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The Scott Correction and the Quasi-classical Limit

Barry Simon[1]

The Scott correction is the second term in a large Z asymptotic expansion of the total binding energy of an atom with nuclear charge Z. The atom is a complicated system with multiparticle correlations among the electrons. Nevertheless, the proof of the Scott correction can be reduced to the study of the semi-classical limit of a one-body system where the electron-electron interaction is replaced by an averaged self-consistent potential.

This reduction is more or less well-known to the experts in the field, so this paper is unabashedly pedagogic. However, previous discussions have so intertwined the reduction to the classical limit with the control of that limit that the simplicity of the reduction has been hidden.

Basically, we will compare a quantum Hamiltonian, H, with a quasi-classical Hamiltonian, H^{QC}, with responding energies E and E^{QC}, and ground states Ψ and Ψ^{QC} and we will show (modulo a fact about the quasi-classical limit) that:

$$E \leq (\Psi^{QC}, H\Psi^{QC}) = E^{QC} + O(Z^{5/3})$$

$$E^{QC} \leq (\Psi, H^{QC}\Psi) = E + O(Z^{5/3})$$

where $E \sim Z^{7/3}$ and the Scott correction is $O(Z^2)$.

To be precise, the N-electron charge Z atomic Hamiltonian acts on $L^2_a\mathbb{R}^{3N}$ by

$$H = \sum_{i=1}^{N}\Big(-\Delta_i - \frac{Z}{|x_i|}\Big) + \sum_{i<j}\frac{1}{|x_i - x_j|} \tag{1}$$

where a point in R^{3N} is written as $(x_1, \ldots, x_N)$ with $x_i \in \mathbb{R}^3$ and L^2_a means those functions $\Psi(x_1, \ldots, x_N)$ in L^2 which are antisymmetric under interchanges of coordinates.

The Hamiltonian H has several simplifications. We ignore electron spin which affects the statistics. It can be easily accommodated by changing the

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constants in the discussion below. We ignore corrections due to a finite nuclear mass. We ignore relativistic corrections.

What will concern us is the total binding energy:

$$E(N,Z) \equiv \inf_{\Psi}(\Psi, H\Psi) = \inf \operatorname{spec}(H)$$

and

$$E(Z) \equiv E(N=Z,Z)$$

We will henceforth take $N = Z$ without further comment.

To describe the quasi-classical problems, we describe the Thomas-Fermi model (invented by Thomas [16] and Fermi [3]). This posits an electron gas with density $\rho(x)$ obeying

$$\int \rho(x)dx = Z \tag{2a}$$

and energy given by

$$\mathcal{E}_{TF}(\rho) = d\int \rho^{5/3}(x)dx - \int \rho(x)|x|^{-1}Z + \frac{1}{2}\int \frac{\rho(x)\rho(y)}{|x-y|} \tag{2b}$$

where d is the universal constant $\frac{3}{5}\left(\frac{3}{4\pi}\right)^{5/3}$ defined so that the sum of the first N eigenvalues of the Dirichlet Laplacian in a cubic region of volume V is asymptotic as $N \to \infty$ to

$$dV(N/V)^{5/3}$$

Thus, the first term is a quasi-classical limit of the kinetic energy term in (1) and the other terms are clearly the nuclear attraction and electron-electron repulsion.

According to Lieb-Simon [7,8], there is a unique ρ, call it ρ_Z^{TF}, minimizing

$$E^{TF}(Z) = \inf\{\mathcal{E}_{TF}(\rho) \,|\, (2a) \text{ holds; } \rho \in L^1 \cap L^{5/3}\}$$

and moreover,

$$E(Z)/E^{TF}(Z) \to 1 \tag{3}$$

as $Z \to \infty$.

It is fairly easy to determine the Z dependence of TF theory:

$$\rho_Z^{TF}(x) = Z^2\rho_1^{TF}(Z^{1/3}x)$$

$$E^{TF}(Z) = Z^{7/3}E^{TF}(1) \equiv Z^{7/3}e_{TF}$$

In what follows, a critical role will be played by the TF potential

$$\varphi_Z^{TF}(x) \equiv \frac{Z}{|x|} - \int |x-y|^{-1}\rho_Z^{TF}(y)dy$$

Note that the Euler-Lagrange equations for minimizing $\mathcal{E}$ read

$$\frac{5}{3}d\rho^{2/3} = \varphi \tag{4}$$

Equation (3) says that $E(Z) \sim e_{TF}Z^{7/3}$ as $Z \to \infty$. There has been work on the next two terms in the asympototic series. Scott [11] looked at the situation where the electron repulsion is dropped and the N-body problem reduces to a one-body problem (Hydrogen atom), which can be exactly solved. He noted the leading corrections to the Thomas-Fermi analog for this model of order Z^2 came from the inner shells where the electron repulsion shouldn't matter; so he posited that the $O(Z^2)$ term was the same for the true atomic case. That

$$E(Z) = e_{TF}Z^{7/3} + e_{\text{Scott}}Z^2 + o(Z^2) \tag{5}$$

was proven recently by Hughes [4] and Siedentop-Weikard [13]. A recent preprint of Ivrii-Sigal [5] provides a new proof and extends the result to the molecular case.

Fefferman-Seco [2] have announced control of the $Z^{5/3}$ term, which has a contribution due to electron exchange (computed originally by Dirac [1]) and one from the higher order classical limit (computed by Schwinger [10]). Actually Fefferman-Seco study $\inf_N E(Z, N)$, not $E(Z)$ but they should be the same to $O(Z^{5/3})$.

These proofs are all over 100 pages and one of our goals here is to hope for a proof of the Scott correction on one foot.

The quasi-classical problem we will relate to H is given by

$$H^{QC} = \sum_{i=1}^{Z}\left(-\Delta_i - \varphi_Z^{TF}(x)\right) - \frac{1}{2}\int \frac{\rho_Z^{TF}(x)\rho_Z^{TF}(y)}{|x-y|}\,d^3x\,d^3y \tag{6}$$

The final term in H^{QC} is a number (constant), which needs to be there because φ_Z overcounts the energy of interaction. In fact, the constant is exactly ([8]),

$$-\frac{1}{3}e_{TF}Z^{7/3}$$

By scaling $\varphi_Z^{TF} = Z^{4/3}\varphi_1^{TF}(Z^{1/2}x)$ so $-\Delta_i - \varphi_Z^{TF}(t)$ is unitarily equivalent to $Z^{4/3}h_Z^{QC}$ where

$$h_Z^{QC} = -Z^{-2/3}\Delta - \varphi_1^{TF}(x)$$

Thus, h^{QC} is a one-body Hamiltonian with $\hbar = Z^{-1/3}$ and $Z \to \infty$ is the $\hbar \to 0$ limit. Let

$$e_1^{QC}(Z) \le e_2^{QC}(Z) \le \cdots$$

be the eigenvalues of h_Z^{QC} with eigenfunction $\eta_1^{QC;Z}$, $\eta_2^{QC;Z}$, ... Then

$$E^{QC}(Z) \equiv \inf \operatorname{spec}(H^{QC}) = Z^{4/3} \sum_{i=1}^{Z} e_i^{QC}(Z) - \frac{1}{3} e_{TF} Z^{7/3}$$

and the one electron density for H^{QC} is

$$\rho_Z^{QC}(x) = Z \sum_{i=1}^{Z} \left| \eta_i^{QC;Z}(Z^{1/3}x) \right|^2$$

Our goal is to prove:

THEOREM.

$$\left| E(Z) - E^{QC}(Z) \right| \leq cZ^{5/3} + \frac{1}{2} \int \frac{\delta\rho(x)\delta\rho(y)}{|x-y|} \, d^3x \, d^3y$$

where

$$\delta\rho(x) = \left[\rho_Z^{TF}(x) - \rho_Z^{QC}(x) \right]$$

The point is that the $\delta\rho$ Coulomb energy is

$$Z^{7/3} \frac{1}{2} \int \frac{\delta\tilde{\rho}(x)\, \delta\tilde{\rho}(y)}{|x-y|}$$

with

$$\delta\tilde{\rho} = \left[\frac{1}{Z} \sum_{i=1}^{Z} |\eta_i(x)|^2 \right] - \rho_1^{TF}(x)$$

The leading order for $\frac{1}{Z} \sum \eta_i^2$ is ρ_1 by (4), so good control of the classical limit should imply that $\delta\tilde{\rho} \sim Z^{-1/3}$ so one expects that

$$\frac{1}{2} \int \frac{\delta\rho(x)\delta\rho(y)}{|x-y|} = O(Z^{5/3}) \tag{7}$$

or less (Seco [12] tells us that it is less). Thus, the Scott correction (5) would follow from control of E^{QC}, a one-body problem, to $O(Z^2)$ and a proof of (7).

We now turn to the proof of the Theorem. We will show that

$$E(Z) \leq E^{QC}(Z) + \frac{1}{2} \int \frac{\delta\rho(x)\delta\rho(y)}{|x-y|} \, d^3x \, d^3y \tag{8a}$$

and

$$E^{QC}(Z) \leq E(Z) + cZ^{5/3} \tag{8b}$$

To prove (8a), let Ψ^{QC} be the ground state of H^{QC}, so

$$\Psi^{QC}(x_1,\ldots,x_N) = (Z!)^{-1/2}\det(\xi_i^{QC}(x_j))$$

with $\xi_i^{QC}(x) = Z^{1/2}\eta_i^{QC;Z}(Z^{1/3}x)$. Then

$$\begin{aligned} E(Z) &= (\Psi^{QC}, H\Psi^{QC}) \\ &= E^{QC}(Z) + (\Psi^{QC}, (H - H^{QC})\Psi^{QC}) \end{aligned}$$

Now $H - H^{QC}$ has three terms:

(a) $(\Psi^{QC}, \sum_i [\varphi_Z^{TF}(x_i) - Z|x_i|^{-1}]\Psi^{QC}) = -\int \frac{\rho^{TF}(y)\rho^{QC}(x)}{|x-y|}\, d^3x\, d^3y$ since $(\Psi^{QC}, (\sum_i W(x_i))\Psi^{QC}) = \int W(x)\rho^{QC}(x)dx$ for any W.

(b) $(\Psi^{QC}, \sum_{i<j} \frac{1}{|x_i - x_j|}\Psi^{QC}) \equiv \frac{1}{2}\int \frac{\rho^{QC}(x)\rho^{QC}(y)}{|x-y|}\, d^3x\, d^3y - Ex(\Psi^{QC})$ where the exchange energy, $Ex(\Psi)$ is defined for any Ψ as:

$$Ex(\Psi) = -\left(\Psi, \sum_{i<j} \frac{1}{|x_i - x_j|}\Psi\right) + \frac{1}{2}\int \frac{\rho_\Psi(x)\rho_\Psi(y)}{|x-y|}\, d^3x\, d^3y \qquad (9)$$

where

$$\rho_\Psi(x) = Z\int |\Psi(x, x_2, \ldots, x_N)|^2 d^3x_2 \ldots d^3x_N$$

is the one particle density. For determinantal Ψ one can compute $Ex(\Psi)$ explicitly and see that

$$Ex(\Psi) \geq 0$$

using the positive definiteness of the kernel $|x-y|^{-1}$. Thus, this term is $\leq \int \frac{\rho^{QC}(x)\rho^{QC}(y)}{|x-y|}\, d^3x\, d^3y$.

(c) The explicit term $\frac{1}{2}\int \frac{\rho^{TF}(x)\rho^{TF}(y)}{|x-y|}\, d^3x\, d^3y$ in the definition of H^{QC}.

Putting these three terms together yields (8a).

To prove (8b), let Ψ be the true ground state of the quantum Hamiltonian and let ρ^Q be its one particle density. Then

$$\begin{aligned} E^{QC}(Z) &\equiv (\Psi, H^{QC}\Psi) \\ &= E(Z) + (\Psi, (H^{QC} - H)\Psi) \end{aligned}$$

The calculation of the second term is identical to the one done for $(\Psi^{QC}, (H - H^{QC})\Psi^{QC})$, viz

$$(\Psi, (H^{QC} - H)\Psi) = Ex(\Psi) - \frac{1}{2}\int \frac{(\delta_1\rho)(x)(\delta_1\rho)(y)}{|x-y|}\, d^3x\, d^3y$$

where

$$(\delta_1\rho)(x) = \rho^Q(x) - \rho^{TF}(x)$$

By the positive definiteness of $|x-y|^{-1}$, the second term is negative. Now we need to pull a rabbit out of our hat, namely, an inequality of Lieb [6]:

$$Ex(\Psi) \leq c\int \rho_\Psi(x)^{4/3} d^3x$$

for any Ψ. Thus, by the Schwartz inequality:

$$E^{QC}(Z) \leq E(Z) + c\Big(\int \rho(x) d^3x\Big)^{1/2}\Big(\int \rho^{5/3}(x) d^3x\Big)^{1/2}$$

Now by definition of ρ:

$$\int \rho(x) d^3x = Z$$

and by the Lieb-Thirring inequality and the virial theorem:

$$\begin{aligned}\int \rho^{5/3}(x) d^3x &\leq c(\Psi, -\Delta\Psi)\\ &\leq c[-E(Z)]\\ &\leq dZ^{7/3}\end{aligned}$$

by an elementary estimate on the quantum binding energy (for example, drop the Coulomb repulsion and use Hydrogen eigenvalues). Thus

$$E^{QC}(Z) \leq E(Z) + c'Z^{1/2}(Z^{7/3})^{1/2} = E(Z) + c'Z^{5/3}$$

proving (8b) and so the Theorem. □

We close with several remarks about the proof:

(1) If one proves that $E - E^{QC} = O(Z)^{5/3}$ (i.e., if one proves that $\int \frac{(\delta\rho)(x)(\delta\rho)(y)}{|x-y|}\, d^3x\, d^3y = O(Z^{5/3})$), then the proof shows that

$$\int \frac{(\delta_1\rho)(x)(\delta_1\rho)(y)}{|x-y|}\, d^3x\, d^3y = O(Z^{5/3})$$

so we get some control on the approach of ρ^Q to ρ^{TF}.

(2) To use these ideas to go to the $Z^{5/3}$ term, we would need to show that the $\delta\rho$ Coulomb energies are $o(Z^{5/3})$, control E^{QC} to $O(Z^{5/3})$ and get control of $Ex(\Psi)$ and $Ex(\Psi^{QC})$. Control of $Ex(\Psi^{QC})$ should be possible as Dirac did his calculation. $Ex(\Psi)$ is a full many-body question.

(3) To prove the Lieb-Simon result on leading order for $E(Z)$, one only proves some leading order results on the quasi-classical limit. For energy, this can be done via path integrals [14], coherent states [15] or Dirichlet-Neumann bracketing [9]. The $\delta\rho$ Coulomb energy should be accessible via L^1 bounds and local L^q convergence of ρ.

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