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# Relativistic Theory of Binding Energies of Heavy Positive Ions

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**Abstract**

The self-consistent relativistic Thomas–Fermi theory of heavy positive ions with $N$ electrons and nuclear charge $Ze$ is shown to lead to a chemical potential $\mu$ which has the scaling property

$$\mu = Z^{4/3} F(N/Z; \varepsilon/Z^{2/3}),$$

with $\varepsilon = \alpha^2 Z^2$, $\alpha$ being the fine structure constant. Combining this with the Layzer–Bahcall expansion for the total energy $E(Z, N)$, namely,

$$E(Z, N) = Z^2 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} E_{nm}(N) \varepsilon^m Z^{-n},$$

it is proved that the coefficients $E_{nm}(N)$ at large $N$ have the asymptotic behavior $N^{n-2m/3+1/3}$. The corresponding result for the scaling of the relativistic Thomas–Fermi energy is

$$E_{\mathrm{TF}}(Z, N) = Z^{7/3} F_1(N/Z; \varepsilon/N^{2/3}).$$

Scaling properties of the higher order terms in $E_{nm}(N)$ and $E(Z, N)$ are also proposed.

## Introduction

To exhibit regularities in the energy $E(Z, N)$ of atomic ions with nuclear charge $Ze$ and $N$ electrons, there have been, historically, two approaches. Many of the earliest utilized the statistical theory of Thomas [1] and Fermi [2], which leads to the result for large $Z$ and $N$ that

$$E_{\mathrm{TF}}(Z, N) = -Z^{7/3} f_1(N/Z)\, e^2/a_0. \tag{1}$$

where the function $f_1(N/Z)$ is known from numerical solution of the Thomas–Fermi equation [3]. Below we shall use atomic units in which the hartree, $e^2/a_0 = 27$ eV, is the unit of energy, $a_0$ being the Bohr radius. Important progress along an apparently different direction resulted when Layzer [4] proposed the $1/Z$ expansion in which $E(Z, N)$ is developed in the form

$$E(Z, N) = -Z^2(E_{00}(N)) + E_{10}(N)/Z + E_{20}(N)/Z^2 + \cdots. \tag{2}$$

March and White [5] demonstrated the connection between Eq. (2) and the statistical limit (1) for heavy positive ions by showing that the general coefficient $E_{n0}(N)$ for large $N$ behaves as

$$E_{n0} = c_n^{(0)} N^{n+1/3} + c_n^{(1)} N^n + c_n^{(2)} N^{n-1/3} + \cdots. \tag{3}$$



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In Eq. (2), $E_{00}(N)$ is determined solely by the bare Coulomb field, while $E_{n0}(N)$ for $n \geq 1$ involves of course the electron–electron interactions. It is also relevant to note here that the convergence of Eq. (2) has been shown by Kato [6] to follow for sufficiently large $Z$.

Everything discussed so far is based on the nonrelativistic Schrödinger equation.

## Self-consistent Relativistic Thomas–Fermi Theory—Scaling Properties

Our object in the present paper is first to exhibit the scaling properties of the self-consistent relativistic Thomas–Fermi theory [7, 8] of positive ions, which will lead us to the appropriate relativistic generalization of Eq. (1). Later, we shall also discuss relativistic generalizations of Eq.(2) and (3), which will be motivated by the results of the relativistic Thomas–Fermi theory.

If we subtract, from the outset, the rest mass energy $mc^2$, we can write the semiclassical energy equation for the fastest electron. This energy is equivalent to the chemical potential $\mu$, which must be a constant throughout the entire electronic cloud of the positive ion. Otherwise, electrons could redistribute in space to lower the total energy. If $p_f(\mathbf{r})$ is the maximum momentum of this electron at position $\mathbf{r}$, while $V(\mathbf{r})$ is the self-consistent potential energy in which the electrons move, then using the customary relativistic expression for the kinetic energy we can write

$$\mu = (c^2 p_f^2(\mathbf{r}) + m^2 c^4)^{1/2} - mc^2 + V(\mathbf{r}). \tag{4}$$

The maximum momentum $p_f(\mathbf{r})$ is related as usual to the electron density $\rho$ by [9]

$$\rho(\mathbf{r}) = (8\pi/3h^3) p_f^3(\mathbf{r}). \tag{5}$$

Third we must add to Eqs. (4) and (5) the requirement of self-consistency embodied in the Poisson equation

$$\nabla^2 V = -\nabla^2(\mu - V) = -4\pi\rho e^2, \tag{6}$$

where we have obviously utilized the constancy of the chemical potential in space.

Following now the scaling conventionally used in the nonrelativistic theory of heavy positive ions [9], we introduce dimensionless quantities $\phi$ and $x$ defined by

$$\mu - V(r) = (Ze^2/r)\phi(x), \qquad r = bx, \qquad b = 0.885 a_0/Z^{1/3}. \tag{7}$$

Equation (6) can then be rewritten

$$\frac{1}{r}\frac{d^2}{dr^2} r(\mu - V) = \frac{1}{r}\frac{d^2}{dr^2} Ze^2\phi = \frac{Ze^2}{b^3 x}\frac{d^2\phi}{dx^2} = 4\pi\rho e^2. \tag{8}$$

At this stage we return to Eq. (4). Rearranging this, and then squaring, almost immediately yields

$$(\mu - V)^2 + 2mc^2(\mu - V) = c^2 p_f^2, \tag{9}$$

and hence in terms of $\phi$, $x$, and $\rho$, we find

$$\frac{p_f^2(r)}{2m} = \frac{1}{2m}\left(\frac{3h^3}{8\pi}\right)^{2/3}\{\rho(r)\}^{2/3} = \frac{(\mu - V)^2}{2mc^2} + (\mu - V)$$

$$= \frac{1}{2mc^2}\left(\frac{Ze^2}{b}\right)^2 \frac{\phi^2}{x^2} + \frac{Ze^2}{b}\frac{\phi}{x}. \tag{10}$$

Utilizing Eq. (8) for the electron density $\rho$ and writing $d^2\phi/dx^2 = \phi''$, we obtain, after a little rearrangement, the result

$$\frac{\text{const}\, Z^{4/3}}{mc^2}\left(\frac{\phi}{x}\right)^2 + \frac{\phi}{x} = \left(\frac{\phi''}{x}\right)^{2/3} \tag{11}$$

where the constant is readily written but is not, in fact, needed for our present purposes. Equation (11) correctly reduces to the dimensionless nonrelativistic Thomas–Fermi equation $\phi'' = \phi^{3/2}/x^{1/2}$ in the limit $c$ tends to infinity. What is of central importance for the present discussion of the scaling properties of the relativistic Thomas–Fermi theory is that, since the fine structure constant $\alpha$ is proportional to $c^{-1}$, and $\varepsilon = \alpha^2 Z^2$ is proportional to $c^{-2}Z^2$, therefore, it is quite clear from Eqn. (11) that the fine structure constant always appears in relativistic Thomas–Fermi theory in the combination $\alpha^2 Z^{4/3} = \varepsilon/Z^{2/3}$.

Having established this scaling property, we next note that, just as for the nonrelativistic Thomas–Fermi theory, the following boundary conditions [9] are obtained for a positive atomic ion with $N$ electrons and nuclear charge $Ze$:

$$\phi(0) = 1, \tag{12a}$$

$$-x_c\left(\frac{\partial\phi}{\partial x}\right)_{x_c} = 1 - \frac{N}{Z}, \tag{12b}$$

where the positive ion has a finite radius $r_c = bx_c$.

Since the electron density $\rho$ is zero at $r_c$, the chemical potential is evidently given from Eq. (10) by

$$\mu - V(r_c) = 0. \tag{13}$$

However just outside $r_c$, it is clear that the positive ion must behave electrostatically as if all its electronic charge were lumped at the point nucleus at $r = 0$ and therefore it follows that

$$V(r_c^+) = -(Z - N)e^2/r_c. \tag{14}$$

Hence, from Eqs. (13) and (14) the chemical potential is

$$\mu = -(Z - N)e^2/r_c. \tag{15}$$

Therefore the scaling of the chemical potential is determined by the scaling of $r_c$.

However now, as is well known [9], in the nonrelativistic Thomas–Fermi theory of positive ions, $x_c = x_c(N/Z)$. This result is now modified because of the presence of the term in $\phi^2/x^2$ proportional to $\varepsilon/Z^{2/3}$ in Eq. (11). Thus one

immediately has the scaling property for the positive ion radius $x_c$ in relativistic Thomas–Fermi theory

$$x_c = x_c(N/Z; \varepsilon/Z^{2/3}). \tag{16}$$

Combining Eqs. (15) and (16), it follows that the scaling of the chemical potential $\mu$ in the relativistic Thomas–Fermi theory is given by

$$\mu = Z^{4/3} F(N/Z; \varepsilon/Z^{2/3}). \tag{17}$$

This is the essential result for discussing the scaling properties of the total binding energy of the relativistic Thomas–Fermi theory.

We want to stress at this point is that it is possible to obtain the result (17) for the chemical potential by focusing on the outer region of the positive ion, i.e., on the positive ion radius. This avoids a severe difficulty, known to Vallarta and Rosen [7], namely, that with a point nucleus the electron density is not normalizable. It is known that the introduction of the finite size of the nucleus will allow one to obtain a normalizable electron density, and since the size of the positive ion is five or six orders of magnitude larger than the nuclear radius, it is evident that the radius of a heavy positive ion must be extremely insensitive to the nuclear radius. Therefore, it is quite appropriate to evaluate the positive ion radius in the limit when the nuclear radius goes to zero, even though we know that just at the limiting point the electron density is not normalizable. This dependence of the normalization on the nuclear radius has been discussed very recently for neutral atoms [10],* which, however, have infinite radius and zero chemical potential.

Having established the important scaling property (17) of the relativistic Thomas–Fermi theory, it will be helpful at this stage to make contact with the relativistic generalization of Eq. (2), due to Layzer and Bahcall [11].

### Generalization of $1/Z$ Expansion to Include Fine Structure Constant

This generalization takes the form

$$E(Z, N) = Z^2 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} E_{nm}(N) \varepsilon^m Z^{-n}. \tag{18}$$

It must be said from the outset that the expansion (18) has some difficult points associated with it which are not present in the nonrelativistic expansion (2). Relevant work, related to these difficulties is that of Ermolaev and Jones [12, 13].† Nevertheless, it can be argued that Eq. (18), which reduces to Eq. (2) if we neglect all terms except $m = 0$, is the natural relativistic expansion, in terms of the parameter $\varepsilon = \alpha^2 Z^2$. We shall see below that from it one can obtain meaningful results in the limit of large $N$. As to the difficult points referred to above, one might mention additionally that, if one uses the Dirac equation as

* The authors of Ref. 10 have rediscovered the Vallarta–Rosen theory of Ref. 7.

† In Ref. 13, some mathematical foundation for the Layzer–Bahcall expansion is provided.

basis, then with a point nucleus there are singularities occurring when $\alpha Z = 1$. Second, one ought strictly to allow for the fact that the coefficients $E_{nm}(N)$ can also depend on $\varepsilon$, as discussed for example by Doyle [14]. This is due to degeneracy and in this paper we shall be considering heavy positive ions with closed shell configurations only. Our main task below will be to obtain the form of $E_{nm}(N)$ for large $N$.

We have the usual relation for the chemical potential that

$$\mu = \left(\frac{\partial E}{\partial N}\right)_Z, \tag{19}$$

and we shall now combine Eqs. (18) and (19) with the relativistic Thomas–Fermi form (17) for the chemical potential. First, from Eqs. (18) and (19) it follows that for large $N$,

$$\mu = Z^2 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{dE_{nm}}{dN} \varepsilon^m Z^{-n}. \tag{20}$$

To compare Eq. (17) of the relativistic Thomas–Fermi theory with Eq. (20), let us introduce the variables $N/Z$ and $\varepsilon/Z^{2/3}$ into this latter equation to obtain

$$\mu = Z^{4/3} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{dE_{nm}(N)}{dN} \frac{1}{N^{n-2m/3-2/3}} \left(\frac{N}{Z}\right)^{n-2m/3-2/3} \left(\frac{\varepsilon}{Z^{2/3}}\right)^m. \tag{21}$$

It follows that to obtain the scaling property (17) at large $N$ and $Z$ we must choose

$$\frac{dE_{nm}(N)}{dN} \approx N^{n-2m/3-2/3}, \tag{22}$$

or, on integration,

$$E_{nm}(N) = c_{nm}^{(0)} N^{n-2m/3+1/3} + \cdots, \tag{23}$$

where the dots represent higher order terms. This result reduces, as it must, to the nonrelativistic equation (3) of March and White when we put $m = 0$. Of course, the higher order terms indicated in Eq. (23) cannot be obtained solely from the relativistic Thomas–Fermi theory. Therefore we shall use the bare Coulomb field example briefly in the next section, the details being relegated to the Appendix, to suggest the appropriate generalization of the power law dependence exhibited in Eq. (23) for the higher order terms. This Coulomb field example is useful also to us in another context; namely, excluding other alternative formulations of the relativistic Thomas–Fermi theory than the Vallarta–Rosen form employed above.

## Relativistic Treatment of Bare Coulomb Field

Though the main interest below is in the energy levels given by the Dirac equation for a bare Coulomb field, let us briefly review the nonrelativistic analogue. With $\mathcal{N}$ closed shells, to which case we shall restrict ourselves, the

total energy, $E_c(Z, N)$ say, is easily written. Each shell of principal quantum number $n$ has energy $-Z^2/2n^2$, and since such a closed shell holds $2n^2$ electrons it follows that the energy per shell is simply $-Z^2$. Hence for $\mathcal{N}$ closed shells, the total energy, which in this noninteracting electron model is simply the sum of the one-electron energies over occupied states, is given by

$$E_c^{\text{nonrel}}(Z, N) = -Z^2\mathcal{N}, \tag{24}$$

where evidently

$$N = \sum_1^{\mathcal{N}} 2n^2 = \frac{\mathcal{N}(\mathcal{N}+1)(2\mathcal{N}+1)}{3}. \tag{25}$$

For a really large number of closed shells, the leading term in the solution of Eq. (25) for $\mathcal{N}$ is given by $\mathcal{N} = (\frac{3}{2})^{1/3}N^{1/3}$, revealing $N^{-1/3}$ as a basic expansion parameter for large $N$.

We have next studied the sum of the one-electron energies over occupied states from the Dirac energy levels for a bare Coulomb field, with potential energy $-Ze^2/r$. These levels are given by [9]

$$mc^2\left[\left(1+\frac{\alpha^2Z^2}{n_r+[(j+\frac{1}{2})^2-\alpha^2Z^2]^{1/2}}\right)^{-1/2}-1\right]. \tag{26}$$

This problem has first been studied numerically, for a set of values of the number of closed shells $\mathcal{N}$, up to $\mathcal{N}$ equal to 20. Though we are primarily interested in the dependence on $N$, the total number of electrons in the atomic ion, Eqs. (24) and (25) indicate that the dependence on $\mathcal{N}$ is likely to be simpler to represent at first than that on the total number of electrons.

We have therefore plotted in Figure 1 the difference between the relativistic and nonrelativistic energies, denoted by $E_{\text{Rel}}$, divided by $\alpha^4Z^4$, against the number of closed shells, for various values of $Z$ from 10 to 136. We stress here that, while from these plots we want to extract the dependence of $E_{\text{Rel}}/\alpha^4Z^4$

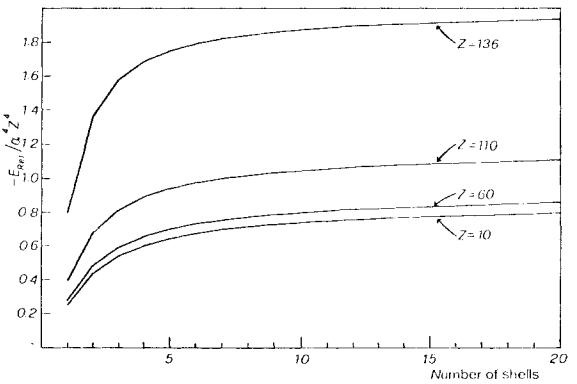


Figure 1. $-E_{\text{rel}}/\alpha^4Z^4$ for bare Coulomb field as a function of the number of closed shells.

on $\mathcal{N}$ for large $\mathcal{N}$, physical significance should not be ascribed to the plots for independent choices for $\mathcal{N}$ and $Z$. To be specific, it is not physical to consider $\mathcal{N} \lesssim 7$ for $Z = 136$ or $\mathcal{N} > 2$ for $Z = 10$ in Figure 1. However, the point which emerges from these numerical studies is that one can write, for large $\mathcal{N}$,

$$E_{\text{rel}}/\alpha^4 Z^4 = D_0(Z) + D_1(Z)/\mathcal{N} + O(1/\mathcal{N}^2). \tag{27}$$

Some approximate analysis which demonstrates that $E_{\text{rel}}$ tends to a constant, independent of $\mathcal{N}$ for large $\mathcal{N}$ is presented in the Appendix. However even without this mathematics, it is quite clear that since the electrons in an atomic ion which move really fast are in the $K$ shell, at most it will be a few inner shells which will dominate the relativistic correction, which must therefore evidently become independent of the number of closed shells as $\mathcal{N}$ becomes large. Evidently for smaller $\mathcal{N}$ there must be a dependence on the number of closed shells and it is shown in the Appendix that there is an expansion of $E_{\text{rel}}$ in powers of $1/\mathcal{N}$ as displayed in Eq. (27).

In the Appendix, further comments are made on the singularity in the Dirac equation for a point nucleus at $\alpha Z = 1$. However, even at $Z = 1/\alpha = 137$, it turns out that the function $D_0(Z)$ in Eq. (27) remains bounded, though the singular behaviour at $\alpha Z = 1$ is reflected in the divergence of its derivative with respect to $Z$ at this point $\alpha Z = 1$.

What has been established here, by study of the bare Coulomb field case, is that in spite of the singularity in the Dirac equation for a point nucleus, there is still a meaningful expansion in $1/\mathcal{N}$ which from Eq. (27) turns out to be equivalent to an expansion in $1/N^{1/3}$. Thus we can hope to make progress, when we treat real atoms with their electron–electron interactions (cf. Fig. 2), by generalizing the result (23) which has been established from the relativistic Thomas–Fermi theory to include higher order terms by an expansion in $1/N^{1/3}$. This will be discussed below, after we have made some brief remarks on the

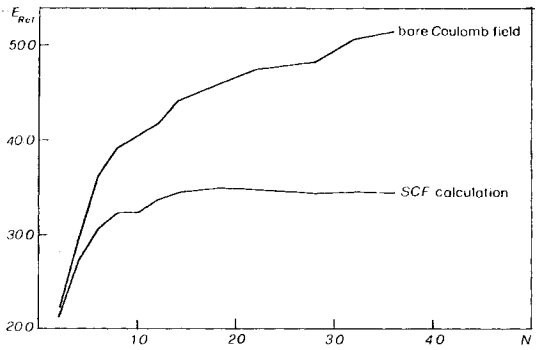


Figure 2. $-E_{\text{rel}}$ in hartree for the krypton ion, $Z = 36$, as a function of the number $N$ of electrons from relativistic self-consistent field theory. Bare Coulomb results are shown for comparison. The inclusion of interactions is seen to speed the convergence to the limiting value as the number of electrons gets large. This is understandable in that the outer electrons contribute less to the binding energy in the presence of the self-consistent field than for the bare Coulomb case.

way this Coulomb field example can be used to demonstrate the less satisfactory nature of the other alternative proposals for a relativistic Thomas–Fermi theory compared with the Vallarta–Rosen form which we use exclusively in the present paper.

Because of the normalization difficulty referred to above for a point nucleus in the Vallarta–Rosen theory, alternative proposals have been put forward by Gilvarry [15] and by Rudkjobing [16]. While the proposal of Gilvarry has been examined numerically by Waber and Canfield [17] and compared with a normalizable modification of the Vallarta–Rosen density, in the course of the present work we have adopted the different approach of studying analytically the relation of the alternative proposals [15, 16] to the summation of the Dirac energy levels for a point nucleus with potential energy $-Ze^2/r$. By comparison with the results presented in the Appendix, it is found that these alternatives lead one to results which are not compatible with the Dirac energy levels for this bare Coulomb field problem. Therefore, since only the Vallarta–Rosen theory is satisfactory for the total energy of the bare Coulomb field problem for many closed shells, the considerations of the present paper are all based on the Vallarta–Rosen form of the relativistic Thomas–Fermi theory. We have already referred to work on normalizable densities in this theory with a finite nucleus [10], and for further discussion related to this aspect of relativistic Thomas–Fermi theory, the work of Müller [18] should also be mentioned here.

## Partial Summation of Layzer–Bahcall Expansion

We turn to the final topic of the paper, namely the way in which a partial summation of the Layzer–Bahcall expansion can be formally achieved, based on an expansion in the parameter $N^{-1/3}$ which emerged from the Coulomb field argument of the previous section.

Expressing the above findings explicitly in a series for the coefficients $E_{nm}(N)$ in the Layzer–Bahcall expansion (18), we propose then for large $N$ the generalization of Eq. (23), established from the relativistic Thomas–Fermi theory, as

$$E_{nm}(N) = c_{nm}^{(0)} N^{n-2m/3+1/3} + c_{nm}^{(1)} N^{n-2m/3} + c_{nm}^{(2)} N^{n-2m/3-1/3} + \cdots. \quad (28)$$

We stress that this proposal has the following limiting cases correctly contained within it: (a) the relativistic Thomas–Fermi theory as the leading term; (b) the March–White nonrelativistic expansion [5] for the limiting case $m = 0$; and (c) the form of the Dirac bare Coulomb field results for $n = 0$.

Adopting this as the series expansion for large $N$, we can insert it back into Eq. (18), the Layzer–Bahcall series then being

$$E(Z, N) = Z^2\Big(\sum_n \sum_m c_{nm}^{(0)} N^{n-2m/3+1/3} \varepsilon^m Z^{-n} + \sum_n \sum_m c_{nm}^{(1)} N^{n-2m/3} \varepsilon^m Z^{-n} + \cdots\Big), \quad (29)$$

which can be formally summed to yield

$$E(Z,N)=Z^{7/3}F_1(N/Z;\varepsilon/N^{2/3})+Z^2F_2(N/Z;\varepsilon/N^{2/3})$$
$$+Z^{5/3}F_3(N/Z;\varepsilon/N^{2/3})+\cdots. \tag{30}$$

This form has (a) the relativistic Thomas–Fermi energy as its leading term, and (b) the nonrelativistic expansion given very recently by March and Parr [19] as the limiting case when the fine structure constant, or equivalently $\varepsilon$, is put equal to zero.

## Conclusion

We have used the relativistic Thomas–Fermi theory of Vallarta and Rosen [7] to establish the scaling property of the chemical potential of heavy positive ions given in Eq. (17). This is then used to prove the asymptotic dependence of the coefficients $E_{nm}(N)$ in the Layzer–Bahcall expansion (18) for large $N$ as proportional to $N^{n-2m/3+1/3}$. This corresponds in the relativistic Thomas–Fermi theory to an energy which scales as $Z^{7/3}F_1(N/Z;\varepsilon/N^{2/3})$. This contains the well known nonrelativistic scaling (1) of the energy of positive ions in the limit as $\varepsilon=\alpha^2Z^2$ tends to zero.

By numerical and analytical study of the bare Coulomb field energy levels as given by the Dirac equation, the generalization of the result (23) for large $N$ is porposed to have the form (28). This then leads to the partial summation of the Layzer–Bahcall expansion as displayed in Eq. (30). While the first term in this Eq. (30) for the total energy of heavy positive ions is just that given by the relativistic Thomas–Fermi theory, one can expect in higher order terms in the expansion in $Z^{-1/3}$ that exchange and correlation corrections must appear, at some order. Equally fundamentally, at some stage in the relativistic expansion in $\varepsilon$, the quantum electrodynamic corrections must appear. This leads on to the final, cautionary remark on the present approach, based on relativistic Thomas–Fermi theory and its relation to the $1/Z$ expansion. While we believe that the analytical structure of the energy $E(Z,N,\varepsilon)$ must be of basic interest for relativistic atomic theory, it has to be stressed that numerical Dirac–Fock calculations can now be routinely made for any atom, and it is unlikely that a relativistic Thomas–Fermi theory, or a $1/Z$ calculation, could add to such numerical knowledge. As emphasized here, one purpose of such approaches is to discuss trends in $E_{\text{rel}}/Z^4$ as a function of $N$ and $Z$. Even here though, it should be cautioned that for small numbers of closed shells the shell structure is pronounced, and for large numbers of closed shells, and therefore in practice for large $Z$, an expansion in $(\alpha Z)^2$ presents problems and, as already remarked, the quantum electrodynamic effects come in. In spite of these somewhat limiting conclusions, the scaling properties proposed here in the asymptotic limit of large $N$ seem nonetheless of some interest for basic theory.

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## Appendix

Some approximate analysis of the sum of the one-electron energies over occupied states using the bare Coulomb field Dirac energy levels will be presented here. This will make clear mathematically why the relativistic energy shift $E_{\text{rel}}$ tends to a constant as the number of closed shells gets large. It will also show why it is not proportional to $\varepsilon^2 = \alpha^4 Z^4$, the reason being that the energy is not an analytic function of $Z$ as $Z$ tends to $1/\alpha = 137$ from Dirac's theory for a point nucleus.

We seek the sum of the first $N = (\mathcal{N}/3)(\mathcal{N}+1)(2\mathcal{N}+1)$ energy levels (26). This we can write in the form

$$E_c(Z,N) = \sum_{n'=1}^{\mathcal{N}} \sum_{n_r=0}^{n'-1} \frac{[(n'-n_r)^2-\varepsilon]^{1/2}+n_r}{n_r^2+(n'-n_r)^2+2n_r[(n'-n_r)^2-\varepsilon]^{1/2}}\, d_{n_r}, \tag{31}$$

where $d_{n_r}$ is the degeneracy of the level and is given by

$$d_{n_r} = \begin{cases} 4(n'-n_r), & \text{if } n_r \neq 0, \\ 2(n'-n_r), & \text{if } n_r = 0. \end{cases}$$

Now if $\varepsilon \ll 1$, we can expand Eq. (31) in powers of $\varepsilon$ and then make the double summation. Otherwise we can split Eq. (31) into parts: (i) a nonanalytic part at $\varepsilon = 1$, and (ii) an analytic part. The nonanalytic part is given by $2(2\mathcal{N}-1)$ terms corresponding to the choice $j = \frac{1}{2}$. Let us denote by $S_N$ the sum of the nonanalytic terms

$$S_N(\varepsilon,\mathcal{N}) = 2(1-\varepsilon)^{1/2} + \sum_{n'=2}^{\mathcal{N}} \frac{4[(1-\varepsilon)^{1/2}+n'-1]}{[(n'-1)+1+2(n'-1)(1-\varepsilon)^{1/2}]^{1/2}}. \tag{32}$$

By using the Euler–Maclaurin summation formula we approximate this by

$$S_N(\varepsilon,\mathcal{N}) \simeq 4[(n'-1)^2+1+2(n'-1)(1-\varepsilon)^{1/2}]\Big|_{1/2}^{\mathcal{N}-1/2} - 2(1-\varepsilon)^{1/2},$$

and then we obtain

$$S_N(\varepsilon,\mathcal{N}) = 4\mathcal{N}\left(1-\frac{3}{\mathcal{N}}-\frac{1}{\mathcal{N}}(1-\varepsilon)^{1/2}+\frac{13}{4}\frac{1}{\mathcal{N}^2}\right)^{1/2} - 4[\tfrac{5}{4}-(1-\varepsilon)^{1/2}]^{1/2} - 2(1-\varepsilon)^{1/2} + \cdots. \tag{33}$$

For large values of $\mathcal{N}$, this formula can be expanded in powers of $1/\mathcal{N}$ and we obtain a series whose coefficients depend on $(1-\varepsilon)$:

$$S_N(\varepsilon, \mathcal{N}) = 4\mathcal{N} + \tfrac{1}{2} f_1(\varepsilon) + f_2(\varepsilon)(1/\mathcal{N}) + \cdots . \tag{34}$$

The summation of the terms containing $j > \frac{1}{2}$ is straightforward; in fact we can now use a Taylor expansion

$$S_A(\varepsilon, \mathcal{N}) = \sum_{n'=2}^{\mathcal{N}} \sum_{n_r=0}^{n'-2} d_{n_r} \frac{[(n-n_r)^2 - \varepsilon]^{1/2} + n_r}{\{n_r^2 + (n-n_r)^2 + 2n_r[(n-n_r)^2\varepsilon]^{1/2}\}^{1/2}}. \tag{35}$$

The evaluation of Eq. (35) reduces to the summation of a series in powers of $\varepsilon$ and we can write

$$S_A(\varepsilon, \mathcal{N}) = \sum_{n'=2}^{\mathcal{N}} \sum_{p=2}^{n'-1} 4p\left[1 - \frac{\varepsilon}{2n'^2} + \varepsilon^2\left(\frac{3}{8n'^4} - \frac{1}{4n'^3 p}\right)\right] + \sum_{n'=2}^{\mathcal{N}} 2n'\left(1 - \frac{\varepsilon}{2n'^2} - \frac{\varepsilon^2}{8n'^4}\right) + O(\varepsilon^3). \tag{36}$$

This then yields the form

$$S_A(\varepsilon, \mathcal{N}) = \left(\frac{\mathcal{N}(\mathcal{N}+1)(2\mathcal{N}+1)}{3} - 4\mathcal{N} + 2\right) - \varepsilon\left((\mathcal{N}-1) - \sum_{n'=2}^{\mathcal{N}} \frac{2}{n'^2}\right) - \varepsilon^2 \sum_{n'=2}^{\mathcal{N}} \left(\frac{1}{4n'^2} - \frac{1}{n'^3} + \frac{3}{2n'^4}\right) + O(\varepsilon^3). \tag{37}$$

The conclusion is now clear. By combining Eqs. (37) and (34), we find that, provided we subtract the nonrelativistic energy, the relativistic energy shift has an expansion in powers of $1/\mathcal{N}$.

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