Density-functional approach to relativistic charge expansion theory

N. H. March*
University of Oxford, Oxford, England
(Received 7 August 1996; revised manuscript received 7 January 1997)

In a recent paper, Weiss and Kim [Phys. Rev. A **51**, 4487 (1995)] have discussed the effects of relativistic corrections on the large atomic number Z behavior of the $1/Z$ expansion. Contact is established here between their study and the simplest version of density-functional theory in the large Z limit, namely, the Thomas-Fermi theory. It is emphasized that this simple density-functional theory sums subseries of the original $1/Z$ expansion to all orders in the nonrelativistic case. Relativistic corrections to this density-functional theory are also discussed [S1050-2947(97)07407-6]

PACS number(s): 31.10.+z, 31.30.Jv

We wish to make contact between the interesting paper by Weiss and Kim (WK) [1] and the results of the simplest density-functional theory DFT, namely, the statistical method of Thomas [2] and Fermi [3] (TF). We begin with the nonrelativistic theory and then discuss relativistic modifications of this DFT, going back to the pioneering work of Vallarta and Rosen [4].

In their Eq. (1), WK write the nonrelativistic total energy of any state of an atom or ion. We shall write their Eq. (1) to show explicitly where the number of electrons N in the atomic ion enters the $1/Z$ expansion. However, we shall restrict all our considerations in this paper to the ground-state energy $E(Z,N)$, Z being the atomic number. Thus, specialized to the ground state, WK's Eq. (1) will be written as

$$E(Z,N)=Z^2[\epsilon_0(N)+Z^{-1}\epsilon_1(N)+Z^{-2}\epsilon_2(N)+\cdots]. \tag{1}$$

To make contact between Eq. (1) and the DFT of Thomas and Fermi, March and White [5] noted that to regain the nonrelativistic DFT energy of Thomas and Fermi [6,7] from Eq. (1), the asymptotic behavior of the coefficients $\epsilon_n(N)$ for large numbers of electrons N must take the form

$$\epsilon_n(N)\sim A_n N^{n+(1/3)}; \quad \text{large } N. \tag{2}$$

Then the result for neutral atoms $Z=N$ of Milne [6] and Hulthén [7] for positive atomic ions (i.e., $0<N/Z\leqslant 1$) is regained, namely,

$$E_{\mathrm{TF}}(Z,N)=Z^{7/3}f_1(N/Z), \tag{3}$$

where $f_1(x)$ is known from numerical solutions of the nonlinear dimensionless TF equation for atomic ions. Subsequently the form of A_n for large n has been shown by Senatore and March [8] to have the form $A/n^{3+\alpha}$, where $\alpha=\frac{1}{3}$ [8] and an accurate analytical approximation is also given for A [8].

The natural extension of Eq. (2) is to write [9]

$$\epsilon_n(N)=A_n N^{n+(1/3)}+B_n N^n+C_n N^{n-(1/3)}+\cdots . \tag{4}$$

Forming $\epsilon_n(N)/Z^n$ and summing over n formally leads then to

$$E_{\mathrm{DFT}}(Z,N)=Z^{7/3}f_1(N/Z)+Z^2 f_2(N/Z)+Z^{5/3}f_3(N/Z)+\cdots , \tag{5}$$

which March and Parr [9] point out reduces to the expansion of Scott [10] in the neutral atom case $N=Z$. For a detailed discussion of the Z^2 term in Eq. (5), following the work of Scott, see Englert and Schwinger [11]. A note about correlation [1] is appropriate here. March and Wind [12] give the approximate result that correlation energy of neutral atoms is approximately proportional to Z, whereas Kais *et al.*, by dimensional scaling theory, argue for the dependence $Z^{4/3}$ at large Z [13].

Having established therefore direct contact between the nonrelativistic $1/Z$ expansion (1) and the statistical DFT of Thomas and Fermi, we turn to comment on relativistic modifications of charge expansion theory [1]. Senatore and March [14] have discussed the changes required in the DFT of Thomas and Fermi in going to the relativistic modification of Vallarta and Rosen [4]. From the way the analyticity properties of $E(Z,N,\alpha)$, where the fine-structure constant $\alpha\neq 0$ now, are altered from the TF theory, Senatore and March [14] propose a Laurent expansion

$$E(Z,N,\alpha,R_n)=Z^2\sum_{n=-\infty}^{\infty}\epsilon_n(N,\alpha,R_n)Z^{-n}, \tag{6}$$

where R_n denotes the nuclear radius. They demonstrate that this includes the expansion of Layzer and Bahcall [15] discussed by WK [1].

Just as for the nonrelativistic case, it can be shown from the Vallarta-Rosen (VR) theory that if one writes the Layzer-Bahcall (LB) expansion as a special case of the Laurent form (6), namely,

$$E_{\mathrm{LB}}(Z,N,\alpha)=Z^2\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}E_{nm}(N)\epsilon^m Z^{-n}, \tag{7}$$

with $\epsilon=\alpha^2Z^2$, then the VR method gives for suitably large N the result [16]

*Permanent address: 6 Northcroft Rd. Egham, Surrey TW20 0DU, England.

$$E_{nm}^{\mathrm{VR}}(N)=c_{nm}N^{n-(2m/3)-(1/3)}. \quad (8)$$

In summary, it has been pointed out that for heavy positive atomic ions with $N \lesssim Z$ the charge expansion theory can be partially summed by appeal to DFT for large Z. Then the natural expansion parameter appears in the nonrelativistic case to be $Z^{-(1/3)}$ rather than Z^{-1}. In the relativistic case, the DFT of Vallarta and Rosen [4] strongly motivates the Laurent expansion (6), of which the Layzer-Bahcall (LB) expansion is a special case. Given the LB result (7), the VR theory then leads to the scaling property (8). Of course, all this is not to deny the interest in the direct use of charge expansion theory for examples such as C-like uranium referred to in WK [1]. The final point takes us back to the least well established area of correlation energy. Recently it has also been pointed out to the writer that, in the thermodynamic limit, the work of Gell-Mann and Brueckner [17] and Kilic [18], leads to a term of the form $N \ln N$. Whether such a term enters the correlation energy in the finite systems that are discussed throughout this paper remains an open question at the time of writing.

This work was carried out during a visit to ICTP, Trieste. The author is much indebted to Professor Yu Lu and his colleagues for hospitality and for stimulating interaction. Partial financial support for work on density-functional theory has been provided by the Leverhulme Trust, UK.

[1] A. W. Weiss and Y.-K. Kim, Phys. Rev. A **51**, 4487 (1995).
[2] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1926).
[3] E. Fermi, Z. Phys. **48**, 73 (1928).
[4] M. S. Vallarta and N. Rosen, Phys. Rev. **41**, 708 (1932).
[5] N. H. March and R. J. White, J. Phys. B **5**, 466 (1972).
[6] E. A. Milne, Proc. Cambridge Philos. Soc. **23**, 794 (1927).
[7] L. Hulthén, Z. Phys. **95**, 789 (1935).
[8] G. Senatore and N. H. March, J. Chem. Phys. **83**, 1232 (1985).
[9] See N. H. March and R. G. Parr, Proc. Natl. Acad. Sci. USA **77**, 6285 (1980).
[10] J. M. C. Scott, Philos. Mag. **43**, 859 (1952).
[11] B.-G. Englert and J. Schwinger, *Semiclassical Theory of Atoms* (Springer-Verlag, Berlin, 1988).
[12] N. H. March and P. Wind, Mol. Phys. **77**, 791 (1992).
[13] S. Kais *et al.*, Int. J. Quantum. Chem. (to be published).
[14] G. Senatore and N. H. March, Phys. Rev. A **30**, 990 (1985).
[15] D. Layzer and J. Bahcall, Ann. Phys. (N.Y.) **17**, 177 (1962).
[16] U. M. B. Marconi and N. H. March, Int. J. Quantum Chem. **20**, 693 (1981).
[17] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).
[18] See also S. Kilic, Fizika A **1**, 135 (1992).