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## Functionals for non-collinear magnetism

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Most formulations of spin density functional theory (SDFT) restrict the magnetization vector field to have global collinearity. Nevertheless, there exists a wealth of strong noncollinearity in nature, for example molecular magnets, spin-spirals, spin-glasses and all magnets at finite temperatures.

The local spin density approximation (LSDA) can be extended to these non-collinear cases [1] but this extension has the undesirable property of having the exchange-correlation (XC) field parallel to the magnetization density at each point in space. When used in conjunction with the equation of motion for the spin magnetization in the absence of spin currents and external fields [2, 3], this local collinearity eliminates the torsional term, resulting in no time evolution. This severe shortcoming of LSDA, where the physical prediction is qualitatively wrong, opens up an important new direction for the development of functionals where this time evolution is correctly described.

Towards this goal we have taken two approaches. The first extends the Kohn-Sham optimized effective potential (OEP) method to the non-collinear case [3, 4], while the second is to develop a new XC functional [5] based on spin-spiral waves which goes beyond the LSDA by using gradients of the magnetization density. In both cases, we require the Kohn-Sham (KS) equation for two-component spinors  $\Phi_i$ , which has the form of a Pauli equation. For non-interacting electrons moving in an effective scalar potential  $v_s$  and a magnetic vector field  $\boldsymbol{B}_s$  it reads as (atomic units are used throughout):

$$-\frac{1}{2}\nabla^2 + v_{\rm s}(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \cdot \mathbf{B}_{\rm s}(\mathbf{r}) \Phi_i(\mathbf{r}) = \epsilon_i \Phi_i(\mathbf{r}). \tag{1}$$

This equation can be derived by minimizing the total energy which, in SDFT, is given as a functional of the density  $\rho(\mathbf{r}) = \sum_{i}^{\text{occ}} \Phi_{i}^{\dagger}(\mathbf{r}) \Phi_{i}(\mathbf{r})$  and the magnetization density  $\boldsymbol{m}(r) = \mu_{B} \sum_{i}^{\text{occ}} \Phi_{i}^{\dagger}(\mathbf{r}) \boldsymbol{\sigma} \Phi_{i}(\mathbf{r})$ .



FIG. 1: Fully non-collinear magnetization density and B field obtained using the LSDA and exchange-only EXX functionals for an unsupported Cr-monolayer in Néel state. Arrows indicate the direction and information about the magnitude (in atomic units) is given in the colour bar.

For a given external scalar potential  $v_{\text{ext}}$  and magnetic field  $\boldsymbol{B}_{\text{ext}}$  this total energy reads:

$$E[\rho, \boldsymbol{m}] = T_{\rm s}[\rho, \boldsymbol{m}] + \int \rho(\mathbf{r}) v_{\rm ext}(\mathbf{r}) d\mathbf{r} + \int \boldsymbol{m}(\mathbf{r}) \cdot \boldsymbol{B}_{\rm ext}(\mathbf{r}) d\mathbf{r} + U[\rho] + E_{\rm xc}[\rho, \boldsymbol{m}] \quad (2)$$
$$= \sum_{i}^{\rm occ} \epsilon_{i} - \int \rho(\mathbf{r}) v_{\rm xc}(\mathbf{r}) d\mathbf{r} - \int \boldsymbol{m}(\mathbf{r}) \cdot \boldsymbol{B}_{\rm xc}(\mathbf{r}) d\mathbf{r} - U[\rho] + E_{\rm xc}[\rho, \boldsymbol{m}]$$

where  $U[\rho] = 1/2 \int \int \rho(\mathbf{r}')\rho(\mathbf{r})/|\mathbf{r}' - \mathbf{r}|d\mathbf{r}'d\mathbf{r}$  is the Hartree energy. The XC potential and XC magnetic field are given by

$$v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[\rho, \boldsymbol{m}]}{\delta \rho(\mathbf{r})} \qquad \qquad \boldsymbol{B}_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[\rho, \boldsymbol{m}]}{\delta \boldsymbol{m}(\mathbf{r})} \tag{3}$$

respectively. The exact functional form of  $E_{\rm xc}[\rho, \boldsymbol{m}]$  is unknown and has to be approximated in practice.

Assuming that the densities  $[\rho, \mathbf{m}]$  are non-interacting  $(v, \mathbf{B})$ -representable one may, equivalently, minimize the total-energy functional (2) over the effective scalar potential and magnetic field. Thus the conditions

$$\frac{\delta E[\rho, \boldsymbol{m}]}{\delta v_{\rm s}(\mathbf{r})}\Big|_{\boldsymbol{B}_{\rm S}} \qquad \text{and} \qquad \frac{\delta E[\rho, \boldsymbol{m}]}{\delta \boldsymbol{B}_{\rm s}(\mathbf{r})}\Big|_{v_{\rm S}} \tag{4}$$

must be satisfied.

If we were to use a functional that depends explicitly on spinor valued wavefunctions we can stay within a single global reference frame, in contrast to the case where functionals originally designed for collinear magnetism are used in a non-collinear context by introducing a local reference frame at each point in space. The most commonly used orbital functional is the EXX energy given by

$$E_{\mathbf{x}}^{\mathbf{EXX}}[\{\Phi_i\}] = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \sum_{i,j}^{\mathrm{occ}} \frac{\Phi_i^{\dagger}(\mathbf{r}) \Phi_j(\mathbf{r}) \Phi_j^{\dagger}(\mathbf{r}') \Phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(5)

where the label occ indicates that the summation runs only over occupied states. From the conditions of Eq. (4) and using the functional form given in Eq. (5) (although generalization to other orbital functionals is straightforward), the OEP equations for the non-collinear systems were derived [3, 4].

In order to explore the impact of treating non-collinear magnetism in the way outlined above and at the same time to ensure that our numerical analysis be as accurate as possible, we implemented the OEP equations for the fully non-collinear case within the full-potential linearized augmented plane wave (FP-LAPW) method implemented within the ELK code [6]. This method is then applied to study the non-collinear spin magnetism in an unsupported Cr (111) monolayer. In Fig. 1 are shown the magnetization density and  $\boldsymbol{B}$  field calculated using both the LSDA and the OEP method.

A striking feature of the OEP B field is that, unlike its LSDA counterpart, it is not locally parallel to the magnetization density and this will produce manifestly different spindynamics. This is because the equation of motion for the spin magnetization reads

$$\frac{d\boldsymbol{m}(\mathbf{r},t)}{dt} = \gamma \boldsymbol{m}(\mathbf{r},t) \times [\boldsymbol{B}_{\rm XC}(\mathbf{r},t) + \boldsymbol{B}_{\rm ext}(\mathbf{r},t)] - \nabla \cdot \boldsymbol{J}_{\rm S}$$
(6)

where  $J_{\rm s}$  is the spin current and  $\gamma$  the gyromagetic ratio. In the time-independent LSDA and conventional GGA,  $\boldsymbol{m}(\mathbf{r})$  and  $\boldsymbol{B}_{\rm xc}(\mathbf{r})$  are locally collinear, as is clear from Fig. 1, and therefore  $\boldsymbol{m}(\mathbf{r}) \times \boldsymbol{B}_{\rm xc}(\mathbf{r})$  vanishes. This also holds true in the adiabatic approximation of time dependent SDFT which, by Eq. (6), implies that these functionals cannot properly describe the dynamics of the spin magnetization. In contrast, already at the static level, for the EXX functional  $\boldsymbol{m}(\mathbf{r}) \times \boldsymbol{B}_{\rm x}(\mathbf{r})$  does not vanish. In fact, in the ground state of a non-collinear ferromagnet without external magnetic field,  $\boldsymbol{m}(\mathbf{r}) \times \boldsymbol{B}_{\rm xc}(\mathbf{r})$  exactly cancels the divergence of the spin current,  $\nabla \cdot \boldsymbol{J}_{\rm s}$ , i.e. these terms are equally important, and it is essential to have a proper description of  $m(\mathbf{r}) \times B_{\rm xc}(\mathbf{r})$ . These results indicate that a time-dependent generalization of our method could open the way to an ab-initio description of spin dynamics. How well this functional really performs in describing the spin dynamics remains a question for future investigations.



FIG. 2: Illustration of spin spiral waves along one spatial coordinate for two different choices of wavevector  $\boldsymbol{q} = \boldsymbol{k}_{1,2}$ . The angle  $\theta$  is determined by s while the angle  $\phi = \boldsymbol{q} \cdot \mathbf{r}$ . Image reproduced from the PhD thesis of F. Eich.

Unfortunately OEP calculations are computationally demanding, leading us to develop [5] a new semi-local XC functional for non-collinear magnetism. This is analogous to the case in DFT, where going from the LDA to the generalized gradient approximations (GGAs) led to additional accuracy. To derive a new functional, our starting point was the spin-spiral wave (SSW) phase of the electron gas, which has magnetization:

$$\boldsymbol{m}(\mathbf{r}) = m(s\cos[\boldsymbol{q}\cdot\mathbf{r}], s\sin[\boldsymbol{q}\cdot\mathbf{r}], \sqrt{1-s^2})$$
(7)

where s is the spin projection on the z-axis and q is the SSW wavevector, it is illustrated in Fig. 2. Using quantum monte-carlo or the random phase approximation (RPA), the XC energy for such a state can be calculated and parameterized. To then construct a functional, we will use gradients of the magnetization to create effective s and q variables which can then be inserted into our parameterization. One particular choice is to use quantities:

$$D(\mathbf{r}) = ||\boldsymbol{m}(\mathbf{r}) \times (\nabla \otimes \boldsymbol{m})||^2$$
 and  $d(\mathbf{r}) = |\boldsymbol{m}(\mathbf{r}) \times \Delta \boldsymbol{m}(\mathbf{r})|^2$  (8)

giving effective s and q:

$$s^{2}(\mathbf{r}) = \frac{D^{2}(\mathbf{r})}{D^{2}(\mathbf{r}) + m^{4}(\mathbf{r})d(\mathbf{r})} \qquad \text{and} \qquad q^{2} = \frac{D^{2}(\mathbf{r}) + m^{4}(\mathbf{r})d(\mathbf{r})}{m^{4}(\mathbf{r})D(\mathbf{r})}$$
(9)



FIG. 3: The magnitude (heat map) and direction (arrows) of the magnetization density (left) and XC magnetic field (right) of the Cr monolayer.

The functional can then be written as:

$$E_{\rm xc}[\rho, \boldsymbol{m}] = \int d\mathbf{r} \ \epsilon_{\rm xc}^{\rm LSDA}(\mathbf{n}, \mathbf{m})(\mathbf{r}) \left(1 + S_{\rm xc}(\mathbf{n}, \mathbf{m}, \mathbf{D}, \mathbf{d})(\mathbf{r})\right) \tag{10}$$

where  $\epsilon_{\rm xc}^{LSDA}(n,m)$  is the non-collinear LSDA functional discussed earlier.  $S_{\rm xc}$  is the enhancement factor based on the parameterization of the SSW energies, and is designed so that the total functional reduces to LSDA in the appropriate limit. It can also be shown that this functional respects the zero-torque theorem.



FIG. 4: Heat map of the z-component of  $m(\mathbf{r}) \times B_{\rm XC}(\mathbf{r})$  around a Chromium atom in the monolayer. Note the three-fold rotation symmetry inherited from the symmetry of the monolayer.

To test this functional, it was implemented in ELK [6] and applied to the same case studied by OEP EXX above. In Fig. 3, we plot the self-consistent magnetization density  $\boldsymbol{m}(\mathbf{r})$  and the XC magnetic field  $\boldsymbol{B}_{\rm XC}(\mathbf{r})$  for a 2*d* slice in the plane of the Cr monolayer. To demonstrate that this functional does lead to locally non-collinear terms, in Fig. 4 we plot the *z*-component of  $\boldsymbol{m}(\mathbf{r}) \times \boldsymbol{B}_{\rm XC}(\mathbf{r})$  in the region around an atom of Chromium. Unlike the LSDA case and similar to the OEP case, this quantity is non-zero implying non-zero spin currents in the ground-state. For TDDFT this functional shows much promise as it contains non-zero local torques on the magnetization density (missing in LSDA) while still a semi-local functional and hence computationally less demanding that OEP.

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