Asymptotic Neutrality of Large-Z Ions

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(Received 4 January 1984)

Let $N(Z)$ denote the number of electrons that a nucleus of charge Z binds in nonrelativistic quantum theory. It is proved that $N(Z)/Z \rightarrow 1$ as $Z \rightarrow \infty$. The Pauli principle plays a critical role.

PACS numbers: 31.10.+z, 03.65.Bz

Mathematically rigorous results about binding energies of multiparticle systems of charged particles in nonrelativistic quantum mechanics are clearly basic to the foundations of atomic, molecular, and solid-state physics. We want to present here a new result in this area which could be called quantum potential theory; details of our proof will appear elsewhere.[1]

Let $H(N,Z)$ be the Hamiltonian of a nucleus of charge Z and N electrons, i.e.,[2]

$$H(N,Z) = \sum_{i=1}^{N} (-\Delta_i - Z|\vec{x}_i|^{-1}) + \sum_{i<j} |\vec{x}_i - \vec{x}_j|^{-1}. \quad (1)$$

Its minimum energy for fermion states[3] will be denoted by $E(N,Z)$ and its minimum over all states[4] by $E_b(N,Z)$. It is useful to study E_b to understand where the Pauli principle plays a central role.

It is a fundamental result of Ruskai and Sigal[5] that for any fixed Z, there is a number[6] $N(Z)$ $[N_b(Z)]$ so that $E(N(Z),Z) = E(N(Z)+j,Z)$ for all j $[E_b(N(Z),Z) = E_b(N(Z)+j,Z)$ for all $j]$. Thus $N(Z)$ is the maximal number of electrons that the nucleus binds.

We are concerned here with the asymptotics of $N(Z)$ for large Z. Sigal[7] proved that

$$\limsup [N(Z)/Z] \leq 2, \qquad \lim [\ln N_b(Z)/\ln Z] = 1. \quad (2)$$

Recently,[8] Lieb has proven the bounds

$$N(Z) < 2Z+1, \quad N_b(Z) < 2Z+1,$$

for all Z (not just Z large). The same result holds in any symmetry sector. We have proven the fundamental result that

$$\lim_{Z\rightarrow\infty} N(Z)/Z = 1. \quad (3)$$

Lest the reader think that (3) is "obvious," we point out that it is *false* for bosons, for Benguria and Lieb[9] have shown that

$$\liminf [N_b(Z)/Z] \geq \lambda_c,$$

where λ_c is the critical charge for the Hartree equation. It is known[10] rigorously that $1 < \lambda_c < 2$; numerically[11] $\lambda_c \simeq 1.2$. In our sketch of the proof of (3), we shall emphasize where the Pauli principle enters.

Although one expects $N(Z) \approx Z + k$ for some constant k $(=1,2)$, our proof of (3) does not rule out a possibility like $Z + Z^{\alpha}$ for some $\alpha < 1$.

One part of our proof follows closely Sigal's[7] proof of (2). Sigal gets $2Z$ because he uses[12] the obvious fact that if one has a nucleus of charge Z and removes the electron farthest from the nucleus, there is a gain in energy as long as $N-1>2Z$ (since the worst case would be to have the other $N-1$ electrons at the opposite side of the nucleus almost as far away). It is intuitively obvious that one can do better by choosing more carefully the particle to be removed. Indeed, an important element for our proof is the following: For any ϵ, there exists an N_0 so that for all configurations $\{x_a\}_{a=1}^{N}$ of $N \geq N_0$ points we have

$$\max_b\left(\sum_{a\neq b}\frac{1}{|\vec{x}_b-\vec{x}_a|}-\frac{(1-\epsilon)N}{|\vec{x}_b|}\right)\geq 0. \tag{4}$$

This, in effect, is a factor of two better than Sigal's estimate.

We prove (4) by first proving a continuum analog; namely, for any positive charge density $\rho\neq\delta(x)$ and any ϵ, we can find a point $x\neq 0$, in the support of ρ,[13] such that

$$\phi_\rho(x)\equiv\int\frac{1}{|\vec{x}-\vec{y}|}d\rho(y)\geq\frac{1-\epsilon}{|\vec{x}|}\int d\rho(y). \tag{5}$$

We obtain (4) from (5) by an argument via contradiction. If (4) fails for arbitrarily large N, we can find a suitable limit[14] of the densities $N^{-1}\sum_a\delta(\vec{x}-\vec{x}_a)$ so that (5) fails.

(5) is proven as follows: First consider the case where ϕ_ρ is continuous, $0\notin \operatorname{supp}\rho$, and $\operatorname{supp}\rho$ is bounded. Then

$$f(x)=\phi_\rho(x)-|x|^{-1}(1-\epsilon)\int d\rho(y)$$

is a function whose average over large spheres is positive. Thus, since f vanishes at ∞ and is harmonic outside $\operatorname{supp}\rho$, f is positive at some points arbitrarily close to $\operatorname{supp}\rho$ and so by continuity of ϕ_ρ, f is nonnegative somewhere on $\operatorname{supp}\rho$. Given the special case, one obtains (5) in general by using a theorem of Choquet[15]: Given any finite positive charge density ρ, and given ϵ, one can find K compact so that the charge outside K is at most ϵ and so that the restriction of ρ to K generates a continuous potential.

(4) and (5) are clearly classical analogs of the basic result (3) that we want to prove. We control the possible quantum corrections to (4) by the same method Sigal used in his proof of (2).

By slightly improving (4) and following Ref. 7, one constructs functions $\{j_a\}_{a=0}^{N}$ on R^{3N} obeying the following: (i) j_0 is symmetric in $X=(\vec{x}_1,\ldots,\vec{x}_N)$ and j_a $(a\neq 0)$ are symmetric in $\{\vec{x}_b\}_{b\neq a}$. (ii) j_0 is supported in the region where $|X|_\infty\equiv\max_a|\vec{x}_a|<R$. (iii) j_a is supported in the region where

$$|X|_\infty\geq(1-\epsilon)R,\qquad \sum_{b\neq a}\frac{1}{|\vec{x}_b-\vec{x}_a|}\geq\frac{N(1-\epsilon)}{|\vec{x}_a|}. \tag{6}$$

(iv) One has the estimate, for the $3N$-dimensional gradients,[16]

$$\sum_{a=0}^{N}(\nabla j_a)^2(X)\leq CN^{1/2}R^{-1}|X|_\infty^{-1}. \tag{7}$$

(v) One has $\sum_{a=0}^{N}|j_a(X)|^2=1$ for all X. To be precise, for any ϵ, there is an N_0, and a positive number C, such that such a set exists for any $N>N_0$ and R. C depends only on ϵ and not on N or R.

To prove (3), we use the localization formula[17]

$$H(N,Z)=\sum_{a=0}^{N}j_aHj_a-\sum_{a=0}^{N}(\nabla j_a)^2=\sum_{a=0}^{N}j_a\Big[H-\sum_{b=0}^{N}(\nabla j_b)^2\Big]j_a.$$

(3) will follow if we prove that if we choose R suitably and $N\geq Z(1+\epsilon')$, Z large, then for each a

$$j_a\Big[H(N,Z)-\sum_{b=0}^{N}(\nabla j_b)^2\Big]j_a\geq j_a^2E(N-1,Z). \tag{8}$$

We shall take[18]

$$R=\alpha N^{-1/3}, \tag{9}$$

with $\alpha<<1$ to be chosen later. To obtain (8) for $a=N$, write

$$H(N,Z)=H(N-1,Z)-\Delta_N-Z|\vec{x}_N|^{-1}+\sum_{b\neq N}|\vec{x}_b-\vec{x}_N|^{-1};$$

use $j_NH(N-1,Z)j_N\geq E(N-1,Z)J_N^2$ (because j_N preserves antisymmetry in $1,\ldots,N-1$), $-\Delta_N\geq 0$, (6), and (7) to see that[16]

$$[\text{left-hand side of (8)}]-[\text{right-hand side of (8)}]\geq j_a^2|\vec{x}_a|^{-1}[-Z+N(1-\epsilon)-CN^{5/6}\alpha^{-1}],$$

which is positive for $N \geqslant Z\{(1-\epsilon)^{-1}+\epsilon\}$ and Z large (for any fixed α). A similar argument applies for any $a \neq 0$.

To control the core (i.e., $a=0$), we write $H(N,Z) = \tilde{H}(N,Z)+$ rep where rep denotes the electron repulsion. By filling up levels in hydrogen we obtain

$$\tilde{H}(N,Z) \geqslant -C_1 Z^2 N^{1/3}. \tag{10}$$

Since $|\vec{x}_i - \vec{x}_j| \leqslant 2|X|_\infty \leqslant 2R$ on the support of j_0, rep $\geqslant \frac{1}{4}N(N-1)R^{-1}$. Thus[16] for $a=0$

$$\text{left-hand side of (8)} \geqslant j_0^2\,[-C_1 Z^2 N^{1/3} + C_2 N^{7/3}\alpha^{-1} - C_3(1-\epsilon)^{-1}\alpha^{-2}N^{7/6}]$$

which is positive [and so larger than the right-hand side of (8)] if $N \geqslant Z$ and α is chosen sufficiently small. This completes our sketch of the proof of our basic result (3).

The fact that we had fermions and not bosons enters in the bound (10). The Pauli principle prevents the collapse[19] from becoming so great that the quantum corrections [as represented, for example, by the size of the "localization error," $\sum_{b=0}^{N}(\nabla j_b)^2$] overcome the basic classical potential theory result Eq. (4).

Parts of this work were done while some of us were visiting others of us: B.S. should like to thank H. Dym and I. Sigal for the hospitality of the Weizmann Institute, and W.T. would like to thank E. Lieb for the hospitality of Princeton University and M. Goldberger and R. Vogt for the hospitality of the California Institute of Technology. This work was supported in part by National Science Foundation Grants No. PHY-81-16101-A01 and No. MCS-81-20833 and by U. S.–Israel Binational Science Foundation Grant No. 3188/83.

[1]E. H. Lieb, I. Sigal, B. Simon, and W. Thirring, to be published.

[2]We choose units of length and energy so that $\hbar^2/2m = e^2 = 1$. In (1), we have taken infinite nuclear mass; our proof of Eq. (3) below extends to finite nuclear mass and to the allowance of arbitrary magnetic fields. See Ref. 1.

[3]We have in mind the Pauli principle with two spin states. The number of spin states (so long as it is a *fixed* finite number) does not affect the truth of Eq. (3).

[4]The minimum without any symmetry restriction occurs on a totally symmetric state, so that we could just as well view $E_b(N,Z)$ as a Bose energy.

[5]The result for E_b is due to M. B. Ruskai, Commun. Math. Phys. 82, 457 (1982). The fermion result was obtained by I. Sigal, Commun. Math. Phys. 85, 309 (1982). M. B. Ruskai, Commun. Math. Phys. 85, 325 (1982), then used her methods to obtain the fermion result.

[6]$N(Z)$ denotes the smallest number obeying this condition.

[7]I. Sigal, to be published.

[8]E. Lieb, Phys. Rev. A (to be published). A summary appears in E. H. Lieb, Phys. Rev. Lett. 52, 315 (1984).

[9]R. Benguria and E. Lieb, Phys. Rev. Lett. 50, 50 (1983).

[10]See R. Benguria, H. Brezis, and E. Lieb, Commun. Math. Phys. 79, 167 (1981); E. Lieb, Rev. Mod. Phys. 53, 603 (1981), and 54, 311(E) (1982).

[11]B. Baumgartner, "On the Thomas–Fermi–von Weizsäcker and Hartree energies as functions of the degree of ionization" (to be published).

[12]He also needs a method to control quantum corrections. This method is discussed later.

[13]The support of ρ, denoted by suppρ, is just those points x where an arbitrarily small ball about x has some charge.

[14]To be sure the limit exists and is not a delta function or zero, one may have to scale the x_a in an N-dependent way.

[15]G. Choquet, C. R. Acad. Sci. 244, 1606–1609 (1957).

[16]Since $|x_a| \leqslant |X|_\infty$ for all a, we can replace the right-hand side of (6) by $CN^{1/2}R^{-1}|x_a|^{-1}$. Since the gradients are all zero if $|X_\infty| < (1-\epsilon)R$, we can replace the right-hand side of (6) also by $C(1-\epsilon)^{-1}N^{1/2}R^{-2}$.

[17]This formula is easy to prove by expanding $\sum_a [j_a,[j_a,H]]$. Versions of it were found in successively more general situations by R. Ismagilov, Sov. Math. Dokl. 2, 1137 (1961); J. Morgan, J. Operator Theory 1, 109 (1979), and J. Morgan and B. Simon, Int. J. Quantum Chem. 17, 1143 (1980). It was I. Sigal in Ref. 5 who realized its significance for bound-state questions.

[18]This is precisely the scaling for Thomas-Fermi and for the real atomic system; see E. Lieb and B. Simon, Adv. Math. 23, 22 (1977).

[19]For bosons, the "electron" density collapses as Z^{-1}, not $Z^{-1/3}$; see Ref. 9.