

**LNF-90/090**

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Estratto da: Solid State Commun. in Phys. Res. Vol. 76, n. 11, 109-111 (1990)



## APPLICATION OF A COMPLEX POTENTIAL TO THE INTERPRETATION OF XANES SPECTRA THE CASE OF Na K-EDGE IN NaCl

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(Received 2 July 1990 by E. Tosatti)

### ABSTRACT

We present an application of a general full multiple scattering scheme with complex potential, to the Na-K edge for the interpretation of inner shell x-ray absorption spectra. This scheme, taking into account the decaying processes of the photoelectron, by mean the imaginary part of Hedin-Lundqvist potential, is able to recover the right experimental intensities without empirical parameters.

Good agreement with experimental data has been obtained using a nine-shells cluster for the NaCl system.

### INTRODUCTION

In the framework of one electron theory several approaches have been suggested to reproduce the first tenths of electronvolts of an X-Ray Absorption Spectra (XAS). Although the shape of the experimental spectra can be reproduced by theory, several problems exist to obtain quantitative agreement respect to the relative intensities of the features in the XAS spectra. [1,2,3] In fact except to an *a posteriori* correction, via phenomenological mean-free-path, all these schemes do not account for the inelastic losses of the photoelectron in the final state.

In this paper we report a multiple scattering (MS) scheme, using complex potential of Hedin-Lundqvist type, that accounts *ab-initio* for the inelastic losses of the photoelectron. As an application the Na K-edge in the NaCl system is presented. The dependence of the MS calculation as a function of different choices for the potential and of the size of the cluster is also discussed.

### A MS SCHEME WITH COMPLEX POTENTIAL

The one-channel approach to the MS problem lets to write the photoabsorption cross-section, in atomic units, as

$$\sigma(\omega) = -4\pi\alpha_0\omega \int d^3r d^3r' \phi_c(\vec{r}) \hat{\epsilon} \cdot \vec{r} \{ \text{Im } G(\vec{r}, \vec{r}'; \omega + E_i) \} \hat{\epsilon} \cdot \vec{r}' \phi_c(\vec{r}') \quad (1)$$

where  $\phi_c(\vec{r})$  is the photoelectron wavefunction in the initial core state with energy  $E_i$ ,  $\omega$  is the photon energy,  $\alpha_0$  is the fine structure constant and  $\epsilon$  is the polarization of the light.  $G$  is the one particle Green function that obeys to the Dyson equation:

$$(\nabla^2 + E - V_c(\vec{r})) G(\vec{r}, \vec{r}'; E) - \int d^3r'' \Sigma(\vec{r}, \vec{r}''; E) G(\vec{r}'', \vec{r}'; E) = \delta(\vec{r} - \vec{r}') \quad (2)$$

where  $V_c$  is the usual Coulombic or Hartree potential and  $\Sigma(\vec{r}, \vec{r}'; E)$  is an energy dependent complex and in general, non-local exchange and correlation potential.

$G(\vec{r}, \vec{r}'; E)$  plays the role of propagator of the excited electron, from site  $\vec{r}$  to  $\vec{r}'$  in the presence of the core hole. The solution of equation (2) is well known in the case of collection of muffin-tin potential, [4] when a local approximation for the self-energy is available. Following Hedin and Lundqvist [5] suggestion the self-energy can be approximated using a density functional formalism [6] and a single plasmon pole approximation for the electron gas dielectric function. In this way, the self energy becomes local and can be written as:

$$V_{xc} \equiv \sum_h (\vec{p}(\vec{r}), E - V_c(\vec{r}); \rho(\vec{r})) \quad (3)$$

where now  $\Sigma_h$  is the self-energy of an electron in an interacting homogeneous electron gas with wavenumber  $\vec{p}(\vec{r})$ , energy  $E - V_c(\vec{r})$  and local electronic density  $\rho(\vec{r})$ . Following Lee and Beni the validity of this scheme is extended even to core region. [7] In this way the real and imaginary part of the self-energy [5] becomes

$$\text{Re } \Sigma_h(\vec{p}, \omega) = - \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} \frac{f(\vec{p}+\vec{q})}{\epsilon[\vec{q}, (\vec{p}+\vec{q})^2 - \omega]} + \omega_p^2 \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} \frac{1}{\omega - \omega_1(\vec{q}) - (\vec{p}+\vec{q})^2} \quad (6)$$

$$\text{Im } \Sigma_h(\vec{p}, \omega) = \frac{\pi}{2} \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} \frac{1}{\omega_1(\vec{q})} \{ f(\vec{p}+\vec{q}) \delta[(\vec{p}+\vec{q})^2 - \omega_1(\vec{q}) - \omega] - [1 - f(\vec{p}+\vec{q})] \delta[(\vec{p}+\vec{q})^2 - \omega_1(\vec{q}) - \omega] \} \quad (7)$$

where  $f(q)$  is the Fermi distribution function,  $\epsilon(\omega, \vec{p})$  is the dielectric function and  $\omega_1(\vec{q})$  the plasmon pole dispersion relation as in ref. 7.

The real part of the self energy (equation 6) is formed by two terms, the first one represents a screened version of an exact HF exchange potential for the electron gas, while the second one is the correlation energy for the Coulomb-hole. The imaginary part of the self energy (equation 7) is formed also by two terms that represent the possibility for an electron to gain or loss (the negative term) energy by interaction with plasmon excitations.

The total cross-section can be now written as: [8]

$$\sigma(\omega) = \frac{8\pi}{3} \alpha_0 \omega \sum_{\ell m} A(\ell_0, \ell) \text{Im} \{ M_{\ell}^{\prime} \tau_{\ell m, \ell m}^{00} M_{\ell}^{\prime} + M_{\ell}^{\prime} \bar{M}_{\ell}^{\prime} \} \quad (8)$$

where  $M$  represents the atomic matrix element coming from the regular part of the solution of equation 2, while  $\bar{M}$  is the same part coming from the singular term.  $A(\ell, \ell_0)$  is a term coming from the angular integration, while  $\tau$  is the multiple scattering path operator. It is important to underline that in the complex potential case, the atomic cross section does not factorize out from the total contribution.

Using this formulation it is also possible to show that the introduction of an absorptive part in the potential is equivalent to perform an appropriate convolution of the total cross-section  $\sigma(\omega)$  calculated with real potential. All these points are discussed in detail in reference [8].

In all the following calculations muffin-tin potentials are built, starting from Clementi and Roetti charge density for neutral or ionized atoms, according to Mattheis prescriptions. The muffin-tin radii are chosen according to Norman criteria starting from the photoabsorber and using touching spheres.

## RESULTS AND DISCUSSION

In fig. 1 we report the comparison between the experimental data of the Na K-edge in the NaCl system with three different calculations obtained using X- $\alpha$  exchange potential, [9] a Dirac-Hara (DH) energy dependent exchange potential, [10] and Hedin-Lundqvist exchange and correlation complex potential.

For these calculations we have used a seven-shells cluster (92 atoms) around the photoabsorber sodium. Because the DH potential is real, the corresponding calculation was convoluted using the imaginary part of the HL potential, while X- $\alpha$  spectra have been convoluted using a lorentzian function of FWHM equal to  $2k/\lambda$  where  $\lambda$  is the photoelectron mean free path (MFP) according to Seah and Dench power law for inorganic materials. [11] The coefficient, for this power law have been chosen in order to reproduce the measurements of attenuation length (AL), for the compounds under study, [12] taking into account that AL measurements give values about 15-30% lower than the corresponding MFP. [13] All the theoretical spectra are also convoluted to take account for the experimental resolution ( $\sim 0.7$  eV at 1 KeV) and for the core-hole lifetime ( $\sim 0.26$  eV for sodium). [14]

The edge region (the first ten electronvolts) of the NaCl spectrum is characterized by the presence of some bound state transitions which cannot be reproduced with correct intensities by the extended continuum MS formalism, due to the different normalization of the wavefunction in the final state. For a complete discussion of this point see ref.15. Excluding this region the results of the calculation are however satisfactory and the DH potential shows the

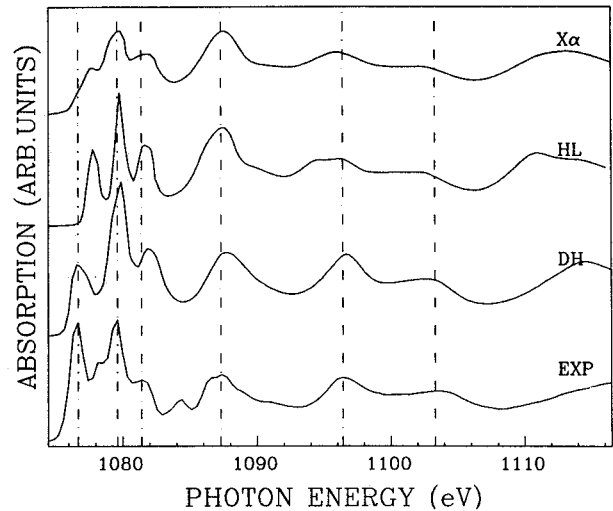


FIG.1 NaCl - Na K-edge. Different choices for the potential (X- $\alpha$ , HL and DH) for a seven shells cluster and comparison with the experiment. (EXP)

best agreement even if this behaviour is not completely understood.

From the comparison of theoretical calculations for the seven-shells cluster, clearly appears that both HL and X- $\alpha$  potentials are too attractive as other works have already shown. [8,16] This effect has been explained with the difficulty of both the Coulomb hole term and the screened term of the exchange, (see equation. 6), to vanish near the edge. In any case the problem cannot be simply addressed to the ionic nature of the compounds because it is present in other non-ionic systems. [16]

Moreover in the NaCl, it is possible to notice other structures that cannot be reproduced by all the calculations: in particular the structure at 1085 eV. This structure could be addressed to an atomic effect such as shake-off satellites.

To clarify these aspects and due to the very large mean free path value for NaCl, we have implemented the calculations for a nine shells cluster (122 atoms) around the Na atom. The results are presented in fig.2.

Although a better general agreement with experimental data are now obtained in all calculations, both concerning the shape and the energy position of the features in comparison with the previous results, it appears clearly that now HL potential shows the best agreement with the experiment.

In fact the relative energy positions and intensities of the features are reproduced quite well including the structure at 1085 eV, while the weak structure at 1078 eV start to be reproduced too. To be noticed the DH potential does not succeed to reproduce the above described structures.

These calculations have allowed us to investigate also the sensitivity to the different choices of the charge density used for the description of the final state. Due to the extreme ionicity of this compound we used the ionic charge density to build the potential. Calculations non presented in this paper indicates that this aspect of the potential determines a different reproduction only of the first 5-10 eV of the spectra. On the contrary the remaining part of the spectra is slightly affected by this choice.

Moreover in fig. 3 we report two different calculations

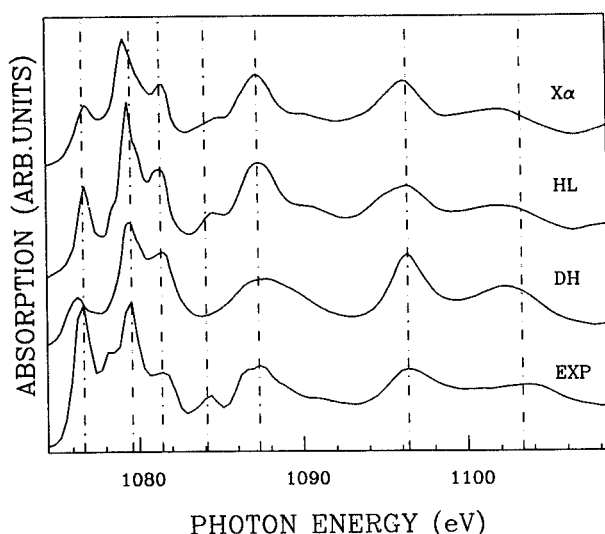


FIG.2 NaCl - Na K-edge. The same of fig. 1 but for a calculation with a nine shells cluster. (123 atoms)

obtained using DH potential with different final states. Comparison has been made between the Z+1 excited potential (exc) and a final potential chosen equal to the one of the ground state (gs). As before, only the first electronvolts of the spectra are affected by these different choices of the final state potential.

Summarizing, the main results of this investigation concerns the best choice of the potential for a multiple scattering calculation. Our results indicates that HL

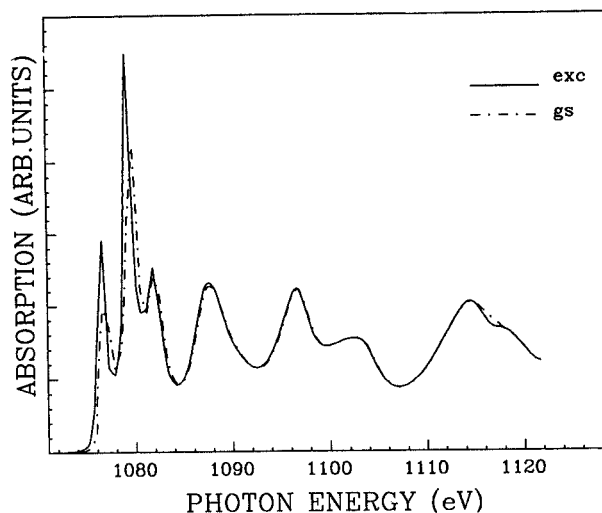


FIG.3 NaCl - Na K-edge. Theoretical spectra built by a DH potential. Comparison between calculations with final state with the Z+1 excited potential (exc) and a final potential equal to the one of the ground state (gs).

potential gives the more accurate calculation in agreement with recent works on Br<sub>2</sub>, GeCl<sub>4</sub> and SF<sub>6</sub> molecules. [15]

#### ACKNOWLEDGEMENT

We are indebted to T. Murata, T. Matsukawa and S. Naoe' which send us experimental data on alkali halides prior to publication.

#### REFERENCES

- 1) J. E. Müller, O. Jepsen, J. W. Wilkins, *Solid State Comm.* **42**, 365 (1982).
- 2) D. Dill, J. L. Dehmer, *J. Chem. Phys.* **61**, 694 (1974)
- 3) C. R. Natoli, D. Misemer, S. Doniach, F. Kutzler, *Phys. Rev. A* **22**, 1104 (1980).
- 4) J. S. Faulkner and G. M. Stocks, *Phys. Rev. B* **21**, 3222 (1980).
- 5) L. Hedin, B. I. Lundqvist, *J. Phys. C: Solid State Phys* **4**, 2347 (1971).
- 6) L. J. Sham, W. Kohn, *Phys. Rev* **145**, 561 (1966).
- 7) P. A. Lee, G. Beni, *Phys. Rev. B* **15**, 2862 (1977).
- 8) Ph. Sainctavit, J. Petiau, M. Benfatto, C. R. Natoli to be publ.
- 9) J. C. Slater, *The Self-Consistent Field for Molecules and Solids; Quantum Theory of Molecules and Solids*, McGraw-Hill, New York (1979).
- 10) S. Hara, *J. Phys. Soc. Jpn* **26**, 376 (1967).
- 11) M. P. Seah, W. A. Dench, *Surf. and Interf. Anal.* **1**, 1 (1979)
- 12) F. L. Battye, J. Liesegang, R. C. G. Leckey, J. G. Jenkin, *Phys. Rev. B* **13**, 2646 (1976).
- 13) C. J. Powell, *J. Electron Spectrosc. Relat. Phenom.* **47**, 197 (1988).
- 14) K. D. Sevier, *Low Energy Electron Spectrometry*, p.220, Wiley-Interscience, Chichester (1972).
- 15) C. R. Natoli, M. Benfatto, T. A. Tyson, K. O. Hodgson, submit. to *Phys. Rev. B*.
- 16) R. F. Pettifer, A. D. Cox, in: *EXAFS and near edge Structure*, eds. A. Bianconi, L. Incoccia and S. Stipcich, p.66, Springer Verlag, Berlin (1982).