labeled TFSS, with the Schrödinger ground state energies, up to $Z = 17$, as deduced in Ref. 7 and the Hartree–Fock (HF) energies for $Z \geq 20$ as obtained from Refs. 8 and 6. (The HF energies would be indistinguishable from the Schrödinger ones on the scales used in this paper.)

II. PADÉ REPRESENTATION

We have attempted, through Padé extrapolation,[9] to reduce the error in Fig. 1 for all Z. Since for $Z = 1$ one has the *exact* Bohr formula

$$E = -\tfrac{1}{2} Z^2 \; (Z = 1), \tag{2}$$

we have constructed *two*-point Padé approximants which

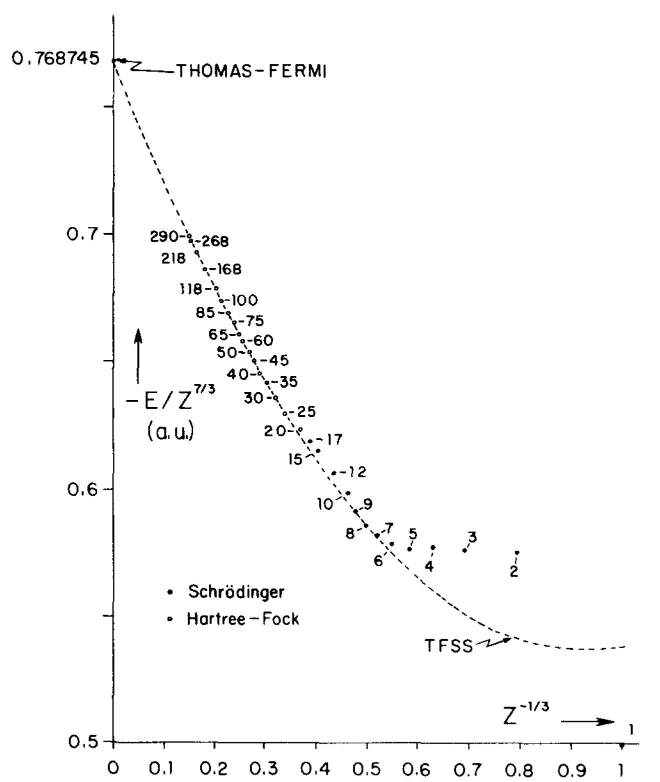

FIG. 1. The TFSS large Z expansion (dashed curve) for $-E/Z^{7/3}$ vs $Z^{-1/3}$, as given by Eq. (1) with $C_4 = 0$, where E is the ground state energy of a neutral atom with Z electrons. Dots refer to the Schrödinger energy as deduced in Ref. 7 for $Z \leq 17$ while open circles refer to the Hartree–Fock energies (Ref. 8) (which, on the scales used in this paper, are indistinguishable from the Schrödinger ones). Numbers refer to Z values.

[a] On leave from Instituto de Física Teórica, Sao Paulo, Brasil.

[b] Permanent address: U.P.I.I.C.S.A del IPN, México 9, D. F.

TABLE I. The coefficients of the [3//3] (t) Padé approximant, defined in Eq. (3), to the series Eq. (4) with $C_4 = 0$.

p_0	−0.284 398 8
p_1	−0.344 147 9
p_2	−0.454 516 0
p_3	−0.5
q_0	+0.369 952 1
q_1	+0.688 295 8
q_2	+0.909 032 1

reduce to Eqs. (1) and (2) in the corresponding limits. These approximants gave results which are, on the whole, superior to a *one*-point Padé approximant which reduces to Eq. (1). Of several expansion variables $Z^{-1/3}$, $(1-Z^{-1/3})^2$, and $(Z-1)^{-1/3} \equiv t$, we found the latter more useful. Then, the nth order Padé two-point approximant

$$[n//n](t) \equiv \frac{p_0 + p_1 t + p_2 t^2 + \cdots + p_n t^n}{q_0 + q_1 t + q_2 t^2 + \cdots + t^n} \tag{3}$$

contains $2n+1$ coefficients which are to be determined

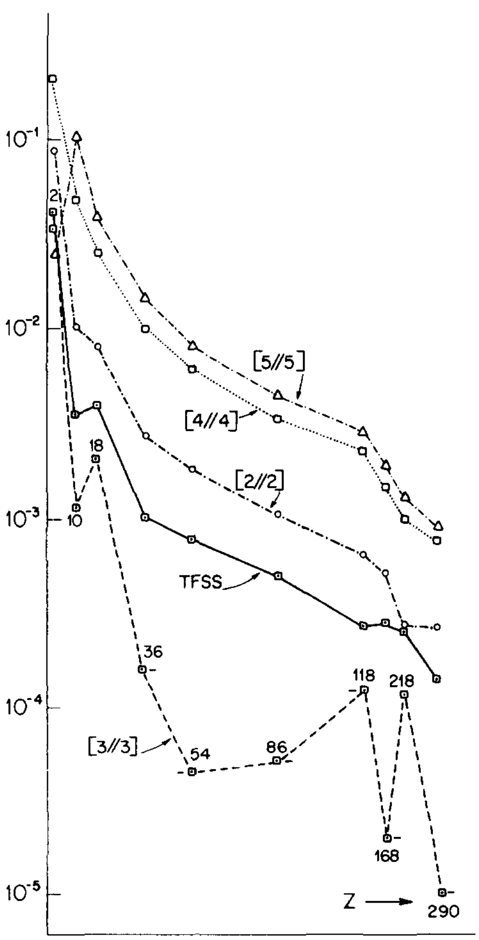

FIG. 2. Difference between $[n//n]$ two point approximants, deduced according to Eq. (3), for $n = 2$, 3, 4, and 5 and the Schrödinger values of $E/Z^{7/3}$. The corresponding difference for the TFSS expansion is also shown. Only closed-shell Z values are considered here, and the numbers refer to these.

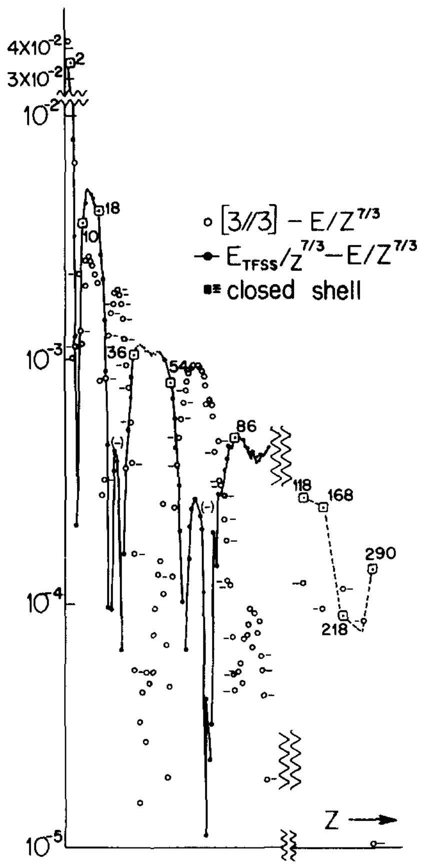

FIG. 3. Same difference as in Fig. 2 but for $n = 3$ and *all* Z values for which we could find Schrödinger or HF data. The minus signs refer to negative differences. Note that the full curves between $Z = 18$ and 36, and between $Z = 54$ and 86, are negative values.

from (a) four equations obtained from matching the small t expansion of Eqs. (3) to (1), now rewritten as

$$E/Z^{7/3} = C_1 + C_2 t + C_3 t^2 + C_4 t^3 + O(t^4) \quad (t \ll 1) \tag{4}$$

and (b) $2n-3$ equations obtained by matching the large t expansion of Eqs. (3) to (2), now rewritten as

$$E/Z^{7/3} = -\frac{1}{2Z^{1/3}} = -\frac{1}{2(1+t^{-3})^{1/3}} = -\frac{1}{2}\left[1 - \frac{1}{3}\frac{1}{t^3} + \frac{2}{9}\frac{1}{t^6} - \frac{14}{81}\frac{1}{t^9} + \cdots\right] \quad (t \gg 1). \tag{5}$$

III. RESULTS

This procedure gives, for example, for $n = 3$ the coefficients of Table I (we use $C_4 = 0$). [We note that since the denominator of Eq. (3) for $n = 3$ is positive for all $t \geq 0$ the extrapolant to $E/Z^{7/3}$ has no poles for $Z \geq 1$.] One- and three-point Padé approximants were also constructed but found to be inferior in quality to the family (3) and within this family the $n = 3$ was found to be the best. This is illustrated in Fig. 2 for closed-shell Z values where the *difference* between Eq. (3), for $n = 2$, 3, 4, and 5, as well as the TFSS values (1), and the Schrödinger energy $E/Z^{7/3}$ is shown. Note that [2//2] relies on only the first term of the expansion (5), whereas [3//3] utilizes the first three. Figure 3 shows the

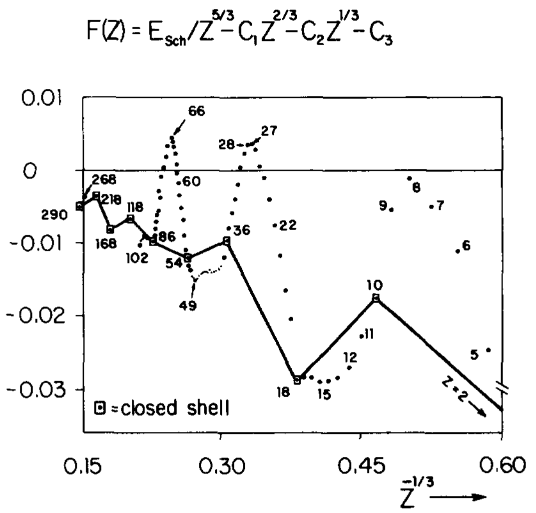

FIG. 4. Difference between the Schrödinger $E/Z^{5/3}$ and the TFSS expansion Eq. (1) times $Z^{2/3}$ for almost all Z. The closed shell Z values are connected by a straight line only to guide the eye.

alluded difference for $n=3$ only, and the TFSS values, for all values $Z=2, 3, \ldots, 102$ and $Z=118, 168, 218, 268$, and 290. The full curve (giving the difference between Eq. (1) and the Schrödinger $E/Z^{7/3}$) is extremely jagged and oscillatory, at least up to $Z=102$ where data are available for all integer $Z \geq 1$, in support of the above mentioned conjecture of Ref. 6. That the series (1) is followed by nonsmooth-in-Z contributions is further suggested by observing that, although our [3//3] approximant gives a *lower* (and hence better) value than TFSS for some 60% of the Z values considered it is clearly *inferior* to the TFSS at the two open shells $Z=(18, 36)$ and $Z=(54, 86)$. Finally, Fig. 4 shows a plot of the Schrödinger $E/Z^{5/3}$ minus the first three terms of Eq. (1) times $Z^{2/3}$. If the terms beyond the C_3 term were a descending series in $Z^{1/3}$ the points would fall on a smooth curve. We note, however, not only huge well-defined oscillations for all Z but also that the closed-shell values themselves are far from defining a smooth curve.

In conclusion, it appears that extending the TFSS large Z expansion for the total binding energy of neutral atoms, even granting its validity as it now stands, will be a challenging endeavor.

Note added in proof: A recent paper by Y. Tal and L. J. Bartolotti [J. Chem. Phys. **76**, 4056 (1982)] exhaustively studies the Hartree–Fock energies of both neutral and ionic systems with the TFSS expansion and also conclude that oscillatory terms must be present.

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