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Many-body aspects of the near-edge structure in x-ray absorption

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The near-edge structure (NES) in x-ray absorption is investigated using a simple reformulation of the Hartree-Fock approach. It is found that the most natural single-particle states are not the usual Hartree-Fock ones but those that explicitly incorporate the exclusion principle in the transition by having the directly excited photoelectron state orthogonal to all *initially* occupied states and the resulting core hole orthogonal to all *finally* occupied states. This reformulation shows clearly that many-body effects are important when the perturbation by the core-hole potential is significant. Only in two limits does the NES reduce to an effective single-particle problem, namely, when a single photoelectron either (a) makes a transition into an initially empty shell (band) or (b) fills that shell (band). In the former case the local density of states of the *final* potential is appropriate, while for the latter the density of states of the *initial* system, before excitation, is appropriate. Spin-dependent effects are illustrated by a model calculation.

I. INTRODUCTION

The interest in x-ray absorption has grown in recent years with the availability of synchrotron sources and the appreciation of the structural information present in the extended x-ray-absorption fine structure (EXAFS). The absorption spectra of x-ray edges can be divided into two intervals.[1] The near-edge region extends about 40 eV beyond the threshold, followed by the EXAFS region which extends typically 1000 eV further. Whereas the EXAFS can be understood largely as a perturbative scattering of free-electron states by nearby atoms, the near-edge structure (NES) requires a detailed calculation of multiple-scattering processes to all orders.

This has advantages and disadvantages. The need for a detailed calculation makes it difficult to extract information from the measurements, especially for samples whose structure is unknown. On the other hand, the NES contains information that is not readily available to the EXAFS region such as the density of unfilled states and angular correlation between atoms. There has been some effort to obtain an understanding of NES.[2–8] One recent motivating force has been the effort to understand the catalytic activity of transition-metal compounds in heterogeneous catalysts.[8,9]

All of the above-mentioned investigations have been based on the one-electron approximation with many-body effects lumped into a Lorentzian smearing function. Yet one must be careful in applying this approximation consistently in the x-ray-absorption problem. When the core electron is excited, its removal changes the potential seen by the rest of the electrons in the atom and in the surrounding environment. The surrounding electrons respond to this change, causing the final states to be different from the initial states. A question that arises is what potential and states should be used in the one-electron approximation: the initial or the final ones as suggested by von Barth and Grossman.[10] Most of the previous investigations either ignored this question and employed the initial states or acknowledged the complication introduced by the hole in the excited atom and neglected it for mathematical convenience. A recent paper[8] confronts this question directly and explicitly uses the final states and potential in the calculation.

X-ray absorption is a many-body problem which has attracted much interest for a core level embedded in a uniform electron gas.[11] In this case the many-body aspect of the electron gas introduces a singularity at the edge. This singularity has evoked experimental interest only for the soft-x-ray region because it is narrow and requires long excited-state lifetimes to observe. Many-body effects, however, do appear for hard x rays in the EXAFS region.[12–15] What we show in this paper is that many-body effects are also important in the NES for hard x rays. The effects are not as spectacular as singularities, but they have an appreciable influence on the shape of the absorption. For example, we will show that the inclusion of many-body effects will resolve the question of which single-particle states to use in calculations. The correct single-particle states are generally neither the initial nor the final ones but something in between. Only in the two limits of transitions to nearly empty and nearly filled bands do the appropriate single-particle states reduce to the final and initial ones, respectively.

In Sec. II we look at a simple problem to illustrate the many-body effects and give a simple physical interpretation. Based on this interpretation we obtain a solution to the general problem. In Sec. III the addition of electron spin is discussed. A simple diatomic model is calculated in Sec. IV to illustrate the multielectron effects including spin. In Sec. V a discussion is given of the relationship of the formalism developed here to other presentations of the x-ray problem. Section VI discusses the relationship between the one-electron and the many-electron problem for the NES, and Sec. VII ends with a summary.

II. MODEL CALCULATIONS

To investigate the many-body aspects of the NES we use the same approximation as employed in the electron-gas problem. These are essentially equivalent to the Hartree-Fock approximation for the wave functions,[16,17] together with a frozen-core level. The assumption of a frozen core is necessary to ensure that the excited states of the final-state Hamiltonian are orthogonal to the ground state; it is generally a very good approximation.

To illustrate the problem, we consider the many-body case with the least number of electrons, namely, a model two-electron atom. For the ground state Ψ_0 the Hartree-Fock orbitals are denoted by ϕ_n. They are taken to be eigenstates of the Hartree-Fock (or other effective one-particle) Hamiltonian for the ground state and are ordered in increasing eigenenergies. The ground state consists of the two lowest states being occupied, ϕ_1 and ϕ_2.

Upon excitation of one of the electrons, the Hartree-Fock potential sensed by the other electron is altered and the resulting eigenstates ϕ_n' are different from the initial ones, ϕ_n. In general, the overlap matrix $\langle \phi_n \mid \phi_m' \rangle$ is not diagonal.

The x-ray transition rate is given by

$$W=\frac{2\pi}{\hbar}\sum_f \mid \langle \Psi_f \mid O \mid \Psi_i \rangle \mid^2 \delta(E_i+\hbar\omega-E_f) , \qquad (1)$$

where O is the transition operator introduced by the electromagnetic field (not necessarily the dipole operator), and Ψ_f and Ψ_i are the Slater determinants of the occupied ϕ_n' and ϕ_n, respectively. The sum is over all final states. Because ϕ_n and ϕ_n' are not orthogonal to one another, cross terms between them occur in the evaluation of (1). Consider the transition of directly exciting the most tightly bound ϕ_1 into the state ϕ_k'. In that case the contribution to W is

$$W=\frac{2\pi}{\hbar}\sum_f \mid M \mid^2 \delta(E_i+\hbar\omega-E_f) , \qquad (2)$$

where

$$M=\langle \phi_k' \mid O \mid \phi_1 \rangle \langle \phi_2' \mid \phi_2 \rangle - \langle \phi_2' \mid O \mid \phi_1 \rangle \langle \phi_k' \mid \phi_2 \rangle . \qquad (3)$$

The matrix element has no obviously simple interpretation. Friedel[16] has described it by a direct transition (induced by the transition operator) and a replacement term where ϕ_k' is reached indirectly by exciting an intermediate transition and using the overlap term $\langle \phi_k' \mid \phi_2 \rangle$ to complete the transition. However, such a description is not edifying since it simply describes in words what the equation states.

More insight can be obtained by noting that we can simplify the matrix element by making a unitary transformation of the final state $S\phi'=\psi'$ such that $\langle \psi_k' \mid \phi_2 \rangle = 0$. Specifically, let

$$\psi_k'=A[\phi_k'\langle \phi_2' \mid \phi_2 \rangle - \phi_2' \langle \phi_k' \mid \phi_2 \rangle] , \qquad (4)$$

$$\psi_2'=A[\phi_k'\langle \phi_k' \mid \phi_2 \rangle + \phi_2' \langle \phi_2' \mid \phi_2 \rangle] , \qquad (5)$$

where

$$A^{-2}= \mid \langle \phi_2' \mid \phi_2 \rangle \mid^2 + \mid \langle \phi_k' \mid \phi_2 \rangle \mid^2 .$$

This transformation does not change the wave function Ψ_f, but now ψ_k' is orthogonal to both initially occupied states. Thus Eq. (2) for M becomes

$$M=\langle \psi_k' \mid O \mid \phi_1 \rangle \langle \psi_2'(k) \mid \phi_2 \rangle , \qquad (6)$$

i.e., a single-particle matrix element and a k-dependent overlap factor, all calculated with *normalized* single-particle states.

This result is physically pleasing since it explicitly incorporates the exclusion principle in the transition guaranteeing that even after the transition there will be no more than one electron per state. Thus the complicated replacement terms in the Friedel description are simply the mathematical terms necessary to correct the nonorthogonality between the ϕ' and the ϕ.

The insight gained in this simple model suggests how one can treat the general case in which N states are initially occupied, including the deep core state ϕ_1. The system need not be limited to an atom but can consist of atoms embedded in an electron gas. Again one can choose a unitary transformation on the final state $S\phi' \rightarrow \psi'$ such that

$$\langle \psi_k' \mid \phi_i \rangle = 0, \quad i=2,\ldots,N .$$

The frozen-core approximation automatically makes

$\langle \phi_1 | \phi_i' \rangle = 0$ $(i > 1)$. Thus

$$M = \langle \psi_k' \,|\, O \,|\, \phi_1 \rangle \det(S_{ij})_{N-1} \,, \tag{7}$$

where $S_{ij} = \langle \psi_i' \,|\, \phi_j \rangle$ and the indices in Eq. (7) range from $i,j = 2, \ldots, N$, i.e., over the passive electrons which are not directly operated on by O.

Defining the Slater determinants of the passive states by Ψ_i^{N-1} and Ψ_f^{N-1} for the initial and final states, respectively, the determinant in (7) is equal to $\langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle$, the overlap between the passive electrons. Thus M can be written as

$$M = \langle \Psi_f^{N-1} \,|\, \Psi_i^{N-1} \rangle \langle \psi_k' \,|\, O \,|\, \phi_1 \rangle \,. \tag{8}$$

This form is similar to that of the simple case of no change in potential when the hole is created. In the simple case the overlap is unity because of orthonormality, and there is no contribution from the passive electrons. In the more general case, where the potential perturbation produced by the hole is not negligible, the states ψ' and ϕ are, in general, not orthogonal to one another. Thus the passive states occupied after the transition need not be adiabatically related to the initial states and the passive electrons can also be left in excited states. Thus the phenomenon of multielectron excitations naturally occurs.

In computing the total absorption cross section at a given energy, one must sum the squares of contribution from each multielectron excitation. Thus one obtains

$$W = \frac{2\pi}{\hbar} \sum_{k',n} |\langle \psi_k'(n) \,|\, O \,|\, \phi_1 \rangle|^2 S_n^2(k') \times \delta(\hbar\omega - (E_{k'} + E_n - E_r)) \,, \tag{9}$$

$$S_n^2(k') = |\langle \Psi_f^{N-1}(k',n) \,|\, \Psi_i^{N-1} \rangle|^2 \,, \tag{10}$$

where $E_k' = E_k - E_n$ (E_n is the excitation energy of the passive electron) and E_r is the relaxation of the ground state caused by the hole.[18] Although it is tempting to try to express this as a convolution of the square of a one-particle matrix element and a universal excitation spectrum, this cannot be accomplished because of the k',n dependence in the overlap factor. If the variation is smooth, then at best one is left with a convolution function which is dependent on the energy of the final state of the active electron. For the NES this dependence is strongest, and its precise form must be taken into account.

III. SPIN

The above account neglected the spin of the electron. We now include spin in cases where the spin-orbit interaction can be neglected and we assume that the operator O of the electromagnetic field can be approximated by the dipole operator D which does not couple to spin variables. Under these conditions the electron spin is conserved in the transition. The notation we now use is the same as before, with the addition of a spin variable ↑ or ↓ to denote the two spin states, e.g., $\psi_k' \rightarrow \psi_{k\uparrow}'$.

The same reasoning as above holds in determining the choice of one-electron states: The active electron must end up in a state orthonormal to all of the *initially* occupied passive states and the final hole must be orthonormal to all of the finally occupied states. Again the frozen-core approximation satisfies the latter condition. In satisfying the initial condition the spin variable accounts for the orthonormality for all electrons of opposite spin. Thus the unitary transformation discussed above need be applied only among electrons with the same spin. If the final active electron is $\psi_{k\uparrow}'$ the appropriate spin-up and spin-down one-electron states are different. They are $\psi_{i\uparrow}'$ and $\phi_{i\downarrow}'$.

Equation (10) still holds, but now Ψ_f^{N-1} separates into the product of the determinants of the single-particle states $\psi_{1\uparrow}'$ by the determinant of $\phi_{i\downarrow}'$. Equation (10) implies that the spins of the passive electrons do not change in the transition. The addition of spin introduces an additional spin dependence into the x-ray-absorption problem for ferromagnetic solids, and even for nonmagnetic solids it modifies the standard result. This is illustrated in the next section by a model calculation.

IV. DIATOMIC MODEL

The model we choose is a two-level diatomic molecule treated in the tight-binding approximation, which is sufficient to illustrate the physical principles involved. The atomic basis states are taken to be s states, one for each atom. Including spin there are four states altogether. As in the preceding section we neglect spin-orbit effects so that the Hamiltonian is spin independent and the initial one-electron states can be determined by diagonalizing the initial Hamiltonian $\mathcal{H}$, which in the atomic basis is assumed to be of the form

$$\mathcal{H} = \begin{bmatrix} \epsilon & -t \\ -t & -\epsilon \end{bmatrix} . \tag{11}$$

The atoms in the molecule thus are dissimilar, the second atom being more attractive (i.e., $\mathcal{H}_{22} = -\epsilon < 0$); also, we assume $t > 0$. It is assumed that the x-ray excites the core state of the first atom, yielding a final-state Hamiltonian of the form

$$\mathcal{H}'=\begin{bmatrix}-\epsilon & -t\\ -t & -\epsilon\end{bmatrix}. \tag{12}$$

The core-hole perturbation V is thus

$$V=\begin{bmatrix}-2\epsilon & 0\\ 0 & 0\end{bmatrix},$$

localized on the first atom.

The eigenvalues of $\mathcal{H}$ and $\mathcal{H}'$ are, respectively,

$$\begin{aligned}&E=\pm\epsilon(1+x^2)^{1/2}\,,\\ &E'=-\epsilon(1\pm x)\,,\end{aligned} \tag{13}$$

where $x=\epsilon/t$.

The eigenfunctions of the initial-state Hamiltonian $\mathcal{H}$, corresponding, respectively, to the ground state ψ_g and the first excited state $\psi_{\rm ex}$ are

$$\begin{aligned}\psi_g&=\begin{bmatrix}\dfrac{1-T}{A}\\ \dfrac{-x}{A}\end{bmatrix},\\ \psi_{\rm ex}&=\begin{bmatrix}\dfrac{1+T}{B}\\ \dfrac{-x}{B}\end{bmatrix},\end{aligned} \tag{14}$$

where

$$\begin{aligned}&T=(1+x^2)^{1/2}\,,\\ &A=[(1-T)^2+x^2]^{1/2}\,,\\ &B=[(1+T)^2+x^2]^{1/2}\,.\end{aligned}$$

In the matrices the top (bottom) term is the amplitude of the atomic state on atom one (two).

The corresponding eigenfunctions of $\mathcal{H}'$ are

$$\begin{aligned}\psi'_g&=\begin{bmatrix}+1/\sqrt{2}\\ 1/\sqrt{2}\end{bmatrix},\\ \psi'_{\rm ex}&=\begin{bmatrix}-1/\sqrt{2}\\ 1/\sqrt{2}\end{bmatrix}.\end{aligned} \tag{15}$$

The model chosen simulates a diatomic molecule which initially has partial ionic binding with some of the charge transferred from the first to the second atom. The excitation of the core perturbs the binding to a pure covalent bond with no charge transfer.

To simulate a ferromagnetic metal the initial state of the system is taken to be $\psi_{g\uparrow}$, as indicated in Table I. The Hartree-Fock (HF) final states are listed in the second column of the table. The standard approach would be to take the Slater determinant of these final HF states as the many-body state. Alternatively, as discussed above, one can transform to another single-particle state basis such that one state (the active electron) is made orthogonal to the initial state. These orthogonalized states are listed in the third column (with the active electron underlined). The HF states are already correctly orthogonalized through the spin variable for every final state except for the third one down. In that case orthogonalization simply transforms the states to the initial basis. The energy of the final states is listed in the fourth column, and the matrix element of the transition is listed in the last column. The first three final states in the table are single-particle excitations in which the passive electron remains in the ground state. The other two nonzero contributions are multielectron (shakeup) transitions. In the fourth state the passive electron is excited to $\psi'_{{\rm ex}\uparrow}$ while the active electron ends up in $\psi'_{g\downarrow}$. In the last state the passive electron is again excited to $\psi'_{{\rm ex}\uparrow}$ as the active electron makes a transition to $\psi'_{{\rm ex}\downarrow}$.

TABLE I. Initial and final states of model.

Initial state	Hartree-Fock	Final state Orthogonal[a]	Energy	Matrix element M of transition[b]
$\psi_{g\uparrow}$	$\psi'_{g\uparrow}\psi_{g\downarrow}$	$\psi'_{g\uparrow}\psi'_{\underline{g\downarrow}}$	$-2\epsilon(1+x)$	$M_1=\langle\psi_{g\uparrow}\mid\psi'_{g\uparrow}\rangle\langle c\mid D\mid\psi'_{g\downarrow}\rangle$
	$\psi'_{g\uparrow}\psi'_{{\rm ex}\downarrow}$	$\psi'_{g\uparrow}\psi'_{\underline{{\rm ex}\downarrow}}$	-2ϵ	$M_2=\langle\psi_{g\uparrow}\mid\psi'_{g\uparrow}\rangle\langle c\mid D\mid\psi'_{{\rm ex}\downarrow}\rangle$
	$\psi'_{g\uparrow}\psi'_{{\rm ex}\uparrow}$	$\psi_{g\uparrow}\psi_{\underline{{\rm ex}\uparrow}}$	-2ϵ	$M_3=\langle\psi_{g\uparrow}\mid\psi_{g\uparrow}\rangle\langle c\mid D\mid\psi_{{\rm ex}\uparrow}\rangle$
	$\psi'_{g\downarrow}\psi'_{{\rm ex}\uparrow}$	$\psi'_{\underline{g\downarrow}}\psi'_{{\rm ex}\uparrow}$	-2ϵ	$M_4=\langle\psi_{g\uparrow}\mid\psi'_{{\rm ex}\uparrow}\rangle\langle c\mid D\mid\psi'_{g\downarrow}\rangle$
	$\psi'_{g\downarrow}\psi'_{{\rm ex}\downarrow}$	$\psi'_{g\downarrow}\psi'_{{\rm ex}\downarrow}$	-2ϵ	0
	$\psi'_{{\rm ex}\uparrow}\psi'_{{\rm ex}\downarrow}$	$\psi'_{{\rm ex}\uparrow}\psi'_{\underline{{\rm ex}\downarrow}}$	$-2\epsilon(1-x)$	$M_5=\langle\psi_{g\uparrow}\mid\psi'_{{\rm ex}\uparrow}\rangle\langle c\mid D\mid\psi'_{{\rm ex}\downarrow}\rangle$

[a] Final states transformed so that the active electron (underlined) is orthogonal to the initial state.

[b] Core state is denoted by c and dipole operator of the x-ray field by D.

For our purposes the three states with the intermediate final energy -2ϵ are the most interesting because core electrons with both spins are involved. In the other two transitions the standard restriction of only one electron per state completely defines the spin possibilities. Of the three intermediate states, two involve a spin-down core electron while one involves a spin-up core electron. Since the two spin-down states, 2 and 4, are distinguishable, the absorption of x rays by spin-down core electrons is proportional to $|M_2|^2+|M_4|^2$, while the absorption of the spin-up core electrons is proportional to $|M_3|^2$. A plot of the various matrix elements squared divided by $|M_A|^2$ is shown in Fig. 1, where M_A is the x-ray-absorption matrix element for an isolated atom of type one. These matrix elements are plotted as a function of

$$\Delta\rho = |\langle \psi'_g | \psi \rangle|^2 - |\langle \psi_g | \psi \rangle|^2 ,$$

where ψ is the atomic wave function for the type-one atom. The term $\Delta\rho$ is the charge transferred to the type-one atom in the ground state of the diatomic molecule as the core electron is excited. From the form of ψ'_g and ψ_g given in Eqs. (14) and (15) it is straightforward to calculate

$$\Delta\rho = \frac{1}{2} - \frac{(1-T)^2}{A^2} . \tag{16}$$

When the core perturbation $V=0$, $\Delta\rho=0$ also.

From the results shown in Fig. 1 no spin effects are present when $V=\Delta\rho=0$. Both core spins have equal probability of being excited. However, as $\Delta\rho$ increases, the core electron with a spin parallel to the initial state has an enhanced probability of being excited. This spin-enhanced effect reveals itself only when charge transfer caused by the core-hole potential V becomes noticeable.

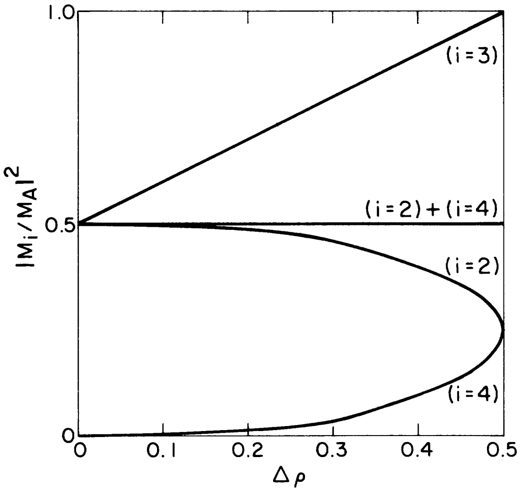

FIG. 1. Calculations of x-ray absorption in a diatomic model relative to that of an isolated atom plotted as a function of $\Delta\rho$, the charge transferred to the ground-state wave function of the x-ray-absorbing atom after excitation. M_A is the matrix element of absorption for an isolated atom, and M_i is the same for the diatomic model for the transitions listed in the last column of the table. M_3 is the matrix element for the core-electron spin-up transitions, while M_2 and M_4 are the spin-down transitions. These matrix elements represent all of the nonzero transitions to the intermediate energy level of -2ϵ in the table.

V. DISCUSSION

The requirement that the active electron be orthogonal to all of the initially occupied states was also suggested by Davis and Feldkamp[19] for the electron-gas problem, but only in the limiting case of excitations far from threshold. In that case the overlap terms $\langle \phi'_k | \phi_i \rangle$ are small and $\psi'_j \simeq \phi'_j$. The orthogonality requirement in that limit is satisfied by letting

$$\psi'_k = \phi'_k - \sum_i \langle \phi_i | \phi'_k \rangle \phi'_i ,$$

that is, by projecting out the overlap terms of ϕ'_k with the ϕ_i. When $\langle \phi_i | \phi'_i \rangle$ is not small, as near threshold, then their approximation breaks down and a different formulism, such as that presented here, must be employed.

The insight gained from the discussion presented here permits a simple physical explanation of the results for a model narrow-band metal which includes the hole perturbation in the x-ray-absorption problem.[20] This interesting calculation showed a dependence of the absorption spectrum as a function of the number of electrons initially in the band. As the band filling progressed from empty to almost full, the emission and absorption spectrum varied from that given by the final density of states to that of the initial density of states. In the former case the spectrum reflects the local impurity density of states, while in the latter it reflects the density of states of the unperturbed system.

In this model, exciting the hole when the band is initially empty places only one electron in the narrow band and no many-body effects occur. For such a one-electron problem it is well known that the transition reflects the local density of states about the impurity. In this single-band model, when the band is almost filled, say, with just one hole, then the requirement that the active electron be orthogonal to all of the initially occupied states forces the active electron to end up in the hole of the *initial* unperturbed matrix. The orthogonality requirement completely defines the final state of the active electron, and the hole can have no impact on the transition. The final states of the passive electrons are also forced to remain the same as their initial states by the fact that the band is completely filled and the overlap factor is therefore unity. Thus, the transition is equivalent to the one-electron case with *no* perturbation introduced by the hole.

The many-body effects in the x-ray-absorption problem impact on the matrix element of Eq. (8) in two ways: (a) The overlap factor, being less than unity, allows excitation of passive electrons, and (b) the state of the effective photoelectron ψ_k' is modified. The problem reduces to an effective one-electron problem in the limiting cases referred to above because the overlap factor of the passive electrons becomes unity and the matrix element depends solely on the active electron, which is the only one excited. However, many-body effects are still evident in these limiting cases in influencing which single-particle states are appropriate. In a real solid the excited atom consists of more than a single core hole. The other bound electrons in the atom are affected by the creation of the core hole in addition to the band electrons. The resulting relaxation of the bound electrons contributes to the overlap factor. This contribution has been calculated for atoms[21] and some molecules[22] in the limit of excitations far from threshold and is found to be a 20–30% effect. The effect comes mainly from the valence electrons which become the band electrons in the solid. The effects of the bound electrons on the NES have not been accurately assessed as yet. Work is in progress to do so.[23]

VI. THE NES

The implications of the above discussion for the NES of transition metals for deep-core transitions are as follows. In transitions from the L_{II} and L_{III} edges the matrix elements from the initial p states to the final d states dominate over the final s states,[24] producing the white-line peaks.[3] The final d state must be chosen to be orthogonal to the initially occupied states in both the atom and the d band of the transition metal. The occupied atomic states are substantially more tightly bound than the d-band states, and their overlap with the HF final states before orthogonalization is negligible compared with that of the d-band states. Thus, to a reasonable approximation, the active electron needs to be orthogonalized only with the d-band states. As discussed at the end of the preceding section, the x-ray-absorption or -emission problem will reflect the local impurity final states for transition metals on the far left-hand side of the Periodic Table and the final states of the initial solid for transition metals on the far right-hand side. Thus, this theory predicts that in x-ray absorption for Pt metal the hole perturbation should be neglected. However, for Ba the hole perturbation should be included. For the transition metals between these two extremes, neither the perturbed nor the unperturbed solid is appropriate, and a full many-body calculation is required for an accurate result.

VIII. SUMMARY

A discussion is given of the x-ray-absorption problem accounting for the hole perturbation similar to the HF treatment of Friedel[16] and Combescot and Nozières.[17] Particular emphasis is given to the NES where many-body effects are especially important. The appropriate one-electron states to describe this transition are those for which the final active-electron state excited directly by the electromagnetic field is orthogonal to all of the initially occupied states and the initial core state that is emptied in the transition is orthogonal to all of finally occupied states. These one-electron states are not the usual HF orbitals except in two limits.

In these two limits the many-body problem can be reduced to a one-electron calculation, namely for nearly empty or nearly full bands (or electron shells in atoms). In the former case the local impurity density of states of the final state with the core hole is appropriate, while in the latter case the density of states of the unperturbed atom is appropriate. In between these two limits the full many-body problem must be solved to obtain an accurate result close to threshold.

There is satisfying symmetry between holes in an almost full shell or band and electrons in an empty shell or band. The x-ray-absorption problem reduces to a one-electron limit in both cases, but note must be taken of the different potentials appropriate for each case. In the former the initial potential holds, while in the latter the final potential is appropriate.

With the introduction of spin, new spin-dependent effects appear in the x-ray-absorption problem mediated by the many-electron effect and activated by the core-hole potential. When the core-hole potential can be neglected the only spin-dependent effects are the usual ones that prohibit transitions to states already filled. With the introducton of the core hole perturbation the transition rate to states initially unfilled with either spin becomes spin dependent in the ferromagnet case.

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