A relativistic optimized potential method for spin-polarized systems

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Motivation

The search for xc-functionals

Tremendous success of Density-Functional-Theory relies on available exchange-correlation functionals

- 1^{st} generation: L(S)DA – n, $(n^{\uparrow}, n^{\downarrow})$
- 2^{nd} generation: GGAs – $n, \nabla n, \ldots$
- 3^{rd} generation: orbital functionals – $E_{xc}[\{\phi_i[n]\}]$

Use of orbital functionals requires method of optimized effective potential (OEP, OPM)

Exact exchange $E_x[\{\phi_i[n]\}]$ functional:

- wishful reductionism
- systematically improve on correlation problem

Relativistic OPM

Why ROPM in relativistic KKR-multiple scattering formalism?

- treat open-shell systems
- treat systems containing atoms with high Z
- study spin-orbit induced properties of solids without recourse to perturbative treatment of SOC
  - improve description of **orbital** magnetism
  - magneto-crystalline anisotropy
- Contribute to current discussions
  - How important is the use of an all-electron approach?
  - EXX treatment of magnetic solids?

Formalism

SDFT version of the ROPM

Spin-polarized systems $\left\{ \begin{array}{l} \text{open shell atoms} \\ \text{magnetic solids} \end{array} \right.$

Starting point – collinear SDFT-ROPM Dirac equation

$$\left[-ic\boldsymbol{\alpha}\cdot\vec{\nabla} + \frac{c^2}{2}(\beta - 1) + V_0(\vec{r}) + \bar{V}_{xc}(\vec{r}) + \beta\Sigma_z B_{xc}(\vec{r}) \right] \phi_k(\vec{r}) = \epsilon_k \phi_k(\vec{r})$$

$$\overline{V}_{xc}(\vec{r}) = \frac{\delta E_{xc}[n,m]}{\delta n(\vec{r})} \quad \text{and} \quad B_{xc}(\vec{r}) = \frac{\delta E_{xc}[n,m]}{\delta m(\vec{r})}$$

(Exact) numerical wave functions with mixed spin-angular character:

$$\phi_k^{\nu}(\vec{r}) = \begin{pmatrix} g^{\nu}_{\Lambda k}(r)\chi_{\Lambda}(\hat{r}) \\ i f^{\nu}_{\Lambda k}(r)\chi_{-\Lambda}(\hat{r}) \end{pmatrix} + \begin{pmatrix} g^{\nu}_{\bar{\Lambda} k}(r)\chi_{\bar{\Lambda}}(\hat{r}) \\ i f^{\nu}_{\bar{\Lambda} k}(r)\chi_{-\bar{\Lambda}}(\hat{r}) \end{pmatrix}, \quad \begin{array}{l} \Lambda = (\kappa, \mu), \\ \bar{\Lambda} = (-\kappa - 1, \mu) \end{array}$$

SDFT-ROPM equations

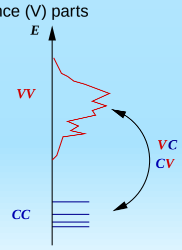
xc-potentials obtained from inverting integral equations

$$\begin{pmatrix} I_V(\vec{r}) \\ I_B(\vec{r}) \end{pmatrix}^T = \int \begin{pmatrix} \bar{V}_{xc}(\vec{r}') \\ B_{xc}(\vec{r}') \end{pmatrix}^T \chi(\vec{r},\vec{r}') d^3r'$$

$$\begin{pmatrix} \frac{\delta E_{xc}}{\delta \bar{V}_{KS}(\vec{r})} \\ \frac{\delta E_{xc}}{\delta B(\vec{r})} \end{pmatrix}^T = \int \begin{pmatrix} \bar{V}_{xc}(\vec{r}') \\ B_{xc}(\vec{r}') \end{pmatrix}^T \begin{pmatrix} \chi_{nn}(\vec{r},\vec{r}') & \chi_{mn}(\vec{r},\vec{r}') \\ \chi_{nm}(\vec{r},\vec{r}') & \chi_{mm}(\vec{r},\vec{r}') \end{pmatrix} d^3r'$$

- non-interacting static KS response functions χ
- inhomogeneities I_V and I_B

Partition contributions into core (C) and valence (V) parts



Response

$$\chi = \chi_C + \chi_V$$

Inhomogeneities of integral equation

$$E_{xc} = E^{CC}_{xc} + E^{CV}_{xc} + E^{VC}_{xc} + E^{VV}_{xc}$$

Core - core contribution

ROPM equations:

$$I_V(\vec{r}) = \frac{\delta E^{CC}_{xc}}{\delta V_{KS}(\vec{r})} = \int \sum_k \frac{\delta \phi^{\dagger}_k(\vec{r}')}{\delta \bar{V}_{KS}(\vec{r})} \frac{\delta E_{xc}[n,m]}{\delta \phi^{\dagger}_k(\vec{r}')} + c.c.\ d^3r'$$

$$I_B(\vec{r}) = \frac{\delta E^{CC}_{xc}}{\delta B_{xc}(\vec{r})} = \int \sum_k \frac{\delta \phi^{\dagger}_k(\vec{r}')}{\delta B_{xc}(\vec{r})} \frac{\delta E_{xc}[n,m]}{\delta \phi^{\dagger}_k(\vec{r}')} + c.c.\ d^3r'$$

From first order perturbation theory

$$\frac{\delta \phi^{\dagger}_k(\vec{r}')}{\delta \bar{V}_{KS}(\vec{r})} = \phi^{\dagger}_k(\vec{r}) G_k(\vec{r},\vec{r}') \qquad \frac{\delta \phi^{\dagger}_k(\vec{r}')}{\delta B_{xc}(\vec{r})} = \phi^{\dagger}_k(\vec{r})\beta\Sigma_z G_k(\vec{r},\vec{r}')$$

G_k orthogonal Green's function

$$\chi_{\mu\nu}(\vec{r},\vec{r}') = \sum_k^{occ} \phi^{\dagger}_k(\vec{r}) O^{\mu} G_k(\vec{r},\vec{r}') O^{\nu} \phi_k(\vec{r}') \qquad \mu,\nu \in \{n,m\}$$

Relativistic orthogonal Green's function

$$G_k(\vec{r}',\vec{r}) = \sum_{i \neq k} \frac{\phi_i(\vec{r}')\phi^{\dagger}_i(\vec{r})}{\epsilon_k - \epsilon_i}$$

- constructed numerically avoiding sum over states approach
- magnetic case ($\vec{B} \neq 0$) & coupled states: G_k built from ***four*** linear independent solutions of SDFT-Dirac equation

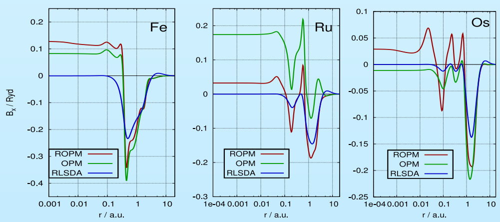
$$\begin{aligned} G_k(\vec{r},\vec{r}') &= \Gamma_k(\vec{r},\vec{r}') + A[\phi_k(\vec{r})] \\ \Gamma_k(\vec{r},\vec{r}') &= \phi_k(\vec{r})\psi^{\dagger}_k(\vec{r}')\Theta(r - r') + \psi_k(\vec{r})\phi^{\dagger}_k(\vec{r}')\Theta(r' - r) \\ &+ \tilde{\phi}_k(\vec{r})\tilde{\psi}^{\dagger}_k(\vec{r}')\Theta(r - r') + \tilde{\psi}_k(\vec{r})\tilde{\phi}^{\dagger}_k(\vec{r}')\Theta(r' - r) \end{aligned}$$

Exact exchange: core-core contribution

$$E^{CC}_x[n,m] = -\sum_{E_i,E_j \le E_F} \int d^3r' \int d^3r'' \frac{\phi^{\dagger}_i(\vec{r}')\,\phi_j(\vec{r}')\,\phi^{\dagger}_j(\vec{r}'')\,\phi_i(\vec{r}'')}{|\vec{r}' - \vec{r}''|}$$

Test of core-core contributions

Exchange field B_x – open shell d^6 valence configuration



First application of relativistic OEP to open shell system
DK, H. Ebert, E. Engel, PRB 77, 045101 (2008)

Valence-valence contribution

$$E^{VV}_x[n,m] = -\frac{1}{\pi^2} \int d^3r' \int d^3r'' \frac{\text{Tr}\left[\int dE\, \Im G(\vec{r}',\vec{r}'',E)\right]\left[\int dE'\, \Im G(\vec{r}'',\vec{r}',E')\right]}{|\vec{r}' - \vec{r}''|}$$

Multiple scattering Green's function - relativistic KKR:

$$\begin{aligned} G(\vec{r},\vec{r}',E) &= \sum_{\Lambda\Lambda'} Z^n_{\Lambda}(\vec{r},E)\tau^{nn'}_{\Lambda\Lambda'}(E) Z^{n'\times}_{\Lambda'}(\vec{r}',E) \\ &- \sum_{\Lambda} \left[Z^n_{\Lambda}(\vec{r},E) J^{n\times}_{\Lambda}(\vec{r}',E)\Theta(r' - r) \right. \\ &\left. + J^n_{\Lambda}(\vec{r},E) Z^{n\times}_{\Lambda}(\vec{r}',E)\Theta(r - r') \right] \delta_{nn'} \end{aligned}$$

with Z_{Λ} and J_{Λ} regular/irregular relativistic WF (numerical)

Inhomogeneities: variation of E^{VV}_x leads to

$$\frac{E^{VV}_x}{\delta V^{\nu}(\vec{r})} = -\frac{1}{\pi^2} \int d^3r' \int d^3r'' \frac{\text{Tr}\left[\int dE\, \Im G(\vec{r}',\vec{r}'',E)\right]\left[\int dE'\, \Im G(\vec{r}'',\vec{r},E')\hat{O}^{\nu} G(\vec{r},\vec{r}',E')\right]}{|\vec{r}' - \vec{r}''|}$$

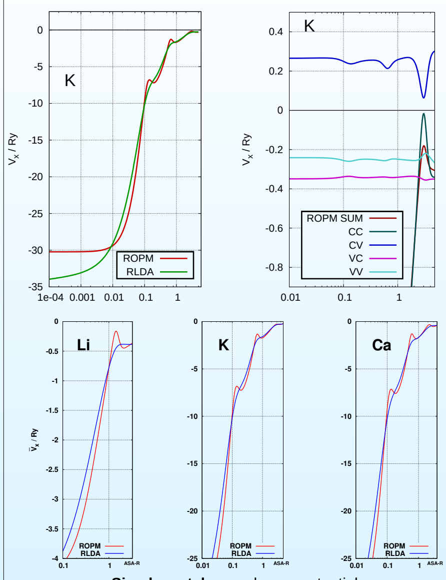
- evaluation on (E, E') mesh, complex contour integration
- real space evaluation of Coulomb-integrals most expensive part of the calculation

Response function:

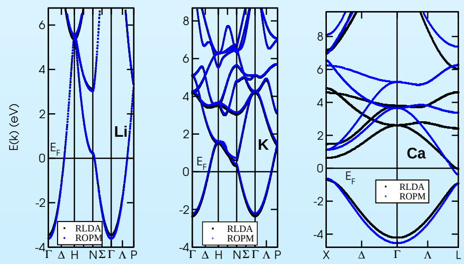
$$\chi_{\mu\nu}(\vec{r},\vec{r}') = \text{Tr}\left[O^{\mu} G(\vec{r},\vec{r}',E) O^{\nu} G(\vec{r}',\vec{r},E)\right]; \qquad \mu,\nu \in \{n,m\}$$

Applications

Relativistic OPM for solids

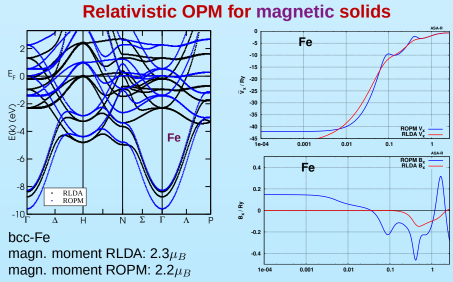


Simple metals – exchange potential



Simple metals – bandstructures

Relativistic OPM for magnetic solids



bcc-Fe
magn. moment RLDA: 2.3μ_B
magn. moment ROPM: 2.2μ_B

Summary & outlook

- relativistic OPM implementation for open-shell atoms PR**B** 77, 045101 (2008)
- relativistic OPM results for solids
- test implementation – various systems and properties
  - semiconductors – check importance of core–valence interactions (compare to Sharma *et al.*, PRL**95**, 136402)
  - all 3d-metals
  - diluted magnetic semiconductors
  - Hyperfine fields
- include correlations using RPA

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