The Ground State Energy of Heavy Atoms

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1 Motivation

- We consider the ground state energy of neutral atoms of nuclear charge Z that are described by a Hamiltonian H_Z
$$E^Z := \inf_{\|\Psi\|=1} \langle \Psi, H_Z \Psi \rangle$$
in $\mathcal{H} := \bigwedge_{i=1}^{Z} L^2(\mathbb{R}^3 : \mathbb{C}^q)$.
- In the non-relativistic case
$$H_Z := \sum_{i=1}^{Z} \left(\frac{\mathbf{p}_i^2}{2} - \frac{Z}{|\mathbf{x}_i|} \right) + \sum_{1 \le i < j \le Z} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$$
the leading order of the ground state energy is given by the infimum $E_{\mathrm{TF}}^Z = E_{\mathrm{TF}}^1 Z^{7/3}$ of the Thomas-Fermi functional
$$\mathcal{E}_{\mathrm{TF}}^Z[\rho] = \frac{3(3\pi^2)^{\frac{2}{3}}}{5 \quad 2} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}}(x)\mathrm{d}x - \int_{\mathbb{R}^3} \frac{Z\rho(x)}{|x|}\mathrm{d}x + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\mathrm{d}x\mathrm{d}y.$$
on a suitable set of electron densities.
- The next order is called Scott correction and originates from quantum effects close to the Coulomb singularity.
$$E^Z = E_{\mathrm{TF}}^1 Z^{7/3} + \frac{1}{2} Z^2 + O(Z^{2-\epsilon})$$
where $E_{\mathrm{TF}}^1 \sim -0.7687[Ha]$.
- However, in reality, due to the high velocities of the electrons near the nucleus relativistic effects have to be accounted for.

2 Relativistic Operators

- The simplest way to include relativity would be to replace the kinetic energy by $\sqrt{c^2\mathbf{p}^2 + c^4} - c^2$.
- More sophisticated models comprise suitably projected Dirac operators, so called no-pair operators. We consider
$$D_{\gamma,\phi} = \boldsymbol{\alpha} \cdot \mathbf{p} + \beta - \frac{\gamma}{|\mathbf{x}|} + \phi$$
with a mean-field potential ϕ on subspaces of $L^2(\mathbb{R}^3 : \mathbb{C}^4)$:

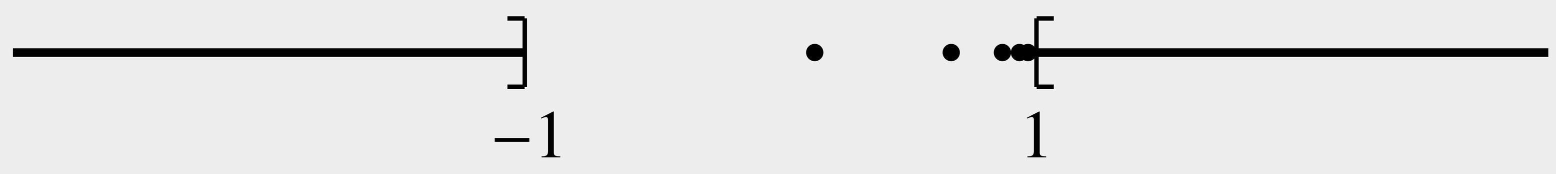
Free picture (Brown & Ravenhall 1951)
$$\mathfrak{H}_0 := 1_{(0,\infty)}(D_0) L^2(\mathbb{R}^3 : \mathbb{C}^4)$$

Furry picture (Furry & Oppenheimer 1934)
$$\mathfrak{H}_\gamma := 1_{(0,\infty)}(D_\gamma) L^2(\mathbb{R}^3 : \mathbb{C}^4)$$

Intermediate or "Fuzzy" picture (Mittleman 1981)
$$\mathfrak{H}_{\gamma,\chi} := 1_{(0,\infty)}(D_{\gamma,\chi}) L^2(\mathbb{R}^3 : \mathbb{C}^4).$$
with a possibly different mean-field potential χ.
- Since $D_{\gamma,\phi}$ is only defined or $\gamma \le 1$ we have to consider the simultaneous limit $c \to \infty$ as $Z \to \infty$, such that $\gamma = \frac{Z}{c} \le 1$ (or $\gamma \le \frac{2}{\pi/2 + 2/\pi}$ in the Brown-Ravenhall case).

3 Relativistic Hydrogen

- The spectrum of $D_{\gamma,\phi}$ consists of the continuous part $(-\infty,-1] \cup [1,\infty)$ and some eigenvalues in the gap $(-1,1)$ accumulating at 1:



Adding projections removes the negative continuous part of the spectrum (no positrons) and shifts the eigenvalues.
- Only for $\phi = \chi = 0$ the eigenvalues λ_n^D and eigenvectors are explicitly known, e.g. the ground state energy is $\lambda_0^D = \sqrt{1-\gamma^2}$.

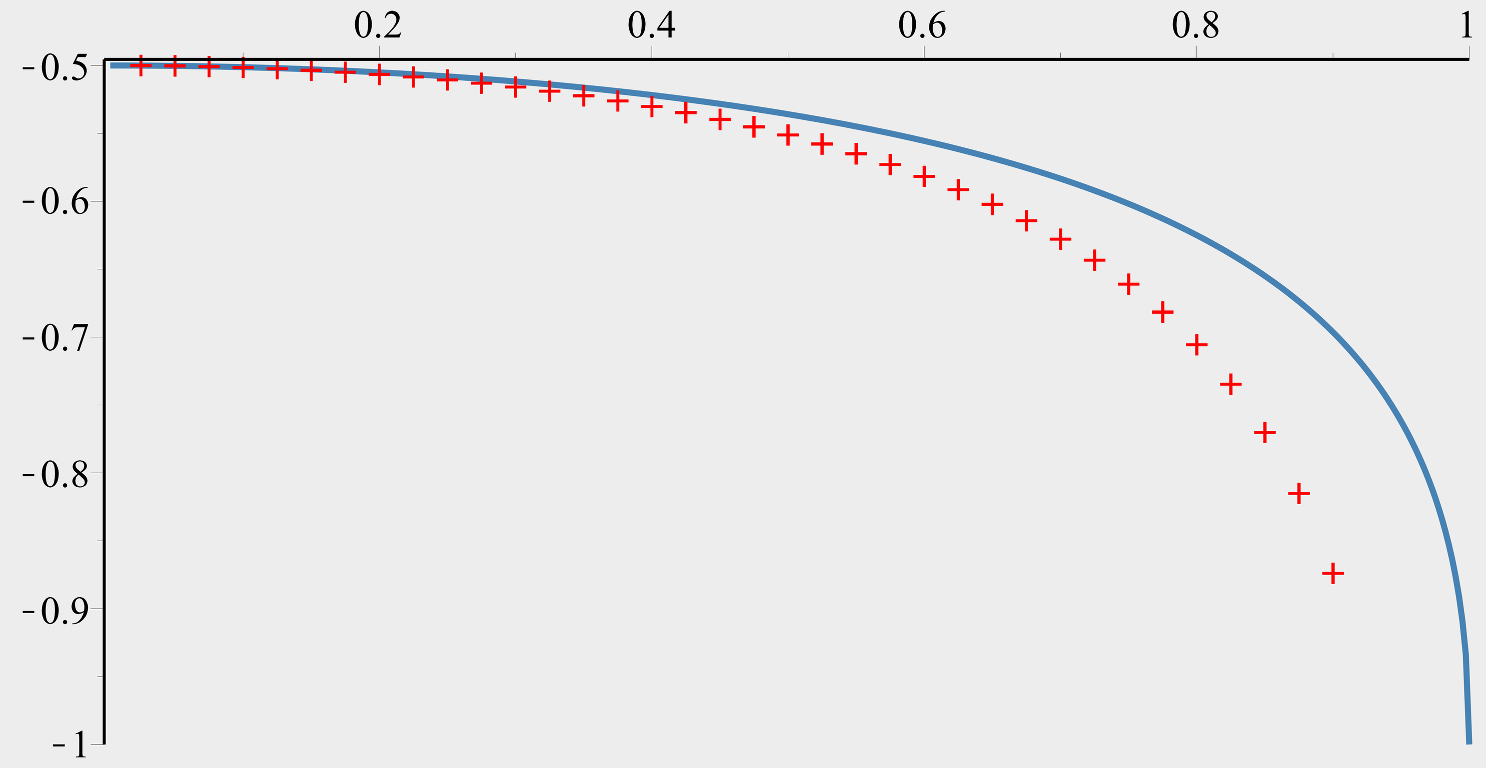


Fig. 1. $\lambda_0^D - 1$ and the ground state energy of the Brown-Ravenhall operator (DIRAC program) divided by γ^2 as a function of γ. For the non-relativistic Schrödinger operator $\lambda_0^{NR}/\gamma^2 = -\frac{1}{2}$.

4 Relativistic Scott correction

For the Furry picture and for a class of mean-field potentials in the intermediate picture we show

Theorem 1. *In the limit $Z, c \to \infty$ such that $\frac{Z}{c} \to \gamma < 1$, the ground state energy of the quadratic form*
$$\mathcal{E}^Z[\Psi] := c^2 \left\langle \Psi, \left(\sum_{i=1}^{Z} (D_{\gamma,i} - 1) + \sum_{1 \le i < j \le Z} \frac{\alpha}{|\mathbf{x}_i - \mathbf{x}_j|} \right) \Psi \right\rangle$$
on $\mathfrak{H}^Z := \bigwedge_{n=1}^{Z} \mathfrak{H}_\gamma$ or $\bigwedge_{n=1}^{Z} \mathfrak{H}_{\gamma,\chi}$ fulfills
$$E^Z = E_{\mathrm{TF}}^1 Z^{7/3} + \left(\frac{1}{2} + s^D(\gamma) \right) Z^2 + o(Z^2),$$
where $s^D(\gamma) := \frac{1}{\gamma^2} \sum_{n=1}^{\infty} \left(\lambda_n^D - \lambda_n^{NR} \right)$.

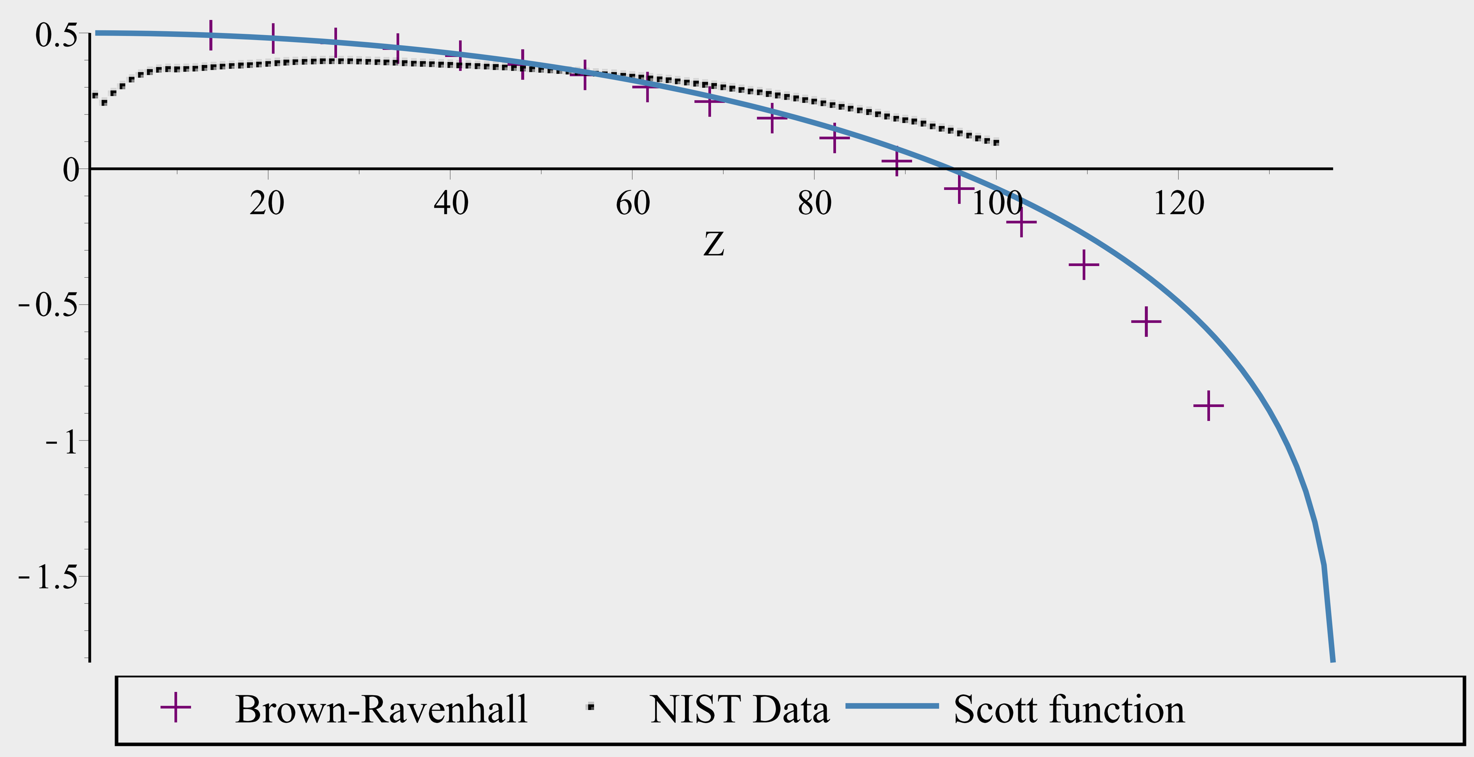


Fig. 2. The Scott function $s^D(Z/c)$ for fixed $c = \frac{1}{\alpha}$ compared to values from the NIST database and numerical computations of the Brown-Ravenhall Scott function.