Full potential multiple scattering calculations of
transition metals K-edges

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Abstract. Following our recent derivation of a Real Space Full-Potential Multiple-Scattering-Theory (RSFP-MST), we calculate the low-energy part of the K-edge absorption spectra of the transition metals of the first row of the periodic table using the Hedin-Lundqvist (HL) and the Dirac-Hara (DH) complex potentials, which are often used in the literature for this kind of calculations. In both cases the complex part is taken from the HL potential. Taking advantage of the fact that in the FP-MS scheme the Schrödinger Equation is solved exactly without approximations (within the limits of the $l$-truncation procedure in MST), we intend to test the \textit{ab initio} validity of these optical potentials in cases that are borderline between the independent particle and the weakly correlated regime. Surprisingly enough, we find better agreement with experiments with the DH potential.

1. Introduction
Recently, we have developed a Real Space Full-Potential Multiple-Scattering-Theory (RSFP-MST) valid both for continuum and bound states, that is free from the drawbacks that up to now have impared its development, in particular the need to use cell shape functions and rectangular matrices. This approach provides a straightforward extension of MST in the Muffin-Tin (MT) approximation, with only one truncation parameter given by the classical relation $l_{\text{max}} = kR_b$, where $k$ is the photo-electron wave vector and $R_b$ the radius of the bounding sphere of the scattering cell \cite{1, 2}. The method provides in principle an exact solution (within the convergence limits of the $l$-truncation procedure) of the Lippmann-Schwinger (LS) equation associated to the scattering solution of the Schrödinger Equation (SE), without making any approximation on the geometrical shape of the scattering potential, as instead done in the MT approach. As well known, this solution is a necessary ingredient for the calculation of various types of Synchrotron Radiation (SR) spectroscopies, in particular photo-absorption. It is therefore natural to try to use this advantage to begin to test the optical potentials commonly used for this spectroscopy, like the Hedin-Lundqvist (HL) and the Dirac-Hara (DH) potentials, in order to understand and possibly amend their defects.

It is also known that a fitting procedure based on absorption signals calculated in the MT approximation provides sometimes excellent fits to the experimental spectra. However this
| Element | Ti | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---------|----|----|----|----|----|----|----|----|
| Z       | 4  | 6  | 7  | 8  | 9  | 10 | 11 | 12 |
| $\hbar \omega_p$ | 17 | 24 | 28 | 31 | 34 | 35 | 36 | 32 |
| $\Delta E_{\text{obs}}$ | 22 | 24 | 22 | 21 | 21 | 23 | 20 | 23 |

Table 1. Expected and observed plasmon energies in TM (in eV)

One way to eliminate this inconvenience is to study the absolute performance of the optical potential itself, by calculating the absorption spectrum without any adjustable parameter. This is our goal in this paper.

2. The Hedin-Lundqvist (HL) and the Dirac-Hara (DH) self-energies

The systems we have chosen to study are the transition metals (TM) of the first row of the periodic table, by considering their K-edge absorption. This choice has the advantage that the quasi-particle approach in this case is reasonably justified, since the photo-electron final state is a $p$ band of the metal, enough extended so that the Coulomb interaction with the localized $3d$ states can be neglected in first approximation. As a consequence a GW approximation to the self-energy as an optical potential (at least to describe extrinsic losses) should be a viable approach. As is well known, the HL potential is the local density approximation of the GW self-energy, which corresponds to the self-energy of a test electron moving in an uniform interacting electron gas (the model system) with density equal to the local density of the real inhomogeneous system. Moreover the inverse dielectric function of the model system is approximated by a single plasmon pole, so that one puts

\[
[\epsilon(k, \omega)]^{-1} = 1 + \omega_p^2 [\omega^2 - \omega_k^2]^{-1}
\]

\[
\hbar \omega_p = \left( \frac{4\pi e^2 n}{m} \right)^{1/2} = \frac{2\sqrt{3}}{r_s^{3/2}} \text{Ryd}
\]

Here $k$ is the local photo-electron momentum and $\hbar \omega_p$ is the plasmon energy, which can be expressed in terms of $r_s = [3/(4\pi n)]^{1/3}$, the interparticle distance in the homogeneous electron gas of density $n$, measured in au. We refer to Ref. [3] for the explicit expression of the HL potential and definition of the other parameters.

The real part of the HL potential is composed of two terms: the static Hartree-Fock (HF) exchange, known also as Dirac-Hara (DH) exchange, coming from the constant part of of the dielectric function in Eq. (1) and the dynamically screened exchange-correlation contribution (HLXC), originating from the $\omega$-dependent part. One would be led to think that the real DH part of the self-energy should perform better than the HLXC part, since this latter is connected to $3d$ interband transitions which deviate quite substantially from the free-electron bands. This fact becomes apparent if one tries to calculate the plasmon energy from Eq. (1). Table 1 gives the expected plasmon energy for selected transition metals, by assuming that $Z$ electrons participate in the charge oscillation, and the observed energy loss $\Delta E_{\text{obs}}$ [4]. It is clear that not all the $3d$ electrons participate in the plasmon oscillations, implying that the $3d$ electrons are not completely free to oscillate.

This discrepancy indicates that the HLXC part of the HL self-energy in the local plasmon pole approximation might not be adequate to describe the diffraction processes that the photoelectron undergoes in its way through the system. Indeed, even the imaginary part might be affected by this drawback, although to a lesser extent, due to the fact that the plasmon pole holds almost
all of the oscillator strength of the particle-hole transitions. Due to lack of space, we shall limit ourselves here to compare the performance of the HL against a DH potential, assuming that the losses are sufficiently well described in both cases by the imaginary part of the HL self-energy.

When we compare the results of Figs. 1, 2, 3, it is clear that the DH potential gives overall better agreement with the experiments than the HL one. A similar result was found in Ref. [5] for $Cu_2MnM$, where $M = Al, Sn, In$, although in the MT approximation. In both cases there seems to be a problem with Chromium. Disagreement with the experiments toward the end of the energy range might be also affected by an insufficient
Figure 2. Comparison between Fe K-edge absorption (top) and Cr (bottom) calculated with complex HL (left) and DH (right) potentials. (Color online)

Figure 3. Comparison between Co K-edge absorption calculated with complex HL (left) and DH (right) potentials. (Color online)

$l_{\text{max}}$ used in the calculations and the neglect of the Debye-Waller effect.

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