Theory of Electron-Phonon Interaction in XAFS and Other Spectroscopies

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Abstract. The electron-phonon interaction in X-ray absorption and photoemission spectra are studied on the basis of nonrelativistic Keldysh Green’s function theory developed by the authors. The X-ray absorption intensity is described in terms of reducible polarization propagator which can be written by using the electron irreducible polarization and the screened Coulomb interaction with and without the electron-phonon interaction. The lowest-order term naturally describes the Debye-Waller and the Franck-Condon factors, and also finite mean free path due to the electron-phonon interaction. We also derive a general formula to discuss low energy photoemission taking the electron-phonon interaction.

Keywords: XAFS, UPS, electron-phonon interaction, Debye-Waller factor, Franck-Condon factor

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INTRODUCTION

For the study of phonon effects on XAFS spectra, the EXAFS Debye-Waller (DW) factors have extensively been discussed, whereas other factors like Franck-Condon (FC) factors and electron-phonon interactions, are rarely discussed. In our previous papers both the DW and the FC factors are taken into account within the single scattering EXAFS theory [1, 2], which confirms the validity of the widely used DW factor after the FC and the interference terms cancel each other. More general discussion beyond the single scattering theory has been given on the basis of the Keldysh Green’s function approach [3, 4]. Ankudinov and Rehr have shown that local atomic displacements are responsible for additional XANES peaks [5].

So far no systematic first principle theory has been proposed to study the influence of electron-phonon interaction on the XAFS and related spectroscopies. Here we propose a first principle theory to handle the phonon effects on XAFS spectra based on the Keldysh Green’s function theory and on the Baym-Hedin approach [6].

BASIC XAFS THEORY

The X-ray absorption intensity $I(\omega)$ for an X-ray photon of energy $\omega$ is given by the correlation function expression [3],

$$I(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \langle H_{ep}^\dagger(t)H_{ep}(0) \rangle \, dt$$

where $\langle \cdots \rangle$ stands for thermal average at finite temperature and $H_{ep}$ is the electron-phonon interaction Hamiltonian

$$H_{ep} = \int dx \psi^\dagger(x) \Delta(x) \psi(x) = \int dx \Delta(x) n(x).$$

In the above equation $\psi$ ($\psi^\dagger$) is the electron annihilation (creation) operator, $n(x) = \psi^\dagger(x) \psi(x)$ is the electron density operator ($x = (r, \alpha)$), and $\Delta \equiv e \cdot r$, where $e$ is the polarization vector of the incident X-ray. We obtain a key formula for the X-ray absorption intensity

$$I(\omega) = i \int dx dx' \Delta^*(x) \Delta(x') \int_{-\infty}^{\infty} \pi_{ee} \bigl(u_t, x'\bigr) e^{i\omega t} \, dt,$$

where we have used the electron reducible polarization notation that $p_e(1) = -n(1)$

$$\pi_{ee}(1, 2) = -i \langle T_0 [\delta \rho_e(1) \delta \rho_e(2)] \rangle,$$

where $T_0$ is the path-ordering operator along the Keldysh contour.

We now discuss some approximations to include phonon effects on XAFS. To calculate the correlation function $\pi_{ee}$ we introduce the electron density - total density fluctuation function $\pi_e$ defined by

$$\pi_e(1, 2) = \frac{\delta \langle \rho_e(1) \rangle}{\delta \phi^{ex}(2)} = -i \langle T_0 [\delta \rho_e(1) \delta \rho(2)] \rangle,$$

where the nuclei charge density operator is $\rho_n(r) = \sum_\alpha Z_\alpha \delta(r - R_\alpha)$, total density operator $\rho(r) = \rho_e(r) + \rho_n(r)$ ($\rho_e(r) = \sum_\alpha \rho_e(\alpha)$). The external potential $\phi^{ex}$ couples with the total density operator. We can eliminate the mixed term $\langle T_0 [\delta \rho_e(1) \delta \rho_n(2)] \rangle$ by use of the Baym’s
technique [7]
\[ -i\langle T_e [\delta \rho_{\sigma}(2) \delta \rho_{\pi}(1)] \rangle = D(1,2) - i\langle T_e [\delta \rho_{\pi}(2) \delta \rho_{\sigma}(1)] \rangle \]
\[ = \left[ (1 - P_e v) - D \right] (1,2) \]  
(6)

which yields [6]
\[ -i\langle T_e [\delta \rho_{\sigma}(1) \delta \rho_{\pi}(2)] \rangle = [P_e W_e D] (1,2), \]  
(7)

where we have used the phonon Green’s function
\[ D(1,2) = -i\langle T_e [\delta \rho_{\sigma}(1) \delta \rho_{\pi}(2)] \rangle \]  
(8)

and \( W_e \) is the screened Coulomb interaction associated with electrons defined by \( W_e = e_r^{-1} v \). We introduced a polarization function \( P_e \) associated with the electrons, which are related by a dielectric function \( \varepsilon_r, \varepsilon_r \equiv 1 - P_e v \). By use of the chain rule in the functional derivative, \( \pi_e \) is given by
\[ \pi_e = P_e + P_e W_e P_e + P_e W_e D e_r^{-1}. \]  
(9)

From eqs. (5), (7) and (9), we finally obtain
\[ \pi_{ee}(1,2) = P_e (1,2) + [P_e W_e P_e] (1,2), \]  
(10)

where we define the total screened Coulomb interaction including the electron-phonon interaction [6],
\[ W = W_e + W_{ph}, \quad W_{ph} = W_e D e_r. \]  
(11)

In comparison with the previous result [3, 4], \( P_e \) is replaced by \( P_e \) and \( W \) includes explicitly the electron-phonon interaction here.

DEBYE-WALLER AND FRANCK-CONDON FACTORS IN XAFS SPECTRA

In this section we show that the present new formula can describe the previous important results [3, 4]. The lowest-order term, the skeleton bubble \( P_e^{(0)} \) in \( P_e^{(\infty)} \) is now given
\[ P_e^{(0)}(1,2) = -ig^{\infty}(1,2)g^{\infty}(2,1^+), \]  
(12)

as shown in Fig. 1(a). We should note that the electron Green’s functions \( g^{\infty} \) and \( g^{\infty} \) have already phonon effects through the self-energy and phonon part in the total Hamiltonian. As we can write \( ig^{\infty}(2,1) \sim -\phi_c(x_1)\phi_c(x_2) (b_1^+ b_2) \) for the core excitation (\( b \) is the annihilation operator of core level \( \phi_c \)), the lowest-order term of the X-ray absorption intensity \( I^{(0)}(\omega) \) is thus written
\[ I^{(0)}(\omega) = \int \frac{d\epsilon}{2\pi} G_{\lambda \lambda}(\epsilon) G_{\lambda \lambda}^{\infty}(\epsilon - \omega), \]  
(13)

where \( G_{\lambda \lambda}^{\infty} \) describes the X-ray absorption processes without core-hole effects, whereas \( G_{\lambda \lambda} \) describes the core effects and the FC factor. In the X-ray absorption process, if the condition \( \epsilon \gg \mu \) is satisfied, we have
\[ G_{\lambda \lambda}^{\infty}(\epsilon) = -\text{Im} \langle c | \Delta \phi_c(\epsilon) | \lambda \rangle \]
\[ \approx -2\text{Im} \langle c | \Delta \phi_c(\epsilon) | \lambda \rangle, \]  
(14)

where \( \phi_c \) is the retarded Green’s function and \( c \) is a core function \( \phi_c \). We should note that \( g^{\infty} \) includes the electron-phonon interaction through the self-energy \( \Sigma \). We thus obtain the convolution formula (13) of the DW and FC factors as before, where the FC factor is unimportant for the EXAFS analyses due to delicate cancellation [3]. In contrast to EXAFS, the white line broadening is temperature dependent which is due to the FC factors [8].

ELECTRON-PHONON INTERACTION IN XAFS

So far no discussion about the electron-phonon interactions has been given for the XAFS analyses. At first the optical potential \( \Sigma \) includes those effects which are responsible for the finite mean-free path at low energy region. It also plays some important role for the phase shift calculation. It can be written
\[ \Sigma^{\infty}(\omega) = \Sigma^{\infty}(\omega) + \Sigma^{ph}(\omega), \]
\[ \Sigma^{\infty}(\omega) = \int \frac{d\epsilon}{2\pi i} \frac{\Sigma^{\infty}(\epsilon) - \Sigma^{\infty}(\epsilon) - \Sigma^{\infty}(\epsilon) - \Sigma^{\infty}(\epsilon)}{\epsilon - \omega - \text{Im} \Sigma^{\infty}(\epsilon)}, \]  
(15)

where \( \Sigma^{\infty} \) and \( \Sigma^{ph} \) are the electron self-energy without and with electron-phonon interaction. In the GW approximation, they are written
\[ \Sigma^{\infty}(1,2) = ig^{\infty}(1,2)w^{\infty}(2,1^+), \]
\[ \Sigma^{ph}(1,2) = ig^{\infty}(1,2) w^{ph}(1,1^+). \]  
(16)

Other electron-phonon interactions come from the higher-order terms in \( \pi_{ee} \) beyond \( P_e^{(0)} \). From \( P_e \) we have the first-order term in the electron-phonon interaction, which is diagrammatically shown by Fig. 1(b),
\[ P_e^{(1)}(1,2) = \int [G(1,3)G(3,2)G(2,4)G(4,1^+)] \times W_{ph}(3,4^+) \]  
(17)

We also obtain the same order term in \( W_{ph} \) from the second term in eq. (10) shown in Fig. 1(c),
\[ [P_e W_{ph} P_e]^{(1)} \approx \left[ P_e^{(0)} W_{ph} P_e^{(0)} \right]^{(1)}. \]  
(18)

These terms can contribute to real and virtual phonon losses due to the electron-phonon interaction. The energy
range influenced by these losses, however, is in order of 0.1 eV. Energy resolution for typical XAFS measurement should be much larger than that. These phonon effects from Figs. 1(b) and (c) should play an unimportant role in XAFS region.

\[ I_p \propto \text{Im} \left( \langle F_p | \Delta g^- (\epsilon_p - \omega) \Delta^+ | F_p \rangle \right). \]  
(19)

In this case, however, the electron Green’s function \( g^- \) implicitly has phonon effects. We thus separate out the "bare" electron Green’s function \( G_e \) which satisfies the equation

\[ G_e = G_0 + G_0 \Sigma \Lambda G_e. \]  
(20)

We should note that \( G_e \) still has phonon effects associated with DW or FC factors, but it has no effects from the electron-phonon interaction \( W_{ph} \). We pick up important contribution to loss related to the electron-phonon interaction,

\[ I_p \propto \text{Im} \left( \langle F_p | \Delta (1 + g^- \Sigma_{ph}^e) \Delta^+ (1 + \Sigma_{ph}^e g^-) \Delta^+ | F_p \rangle \right). \]  
(22)

This basic formula describes the photoemission processes from the hole Green’s function \( g^\pm (\epsilon_p - \omega) \) to the photoelectron state \( F_p \) excited by the interaction \( \Delta \). In addition to this direct excitation, the hole states are influenced by the electron-phonon interaction through \( \Sigma_{ph} \) before the photoexcitation. We should notice that the photoelectron state \( F_p \) is influenced by the electron-phonon interaction self-energy \( \Sigma_{ph}(\epsilon_p - \omega) \) after the photoexcitation. So far no detailed study has been found on these problems.

CONCLUSION

We propose a first principle theory to handle phonon effects on X-ray absorption and photoemission spectra based on the Keldysh Green’s function approach and on the Baym-Hedin approach. General basic formulas to calculate XAFS and UPS intensity are obtained which allow us to classify some phonon effects on these spectra. The DW and FC factors are different from the effects caused by the electron-phonon interaction which is described in terms of the factor \( W_{ph} \): \( F_p \cdot g^- \cdot \cdots \) implicitly include those effects.

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REFERENCES