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On the Leading Correction of the Statistical Atom: Lower Bound.

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Abstract. – It is shown that the quantum-mechanical ground-state energy of an atom with nuclear charge Z can be bounded from below by the sum of the Thomas-Fermi energy of the problem plus $(q/8)Z^2$ plus terms of lower order.

Given the Hamiltonian of N electrons having q spin states each moving in the field of a nucleus of charge Z

$$H = \sum_{i=1}^{N} \left(-\Delta_i - \frac{Z}{|\mathbf{r}_i|} \right) + \sum_{\substack{i,j=1 \\ i<j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

as self-adjoint realization on $\bigwedge_{i=1}^{N} (L^2(\boldsymbol{R}^3) \otimes \boldsymbol{C}^q)$, we are interested in a lower bound on the ground-state energy $E_Q(Z, N)$ of H that has the behaviour conjectured by Scott:

Theorem 1:

$$E_Q(Z, Z) \geq Z^{7/3} E_{\mathrm{TF}}(1, 1) + \frac{q}{8} Z^2 + o(Z^2), \tag{2}$$

where $E_{\mathrm{TF}}(Z, N)$ *is the Thomas-Fermi energy of the above Hamiltonian.*

This result was claimed in Hughes' thesis [1]. However, doubts were raised on the conclusiveness of the proof, since it appears in a rather rough formulation, in particular some of his «theorems» may be formulated more clearly and more generally, some of the proofs contain gaps, and some of them are not correct. Our main result is a correct proof of the above theorem. However, in some sense, our work refutes the criticism concerning Hughes' work: it turns out that his idea is essentially correct, since we may follow the general strategy clarifying some cryptic points, giving a more concise treatment at other points, and strengthening some of his results.—We may remark that the motivation for this work stems from the fact that the corresponding upper bound was obtained in [2, 3] thus, given the validity of Hughes' result, settling Scott's conjecture.

The strategy of the proof (see [4] for details) is as follows: in the first step—following an old idea of Slater [5]—the full N-particle Hamiltonian H is bounded by an effective one-particle Hamiltonian H_{eff} with exchange hole:

$$H \geq H_{\text{eff}} = \sum_{i=1}^{N} \left(-\Delta_i - \frac{Z}{|x_i|} + \chi(x_i) \right) - \frac{1}{2} \int \int \frac{\rho_{\text{TF}}(x)\rho_{\text{TF}}(y)}{|x-y|} \mathrm{d}^3x \, \mathrm{d}^3y \,, \tag{3}$$

where ρ_{TF} is the Thomas-Fermi density of the system,

$$\chi(x) = \int_{|y-x| > R(x)} \frac{\rho_{\text{TF}}(x)}{|x-y|} \mathrm{d}^3y + \frac{1}{2R(x)} \,,$$

and $R(x)$ is the radius of the ball centred at x that contains charge one, *i.e.*

$$\int_{|x-y| < R(x)} \rho_{\text{TF}}(y) \, \mathrm{d}^3y = 1 \,.$$

This bound is essentially due to Lieb [6].

In the second step one shows that the exchange hole may be dropped in all expressions so that χ becomes just the classical potential generated by the Thomas-Fermi density. This may be done without paying a high price, *i.e.* the difference of the corresponding ground-state energies is only of order $O(Z^{5/3})$. Furthermore, the resulting one-particle Hamiltonian has spherical symmetric potential. Thus a partial-wave analysis is possible.

In the third step the problem is decomposed into the various angular-momentum channels and the low l-channels ($l < Z^{1/9}$) are treated by estimating the screened potential by the bare Coulomb potential from below and calculating the energies explicitly. This reflects the fact that the nucleus-electron interaction dominates the electron-electron interaction in the vicinity of the nucleus (see [3, 2]).

In the fourth step the radial equations are rescaled for large angular momenta ($r \to bZ^{1/3} r$, $b = (2q/3\pi)^{2/3}$), and the problem is turned into a quasi-classical one where $Z^{-1/3}$ plays the role of the quasi-classical expansion parameter. The scaled radial equation reads

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{Z^{2/3}}{b} \left(\frac{b}{Z^{2/3}} \frac{l(l+1)}{r^2} - \frac{y(r)}{r} \right) \right] \psi = E\psi \,, \tag{4}$$

where y is the Thomas-Fermi function, *i.e.* the solution of $y''(r) = y(r)^{3/2} r^{-1/2}$ with boundary conditions $y(0) = 1$, $y(\infty) = 0$.

In the fifth step it is shown that the phase space volume of the $(k+1)$-th eigenvalue E_k of a high-angular-momentum radial equation generates a quasi-classical phase space volume

$$G(E_k) = \int_{-\infty}^{\infty} \mathrm{d}p \int_{0}^{\infty} \mathrm{d}q \, \theta(E_k - H_l(p, q))$$

that is about $2\pi(k + 1/2)$. Here H_l is the classical Hamiltonian function corresponding to the radial equation (4). The main result of this step is to give a definite error bound for the deviation of $G(E_k)$ from the Bohr-Sommerfeld quantum number. This is done by treating the low-lying states directly through a harmonic-oscillator approximation and making rigorous a WKB-analysis for the higher states in each channel.

In a sixth and last step the error bounds on the quantum numbers obtained in the fifth step are transformed into bounds on eigenvalues. This may be done by obtaining several properties of the phase space volume as function of the energy.

Finally, all estimates for the various channels are put together by using a Poisson summation as in [2, 7] or, alternatively, by a convexity argument. This yields the Thomas-Fermi energy plus the desired Scott correction.

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