

Improved Z-dependence of the ground-state energies of neutral atoms

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Abstract. Three *simulated* expressions are suggested regarding the Z-dependence of ground-state energies of neutral atoms at the Hartree-Fock, exact nonrelativistic and relativistic levels. The Hartree-Fock-level $Z^{-1/3}$ -expansion contains three previously derived *plus* two newly derived terms, the latter signifying exchange corrections from the 'inner core' and the 'core mantle' of the Lieb atom. This leads to better agreement than any previous expression, with every coefficient being physically transparent. The Z-dependence of the correlation energy is obtained from a semiempirical Wigner-type correlation potential while the relativistic correction is taken to be in between the values suggested separately by Scott and Schwinger. Agreement with reference values is again better than before. It appears, however, that the atomic $Z^{-1/3}$ -expansion should not proceed beyond terms $O(Z)$.

Keywords. $Z^{-1/3}$ -expansion; atomic binding energy; Thomas-Fermi theory; exchange-correlation energy; single-particle density.

1. Introduction

Based on the Thomas-Fermi (TF) method and its various refinements, the search for a $Z^{-1/3}$ -expansion for the non-relativistic ground-state energies of neutral atoms has been a vintage problem in atomic physics (Dirac 1930; Scott 1952; March 1953, 1957; Ballinger and March 1955; March and Plaskett 1956; Dmitrieva and Plindov 1975; Lieb 1976, 1981; March and Parr 1980; Schwinger 1980, 1981; Shakeshaft *et al* 1981; Shakeshaft and Spruch 1981; Tal and Levy 1981; Aguilera-Navarro *et al* 1982; Bander 1982; Tal and Bartolotti 1982; Conlon 1983). This involves writing the energy as the following function of Z (nuclear charge or the number of electrons)

$$-E(Z) = C_7 Z^{7/3} + C_6 Z^2 + C_5 Z^{5/3} + \dots, \quad (\text{A})$$

where all the C_i 's are, in principle, *known universal numbers arising from well-defined physical effects*. However, the present situation concerning (A) is not quite satisfactory on the basis of *three* criteria: (i) clear physical significance is known only for C_7 , C_6 and C_5 ; (ii) agreement with Hartree-Fock (HF) and nonrelativistic (NR) atomic energies, especially at low Z, is not excellent; and (iii) the length of the above expansion is not known.

There have been two types of studies on (A). The first has tried to calculate C_7 , C_6 and C_5 from first principles (Dirac 1930; Scott 1952; March 1953, 1957; Ballinger and

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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March 1955; March and Plaskett 1956; Schwinger 1980, 1981; Dmitrieva and Plindov 1975; Lieb 1976, 1981; Bander 1982; Conlon 1983) whereas the second has tried to obtain either C_5 or all three by fitting calculated energies to experimental or *ab initio* energies (Scott 1952; March and Parr 1980; Shakeshaft *et al* 1981; Shakeshaft and Spruch 1981; Tal and Levy 1981; Aguilera-Navarro *et al* 1982; Tal and Bartolotti 1982). The derived values are $C_7 = 0.76874512$ a.u.* (TF value), $C_6 = -0.5$ a.u. [Scott value (1952)] and $C_5 = 0.2699$ a.u. [(Schwinger value (1980))]. With these, the 3-term expansion in (1) reproduces known energy values for $6 \leq Z \leq 80$ at 2% error and at 7% error for the hydrogen atom (Schwinger 1980). If one takes the $Z^{7/3}$ term alone then, in the limit $Z \rightarrow \infty$, this gives the exact NR energy (Lieb 1976; Lieb and Simon 1977), but it overestimates energy badly at low Z with $\approx 30\%$ error (figure 1). On the other hand, workers studying various fitting or interpolation schemes have commented on the presence of oscillatory and/or discontinuity features, depending on the scheme of interpolation.

This paper is an attempt to improve the situation *vis-a-vis* criteria (i)–(iii) above. In §2 we discuss the basis on which two new constants C_4 and C_3 are derived in §3. The results of energy simulation at the HF, NR and relativistic levels are then described in §4, while §5 takes stock of the resulting situation.

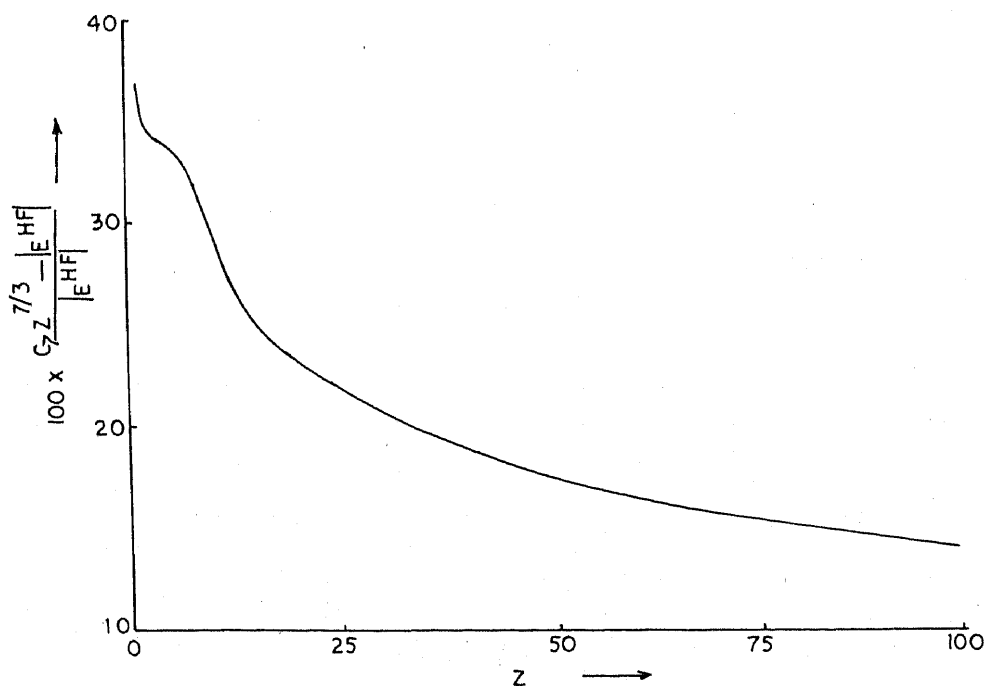


Figure 1. Percent deviation of $C_7 Z^{7/3}$ from atomic ground-state Hartree-Fock energies (Clementi and Roetti 1974; McLean and McLean 1981) as a function of Z .

* Atomic units will be employed throughout this paper.

2. The approach to the problem

The analysis of the present problem requires us to obtain the integral of any local function of the charge density $\rho(\mathbf{r})$ as a function of the nuclear charge Z . This we do below, using an average-density argument. We also utilize Lieb's (1976; 1981) analysis of the Z -dependence of r and ρ in different regions of an atom (in particular, see § Vc of Lieb 1981). Specifically, we consider almost the whole of the atom to consist of an 'inner core', a 'core' and a 'core mantle'. The $Z^{7/3}$ -dependent kinetic energy term arises from the 'core' whereas the Z^2 and $Z^{5/3}$ terms arise from the 'inner core' and 'core mantle' respectively. Similarly, the $Z^{5/3}$ term for exchange energy arises from the 'core', while the 'inner core' and 'core mantle' contribute, respectively, the $Z^{4/3}$ and Z terms. Note that the problem is really open-ended since the $Z^{4/3}$ and Z terms would also contain small kinetic-energy contributions from the region outside the 'core mantle'. However, we feel it is necessary that the included terms correspond to a consistent physical picture and, therefore, we do not consider here the region outside the 'core mantle' (since then, one will also have to consider exchange contributions from this region, and so on again for kinetic energy, etc.).

Let $f(\rho)$ be a local function of $\rho(\mathbf{r})$ and $F[\rho]$ its volume integral. Then the Z -dependence of F is given by

$$\begin{aligned} F &= f(\bar{\rho})V \\ &= f(Z^2/V_0)V_0Z^{-1}, \end{aligned} \quad (1)$$

where V is the TF volume (Lieb 1976) of a neutral atom with Z electrons, $\bar{\rho} (= Z/V)$ is the average density and the volume V_0 is a universal constant. Writing

$$-E_{TF} = C_k \int \rho^{5/3} d\mathbf{r} = C_7 Z^{7/3} \quad (2)$$

and $V = V_0 Z^\alpha$, one can readily show that $\alpha = -1$ and $V_0 = (C_k/C_7)^{3/2} = 7.218207$ a.u., since $C_k = (3/10)(3\pi^2)^{2/3}$.

Now, in order to find the correction from the 'inner core', consider all the electrons as having been incorporated into a spherical Scott atom (1952) of radius R , where R may extend a little outside the 'inner core' into the 'core'. For this atom, let

$$\rho = Cr^\alpha, \quad (3)$$

where C is a universal constant. The Z -dependence of ρ enters through that of r . The density normalization is

$$4\pi \int_0^R \rho r^2 dr = Z. \quad (4)$$

Taking $Z \sim R^{-1}$ (see Lieb 1981) and using (3), this gives $\alpha = -4$. To obtain C , we equate the Scott (1952) and Weizsäcker energies, viz.,

$$\begin{aligned} \frac{1}{2}Z^2 &= \frac{1}{8} \int \frac{(\nabla\rho)^2}{\rho} d\mathbf{r} \\ &= 2C^{-1/2} \int \rho^{3/2} d\mathbf{r}, \end{aligned} \quad (5)$$

for a spherical atom, using $\rho = Cr^{-4}$. Using (1) and (2) we obtain

$$\rho = 16V_0^{-1}r^{-4}. \quad (6)$$

This gives the radial dependence of electron density in a spherical Scott atom.

Consider now the correction from the 'core mantle'. Here $Z \sim R^{-3}$ (Lieb 1981), where R is the radius of the 'mantled' atom (as before, R may extend a little into the 'core'). Using (3) and (4), we now find $\alpha = -6$, i.e.

$$\rho = Cr^{-6}. \quad (7)$$

Replacing $(\nabla\rho)^2$ by $(d\rho/dr)^2$ as well as using (1) and (2), we obtain the Weizsäcker energy for this region as

$$\frac{1}{8} \int \frac{(\nabla\rho)^2}{\rho} dr = 4.5 Z^{5/3} (CV_0)^{-1/3}. \quad (8)$$

This ought to be identified with the δE_{qu} correction of Schwinger (1980), where

$$\delta E_{qu} = 2 (0.2699) Z^{5/3} / 11. \quad (9)$$

Then

$$\rho = (99/1.0796)^3 V_0^{-1} r^{-6}, \quad (10)$$

which gives the radial dependence of the electron density in the 'core mantle' and in its region of overlap with the 'core'.

Equations (1), (2), (6) and (10) form the backbone of the present work leading to the following results.

3. Simulation of the ground-state energies of neutral atoms at the Hartree-Fock, exact nonrelativistic and relativistic levels

3.1 The Hartree-Fock level

We write the energy as

$$-E_{HF}(Z) = C_7 Z^{7/3} + C_6 Z^2 + C_5 Z^{5/3} + C_4 Z^{4/3} + C_3 Z, \quad (11)$$

where C_7 is the TF value, C_6 is the Scott value and C_5 is the Schwinger value. C_4, C_3 are the exchange corrections to be calculated in view of the fact that the magnitude of the Dirac exchange is less (Shih 1976) than that of the HF exchange.

For a homogeneous electron gas or a gas of slowly varying density, the leading gradient correction to the Dirac exchange is taken as (Kohn and Sham 1965; Shih 1980; Shih *et al* 1980; Gross and Dreizler 1981; Hernandez and Gazquez 1982; Csavinszky and Vosman 1983):

$$K_2[\rho] = \beta \int \frac{(\nabla\rho)^2}{\rho^{4/3}} dr, \quad (12)$$

where β is given by (Kohn and Sham 1965; Shih 1980; Shih *et al* 1980; Gross and Dreizler 1981; Csavinszky and Vosman 1983):

$$\beta = (-7)/[432\pi(3\pi^2)^{1/3}].$$

Replacing $(\nabla\rho)^2$ by $(d\rho/dr)^2$ for a spherical Scott atom and using (6), we obtain

$$K_2^1[\rho] = 16\beta(16/V_0)^{-1/2} \int \rho^{7/6} dr. \quad (13)$$

Use of (1) and (2) then gives

$$K_2^i(Z) = 4\beta V_0^{1/3} Z^{4/3}, \quad (14)$$

i.e.

$$C_4 = 0.0129783 \text{ a.u.} \quad (15)$$

Similarly, using (1), (2) and (10) for the 'core mantle', we obtain

$$K_2^m(Z) = 36\beta Z C^{-1/3}. \quad (16)$$

Hence,

$$C_3 = 0.00126492 \text{ a.u.} \quad (17)$$

Note that both the exchange corrections, C_4 and C_3 , have the same sign as the original $Z^{5/3}$ -exchange term. Thus, at the HF level all the five C_i 's are *derived*, and not *adjusted*, with the physical effects clearly delineated.

3.2 The exact nonrelativistic level

Since both exchange and correlation have a similar origin in interelectronic repulsion, one may think of extending the above picture to cover electron correlation as well. As we shall see below, this does not work, casting doubt on any $Z^{-1/3}$ -expansion for correlation energy.

In the local density approximation, correlation energy is given by

$$E_c[\rho] = \int \varepsilon_c[\rho] \rho \, dr. \quad (18)$$

In order to apply (1) and (2), one must start with a reliable correlation potential $\varepsilon_c[\rho]$. We have examined the parametric forms for $\varepsilon_c[\rho]$ of McWeeny (1976) and Vosko and coworkers (Vosko *et al* 1980; Wilk *et al* 1981) for $0.5 \leq r_s \leq 20$, where $(4/3)\pi r_s^3 = \rho^{-1}$. The values of Vosko and coworkers agree with reference values (Ceperley and Alder 1978, 1980) better than those of McWeeny. However, using Hartree-Fock atomic densities (Clementi and Roetti 1974), we observed that both these correlation potentials overestimate atomic correlation energies, especially at low Z , by 100–250%; such a situation also occurs with Cowan's (1981) statistical prescription for correlation. Therefore, we will employ the Wigner-type parametric formula

$$\varepsilon_c^{\text{at}}[\rho] = -(9.810 + 21.437 \rho^{-1/3})^{-1}, \quad (19)$$

suggested by Bruil and Rothstein (1978). As seen in table 1, this gives a much better reproduction of atomic correlation energies (Veillard and Clementi 1968). Using (1) and (2), (19) leads to

$$-E_c^{\text{at}}(Z) = Z[9.810 + 21.437(Z^2/V_0)^{-1/3}]^{-1}. \quad (20)$$

Table 1 lists these values. Comparing columns 2 and 5, we see that the average-density argument via (1) and (2) leads to some overestimation. This is a characteristic feature. Nevertheless, the values from (20) are still better than those from the ε_c 's of McWeeny (1976), Vosko *et al* (1980) and Wilk *et al* (1981).

Thus, the sum of (11) and (20) simulates the exact nonrelativistic energy. Note that (20) contains two adjusted parameters.

Using (1) and (2), one can readily argue that $E_c(Z)$ cannot have terms containing $Z^{2/3}$, $Z^{1/3}$, etc. If $E_c(Z)$ has any term Z^k , $k < 1$, then the corresponding $\varepsilon_c[\rho]$ has a ρ^l term, $l < 0$. Such an $\varepsilon_c[\rho]$ diverges when $\rho \rightarrow 0$, although the correlation energy density

Table 1. Calculated values (a.u.) of $-E_c(Z) = -\int \varepsilon_c[\rho]\rho dr$, using Hartree-Fock atomic densities⁽ⁱ⁾.

Z	Reference value ⁽ⁱⁱ⁾	Brual-Rothstein value ⁽ⁱⁱⁱ⁾	McWeeny value ^(iv)	Vosko <i>et al</i> value ^(v)	Equation (20)
3	0.0454	0.06472	0.1770	0.1620	0.1010
4	0.0940	0.09163	0.2431	0.2247	0.1525
6	0.1551	0.1593	0.4034	0.3738	0.2684
7	0.1861	0.2044	0.4986	0.4636	0.3313
10	0.381	0.3567	0.7828	0.7464	0.5337
12	0.428	0.4377	0.9119	0.8916	0.6774

⁽ⁱ⁾ Clementi and Roetti 1974; ⁽ⁱⁱ⁾ Veillard and Clementi 1968; ⁽ⁱⁱⁱ⁾ Brual and Rothstein 1978; ^(iv) McWeeny 1976; ^(v) Vosko *et al* 1980; ^(vi) Wilk *et al* 1981.

vanishes giving a finite $E_c[\rho]$. If, like exchange, one expresses $E_c(Z)$ as a sum of $Z^{5/3}$, $Z^{4/3}$ and Z terms, then $\varepsilon_c[\rho]$ becomes

$$\varepsilon_c[\rho] = A\rho^{1/3} + B\rho^{1/6} + C. \quad (21)$$

If the three parameters A , B and C are now adjusted to reproduce atomic correlation energies (Veillard and Clementi 1968), then the parameters do not have the same sign leading to the unphysical result that $\varepsilon_c[\rho]$ vanishes at a nonzero ρ . An identical situation results if one takes any two of the three Z -dependent terms. Further, one should not take $E_c(Z)$ as either a single $Z^{5/3}$, $Z^{4/3}$ or Z term, because this will again lead to an $\varepsilon_c[\rho]$ which is not in accord with experience (see (21)). Therefore, it is obvious that if one requires good reproduction of atomic correlation energies, then $E_c(Z)$ should not contain $Z^{5/3}$ to $Z^{1/3}$ terms.

3.3 The relativistic level

For simulation at this level we employ the expression (Scott 1952; Schwinger 1980)

$$-E_{\text{Rel}}(Z) \times 10^6 = C_R Z^{9/2}, \quad (22)$$

where we take $C_R = 3.5$ a.u. This provides better agreement with Dirac-Hartree-Fock values (Desclaux 1973) than the values of 4.0 and 2.4 suggested by Scott (1952) and Schwinger (1980). The $Z^{9/2}$ -term is the leading relativistic correction to the kinetic energy. Note that this is the only parameter adjustment done in this paper.

Thus, the sum of (11), (20) and (22) simulates the relativistic atomic energy. The diminishing relative importance of correlation and increasing importance of relativistic corrections with increasing Z are faithfully mimicked by (20) and (22).

4. Results

Using (11), (20) and (22), we have calculated atomic ground-state energies for $2 \leq Z \leq 110$ and compared them with the appropriate reference values as well as the values of Shakeshaft *et al* (1981) with their median value (0.275) for C_s which includes

correlation. The largest error occurs with $Z = 2$, viz. 3.1%, 2.8% and 1.4% for (11), (20) and (22) respectively. On the whole, the present energies are better than the previous ones, especially at low Z . Table 2 reports values for 10 atoms. A pleasing situation is that for most of the atoms, the simulated HF and nonrelativistic energies lie *above* the corresponding true energies. However, due to parameter adjustment, the physical

Table 2. Comparison of $-E(Z)$ values (a.u.) for neutral atoms with Hartree-Fock, nonrelativistic and relativistic energies.

Z	Hartree-Fock level ⁽ⁱ⁾	Nonrelativistic level ⁽ⁱⁱ⁾	Relativistic level ⁽ⁱⁱⁱ⁾
2	2.86168	2.9037	2.90382
	2.76634	2.7473	2.86175
3	7.43272	2.8220	2.82212
	7.22269	7.4781	7.4780
		7.1946	7.43327
4		7.3236	7.32410
	14.57302	14.6670	14.6685
	14.33280	14.2967	14.5752
		14.4852	14.4870
5	24.52906	24.6530	24.6579
	24.42664	24.3839	24.5350
		24.6352	24.6401
10	128.54705	128.928	129.056
	128.44103	128.385	128.674
		128.975	129.085
15	340.71869	341.240	342.025
	339.19779	339.164	341.420
		340.100	340.786
20	676.75803	—	—
	675.18084	675.202	679.502
		676.477	678.981
40	3538.9172	—	—
	3534.6109	3535.171	3594.81
		3537.607	3594.27
80	18408.984	—	—
	18404.965	18407.963	19623.5
		18411.609	19693.9
90	24359.726	—	—
	24348.155	24352.024	26471.9
		24355.735	26534.2

⁽ⁱ⁾ In this column for every Z , the first number is from Clementi and Roetti (1974) for $2 \leq Z \leq 40$ and from McLean and McLean (1981) for $Z = 80-90$. The second number is from eq. (11).

⁽ⁱⁱ⁾ In this column, for every Z , the first number is from Veillard and Clementi (1968); the second number is from Shakeshaft *et al* (1981), with $C_5 = 0.275$; the third number is from the sum of (11) and (20). For $Z > 15$, the first number is not entered.

⁽ⁱⁱⁱ⁾ In this column, for every Z , the first number is the experimental energy (Veillard and Clementi 1968); the second number is the Dirac-Hartree-Fock value (Desclaux 1973); the third number is from the sum of (11), (20) and (22). For $Z > 15$, the first number is not entered.

meaning of the constants in (20) and (22) is not completely clear. Note that the overestimation in energy due to the use of the average-density argument, in converting ρ -dependence into Z -dependence, compensates to a certain extent for the underestimation resulting from C_7 , C_6 and C_5 together.

5. Conclusions

By incorporating the exchange corrections $C_4 Z^{4/3}$ and $C_3 Z$, we have obtained better agreement with HF values than observed before, especially at low Z . Except for the few atoms where the simulated energy has gone below the HF energy, the agreement would improve further if $Z^{4/3}$ - and Z -dependent kinetic-energy contributions are also incorporated. In order to retain physical consistency, we have refrained from doing this. At this level, the physical meanings of all the co-efficients are clear. However, at the NR and relativistic levels this physical clarity is partly lost due to parameter adjustment, although the numerical agreement with reference values improves further. The relativistic situation deserves a first-principles attack.

For practical purposes, if one neglects exchange contributions from outside the 'core mantle', then expansion (A) proceeds only up to $C_3 Z$. We have argued in §3 that the atomic correlation energy should not be expanded in $Z^{-1/3}$, i.e. it should not contain terms from $Z^{5/3}$ to $Z^{1/3}$, if a satisfactory correlation potential and good agreement with atomic correlation energies are desired. It is also worthwhile to note that hardly any work seems to have been done on the Z -dependence of excited states.

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