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Variational principle for the chemical potential in the Thomas–Fermi model

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Abstract. We derive a variational characterization for the chemical potential in the Thomas–Fermi model of atoms and molecules. We use this variational principle to obtain accurate upper bounds for the chemical potential $\epsilon_F(N, Z)$ as a function of the atomic number Z and the number of electrons N. In particular we study the behaviour of $\epsilon_F(N, Z)$ for a weakly ionized atom.

1. Introduction

Variational principles are often good alternative procedures for estimating physical quantities. The purpose of this paper is to give a variational principle for the chemical potential in the Thomas–Fermi model of atoms and molecules. The Thomas–Fermi (TF) model [1, 2] is defined by the energy functional

$$\mathcal{E}(\rho) = \frac{3}{5}\int \rho^{5/3}(x)\,\mathrm{d}^3x - \int V(x)\rho(x)\,\mathrm{d}^3x + D(\rho,\rho) \tag{1.1}$$

where

$$D(\rho,\rho) = \frac{1}{2}\int \rho(x)|x-y|^{-1}\rho(y)\,\mathrm{d}^3x\,\mathrm{d}^3y \tag{1.2}$$

and

$$V(x) = \sum_{j=1}^{k} z_j|x-R_j|^{-1}. \tag{1.3}$$

Throughout the paper we use units for which $h^2(8m)^{-1}(3/\pi)^{2/3} = 1$ and $|e| = 1$, where e and m are the electron charge and mass, respectively, and h is Planck's constant. In these units, the Bohr radius $a_0 \equiv h^2/(4\pi^2 me^2) \approx 0.208\,97$. Here $z_1, \ldots, z_k \geqslant 0$ are the charges of k fixed nuclei located at $R_1, \ldots, R_k$. $\mathcal{E}(\rho)$ is defined for electronic densities $\rho(x) \geqslant 0$ such that $\int \rho\,\mathrm{d}^3x$ and $\int \rho^{5/3}\,\mathrm{d}^3x$ are finite. The TF electronic energy for N (not necessarily an integer) electrons is defined by

$$E(N) = \min\left\{\mathcal{E}(\rho)\,\middle|\,\int \rho\,\mathrm{d}^3x = N\right\}. \tag{1.4}$$

It is known [3, 4] that for $N \leqslant Z \equiv \sum_{j=1}^{k} z_j$ there is a unique minimizing ρ for (1.4). It is the unique solution to the Thomas–Fermi equation

$$\rho(x)^{2/3} = \max(\varphi + \epsilon_F, 0) \tag{1.5}$$

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for some $\epsilon_F \leqslant 0$ and with

$$\varphi(x) = V(x) - \int \frac{\rho(y)}{|x-y|}\, d^3y. \tag{1.6}$$

$\epsilon_F(N; z_1, \ldots, z_k)$ is the chemical potential, i.e.

$$\epsilon_F = \frac{dE}{dN}. \tag{1.7}$$

There is extensive literature on the TF model, and we refer the interested reader to two review articles by Lieb [5] and Spruch [6] for details.

As we mentioned at the beginning, our interest here is in proving a variational characterization of the chemical potential ϵ_F. A minimax and a maximin principle for ϵ_F were proven by Lieb and Simon (see [4], Theorems II.28 and II.29). In short, their maximin principle reads as follows: let ρ be an admissible density, define $\phi_\rho(x) = \int \rho(y)|x-y|^{-1}\, d^3y$; let $T(\rho) = \inf_x(\rho^{2/3}(x) - \phi_\rho)$, then $\epsilon_F(N, Z) = \sup\{T(\rho) | \int \rho\, d^3x = N\}$. Their minimax principle is analogous with the operations on x and ρ reversed. These minimax principles are of the same type as Barta's (or Duffin's) principle for the Schrödinger equation (see [7], pp 154–5). On the other hand, the variational characterization we give here for ϵ_F is closer to the Rayleigh–Ritz principle for the ground-state energy of the Schrödinger equation.

Our main results are the following two theorems.

Theorem 1 (atomic case, $k = 1$). Let $\mathcal{D}$ be the set of non-negative, radially symmetric, bounded, subharmonic functions g on $\Re^3$ (i.e. with $\Delta g \geqslant 0$), with piecewise continuous second derivatives and such that both Δg and $(\Delta g)^3/g^2$ are integrable. For any $g \in \mathcal{D}$ let

$$\mathcal{I}(g) = \left(\int \Delta g\, d^3x\right)^{-1}\left(4\pi g_\infty(Z-N) - 4\pi g_0 Z - \frac{1}{108\pi^2}\int \frac{(\Delta g)^3}{g^2}\, d^3x\right) \tag{1.8}$$

where g_0 is the value of g at the nucleus and g_∞ is the limit of $g(x)$ as $|x| \to \infty$ (such a limit always exists for $g \in \mathcal{D}$).

Then

$$-\epsilon_F(N, Z) = \max\{\mathcal{I}(g) | g \in \mathcal{D}\} \tag{1.9}$$

and the maximum is attained at $\hat{g}$, the (unique up to a multiplicative constant) solution of equation (2.15) below.

Theorem 2 (molecular case, $k > 1$). Let $\mathcal{H}$ be the set of non-negative, bounded, subharmonic functions g on $\Re^3$ (i.e. with $\Delta g \geqslant 0$), with piecewise continuous second derivatives and such that both Δg and $(\Delta g)^3/g^2$ are integrable. For any $g \in \mathcal{H}$ let

$$\mathcal{I}(g) = \left(\int \Delta g\, d^3x\right)^{-1}\left(4\pi g_\infty(Z-N) - 4\pi \sum_{j=1}^{k} g_j z_j - \frac{1}{108\pi^2}\int \frac{(\Delta g)^3}{g^2}\, d^3x\right) \tag{1.10}$$

where g_j is the value of g at the nucleus located at R_j and g_∞ is the limit of the spherical average of $g(x)$, over a ball of radius R enclosing all the nuclei, as $R \to \infty$ (such a limit always exists for $g \in \mathcal{H}$).

Then

$$-\epsilon_F(N; z_1, \ldots, z_k) = \max\{\mathcal{I}(g) | g \in \mathcal{H}\} \tag{1.11}$$

and the maximum is attained at $\hat{g}$, the (unique up to a multiplicative constant) solution of equation (2.15) below.

Techniques similar to these used in the derivation of the variational principle for the chemical potential of the Thomas–Fermi model have been used recently in the derivation of analogous variational characterizations of other nonlinear eigenvalue problems. In particular, they have been used to characterize the asymptotic speed of propagation of fronts of the one-dimensional reaction–diffusion equation [8, 9]. They have also been used in deriving a variational principle for the bifurcation branches of the nonlinear one-dimensional eigenvalue problem $-u'' + N(u) = \lambda u$, with two point boundary conditions (here N is a rather general nonlinear term) [10].

The rest of the paper is organized as follows. In section 2, we prove theorem 1, and we indicate how to proceed with the proof of theorem 2. In section 3, we study the behaviour of the chemical potential for a weakly ionized atom. Finally in section 4 we give more applications of our variational characterization of $\epsilon_F(N, Z)$ for subneutral atoms.

2. Variational characterization for $\epsilon_F(N, Z)$

In this section we derive the variational characterization for ϵ_F. We will only give the details for the atomic case. For molecules the derivation is analogous and we will just make a few remarks and state the result in that case. Our starting point is the TF equation for the electronic density ρ

$$\rho^{2/3} = \max(\phi - \phi_0, 0) \tag{2.1}$$

where

$$\phi(x) = \frac{Z}{|x|} - \int \frac{\rho(y)}{|x-y|}\, \mathrm{d}^3 y \tag{2.2}$$

is the electrostatic potential and $-\phi_0 = \epsilon_F(N, Z)$ is the chemical potential.

Proof of theorem 1. Consider now any non-negative, radially symmetric function $g(x)$, bounded, with piecewise continuous second derivatives and with non-negative Laplacian (i.e. with $\Delta g \geqslant 0$, in other words a subharmonic function). Multiplying equation (2.1) by Δg we obtain

$$\rho^{2/3}\Delta g \geqslant \phi \Delta g - \phi_0 \Delta g. \tag{2.3}$$

We will integrate equation (2.3) in the region between two concentric balls (B_ε, of radius ε, and B_R of radius $R > \varepsilon$) centred at the nucleus. Eventually we will let ε go to zero and R go to infinity. Thus we have

$$\int_{B_R \setminus B_\varepsilon} \rho^{2/3}\Delta g \, \mathrm{d}^3 x \geqslant \int_{B_R \setminus B_\varepsilon} \phi \Delta g \, \mathrm{d}^3 x - \phi_0 \int_{B_R \setminus B_\varepsilon} \Delta g \, \mathrm{d}^3 x. \tag{2.4}$$

Integrating the first term on the right-hand side of (2.4) by parts, using Green's formula, we can write

$$\int_{B_R \setminus B_\varepsilon} (\phi \Delta g)\, \mathrm{d}^3 x = \int_{B_R \setminus B_\varepsilon} (g \Delta \phi)\, \mathrm{d}^3 x + I_R - I_\varepsilon \tag{2.5}$$

where

$$I_R = \int_{\partial B_R} (\phi \nabla g - g \nabla \phi) \cdot \mathrm{d}\boldsymbol{S} \tag{2.6}$$

and

$$I_\varepsilon = \int_{\partial B_\varepsilon} (\phi \nabla g - g \nabla \phi) \cdot \mathrm{d}\boldsymbol{S}. \tag{2.7}$$

The integrals I_R and I_ε are performed over the surfaces of the spheres of radius R and ε, respectively. In both cases the normal is pointing outwards (in the radial direction $\hat{r}$). Since $\varepsilon > 0$, it follows from (2.2) that the first integral on the right-hand side of (2.5) may be written as

$$\int_{B_R \setminus B_\varepsilon} (g\Delta\phi)\, \mathrm{d}^3x = 4\pi \int_{B_R \setminus B_\varepsilon} (g\rho)\, \mathrm{d}^3x. \tag{2.8}$$

By Gauss' theorem, the leading behaviour of the electric field $-\nabla\phi$, at a distance R from the nucleus, as R goes to infinity is given by

$$-\nabla\phi \approx \frac{1}{R^2}(Z-N)\hat{r} \tag{2.9}$$

where $\hat{r}$ is the radial unit vector. Since the function g is radially symmetric, bounded and subharmonic it has a limit as $r = |x|$ goes to infinity. We will denote this limit by g_∞. Moreover, ∇g goes to zero at infinity as $1/|x|^2$ or faster. Thus, using (2.9) we get from (2.6) that

$$\lim_{R\to\infty} I_R = 4\pi g_\infty (Z-N) \tag{2.10}$$

(since $\mathrm{d}\boldsymbol{S} = \hat{r}R^2\,\mathrm{d}\Omega$ and $\int \mathrm{d}\Omega = 4\pi$). On the other hand, as ε goes to zero, it follows from Gauss' theorem again that at a distance ε from the nucleus

$$-\nabla\phi \approx \frac{1}{\varepsilon^2} Z\hat{r}. \tag{2.11}$$

Since the function g together with its first derivatives are continuous, denoting by g_0 the value of g at the nucleus, we get from equations (2.7) and (2.11) that

$$\lim_{\varepsilon\to 0} I_\varepsilon = 4\pi g_0 Z. \tag{2.12}$$

Taking the limits ε going to zero and R going to ∞ in (2.4), and using (2.5), (2.10), (2.12) and (2.8) we get

$$\phi_0 \int \Delta g\, \mathrm{d}^3x \geqslant \int (4\pi g\rho - \rho^{2/3}\Delta g)\, \mathrm{d}^3x + 4\pi g_\infty (Z-N) - 4\pi g_0 Z. \tag{2.13}$$

(Notice that now the integrals are performed over the whole space.) Since ρ, g and Δg are non-negative

$$4\pi g\rho - \rho^{2/3}\Delta g \geqslant -\frac{1}{108\pi^2}\frac{(\Delta g)^3}{g^2}. \tag{2.14}$$

To obtain the right-hand side of equation (2.14) we just minimize the left-hand side with respect to ρ. Equality is obtained in (2.14) for all x if and only if g satisfies the equation

$$\Delta g = 6\pi\rho^{1/3} g. \tag{2.15}$$

We will denote by $\hat{g}$ the positive solution to (2.15), which is unique up to a multiplicative constant. (A proof of the existence and uniqueness of $\hat{g}$ as well as other mathematical aspects related to the variational characterization of $\epsilon_\mathrm{F}(N, Z)$ is given elsewhere [11].)

From equations (2.13) and (2.14) we finally get the desired lower bound on ϕ_0, namely

$$\phi_0 \geqslant \left(\int \Delta g\, \mathrm{d}^3x\right)^{-1} \left(4\pi g_\infty (Z-N) - 4\pi g_0 Z - \frac{1}{108\pi^2}\int \frac{(\Delta g)^3}{g^2}\, \mathrm{d}^3x\right). \tag{2.16}$$

To conclude with the proof of the variational characterization of $\epsilon_\mathrm{F}(N, Z)$ (or, equivalently of ϕ_0), we need only show that equality is attained in (2.16) if $g = \hat{g}$. As we remarked above, equality is attained in (2.14) if $g = \hat{g}$. On the other hand, $\hat{g}$ is harmonic outside the support of ρ, since $\hat{g}$ is a solution of (2.15) (i.e. $\Delta\hat{g} = 0$ whenever ρ vanishes). Hence, if $g = \hat{g}$ equation (2.3) becomes an equality. Therefore, if $g = \hat{g}$, (2.16) becomes an equality and theorem 1 follows. □

The Thomas–Fermi model has simple scaling properties. In particular, the natural length scale is $Z^{-1/3}$ [5, 6]. These scaling properties imply that in the atomic case one can write

$$\epsilon_{\mathrm{F}}(N, Z) = Z^{4/3}\epsilon_{\mathrm{F}}(n) \tag{2.17}$$

with $\epsilon_{\mathrm{F}}(n) \equiv \epsilon_{\mathrm{F}}(N/Z, 1)$. This fact can be easily recovered from our variational principle, by introducing trial functions of the form $g(x) = h(Z^{1/3}x)$. If we introduce such a g in (2.16), and if we write $\epsilon_{\mathrm{F}}(N, Z) = Z^{4/3}\epsilon_{\mathrm{F}}(n)$, with $n = N/Z$, then the bound (2.16) becomes a bound on $\epsilon_{\mathrm{F}}(n)$, which reads as follows:

$$-\epsilon_{\mathrm{F}}(n) \geqslant \left(\int \Delta h \, \mathrm{d}^3x\right)^{-1}\left(4\pi h_\infty(1-n) - 4\pi h_0 - \frac{1}{108\pi^2}\int \frac{(\Delta h)^3}{h^2}\,\mathrm{d}^3x\right). \tag{2.18}$$

This is the form that we will use in sections 3 and 4. Of course this bound is saturated for an appropriate h satisfying an equation analogous to (2.15).

With respect to the proof of theorem 2, which we omit here (see [11] for details), the idea is the same as in the proof of theorem 1, except that now we have to cut k small balls, one around each nucleus, and we have to consider a ball of radius R that encircles all the nuclei. Eventually the radii of the small balls go to zero, and now one picks one boundary term from each nuclei of the form $g_j z_j$, where g_j is the value of g at the nucleus j. On the other hand, as R goes to infinity (while keeping all the nuclear charges inside) one picks a boundary term proportional to $g_\infty(Z - N)$. However, now g_∞ is the limit of the spherical average of g over the ball of radius R as R goes to infinity, since g does not need to be spherically symmetric.

Before closing this section we would like to remark on the meaning of the function g that saturates the variational bound (i.e. the function $\hat{g}$). It turns out that $\hat{g}$ is (up to a multiplicative constant) the derivative of $\phi - \phi_0$ with respect to the number of electrons N. This can be seen formally by taking the derivative of the TF equation ($\Delta\phi = 4\pi \max(\phi - \phi_0, 0)^{3/2}$) with respect to N and checking that the derivative of $\phi - \phi_0$ with respect to N satisfies precisely equation (2.15). A rigorous proof of this fact is presented in [11].

3. Chemical potential for a weakly ionized atom in the Thomas–Fermi model

The behaviour of the chemical potential $\epsilon_{\mathrm{F}}(N, Z)$ for a weakly ionized atom in the TF model (i.e. as N approaches Z from below) has been considered by several authors in the past 20 years. Lieb and Simon ([4], theorem IV.11, p 81) found upper and lower bounds for $\epsilon_{\mathrm{F}}(n)$ for both the atomic and the molecular case. In the units we are using in this paper, they proved that

$$-0.6496\ldots = -\left(\frac{\pi^2}{36}\right)^{1/3} \leqslant \limsup_{n\to 1} \epsilon_{\mathrm{F}}(n)(1-n)^{-4/3} \leqslant -\frac{3}{4}\left(\frac{\pi^2}{36}\right)^{1/3} = -0.4872\ldots \tag{3.1}$$

and conjectured that $\lim_{n\to 1} \epsilon_{\mathrm{F}}(n)(1-n)^{-4/3}$ exists ([4], problem 5, p 33). This conjecture was proved by Bénilan and Brézis [12, 13]. Although Bénilan and Brézis did not compute the numerical value of this limit explicitly, they characterized it as the value at 1 of the solution of some nonlinear explicit ordinary differential equation on [0, 1] taking the value 0 at 0. We have solved the ordinary differential equation of Bénilan and Brézis numerically (using Maple) finding the value $-0.5282\ldots$ for this limit. Dmitrieva and Plindov using asymptotic expansions ([14, 15]) showed that in the neighbourhood of $n = 1$

$$\epsilon_{\mathrm{F}}(n) \approx -0.1103(1-n)^{4/3}[1 + 0.9102(1-n)^{\sigma/3} + \cdots]\frac{e^2}{a_0} \tag{3.2}$$

where $\sigma = (\sqrt{73} - 7)/2 \approx 0.7720$ and a_0 is the Bohr radius. In the units we are using here, $a_0 \approx 0.208\,97$, and the numerical constant of Dmitrieva and Plindov becomes $0.1103e^2/a_0 = 0.5278$, in excellent agreement with the exact value of Bénilan and Brézis.

Again, using asymptotic expansions (but keeping only the first-order correction in the screening function of a neutral atom) March [16] showed that

$$\epsilon_F(n) \approx -\frac{2}{3}\frac{1}{(3\pi^2(7+\sigma))^{1/3}}(1-n)^{4/3}\frac{e^2}{a_0} \approx -0.5206(1-n)^{4/3} \tag{3.3}$$

in the units used here. The numerical constant in (3.3) is slightly lower (by about 1.3%) than the value obtained by Dmitrieva and Plindov.

Here we will use the variational characterization of $\epsilon_F(n)$, derived in section 2, to get an upper bound on $\epsilon_F(n)$ suited in the neighbourhood of $n = 1$ (i.e. for the weakly ionized atom).

In order to obtain a good estimate for $\epsilon_F(n)$ in the vicinity of $n = 1$ we will use the following

$$h(r) = \begin{cases} r^\alpha & \text{if } r < R \\ h_\infty - \alpha R^{\alpha+1}/r & \text{if } r \geqslant R \end{cases} \tag{3.4}$$

as a trial function in the variational principle given by (2.18). Here $\alpha > 3$ and R are free parameters and $h_\infty = (1+\alpha)R^\alpha$. It is easy to check that $h \in \mathcal{D}$. The justification of this choice of trial function, together with the approximate meaning of α and R will be given at the end of this section. An explicit computation, using (3.4) yields

$$\int \Delta h \, \mathrm{d}^3x = 4\pi\alpha R^{\alpha+1} \tag{3.5}$$

and

$$\int \frac{(\Delta h)^3}{h^2}\, \mathrm{d}^3x = 4\pi(\alpha(\alpha+1))^3(\alpha-3)^{-1}R^{\alpha-3}. \tag{3.6}$$

Hence, using (3.5) and (3.6) together with the values $h(0) = 0$ and $h_\infty = (1+\alpha)R^\alpha$ in the variational principle (2.18) we get

$$-\epsilon_F(n) \geqslant \frac{1+\alpha}{\alpha}(1-n)R^{-1} - \frac{1}{108\pi^2}\frac{\alpha^2(\alpha+1)^3}{\alpha-3}R^{-4}. \tag{3.7}$$

Maximizing the right-hand side of (3.7) with respect to R we get

$$-\epsilon_F(n) \geqslant \frac{3}{4}(27\pi^2)^{1/3}\left[\frac{(\alpha-3)(\alpha+1)}{\alpha^6}\right]^{1/3}(1-n)^{4/3}. \tag{3.8}$$

The maximizing R, $\hat{R}$ say, is given by

$$\hat{R} = \left[\frac{\alpha^3(1+\alpha)^2}{27\pi^2(\alpha-3)}\right]^{1/3}(1-n)^{-1/3}. \tag{3.9}$$

Finally, in order to get the best possible lower bound on $-\epsilon_F(n)$ we maximize the right-hand side of (3.8) with respect to α. The maximizing α, $\hat{\alpha}$ say, is given by

$$\hat{\alpha} = \frac{\sqrt{97}+5}{4} \approx 3.7122\ldots. \tag{3.10}$$

Replacing this value of α in (3.8) we get

$$-\epsilon_F(n) \geqslant 9\pi^{2/3}\frac{(17+\sqrt{97})^{1/3}}{61+5\sqrt{97}}(1-n)^{4/3} \approx 0.5243\ldots(1-n)^{4/3}. \tag{3.11}$$

The numerical constant on the right-hand side of (3.11) is within 0.6% difference from the values of March (equation (3.3)) and Dmitrieva and Plindov (equation (3.2)). However, the fact that the right-hand side of (3.11) is a lower bound to $-\epsilon_F(n)$ rules out the value of March.

Before closing this section we would like to justify our choice of the trial function h given by (3.4). If the exponent α were exactly the positive root of $\alpha(\alpha+1)=18$ (i.e. $\alpha = 3+\sigma = 3.772\,0018\ldots$) our h would be the exact solution to equation (2.15) with ρ given by the Sommerfeld formula [17] (i.e. $\rho(x) = 27\pi^{-3}/|x|^6$) which represents the correct asymptotic behaviour of the TF density for the neutral atom. As it is natural to expect, the optimal choice of α, given by (3.10) is very close to $3+\sigma = 3.7720\ldots$. On the other hand, the optimal choice of R given by (3.9) has precisely the right dependence in n as the radius of the atom (i.e. the radius of the support of ρ) in the TF model [4].

4. Estimates on the chemical potential for $N \leqslant Z$

In this section we consider the behaviour of $\epsilon_F(n)$ as a function of $n = N/Z$ for $0 \leqslant n \leqslant 1$. As in the case of the weakly ionized atom, there are several results in the literature concerning $\epsilon_F(n)$ for $0 \leqslant n \leqslant 1$. Lieb and Simon showed that $\epsilon_F(n) \approx -(\pi^2/4)^{2/3}n^{-2/3} \approx 1.8259\ldots n^{-2/3}$ as n goes to 0 and determined upper and lower bounds on $\epsilon_F(n)$ (see [4], theorem II. 31). Kobayashi [18] and Tal and Levy [19] computed the function $\epsilon_F(n)$ numerically for $0 \leqslant n \leqslant 1$ and Dmitrieva and Plindov obtained two analytic approximations (see [15], equations (9) and (11)) which are in good agreement with the numerical values obtained in [18, 19].

In what follows we will exemplify the use of the variational principle given by (2.18) together with simple trial functions to estimate $\epsilon_F(n)$ in the interval $(0, 1)$.

Consider the trial function

$$h(r) = \begin{cases} 1 + Br^{3/2} - Cr^{\alpha} & \text{if } r \leqslant R \\ (D/r) + h_{\infty} & \text{if } r \geqslant R \end{cases} \tag{4.1}$$

with $h_0 = h(0) = 1$. Requiring continuity of $h(r)$, $h'(r)$ and $\Delta h(r)$ at $r = R$ implies

$$C = \frac{15}{4\alpha(\alpha+1)} BR^{(3/2)-\alpha} \tag{4.2}$$

$$D = -\frac{3(2\alpha-3)}{4(\alpha+1)} BR^{5/2} \tag{4.3}$$

and

$$h_{\infty} = 1 + \frac{5(2\alpha-3)}{4\alpha} BR^{3/2}. \tag{4.4}$$

Here, $\alpha > 3/2$, $R > 0$ and $B \geqslant 0$ are variational parameters. It then follows from (4.1), (4.2) and (4.3) that

$$\int \Delta h \, \mathrm{d}^3x = 4\pi R^2 h'(R) = -4\pi D \tag{4.5}$$

and

$$J(B, R) \equiv \frac{1}{4\pi} \int \frac{(\Delta h)^3}{h^2} \, \mathrm{d}^3x = \left(\frac{15}{4}\right)^3 B^3 R^{3/2} \times \int_0^1 \frac{y^{1/2}(1 - y^{\alpha-(3/2)})^3 \, \mathrm{d}y}{(1 + BR^{3/2}(y^{3/2} - 15y^{\alpha}/(4\alpha(\alpha+1))))^2}. \tag{4.6}$$

Finally, using (4.4), (4.5), and (4.6) in (2.18), we obtain

$$-\epsilon_{\mathrm{F}}(n) \geqslant a(\alpha)\left(-B^{-1}R^{-5/2}n + b(\alpha)R^{-1}(1-n) - \frac{B^{-1}}{108\pi^2 R^{5/2}}J(B,R)\right) \tag{4.7}$$

with

$$a(\alpha) \equiv \frac{4(\alpha+1)}{3(2\alpha-3)} \tag{4.8}$$

and

$$b(\alpha) \equiv \frac{5(2\alpha-3)}{4\alpha}. \tag{4.9}$$

There are two ways in which we will use (4.7) in the following. First, for a fixed value of n, in the interval $(0, 1)$, we maximize numerically the right-hand side of (4.7) as a function of the parameters B, R and α to obtain a good lower bound on $-\epsilon_{\mathrm{F}}$. In order to compare with [19] and [15] we choose the value $n = 0.550\,28$. Using Maple, we find that the right-hand side of (4.7) is maximized approximately at $\alpha = 7.5$, $R = 0.655$ and $B = 4.4686$. At these values of the parameters the right-hand side of (4.7) is given approximately by $0.721\,66\ldots$ (in the units used here). The value of $-\epsilon_{\mathrm{F}}(n)$, for $n = 0.550\,28$, given by Dmitrieva and Plindov [15] is $0.150\,95/a_0 \approx 0.722\,35$ (recall that the value of the Bohr radius in our units is $0.208\,969\ldots$), while the numerical value obtained by Tal and Levy at this particular value of n is $0.151\,04/a_0 = 0.722\,78$. Our lower bound on $-\epsilon_{\mathrm{F}}(n)$ is therefore less than 0.16%, apart from the value of [15] and [19].

The second use we will make of equation (4.7) is to obtain a lower bound on $-\epsilon_{\mathrm{F}}(n)$ just in terms of n. One can estimate J from above by approximating by one the denominator appearing inside the integral in the definition of J (i.e. in (4.6)). This is in fact a crude estimate except for very low values of n. Dropping in this way the denominator, allows us to compute the integral. Thus we obtain

$$\frac{J}{108\pi^2} \leqslant B^3 R^{3/2} d(\alpha) \tag{4.10}$$

with

$$d(\alpha) \equiv \frac{1}{\pi^2}\frac{5^3(2\alpha-3)^3}{4^4 3\alpha(\alpha-1)(4\alpha-3)}. \tag{4.11}$$

Hence from (4.7) and (4.10) we get

$$-\epsilon_{\mathrm{F}}(n) \geqslant a(\alpha)\frac{1}{BR^{5/2}}(-n + BR^{3/2}b(\alpha)(1-n) - B^3R^{3/2}d(\alpha)). \tag{4.12}$$

For fixed n and α the right-hand side of (4.12) can be easily maximized with respect to B and R. The maximum occurs at

$$B = \left(\frac{b(\alpha)(1-n)}{6d(\alpha)}\right)^{1/2} \tag{4.13}$$

and

$$R = \frac{3(2n^2 d(\alpha))^{1/3}}{b(\alpha)(1-n)}. \tag{4.14}$$

Replacing these values of B and R in (4.12) gives the bound

$$-\epsilon_{\mathrm{F}}(n) \geqslant \frac{1}{6}\frac{a(\alpha)b(\alpha)^2}{(2d(\alpha))^{1/3}}(1-n)^2 n^{-2/3}. \tag{4.15}$$

The prefactor $a(\alpha)b(\alpha)^2/(2d(\alpha))^{1/3}$ can be easily maximized with respect to the parameter α. Using (4.8), (4.9) and (4.11) we observe that the maximum of this prefactor as a function of α occurs at $\alpha = (11 + \sqrt{46})/5 \approx 3.5564\ldots$ and it is given by $1.8227\ldots$, so we finally obtain

$$-\epsilon_{\mathrm{F}}(n) \geqslant 1.8227\ldots n^{-2/3}(1-n)^2 \tag{4.16}$$

for all $0 \leqslant n \leqslant 1$. As we have seen in the previous section, the right-hand side of (4.16) does not reproduce the correct behaviour of $\epsilon_{\mathrm{F}}(n)$ near $n = 1$ (i.e. at the weakly ionized limit). This is due to the coarse approximation we did when dropping the denominator in the integral defining J. On the other hand, for small n, the dependence of the lower bound in n is correct and the numerical prefactor we get is quite close to the exact value $(\pi^2/4)^{2/3} \approx 1.8259\ldots$ proven by Lieb and Simon [4].

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