On the total magnetic moment of large atoms in strong magnetic fields

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Abstract

We look at the magnetisation of neutral atoms in large magnetic fields. Asymptotic formulas for the energy exist with high precision in different regions depending on how large the nuclear charge Z is compared to the magnetic field strength B. All these formulas take the splitting of the kinetic energy into Landau levels as the principal feature and then treat the electric potential as a perturbation. We prove that these approximate formulas predict correctly (to highest order) the total magnetic moment of the atom. The proof of this fact relies on a "virial theorem" for Coulomb systems in a constant magnetic field.

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1 Introduction

The magnetisation of atoms in low magnetic fields is given by the famous Zeeman effect of elementary atomic physics. This effect comes purely from the coupling of the electronic spin with the external magnetic field. For atoms in strong magnetic fields, however, this is no longer the case: The electrons in the atom produce a *persistent current* which cancels the *spin-current* to a very high precision and the resulting magnetisation is of lower order. It will be the purpose of this paper to calculate the resulting total magnetic moment in different regions.

In the important work [5] a number of approximating density-type theories for large atoms in strong magnetic fields were studied (see [5] for references to earlier work). If one introduces the two parameters; B that measures the strength of the external, constant magnetic field, and Z that measures the nuclear charge of the neutral atom, then the final result is that these different theories (some of them simple limits of each other, others *qualitatively* very different) reproduce correctly the ground state energy of the atom in the limit where $(B, Z) \to \infty$, in different parameter regions that depend on the relative magnitude of B and Z. It follows then by a convexity argument (called the Feynman-Hellman theorem in the physics litterature) that these approximating theories also reproduce the ground state *density* correctly to highest order. However, in the presence of a magnetic field, one is also interested in the magnetic moment of the atom, but the magnetic field appears in a somewhat more complicated way in the Hamiltonian, so the convexity argument does not work for the magnetic moment. In general, it seems complicated to find the distribution of the magnetic moment (or the current) over the atom, but for the *total magnetic moment* we will in this article exploit a *magnetic virial theorem* to get very simple proofs that all the approximating theories from [5] give (each in their parameter region) correct highest order predictions for the total magnetic moment. Now the virial theorem is really just a scaling relation upon scaling the space variables - it depends on the perfect scaling of the Coulomb potential and the magnetic vector potential - and the approximating theories scale the same way, so they satisfy the same virial theorem. This reduces the convergence of the total magnetic momemt to the convergence of the different parts of the energy (kinetic, potential), for which convexity arguments (Feynman-Hellman) can be used.

1.1 The model:

The model of a nonrelativistic atom in a constant magnetic field that we will use in this paper is that of the Pauli operator; with the assumption that the nucleus is infinitely heavy. Therefore the Hamiltonian governing the system is:

$$\begin{aligned}\mathbf{H}(B,Z) &= \sum_{j=1}^{Z}\left((-i\nabla_j + B\vec{A}(x_j))^2 + \vec{B}\cdot\vec{\sigma}_j - \frac{Z}{|x_j|}\right) \\ &\quad + \sum_{1\leq j<k\leq Z}\frac{1}{|x_j - x_k|}.\end{aligned}$$

Here we choose $\vec{A}(x) = (-x^{(2)}/2, x^{(1)}/2, 0)$ and get $\vec{B} = (0,0,B)$, and $\vec{\sigma}$ denotes the vector of Pauli spin matrices. Notice, that we have assumed for simplicity that the atom is neutral.
We will study the total magnetic moment m of this system defined as:

$$m = \langle\Psi|\mathbf{J}(\vec{A})|\Psi\rangle, \tag{1}$$

where Ψ is a ground state of $\mathbf{H}(B,Z)$ and where $\mathbf{J}(\vec{a})$ for any vector function $\vec{a}$ is the operator

$$\mathbf{J}(\vec{a}) = \sum_{j=1}^{Z}\left(\vec{a}(x_j)\cdot(-i\nabla_j + B\vec{A}(x_j)) + (-i\nabla_j + B\vec{A}(x_j))\cdot\vec{a}(x_j) + \vec{b}(x_j)\cdot\vec{\sigma}_j\right),$$

with $\vec{b} = \operatorname{curl}\vec{a}$.
It will be a standing hypothesis all through the paper that such a ground state Ψ exists, though we will not assume that it is unique.
Let us define $E^Q(Z,B)$ to be the ground state energy of the atom, i.e. the bottom of the spectrum of $\mathbf{H}(B,Z)$, then an easy argument (using the variational definition of the ground state energy), gives that

$$m = \frac{dE^Q(Z,B)}{dB},$$

when the derivative exists. Therefore we will abuse notation and write $\frac{dE^Q(Z,B)}{dB}$ instead of m even though we do not assume that the derivative exists.

There are several different asymptotic theories for atoms in large magnetic fields - in practise the distinction between them should be made on the grounds of the relative magnitude between the two parameters Z and B. A mathematically precise way of formulating them is to consider both Z and B as parameters which may be allowed to tend to $+\infty$.

- $Z \to \infty, B/Z^{4/3} \to 0$.
  This is the region of usual Thomas-Fermi theory. The magnetic field has no effect on the highest order energy term and correspondingly, the magnetic moment vanishes to highest order.

- $B, Z \to \infty,\ B/Z^3 \to 0$.
  In this region a modified Thomas Fermi theory, *Magnetic Thomas-Fermi Theory* (MTF) exists which correctly describes the energy of the atom to highest order ([6]). We will prove that this theory also gives the correct prediction for the magnetisation. In a part of this region ($BZ^{-4/3} \leq const$) a calculation of the *current* or local magnetic moment exists, which is more precise information than the total magnetic moment (see [2]).
  If $B/Z^{4/3} \to \infty$ then a simplified MTF-theory, viz. *Strong Thomas Fermi Theory* (STF) becomes valid.

- $B, Z \to \infty,\ B/Z^{4/3} \to \infty$ (notice overlap with the above region).
  Here a *density matrix theory* (DM) developed in [5] gives the energy of the atom to highest order. We prove that the total magnetic moment is also correctly described by this model (for technical reasons we have to restrict to B's which are at most polynomial in Z). This region is also correctly described by the the *Discrete Density Matrix* (DDM) theory from [3].

For clarity let us state the result as a theorem:

Theorem 1.1. *Let $E^A(B,Z)$ denote the energy in one of the approximating models (MTF, STF, DM or DDM) and let (B_n, Z_n) be a sequence that tends to infinity i.e. $|(B_n, Z_n)| \to \infty$ as n tends to infinity. Suppose now that*

$$E(B_n, Z_n)/E^A(B_n, Z_n) \to 1, \tag{2}$$

and that

$$Z_n^{-1/6}\max\{1,\log(B_n/Z_n^3)\}\to 0. \tag{3}$$

Then also

$$\frac{dE}{dB}(B_n,Z_n)/\frac{dE^A}{dB}(B_n,Z_n)\to 1.$$

Remark 1.2. *The "subexponential condition" (3) on B is purely technical. It comes, in particular, from the fact that we have only fairly weak control of correlations between the individual electrons in the atom.*

Remark 1.3. *The regions (in (B,Z)) where (2) is satisied for the individual theories (MTF, STF, DM or DDM) is given by the discussion above.*

Let us finally discuss the *magnetisation* of the atom, i.e. $M=m/V$, where V is the volume of the atom. In the extreme case of $B/Z^3\to\infty$ the atom is approximately a cylinder of length $\approx Z^{-1}[\log(B/Z^3)]^{-1}$ and radius $\approx\sqrt{Z/B}$. The energy behaves as $E\approx Z^3[\log(B/Z^3)]^2$ and therefore $m\approx(Z^3/B)\log(B/Z^3)$. Thus

$$M\approx\frac{(Z^3/B)\log(B/Z^3)}{Z^{-1}[\log(B/Z^3)]^{-1}(Z/B)}=Z^3[\log(B/Z^3)]^2\ll B.$$

2 Virial-type theorems

2.1 Quantum mechanics

Using scaling (as in the proof of the usual virial theorem for Coulomb systems) it is easy to see for the full quantum model that[1] :

Theorem 2.1 (Magnetic Virial Theorem). *Let Ψ be any eigenfunction of $\mathbf{H}(B,Z)$, then*

$$2B\langle\Psi|\mathbf{J}(\vec{A})|\Psi\rangle=2\langle\Psi|\mathbf{K}|\Psi\rangle+\langle\Psi|\mathbf{V}|\Psi\rangle+\langle\Psi|\mathbf{I}|\Psi\rangle,$$

[1]This theorem appeared first in [4] and a more general form was found independently by the author in e.g. [1]

where the operators on the right are the total kinetic, potential and interaction energies.

$$\begin{aligned}
\mathbf{K} &= \sum_{j=1}^{Z} \left((-i\nabla_j + B\vec{A}(x_j))^2 + \vec{B}\cdot\vec{\sigma}_j \right), \\
\mathbf{V} &= \sum_{j=1}^{Z} \left(-\frac{Z}{|x_j|} \right), \\
\mathbf{I} &= \sum_{1\le j<k\le Z} \frac{1}{|x_j - x_k|}.
\end{aligned}$$

If we only apply scaling to the electron coordinates orthogonal to the magnetic field ($x_j^{(1)}, x_j^{(2)}$ for all j) we will obtain a similar expression for the magnetisation which will be more useful in the case of very strong magnetic fields.

Theorem 2.2. *Let Ψ be any eigenfunction of $\mathbf{H}(B,Z)$, then*

$$\langle\Psi|\mathbf{J}(\vec{A})|\Psi\rangle = 2\langle\Psi|\hat{\mathbf{K}}|\Psi\rangle + \langle\Psi|\hat{\mathbf{V}}|\Psi\rangle + \langle\Psi|\hat{\mathbf{I}}|\Psi\rangle,$$

where the operators on the right are:

$$\begin{aligned}
\hat{\mathbf{K}} &= \sum_{j=1}^{Z} \left((-i\partial_{x_j^{(1)}} - B/2x_j^{(2)}))^2 + (-i\partial_{x_j^{(2)}} + B/2x_j^{(1)}))^2 + \vec{B}\cdot\vec{\sigma}_j \right), \\
\hat{\mathbf{V}} &= \sum_{j=1}^{Z} \left(-Z\frac{(x_j^{(1)})^2 + (x_j^{(2)})^2}{|x_j|^3} \right), \\
\hat{\mathbf{I}} &= \sum_{1\le j<k\le Z} \frac{(x_j^{(1)} - x_k^{(1)})^2 + (x_j^{(2)} - x_k^{(2)})^2}{|x_j - x_k|^3}.
\end{aligned}$$

Remark 2.3. *The above theorem is particularly useful in very high magnetic fields where the electrons are essentially localised to the lowest Landau band, since in that case the first term on the right $2\langle\Psi|\hat{K}|\Psi\rangle$ is of lower order than the remaining terms.*

Using the above "virial theorems" we obtain information on the movement paralel to the magnetic field axis:

Corollary 2.4. *Let* Ψ *be any eigenfunction of* $\mathbf{H}(B,Z)$*, then*

$$0 = \langle \Psi | \sum_{j=1}^{Z} \left(-2\partial^2_{x_j^{(3)}} - Z\frac{(x_j^{(3)})^2}{|x_j|^3} \right) + \sum_{1\le j<k\le Z} \frac{(x_j^{(3)} - x_k^{(3)})^2}{|x_j - x_k|} |\Psi\rangle.$$

2.2 Approximating theories

It is interesting to note the the magnetic virial theorems hold for the approximating theories as well. In [5] the following theories are discussed: Magnetic Thomas Fermi (MTF), Strong Thomas Fermi (STF), Density Matrix (DM) and Super Strong (SS). Furthermore a Discrete Density Matrix theory (DDM) has recently been proposed in [3]. All these models are functionals on a space of densities or density matrices, and give the energy as a sum of kinetic, potential and interaction energies. The sets of admissible densities (or density matrices) may depend on both B and Z. In all cases it is a simple task to go through and check by scaling in the space variables and/or variation of the magnetic field strength B, that the following holds:

Proposition 2.5. *Let* $E^A(B,Z) = K^A(B,Z) + U^A(B,Z)$ *be one of the above approximating energies to the true quantum mechanical ground state of a neutral atom with* Z *electrons in the magnetic field of strength* B*. Here* $K^A(B,Z)$ *denotes the kinetic energy and* $U^A(B,Z)$ *the total potential energy. Then the following (virial) relation holds:*

$$2B\frac{dE^A(B,Z)}{dB} = 2K^A(B,Z) + U^A(B,Z).$$

Remark 2.6. *It was noticed in [4] that this relation holds for the STF theory (denoted by MTF in their paper).*

For high fields ($B \ge Z^3$) it is more interesting to have a relation like Thm. 2.2. This holds true for the theories which are exact in this regime. It would be too involved to state all the different cases, so we restrict attention to the Super Strong (SS) case, but similar relations are true for the Discrete Density Matrix (DDM) and Density Matrix (DM) theories.

First a bit of notation: The admissible functions $\mathcal{C}^{SS}(Z,B)$ for the *Super Strong Magnetic Field Density Functional* is the set of positive measurable functions on $\mathbb{R}^3$, satisfying:

- $\int_{\mathbb{R}^3} \rho(x)\, dx = Z$,

- $\int_{\mathbb{R}} \rho(x_\perp, x_3)\, dx_3 \leq \frac{B}{2\pi}$ for all $x_\perp \in \mathbb{R}^2$.
- The distributional derivative $\frac{\partial\sqrt{\rho}}{\partial x_3}$ is a function in $L^2(\mathbb{R}^3)$.

The functional itself is defined for $\rho \in \mathcal{C}^{SS}(Z,B)$ as:

$$\mathcal{E}^{SS}[\rho] = \int_{\mathbb{R}^3} \frac{\partial\sqrt{\rho}}{\partial x_3}\, dx - Z \int_{\mathbb{R}^3} \frac{\rho(x)}{|x|} dx + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} dxdy.$$

Now, notice that the scaling of the variables perpendicular to the field: $\rho(x_\perp, x_3) \mapsto \rho_t \equiv t^2 \rho(tx_\perp, x_3)$ maps $\mathcal{C}^{SS}(Z,B)$ to $\mathcal{C}^{SS}(Z, t^2 B)$. Now by calculating $\mathcal{E}^{SS}[\rho_t]$ and differentiating in t at $t=1$, we get

$$2B\frac{dE^{SS}}{dB} = -Z \int_{\mathbb{R}^3} \frac{\rho(x) x_\perp^2}{|x|^3} dx + \frac{1}{2} \iint \frac{\rho(x)\rho(y)|x_\perp - y_\perp|^2}{|x-y|^3} dxdy.$$

This, of course, is readily comparable to Thm. 2.2.

3 Correctness of approximating theories

The mechanism that makes it possible for us to calculate the total magnetisation is given by the following theorem:

Theorem 3.1. *Let $\mathbf{H}(B,Z)$, $\mathbf{K}(B,Z)$ and $\mathbf{U}(B,Z)$ denote the quantum mechanical operators of total energy, kinetic energy and potential energy, and let $E^Q(B,Z)$, $K^Q(B,Z)$ and $U^Q(B,Z)$ denote the ground state total, kinetic and potential energies, i.e. the expectations of the corresponding operators in the ground state.*
Let furthermore, $\mathcal{E}^A(B,Z) = \mathcal{K}^A(B,Z) + \mathcal{U}^A(B,Z)$ denote an approximating functional, defined on the space $\mathcal{C}^A(B,Z)$, and let $E^A(B,Z)$, $K^A(B,Z)$ and $U^A(B,Z)$ denote the corresponding approximating total, kinetic and potential energies.
Let furthermore $\mathbf{H}_t(B,Z) = t\mathbf{K}(B,Z) + \mathbf{U}(B,Z)$, for $t \in (1/2, 3/2)$, and define $E_t^Q(B,Z)$, $K_t^Q(B,Z)$ and $U_t^Q(B,Z)$ by means of the ground state of $\mathbf{H}_t^Q(B,Z)$.
Define corresponding approximating quantities analogously on the space $\mathcal{C}^A(B,Z)$ (the space is independent of t).
Let Σ denote an unbounded subset of $\{(B,Z) \in \mathbb{R}_+^2\}$.
Suppose now

1. *that the virial theorem is satisfied for the approximating energies i.e.*

$$2B\frac{dE^A(B,Z)}{dB} = 2K^A(B,Z) + U^A(B,Z),$$

2. *that*

$$\left|E_t^A(B,Z) - E_1^A(B,Z) - (t-1)\frac{dE_t^A(B,Z)}{dt}\right| \leq |t-1|g(t)|E^A(B,Z)|,$$

   where the positive function $g(t) \to 0$ *as* $t \to 1$ *is independent of* (B,Z)*,*

3. *and that the approximating theory is indeed approximating in the following sense:*

$$|E^Q(B,Z)_t - E_t^A(B,Z)| \leq c\epsilon^2(B,Z)|E^Q(B,Z)|,$$

   where $\epsilon(B,Z) \to 0$ *as* $(B,Z) \to \infty$ *in* Σ*, and where* ϵ *and the constant* c *do not depend on* t*.*

Then

$$|B\frac{dE^Q(B,Z)}{dB} - B\frac{dE^A(B,Z)}{dB}| \leq c\epsilon(B,Z)|E^Q(B,Z)|.$$

Proof. By the virial theorems for both quantum and approximating theories it is enough to show that the the kinetic and potential energies are correctly given by the approximating theories. The proof of this fact is simple by convexity arguments of the following type:
Let Ψ_1 be a ground state of $\mathbf{H}_1(B,Z)$, then

$$\begin{aligned}
(t-1)K^Q(B,Z) &= \langle\Psi_1|\mathbf{H}_t(B,Z) - \mathbf{H}_1(B,Z)|\Psi_1\rangle \\
&\leq E_t^Q(B,Z) - E_1^Q(B,Z) \\
&= E_t^A(B,Z) - E_1^A(B,Z) + O(\epsilon^2(B,Z)E^Q(B,Z)) \\
&\leq (t-1)K_1^A(B,Z) + |t-1|g(t)|E^Q(B,Z)| \\
&\quad +O(\epsilon^2(B,Z)E^Q(B,Z)).
\end{aligned}$$

Then we choose $t = 1 + c\epsilon(B,Z)$, first with $c > 0$ and then with $c < 0$, to get

$$K^Q(B,Z) = K^A(B,Z) + O(\epsilon(B,Z)E^Q(B,Z)).$$

□

Corollary 3.2. *For all the approximating theories (MTF, STF, DM, DDM and SS) the following holds:*

$$|B\frac{dE^Q(B,Z)}{dB} - B\frac{dE^A(B,Z)}{dB}| = o(E^Q(B,Z)),$$

in their respective domains (in (B,Z)) of validity.

In the regimes where the energy is described by a power law in B, the three terms in Cor. 3.2 above are of the same order, and we can therefore use it to find the main term of the magnetic moment. However, for $B, Z \to \infty$, such that $B/Z^3 \geq const$, the energy has logarithmic behaviour:

$$E(B,Z) \approx Z^3[\log(B/Z^3)]^2.$$

If we differentiate this relation (assuming that they are strictly equal) we get $B\frac{E(B,Z)}{dB} \approx Z^3 \log(B/Z^3) \ll E(B,Z)$. Therefore we would like to choose the $\epsilon(B,Z)$ in Thm 3.1 as small as possible, and at least smaller than $1/|\log(B/Z^3)|$. Luckily it turns out that this precision is already contained in the work of Lieb, Solovej and Yngvason:

Theorem 3.3 (Error bounds for DM-theory when $B \geq Z^3$). *Suppose that $B \geq cZ^3$, then the quantum mechanical energy $E^Q(B,Z)$ and the energy from LSY's density matrix theory $E^{DM}(B,Z)$ satisfy the bound:*

$$|E^Q(B,Z) - E^{DM}(B,Z)| = O(Z^{-1/3}Z^3(1 + [\log(B/Z^3)]^2)).$$

Proof. The proof is essentially a careful reading of the paper [5]. Upon inspection of the proof, we see that the only error term from that paper which is not already given as compatible with the above error bound, is the concentration to the lowest Landau band (notice in particular that the bound above fits with the bound on the exchange energy [5, 7.1. Theorem]). However, from the discussion on the beginning of [5, p. 57] we see that for $B \geq cZ^3$, we may choose $\epsilon = Z/\sqrt{B}$ in [5, (6.12)]. This finishes the proof. □

Corollary 3.4. *For the approximating theories for high fields (DM, DDM and SS) the following holds:*

$$|B\frac{dE^Q(B,Z)}{dB} - B\frac{dE^A(B,Z)}{dB}| = O(Z^{-1/6}Z^3(1 + [\log(B/Z^3)]^2)),$$

when $B \geq cZ^3$.

Together Cor. 3.2 and 3.4 give the statement in Thm. 1.1. Thus the total magnetic moment is given correctly to highest order by the approximating theories - at least up to B's which are exponential in Z.

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