Asymptotic Neutrality of Large-Z Ions

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

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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.,

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

Its minimum energy for fermion states² will be denoted by $E(N,Z)$ and its minimum over all states³ 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 Sigal⁴ that for any fixed $Z$, there is a number $6 N(Z)$ $[N_b(Z)]$ so that $E(N(Z),Z) = E_b(N(Z) + j,Z)$ 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 $Z$. Sigal⁵ proved that

$$\limsup \frac{N(Z)}{Z} \leq 2,$$

$$\lim \frac{\ln N_b(Z)}{\ln Z} = 1. \quad (2)$$

Recently,⁶ 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

$$\lim_{Z \to \infty} \frac{N(Z)}{Z} = 1. \quad (3)$$

Lest the reader think that (3) is "obvious," we point out that it is false for bosons, for Benguria and Lieb⁷ have shown that

$$\liminf \frac{N_b(Z)}{Z} \geq \lambda_c,$$

where $\lambda_c$ is the critical charge for the Hartree equation. It is known⁸ rigorously that $1 < \lambda_c < 2$; numerically⁹ $\lambda_c \approx 1.2$. 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 $k \approx 1,2$, 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's⁵ proof of (2). Sigal gets $2Z$ because he uses¹² the

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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 $\epsilon$, there exists an $N_0$ so that for all configurations $\{x_b\}_{b=1}^N$ of $N \geq N_0$ points we have

$$\max_b \left( \sum_{a \neq b} \frac{1}{|x_b - x_a|} - \frac{(1 - \epsilon)N}{|x_b|} \right) \geq 0.$$  \(4)\)

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

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

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

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 $N^{-1} \sum_a \delta(x - x_a)$ so that (5) fails.

(5) is proven as follows: First consider the case where $\phi_\rho$ is continuous, $0 \notin \text{supp}(\rho)$, and $\text{supp}(\rho)$ 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 $\infty$ and is harmonic outside suppp, $f$ is positive at some points arbitrarily close to suppp and so by continuity of $\phi_\rho$, $f$ is nonnegative somewhere on suppp. Given the special case, one obtains (5) in general by using a theorem of Choquet$^{15}$. Given any finite positive charge density $\rho$, and given $\epsilon$, one can find $K$ compact so that the charge outside $K$ is at most $\epsilon$ and so that the restriction of $\rho$ 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 $R^{2N}$ obeying the following: (i) $j_0$ is symmetric in $X = (x_1, \ldots, x_N)$ and $j_a$ ($a \neq 0$) are symmetric in $[x_b]_{b \neq a}$. (ii) $j_0$ is supported in the region where $|X|_\infty = \max_a |x_a| < R$. (iii) $j_a$ is supported in the region where

$$|X|_\infty \geq (1 - \epsilon)R.$$  \(6)\)

$$\sum_{b \neq a} \frac{1}{|x_b - x_a|} \geq N(1 - \epsilon) |x_a|.$$  \(7)\)

(iv) One has the estimate, for the $3N$-dimensional gradients,$^{16}$

$$\sum_{a=0}^N (\nabla_jj_a)^2(X) \leq CN^{12}R^{-1}|X|_\infty^{-1}.$$  \(8)\)

(v) One has $\sum_{a=0}^N |j_a(X)|^2 = 1$ for all $X$. To be precise, for any $\epsilon$, 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 $\epsilon$ and not on $N$ or $R$.

To prove (3), we use the localization formula$^{17}$

$$H(N,Z) = \sum_{a=0}^N j_a^2 - \sum_{a=0}^N (\nabla_jj_a)^2.$$  \(9)\)

(3) will follow if we prove that if we choose $R$ suitably and $N \gg Z(1 + \epsilon')$, $Z$ large, then for each $a$
which is positive for $N \gg Z \{(1 - e)^{-1} + \epsilon\}$ and $Z$ large (for any fixed $\alpha$). A similar argument applies for any $a \neq 0$.

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

$$\tilde{H}(N, Z) \geq -C_1 Z \sqrt[4]{3/3}.$$

Since $|x_i - x_j| \leq 2|x_i|\leq 2R$ on the support of $j_0$, rep $\geq \frac{1}{4} N(N - 1) R^{-1}$. Thus for $a = 0$

$$\text{left-hand side of (8)} \geq \int_0^1 \left[ - C_1 Z \sqrt[4]{3/3} + C_2 N^{7/3}\alpha^{-1} - C_3 (1 - e)^{-1}\alpha^{-2} N^{7/6}\right]$$

which is positive [and so larger than the right-hand side of (8)] if $N \gg Z$ and $\alpha$ 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 from becoming so great that the quantum corrections [as represented, for example, by the size of the “localization error,” $\sum_{j} |j\langle x_j |j\rangle^2|$ overcome the basic classical potential theory result Eq. (4).

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1E. H. Lieb, I. Sigal, B. Simon, and W. Thirring, to be published.
2We 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.
3We have in mind the Pauli principle with two spin states. The number of spin states (so long as it is a fixed number) does not affect the truth of Eq. (3).
4The minimum without any symmetry restriction occurs on a totally symmetric state, so that we could just as well view $E_0(N, Z)$ as a Bose energy.
7I. Sigal, to be published.
12He also needs a method to control quantum corrections. This method is discussed later.
13The support of $\rho$, denoted by supp $\rho$, is just those points $x$ where an arbitrarily small ball about $x$ has some charge.
14To be sure the limit exists and is not a delta function or zero, one may have to scale the $x_i$ in an $N$-dependent way.
16Since $|x_i| \approx |x_i|/\alpha$ for all $\alpha$, we can replace the right-hand side of (6) by $\alpha^{1/2} R^{-1/3}|x_i|^{-1}$. Since the gradients are all zero if $|x_i| < (1 - e) R$, we can replace the right-hand side of (6) also by $(1 - e)^{-1}|x_i|^{-1} N^{1/2} R^{-2}$.
17This formula is easy to prove by expanding $\sum_{j} \langle j_0,j_0 | H \rangle$. 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.
18This is precisely the scaling for Thomas-Fermi and for the real atomic system; see E. Lieb and B. Simon, Adv. Math. 23, 22 (1977).
19For bosons, the “electron” density collapses as $Z^{-1}$, not $Z^{-1/3}$; see Ref. 9.