Scott correction in models of atoms and molecules with magnetic and relativistic corrections

Jan Philip Solovej
Department of Mathematics
University of Copenhagen

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Abstract of Talk

The topic of this talk is the **energy asymptotics of large atoms and molecules**. I will discuss

- Joint work with Østergaard-Sørensen and Spitzer on **relativistic corrections** to the energy
- Joint work with Erdős and Fournais on including **magnetic self-interactions**
- The relativistic corrections will be seen to be stronger than the magnetic corrections.
- In all cases the leading Thomas-Fermi (semiclassical) order of the energy is not affected by the corrections
- The corrections come in to second order, **the Scott order**.

Atomic Units: $\hbar = 1$, $m_e = 1$, $e = 1$, Fine structure constant $\alpha = e^2/(\hbar c) = c^{-1} \approx 1/137$. We will however consider α a small parameter.

Outline of Talk

1. Hamiltonian for molecule
2. The magnetic interaction
3. Two magnetic models
4. (Pseudo)-Relativistic models
5. The main results
6. Collaborators and history
7. The Scott function S
8. The main technical result

Hamiltonian for molecule

$$H_N = \sum_{j=1}^{N} \left[T(i\nabla_{\mathbf{A}})_j - \sum_{k=1}^{K} \frac{Z_k}{|x_j - R_k|} \right] + \sum_{i<j} \frac{1}{|x_i - x_j|} + \mathcal{U}$$

acts on $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$.

- **Kinetic energy**: $T(i\nabla_{\mathbf{A}})$ on $L^2(\mathbb{R}^3, \mathbb{C}^2)$.
- **Magnetic potential**: $\nabla_{\mathbf{A}} = \nabla - i\mathbf{A}$, $\mathbf{A} \in C_0^1(\mathbb{R}^3; \mathbb{R}^3)$,
- **Field energy**: $\mathbf{B} = \nabla \times \mathbf{A}$, α **fine structure constant**

$$\mathcal{U} = (8\pi\alpha^2)^{-1} \int \mathbf{B}^2 + \sum_{k<\ell} \frac{Z_k Z_\ell}{|R_k - R_\ell|}$$

Ground state energy: (fixed $\mathbf{A}$)

$$E = \inf \mathrm{spec}_{\mathcal{H}_N} H_N \text{ for } N = Z.$$

The magnetic interaction

We are however interested in the **magnetic interaction** so $\mathbf{A}$ not fixed. The **ground state energy** rather defined as

$$E(Z,\alpha) = \inf_{\mathbf{A}} \inf \text{spec} H_N \text{for } N = Z.$$

Remark: The variational equation is the **coupled Schrödinger-Maxwell** system:

$$H_N \Psi = E\Psi, \quad \nabla \times \mathbf{B} = 4\pi\alpha^2 \mathbf{j}_\Psi$$

$\mathbf{j}_\Psi$ is the **current** of Ψ:

$$\mathbf{j}_\Psi = -\frac{\delta}{\delta \mathbf{A}}(\Psi, \sum_{j=1}^{N} T(i\nabla_{\mathbf{A}})_j \Psi).$$

We study the **large Z asymptotics** $Z \to \infty$ (and $\alpha \to 0$)

$$Z_k = Z z_k, \quad R_k \geq r_k Z^{-1/3}, \quad z_k, r_k \text{ fixed}.$$

Two magnetic models

Atoms for simplicity:

$$H_N = \sum_{j=1}^{N} \left[T(i\nabla_{\mathbf{A}})_j - \frac{Z}{|x_j|} \right] + \sum_{i<j} \frac{1}{|x_i - x_j|} + \frac{1}{8\pi\alpha^2} \int \mathbf{B}^2$$

- **Magnetic-Schrödinger model**: $T(i\nabla_{\mathbf{A}}) = \frac{1}{2}(i\nabla_{\mathbf{A}})^2$

$$E = E_{\mathrm{MS}}(Z,\alpha) = \inf_{\mathbf{A}} E = \inf_{\mathbf{A}} \inf \mathrm{spec} H_N$$

- **Magnetic-Pauli model**: With $\boldsymbol{\sigma}$ = Pauli matrices:

$$T(i\nabla_{\mathbf{A}}) = \frac{1}{2}(i\nabla_{\mathbf{A}} \cdot \boldsymbol{\sigma})^2 = \frac{1}{2}(i\nabla\!\!\!/_{\mathbf{A}})^2 = \frac{1}{2}(i\nabla_{\mathbf{A}})^2 + \frac{1}{2}\boldsymbol{\sigma} \cdot \mathbf{B},$$

$$E = E_{\mathrm{MP}}(Z,\alpha) = \inf_{\mathbf{A}} E = \inf_{\mathbf{A}} \inf \mathrm{spec} H_N$$

E depends on Z and on the fine structure constant α, although the models are **essentially non-relativistic**.

(Pseudo)-Relativistic models

Relativistic magnetic atoms:

- **Schrödinger case;**

$$T(i\nabla_{\mathbf{A}}) = \sqrt{\alpha^{-2}(i\nabla_{\mathbf{A}})^2 + \alpha^{-4}} - \alpha^{-2},$$

The energy denoted $E_{\rm RMS}(Z,\alpha)$.

- **Pauli case;**

$$T(i\nabla_{\mathbf{A}}) = \sqrt{\alpha^{-2}(i\not{\nabla}_{\mathbf{A}})^2 + \alpha^{-4}} - \alpha^{-2},$$

The energy denoted $E_{\rm RMP}(Z,\alpha)$.

Remark: In all cases $\alpha = 0$ corresponds to
Non-relativistic/non-magnetic case:

$$E_{\rm MS}(Z,0) = E_{\rm MP}(Z,0) = E_{\rm RMS}(Z,0) = E_{\rm RMP}(Z,0) = E_{\rm NR}(Z),$$

corresponding to

$$T(i\nabla) = -\frac{1}{2}\Delta, \quad \mathbf{A} = 0, \quad \mathcal{U} = 0.$$

The main results

Theorem (Scott correction for atoms)

There exist constants $C_{\mathrm{TF}}, \kappa_c > 0$ *and* **continuous functions**

$$S_{\mathrm{R}} : [0, 2/\pi] \to \mathbb{R},\ \ S_{\mathrm{MS}} : [0, \infty] \to \mathbb{R},\ \ S_{\mathrm{MP}} : [0, \kappa_c] \to \mathbb{R}$$

with $S_{\mathrm{R}}(0) = S_{\mathrm{MS}}(0) = S_{\mathrm{MP}}(0) = 1/2$ *such that*

$$E_{\mathrm{RMS}}(Z, \alpha) = E_{\mathrm{RMP}}(Z, \alpha) = -C_{\mathrm{TF}} Z^{7/3} + Z^2 S_{\mathrm{R}}(Z\alpha) + o(Z^2)$$

as $Z \to \infty$, $\alpha \to 0$ *with* $0 \leq Z\alpha \leq \kappa < 2/\pi$. *To the* **order** $o(Z^2)$ *the* **ground state energy** *is achieved with* $\mathbf{A} = 0$.

$$E_{\mathrm{MS,MP}}(Z, \alpha) = -C_{\mathrm{TF}} Z^{7/3} + Z^2 S_{\mathrm{MS,MP}}(Z^{1/2}\alpha) + o(Z^2)$$

as $Z \to \infty$, $\alpha \to 0$ *with* $0 \leq Z^{1/2}\alpha \leq \kappa$ *(with* $\kappa \leq \kappa_c$ *for MP).*

TF=Thomas-Fermi. Holds for molecules: **Scott term additive**.

Collaborators and history

Collaborators:

- **Relativistic Scott ($\mathbf{A} = 0$):** Joint with Østergaard-Sørensen and Spitzer. Can take $Z\alpha = 2/\pi$.
- **Magnetic (-relativistic) Scott:** Joint with Erdős and Fournais

History and other results:

- **Leading term (of semiclassical origin):** Thomas and Fermi, Lieb-Simon.
- **Non-relativistic Scott correction:** Scott, Schwinger, Schwinger-Englert, Hughes, Siedentop-Weikard, Ivrii-Sigal, Solovej-Spitzer
- **Relativistic Scott:** Schwinger, Østergaard-Sørensen (leading term) , Frank-Siedentop-Warzel (alternative proof only atoms)
- **Magnetic leading term:** Erdős-Solovej

Open probem: Quantized fields!

The Scott function S

Theorem (Scott function S)

The function S is given by

$$S(\alpha) \;=\; \lim_{\mu\to 0}\Big[\;\inf_{\mathbf{A}}\Big(\mathrm{Tr}\,[T(i\nabla_{\mathbf{A}})-|x|^{-1}+\mu]_- + \frac{1}{8\pi\alpha^2}\int \mathbf{B}^2\Big)$$

$$-\,(2\pi)^{-3}\iint [\tfrac{1}{2}p^2-|q|^{-1}+\mu]_-dpdq\Big]$$

Remark: Note that we may replace

$$\int \mathbf{B}^2 \to \int |\nabla\otimes\mathbf{A}|^2 \geq \int \mathbf{B}^2.$$

with equality if div$\mathbf{A}=0$, which can be achieved by a gauge choice.

The main technical result

Theorem (The local semiclassical estimate)

$B = \{|x| < 1\}$, $V \in C^\infty(\overline{B})$, $\phi \in C_0^\infty(B)$. *There is* $\varepsilon > 0$ *such that for all* $\alpha_0 > 0$

$$\left| \inf_{\mathbf{A}} \left[\mathrm{Tr}\left[\phi(T(ih\nabla_{\mathbf{A}}) + V)\phi\right]_- + \frac{1}{8\pi\alpha^2}\int_{2B} |\nabla \otimes \mathbf{A}|^2 \right] - \frac{1}{(2\pi h)^3} \iint \phi(q)^2 [\tfrac{1}{2}p^2 + V(q)]_- dp dq \right| \leq Ch^{-2+\varepsilon}$$

for all $\alpha < \alpha_0$. C *depends on* α_0 *and finitely many derivatives of* ϕ *and* V.
The upper bound *achieved (in all cases) with* $\mathbf{A} = 0$ *and an explicit approximation for the proj.* $\mathbf{1}_{(-\infty,0]}(\phi(T(ih\nabla) + V)\phi)$.

Main difficulty lies in lack of regularity of $\mathbf{A}$.