Optimized Effective Potential method for (Non)-collinear Magnets

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Plan of the talk

1. Overview
2. Results for semiconductors and insulators
3. OEP for a general case (insulators, (non)-collinear magnets)
4. Results for magnetic metals
5. Outlook
Hohenberg-Kohn Theorems (1964)

1. External potential $v(r)$ is uniquely determined by $n(r)$
2. The variational principle holds

$$E_0 = E_{v_0}[n_0] < E_{v_0}[n]$$

3. $E_{v_0}[n] = F[n] + \int dr \ v_0(r)n(r)$

$$F[n] = \min_{\Phi \rightarrow n} \langle \Phi | T + V_{ee} | \Phi \rangle$$
Kohn-Sham equations

Auxiliary non-interacting system in an effective potential.

\[ T_s[n] = \min_{\Phi \to n} \langle \Phi | T | \Phi \rangle \]

\[ E_{xc}[n] = F[n] - T_s[n] - U[n] \]

\[ \left[ -\frac{1}{2} \nabla^2 + v_s(r) \right] \phi_i(r) = \epsilon_i \phi_i(r) \]

and

\[ n(r) = \sum_{i}^{\text{occ}} |\phi_i(r)|^2. \]
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Kohn-Sham equations

\[ v_s[n(r)] = v(r) + \int dr' \frac{n(r')}{|r - r'|} + v_{xc}[n(r)] \]

where

\[ v_{xc}[n(r)] = \frac{\delta E_{xc}[n]}{\delta n(r)} . \]

Many sins hidden in \( E_{xc}[n] \)!
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Exchange-correlation functionals

First generation: Local density approximation (LDA)

\[ E^{\text{LDA}}_{xc}[n] = \int d\mathbf{r} \ n(\mathbf{r}) e^{\text{unif}}_{xc}(n(\mathbf{r})) \]

Second generation: Generalised gradient approximations

\[ E^{\text{GGA}}_{xc}[n] = \int d\mathbf{r} \ f(n(\mathbf{r}), \nabla n(\mathbf{r})) \]

\[ E^{\text{Meta-GGA}}_{xc}[n] = \int d\mathbf{r} \ g(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r})) \]
Exchange-correlation functionals

**First generation**: Local density approximation (LDA)

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E_{xc}^{\text{LDA}}[n] = \int dr \, n(r) e_{xc}^{\text{unif}}(n(r))
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E_{xc}^{\text{GGA}}[n] = \int dr \, f(n(r), \nabla n(r))
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E_{xc}^{\text{Meta-GGA}}[n] = \int dr \, g(n(r), \nabla n(r), \tau(r))
\]
Problems and solutions

Problems

1. Band-gap and band positions in semiconductors and insulators are incorrect.
2. Band widths in simple magnetic metals.
4. Non-collinear magnets cannot be treated beyond LSDA.
Problems and solutions

Solutions

1. LDA+$U$ : improves correlations.
2. SIC : corrects for self interaction in Hartree potentials hence doing the job of exchange.
3. LDA+DMFT : quasi particle.
4. GW : quasi particle.
Orbital exchange-correlation functionals

Third generation: Exact exchange (EXX)

Neglect correlation and use the Hartree-Fock exchange energy

\[ E_x[n] = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int d\mathbf{r} \, d\mathbf{r}' \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \]

Optimized Effective Potential

To solve the Kohn-Sham system we require

\[ v_x[n](\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} \]
Third generation: Exact exchange (EXX)

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E_x[n] = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int dr \, dr' \frac{\phi_i^*(r)\phi_j^*(r')\phi_j(r)\phi_i(r')}{|r - r'|}
\]

Optimized Effective Potential
To solve the Kohn-Sham system we require

\[
v_x[n](r) = \frac{\delta E_x[n]}{\delta n(r)}
\]
Using the functional derivative chain rule:

\[
v_x[n](\mathbf{r}) = \sum_i^{\text{occ}} \int d\mathbf{r} \, d\mathbf{r}' \left[ \frac{\delta E_x}{\delta \phi_i(\mathbf{r}'')} \frac{\delta \phi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}') \delta n(\mathbf{r})} + \frac{\delta E_x}{\delta \phi_i^*(\mathbf{r}'')} \frac{\delta \phi_i^*(\mathbf{r}'')}{\delta v_s(\mathbf{r}') \delta n(\mathbf{r})} \right] \frac{\delta v_s(\mathbf{r}')}{\delta n(\mathbf{r})}
\]

\[
= \int d\mathbf{r}' \left[ \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \langle \phi_i | \hat{v}_x^{\text{NL}} | \phi_j \rangle \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j} + \text{c.c.} \frac{\delta v_s(\mathbf{r}')}{\delta n(\mathbf{r})} \right],
\]

where

\[
\langle \phi_{ik} | \hat{v}_x^{\text{NL}} | \phi_{jk} \rangle = \sum_{lk'}^{\text{occ}} w_{k'} \int d\mathbf{r} \, d\mathbf{r}' \frac{\phi_{ik}^*(\mathbf{r}) \phi_{lk'}(\mathbf{r}) \phi_{lk'}^*(\mathbf{r}') \phi_{jk}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.
\]
Using the linear-response operator

$$\chi(r, r') \equiv \frac{\delta n(r)}{\delta v_s(r')}$$

$$= \sum_i \sum_j^{\text{occ unocc}} \frac{\phi_i^*(r) \phi_j(r) \phi_j^*(r') \phi_i(r')}{\epsilon_i - \epsilon_j} + \text{c.c.}$$

we have

$$\frac{\delta v_s(r')}{\delta n(r)} = \tilde{\chi}^{-1}(r, r').$$
Semiconductors and insulators: band-gaps

PP-EXX: Städele et al. PRB 59 10031

PP-EXX: Magyar et al. PRB 69 045111

Optimized Effective Potential method for (Non)-collinear Magnets
The fundamental band-gap for materials:

\[ E_g = A - I = (E_{N+1} - E_N) - (E_N - E_{N-1}) \]

\[ E_g = \frac{\delta E}{\delta n^+} - \frac{\delta E}{\delta n^-} \]

\[ E[n] = T[n] + U_s[n] + E_{xc}[n] \]

\[ E_g = \left( \frac{\delta T}{\delta n^+} - \frac{\delta T}{\delta n^-} \right) + \left( \frac{\delta v_{xc}}{\delta n^+} - \frac{\delta v_{xc}}{\delta n^-} \right) \]

\[ E_g = E_{g}^{KS} + \Delta_{xc} \]
Semiconductors and insulators: band-gaps


<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.74</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.43</td>
</tr>
<tr>
<td>CdS</td>
<td>2.41</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.67</td>
</tr>
</tbody>
</table>

- $E_g$ denotes the bandgap energy of the materials.
- The figure compares different theoretical methods: FP-EXX, PP-EXX, LMTO-ASA-EXX, and FP-LDA.

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Optimized Effective Potential method for (Non)-collinear Magnets
Semiconductors and insulators: d-band positions

![Graph showing d-band positions for various materials with different theoretical methods.](image)

**Figure Caption:**


**Materials and Methods:**

Semiconductors and insulators: d-band positions

- Ge
- GaAs
- InP
- ZnS
- CdS

- EFEX
- PP-EXX
- GW-FPLMTO
- GW-LMTO-ASA
- GW-PP-EXX
- SIRC
- PP-SIC
- FP-EXX-ncv
- FP-LDA

**Summary:**

- Theory and motivation
- Example: Semiconductors and insulators
- OEP for a general case
- Outlook

**References:**


**Authors:**

S. Sharma

**Title:** Optimized Effective Potential method for (Non)-collinear Magnets
Non-collinear magnetism within OEP

$$E[n, m]$$

$$\left. \frac{\delta E}{\delta n(r)} \right|_m = 0; \quad \left. \frac{\delta E}{\delta m(r)} \right|_n = 0$$

$$E[v_s, B_s]$$

$$\left. \frac{\delta E}{\delta v_s(r)} \right|_{B_s} = 0; \quad \left. \frac{\delta E}{\delta B_s(r)} \right|_{v_s} = 0$$
Non-collinear magnetism within OEP

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Non-collinear magnetism within OEP

Iterative solution of following equations

\[ R_v(r) \equiv \left. \frac{\delta E[\rho, m]}{\delta v_s(r)} \right|_{B_s} = \sum_{i}^{\text{occ}} \sum_{j}^{\text{un}} \left( \Lambda_{ij} \frac{\rho_{ij}(r)}{\varepsilon_i - \varepsilon_j} + \text{c.c.} \right) = 0 \quad (1) \]

\[ R_B(r) \equiv \left. \frac{\delta E[\rho, m]}{\delta B_s(r)} \right|_{v_s} = \sum_{i}^{\text{occ}} \sum_{j}^{\text{un}} \left( \Lambda_{ij} \frac{m_{ij}(r)}{\varepsilon_i - \varepsilon_j} + \text{c.c.} \right) = 0, \quad (2) \]

\[ \Lambda_{ij} = \left( V_{ij}^{NL} \right)^* - \int \rho^*_{ij}(r) v_x(r) \, dr - \int m^*_{ij}(r) \cdot B_x(r) \, dr, \]
Non-collinear magnetism in unsupported Cr-monolayer

cond-mat/0510800
Classic collinear magnets

Magnetic moment

<table>
<thead>
<tr>
<th>Metal</th>
<th>Expt</th>
<th>FP-OEP</th>
<th>LMTO-OEP</th>
<th>FP-LDA</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1.59</td>
<td>1.77</td>
<td>2.25</td>
<td>1.61</td>
<td>1.90</td>
</tr>
<tr>
<td>Fe</td>
<td>2.12</td>
<td>2.78</td>
<td>3.40</td>
<td>2.18</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Isostructural phase transition: $\gamma$-\( \alpha \) Ce

**Mott localization:** phase transition is controlled by \( f \)-states and \( spd \)-states are just spectators.

**Kondo volume collapse:** phase transition is controlled by hybridization of \( spd \) and \( f \)-states.
LDA+SIC study

(a) Soztek et al. PRL 72 1244 (94)

(b) $m_{\mu B} \ [\mu B]$

Volume [\text{a.u.}^3]
Isostructural phase transition: $\gamma - \alpha$ Ce: captured by OEP

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Outlook

1. OEP is being generalised to handle spin-spirals
2. Current Density Functional Theory
3. Density Matrix Functional Theory
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Code used: EXCITING

K. Dewhurst, S. Sharma, C. Ambrosch-Draxl and L. Nordström
The code is released under GPL and is freely available at:
http://exciting.sourceforge.net/