Proof of the Stability of Highly Negative Ions in the Absence of the Pauli Principle

Rafael Benguria
Departamento de Fisica, Universidad de Chile, Casilla 5487, Santiago, Chile

and

Elliott H. Lieb
Departments of Mathematics and Physics, Princeton University, New Jersey 08544
(Received 31 January 1983)

It is well known that ionized atoms cannot be both very negative and stable. The maximum negative ionization is only one or two electrons, even for the largest atoms. The reason for this phenomenon is examined critically and it is shown that electrostatic considerations and the uncertainty principle cannot account for it. The exclusion principle plays a crucial role. This is shown by proving that when Fermi statistics is ignored, then the degree of negative ionization is at least of order z, the nuclear charge, when z is large.

PACS numbers: 31.10.+z, 03.65.Ge

One of the interesting and important facts about atoms is that they cannot be very negatively ionized (in a stable state, as distinguished from metastable state). For a nucleus of charge z, let $N_c(z)$ denote the maximum number of electrons that can be bound to this nucleus (*in vacuo*, not in water or other matter). Experiments indicate that $N_c(z)-z$ is one, or possibly two, as z varies over the periodic table. It is often said that this striking fact, which begs for an explanation, is a consequence of electrostatics; namely, if an atom has a net negative charge then an additional electron will not bind because the electron can lower its energy by escaping to infinity. The purpose of this note is to examine this simple, but important physical problem in a critical way and to show that the correct explanation does not lie with electrostatics alone—*the Pauli exclusion principle plays a central role in the correct explanation.* We are not able to offer an explanation of the phenomenon, but we thought it worthwhile at least to expose the fallacy in the "simple electrostatic" explanation and thereby show that the phenomenon is really a deep consequence of quantum mechanics.

To prove that the Pauli principle is essential we shall consider an atom in which the electrons are spinless bosons. (Since the ground state of a many-body system is nodeless, it is automatically symmetric; therefore "bosons" and "ignoring statistics" are synonymous.) We shall prove that in this model, $N_c(z)-z \geq \gamma z$ when z is large, and where $\gamma > 0$ is some fixed constant. We do not know the numerical value of γ, except that $0<\gamma<1$. It can be found by solving an equation [namely (11) with $\mu=0$] on a computer, if there is sufficient interest in doing so. The exact numerical value of γ is not as important as the fact that "bosonic" atoms would not obey the $N_c(z)-z\approx 1$ rule for sufficiently large z. Just how large z has to be in order to violate the rule substantially, we do not know. Equation (11) has to be solved to answer the question.

One can adopt different points of view about this. It is possible that the rule is not really a rule at all for fermions, and that $N_c(z)-z$ grows at least as fast as z for large z. In this case the fact that $N_c(z)-z\approx 1$ within the periodic table is fortuitous, and in reality bosons and fermions are qualitatively similar as far as the phenomenon goes. Another possibility is that $N_c(z)/z - 1 \to 0$ as $z\to\infty$ [thereby allowing the possibility that $N_c(z)-z\approx z^{1/2}$, for example], in which case the Pauli principle is crucial. We, of course, do not know which point of view will ultimately prevail. It is to be hoped that if it is the second one then someone will find a simple, but rigorous explanation. In any case, the phenomenon should not be left merely as a numerical statement about the periodic table but should be understood on a deeper level.

While we use the nonrelativistic Schroedinger equation and we regard the nucleus as fixed, it will be clear, at least intuitively, that our conclusions are not limited by these approximations. The lack of the Pauli principle is, however, crucial.

Before turning to the mathematical proof, let us consider the problem from a heuristic viewpoint. Suppose N electrons are bound to the nucleus. With neglect of many-body effects, the effective potential that an $(N+1)$th electron feels is approximately

$$\varphi_\rho(\vec{x}) = V(\vec{x}) + \int |\vec{x} - \vec{y}|^{-1}\rho(\vec{y})d^3y , \quad (1)$$

where $V(\vec{x}) = -z/|\vec{x}|$, and units in which the electron charge is unity are used. $\rho(\vec{x})$ is the density of the N electrons, $\int \rho = N$. The effective Hamiltonian for the $(N+1)$th electron is approximately

$$h_{\text{eff}} = -m^{-1}\Delta + \varphi_\rho(\vec{x}) , \quad (2)$$

where m is the electron mass and $\hbar^2 = 2$.

As N increases from zero, φ_ρ increases in some average sense. When $N > z$, $\varphi_\rho(\vec{x})$ is positive for large $|\vec{x}|$ [by Newton's theorem, $\varphi_\rho(\vec{x}) \approx (N-z)/|\vec{x}|$ for large $|\vec{x}|$]. However, $\varphi_\rho(\vec{x})$ is still very large and negative for x near zero, namely, $-z/|\vec{x}|$. The uncertainty principle is crucial here; it prevents $\rho(\vec{x})$ from being a delta function and thereby screening the nucleus for small $|\vec{x}|$. Thus, even if $N > z$, h_{eff} might have a genuine bound state and the $(N+1)$th electron might be bound. Eventually, of course, the region of negative φ_ρ will be too small and binding will cease. Implicit in this discussion is the fact that the $(N+1)$th electron is allowed to go into any available bound state of h_{eff}. In other words, the argument works if statistics is ignored, which is the same thing as saying that we are dealing with bosons. If, on the other hand, the electrons are fermions then, for binding, h_{eff} must have something like $N+1$ bound states in order that the $(N+1)$th electron can go into an orbital that is orthogonal to the previously occupied orbitals. It is a remarkable fact about Fermi statistics that the $(N+1)$th bound state of h_{eff} disappears when $N \approx z$, if the $N_c(z) - z \approx 1$ rule is obeyed.

The above argument is not completely convincing, even on the heuristic level, because it is not obvious that h_{eff} indeed has a bound state when $N = (1+\gamma)z$.

A proper proof, starting from the correct Schroedinger equation, and without any approximations, will now be given. Let

$$H(N) = \sum_{i=1}^{N} [-m^{-1}\Delta_i + V(\vec{x}_i)] + \sum_{1 \le i < j \le N} |\vec{x}_i - \vec{x}_j|^{-1} \quad (3)$$

be the Hamiltonian for N bosonic electrons [$V(\vec{x}) = -z/|\vec{x}|$]. Let $E(N)$ be the ground-state energy of $H(N)$. We shall find two bounding functions, $E_\pm(N)$, with $E_-(N) \le E(N) \le E_+(N)$ and

$$E_+(N) = -mz^3 e(N/z) , \quad (4a)$$

$$E_-(N) = -mz^3[e(N/z)^{1/2} + bz^{-3/2}N^{5/6}]^2 . \quad (4b)$$

Here, $b = 0.36$ and $e(t)$ is a monotone nondecreasing, concave function ($\dot{e} \ge 0$, $\ddot{e} \le 0$), defined for all real $t \ge 0$, with $e(0) = 0$. $E_+(N)$ is essentially the Hartree energy. The *crucial point* about $e(t)$ is that it is *strictly increasing* in t up to some $t_c = 1+\gamma$ and $0 < \gamma < 1$. We do not know the numerical value of γ, but that is unimportant. [It can be found by solving Eq. (11), as explained below.] From Eq. (4) we see that if $N < \bar{N}$, where

$$E_-(\bar{N}) = E_+(zt_c) \quad (5)$$

(which means that $\bar{N}$ is not necessarily an integer), then the energy can be lowered by adding some number of electrons because $E(N) \ge E_-(N) > E_-(\bar{N}) = E_+(zt_c) = E_+([zt_c]) \ge E([zt_c])$. Here, $[x]$ denotes the smallest integer $\ge x$. [Note that Eq. (5) has a unique solution; $E_-(N)$ is monotone in N since $e(N/z)$ is monotone in N.] In other words

$$N_c(z) \ge [\bar{N}] . \quad (6)$$

As $z \to \infty$, $\bar{N} \to z(1+\gamma)$ because (5) reads (with $\bar{N}/z \equiv t$)

$$e(t)^{1/2} + bz^{-2/3}t^{5/6} = e(t_c)^{1/2} . \quad (7)$$

Since the solution to Eq. (7) satisfies $t < t_c < 2$ and since $e(t)$ is continuous, we have that $t \to t_c$ as $z \to \infty$. Thus, our main point is proved, namely, asymptotically

$$N_c(z) - z \ge \gamma z , \text{ large } z . \quad (8)$$

An *upper* bound for $N_c(z)$ was first given by Ruskai in the form $N_c(z) \le (\text{const})z^2$ for bosons.[1] Sigal[2] proved for fermions that $N_c(z) \le cz$ for z sufficiently large, with $c > 2$ being some constant. For fermions Ruskai[3] proved that $N_c(z) \le (\text{const}) \times z^{6/5}$. Sigal[4] improved his result for fermions to $N_c(z) \le \alpha(z)z$, with $\alpha(z) \le 12$ and $\alpha(z) \to 2$ as $z \to \infty$.

Now we turn to the proof of Eq. (4).

Upper bound for E(N).—We take a product trial function $\psi = \prod_{i=1}^{N} f(\vec{x}_i)$, with $\int f^2 = 1$ and with $f(\vec{x})$ real and nonnegative, and use the variational principle:

$$E(N) \le \langle \psi | H(N) | \psi \rangle \le \int \{ m^{-1} |\nabla \rho(\vec{x})^{1/2}|^2 + V(\vec{x})\rho(\vec{x}) \} d^3x + \tfrac{1}{2} \iint \rho(\vec{x})\rho(\vec{y}) |\vec{x} - \vec{y}|^{-1} d^3x\, d^3y \equiv L(\rho) , \quad (9)$$

where $\rho(\vec{x}) \equiv N f(\vec{x})^2$. [We could insert a factor $(N-1)/N$ before the last integral, but choose not to do so because we want $L(\rho)$ to be independent of N.] Next we define

$$E_+(N) = \inf\{L(\rho) \mid \int \rho = N, \rho(\vec{x}) \geq 0\}\,. \tag{10}$$

Equation (10) means that we try to minimize $L(\rho)$ under the stated conditions. The minimum may not be achieved by any ρ (it is achieved if and only if $N \leq 1+\gamma$ as stated below), but in any case E_+ cannot exceed the "greatest lower bound" or "infimum" of $L(\rho)$. The problem posed by Eq. (10) is a special case of the generalized Thomas–Fermi–von Weizsaecker problem analyzed earlier.[5,6] In our case, by the simple scaling $\rho(\vec{x}) \to m^3 z^4 \rho(mz\vec{x})$ the problem can be reduced to the case in which $m=1$, $z=1$, and $\int\rho = N/z$. Equation (4a) is thus seen to hold. Moreover, the m dependence of e is $e(N/z, m) = me(N/z, m=1)$ as in Eq. (4a). (Incidentally, this scaling shows that the radius of bosonic atoms *shrinks* as z^{-1}, whereas it *shrinks* as $z^{-1/3}$ for fermions.) There is a minimizing ρ for $L(\rho)$ (and it is unique) if and only if $N/z \leq t_c$ for some definite number $t_c > 1$. (Note that t_c is independent of m.) This ρ satisfies

$$[-m^{-1}\Delta + \varphi_\rho(\vec{x})]\rho(\vec{x})^{1/2} = -\mu\rho(\vec{x})^{1/2} \tag{11}$$

with $\mu \geq 0$, and $\mu = 0$ when $N = t_c z$. The proof that $t_c > 1$ is given in Ref. 5, lemma 13, and Ref. 6, theorem 7.16 (note: in these proofs take $p = \frac{5}{3}$ and $\gamma = 0$). The proof that $t_c < 2$ is given in Ref. 6, theorem 7.23. [The reason that $t_c > 1$ is that when $N = z$ then $\varphi_\rho(\vec{x}) < 0$ and one can prove that this potential has a bound state; thus μ cannot be zero. To prove that $t_c < 2$, set $\mu = 0$, multiply Eq. (11) by $|\vec{x}|\rho(\vec{x})^{1/2}$ and integrate. One can show, by partial integration, that $\int |\vec{x}|\rho(\vec{x})^{1/2}\Delta\rho(\vec{x})^{1/2} \leq 0$. Obviously, $\int V(\vec{x})|\vec{x}|\rho(\vec{x}) = -zN$. Finally, $I \equiv \iint |\vec{x}|\rho(\vec{x})\rho(\vec{y})|\vec{x}-\vec{y}|^{-1} = \frac{1}{2}\iint \rho(\vec{x})\rho(\vec{y})|\vec{x}-\vec{y}|^{-1}(|\vec{x}| + |\vec{y}|)$. But $(|\vec{x}| + |\vec{y}|)|\vec{x}-\vec{y}|^{-1} \geq 1$, so that $I \geq N^2/2$. Since $I \leq zN$, $N \leq 2z$.] That $e(t)$ is concave (and strictly concave when $t \leq t_c$) is a consequence of the fact that when $\int\rho$ is increased the additional density can be placed, if need be, at infinity where its energy contribution is zero (see Refs. 5 and 6).

Lower bound for $E(N)$.—Let $\psi(\vec{x}_1, \ldots, \vec{x}_N)$ be *any* normalized function. We want to show that

$$F(\psi) \equiv \langle\psi|H(N)|\psi\rangle \geq \text{right side of (4b)}\,. \tag{12}$$

Let

$$\rho_\psi(\vec{x}) = \sum_{i=1}^{N} \int |\psi(\vec{x}_1, \ldots, \vec{x}_{i-1}, \vec{x}, \vec{x}_{i+1}, \ldots, \vec{x}_N)|^2 d^3x_1 \cdots d^3x_{i-1} d^3x_{i+1} \cdots d^3x_N \tag{13}$$

be the single-particle density associated with ψ; $\int\rho_\psi = N$. We shall use several known inequalities. The first is the kinetic energy inequality of Hoffmann-Ostenhof[7] (see also Ref. 8 for a further discussion of kinetic energy inequalities):

$$\langle\psi| -\sum_{i=1}^{N} \Delta_i |\psi\rangle \geq \int |\nabla\rho_\psi(\vec{x})^{1/2}|^2 d^3x\,. \tag{14}$$

This follows by taking the gradient in (13) and then using the Schwarz inequality. The second is the "exchange and correlation" inequality[9,10]:

$$\langle\psi| \sum_{1\leq i<j\leq N} |\vec{x}_i - \vec{x}_j|^{-1} |\psi\rangle \geq \tfrac{1}{2}\iint \rho_\psi(\vec{x})\rho_\psi(\vec{y})|\vec{x}-\vec{y}|^{-1} d^3x\, d^3y - (1.68)\int \rho_\psi(\vec{x})^{4/3} d^3x\,. \tag{15}$$

Inserting Eqs. (14) and (15) in (12) we have, for any ψ,

$$F(\psi) \geq L(\rho_\psi) - (1.68)\int \rho_\psi(\vec{x})^{4/3}\, d^3x\,. \tag{16}$$

To bound the right side of (16) from below, let us first explicitly denote the m dependence of $L(\rho)$ by $L(\rho, m)$. Choose $\epsilon > 0$ and let $m_\epsilon = (1+\epsilon)m$. Then Eq. (16) reads

$$F(\psi) \geq L(\rho_\psi, m_\epsilon) + P(\rho_\psi, m_\epsilon)\,, \tag{17}$$

$$P(\rho_\psi, m_\epsilon) = \epsilon m_\epsilon^{-1} \int |\nabla\rho_\psi(\vec{x})^{1/2}|^2 d^3x - (1.68)\int \rho_\psi(\vec{x})^{4/3}\, d^3x\,. \tag{18}$$

We have already seen that [see Eq. (10) and the following remark about scaling]

$$L(\rho_\psi, m_\epsilon) \geq (m_\epsilon/m)E_+(N) = (1+\epsilon)E_+(N)\,. \tag{19}$$

To bound P, we use the Sobolev inequality[6,11]

$$\int |\nabla g(\vec{x})|^2 \, d^3x \geq 3(\pi/2)^{4/3}\{\int |g(\vec{x})|^6 \, d^3x\}^{1/3} \tag{20}$$

for any g. Thus

$$P(\rho_\psi, m_\epsilon) \geq 3(\pi/2)^{4/3}\epsilon m_\epsilon^{-1}\{\int \rho_\psi(\vec{x})^3 \, d^3x\}^{1/3} - (1.68)\int \rho_\psi(\vec{x})^{4/3} \, d^3x. \tag{21}$$

By Hoelder's inequality, $\int \rho^{4/3} \leq X\{\int\rho\}^{5/6}$ with $X = \{\int \rho^3\}^{1/6}$. Inserting this in (21), and then minimizing the right side with respect to the unknown X, we have

$$P(\rho_\psi, m_\epsilon) \geq -b^2 m_\epsilon N^{5/3}/\epsilon, \tag{22}$$

$$b = (1.68)2^{-1/3}3^{-1/2}\pi^{-2/3} = 0.36. \tag{23}$$

Inserting Eqs. (19) and (22) in (17) we have, for any $\epsilon > 0$, and any normalized ψ,

$$\langle \psi | H(N) | \psi \rangle \geq (1+\epsilon)E_+(N) - (1+1/\epsilon) m b^2 N^{5/3}. \tag{24}$$

Maximizing this with respect to ϵ yields Eq. (4b).

One of the authors (E.L.) acknowledges gratefully the hospitality and support of the Departamento de Física, Universidad de Chile, where this work was carried out. He also acknowledges the support of the U. S. National Science Foundation under Grant No. PHY-8116101 A01. We thank Barry Simon for valuable comments.

[1] M. B. Ruskai, Commun. Math. Phys. 82, 457 (1982).
[2] I. M. Sigal, Commun. Math. Phys. 85, 309 (1982). See also *Mathematical Problems in Theoretical Physics*, Lecture Notes in Theoretical Physics Vol. 153 (Springer-Verlag, Berlin, 1982), pp. 149–156.
[3] M. B. Ruskai, Commun. Math. Phys. 85, 325 (1982).
[4] I. M. Sigal, Institute Mittag-Leffler Report No. 12, 1982 (unpublished).
[5] R. Benguria, H. Brezis, and E. H. Lieb, Commun. Math. Phys. 79, 167 (1981).
[6] E. H. Lieb, Rev. Mod. Phys. 53, 603 (1981).
[7] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, Phys. Rev. A 16, 1782 (1977).
[8] E. H. Lieb, *Density Functionals for Coulomb Systems*, in *Physics as Natural Philosophy: Essays in Honor of Laszlo Tisza on His 75th Birthday*, edited by A. Shimony and H. Feshbach (MIT Press, Cambridge, Mass., 1982), pp. 111–149.
[9] E. H. Lieb, Phys. Lett. 70A, 444 (1979).
[10] S. Oxford and E. H. Lieb, Int. J. Quantum Chem. 19, 427 (1981).
[11] E. H. Lieb, Rev. Mod. Phys. 48, 553 (1976).