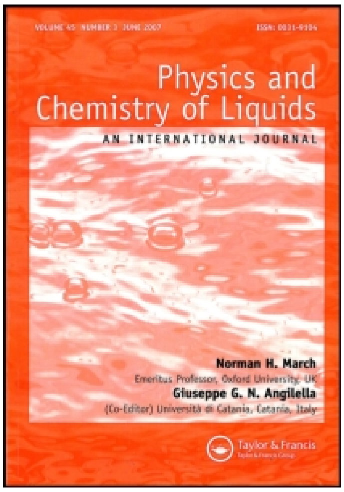

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Thomas-Fermi Modelling of Atoms in Cold Dense Plasmas

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THOMAS-FERMI MODELLING OF ATOMS IN COLD DENSE PLASMAS

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The dimensionless Thomas-Fermi equation for isolated atoms is first generalized to apply to atoms in cold dense plasmas. The form of the potential distribution for an atom in an electron liquid, such as exists in the conduction band of a molten metal, is then characterized by the ratio $s = \mu_0 b/Ze^2$ of the chemical potential μ_0 of the plasma to a characteristic energy Ze^2/b of the Thomas-Fermi atom with nuclear charge Ze, b being a length proportional to $Z^{-1/3}$. A WKB approach to the bound-state level spectrum ε_{nl} for the atom in the plasma is presented and some qualitative deductions made. Finally, such potential distributions, scaling with the parameter s, plus the pair correlation function $g(r)$, yield an approximate partition function and electronic density of states of a liquid metal.

KEY WORDS: WKB levels, partition function, liquid metals.

1. INTRODUCTION

Following the experiments of Flynn and co-workers[1, 2] on rare gas atoms implanted in the alkali metals Li through to Cs, it has been pointed out[3] that the optically measured threshold energies for Kr and for Xe vary linearly with the mean interelectronic spacing r_s through the alkali series. In ref. 3 it was stressed that such simple behaviour supported the utility of the concept of an atom in a cold dense plasma and in the present work attention is focussed on modelling such atoms using the Thomas-Fermi (TF) approximation.

However, before embarking on such a programme, it is important to comment on the range of validity to be anticipated for such results. To do so, consider specifically the binding energy formula for heavy atoms as a function of atomic number Z:

$$E/(e^2/a_0) = -0.77Z^{7/3} + \tfrac{1}{2}Z^2 - 0.27Z^{5/3} + \cdots \qquad (1.1)$$

Here the leading term is the TF result,[4] the term of $O(Z^2)$ is due to density gradient corrections[5,6] while the last term exhibited in eqn. (1.1) is largely from exchange.[5] Correlation is expected to enter the formula (1.1) at O(Z). If one requires, say, that the TF approximation be accurate to $\sim 1\%$, then one would require $Z^{1/3} \sim 100$. Thus, one should apply the theory to 'superheavy elements'. Needless to say, relativistic considerations should then enter, but in the present work one will suppose that the predictions of the non-relativistic Schrödinger equation are the focus of the discussion, even though there is recent progress relating to relativistic TF theory.[7,8] Also, the potential distribution for isolated atoms given by the TF approximation is known to be widely useful in the range of the Periodic Table, so this aspect will be emphasized especially in the present work on atoms in cold dense plasmas. For some further relevant background, the article by More[9] may be consulted.

The outline of the present paper is then as follows. In section 2, the TF approximation is used to show that the potential distribution $V(r)$ created by embedding a nuclear charge Ze in a plasma of chemical potential μ_0 can be characterized by a generalization of the dimensionless TF equation for neutral atoms to take account of the non-zero value of the dimensionless ratio $s = \mu_0 b/Ze^2$ of the chemical potential to Ze^2/b, a characteristic energy of the TF isolated atom, with b its characteristic length

$$b = \frac{1}{4}\left(\frac{9\pi^2}{2}\right)^{1/3} \frac{a_0}{Z^{1/3}} = \frac{0.88534a_0}{Z^{1/3}} : a_0 = \frac{\hbar^2}{me^2}. \tag{1.2}$$

Section 3 then sets out the way the WKB method can be used to calculate both bound-state eigenvalues and some continuum properties of such TF potentials: some contact being made with known isolated atom results.

Then in section 4, because of the usefulness of such potentials as a starting point for electronic structure calculations on liquid metals, a method due to Hilton *et al.*,[10] is briefly summarized for computing the canonical or Bloch density matrix in terms of an effective potential $U(r, \beta, s)$ derivable from the TF potentials discussed in section 2. The first-order approximation U_1 to U is shown to scale simply when the TF potential for an atom in a plasma is taken as starting point. The resultant effective potential determines, together with the pair correlation function $g(r)$, the partition function, and hence the electronic density of states, of the liquid metal.[11] Section 5 constitutes a summary, together with suggestions for further work.

2. GENERALIZATION OF DIMENSIONLESS TF EQUATION TO TREAT ATOMS IN COLD DENSE PLASMAS

The basic density-potential relation of the TF method is given by

$$n(r) = \frac{8\pi}{3h^3}(2m)^{3/2}(\mu - V(r)^{3/2} \tag{2.1}$$

where $n(r)$ is the electron density, $V(r)$ the one-body potential energy and μ the chemical potential. The Poisson equation for the electrostatic potential $\chi(r) = -V(r)/e$, created by a charge Ze embedded in an initially uniform cold plasma, namely

$$\nabla^2\chi = 4\pi[n_+ - n(r)]e, \tag{2.2}$$

where $n_+ = \frac{8\pi}{3h^3}(2m)^{3/2}\mu^{3/2}$, then can be rewritten with the substitution

$$(\mu - V) = \frac{Ze^2}{r}\phi(x): r = bx, \tag{2.3}$$

where b is given by eqn (1.2) in the form

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} - s^{3/2}x \tag{2.4}$$

where s is the ratio $\mu/(\mathrm{Ze}^2/b)$; μ being a characteristic (Fermi) energy of the cold plasma and (Ze^2/b) an appropriate energy scale for the isolated TF atom.

Since the chemical potential μ is identically zero for the isolated TF atom, this is included, in fact, in eqn (2.4) corresponding to the limit $s = 0$. However, in the present work we are concerned with the form of the solutions of eqn (2.4) satisfying the boundary conditions

$$\phi(x = 0) = 1;\ \phi(x \to \infty) = s(x). \tag{2.5}$$

The first of these conditions (2.5) follows immediately from eqn (2.3) since $V \to -\mathrm{Ze}^2/r$ as $r \to 0$ with nuclear charge Ze at the origin of coordinates. Since, in a conducting medium, Ze is perfectly screened at large distances, it is also clear from eqn (2.3) plus the definition of s that $(\phi/x) \to s$ as $r \to \infty$, which completes the discussion of the boundary conditions (2.5).

Though the focus of the present work is on solutions of eqn (2.4) satisfying the conditions (2.5) well away from $s = 0$, it seemed of interest to depict in Fig. 1 the relation of the isolated atom solution at $s = 0$ to that for an atom in a cold dense plasma for finite s, these solutions corresponding to curves 1 and 2 in Fig. 1.

2.1 *Asymptotic behaviour of* $\phi(x, s)$ *satisfying eqns* (2.4) *and* (2.5)

Let us next exhibit the way in which curve 2 of Fig. 1. approaches its asymptote sx by writing

$$\phi = sx + \Delta \tag{2.6}$$

where evidently, for $s \neq 0$; $\Delta \ll sx$ for sufficiently large x. The non-linear term $\phi^{3/2}$ in eqn (2.4) can then be written as $s^{3/2}x^{3/2} + \frac{3}{2}s^{1/2}x^{1/2}\Delta + \mathrm{O}(\Delta^2)$, and hence at large x one has

$$\frac{d^2\Delta}{dx^2} = \tfrac{3}{2}s^{1/2}\Delta, \tag{2.7}$$

the solution tending to zero at infinity being evidently

$$\Delta(x, s) = \alpha(s)\exp(-\sqrt{\tfrac{3}{2}}\,s^{1/4}x). \tag{2.8}$$

Clearly the amplitude $\alpha(s)$ in eqn (2.8) must be determined by matching the asymptotic form of eqn (2.8) on to the small x expansion of eqn (2.4) given in Appendix 1.

Fortunately, information about $\alpha(s)$ can be extracted from early numerical solutions of Alfred and March.[12] These workers show that the screened potential $\mathrm{V}(r)$ has the large r form

$$\mathrm{V}(r) = -\frac{\mathrm{Ze}^2}{r}\alpha\exp(-qr) \tag{2.9}$$

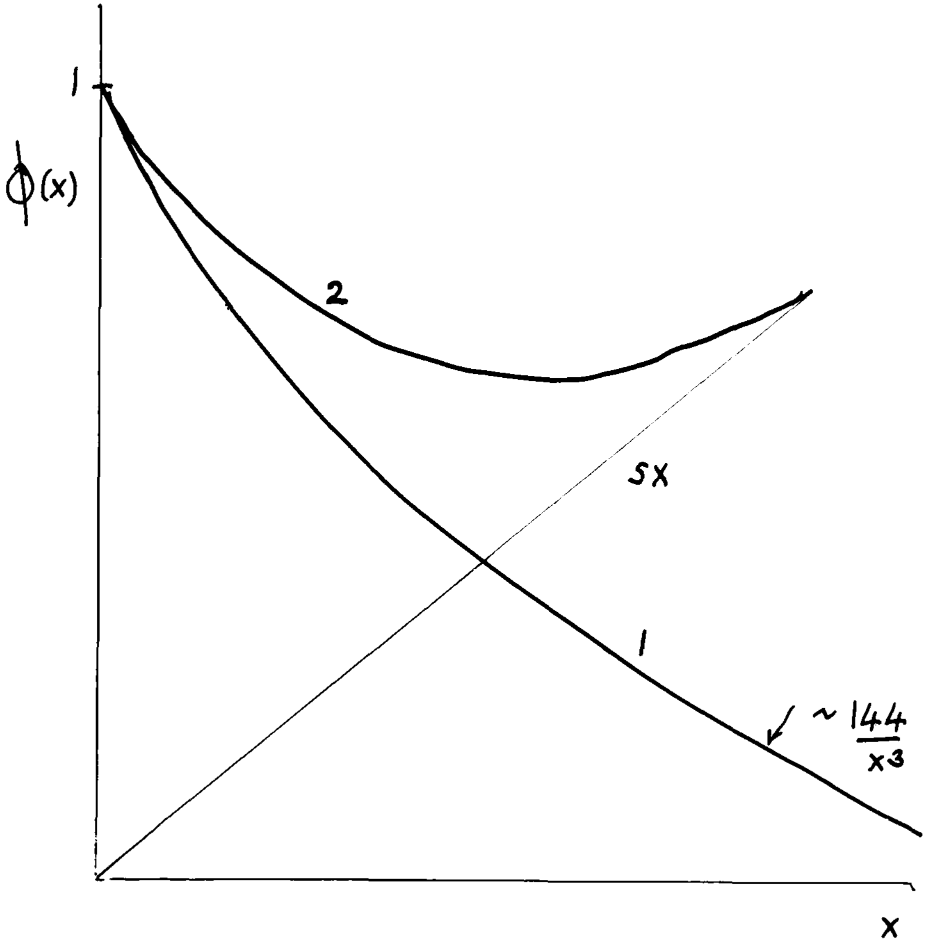

Figure 2 Shows nature of solutions of eqn (2.4) with boundary conditions (2.5). Curve 1 $s = 0$. Isolated atom. Curve 2 $s \neq 0$. Atom in plasma

where q^{-1} is the usual TF screening length given by

$$q^2 = \frac{4k_f}{\pi a_0} \tag{2.10}$$

with k_f the Fermi wave number. These workers solved eqns (2.1) and (2.2) with μ calculated from the mean conduction electron density of Cu metal, for the cases $Z = 1$ to 4. The values of α thereby obtained are recorded in Table 2.1.

Also recorded in Table 2.1 is the constancy of the quantity $(1 - \alpha)/Z^{1/2}$ noted by Alfred and March.[12]

Table 2.1 Values of α in eqn (2.9) for charges $Z = 1 - 4$ in Cu metal

Z	1	2	3	4
α	0.77	0.67	0.60	0.55
$(1-\alpha)/Z^{1/2}$	0.23	0.23	0.23	0.22(5)

In view of the scaling with s made clear in eqn (2.4), this constancy can be translated into the form for $\alpha(s)$ in eqn (2.8):

$$\alpha(s) = 1 - \frac{\text{const}}{s^{3/8}} + O(s^{-1/2}) \tag{2.11}$$

where the constant is determined from the equation

$$s = \mu/(Ze^2/b) = \frac{0.88534a_0}{Z^{4/3}e^2}\mu \tag{2.12}$$

using the value of μ for Cu metal and the constant 0.23 from Table 2.1. It must be emphasized, of course, that eqn (2.11) must only be used when the term proportional to $s^{-3/8}$ is small compared with unity; it must not be used near the neutral atom limit $s \to 0$.

In modelling the potential distribution for atoms in cold dense plasmas, a simple, though obviously approximate representation of the screened potential $V(r)$ can be written as

$$V(r) = -\frac{Ze^2}{r}\frac{\alpha(s)}{[\exp(qr) + \alpha(s) - 1]}. \tag{2.13}$$

This form has been chosen to interpolate between the correct TF asymptotic behaviour (2.9) and the $r \to 0$ limit in which $V(r) \to -Ze^2/r$. It is not claimed that eqn (2.13) gives an accurate quantitative fit of the numerical solutions of Alfred and March,[12] but it does reflect (i) the general form of the potential distribution and (ii) the scaling with s reflected in eqn (2.4). Some discussion of the eigenvalue spectrum of $V(r)$ in eqn (2.13) is given in section 3 below.

3 EIGENVALUE SPECTRUM FOR ATOMS IN DENSE PLASMAS

Senatore and March[13] have examined the eigenvalue spectrum ε_{nl} for the isolated TF atom, using the solution of eqn (2.4) with $s = 0$, plus the boundary conditions (2.5) at $s = 0$. This was done by using the WKB method, evaluated then by expansion to lowest order in $Z^{-1/3}$. One result which emerged was the value of the atomic number, Z_l say, for the first appearance of a given l. Their condition reads;

$$Z_l \geq 0.15641(2l+1)^3 \tag{3.1}$$

which was quite similar to a condition derived differently by Abrahamson,[14] which differs from the inequality (3.1) only by replacing the numerical factor by 1/6.

Since Abrahamson's result was derived starting from an effective potential energy

$$V_{\mathrm{eff}}(r) = V(r) + \frac{(l+\frac{1}{2})^2}{2r^2}e^2a_0 \tag{3.2}$$

with the usual factor $l(l+1)$ in the centrifugal potential energy term replaced by its WKB equivalent $(l+\frac{1}{2})^2$, by requiring that for an electron to be bound there must exist a region where V_{eff} is negative, we take this inequality thereby derived from eqn (3.2):

$$-(r^2V)_{\max} \geq \tfrac{1}{2}e^2a_0(l+\tfrac{1}{2})^2 \tag{3.3}$$

as a simple starting point for the discussion of an atom in a cold plasma.

Taking first the form (2.9), valid at large r, and evaluating $(r^2V)_{\max}$ to insert in the inequality (3.3) one readily finds the maximum is at r_m such that

$$qr_m = 1 \tag{3.4}$$

which when re-inserted in eqn (2.9) yields

$$Z_1e^2q^{-1}\alpha(s_1)\exp(-1) \geq \tfrac{1}{8}e^2a_0(2l+1)^2.\ s_1 = \mu b/Z_1e^2. \tag{3.5}$$

In the large s limit, where $\alpha = 1$ from eqn (2.1), this yields immediately

$$Z_1 \geq \tfrac{1}{8}qa_0\exp(1)(2l+1)^2. \tag{3.6}$$

A presumably more accurate treatment is set out in Appendix 2, based on the forms (2.13) and (2.11).

For a fuller study of the WKB eigenvalues ε_{nl}, one can follow Senatore and March[13] and write

$$\pi(s^*+\tfrac{1}{2}) = Z^{1/3}\int_{x_1}^{x_2} dx\left[2C\frac{\phi(x,s)}{x} - \frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3} + \varepsilon_{s*l}C^2Z^{-4/3}\right]^{1/2} \tag{3.7}$$

where b in eqn (12) has been written as $Ca_0/Z^{1/3}$. In eqn (3.7) the integer s^* is related to the usual quantum number n by

$$n = s^* + l + 1, \tag{3.8}$$

while x_1 and x_2 denote the classical turning points of the motion in dimensionless units, the energy being in Rydbergs.

Eqn (3.7) is a concrete demonstration of the qualitative assertion now being made that each plasma, characterized by μ in eqn (2.1), generates its own Periodic Table, the behaviour of isolated atoms (with large Z) following from the case $s = 0$ studied in detail by Senatore and March.[13]

When further solutions of the generalization (2.4) of the dimensionless TF equation for isolated atoms become available for larger Z than in the study of Alfred and March[12] (their results can be used at larger Z, in fact, but at the price of greatly increased chemical potential μ to keep s unchanged) it will be a relatively straightforward matter to map out quantitatively the WKB eigenvalue spectrum ε_{nl} for a chosen plasma, as a function of atomic number Z, and thus to investigate the (usually different) Periodic Table for the plasma. In this connection the work of Green, Sellin and Zachor[15] is highly relevant for the potential (2.13) and its eigenvalues, without invoking the WKB approximation.

4. LIQUID METALS BUILT UP FROM ATOMS IN A COLD PLASMA

Having discussed an individual atom in a plasma, let us now turn to the use of such an atom as a building block for treating liquid metals. Such a treatment was, in fact, set up by Rousseau, Stoddart and March,[11] based on the one-centre calculations of Hilton, March and Curtis,[10] who started from the potential distribution of Alfred and March[12] for Z = 4 in a Cu metal conduction electron density.

The first step in this method is to calculate the so-called effective potential $U(r\beta)$, which determines the diagonal element of the Bloch or canonical density matrix, say $C(r, \beta)$ through

$$C(r\beta) = \frac{1}{(2\pi\beta)^{3/2}} \exp(-\beta U(r\beta)). \tag{4.1}$$

To first order in the potential $V(r)$, U is given by

$$U_1(r, \beta, Z, s) = \int \mathcal{G}(\mathbf{r}, \mathbf{r}', \beta)\left(-\frac{Ze^2}{r'}\right)\phi\left(\frac{r'}{b}, s\right) d\mathbf{r}' \tag{4.2}$$

where $\mathcal{G}$ was given explicity in ref. 10 as

$$\mathcal{G}(\mathbf{r}, \mathbf{r}', \beta) = \frac{1}{2\pi\beta}\frac{2}{|\mathbf{r}-\mathbf{r}'|}\exp\left\{-2\frac{|\mathbf{r}-\mathbf{r}'|^2}{2\beta}\right\}. \tag{4.3}$$

Evidently, the scaling properties of the potential distributions obtained by solution of eqn (2.4) lead to simplifications in this first-order approximation to the effective potential $U(\mathbf{r}\beta)$. In the next step, the density matrix C_1 corresponding to this first-order U_1 is orthogonalized to the lowest bound state,[10] which has to be directly calculated. Hence, by iteration, $U(\mathbf{r}\beta)$ is obtained for a given starting potential $V(r) = -\frac{Ze^2}{r}\phi\left(\frac{r}{b}, s\right)$.

4.1 *Liquid metal partition function and electronic density of states*

The assumption customarily made in the liquid metal problem is that the total potential energy $V(r)$ to be inserted in the Schrödinger equation for a given fixed configuration of ions $\{\mathbf{R}_i\}$ is the superposition of atomic-like localized potentials $v(r)$ centred on $\{\mathbf{R}_i\}$, i.e.

$$V(\mathbf{r}) = \sum_{R_i} v(|\mathbf{r} - \mathbf{R}_i|). \tag{4.4}$$

The TF approximation to $C(r\beta)$ in the liquid metal is then

$$C(r\beta) = \frac{1}{(2\pi\beta)^{3/2}} \exp(-V(\mathbf{r})) = \frac{1}{(2\pi\beta)^{3/2}} \prod_i \exp(-\beta v(\mathbf{r} - \mathbf{R}_i)). \tag{4.5}$$

In the method of ref. 11, one simply replaces in eqn (4.5) the potential $v(r)$ by $U(r, \beta)$ for the atom in a plasma, calculated as above.

Once $U(r, \beta)$ is known, the partition function $Z(\beta) = \int C(r, \beta) d\mathbf{r}$ can be calculated, albeit approximately, once one has the liquid pair function $g(r)$. In brief, the result may be expressed in the form

$$Z(\beta) = \frac{1}{(2\pi\beta)^{3/2}} \exp(\beta\Gamma(\beta)) \tag{4.6}$$

where

$$\exp(\beta\Gamma(\beta))] = 1 + \int d\mathbf{r}' \frac{f(\mathbf{r}', \beta)[\exp\{\rho G(\mathbf{r}')\} - 1]}{G(\mathbf{r}')}, \tag{4.7}$$

f denoting the Mayer-like function

$$f(r, \beta) = \exp[-\beta U(r, \beta)] - 1. \tag{4.8}$$

Finally $G(\mathbf{r}')$ is given explicitly in terms of f and the pair function $g(r)$ of the liquid metal by

$$G(\mathbf{r}') = \int d\mathbf{r}'' f(\mathbf{r}''\beta) g(|\mathbf{r}' - \mathbf{r}''|). \tag{4.9}$$

Hence, knowledge of the $U(r, \beta)$ for an individual atom in a cold plasma having a density equal to that in the conduction band of the specified liquid metal, together with the liquid pair function $g(r)$, suffices to yield the partition function $Z(\beta)$ of the liquid metal, the electronic density of states following by inverse Laplace transform.[11]

5 SUMMARY

The main result of the present work is to show that the potential distribution around an atom in a cold dense plasma can be modelled in the Thomas-Fermi regime by the generalized non-linear differential equation (2.4), to be solved with the boundary conditions (2.5). The fact that the solution for the potential can be characterized by the single parameter s has implications for the eigenvalue spectrum of an atom in a plasma, as well as for the electronic structure of liquid metals, which can be built from quantitative knowledge of an atom in the plasma formed by the conduction electrons, plus the short-range atomic order in the liquid metals, described by the experimentally accessible pair function $g(r)$.

Clearly, a further worthwhile step would be to generate, for a wider range of the parameter s than is hitherto available, solutions of the non-linear equation (2.4). With such solutions available, the eigenvalues ε_{nl} in the WKB approximation should be readily calculable from eqn (3.7). A further use of such solutions would be to yield the first-order approximation $U_1(\mathbf{r}\beta)$ to the effective potential $U(\mathbf{r}\beta)$ for an atom in a cold dense plasma from eqns (4.2) and (4.3), to provide the first step in a more extensive study than made hitherto of the electronic structure of liquid metals.

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APPENDIX 1

Power series solution of generalized TF eqn (2.4) for small x

It was already known to Baker[16] that the small x series solution of eqn (2.4) for the particular case $s = 0$ had the form

$$\phi(x) = 1 + a_2 x + a_3 x^{3/2} + a_4 x^2 + a_5 x^{5/2} + \cdots \tag{A1.1}$$

The purpose of this Appendix is to generalize Baker's coefficients to apply to arbitrary s. To do so, eqn (A1.1) suggests the substitutions $x^{1/2} \to y$, $\phi(x) \to \chi(y)$. Then eqn (2.4) is readily rewritten as

$$y\frac{d^2\chi}{dy^2} - \frac{d\chi}{dy} = 4y^2\chi^{3/2} - 4s^{3/2}y^5. \tag{A1.2}$$

Table A1.1 Coefficients in Eqn. (A1.1) for arbitrary values of the parameter s in Eqn. (2.4)

a_3	a_4	a_5	a_6	a_7	a_8
$\frac{4}{3}$	0	$\frac{2}{5}a_2$	$\frac{1}{3}-\frac{s^{3/2}}{6}$	$\frac{3}{70}a_2^2$	$\frac{2}{15}a_2$
a_9	a_{10}	a_{11}			
$\frac{2}{27}-\frac{a_2^3}{252}-\frac{s^{3/2}}{63}$	$\frac{a_2^2}{175}$	$\frac{31}{1485}a_2-\frac{a_2s^{3/2}}{198}+\frac{a_2^4}{1056}$			
a_{12}	a_{13}				
$\frac{4}{405}+\frac{4a_3^3}{1575}-\frac{2}{315}s^{3/2}$	$\frac{557}{100100}a_2^2-\frac{3a_2^5}{9152}+\frac{a_2^2s^{5/2}}{1144}$				

Using the form (A1.1), the left-hand side of eqn (A1.2) is

$$y\frac{d^2\chi}{dy^2}-\frac{d\chi}{dy}=\sum_{n=3}^{\infty}n(n-2)a_n y^{n-1} \tag{A1.3}$$

while

$$\begin{aligned}4y^2\chi^{3/2}-4s^{3/2}y^5 &= 4y^2+6a_2y^4+[6a_3-4s^{3/2}]y^5\\ &\quad+[\tfrac{3}{2}a_2^2+6a_4]y^6+[3a_2a_3+6a_5]y^7\\ &\quad+[-a_2^3/4+\tfrac{3}{2}a_3^2+6a_6]y^8\\ &\quad+\cdots\end{aligned} \tag{A1.4}$$

Equating coefficients of powers of y^n in eqns (A1.3) and (A1.4) yields the results recorded in Table A1.1. These reduce correctly to the results for $s = 0$ given earlier by the writer,[17] who calculated additional terms, and made one correction, to the results of Baker[16] already referred to.

APPENDIX 2

Consequences of scaling property of generalized Thomas-Fermi potential for the first-order effective potential U_1 in eqn (4.2)

Introducing the quantity Δ defined by eqn (2.6), namely

$$\frac{\Delta}{sx}=\frac{\phi}{sx}-1 \tag{A2.1}$$

the effective potential U_1 to first-order in the TF potential can be written

$$\frac{U_1(r,\beta)}{\mu}=\int G(\mathbf{r},\mathbf{r}_1,\beta)\frac{\Delta(x_1)}{sx_1}d\mathbf{x}_1 \tag{A2.2}$$

Here the Green function G is given by

$$G=\frac{1}{\pi\beta}(b|\mathbf{x}-\mathbf{x}'|)^{-1}\exp\left(-\frac{2b^2|\mathbf{x}-\mathbf{x}'|^2}{2\beta}\right) \tag{A2.3}$$

Thus one has

$$\frac{U(r_1,\beta)}{\mu}=\frac{b^2}{\beta s}F(x,b^2/\beta) \tag{A2.4}$$

where

$$F(x,b^2/\beta)=\pi^{-1}\int\frac{1}{|\mathbf{x}-\mathbf{x}'|}\exp\left(-\frac{2b^2}{\beta}|\mathbf{x}-\mathbf{x}'|^2\right)\frac{\Delta(x_1,s)}{sx_1}d\mathbf{x}_1. \tag{A2.5}$$

or finally

$$\frac{U_1(r,\beta,Z,\mathrm{s},\mu)}{\mu}=\frac{b^2}{\beta s}F\left(x,\frac{b^2}{\beta},s\right). \tag{A2.6}$$

Of course, it is not implied that such a simple scaling will be preserved in higher order approximations to the effective potential U.