Time dependent density functional spin dynamics and its application for Fe and Ni

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Abstract

The main equations of time dependent density functional spin dynamics are analyzed. Their relation with phenomenological spin dynamics is discussed. The finite temperature calculations in local density approximation are performed for ferromagnetic Fe and Ni. The strong magnetic short range order has been found in Ni. The influence of this dynamical order on observed physical properties of magnets is shortly discussed.

Ab-initio spin dynamics[1–3] recently attracted a lot of attention due to a possibility to describe magnetic properties of real materials at finite temperatures without adjustable parameters. In this short communication we describe the main equations of spin dynamics and analyze their meaning with emphasis on recently discussed in literature issues. We also present the results of the application of this dynamics for the studies of finite temperature properties of 3d ferromagnets.

The evolution of the many-electron system in the presence of the external field is defined in a unique way by the time-dependent one-particle density matrix $\rho_{\alpha\beta}(\mathbf{r},\mathbf{r},t)$, where α,β are spin indices. Equivalently, one can introduce the charge $n(\mathbf{r},t) = Tr\rho(\mathbf{r},\mathbf{r},t) = \sum_\nu f(\varepsilon_\nu) n_\nu(\mathbf{r},t)$ and magnetization $\mathbf{m}(\mathbf{r},t) = Tr\rho(\mathbf{r},\mathbf{r},t)\sigma = \sum_\nu f(\varepsilon_\nu)\mathbf{m}_\nu(\mathbf{r},t)$ densities, where σ are Pauli matrices, $f(\varepsilon)$ is the Fermi function and ν is a one electron state. Below we will assume a sum over repeated indices. Starting from the Schroedinger equation for the many-electron system one can formally obtain the exact set of the equations for these quantities:

$$\dot{\mathbf{m}}(\mathbf{r},t) = \gamma\mathbf{m}(\mathbf{r},t)\times\mathbf{B}_{ext}(\mathbf{r},t)+\frac{i}{2}\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}(\rho_{\alpha\beta}(\mathbf{r},\mathbf{r}',t)\sigma_{\beta\alpha}-c.c.)_{\mathbf{r}'=\mathbf{r}}, \tag{1}$$

$$\dot{n}(\mathbf{r},t) = \frac{i}{2}\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}(\rho_{\alpha\alpha}(\mathbf{r},\mathbf{r}',t) - c.c.)_{\mathbf{r}'=\mathbf{r}} \tag{2}$$

where $\mathbf{B}_{ext}(\mathbf{r},t)$ is the external magnetic field. These equations are not closed since, generally speaking, the quantity $\nabla_{\mathbf{r}'}\rho_{\alpha\beta}(\mathbf{r},\mathbf{r}',t)_{\mathbf{r}'=\mathbf{r}}$ cannot be described directly in terms of $\rho_{\alpha\beta}(\mathbf{r},\mathbf{r},t)$. Introducing the wave functions of Kohn-Sham quasiparticles $\varphi_{\nu\alpha}$ as the solution of one-particle perturbed Schroedinger equation we can obtain a set of equations describing charge and spin dynamics (see Ref.[1–3] and references therein):

$$\dot{\mathbf{m}}(\mathbf{r},t) = \gamma\mathbf{m}(\mathbf{r},t)\times\mathbf{B}_{tot}(\mathbf{r},t)+ \frac{i}{2}\nabla_{\mathbf{r}}(\varphi^*_{\nu\alpha}(\mathbf{r},t)\nabla_{\mathbf{r}}\varphi_{\nu\beta}(\mathbf{r},t)\cdot\sigma_{\beta\alpha} - c.c.), \tag{3}$$

$$\dot{n}(\mathbf{r},t) = \frac{i}{2}\nabla_{\mathbf{r}}(\varphi^*_{\nu\alpha}(\mathbf{r},t)\nabla_{\mathbf{r}}\varphi_{\nu\alpha}(\mathbf{r},t) - c.c.), \tag{4}$$

To make the system complete we have to add the equation for the velocity function

$$\mathbf{v}(\mathbf{r},t) = \frac{\hbar^2}{2mi}\left(\frac{\varphi^*_{\nu\alpha}(\mathbf{r},t)\nabla\varphi_{\nu\alpha}(\mathbf{r},t)}{n_\nu(\mathbf{r},t)} - c.c.\right). \tag{5}$$

Then the closed system of non linear *one electron* equations for the local functions $n_\nu(\mathbf{r},t)$, $\mathbf{m}_\nu(\mathbf{r},t)$ and $\mathbf{v}_\nu(\mathbf{r},t)$ can be presented as (indices of initial and one-electron states are omitted)

$$\frac{\partial n}{\partial t} + \partial_k(v_k n) = 0 \tag{6}$$

$$\frac{\partial v_i}{\partial t}+v_k\partial_k v_i = -\frac{1}{m}\partial_i(V_{Coul}+V_q)+\frac{1}{m}\frac{\mathbf{m}}{n}\cdot\partial_i\mathbf{B}_{tot}-\frac{1}{mn}\partial_k T_{ki} \tag{7}$$

$$\frac{\partial\mathbf{m}}{\partial t} + \partial_k(v_k\mathbf{m}) = \frac{1}{\hbar}(\mathbf{m}\times\mathbf{B}_{tot}) + \frac{\hbar}{2m}\partial_k\frac{1}{n}(\mathbf{m}\times\partial_k\mathbf{m}) \tag{8}$$

where

$$V_q = \frac{\hbar^2}{4m}\left(\frac{1}{2}\left|\frac{\nabla n}{n}\right|^2 - \frac{\triangle n}{n}\right) + V_{exc} \tag{9}$$

is the potential energy,

$$T_{ki} = T_{ik} = \frac{\hbar^2}{4m}n\partial_i\left(\frac{\mathbf{m}}{n}\right)\cdot\partial_k\left(\frac{\mathbf{m}}{n}\right) \tag{10}$$

is the 'magnetic' stress tensor and ∂_k is $\nabla_{k=x,y,z}$. V_{exc} is the non-magnetic part of the exchange correlation potential. These equations are not all independent. We have two constraints (in insulating case) imposed on those variables

$$n^2 = \mathbf{m}\cdot\mathbf{m} \tag{11}$$

$$\nabla\times\mathbf{v} = \frac{\hbar}{2m}\nabla\left(\frac{m_z}{n}\right)\times\frac{m_y\nabla m_x - m_x\nabla m_y}{m_x^2+m_y^2} \tag{12}$$

In addition we have the Poisson equation

$$\triangle V_{Coul} = -4\pi\langle n\rangle \tag{13}$$

and exchange correlation field which in the local spin density approximation (LSDA) is presented as

$$\mathbf{B}_{exc} = B_{exc}\frac{\langle\mathbf{m}\rangle}{|\langle\mathbf{m}\rangle|}. \tag{14}$$

In the equilibrium

$$\mathbf{m}_\nu = \left(0,0,\sigma n^0_\nu\right),\ T_{ik} = 0, \tag{15}$$

$$\nabla\times\mathbf{v}_\nu = 0,\ \mathbf{B}_{tot} = \left(0,0,B^0_{ext}+B^0_{exc}\right). \tag{16}$$

To demonstrate a connection with phenomenological approaches in the magnetism theory one can transform second term in the right part of Eq.8 which represent the kinetic energy contribution to the spin dynamics. It is evident that a part of this contribution has term proportional to $\mathbf{m}_\nu \times \Delta\mathbf{m}_\nu$ which is similar to the generic structure of the torque term in the phenomenological spin dynamics equation for the total magnetization[5]

$$\dot{\mathbf{m}} \sim \mathbf{m}\times\Delta\mathbf{m} = \left(\sum_\nu f(\varepsilon_\nu)\,\mathbf{m}_\nu(\mathbf{r},t)\right)\times\Delta\left(\sum_\mu f(\varepsilon_\mu)\,\mathbf{m}_\mu(\mathbf{r},t)\right) \tag{17}$$

However, in our case

$$\dot{\mathbf{m}} \sim \sum_\nu f(\varepsilon_\nu)\,\mathbf{m}_\nu(\mathbf{r},t)\times\Delta\mathbf{m}_\nu(\mathbf{r},t)\,. \tag{18}$$

Evidently the phenomenological Eq.17 is written in rigid spin approximation and includes many off-diagonal terms of $\mathbf{m}_\nu \times \Delta\mathbf{m}_\mu$ type which are absent in the quantum mechanical Eq.18.

A connection with the relaxation term in the macroscopical equation of motion is more complicated. A first type of non-adiabatic processes comes from the fact that the local magnetization is not an independent dynamic variable. In general, the dynamics of the local electronic velocity and charge densities is expected to influence pure spin dynamics in the itinerant magnets. Another source of non-adiabaticity is related to the summation in Eq(18). This summation over different states (which might have different time dependences) leads to such effects as decoherence, the appearance of the optical modes in systems with one atom per cell and so on. While most of the terms in Eq.8 have one-electron nature, the exchange-correlation term (V_{exc}) can not be presented as such and, in general, takes into account influence of other electrons in the density functional approach. In LSDA the influence of $\mathbf{B}_{exc}$ on the dynamics of the total magnetization is absent [2], however this term must be included when the dynamics of one-electron magnetization is studied.

In the non-local case $\mathbf{B}_{exc}$ contributes to the total magnetization dynamics. Under condition of a weak non-locality one can use a gradient expansion

$$\mathbf{B}_{exc}(\mathbf{r},\mathbf{r}') = \mathbf{B}_{exc}(\mathbf{r},\mathbf{r}) + A\Delta\mathbf{m}(\mathbf{r})\,. \tag{19}$$

These non-local corrections ultimately lead to the familiar torque of $\mathbf{m}\times\Delta\mathbf{m}$ type (similar to Eq.17).This term has functional dependence similar to the kinetic energy term but has a material coefficient and is obtained in the perturbative way. In general, one can expect its smallness in the case of well defined local moment systems. The influence of such gradient terms (non-locality of $\mathbf{B}_{exc}$) on acoustical branches of spin-wave spectra of 3d ferromagnets was recently studied[3]. It appears that in the adiabatic regime the addition of spin angular gradient corrections practically does not change the results obtained in LSDA. These results justify the usage of weakly correlated LSDA in cases when magnons are well defined. Also, it indicates that the kinetic energy term (second in right part of Eq.8) is a *main* source of spin dynamics, while the exchange correlation field practically *static* on this scale of frequencies.

The next source of non-adiabaticity is a time dependence of $\mathbf{B}_{exc}$. In the first order

$$\mathbf{B}_{exc}(t) \simeq \mathbf{B}_{exc}(0) + t\frac{\partial}{\partial t}\mathbf{B}_{exc} = B_{exc}\frac{\mathbf{m}}{|\mathbf{m}|} + C(t)\dot{\mathbf{m}} \tag{20}$$

and such an expansion naturally leads to the appearance of the famous relaxation term of Landau-Lifshitz equation

$$\mathbf{m}\times\mathbf{B}\times\mathbf{m} \sim \dot{\mathbf{m}}\times\mathbf{m} \tag{21}$$

This term is not expected to influence the spin wave spectra but will contribute to the spin wave decay. It can be easily taken into account in frame of *ab-initio* spin dynamics described above.

The structure (21) is written in non-relativistic case when the total magnetic moment of the system is conserved. The account of relativistic effects will ultimately lead to the appearance of the additional terms in Eq.(21).

Recently Eq.3 was also discussed in Ref.[4] and different reasons have been used to eliminate kinetic energy from spin dynamics equations. It was stated also that spin dynamics in real materials exists only due to correlations effects. Consequently, it was concluded that spin dynamics in LSDA is not correct. However, all these conclusions have been obtained without any physical or mathematical analysis of Eq.3 and should be ignored. We demonstrated above that the main contribution to the spin dynamics comes from the kinetic energy which was completely overlooked in Ref.[4].

We applied the technique described above for the temperature dependent spin dynamical simulations of ferromagnetic Fe and Ni in frame of LSDA using linear muffin tin orbital method. 20-30 $\mathbf{k}$-points in the irreducible part of the Brillouine zone in typical calculations with 100-120 atoms per cell have been used. The correct description of possible long range magnetic order especially at low temperatures requires the usage of many atoms in simulation cell. To avoid this numerical difficulty we added spin spiral temperature dependent boundary conditions[6]. Effectively such combined real/reciprocal space spin dynamics allows us to reduce the number of real atoms per cell in simulations (by factor of 30-35 at $T_c/2$ in Ni) and make statistical calculations possible. From a physical point of view the simultaneous inclusion of the real space short range modes (inside supercell) and the long wavelength modes (between supercells) allows us to describe the magnetic excitations developing on different length scales and their interactions on equal footing.

The obtained values of T_c are very reasonable from a point of view of experiment and theory. While in Fe we obtained a nearly perfect agreement with the experiment 1070K (1023K), in Ni the obtained number is about 25% smaller than the experimental value (470 K versus 623

K). We believe that our number in Ni is in compliance with LSDA limitations.

The main result of our calculations is a discovery of a very unusual picture of magnetic short range order (MSRO) at high temperatures in these ferromagnets. The degree of MSRO was analyzed by calculating the spin-spin correlation function $S(\mathbf{r},\mathbf{r}',T) = \langle\langle \mathbf{m}(\mathbf{r})\,\mathbf{m}(\mathbf{r}')\rangle\rangle$.

It was obtained that the average angle between nearest neighbors moments near T_c is 72^0 in bcc Fe, while the corresponding angle in fcc Ni appears to be just 24^0. Such values indicate that in Fe MSRO is relatively small, while in Ni it is enormous. Further study indicated that in Ni at high temperature the dynamical ordering of the distorted spin spiral or domain wall type is realized with a period of about 6 lattice constants. In Fe, however, nearest neighbor spin fluctuations are more relevant (soft modes) at T_c and relatively weak MSRO of superparamagnetism type arises.

The presence of such MSRO at T_c indicates that nearest neighbors interactions in these materials are larger then T_c. However, the exchange parameters in these materials are well known (see, for instance, Ref.[2]) and the corresponding numbers are somewhat lower then T_c. This contradiction can be eliminated using our recent analysis[7]. It has been shown that the usage of the exact adiabatic definition of $J_{ij} \sim (\chi)^{-1}_{ij}$(instead of commonly accepted long wavelength approximation(LWA)) leads to a very different result. First of all, the traditional LWA is suitable for such a 'localized' system as Fe, and the corresponding modification of the nearest neighbor J_{01} is relatively small ($\sim$15%). Ferromagnetic Ni represents a rather itinerant system and any local approach (LWA in particular) might produce a large error. In our case, a large increase in J_{01} for Ni ($\sim$350% of LWA J_{01}) also support strong MSRO and makes the traditional mean field approach meaningless (T_c $\sim$1000K). Correspondingly, LWA can not be used in the itinerant or any other systems with strong MSRO.

The magnetic itineracy strongly affects the short-ranged part of $S(\mathbf{r}-\mathbf{r}',T)$, which, in turn, influences the effective range a fixed amount of itinerant electrons with quantum number l and spin σ propagates at distance L from a point $\mathbf{r}$ during thermal fluctuation time $\tau \sim 1/T_c$

$$L_l^\sigma(\mathbf{r}) \sim v_l^\sigma(\mathbf{r})\,\tau S\left(L_l^\sigma, T_c\right), \tag{22}$$

where $v_l^\sigma(\mathbf{r})$ is the electronic velocity for given state. The quantity L_l^σ characterizes the degree of itineracy of the different electrons in magnets.

The discovered MSRO also lead to a new interpretation of the results for the high temperature susceptibility. The MSRO increase of the effective magnetic moment in Curie Weiss law is directly related to a clustering (like superparamagnetism type in Fe) when the effective moment of a cluster is several times larger then the original atomic moment. The effective moment in terms of atomic moments is much larger in Ni then in Fe in compliance with more extended MSRO and experimental data.

Such strong MSRO also allow us to resolve a very old issue of the importance of quantum corrections for T_c and high-temperature susceptibility calculations. These corrections are traditionally small in the localized systems (4f magnets), but always considered to be significant in the itinerant systems. Discovered in Ni MSRO also strongly suppress quantum corrections in the case of itinerant magnets by increasing the effective moment. We will describe all these effects in details in our extended publications.

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