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The most negative ion in the Thomas–Fermi–von Weizsäcker theory of atoms and molecules

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Abstract. Let N_c denote the maximum number of electrons that can be bound to an atom of nuclear charge z, in the Thomas-Fermi-von Weizsäcker theory. It is proved that N_c cannot exceed z by more than one, and thus this theory is in agreement with experimental facts about real atoms. A similar result is proved for molecules, i.e. N_c cannot exceed the total nuclear charge by more than the number of atoms in the molecule.

1. Introduction

The Thomas-Fermi-von Weizsäcker (TFW) theory (von Weizsäcker 1935, Benguria *et al* 1981, Lieb 1981) is defined by the energy functional (see Lieb 1981, § VII) (in units in which $\hbar^2(2m)^{-1} = |e| = 1$, where e and m are the electron charge and mass)

$$\xi(\rho) = A \int (\nabla \rho^{1/2}(x))^2 \, dx + \tfrac{3}{5}\gamma \int \rho(x)^{5/3} \, dx - \int V(x)\rho(x) \, dx + D(\rho, \rho) \tag{1}$$

where

$$D(\rho, \rho) = \tfrac{1}{2} \int \rho(x)|x-y|^{-1}\rho(y) \, dx \, dy \tag{2}$$

$$V(x) = \sum_{j=1}^{K} z_j |x - R_j|^{-1}. \tag{3}$$

Here $z_1, z_2, \ldots, z_K \geq 0$ are the charges of K fixed nuclei located at $R_1, \ldots, R_K$. The total nuclear charge is denoted by Z, $Z = \sum_{j=1}^{K} z_j$. $K = 1$ is the atomic case and here we shall simply write $Z = z_1 = z$. dx is always a three-dimensional integral. $\xi(\rho)$ is defined for electronic densities $\rho(x) \geq 0$ such that each of the terms of $\xi(\rho)$ in (1) is finite. In the physical situation, $\gamma = \gamma_{\text{phys}} = (3\pi^2)^{2/3}$ but, for generality, we shall allow γ to be an arbitrary positive constant in what follows. The TFW energy for N (not necessarily an integer) electrons is defined by

$$E(N) = \inf\left(\xi(\rho) \,\middle|\, \int \rho = N \right). \tag{4}$$

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On energetic grounds, the value of A should be chosen to reproduce the Scott term in the expression of the atomic or molecular energy $E(N)$ as a function of N and the nuclear charges, (see Lieb 1981, §§ V.B, VII.D). Numerically one finds (Lieb and Liberman 1982, Lieb 1982), $A = 0.1859$. However, we should retain A as an arbitrary positive constant. In the original TFW model (von Weizsäcker 1935) the numerical value of A is 1.

It is known (Benguria *et al* 1981, Lieb 1981) that there exists a critical value of N (depending on A, γ and the z_j and R_j), which we denote by N_c, such that for $N \leq N_c$ the minimisation problem (4) has a unique solution, whereas for $N > N_c$ there is no solution. In other words, N_c is the maximum number of 'electrons' that can be bound to the atom or molecule. The aim of this paper is to find an upper bound for N_c. The value of N_c is given by $\int \rho$, where $\rho \geq 0$ is the unique minimising function of $\xi(\rho)$ without constraints. Let $\psi = \rho^{1/2}$. Then ψ is the *unique* positive solution of the TFW equation (for a saturated system),

$$-A\,\Delta\psi(x) + (\gamma\psi(x)^{4/3} - \phi(x))\psi(x) = 0 \tag{5}$$

where

$$\phi(x) = V(x) - |x|^{-1} * \rho \qquad \text{with } \rho = \psi^2. \tag{6}$$

Note that (5) is the Euler equation corresponding to the functional $\xi(\psi^2)$. The only previous rigorous results (Lieb 1981, Benguria *et al* 1981) for N_c were that $Z < N_c < 2Z$.

Our main result is the following.

Theorem 1. For a TFW molecule of $K \geq 1$ atoms,

$$0 < N_c - Z \leq 270.74(A/\gamma)^{3/2}K \tag{7}$$

for all choices of $z_1, \ldots, z_K$ and $R_1, \ldots, R_K$. In particular, for the value of A chosen in Lieb (1981) and Lieb and Liberman (1982) to reproduce the Scott term in the energy (i.e. $A = 0.1859$) and for the physical $\gamma = (3\pi^2)^{2/3}$,

$$0 < N_c - Z < 0.7335K. \tag{8}$$

In the TFW model the number of electrons is not generally an integer, but in a real atom N and z are required to be integral. How can theorem 1 be interpreted in the light of this additional requirement? One way is the energetic point of view: since $E(N)$ is strictly decreasing for $N < N_c$ and constant for $N \geq N_c$ (Lieb 1981, § VII.A), theorem 1 implies that $E(z) > E(z+1) = E(z+2)$. Thus, the $(z+1)$th electron has a positive binding energy, while the $(z+2)$th does not, and we can say that a singly ionised atom (but not a doubly ionised atom) is stable. This interpretation, however, suffers from the drawback that there is no solution to (5) when $N = z+1$. A second interpretation that leads to the same conclusion about atomic ionisation, but eliminates the problem that (5) has no solution for $N = z+1$, was kindly provided by John Morgan: introduce the Fermi-Amaldi correction (i.e. replace $D(\rho, \rho)$ in (1) by $(1 - 1/N)D(\rho, \rho)$). This has the effect of replacing z by $z'(N) = Nz/(N-1)$. (It also effectively changes A and γ, but not A/γ.) Theorem 1 now states that a solution to (5) always exists if $N \leq z'(N)$ while it never exists if $N - 0.74 \geq z'(N)$. This implies that a solution exists (with N and z integral) if and only if $N \leq z+1$. However it is not clear that $E(z+1) < E(z)$ in this Fermi-Amaldi model.

The best previous upper bound on N_c is, as we said, $N_c < 2Z$ (Lieb 1981, theorem 7.23), a result which is valid for both atoms and molecules. It turns out that such a bound also holds for the Hartree (bosonic) atom. More recently one of us (Lieb 1984a, Lieb *et al* 1984) has proved a similar bound for the real Schrödinger equation namely, $N_c < 2z+1$ for an atom and $N_c < 2Z+K$ for a molecule of K atoms. This result (Lieb 1984a, Lieb *et al* 1984) is valid regardless of the statistics of the bound particles. However, if the bound particles are fermions, as is the case for real matter, N_c should presumably not exceed z (for an atom) by more than one or two electrons. This is still a conjecture; however, it has been proved that $N_c/z \to 1$ as $z\to\infty$ for fermions (Lieb *et al* 1984). On the other hand, we know that $N_c - z > 0.2z$ for the Schrödinger equation of an atom with bosonic particles and for large z (Benguria and Lieb 1983, Baumgartner 1983, 1984). See (Lieb 1984b) for a review of the recent literature on the subject.

In the Thomas-Fermi theory, defined by the energy functional (1) with $A=0$, N_c is exactly Z even in the molecular case (Lieb 1981, theorem 3.18, Lieb and Simon 1977). Equation (7) implies that for the TFW atom or molecule $N_c \to Z$ as $A \to 0$. However, we do not expect $N_c(A)$ to be analytic around $A=0$ because the von Weizsäcker correction is a singular perturbation to Thomas-Fermi theory. It is an *open problem* to derive an asymptotic expansion for $N_c(A)$ around $A=0$.

Two other open problems arise from the results of this paper. The first is that while we prove an upper bound for $N_c - Z$, we have no *lower* bound. We conjecture that $N_c - Z \to \text{constant} > 0$ as $Z\to\infty$. The second problem is related to the first: it is highly plausible that $N_c - Z$ is a monotonically increasing function of all the z_j (for fixed $R_1, \ldots, R_K$). Is this true?

This article is organised as follows: in § 2 we give the proof of theorem 1; in § 3 we determine the behaviour of N_c as Z goes to zero. Finally in § 4 we give a bound for the chemical potential of a neutral molecule. Such a bound is independent of the charge of the nuclei.

We should like to emphasise that many of the results herein can be extended in two ways: (i) to spherically symmetric 'smeared out' nuclei; (ii) to the TFW theory in which the exponent $\frac{5}{3}$ in (1) is replaced by some $p \neq \frac{5}{3}$ (cf Lieb 1981). For simplicity and clarity we confine ourselves here to point nuclei and $p=\frac{5}{3}$.

2. Proof of theorem 1

The proof of theorem 1 will be divided into three steps. First, we estimate the excess charge $Q \equiv N_c - Z$ in terms of the electronic density ρ and the TFW potential ϕ evaluated at an arbitrary, but fixed, distance r from all the nuclei. Then we find a local bound for ρ in terms of ϕ. These two estimates do not involve the z_j explicitly. Therefore, if we can prove that at some distance of order one, (i.e. independent of the z_j) the potential ϕ is bounded by a constant independent of the z_j, then the two previous results will imply that Q is less than a constant independent of the z_j, which is basically what theorem 1 says. Proving this last fact about ϕ is our third step. We begin with

Lemma 2. Let $\psi \geq 0$, ϕ be the unique solution pair for the TFW equation (5), (6) with V being the potential (3) for a molecule. Then, the function

$$p(x) = (4\pi A\psi(x)^2 + \phi(x)^2)^{1/2} \tag{9}$$

is subharmonic away from the nuclei, i.e. on $\mathscr{R}^3 \backslash \bigcup_{j=1}^{K} R_j$.

Proof. By direct computation

$$\Delta p = p^{-1}(4\pi A\psi\, \Delta\psi + \phi\, \Delta\phi) + h \tag{10}$$

with

$$h = 4\pi A p^{-3}|\phi\nabla\psi - \psi\nabla\phi|^2 \geqslant 0.$$

By (5), (6) the sum of the first two terms in (10) is (away from the nuclei so that $\Delta V = 0$): $4\pi\gamma\psi^{10/3} \geqslant 0$. Thus, $\Delta p \geqslant 0$, so p is subharmonic. □

Remark. Let

$$W(x) \equiv \gamma\psi(x)^{4/3} - \phi(x) \tag{11}$$

be the 'potential' in the TFW equation (5). Proceeding as in the proof of lemma 2, one can show that

$$(4\pi A\psi(x)^2 + W(x)^2)^{1/2} \tag{12}$$

is subharmonic whenever $W(x) \geqslant 0$.

The next lemma gives a local bound for ψ in terms of ϕ. This bound is independent of the nuclear charges z_j.

Lemma 3. For all $\lambda \in (0, 1)$ and all $x \in \mathscr{R}^3$

$$\gamma\lambda\psi(x)^{4/3} \leqslant \phi(x) + c(\lambda)A^2\gamma^{-3} \tag{13}$$

with

$$c(\lambda) \equiv (9/4)\pi^2\lambda^{-2}(1-\lambda)^{-1}. \tag{14}$$

Proof. Define $u(x) \equiv \psi(x)^{4/3}$. Then, from the TFW equation (5),

$$-\Delta u + (4/3A)(\gamma u - \phi)u + |\nabla u|^2/4u = 0$$

and hence

$$-\Delta u + (4/3A)(\gamma u - \phi)u \leqslant 0. \tag{15}$$

Also, from (6)

$$-\Delta\phi = -4\pi\psi^2 = -4\pi u^{3/2} \qquad x \neq R_j, \text{ all } j. \tag{16}$$

Let $v(x) = \gamma\lambda u(x) - \phi(x) - d$, with d a positive constant. We shall show that $v(x) \leqslant 0$, all x, for appropriate d and λ. From equations (15) and (16),

$$-\Delta v \leqslant -(4\gamma\lambda/3A)(\gamma u - \phi)u + 4\pi u^{3/2}.$$

Let $S = \{x|v(x) > 0\}$. ψ is continuous and goes to zero at infinity; ϕ is continuous away from the R_j and it also goes to zero at infinity (Benguria *et al* 1981, § III). Therefore v is continuous away from all the R_j and goes to $-d$ at infinity. Hence S is open and bounded. Moreover, $R_j \notin S$, all j since $\phi = +\infty$ at the R_j. On S, $\phi < \gamma\lambda u - d$ so

$$\begin{aligned}-\Delta v &\leqslant -(4\gamma\lambda/3A)(\gamma u + d - \gamma\lambda u)u + 4\pi u^{3/2}\\ &\leqslant u[4\pi u^{1/2} - (4/3A)\gamma^2\lambda(1-\lambda)u - (4/3A)\gamma\lambda d]\\ &\leqslant 0\end{aligned}$$

provided we choose $\lambda \in (0, 1)$ and $d = \frac{9}{4}(\pi A/\lambda)^2\gamma^{-3}(1-\lambda)^{-1}$ in order that the quantity in brackets [ ] be non-negative for all possible (unknown) values of $u(x)$. With that choice of λ and d, v is subharmonic on S. On ∂S $v = 0$, and therefore S is empty. □

Corollary. For all $x \in \mathscr{R}^3$

$$\phi(x) \geq -3^5 2^{-4}\pi^2 A^2\gamma^{-3} \geq -150A^2\gamma^{-3}. \tag{17}$$

If x is such that $\phi(x) \leq 0$, then $p(x) = (4\pi A\psi(x)^2 + \phi(x)^2)^{1/2}$ satisfies

$$p(x) \leq (\tfrac{4}{3})^{3/4} 16\pi^2 A^2\gamma^{-3} \leq 196A^2\gamma^{-3}. \tag{18}$$

Proof. By (13) and the fact that $\psi(x)^{4/3} \geq 0$, $\phi(x) \geq -c(\lambda)A^2\gamma^{-3}$ for all $\lambda \in (0, 1)$. Minimising $c(\lambda)$ (at $\lambda = \frac{2}{3}$) gives (17). To prove (18), take $\lambda = \frac{3}{4}$ (which minimises $c(\lambda)/\lambda$), let $a = -\frac{4}{3}cA^2\gamma^{-3}$ and observe from (13) that

$$p(x)^2 \leq \max_{a \leq \phi \leq 0} [4\pi A(3\gamma/4)^{-3/2}(\phi - a)^{3/2} + \phi^2]. \tag{19}$$

The right-hand side of (19) is convex in ϕ, so its maximum occurs either at $\phi = 0$ or $\phi = a$. $\phi = 0$ prevails and gives (18). □

In our next lemma, starting from ρ and ϕ, we introduce a smeared density $\tilde{\rho}$ and potential $\tilde{\phi}$. We find that $\tilde{\rho}$ and $\tilde{\phi}$ satisfy an inequality resembling the Thomas-Fermi equation for smeared nuclei. Then we use a comparison theorem to get an upper bound for the smeared potential $\tilde{\phi}$ in terms of a universal function (independent of the z_j). Finally, noting that ϕ is subharmonic away from the nuclei, we see that essentially the same bound applies to ϕ. In particular, this lemma says that at distances of order one from all the nuclei, in atomic units, ϕ is of order one and, in any case, independent of the z_j. We note, however, that this bound is not satisfactory both very close and very far from the nuclei. Near the nuclei it diverges too fast. On the other hand, the bound is always positive, whereas ϕ is negative at large distances because $Q = N_c - Z$ is strictly positive.

Lemma 4. Let $\psi \geq 0$, ϕ be the solution of the TFW equation (5), (6) with V given by (3). Choose any $R > 0$ and define

$$\delta \equiv 25\pi^{-2}\gamma^3 = 2.53\gamma^3 \tag{20}$$

which is independent of the z_j. Suppose $x \in \mathscr{R}^3$ is such that $|x - R_j| > R$ for all $j = 1, 2, \ldots, K$. Then

$$\phi(x) \leq A\pi^2 R^{-2} + \delta \sum_{j=1}^{K} (|x - R_j| - R)^{-4}. \tag{21}$$

Proof. Let $W = \gamma\rho^{2/3} - \phi$, $\rho \equiv \psi^2$ and consider the Hamiltonian $H = -A\Delta + W$. H is a non-negative operator, since its ground state, the TFW function ψ, has zero energy (chemical potential). Therefore for any function $b \in L^2$ with $\nabla b \in L^2$ we have

$$A\int |\nabla b(x)|^2\,dx + \int W(x)b(x)^2\,dx \geq 0. \tag{22}$$

We shall choose $b(x)$ to be a translate of the normalised ground state, $e(x)$, of the Laplacian on a ball of radius R with Dirichlet boundary condition. That is, let

$e(x)=(2\pi R)^{-1/2}\sin(\pi|x|R^{-1})/|x|$, for $|x|\leq R$ and $e(x)=0$ otherwise. Clearly, $e(x)$ is spherically symmetric, decreasing and it has compact support. Let $b_x(y)=e(y-x)$ denote the translate of e and define $g(x)=e(x)^2$ and $g_x(y)=g(y-x)$. Let $B=A\int|\nabla b_x(y)|^2\,dy$. Clearly B does not depend on x. With this choice of b, $B=(\pi/R)^2A$. From equation (22) we have,

$$\int W(y)g_x(y)\,dy\geq -B \qquad \text{all } x. \tag{23}$$

Note that $\int W(y)g_x(y)\,dy=(g*W)(x)$, where an asterisk denotes convolution. Define

$$\tilde{\phi}\equiv\phi*g-B. \tag{24}$$

Since $\phi\in L^{3+\varepsilon}+L^{3-\varepsilon}$, $\varepsilon>0$, (Benguria *et al* 1981, proof of lemma 7) and $g\in L^p$, all $p\geq 1$, $\tilde{\phi}$ is continuous and goes to $-B$ at infinity (Lieb 1981, lemma 3.1). Using Hölder's inequality, we have for all x

$$(g*\rho^{2/3})(x)\leq[(g*\rho)(x)]^{2/3}\left(\int g(y)\,dy\right)^{1/3}=[(g*\rho)(x)]^{2/3} \tag{25}$$

where we have used $\int g(y)\,dy=1$. Let us also define

$$\tilde{\rho}\equiv g*\rho. \tag{26}$$

From equations (23)-(26) we obtain for all x

$$B\geq(\phi*g)(x)-\gamma(\rho^{2/3}*g)(x)\geq\tilde{\phi}(x)+B-\gamma\tilde{\rho}(x)^{2/3}.$$

In other words

$$\tilde{\phi}\leq\gamma\tilde{\rho}^{2/3}. \tag{27}$$

Notice that ϕ is subharmonic away from the nuclei and that $\tilde{\phi}=g*\phi-B$ with g being spherically symmetric, positive, of total mass one and having support in a ball of radius R. From this it follows easily that

$$\phi(x)\leq\tilde{\phi}(x)+B \tag{28}$$

for all x such that $|x-R_j|>R$ (for all j). Thus, to prove (21) we need a bound on $\tilde{\phi}$.

From equations (6) and (24), using the bound (27) and the fact that the Laplacian commutes with convolution, we compute

$$-(4\pi)^{-1}\Delta\tilde{\phi}(x)=\tilde{V}(x)-\tilde{\rho}(x)\leq\tilde{V}(x)-\gamma^{-3/2}[\tilde{\phi}_+(x)]^{3/2} \tag{29}$$

with

$$\tilde{V}(x)=\sum_{j=1}^{K}z_jg(x-R_j) \tag{30}$$

and with $\tilde{\phi}_+(x)=\max(\tilde{\phi}(x),0)$.

Note that equation (29) resembles a Thomas–Fermi (TF) equation with smeared nuclei of spherical charge density $z_jg(x-R_j)$. Indeed, let $\hat{\phi}$ be the TF potential for this system (i.e. with equality in (29)):

$$-(4\pi)^{-1}\,\Delta\hat{\phi}(x)=\tilde{V}(x)-\gamma^{-3/2}\hat{\phi}(x)^{3/2}. \tag{31}$$

It is known from general TF theory that (31) has a unique solution, $\hat{\phi}$, that goes to zero at infinity.

It is easy to see that

$$\tilde{\phi}(x) \leqslant \hat{\phi}(x) \qquad \text{for all } x \tag{32}$$

by observing that if the set $M = \{x | \hat{\phi}(x) - \tilde{\phi}(x) < 0\}$, then $\hat{\phi} - \tilde{\phi}$ is superharmonic on M and zero on the boundary of M and infinity, so M is empty.

The next step is to bound $\hat{\phi}$. First consider an atom with $V = z/r$, $r = |x|$, and consider the function $f(r) = \delta(r-R)^{-4}$ which satisfies

$$(4\pi)^{-1} \Delta f \leqslant \gamma^{-3/2} f^{3/2} \qquad \text{for } r > R. \tag{33}$$

Outside the ball of radius R (centred at the origin) $\hat{\phi}$ satisfies

$$(4\pi)^{-1} \Delta \hat{\phi} = \gamma^{-3/2} \hat{\phi}^{3/2}. \tag{34}$$

Again, by a comparison argument (and using the fact that $f(r) - \hat{\phi}(r) = \infty$ when $r = R$)

$$\hat{\phi}(r) \leqslant f(r) \qquad \text{for } r > R. \tag{35}$$

This, together with (28), proves (21) in the atomic case.

For the molecular case, let $\hat{\phi}_j(x)$ be the solution to (31) for an atom of (smeared) nuclear charge z_j located at R_j. By another comparison argument (Lieb and Simon 1977, theorem V.12 or Lieb 1981, corollary 3.6), $\hat{\phi}(x) \leqslant \Sigma_{j=1}^{K} \hat{\phi}_j(x)$. This, together with (35) and (28) proves (21). □

We conclude this section with

Proof of Theorem 1: atomic case. Let us start with the atomic case, $V(x) = z/|x|$, in order to expose the ideas most simply. The following facts have been established:

$$p(x) = (4\pi A \psi(x)^2 + \phi(x)^2)^{1/2} \tag{36}$$

is subharmonic for $|x| > 0$.

$$p(x) \leqslant (4/3)^{3/4} 16\pi^2 A^2 \gamma^{-3} \tag{37}$$

if $\phi(x) \leqslant 0$.

$$\phi(x) \leqslant \delta(|x| - R)^{-4} + \pi^2 A R^{-2} \tag{38}$$

for all $|x| > R > 0$, with $\delta = 25\gamma^3\pi^{-2}$ and with arbitrary $R > 0$.

$$\gamma\lambda\psi(x)^{4/3} \leqslant \phi(x) + c(\lambda) A^2 \gamma^{-3} \tag{39}$$

for all $|x|$, $0 < \lambda < 1$ with $c(\lambda) = 9\pi^2[4\lambda^2(1-\lambda)]^{-1}$.

The functions p, ϕ, ψ are functions only of $|x| = r$. As $r \to \infty$, $\psi(r) \to 0$ faster than any power of r (Lieb 1981, theorem 7.24) and $r\phi(r) \to -Q$. Thus,

$$rp(r) \to Q \qquad \text{as} \qquad r \to \infty. \tag{40}$$

The subharmonicity and the fact that $p(r) \to 0$ as $r \to \infty$ imply that $rp(r)$ is monotonically decreasing and convex. (This may be seen from the fact that $\Delta p \geqslant 0$ is equivalent, in polar coordinates, to $\mathrm{d}^2(rp(r))/\mathrm{d}r^2 \geqslant 0$.) Using (40) we conclude that

$$Q \leqslant rp(r) \qquad \text{for any } r > 0. \tag{41}$$

The same conclusion, (41), can be reached from another viewpoint, which will be important for the molecular case: fix $r > 0$ and consider the domain $D_r = \{x | |x| > r\}$. Let P be any *harmonic* function on D_r with $P(x) \to 0$ as $|x| \to \infty$ and $P(x) \geqslant p(x)$ on the boundary $|x|=r$. Then $P(x)\geqslant p(x)$ for all $x\in D_r$. (Proof: on the set $E=\{x|P(x)<p(x)\}\subset D_r$, $p-P$ is positive, subharmonic and $p-P$ vanishes on the boundary of E, so E is empty.) Now choose $P(x)=rp(r)/|x|$ for $|x|>r$. Then $rp(r)\geqslant|x|p(x)$, for $|x|>r$. However, $|x|p(x)\to Q$ as $|x|\to\infty$, and this establishes (41).

To complete the proof, we make the following specific choices for r, R, λ:

$$r=0.9086\,(\gamma^3/A)^{1/2}\qquad R=0.4020\,(\gamma^3/A)^{1/2}\qquad \lambda=0.7825. \tag{42}$$

If $\phi(r)$ happens to be positive, we use the bound (38), followed by (39) and insert these in (36). (41) then implies that if $\phi(r)>0$ then

$$Q\leqslant 270.74\,(A/\gamma)^{3/2}. \tag{43}$$

(The numbers in (42) were chosen to minimise the coefficient in (43).) On the other hand, if $\phi(r)\leqslant 0$ we can use (37) and (41) to conclude that

$$Q\leqslant 178.03\,(A/\gamma)^{3/2}. \tag{44}$$

Clearly, (43) is the worst case, and this gives theorem 1. Note, however, that if it were to be shown that $\phi(r)\leqslant 0$, then the bound (44) would be valid, and, using the physical values of A and γ, one would obtain $Q\leqslant 0.49$.

Molecular case. Equation (36) is still valid, except that p is subharmonic only on the set $x\neq R_j$ (all $j=1,\ldots,K$). Equations (37) and (39) are also valid. Equation (38) must be replaced by (21) on the set

$$D_R=\{x\,|\,|x-R_j|>R \text{ for all } j=1,\ldots,K\}. \tag{45}$$

Now choose r, R and λ as in (42) and consider the smaller domain

$$D_r=\{x\,|\,|x-R_j|>r \text{ for all } j=1,\ldots,K\}. \tag{46}$$

Consider the following function which is harmonic on D_r:

$$P(x)=Q_1\sum_{j=1}^{K}|x-R_j|^{-1} \tag{47}$$

where Q_1 is the right-hand side of (43), namely the value of the upper bound for $rp(r)$ computed in the atomic case under the assumption $\phi(r)\geqslant 0$. As explained above, if we can show that $P(x)\geqslant p(x)$ for all x on the boundary of D_r, then $P(x)\geqslant p(x)$ for all $x\in D_r$. Taking the limit $|x|\to\infty$ yields

$$Q=\lim_{|x|\to\infty}|x|p(x)\leqslant\lim_{|x|\to\infty}|x|P(x)=KQ_1 \tag{48}$$

which is the desired result.

Let x be on the boundary of D_r, so that $|x-R_j|=r$ for some j (say $j=m$). If $\phi(x)\leqslant 0$, the bound (37) is valid and $p(x)\leqslant Q_2/r$, where $Q_2<Q_1$ is the right-hand side of (44). However, $P(x)\geqslant Q_1|x-R_m|^{-1}=Q_1/r$, so $P(x)>p(x)$. On the other hand, suppose $\phi(x)\geqslant 0$, in which case we can use (21) and (39). Now use proposition 5 below with the choices $t=\frac{3}{2}$, $s=2$ and

$$a_j=\delta(|x-R_j|-R)^{-4}\qquad b_j=a_j(4\pi A)^{2/3}/\gamma\lambda\qquad \text{for } j\neq m$$

$$a_m=\delta(|x-R_m|-R)^{-4}+A\pi^2R^{-2}$$

$$b_m=(a_m+c(\lambda)A^2\gamma^{-3})(4\pi A)^{2/3}/\gamma\lambda.$$

Recalling that $|x-R_m|=r$ we have

$$p(x)\leq p_1(r)+\sum_{j\neq m}\hat{p}(x-R_j) \tag{49}$$

where $p_1(r)$ is precisely the number we calculated before in the atomic case and

$$\hat{p}(x-R_j)=(b_j^{3/2}+a_j^2)^{1/2}. \tag{50}$$

By construction, $p_1(r)=Q_1/r$. Thus, $p(x)\leq P(x)$ if we can show that $\hat{p}(x-R_j)\leq Q_1/|x-R_j|$ for $j\neq m$. Let $|x-R_j|=u\geq r$. We require that

$$u^2[4\pi A(\gamma\lambda)^{-3/2}\delta^{3/2}(u-R)^{-6}+\delta^2(u-R)^{-8}]\leq Q_1^2. \tag{51}$$

However, the functions $u^2(u-R)^{-6}$ and $u^2(u-R)^{-8}$ are monotonically decreasing in u for $u>R$. Hence, the left-hand side of (51) is less than its value at $u=r$. But this is obviously less than $r^2p_1(r)^2$ which is Q_1^2. □

Proposition 5. Let $0\leq s\leq 2$, $0\leq t\leq 2$ and let $a_1,\ldots,a_K$, $b_1,\ldots,b_k$ be $2K$ non-negative numbers. Then

$$\left[\left(\sum_{j=1}^{K}a_j\right)^s+\left(\sum_{j=1}^{K}b_j\right)^t\right]^{1/2}\leq\sum_{j=1}^{K}(a_j^s+b_j^t)^{1/2}. \tag{52}$$

Proof. It suffices to prove the proposition for $K=2$ namely, for $a, A, b, B\geq 0$,

$$[(a+A)^s+(b+B)^t]^{1/2}\leq(a^s+b^t)^{1/2}+(A^s+B^t)^{1/2}. \tag{53}$$

If (53) holds then simply take $a=a_1$, $A=\Sigma_2^K a_j$ (and similarly for b, B) and use induction. Now $(a+A)^s=(a+A)^2/(a+A)^{2-s}\leq(a^2+2aA+A^2)/\max(a^{2-s}, A^{2-s})\leq a^s+2a^{s/2}A^{s/2}+A^s$. A similar inequality holds for $(b+B)^t$. Squaring (53) and using these inequalities, it suffices to prove that

$$a^{s/2}A^{s/2}+b^{t/2}B^{t/2}\leq(a^s+b^t)^{1/2}(A^s+B^t)^{1/2}.$$

This, however follows from the Cauchy-Schwarz inequality. □

3. Behaviour of N_c for small Z or small γ or large A

Although theorem 1 gives an upper bound for all values of the z_j, it is primarily useful for the large-Z behaviour of Q. In fact, the comparison function f we chose in the proof of lemma 4, (i.e. $f(x)=\delta(|x|-R)^{-4}$ may be too big when we consider small z. Since the atomic $\phi(x)$ is bounded from above by $V(x)=z|x|^{-1}$ and the function g has support on a ball of radius R and total mass 1, $\tilde{\phi}(x)\leq z|x|^{-1}$ for $|x|\geq R$. In particular $\tilde{\phi}(R)\leq z|R|^{-1}$, whereas the comparison function f goes to infinity at $|x|=R$. Therefore it is somewhat better to choose $f(x)=\delta(|x|-\alpha R)^{-4}$, where $\alpha=\alpha(z)=1-(\delta/zR^3)^{1/4}$ is such that $f(R)=zR^{-1}$. Then, proceeding as in the proof of theorem 1, one gets a z_j-dependent bound for Q. Although we do not give any details here, we point out that as z goes to zero, for an atom, this upper bound goes to $3.057A^{3/2}$ with $\gamma=\gamma_{\text{phys}}$. We know, however, that as Z goes to zero, Q vanishes because $Q<Z$ (Lieb 1981, theorem 7.23). Thus, the previous bound is not good for small Z. Getting the behaviour of Q as a function of Z for small Z is the subject of this section. The main result for Q is contained in equation (63) below.

We begin with a normalisation convention. Choose $z_1^0, \ldots, z_K^0 > 0$ such that

$$\sum_{j=1}^{K} z_j^0 = 1 \tag{54}$$

and let $R_1^0, \ldots, R_K^0$ be fixed, distinct points in $\mathcal{R}^3$. Let $Z > 0$ be the total nuclear charge in a molecule in which

$$z_j = Zz_j^0 \qquad R_j = (A/Z)R_j^0. \tag{55}$$

In this molecule the length scale is A/Z. In TF theory, by comparison, it is $Z^{-1/3}$. As $Z \to 0$ the atoms move apart. One can also treat the case in which the R_j remain fixed as $Z \to 0$; we do not do so explicitly here, but note that in the limit $Z \to 0$ this is obviously the same as placing all the R_j at one common point.

Let us write the solution to (5) as

$$\psi(x) = Z^2 A^{-3/2} \tilde{\psi}((Z/A)x) \tag{56}$$

whence

$$\int \psi(x)^2 \, dx = Z \int \tilde{\psi}(x)^2 \, dx. \tag{57}$$

The TFW equation (5) then reads

$$(-\Delta + \tilde{\gamma}\tilde{\psi}(x)^{4/3} - \tilde{\phi}(x))\tilde{\psi}(x) = 0 \tag{58}$$

with

$$\tilde{\gamma} = \gamma Z^{2/3}/A \tag{59}$$

$$\tilde{\phi}(x) = \tilde{V}(x) - (|x|^{-1} * \tilde{\psi}^2)(x) \tag{60}$$

$$\tilde{V}(x) = \sum_{j=1}^{K} z_j^0 |x - R_j^0|^{-1}. \tag{61}$$

With this scaling there is only one non-trivial parameter in the problem, $\tilde{\gamma}$. The potential $\tilde{V}$ is that of a molecule with unit total nuclear charge and $A = 1$. Our goal is to elucidate the behaviour of (58) as $\tilde{\gamma} \to 0$. From now on we shall omit the tilde on the various quantities in (58)-(61).

Formally, at least, as $\gamma \to 0$ the solution ψ_γ to (58) approaches the solution ψ_H to the Hartree equation

$$(-\Delta - \phi(x))\psi_H = 0 \tag{62}$$

with ϕ given by (61) and (60) with ψ_H^2. This equation (which was also used in Benguria and Lieb 1983) has a unique positive solution, ψ_H, because the proof in Benguria *et al* (1981), Lieb (1981), that (1) has a unique minimum and that this minimum is the unique solution to (5) only uses the fact that $\gamma \geq 0$. Assuming that $\int \psi^2 \to \int \psi_H^2$, (57) tells us that

$$\lim_{Z \to 0} Q/Z = \int \psi_H^2(x) \, dx - 1. \tag{63}$$

Proving (63) is the goal of this section.

As stated earlier, $1<\int \psi_{\mathrm{H}}^2<2$. For the atomic case $K=1$, $z_1^0=1$, (62) has been solved numerically (Baumgartner 1983) with the result that

$$\int \psi_{\mathrm{H}}(x)^2\,\mathrm{d}x=1.21. \tag{64}$$

Thus, as $Z\to 0$, $Q\simeq 0.21Z$ for an atom. The right-hand side of (63) is not known for a molecule, but we conjecture that

$$\int \psi_{\mathrm{H}}(x)^2\,\mathrm{d}x\leqslant 1+0.21\ \mathrm{K}. \tag{65}$$

The point $\gamma=0$ is not special. We shall prove the following general theorem which says that if $\gamma\to\Gamma\geqslant 0$ then the solution $\psi_\gamma\to\psi_\Gamma$ in a very strong sense. In particular there is strong L^2 convergence so that (63) is justified.

Theorem 6. Let ψ_γ (and $\rho_\gamma=\psi_\gamma^2$) denote the unique positive solution to the TFW equation (5) for $\gamma\geqslant 0$, with A fixed and with V in equation (3) fixed. (Note: condition (54) is irrelevant here.) Let $\Gamma\geqslant 0$ be fixed. Then, as $\gamma\to\Gamma$, $\psi_\gamma\to\psi_\Gamma$ in the following senses:

$$\nabla\psi_\gamma\to\nabla\psi_\Gamma \text{ strongly in } L^2. \tag{66}$$

$$\psi_\gamma\to\psi_\Gamma \text{ and } \rho_\gamma\to\rho_\Gamma \text{ strongly in } L^p \tag{67}$$

for all $1\leqslant p\leqslant\infty$.

$$|x|^{-1}*\psi_\gamma^2\to|x|^{-1}*\psi_\Gamma^2 \text{ strongly in } L^p \tag{68}$$

for all $3<p\leqslant\infty$.

$$D(\psi_\gamma^2,\psi_\gamma^2)\to D(\psi_\Gamma^2,\psi_\Gamma^2) \tag{69}$$

(cf (2)).

Proof. Let $\gamma_n\geqslant 0$ be any sequence with $\gamma_n\to\Gamma$ and let $\psi_n\equiv\psi_{\gamma_n}$. Since ψ_Γ is unique, it suffices to show that some subsequence of ψ_n converges to ψ_Γ in the indicated senses. In the appendix it is proved that $\|\psi_\gamma\|_\infty<C_\infty=$ constant, independent of γ. Since $\|\psi_\gamma\|_2^2<2$, then for all $2\leqslant p\leqslant\infty$ we have $\|\psi_\gamma\|_p<C_p=$ constant. With ξ_γ given by (1) and with E_γ being the minimum of ξ_γ we easily find, by considering $\xi_\gamma(\psi_\Gamma^2)$ and $\xi_\Gamma(\psi_\gamma^2)$, that

$$\lim_{\gamma\to\Gamma}E_\gamma=E_\Gamma \tag{70}$$

and also that ψ_n^2 is a minimising sequence for ξ_Γ. By the proof in Lieb (1981) and Benguria *et al* (1981) of the existence of a minimum for ξ_Γ, and the lower semicontinuity of ξ_Γ, we conclude that there is a subsequence (which we continue to denote by ψ_n) such that

$$\nabla\psi_n\to\nabla\psi_\Gamma \text{ strongly in } L^2 \tag{71}$$

$$D(\psi_n^2,\psi_n^2)\to D(\psi_\Gamma^2,\psi_\Gamma^2) \tag{72}$$

$$\psi_n\to\psi_\Gamma \text{ almost everywhere} \tag{73}$$

This proves (66) and (69). ((73) follows from the Rellich–Kondrachov theorem.)

Not only is $\psi_n(x) \leq C_\infty$ for all x, but we also have the bound (with some constants M and α)

$$\psi_n(x) \leq M \exp(-\alpha |x|^{1/2}) \tag{74}$$

for $|\gamma_n - \Gamma|$ small enough and for $|x| > R$ for some fixed R. To prove (74) we note that for some R_1 and some $Q > 0$

$$\int_B \psi_\Gamma(x)^2 \, dx > Z + Q/2$$

with $B = \{x \| x| < R_1\}$. Since $H^1(B)$ is compactly imbedded in $L^2(B)$ (Rellich-Kondrachov), there is a further subsequence such that $\psi_n \to \psi_\Gamma$ strongly in $L^2(B)$. Hence the entire sequence (see the remark at the beginning of the proof) converges strongly to ψ_Γ in $L^2(B)$. Thus,

$$\int_B \psi_n(x)^2 \, dx > Z + Q/4 \tag{75}$$

for n large enough. (74) follows by the proof in Benguria *et al* (1981), lemma 8 or Lieb (1981), lemma 7.24(ii). Consequently, $\psi_n(x) \leq F(x)$ for all x and n large enough, where $F(x) = C_\infty$ for $|x| \leq R$ and $F(x)$ is the right-hand side of (74) for $|x| > R$. Since $F \in L^p$ for $1 \leq p \leq \infty$, (67) follows from (73) for $1 \leq p < \infty$ by dominated convergence.

The upper bound F and (73) also imply (by dominated convergence) that the convergence in (68) is pointwise almost everywhere and that $g_\gamma \equiv |x|^{-1} * \psi_\gamma^2$ is bounded by a function of the form $G = \min(s, t/|x|)$ for suitable s and t. Again, by dominated convergence, we obtain strong convergence in (68) in L^p for $3 < p < \infty$. The L^∞ convergence in (68) follows easily from the L^2 convergence of ρ_γ to ρ_Γ together with the large $|x|$ bound (74).

To prove the L^∞ convergence in (67) note that in view of (74) it suffices to prove L^∞ convergence on bounded sets. But this follows from the fact (Benguria *et al* 1981, lemma 7, or Lieb 1981, theorem 7.9) that for any bounded set S and all $x, y \in S$, $|\psi_n(x) - \psi_n(y)| < M|x-y|^{1/2}$ for some constant M which depends on S but (it is easy to see from the proof) not on n. □

4. Lower bound for the chemical potential of a neutral atom or molecule

Here, we prove a result which is somewhat related to the bound on N_c. We shall show that the chemical potential of a neutral system (K not necessarily one) is bounded from below by a constant independent of the nuclear charge. We *conjecture* that a similar bound from above should hold.

The chemical potential, $-\mu(N) = dE/dN$, as a function of N is nonpositive, continuous and monotonically increasing in N (for fixed nuclear charges) since $E(N)$ is convex in N in TFW theory (Lieb 1981, theorem 7.2 and theorem 7.8(iii)). Therefore the binding energy ΔE (or affinity) satisfies $|\Delta E| < \mu_0 Q$, where Q is the added charge ($Q = 1$ for an electron).

The fact that the chemical potential, $-\mu_0 = -\mu(Z)$, for a neutral atom or molecule is bounded independent of the nuclear charges agrees with what is believed to be the case for the Schrödinger equation.

Consider the TFW equation for a neutral system (which is a generalisation of (5)), i.e.

$$-A\,\Delta\psi + (\gamma\psi^{4/3} - \phi)\psi = -\mu_0\psi \tag{76}$$

with ϕ given by (6), (3), or equivalently,

$$-\Delta\phi = -4\pi\psi^2 \qquad x \neq R_i,\ i = 1, 2, \ldots, K. \tag{77}$$

Here $\int \psi^2\,\mathrm{d}x = Z = \Sigma_{i=1}^K z_i$. Our bound is the following.

Theorem 7. For a neutral system, i.e. for $\int \psi^2\,\mathrm{d}x = Z$, the chemical potential is bounded from below by,

$$-\mu_0 \geqslant -27\pi^2 A^2 \gamma^{-3} \qquad \text{all } Z \tag{78}$$

in the units chosen in the Introduction. In particular, for the value of A chosen in Lieb (1981) to fit the Scott term in the energy, i.e. $A = 0.1859$, and with $\gamma = \gamma_{\text{phys}}$, $\mu_0 \leqslant 0.0105$.

Remark. Since $N_c > Z$ (Lieb 1981, theorem 7.19), μ_0 is strictly positive.

Proof. First consider the TFW equation with arbitrary $N = \int \psi^2 \leqslant N_c$, in which case the right side of (76) is replaced by $-\mu(N)\psi$. We know that $\mu(N) = -\mathrm{d}E(N)/\mathrm{d}N$ and that $\mu(N)$ is *continuous* and monotonically decreasing (Lieb 1981, theorem 7.8(iii)). Therefore (78) will be proved if we can show that for every $N > Z$, $\mu(N) < 27\pi^2 A^2 \gamma^{-3}$. This, we shall now proceed to do.

For every positive b and for all numbers $\psi \geqslant 0$ we have the algebraic inequality

$$b\psi^2 \leqslant \gamma\psi^{7/3} + d(b)\psi \tag{79}$$

with

$$d(b) = 27b^4\gamma^{-3}/256. \tag{80}$$

The TFW equation (with $\int \psi^2 = N > Z$) implies

$$-A\,\Delta\psi + b\psi^2 - \phi\psi \leqslant (d(b) - \mu(N))\psi.$$

Therefore, if $\mu(N) \geqslant d(b)$

$$-A\,\Delta\psi + b\psi^2 - \phi\psi \leqslant 0. \tag{81}$$

Now, as long as b is chosen so that $b > 4(\pi A)^{1/2}$, (77) and (81) imply that $\psi < \beta\phi$, all $x \in \mathscr{R}^3$, where β is the positive root of $b = \beta^{-1} + 4\pi\beta A$. To prove this, let $S = \{x | \psi(x) > \beta\phi(x)\}$. Obviously $R_i \notin S$. Since $\psi - \beta\phi$ is continuous in $\mathscr{R}^3 \backslash \{R_i\}$, S is open. On S,

$$\begin{aligned} -A\,\Delta(\psi - \beta\phi) &\leqslant -b\psi^2 + \phi\psi + 4\pi A\beta\psi^2 \\ &= \beta^{-1}[\beta\phi - \beta(b - 4\pi A\beta)\psi]\psi \\ &= \beta^{-1}(\beta\phi - \psi)\psi \leqslant 0, \end{aligned}$$

where we have used the fact that $b - 4\pi A\beta = \beta^{-1}$. Hence $\psi - \beta\phi$ is subharmonic on S. Moreover $\psi - \beta\phi = 0$ on $\partial S \cup \{\infty\}$. Therefore S is empty and $\beta\phi(x) \geqslant \psi(x)$ for all $x \in \mathscr{R}^3$. Since $\psi \geqslant 0$, ϕ must be non-negative everywhere. On the other hand, $\phi =$

$V-|x|^{-1} * \psi^2$ and $\int \psi^2 > Z$; consequently, $\phi(x)<0$ for sufficiently large $|x|$. This is a contradiction, and we conclude that $\mu(N)<d(b)$ whenever $b=\beta^{-1}+4\pi\beta A$ for some $0<\beta<\infty$. Choosing $\beta=(4\pi A)^{-1/2}$ yields the desired result, i.e. $\mu(N)<27\pi^2A^2\gamma^{-3}$. □

Remark. From the asymptotics of the solution of equation (76) we see that $\mu_0^{-1/2}$ somehow measures the range of the electronic density. If our conjecture is true, such a range would be independent of Z.

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Appendix

Here, we give a bound for the L^∞ norm of the solution to the TFW equation. Such a bound is independent of γ, the constant in front of the $\psi^{7/3}$ term. This bound is used in § 3.

Lemma A.1. Let ψ be the positive solution to the TFW equation for a molecule with $V(x)$ given by (3). Then for all $\gamma>0$

$$\|\psi\|_\infty \leqslant (27/16\pi)^{1/2}(Z/A)^{3/2}\|\psi\|_2$$

with $\|\psi\|_2<(2Z)^{1/2}$ (Lieb 1981, theorem 7.23).

Proof. Because of lemma 9 in Benguria *et al* (1981), $\psi \in L^\infty$. From equation (5), $-A\,\Delta\psi(x) \leqslant V(x)\psi(x)$. First, consider a single atom with $V(x)=z|x|^{-1}$. In this case, therefore,

$$A\psi(x) \leqslant (4\pi)^{-1}\int z|y|^{-1}|x-y|^{-1}\psi(y)\,\mathrm{d}y. \tag{A.1}$$

Hence

$$\begin{aligned}8\pi z^{-1}A\psi(x) &\leqslant \int (|y|^{-2}+|x-y|^{-2})\psi(y)\,\mathrm{d}y \\ &= \int |y|^{-2}(\psi(y)+\psi(x-y))\,\mathrm{d}y.\end{aligned} \tag{A.2}$$

We decompose this last integral into two terms. One integral over $\{|y|<r\}$ and the other over $\{|y|>r\}$ for any fixed $r>0$. We have,

$$\int_{|y|<r} |y|^{-2}(\psi(y)+\psi(x-y))\,\mathrm{d}y \leqslant 8\pi r\|\psi\|_\infty \tag{A.3}$$

$$\int_{|y|>r} |y|^{-2}(\psi(y)+\psi(x-y))\,\mathrm{d}y \leqslant 2\|\psi\|_2(4\pi/r)^{1/2} \tag{A.4}$$

by Hölder's inequality. Thus, substituting (A.3) and (A.4) into (A.2), we have

$$8\pi z^{-1}A\psi(x) \leq 8\pi r\|\psi\|_\infty + 2\|\psi\|_2(4\pi/r)^{1/2} \qquad \text{all } r>0 \tag{A.5}$$

and minimising the right-hand side with respect to r we get

$$8\pi A\psi(x) \leq 6z\|\psi\|_\infty^{1/3}\|\psi\|_2^{2/3}(2\pi)^{2/3} \qquad \text{all } x. \tag{A.6}$$

In the molecular case

$$A\psi(x) \leq (4\pi)^{-1}\sum_{j=1}^{K}\int z_j|y-R_j|^{-1}|x-y|^{-1}\psi(y)\,\mathrm{d}y. \tag{A.7}$$

Using the same analysis (A.2)-(A.6) for each term on the right-hand side of (A.7) (but with $\{|y-R_j| \gtrless r_j\}$ and with r_j depending on j) we have that

$$8\pi A\psi(x) \leq 6Z\|\psi\|_\infty^{1/3}\|\psi\|_2^{2/3}(2\pi)^{2/3}. \tag{A.8}$$

The lemma is proved by taking the supremum over x on the left-hand side of (A.8). □

Remark. By making a similar decomposition, one can show that

$$\|B\psi^2\|_\infty \leq 3(\pi/2)^{1/3}\|\psi\|_2^{4/3}\|\psi\|_\infty^{2/3} \leq \|\psi\|_2^2(Z/A)\times 9\times 2^{-5/3}. \tag{A.9}$$

where

$$(B\psi^2)(x) = \int |x-y|^{-1}\psi(y)^2\,\mathrm{d}y$$

and $\|\psi\|_2^2 < 2Z$ (Lieb 1981, theorem 7.23). The second inequality in (A.9) comes from lemma A.1. Actually, the sharp constant in the middle term of (A.9) is $3(\pi/6)^{1/3}$, not $3(\pi/2)^{1/3}$. One can show that the maximising ρ for $\|B\rho\|_\infty/(\|\rho\|_1^{2/3}\|\rho\|_\infty^{1/3})$ is $\rho =$ characteristic function of a ball.

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Part V
Stability of Matter