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Electronic Density at the Nucleus. On a Conjecture of Lieb – Draft of the Manuscript of the Talk in St. Jean de Monts, June 1994

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Abstract

In the this talk we outline how to bound the atomic and molecular ground state density at the nucleus by a certain explicitly given positive constant times the third power of the nuclear charge. We discuss the relation of this result with a conjecture of Lieb, the "The Strong Scott Conjecture". We will indicate how the proof generalizes to proof this conjecture in a weak sense.

1 Introduction

The Hamiltonian of an atom of N electrons with q spin states each and a fixed nucleus of charge Z located at the origin is given by

$$H_{N,Z} = \sum_{\nu=1}^{N} \left(-\Delta_\nu - \frac{Z}{|\mathfrak{r}_\nu|} \right) + \sum_{\substack{\mu,\nu=1 \\ \mu<\nu}}^{N} \frac{1}{|\mathfrak{r}_\mu - \mathfrak{r}_\nu|} \tag{1}$$

self-adjointly realized in $\bigwedge_{\nu=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$. Furthermore we write ψ for an eigenfunction that belongs to the bottom of the spectrum of $H_{N,Z}$, i.e., a ground state eigenfunction and

$$\begin{aligned} &\rho_\psi(\mathfrak{r}) \\ &= \sum_{\sigma_1,\ldots,\sigma_N=1}^{q} \sum_{\nu=1}^{N} \int_{\mathbb{R}^{3(N-1)}} |\psi(\mathfrak{r}_1,\sigma_1;\ldots;\mathfrak{r}_{\nu-1},\sigma_{\nu-1};\mathfrak{r},\sigma_\nu;\mathfrak{r}_{\nu+1},\sigma_{\nu+1};\ldots;\mathfrak{r}_N,\sigma_N)|^2 \\ &\quad d\mathfrak{r}_1\ldots d\mathfrak{r}_{\nu-1} d\mathfrak{r}_{\nu+1}\ldots d\mathfrak{r}_N \end{aligned} \tag{2}$$

for the corresponding density.

A quantity of particular interest is the ground state density $\rho_\psi(0)$ at the nucleus. Recently Narnhofer [4] argued that one might expect for an atom $\rho_\psi(0) = O(Z^3)$. In this talk we will outline a proof of this conjecture. In fact we can prove

Theorem 1 *Let ρ_ψ be a ground state density of $H_{N,Z}$ and $N = Z$, then*

$$\rho_\psi(0) \leq \frac{\pi}{48} q Z^3 + const\ Z^{161/54}.$$

This value is not in disagreement with Lieb's Strong Scott Conjecture [3] which is actually older and stronger than Narnhofer's: according to Lieb the scaled atomic density $\rho_\psi(\mathfrak{r}/Z)/Z^3$ should converge to the corresponding quantity of the bare Schrödinger operator $H_{N,Z}^0$ which equals $H_{N,Z}$ except for the omission of the second sum, the electron-electron interaction. If one assumes this convergence to be pointwise this would predict $\rho_\psi(0) = \frac{\zeta(3)}{8\pi} q Z^3 + o(Z^3)$ (Lieb [3], (7.35)). We are now explicitly able to see that our theorem does support this conjecture, since $\frac{\pi}{48}$ which is about 0.065 is bigger than $\frac{\zeta(3)}{8\pi}$ which is about 0.048. On the other hand it shows that our estimate is rather good – we loose only using (3) – but presumably not yet sharp.

To conclude the introduction we note that Solovej announced recently that the ground state energy of molecules having a certain reflection symmetry, e.g., molecules consisting of two equal atoms, is equal to the sum of ground state energies of the corresponding atoms up to order $o(Z^{5/3})$. Given this fact our proof immediately generalizes to such molecules.

2 Outline of the Proof

The starting point of our proof is the inequality

$$\rho_\psi(0) \leq \frac{Z}{4\pi} \int_{\mathbb{R}^3} \frac{\rho_\psi(\mathfrak{r})}{|\mathfrak{r}|^2} d\mathfrak{r} \tag{3}$$

of Hoffmann-Ostenhof et al. [1]. The evaluation of the right hand side will be done by controlling the ground state energy up to second order in Z which in turn requires control of the ground states on distances Z^{-1} and $Z^{-1/3}$ from the origin. To do so we pursue a strategy similar to [6].

For the sake of notational simplicity we formulate our theorem and this outline of the proof for the most canonical case only, namely neutral atoms, i.e., $N = Z$.

First we define for $\epsilon \in [0, \frac{1}{4})$

$$H^\epsilon_{N,Z} = H_{N,Z} - \sum_{\nu=1}^{N} \frac{\epsilon}{|\mathfrak{r}_\nu|^2}.$$

With this notation we may write for positive ϵ

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{\rho_\psi(\mathfrak{r})}{|\mathfrak{r}|^2} d\mathfrak{r} &= \frac{1}{\epsilon}\left[(\psi, H_{N,Z}\psi) - (\psi, H^\epsilon_{N,Z}\psi)\right] \\ &\leq \frac{1}{\epsilon}\left[E_{TF}(N,Z) + \frac{q}{8}Z^2 - \inf\sigma(H^\epsilon_{N,Z}) + const Z^{47/24}\right] \end{aligned} \tag{4}$$

where we use [5], Theorem 1. (We denote by $E_{TF}(N, Z)$ the infimum of the Thomas-Fermi functional

$$\mathcal{E}_{TF}(\rho) = \int_{\mathbb{R}^3} \frac{3}{5}\gamma\rho(\mathfrak{r})^{5/3} - \frac{Z}{|\mathfrak{r}|}\rho(\mathfrak{r})d\mathfrak{r} + D(\rho,\rho)$$

on $\mathcal{I} = \{\rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3) | \rho \geq 0,\ \int \rho \leq N\}$ where $\gamma = (6\pi^2/q)^{2/3}$ and

$$D(\sigma, \rho) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\overline{\sigma(\mathfrak{r})}\rho(\mathfrak{s})}{|\mathfrak{r}-\mathfrak{s}|} d\mathfrak{r} d\mathfrak{s}$$

is the usual Coulomb scalar product.)

To proceed we need to estimate the infimum $\inf \sigma(H^\epsilon_{N,Z})$ of the spectrum of $H^\epsilon_{N,Z}$ from below. To this end we use Lieb's inequality on correlation (Lieb [2]) and the Lieb-Thirring inequality to obtain

$$\begin{aligned} & \inf \sigma(H^\epsilon_{N,Z}) \\ \geq \ & \inf \sigma(\textstyle\sum_{\nu=1}^N \underbrace{1 \otimes ... \otimes 1}_{\nu-1 \ factors} \otimes h^{\epsilon,TF}_{N,Z} \otimes \underbrace{1 \otimes ... \otimes 1}_{N-\nu \ factors}) - D(\rho_{TF}, \rho_{TF}) - const Z^{5/3} \end{aligned} \quad (5)$$

where

$$h^{\epsilon,TF}_{N,Z} = -\Delta - \frac{\epsilon}{|.|^2} - \frac{Z}{|.|} + \rho_{TF} \star \frac{1}{|.|}. \quad (6)$$

The first term on the right hand side can be estimated by the sum of all negative eigenvalues of (6) which are in turn given by

$$\begin{aligned} h^\epsilon_l \varphi_{n,l}(r) &:= \left(-\frac{d^2}{dr^2} + \frac{l(l+1)-\epsilon}{r^2} - \frac{Z}{r} + \int_0^\infty \frac{\sigma(r')}{\max\{r,r'\}} dr' \right) \varphi_{n,l}(r) \\ &= \epsilon^Z_{n,l} \varphi_{n,l}(r) \end{aligned}$$

($l = 0, 1, 2, ...$) using separation of variables. Here $\sigma(r) = 4\pi r^2 \rho_{TF}(\mathfrak{r})$ for $r = |\mathfrak{r}|$. (Note that ρ_{TF} is spherically symmetric.)

We treat small l, i.e., $l < L = [Z^{4/27}]$, and large l, i.e., $l \geq L$, differently:

Small l: we estimate h^ϵ_l from below by

$$-\frac{d^2}{dr^2} + \frac{l(l+1)-\epsilon}{r^2} - \frac{Z}{r}.$$

The eigenvalues of this operator are

$$-\frac{Z^2}{4(\lambda_{l,\epsilon} + n)^2}$$

where $n = 1, 2, ...$ and $\lambda_{l,\epsilon}$ is the positive root of $\lambda(\lambda+1) = l(l+1) - \epsilon$; more explicitly $\lambda_{l,\epsilon} = \sqrt{(l+\frac{1}{2})^2 - \epsilon} - \frac{1}{2}$. Thus

$$
\begin{aligned}
&-\sum_{l=0}^{L-1} q(2l+1)\,\mathrm{tr}\, h_l^\epsilon \geq -\sum_{l=0}^{L-1} q(2l+1) \sum_{n=1}^{\infty} \frac{Z^2}{4(\lambda_{l,\epsilon}+n)^2} \\
= \; & -q\frac{Z^2}{4} \sum_{l=0}^{L-1} q(2l+1) \sum_{n=1}^{\infty} \left(\frac{1}{(l+n)^2} + \frac{\epsilon}{\left(\sqrt{(l+\frac{1}{2})^2} - \frac{1}{2} + n\right)^3 \sqrt{(l+\frac{1}{2})^2}} \right. \\
& \left. + \frac{\epsilon^2}{4} \frac{3((l+\frac{1}{2})^2 - \xi)^{1/2} + \sqrt{(l+\frac{1}{2})^2 - \xi} - \frac{1}{2} + n}{(\sqrt{(l+\frac{1}{2})^2 - \xi} - \frac{1}{2} + n)^4((l+\frac{1}{2})^2 - \xi)^{3/2}} \right)
\end{aligned}
$$

for some ξ with $0 < \xi < \epsilon$. We obtain a lower bound by replacing ξ by any number bigger or equal to ϵ and smaller than $1/4$.

Note that the sum over n is convergent for each term separately. Moreover, for the last two terms the summation over l when extended to infinity is convergent, too. The term of interest is the one that is homogeneous of degree one in ϵ:

$$
\begin{aligned}
& -q\frac{Z^2}{2} \sum_{l=0}^{L-1} \sum_{n=1}^{\infty} \frac{\epsilon}{(l+n)^3} \geq -q\frac{Z^2}{2} \sum_{l=0}^{\infty} \sum_{n=1}^{\infty} \frac{\epsilon}{(l+n)^3} \\
= \; & -q\frac{Z^2}{2} \sum_{\mu=1}^{\infty} \frac{\epsilon}{\mu^2} = -\frac{\pi^2}{12} q Z^2 \epsilon. \qquad (7)
\end{aligned}
$$

Large l: we follow the treatment in [6] which yields

$$
\sum_{l=L}^{\infty} q(2l+1)\,\mathrm{tr}\, h_l^\epsilon = \sum_{l=L}^{\infty} q(2l+1)\,\mathrm{tr}\, h_l^0 + O(Z^{53/27}) \qquad (8)
$$

uniformly in ϵ.

Summation over l analogously to [6] yields

$$
\inf \sigma(H_{N,Z}^\epsilon) \geq E_{TF}(N,Z) + \left(\frac{1}{8} - \frac{\pi^2}{12}\right) q Z^2 \epsilon - const \left(Z^2 \epsilon^2 + Z^{53/27}\right). \qquad (9)
$$

Picking now $\epsilon = Z^{-\frac{1}{54}}$ and putting together (3), (4), and (9) yields the desired result.

3 Some Remarks on the "Strong Scott Conjecture" in a Weak Sense

Our main tool was the estimate of the ground state energy of the modified Hamiltonian $H^{\epsilon}_{N,Z}$ where added a $Z^2\frac{1}{(Zr)^2}$-term to the original Schrödinger operator. Instead of this term we may add a function $Z^2U(Zr)$ where U is, e.g., any $C_0^{\infty}(\mathbb{R}_+)$. The estimates for large l go through unchanged and the explicit calculation for small l may be substituted by first order perturbation theory. In this way one can show that the scaled ground state density does indeed converge to hydrogenic density weakly. This is part of an ongoing investigation with A. Iantchenko and E.H. Lieb.

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