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Energy of Heavy Atoms

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Notation and Main Result

Notation:

$$D_{c,Z} = c\mathbf{p}\cdot\boldsymbol{\alpha} + c^2\beta - \frac{Z}{|x|} \tag{1}$$

hydrogenic Dirac. Z atomic number, $\mathbf{p} := -\mathrm{i}\nabla$ momentum, $\boldsymbol{\alpha}$, β four Dirac matrices, c velocity of light, and $\kappa := Z/c \in (0,1)$ fixed in the following.

Energy of relativistic Coulomb system in state Ψ

$$\mathcal{E}_{c,Z,N}[\Psi] := \left\langle \Psi, \left(\sum_{n=1}^{N}(D_{c,Z}-c^2)_n + \sum_{1\leq m<n\leq N}\frac{1}{|x_n - x_m|}\right)\Psi \right\rangle \tag{2}$$

Allowed states: electronic states only (Dirac sea: negative energy states filled). Implementation by Brown and Ravenhall [2], Bethe and Salpeter [1], Sucher [8]:

1-electron space and form domain:

$$\begin{aligned}\mathfrak{H}^W &:= \mathbb{1}_{(0,\infty)}(D_{c,Z}+W)(\mathfrak{H}),\ \mathfrak{H} := L^2(\mathbb{R}^3:\mathbb{C}^4)\\ \mathfrak{Q}^W &:= \mathbb{1}_{(0,\infty)}(D_{c,Z}+W)(\mathfrak{Q}),\ \mathfrak{Q} := H^{\frac12}(\mathbb{R}^3:\mathbb{C}^4)\end{aligned} \tag{3}$$

with some potential W.

N-electron Hilbert space:

$$\mathfrak{H}_W^N := \bigwedge_{n=1}^{N}\mathbb{1}_{(0,+\infty)}(D_{c,Z}^W)(\mathfrak{H}), \qquad \mathfrak{Q}_W^N := \bigwedge_{n=1}^{N}\mathbb{1}_{(0,+\infty)}(D_{c,Z}^W)(\mathfrak{Q}) \tag{4}$$

Sucher terminology: choice of W defines a ”picture”:

- **Free picture (Brown–Ravenhall [2])** Here $W = \frac{Z}{|x|}$, i.e., $D_{c,Z}^W = Dc, 0$.
- **Furry picture (Furry and Oppenheimer [4])** Here $W = 0$, i.e., $D_{c,Z}^W = D_{c,Z}$.
- **Intermediate or Fuzzy picture (Sucher [9])** some W mean field, e.g., $W = \rho * |\cdot|^{-1}$. Optimal choice: mean field of MCSCF type (Mittleman [6]). Studied numerically in quantum chemistry, see Saue [7].

Ground-state energy of the atom for given W

$$E_{c,Z,N,W} := \inf \mathcal{E}_{c,Z,N}[\{\Psi \in \mathfrak{Q}_W^N|\ \|\psi\| \leq 1\}]. \tag{5}$$

Physical ground-state energy (Mittleman [6]): take supremum over W.

Theorem 1. *Pick $N = Z$ and $W = A + \rho_* * |\cdot|^{-1}$, A admissible (see Definition 3), ρ_* a Séré density (see Definition 1). Then, as $Z \to \infty$,*

$$E_{c,Z,Z,W(Z)} \leq E_{c,Z,Z,0} + o(Z^2) = -C_{\mathrm{TF}}Z^{\frac73} + C_{\mathrm{Scott-Furry}}(\kappa)Z^2 + o(Z^2). \tag{6}$$

In particular

- The Furry picture gives the highest Scott correction

Outline of the proof

Lower bound: Consequence of Handrek and Siedentop [5]

Upper bound: **Séré’s ground state energy**

Starting point of the upper bound: Solution of simplified relativistic Hartree-Fock equation in spirit Séré [10] and its energy by Fournais, Lewin, and Triay [3]:

Reduced relativistic Hartree-Fock operator for $\sqrt{\rho} \in \mathfrak{Q}$

$$D_{c,Z,\rho} := D_{c,Z} + \rho * |\cdot|^{-1} \tag{7}$$

Reduced relativistic Hartree-Fock functional reads

$$\mathcal{E}_Z^{\mathrm{HF}}(\gamma) := \mathrm{tr}\,[(D_{c,Z}-c^2)\gamma] + \underbrace{\frac12\int_{\mathbb{R}^3}\mathrm{d}x\int_{\mathbb{R}^3}\mathrm{d}y\frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}}_{=:\mathcal{D}[\rho_\gamma]}. \tag{8}$$

Density matrices γ:

$$X := \{\gamma \in \mathfrak{S}^1(\mathfrak{H})|\mathrm{tr}\left[(1+\mathbf{p}^2)^{1/4}|\gamma|(1+\mathbf{p}^2)^{1/4}\right] < \infty\}. \tag{9}$$

$$\Gamma_{c,Z,N} := \{\gamma \in X | 0 \leq \gamma \leq 1,\ \mathrm{tr}\,(\gamma) \leq N,\ P_{c,Z,\rho_\gamma}\gamma P_{c,Z,\rho_\gamma} = \gamma,\ \rho_\gamma \text{ spherically symmetric}\} \tag{10}$$

with

$$P_{c,Z,\rho} := \mathbb{1}_{(0,+\infty)}(D_{c,Z,\rho}). \tag{11}$$

Definition 1:

Séré functional and energy $\mathcal{E}_{c,Z,N}^{\mathrm{S}} := \mathcal{E}_{c,Z}^{\mathrm{HF}}\Big|_{\Gamma_{c,Z,N}}$, $E_{c,Z,N}^{\mathrm{S}} := \inf \mathcal{E}_{c,Z}^{\mathrm{HF}}(\Gamma_{c,Z,N})$

Séré minimizer, density, operator γ_* minimizer, ρ_*, $D_* = D_{c,N,\rho_*}$

Theorem 2. (Séré’s ground states [10]) *For Z large enough and $N \leq Z$, the Séré functional $\mathcal{E}_{c,Z,N}^{\mathrm{S}}$ has a minimizer $\gamma_* \in \Gamma_{c,Z,N}$.*

Theorem 3. (Properties of Séré minimizers) *Fix $N = Z$. Then, as $Z \to \infty$*

$$Z\mathrm{tr}\,[|\cdot|^{-1}\gamma_*] + \mathcal{D}[\rho_*] = O(Z^{7/3}), \tag{12}$$

$$\mathrm{tr}\,[(|D_{c,0}| - c^2)\gamma_*] = O(Z^{7/3}), \tag{13}$$

$$\|\rho_* * |\cdot|^{-1}\|_\infty \leq \frac{\pi}{2}\mathrm{tr}\,[|\mathbf{p}|\gamma_*] = O(Z^{5/3}). \tag{14}$$

The proof is based on the asymptotic behavior of the Séré energy [3]:

Theorem 4. *For Z large, $E_{c,Z,Z}^{\mathrm{S}} = E_{c,Z,Z,0} + o(Z^2)$.*
(Recall: $E_{c,Z,Z,0}$ Furry ground state energy.)

Allowed potentials

The allowed potentials W will rely on γ_*.

Definition 2. *Pick a Séré minimizer $\gamma_* \in \Gamma_{c,Z,Z}$. $\mathfrak{A}$ is set of symmetric operators A with form domain $\mathfrak{Q}(A) \supset \mathfrak{Q}$ such that $D_{c,0} - Z|\cdot|^{-1} + \rho_* * |\cdot|^{-1} + A$ has a distinguished self-adjoint extension $D_{*,A}$ in the sense of Nenciu such that $\mathfrak{D} \subset \mathfrak{D}(D_{*,A}) \subset \mathfrak{Q}(D_{*,A}) \subset \mathfrak{Q}$. and the following inequalities*

$$C^{-1}|D_{c,0}| \leq |D_{*,A}| \leq C|D_{c,0}| \tag{15}$$

$$-A \leq |D_{*,A}| + c^2. \tag{16}$$

hold with constant C uniformly in c and A.

We consider subfamilies of $\mathfrak{A}$. Set $P_A := \mathbb{1}_{(0,\infty)}(D_{*,A})$.

Definition 3. *Given a Séré minimizer γ_*, we call a family of operators $A : [Z_0,\infty) \to \mathfrak{A}$ for some Z_0, admissible, if and only if*

$$\mathrm{tr}\left(\gamma_* A(Z)P_A^\perp\frac{1}{\lambda_1(D_*) - P_A^\perp D_{*,A(Z)}}P_A^\perp A(Z)\right) = o(Z^{\frac{12}{5}}). \tag{17}$$

will be central.

Note

- If $A_1 + A_2 \in \mathfrak{A}$, and A_1 and A_2 are admissible, so is $A_1 + A_2$
- Sufficient for (17) is

$$\mathrm{tr}\,(|A(Z)|\gamma_*)\||D_{c,0}|^{-1/2}|A(Z)||D_{c,0}|^{-1/2}\| = o(Z^{\frac{12}{5}}). \tag{18}$$

Examples of allowed potentials

The Fuzzy picture and beyond

Lemma 1. *Pick a family $A(Z) := \rho_Z * |\cdot|^{-1}$ with $\rho_Z \in L^{\frac32-} \cap L^{\frac32+}$ such that*

$$\||\cdot|^{-1} * \rho_Z\|_\infty = o(Z^2) \tag{19}$$

and

$$\mathcal{D}[|\rho_Z|]\|\rho_Z * |\cdot|^{-1}\|_\infty^2 = o(Z^{\frac{97}{15}}). \tag{20}$$

Then $\rho_Z * |\cdot|^{-1}$ is admissible.

In other words, the Furry energy maximizes the Mittleman energy within the class of mean field potentials of Hartree type. Note also that the class of densities generating the mean field exceeds by far those that are physically expected: A physical Hartree term is expected to be $O(Z^{\frac73})$ and a pointwise bound on the mean field is $O(Z^{\frac53})$. This leads to a physical expected bound of $O(Z^{\frac{17}{3}})$ which is less than $97/15$.

We define the exchange term:

$$X_\gamma u = \frac12\int_{\mathbb{R}^3}\frac{\gamma(x,y)u(y)}{|x-y|}dy. \tag{21}$$

Then,
Lemma 2. *Pick a family $A(Z) := \rho_\gamma * |\cdot|^{-1} - \rho_* * |\cdot|^{-1} - X_\gamma$ with γ a family of charge density matrices in X such that*

$$\||\cdot|^{-1} * \rho_{|\gamma|}(Z)\|_\infty = o(Z^2) \tag{22}$$

and

$$\mathcal{D}[\rho_{|\gamma|}(Z)]\|\rho_{|\gamma|}(Z) * |\cdot|^{-1}\|_\infty^2 = o(Z^{\frac{97}{15}}) \tag{23}$$

Then $\rho_\gamma * |\cdot|^{-1} - \rho_* * |\cdot|^{-1} - X_\gamma$ with $Z \geq Z_0$ is admissible.

Weird potentials

Weird potentials expected to lead to wrong Scott corrections are covered.

Lemma 3. *Pick the family $A(Z) := aZ|\cdot|^{-1} - \rho_* * |\cdot|^{-1}$ with $a \in [-\epsilon_0, 1+\kappa^{-1})$ and some $\epsilon_0 > 0$ small enough. Then $A(Z)$ is admissible .*

In particular, when $a = -1$, the projection P_A is the free picture, i.e., $P_A = \mathbb{1}_{(-\infty,0)}(D_{c,0})$.

The case of moderate Coulomb singularities at a location different from the location of the nucleus is also covered:

Lemma 4. *Pick a family of signed measures ν, such that $\nu(Z) * |\cdot|^{-1}$ is relative operator bounded with respect to $D_{c,Z}$ with a small enough constant uniform in Z and set $A(Z) := \nu(Z) * |\cdot|^{-1} - \rho_* * |\cdot|^{-1}$. Then $A(Z)$ is admissible.*

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