THE GROUND STATE ENERGY OF HEAVY ATOMS

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ABSTRACT. We review results on the asymptotic behavior of the groundstate energy and the reduced one-particle ground state density of large atoms.

1. MODELS OF AN ATOM

We will review the description of large atoms, in particular the asymptotic behavior of the ground state energy and the ground state density. This can be done in the context of various models which – heuristically – should describe the atom – when compared with experimental values of these quantities – to increasing order of correctness. Some of those models for N electrons are discussed here. For simplicity we will focus on the one center case, i.e., the external field is generated by a nucleus of charge Z although some of the results are also true for molecules. Moreover, we will concentrate on the most prominent case, namely neutral atoms, i.e., $N = Z$.

Thomas-Fermi: The Thomas-Fermi energy $E_{\mathrm{TF}}(N, Z)$ of N electrons in the field of a nucleus of charge Z is the infimum of the Thomas-Fermi functional (Lenz [37])

$$\mathcal{E}_{\mathrm{TF}}(\rho) := \int_{\mathbb{R}^3} \left(\frac{3}{10} \left(3\pi^2\right)^{2/3} \rho(x)^{5/3} - \frac{Z}{|x|} \right) \mathrm{d}x + D[\rho]$$

where

$$D[\rho] := \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y \frac{\rho(x)\rho(y)}{|x - y|}$$

and ρ is taken over all $\rho \geq 0$ in $L^{5/3}(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} \mathrm{d}x\rho(x) \leq N$. Lieb and Simon [38] analyzed the functional mathematically and showed among other facts the existence and uniqueness of a minimizer. From the physical point Gombas [24] offers a classical review.

Schrödinger: The Schrödinger energy is the lowest spectral point $E_S(N, Z) := \inf \sigma(S_{N,Z})$ of the Schrödinger operator

$$S_{N,Z} = \sum_{n=1}^{N} \left(T_n - \frac{Z}{|x_n|} \right) + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}$$

defined by the associated quadratic form on the anti-symmetric Schwartz functions $\bigwedge_{n=1}^{N} \mathfrak{h}$ with $\mathfrak{h} := \mathcal{S}(\mathbb{R}^3 : \mathbb{C}^2)$ (Friedrichs extension). Here $T := p^2/2$ with $p := -i\nabla$.

Chandrasekhar: The Chandrasekhar operator $C_{N,Z,c}$ is motivated by the naive quantization of the classical relativistic Hamiltonian. It can be defined as the Schrödinger operator $S_{N,Z}$ but with the operator of kinetic energy $T := \sqrt{c^2 p^2 + c^4} - c^2$. The additional parameter c is – in physical terms – known as the velocity of light. The Chandrasekhar energy $E_C(N, Z)$ is the lowest spectral point of $C_{N,Z,c}$.

Of course this is only meaningful, if and only if $Z/c \leq 2/\pi$, the necessary and sufficient condition for the form being bounded from below (Kato [35, p. 307], see also Herbst [29] and Chen and Siedentop [7]).

Brown-Ravenhall: The no-pair operator $B_{N,Z,c}$ in the free picture (Sucher [59]), also called Brown-Ravenhall operator (Brown and Ravenhall [6], see also Bethe and Salpeter [5]), can again be defined similarly to Schrödinger operator $S_{N,Z}$, however, with

$$T := D_{0,c} := c\boldsymbol{\alpha} \cdot p + \beta c^2 - c^2$$

and one-particle states in $\mathfrak{h} = \chi_{\mathbb{R}_+}(D_{0,c})(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4))$ which intuitively is interpreted as the orthogonal space of the Dirac sea – here of the free Dirac operator $D_{0,c}$ – which is not accessible to electrons, i.e., poetically speaking the electrons are the vapor over the free Dirac sea. The Brown-Ravenhall energy $E_B(N, Z)$ is the lowest spectral point of $B_{N,Z,c}$.

Again, as in the Chandrasekhar case, this requires a restriction of the allowed coupling constant. For boundedness from below $Z/c \leq 2/(2/\pi + \pi/2)$ is necessary and sufficient (Evans et al [10], see also Tix [61, 62]).

Furry & Oppenheimer: The no-pair operator $F_{N,Z,c}$ in the Furry picture [59], for short the Furry operator, is defined as the Brown-Ravenhall operator, however, with one particle states $\mathfrak{h} = \Lambda_{Z,c}(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4))$ where $\Lambda_{Z,c}$ is the spectral projection of the Coulomb Dirac operator

$$D_{Z,c} := c\boldsymbol{\alpha} \cdot \tfrac{1}{i}\nabla + c^2(\beta - 1) - \frac{Z}{|x|}$$

to the positive spectral subspace, i.e., $\Lambda_{Z,c} := \chi_{(0,\infty)}(D_{Z,c})$. In other words, the Furry electrons are the vapor over the Dirac sea defined as the negative spectral subspace of the one-particle Dirac operator with external potential. – Again there is a natural restriction on the coupling constant, namely $Z/c < 1$.

2. SOME CLASSICAL RESULTS

2.1. Non-Relativistic Hamiltonian.
The classical Hamiltonian was introduced by Schrödinger [45, 46, 44] and solved for $N = 1$. But motivation for taking anti-symmetric states predates these works and goes back to Pauli [33]. However, it was Kato [34] (see also Kato [35]) who showed that $S_{N,Z}$ can be self-adjointly realized in $\bigwedge_{n=1}^{N} L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ and can be viewed as perturbation of the Laplacian.

Shortly after Schrödinger's work it became clear that the hope for an analytical solution of the N-electron problem in quantum mechanics is at least as unrealistic as in classical mechanics. Driven by this insight, Thomas [60] and Fermi [20, 21] saw the necessity of an approximation which describes N electron systems in a simple way; they derived – on a physical level – the Thomas-Fermi theory with the intention to describe the energy and density roughly correct when many particles are involved and the external potential does not change much, i.e., in a certain

sense, the potential would commute locally with the momentum operator. The expectation was that $E_S(Z) \approx E_{\mathrm{TF}}(Z)$. In fact Lieb and Simon [38] showed in their seminal paper published fifty years after Thomas and Fermi that indeed

$$E_S(Z) = E_{\mathrm{TF}}(Z) + o(Z^{7/3}).$$

(Note that we find it convenient to formulate our results for the neutral case only, i.e., $N = Z$. In this case – when no confusion is possible – we tend to drop the index N. Note also that the Thomas-Fermi energy has the simple scaling relation $E_{\mathrm{TF}}(Z) = E_{\mathrm{TF}}(1)Z^{7/3}$.)

Based on the local commutativity assumption it was clear that a correction of the TF-model should come from the electrons close to the attractive singularity. In fact Scott [48] conjectured on this basis the following formula

$$E_S(Z) = E_{\mathrm{TF}}(Z) + \frac{1}{2}Z^2 + o(Z^2)$$

which – was proven another ten years later (Siedentop and Weikard [54, 49, 50, 51, 52] (upper and lower bound) and Hughes [30, 31] (lower bound). The formula has been physically rederived, mathematically reproven and extended by various methods (Bach [1, 2], Ivrii and Sigal [32], Solovej and Spitzer [56], [4]). In fact Fefferman and Seco [16, 17, 18, 11, 19, 14, 12, 13, 15] obtained a three terms asymptotics.

2.2. Relativistic Hamiltonians.

2.3. The Chandrasekhar Energy.
Since states at large distances from the nucleus have – at least intuitively – small kinetic energy, a non-relativistic description should still be appropriate for those states. However, at small distance the electrons are moving much faster. Thus, using a non-relativistic model for large Z atoms is physically inappropriate. Although mathematically possible as mentioned above, it cannot be expected to give physically relevant results. Instead a relativistic description is required. It should influence the electrons close to the nucleus strongly and thus contribute to the Scott correction. Since the relativistic energy is much weaker for large momenta, a lowering of the Scott term should occur. This was predicted by Schwinger [47] based on a heuristic modification of Scott's original observation. In fact, for large Z and $\gamma = Z/c$ fixed and less or equal $2/\pi$ one obtains for the Chandrasekhar ground state

$$(1) \qquad E_C(Z) = E_{\mathrm{TF}}(Z) + (\frac{1}{2} - s_C(\gamma))Z^2 + o(Z^2)$$

where $s_C(Z/c)$ is the sum of the difference of the negative eigenvalues of the operators $p^2/2 - \gamma/|x|$ and $(p^2 + 1)^{1/2} - 1 - \gamma/|x|$, i.e.,

$$(2) \qquad s_C(\gamma) = \mathrm{tr}((S_{1,\gamma})_- - (C_{1,\gamma,1})_-).$$

This result is due to Solovej, Sørensen, and Spitzer [55] and Frank, Siedentop, and Warzel [22].

Note, that this model can be considered as a mathematical warm-up only, since its eigenvalues are – even in the one-particle case – too low compared with the one-particle Dirac eigenvalues. Moreover, it does not even cover the all known elements for the physical values of c and Z.

2.4. **The Energy of the Brown-Ravenhall Operator.** The above general consideration on fast moving inner electrons applies to all relativistic operators, i.e., also for the Brown-Ravenhall operator a lowering of the Scott term is expected. In fact on gets

$$(3) \qquad E_B(Z) = E_{\mathrm{TF}}(Z) + (\frac{1}{2} - s_B(\gamma))Z^2 + o(Z^2)$$

where, analogously to the Chandrasekhar case,

$$(4) \qquad s_B(\gamma) = \mathrm{tr}((S_{1,\gamma})_- - (B_{1,\gamma,1})_-)$$

with γ is fixed in $[0, (\pi/2 + 2/\pi)/2]$ (Frank, Siedentop, and Warzel [23]).

Although the eigenvalues of the one-particle Coulomb Brown-Ravenhall operator majorize the eigenvalues of the Coulomb Chandrasekhar operator and although it covers all known elements for the physical value of c the one-particle eigenvalues are still too low compared to the Dirac eigenvalues.

2.5. **The Energy of the Furry Operator.** The Furry operator is expected to yield the right asymptotic behavior of the ground state energy. Therefore we indicate the strategy of the proof in this case.

First we note that the hydrogenic Dirac operator $D_{Z,c}$ can be defined in a natural way with form domain $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^3)$ when $Z/c < 1$ (Nenciu [42]). Furthermore, it is obvious that

$$D_{N,Z,c} := \sum_{n=1}^{N} D_{Z,c_n} + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}$$

defined on all 4^N-spinors in the Schwartz space is a symmetric operator with corresponding form

$$(5) \qquad \mathcal{E}[\psi] := (\psi, D_{N,Z,c}\psi).$$

However, we will admit only normalized anti-symmetric spinors because of the Pauli principle and require $\otimes_{n=1}^{N}\Lambda_{Z,c}\psi = \psi$ implementing the Dirac sea. Note that $\mathcal{E}$ is bounded from below on those functions. Obviously, $\mathcal{E}[\psi] \geq -c^2 N\|\psi\|^2$. This allows to define the Furry operator $F_{N,Z,c}$ as the self-adjoint operator associated with the form $\mathcal{E}$ restricted to those spinors.

For $\gamma \in (0,1)$ we define

$$(6) \qquad \lambda_n^{\mathrm{S,H}} : \text{n-th eigenvalue of} \qquad \left(p^2 - \frac{\gamma}{|x|}\right) \otimes 1_{\mathbb{C}^2}$$

$$(7) \qquad \lambda_n^{\mathrm{D,H}} : \text{n-th eigenvalue of} \qquad \boldsymbol{\alpha} \cdot p + \beta - 1 - \frac{\gamma}{|x|}$$

This allows to define the relativistic correction of the Scott term:

$$(8) \qquad s_F(\gamma) := \frac{1}{\gamma^2} \sum_{n=1}^{\infty} \left(\lambda_n^{\mathrm{S,H}} - \lambda_n^{D,H}\right)$$

for $\gamma \in (0,1)$. Note that not only the non-relativistic eigenvalues but also the relativistic eigenvalues are explicitly known (Schrödinger [45], Gordon [25], Darwin [8]). In fact those energy levels were known before the Schrödinger equation and the Dirac equation (Balmer [3] and Sommerfeld [57]).

Since the Coulomb eigenvalues are ordered as follows: Schrödinger (including spin) bigger than Dirac bigger than Brown-Ravenhall bigger than Chandrasekhar (including spin) eigenvalues, one has

$$0 < s_F(\gamma) < s_B(\gamma) < s_c(\gamma).$$

This is a consequence of the variational principle for eigenvalues in gaps (see Griesemer et al. [27, 26], Morozov and Müller [40] and Müller [41]).

2.5.1. *Main Result.* We can now formulate the main result.

Theorem 1 (Handrek and Siedentop [28]). *There exists a constant $C > 0$ such that for all $Z > 0$ and $\gamma = \frac{Z}{c} \leq d < 1$ for some d one has*

$$(9) \qquad \left| E_F(Z) - \left[E_{\mathrm{TF}}(Z) + \left(\frac{1}{2} - s_F(\gamma) \right) Z^2 \right] \right| \leq C Z^{47/24}.$$

Put differently: Fix $\gamma \in (0, 1)$. As $Z \to \infty$

$$(10) \qquad E_F(Z) = E_{\mathrm{TF}}(Z) + \left(\tfrac{1}{2} - s^D(\gamma) \right) Z^2 + o(Z^2)$$

uniformly in $\gamma = \frac{Z}{c} \leq d < 1$.

We indicate the strategy of proof here. The main point is that we do not control the relativistic energy directly but only relatively to the non-relativistic energy. Physically speaking we renormalize the energy. We outline this procedure for the lower bound. The upper bounds is – in spirit – similar.

2.5.2. *The Energy Shift from Hydrogenic Schrödinger to Hydrogenic Dirac Energies.*
Using the explicit formulae for the eigenvalues one proves the following lemma:

Lemma 1. *Assume $\gamma_0 < 1$. Then there exists a constant $C \in \mathbb{R}$ such that for all $l \in \mathbb{N}$, $j = l \pm 1/2$, $j \geq 1/2$, and $\gamma \in [0, \gamma_0)$*

$$(11) \qquad \left| \lambda_{\gamma,n,l,j}^{\mathrm{D,H}} - \lambda_{\gamma,n,l}^{S,H} + \frac{\gamma^4}{2(n+l)^3} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4} \frac{1}{n+l} \right) \right| \leq C \gamma^6 \frac{n}{(n+l)^4 l}.$$

This has the two important consequences:

Corollary 1. *Under the above assumptions*

$$(12) \qquad 0 \leq \lambda_{\gamma,n,l}^{\mathrm{S,H}} - \lambda_{\gamma,n,l,j}^{\mathrm{D,H}} \leq \frac{C\gamma^4}{(n+l)^3 l}.$$

and

Corollary 2. *For $\gamma < 1$ the energy shift $s_F(\gamma)$ exists and is positive.*

2.5.3. *The Shift from Screened Schrödinger to Screened Dirac.* In the next step, one needs to control the error when replacing screened Dirac eigenvalues by Schrödinger eigenvalues for large angular momenta:

Lemma 2.

$$\sum_{l, 0 \leq j = l \pm \frac{1}{2}, n} \left(\lambda_{n,l,j}^{\mathrm{S,TF}} - \lambda_{n,l,j}^{\mathrm{D,TF}} \right) = O \left(\frac{\gamma^2 Z^2}{l^2} \right)$$

2.5.4. *Correlation Inequality.* An important step is the reduction to a one-particle problem. This is accomplished by using the correlation inequality of Mancas et al [39]

$$(13) \qquad \sum_{1 \leq \nu < \mu \leq N} \frac{1}{|\mathbf{x}_\nu - \mathbf{x}_\mu|} \geq \sum_{\nu=1}^{N} \left(\rho_Z^{\mathrm{TF}} * |\cdot|^{-1}(x_\nu) - \chi(\mathbf{x}_\nu) \right) - D[\rho_Z^{\mathrm{TF}}].$$

where

$$(14) \qquad \chi(\mathbf{x}) = \int_{|\mathbf{x}-\mathbf{y}| < R_Z(\mathbf{x})} \frac{\rho_Z^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \mathrm{d}\mathbf{y}$$

$R_Z(x)$ radius of the exchange hole defined by

$$(15) \qquad \int_{|\mathbf{x}-\mathbf{y}| \leq R_Z(\mathbf{x})} \rho_Z^{\mathrm{TF}}(\mathbf{y})\mathrm{d}\mathbf{y} = \frac{1}{2}.$$

This gives a lower bound on the total Furry energy in terms of one- and zero-particle operators

Corollary 3 (Lower Bound on Furry).

$$\mathcal{E}[\psi] \geq \sum_{\nu=1}^{N} (\psi, (D_{0\nu} - 1 - \varphi_{\mathrm{TF}}(x_\nu)\psi)) - D[\rho_Z^{\mathrm{TF}}] - \mathrm{C}Z^{5/3}$$

Now, we use the following consequece of the upper and lower bounds of Siedentop and Weikard [49, 52], see also [53]:

Theorem 2. *Pick* $L = [Z^{1/9}]$. *Then*

$$E_S(Z) = \sum_{n,l \leq L-1, 0 \leq j = l \pm \frac{1}{2}} \lambda_{n,l,j}^{\mathrm{S,H}} + \sum_{n, L \leq l, 0 \leq j = l \pm \frac{1}{2}} \lambda_{n,l,j}^{\mathrm{TF}} - D[\rho_Z^{\mathrm{TF}}] + \mathrm{C}Z^{47/24}$$

Armed with this result, we get the following lower bound on the shift of the total energy

$$(16) \qquad E_S(Z) - E_F(Z)$$

$$(17) \qquad \geq \sum_{l=0}^{L-1} \sum_{0 \leq j = l \pm \frac{1}{2}, n} \left(\lambda_{n,l,j}^{\mathrm{S,H}} - \lambda_{n,l,j}^{\mathrm{D,H}} \right)$$

$$(18) \qquad - \sum_{l=L}^{\infty} \sum_{0 \leq j = l \pm \frac{1}{2}, n} \left(\lambda_{n,l,j}^{\mathrm{S,TF}} - \lambda_{n,l,j}^{\mathrm{D,TF}} \right) - \mathrm{C}Z^{47/48}$$

$$(19) \qquad \geq s^D(\gamma)Z^2 - \mathrm{C}Z^{47/48}.$$

This finishes the outline of the proof.

2.6. **Comparison with Experiment.** As already mentioned, one cannot expect that the Chandrasekhar and Brown-Ravenhall operators give quantitatively correct result for heavy atoms. However, the Furry picture gives numerical values up to chemical accuracy (Reiher and Wolf [43]).

If one is emboldened by this fact and dares to apply Stell's *Principle of Unreasonable Utility of Asymptotic Expansions* (G. Stell [58]) one gets the following graph.

- red diamonds, crosses: $(E_{\text{experimental}}(Z) - E_{\text{TF}}(Z))Z^{-2}$
- red solid: Schwinger's approximation
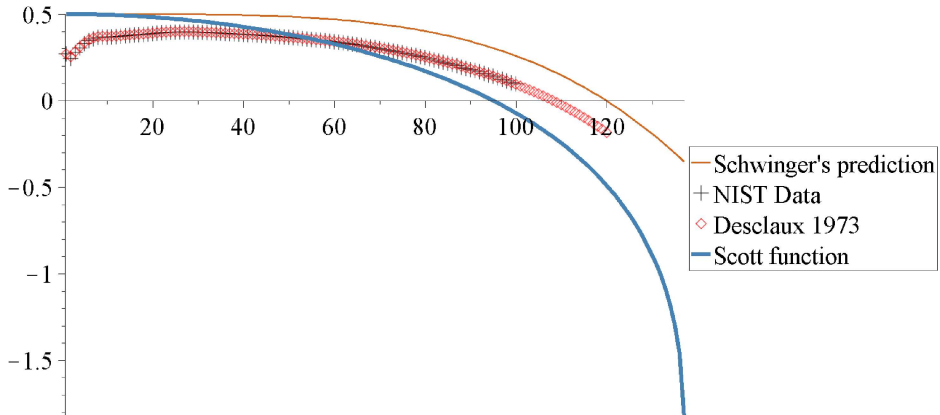- blue: $\frac{1}{2} - s^D(Z/137)$

FIGURE 1. Comparison (see [28]) of the relativistic Scott function with data taken from the NIST database [36], Dirac-Fock calculations (Desclaux [9]), and Schwinger's original prediction (Schwinger [47]) plotted over Z for $c = 137$.

3. THE GROUND STATE DENSITY

Energetic control yields also convergence of the ground state. Using a linear response argument Lieb and Simon[38] show

Theorem 3. *Assume ψ^S to be a groundstate of $S_{Z,Z}$; write $\tilde{\rho}_{\psi^S}$ for the associated one-particle groundstate density and ρ_{TF} the minimizer of the Thomas-Fermi functional with $Z = 1$. Moreover, let B be any measurable bounded subset of $\mathbb{R}^3$. Then the rescaled density ρ^S defined by*

$$\rho^S(x) := Z^{-2}\tilde{\rho}_{\psi^S}(Z^{-1/3}x)$$

converges to the Thomas-Fermi density in the following sense:

$$\lim_{Z \to \infty} \int_B \mathrm{d}x \rho(x) = \int_B \mathrm{d}x \rho_{\text{TF}}(x).$$

Fefferman and Seco [17] observed that the missing term in the correlation inequality yields automatically the convergence in Coulomb norm

Theorem 4. *As $Z \to \infty$*

$$D[\rho^S - \rho_{\text{TF}}] = O(Z^{-1/3}).$$

Corresponding considerations can be also carried through for the Chandrasekhar and Brown-Ravenhall operator (Merz [in preparation] and Merz and Siedentop [in preparation]). In particular one obtains in the Brown-Ravenhall case the following result:

Theorem 5. *Let ψ^B be a groundstate of $B_{Z,z,c}$, let ρ^B be the rescaled groundstate density (as above) and fix $Z/c < 2/(2/\pi + \pi/2)$. Then, as $Z \to \infty$*

$$D[\rho^B - \rho_{\mathrm{TF}}] = O(Z^{-1/48}).$$

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