

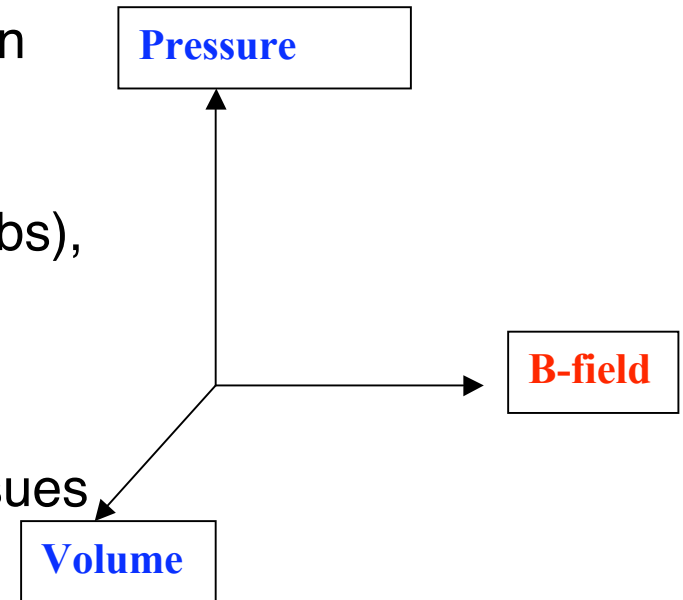


Large-scale, Grid-enabled Gaussian Orbital Implementation of Current-density and Spin- density Functional Theory for Ordered Systems

**J. Ashley Alford, Wuming Zhu,
Samuel B. Trickey
NSF DMR 0218957**

Institute for Theory and Computation
in Molecular and Materials Sciences
“Quantum Theory Project”
Depts. of Physics and of Chemistry

♣ Objective: Extend the success of all-electron DFT methodology from the P-V (stress-strain) plane into the P-V-B space for 1D (ordered polymers), 2D (ordered Ultra-Thin Films & slabs), & 3D systems (crystals).



♣ Even at $B = 0$, there are many important issues beyond equilib.volume V_0 and equilib.bulk modulus B_0 :

- (a) $T = 0$ K eqn of state & sequence of ordered phases *including* metal-insulator and magnetic-non-magnetic transitions (diamond anvil cell data to approx. 2 Mbar);
- (b) epitaxy & reconstruction in surfaces and over-layers;
- (c) force constant matrices (dynamical matrices), elastic constant anisotropies & Cauchy relations,
- (d) susceptibilities, etc.

What happens for $B \neq 0$?

$B \neq 0$ relatively little-explored. Physically important ranges:

$0 < B \leq 50 \text{ T}$ (terrestrial; Natl. High Mag. Field Lab.)

$10^3 \text{ T} \leq B \leq 10^8 \text{ T}$ (white dwarves, neutron stars)

(1 gauss = 10^{-4} T \approx field near Earth's surface)

External B fields break periodicity, **but** -

1 Hartree au of B field = $2.3505 \times 10^5 \text{ T}$ _

terrestrial: $0 < B \leq 0.0002 \text{ au}$

astrophysical: $0.004 \text{ au} \leq B \leq 425 \text{ au}$

Low field: weak perturbation

High field: rational fields restore periodicity on a supercell -

$B \approx 2.5 (L/N) \times 10^4 \text{ T}$; L, N integers with no common factor

$\approx 0.1 (L/N) \text{ au}$

- Computational Tool: **GTOFF** Code
GTOFF = A general, periodic system (1D, 2D, 3D), all-electron DFT code that uses **G**aussian **T**ype **O**rbitals with **F**itting **F**unction techniques for speed.
- Basic scheme – Gaussian basis (materials are made of molecules and molecules are computed mostly in Gaussian basis). Gain speed by fitting the charge density to a linear expansion in an auxiliary set of Gaussians (no 4-center Coulomb integrals). Use “fit-to-fit” to obtain XC densities in a second Gaussian expansion (efficient numerical integral scheme).
- Recent review article on **GTOFF** methods and algorithms: S.B Trickey, J. Ashley Alford, and J.C. Boettger in “Computational Materials Science”, vol. 15 of *Theoretical and Computational Chemistry*, J. Leszczynski, ed. (Elsevier, 2004) pp 171 – 228

- **Opportunity –**
Add **C**urrent **D**ensity **F**unctional **T**heory to **GTOFF**.
- **Barriers –**
 1. **GTOFF** is written in fast, efficient, robust but baroque FORTRAN, its data structures are messy and many, ..._ almost hopeless to add physics by modifying present version.
 2. Little is known about **CDFT** implementation:
 - Magnetic susceptibilities & nuclear shielding constants for atoms & small molecules (Handy and co-workers)
 - Perturbative shifts of atomic KS orbital energies at $B \neq 0$ (Capelle and co-workers)
 - Few approximations for
 3. Need experience with $B \neq 0$ **CDFT** behavior up to at least $B = 5\text{--}10$ au

- Implementation Objectives

Build a new **GTOFF** (“_**GTOFF**”) that is

 } modular, maintainable, shareable _ Objects,
 C++...

 } most of all, extensible to new physics

Design implications -

 Drastic simplification of user interface including:

*Automated generation of direct and reciprocal lattice
 grids (with simpler, cleaner symmetry info input)*

*Automatic detection of symmetries and structure
 space group operations*

Integrals Package -

*Matrix elements of general 1-body operators with
 parallelization options both by **k**-points & orbitals*

*2- and 3-center coulomb integrals: Generalized Ewald
 summations have distinct real-space and
 reciprocal-space optimization requirements
 (parallelization, evaluation*

*of a characteristic special function determined by
 dimension; e.g. 1-D requires evaluation &*

Design implications (continued) -

Integrals Package (continued)

*Efficient implementation of numerical integrals for
fit-to-fit expansion of XC potentials and energy
densities*

*Add the integrals needed for Douglas-Kroll-Hess
relativis-*

*tic corrections (presently in **R-GTOFF**)*

SCF Package –

*Incorporate the relativistic corrections (presently
separate)*

*Make independent of details of the integrals package
(allow possibility of using at least parts of quantum
chemistry integrals packages)*

*Incorporate hooks for **CDFT***

- Work begun January 2003
- Detailed Status and Progress Report in Ashley Alford's poster:

**“Object-oriented Design of an All-Electron Gaussian
Basis**

DFT Code for Periodic Systems”

-GTOFF: Development status

1.) **Flexible input module** that separates form of input data from objects that need the data.

The **parser** reads and stores data with associated **keywords** (which can be nested, associated other keywords), and provides a simple interface through which other modules can access the data.

2.) **Determination of Symmetry and Brillouin Zone Reduction.**

Old: Separate module GMESH.F outputs real or reciprocal space grids and requires input of mirror planes and rotation axes.

New: Automatic calculation of space group operations and reduced grids via the **Crystal** class and user input of desired grid density.

3.) **One-electron Integrals:**

The **Int1e** template class allows for calculation and storage or output of orbital matrix elements of a general class of simple 1-body operators (e.g. overlap, kinetic energy). For any such operator, the program constructs a simple function and passes it as a template parameter to **Int1e**.

4.) **Processor Group Handler:**

Simple functions comprising MPI code for posting warnings and/or a global kill signal. Provides a guaranteed clean exit in an MPI environment.

(continued)

-GTOFF: Development status (cont'd)

5.) Two and Three Electron Coulomb Integrals:

The **Int3c** class (3e integrals) is derived from the base class **Int2c** (2e integrals) because 3-center integrals are simply a linear combination of 2- center integrals.) For integrals calculated in real space, **Int3c** contains an extra member function where the usage of the recursion relations that generate the integrals is optimized

Basic message: first Integrals package by late Summer,
first version of SCF by end of the year.

- Implementation Objective:

Understand **CDFT** by studying isolated atoms in GTO basis

} Understand implications of non-spherical Gaussians:

The usual GTO procedure

$$\phi_k^m(\mathbf{r}) = \sum_l R_k^{lm}(r) Y_{lm}(\theta, \varphi) \quad R_k^{lm}(\mathbf{r}) = r^l \sum_i c_{ki}^{lm} e^{-\alpha_i^l r^2}$$

goes over to expansion in

$$\chi_i(\rho, z, \varphi) = \rho^{n_{\rho i}} z^{n_{z i}} e^{-\alpha_i \rho^2 - \beta_i z^2} e^{im_i \varphi}$$

} Understand basis set effects (impracticably large basis sets are the norm for Hartree-Fock atoms in magnetic fields)

} Understand limits of approximations, magnitude relative to external field, compare with “naïve B-DFT”

} Study numerical behavior [*c.f.* Orestes *et al.* remark, Phys. Rev. A **66**, 022105 (2003) that full scf for **CDFT** is “still quite demanding”, hence they do pert. theory.]

- Reminder: In DFT the ground state is parameterized by $\psi(\mathbf{r})$
However, not true in the presence of an external magnetic field.
- G. Vignale *et. al.* : must use gauge-invariant combination of paramagnetic current density \mathbf{j}_p and \mathbf{j}_m . **CDFT**
thus parameterizes with \mathbf{j}_m

the “vorticity”

- In contrast “Naïve DFT-B” keeps external B contributions but has no CDFT terms (no \mathbf{j}_m)

- Energy functional written in terms of KS eigenvalues and potentials:

- The XC functional always is the challenge in implementing DFT.

Write $E_{xc}[n(\mathbf{r}), \mathbf{j}_p(\mathbf{r})] = \tilde{E}_{xc}[n(\mathbf{r}), \mathbf{v}(\mathbf{r})]$

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

Separate the vorticity-dependent part

$$E_x[n^k, \mathbf{j}_p^k] = k E_x[n, \mathbf{j}_p]$$

Known eXchange scaling

Assume: exchange dominates and that some sort of local approximation

is possible. Then this scaling leads to

- Vignale *et al.* weak-field approximation [Adv. Quantum Chem. 21, 235 (1990)]

Perhaps the simplest possible assumption (but severe)

Interacting HEG orbital magnetic susceptibility

Non-interacting HEG susceptibility

Lee, Colwell, & Handy, Chem.Phys. Lett. 217, 271 (1994) Fit to Vignale & Rasolt tabulation of susceptibilities. $1 \leq r_s \leq 10$

Sign of trouble: There are 3 different fits to the same data. They differ dramatically outside the original range of r_s

- Implementation in Gaussian-Type Orbital (isotropic, anisotropic) basis sets

KS Hamiltonian with B along z-axis;
drop 2nd line to get “naïve DFT-B”

$$\phi_k^m(\mathbf{r}) = \sum_l R_k^{lm}(r) Y_{lm}(\theta, \varphi)$$

KS orbitals in isotropic basis

$$R_k^{lm}(\mathbf{r}) = r^l \sum_i c_{ki}^{lm} e^{-\alpha_i^l r^2}$$

KS orbitals in anisotropic basis

$$\chi_i(\rho, z, \varphi) = \rho^{n_{\rho_i}} z^{n_{z_i}} e^{-\alpha_i \rho^2 - \beta_i z^2} e^{im_i \varphi}$$

$$n_{\rho_i} = |m_i| + 2k_i, \quad k_i = 0, 1, L$$

$$m_i = L, -2, -1, 0, 1, 2, L$$

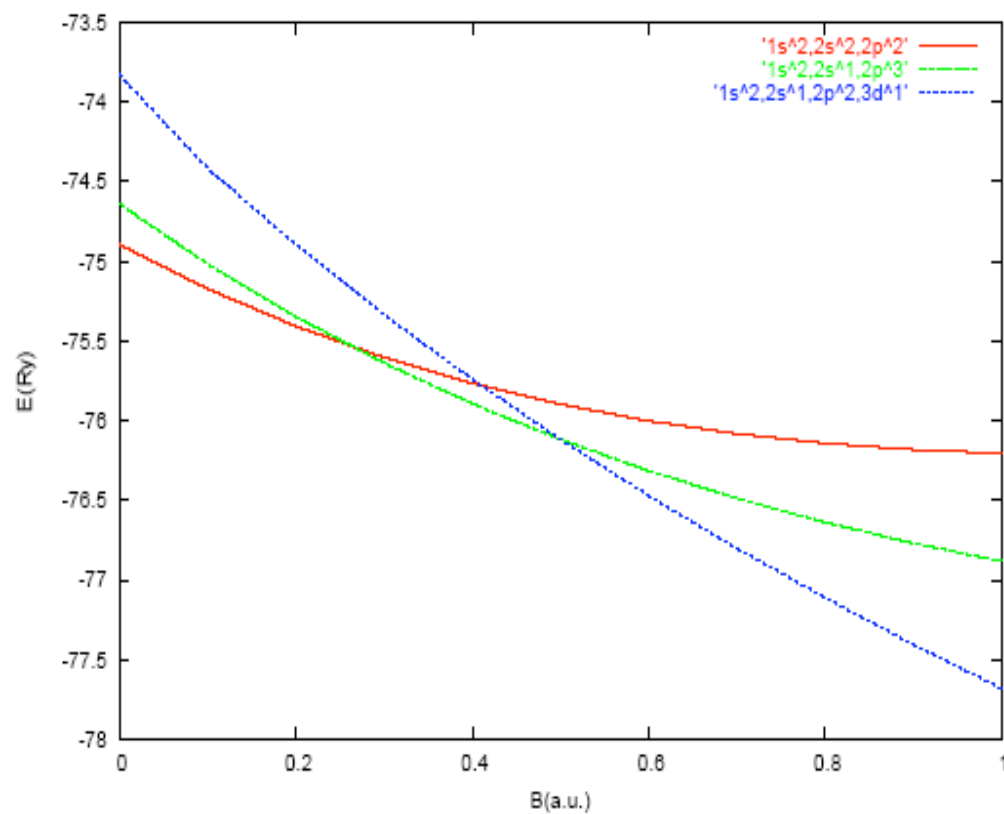
$$n_{z_i} = \pi_{z_i} + 2l_i, \quad l_i = 0, 1, L$$

$$\pi_{z_i} = 0, 1.$$

$$\alpha_i - \beta_i = \begin{cases} B\Delta_1 & , B \leq 1 \\ B[\Delta_\infty - \frac{\Delta_\infty - \Delta_1}{1 + \ln(B)}] & , B > 1 \end{cases}$$

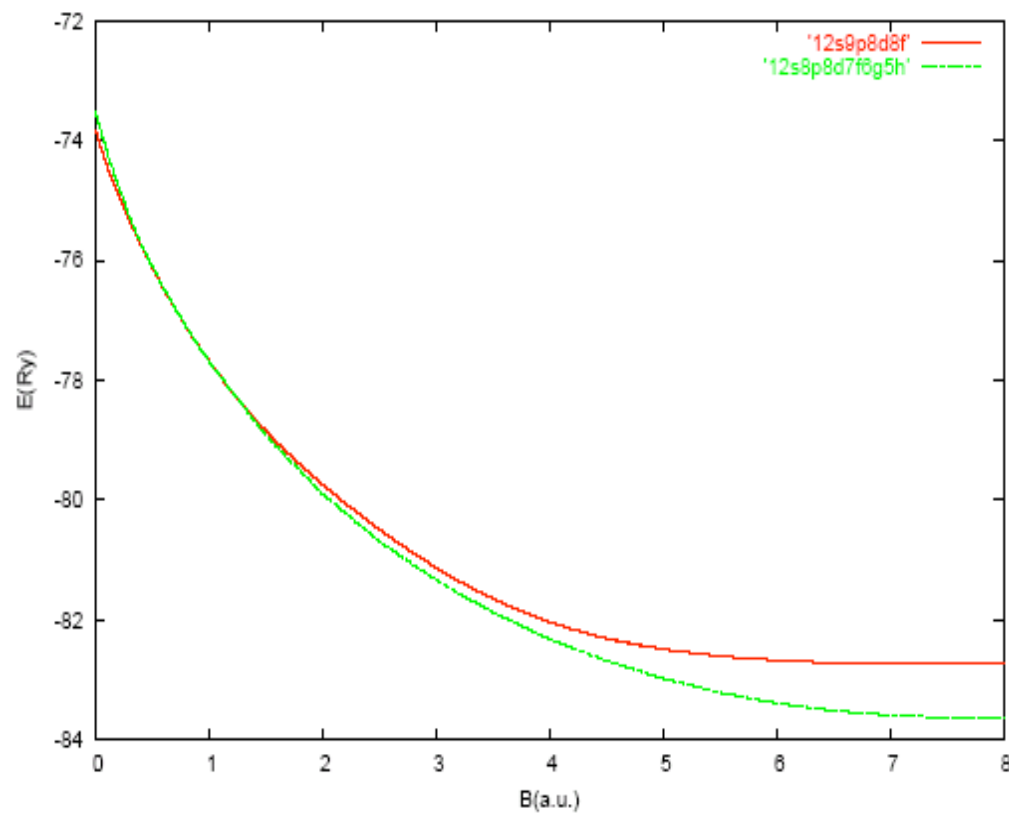
Partial optimization

- Results – Carbon atom.
Basis A: 12s9p8d8f isotropic
Naïve DFT-B



1au B field = 2.3505E05 Tesla

- Results – Carbon atom; Naïve DFT-B
 Basis A: 12s9p8d8f isotropic
 Basis B: 12s9p8d7f6g5h isotropic

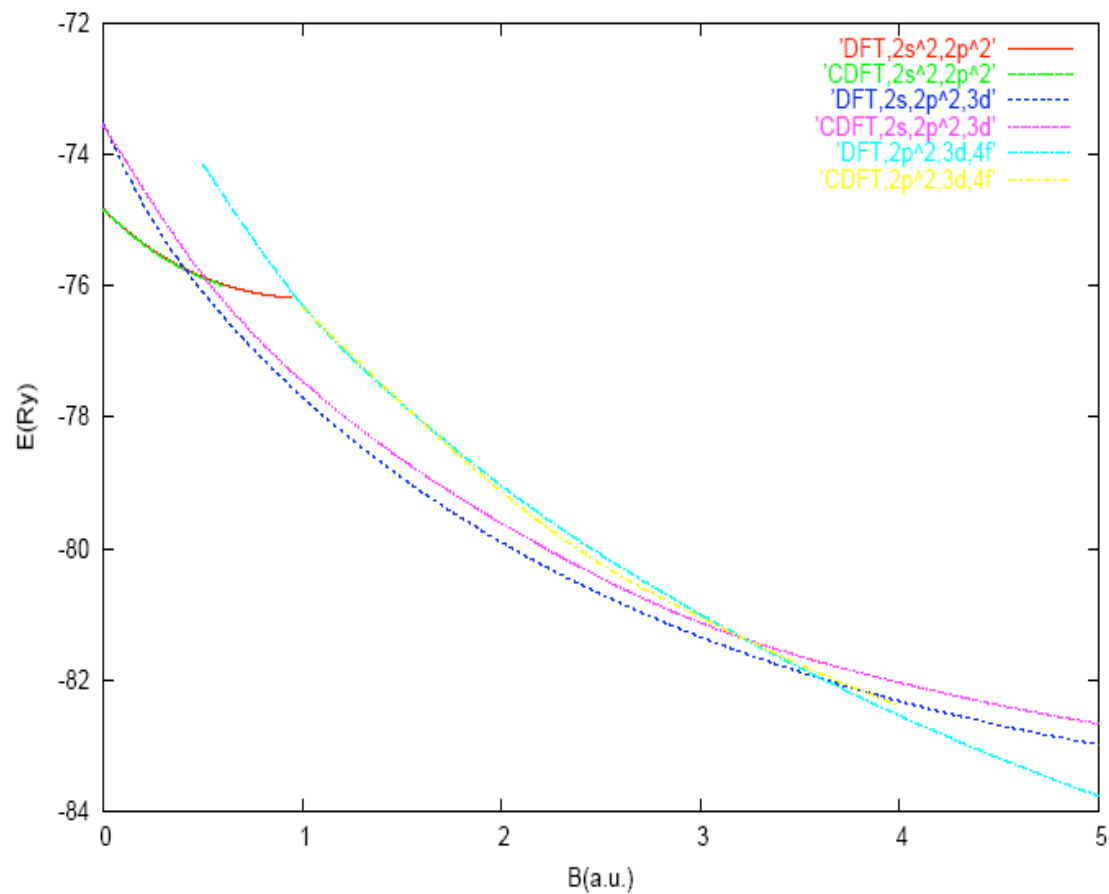


Naïve DFT-B; Basis Set effect. Fixed configuration: $1s^2 2s 2p_0 2p_{-1} 3d_{-2}$
 1au B field = 2.3505E05 Tesla

- Results – Carbon atom.

Basis A: 12s9p8d8f

Basis B: 12s9p8d7f6g5h



CDFT vs. naïve DFT-B. 1au B field = 2.3505E05 Tesla

- Results – Carbon atom. Isotropic basis sets
- Basis A: 12s9p8d8f
- Basis B: 12s9p8d7f6g5h

Ground state configuration $1s^2 2s^2 2p^2 3d^2 4f^3$ $1s^2 2s^2 2p_0 2p_1$	Hartree -Fock calculation ^a	DFT calculation (basis set A)	DFT calculation (basis set B)	CDFT calculation (basis set B)
	0 ~ 0.1862	0 ~ 0.273	0 ~ 0.285	0 ~ 0.297
	0.1862 ~ 0.4903	0.273 ~ 0.504	0.285 ~ 0.489	0.297 ~ 0.676
	0.4903 ~ 4.207	0.504 ~ 4.42	0.489 ~ 3.61	0.676 ~ 3.03
	4.207 ~ 7.920	4.42 ~	3.61 ~	3.03 ~

Range of B fields for which indicated configuration lies lowest. “DFT” is actually naïve DFT-B. 1au B field = 2.3505E05 Tesla. Ref. “a” is Ivanov and Smelcher, Phys. Rev. A 60, 3558 (1999)

Note that our results differ significantly from the perturbative CDFT results at B=0 au of Orestes *et al.*, Phys. Rev. A 68, 022105 (2003) For example, the 2p₀ eigenvalue shift from DFT to CDFT is +0.0022 Ry vs. the pert-CDFT shift of -0.045 eV.

Total Energy (Hartrees) Calculation of Carbon Atom in
Magnetic Field; Basis construction C.

B field (a.u.)	Ground State Configuration	Hartree-Fock (present work)	Numerical HF Note a)	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 Note b)	As at left	0
0	$1s^2 2s^2 2p_0 2p_{-1}$	-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	$1s^2 2s 2p_0 2p_{-1} 3d_{-2}$	-39.1573	-39.1577	-38.8662	-38.8740	-0.0079
10	$1s^2 2p_{-1} 3d_{-2} 4f_{-3} 5g_{-4}$	-44.3862	-44.3872	-44.0706	--- Note c)	-0.192
100	$1s 2p_{-1} 3d_{-2} 4f_{-3} 5g_{-4} 6h_{-5}$	-92.4520	-92.4552	-92.6156	---Note c)	-1.85

a) Ivanov & Smelcher, Phys. Rev. A **60**, 3558 (1999)

b) Kotochigova *et al.*, Phys. Rev. A **55**, 191 (1997)

c) Estimated from DFT KS orbitals; CDFT calc. would not converge.

Basis set effect on total energy calculation of carbon atom in
magnetic field of 1.0 a.u. Energies in Hartree au.

Basis Set ^a	Hartree-Fock calculation	DFT (VWN)	CDFT (VWN+VRG)	ΔE_{VRG}^{cdft}
Set A	-39.1141	-38.8228	-38.8283	-0.0055
Set B	-39.1524	-38.8610	-38.8680	-0.0070
Set C	-39.1573	-38.8662	-38.8740	-0.0079
Numerical basis	-39.1577 ^b	----	----	----

Note that CDFT shifts w/r naïve DFT-B are larger than the B_C basis set
improvement

a) see Wuming Zhu's Poster for details of basis sets A, B and C;

b) Ivanov and Smelcher, Phys. Rev. A **60**, 3558 (1999)

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- **SUMMARY:** A work in progress
 - θ Software: complete rebuild of GTOFF (review article of key methods and algorithms; design, coding, testing)
 - θ CDFT: exploration of $B \neq 0$ in atoms (anisotropic basis sets, approximate gauge-inclusion; BIG issue is better XC approximations)