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EFFECTS OF MANY-BODY INTERACTIONS IN EXTENDED X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY (EXAFS)

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ABSTRACT: We present the first a priori derivation of a many-body theory for EXAFS with clearly defined approximations and with final expressions which are feasible for quantitative evaluations. We conclude that the conventional EXAFS expression should be complemented with a term that crudely is the main term, energy-shifted and scaled down by a factor of order 0.2-0.3. Further the f-factors depend significantly, not only on the scattering properties of the individual ions, but also on the electron energy-loss properties of the material itself.

1- INTRODUCTION

It is well-known from core-electron photoemission that strong **shake-up** effects occur (intrinsic losses), as well as extrinsic losses, and there has been many discussions on how these effects could influence EXAFS and on the importance of possible interferences between them. There has also been a number of qualitative discussions on how fast the **relaxation** around a core hole is at different photoelectron energies (adiabatic and sudden limits), and the proper choice of one-electron potentials. We here present a theory using similar techniques as in our earlier work[1] on photoemission. We show that, in our formalism, only completely relaxed potentials appear, and we find an explanation why a constant damping factor in the propagating waves can be used. Our results predict strong deviations from the conventional theory, however much of the deviations can be absorbed into renormalized ionic scattering amplitudes. We have only made pilot calculations but our expressions are quite feasible also for quantitative calculations. This is the first comprehensive many-body theory for EXAFS, and in our view represents a major break-through.

The conventional expression for the EXAFS spectrum can be written as [2] $\sigma(\omega) = -\text{Im} \langle c | p G_0(\omega) p | c \rangle$, where G_0 is a damped one-electron Green's function, $G_0(\omega) = (\hbar \omega - h + i \Gamma)^{-1}$, h is a one-electron Hamiltonian (including the ionic scattering terms), Γ is a constant and p is the one-electron transition operator ($p = -i \hbar \epsilon \nabla$). Here we develop a many-body theory which results in

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replacing G_0 by (from now on we put f_1 equal to one)

$$G = e^{-n} [G_0(\omega) + \sum_v (V_{cc}^v/\omega_v)^2 G_0(\omega - \omega_v) - 2 \sum_v (V_{cc}^v/\omega_v) G_0(\omega - \omega_v) V^v G_0(\omega)] \quad (1)$$

We have represented the valence electron excitations in the **quasi-boson approximation** as $\sum_v \omega_v a_v^\dagger a_v$. The boson operators a_v can describe extended elementary excitations like plasmons and electron-hole pairs in "simple" metals, as well as localized excitations where say d- or f-electrons are involved. The potentials V_{cc}^v (a scalar) and V^v (a one-electron operator) give the coupling from the core-hole respectively the photo-electron to the quasi-boson "v". The n in $\exp(-n)$ is the total coupling strength,

$n = \sum_v (V_{cc}^v/\omega_v)^2$. The first term in the expression for G thus gives the conventional EXAFS spectrum scaled down by an expected "shake-up" exponential $\exp(-n)$. The second term gives the contribution from the purely "intrinsic" losses and the last term is a "cross" contribution involving both "intrinsic" and "extrinsic" losses. In our theory G_0 actually has the form

$G_0(\omega) = (\omega - h - \Sigma(\omega))^{-1}$, where $\Sigma(\omega)$ is a (complex) one-electron operator which accounts for the purely "extrinsic" losses. When we evaluate the electron gas expression for the spatial representation $G_0(r, r'; \omega)$, we however find that for $|r - r'|$ equal and larger than the shortest interatomic distance the result is closely the same as if we had used $-i\Gamma$ and not $\Sigma(\omega)$. The effect of the last ("cross") term of G can approximately be absorbed in the two first by renormalizing the ionic scattering factors.

II - THEORY

In a recent theory of photoemission [1] a new description of the many-body effects was presented. In principle one should be able to obtain the result for x-ray absorption by just integrating this expression for the photoemission distribution. In practice this is not feasible. The reason is that photoemission basically is a surface effect, and the scattering states for the photoelectron are a basic ingredient in the theory. The scattering states are stable eigenstates with a well-defined photoelectron momentum of an unperturbed Hamiltonian also describing a solid with many-electron interactions. The perturbation is the interaction between the photoelectron and the remaining solid. The correspondence in x-ray absorption to the photoelectron scattering states are states which describe the propagation out from the excited ion core, are scattered by the surrounding ions and then come back to the excited ion core again. These propagating states are not natural to represent by timeinverted LEED states, and the description of x-ray absorption has to find its own theory.

In the photoemission theory a novel very simple perturbation scheme was developed [1]. This scheme uses infinite summations to get rid of those intermediate states which have occurred earlier in the expansion. It represents an extension of the method used by Heitler to isolate self-energy terms. In this scheme we represent the interaction term with a fermion-boson coupling

$$V = \sum_{v, k, k'} V_{kk'}^v a_v^\dagger c_k^\dagger c_{k'} + hc \quad (2)$$

where a_v stands for a boson and c_k for a fermion operator. Many problems can, to a good approximation, be mapped on such a polaron-type of interaction, and this approach should represent no serious draw-back. We also neglect exchange couplings between the photoelectron and the other electrons, which excludes the near-threshold region from our considerations.

The well-known basic many-electron expression which gives x-ray absorption is [2]

$$\sigma = -\text{Im} \langle \Psi_{GS} | \Delta^\dagger (E - H + i\delta)^{-1} \Delta | \Psi_{GS} \rangle, \quad (3)$$

where $\Delta = \sum_{ij} \langle i | p | j \rangle c_i^\dagger c_j$, and H is the fully interacting many-electron Hamiltonian. Writing the statevector as a product of a core and a valence electron part (again neglecting exchange couplings) we have, after separating out the core electron part

$$\sigma = -\text{Im} \langle N_{v,0} | T^\dagger (E - h - H_v - V_c - V + i\delta)^{-1} T | N_{v,0} \rangle \quad (4)$$

where $T = \sum_k \langle k | p | c \rangle c_k^\dagger$, h is the (one-electron) Hamiltonian for the photoelectron in the presence of the valence electron system (with core-hole), H_v is the fully interacting many-electron Hamiltonian for valence electrons in a system without core hole, V_c is the core hole potential, and V as before is the coupling between the photoelectron and the solid (eq 2). As we said earlier we represent H_v by $\sum_v \omega_v a_v^\dagger a_v$. Proceeding in a similar way as we did for photoemission we obtain

$$\sigma(\omega) = -\text{Im} \langle c | p G(\omega) p | c \rangle \quad (5)$$

where $G(\omega)$ is a one-electron Green's function for the photoelectron

$$G(\omega) = \langle N_{v,0} | (\omega - h - H_v - V_c - V + i\delta)^{-1} | N_{v,0} \rangle \quad (6)$$

We let $\omega = 0$ correspond to an energy which just carries the photoelectron to the Fermi surface. $|N_{v,0}\rangle$ is an eigenfunction of H_v and not of $H_v + V_c$, and thus an "unrelaxed function". We write (cf eq 2)

$$V^c = -\sum_v V_{cc}^v (a_v^\dagger + a_v) \quad (7)$$

and make the transformation

$$|N_{v,0}\rangle = \exp(-S) |N_{v,0}^\dagger\rangle$$

$$S = \sum_v [(V_{cc}^v / \omega_v) a_v^\dagger + 1/2 (V_{cc}^v / \omega_v)^2] \quad (8)$$

to obtain the relation to the eigenfunction $|N_{v,0}^\dagger\rangle$ of $H_v^\dagger = H_v + V_c$.

Substituting in eq (6) we have

$$G(\omega) = \langle N_{v,0}^\dagger | \exp(-S^\dagger) (\omega - h - H_v^\dagger - V + i\delta)^{-1} \exp(-S) | N_{v,0}^\dagger \rangle \quad (9)$$

Expanding to lowest order in V and V_c , using the same technique as in the photoemission case, we obtain eq (1)

$$G(\omega) = e^{-\Gamma} [G_0(\omega) + \sum_v (V_{cc}^v / \omega_v)^2 G_0(\omega - \omega_v) - 2 \sum_v (V_{cc}^v / \omega_v) G_0(\omega - \omega_v) V^v G_0(\omega)] \quad (1)$$

Here $V^v = \sum_{kk'} V_{kk'}^v c_{k'}^\dagger c_k$ and $G_0(\omega) = [\omega - h - \Sigma_0(\omega)]^{-1}$. The optical potential $\Sigma_0(\omega)$ includes the effects of the photoelectron-solid interaction V , and is to lowest order given by,

$$\Sigma_0(\omega) = \sum_{v, k_1, k_1'} V_{k_1, k_1'}^v (\omega - \omega_v - \varepsilon_{k_1})^{-1} V_{k_1, k_1'}^v c_{k_1'}^\dagger c_{k_1} \quad (10)$$

This is essentially the same expression as the "GW-approximation". To proceed further we have to expand our Green's function $G_0(\omega)$. From $\Sigma_0(\omega)$ we take out terms which are well localized on individual atoms and combine them with the ionic potential in h . We can then write $h = T + \sum_i t_i$, where T is the pure kinetic energy and $\sum_i t_i$ gives the ionic potentials plus the localized parts in $\Sigma_0(\omega)$. These parts are complex, and we obtain scattering potentials with complex phase shifts. The remaining part in $\Sigma_0(\omega)$, which comes from delocalized electrons, is called $\Sigma_{0h}(\omega)$. We treat $G_{0h} = (\omega - T - \Sigma_{0h}(\omega))^{-1}$ as the unperturbed Green's function, and $t = \sum_i t_i$ as the perturbation. A numerical study of $(\omega - T - \Sigma_{0h}(\omega))^{-1}$ shows that it is a good approximation to replace $\Sigma_{0h}(\omega)$ by a constant $-i\Gamma$.

The further development follows similar lines as in conventional EXAFS theory. To see the structure in the theory, we make some simplifications in our basic eq (1). First we replace the energy argument ω_v in $G_0(\omega-\omega_v)$ with an average value ω_0 , and introduce the notation $V_{\text{cross}} = \sum_v (V_{cc}^v/\omega_v) V^v$, for the one-electron potential that gives the cross term between the core electron and the photoelectron potentials. Eq (1) then becomes

$$G(\omega) = e^{-n} [G_0(\omega) + nG_0(\omega-\omega_0) - 2G_0(\omega-\omega_0)V_{\text{cross}}G_0(\omega)] \quad (11)$$

As usual in EXAFS theory we expand in the scattering potential. To lowest order (single-scattering or kinematical theory) we have $G_0 = G_{0h} + G_{0ht}G_{0h}$. The first term G_{0h} gives the smooth part in the cross section. It is found that the V_{cross} term in eq (11) can be approximately absorbed in the other two terms by redefining the ionic scattering factors. One is then left with the same expression for EXAFS as in conventional theory plus a term from the intrinsic processes, which is identical to the conventional one but shifted in energy and scaled down in amplitude

III - CONCLUSIONS

The main features of EXAFS data should be possible to fit with the conventional EXAFS expression, but the f-factors depend strongly on the quasi-boson excitation spectrum in the material. Phaseshift transferability is thus limited to compounds with similar electron energy loss properties. Accurately calculated free atom f-factors should give poor results, due to the largeness of the correction factor.

The spectra have an appreciable component which is energy-shifted (the term associated with $G_0(\omega-\omega_0)$). This shifted component gives rise to a beating in the spectrum which can be misinterpreted as an ionic scattering component.

Our quantitative calculation is a only pilot study with very crude approximations of our basic expressions, involving use of electron-gas plasmons for the quasi-bosons and single scattering expressions. However our qualitative conclusions should be quite reliable.

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