Density-functional theory of atoms in strong magnetic fields

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A density-functional model of atoms in strong magnetic fields is proposed along lines parallel to Hohenberg-Kohn-Sham density-functional theory. We derive a Thomas-Fermi-Weizäcker-like (TFW) functional by using the classical-path approximation to the relevant one-particle Green's function. We also address the correlation effect between the effective potential and the magnetic field. The TFW-like model provides a simple way of calculating ground-state energies and charge densities of atoms in magnetic fields, and can be systematically improved.

I. INTRODUCTION

Ordinary perturbation approaches fail in calculating the properties of atoms in strong magnetic fields, objects of obvious astrophysical importance. A variety of nonperturbative approaches to ground-state energies and charge densities of these systems have therefore been developed in the past few decades, Thomas-Fermi-like (TF) statistical models[1–5] among them. More detailed, but still phenomenological, models of the Kohn-Sham-type (KS) depend upon solving Hartree-Fock-like equations. This paper aims at providing a density-functional framework for such problems via the Feynman path integral formulation of quantum mechanics. Even the lowest order of this theory leads to a Thomas-Fermi-Weizsäcker-like (TFW) functional which can be easily analyzed, and higher order can be incorporated with little difficulty. For simplicity, we here consider electrons as spinless particles, a supposition which becomes exact in very intense magnetic fields.

II. KOHN-SHAM DENSITY FUNCTIONAL

Subject to caveats concerning V representability,[6] the density-functional format, known mainly through the work of Hohenberg and Kohn, can be regarded as proceeding as follows. If we neglect the magnetic field for the moment, then the ground-state energy of an atom with fixed nucleus and associated external Coulomb potential $u(\mathbf{x})$ can be written as

$$E=\min_{\Psi}\left[\int u(\mathbf{x})\rho_{\Psi}(\mathbf{x})d\mathbf{x}+\langle T+\Phi\rangle_{\Psi}\right], \tag{1}$$

where T is the kinetic energy operator, Φ the total Coulomb interaction potential, and ρ_{Ψ} the one-body density belonging to the N-Fermion wave function Ψ. Normalization of Ψ is equivalent to

$$\int \rho_{\Psi}(\mathbf{x})d\mathbf{x}=N . \tag{2}$$

Now in (1), we may fix $\rho_{\Psi}(\mathbf{x})=\rho(\mathbf{x})$, and then minimize over $\rho(\mathbf{x})$, subject to (2), yielding

$$\begin{aligned}E&=\min_{\rho}E[\rho]\\&=\min_{\rho}\left[\int u(\mathbf{x})\rho(\mathbf{x})d\mathbf{x}+(T+\Phi)[\rho]\right],\end{aligned} \tag{3}$$

where $Q[\rho]\equiv\min_{\rho_{\Psi}=\rho}\langle Q\rangle_{\Psi}$.

In the Kohn-Sham model,[7] one makes the separation ansatz (atomic units throughout)

$$(T+\Phi)[\rho]=T_s[\rho]+\frac{1}{2}\int\frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{|\mathbf{x}_1-\mathbf{x}_2|}d\mathbf{x}_1d\mathbf{x}_2+E_{\mathrm{xc}}[\rho] , \tag{4}$$

with $E_{\mathrm{xc}}[\rho]$ an appropriate exchange-correlation functional. Minimization of (3) then results in a one-body density matrix

$$\gamma(\mathbf{x},\mathbf{x}')=\sum_{i=1}^{N}\psi_i(\mathbf{x})\psi_i^{\dagger}(\mathbf{x}') , \tag{5}$$

and associated nonrelativistic kinetic energy functional

$$\begin{aligned}&T_s[\rho]=\int t_s(\mathbf{x})d\mathbf{x} ,\\&t_s(\mathbf{x})=\tfrac{1}{2}\nabla_{\mathbf{x}}\cdot\nabla_{\mathbf{x}'}\gamma(\mathbf{x},\mathbf{x}')|_{\mathbf{x}'=\mathbf{x}} ,\end{aligned} \tag{6}$$

where

$$\begin{aligned}&(H_{\mathrm{KS}}-E_i)\psi_i=0,\quad H_{\mathrm{KS}}=-\tfrac{1}{2}\nabla^2+u_{\mathrm{EF}}(x) ,\\&u_{\mathrm{EF}}(\mathbf{x})=u(\mathbf{x})+\int\frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d\mathbf{x}'+\frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{x})} .\end{aligned} \tag{7}$$

III. TFW-LIKE FUNCTIONAL

Application of a magnetic field B in the z direction has the sole effect of replacing ∇^2 by $[\nabla+i\,\mathbf{A}(\mathbf{x})]^2$, i.e., now

$$H_{\mathrm{KS}}=-\frac{1}{2}\nabla^2+\frac{B}{2}l_z+\frac{B^2}{8}(x^2+y^2)+u_{\mathrm{EF}}(\mathbf{x}) , \tag{8}$$

but our approach to $T[\rho]$ will avoid the use of the KS orbitals ψ_i. For this purpose, we write instead

$$\gamma(\mathbf{x},\mathbf{x}')=\langle\mathbf{x}|\Theta(\mu-H_{\mathrm{KS}})|\mathbf{x}'\rangle , \tag{9}$$

where Θ is the Heaviside step function and μ the Fermi energy. Expressing the step function as an inverse Laplace transform relates (9) to the one-body Green's function[8]

$$\begin{aligned}&\gamma(\mathbf{x},\mathbf{x}')=\int_{-\infty-i\alpha}^{\infty-i\alpha}dT(2\pi iT)^{-1}e^{i\mu T}G(\mathbf{x},\mathbf{x}';T) ,\\&G(\mathbf{x},\mathbf{x}';T)=\langle\mathbf{x}|e^{-iH_{\mathrm{KS}}T}|\mathbf{x}'\rangle ,\end{aligned} \tag{10}$$

which in turn can be evaluated as a Feynman path integral[9]

$$G(\mathbf{x},\mathbf{x}';T)=\int e^{iS(\mathbf{x}(t))}D\mathbf{x}(t)\ ,$$

$$\text{with } \mathbf{x}(0)=\mathbf{x}',\ \mathbf{x}(T)=\mathbf{x}\ . \quad (11)$$

Here, $S(\mathbf{x}(t))$ is the classical action

$$S(\mathbf{x}(t))=\int_0^T L(\mathbf{x}(t),\dot{\mathbf{x}}(t),t)dt\ , \quad (12)$$

with the corresponding KS Lagrangian

$$L_{\rm KS}=\frac{1}{2}(\dot{x}^2+\dot{y}^2+\dot{z}^2)-\frac{B}{2}(x\dot{y}-y\dot{x})-u_{\rm EF}(\mathbf{x})\ . \quad (13)$$

It is well known[9] that the path integral (11) is dominated by classical paths in the classical limit $T\to 0$. Furthermore, it turns out that every Green's function that has been evaluated exactly in closed form is a sum over classical paths alone.[10] These facts encourage us to use the classical path of some nearby reference system to approximate the Green's function (11). For this purpose, we first make the separation $S=S_0+\Delta S$, and rewrite (11) as[11]

$$G(\mathbf{x},\mathbf{x}';T)=G_0(\mathbf{x},\mathbf{x}';T)\langle e^{i\Delta S(\mathbf{x}(t))}\rangle_0\ , \quad (14)$$

where the path average designated by subscript zero employs the probability weight $\exp iS_0(\mathbf{x}(t))/G_0(\mathbf{x},\mathbf{x}';T)$. Let us choose the reference Lagrangian L_0 as (13) in the absence of $u_{\rm EF}(\mathbf{x})$. The Green's function for an electron in a constant magnetic field is one of the few known exactly in closed form[10]

$$G_0(\mathbf{x},\mathbf{x}';T)=\frac{1}{(2\pi iT)^{3/2}}\frac{aT}{\sin(aT)}\exp\left[\frac{i}{2T}(z-z')^2+\frac{ia}{2}\cot(aT)[(x-x')^2+(y-y')^2]+ia(xy'-yx')\right]\ , \quad (15)$$

where $a=B/2$. Equation (14) then becomes

$$G(\mathbf{x},\mathbf{x}';T)=G_0(\mathbf{x},\mathbf{x}';T)e^{-i\int_0^T u_{\rm EF}(\mathbf{x}_{\rm cl}(t))dt}\ , \quad (16)$$

where $\mathbf{x}_{\rm cl}(t)$ is the classical path of an electron in the magnetic field, a helix satisfying the boundary conditions (11)

$$x_{\rm cl}(t)=x'+\frac{(x-x')(1-\cos BT)-(y-y')\sin BT}{2(1-\cos BT)}\times(1-\cos Bt)+\frac{(x-x')\sin BT+(y-y')(1-\cos BT)}{2(1-\cos BT)}\times\sin Bt\ , \quad (17)$$

$$y_{\rm cl}(t)=y'+\frac{(y-y')\sin BT-(x-x')(1-\cos BT)}{2(1-\cos BT)}\times\sin Bt+\frac{(x-x')\sin BT+(y-y')(1-\cos BT)}{2(1-\cos BT)}\times(1-\cos Bt)\ , \quad (18)$$

$$z_{\rm cl}(t)=z'+\frac{z-z'}{T}t\ . \quad (19)$$

The basic semiclassical approximation that we now make is valid for $(T\to 0)$. This is to restrict the average in (16) to the straight-line free-particle path from $\mathbf{x}'$ to $\mathbf{x}$,

$$\mathbf{x}_{\rm cl}(t)=\mathbf{x}'+\frac{\mathbf{x}-\mathbf{x}'}{T}t\ . \quad (20)$$

We therefore can expand $x_{\rm cl}(t)$ and $y_{\rm cl}(t)$ about $T=0$. As a matter of fact, for sufficiently small T, any classical path satisfying the boundary conditions (11) can be approximated by a straight line if the field is not singular. Corresponding to the small T approximation (18), retaining terms only through $O(T)$ in the exponent of (15) results in the semiclassical Green's function

$$G_{\rm sc}(\mathbf{x},\mathbf{x}';T)=e^{ia(xy'-yx')}\frac{1}{(2\pi iT)^{3/2}}\frac{aT}{\sin aT}\times\exp\left[\frac{i(\mathbf{x}-\mathbf{x}')^2}{2T}-iT\int_0^1 u_{\rm EF}(\mathbf{x}'+(\mathbf{x}-\mathbf{x}')t)dt-\frac{iT}{6}a^2[(x-x')^2+(y-y')^2]\right]\ . \quad (21)$$

The combination of (21), (10), and (6) then leads, after some computation, to the density and the kinetic functional

$$\rho(\mathbf{x})=(1/6\pi^2)k_F^3(\mathbf{x})\Theta(k_F^2(\mathbf{x}))\ , \quad (22)$$

$$k_F^2(\mathbf{x})=2[\mu-u_{\rm EF}(\mathbf{x})]\ , \quad (23)$$

$$t_s(\mathbf{x})=t_{\rm TF}(\mathbf{x})+\frac{1}{9}t_W(\mathbf{x})+\frac{B^2}{16}\frac{1}{(6\pi^2)^{2/3}}\rho^{1/3}(\mathbf{x})\ . \quad (24)$$

In the derivation, we have replaced ∇ in Eq. (6) by $\nabla + i\,\mathbf{A}$, and kept only the leading orders in T. t_{TF} and t_W denote the usual Thomas-Fermi and Weizsäcker expressions

$$t_{\mathrm{TF}}(\mathbf{x}) = \frac{3}{10}(6\pi^2)^{2/3}\rho^{5/3}(\mathbf{x}) ,$$
$$t_W(\mathbf{x}) = \frac{1}{8}\frac{|\nabla\rho(\mathbf{x})|^2}{\rho(\mathbf{x})} . \tag{25}$$

Hence combining (24) and (25) with (3), (4), and (6), we obtain the density functional

$$E[\rho] = T_{\mathrm{TF}}[\rho] + \frac{1}{9}T_W[\rho] + \frac{B^2}{16}\frac{1}{(6\pi^2)^{2/3}}\int \rho^{1/3}(\mathbf{x})d\mathbf{x} + \int u(\mathbf{x})\rho(\mathbf{x})d\mathbf{x} + \frac{1}{2}\int \frac{\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)}{|\mathbf{x}_1-\mathbf{x}_2|}d\mathbf{x}_1 d\mathbf{x}_2 + E_{\mathrm{xc}}[\rho] , \tag{26}$$

where

$$T_{\mathrm{TF}}[\rho] = \int t_{\mathrm{TF}}(\mathbf{x})d\mathbf{x}, \quad T_W[\rho] = \int t_W(\mathbf{x})d\mathbf{x} . \tag{27}$$

On minimizing (26) with respect to ρ, with the Fermi energy μ as Lagrange multiplier for the condition $\int\rho(\mathbf{x})d\mathbf{x} = N$, we have as well the corrected profile equation

$$\frac{1}{2}(6\pi^2)^{2/3}\rho^{2/3} - \frac{1}{18}\frac{\nabla^2\rho^{1/2}}{\rho^{1/2}} + \frac{B^2}{48}\frac{1}{(6\pi^2)^{2/3}}\frac{1}{\rho^{2/3}} + u(\mathbf{x}) + \int\frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d\mathbf{x}' + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho} = \mu . \tag{28}$$

The density functional (26), with its nontrivial $\rho^{1/3}$ B dependence,[12] and the associated profile equation (28) are simple and practical tools for dealing with magnetic fields. But the range of validity of B in the above functional needs to be checked even though the magnetic field is not necessarily weak in the short-time (ST) approximation. Furthermore, even at the stage represented by Eqs. (17)–(19) (classical path approximation), a direct correlation effect between the effective potential and the magnetic field still exists. Unfortunately, this effect cannot be incorporated in the ST approximation. We will discuss these topics in future articles.

IV. DISCRETIZED PROPAGATOR REPRESENTATION

The discretized propagator approach, developed by Handler,[13] Harris and Pratt,[14] has recently been used by Yang[15] to construct an integral formulation of the Hohenberg-Kohn-Sham (HKS) density functional theory for atoms. This formation makes full use of the advantages given by density functional theory (DFT) because it does not invoke the self-consistent orbitals. The multidimensional integration formulas offer the possibility of *ab initio* calculations for systems with a very large number of electrons. We now use the same method to develop formulations for atoms in magnetic fields. The one-body Green's function G can be expressed in the form

$$G(\mathbf{x},\mathbf{x}';T) = \langle\mathbf{x}|(e^{-iH_{\mathrm{KS}}T/n})^n|\mathbf{x}'\rangle = \int d\mathbf{x}_1\cdots d\mathbf{x}_{n-1}\prod_{m=0}^{n-1}\langle x_{m+1}|e^{-iH_{\mathrm{KS}}T/n}|\mathbf{x}_m\rangle , \tag{29}$$

where $\mathbf{x}_0 = \mathbf{x}'$, $\mathbf{x}_n = \mathbf{x}$, and the KS Hamiltonian is defined by Eq. (8). From the previous discussion, we know that Green's function G takes the form given by Eq. (21) at the zero time limit. Therefore the discretized propagator in the integrand can be approximated by

$$\langle\mathbf{x}_{m+1}|e^{-iH_{\mathrm{KS}}T/n}|\mathbf{x}_m\rangle = G(\mathbf{x}_{m+1},\mathbf{x}_m;T/n) + O[(T/n)^2] , \tag{30}$$

$$G(\mathbf{x}_{m+1},\mathbf{x}_m;T/n) = e^{ib_0(m+1,n)}\left[\frac{n}{2\pi iT}\right]^{3/2} \times\exp\left[\frac{in}{2T}(\mathbf{x}_{m+1}-\mathbf{x}_m)^2 - \frac{iT}{n}u(m+1,m) - \frac{iT}{n}b_1(m+1,m)\right] , \tag{31}$$

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

$$u(m+1,m) = \int_0^1 u_{\mathrm{EF}}(x_m + (\mathbf{x}_{m+1}-\mathbf{x}_m)t)dt ,$$
$$b_0(m+1,m) = a(x_{m+1}y_m - y_{m+1}x_m) ,$$
$$b_1(m+1,m) = \frac{a^2}{6}[(x_{m+1}-x_m)^2 + (y_{m+1}-y_m)^2] .$$

Substituting Eq. (30) into Eq. (29), we have

$$G_n(\mathbf{x},\mathbf{x}';T) = \left[\frac{n}{2\pi iT}\right]^{3n/2}\int d\mathbf{x}_1\cdots d\mathbf{x}_{n-1}\exp\left[i\sum_{m=0}^{n-1}b_0(m+1,m)\right] \times\exp\left[\frac{in}{2T}\sum_{m=0}^{n-1}(\mathbf{x}_{m+1}-\mathbf{x}_m)^2 - \frac{iT}{n}\sum_{m=0}^{n-1}u(m+1,m) - \frac{iT}{n}\sum_{m=0}^{n-1}b_1(m+1,m)\right] . \tag{32}$$

From Eq. (30), it is obvious that

$$G(\mathbf{x},\mathbf{x}';T)=G_n(\mathbf{x},\mathbf{x}';T)+O(T^2/n) . \tag{33}$$

Thus G_n converges to G as n goes to infinity. The corresponding density matrix is given by

$$\gamma_n(\mathbf{x},\mathbf{x}')=\int d\mathbf{x}_1\cdots d\mathbf{x}_{n-1}\exp\left[i\sum_{m=0}^{n-1}b_0(m+1,m)\right] \times\left[\frac{nk_n}{2\pi l_n}\right]^{3n/2}J_{3n/2}(k_n l_n)\Theta(k_n^2) , \tag{34}$$

where $J_{3n/2}$ is the Bessel function and

$$k_n^2=2\left[\mu-\frac{1}{n}\sum_{m=0}^{n-1}u(m+1,m)-\frac{1}{n}\sum_{m=0}^{n-1}b_1(m+1,m)\right] , \tag{35}$$

$$l_n^2=n\sum_{m=0}^{n-1}(\mathbf{x}_{m+1}-\mathbf{x}_m)^2 . \tag{36}$$

The convergence of γ_n is ensured by that of G_n.[15] The diagonal elements of γ_n yield the electron density

$$\rho_n(\mathbf{x})=\rho_n(u_{\mathrm{EF}}(\mathbf{x});\mathbf{x},B) , \tag{37}$$

which is an explicit functional of $u_{\mathrm{EF}}(\mathbf{x})$ with the magnetic field B as a parameter. The kinetic functional $t_n(\mathbf{x})$ is given by the differential relation (6),

$$t_n(\mathbf{x})=\tfrac{1}{2}(\nabla_{\mathbf{x}}+i\,\mathbf{A})\cdot(\nabla_{\mathbf{x}'}+i\,\mathbf{A}')\gamma_n(\mathbf{x},\mathbf{x}')|_{\mathbf{x}'=\mathbf{x}} =t_n(u_{\mathrm{EF}}(\mathbf{x});\mathbf{x},B) , \tag{38}$$

The calculation of t_n is elementary but very tedious.

Combining Eqs. (2), (3), (4), (7), (37), and (38), the ground-state energy of atoms in the magnetic field can be calculated, provided the exchange-correlation functional is given. The above integral formulation approaches the KS orbital method as n goes to infinity.

V. CONCLUDING REMARKS

A TFW-like density functional model for atoms in magnetic fields has been obtained through the path integral formulation of the one-body Green's function. The integral formulation of DFT proposed in Sec. IV is expected to provide a more efficient way for accurate calculation of ground-state energies and charge densities for atoms with very many electrons in intense magnetic fields.

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