Magnetic-field density-functional theory

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We discuss the formal basis and general advantages of magnetic-field-and-density functional theory (BDFT) for the ground-state magnetic properties of many-electron systems. The ground-state density $\rho(\mathbf{r})$ and the magnetic field $\mathbf{B}(\mathbf{r})$ are the variables appearing in the energy functionals that are the fundamental elements of BDFT. This is in contrast to the energy functionals of current-and-density functional theory (CDFT), the most general density-functional way of treating systems in a magnetic field, where the variables are $\rho(\mathbf{r})$ and the ground-state paramagnetic current $\mathbf{j}_p(\mathbf{r})$. Explicit calculations of magnetic properties have already been made that can be recognized as belonging to the BDFT paradigm, which this work therefore puts on a formal foundation. There are also aspects of BDFT discussed here that may make it an attractive alternative to the more general CDFT in some situations. In particular, we show that Kohn-Sham equations may be derived that use purely real orbitals and for which the energy does not separate into para- and diamagnetic contributions. We also show that in BDFT the zero-field electron density alone is sufficient to calculate the energy to *second* order in the magnetic field. Thus calculation of, e.g., diamagnetic susceptibilities or chemical shifts can in principle be made directly from zero-field electron distributions, without any need for the calculation of first-order corrections.

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I. INTRODUCTION

The linchpin of density-functional theory is the universality of its energy functionals. Electronic density-functional theory (DFT) begins by writing the ground-state energy E of an interacting many-electron system, characterized by an external scalar potential $V(\mathbf{r})$, in the following way [1,2]:

$$E = G[\rho] + \int d^3r\, \rho(\mathbf{r})V(\mathbf{r}) + \frac{1}{2}\int d^3r\, d^3r'\, \frac{\rho(\mathbf{r})\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|},$$

(1)

where $\rho(\mathbf{r})$ is the ground-state density. Equation (1) is useful precisely because of the universality of the kinetic-exchange-correlation functional $G[\rho]$. Although constructing an accurate approximation to $G[\rho]$ is a formidable task, it need only be done once because the form of G is independent of the form of $V(\mathbf{r})$.

It is therefore natural that when density-functional theory was extended to systems characterized by an external vector as well as scalar potential the most universal form of G was sought [3–8]. Unfortunately it turns out that if G is to be independent of the vector potential $\mathbf{A}(\mathbf{r})$, it cannot be written as a functional of $\rho(\mathbf{r})$ alone. The canonical or "paramagnetic" current $\mathbf{j}_p(\mathbf{r})$ must enter G as an additional independent functional variable [5,8]. Thus the natural equivalent of density-functional theory when a magnetic field is present is current-and-density functional theory (CDFT), in which the equivalent of Eq. (1) is [8]

$$E = G[\rho, \mathbf{j}_p] + \int d^3r\, \rho(\mathbf{r})V(\mathbf{r}) + \frac{1}{2}\int d^3r\, d^3r'\, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+ \int d^3r\, \left\{ \mathbf{j}_p(\mathbf{r}) + c^{-1}\rho(\mathbf{r})\mathbf{A}(\mathbf{r}) \right\} \cdot c^{-1}\mathbf{A}(\mathbf{r}).$$

(2)

The functional $G[\rho, \mathbf{j}_p]$ in this equation will in general bear no resemblance to the functional $G[\rho]$ of zero-field DFT that appears in Eq. (1).

The presence of $\mathbf{j}_p(\mathbf{r})$ as an additional independent variable makes CDFT a more complex theory than DFT, and although approximate forms of pieces of $G[\rho, \mathbf{j}_p]$ have been made in the equivalent of the local-density approximation (LDA) [5,6,9], no calculations using CDFT have yet been reported.

Meanwhile, non-CDFT calculations have been made of the lowest-order responses of many-electron systems to weak magnetic fields [10–13]. The approaches have been from different viewpoints, Thomas-Fermi-Dirac theory [10,12], $X\alpha$ theory [11], and analogy to coupled Hartree-Fock theory [13], but in all of them only $\rho(\mathbf{r})$ appears as an independent variable in the energy functional. How can one reconcile this with the foundation of CDFT that both $\rho(\mathbf{r})$ and $\mathbf{j}_p(\mathbf{r})$ should be independent variables in the energy functional? If this can be done, and a general approach other than CDFT exists, what advantages are there to proceeding in such a way? The work we present here addresses these questions.

Our first and most essential result is that there does exist a formal basis for ground-state magnetic property calculations in which only $\rho(\mathbf{r})$ appears as an independent variable. Such an approach is what we call magnetic-

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field-and-density functional theory (BDFT) because the magnetic field $\mathbf{B}(\mathbf{r})$ instead of the current $\mathbf{j}_p(\mathbf{r})$ appears explicitly in the energy functional. That is, an equivalent of Eq. (2) can be written which is

$$E = G[\rho, \mathbf{B}] + \int d^3r\, \rho(\mathbf{r}, \mathbf{B})\, V(\mathbf{r})$$
$$+ \frac{1}{2} \int d^3r\, d^3r'\, \frac{\rho(\mathbf{r}, \mathbf{B})\rho(\mathbf{r}, \mathbf{B})}{|\mathbf{r} - \mathbf{r}'|}. \qquad (3)$$

While G has the same form for all $V(\mathbf{r})$, it depends explicitly on the form of $\mathbf{B}(\mathbf{r})$. That is, G is still universal with respect to the scalar potential, but it is *not universal* with respect to the vector potential.

At first glance it would appear silly to abandon the universality of G—which we labeled the linchpin of DFT—when the option not to (i.e., CDFT) exists. Doing so does of course allows a reduction in complexity by eliminating $\mathbf{j}_p(\mathbf{r})$ as an independent variable. Moreover there are potential practical advantages of working with the magnetic field directly, which we mention below. But the essential reason why BDFT is *not* pointless is because the nonuniversality of G is a lot less important when it applies to external vector potentials than it would be if it applied to external scalar potentials. It is totally impractical to construct a different $G[\rho]$ for each scalar potential because there are an unlimited number of forms for $V(\mathbf{r})$ (e.g., possible arrangements of nuclei) that are of practical interest. This cannot be said for external vector potentials. In fact just a few forms of $\mathbf{A}(\mathbf{r})$ cover a large number of the problems of practical interest. For example, when studying the magnetic properties of molecules in the gas or liquid phase it is unusual to consider forms of $\mathbf{A}(\mathbf{r})$ other than those corresponding to a constant magnetic field, one or two spin magnetic dipoles, or a combination of these. Constructing different $G[\rho, \mathbf{B}]$ for different forms of $\mathbf{B}(\mathbf{r})$ is therefore not impractical.

In what follows we first present the formal basis for BDFT, which is essentially the Hohenberg-Kohn [1] theorem. We then show the formal derivation of the one-electron (Kohn-Sham [14]) equations that allow one to avoid construction of the kinetic part of G. We point out that in BDFT there is no unique separation of the one-electron Hamiltonian into "kinetic" and "potential" operators and that one can define purely real one-electron orbitals for which the energy does not divide into para- and diamagnetic terms. Finally, we discuss the use of BDFT for the calculation of the second-order responses of a system to a weak external field, e.g., diamagnetic susceptibilities or the shielding tensors (chemical shifts) of spin magnetic dipoles [15]. We prove that in principle these *second*-order energy changes may be extracted from the *zero*-order ($\mathbf{B} = 0$) electron density alone. There is no *a priori* necessity for the calculation of the corrections to the zero-field wave function that enters an ordinary *ab initio* calculation of second-order energies such as coupled Hartree-Fock theory [16]. This suggests that BDFT may have a powerful and perhaps unique role to play in this particular kind of calculation.

II. THE FORMAL BASIS OF BDFT

We wish to describe completely the ground state of an N-electron system in an external scalar potential $V(\mathbf{r})$ and vector potential $\mathbf{A}(\mathbf{r})$. The formal basis of current-and-density functional theory [8] is the proof that this can be done with the ground-state density $\rho(\mathbf{r})$ and the canonical or paramagnetic current $\mathbf{j}_p(\mathbf{r})$. However, in a fixed gauge we argue that this can also be done with $\rho(\mathbf{r})$ and the magnetic field $\mathbf{B}(\mathbf{r})$. The proof is in two steps.

First, in the absence of accidental degeneracy and for a fixed gauge, the ground-state N-electron wave function Ψ_0 is a unique functional of $\mathbf{B}(\mathbf{r})$ and $V(\mathbf{r})$ because we may explicitly construct Ψ_0 from them by solving the N-electron Schrödinger equation. [Note that fixing the gauge means $\mathbf{B}(\mathbf{r})$ determines $\mathbf{A}(\mathbf{r})$ uniquely.]

Second, there is a one-to-one correspondence [17] between $V(\mathbf{r})$ and $\rho(\mathbf{r})$ for a fixed $\mathbf{B}(\mathbf{r})$. This is a result of the Hohenberg-Kohn theorem [1], which holds *within* but not *across* each domain defined by the set of all many-electron Hamiltonians with a fixed $\mathbf{B}(\mathbf{r})$ and any $V(\mathbf{r})$.

This last statement can be illustrated in a different context that is familiar to electronic density-functional theory: the Kohn-Sham [14] construction of one-electron equations for the density $\rho(\mathbf{r})$. In the Kohn-Sham construction one assumes that the *exact same density* $\rho(\mathbf{r})$ results from two different Hamiltonians containing two different external potentials. One Hamiltonian is that of the system of interest in its particular external potential $V(\mathbf{r})$. The other is that of the reference or noninteracting system in the effective external potential $V_{\text{eff}}(\mathbf{r})$ that contains the usual exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$. The fact that two different external potentials give the same density would at first glance seem to violate the Hohenberg-Kohn theorem. But it does not because the electron-electron interaction is different in the two Hamiltonians (the noninteracting Hamiltonian has no electronic-repulsion term), that is, the Hamiltonians belong to different domains defined by the set of all Hamiltonians with a fixed form of electron-electron interaction and any $V(\mathbf{r})$. The Hohenberg-Kohn theorem does not hold across such domains, but only within each. This particular domain definition is also apparent in classical density functional theory [18], where different forms of particle pair interactions are commonplace.

We have thus established that Ψ_0 and hence all ground-state properties are determined uniquely by $\mathbf{B}(\mathbf{r})$ and $\rho(\mathbf{r})$. We may therefore write Eq. (3) for the ground-state energy and define the kinetic-exchange-correlation functional $G[\rho, \mathbf{B}]$, which is "nonuniversal" in that it depends explicitly on $\mathbf{B}(\mathbf{r})$.

As there is no practical value in regarding $\mathbf{B}(\mathbf{r})$ as an independent variable, we regard it in the energy functional as a parametric variable. The ground-state density $\rho(\mathbf{r}, \mathbf{B})$ is then the only independent variable in Eq. (3). The variational principle is easily shown in the usual way [1], and so we may find the actual ground-state density $\rho(\mathbf{r}, \mathbf{B})$ for any particular $V(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ by minimizing the right-hand side of Eq. (3) with respect to trial densities $\tilde{\rho}(\mathbf{r}, \mathbf{B})$ [17]. Then, with $\rho(\mathbf{r}, \mathbf{B})$ inserted into it, Eq. (3) provides the actual ground-state energy or,

when subjected to appropriate derivatives, other observable ground-state properties. $E[\rho, \mathbf{B}]$ can also be used directly, e.g., within a Kim-Gordon [19,20,10,12] calculation for the contribution to ground-state properties of nonbonded interaction.

Practical construction of a magnetic-field density-functional theory requires an approximation for $G[\rho, \mathbf{B}]$. Some of these have already been constructed, in whole or in part, for various forms of $\mathbf{B(r)}$. In particular, LDA forms have been constructed for $\mathbf{B(r)}$ weak and constant or slowly varying [10,21] and for $\mathbf{B(r)}$ consisting of a weak constant field plus a magnetic dipole field, i.e., the field seen by an electron in a spin magnetic resonance experiment [13,22]. It should also be straightforward, using the propagator methods developed in Ref. [22], to construct an approximation for $G[\rho, \mathbf{B}]$ for another $\mathbf{B(r)}$ of general interest: that due to two magnetic dipoles. With this G one could address at a rigorous level spin-spin coupling experiments in many electron systems, which are important in the determination of the solution structure and dynamics of macromolecules [23].

For certain forms of $\mathbf{B(r)}$ it is likely to be easier to construct approximations to $G[\rho, \mathbf{B}]$ than to the CDFT functional $G[\rho, \mathbf{j}_p]$, because the form of $\mathbf{B(r)}$—unlike that of $\mathbf{j}_p(\mathbf{r})$—is fixed and known at the beginning. This extra information may be used to advantage in constructing $G[\rho, \mathbf{B}]$. For example, if $\mathbf{B(r)}$ contains a laboratory field $\mathbf{B}_{lab}(\mathbf{r})$, its magnitude B_{lab} must be very weak (one atomic unit of magnetic field is more than a billion gauss), so perturbation theory in B_{lab} may be used in constructing $G[\rho, \mathbf{B}]$ [22]. A more general issue affected by the form of $\mathbf{B(r)}$ is the ability to treat separately exchange and correlation contributions to G. If one makes the LDA, as is almost inevitable, and $\mathbf{B(r)} = \mathbf{B}$, a constant field, then the $\mathbf{B}$-dependent pure exchange contribution to $G[\rho, \mathbf{B}]$ diverges [9]. Consequently the $\mathbf{B}$-dependent parts of exchange and correlation must be treated together. This is true also if $\mathbf{B(r)}$ is assumed to vary slowly and its position dependence is treated classically, as in the present incarnations of CDFT [8]. On the other hand, for nonuniform fields, when the spatial variation of $\mathbf{B(r)}$ is treated quantum mechanically, the $\mathbf{B}$-dependent exchange contribution may be well behaved even within the LDA. This has been shown to be true explicitly for the spin magnetic resonance experiment fields [22]. In these cases one can include $\mathbf{B}$-dependent exchange contributions to G without having to treat $\mathbf{B}$-dependent correlation.

III. ONE-ELECTRON EQUATIONS

Little density-functional theory is attempted with the full functional G. Generally one tries to avoid error in the kinetic contribution to G, which is the largest, by writing this part as the Hartree-Fock form of the kinetic energy plus a correction. As the Hartree-Fock kinetic energy is the expectation value of a kinetic-energy operator between one-electron orbitals, one must therefore introduce such orbitals and the eigenvalue equations with which to calculate them. These are the Kohn-Sham one-electron equations [14,2], which we write here for a closed-shell

system:

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \right\} \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}). \qquad (4)$$

The effective one-electron potential appearing in Eq. (4) is given by

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}[\rho], \qquad (5)$$

where $E_{\text{xc}}[\rho]$ is the usual exchange-correlation energy functional. The density is given by twice (for double occupancy) the sum of the squares of the $(N/2)$ lowest eigenfunctions ϕ_n,

$$\rho(\mathbf{r}) = 2 \sum_{n=1}^{N/2} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}) \qquad (6)$$

and the total energy by the sum of the corresponding eigenvalues, less overcounting terms,

$$E = 2 \sum_{n=1}^{N/2} \epsilon_n + E_{\text{xc}}[\rho] - \frac{1}{2} \int d^3r \, d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$- \int d^3r \, \rho(\mathbf{r}) \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}. \qquad (7)$$

The explicit construction of the kinetic part of $G[\rho, \mathbf{B}]$ in BDFT can be avoided by deriving one-electron equations in an essentially identical manner. The most natural generalization of Eq. (4) is

$$\left\{ \frac{1}{2} \left[-i\nabla + c^{-1}\mathbf{A(r)} \right]^2 + V_{\text{eff}}(\mathbf{r}, \mathbf{B}) \right\} \phi_n(\mathbf{r}, \mathbf{B})$$

$$= \epsilon_n(\mathbf{B})\phi_n(\mathbf{r}, \mathbf{B}), \qquad (8)$$

where $\mathbf{A(r)}$ is the particular form of vector potential that was chosen to give the particular $\mathbf{B(r)}$ in the problem. We then define as usual the noninteracting kinetic-energy functional T_s as the expectation value of the kinetic operator in Eq. (8) between the one-electron orbitals

$$T_s[\rho, \mathbf{B}] = 2 \sum_{n=1}^{N/2} \int d^3r \, \phi_n^*(\mathbf{r}, \mathbf{B})$$

$$\times \frac{1}{2} \left[-i\nabla + c^{-1}\mathbf{A(r)} \right]^2 \phi_n(\mathbf{r}, \mathbf{B}) \qquad (9)$$

and write $G[\rho, \mathbf{B}]$ as T_s plus a correction

$$G[\rho, \mathbf{B}] = T_s[\rho, \mathbf{B}] + E_{\text{xc}}[\rho, \mathbf{B}]. \qquad (10)$$

Using Eq. (10) in Eq. (3) we can show in the usual way that the energy is given by an equation identical to Eq. (7) except that the eigenvalues ϵ_n, density $\rho(\mathbf{r})$, and exchange-correlation functional E_{xc} all depend on $\mathbf{B(r)}$. Minimizing the energy with respect to the density we can then show that $V_{\text{eff}}(\mathbf{r}, \mathbf{B})$ is given by the natural generalization of Eq. (5),

$$V_{\text{eff}}(\mathbf{r}, \mathbf{B}) = V(\mathbf{r}) + \int d^3 r' \frac{\rho(\mathbf{r}, \mathbf{B})}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}[\rho, \mathbf{B}]. \quad (11)$$

Solving the self-consistent equations (8) and (11) for the $V(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ that characterize a system gives the eigenvalues $\epsilon_n(\mathbf{B})$ and, via Eq. (6), the density $\rho(\mathbf{r}, \mathbf{B})$. Using the $\epsilon_n(\mathbf{B})$ and $\rho(\mathbf{r}, \mathbf{B})$ in Eq. (7) then gives the ground-state energy or, through appropriate derivatives, other observable ground-state properties. The difficult step in this procedure is as always constructing a good approximation to $E_{\text{xc}}[\rho, \mathbf{B}]$.

Note that $\mathbf{B}(\mathbf{r})$ appears explicitly not only in the one-electron kinetic operator in Eq. (8) but also in the potential operator $V_{\text{eff}}(\mathbf{r}, \mathbf{B})$. The presence of the magnetic field in a potential operator might seem peculiar, but there is in fact no significance to this. The operators in Eq. (8) describe effective interactions that have *no relationship* to the real interactions in the system. As a matter of fact, we are perfectly free to choose another form for the kinetic operator in the Kohn-Sham-like equations. While the general success of the Kohn-Sham equations themselves compared to straight Thomas-Fermi theory [24] strongly suggests retaining the ∇^2 operator in the kinetic operator, we have no such insight about keeping the vector potential there. Suppose we choose *not* to and instead put all of the explicit magnetic-field dependence of the one-electron "Hamiltonian" into the one-electron potential operator. Then we have a different set of one-electron equations,

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}, \mathbf{B}) \right\} \phi_n(\mathbf{r}, \mathbf{B}) = \epsilon_n(\mathbf{B})\phi_n(\mathbf{r}, \mathbf{B}). \quad (12)$$

There is no reason why we cannot choose these ϕ_n to be purely real, and for convenience [in particular the Hermiticity of the potential $V_{\text{eff}}(\mathbf{r}, \mathbf{B})$] we do so. Now it is certainly curious to construct single-electron "orbitals" *in a magnetic field* that are purely real. This serves as a reminder that the solutions to Eq. (12) have no significance other than as auxiliary functions with which the density $\rho(\mathbf{r})$ may be constructed via Eq. (6) and the energy via Eq. (7). In particular they bear no relationship to the actual N-electron ground-state wave function $\Psi_0(\mathbf{B})$. Note that, for example, the expectation value of the canonical particle current operator is generally nonzero for $\Psi_0(\mathbf{B})$, but identically zero for the "wave function" formed by the Slater determinant of the $(N/2)$ doubly occupied ϕ_n.

We now define T_s as

$$T_s[\rho, \mathbf{B}] = 2 \sum_{n=1}^{N/2} \int d^3 r \, \phi_n^*(\mathbf{r}, \mathbf{B}) \left(-\frac{1}{2}\nabla^2 \right) \phi_n(\mathbf{r}, \mathbf{B}) \quad (13)$$

instead of through Eq. (9). As usual we write $G[\rho, \mathbf{B}]$ as T_s plus a correction,

$$G[\rho, \mathbf{B}] = T_s[\rho, \mathbf{B}] + E_{\text{kxc}}[\rho, \mathbf{B}]. \quad (14)$$

But now the correction functional E_{kxc} contains not only the normal exchange and correlation contributions, but also the explicitly $\mathbf{B}$-dependent kinetic contribution to the energy of the interacting system.

The total energy E may be shown to be given once again by Eq. (7), but with $E_{\text{kxc}}[\rho, \mathbf{B}]$ appearing instead of $E_{\text{xc}}[\rho]$ and with $\mathbf{B}(\mathbf{r})$ appearing again in the eigenvalues $\epsilon_n(\mathbf{B})$ and density $\rho(\mathbf{r}, \mathbf{B})$. Minimizing E with respect to the density in the usual way gives the potential $V_{\text{eff}}(\mathbf{r}, \mathbf{B})$ that appears in Eq. (12) and $V_{\text{eff}}(\mathbf{r}, \mathbf{B})$ turns out to be given by an equation identical to Eq. (11), except that E_{kxc} appears instead of E_{xc}.

One would have to construct some approximation to $E_{\text{kxc}}[\rho, \mathbf{B}]$ in order to use Eq. (12), but this may not be more difficult than the approximation of $E_{\text{xc}}[\rho, \mathbf{B}]$ that enters Eq. (8).

The general advantages of using Eq. (12) over Eq. (8) are that one need only work with real orbitals and there is no separation of the energy into paramagnetic and diamagnetic terms. (There is also a further advantage when calculating second-order susceptibilities, which is discussed at the end of Sec. IV.) Whether Eq. (12) or the more challenging Eq. (8) is numerically superior depends on whether retaining the magnetic field in the kinetic one-electron operator is a better choice in practice, with approximate forms of E_{xc} and E_{kxc}. This cannot be known without a direct test and may also depend on the particular form of $\mathbf{B}(\mathbf{r})$ in the problem.

IV. SECOND-ORDER SUSCEPTIBILITIES

One is often interested in the magnetic properties of a many-electron system only to second order in the field strength B, which is in such things as diamagnetic susceptibilities or chemical shifts. Perturbation theory in the strength of the magnetic field is then a natural approach. Because the energy is required to second order in $\mathbf{B}$, one needs in all current *ab initio* methods (e.g., Hartree-Fock [16] or CDFT [21]) to calculate wave functions to first order in $\mathbf{B}$. An interesting point about BDFT is that the *zero*-order ($\mathbf{B} = 0$) density is in principle sufficient to calculate the *second*-order corrections to the ground-state energy and hence to calculate the magnetic susceptibilities. One can avoid entirely calculating $\mathbf{B}$-dependent corrections to the ground-state wave function.

The proof of this statement is as follows. We expand the functional $G[\rho, \mathbf{B}]$ to second order in the field strength. First we expand with respect to the explicit dependence on the magnetic field

$$G[\rho, \mathbf{B}] = G[\rho, 0] + B^2 \frac{\partial^2 G}{\partial B^2}[\rho, 0] + \cdots. \quad (15)$$

Note that only even powers of B can appear in the expansion by time-reversal symmetry [25]. Now we expand each term of Eq. (15) with respect to its implicit dependence on $\mathbf{B}$ via the density

$$G[\rho, \mathbf{B}] = G[\rho^{(0)}, 0]$$
$$+ \int d^3 r \, \rho^{(2)}(\mathbf{r}, \mathbf{B}) \frac{\delta G}{\delta \rho(r)}[\rho^{(0)}, 0] + \cdots$$
$$+ B^2 \frac{\partial^2 G}{\partial B^2}[\rho^{(0)}, 0] + \cdots, \quad (16)$$

where the density can also by time-reversal symmetry only have even powers of B in it,

$$\rho^{(0)}(\mathbf{r}) = \rho(\mathbf{r}, 0),$$

$$\rho^{(2)}(\mathbf{r}, \mathbf{B}) = B^2 \frac{d^2\rho}{dB^2}(\mathbf{r}, 0), \tag{17}$$

and we note, for future use, that normalization of $\rho(\mathbf{r})$ requires

$$\int d^3r\, \rho^{(2)}(\mathbf{r}, \mathbf{B}) = 0. \tag{18}$$

We introduce the abbreviated notation for the part of energy functionals second order in $\mathbf{B}$ only by virtue of an *explicit* $\mathbf{B}$ dependence,

$$\tilde{G}^{(2)}[\rho^{(0)}, \mathbf{B}] \equiv B^2 \frac{\partial^2 G}{\partial B^2}[\rho^{(0)}, 0]. \tag{19}$$

Now inserting Eq. (16) into Eq. (3) and using the definitions in Eq. (17) we find that the energy to second order is given by

$$E[\rho, \mathbf{B}] = E^{(0)}[\rho^{(0)}] + \tilde{G}^{(2)}[\rho^{(0)}, \mathbf{B}]$$
$$+ \int d^3r \rho^{(2)}(\mathbf{r}, \mathbf{B}) \left\{ \frac{\delta G}{\delta \rho(\mathbf{r})}[\rho^{(0)}, 0] + V(\mathbf{r}) \right.$$
$$\left. + \int d^3r' \frac{\rho^{(0)}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right\} + \cdots, \tag{20}$$

where $E^{(0)}$ is the energy in the absence of the field. The requirement that the zero-field density minimize the zero-field energy is expressed by the variational condition

$$\frac{\delta E^{(0)}}{\delta \rho(r)} - \lambda = 0, \tag{21}$$

where λ is a Lagrange multiplier. Using the result of applying Eq. (21) to Eq. (1), and using Eq. (18), it can be shown that the last term in Eq. (20) is zero for the actual ground-state density. (Note that $G[\rho, \mathbf{B}]$ as defined by Eq. (3) reduces to $G[\rho]$ as defined in Eq. (1) in the limit of $\mathbf{B} \to 0$.) So finally we have

$$E[\rho, \mathbf{B}] = E^{(0)}[\rho^{(0)}] + \tilde{G}^{(2)}[\rho^{(0)}, \mathbf{B}] + \cdots. \tag{22}$$

Only the zero-field density $\rho^{(0)}$ is required to calculate the right-hand side of this expression, which completes the proof.

If the full functional $G[\rho, \mathbf{B}]$ is available, using Eq. (22) is straightforward since the explicitly $\mathbf{B}$-dependent part of G can be picked out by inspection. If, on the other hand, the one-electron (Kohn-Sham) approach discussed in Sec. III is taken, then G is only available in the form of T_s plus a correction functional $E_{\text{correct}}[\rho, \mathbf{B}]$, where $E_{\text{correct}} = E_{\text{xc}}$ if Eq. (8) defines the one-electron equations and $E_{\text{correct}} = E_{\text{kxc}}$ if Eq. (12) defines the one-electron equations. In this case Eq. (22) takes the form

$$E[\rho, \mathbf{B}] = E^{(0)}[\rho^{(0)}] + \tilde{T}_s^{(2)}(\rho^{(0)}, \mathbf{B})$$
$$+ \tilde{E}_{\text{correct}}^{(2)}[\rho^{(0)}, \mathbf{B}] + \cdots. \tag{23}$$

While $\tilde{E}_{\text{correct}}^{(2)}$, the explicitly $\mathbf{B}$-dependent part of $E_{\text{correct}}^{(2)}$, can presumably be picked out by inspection, the same is not true of $\tilde{T}_s^{(2)}$, the explicitly $\mathbf{B}$-dependent part of $T_s^{(2)}$. Because the Kohn-Sham orbitals are found as functions of $\mathbf{r}$ and not functionals of $\rho(\mathbf{r}, \mathbf{B})$, one cannot look at the actual expectation values in, e.g., Eq. (9) or (12) and just pick out which of the $\mathbf{B}$-dependent terms come about because of the $\mathbf{B}$ dependency of $\rho(\mathbf{r}, \mathbf{B})$ and which represent an explicit $\mathbf{B}$ dependency. [The Kohn-Sham orbitals can in principle be expressed as functionals of $\rho(\mathbf{r}, \mathbf{B})$ and $\mathbf{B}$ because T_s can. Doing this would certainly obviate the problem of identifying the origin of the $\mathbf{B}$ dependency in each expectation value in, e.g., Eq. (9), but of course if we know how to write the Kohn-Sham orbitals in terms of $\rho(\mathbf{r}, \mathbf{B})$ and $\mathbf{B}$, there is no need for the one-electron equations in the first place.]

We can get around this problem by using the technique by which the coupled Hartree-Fock equations can be derived [16]. First we write the generic T_s as the expectation value of a one-electron kinetic operator t,

$$T_s = 2 \sum_{n=1}^{N/2} \langle n|t|n \rangle, \tag{24}$$

where we have switched to Dirac notation for the expectation values in, e.g., Eq. (9) or (13). The entire second-order dependence of T_s on $\mathbf{B}$ is then

$$T_s^{(2)} = 2 \sum_{n=1}^{N/2} \left\{ \langle n^{(0)}|t^{(2)}|n^{(0)} \rangle + \langle n^{(1)}|t^{(0)}|n^{(1)} \rangle \right.$$
$$+ \langle n^{(0)}|t^{(1)}|n^{(1)} \rangle + \langle n^{(1)}|t^{(1)}|n^{(0)} \rangle$$
$$\left. + \langle n^{(0)}|t^{(0)}|n^{(2)} \rangle + \langle n^{(2)}|t^{(0)}|n^{(0)} \rangle \right\}, \tag{25}$$

where the superscripts (1) and (2) indicate corrections to order B^1 and B^2, respectively. The eigenkets $|n\rangle$ satisfy the one-electron equations

$$\{t + V_{\text{eff}}\}|n\rangle = \epsilon_n|n\rangle. \tag{26}$$

If we use the equations that come from requiring Eq. (26) to hold order by order in $\mathbf{B}$, and the orthonormality of the $|n\rangle$, we can show that

$$T_s^{(2)} = 2 \sum_{n=1}^{N/2} \left\{ \langle n^{(0)}|t^{(2)}|n^{(0)} \rangle \right.$$
$$\left. + \frac{1}{2} \langle n^{(0)}|t^{(1)}|n^{(1)} \rangle + \frac{1}{2} \langle n^{(1)}|t^{(1)}|n^{(0)} \rangle \right\}$$
$$- \int d^3r\, \rho^{(2)}(\mathbf{r}, \mathbf{B})\, V_{\text{eff}}^{(0)}(\mathbf{r}). \tag{27}$$

Now we can pick out by inspection from Eq. (27) which parts of $T_s^{(2)}$ derive the $\mathbf{B}$ dependency from that of the density. Certainly the last term does so. Equally clearly, the other terms do not: First of all, the $|n^{(0)}\rangle$ have no $\mathbf{B}$ dependency at all. Second, the $|n^{(1)}\rangle$ depend linearly on $\mathbf{B}$, which must be an explicit $\mathbf{B}$ dependence because the

density can only cause dependency on even powers of **B**.

Thus we have an expression for the explicitly **B**-dependent part of $T_s^{(2)}$ in terms of the Kohn-Sham orbitals

$$\tilde{T}_s^{(2)} = 2 \sum_{n=1}^{N/2} \left\{ \langle n^{(0)} | t^{(2)} | n^{(0)} \rangle \right. $$
$$\left. + \frac{1}{2} \langle n^{(0)} | t^{(1)} | n^{(1)} \rangle + \frac{1}{2} \langle n^{(1)} | t^{(1)} | n^{(0)} \rangle \right\}. \qquad (28)$$

This expression can be used in Eq. (23) to find the second-order changes in E when Kohn-Sham orbitals are used to calculate T_s. We note that Eq. (23) with Eq. (28) inserted into it differs by the presence of $\tilde{E}_{\text{correct}}^{(2)}$ from the equivalent expression in coupled Hartree-Fock theory. More importantly, Eq. (23) cannot be derived from zero-field DFT because zero-field DFT has no provision for the *explicit* appearance of the magnetic field in $E_{\text{correct}}^{(2)}$. This explicit appearance must be considered in a consistent theory of weak responses to magnetic fields since the explicit appearance of **B**(**r**) in the energy functional is what allowed at the beginning the elimination from the energy functional of $\mathbf{j}_p(\mathbf{r})$ as an independent variable. That is, *density*-functional theory by itself, where the magnetic field can only enter through the density, cannot consistently describe systems in a magnetic field. It is only *current-and-density* functional theory or *magnetic-field-and-density* functional theory that can do so.

If Eq. (8) defines the one-electron equations, that is, if the one-electron kinetic operator is given by

$$t = \frac{1}{2} \left[-i\nabla + c^{-1}\mathbf{A}(\mathbf{r}) \right]^2, \qquad (29)$$

then the terms in Eq. (28) are all generally present. That means we have to solve Eq. (8) to linear order in **B**; that is, we must calculate the first-order **B**-dependent corrections to the Kohn-Sham orbitals in order to get the second-order changes in the energy. This does *not* constitute an exception to the general theorem above, because we can calculate these linear corrections with the zero-field density $\rho^{(0)}(\mathbf{r})$ alone. The effective potential $V_{\text{eff}}[\rho, \mathbf{B}]$ appearing in Eq. (8) is given to *linear* order in **B** by $V_{\text{eff}}[\rho^{(0)}, \mathbf{B}]$.

Note that, since it is only through V_{eff} that the one-electron equation for each Kohn-Sham orbital ϕ_n depends on the other orbitals $\phi_{m \neq n}$, the first-order corrections $\phi_n^{(1)}$ to the Kohn-Sham orbitals do not depend on each other. That is, if the zero-field $\phi_n^{(0)}$ are known, the perturbation equations that must be solved to find the $\phi_n^{(1)}$ are uncoupled. This is in distinct contrast to the Hartree-Fock equations, where the first-order corrections do depend on one another and the perturbation equations to find them are coupled. Using BDFT to find the second-order energy changes, even in the Kohn-Sham formalism, even with Eq. (8) defining the one-electron orbitals, is therefore much easier than solving the coupled Hartree-Fock equations.

As a matter of fact if we have available enough informa-

tion about the kinetic part of G to define the one-electron equations through Eq. (12) instead of Eq. (8), then the one-electron kinetic operator is

$$t = -\frac{1}{2}\nabla^2 \qquad (30)$$

instead of as in Eq. (29), and from Eq. (28)

$$\tilde{T}_s^{(2)} = 0 \qquad (31)$$

and the energy to second order in **B** is given by

$$E[\rho, \mathbf{B}] = E^{(0)}[\rho^{(0)}] + \tilde{E}_{\text{kxc}}^{(2)}[\rho^{(0)}, \mathbf{B}]. \qquad (32)$$

No **B**-dependent corrections to the Kohn-Sham orbitals need to be calculated at all. The prospect represented by Eq. (32) of being able to calculate ground-state second-order magnetic susceptibilities for an arbitrary closed-shell system without solving any differential equations at all may make the effort required to contruct accurate forms for E_{kxc} very worthwhile.

V. CONCLUSIONS

We have outlined basic features of magnetic-field-and-density functional theory, an approach to the problem of the *ab initio* calculation of the properties of interacting many-electron systems in the presence of a magnetic field. The theory is grounded in the Hohenberg-Kohn theorem, which we emphasize is still perfectly valid in the presence of a magnetic field **B**(**r**) *provided* that all the Hamiltonians for which it is required to hold have the same form of vector potential **A**(**r**). The energy in BDFT is written as a functional of the ground-state density $\rho(\mathbf{r})$, as usual, and also explicitly of **B**(**r**). Thus the knotty part of density-functional energy functionals, the kinetic-exchange-correlation functional G, is for BDFT *nonuniversal* in (i.e., depends explicitly on) the vector potential. It is, however, still universal for all possible scalar potentials, e.g., arrangement of nuclei.

While presumably in the most general situations the universality of current-and-density functional theory makes it the method of choice for calculating ground-state magnetic properties of many-electron systems, it seems possible that in certain situations the use of BDFT may be as or more practically tractable. These situations would in general presumably be where properties of the exact form of **B**(**r**) make the construction of an accurate approximation to $G[\rho, \mathbf{B}]$ easier than an approximation of equal accuracy to $G[\rho, \mathbf{j}_p]$. It is also possible that in situations where the kinetic part of G is actually used [12,20], instead of being represented with the Kohn-Sham formalism, BDFT may be of more use since kinetic contributions to $G[\rho, \mathbf{B}]$ are known in some cases already, while the only attempts as yet to formulate the kinetic part of $G[\rho, \mathbf{j}_p]$ are not computationally tractable [9].

We have demonstrated the construction of one-electron (Kohn-Sham) equations to avoid construction of the kinetic-energy part of $G[\rho, \mathbf{B}]$ and pointed out the inter-

esting opportunity of constructing one-electron equations not based on the obvious partitioning of the magnetic-field dependency between kinetic and potential operators in the one-electron equations. Such equations give purely real Kohn-Sham orbitals and no division of the energy into para- and diamagnetic contributions. Furthermore, when these orbitals are used to calculate second-order susceptibilities one does not need to calculate the magnetic-field-dependent corrections to these orbitals.

Finally, we have presented a theorem for the calculation within BDFT of the second-order magnetic properties of the ground state, e.g., diamagnetic susceptibilities and chemical shifts. This theorem shows that knowledge of the zero-field density alone is sufficient in principal

to find these quantities and, unlike any other *ab initio* method, there is no *a priori* need to calculate the changes in the ground-state wave function due to the magnetic field.

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