Hole counts from X-ray absorption spectra

A. L. Ankudinov,* A. I. Nesvizhskii and J. J. Rehr

Dept. of Physics, University of Washington, Seattle, WA 98195-1560, USA. E-mail: alex@phys.washington.edu

The interpretation of X-ray absorption spectra in terms of electronic structure has long been of interest. Hole counts derived from such spectra are often interpreted in terms of free-atom occupation numbers or Mülliken counts. It is shown here, however, that renormalized-atom (RA) and cellular counts are better choices to characterize the configuration of occupied electron states in molecules and condensed matter. A projection-operator approach is introduced to subtract delocalized states and to determine quantitatively such hole counts from X-ray absorption spectra. The described approach is based on multiple-scattering theory (MST) and on atomic calculations of a smooth transformation relating the X-ray absorption spectra to local projected densities of states (LDOS). Theoretical tests for the *s* and *d* electrons in transition metals show that the approach works well.

Keywords: hole counts; Mülliken counts; electronic structure; X-ray absorption spectra; fine structure.

1. Introduction

X-ray absorption spectroscopy (XAS) directly probes the unoccupied excited states of a system. The determination of hole counts from XAS has been of interest for many years, since the XAS spectrum is directly related to the final-state angular-momentum ℓ projected density of states (LDOS). In the 1970s, the Pt white line was related to the number of *d* holes (Brown *et al.*, 1977). Later, a quantitative procedure to obtain such hole counts was proposed (Mansour *et al.*, 1984). These methods are based on a tight-binding linear combination of atomic orbitals (LCAO) picture and thus essentially give occupation numbers in terms of Mülliken counts. However, the procedure is complicated by the presence of contributions to the XAS spectra from both the localized atomic orbitals and the delocalized atomic continuum states. Their separation is typically performed with an *ad hoc* step-function subtraction of delocalized states. Also, the procedure needs an *a priori* estimate of the number of holes or the reduced matrix element for the $p \rightarrow d$ transition. Thus a better approach is desirable.

The number of holes can be calculated theoretically in several ways, as reviewed by Müller *et al.* (1998). These authors criticized cellular counts, since the separation of space into cells is ambiguous, and argued in favor of a Mülliken analysis, based on atomic orbitals. However, as discussed below, XAS from deep core levels is not sensitive to the density matrix beyond the cell boundaries and thus cannot precisely determine such Mülliken counts, which depend on the density matrix throughout the range of a given orbital. Also, the LCAO picture has a fundamental problem connected with nonzero amplitude of atomic orbitals at neighboring sites. This can be regarded as a violation of the Pauli principle (Hodges *et al.*, 1972), since the orbital tails do not satisfy the Schrödinger equation in the potential near the neighbors. As a result, the total number of such *d* electrons per site is not 10. To cope with this problem, Hodges *et al.* (1972) suggested the renormalized-atom (RA) method, which has many advantages with regard to transition-metal properties.

In the present paper, we develop a procedure to extract hole counts from XAS and compare them to directly calculated RA, cellular and Mülliken counts. Our approach is based in part on *ab initio* atomic calculations of a smooth transformation relating the XAS spectrum to the LDOS.

2. Theory

The central quantity of interest here is the electron density matrix $\hat{\rho}$. We begin with the expression for $\hat{\rho}$ within multiple-scattering theory (MST) and then outline its connection to XAS. Next we discuss the use of projection operators to obtain hole counts, *e.g.* Mülliken and RA counts, from $\hat{\rho}$ and to separate the LDOS into localized and delocalized parts. Such a separation of XAS data is ambiguous, owing to the presence of localized–delocalized cross terms.

The transformation from the XAS $\mu(E)$ to the LDOS $\rho(E)$, *i.e.* the number of electrons per unit energy, can be derived within MST (Müller & Wilkins, 1984). Starting from the 'golden rule' $\mu(E) = \sum_f |\langle f|d|c\rangle|^2 \delta(E - E_f)$, one obtains a linear relation between $\mu(E)$ and the electron-density matrix $\hat{\rho}(E)$, *i.e.* $\mu(E) = M_\Gamma \hat{\rho}(E)$, where M_Γ is a linear operator containing dipole matrix elements and final state broadening, and the density matrix is given as a sum over angular momenta $L = (\ell, m)$,

$$\hat{\rho}(\mathbf{r}, \mathbf{r}', E) = \sum_{L,L'} R_L^*(\mathbf{r})\,(\delta_{L,L'} + \chi_{L,L'})\,R_{L'}(\mathbf{r}'), \qquad (1)$$

$$\rho_\ell(E) = \sum_m \langle L\,|\,\hat{\rho}(E)\,|\,L\rangle = \rho_0(1 + \chi), \qquad (2)$$

$$\mu(E) = \sum_{i,\ell} |\langle i\,||\,p\,||\,\ell\rangle|^2 \sum_m \langle L\,|\,\hat{\rho}(E)\,|\,L\rangle = \mu_0(1 + \chi), \qquad (3)$$

where $\chi = \sum_m \chi_{L,L}/(2\ell + 1)$, and ℓ depends on the initial core orbital momentum as $\ell = \ell_c + 1$ since it represents the dominant absorption channel. To simplify the relationship between XAS and LDOS, we note that from MST both the XAS $\mu(E) = \mu_0(1 + \chi)$ and the LDOS $\rho_\ell(E) = \rho_0(1 + \chi)$ have similar decompositions in terms of the smooth atomic background μ_0 and fine structure or XAFS χ. Consequently,

$$\rho_\ell(E) = [\rho_0(E)/\mu_0(E)]\,\mu(E). \qquad (4)$$

The ratio $\rho_0(E)/\mu_0(E)$ is essentially an atomic quantity which can be calculated by any code based on MST or even appropriately modified atomic codes. Strictly speaking, both μ_0 and ρ_0 refer to embedded atomic quantities, *i.e.* the effective atomic states defined by the local molecular potential at a given site. MST is based on the separation of space into cells (Voronoi polyhedra) and thus the number of holes (or the change in the number of holes) corresponds to space-separation counts. Such a space separation is not unique and therefore one faces difficulty in interpreting the results.

Using equation (4), one can transform the experimental XAS spectrum into the normalized LDOS above the Fermi level. However, this unoccupied LDOS contains contributions both from localized atomic-like states and from delocalized atomic continuum states. A projection operator can then be used to obtain the localized contribution to the LDOS. In particular, the Mülliken count is given by projection of all occupied states onto a particular atomic orbital,

$$n_L = \sum_n^{\rm occ} |\langle \varphi_L^{\rm at}\,|\,\psi_n\rangle|^2 = \int_{-\infty}^{E_F} \langle \varphi_L^{\rm at}\,|\,\hat{\rho}\,|\,\varphi_L^{\rm at}\rangle. \qquad (5)$$

The main disadvantage of Mülliken counts is that if one sums the occupied and unoccupied 3*d* states, one obtains a total count that is different from 10, as a result of the overlap of the 3*d* orbital with orbitals centered on neighbors. Indeed, our estimate for the total

Table 1
Occupied and total (where applicable) d-electron counts determined by various methods.

The last column gives the RA hole counts from simulated X-ray absorption spectra. The discrepancy between the last two columns arises from $\Gamma_{\rm ch}$ broadening, as discussed in the text.

	Cellular	Mülliken	RA	RA holes (XAS)
Fe, $3d$	6.76	7.82	6.56	2.96
Fe, $3d$ total		10.41	9.94	
Co, $3d$	7.52	8.43	7.32	2.26
Co, $3d$ total		10.39	9.95	
Ni, $3d$	8.57	9.26	8.36	1.48
Ni, $3d$ total		10.37	9.96	
Pt, $5d_{3/2}$	3.56	4.40	3.49	0.46
Pt, $5d_{3/2}$ total		4.44	3.97	
Pt, $5d_{5/2}$	4.68	6.58	4.60	1.14
Pt, $5d_{5/2}$ total		6.81	5.94	

Mülliken d count in Fe, Co and Ni is 10.4 (Table 1). Therefore, one faces the problem of separating tail contributions from Mülliken counts to obtain physically meaningful total $3d$ counts. The situation is even worse for s and p electrons, which extend much further.

The RA method (Hodges *et al.*, 1972) has been proposed to overcome the above difficulty. In this method, each atomic orbital is set to zero outside a given radius R_0, and is multiplied by a constant factor inside to recover unit normalization. The RA states are therefore better approximations to embedded atom states inside a cell. Also, the wave functions used in the projection operator become essentially orthonormal to one another and the tail contribution is much smaller. The RA counts thus overcome the problem of nonorthogonality with the LCAO method, and also justify the use of the MST formula $\rho_\ell = \rho_0(1 + \chi)$. The error in total RA count for occupied and unoccupied states was found to be an order of magnitude smaller for each d_j subshell than the corresponding Mülliken count (Table 1). Our calculations were performed with the self-consistent real-space multiple-scattering code *FEFF*8 (Ankudinov *et al.*, 1998). The total number of $3d$ electrons obtained with RA counts is 9.95 for Fe, Co, Ni and an integration up to 100 eV above the edge. The $4s$ RA count is 1.90 for all tested cases, with integration up to 400 eV. The error mostly arises from inaccuracy of our grid for the integration to that high energy. Thus, with the RA method one can easily transform hole counts to meaningful electron counts and this transformation is valid for localized d and f electrons, as well as for highly delocalized s and p electrons.

The RA counts depend on the choice of the embedded atomic radius R_0. The most natural choice is that for which the total count for occupied and unoccupied d states is equal to 10. Thus unlike the ambiguous cellular counts, the RA method fixes the radius of cells. The present work shows that this radius is very close to the Norman radius r_N, *i.e.* the radius for which the net charge enclosed is the atomic number (Norman, 1974). With such a definition of a cell, both s and d total counts per site are simultaneously close to the numbers expected from the Pauli principle. Charge transfer also has a natural definition as the net charge within the Norman sphere, which can be separated unambiguously into s, p, d and f electron contributions.

Table 1 summarizes our results for d-electron counts. The first three columns show the occupation numbers for cellular, Mülliken and RA counts. All of them show an expected change of about one d electron from Fe to Co and from Co to Ni. The cellular and RA counts are very close to each other, while the Mülliken count is about one d electron larger. The fractional counts can be interpreted as the wave function being a mixture of d^ns and d^{n+1} states. Note that the RA counts are much closer to those expected from atomic multiplet calculations, where Ni is regarded as having a d^8 configuration (de Groot, 1994). For Pt we find that the calculated ratio of $d_{5/2}$ holes to $d_{3/2}$ holes is 2.8, in agreement with the value of 2.9 calculated by Mattheiss & Dietz (1980), thus updating an earlier estimate (Brown *et al.*, 1977). The total number of d holes for Pt according to the RA count is 1.8, which is also consistent with the results of Mattheiss & Dietz (1980).

Table 2
Occupied (cellular and RA) and total (RA) s-electron counts determined by the cellular and renormalized-atom methods.

The total RA number is obtained by integration up to 400 eV above the Fermi level.

	Cellular	RA	RA total
Fe, $4s$	0.61	0.61	1.90
Co, $4s$	0.62	0.61	1.90
Ni, $4s$	0.63	0.63	1.90
Pt, $6s$	0.73	0.72	1.90

Table 2 presents the s-electron counts determined by the cellular and RA methods. We could not make a reliable estimate of the Mülliken counts in this case, since the $4s$ orbital extends significantly beyond the nearest-neighbor distance. Note that for s electrons, the occupied RA and cellular counts are also practically equal. The RA total count is 1.9 for all cases, which shows that the RA method works well with highly non-localized s and p orbitals.

3. RA counts from XAS

In this section we describe a procedure to obtain hole counts from XAS and apply it to a theoretically calculated XAS spectrum. Such a theoretical test is necessary, both to check the validity of the procedure and also to estimate the possible systematic error of the method. For example, in theoretical calculations, one can include or exclude the $\ell \rightarrow \ell - 1$ transition, and thus estimate the error in hole count caused by its inevitable presence in the measured signal.

In order to separate the localized and continuum contributions, it is natural to use the projection operator $P_{\rm at}$ which projects onto a particular atomic orbital (free or renormalized atom), *i.e.* $\hat{P}_{\rm at} = |\varphi_{\rm at}\rangle\,\langle\varphi_{\rm at}|$. In theoretical calculations, it is also possible to project onto any particular orbital character: *e.g.* to atomic t_{2g} or e_g orbitals. These orbitals result from splitting of d states by a cubic crystal field, and their occupation and ordering is often used to explain properties of $3d$ elements. However, such a projection cannot be performed for an experimental spectrum. Within the dipole approximation, only six irreducible operators can be extracted from polarization-dependent XAS (Ankudinov & Rehr, 1995) and the number of holes is one of them. A direct separation of the XAS spectrum into localized (*i.e.* projected atomic) and delocalized (*i.e.* continuum) parts cannot be made unambiguously. If the projection operator is used to separate the final state wave function, the XAS spectrum can be expressed as

$$\mu \propto \langle\, i\,|\varepsilon\cdot\mathbf{r}\,|\,\psi_{\rm loc}+\psi_{\rm cont}\,\rangle|^2 = \mu_{\rm loc}+\mu_{\rm cont}+\mu_{\rm cross},$$

where the cross term is nonzero. Previous procedures (Brown *et al.*, 1977) ignore $\mu_{\rm cross}$. But the cross term has the largest contribution exactly where localized and delocalized contributions are comparable and the *ad hoc* separation of $\mu_{\rm cross}$ or its neglect can lead to erroneous results. In contrast to XAS, the separation of LDOS into localized atomic and continuum parts is completely unambiguous. By substituting $\hat{\rho}(E) = \hat{P}_{\rm at}\hat{\rho}(E) + (1 - \hat{P}_{\rm at})\hat{\rho}(E)$ in equation (1) for the density matrix, we can decompose the total LDOS $\rho_\ell(E)$ into localized and delocalized parts:

$$\rho_\ell(E) = \rho_{\rm loc}(E) + \rho_{\rm cont}(E).$$

In this case, the cross term is exactly zero, as a result of the definition of the projection operator.

The projection operator acts only on the radial part in equation (1) and both the localized and the delocalized contributions should have the same χ, which is, therefore, the same as for XAS. Thus one can transform the XAS spectrum directly into the localized part of the LDOS using atomic ratios:

$$\rho_{\rm loc}(E) = \frac{\rho^0_{\rm loc}(E)}{\rho^0(E)}\frac{\rho^0(E)}{\mu^0(E)}\mu(E) = \frac{\rho^0_{\rm loc}(E)}{\mu^0(E)}\mu(E). \qquad (6)$$

This equation provides the basis for our projection-operator procedure to obtain the occupied electron configuration counts from experimental XAS. Thus, one simply multiplies the normalized experimental XAS data by the theoretically calculated atomic-like ratio $\rho^0_{\rm loc}(E)/\mu^0(E)$ to obtain the contribution to the LDOS from localized electrons. The integral over energy of this contribution gives the number of holes in the electron configuration for a particular orbital character. Unfortunately, because of the dipole selection rule, the determination of the number of *s* holes, especially when the *d* shell is partially occupied, is not reliable. However, one can obtain from XAS an estimate of the number of *p*, *d* and *f* electrons in terms of RA counts.

Our procedure, which can be generalized for various experimental applications, has several steps, as follows.

(i) Subtract the pre-edge contribution and (if possible) separate edges. This was not necessary in our theoretical tests since one can calculate the L_2 and L_3 edges separately.

(ii) Normalize experimental XAS background about 50 eV above the edge to that theoretically calculated or measure the absorption coefficient in absolute units. This step was also not needed in our theoretical tests.

(iii) Transform the XAS spectrum into LDOS projected onto a particular renormalized atomic orbital using equation (6).

(iv) Integrate to obtain the RA hole count for the electron configuration.

(v) Multiply by a theoretical factor to correct for lifetime broadening effects.

For final *d* and *f* states, one can obtain separately the number of electrons with total angular momentum $j = \ell \pm 1/2$ when the corresponding $L_{2,3}$ or $M_{4,5}$ edges are well separated. Only the total number of *p* electrons can be estimated from *K* and L_1 edges.

Numerical tests of the first four steps of this approach for 3*d* transition metals show that typically the number of holes obtained from XAS is underestimated by about 10–20%. The main source of this reduction stems from the strong effect of core-hole lifetime broadening on white lines, as verified by observing that the reduction vanishes when $\Gamma_{\rm ch}$ is reduced to zero. This also provides a way of calculating the reduction factor of step (v). To understand the effect, suppose that all states below E_0 are localized and all states above are delocalized. Then as a result of the core-hole broadening, the localized LDOS will leak above E_0, while the delocalized will leak below E_0. However, since for the case of white lines the localized LDOS is larger, the integration to the ideal localized–delocalized separation energy will give a reduced number of localized states. The theoretically calculated reduction factor for the *d*-hole count due to $\Gamma_{\rm ch}$ broadening is 1.14 for Fe, 1.16 for Co, 1.07 for Ni, 1.04 for Pt $d_{3/2}$, and 1.18 for Pt $d_{5/2}$ holes.

In the analysis of X-ray magnetic circular dichroism (XMCD), one can avoid the use of such a reduction coefficient if the goal is to obtain spin and orbital moments in terms of cellular counts (Nesvizhskii *et al.*, 2000). In that case one can use the smooth ratio of equation (4) instead of equation (6). As one can see from Tables 1 and 2, the cellular counts within a Norman sphere are very close to the RA counts. Their agreement means that the shape of *d* and *s* orbitals practically does not change within the Norman radius. The smoothness is important since, for example, multiplet effects can lead to an additional splitting of the order of 5 eV. But with a smooth ρ_0/μ_0, the error in hole counts caused by this effect is expected to be smaller than for the transformation to the localized LDOS $\rho_{\rm loc}/\mu_0$, which has a significant rise at the border between localized and delocalized states. As one can see from the hole-count calculations, such a procedure can lead to a significant error.

In Fig. 1, we demonstrate the separation of XAS data into localized and delocalized contributions. The directly calculated total XAS spectrum is represented by a solid line. The delocalized contribution is obtained by transforming XAS data into LDOS, subtracting the localized LDOS contribution and transforming the delocalized LDOS back to an XAS spectrum. As expected, at high energies, the delocalized contribution dominates, while near the edge, practically all absorption comes from the localized part. For comparison, we also present an *ad hoc* two edge-step modeling of the delocalized contribution, which is often employed in XMCD analysis and clearly gives a poor approximation to the unambiguous delocalized contribution calculated by *FEFF*8.

In the procedure of Brown *et al.* (1977), the difference between Pt L_2 and L_3 XAS is interpreted as solely caused by the localized contribution to the XAS data. If this were the case, the division of the difference signal by the square of the $p \rightarrow d$ matrix element would yield the difference in the number of $d_{3/2}$ and $d_{5/2}$ holes. However, this analysis must be modified for the presence of the cross term, because the difference in $d_{3/2}$ and $d_{5/2}$ occupation will show up both in localized and in cross-term contributions. Our procedure specifically avoids the cross-term problem by transforming XAS spectra into LDOS, and hence yields, we believe, a more reliable analysis of occupation numbers.

Fig. 2 represents the application of this procedure to Pt $L_{2,3}$ data. The *FEFF*8 calculations agree well with Pt XAS, as shown by

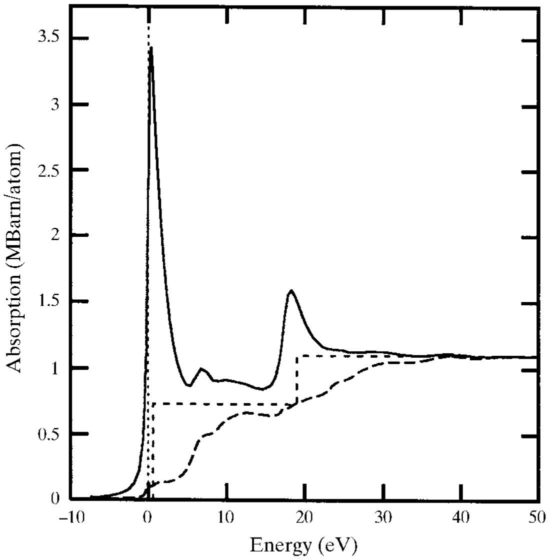

Figure 1
Separation of the Ni XAS spectrum (solid line) into delocalized (continuum) parts (long dashes) using the procedure described in the text. The short dashes show the *ad hoc* step function representation of delocalized states in the conventional procedure.

Ankudinov *et al.* (2001, Fig. 1 therein). Even though the peak positions are not changed by our procedure, the ratio of peak intensities in the total LDOS is significantly altered compared to the XAS spectrum. The localized LDOS is mostly limited to the region of first two peaks, *i.e.* about 40 eV above the edge. By inspection, one sees that the ratio of $5d_{5/2}$ to $5d_{3/2}$ hole counts should be around 3.

Several many-electron effects may be important for the extraction of hole counts. For example, the usual dipole matrix elements, which are not corrected with respect to local screening of the X-ray electric field, are not accurate for most $3d$ metals, as the screening effect modifies the L_3/L_2 white-line ratio (Schwitalla & Ebert, 1998). Our procedure can account for this effect by including screening in the calculated μ_0. Multiplet splitting and multi-electron excitations are neglected in our single-particle derivation. However, such effects are not expected to change the counts significantly, since such splitting is expected to transfer spectral density only within about 5 eV of the absorption edge, where the ratio is smooth. Thus one expects a greater cancellation of these effects in equation (4) than in equation (6). Equation (4) can be used to obtain S_z and L_z from XMCD, but is inapplicable to the problem of hole determination.

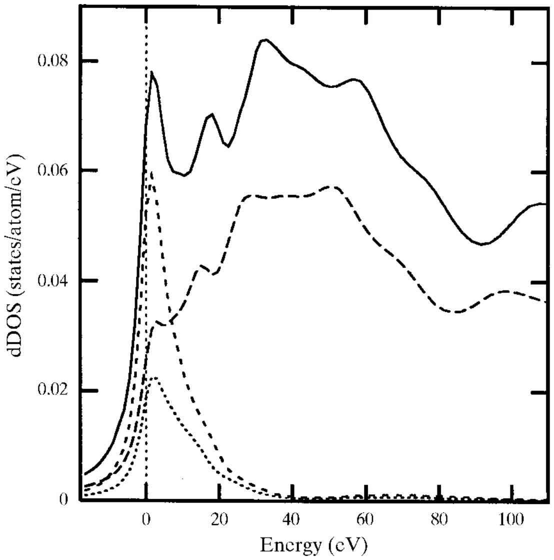

Figure 2
Pt d LDOS obtained from L-edge XAS using the transformations described in the text: total $d_{5/2}$ LDOS (solid line), total $d_{3/2}$ LDOS (long dashes), localized $d_{5/2}$ LDOS (short dashes), and localized $d_{3/2}$ LDOS (dots).

4. Conclusions

The present work updates previous techniques for hole-count determination. We have found that RA counts are more appropriate than Mülliken counts for the interpretation of both electronic structure and XAS. Noteworthy is the fact that occupied RA counts are very close to cellular counts when the chosen cell has the volume of a Norman sphere. We have introduced a quantitative technique, based on the use of projection operators, to subtract atomic delocalized states and hence to determine the electron configuration, in terms of RA counts, from XAS. In this approach, one transforms the measured XAS spectrum to a localized projected LDOS, using a calculated atomic ratio $\rho^0_{\rm loc}/\mu^0$ and a calculated correction factor to account for lifetime broadening. As a result, physically meaningful p, d and f counts can all be obtained from experimental XAS data to an accuracy of a few percent.

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