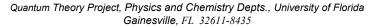


Current DFT versus Ordinary DFT for Atomic Ground States in External Magnetic Fields

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Density functional theory (DFT) is based upon the proof that the charge density of a system is the unique variable that determines all the ground state observables. However, this statement does not hold in the presence of a magnetic field. G. Vignale et. al. (ref. 1) argued that the paramagnetic current density $\tilde{J}_r(\tilde{r})$ together with the electron density $n(\vec{r})$ are the basic variables for such a system. This generalization of DFT is called current density functional theory (CDFT). We have implemented the CDFT formalism in our Gaussian basis atomic code. Some results from the ongoing work are presented in this poster. In particular, the effects of aniostropic basis sets are considered. A comparison is made with results from both naïve inclusion of an external B-field in ordinary

Theory

CDFT is formulated in terms of a gauge-invariant combination of the charge density

$n(\vec{r}) = \sum \phi_k(\vec{r}) ^2$		(1)
and the paramagnetic current density	$\vec{j}_p(\vec{r}) = \frac{\hbar}{2mi} \sum_k [\phi_k^*(\vec{r}) \nabla \phi_k(\vec{r}) - c.c.]$	(2)

The one electron Kohn-Sham (KS) equation takes the form $\hat{h}\phi_{\iota}(\vec{r}) = \mathcal{E}_{\iota}\phi_{\iota}(\vec{r})$

$$\hat{h} = \frac{1}{2m_e} \left(\frac{\hbar}{c} \nabla + \frac{e}{c} \vec{A}_{eff}(\vec{r}) \right)^2 + V_{eff}(\vec{r})$$

$$\vec{A}_{eff}(\vec{r}) = \vec{A}_{ee}(\vec{r}) + \vec{A}_{ee}(\vec{r})$$

$$V_{eff}(\vec{r}) = V_s(\vec{r}) + \frac{e^2}{2m_e c^2} [\vec{A}_{se}^2(\vec{r}) - \vec{A}_{eff}^2(\vec{r})]$$
 (6)

$$V_x(\vec{r}) = V_{xx}(\vec{r}) + V_H(\vec{r}) + V_{xx}(\vec{r})$$

$$V_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

$$V_{n}(\vec{r}) = \frac{\partial \mathbb{E}_{n}[n(\vec{r}), \tilde{f}_{p}(\vec{r})]}{\partial i(\vec{r})}$$

$$\tilde{A}_{n}(\vec{r}) = \frac{\partial \mathbb{E}_{n}[n(\vec{r}), \tilde{f}_{p}(\vec{r})]}{\partial \tilde{f}_{p}(\vec{r})}$$
(6)

$$E_{G} = \sum_{i} \mathcal{E}_{k} \frac{e^{2}}{2} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{m}[n(\vec{r}), \vec{J}_{p}(\vec{r})] - \int [n(\vec{r}) V_{m}(\vec{r}) + \frac{e}{c} \vec{J}_{p}(\vec{r}) \vec{A}_{m}(\vec{r})] d\vec{r}$$
(11)

Those formulas bury all the complexity of an interacting system in the exchange-correlation functional $E_{n}[n(\vec{r}),\vec{j}_{n}(\vec{r})]$ Gauge invariance considerations show that $E_{\nu}[n(\vec{r}), \vec{j}_{\nu}(\vec{r})]$ is actually a functional of $n(\vec{r})$ and the so-called

$$\vec{v}(\vec{r}) = \nabla \times \left(\frac{\vec{J}_p(\vec{r})}{n(\vec{r})} \right)$$
(12)

$$E_{_{M}}[n(\vec{r}), \vec{J}_{_{\vec{p}}}(\vec{r})] = \vec{E}_{_{M}}[n(\vec{r}), \vec{v}(\vec{r})]$$
(13)

It is useful to separate the exchange-correlation functional into a current-independent term and an explicitly

$$\widetilde{E}_{xc}[n(\vec{r}), \vec{v}(\vec{r})] = E^{0}[n(\vec{r})] + \Delta E_{xc}[n(\vec{r}), \vec{v}(\vec{r})]$$

(14) By homogeneous scaling of both the electron density and the paramagnetic current density, Erhard and Gross deduced that the current density exchange functional scales homogeneously as

current density exchange functional scales homogeneously as
$$E_{\nu}[n^{k}, \vec{j}_{n}^{k}] = kE_{\nu}[n, \vec{j}_{n}] \qquad (15)$$

where n^k and \vec{j}_n^k are scaled charge density and paramagnetic current density, respectively.

Assuming that the exchange part dominates the exchange-correlation energy, a local approximation for the exchange-correlation functional takes the form

$$E_{\infty}[n(\vec{r}), \vec{v}(\vec{r})] = E_{-}^{0}[n(\vec{r})] + \int g([n(\vec{r}), \vec{v}(\vec{r})], \vec{r}) |\vec{v}(\vec{r})|^{2} d\vec{r}$$
(16)

A further (drastic) approximation is to assume

 $g([n(\vec{r}),\vec{v}(\vec{r})],\vec{r}) = g(n(\vec{r}))$

For implementation purposes, of course, an explicit expression for the exchange-correlation functional is required. Unfortunately we know little about its form. Vignale et. al. gave a weak-field approximation

$$g(\vec{r}) = g(n(\vec{r})) = \frac{m_e k_F}{24\pi^2} \left[\frac{\chi(n(\vec{r}))}{\chi_0(n(\vec{r}))} - 1 \right]$$

by analyzing the homogeneous electron gas (HEG). Here k_F is the Fermi momentum, and χ and χ_0 are the orbital magnetic susceptibilities for the interacting and non-interacting HEG, respectively.

From the tabulation of γ/γ_c in Vignale's paper, Lee, Colwell, and Handy (LCH) obtained the fitted form (ref. 7),

$$s_{LCH} = \chi / \chi_0 = (1.0 + 0.028 r_s) e^{-0.042 r_s}$$

here
$$r_s = (\frac{3}{4 - \sqrt{z}})^{1/3}$$
 (26)

chose the LCH fit because it seems least ill-behaved. However, even it needs modification for B#0.

Rewrite equation (4) in a slightly different form:

$$\hat{h} = \frac{1}{2m_e} \left(\frac{h}{l} \nabla + \frac{e}{c} \vec{A}_{cu}(\vec{r}) \right)^2 + \{V_{cv}(\vec{r}) + V_{ff}(\vec{r}) + V_{x}(\vec{r})\} + \frac{he}{2im_e} (\vec{A}_{x}(\vec{r}) \cdot \nabla + \nabla \cdot \vec{A}_{x}(\vec{r}))$$
(22)

$$\hat{h} = \left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{r} + V_H(\vec{r}) + V_{rc}(\vec{r}) \right] + \left[\frac{eB}{2m_e c} (l_z + 2s_z) + \frac{e^2B^2}{8m_e c^2} (x^2 + y^2) \right] - \frac{\hbar kc}{2m_C} (\bar{A}_{rc}(\vec{r}) \cdot \nabla + \nabla \cdot \bar{A}_{rc}(\vec{r}))$$
(23)

Gaussian-type basis sets are widely used in many atomic, molecular, and cluster codes. The periodic system code we use and develop. GTOFF, also uses a GTO basis. On the other hand, in the high magnetic field situation, cylindrical coordinates are preferred. Numerical basis sets are also used in some studies. For the reason of consistency with the B=0 limit and the motive of adding CDFT to the GTOFF code, here we use an anisotropic Gaussian basis as in reference 6 and follow their scheme for electron-electron integrals

$$\chi_i(\rho, z, \phi) = \rho^{n_{\rho_i}} z^{n_{z_i}} e^{-\alpha_i \rho^2 - \beta_i z^2} e^{im_i \phi}$$
 $i = 1, 2, 3, \dots$

where
$$n_{\rho_i} = |m_i| + 2k_i$$
, $k_i = 0,1, \cdots$ with $m_i = \cdots, -2, -1, 0, 1, 2, \cdots$
 $n_i = \pi_- + 2l_i$, $l_i = 0,1, \cdots$ with $\pi_z = 0,1$. (24)

If we let $\alpha = \beta$, this basis returns to the isotropic Gaussian one, appropriate for B=0. For B>0, anisotropic Gaussians are better adapted for the description of the elongation of the electron density distribution caused by the field. From our studies of the History in an external magnetic field, we propose the following expression

$$\alpha_i - \beta_i = \begin{cases} B\Delta_1 & , B \leq 1 \\ B(\Delta_1 - \Delta_2 - \Delta_1) & B > 1 \end{cases}$$

where $\Delta_{_{1}}=0.11$, $\Delta_{_{10}}=0.21$ and B is in Hartree atomic units (1 a.u. B field $\approx 2.3505 \cdot 10^6$ Tesla). Reference 5 gave a slightly different value for $\Delta_- = 0.25$ This basis construction will be referred to as anisotropic basis

Thus obtained anisotropic basis can be further optimized by minimizing calculated Hartree-Fock or DFT total atomic energy resulting into optimized basis. Note this nonlinear optimization step needs to be done for each B field strength and fully optimization is difficult. Basis sets used in this work are only partially optimized and no optimization is done for $B \le 0.1$. The quality of calculation also depends on the size of the basis. For $B \le 10$ a.u., we use basis sets of 28s15p12d12f11g10h; for B=100 a.u., the basis set is 28s16p16d13f13g13h.

Turn next to the calculation of the exchange-correlation vector potential $\vec{A}_{-}(\vec{r})$. Equations (10) and (16)

imply
$$\frac{e}{c}\vec{A}_{w}(\vec{r}) = \frac{-1}{n(\vec{r})} \left(\nabla \times \frac{\delta \vec{E}_{w}[n,\vec{v}]}{\delta \vec{v}(\vec{r})} |_{u(\vec{r})} \right) = \frac{-2}{n(\vec{r})} \nabla \times (g(\vec{r}))\vec{v}(\vec{r}))$$

$$\vec{V}(\vec{r})$$
 is calculated analytically according to $\vec{v}(\vec{r}) = -\frac{\nabla n(\vec{r})}{n^2 \cdot (\vec{r})} \times \vec{J}_{\rho}(\vec{r}) + \frac{\nabla \times \vec{J}_{\rho}(\vec{r})}{n(\vec{r})}$
Then the curl in equation (28) is taken numerically on the mean.

Integrals of the last term in eqn. (23) are not necessarily convergent, since the function $g_{con}(n(\vec{r}))$ behaves inappropriately in low density regions. It is desirable to know its behavior in this region, but unfortunately, Ref. 1 did not give data for r_s> 10, nor do we know its asymptotic form. Ref. 8 suggested (but did not use) a smooth, rapid cutoff for $\varrho\left(n(\vec{r}\,)\right)$. Here we pursue the idea and introduce a cutoff function

$$g_{conf} = \frac{m_x k_F}{24 \, \pi^2} (c_1 + c_2 r_r) e^{-\sigma_{coff} r_r} \tag{28}$$
 where α_{conff} is the cutoff exponent, which determines how fast the function dies cut. Two constants c_1 c_2 are determined by the smooth connection between g_{LCR} and g_{conff} at the designated cutoff density n_{conff}

$$g_{colof}(n_{colof}) = g_{LCH}(n_{colof}), \frac{dg_{colof}}{dn}|_{n_{colof}} = \frac{dg_{LCH}}{dn}|_{n_{colof}}$$
In this work, we use $n_{colof} = 0.001a_0^{-1}, \alpha_{colof} = 2.0a_0^{-1}$ unless other values are explicitly specified. (29)

Table I. Total Energy Calculation of Carbon Atom in Magnetic Field (energy in Hartree)

B field (a.u.)	Ground State Configuration	Hartree-Fock in present work	Numerical HI ^P	DFT (VWN)	CDFT (VWN+VRG)	ΔE_{VRG}^{cdft}
0	1s ² 2s ² 2p ₀ ^{2/3} 2p ₋₁ ^{2/3} 2p ₁ ^{2/3}	-37.5313		-37.470028 (-37.470031 ^b)	as left	0
0	1 s 2 2 s 2 2 p a 2 p -1	-37.69092	-37.69096	-37.4698	-37.4708	-0.0011
0.001	as above	-37.6924	-37.6925	-37.4713	-37.4723	-0.0011
0.01	as above	-37.7058	-37.7059	-37.4847	-37.4857	-0.0011
0.1	as above	-37.8299	-37.8302	-37.6083	-37.6094	-0.0011
1.0	1 s 2 2 s 2 p a 2 p -1 3 d -2	-39.1573	-39.1577	-38.8662	-38.8740	-0.0079
10	1 s 2 2 p - 1 3 d - 2 4 f - 3 5 g - 4	-44.3862	-44.3872	-44.0706		-0.192 °
100	1s2p_3d_24f_55g_6h_5	-92.4520	-92.4552	-92.6156		-1.85 °

a) Reference 2 6) Reference 4 c) Estimated from SCE-DET orbitals CDET calculation failed to converge

Table II. Total Energy Calculation of Boron Atom in Magnetic Field (energy in Hartree)

Basi	s optimized for C atom a	is function of B	-field and ur	icnanged.			
B Field (a.u.)	Ground State Configuration	Hartree-Fock in present work	Numerical HI ⁰	DFT (VWN)	CDFT (VWN+VRG)	$\Delta E_{VRG}^{cd/0}$	
0	1s 2 2 s 2 2 p 1/3 2 p 1/3 2 p 1/3	-24.4150		-24.353613 (-24.353614 ^b)	as left	0	1
0	1s22s2p-1	-24.53024	-24.53029	-24.3545	-24.3555	-0.0010	1
0.001	as above	-24.53124	-24.53133	-24.3555	-24.3565	-0.0010	1
0.01	as above	-24.54009	-24.54018	-24.3643	-24.3653	-0.0010	1
0.1	1 s 2 2 s 2 p 0 2 p -1	-24.63892	-24.63932	-24.4219	-24.4231	-0.0012	1
1.0	as above	-25.64663	-25.64711	-25.4190	-25.4208	-0.0018	1
10	1s2p_13d_24f_15g_4	-30.06282	-30.06363	-29.8747		-0.20°	1
100	as above	-66.99485	-66.99699	-67.1169			1

a) Reference 3. b) Reference 4. c) Estimated from SCF-DFT wave function. CDFT calculation failed to converge.

Table III. Total Energy Calculation of Boron Ion in Magnetic Field (energy in Hartree)

B Field (a. u.)	Ground State Configuration	Hartree-Fock in present work	Numerical HF ^a	DFT (VWN)	CDFT (VWN+VRG)	$\Delta E_{\rm FBG}^{\rm edf}$
0	1s22s2	-24.23757	-24.23758	-24.038275 (-24.038275 ^b)	as left	0
0.001	as above	-24.23757	-24.23758	-24.03827	as left	0
0.01	as above	-24.23751	-24.23752	-24.03821	as left	0
0.1	1s22s2p.,	-24.26342	-24.26360	-24.02913	-24.03135	-0.00223
1.0	as above	-25.07016	-25.07026	-24.83998	-24.84269	-0.00272
10	1s2p_13d_24f_1	-28.93421	-28.93504	-28.71343		0.163
100	as above	-63.94533	+63.94727	-63.81585		1.32 °

a) Reference 3. b) Reference 4. c) Estimated from SCF-DFT orbitals. CDFT calculation failed to converge.

Tables I-III give calculated total energies for the carbon and boron atoms, and the boron positive ion in different field strengths. Hartree-Fock and naïve DFT energies in the same basis set are also listed. We use VWN (ref. 11) XC functional in the DFT calculation,augmented by the VGR functional (ref. 1) for CDFT. Numerical HF values from reference 2 and 3 are also listed for comparison.

There is generally good agreement between our HF calculation with Gaussian type orbitals and Ivanov and Schmelcher's numerical mesh HF values. The slightly larger difference for high field values shows the increasing demands on basis sets with increasing field strength. For the naïve DFT calculation, we compare with the spherical averaged value from reference 4. The agreement is excellent.

Reference 2 and 3 show the ground states of C, B, and B* undergo several configuration transitions with increasing B field. Similar crossovers occur in our DFT and CDFT calculations. The CDFT correction is mainly determined by the ground state configuration, which is in turn determined by the field strength.

GL+VRG

-38.9059

2.0

1.0

	of 1.0 a.u.	(energy in	correlation functionals (energy in a.u.)			
	HF	DFT	CDFT		PZ"	-38.8639
lasis Set		(VWN)	(VWN+ VRG)		PW92 ^b	-38.8652
et A	-39.1141	-38.8228	-38.8283	-0.0055	VWN "	-38.8662
let B	-39.1524	-38.8610	-38.8680	-0.0070	GL'	-38.9697
iet B	-39.1524	-38.8610		-0.0070	HL-JMW "	-38.8981
let C	-39.1573	-38.8662	-38.8740	-0.0079	PZ+VRG ^f	-38.8717
èum.	-39.1577 ^b			-	PW92+VRG	-38.8730
nasis					VWN+VRG	-38.8740

IV. Sets A.B.C are isotropic, anisotropic. and optimized aniso. basis sets, respec-Appropriately optimized basis sets are necessary and sufficient for a wide range of B field range from 0 to several

hundreds of a u The performance of different functionals is compared in table V. The CDFT/VRG correction is roughly half the imprecision among LDA models. It's not clear whether the VRG functional can give systematic improvement on DFT values.

The VPC functional with LCH fit has a major deficiency for finite systems at high

B fields. Using a smooth cutoff function and a sensible cutoff density, one hopes the VRG contribution to $E_{\rm total}$ would be insensitive to the cutoff choice but this is not the case. Table VI shows the effects of cutoff choices: they are undesirable. Ref. 16 gave two alternative fits to the data in ref. 1, but they also have the same problem.

A fully self-consistent CDFT approach is implemented in our atomic code with external magnetic field Anisotropic Gaussian basis sets are used in the expansion of KS orbitals. Numerical tests show that a rich basis set is required for accurate calculation, especially in the high field regime. The current density correction to the total atomic energy appears to be two or three orders smaller than the interaction between the magnetic field and atom angular momentum. The CDFT correction is strongly configuration related. While our HF and DFT calculations give reliable results, the CDFT calculation should be understood to be only qualitatively correct (or optimistically, semi-quantitative), since the VRG functional we investigated is sensitive to an unavoidable cutoff. Keeping in mind (a) that the local density approximation of eqn. (16) presumes the variation of electron density and current density both to be small in an atomic scale, (a constraint not satisfied in the high field regime), and (b) that eqn. (18) was proposed and fitted only in the low field regime, it is not surprising that use of those functionals may have serious limitations. The lack of general and accurate CDFT XC functionals is still the biggest problem as of today. Recently, some other currentdependent functionals were proposed (ref. 14, 15). Though not manifestly gauge invariant, we are going to investigate how the behave in the high field regime. CDFT is expected to be more useful with the advent of high quality CDFT exchange-correlation functionals

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References: 1. G. Vigrale, M. Rasolt and D. J. W. Geldarf, Advan. Quantum Chem. 21, 235 (1990) 2. M. V. Ivanov and P. Schmelcher, Phys. Rev. A 60, 3558 (1999)

3. M. V. Ivanov and P. Schmelcher, J. Phys. B: At. Mol. Opt. Phys. 34, 2031 (2001)

4. S. Kotochigova, et. al., Phys. Rev. A 55, 191 (1997)

Y. P. Kinzchenko and M. A. Liberman, Int. J. Chaesham Chien. 64, 513 (1997)
 W. Becken and P. Schmeicher, J. Phys. B: At. Mol. Opt. Phys. 33, 545 (2003)
 A. M. Lee, S. M. Colwell, and N. C. Handy, Chiem Phys. Lett. 229, 225 (1994)

8. A. M. Lee, N. C. Handy, and S. M. Colwell, J. Chem. Phys. 103, 10095 (1995)

J. P. Pendew and A. Zinger, Phys. Rev. B 23, 5048 (1981)
 J. P. Pendew and Y. Wang, Phys. Rev. B 45, 13244 (1992)
 S. H. Vosko, L. Wilk, and M. Nussir, Can. J. Phys. 58, 1200 (1980)

12. O. Gunnarsson and B. I. Lundovist, Phys. Rev. B 13, 4274, (1975)

13. J. F. Janak, V. L. Moruzzi, and A. R. Williams, Phys. Rev. B 12, 1257 (1975) 14. S. N. Maximoff, M. Emperhof, and G. E. Scuseria, J. Chem. Phys. 120, 2105 (2004)

A. D. Becke, J. Chem. Phys. 117, 6935 (2002)
 E. Crestes, T. Marcasso, and K. Capelle, Phys. Rev. A 68, 022105 (200