

Finite-Temperature Density Functional Theory of Atoms in Strong Magnetic Fields

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The density functional theory of atomic electrons in strong magnetic fields is generalized to finite-temperature systems. General integral formulations are developed in the format of Mermin–Kohn–Sham finite-temperature density functional theory. The lowest order of the general theory leads to a temperature-dependent extended Thomas–Fermi (TETF)-like functional, which is simple enough to be analyzed. The general theory provides a new way of calculating the equilibrium properties of many-electron systems in strong magnetic fields.

KEY WORDS: Density functional; magnetic fields; finite temperature.

1. INTRODUCTION

Atoms in strong magnetic fields^(1–5) have obvious importance in studying the atmospheres of neutron stars. In the deep atmosphere of a neutron star, temperature effects are not negligible even though they have little effect on total atomic energies. Thus, when the temperature gets to the order of the lowest excitation energy, finite-temperature statistical models are needed. And when temperature is not small compared to lowest ionization energy, the electrons must be studied in terms of a grand canonical ensemble. The generalized Hohenberg–Kohn theorem⁽⁶⁾ appropriate to such a system has a long history, presented in various forms by Gibbs and von Neumann, Mermin,⁽⁷⁾ Stillinger and Buff,⁽⁸⁾ Lebowitz and Percus,⁽⁹⁾ and others. It sets up a density functional theory (DFT) for finite-temperature ensembles, in which the thermal properties of the interacting many-electron system are uniquely determined by the electron density which minimizes a grand

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canonical potential density functional. Whereas the original MKS (Mermin–Kohn–Sham) scheme⁽¹⁰⁾ relied on solving a set of self-consistent equations, as in the ground-state DFT, the finite-temperature approach proposed by Brack in his temperature-dependent extended Thomas–Fermi (TETF)^(11,12) approach has recently been used by Yang⁽¹³⁾ to construct an integral formulation of DFT. In the present paper, we use the same approach to generalize the ground-state DFT of atoms in strong magnetic fields⁽¹⁴⁾ to finite temperature. A semiclassical approximation for the required Green’s function results in a TETF-like density functional, a simple and practical tool. We also make the convenient, but not necessary, simplification that in high magnetic field, the electrons can be considered as spinless fermions. We conclude by describing the use of a many-interval discretized propagator, displaying a new method for accurate calculation of thermal properties of many-electron systems in strong magnetic fields.

2. MERMIN–KOHNSHAM DENSITY FUNCTIONAL

Consider a many-electron Hamiltonian H . The grand canonical potential of the system is given by (a.u. throughout)

$$\Omega = \text{Min}_\Gamma \text{Tr} \Gamma (H - \mu N + \tau \ln \Gamma) \quad (1)$$

where Γ is the grand canonical density matrix operator having the minimizing value

$$\Gamma = e^{-(H - \mu N)/\tau} / \text{Tr} e^{-(H - \mu N)/\tau} \quad (2)$$

Here, μ is the chemical potential and τ the temperature in energy units. The electron density is obtained from Γ as

$$\rho_\Gamma(\mathbf{x}) = \text{Tr} \Psi^\dagger(\mathbf{x}) \Psi(\mathbf{x}) \Gamma \quad (3)$$

where Ψ^\dagger and Ψ are the usual electron field operators. Denoting the kinetic energy operator by K , the internal Coulomb energy by Φ , and restricting attention for the moment to an external potential $u(\mathbf{x})$, we can write (1) as

$$\Omega = \text{Min}_\rho \Omega[\rho]$$

where

$$\Omega[\rho] = \text{Min}_{[\Gamma^\dagger \rho \Gamma = \rho]} \text{Tr} \Gamma (K + \Phi + \tau \ln \Gamma) + \int [u(\mathbf{x}) - \mu] \rho(\mathbf{x}) d\mathbf{x} \quad (4)$$

In the MKS model,⁽⁷⁾ one makes the following assumption:

$$\begin{aligned} \Omega[\rho] = G_s[\rho] + \int [u(\mathbf{x}) - \mu] \rho(\mathbf{x}) d\mathbf{x} \\ + \frac{1}{2} \int \frac{\rho(\mathbf{x}_1) \rho(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_1 d\mathbf{x}_2 + \mathcal{F}_{xc}[\rho] \end{aligned} \quad (5)$$

where G_s is the Helmholtz free energy of the auxiliary noninteracting system of Hamiltonian K , and \mathcal{F}_{xc} is an appropriate exchange-correlation functional. Minimizing Eq. (5) leads to a set of self-consistent equations for the KS eigenstates ψ_i :

$$(H_{ks} - E_i) \psi_i = 0 \quad (6)$$

$$H_{ks} = -\frac{1}{2} \nabla^2 + u_{ef}(\mathbf{x}) \quad (7)$$

$$u_{ef}(\mathbf{x}) = u(\mathbf{x}) + \int \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' + \frac{\delta \mathcal{F}_{xc}}{\delta \rho(\mathbf{x})} \quad (8)$$

in terms of which the finite-temperature one-body density matrix and density can then be constructed explicitly,

$$\gamma(\mathbf{x}, \mathbf{x}'; \tau) = \sum_i \psi_i(\mathbf{x}) \psi_i^\dagger(\mathbf{x}') f_\tau(\mu - E_i), \quad \rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x}) \quad (9)$$

where f_τ is the Fermi function,

$$f_\tau(\mu - E_i) = 1/(1 + e^{-(\mu - E_i)/\tau}) \quad (10)$$

Then the Helmholtz free energy is given by

$$G_s[\rho] = T_s[\rho] - \tau S_s[\rho] \quad (11)$$

with the kinetic energy and entropy functionals

$$\begin{aligned} T_s[\rho] &= \int t_s(\mathbf{x}) d\mathbf{x} \\ t_s(\mathbf{x}) &= \frac{1}{2} \nabla_{\mathbf{x}} \nabla_{\mathbf{x}'} \gamma(\mathbf{x}, \mathbf{x}'; \tau) \Big|_{\mathbf{x}' = \mathbf{x}} \end{aligned} \quad (12)$$

$$S_s = -\sum_i [f_\tau \ln f_\tau + (1 - f_\tau) \ln(1 - f_\tau)] \quad (13)$$

The diagonal elements of $\gamma(\mathbf{x}, \mathbf{x}'; \tau)$ yield the one-body density $\rho(\mathbf{x})$.

3. THE TETF-LIKE DENSITY FUNCTIONAL

We now introduce a magnetic field. The KS Hamiltonian for an atomic electron in a constant external magnetic field B in the z direction is

$$H_{ks'} = -\frac{1}{2}\nabla^2 + \frac{B}{2}l_z + \frac{B^2}{8}(x^2 + y^2) + u_{ef}(\mathbf{x}) \quad (14)$$

In order to avoid the KS orbitals, we rewrite $\gamma(\mathbf{x}, \mathbf{x}'; \tau)$ in the form

$$\gamma(\mathbf{x}, \mathbf{x}'; \tau) = \langle \mathbf{x} | f_\tau(\mu - H_{ks'}) | \mathbf{x}' \rangle \quad (15)$$

If we express the Fermi function by a two-sided inverse Laplace transform, the following relationship can be established⁽¹²⁾:

$$\gamma(\mathbf{x}, \mathbf{x}'; \tau) = \mathcal{L}_\mu^{-1} \frac{1}{\beta} \frac{\pi\tau\beta}{\sin \pi\tau\beta} G(\mathbf{x}, \mathbf{x}'; \beta) \quad (16)$$

$$G(\mathbf{x}, \mathbf{x}'; \beta) = \langle \mathbf{x} | \exp(-\beta H_{ks'}) | \mathbf{x}' \rangle \quad (17)$$

where G is the one-electron Green's function. Accordingly, the entropy functional can also be expressed in terms of the Green's function

$$S_s[\rho] = \int \sigma(\mathbf{x}) d\mathbf{x}, \quad \sigma(\mathbf{x}) = \frac{\partial}{\partial\tau} A(\mathbf{x}, \mathbf{x}; \tau) \quad (18)$$

$$A(\mathbf{x}, \mathbf{x}'; \tau) = \mathcal{L}_\mu^{-1} \frac{1}{\beta} \frac{\pi\tau}{\sin \pi\tau\beta} G(\mathbf{x}, \mathbf{x}'; \beta)$$

It should be noted that the above relations are an exact transcription of (9) and (10). We now replace the exact Green's function by its semiclassical approximation.⁽¹⁴⁾ Here, we take the known ($u_{ef} = 0$) Green's function as reference in the Feynman-Kac path integral expression, and keep only up to first order in β in the exponent. This results in

$$\begin{aligned} G_{sc}(\mathbf{x}, \mathbf{x}'; \beta) = & \left\{ \exp[ia(xy' - yx')] \right\} \frac{1}{(2\pi\beta)^{3/2}} \frac{a\beta}{\sinh a\beta} \\ & \times \exp \left\{ -\frac{1}{2\beta} (\mathbf{x} - \mathbf{x}')^2 - \beta \int_0^1 u_{ef}(\mathbf{x}' + (\mathbf{x} - \mathbf{x}')t) dt \right. \\ & \left. - \frac{\beta}{6} a^2 [(x - x')^2 + (y - y')^2] \right\} \quad (19) \end{aligned}$$

where $a = B/2$. The corresponding one-body density and the kinetic functional are given by

$$\rho(\mathbf{x}) = C_\tau F_{1/2}(\chi), \quad C_\tau = \frac{2^{1/2} \tau^{3/2}}{2\pi^2} \quad (20)$$

and

$$t_{sc}(\mathbf{x}) = C_\tau \left[\tau F_{3/2}(\chi) - \frac{1}{24} \tau^{-1} F_{-1/2}(\chi) \nabla^2 u_{ef} - \frac{1}{32} \tau^{-2} F_{-3/2}(\chi) |\nabla u_{ef}|^2 + \frac{B^2}{96} \tau^{-1} F_{-1/2}(\chi) \right] \quad (21)$$

where, throughout, $\chi \equiv [\mu - u_{ef}(\mathbf{x})]/\tau$ is defined by Eq. (20), and F_α is the Fermi-Dirac function

$$F_\alpha(x) = \int_0^\infty \frac{t^\alpha}{1 + e^{t-x}} dt \quad (\alpha > -1) \quad (22)$$

$$F_\alpha(x) = \frac{1}{\alpha + 1} \frac{d}{dx} F_{\alpha+1}(x) \quad (\alpha \neq -1) \quad (23)$$

If $\alpha < -1$, where the integral (22) is divergent, the recursion relation (23) must be used as the definition of $F_\alpha(x)$.⁽¹²⁾ In the derivation, we have replaced ∇ in Eq. (12) by $\nabla + iA$, and kept only the leading order in β . In order to eliminate the gradients of $u_{ef}(\mathbf{x})$ from the above expression, we use the relations

$$|\nabla u_{ef}|^2 = \frac{4\tau^2}{C_\tau} \frac{F_{1/2}}{F_{-1/2}^2} \frac{|\nabla \rho|^2}{\rho} \quad (24)$$

$$\nabla^2 u_{ef} = -\frac{2\tau}{C_\tau F_{-1/2}} \left(\nabla^2 \rho + \frac{F_{1/2} F_{-3/2}}{F_{-1/2}^2} \frac{|\nabla \rho|^2}{\rho} \right) \quad (25)$$

which stem from Eq. (20). Combination of Eqs. (21), (24), and (25) results in a TETF-like kinetic functional

$$t_{sc}(\mathbf{x}) = t_{TF}(\mathbf{x}) + t_W(\mathbf{x}) + \frac{1}{12} \nabla^2 \rho + \frac{B^2}{96} C_\tau \tau^{-1} F_{-1/2} \quad (26)$$

with

$$t_{TF}(\mathbf{x}) = C_\tau \tau F_{3/2}, \quad t_W(\mathbf{x}) = \kappa \frac{|\nabla \rho|^2}{\rho} \quad (27)$$

where

$$\kappa = -\frac{1}{24} \frac{F_{1/2} F_{-3/2}}{F_{-1/2}^2} \equiv -\frac{1}{12} F_{1/2} \frac{\partial}{\partial \chi} \frac{1}{F_{-1/2}(\chi)} \quad (28)$$

Similarly, replacing G by G_{sc} in Eq. (18) leads to the results

$$\sigma_{sc}(\mathbf{x}) = \frac{\partial}{\partial \tau} A_{sc}(\mathbf{x}, \mathbf{x}; \tau) = \frac{5}{3} C_\tau F_{3/2} - \rho \chi \quad (29)$$

Combining Eqs. (5), (11), (26), and (29), we obtain the grand canonical potential functional

$$\begin{aligned} \Omega[\rho] = & -\frac{2}{3} T_{TF}[\rho] + T_W[\rho] + \frac{B^2}{96} C_\tau \tau^{-1} \int F_{-1/2} d\mathbf{x} + \tau \int \rho \chi d\mathbf{x} \\ & + \int [u(\mathbf{x}) - \mu] \rho(\mathbf{x}) d\mathbf{x} + \frac{1}{2} \int \frac{\rho(\mathbf{x}_1) \rho(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} d\mathbf{x}_1 d\mathbf{x}_2 + \mathcal{F}_{xc}[\rho] \end{aligned} \quad (30)$$

with

$$T_{TF}[\rho] = \int t_{TF}(\mathbf{x}) d\mathbf{x}, \quad T_W[\rho] = \int t_W(\mathbf{x}) d\mathbf{x} \quad (31)$$

Minimizing (30), we have as well the Euler profile equation

$$\begin{aligned} -\frac{2}{3} C_\tau \tau \frac{dF_{3/2}}{d\rho} - 4\kappa \frac{\nabla^2 \rho^{1/2}}{\rho^{1/2}} - \frac{|\nabla \rho|^2}{\rho} \frac{d\kappa}{d\rho} + \frac{B^2}{96} C_\tau \tau^{-1} \frac{dF_{-1/2}}{d\rho} \\ + u(\mathbf{x}) + \tau \frac{d(\rho \chi)}{d\rho} + \int \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' + \frac{\delta \mathcal{F}_{xc}[\rho]}{\delta \rho} = \mu \end{aligned} \quad (32)$$

We have used the fact that $F_\alpha(\chi)$ is a function of electron density $\rho(\mathbf{x})$, which is clear from Eq. (20). With the help of the following asymptotic expansion of $F_\alpha(\chi)$,⁽¹⁵⁾

$$F_\alpha(\chi) = \frac{1}{\alpha + 1} \chi^{\alpha+1} \left[1 + \alpha(\alpha + 1) \frac{\pi^2}{6} \chi^{-2} + \dots \right] \quad (\chi \gg 1) \quad (33)$$

it is easy to show that Eqs. (30) and (32) reduce to the energy functional (26) and the profile equation (28) of ref. 14, respectively, in the limit of $\tau \rightarrow 0$. It is also interesting to study another limit, $B \rightarrow 0$. Because of the simple coupling with the magnetic field in Eqs. (30) and (32), taking the limit means dropping the terms in B in both equations. It turns out that

the grand potential functional, after dropping the magnetic terms, is exactly the same as that obtained by Perrot, which is slightly different from the Brack's result. From the minimized grand canonical potential, all the equilibrium properties can be determined. As discussed for the ground-state case,⁽¹⁴⁾ the range of validity of B in the above functional needs to be checked because of the "short-time" approximation to the Green's function.

4. MULTIDIMENSIONAL INTEGRAL FORMULATION

The semiclassical approximation of the Green's function can be systematically improved by the discretized propagator approach developed by Handler,⁽¹⁶⁾ Harris and Pratt,⁽¹⁷⁾ and other authors. The exact Green's function defined by Eq. (17) can be well approximated by the multi-interval discretized propagator formulation⁽¹⁴⁾ (where the known factor $a\beta/\sinh a\beta$ can be recognized and removed at any stage)

$$G_n(\mathbf{x}, \mathbf{x}'; \beta) = \left(\frac{n}{2\pi\beta}\right)^{3n/2} \int d\mathbf{x}_1 \cdots d\mathbf{x}_{n-1} \exp \left[i \sum_{m=0}^{n-1} b_0(m+1, m) \right] \\ \times \exp \left[-\frac{n}{2\beta} \sum_{m=0}^{n-1} (\mathbf{x}_{m+1} - \mathbf{x}_m)^2 - \frac{\beta}{n} \sum_{m=0}^{n-1} u(m+1, m) \right. \\ \left. - \frac{\beta}{n} \sum_{m=0}^{n-1} b_1(m+1, m) \right] \quad (34)$$

where $u(m+1, m)$, $b_0(m+1, m)$, and $b_1(m+1, m)$ are defined by

$$u(m+1, m) = \int_0^1 u_{ef}(\mathbf{x}_m + (\mathbf{x}_{m+1} - \mathbf{x}_m)t) dt \quad (35)$$

$$b_0(m+1, m) = a(x_{m+1}y_m - y_{m+1}x_m) \quad (36)$$

$$b_1(m+1, m) = \frac{a^2}{6} [(x_{m+1} - x_m)^2 + (y_{m+1} - y_m)^2] \quad (37)$$

The boundary conditions $\mathbf{x}_0 = \mathbf{x}'$ and $\mathbf{x}_n = \mathbf{x}$ are combined with Eq. (34). It has been shown that G_n converges to G as n goes to infinity. Using G_n in Eqs. (16) and (18) leads to the expressions

$$\gamma_n(\mathbf{x}, \mathbf{x}'; \tau) = \left(\frac{n\tau}{2\pi}\right)^{3n/2} \int d\mathbf{x}_1 \cdots d\mathbf{x}_{n-1} \\ \times \left\{ \exp \left[i \sum_{m=0}^{n-1} b_0(m+1, m) \right] \right\} D_{3n/2}(k_n^2/2\tau, l_n^2\tau/2) \quad (38)$$

$$A_n(\mathbf{x}, \mathbf{x}'; \tau) = \tau \left(\frac{n\tau}{2\pi} \right)^{3n/2} \int d\mathbf{x}_1 \cdots d\mathbf{x}_{n-1} \\ \times \left\{ \exp \left[i \sum_{m=0}^{n-1} b_0(m+1, m) \right] \right\} D_{3n/2+1}(k_n^2/2\tau, l_n^2\tau/2) \quad (39)$$

where D_α is defined by⁽¹³⁾

$$D_\alpha(x, y) = \mathcal{L}_x^{-1} \frac{\pi}{\beta^\alpha \sin \pi\beta} e^{-y/\beta} \\ \frac{\partial}{\partial x} D_\alpha(x, y) = D_{\alpha-1}(x, y), \quad \frac{\partial}{\partial y} D_\alpha(x, y) = -D_{\alpha+1}(x, y) \quad (40)$$

with

$$k_n^2 = 2 \left[\mu - \frac{1}{n} \sum_{m=0}^{n-1} u(m+1, m) - \frac{1}{n} \sum_{m=0}^{n-1} b_1(m+1, m) \right] \quad (41)$$

$$l_n^2 = n \sum_{m=0}^{n-1} (\mathbf{x}_{m+1} - \mathbf{x}_m)^2 \quad (42)$$

The diagonal element of γ_n gives the electron density

$$\rho_n(\mathbf{x}) = \rho_n[u_{ef}(\mathbf{x}); \mathbf{x}, B, \tau] \quad (43)$$

which is an explicit functional of $u_{ef}(\mathbf{x})$ with the magnetic field B and the temperature τ as parameters. The kinetic functional $t_n(\mathbf{x})$ is given by

$$t_n(\mathbf{x}) = \frac{1}{2} (\nabla_{\mathbf{x}} + iA) \cdot (\nabla_{\mathbf{x}'} + iA') \gamma_n(\mathbf{x}, \mathbf{x}'; \tau) \Big|_{\mathbf{x}' = \mathbf{x}} \\ = t_n[u_{ef}(\mathbf{x}); \mathbf{x}, B, \tau] \quad (44)$$

Direct calculation of $t_n(\mathbf{x})$ is elementary, but very tedious. We use instead the identity

$$t'(\mathbf{x}) = [\mu - u_{ef}(\mathbf{x})] \rho(\mathbf{x}) + \tau \sigma(\mathbf{x}) - A(\mathbf{x}, \mathbf{x}; \tau) \quad (45)$$

for an indirect calculation. It is believed that both t_n and t'_n converge to an exact kinetic functional as $n \rightarrow \infty$. The corresponding entropy is

$$\sigma_n(\mathbf{x}) = \left(\frac{n\tau}{2\pi} \right)^{3n/2} \int d\mathbf{x}_1 \cdots d\mathbf{x}_{n-1} \\ \times \left[\left(\frac{3n}{2} + 1 \right) D_{3n/2+1} - \frac{k_n^2}{2\tau} D_{3n/2} - \frac{l_n^2\tau}{2} D_{3n/2+2} \right] \quad (46)$$

We have used the differential recursion relations (40) in the calculation of the entropy. The Helmholtz free energy is given by

$$G_n[\rho] = \int d\mathbf{x} [t'_n(\mathbf{x}) - \tau\sigma_n(\mathbf{x})] \\ = \int d\mathbf{x} \{ [\mu - u_{ef}(\mathbf{x})] \rho_n(\mathbf{x}) - A_n(\mathbf{x}, \mathbf{x}; \tau) \} \quad (47)$$

By solving the self-consistent equations (8) and (43), we can obtain ρ_n and u_{ef} , then t_n and σ_n , and all other thermal properties can be uniquely determined by ρ_n .

5. CONCLUDING REMARKS

A new TETF-like density functional model for atoms in magnetic fields is created through the semiclassical approximation of the Green's function. The integral formulation of DFT proposed for ground-state atoms in strong magnetic fields has been generalized to finite temperatures. The so-called better short-time expansion of the one-body Green's function, known mainly through the work of Fujiwara *et al.*,⁽¹⁸⁾ is easily accomplished in the integral formulation of the last section. It is expected that the integral formulation will provide an efficient way of calculating the thermal properties of atoms in strong magnetic fields.

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