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Electronic Structure of Transition Metals Fe, Ni and Cu in the *GW* Approximation

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The quasiparticle band structures of 3*d* transition metals, ferromagnetic Fe, Ni and paramagnetic Cu, are calculated by the *GW* approximation. The width of occupied 3*d* valence band, which is overestimated in the LSDA, is in good agreement with experimental observation. However the exchange splitting and satellite in spectra are not reproduced and it is required to go beyond the *GW* approximation. The effects of static screening and dynamical correlation are discussed in detail in comparison with the results of the static COHSEX approximation. The dynamical screening effects are important for band width narrowing.

KEYWORDS: density functional theory, GW approximation, LMTO, product-basis, transition metal, dynamical screening
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1. Introduction

Lattice structure, lattice constants and bulk moduli in 3*d* transition metal are well described by the local-spin-density approximation (LSDA)[1,2] or the generalized gradient approximation (GGA).[3,4] However, the occupied 3*d* band width is too broad, and the exchange splitting is overestimated. The good agreement is essentially related with the property of the ground-state, and the discrepancies are associated with excitation properties.

The *GW* approximation (GWA) is based on the many-body perturbation theory[5–7] and can describe the quasiparticle property. The self-energy of GWA is the first term in a series expansion of dynamical correlation and it is treated by the random-phase approximation (RPA).

The plane wave basis set based on the pseudopotential method is used in many *GW* calculations. In simple metals and semiconductors, the single plasmon peak is often assumed within the plane wave framework (the plasmon pole approximation).[8] However the plasmon peak of transition metal cannot be well-defined isolated peak due to interband transition in the same energy region. The transition metal has strong atomic potential for 3*d* electrons, the 3*d* orbital is localized and the plane wave formalism cannot be applied. Moreover it is essentially important to include core electrons in many cases. Therefore the plasmon peak approximation is not applicable to the dielectric function of transition metals and all-electron calculation and localized orbital basis set are needed.

In this paper, the *GW* method based on the linear muffin-tin orbital (LMTO) method[9] and the product-basis method[10] are applied to the series of transition metal. There is a numerical difficulty in the $\boldsymbol{k}$-point summation of self-energy with the momentum transfer $\boldsymbol{q} \cong 0$. This summation is treated by the offset method,[11] and test calculation of the exchange energy in the electron gas is performed. The paper is organized as follows. The theoretical framework is described in §2. The numerical technique and test calculation of electron gas are also given in this section. The results for these systems and detailed discussion are presented in §3. Finally, in §4 we present our summary.

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2. Theory

2.1 GW approximation

In the GWA the self-energy is replaced by the lowest order term of the expansion as $\Sigma(1,2) = \mathrm{i}G(1,2)W(1,2)$. G is the one particle Green function and the dynamically screened interaction W is defined by

$$W(1,2) = \int \mathrm{d}(3)\epsilon^{-1}(1,3)v(3,2) \tag{1}$$

$$= v(1,2) + \int \mathrm{d}(34)v(1,3)\chi^0(3,4)W(4,2), \tag{2}$$

where ϵ^{-1} is the inverse dynamical dielectric function, v is the bare Coulomb potential and χ^0 is the irreducible polarization function $\chi^0(1,2) = -\mathrm{i}G(1,2)G(2,1)$. Here we use an abbreviated notation $(1) = (\boldsymbol{r}_1, \sigma_1, t_1)$ and $v(1,2) = v(\boldsymbol{r}_1, \boldsymbol{r}_2)\delta(t_1 - t_2)$. Equation (2) is treated by the RPA.

We adopt the LSDA Hamiltonian to be the unperturbed one $H^0 = T + V^{\mathrm{H}} + V^{\mathrm{xc}}_{\mathrm{LSDA}}$. Here T is the kinetic energy, V^{H} is the Hartree potential, and $V^{\mathrm{xc}}_{\mathrm{LSDA}}$ is the exchange–correlation potential in the LSDA. We presume the wavefunctions $\{\psi_{\boldsymbol{k}n}(\boldsymbol{r})\}$ of the LSDA to be a reasonably good starting wavefunctions. Then the self-energy can be written by three terms as $\Delta\Sigma = \Sigma^{\mathrm{x}} + \Sigma^{\mathrm{c}} - V^{\mathrm{xc}}_{\mathrm{LSDA}}$, where Σ^{x} $(= \mathrm{i}Gv)$ is the exchange part (the Fock term) and Σ^{c} $(= \mathrm{i}GW^c)$ is the dynamical correlation part. W^c is the second term in eq. (2). The quasiparticle energy is given as

$$E_{\boldsymbol{k}n} = \epsilon_{\boldsymbol{k}n} + Z_{\boldsymbol{k}n}\Delta\Sigma_{\boldsymbol{k}n}(\epsilon_{\boldsymbol{k}n}), \tag{3}$$

where $\epsilon_{\boldsymbol{k}n}$ is the LSDA eigenvalue. The self-energy is $\Delta\Sigma_{\boldsymbol{k}n}(\epsilon_{\boldsymbol{k}n}) = \langle\psi_{\boldsymbol{k}n}|\Sigma^{\mathrm{x}} + \Sigma^{\mathrm{c}}(\epsilon_{\boldsymbol{k}n}) - V^{\mathrm{xc}}_{\mathrm{LSDA}}|\psi_{\boldsymbol{k}n}\rangle$ and the renormalization factor is $Z_{\boldsymbol{k}n} = (1 - \partial\Delta\Sigma_{\boldsymbol{k}n}(\epsilon_{\boldsymbol{k}n})/\partial\omega)^{-1}$. The renormalization factor $Z_{\boldsymbol{k}n}$ is a measure of the occupation number and should equal to the discontinuity of occupation number at the Fermi energy. Therefore it should satisfy the condition $Z_{\boldsymbol{k}n} \leq 1$. In the present work we perform one iteration calculation without self-consistency.[12]

2.2 LMTO minimal basis set and product-basis

Because the plane wave basis becomes very costly for systems containing 3*d* electrons, the LMTO method[9] is more appropriate. We use the LMTO basis set $\chi_{\boldsymbol{R}L\nu}(\boldsymbol{r})$ within the atomic sphere approximation (ASA) for the LSDA

calculation. Here L is angler momentum $L = (l, m)$. The LMTO can be expanded by the muffin-tin orbital $\phi_{RL\nu}(\boldsymbol{r})$ and it's energy derivative $\dot{\phi}_{RL\nu}(\boldsymbol{r})$.

The functional space of basis for Σ is spanned as

$$\{\Sigma\} = \{\psi\psi\} = \{\chi\chi\} = \{\phi\phi\} + \{\phi\dot{\phi}\} + \{\dot{\phi}\dot{\phi}\}. \quad (4)$$

In fact the mixing coefficients of $\dot{\phi}$ to ϕ are less than 0.1 for the most part and the norm of $\dot{\phi}$, $\langle\dot{\phi}\dot{\phi}\rangle$, is 0.1–0.3 even in the largest case, so the terms including $\dot{\phi}$ can be dropped out. More detailed description is shown in ref. 13.

2.3 Numerical technique

The Coulomb matrix $v(\boldsymbol{q})$ has a singularity at $\boldsymbol{q} = 0$ as $F(\boldsymbol{q}) = 1/|\boldsymbol{q}|^2$. The integration of $v(\boldsymbol{q})$ over the Brillouin zone does not diverge but special cares are needed not only for the $\boldsymbol{q} = 0$ term but for small finite $\boldsymbol{q}$. For a choice of the discrete points near $\boldsymbol{q} = 0$, we use the offset Γ-point method,[11] where the integration of $F(\boldsymbol{q})$ over the Brillouin zone can be performed analytically and the offsetted points $\boldsymbol{Q}$'s are chosen near $\boldsymbol{q} = 0$ so as to satisfy a relation

$$\int_{\text{B.Z.}} F(\boldsymbol{q})\mathrm{d}\boldsymbol{q} = \sum_{\boldsymbol{Q}} F(\boldsymbol{Q}) + \sum_{\boldsymbol{k}\neq 0} F(\boldsymbol{k}). \quad (5)$$

Here $\boldsymbol{k}$'s are the discrete mesh points in the Brillouin zone.

The exchange energy of the electron gas system is given as a function of a wave vector k as $\Sigma^{\text{x}}(k) = \frac{e^2 k_{\text{F}}}{\pi} S(y)$, where $S(y) = -(1 + \frac{1-y^2}{2y} \ln|\frac{1+y}{1-y}|)$, $y = \frac{k}{k_{\text{F}}}$ and k_{F} is the Fermi wave vector. The empty lattice calculation is done with $spdf$ orbitals in the LMTO method. We calculate the exchange energy of the electron gas in a fcc lattice with a lattice constant $a = 6.824a_0$ which corresponds to the fcc copper and a_0 is the Bohr radius. The corresponding electron gas parameter is $r_s = 2.6668$. The calculated $S(y)$, by the simple summation, by the offset method and by the exact $S(y)$, are shown in Fig. 1. In the simple summation, the diverging term $1/|\boldsymbol{q}|^2$ is simply averaged inside a sphere of a volume equal to that of one $\boldsymbol{k}$-mesh point. The number of $\boldsymbol{k}$-mesh of the Brillouin-zone in the calculation is (a) 64 points ($4 \times 4 \times 4$) and (b) 512 points ($8 \times 8 \times 8$). In case of 512 points of these structure, eight offsetted points $\boldsymbol{Q}$ are $\frac{2\pi}{a}(\pm 0.038, \pm 0.038, \pm 0.038)$. The derivative of $S(y)$ has a logarithmic singularity at the Fermi energy ($y = 1$). Unphysical gap still remains at the Fermi energy in the simple summation of these examples. A large number of $\boldsymbol{k}$ points is necessary for a convergence in the simple summation. But the offset method can reduce the number of $\boldsymbol{k}$ points for rapid convergence even in case of small number of mesh points. The careful treatment of the Coulomb matrix at or near $\boldsymbol{q} = 0$ is very crucial near the band gap or the Fermi energy.

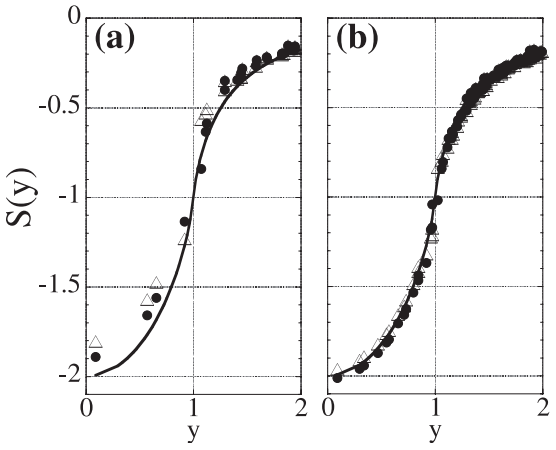

Fig. 1. Exchange energy $S(y)$ of the electron gas as a function of $y = k/k_{\text{F}}$. The solid lines for the exact result, the open triangles for the simple summation and the closed circles for the offset method. The numbers of the mesh points in the Brillouin zone are (a) $64 = (4 \times 4 \times 4)$ and (b) $512 = (8 \times 8 \times 8)$.

3. Results and Discussions

In the calculation of LSDA, the lattice structure and constants of Fe, Ni and Cu are bcc and $a = 2.87$ Å, fcc and 3.52 Å, fcc and 3.61 Å, respectively.[14] The band structures of Fe, Ni and Cu, calculated both in the LSDA and the GWA, are shown in Fig. 2 along high symmetric lines. The localized $3d$ orbital has a weak hybridization with the extended $4s$, $4p$ orbitals and is below Fermi energy.

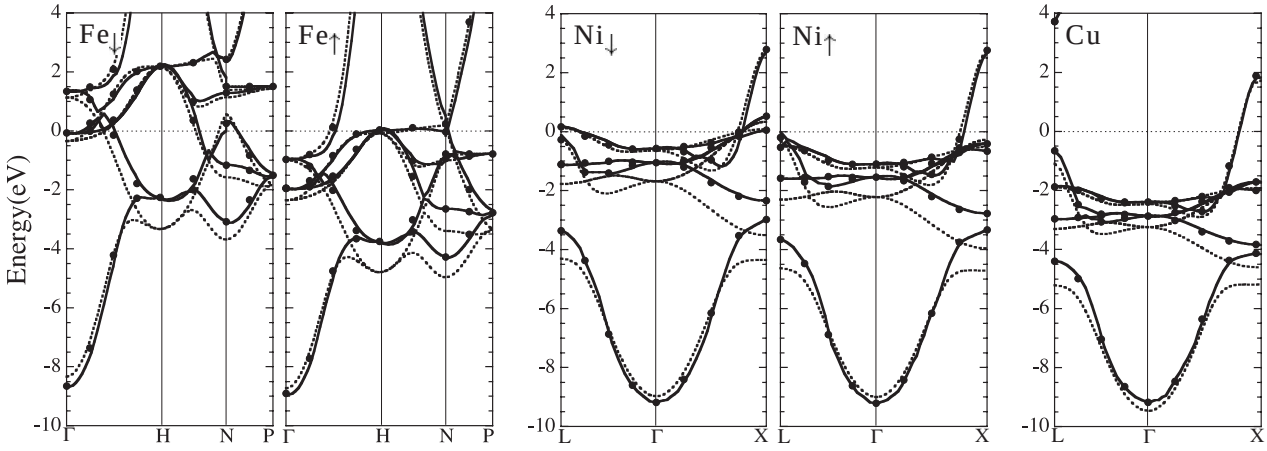

Fig. 2. The energy bands of Fe, Ni and Cu, calculated by the LSDA (dotted lines) and the GWA (solid lines) along high symmetric lines. The closed circles are the calculated points in the GWA. In Fe and Ni, left side and right side show minority spin and majority spin, respectively. The high symmetric points are $\Gamma = (0, 0, 0)$, $\text{H} = (1, 0, 0)$, $\text{N} = (1/2, 1/2, 0)$ and $\text{P} = (1/2, 1/2, 1/2)$ in bcc lattice (Fe), and $\text{L} = (1/2, 1/2, 1/2)$, $\Gamma = (0, 0, 0)$ and $\text{X} = (1, 0, 0)$ in fcc lattice (Ni and Cu). Fermi energy is set to zero. ($E_{\text{F}} = 0$)

The magnetic moment, the exchange splitting and the band width of the occupied 3*d* valence bands in the GWA are summarized in Table I, in comparison with those by the LSDA and the static COHSEX approximation.[6] Our results of Ni are in good agreement with those of the previous *GW* calculation.[15] The spectral function $A(\omega) = -(1/\pi)\,\mathrm{Im\,Tr}\,G(\omega)$ is shown in Fig. 3.

Table I. The Magnetic moment μ_{spin} (μ_{B}) of Fe and Ni, the exchange splitting δE_{ex} (eV) of Fe and Ni, the band width of the occupied 3*d* valence bands $W_{d,\mathrm{occ}}$ (eV) of Fe, Ni and Cu.

			LSDA	COHSEX	GW	Expt.
μ_{spin}	Fe		2.27	2.04	2.31	2.13[16,17]
	Ni		0.54	0.62	0.55	0.57[16,17]
δE_{ex}	Fe	Γ_{25}	2.0	1.7	1.9	2.1[18]
		H_{25}	2.3	2.1	1.8	1.8[19]
		P_4	2.2	2.5	2.3	1.5[20]
	Ni	L_3	0.6	0.5	0.7	0.3[20]
		X_2	0.6	0.5	0.7	0.2[21]
$W_{d,\mathrm{occ}}$	Fe		3.7	4.6	3.4	3.3[22–24]
	Ni		4.5	5.1	3.3	3.2[25]
	Cu		3.3	3.7	2.9	3.0[26]

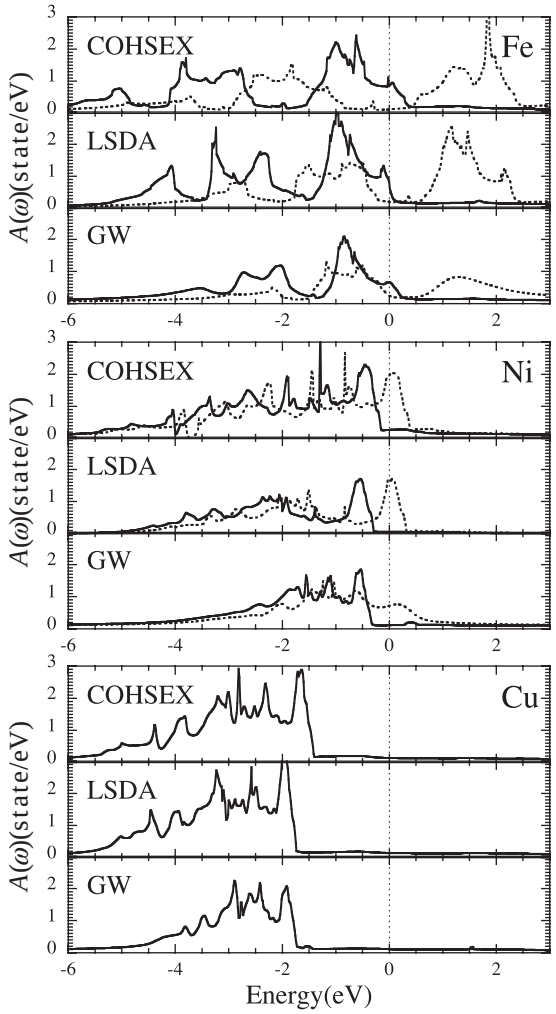

Fig. 3. The spectral function $A(\omega)$ in the transition metals Fe, Ni and Cu by the GWA (bottom), the LSDA (middle) and the static COHSEX approximation (top). In Fe and Ni, the solid lines show majority spin and the dotted lines show minority spin, respectively.

The occupied 3*d* valence band width of transition metals Fe, Ni and Cu in the LSDA is overestimated in comparison with experimental observation, especially in Ni. The valence band width is in reasonably agreement with experiment in the GWA. In Fig. 3, the band narrowing occurs in the occupied valence band of both the majority and the minority spin in Fe and Ni. But the width of unoccupied 3*d* band of Fe is unchanged in the GWA. The source of band narrowing is the screening for the valence electrons. In the spectral function of the GWA, the plasmon-like excitation appears around 30 eV above and below the Fermi energy and also the long tail extends over wide lower energy region. The intensity of spectrum is totally suppressed by the excitations in wide energy region. The intensity of the *GW* spectrum is actually reduced by a factor of Z_{kn} and, in Fig. 3, the reduction factor is $Z_d \approx 0.5$–0.6. In the Hartree Fock (HF) approximation which includes no screening effects, the band width is overestimated. No screening in the HF gives zero density of states at the Fermi level in the electron gas and also gives overestimated band gap in insulators and semiconductors. In the static COHSEX approximation, which includes static screening, the band width is much smaller than the HF results, and is almost the same as the one in the LSDA or still wider. Moreover the 4*s* state is located too much deep because it exists far from Fermi level. The band width in the GWA is in good agreement with experiment. We can see that the dynamical correlation effect is important for the band width in the transition metals from the comparison between the GWA and the static COHSEX approximation.

The magnetic moment μ_{spin} of Fe and Ni is almost the same as the result of LSDA and is in good agreement with experiment. The difference of the exchange splitting δE_{ex} between the LSDA and experiments in Fe ($\sim$30%) is smaller than that in Ni ($\sim$50%). δE_{ex} of Fe becomes close to the experimental value in the GWA. In Ni, the discrepancy of δE_{ex} is not improved by the GWA. In the HF, δE_{ex} is overestimated. The screening effects of correlation term Σ^{c} in the GWA or the static COHSEX approximation reduce δE_{ex} of HF. However the GWA only includes long-range correlation effects, and cannot describe short-range effects such as electron-electron or hole–hole scattering process. Higher order diagrams (*e.g.* vertex corrections) is needed for electron-electron and hole–hole scattering. Especially two-hole bound states are very important to the exchange splitting and the satellite structure of spectrum if on-site Coulomb interaction between *d* electrons is large.[27,28] The effective Coulomb interaction is obtained from an analysis of Auger spectra, Ni is $U \approx 4.0$ eV and Fe is $U \approx 1.0$ eV.[29] The discrepancy between experiments and the GWA in Ni is caused by the short-range correlation effects from large *U*. The clear satellite in Ni can be also explained, and the GWA cannot reproduce it. Since the 3*d* band is full in Cu, there is no hole–hole correlation and the GWA can work quite well.

The renormalization factor of transition metal 3*d* states is $Z = 0.52$–0.58 in Fe, $Z = 0.48$–0.53 in Ni and $Z = 0.53$–0.66 in Cu. Z of 4*s* states is about 0.7–0.8 in these systems. Those results of the renormalization factor show that the interaction between 3*d* electrons is large, and the correlation in Ni is strongest, which is consistent with the

large Coulomb interaction U.

The static screened d–d Coulomb interaction $\langle\phi_d\phi_d|W(\omega=0)|\phi_d\phi_d\rangle$ is calculated to be about 1.4 eV, 1.2 eV and 3.9 eV in Fe, Ni and Cu, respectively. The bare Coulomb interaction $\langle\phi_d\phi_d|v|\phi_d\phi_d\rangle$ is actually 23.7 eV, 25.9 eV, and 27.4 eV in Fe, Ni and Cu. This values become larger with increasing the number of $3d$ occupation. Then the correlation term $\langle\phi_d\phi_d|W^c(\omega=0)|\phi_d\phi_d\rangle$ is -22.3 eV, -24.7 eV and -23.5 eV in Fe, Ni and Cu. Therefore, the correlation effects and the static screening are quite important in transition metals. The screened correlation of Ni is largest and this is consistent with the smallest Z in these systems. We should mention that the d–d Coulomb interaction $\langle\phi_d\phi_d|W(0)|\phi_d\phi_d\rangle$ is different from the Hubbard U evaluated from the constrained LSDA, which includes only screening by on-site d electrons. The term $\langle\phi_d\phi_d|W(0)|\phi_d\phi_d\rangle$ includes the screening effects by both on-site and off-site electrons.[30)]

In the transition metals, the Hubbard U parameter is overestimated within the constrained LSDA, for example $U \approx 6$ eV for Fe, due to incomplete metallic screening in the LSDA.[31)] We should mention that our value of Ni with offset method is smaller than the previous estimate ($\langle\phi_d\phi_d|W(0)|\phi_d\phi_d\rangle = 2.2$ eV).[30)] The discrepancy may be caused by the absence of the present offset method since we also obtained the value without the offset method similarly to be previous one.

4. Summary

In this paper the GW approximation is applied to ferromagnetic transition metals Fe and Ni, and paramagnetic Cu. We showed that the occupied $3d$ band width of transition metal is improved within our GW calculation.

We also investigated the effects of dynamical screening by comparison between the GWA and the static COHSEX approximation and showed the crucial role of the dynamical correlation for band width.

The self-energy is discussed systematically. The renormalization factor Z showed that the interaction between d-electrons in Ni is larger than that in Fe, and this is consistent with the interaction strength from Auger spectra.

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