Report for the spin-related calculation

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ABINIT is a software suite to calculate the optical, mechanical, vibrational, and other observable properties of materials based on the density function theory (DFT). In this report, we present some numerical calculation related the spin property of electrons, i.e. magnetism, antiferromagnetism and spin-orbital coupling. Abundant techniques are used in the spin-dependent calculation, and relatively accurate result is obtained, compared with the experiments.

I. THEORY AND ALGORITHM

In this report, we calculate the magnetic property of Fe with DFT method, as a practice of spin-dependent numerical calculation. In the homogeneous electron gas, the energy of electrons is comprised of kinetic energy \mathcal{E}_k and exchange energy \mathcal{E}_x . Base on the uncertainty relation, the momentum of the electron is proportion to $1/r_s$, therefore, the kinetic energy has the form $\mathcal{E}_k \propto r_s^{-2} \propto n_e^{2/3}$, where r_s is the average distance of electrons, and n_e is the average density of electrons. Meanwhile, from quantum Monte Carlo method, one can show that the exchange energy has the following form $\mathcal{E}_x \propto -r_s^{-1} \propto -n_e^{1/3}$. As a result, the full energy is

$$E = n_e(\mathcal{E}_k + \mathcal{E}_x) = An_e^{5/3} - Bn_e^{4/3}.$$
 (1)

One can observe that the total energy is dependent on the electron density explicitly.

In the discussion above, we do not include the spin freedom into consideration. Here, note that $n_e = n_{\uparrow} + n_{\downarrow}$. Based on the fact that only the electrons with the same spin can have a non-vanishing exchange energy, the total energy can be separated into two parts which represent the different spin orientations, i.e. $E = E_{\uparrow} + E_{\downarrow}$, and $E_{\sigma} = An_{\sigma}^{5/3} - Bn_{\sigma}^{4/3}$. In a non-magnetic system, the population of spin-up electrons is the same as the one of spin-down electrons, i.e. $n_{\uparrow} = n_{\downarrow} = n_e/2$. Hence,

$$E_{non-mag} = 2E\left(\frac{n_e}{2}\right).\tag{2}$$

However, in the magnetic system, there is a population difference between the electrons of different spin orientations. Denote $n_{\uparrow} = n_e/2 + \delta n$ and $n_{\downarrow} = n_e/2 - \delta n$, then,

$$E_{mag} = E\left(\frac{n_e}{2} + \delta n\right) + E\left(\frac{n_e}{2} - \delta n\right) \tag{3}$$

If $E_{non-mag} < E_{mag}$, the system would become non magnetic. Likewise, if $E_{non-mag} > E_{mag}$, which means that the magnetic state is energy preferable, the system would become magnetic with non zero population difference of electron in different spin orientations. One can show the magnetic property is related to the concavity and convexity of the energy function E dependence of average electron density n_e .

Suppose the ground state of such system is magnetic, we have

$$E_{xc}^{homo} = n_{\uparrow} \mathcal{E}_{xc}^{homo}(n_{\uparrow}) + n_{\downarrow} \mathcal{E}_{xc}^{homo}(n_{\downarrow}), \tag{4}$$

while the potetial is defined as

$$V_{xc}^{\sigma} = \frac{\partial E_{xc}^{homo}}{\partial n_{\sigma}} = \mathcal{E}_{xc}^{homo}(n_{\sigma}) + n_{\sigma} \frac{\mathrm{d}\mathcal{E}_{xc}^{homo}}{\mathrm{d}n} \bigg|_{n=n_{\sigma}}.$$
(5)

In the colinear spin configuration, where the spin is along the z direction, $\mathbf{m}(\mathbf{r}) = m(\mathbf{r})\hat{z}$ one can write down the Kohn-Sham Hamiltonian as

$$H_{KS} = -\frac{1}{2}\nabla^2 + V_{ion-e}(\mathbf{r}) + V_H(\mathbf{r}) + \begin{pmatrix} V_{xc}^{\uparrow}(\mathbf{r}, n_{\uparrow}(\mathbf{r})) & 0\\ 0 & V_{xc}^{\downarrow}(\mathbf{r}, n_{\downarrow}(\mathbf{r})) \end{pmatrix}.$$
(6)

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However, for noncolinear spin configuration, the direction of magnetization is dependent on the real space coordinate \mathbf{r} , i.e. $\mathbf{m}(\mathbf{r}) = m(\mathbf{r})\hat{d}(\mathbf{r})$. As a result,

$$H_{KS} = -\frac{1}{2}\nabla^2 + V_{ion-e}(\mathbf{r}) + V_H(\mathbf{r}) + U_d^{\dagger}(\mathbf{r}) \begin{pmatrix} V_{xc}^{\dagger}(\mathbf{r}, n_{\uparrow}(\mathbf{r})) & 0\\ 0 & V_{xc}^{\downarrow}(\mathbf{r}, n_{\downarrow}(\mathbf{r})) \end{pmatrix} U_d(\mathbf{r}).$$
(7)

With the Kohn-Sham Hamiltonian given above, one can conduct the two-component self-consistent DFT calculation.

II. NUMERICAL CALCULATION

We first calculate the magnetism of bcc Fe in a non-magnetic DFT calculation and magnetic DFT calculation. The non-magnetic calculation is the same as the calculation we conducted in the former report, while in the magnetic calculation we specify two new input variables, named **nsppol**, which gives the number of spin polarization, and **spinat**, which gives the initial electronic spin-magnetization for each atom in the unit of $\hbar/2$.

Due to the calculation, we find that the occupation in each bands in different for up and down spins, which indicates that the energy eigenvalues are shifted, due to the alternation of exchange-correlation potential, and therefore of the total effective potential. Note that the exchange-correlation is proportional to the density of spin-up or spin-down electrons independently. The magnetization density is the difference between the up and down densities. The magnetization density, divided by the total density is denoted as zeta, which quantifies the magnetization. In the output file, we find that the zeta varies from points to points, and has minimum and maximum value. The total magnetization integrated in the unit cell is 1.9674 in Bohr magneton, as a difference of spin-up occupation number 4.9867 and spin-down occupation number 3.0163. Moreover, the non-magnetic method shows the system energy as -2.46617 Hartree while the magnetic method shows the system energy as -2.46617 Hartree, which is lower than the result from non-magnetic calculation. This means that the magnetic ground state is energetically favored, as expected since bcc Fe is a ferromagnet.



FIG. 1. Density of state from non-magnetic calculation of bcc Fe. The yellow line is the integrated density of state, while the other three lines are the density of state with different smooth parameters.

The density of state from the non-magnetic and magnetic calculation is plotted in Fig.1 and Fig.2. We observe that the spin up and down DOS have been shifted with respect to each other. The integrated density of states yields the number of electrons for each spin direction, and we see the magnetization which arises from the fact that there are more up than down electrons at the Fermi level, which is -0.26471 Hartree in the magnetic calculation.

Then, we take fcc Fe, which is in an antiferromagnetic order, as our second example. Here, we conduct an antiferromagnetic calculation by selecting the input variable **nsppol** as 1, and **nspden** as 2. Like the former magnetic calculation, we set the **spinat** following the requirement of antiferromagnetism. In the calculation, there are two Fe atoms in one unit cell with the opposite spin orientations.



FIG. 2. Density of state from magnetic calculation of bcc Fe. The yellow line is the integrated density of state, while the other three lines are the density of state with different smooth parameters.

The computation result reveals that the magnetization of each atoms is 0.33696 and -0.33693, respectively. Furthermore, if we use the cut3d tool, which performs an integration of the magnetization in a cube of size acell/2 around each atom. Note that the overall magnetization for antiferromagnetism is zero, and we cannot analysis the density of state for spin up or down electrons to directly observe the magnetic order of the antiferromagnetic system, as shown in Fig.3.

Instead of treating fcc Fe directly as an antiferromagnetic material, we can start the calculation without any hypothesis on its magnetic structure. In this case, we will not predesignate the initial spins of the atoms. In this calculation, we use the angular momentum projected densities of state. In such calculation, we specify **natsph**, **iatsph** and **ratsph**.



FIG. 3. Density of state from antiferromagnetic calculation of fcc Fe. The yellow line is the integrated density of state, while the other three lines are the density of state with different smooth parameters.

After the calculation, we can see the density of state which is labeled with the angular momentum. In the output file, we find that the energy of the system is -4.9249 Hartree, which matches the result from the antiferromagnetic calculation. Additionally, we see the face-centered atom and the cornered atom have the opposite magnetization. The difference of up and down density is 0.395989 and its opposite.

As the last experiment in this report, we conduct a calculation where the spin-orbital coupling is taken into the consideration. With a new pseudopotential, which has already contained the spin-orbital coupling, i.e. HGH pseudopotential with semicore states. In such calculation, we can recover the splitting of the atomic level. In the program, we consider 26 bands in the tantalum, and the energy of each bands are shown in the following block.

Information	of	band	structure	calcula	tion
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Eigenvalues (hartree) for nkpt= 1 k points:								
kpt# 1, n	band = 26, w	tk= 1.0000	0, kpt = 0.	0000 0.000	0			
0.0000 (red	uced coord)							
-2.43258	-2.43258	-1.67294	-1.67294	-1.35468	-1.35468			
-1.35468	-1.35468	-0.16788	-0.16788	-0.11629	-0.11629			
-0.11629	-0.11629	-0.09221	-0.09221	-0.09120	-0.09120			
-0.09120	-0.09120	-0.00959	-0.00959	0.01473	0.01473			
0.01473	0.01473							

One can show that the first two bands are s-orbital, while the latter six bands are the splitting p-orbital. The following two bands are s-orbital again, while the latter ten bands are from d-orbital. There are splittings in both p-orbital and d-orbital, due to the finite size of the simulation box, and in particular the cubic shape, which gives a small crystal field splitting of the d-orbitals between e_g and t_{2g} states. We can calculate the splitting of the level based on the former data, and find it is in a good agreement with the NIST data.

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