Non colinear magnetism

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November 19, 2006

1 Notations and theoretical considerations

* We will denote the spinor by $\Psi^{\alpha\beta}$, α, β being the two spin indexes.

* The magnetic properties are well represented by introducing the spin density matrix: $\rho^{\alpha,\beta}(r) = \sum_n f_n < r|\Psi_n^\alpha >< \Psi_n^\beta|r >$ where the sum runs over all states and f_n is the occupation of state n.

* With $\rho^{\alpha,\beta}(r)$, we can express the scalar density by $\rho(r) = \sum_{\alpha,\alpha} \rho^{\alpha,\alpha}(r)$ and the magnetisation density $\vec{m}(r)$ (in units of $\hbar/2$) whose components are $m_i(r) = \sum_{\alpha,\beta} \rho^{\alpha,\beta}(r)\sigma_i^{\alpha,\beta}$, where the σ_i are the Pauli matrices.

* In general, E_{xc} is a functional of $\rho^{\alpha,\beta}(r)$, or equivalently of $\vec{m}(r)$ and $\rho(r)$. It is therefore denoted as $E_{xc}(n(r), \vec{m}(r))$

* The expression of V_{xc} taking into account the above expression of E_{xc} is:

$$V_{xc}^{\alpha,\beta}(r) = \frac{\delta E_{xc}}{\delta \rho(r)} delta_{\alpha,\beta} + \sum_{i=1}^{3} \frac{\delta E_{xc}}{\delta m_i(r)} \sigma_i^{\alpha,\beta}$$

* In the LDA approximation, due to its rotational invariance, E_{xc} is indeed a functional of $n(r)$ and $|m(r)|$ only. In the GGA approximation, we *assume* that it is a functional of $n(r)$ and $|m(r)|$ and their gradients.(This is not the most general functional of $\vec{m}(r)$ dependent upon first order derivatives, and rotationally invariant.) We therefore use exactly the same functional as in the spin polarized situation, using the local direction of $\vec{m}(r)$ as polarization direction. We the have $\frac{\delta E_{xc}}{\delta m_i(r)} = \frac{\delta E_{xc}}{\delta |m_i(r)|} \widehat{m(r)}$, where $\widehat{m(r)} = \frac{m(r)}{|m(r)|}$. Now, in the LDA-GGA formulations, $n \uparrow + n \downarrow = n$ and $|n \uparrow - n \downarrow| = |m|$ and therefore, if we set $n \uparrow = (n + m)/2$ and $n \downarrow = (n - n \uparrow)$, we have:

$$\frac{\delta E_{xc}}{\delta \rho(r)} = \frac{1}{2}\left(\frac{\delta E_{xc}}{\delta n \uparrow (r)} + \frac{\delta E_{xc}}{\delta n \downarrow (r)}\right)$$

and

$$\frac{\delta E_{xc}}{\delta |m(r)|} = \frac{1}{2}(\frac{\delta E_{xc}}{\delta n\uparrow(r)} - \frac{\delta E_{xc}}{\delta n\downarrow(r)})$$

This makes the connection with the more usual spin polarized case.

* Expression of V_{xc} in LDA-GGA

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}\delta_{\alpha,\beta} + \frac{\delta E_{xc}}{\delta|m(r)|}\widehat{m}(r).\sigma$$

* Implementation

* Computation of $\rho^{\alpha,\beta}(r) = \sum_n f_n < r|\Psi^\alpha >< \Psi^\beta|r >$ One would like to use the routine `mkrho.f` which does precisely this. But this routine transforms only real quantities, whereas $\rho^{\alpha,\beta}(r)$ is hermitian and can have complex elements. The "trick" is to use only the real quantities:

$$\begin{aligned}
\rho^{1,1}(r) &= \sum_n f_n < r|\Psi^1 >< \Psi^1 > \\
\rho^{2,2}(r) &= \sum_n f_n < r|\Psi^2 >< \Psi^2 > \\
\rho(r) + m_x(r) &= \sum_n f_n(\Psi^1 + \Psi^2)^*_n(\Psi^1 + \Psi^2)_n \\
\rho(r) + m_y(r) &= \sum_n f_n(\Psi^1 - i\Psi^2)^*_n(\Psi^1 - i\Psi^2)_n
\end{aligned}$$

and compute $(\rho(r), \vec{m}(r))$ with the help of the aditionnal:

$$\begin{aligned}
\rho(r) &= \rho^{1,1}(r) + \rho^{2,2}(r) \\
m_z(r) &= \rho^{1,1}(r) - \rho^{2,2}(r)
\end{aligned}$$

Note that only the forurier transform are performed in `mkrho.f` the final transformation to $(\rho(r), \vec{m}(r))$ is performed in `symrhg.f`.

* The computation of V_{xc} is performed in `rhohxc.f`. The only transformation to this routine, is to compute $|\vec{m}(r)|$ as input of the usual (i.e spin polarized) `rhohxc.f` and yield back the four component V_{xc}, from the expression of $\frac{\delta E_{xc}}{\delta|m(r)|}$.

* For more information, see: Hobbs et al., PRB, 62, 11556 ; Perdew et al. PRB, 46, 6671 (for the xc functional)