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ANALYSIS OF THE BOUNDARY VALUE PROBLEM ASSOCIATED WITH THE NONRELATIVISTIC THOMAS–FERMI EQUATION FOR HEAVY ATOMS IN INTENSE MAGNETIC FIELDS

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Abstract. This article presents a firm mathematical foundation for the boundary value problem associated with the nonrelativistic Thomas-Fermi equation for heavy atoms in intense magnetic fields. Our approach uses an application of differential inequalities and ideas from nonlinear analysis, including: the technique of lower and upper solutions; and fixed-point theory. We present new results that ensure existence, uniqueness, location and approximation of solutions. We thus establish that the Thomas-Fermi model leads to a robust theory of heavy atoms in intense magnetic fields in spite of the severe approximations that it employs.

A YouTube video from the first author that is designed to complement this paper can be found here http://tinyurl.com/ThomasFermi.

1. Introduction

A mathematically rigorous theory of the electronic structure of atoms in intense magnetic fields is of fundamental physical interest. In astrophysics, for example, one would like to understand the behaviour of atoms in the magnetic fields of neutron stars, which ranges from $\sim 10^{12}$ G for pulsars to $\sim 10^{15}$ G for magnetars, for example, see [26]. Atoms with high nuclear binding energies and stability, such as iron (atomic number $Z = 26$), are of particular interest [3].

The semiclassical Thomas-Fermi theory [18, 41] of atoms has appealing physical simplicity. Its venerable history spans some eighty years with a vast literature, see [2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 19, 21, 23, 28, 31, 32, 33, 34, 37, 39] and references therein. In spite of its failure to predict an atom's shell structure and chemical bonding [36], the theory has nevertheless been shown to be an asymptotically exact description of "heavy" atoms in the $Z \to \infty$ limit, when interpreted as describing the "core and mantle" of the electron distribution [33].

The standard case with no magnetic field leads to the "singular" differential equation $x^{1/2}y'' = y^{1/2}$. Coupled with various boundary conditions, this problem has been extensively studied from theoretical, physical and computational points of view, for example, see [18, 20, 25, 41] and references therein.

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The case of heavy atoms in intense magnetic fields has been studied within the framework of the Thomas-Fermi theory and much is known, both quantitatively and qualitatively, for example, see [19, 24, 27, 29, 30, 35] and references therein. In particular, variational methods have been used to prove the existence and uniqueness of the electron density that minimizes the Thomas-Fermi energy functional [30].

Here, we take a different approach by analyzing the associated boundary value problem (BVP) for the electron density in the case of atoms in strong magnetic fields, which has been subjected to only limited mathematical analysis. The associated ordinary differential equation is

$$y'' = \sqrt{xy}, \qquad x \in [0, x_0], \tag{1.1}$$

subject to appropriate (Dirichlet) boundary conditions (with the notation made precise in Section 2).

In Section 2 we briefly review and derive the Thomas-Fermi BVP for heavy atoms in intense magnetic fields.

In Section 3 we prove that the BVP for heavy atoms in an intense magnetic field is well posed with a unique solution that can rigorously be bounded to lie between simple functions on a finite interval $[0, x_0]$ of the non-dimensional radial distance. The methods chosen herein involve differential inequalities and ideas from nonlinear analysis. This includes such approaches as: an application of the technique of lower and upper solutions [16]; and a particular application of fixed-point theory known as Schauder's fixed-point theorem [44, Theorem 2.A, p.57].

In Section 4 we present a discussion of the results and our conclusions.

2. The Thomas-Fermi model for heavy atoms in an intense magnetic field

To place the boundary value problem considered here in its physical context, we now sketch a derivation of the Thomas-Fermi model as applied to heavy atoms in intense magnetic fields following [27, 35]. We adopt Gaussian units.

The basic idea of the Thomas-Fermi approach is to model the atomic electrons as a degenerate Fermi gas, which allows both kinetic and potential energies of the electrons to be expressed entirely in terms of the number density $n(\mathbf{r})$ of the electrons. Exchange energies are neglected but can be included in refinements of the theory [17].

In the presence of an intense magnetic field (precisely what is meant by "intense" will be quantified below), the electrons are modelled as a one-dimensional Fermi gas moving along the field lines but localized to the atom by the Coulomb potential of the nucleus. The kinetic energy of the electrons associated with their cyclotron orbits is assumed to be unperturbed by the Coulomb potential so that it does not contribute to the energy relative to the free state in the magnetic field. The kinetic energy associated with the orbital motion in the Coulomb potential is assumed to be negligible compared to the kinetic energy of the motion along the field. The range of validity of these assumptions can be justified *a posteriori* for large Z, for example, see, [27, 35, 30] and also below. The number of states per unit volume is then set by the density of Landau levels per unit transverse area, $(eB)/(hc)$, and the density of momentum states per unit length and per unit momentum for the motion parallel to the magnetic field, $2/h$. Assuming temperatures sufficiently low so that all electron spins remain anti-aligned with the field and so that the Fermi momentum cannot be exceeded, there is exactly one electron per state up to the Fermi momentum p_F so that $n(\mathbf{r}) = 2eBp_F/(h^2c)$. Thus, the kinetic energy density per unit volume is given by

$$\frac{eB}{hc}\frac{2}{h}\int_0^{p_F}\frac{p^2}{2m}dp = e^2L^5n^3$$

where the length $L = (c^2h^4)^{1/5}/(24mB^2e^4)^{1/5}$ and m denotes the mass of the electron.

The energy functional of the electron gas is given by the sum of its kinetic energy, its electric potential energy in the field of the nucleus, and the electric potential energy due to Coulomb interactions of the electrons with each other:

$$\mathscr{E}_{TF}[n(\mathbf{r})] = e^2L^5\int n^3(\mathbf{r})d^3r - e^2Z\int\frac{n(\mathbf{r})}{|\mathbf{r}|}d^3r + \frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r'. \tag{2.1}$$

The corresponding ground-state energy scales with field strength B, number of electrons N, and atomic number Z like $(B/B_0)^{2/5}N^{3/5}Z^{6/5}$ for $N \leqslant Z$. Thus, for neutral atoms with $N = Z$, the ground-state energy scales like $(B/B_0)^{2/5}Z^{9/5}$, compared with the neutral zero-field case whose ground-state energy scales like $Z^{7/3}$. Here the natural scale for the magnetic field, B_0, is the field for which the energy of the lowest Landau level equals the ionization energy of a hydrogen atom in its ground state. Thus, $B_0 \equiv cm^2e^3/\hbar^3 \sim 2\times 10^9$ G. Interestingly, the presence of the magnetic field does not spoil the spherical symmetry of the electron density for the magnetic field range for which this model is valid, for example, see [27, 35, 29, 30] and see below. Thus, $n(\mathbf{r}) = n(r)$, where $r = |\mathbf{r}|$.

The electron density that minimizes $\mathscr{E}_{TF}$ subject to the constraint that $\int n(r)d^3r = N$, the number of electrons $N \leqslant Z$, is obtained by variation with respect to n. Setting $\delta(\mathscr{E}_{TF}[n] - eN\varphi_0)/\delta n = 0$, where φ_0 is the Lagrange multiplier associated with the constraint, one immediately obtains

$$3e^2L^5n^2(r) = -e[\varphi(r) - \varphi_0], \tag{2.2}$$

where $\varphi(r)$ is the total Coulomb potential.

For neutral atoms, the Lagrange multiplier $\varphi_0 = 0$. This potential is forced to be self-consistent with the electron density by demanding that $n(r)$ be its source in Gauss' law

$$\nabla^2\varphi(r) = -4\pi en(r), \tag{2.3}$$

subject to the boundary condition that the nuclear potential dominates at the origin:

$$\lim_{r\to 0} r\varphi(r) = -Ze. \tag{2.4}$$

Before defining the associated BVP, it is appropriate to review the limits of validity of the radially symmetric Thomas-Fermi electron density. For there to be well defined momentum states parallel to the magnetic field, the majority of electrons cannot be in deep bound states with nodeless wave functions. The condition for this is that the cyclotron radius of the m^{th} Landau level with $m \sim N \sim Z$ be much larger than the Bohr radius for nuclear charge $-Ze$, which gives the condition $B/B_0 \ll Z^3$. At the lower range of B, the requirement that the binding energy in the presence of a strong magnetic field be significantly greater than that with no field, gives $Z^{4/3} \ll B/B_0$, which follows immediately from the different scaling of the energy with B and Z in the two cases. With respect to the classification scheme of Lieb et al. [29, 30] for the different asymptotic regimes that are realized depending on the powerlaw with which $B \to \infty$ as $Z \to \infty$, we are thus concerned with "region 3" for which $Z^{4/3} \ll B/B_0 \ll Z^3$.

2.1. The boundary value problem

To combine (2.2) and (2.3) into a single nonlinear ordinary differential equation one defines the nondimensional function

$$y(r) := -\frac{r}{Ze}[\varphi(r) - \varphi_0]$$

and nondimensional radial distance $x = r/R$, with $R = (4\pi)^{-2/5}(3Z)^{1/5}L$.

Changing the variable from r to x, (2.2) and (2.3) combine to give

$$y'' = \sqrt{xy}. \tag{2.5}$$

Equation (2.5) must be solved under suitable boundary conditions, namely (2.4), which becomes

$$y(0) = 1, \tag{2.6}$$

and to ensure a finite-size atom one must also have

$$y(x_0) = 0, \tag{2.7}$$

for sufficiently large $x_0 > 0$.

2.2. Necessary notation and definitions

We now give a few mathematical definitions that are necessary for the sections that follow.

DEFINITION 1. A *solution to* (2.5)-(2.7) is defined to be a twice continuously differentiable function $y = y(x)$, denoted by $y \in C^2([0,x_0])$, such that y satisfies (2.5) on $[0,x_0]$ and satisfies (2.6)-(2.7).

Our analysis will be set in the Banach space $(Y, \|\cdot\|_0)$ where: Y is the set of continuous functions on $[0,x_0]$, denoted by $C([0,x_0])$; coupled with the maximum norm, that is,

$$\|y\|_0 := \max_{x\in[0,x_0]} |y(x)|, \quad \text{for all } y \in C([0,x_0]).$$

DEFINITION 2. Let T be a map between Banach spaces, i.e., $T : Y \to Y$. The map T is defined to be *compact* if: T is continuous; and T maps bounded sets into relatively compact sets.

The following result is known as Schauder's fixed-point theorem [44, Theorem 2.A, p.57] and will be required in Section 3.

THEOREM 1. (Schauder) *Let Ω be a nonempty, closed, bounded and convex subset of the Banach space Y. If $T : \Omega \to \Omega$ is a compact map then there is at least one $y \in \Omega$ such that $Ty = y$.*

3. Main results

We first consider the BVP (2.5)-(2.7) and illustrate that a unique solution exists. We prove that the unique solution lies between two simple functions, generally known as lower and upper solutions.

Let us first ensure that the BVP (2.5)-(2.7) has, at most, one solution. We will then build on this result.

THEOREM 2. *For arbitrary (but finite) $x_0 > 0$, the BVP (2.5)-(2.7) has, at most, one solution on $[0, x_0]$.*

Proof. The proof involves exploiting the monotonicity of the right-hand-side of (2.5) in y. Let u and v be two solutions to (2.5)-(2.7). We show that $u \equiv v$ on $[0, x_0]$ so that there is, at most, one solution to (2.5)-(2.7).

Let

$$r(x) := u(x) - v(x), \quad \text{for all } x \in [0, x_0]. \tag{3.1}$$

Since r is continuous on $[0, x_0]$, it must achieve its maximum (and minimum) values on $[0, x_0]$. Let $x_1 \in [0, x_0]$ be such that

$$r(x_1) = \max_{x \in [0, x_0]} r(x) > 0 \tag{3.2}$$

that is, $u(x_1) > v(x_1)$. We show that (3.2) cannot hold in the sense that $r(x_1)$ cannot be positive.

If $x_1 = 0$ then (2.6) ensures $r(0) = 0$ and so (3.2) cannot hold for $x_1 = 0$. Similarly, (2.7) ensures that (3.2) cannot hold for $x_1 = x_0$.

If $x_1 \in (0, x_0)$ then the maximum principle [40, p.1] gives $r'(x_1) = 0$ and $r''(x_1) \leqslant 0$. From (3.1) we also have

$$\begin{aligned} r''(x_1) &= u''(x_1) - v''(x_1) \\ &= (x_1 u(x_1))^{1/2} - (x_1 v(x_1))^{1/2} \\ &> 0 \end{aligned}$$

as $u(x_1) > v(x_1)$. Thus, we reach a contradiction and so (3.2) cannot hold for any $x_1 \in (0, x_0)$.

Combining the above cases we see that $r \leqslant 0$ on $[0,x_0]$.

In a similar fashion to the above argument, it can be shown that $r \geqslant 0$ on $[0,x_0]$ by applying the maximum principle to $-r$ on $[0,x_0]$.

Thus, $r \equiv 0$ on $[0,x_0]$ and so $u \equiv v$ on $[0,x_0]$, that is, there is a most one solution to (2.5)-(2.7). □

The next result guarantees that the BVP (2.5)-(2.7) has a unique solution and also gives a location on the solution, that is, we provide a function that bounds the solution from below and another function that bounds the solution from above, thus "sandwiching" the solution between two functions.

THEOREM 3. *For arbitrary (but finite) $x_0 > 0$, the BVP (2.5)-(2.7) has a unique solution $y \in C^2([0,x_0])$ such that*

$$0 \leqslant y(x) \leqslant 1 - \frac{x}{x_0}, \quad \textit{for all } x \in [0,x_0]. \tag{3.3}$$

Proof. The basic idea is to modify (2.5) to form a related differential equation whose right-hand-side is continuous and uniformly bounded on $[0,x_0] \times \mathbb{R}$. At least one solution to the modified BVP is then guaranteed to exist by Schauder's fixed-point theorem. These solutions are shown to be solutions to (2.5)-(2.7) by a forming a particular pair of "lower and upper solutions". Finally, an application of Theorem 2 shows that this solution is unique.

Consider the modified differential equation

$$y'' = g(x,y), \quad x \in [0,x_0] \tag{3.4}$$

subject to (2.6) and (2.7), where

$$g(x,y) := \begin{cases} \left[x\left(1-\dfrac{x}{x_0}\right)\right]^{1/2} + \dfrac{y-\left(1-\dfrac{x}{x_0}\right)}{1+\left(y-\left(1-\dfrac{x}{x_0}\right)\right)^2}, & \text{for } y \geqslant 1-\dfrac{x}{x_0}; \\ (xy)^{1/2}, & \text{for } 0 \leqslant y \leqslant 1-\dfrac{x}{x_0}; \\ \dfrac{-y}{1+y^2}, & \text{for } y \leqslant 0. \end{cases}$$

Note that g is continuous and uniformly bounded on $[0,x_0] \times \mathbb{R}$ and we let this bound be denoted by $M > 0$. The BVP (3.4), (2.6), (2.7) is equivalent to the integral equation

$$y(x) := \left(1-\frac{x}{x_0}\right) + \int_0^{x_0} G(x,s)g(s,y(s))\,ds, \quad x \in [0,x_0] \tag{3.5}$$

where

$$G(x,s) := \begin{cases} -\dfrac{(x_0-x)s}{x_0}, & \text{for } 0 \leqslant s \leqslant x \leqslant x_0; \\ -\dfrac{x(x_0-s)}{x_0}, & \text{for } 0 \leqslant x \leqslant s \leqslant x_0. \end{cases}$$

The proof of this equivalence is found in Theorem 6 of the appendix.

It is straightforward to show that G satisfies

$$\int_0^{x_0} |G(x,s)|\, ds \leqslant \frac{x_0^2}{8}, \quad \text{for all } x \in [0,x_0] \tag{3.6}$$

see, for example, [22, Chap.XII, Sec.4].

Now, form a Banach space by choosing $Y = C([0,x_0])$, the space of continuous functions on $[0,x_0]$, and coupling it with the maximum norm. Consider the map T defined by

$$[Ty](x) := \left(1 - \frac{x}{x_0}\right) + \int_0^{x_0} G(x,s)g(s,y(s))ds, \quad x \in [0,x_0]. \tag{3.7}$$

The continuity of G, g and the properties of the integral ensure that for all $y \in C([0,x_0])$ we have $Ty \in C([0,x_0])$. In addition, comparing (3.5) with (3.4) we see that y is a solution to (3.4), subject to (2.6) and (2.7), if and only if $Ty = y$.

If we define the nonempty, closed, bounded and convex set

$$\Omega := \left\{ y \in C([0,x_0]) : \|y\|_0 = \max_{x\in[0,x_0]} |y(x)| \leqslant 1 + \frac{Mx_0^2}{8} \right\} \subset C([0,x_0]) \tag{3.8}$$

then the continuity of g and the bounds (3.6) and M ensure that for all $y \in C([0,x_0])$ we have

$$\|Ty\|_0 = \max_{x\in[0,x_0]} |[Ty](x)| \leqslant 1 + \frac{Mx_0^2}{8}$$

with the calculations contained in the proof of Theorem 7 in the appendix. Thus, $T : C([0,x_0]) \to \Omega$ and so $T : \Omega \to \Omega$.

Furthermore, T is a compact map, as shown in Theorem 10 in the appendix (or see [44, p.55-56]).

Hence, all of the conditions of Schauder's theorem are satisfied so there is at least one $y \in \Omega$ such that $Ty = y$. These y are not only in $C([0,x_0])$, but are actually in $C^2([0,x_0])$ due to the continuity of f (and g).Thus, the modified BVP (3.4), (2.6), (2.7) has at least one solution $y \in C^2([0,x_0])$.

We now show that solutions y to (3.4), (2.6), (2.7) must satisfy (3.3) and so they must be solutions to the unmodified BVP (2.5)-(2.7).

We first show that

$$y(x) \leqslant 1 - \frac{x}{x_0}, \quad \text{for all } x \in [0,x_0]. \tag{3.9}$$

The case showing $y \geqslant 0$ on $[0,x_0]$ is similar and so is omitted for brevity.

Let

$$w(x) := y(x) - \left(1 - \frac{x}{x_0}\right), \quad \text{for all } x \in [0,x_0]. \tag{3.10}$$

Since w is continuous on $[0,x_0]$, it must achieve its maximum value on $[0,x_0]$. Let $x_2 \in [0,x_0]$ be such that

$$w(x_2) = \max_{x\in[0,x_0]} w(x) > 0 \tag{3.11}$$

that is, $y(x_2) > 1 - x_2/x_0$. We show that (3.11) cannot hold in the sense that $w(x_2)$ cannot be positive.

The boundary conditions (2.6) and (2.7) ensure that (3.11) cannot hold, respectively, for $x_2 = 0$ or $x_2 = x_0$.

If $x_2 \in (0, x_0)$ then the maximum principle [40, p.1] gives $w'(x_2) = 0$ and $w''(x_2) \leqslant 0$. From (3.10) and (3.4) we also have

$$\begin{aligned} w''(x_2) &= y''(x_2) \\ &= g(x_2, y(x_2)) \\ &= \left[x_2\left(1 - \frac{x_2}{x_0}\right)\right]^{1/2} + \frac{y(x_2) - \left(1 - \frac{x_2}{x_0}\right)}{1 + \left(y(x_2) - \left(1 - \frac{x_2}{x_0}\right)\right)^2} \\ &> 0. \end{aligned}$$

Thus, we reach a contradiction and so (3.11) cannot hold for any $x_2 \in (0, x_0)$. Combining the above cases we conclude that (3.9) must hold.

In a similar fashion to the above, we also have $y \geqslant 0$ on $[0, x_0]$. Thus, (3.3) holds and the solutions to (3.4), (2.6), (2.7) must also be solutions to (2.5)-(2.7). By Theorem 2, there is, at most, one solution and so solutions to (2.5)-(2.7) are unique. □

The following result provides estimates on the slope of the solution to (2.5)-(2.7) at x_0.

THEOREM 4. *The solution y to (2.5)-(2.7) furnished by Theorem 3 satisfies*

$$-\frac{1}{x_0} \leqslant y'(x_0) \leqslant 0 \tag{3.12}$$

so that, for large (but finite) x_0, the solution will satisfy $y'(x_0) \approx 0$.

Proof. From a geometric point of view, inequality (3.12) is immediately apparent as Theorem 3 ensures the solution y to (2.5)-(2.7) is squeezed between the two functions $\alpha \equiv 0$ and $\beta(x) := 1 - x/x_0$ at $x = x_0$. Thus, $y'(x_0)$ must lie between $\beta'(x_0)$ and $\alpha'(x_0)$. □

REMARK 1. The bounds on $y'(x_0)$ established by Theorem 4 can be recast as bounds on the atom's ionization state. The number of electrons, N, is given by the integral of the number density, $N = \int_0^\infty n(r) 4\pi r^2\, dr$, which in terms of the non-dimensional variable $y(x)$, combined with the boundary condition $y(x_0) = 0$, maps onto

$$\frac{N}{Z} = \int_0^{x_0} x^{3/2} \sqrt{y}\, dx, \tag{3.13}$$

where Z is the atomic number. Using $\sqrt{y} = y''/\sqrt{x}$ from (1.1), integrating by parts, and applying the boundary condition $y(0) = 1$ and the fact that the solution bounds (3.3) guarantee that $\lim_{x\to 0^+} xy'(x) = 0$, we have

$$\frac{N}{Z} = 1 + x_0 y'(x_0). \tag{3.14}$$

The bounds on $y'(x_0)$ of Theorem 4 therefore become the condition

$$0 \leqslant N \leqslant Z \tag{3.15}$$

on the number of electrons. Thus, the bounds placed on the solution guarantee that the unique solution we have proven to exist has a physically realizable ionization state somewhere between completely neutral $(N = Z)$ and completely ionized, with all electrons stripped off the atom $(N = 0)$.

In Theorem 3, the solution to (2.5)-(2.7) is bounded between two simple functions. In fact, we can bound the solution by a range of functions, with the general technique known as the method of upper and lower solutions [16].

THEOREM 5. *If there exist functions $l, u \in C^2([0, x_0])$ such that $0 \leqslant u \leqslant l$ on $[0, x_0]$ and*

$$l''(x) \geqslant \sqrt{xl(x)}, \quad \textit{for all } x \in [0, x_0] \tag{3.16}$$

$$u''(x) \leqslant \sqrt{xu(x)}, \quad \textit{for all } x \in [0, x_0] \tag{3.17}$$

$$l(0) \geqslant 0, \quad u(0) \geqslant 1$$

$$l(x_0) = 0, \quad u(x_0) = 0$$

then the BVP (2.5)-(2.7) has a unique solution $y \in C^2([0, x_0])$ such that $l(x) \leqslant y(x) \leqslant u(x)$ for all $x \in [0, x_0]$. In addition, $u'(x_0) \leqslant y'(x_0) \leqslant l'(x_0)$.

Proof. The proof is very similar to that of Theorem 3 and so is omitted. □

REMARK 2. In Theorem 3 we constructed the following lower and upper solutions, respectively, to (2.5)-(2.7)

$$l \equiv 0, \quad u(x) = 1 - \frac{x}{x_0}. \tag{3.18}$$

The advantage in this choice is its simplicity.

REMARK 3. The function g in (3.4) is not Lipschitz [42] and so Banach's fixed-point theorem [43] cannot be applied to the modified BVP in the proof of Theorem 3. Furthermore, the operator T in (3.7) is not monotone and hence the theory of monotone operators is not applicable to the problem $T(y) = y$ in the proof of Theorem 3.

REMARK 4. The arguments of this paper extend to the case when

$$y'' = f(x,y).$$

For example, the same argument as used in the proof for Theorem 2 will ensure non-mulitiplicity of solutions if $f(x,y)$ is increasing in y. In addition, Theorems 2 and 3 can be proved by applying more general theorems in the literature, for example, [1, Theorem 7.6] or [16, Theorem 1.5].

4. Discussion and Conclusions

We considered the Thomas-Fermi model for heavy atoms in intense magnetic fields in the regime $Z^{4/3} \ll B/B_0 \ll Z^3$, where spherical symmetry is preserved. In this regime, the model reduces to the Thomas-Fermi equation $y'' = \sqrt{xy}$, where x is the non-dimensional distance from the nucleus, and the non-dimensionalized electron number density $\widehat{n} \equiv n\sqrt{3L^5R/Z}$ is given by $\widehat{n}(x) = \sqrt{y(x)/x}$. This Thomas-Fermi equation is highly nonlinear and in the absence of exact solutions requires approximations, such as numerical solutions. It is therefore natural to focus on the boundary value problem over the finite interval $x \in [0,x_0]$, with the boundary conditions $y(0) = 1$ and $y(x_0) = 0$. Given the severe approximations made in the Thomas-Fermi approach and the nonlinearity of the resulting equation, neither the well-posedness of the boundary value problem, nor the existence of unique solutions can be taken for granted. Indeed, the Thomas-Fermi model is known to give an exact description of atoms only in the asymptotic limit of infinite atomic number and infinitely strong magnetic fields [33]. This paper provides proof that the boundary value problem is well-posed with a unique solution for any finite x_0, vindicating the physical approximations made in the Thomas-Fermi approach. In this sense the Thomas-Fermi model constitutes a robust theory.

Our analysis also brackets the solution between upper and lower bounds. The lower bound of zero guarantees a positive definite electron density as physically required. We note in passing that the non-negativity of solutions to the boundary value problem of a wide class of differential equations that includes the Thomas-Fermi equation considered here has been proved also for the semi-infinite domain $x \in [0,\infty)$ by O'Regan [38, p,117], although uniqueness was not obtained. The upper bound constrains possible solutions $y(x)$ to lie below the straight line $1 - x/x_0$. which in terms of $y(x)$ and the boundary condition $y(x_0) = 0$ maps to the constraint $\int_0^{x_0} x^{3/2}y^{1/2}dx = 1$, the solution to the Thomas-Fermi equation for heavy atoms in intense magnetic fields is strongly constrained. These constraints provide powerful checks on any numerical or other approximate solutions. These bounds provide powerful checks on any numerical or other approximate solution. In addition, these bounds guarantee that the unique solution that we have shown to exits has a physically realizable ionization state, with the electron number lying between zero (fully ionized cation) and the atomic number (neutral atom).

There are a number of possible directions for further research. For example, our choice of upper and lower solutions in Section 3 involve very simple functions. In view of the more general result, Theorem 5, it may be interesting to construct upper and lower solutions with a more detailed structure to gain further qualitative information about the electron density. In particular, it may be possible to obtain sharper bounds on the solution to the BVP (2.5)-(2.7) at the end points of the interval $[0,x_0]$.

5. Appendix

To keep the paper reasonably self-contained, we present some known results in this section that are used in the proof of the main result, Theorem 3.

THEOREM 6. *The BVP* (3.4), (2.6), (2.7) *is equivalent to the integral equation* (3.5).

Proof. Let y be a solution to the integral equation (3.5) on $[0,x_0]$. Direct differentiation of both sides of (3.5) will yield (3.4). Direct substituion of $x=0$ and $x=x_0$ into (3.5) will yield (2.6) and (2.7), respectively. Thus, every solution to (3.5) must also be a solution to (3.4), (2.6), (2.7).

Now let y be a solution to the BVP (3.4), (2.6), (2.7) on $[0,x_0]$. Integration of (3.4) from 0 to z yields

$$y'(z) = y'(0) + \int_0^z g(q,y(q))\,dq, \qquad z \in [0,x_0]$$

and yet another integration from 0 to x gives

$$y(x) = y(0) + xy'(0) + \int_0^x \int_0^z g(s,y(s))\,ds\,dz \tag{5.1}$$

$$= 1 + xy'(0) + \int_0^x (x-s)g(s,y(s))\,ds, \qquad x \in [0,x_0] \tag{5.2}$$

where we have incorporated (2.6), integrated the final term in (5.1) by parts and then employed a suitable change of independent variable ($z \to s$).

Now, (5.2) evaluated at $x=x_0$ and coupled with (2.7) yields

$$0 = y(x_0) = 1 + x_0 y'(0) + \int_0^{x_0} (x_0-s)g(s,y(s))\,ds. \tag{5.3}$$

A rearrangement in (5.3) gives

$$y'(0) = -\frac{1}{x_0}\left[1 + \int_0^{x_0} (x_0-s)g(s,y(s))\,ds\right]$$

which may be substituted into (5.2) and rearranged to form (3.5). □

THEOREM 7. *If T is defined in* (3.7) *and Ω defined in* (3.8) *then $T(\Omega)$ is uniformly bounded.*

Proof. Let $y \in \Omega$ and consider

$$\begin{aligned}
\|Ty\|_0 &:= \max_{x\in[0,x_0]} |[Ty](x)| \\
&= \max_{x\in[0,x_0]} \left| \left(1 - \frac{x}{x_0}\right) + \int_0^{x_0} G(x,s)g(s,y(s))\, ds \right| \\
&\leqslant \max_{x\in[0,x_0]} \left[\left| 1 - \frac{x}{x_0} \right| + M \int_0^{x_0} |G(x,s)|\, ds \right] \\
&= 1 + \frac{Mx_0^2}{8}.
\end{aligned}$$

Thus $T(\Omega)$ is uniformly bounded by $1 + Mx_0^2/8$.

THEOREM 8. *If T is defined in (3.7) and Ω defined in (3.8) then $T(\Omega)$ is equicontinuous.*

Proof. Let $y \in \Omega$ and $x_1, x_2 \in [0, x_0]$. To show $T(\Omega)$ is equicontinuous, we illustrate that for any given $\varepsilon > 0$ there exists a $\delta = \delta(\varepsilon)$ such that

$$|[Ty](x_1) - [Ty](x_2)| < \varepsilon \quad \text{whenever} \quad |x_1 - x_2| < \delta$$

Since G has continuous partial dertivatives we have

$$\begin{aligned}
|G(x_1,s) - G(x_2,s)| &= \left| \int_{x_2}^{x_1} \frac{\partial G}{\partial x}(x,s)\, ds \right| \\
&\leqslant |x_1 - x_2|.
\end{aligned}$$

Thus, for any given $\varepsilon > 0$ we have

$$\begin{aligned}
|[Ty](x_1) - [Ty](x_2)| &\leqslant \frac{|x_1 - x_2|}{x_0} + \int_0^{x_0} |G(x_1,s) - G(x_2,s)||g(s,y(s))|\, ds \\
&\leqslant \frac{|x_1 - x_2|}{x_0} + M \int_0^{x_0} |x_1 - x_2| \\
&= |x_1 - x_2| \left[\frac{1}{x_0} + Mx_0 \right] \\
&< \varepsilon
\end{aligned}$$

whenever $|x_1 - x_2| < \delta$ for the choice

$$\delta(\varepsilon) = \frac{\varepsilon}{\frac{1}{x_0} + Mx_0}. \quad \square$$

THEOREM 9. *If T is defined in (3.7) and Ω defined in (3.8) then T is continuous on Ω.*

Proof. Let y_n be a sequence of functions in Ω that converges uniformly on $[0,x_0]$ to some $y \in \Omega$, that is $y_n \to y$, as $n \to \infty$. We show that $Ty_n \to Ty$, as $n \to \infty$.

Consider the rectangular region in $\mathbb{R}^2$ defined by

$$\Omega_1 := \left\{ (x,p) \in [0,x_0] \times \mathbb{R} : |p| \leqslant 1 + \frac{Mx_0^2}{8} \right\}.$$

Now, as g is uniformly continuous on Ω_1 we have

$$g(x,y_n(x)) \to g(x,y(x)) \qquad \text{as} \quad n \to \infty$$

with the convergence being uniform on $[0,x_0]$. Thus, on $[0,x_0]$ we have

$$\begin{aligned} \|Ty_n - Ty\|_0 &= \max_{x\in[0,x_0]} \left| \int_0^{x_0} G(x,s)[g(s,y_n(s)) - g(s,y(s))]\,ds \right| \\ &\leqslant \max_{x\in[0,x_0]} \int_0^{x_0} |G(x,s)||g(s,y_n(s)) - g(s,y(s))|\,ds \\ &\to 0, \quad \text{as} \quad n \to \infty. \quad \square \end{aligned}$$

THEOREM 10. *If T is defined in* (3.7) *and Ω defined in* (3.8) *then T is a compact map.*

Proof. In view of the definition of compactness given in Section 2.2 we need to show that T is continuous and T maps bounded sets into relatively compact sets.

Firstly, continuity of T on Ω is ensured from Theorem 9.

Secondly, the uniform boundedness and equicontinuity of $T(\Omega)$ illustrated in Theorems 7 and 8 may be applied to show that $T(\Omega)$ is relatively compact, that is, $\overline{T(\Omega)}$ is a compact set. The properties of uniform boundedness and equicontinuity of $T(\Omega)$ ensure that the Arzelà-Ascoli theorem [44, (24g), p.772] may be applied to $T(\Omega)$ to guarantee it is relatively compact. $\square$

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