Orbital Functionals in Current-Density Functional Theory

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Outline

- Motivation for CDFT
- Orbital functionals in CDFT: OEP and KLI
- Preliminary Results for open-shell atoms
- New Projects
  - self-consistent CDFT with other orbital-dependent functionals, non-collinear magnetism in quantum dots
  - self-consistent potentials for RPA-like functionals
  - correlation functionals in DFT from linear response in CDFT

Motivation for CDFT

- Describe systems in magnetic field which couples to both spins and currents
- of particular interest: open-shell systems where ground state may carry a current
- problem of LDA: derivative discontinuities of $e_{xc}^{unif}(n, \mathbf{B})$ as function of $\mathbf{B}$ whenever new Landau level is filled; difficult to handle in practice

$\longrightarrow$ try orbital-dependent functionals: appearance of Landau levels is orbital effect

Current Density Functional Theory

Energy functional for electrons in magnetic field

$$E[n, \mathbf{m}, \mathbf{j}_p] = T_s[n, \mathbf{m}, \mathbf{j}_p] + \int \mathrm{d}^3 r \; v_0(\mathbf{r}) n(\mathbf{r})$$
$$- \int \mathrm{d}^3 r \; \mathbf{m}(\mathbf{r}) \mathbf{B}_0(\mathbf{r}) + \frac{1}{c} \int \mathrm{d}^3 r \; \mathbf{j}_p(\mathbf{r}) \mathbf{A}_0(\mathbf{r})$$
$$+ \frac{1}{2c^2} \int \mathrm{d}^3 r \; n(\mathbf{r}) \mathbf{A}_0(\mathbf{r})^2 + U[n] + E_{xc}[n, \mathbf{m}, \mathbf{j}_p]$$

with non-interacting kinetic energy T_s, Hartree energy U, and exchange-correlation energy E_{xc}

densities

$$n(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow} \langle \hat{\psi}^\dagger_\alpha(\mathbf{r}) \hat{\psi}_\alpha(\mathbf{r}) \rangle$$

$$\mathbf{m}(\mathbf{r}) = -\mu_B \sum_{\alpha,\beta} \langle \hat{\psi}^\dagger_\alpha(\mathbf{r}) \boldsymbol{\sigma}_{\alpha\beta} \hat{\psi}_\beta(\mathbf{r}) \rangle$$

$$\mathbf{j}_p(\mathbf{r}) = \frac{1}{2i} \sum_{\alpha=\uparrow,\downarrow} \left(\langle \hat{\psi}^\dagger_\alpha(\mathbf{r}) \nabla \hat{\psi}_\alpha(\mathbf{r}) - \nabla \hat{\psi}^\dagger_\alpha(\mathbf{r}) \hat{\psi}_\alpha(\mathbf{r}) \rangle \right)$$

Kohn-Sham scheme

$$\left(\frac{1}{2}(-i\nabla + \frac{1}{c}\mathbf{A}_s(\mathbf{r}))^2 + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma}\mathbf{B}_s(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

with effective potentials

$$v_s(\mathbf{r}) = v_0(\mathbf{r}) + \int \mathrm{d}^3r' \, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r}) + \frac{1}{2c^2}\left(\mathbf{A}_0(\mathbf{r})^2 - \mathbf{A}_s(\mathbf{r})^2\right)$$

$$\mathbf{B}_s(\mathbf{r}) = \mathbf{B}_0(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r})$$

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}_0(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r})$$

Exchange-correlation potentials

$$v_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta n(\mathbf{r})}$$

$$\mathbf{B}_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = -\frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta \mathbf{m}(\mathbf{r})}$$

$$\mathbf{A}_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = c\frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta \mathbf{j}_p(\mathbf{r})}$$

Exchange-correlation potentials

$$v_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta n(\mathbf{r})}$$

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$$\mathbf{A}_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = c\frac{\delta E_{xc}[n, \mathbf{m}, \mathbf{j}_p]}{\delta \mathbf{j}_p(\mathbf{r})}$$

if xc functional satisfies $E_{xc}[n, \mathbf{m}, \mathbf{j}_p] = E_{xc}[n, \mathbf{j}_p - c\nabla \times \mathbf{m}]$
$\longrightarrow$ usual relation between vector potential and magnetic field

$$\mathbf{B}_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r}) = \nabla \times \mathbf{A}_{xc}[n, \mathbf{m}, \mathbf{j}_p](\mathbf{r})$$

Optimized Effective Potentials in CDFT

variation with respect to potentials gives OEP equations (Helbig and Gross)

$$\int \mathrm{d}^3 r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{1}{c} A_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta v_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right)$$
$$= \sum_{i=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right)$$

$$\int \mathrm{d}^3 r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \frac{1}{c} A_{xc}(\mathbf{r}') \frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} \right)$$
$$= \sum_{i=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + c.c. \right)$$

CDFT-OEP equations in short form

use “orbital shifts”

$$\sum_{i=1}^{N} \left(\psi_i^\dagger(\mathbf{r}) \varphi_i(\mathbf{r}) + c.c. \right) = 0$$

$$\sum_{i=1}^{N} \left(\psi_i^\dagger(\mathbf{r}) \boldsymbol{\sigma} \varphi_i(\mathbf{r}) + c.c. \right) = 0$$

$$\sum_{i=1}^{N} \left(\psi_i^\dagger(\mathbf{r}) \nabla \varphi_i(\mathbf{r}) - (\nabla \psi_i^\dagger(\mathbf{r})) \varphi_i(\mathbf{r}) + c.c. \right) = 0$$

first-order changes in the densities vanish: Kohn-Sham already gives correct densities by construction

KLI equations in CDFT

usual trick of Krieger, Li, and Iafrate: replace energy denominators $(\varepsilon_i - \varepsilon_j) \longrightarrow \Delta\varepsilon$: KLI equations in CDFT with similar structure than in non-collinear spin DFT

$$\begin{pmatrix} n & -m_1 & -m_2 & -m_3 \\ -m_1 & \mu_B^2 n & 0 & 0 \\ -m_2 & 0 & \mu_B^2 n & 0 \\ -m_3 & 0 & 0 & \mu_B^2 n \end{pmatrix} \begin{pmatrix} v_{xc}(\mathbf{r}) \\ B_{xc,1}(\mathbf{r}) \\ B_{xc,2}(\mathbf{r}) \\ B_{xc,3}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} g_1(\mathbf{r}) \\ g_2(\mathbf{r}) \\ g_3(\mathbf{r}) \\ g_4(\mathbf{r}) \end{pmatrix}$$

remark: the $g_i(\mathbf{r})$ depend linearly on $\mathbf{A}_{xc}(\mathbf{r})$

Iterative scheme for KLI equations

1. with guess for $v_{xc}, \mathbf{A}_{xc}, \mathbf{B}_{xc} = \nabla \times \mathbf{A}_{xc}$ compute orbitals, then r.h.s. and matrix on l.h.s. of KLI equation
2. solve matrix equation for new $v_{xc}, \mathbf{B}_{xc}$ for each point $\mathbf{r}$
3. from $\mathbf{B}_{xc}$ compute new $\mathbf{A}_{xc}$ by inverting $\mathbf{B}_{xc} = \nabla \times \mathbf{A}_{xc}$ (see also Eschrig et al, 1985)

$$\mathbf{A}_{xc}(\mathbf{r}) = \frac{1}{4\pi} \int \mathrm{d}^3 r' \, \frac{\nabla' \times \mathbf{B}_{xc}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

4. go back to point 1. and iterate

Open-shell atoms: no external magnetic field

Lifting of degeneracies in DFT: spurious energy shifts between current-carrying and zero-current states

Becke (2002): include $\mathbf{j}_p$ in E_{xc} to reduce energy shifts.

Energy shifts in Kcal/mol.

Atom	BRx	jBRx	KLIx(S)	KLIx(C)	KLIx(D)
B	5.7	0.6	1.7		
C	5.9	0.7	1.6		
O	10.3	1.2	1.7		
F	10.0	1.5	2.3		

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Energy shifts in Kcal/mol.

Atom	BRx	jBRx	KLIx(S)	KLIx(C)	KLIx(D)
B	5.7	0.6	1.7	11	
C	5.9	0.7	1.6	70	
O	10.3	1.2	1.7	-57	
F	10.0	1.5	2.3	-6	

Open-shell atoms: no external magnetic field

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Energy shifts in Kcal/mol.

Atom	BRx	jBRx	KLIx(S)	KLIx(C)	KLIx(D)
B	5.7	0.6	1.7	11	0.1
C	5.9	0.7	1.6	70	0.1
O	10.3	1.2	1.7	-57	-0.2
F	10.0	1.5	2.3	-6	0.1

essentially degenerate states in DFT in x-only KLI !

Second-row atoms:

Energy shifts in Kcal/mol.

Atom	jBRx	jPBEx	KLIx(S)	KLIx(D)
Al	1.0	0.2	1.3	-0.7
Si	0.8	-0.1	-0.7	0.0
S	2.0	-0.7	3.0	0.3
Cl	1.7	-0.3	3.1	0.3

New Projects: Project 1

- CDFT implementation of other functionals

  meta-GGA's depending on $\tau = \frac{1}{2}\sum_{i=1}^{N} |\nabla \varphi_i(\mathbf{r})|^2$,

  Becke's functional depending on $\mathbf{j}_p$

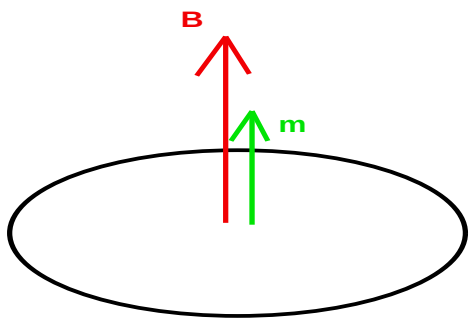
  none of these satisfy $\mathbf{B}_{xc} = \nabla \times \mathbf{A}_{xc}$

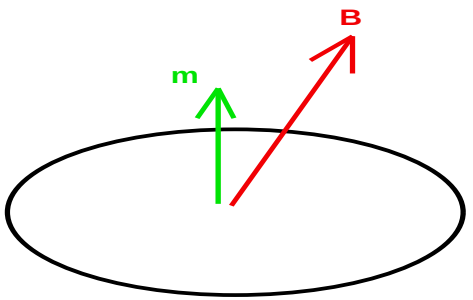
  $\longrightarrow$ 3 OEP/KLI equations have to be solved

- noncollinear magnetism

  ongoing project: 2D quantum dot in perpendicular magnetic field with collinear magnetization

  if magnetic field is tilted: expect magnetization (locally) to be non-collinear





Project 2:

Self-consistent xc potentials for RPA-like functionals

correlation energy expressed with fluctuation-dissipation theorem (also describes van-der-Waals interaction)

$$E_c[n] = -\int_0^1 \mathrm{d}\lambda \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{1}{|\mathbf{r}-\mathbf{r}'|} \int_0^\infty \frac{\mathrm{d}u}{2\pi} \left(\chi^\lambda(\mathbf{r},\mathbf{r}',iu) - \chi_s(\mathbf{r},\mathbf{r}',iu) \right)$$

with linear density response function at coupling strength λ and xc kernel f_{xc}^λ of TDDFT

$$\chi^\lambda = \chi_s + \chi_s \left(\lambda v_{Clb} + f_{xc}^\lambda \right) \chi^\lambda$$

write OEP equation in terms of orbital shifts

$$v_c(\mathbf{r}) = \frac{1}{2n(\mathbf{r})}\sum_{i=1}^{\infty}\left(\varphi_i(\mathbf{r})\frac{\delta E_c}{\delta\varphi_i(\mathbf{r})} + (n_i\bar{v}_{xci} - \bar{u}_{xci})|\varphi_i(\mathbf{r})|^2 + c.c.\right)$$
$$+\frac{1}{2n(\mathbf{r})}\sum_{i=1}^{\infty}\left(\varphi_i(\mathbf{r})\frac{\nabla^2}{2}\psi_i^*(\mathbf{r}) - \psi_i^*(\mathbf{r})\frac{\nabla^2}{2}\varphi_i(\mathbf{r}) + c.c.\right)$$

Problem: summation includes all states, asymptotic behavior numerically very difficult (Engel et al)
pragmatic approach: tag on analytic result (Niquet et al)

observation: in RPA, first term can be written explicitly in terms of response function

Project 3:

Correlation Functionals in DFT from linear response in CDFT

linear response of current

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int \mathrm{d}^3 r' \mathbf{X}(\mathbf{r},\mathbf{r}',\omega)\delta\mathbf{a}(\mathbf{r}',\omega)$$

with current-current response tensor

$$\mathbf{X} = \mathbf{X}_s + \mathbf{X}_s \mathbf{f}_{xc} \mathbf{X}$$

connected to TDDFT by continuity equation

$$\delta n(\mathbf{r},\omega) = -\frac{1}{i\omega}\nabla\delta\mathbf{j}(\mathbf{r},\omega)$$

consider $\delta\mathbf{a}(\mathbf{r},\omega)$ obtained from pure scalar potential $\delta v(\mathbf{r},\omega)$ by gauge transformation

$$\delta\mathbf{a}(\mathbf{r},\omega) = \frac{1}{i\omega}\nabla\delta v(\mathbf{r},\omega)$$

$\longrightarrow$ relation between density and current response

$$\chi(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{\omega^2}\sum_{j,k=1}^{3}\frac{\partial}{\partial r_j}\frac{\partial}{\partial r'_k}\mathbf{X}_{jk}(\mathbf{r},\mathbf{r}',\omega)$$

idea: use simple approximations for kernel $\mathbf{f}_{xc}$ of CDFT to get density response χ (simple $\mathbf{f}_{xc}$ can lead to $1/q^2$ divergence for f_{xc} in limit $q \to 0$ needed to describe excitons in semiconductors)

Summary

- OEP and KLI equations in CDFT: self-consistent KLI
- Open-shell atoms: lifting of degeneracies much smaller in DFT than SDFT but (preliminary!) much larger in CDFT
- new projects
  - self-consistent CDFT with other orbital-dependent functionals, non-collinear magnetism in quantum dots
  - self-consistent potentials for RPA-like functionals
  - correlation functionals in DFT from linear response in CDFT