

***Ab initio* calculation of the 3s and 1s core-level x-ray photoemission spectra of iron**Manabu Takahashi,¹ Jun-ichi Igarashi,² and Noriaki Hamada³¹*Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan*²*Faculty of Science, Ibaraki University, Mito, Ibaraki 310-8512, Japan*³*Faculty of Science and Technology, Tokyo University of Science, Chiba 278-8510, Japan*

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We develop a method of the *ab initio* calculation for the core-level x-ray photoemission spectroscopy (XPS). By calculating one-electron states in the presence of core-hole potential, excited states are constructed by distributing electrons on these one-electron states. The overlap integrals between the excited states and the ground state are evaluated by using the wave functions with and without the core-hole potential, and finally the XPS spectra are obtained. Implementing the procedure, we obtain the spin-resolved 3s-core XPS spectra in ferromagnetic iron without any adjustable parameters, in good agreement with the experiment. The spectral shapes are quite different for different spin channels. We explain the behavior in terms of the difference in the one-electron states screening the core-hole potential.

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I. INTRODUCTION

Electronic structure calculations based on the density-functional theory with the local approximation have provided valuable information on the ground-state properties.¹ Various attempts beyond the local-density approximation (LDA) have also been worked out. These approaches have had great success in predicting accurate electronic structures without introducing any adjustable parameters.² However, the LDA and its extensions have not been suited to treat highly excited states, and are usually limited to calculate the ground-state properties. For example, although the x-ray photoemission spectroscopy (XPS) from inner-core states is a powerful method to investigate the dynamical response to the local perturbation associated with the photoexcited core hole,³ the corresponding spectra have not been calculated from first principles.

The purpose of this paper is to develop a method of the *ab initio* calculation for the inner-core-level XPS spectra. It is known that the spectra show asymmetric shape as a function of binding energy near the threshold in metals.⁴ This phenomenon is related to the singularity in the response function near the Fermi edge.⁵⁻⁷ The spectra sometimes show extra peaks called satellites in systems of strongly correlated electrons. One example is in systems of rare-earth-metal compounds, where the main and satellite peaks are explained as “well-screened” and “poorly screened” states, respectively.^{8,9} Another notable example is a satellite around 6 eV separate from the threshold on the 2p-XPS in a ferromagnetic metal Ni.¹⁰ It arises from a combined effect of screening the core-hole potential and the interaction between electrons. Feldkamp and Davis (FD) (Ref. 11) analyzed the 2p-XPS spectra in Ni by developing a numerical method on the Hubbard model. Evaluating the overlap between the excited states and the ground state, they obtained the spectra in good agreement with the experiment.

The method we develop in this paper is as an extension of the FD theory to an *ab initio* level. First, we carry out the band calculation within the LDA to obtain the one-electron states in the ground state. We use the augmented plane-wave

(APW) method instead of the Korringa-Kohn-Rostoker (KKR) method, since we need the wave functions later. Next, we consider a system of supercells with one core hole per cell. The core hole is introduced by removing an electron from the core level, whose wave function is assumed to be localized. In this system, we carry out the band calculation to obtain the one-electron states. To guarantee the charge neutrality, we add one extra electron in each supercell. To be exact, there should exist only one core hole in crystal for the XPS event. In this situation, as known in the impurity problem, the local charge neutrality is naturally satisfied according to the Friedel sum rule.¹² The supercell method works better as the cell size increases. Note that not only the effect of core-hole potential but also that of electron-electron interactions are taken into account in the one-electron states thus obtained through the exchange-correlation potential. Discretizing the momentum space into finite number of points, we distribute electrons into the one-electron states to construct the excited states. The lowest-energy state with core hole is given by piling electrons into all one-electron levels up to the Fermi level. One electron-hole pair, two electron-hole pairs, and so on, are created from this core-hole state. Finally, we calculate the XPS spectra by evaluating the overlaps between these excited states and the ground states with the help of the one-electron wave functions.

We substantiate this scenario by applying the procedure to the 3s-core XPS in the ferromagnetic Fe metal.¹³⁻¹⁹ The spectra are resolved with respect to the spin of photoelectron or equivalently the spin of core hole. Hereafter we call the majority and minority spin as the up and down spin, respectively. The core hole with up (down) spin indicates that one core electron with up (down) spin is missing. The spectra show a strong dependence on the spin;¹⁶ for the core hole with up spin, the spectral intensity is distributed in a wide region of binding energy with a clear satellite peak; for the core hole with down spin, the spectra have a slightly asymmetric peak with no satellite peak. These features indicate that the screening effect on the core hole with up spin is quite different from that with down spin. So far, such spectra have been analyzed using a single band Hubbard model,²⁰ but it is too simple to compare quantitatively the experimental data.¹⁶

We demonstrate that the present scheme works well by comparing the calculated spectra with the experimental data.

Since the core hole has spin degrees of freedom, the exchange effect plays an important role, which is different from the impurity potential problem in dilute alloys.^{21,22} We could explain the strong spin dependence of the spectra in relation to $3d$ bands changed by the core hole. For the core hole with up spin, the $3d$ electrons with down spin are strongly attracted by the core-hole potential, resulting in an overscreening, while the $3d$ electrons with up spin are influenced little by the core-hole potential because of the exchange effect, resulting in an antiscreening due to the repulsion between $3d$ electrons. The local spin moment is reversed at the core-hole site. On the other hand, for the core hole with down spin, the $3d$ electrons with up spin are strongly attracted by the core-hole potential, but the unoccupied $3d$ states available to the screening are limited, resulting in an incomplete screening. The shortage of the screening is compensated by the $3d$ electrons with down spin. The spin-dependent XPS spectra are interpreted in terms of these changes in the $3d$ one-electron states.

Note that the $3s$ satellite is conventionally interpreted as a multiplet splitting between the $3s$ and $3d$ electrons on the basis of the atomic model.¹⁵ However, the electronic structure given in this paper is quite different from what the atomic model predicts. The number of $3d$ electrons is increased by nearly one at the core-hole site in accordance with Friedel sum rule, and the one-electron states are strongly modified from the ground state, and even quasibound states appear.

Furthermore, we calculate the $1s$ -core XPS spectra to clarify the situation by comparison with the $3s$ -core spectra. Since the $1s$ wave function is so localized the exchange effect on the $3d$ one-electron states is expected to be relatively small. This is actually the case, and we obtain the XPS spectra, which are less dependent on the spin.

The present paper is organized as follows. In Sec. II, we formulate the XPS spectra with the *ab initio* method. In Sec. III, we present the calculated XPS spectra for Fe $3s$ - and $1s$ -core in comparison with the experiment. Section IV is devoted to the concluding remarks.

II. FORMULATION

A. XPS spectra

We consider the situation that a core electron is excited to a high energy state with energy ϵ by absorbing the x ray with energy ω_q . Then the probability of finding a photoelectron with energy ϵ may be proportional to

$$I_{\sigma}^{\text{XPS}}(\omega_q - \epsilon) = 2\pi |w|^2 \sum_f |\langle f | s_{\sigma} | g \rangle|^2 \delta(\omega_q + E_g - \epsilon - E_f), \quad (1)$$

where w represents the transition matrix element from the core state localized at a particular site to the state of photoelectron. The s_{σ} is the annihilation operator of a relevant core electron, which is assumed to have only spin σ as the internal degrees of freedom. State $|g\rangle$ represents the ground state

with energy E_g , while $|f\rangle$ represents the final state with energy E_f . For the definition of $|f\rangle$, the photoelectron is excluded. In the actual calculation, we replace the δ -function by the Lorentzian function with the full width at half maximum (FWHM) $2\Gamma_s$ to take account of the lifetime broadening of the core level. It should be noted here that we can specify the spin of core hole by resolving the spin of photoelectron. Since the core-hole potential induces the screening in the final state, the electronic structure would become different from the ground state. Therefore, the spectra would be spin dependent in the magnetic system, due to the exchange interaction.

B. Overlap integrals

The KKR method could solve a single core-hole problem in the final state. Actually it is successfully applied to alloy problems combined with the coherent-potential approximation (CPA).^{23,24} However, it may not be useful in the present problem, because we need the information of wave functions. Instead, we consider a periodic array of supercells containing one core hole per cell, and calculate the one-electron states by means of the APW method. The larger the unit cell size is, the better results are expected to come out. Inner-core states, for example $1s$, $2s$, $2p$, and $3s$ in Fe, are treated as localized states within a muffin-tin sphere, so that we could directly specify the core-hole site. To ensure the charge neutrality, we assume $n_e + 1$ band electrons per unit cell instead of n_e band electrons in the ground state. One additional electron per unit cell would not cause large errors in evaluating one-electron states in the limit of large unit cell size. We write the resulting single particle states with energy eigenvalue $\epsilon_n(\mathbf{k})$ as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_c}} \sum_j \phi_{n\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) \exp(i\mathbf{k}\mathbf{R}_j), \quad (2)$$

with

$$\phi_{n\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}(\mathbf{r} - \mathbf{R}_j)}, \quad (3)$$

where $u_{n\mathbf{k}}(\mathbf{r} - \mathbf{R}_j)$ is a periodic function with changing unit cells, and j runs over N_c unit cells. We use these one-electron states as substitutes for the states under a single core hole. We distribute N_e ($\equiv n_e N_c$) band electrons on these states to construct excited states. In addition, we carry out the band calculation in the absence of the core hole by assuming n_e band electrons per unit cell. The wave function and eigenenergy are denoted as $\psi_{n\mathbf{k}}^{(0)}(\mathbf{r})$ and $\epsilon_n^{(0)}(\mathbf{k})$, respectively. All the lowest N_e levels are occupied in the ground state. Then, the matrix elements connecting the ground and final states are expressed as

$$\langle f | s_{\sigma} | i \rangle = \begin{vmatrix} S_{1,1} & S_{2,1} & \cdots & S_{N_e,1} \\ S_{1,2} & S_{2,2} & \cdots & S_{N_e,2} \\ \cdots & \cdots & \cdots & \cdots \\ S_{1,N_e} & S_{2,N_e} & \cdots & S_{N_e,N_e} \end{vmatrix}, \quad (4)$$

with

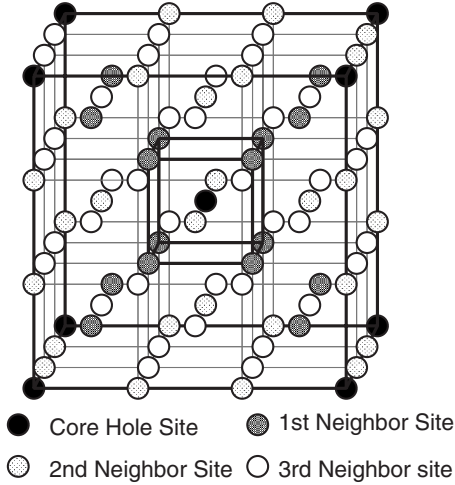


FIG. 1. Sketch of a supercell containing core holes in bcc Fe.

$$S_{i,i'} = \int \phi_i^*(\mathbf{r}) \phi_{i'}^{(0)}(\mathbf{r}) d^3r, \quad (5)$$

where the integral is carried out within a unit cell. Subscripts $i=(n, \mathbf{k})$ and $i'=(n', \mathbf{k}')$ are running over occupied states in the final state and in the ground state, respectively. The corresponding energies are

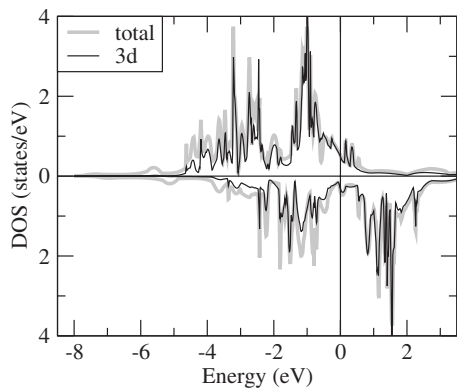
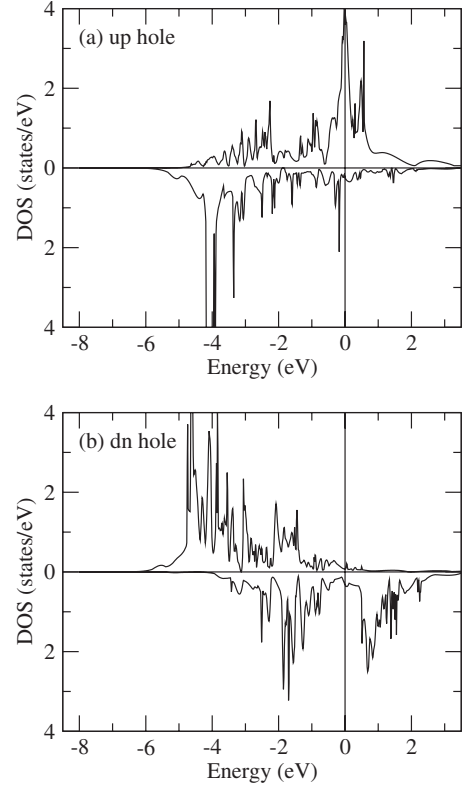
$$E_f = \epsilon_1 + \epsilon_2 + \dots + \epsilon_{N_e}, \quad (6)$$

$$E_g = \epsilon_1^{(0)} + \epsilon_2^{(0)} + \dots + \epsilon_{N_e}^{(0)}. \quad (7)$$

Substituting Eqs. (4), (6), and (7) into Eq. (1), we obtain the XPS spectra.

III. CALCULATED RESULTS

We apply the above method to calculate the XPS spectra for the 3s and 1s cores in Fe metal. We use a supercell containing 27 iron atoms, as illustrated in Fig. 1. The first Brillouin zone (BZ) for the supercells becomes much smaller than the original first BZ. Accordingly, the energy bands in the absence of core hole are folded. To demonstrate the reli-


 FIG. 2. DOS calculated in a system of supercells with no core hole in ferromagnetic iron. The solid line represents the DOS projected onto the d symmetry within the muffin-tin sphere.

 FIG. 3. The d -DOS at the site of 3s-core hole with (a) up spin and (b) down spin.

ability of our supercell calculation, we show in Fig. 2 the DOS calculated in the supercell system without core hole. The DOS resolved into the majority (up) spin and minority (down) spin reproduces well the previous results.²⁵ In addition, the DOS is projected onto the d symmetry (d -DOS) within the muffin-tin sphere, whose curve is close to the total DOS. This indicates that the most part of the DOS arises from the 3d states.

A. 3s-core hole

1. One-electron states

How are the one-electron states modified by the core-hole potential? We explain the change through the change in the d -DOS at the core-hole site. Figure 3 shows the d -DOS calculated in the presence of the 3s-core hole, and Table I lists the screening charge Δn_d , which is defined by the change in the occupied electron number caused by the core-hole potential within the muffin-tin sphere at the core-hole site.

2. Up-spin core hole

Figure 3(a) shows the d -DOS at the site of core hole with up spin. By comparing with the d -DOS with no core hole, we

 TABLE I. Screening charge with respect to the d symmetry within the muffin-tin sphere on the 3s-core-hole site.

	$\Delta n_{d\uparrow}$	$\Delta n_{d\downarrow}$	Δn_d (Total)
Up-spin hole	-1.44	2.38	0.94
Down-spin hole	0.47	0.48	0.95

notice that the attractive core-hole potential is strongly working on the $3d$ electrons with *down* spin, pulling down the d -DOS. A large weight develops around the bottom of the band. Even quasibound states seem to be formed. It looks like an overscreening (the screening charge reaches 2.38). On the other hand, the $3d$ electrons with up spin are prevented from coming close to the core hole by the exchange effect, thereby the attractive potential would be less effective. The repulsion between $3d$ electrons pushes the $3d$ states upward, resulting in a compensation of the overscreening (the screening charge -1.44). As a total, the screening charge is 0.94. This indicates that the screening is almost complete within the muffin-tin sphere on the core-hole site.

3. Down-spin core hole

Figure 3(b) shows the d -DOS at the site of the core hole with down spin. The attractive potential is now strongly working on the *up*-spin states, pulling down the d -DOS. Again a large weight develops around the bottom of the band. The difference is that the screening charge is limited to 0.47 in the up-spin $3d$ states, even after nearly all occupied states are pulled down below the Fermi level. Therefore, the screening has to be completed by the down-spin $3d$ states. Since the attractive potential is less effective on the minority spin electrons due to the exchange effect, there is no appreciable weight around the bottom of the band. The screening is completed only through a moderate transfer of weight from unoccupied levels to the occupied levels.

4. XPS spectra

We construct the excited states by distributing N_e band electrons on the one-electron states in the presence of the core hole. Since the first BZ is quite small, we pick up only the Γ -point and distribute 8×27 electrons on $3d$, $4s$, and $4p$ bands. The excited state with the lowest energy is given by piling one-electron states up to the Fermi level. Then, picking up an occupied electron from these states and placing it on an unoccupied state, we create one electron-hole pair. We create two electron-hole pairs in a similar way. We calculate Eq. (1) with these excited states by evaluating the Slater determinant in Eq. (4) with the use of the APW wave functions. Since the first BZ is quite small, we take account of the states at the Γ -point only. Figure 4 shows the calculated XPS spectra as a function of the binding energy $\omega_q - \epsilon$ in comparison with the experiment.¹⁶ The contributions from zero, one, and two electron-hole pairs are separately shown. The calculated spectra reproduce well the experimental data. In the following, we discuss the origin of the spectra.

5. Up-spin core hole

The excited state with the lowest energy (no electron-hole pair), denoted as $|f_0\rangle$, has a finite overlap with the ground state $|g\rangle$, giving rise to intensities on the threshold (broadened by a Lorentzian function with FWHM $2\Gamma_s = 2.0$ eV). The energy of threshold is adjusted to coincide with the experimental value. The overlap is given by $\langle f_0 | s_{\uparrow} | g \rangle = A_{\uparrow} A_{\downarrow}$ with $A_{\uparrow} = 0.980 + i0.079$ and $A_{\downarrow} = -0.055 - i0.352$, where A_{\uparrow} and A_{\downarrow} represent the overlap with respect to up-spin electrons

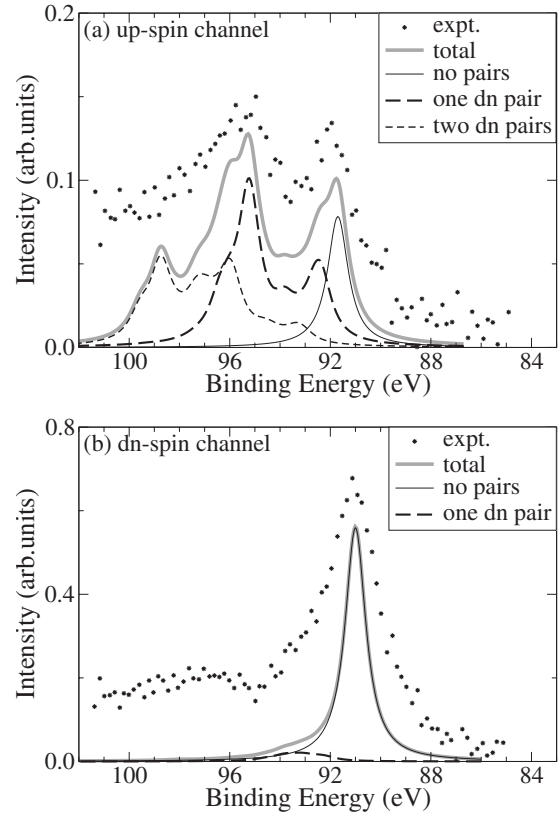


FIG. 4. XPS spectra as a function of binding energy for the $3s$ -core hole with (a) up spin and (b) down spin. The experimental data are taken from Ref. 16.

and with respect to down-spin electrons, respectively. In principle, such overlap tends to be zero with $N_e \rightarrow \infty$, according to the Anderson orthogonality theorem.⁶ In such infinite systems, energy levels become continuous near the Fermi level and thereby infinite numbers of electron-hole pairs could be created with small excitation energies, leading to the so-called Fermi edge singularity in the XPS spectra. The finite contribution obtained above arises from the discreteness of energy levels and could be interpreted as the integral intensity of singular spectra near the threshold, according to the model calculations to other systems.^{9,11} Note that $|A_{\uparrow}|^2 = 0.966$, which is close to 1, in spite of the large modification of the local $3d$ -DOS at the core-hole site [see Fig. 3(a)]. This may be understood as follows. Since the $3d$ bands with up spin are almost occupied in the ground state, the wave functions of the $3d$ bands in the presence of core hole could be nearly represented by a unitary transform of the wave functions of the occupied $3d$ electrons in the ground states. Therefore the value of the Slater determinant in the up-spin channel could not be changed by the presence of the core hole. On the other hand, $|A_{\downarrow}|^2 = 0.127$, suggesting that the wave functions of the occupied levels are considerably modified from those of the ground state in the down-spin channel, whose modifications are brought about by the mixing of the unoccupied states of the ground state, because the $3d$ bands are only partially occupied in the ground state. This change reduces the value of the Slater determinant in the down-spin channel.

For the excitation of one electron-hole pair, the contributions from the up-spin channel are negligibly small. Since the wave functions of the unoccupied levels are almost orthogonal to the wave functions of the 3d bands of the ground state, the Slater determinant corresponding to the occupation of such states would be almost vanishing. On the other hand, the excitations of one electron-hole pair in the down-spin channel could give rise to a considerable contribution to the spectra; each one-electron wave function of occupying electrons is modified from those of the ground state by the mixing of the unoccupied states, resulting in nonvanishing Slater determinants. As a result, we obtain the intensities distributed with wide range of binding energy, corresponding to various kinds of one electron-hole pairs. They consist of two peaks; one is located around $\omega_q - \epsilon = 92.5$ eV and another is around 95 eV. The latter peak corresponds to the excitation from the quasibound states around the bottom of the 3d band in the down-spin channel.

For the excitation of two electron-hole pairs, the contributions from the up-spin channel are extremely small by the same reason as for the case of one electron-hole pair. The contributions arise from the down-spin channel; they consist of three peaks, one small peak around 93.2 eV, and large peaks around 96 and 99 eV. The excitation of three electron-hole pairs gives rise to only minor contribution to the spectra.

6. Down-spin core hole

The excited state with the lowest energy (no electron-hole pair) has an overlap with the ground state, $\langle f_0 | s_{\downarrow} | g \rangle = A_{\uparrow} A_{\downarrow}$ with $A_{\uparrow} = 0.708 + i0.684$, $A_{\downarrow} = 0.758 + i0.576$. Note that $|A_{\uparrow}|^2 = 0.969$, which is close to 1, although the local 3d-DOS is strongly modified from that in the ground state [see Fig. 3(b)]. This means that, by the same reason as explained in the up-spin core hole, the one-electron states in the presence of core hole are nearly represented by a unitary transform of occupied 3d states of the ground state, and thereby the corresponding Slater determinant is close to 1. In the down-spin channel, $|A_{\downarrow}|^2 = 0.906$, which is less than $|A_{\uparrow}|^2$ but close to 1. This simply means that the modification of the one-electron states by the core-hole potential is small, due to the exchange potential. Thereby we obtain a large spectral weight around the threshold.

For the excitation of one electron-hole pair, we again have extremely small contributions in the up-spin channel because of the vanishing overlap with the ground state. In the down-spin channel, since the modification of one-electron states by the core-hole potential is small, the creation of electron-hole pair makes the corresponding state nearly orthogonal to the ground state, and thereby small contributions come out, as shown in Fig. 4.

B. 1s-core hole

1. One-electron states

Figure 5 shows the d -DOS at the 1s-core-hole site. It is a little modified from that with no core hole (Fig. 2). It depends little on the spin of the core hole, indicating that the

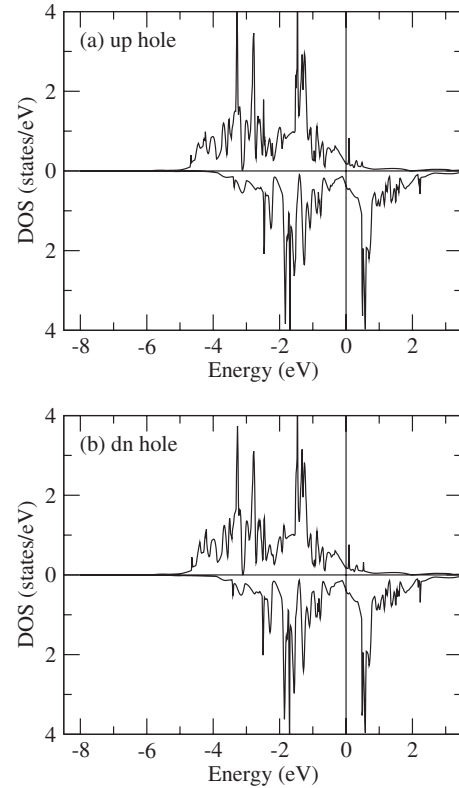


FIG. 5. The d -DOS at the site of 1s-core hole with (a) up spin and (b) down spin.

exchange effect is rather small. This is anticipated from the fact that the 1s core is much localized around the origin than the 3s core. In addition, no quasibound state exists around the bottom of the 3d bands. Table II lists the screening charges caused by the core-hole potential within the muffin-tin sphere at the core-hole site. The screening charges are nearly independent of the spin of core hole.

2. XPS spectra

Figure 6 shows the XPS spectra for the core hole with up spin and down spin, respectively. The spectra are broadened by a Lorentzian function with FWHM $2\Gamma_s = 2.0$ eV to take account of the lifetime broadening of the 1s core. The lowest-energy state (no electron-hole pair) in the presence of core hole has a finite overlap with the ground state; $\langle f_0 | s_{\uparrow} | g \rangle = A_{\uparrow} A_{\downarrow}$ with $A_{\uparrow} = 0.836 - i0.521$ ($A_{\uparrow} = -0.848 + i0.501$), $A_{\downarrow} = 0.737 + i0.538$ ($A_{\downarrow} = -0.708 + i0.578$) for the core hole with up (down) spin. Since $|A_{\uparrow} A_{\downarrow}|^2$ is 0.808 (0.810) for the core hole with up (down) spin, most intensities are concentrated near the threshold. Only small intensities arise from the creation of electron-hole pair with no appreciable

TABLE II. Screening charge with the d symmetry within the muffin-tin sphere at the 1s-core-hole site.

	$\Delta n_{d\uparrow}$	$\Delta n_{d\downarrow}$	Δn_d (Total)
Up-spin hole	0.35	0.74	1.09
Down-spin hole	0.36	0.73	1.09

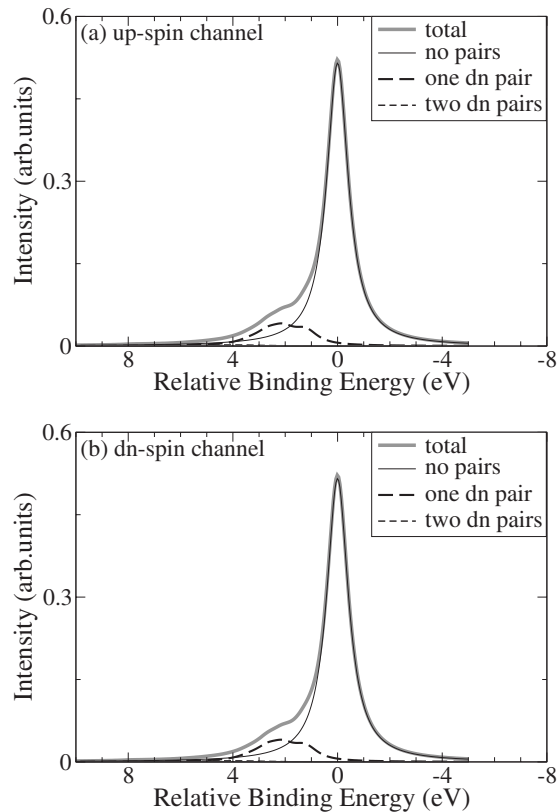


FIG. 6. XPS spectra as a function of binding energy for the 1s-core hole with (a) up spin and (b) down spin.

satellite. Unfortunately, we do not know the experimental data to be compared with.

IV. CONCLUDING REMARKS

We have developed an *ab initio* method to calculate the inner-core XPS spectra. We have applied the method to the 3s-core XPS in a ferromagnetic metal Fe, where the spectra are resolved by the spin of photoelectron. We have found that the spectral intensity distributes in a wide range of binding energy with a clear satellite for the core hole with up spin, while the intensity is concentrated near the threshold with no

satellite peak for the core hole with down spin, in good agreement with the experiment. The origin of such behavior has been explained in relation to the 3d band modified by the core-hole potential.

We have considered only the states on the Γ point in the first BZ to which electrons are distributed in the calculation of the XPS spectra. Since the first BZ is reduced to a small size in a system of supercells, this may not cause large errors. With increasing the states to which electrons are distributed, one may expect that the overlap between the lowest-energy state in the presence of core hole and the ground state would be reduced, and that the contributions from electron-pair creation would increase near the threshold, leading to an asymmetric peak near the threshold as a function of binding energy. Such behavior has been demonstrated in numerical calculations on finite-size systems.^{9,11} On the other hand, the structures with high binding energy are expected to be only a little influenced by such a refined treatment. In any case, to be more quantitative, we need to increase k points to which electrons are distributed as well as to enlarge the size of supercells in the calculation of the XPS spectra.

Acker *et al.*¹³ pointed out that there is poor correlation between the satellite position and the magnetic moment on the Fe atom in various alloys and compounds, and that the satellite splitting is observed even in some Pauli paramagnets. We have interpreted the satellite as arising from an excitation from quasibound states to unoccupied states in one-electron states. At present it is not clear how the position of quasibound state is correlated with the magnetic moment in various systems and whether the satellite appears even in Pauli paramagnets within the present approach. We need further studies to clarify these points.

The present method could be extended to analyze XPS spectra from other core holes, for example 2p core in Ni, and the x-ray absorption spectra.²⁶ These extensions are left for future studies.

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