Density functional theory of magnetic systems revisited

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Abstract

The Hohenberg–Kohn theorem of density functional theory (DFT) for the case of electrons interacting with an external magnetic field (that couples to spin only) is examined in more detail than previously. An unexpected generalization is obtained: in certain cases (which include half-metallic ferromagnets and magnetic insulators), the ground state, and hence the spin density matrix, is invariant for some non-zero range of a shift in uniform magnetic field. The energy gap in an insulator or a half-metal is shown to be a ground state property of the N-electron system in magnetic DFT. Its relation to the gap in the Kohn–Sham eigenvalue spectrum is analyzed. © 2001 Elsevier Science Ltd. All rights reserved.

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The half-metallic state of a ferromagnet has been receiving increased attention since its prediction from band theory [1,2] to be the ground state of important magnetic materials such as CrO_2 [3,4], NiMnSb [5] and Sr_2FeMoO_6 [6], and several other intermetallics and oxides, and its unusual physical properties [7]. Such systems have become very attractive for magnetoelectronic applications, where control of the spin degree of freedom is already leading to new devices [8]. Materials thought to be half-metals have been connected with the phenomena of colossal magnetoresistance (CMR) [9,10], large tunneling MR [11], and large, low-field intergrain MR [12], and they would be optimal for applications of spin valve systems [5] for non-volatile magnetic memory and for high-density magnetic storage.

The half-metallic state, in a one-electron picture, is a collinear magnetic state in which one spin direction is metallic while the other is gapped (insulating). This state is half-metallic in another sense: the absence of low energy spin-flips leads to a vanishing magnetic susceptibility like an insulator, but its charge response (conductivity) is that of a metal. These properties combine to give a one-electron description of a spin-charge separated state. In fact, almost all understanding of half-metals so far is based on the one-electron picture, which opens up questions such as (1) What is a half-metal in many body context? (2) Are there other unusual possibilities in magnetic systems? One general characterization might be in terms of conductivity (charge response) and susceptibility (spin response) alluded to above: in an insulator, both vanish, in a conventional (even ferromagnetic) metal, both are non-zero, and in a half-metal, the conductivity is non-zero while the susceptibility vanishes. A clear many-body formulation is however lacking.

Since density functional theory (DFT) is a rigorous many body theory for (chosen) ground state properties, we revisit the foundations of DFT with magnetic properties in mind. Originally, DFT was based on the first Hohenberg–Kohn (HK) theorem [13] for spin-independent densities, which demonstrates the existence of a unique map

$$n(\mathbf{r}) \mapsto v(\mathbf{r}) \bmod(\text{constant}), \tag{1}$$

where v is the external potential and n is the ground state particle density. According to the second HK theorem, the ground state energy and density are obtained as the solution

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to a variational principle:

$$E[v - \mu] = \min_n \left\{ F[n] + \int n(v - \mu) \, d^3 r \right\}, \tag{2}$$

where μ is the chemical potential. Then, von Barth and Hedin [14] pointed out that (1) cannot be generalized to spin-dependent densities and potentials (including external magnetic fields). Instead, they proved a direct unique map $n_{ss'} \mapsto \Psi$ from spin densities to ground state wavefunctions. These maps were used to define $F[n]$. However, later on, the variational principle has been put on an independent, more general basis [15,16] and those maps are not needed to define the density functional anymore. Nevertheless, the uniqueness of the map (1) remains an important issue regarding the existence and uniqueness of the functional derivative $\delta F/\delta n = -(v - \mu)$ needed to justify the application of Euler's equation (Kohn–Sham equation) for solving (2). A non-uniqueness of $\mu(n)$ $(\mu(N))$ produces the well-known gap problem. DFT, as extended by Kohn and Sham [17] and many others, forms the basis of our understanding of the electronic behavior of real materials. The theory and its extension to spin-dependent densities [14,18] has been applied heavily, however, the HK theorem for interacting particles with spin has been repeatedly stated to be analogous to the HK theorem, although this was already disproved in [14]. Zero susceptibility, however, would imply that the ground state spin density does not change when an external magnetic field is changed. In this paper, we construct a more revealing generalization of the HK theorem, obtain explicitly the conditions that allow half-metallicity, and demonstrate some unexpected consequences.

We consider the system in an external magnetic field $B(\mathbf{r})$ in the (commonly considered) non-relativistic limit, in which the field acts only on the electron spin, and the dipolar interaction between spins is neglected. The potentials can be combined into 2×2 spin matrix

$$u_{ss'}(\mathbf{r}) = v(\mathbf{r})\delta_{ss'} - \mu_B \mathbf{B}(\mathbf{r}) \cdot \vec{\sigma}_{ss'}. \tag{3}$$

The external field $\mathbf{B}$ may vary in magnitude and direction.

Realizing that two different scalar potentials cannot lead to the same ground state Ψ, the original derivation of HK [13] concluded that if $\Psi \mapsto v - \mu$ is unique then $n \mapsto v - \mu$ is also unique. Following the original derivation of HK [13], we begin by supposing that there are two different potentials u, u', which lead to the same ground state Ψ. We show again that $\Psi \mapsto (v - \mu, \mathbf{B})$ is not a unique mapping in general and present a complete analysis of this relation.

The many-body Hamiltonian of the system is

$$\hat{H} = \hat{T} + \hat{W} + \hat{U}, \tag{4}$$

where $\hat{T}$ is the kinetic energy operator, $\hat{W}$, the Coulomb interaction energy and $\hat{U}$, the interaction with the external potential. The fermionic many-particle Schrödinger

equation is (in atomic units)

$$\left[\sum_i^N \frac{-\nabla_i^2}{2} + \sum_{i<j}^N w(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N)$$

$$+ \sum_i^N \sum_{\beta_i} u_{\alpha_i, \beta_i}(\mathbf{r}_i) \Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_i\beta_i, ..., \mathbf{r}_N\alpha_N)$$

$$= E\Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N), \tag{5}$$

where $\mathbf{r}_i$, α_i are the space and spin coordinates of the ith electron; $w(\mathbf{r}, \mathbf{r}') = e^2/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb interaction.

Assume there are two external potentials, u, u', with energies E, E' that have the same ground state wave function $\Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N)$. Subtracting the two many-particle Schrödinger equation leads to

$$\sum_{i=1}^N \sum_{\beta_i} \Delta u_{\alpha_i, \beta_i}(\mathbf{r}_i) \Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_i\beta_i, ..., \mathbf{r}_N\alpha_N)$$

$$= \Delta E \Psi(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N), \tag{6}$$

where $\Delta u = u - u'$, $\Delta E = E - E'$. Now, we perform a unitary spin rotation $Q_{ss'}(\mathbf{r})$ at each point of space that diagonalizes the difference in potentials (i.e. rotates $\mathbf{B}$ to lie along the $\hat{z}$ direction:

$$\{Q(\mathbf{r})[\Delta u(\mathbf{r})]Q^\dagger(\mathbf{r})\}_{ss'} = \Delta \tilde{u}_s(\mathbf{r})\delta_{ss'}. \tag{7}$$

The wavefunction is transformed according to

$$\prod_i^N Q_{\alpha_i\alpha_i'}(\mathbf{r}_i) \Psi(\mathbf{r}_1\alpha_1', ..., \mathbf{r}_N\alpha_N') \equiv \tilde{\Psi}(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N),$$

where $\prod_i^N Q_{\alpha_i\alpha_i'}(\mathbf{r}_i)$ is the operator that rotates each of the (α_i). Collecting these results gives

$$\sum_{i=1}^N \Delta \tilde{u}_{\alpha_i}(\mathbf{r}_i) \tilde{\Psi}(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N) = \Delta E \tilde{\Psi}(\mathbf{r}_1\alpha_1, ..., \mathbf{r}_N\alpha_N).$$

$\tilde{\Psi}$ is some $\{\mathbf{r}_i\}$-dependent multi-component function of the 2^N possible spin configurations, at least one of which must be non-zero. Choose a non-zero component $\tilde{\Psi}_c$ and denote by $N_\uparrow$, the number of $\alpha_i = \uparrow$ values in this component. Since $\tilde{\Psi}$ is antisymmetric (as was Ψ) with respect to permutations of $(\mathbf{r}_i\alpha_i)$ with $(\mathbf{r}_j\alpha_j)$, we may renumber the particle indices in such a way that $\alpha_1 = \alpha_2 = \cdots = \alpha_{N_\uparrow}$, $\alpha_{N_\uparrow+1} = \alpha_{N_\uparrow+2} = \cdots = \alpha_N$. This ordering lets us write

$$\left\{ \sum_{i=1}^{N_\uparrow} \Delta \tilde{u}_\uparrow(\mathbf{r}_i) + \sum_{i=N_\uparrow+1}^N \Delta \tilde{u}_\downarrow(\mathbf{r}_i) \right\} \tilde{\Psi}_c(\mathbf{r}_1\uparrow, ..., \mathbf{r}_N\downarrow)$$

$$= \Delta E \tilde{\Psi}_c(\mathbf{r}_1\uparrow, ..., \mathbf{r}_N\downarrow). \tag{8}$$

This equation must hold for all values of $(\mathbf{r}_1, ..., \mathbf{r}_N)$. (We suppose u, u' are analytic in $\mathbf{r}$ except possibly at isolated points, so that $\tilde{\Psi}_c$ is non-zero almost everywhere.) By varying only $\mathbf{r}_1$, and then separately varying only $\mathbf{r}_N$, we obtain

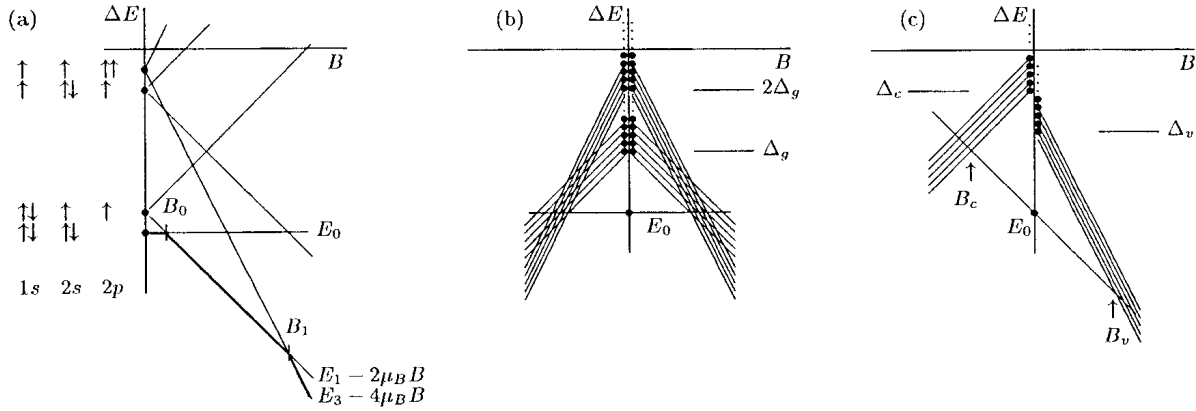$$\Delta \tilde{u}_\uparrow = C_\uparrow, \Delta \tilde{u}_\downarrow = C_\downarrow, \tag{9}$$

Fig. 1. Energy change with field B for: (a) Be atom, the levels are discrete and the variation is $-S_z\mu_B B$; (b) a nonmagnetic insulator, the ground state energy is constant over a range of field $-\Delta_g < \mu_B B < \Delta_g$, beyond which magnetization is induced; (c) a half metal, the ground state energy varies as $-\mu_B(N_\uparrow - N_\downarrow)B$ in the range $B_c < B < B_v$ ($\Delta_v < \mu_B B < \Delta_c$). In (b) and (c), the small dots indicate a continuum extending upwards. See text for further explanation.

where $C_\uparrow$, $C_\downarrow$ are constants. The special cases $N_\uparrow = 0$ or $N_\uparrow = N$ do not lead to new consequences. For further analysis, we consider separate cases.

Case A: impure spin states. Suppose that there are at least two components of $\tilde{\Psi}$ with different values of $N_\uparrow$ and hence $N_\downarrow = N - N_\uparrow$. Then

$$N_\uparrow C_\uparrow + (N - N_\uparrow)C_\downarrow = \Delta E. \tag{10}$$

Since this holds for two different values of $N_\uparrow$, it follows that $C_\uparrow = C_\downarrow \equiv C$, which leads to $\Delta\tilde{u}_\uparrow = \Delta\tilde{u}_\downarrow$ so $\Delta u_{\alpha,\beta} = C\delta_{\alpha,\beta}$. By the ground state energy minimum principle, this recovers the usual Hohenberg–Kohn result

$$n_{ss'} = n'_{ss'} \rightarrow \begin{pmatrix} v(\mathbf{r}) - v'(\mathbf{r}) \equiv C, \\ \mathbf{B}(\mathbf{r}) - \mathbf{B}'(\mathbf{r}) \equiv 0 \end{pmatrix}, \tag{11}$$

implying a non-zero susceptibility.

Case B: pure spin states. Suppose now that all non-zero components of $\tilde{\Psi}$ have the same value of $N_\uparrow$ and $N_\downarrow$. These may be considered as 'pure spin' states, eigenfunctions of the operator $\hat{S}^z = \sum_i \sigma^z_{\alpha_i\beta_i}/2$ with eigenvalues $S_z = N_\uparrow - (N/2) = (N_\uparrow - N_\downarrow)/2$. Then $C_\uparrow$ and $C_\downarrow$ need not be equal and we can write

$$\Delta\tilde{u} = \begin{pmatrix} C_\uparrow & 0 \\ 0 & C_\downarrow \end{pmatrix} = \bar{C}\mathbf{1} - \mu_B\bar{B}\sigma^z, \tag{12}$$

where $\bar{C} = (C_\uparrow + C_\downarrow)/2$ and $-\mu_B\bar{B} = (C_\uparrow - C_\downarrow)/2$.

Backtransforming according to the inverse of Eq. (7) gives

$$\Delta u_{\alpha\beta}(\mathbf{r}) = \bar{C}\delta_{\alpha\beta} - \mu_B\bar{B}[Q^\dagger(\mathbf{r})\sigma_z Q(\mathbf{r})]_{\alpha\beta}. \tag{13}$$

The last term on the right is position-dependent, non-diagonal, and non-vanishing in general. In this case, the conditions for identical ground state wavefunctions are

$$\Psi = \Psi' \rightarrow \begin{pmatrix} v(\mathbf{r}) - v'(\mathbf{r}) = \bar{C}, \\ \mathbf{B}(\mathbf{r}) - \mathbf{B}'(\mathbf{r}) = \bar{B}\hat{e}(\mathbf{r}) \end{pmatrix}. \tag{14}$$

where $\hat{e}$ is the unit vector $(1/2)\,\text{Tr}\{\bar{\sigma}Q^\dagger(\mathbf{r})\sigma_z Q(\mathbf{r})\}$. The result (11) is modified accordingly. This result is a highly non-trivial generalization of the HK theorem: *two magnetic fields whose difference is constant in magnitude, but possibly is non-unidirectional, may give rise to the same ground state.*

Now we investigate the conditions on Q for which $\tilde{\Psi}$ is an eigenstate of $\hat{S}^z$, i.e. $\tilde{\Psi}$ describes a collinear spin arrangement. Considering the Hamiltonian Eq. (4), there must be an operator

$$\hat{U}_o = \sum_{i=1}^N Q^*_{\alpha'_i\alpha_i}(\mathbf{r}_i)\sigma^z_{\alpha'_i\beta'_i}Q_{\beta'_i\beta_i}(\mathbf{r}_i) \tag{15}$$

that commutes with $\hat{T} + \hat{U} + \hat{W}$. We now specialize to the particular important case where one of the external fields, $\mathbf{B}'$, is zero. This yields the behavior of a spontaneously (without external $\mathbf{B}$-field) spin-polarized system when a magnetic field is switched on. Since the interaction $\hat{W}$ is spin independent, $\hat{U}_o$ will commute with H' if and only if it commutes with $\hat{T}$. One can show that this necessitates that Q be $\mathbf{r}$-independent, so that Ψ itself is an eigenstate of $\hat{S}^z$, and hence is a collinear spin state. The second condition in Eq. (14) reduces to $\mathbf{B} - \mathbf{B}' = B\hat{z}$: a turning on of a uniform magnetic field leaves the ground state invariant. Restated: in the subspace of collinear magnetizations, *the ground state determines the magnetic field only up to some codirectional uniform field*, and this is the most general possibility which can appear with a *spontaneously* spin-polarized ground state.

In the collinear case, inserting $\Delta u = \mu_B B\sigma_z$, Eq. (6) yields

$$\Delta E(B) = -(N_\uparrow - N_\downarrow)\mu_B B, \tag{16}$$

which gives the well known dependence of energy vs field for a system of fixed spin. Consider as a simple example a Be atom in a uniform magnetic field, with its ground state

characterized as $1s^2 2s^2$ ($N = 4$, $N_\uparrow = 2$). The lowest excited $\hat{S}_z$-eigenstate is $1s^2 2s2p$ with $N_\uparrow = 3$. Its excitation energy is that of a $2s \rightarrow 2p$ promotion. There is another excited state $1s2s^2 2p$ with the same $N_\uparrow$, but the much higher excitation energy of a $1s \rightarrow 2p$ core excitation. The energetically lowest $N_\uparrow = 4$ state is $1s2s2p^2$ whose excitation energy is roughly the sum of the previous two. The situation is sketched in Fig. 1(a), where the lines with positive slopes correspond to states with all spins reversed.

Since states with $N_\uparrow = N/2 \pm n$ are degenerate for $B = 0$, Fig. 1(a) may be supplemented symmetrically to the vertical axis. Hence, for $|B| < B_0$, the groundstate is $1s^2 2s^2$ with energy E_0, for $B_0 < B < B_1$, the ground state is $1s^2 2s2p$ with energy $E_1 - 2\mu_B B$, and for $B \geq B_1$, the ground state is $1s2s2p^2$ with energy $E_3 - 4\mu_B B$. The ground state does not change with field except at certain isolated values.

In an extended system, say a non-magnetic insulator with gap Δ_g, there is a continuum above Δ_g (one excited electron with reversed spin), another continuum above $2\Delta_g$ (two excited electrons) and so on, as illustrated in Fig. 1(b). In an extended system, one would prefer to consider the intensive quantity

$$\frac{\Delta E(B)}{N} = -\mu_B B \left(\frac{N_\uparrow - N_\downarrow}{N} \right) \tag{17}$$

instead of ΔE itself. Then, one finds that for $\mu_B B < \Delta_g$, the ground state is independent of B, beyond which the state changes and $\Delta E/N$ veers off. Thus while the gap Δ_g is not a ground state property of the N particle system in paramagnetic DFT (it involves the $N \pm 1$ particle ground states), it is a ground state property in the presence of a uniform field.

For a stoichiometric half-metal with moment per cell $\mu_B M$ (M is an integer) the picture is related, except there is an overall bias — a slope of $-\mu_B M$ in the energy per cell — and the positive and negative B directions are not symmetric. The situation that is sketched in Fig. 1(c) has a gap $\Delta_v + \Delta_c$ for $\downarrow$ spin states, with no gap for $\uparrow$ spin. The chemical potential μ corresponds to the energy to remove an $\uparrow$ spin, and the quantities $\Delta_v = \mu_B B_v$, $\Delta_c = \mu_B |B_c|$ represent the energy, or field, required to flip a spin from $\downarrow$ to $\uparrow$, or vice versa. Note again that the interval of B for which the state does not change, which is the gap in the $\downarrow$ spectrum, is a ground state property of the N particle system in an external magnetic field.

It is useful to consider the form of constrained DFT in which $N_\uparrow$ and $N_\downarrow$ are specified, which leads to two associated chemical potentials $\mu_\uparrow$, $\mu_\downarrow$. Then as N_s is changed to $N_s \pm 1$, μ_s may vary only to order $1/N_s$ (metallic behavior) or it may jump discontinuously across a gap, just as is the case for insulators [19,20]. The half-metal is defined as that situation in which one and only one of μ_s (we have chosen $\downarrow$) is discontinuous upon addition of one electron. For an insulator, there is a discontinuity in μ for both spins.

We now consider the KS eigenvalue spectrum. As long as the external field shifts the bands sufficiently little not to disturb the half-metallicity ($B_c < B < B_v$), the ground state, and hence the charge density in each spin channel, remain unchanged. Using the same arguments as were applied to establish the discontinuity in $v_{xc}(N(\mu))$ for an insulator as μ crosses the gap (the kinetic energy is discontinuous across the gap) [19,20], one finds that there is a discontinuity in $v_{xc,\downarrow}(N_\uparrow, N_\downarrow)$ if the filling, with $N_\downarrow$ moves $\mu_\downarrow$ across the gap.[1]

The Kohn–Sham gap $\varepsilon_{g\downarrow}$ is smaller than the true (quasiparticle) gap $\Delta_g = \Delta_c + \Delta_v$. When the magnetic field is large enough that μ reaches the KS band minimum $\varepsilon_c(N_\downarrow)$, the occupation of that channel becomes $N_\downarrow + \epsilon$ (with $\epsilon \rightarrow 0$). This is the point of the discontinuity, where the KS conduction eigenvalue (in fact, the entire $\downarrow$ spectrum) jumps upward. By comparison with Dyson's equation, and the fact that the system ground state spin densities must be the same whether obtained from DFT or the quasiparticle Greens functions, this jump must be such as to make $\varepsilon_{c\downarrow}(N_\uparrow, N_\downarrow + \epsilon) \equiv \Delta_c$, the quasiparticle conduction band edge, for $\epsilon \rightarrow 0$.

It is apparent then that the KS gap in the insulating channel is not equal to the true gap in that channel, and that $\varepsilon_c(N_\uparrow, N_\downarrow) - \mu$ is not the true spin flip energy (which is $\Delta_c - \mu$). By our definition (see Footnote 1), as the reverse field is applied and μ is driven toward the valence band maximum $\varepsilon_{v\downarrow}$, there is no discontinuity, and the other spin flip energy — a true excitation energy — is given correctly by DFT. Needless to say, an approximation such as the local density approximation that interpolates across the discontinuity, will fail to predict both Δ_c and Δ_v.

We now summarize that we have presented new, rigorous results for the Hohenberg–Kohn mapping in a magnetic field. We obtain conditions that characterize half-metals: (1) two collinear systems in different uniform magnetic fields may have the same half-metallic (or magnetic insulating) ground state; (2) exactly one of the chemical potentials μ_s is discontinuous upon particle addition to a half-metal. We have pointed out other consequences, primary among them being that the ground state energy of a system is no longer a unique functional of the density $n_{ss'}$ when magnetic fields are allowed (although the ground state itself is), and that the gap in a half-metal is a ground state property of the N particle system. These results are only exact in the non-relativistic ($c \rightarrow \infty$) limit. For c finite, half-metallicity is an approximate notion due to orbital currents and orbital moments and spin–orbit coupling that mixes them, and the general theory [21] probably restores the conventional theorems of DFT. Still, the notion of half-metallicity will be an important model limit.

Acknowledgements

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[1] We define $v_{xc\downarrow}(N_\uparrow, N_\downarrow)$ to be left semicontinuous at $N_\downarrow(\mu = \varepsilon_v)$.

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