

Invited Paper

Theory of High-energy Photoemission

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We theoretically study some specific features in high-energy photoemission. At first we discuss the breakdown of the electric dipole approximation. The relative importance of electric quadrupole and magnetic dipole transitions can be estimated by the photoelectron angular distribution. Next we discuss the recoil effects exciting phonon modes around an X-ray absorbing atom. In the single-site approximation where elastic scatterings from neighboring atoms are completely neglected, we have free atom recoil energy shift without any further approximation within the harmonic approximation. Additional effects like photoelectron diffraction are also studied. Finally we discuss overall spectral features of high-energy XPS spectra by using an exponential form. We explicitly calculate intrinsic and extrinsic losses on the basis of quantum mechanics, which naturally gives their interference term.

1. Introduction

In contrast to soft X-ray photoelectron spectroscopy (XPS), high-energy XPS has been employed to study bulk electronic structures.

High-energy XPS spectra provide new information, however they raise some questions about recoil effects [1, 2, 3] and breakdown of the electric dipole (E1) approximation [1, 4, 5]. In this paper we discuss some theoretical problems inherent to high-energy XPS spectra. Detailed discussion on the non-dipole effects and recoil effects has been given in our previous papers, we, however, add some comments here. Furthermore some discussion on overall spectral features of high-energy XPS spectra has been given on the basis of a pure quantum theory. In particular we describe a new method to take both elastic and inelastic (extrinsic+intrinsic) losses into account.

2. Nondipole Effects

Electron-photon interaction operator is usually expanded as

$$\begin{aligned}\Delta &= \exp(iqx)p_z \\ &= p_z + iqx p_z - q^2 x^2 p_z / 2 + \dots \\ &= p_z + \frac{iq(xp_z + p_x z)}{2} - \frac{iqL_y}{2} \dots\end{aligned}\quad (1)$$

where X-ray photons propagate in the x-direction with linear polarization in the z-direction. In the soft X-ray region, the length of photon propagation vector q is much smaller r_c^{-1} than (r_c is the size of the core orbital from which a photoelectron is excited). In this case we can use the E1 approximation. In the analyses of high-energy XPS spectra the second (E2) and the third (M1) terms of eq.(1) have finite contribution since q is large enough. More sophisticated expansion of the operator Δ is irreducible tensor expansion

$$\Delta = 4\pi \sum_L i^l j_l(qr) Y_L^*(\hat{\mathbf{q}}) Y_L(\hat{\mathbf{r}}) p_z, \quad (2)$$

Numerical calculations show that the conventional power series expansion (1) works so well even up to quite high energy (~ 10 keV) [2].

How can we estimate the relative importance of E2 and M1 transitions? Let consider photoelectron angular distribution excited from deep 1s or 2p core orbitals in free atoms (Ne, Ar, ..). General formula to describe the angular distribution is well known as Cooper formula in atomic physics [6].

$$I(\theta) = \frac{\sigma}{4\pi} \left[1 + \beta P_2(\cos \theta) + (\delta + \gamma \cos \theta) \sin \theta \cos \phi \right]. \quad (3)$$

where σ is the total cross section. In the E1 approximation we have $\delta = \gamma = 0$. The asymmetric parameter β is in the range $-1 \leq \beta \leq 2$, and $\beta = 2$ for the photoemission from a deep s orbital. In the E1 approximation, we expect symmetric angular distribution around $\theta = 0^\circ$, whereas the nondipole effects give rise to asymmetric angular distribution. Both theoretical calculations and experimental results show these asymmetries even at ε_k (photoelectron energy) < 1 keV.

Can we safely use the expansion (1) for the analyses of photoemission from extended levels? Typically $qr_c \gg 1$ is satisfied in these cases so that we are afraid of complete breakdown of the expansion. We assume that the initial level ϕ_i can be written as linear combination of atomic orbital

$$\phi_i(\mathbf{r}) = \sum_{\alpha} C_{i\alpha} \chi_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}) \quad (4)$$

where χ_{α} is α th atomic orbital (AO) centered on the site \mathbf{R}_{α} and $C_{i\alpha}$ is the expansion coefficient. In the lowest order approximation where elastic scatterings are completely neglected, the photoemission intensity is given by

$$I(\mathbf{k}) \propto I(\mathbf{k})_i^1 + I(\mathbf{k})_i^2 \quad (5)$$

where I^1 and I^2 are the one- and two-center terms. The former describes the photoemission excited from the same atomic site, whereas the latter the interference between two waves coming from different sites. The explicit formulas for them are written by

$$I(\mathbf{k})_i^1 = \text{Re} \left[\sum_{\alpha\alpha'} C_{i\alpha}^* C_{i\alpha'} \sum_{LL'} Y_L^*(\hat{\mathbf{k}}) Y_{L'}(\hat{\mathbf{k}}) \times M_{LL\alpha}^* M_{L'L\alpha'} \right], \quad (6)$$

$$I(\mathbf{k})_i^2 = \text{Re} \left[\sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \exp[i\mathbf{Q} \cdot (\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})] \times \sum_{LL'} Y_L^*(\hat{\mathbf{k}}) Y_{L'}(\hat{\mathbf{k}}) M_{LL\alpha}^* M_{L'L\beta} \right] \times \exp[-Q^2 < \Delta_{\alpha\beta}^2 > / 2], \quad (\mathbf{Q} = \mathbf{q} - \mathbf{k}), \quad (7)$$

where AO's α and α' are on the same site, but α and β are on the different sites, \mathbf{R}_{α} and \mathbf{R}_{β} . We have used the matrix elements,

$$M_{LL\alpha} = \sqrt{2/\pi} i^{-l} \exp(i\delta_l^{\alpha}) \times \langle R_l Y_L | \Delta | R_{l\alpha} Y_{L\alpha} \rangle, \quad (8)$$

$$\chi_{\alpha} = R_{l\alpha} Y_{L\alpha}.$$

Even though the initial state is delocalized over many-atomic sites, we should only consider the phase factor $\exp[i\mathbf{Q} \cdot (\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})]$ and the DW factor $\langle \Delta_{\alpha\beta}^2 \rangle$ in eq. (7). In eq. (8) the multipole expansion (1) works so well.

The one-center term is not influenced by the nuclear vibrations, but the two-center term is strongly influenced by them. The DW factor is the same as those used in EXAFS analyses, and is in the order of 10^{-2} a.u.² We thus have $\exp(-Q^2 < \Delta_{\alpha\beta}^2 > / 2) \approx 0.15$ at $\varepsilon_k = 5$ keV. In addition to this, we can expect that random cancellation works in the sum over α and β in eq. (7), which allows us to neglect the two center term $I(\mathbf{k})_i^2$.

For randomly oriented systems we can simplify the one-center term one step further. We can apply eq. (3) even for randomly orienting polyatomic systems such as free molecules and polycrystals. The total cross section σ is now well approximated by well known Gelius formula [7, 15]

$$\sigma = \sum_{\alpha} |C_{i\alpha}|^2 \sigma_{\alpha}, \quad (9)$$

$$\sigma_{\alpha} = \sum_L |M_{LL\alpha}|^2, \quad (10)$$

where σ_{α} is the total photoionization cross section of α th AO.

3. Recoil Effects

Recent experimental work by Takata et al. clearly shows the peak shift to high binding energy side with increase of photon energy [3]. The energy shift is well explained by

$$\Delta\varepsilon_k = -k^2/2M_A, \quad (11)$$

where M_A is the mass of an X-ray absorbing atom A . This is just free atom recoil energy shift. From physical point view, this result looks so funny because the X-ray

absorbing atom is tightly bound in the solid.

As the kinetic energies of the photoelectrons are large enough, it is sufficient to take single scatterings into account. We can also safely use the plane wave approximation for the photoelectron wave function. In this approximation we have the photoemission intensity formula as a sum

$$I(\mathbf{k})_c = I_0(\mathbf{k})_c + I_1(\mathbf{k})_c + I_2(\mathbf{k})_c \quad (12)$$

where I_0 describes the direct photoemission intensity without suffering elastic scatterings from surrounding atoms (*single-site approximation*). It can be written as

$$I_0(\mathbf{k})_c \propto \sum_{m_c} \left| \sum_L Y_L(\hat{\mathbf{k}}) M_{LLc} \right|^2 \times \int_{-\infty}^{\infty} \frac{dt}{2\pi} \exp(i\varepsilon t) D_0(\mathbf{Q}; t) \quad (13)$$

where $\mathbf{Q} = \mathbf{q} - \mathbf{k}$, and M_{LLc} is defined by eq. (8). By neglecting the Franck-Condon effects which play a minor role compared with the recoil effects as demonstrated by explicit numerical calculations [4], the correlation function D_0 is given within harmonic approximation

$$D_0(\mathbf{Q}; t) = \exp[-F(t)].$$

$$F(t) = \sum_s |\mathbf{Q} \cdot \mathbf{u}_s^A|^2 [n_s(e^{-i\omega_s t} - 1) + (1 + n_s)(e^{i\omega_s t} - 1)], \quad (14)$$

$$\mathbf{u}_s^A = \frac{\mathbf{e}(A|s)}{\sqrt{2N\omega_s M_A}}, n_s = (\exp(\beta\omega_s) - 1)^{-1}$$

where s is abbreviation of phonon momentum \mathbf{P} and its polarization λ , $s = (\mathbf{p}, \lambda)$. We designate the eigenvector $\mathbf{e}(A|s)$ with the polarization λ at the X-ray absorbing site A for the dynamical matrix with momentum \mathbf{P} . From the correlation function we can calculate the energy shift, peak width and asymmetry caused by the recoil effects [4]. The recoil energy shift in the single-site approximation thus yields

$$\Delta\varepsilon_k = - \sum_s \omega_s |\mathbf{Q} \cdot \mathbf{u}_s^A|^2 = - \frac{Q^2}{2M_A} \quad (15)$$

without reference to any approximation like Debye, Einstein approximations [9]. We can see that the simple formula (15) works for any harmonic crystals. In typical XPS experiments, $q \ll k$ is satisfied which yields the

formula (11).

In eq. (12) $I_1(\mathbf{k})_c$ describes the interference between the direct and the single scattering waves, which is explicitly written

$$I_1(\mathbf{k}) \propto 2 \sum_{m_c} \text{Re} \sum_{\alpha} \sum_{LL'} \left[Y_L^*(\hat{\mathbf{k}}) M_{LLc}^* \times \frac{\exp(ikR_{\alpha}(1 - \cos\theta_{\alpha}))}{R_{\alpha}} f_{\alpha}(\theta_{\alpha}) M_{L'Lc} \right] \times \int_{-\infty}^{\infty} \frac{dt}{2\pi} \exp(i\varepsilon t) D_1^{\alpha}(\mathbf{Q}; t), \quad (16)$$

where $f_{\alpha}(\theta_{\alpha})$ is scattering amplitude at nearby α th atom with scattering angle θ_{α} . In the harmonic approximation, we can exactly write D_1^{α} as

$$D_1^{\alpha}(\mathbf{Q}; t) = \exp[-F(t) - k^2 \langle \Delta_{\alpha A}^2 \rangle / 2] \times \exp[-\delta F(t)]. \quad (17)$$

In the above formula $F(t)$ is given by eq. (14), $\langle \Delta_{\alpha A}^2 \rangle$ is the Photoelectron Diffraction Debye-Waller factor, $\delta F(t)$ is responsible for the interference between the recoil and the DW damping. The above correlation function provides the energy shift

$$-\frac{Q^2}{2M_A} + \frac{k}{2M_A} \mathbf{Q} \cdot (\hat{\mathbf{R}}_{\alpha} - \hat{\mathbf{k}}) \quad (18)$$

when the α th surrounding atom is in the same unit cell and is different kind of element. The recoil effects are large for photoemission from light elements like Li, Be,.. whereas elastic scatterings are strong from heavy elements like Mn, I,.. A good system to enhance the scattering effects on the recoil energy shift is thus LiI: The calculated results show that the weighted recoil energy shift shows oscillation as a function of ε_k because the interference term I_1 should oscillate. The recoil energy shift caused by the elastic scatterings amounts to 100 meV for this model system LiI₆, but is less than 10 meV for graphite; C is light element and is a weak scatterer [9]. The recoil energy shift has very weak temperature dependence through the DW factor in $I_1(\mathbf{k})_c$.

On the other hand the peak width is sensitive to temperature. In the single-site approximation, the peak width $\Delta\omega$ is explicitly calculated from the correlation function $D_0(\mathbf{Q}; t)$ in eq. (14),

$$(\Delta\omega)^2 = \sum_s \omega_s^2 |\mathbf{Q} \cdot \mathbf{u}_s^A|^2 (2n_s + 1). \quad (19)$$

For the detailed estimation, heavy computation is necessary. So far only Debye approximations have been applied for the practical purposes [3,4]. We, however, obtain very simple formula at high temperature without any further approximation,

$$(\Delta\omega)^2 = \frac{Q^2 k_B T}{M_A}. \quad (20)$$

This formula shows no anisotropy in the angular distribution. On the other hand, at low temperature $T \ll \theta$ (θ ; Debye temperature), the width shows the anisotropy as observed in C 1s photoemission from graphite [3].

So far our discussion has been focused on the harmonic solids. Beyond the harmonic approximation, for example, $F(t)$ in eq. (14) has additional terms in order Q^3 , $Q^4 \dots$. These terms could be detected for large Q in the high-energy photoemission. No detailed discussion has been found yet.

4. Overall Spectral Features

In this section we discuss overall spectral features of high-energy XPS spectra. Main XPS band (no loss band) measuring photoelectrons with momentum \mathbf{P} excited by X-ray photons with energy ω is described in terms of the damping photoelectron wave function $f_{\mathbf{p}}^-$ under the influence of the optical potential

$$I(\mathbf{p}; \omega) = 2\pi \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle S_0 \right|^2 \times \delta(E_0 + \omega - E_0^* - \varepsilon_p). \quad (21)$$

The intrinsic no-loss amplitude S_0 should be close to 1. The ground state energies with and without core hole are E_0^* and E_0 . On the other hand single-loss XPS intensity whose loss energy is ω_m , is written by

$$I(\mathbf{p}; \omega)^1 = 2\pi \sum_m \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle S_m \right|^2 + \left| \langle f_{\mathbf{p}}^- | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle S_0 \right|^2 \times \delta(E_0 + \omega - E_0^* - \omega_m - \varepsilon_p) \quad (22)$$

where v_m is the fluctuation potential responsible for intrinsic and extrinsic excitations and g is the causal Green's function. In the high-energy region, it can be replaced by the corresponding scattering Green's function. These formulas (21) and (22) can be derived both from many-body scattering theory [10] and Keldysh Green's function theory [11,12]. In the high-energy photoemission, the extrinsic loss amplitude (the second term in $|\dots|^2$ in eq. (22)) is well approximated

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$$\begin{aligned} & \langle f_{\mathbf{p}}^- | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle \\ & \approx \tau_m^{ex}(\mathbf{p}) \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle, \\ & \tau_m^{ex}(\mathbf{p}) \\ & = \int d\mathbf{r} f_{\mathbf{p}}^{-*}(\mathbf{r}) v_m(\mathbf{r}) g(\mathbf{r}, \mathbf{R}_c; \omega + E_0 - E_0^*), \end{aligned} \quad (23)$$

where \mathbf{R}_c is the site of the core function ϕ_c . In the low- and intermediate-energy region, say $\varepsilon_p < 200-300$ eV, the above factorization is a poor approximation. We have to take coherent sum, inelastic + elastic \rightarrow inelastic + inelastic \rightarrow elastic+.. for the calculation of the amplitude $\langle f_{\mathbf{p}}^- | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle$ [11].

To recover the lowest sum $I(\mathbf{p})^0 + I(\mathbf{p})^1$ and also satisfy the normalization condition, the overall photoemission profile is now written by the exponential form with aid of the approximation (23)

$$\begin{aligned} I(\mathbf{p}; \omega)_c^\infty & = \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle \right|^2 \\ & \times \int_{-\infty}^{\infty} dt \exp[i(\omega + E_0 - E_0^* - \varepsilon_p)t] \\ & \times \exp \left[\int_0^{\infty} d\varepsilon \frac{\alpha(\varepsilon)}{\varepsilon} (e^{-i\varepsilon t} - 1) \right] \end{aligned} \quad (24)$$

where we have defined an "asymmetric function" $\alpha(\omega)$ [13]

$$\begin{aligned} \frac{\alpha(\omega)}{\omega} & = \sum_m |\tau_m|^2 \delta(\omega - \omega_m), \\ \tau_m(\mathbf{p}) & = \tau_m^{ex}(\mathbf{p}) + S_m. \end{aligned} \quad (25)$$

This exponential form (24) is known as Landau formula which was derived on the basis of classical transport theory. Very similar quantum derivation is developed by Hedin [13] where time-reversed LEED function is used instead of renormalized damping photoelectron wave function $f_{\mathbf{p}}^-$. This generalization is crucial to discuss quantum depth distribution function (DDF) [14]. It is important to note that $\tau_m^{ex}(\mathbf{p})$ depends on \mathbf{P} as shown by eq. (23).

The amplitude $\langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle$ can be calculated by using full multiple scattering formula [15]

$$\begin{aligned} \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle & = \sum_{\alpha} \exp(-i\mathbf{p} \cdot \mathbf{R}_{\alpha c}) \\ & \times \exp(-\kappa d_{\alpha}(\hat{\mathbf{p}})) \sum_{LL'} Y_{L'}(\hat{\mathbf{p}}) \left[(1 - X)^{-1} \right]_{L'L}^{\alpha c} \\ & \times M_{LLc}, \\ X_{L'L}^{\alpha\beta} & = t_{L'}^{\alpha}(p) G_{L'L}(p \mathbf{R}_{\alpha\beta}) (1 - \delta_{\alpha\beta}), \end{aligned} \quad (26)$$

where matrix X is labeled by a set of atomic site α, β, \dots , and angular momentum L , $d_\alpha(\hat{\mathbf{p}})$ is the distance from the site α to the surface along \mathbf{P} . The full multiple scattering is taken into account by use of the inverse matrix $(1 - X)^{-1}$. The damping of the photoelectron wave is taken into account from first principle theory, since $f_{\mathbf{p}}^-$ is influenced by the non-Hermitian optical potential. The nonlocal optical potential $\Sigma(\varepsilon_p)$ have two different parts,

$$\Sigma(\varepsilon_p) = \Sigma_r(\varepsilon_p) - i\Gamma(\varepsilon_p).$$

The real (Hermitian) part Σ_r has substantial effects on the T -matrix $t_i^\alpha(p)$, and the imaginary (anti-Hermitian) part $-i\Gamma$ is responsible for the photoelectron wave damping which is usually approximated by a constant. In order to derive the multiple scattering formula (26), we apply the site T -matrix expansion [15]. For that purpose it is convenient to use a damping free propagator $g_0(\varepsilon)$,

$$g_0(\varepsilon) = \frac{1}{\varepsilon - T_e + i\Gamma}, \quad T_e = p^2/2 \quad (27)$$

where T_e is the kinetic energy operator. This choice makes unperturbed plane wave have the complex wave number p'

$$p' = \sqrt{2(\varepsilon_p + i\Gamma)} = p_r + i\kappa, \quad (\mathbf{p}' \parallel \mathbf{p}).$$

When we determine Γ as a muffin-tin constant which is small enough in each atomic sphere, the phase shift calculations are only influenced by the real potential. In the high-energy region, we have the well-known formula

$$\kappa \approx \Gamma/p \approx -\text{Im}\Sigma/p.$$

It is often reasonable to split $\alpha(\omega)$ in a "low-energy" flat part $\alpha_1(\omega)$ and a "high-energy" stronger part $\alpha_2(\omega)$ [13],

$$\begin{aligned} \alpha(\omega) &= \alpha_1(\omega) + \alpha_2(\omega), \\ \alpha_1(\omega) &= \alpha_0\theta(\omega_0 - \omega). \end{aligned} \quad (28)$$

We thus have from eq. (24)

$$\begin{aligned} I(\mathbf{p}; \omega)_c^\infty &= \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle \right|^2 \\ &\times 2\pi \int d\omega' D_1(\varepsilon - \omega') D_2(\omega') \\ &\times \exp \left[- \int_0^\infty d\omega' \frac{\alpha(\omega')}{\omega'} \right], \quad (29) \\ \varepsilon &= \omega + E_0 - E_0^* - \varepsilon_p, \end{aligned}$$

where low- (D_1) and high-energy (D_2) spectral functions are defined by ($j = 1, 2$)

$$\begin{aligned} D_j(t) &= \int_{-\infty}^\infty dt D_j(\omega) e^{-i\omega t} \\ &= \exp \left[\int_0^\infty d\omega \frac{\alpha_j(\omega)}{\omega} e^{-i\omega t} \right]. \end{aligned}$$

The low-energy spectral function $D_1(\omega)$ describes X-ray singularity for metallic systems and recoil energy shift, broadening and asymmetry of the main photoemission band. The high-energy spectral function $D_2(\omega)$ describes the plasmon losses taking both intrinsic and extrinsic ones into account, which can be expanded as

$$\begin{aligned} D_2(\omega) &= \delta(\omega) + \beta(\omega) + \frac{1}{2!}(\beta * \beta)(\omega) \\ &+ \frac{1}{3!}(\beta * \beta * \beta)(\omega) + \dots, \quad (30) \\ \beta(\omega) &= \alpha_2(\omega)/\omega, \end{aligned}$$

where $(A * B)(\omega) = \int d\omega' A(\omega - \omega') B(\omega')$ is the convolution of A and B . Substitution of eq. (28) into (27) yields the photoemission intensity from the core site \mathbf{R}_c ,

$$\begin{aligned} I(\mathbf{p}; \omega)_c^\infty &= \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle \right|^2 \\ &\times \exp \left[- \int_0^\infty d\omega \frac{\alpha(\omega)}{\omega} \right] \\ &\times \left[D_1(\varepsilon) + (D_1 * \beta)(\varepsilon) + \frac{1}{2!}(D_1 * \beta * \beta)(\varepsilon) \right. \\ &\left. + \dots \right]. \quad (31) \end{aligned}$$

The first term $D_1(\varepsilon)$ describes the main band with no plasmon loss, and it also describes the recoil effects and asymmetry due to the X-ray singularity. The second term $D_1 * \beta$ describes one-plasmon loss, and so on. As pointed out before $\beta(\omega)$ depends on \mathbf{P} , so that plasmon loss bands show the angular dependence. At low energy prominent angular dependence of the plasmon loss spectra is observed, whereas no angular dependence is observed at high-energy excitation ($\varepsilon_p > 1$ keV) [16]. Some experimental results show that the relative plasmon loss intensity changes very slowly as a function of photoelectron energy [17, 18]. Osterwalder et al. measured azimuthal PD patterns of Al 2s plasmon loss peak $\varepsilon_p \approx 1120$ eV) compared with the main Al 2s band, and found very similar PD patterns [19, 20] These results imply that $\beta(\omega)$ should weakly depend on \mathbf{P} in the

high-energy region. Hedin et al. have shown that the interference terms in $\beta(\omega)$ drop out in the high-energy limit [13, 21]. Our numerical calculations, however, show that the rate of the drop out is very slow. Even at $\hbar\omega = 5$ keV for Al $2p$ excitation, the interference term still has considerably important contribution. In the energy range $\hbar\omega = 1-5$ keV, the extrinsic amplitude is much larger than the intrinsic one.

5. Concluding Remarks

In this work we investigate some theoretical problems in high-energy photoemission. Up to $\hbar\omega = 10$ keV, widely used multipole expansion (1) works so well. The relative importance of the nondipole transition can be estimated by Cooper parameters δ and γ .

The energy shift caused by the recoil processes is well described by the formula for free atom recoil even though the excited atom is tightly bound in a solid. In the photoemission processes phonon modes should be excited, and the above simple formula is derived without use of detailed phonon dispersion. On the other hand the recoil broadening depends on the details of projected phonon modes, which shows the angular dependence as observed for graphite excitation [3]. Photoelectron diffraction from heavy surrounding atoms can give rise to recoil energy shifts, which should oscillate as a function of photoelectron energy.

Overall XPS spectral features are conveniently described by the exponential formula which includes both the intrinsic, extrinsic and their interference in addition to X-ray singularities and recoil effects. The interference terms drop out very slowly with the photoelectron energy. For quantitative studies it is important to obtain reliable fluctuation potentials; at present it is far from the goal.

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