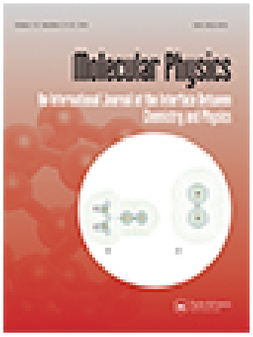

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Absence of proof for the Hohenberg–Kohn theorem for a Hamiltonian linear in the magnetic field

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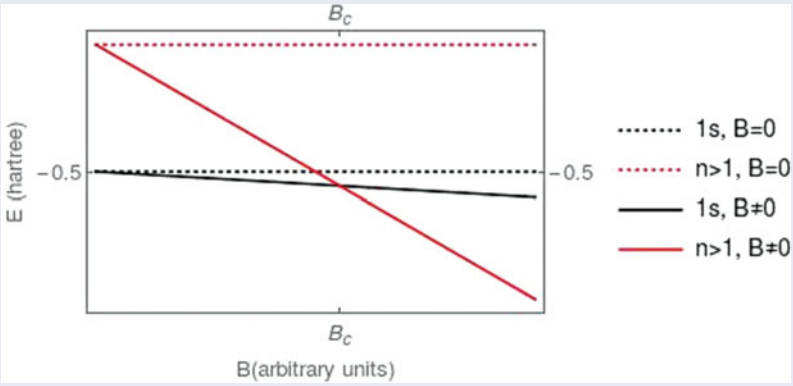
ABSTRACT

The widespread idea that spin-density functional theory is based upon the extension of the Hohenberg–Kohn theorem to weak magnetic fields is contested. First, it is assumed that only the term linear in magnetic field can be kept in the Hamiltonian. Second, once this is done, two problems arise (1) not only the spin-dependent, but also the orbital-dependent term should be taken care of, and (2) the latter produces eigenvalues that are not bounded from below, thus invalidating the proof of the Hohenberg–Kohn theorem.



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1. Introduction

The success of density functional theory is largely due to its extension to spin-polarised systems: spin-density functional theory 'is much more amenable to semilocal approximation than density functional theory' [1]. In textbooks, the Hohenberg–Kohn theorem is extended for spin polarised systems as

$$E_0 = \min_{\rho,m} F[\rho, m] + \int \rho(r)v(r)d^3r + \mu_0 \int B(r)m(r)d^3r. \quad (1)$$

Here, E_0 is the ground state energy, $\rho(r)$ is the ground state density, the sum of the up- ($\rho_\uparrow$) and down-spin density ($\rho_\downarrow$), $m(r) = \rho_\uparrow(r) - \rho_\downarrow(r)$, $v(r)$ is a potential describing the electrostatic interactions of the electrons with an external (usually Coulomb) field, $B(r)$ is a magnetic field, μ_0 is the Bohr magneton and F is a functional that depends only on ρ and m, but not on v and B. To obtain this, the proof of the Hohenberg–Kohn theorem for $B = 0$ is repeated step by step. One starts with a Hamiltonian that contains a term linear in the magnetic field, additionally to the usual ones: kinetic energy, interaction between electrons, and between the electrons and the external (usually nuclear) field. Quadratic terms in B should be present, but one argues that they are irrelevant at small B. There is also a practical argument for neglecting them: theory would become more complicated, as the current density would be needed, too. To derive the Hohenberg–Kohn theorem in small magnetic fields, one makes use of the variation principle that states that for any wave function, the expectation value of the Hamiltonian is larger than E_0.

The aim of this paper is to show that

- the orbital contribution cannot be neglected, even for small magnetic fields,

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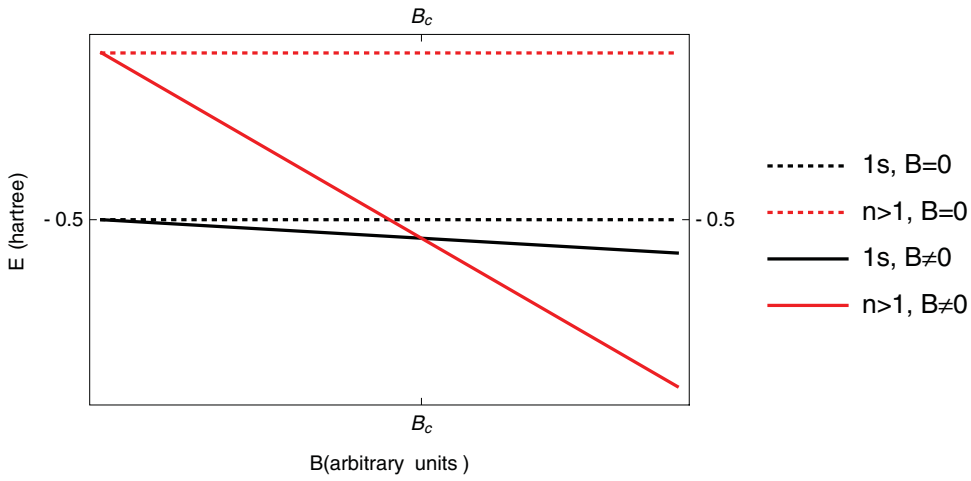

Figure 1. Schematic plot of lowest energies of the hydrogen atomic levels, when only the term linear in the magnetic field is retained, as a function of the magnetic field, $E(n, B)$, for the states having the principal quantum number $n = 1$, and $n > 1$. The dotted horizontal lines correspond to the energies in the absence of the magnetic field. For magnetic fields stronger than B_c, $E(n > 1, B)$ is lower than that of $E(n = 1, B)$.

- in the presence of a vanishingly small, but non-zero B, an infinity of states that are above the ground state in the absence of the magnetic field get below it when the magnetic field is switched on; in fact, the ground state of the Hamiltonian with a term linear in B becomes unbounded from below,

and thus invalidates the extension of the Hohenberg–Kohn theorem that relies on the variation principle. The argumentation given below follows the example given in the classic book of F. Rellich, section 'A Term of Second Order in the Perturbation Parameter cannot always be neglected in Comparison with the First Order Term' [2]. As in this book, the hydrogen atom will be considered to exemplify the issue.

2. Even for weak magnetic fields, orbital contribution should not be neglected

According to the textbook, quantum mechanical treatment of the Zeeman effect, (e.g. [3]), i.e. taking into account terms linear in the magnetic field, the Hamiltonian is given by

$$\hat{H}(B) = \hat{H}(B = 0) + \mu_0 \left(\hat{L} + 2\hat{S}\right) \cdot B. \qquad (2)$$

Please notice that both $\hat{L}$ and $\hat{S}$ commute with $\hat{H}$, and thus the eigenfunctions can be chosen not to change with the constant field B, while the eigenvalues do change with B. The maximum stabilisation by the magnetic field is $-\mu_0(L + 2S)B$, and because L can take any integer value, its contribution can be much larger than that of S. Thus, we consider below the inclusion of the orbital term, due to L.

3. There is no lower bound to the energy for the Hamiltonian linear in *B*

Using the Hamiltonian of Equation (2), the degenerate states for quantum number n have the maximal energy lowering due to the magnetic field given by $-\mu_0 nB$. Its energy is

$$E(n, B) = -\frac{1}{2n^2} - \mu_0 nB.$$

Figure 1 shows schematically the behaviour of $E(n, B)$ as a function of B, for two values of n: $n = 1$, connected to the 1s ground state in the absence of the magnetic field, and some large value of n: beyond a certain value of the field, B_c, $E(n > 1, B) < E(n = 1, B)$: the stabilisation by the magnetic field overcomes the difference between the energies at zero field.

Inversely, we can fix B to some value, and ask if there are values of n for which $E(n, B) < E(n = 1, B)$. The behaviour of $E(n, B)$ at fixed B, is schematically shown in Figure 2. At large n, $E(n \gg 1, B) - E(n = 1, B_c)$ is dominated by the term that decreases linearly with n. There is a critical n, n_c, beyond which all states have an energy lower than that of the state corresponding to the 1s ground state in the absence of the field. As n can take any integer value, there is an infinity of states with $n > n_c$. Furthermore, as n increases, $E(n, B_c)$ goes to $-\infty$.

In the argumentation above, no assumption was made about the magnitude of the field, and holds for any non-zero value, no matter how small. It follows that for the form of the Hamiltonian given by Equation (2), and any non-zero magnetic field, not only the state corresponding to the ground state at $B = 0$ does not remain the ground

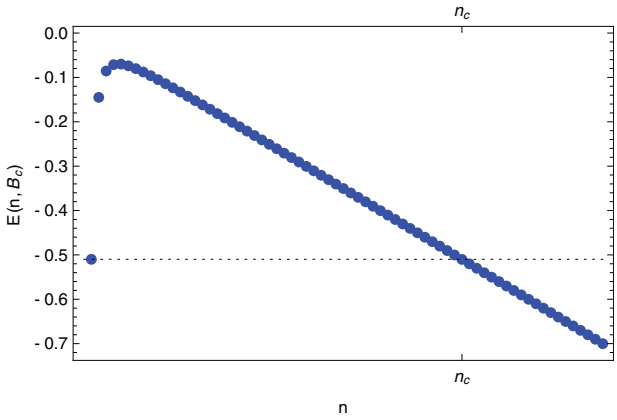

Figure 2. Schematic plot of the energies of the hydrogen atomic levels, when only the terms linear in the magnetic field are retained, as a function of the principal quantum number n, for a given magnetic field. The states with $n > n_c$ have lower energies than that with $n = 1$.

state, but also that there is now lower bound to the energy. Consequently, the variation principle used in deriving the Hohenberg–Kohn theorem cannot be applied for this form of Hamiltonian.

4. Conclusion

Using the Hohenberg–Kohn theorem, only linear terms in the magnetic field is questionable because terms originating from $\hat{L} \cdot B$ can become more important than those originating from $\hat{S} \cdot B$. These terms produce energies that are not bounded from below, and the Hohenberg–Kohn theorem derivation for Hamiltonians linear in B, Equation (2), is not valid.

This does not mean that the Hohenberg–Kohn cannot be applied, under certain conditions, when a magnetic field is present (see, e.g. [4]). It only means that the Hamiltonian linear in the magnetic field is not suited for it; the quadratic terms, with all the complications they bring, have to be taken into account for a proper derivation of the Hohenberg–Kohn theorem when magnetic fields are present.

The question of the meaning of spin-density functional theory, as largely used nowadays, derived from a Hamiltonian linear in the magnetic field, remains open.

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Disclosure statement

No potential conflict of interest was reported by the author.

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