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New high-energy approximation for x-ray-absorption near-edge structure

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Spherical-wave corrections in x-ray-absorption fine structure (XAFS) are incorporated using a novel high-energy approximation which replaces the plane-wave approximation and is found to be in excellent agreement all the way to the absorption edge. The single-scattering theory of XAFS is recovered in terms of distance-dependent backscattering amplitudes. Application to the K-shell XAFS of Cu yields results in close agreement with the corresponding exact treatment. Multiple-scattering contributions in XAFS and spherical-wave corrections in angle-resolved photoemission are treated similarly.

Extended x-ray-absorption fine structure (EXAFS) is a valuable technique for determining local atomic structure in molecules and solids.[1] The usual approximations in EXAFS analysis[1-4] are the small-atom, plane-wave approximation (PWA), and the restriction to single-scattering paths. Recent evidence[5] suggests that the discrepancy between this EXAFS theory and experiment in x-ray-absorption near-edge structure (XANES) is due primarily to the failure of the PWA. This is corroborated here. It has also been thought that correcting the PWA requires exact calculations. We show, in fact, that the appropriate high-energy approximation is not the PWA, but rather an asymptotic theory which is almost as simple that includes spherical-wave corrections.[6] This approximation is termed the spherical-wave approximation (SWA). We find that the SWA yields excellent agreement with exact calculations all the way to the absorption edge, thereby giving a unified treatment of XAFS, i.e., both EXAFS and XANES. As recognized previously[2] the exact theory can be recovered by replacing the backscattering amplitude $f(\pi)$ in the PWA EXAFS formula [Eq. (1) below] with an effective, distance-dependent backscattering amplitude, $\tilde{f}(\pi,R)$. Here we give an explicit expression for $\tilde{f}(\pi,R)$ in terms of atomic phase shifts, together with an accurate SWA formula. The smooth dependence on $1/R$ permits $\tilde{f}(\pi,R)$ to be tabulated for analysis purposes. Similar SWA's are developed for multiple-scattering terms in XAFS and for spherical-wave corrections in photoemission. A model calculation of the K-shell XAFS spectrum for Cu is presented as an initial application.

Before describing our approximation, we briefly recall the results of single-scattering XAFS theory. For simplicity we restrict our attention in this paper to K-shell absorption in polycrystalline materials. The normalized XAFS spectrum is defined in terms of the x-ray-absorption coefficient μ as $\chi(E)=(\mu-\mu_0)/\mu_0$, where μ_0 is the atomiclike background. The PWA formula for $\chi(E)$ is[4]

$$\chi(E)=-\sum_{\mathbf{R}}\frac{|f(\pi)|}{kR^2}\sin[2kR+2\delta_1(0)+\Phi]e^{-2R/\lambda}e^{-2\sigma^2k^2}. \tag{1}$$

Here the sum is over scattering sites $\mathbf{R}$ with backscattering amplitude $f(\pi)=|f(\pi)|e^{i\Phi}$, $k=\sqrt{\varepsilon}$ is the photoelectron wave number (in atomic Rydberg units, $\hbar=2m=e^2/2=1$), $\varepsilon=E-E_0$ is the energy relative to the muffin-tin zero in Rydbergs and $\delta_1(0)$, the $l=1$ phase shift of an absorbing atom at $\mathbf{R}=0$. The exponential decay factors are due to the mean free path λ and to the Debye-Waller factor (assuming small disorder), respectively.

The starting point for our SWA is the exact single-scattering XAFS formula[2,3]

$$\chi(E)=-\mathrm{Im}e^{2i\delta_1(0)}\tfrac{1}{3}\sum_{\bar{m},L,\mathbf{R}}G_{1\bar{m},L}(\mathbf{R})t_L(\mathbf{R})G_{L,1\bar{m}}(-\mathbf{R}), \tag{2}$$

where $G_{L,L'}(\mathbf{R})$ is the dimensionless free propagator in an angular momentum $L\equiv(l,m)$, and site $\mathbf{R}$ basis, and $t_L(\mathbf{R})\equiv e^{i\delta_l}\sin\delta_l$ is the dimensionless atomic t matrix at site $\mathbf{R}$. Formally $G_{L,L'}$ is given by the expansion[3]

$$G_{L,L'}(\mathbf{R})=4\pi\sum_{L''}\langle Y_LY_{L''}|Y_{L'}\rangle h_{L''}^{+}(\mathbf{R}), \tag{3}$$

where $h_L^+(\mathbf{R})\equiv i^l h_l^+(\rho)Y_L(\hat{R})$, h_l^+ is a spherical Hankel function, and $\rho=kR$. Carrying out the L sums in Eq. (2) using Eq. (3) and 3-j symbol identities gives the Müller-Schaich XAFS formula.[7]

The PWA theory can be derived by using an extreme-

high-energy limit for the G's in Eq. (2). Our SWA consists of replacing this form with a better high-energy approximation, based on rapidly convergent, asymptotic expansions of modulus and phase similar to the WKB approximation, which takes into account the centrifugal barrier seen by the photoelectron. We then obtain an approximate XAFS formula that has exactly the same form as Eq. (1), but with $f(\pi)$ replaced by $\tilde{f}(\pi,R)$.

Our derivation is summarized as follows; details will be presented elsewhere.[8] Choosing the z axis along the R direction, we may define $G_{L,L'}$ in terms of its *extreme*-high-energy behavior and a dimensionless correction factor $g_{ll'}^{(|m|)}(\rho)=g_{l'l}^{(|m|)}(\rho)$ as

$$G_{L,L'}(\mathbf{R})=4\pi Y_{l0}^{*}(\hat{\mathbf{R}})Y_{l'0}(\hat{\mathbf{R}})\frac{e^{i\rho}}{\rho}g_{ll'}^{(|m|)}(\rho)\delta_{m,m'}\,, \qquad (4)$$

$$\mathbf{R}=\pm R\hat{\mathbf{z}}\,.$$

In the extreme-high-energy limit, i.e., $\rho\gg l(l+1)+l'\times(l'+1)$, $g_{ll'}^{(m)}(\rho)\rightarrow\delta_{m,0}$ as $\rho\rightarrow\infty$. If one uses this limit to evaluate Eq. (2), the conventional PWA EXAFS formula is recovered. Unfortunately, this extreme limit cannot be achieved for all l and is therefore not the appropriate high-energy limit for EXAFS. The physical reason is that the centrifugal barrier introduces a phase correction in each partial wave of order $l(l+1)/kR$ which is not negligible. To see this note that l-wave scattering is only important when the turning point is smaller than the muffin-tin radius, i.e., $\sqrt{l(l+1)}/k\leq R_{\mathrm{MT}}$. Hence $l(l+1)/kR\leq\sqrt{l(l+1)}R_{\mathrm{MT}}/R$, but this is not negligible for all significant l, especially for small R. Although this phase error grows with l, t_l becomes smaller, and hence the EXAFS still converges to the PWA at sufficiently high energies. Using the PWA together with an *ad hoc* energy shift, such phase shifts can be accounted for only in some average sense, since this prescription introduces an l-independent phase correction varying as $1/k$. However, a significant improvement at all energies results by using our SWA as we now show.

We find it advantageous to calculate $g_{ll'}^{(m)}(\rho)$ in two ways, depending on whether l or l' is small or large: (1) For small l or l', the number of nonvanishing coefficients $\langle Y_L Y_{L''} Y_{L'}\rangle$ in Eq. (3) is small, so $G_{L,L'}$ reduces to a sum over a small number of spherical Hankel functions. For example, for $l=1$ (i.e., for single-scattering, K-shell absorption), $g_{l1}^{(m)}(\rho)$ is given exactly by

$$g_{l1}^{(0)}(\rho)=\frac{(l+1)c_{l+1}(\rho)+lc_{l-1}(\rho)}{2l+1}\,, \qquad (5a)$$

$$g_{l1}^{(1)}(\rho)=\left[\frac{l(l+1)}{2}\right]^{1/2}\frac{c_{l+1}(\rho)-c_{l-1}(\rho)}{2l+1}\,, \qquad (5b)$$

where $c_l(\rho)$ are the correction factors to limiting high-energy form of spherical Hankel functions, i.e., $h_l^{+}(\rho)\equiv i^{-l}(e^{i\rho}/\rho)c_l(\rho)$. Replacing the exact $c_l(\rho)$ with that from the leading terms of asymptotic expansions of the *modulus and phase* of $h_l^{+}(\rho)$, we obtain[9]

$$c_l(\rho)\equiv g_{l0}^{(0)}(\rho)\approx\left[1+\frac{L^2}{2\rho^2}\right]^{1/2}e^{iL^3/2\rho}\,, \qquad (6)$$

where $L^2\equiv l(l+1)$. Note that when l-wave scattering is significant (i.e., t_l non-negligible), $l/\rho<R_{\mathrm{MT}}/R<1$, which implies the high-energy limit. Subsequent terms are smaller than those retained in Eq. (6) and can be neglected. The dominant spherical-wave correction is seen to be the non-negligible phase shift $L^2/2\rho$. Formulae similar to Eqs. (5a) and (5b) can be developed for larger l or l', but they involve an intermediate l sum and hence become progressively more cumbersome.[7] Thus we adopt an alternative procedure: (2) For general l or $l'\neq1$ (i.e., for higher shells L_2, L_3, M, etc., and for multiple-scattering corrections) we develop[8] new asymptotic expansions for the modulus and phase of $g_{ll'}^{(m)}(\rho)$, starting from a more general integral equation for $G_{L,L'}$. The leading terms are

$$g_{ll'}^{(0)}(\rho)\approx\left[1+\frac{L^2+L'^2}{2\rho^2}\right]^{1/2}e^{i[L^2+(L')^2]/2\rho}J_0\left[\frac{L^2L'^2}{\rho^2}\right]^{1/2}\,, \qquad (7a)$$

$$g_{ll'}^{(1)}(\rho)\approx i\left[\frac{L^2L'^2}{\rho^2}\right]^{1/2}e^{i[L^2+(L')^2-2]/2\rho}\,, \qquad (7b)$$

where J_0 is the Bessel function of order zero. For nonshadowing multiple-scattering contributions to $\chi(E)$, one also needs propagators for general directions $\hat{\mathbf{R}}\neq\hat{\mathbf{z}}$. Applying rotation matrices to Eq. (3), and keeping only the dominant term, we find

$$G_{L,L'}(\mathbf{R})\approx4\pi Y_L^{*}(\hat{\mathbf{R}})Y_{L'}(\hat{\mathbf{R}})\frac{e^{i\rho}}{\rho}g_{ll'}^{(0)}(\rho)\,. \qquad (8)$$

The leading corrections to Eq. (8) are proportional to $g_{ll'}^{(1)}(\rho)$.

An exact single-scattering XAFS equation can now be obtained by using Eqs. (5a) and (5b) in (4) and summing over m. The result now has the same form as Eq. (1), except that the backscattering amplitude and phase Φ are replaced by $\tilde{f}(\pi,R)=|\tilde{f}(\pi,R)|e^{i\Phi(R)}$, where

$$\tilde{f}(\pi,R)=\frac{1}{k}\sum_l(-1)^l(2l+1)t_l\times\left[\frac{(l+1)c_{l+1}^2(kR)+lc_{l-1}^2(kR)}{2l+1}\right]\,. \qquad (9)$$

As $R\rightarrow\infty$ the term in brackets in Eq. (9) becomes unity, and $\tilde{f}(\pi,R)$ reduces to $f(\pi)$. We emphasize that this result is exact. Our approximate (SWA) expresssion for $\tilde{f}(\pi,R)$ results by replacing $c_l(\rho)$ in Eq. (9) with the asymptotic formula in Eq. (6) and thereby avoids the explicit calculation of spherical Hankel functions.

We have applied our SWA to a model calculation of the K-shell XAFS of fcc Cu. The potential and lattice constant used are those of the self-consistent linear augmented-plane-wave band-structure calculations of Ref. 10. Thus the core-hole potential is neglected, a reasonable approximation for metallic Cu. To achieve good convergence, we used $0\leq l\leq19$ phase shifts and 34 shells of neighbors. Finally, the resultant spectrum was Lorentzian broadened using a constant imaginary potential,[2] $\eta=4$ eV. To illustrate the importance of spherical-wave effects we plot in Fig. 1 the amplitude and phase of the effective backscattering amplitude $\tilde{f}(\pi,R)$ given by Eqs. (9) and (6); this is compared with the usual definition,

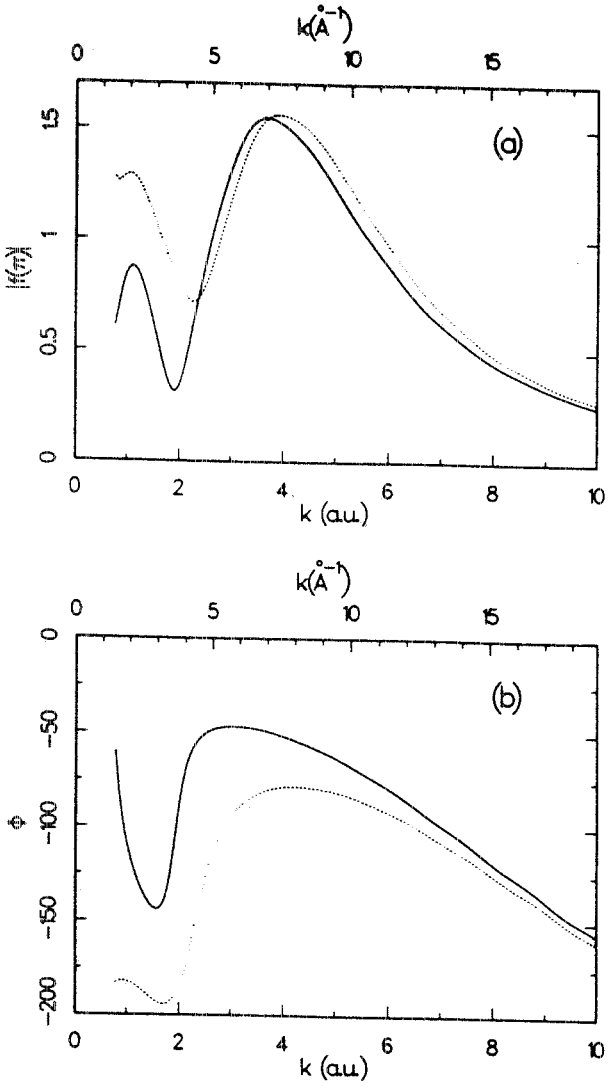

FIG. 1. (a) Modulus and (b) phase of the effective backscattering amplitude $\tilde{f}(\pi,R)$ vs wave number k beyond k_F for the first (solid line) and fourth (dotted line) neighbors in Cu ($R_1=4.80$ and $R_4=2R_1=9.60$ bohrs) and for the standard backscattering amplitude, $f(\pi)=\tilde{f}(\pi,\infty)$ (dashed curves). For other R, $\tilde{f}(\pi,R)$ is given approximately by interpolation in $1/R$.

$f(\pi)=\tilde{f}(\pi,\infty)$. At $k\approx 10$ a.u., $l_{\max}$ was increased to 29 for better convergence. Note that there are sizable corrections to the amplitude and phase at low energies. Since the phase difference $\tilde{\Phi}(R)-\Phi$ is slowly varying at high energies, the PWA can eventually approximate the SWA, but it requires an (unphysical) *ad hoc* energy shift to do so.

In Fig. 2 we compare our SWA result for $\chi(E)$ both with corresponding exact results, and with band-structure calculations.[10] We have included, in addition to single-scattering terms, multiple-scattering contributions due to shadowing[2,7] for the fourth, eighth, and twelfth shells. Note that the SWA and the exact results are practically indistinguishable all the way to the edge (≈ 7 eV for Cu). Thus the high-energy regime where the SWA is valid is indeed reached rapidly, i.e., within several eV of the muffin-tin zero which is comparable to threshold energies. Note too (cf. Ref. 7) that XAFS theory agrees fairly well

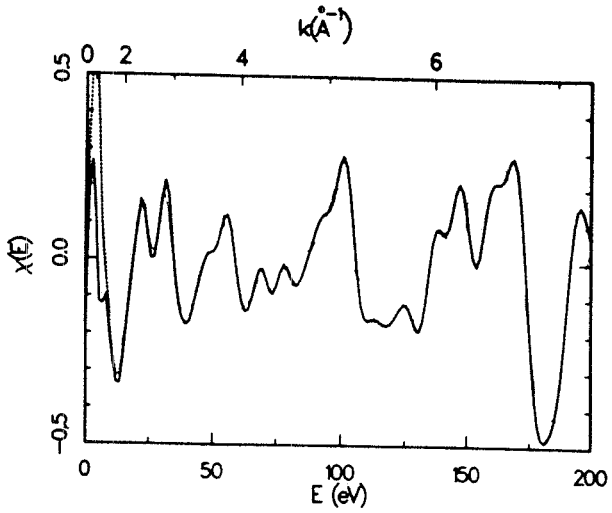

FIG. 2. K-shell EXAFS spectrum $\chi(E)$ for Cu as calculated using SWA formulae for single-scattering and shadowing corrections (solid line), the corresponding exact formulae (Ref. 7) (dashed line), and the LAPW band-structure approach (Ref. 10) (dotted line). All spectra are broadened by a Lorentzian of half-width $\eta=4$ eV. The absorption edge begins at ≈ 7 eV.

with band-structure calculations for $\varepsilon<10$ Ry. However, significant deviations are evident in the EXAFS region beyond about 10 Ry, which cannot be fully explained by shadowing corrections.[2] We will discuss general (i.e., type-1 and type-2) multiple-scattering corrections[5] using the SWA formulae Eqs. (7a), (7b), and (8) in a subsequent paper.[8]

Finally, we note that analogous SWA can be developed for other physical processes. For example, angle-resolved photoemission[11,12] also exhibits EXAFS-like oscillatory structure and spherical-wave corrections are substantial. The intensity of a beam of outgoing p waves at large distances $\mathbf{R}_0=R_0\hat{\mathbf{k}}$, with interfering single-scattering contributions from scatterers at sites $\mathbf{R}$, is given by $I\propto|\hat{\epsilon}\cdot\hat{\mathbf{k}}+\sum_{\mathbf{R}}\hat{\epsilon}\cdot\hat{\mathbf{R}}(\tilde{f}(\theta,R)/R)e^{ikR(1-\cos\theta)}|^2$. Here the angular dependence of the outgoing p wave is $Y_{10}(\hat{\mathbf{r}})\sim\hat{\epsilon}\cdot\hat{r}$, $\theta=\cos^{-1}(\hat{\mathbf{R}}\cdot\hat{\mathbf{k}})$ is the scattering angle; and $\tilde{f}(\theta,R)$ is the effective scattering amplitude given by

$$\tilde{f}(\theta,R)=\frac{1}{k}\sum_l(2l+1)t_lP_l(\cos\theta)g_{l1}^{(0)}\ , \qquad (10)$$

where P_l is the Legendre polynomial of order l. Our expression for $\tilde{f}(\theta,R)$ differs from the PWA formula[11] by the factor $g_{l1}^{(0)}(p)$; a SWA results by evaluating (10) using Eqs. (5a) and (6). Applications of Eq. (10) will be given separately.[13]

In summary, we have introduced a new, efficient high-energy approximation of XAFS which replaces the PWA yet is accurate all the way to the absorption edge. Remarkably, XANES can be treated as a high-energy phenomenon. This was not recognized previously because of the failure to incorporate spherical-wave effects correctly at high energies. The appropriate limit leads to simple, analytical forms for the electron propagators, even when spherical-wave effects are important. Compared to the exact formulae, our SWA is simpler and hence faster compu-

tationally with little loss of accuracy. These advantages are especially important for multiple-scattering contributions; for example, for the calculations presented here including shadowing, the SWA is more efficient by a factor of about 20 on a CRAY-1A computer. By comparison,[12,14] other formulations seem unnecessarily complicated; also, due to various uncertainties in the theory (e.g., muffin-tin corrections, and many-body effects) even the "exact" treatments are only approximate at low energies. The standard EXAFS formula can be recovered and extended by using, in place of $f(\pi)$, the effective scattering amplitude $\tilde{f}(\pi,R)$ defined in Eq. (9). Because $\tilde{f}(\pi,R)$ is an *atomic* quantity and is smoothly varying in $1/R$, it is conveniently tabulated. We plan to do so for a number of elements.[8] Finally, our approach yields a unified treatment of XAFS, valid for both EXAFS and XANES. Because it permits XAFS data to be analyzed all the way to the edge using standard techniques,[1] it should improve the utility of XAFS for determinations of local atomic structure, particularly for low-Z atoms and/or large disorder.

Note added. McKale, Knapp, and Chan[15] have recently calculated backscattering amplitudes $\tilde{f}(\pi,R)$ based on the exact Müller-Schaich formula [cf. Eq. (9)], confirming their utility in practice.

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