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Quanty for core level spectroscopy - excitons, resonances and band excitations in time and frequency domain

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Abstract. Depending on the material and edge under consideration, core level spectra manifest themselves as local excitons with multiplets, edge singularities, resonances, or the local projected density of states. Both extremes, i.e., local excitons and non-interacting delocalized excitations are theoretically well under control. Describing the intermediate regime, where local many body interactions and band-formation are equally important is a challenge. Here we discuss how ***Quanty***, a versatile quantum many body script language, can be used to calculate a variety of different core level spectroscopy types on solids and molecules, both in the frequency as well as the time domain. The flexible nature of ***Quanty*** allows one to choose different approximations for different edges and materials. For example, using a newly developed method merging ideas from density renormalization group and quantum chemistry [1–3], ***Quanty*** can calculate excitons, resonances and band-excitations in x-ray absorption, photoemission, x-ray emission, fluorescence yield, non-resonant inelastic x-ray scattering, resonant inelastic x-ray scattering and many more spectroscopy types. ***Quanty*** can be obtained from: http://www.quanty.org.

Core level spectroscopies have long been valuable tools in the field of material research for a huge range of compounds with different degree of correlations. The theoretical interpretation can be roughly divided into two different approaches. The first approach is based on density functional theory. These methods include the full band formation, either using a one electron basis [4–6] or using multiple scattering theory [7, 8]. At this level of approximation, x-ray absorption is identified as the unoccupied density of states, which works quite well for several edges [9–12]. The core-valence interaction can be modeled as an additional potential resulting in an edge singularity in the spectral function [13–15]. The inclusion of the full band-structure comes at a price and in order to make the calculations tractable approximations have to be made on the local Coulomb interaction and multiplets. The second approach starts from a local ansatz. The method approximates the solid by a small cluster in which all local Coulomb interactions and multiplets can be accounted for. Very good agreement with experiment exists for many transition metal $L_{2,3}$ and rare earth $M_{4,5}$ edges, which are strongly influenced by multiplet effects [16, 17]. The resulting spectra are intrinsically many-body and must not be confused with the unoccupied density of states. In order to make the calculations tractable, the full multiplet methods neglect band formation and non-local dispersions. The later approach used to be parameter based, but several groups recently managed to calculate *ab intio* spectra including full multiplet theory [1, 18–21].

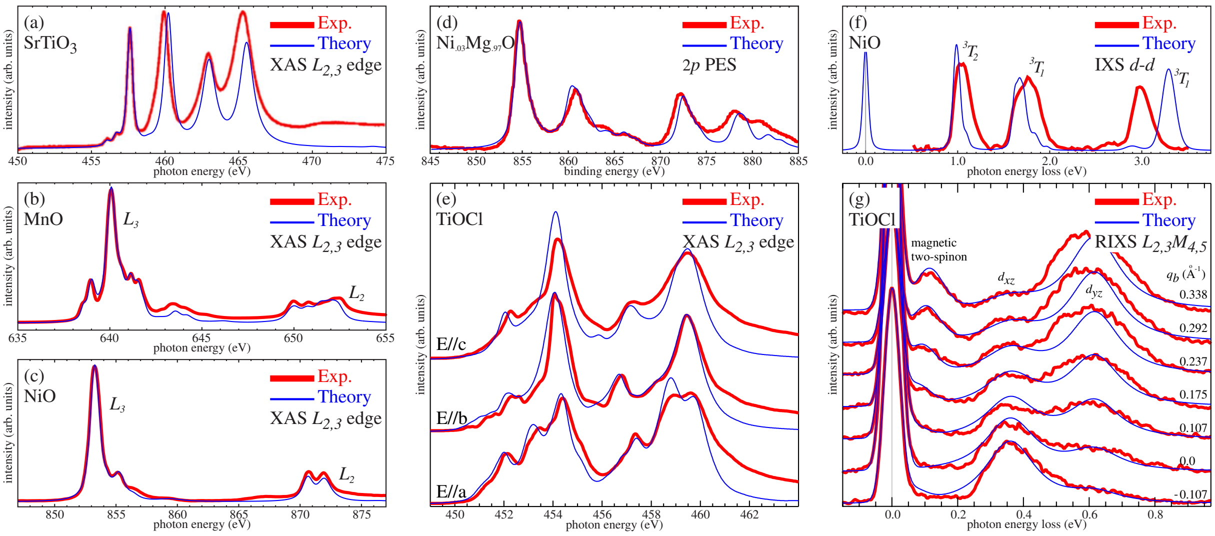

Figure 1. *Ab initio* theoretical and experimental core level spectra for several materials and experimental techniques. (a-c) $2p$ to $3d$ x-ray absorption in transition metal compounds. (d) $2p$ core level photoemmission of Ni impurities in MgO. (e) $2p$ to $3d$ x-ray absorption in TiOCl, including the natural linear dichroism induced due to the low crystal symmetry. (f) $d-d$ excitations in NiO induced by inelastic x-ray scattering. (g) $d-d$ and dispersive magnetic excitations in TiOCl induced by resonant inelastic x-ray scattering at the Ti L edge. Experimental spectra reproduced from: (a) Uehara *et al.* [22], (b) Csiszar *et al.* [23], (c) Alders *et al.* [24], (d) Altieri *et al.* [25], (e) Glawion *et al.* [19, 26], (f) Verbeni *et al.* [27, 28], (g) Glawion *et al.* [19, 26]. Theory reproduced from: (a-d,f) Haverkort *et al.* [1], (e,g) Glawion *et al.* [19, 26].

There is a range of materials, for example correlated metals and a set of experiments, including excitations involving resonances with multiplets, where neither of the two approaches give a satisfactory result. For insulators with a large core-valence interaction a bound state of the core-hole and additional valence electron can form. These bound states are called excitons and show in the spectrum as sharp peaks outside the continuum. If the exciton is degenerate with a set of continuum excitations the core hole and valence electron do not form a perfect bound state. One still can find an enhancement in the absorption, but these peaks are broader than excitonic excitations and have an asymmetric lineshape [29]. These virtually bound states are called (Fano) resonances. Resonances are generally difficult to describe as both local multiplets and non-local band-formation is important. This problem is not unique to core level spectroscopy, but also exists at low photon energies related to visible light. Describing the absorption of light into a local resonance with multiplets and the subsequent decay into a delocalized hole and electron state is a true theoretical challenge. The exponential scaling of the computational effort with system size makes the calculation intractable without further approximations. Despite the difficulty of the problem, progress is made into merging the two different approaches for the calculation of core level spectroscopy. On the side of the band-structure approaches several groups implemented the Bethe Salpeter equations, which allows one to include core-valence interactions in the final state for band-insulators, i.e. Ti^{4+} and Ca^{2+} compounds [30, 31]. The local cluster models can be extended to include the band width of the material at the level of an Anderson impurity model [32–36]. Using a newly developed method to solve the Anderson impurity model [2], this has recently been applied to metals and correlated metals [3].

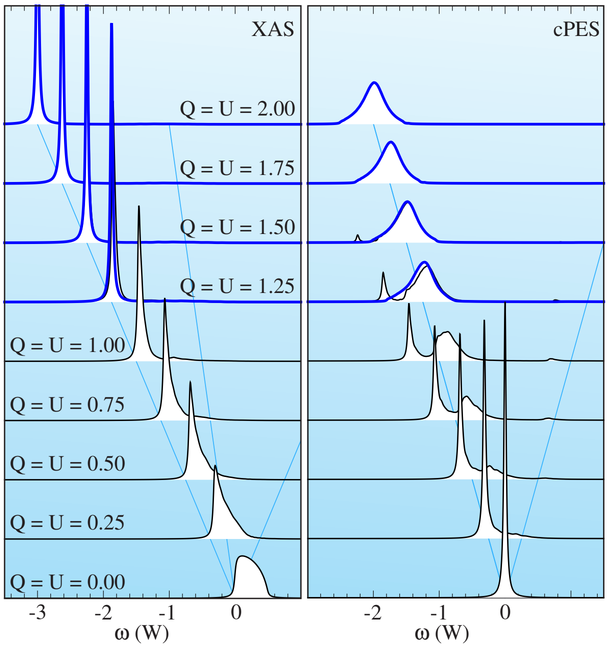

Figure 2. Theoretical model calculations of x-ray absorption (left) and core level photoemission (right) spectra of a band-metal (bottom) to a correlated Mott-insulator (top). The calculations include core-valence interactions (Q) and local valence-valence interactions (U). The infinite correlated lattice is exactly solved locally and non-locally approximating the many body interactions on a (dynamical) mean-field level. For small Coulomb interaction ($U \leq 1.50$) the ground-state is a metal (thin lines) for large Coulomb interactions ($U \geq 1.25$) the ground-state is insulating (thick blue lines). For intermediate correlation strength ($1.25 \leq U \leq 1.50$) we show results for both a metallic and an insulating ground-state. Reproduced from Haverkort *et al.* [3].

Quanty is a program, or script language that can be used to calculate several core level spectroscopies within different approximations. In the first part of the paper we will show *ab initio* results obtained with ***Quanty***. We show multiplet ligand field theory calculations, where the band dispersion is neglected and also show calculations that include the non-local interactions on a (dynamical) mean-field level, governing the complete range of possible spectra. The second part of the paper shows how these calculations can be implemented in ***Quanty***.

In multiplet ligand field theory, the solid is approximated by a single (transition-metal) ion surrounded by an effective set of ligand orbitals mimicking the effect of the solid. For transition metal oxides one can think of these as the O-2p orbitals. Traditionally, multiplet ligand field theory was parameter based [16, 17]. One can implement this method as a post density functional theory method which removes the need to fit parameters [1]. In Fig. 1 we show the result for a large variety of different spectroscopy techniques and transition metal compounds. As one can see, there is good agreement between theory and experiment.

Multiplet ligand field theory is, by the construction of its local basis, not able to describe band excitations or resonances well. The spectra in Fig. 1 are all excitonic excitations in insulators. An extension, which can deal with metals, can be made using the dynamical mean field approximation. Within this approximation locally all correlations are included, but non-locally these are approximated on a mean field level. In Fig. 2 we show the x-ray absorption and core-level photoemission spectra of a one band model for different interaction strengths. The entire range of spectral features, from density of states to resonances to edge singularities to excitons is captured on this level of theory.

Being able to handle both excitons with multiplets as well as resonances in one theory, is for example, important in the description of shallow core level spectra [38]. In Fig. 3 we show the 3p to 3d excitation in MnO as measured with non-resonant inelastic x-ray scattering. For small momentum transfer (panel c and f) one measures a dipole transition. For large momentum transfer (panel a,b,d,e) one measures an octupole transition [39]. Note that although a dipole transition does not possess linear dichroism in a cubic crystal, an octupole transition does, thereby making it possible to distinguish between transitions into the t_{2g} and e_g orbitals by

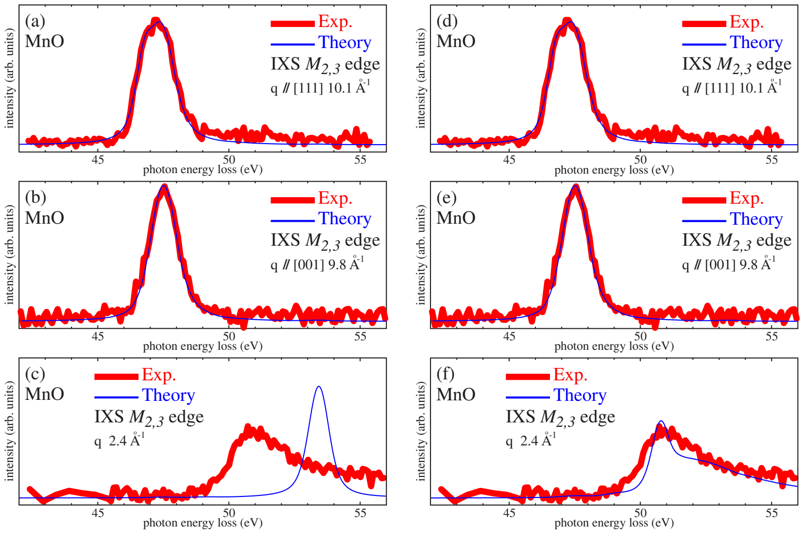

Figure 3. $3p$ to $3d$ IXS excitations in MnO. (a,b,d,e) large momentum transfer, octupole transitions into excitonic states. (c,f) small momentum transfer, dipole transitions into resonances. (a-c) including only a local basis, (d-f) including local correlations as well as the full (dynamical) mean-field approximated band-structure in the theory. Experimental data reproduced from Gordon *et al.* [37]

symmetry[37, 40]. In panel a to c we compare the experiment to the theoretical performed calculations on an *ab initio* multiplet ligand field theory level. The excitonic bound transitions below the continuum edge at $\approx$ 50 eV are well described. The dipole transition above the continuum edge is in the ligand field theory a sharp peak, whereas it is a broad continuum, showing resonant like features in the experiment. Including the continuum in the theory on a dynamical mean field level does not change the excitonic bound states, but does allow one to also capture the resonances correctly as can be seen in panel d to f.

Quanty is a script language which enables its users to calculate these spectra and allows one to solve many other problems in quantum mechanics with a minimal amount of coding. As a first step ***Quanty*** needs to know the basis set used. Although ***Quanty*** is a many body code, the basis set is defined by one particle modes. These are the boxes (basis states) one can place a particle in. The minimal information ***Quanty*** needs to define a basis is the number of Fermionic and Bosonic modes. Fermionic modes can be different orbitals with different spins (spin-orbitals) or different lattice sites. For calculations in solid state physics or chemistry these could refer to the Wannier orbitals in a solid or the molecular orbitals for a molecule. We generally would obtain those with the use of either DFT or Hartree Fock calculations.

```
NF = 6 -- Number of spin-orbitals
NB = 0 -- Number of phonon-modes
```

Once a basis set is defined one can create operators using second quantization. Any operator can be written as:

$$\alpha^{(0,0)} + \sum_i \alpha_i^{(1,0)} a_i^\dagger + \alpha_i^{(0,1)} a_i + \sum_{i,j} \alpha_{i,j}^{(2,0)} a_i^\dagger a_j^\dagger + \alpha_{i,j}^{(1,1)} a_i^\dagger a_j + \alpha_{i,j}^{(0,2)} a_i a_j + \sum_{i,j,k} \ldots, \tag{1}$$

with α numerical prefactors and $a_i^\dagger$ an operator creating an electron in spin-orbital i. In ***Quanty*** one can create a creation operator on spin-orbital $i = 0$ ($a_0^\dagger$) with the function:

```
OppC0 = NewOperator("Cr",NF,0)
```

Annihilation operators are created by replacing the string "Cr" by "An":

```
OppA0 = NewOperator("An",NF,0)
```

One is allowed to multiply operators, either with (complex) numbers or by other operators. Furthermore, one can add operators. In this way one is able to create all possible operators needed.

```
OppNO = OppCO * OppAO                -- Number operator
```

Several standard operators for atomic physics, ligand field theory and different model calculations are pre-defined. It is possible to read the results of several density functional theory codes and obtain a tight-binding Hamiltonian from these codes. This tight binding Hamiltonian can be used as a starting point for many-body calculations and spectroscopy [1, 41].

Wavefunctions are defined by the command:

```
psi = NewWavefunction(NF, NB, {{"100000",sqrt(1/2)}, {"000010",sqrt(1/2)}})
```

where the string defines a Slater determinant and the total function is a sum over different determinants. Expectation values can be obtained by multiplying a wavefunction with an operator with a wavefunction.

```
NO = psi * OppNO * psi
```

For a given operator (H) one can calculate the N_{psi} lowest eigenstates with the function "Eigensystem()". ***Quanty*** does not need to keep the number of electrons fixed. In order to restrict the solutions to a fixed number of electrons one can specify restrictions. This also allows one to do restrictive active space calculations when needed.

```
StartRestrictions = {NF, NB, {"111111",2,2}}
Npsi = 3
psiList = Eigensystem(H, StartRestrictions, Npsi)
```

Spectra are implemented by calculating the Green's function. We calculate the complex energy dependent quantity:

$$G(\omega) = \left\langle \psi_i \middle| T^{\dagger} \frac{1}{\omega - H + \imath\Gamma/2} T \middle| \psi_i \right\rangle, \tag{2}$$

with T and H operators given in second quantization and ψ_i a many particle wavefunction.

```
G = CreateSpectra(H,T,psi)
```

For photoemission, the transition operator T would be an annihilation operator, for absorption it is the product of a creation and annihilation operator and for inverse photoemission T becomes a creation operator. ***Quanty*** has many transition operators for standard types of spectroscopy predefined, but you are always able to create your own transition operator.

Resonant spectra are implemented by calculating a third order Green's function or susceptibility (χ_3):

$$G^3(\omega_1, \omega_2) = \left\langle \psi_i \middle| T_1^{\dagger} \frac{1}{\omega_1 - H_1 - \imath\Gamma/2} T_2^{\dagger} \frac{1}{\omega_2 - H_2 + \imath\Gamma/2} T_2 \frac{1}{\omega_1 - H_1 + \imath\Gamma/2} T_1 \middle| \psi_i \right\rangle. \tag{3}$$

For $2p$ core level resonant inelastic x-ray scattering measuring magnons or $d-d$ excitations T_1 would excite a $2p$ core electron into the $3d$ valence orbitals and T_2 would de-excite a $3d$ electron into the $2p$ core hole. For core-core excitations T_2 would de-excite for example a $3s$ core electron into the $2p$ core hole. ***Quanty*** can calculate resonant spectra with the function:

```
G3 = CreateResonantSpectra(H1, H2, T1, T2, psi)
```

The Green's functions calculated do not only describe the spectra one can measure in the frequency domain, but also spectra one can measure in the time domain. These Green's functions are on a fundamental level related to how an excitation propagates through the sample. The Green's function $G(t) = \langle\psi_i|T^{\dagger}(t)T(0)|\psi_i\rangle$ describes the probability where an excitation made at $t = 0$ can be found at $t = t$. The relation between $G(\omega)$ and $G(t)$ is given by a Fourier transform: $G(\omega) = \imath \int_0^{\infty} e^{\imath\omega t} G(t)$. Pump probe spectroscopy where one investigates the propagation of one excitation by a second excitation is expressed as the Fourier transform of G^3.

In conclusion, we here present several calculations of different forms of x-ray spectroscopy (XAS, cPES, RIXS, nIXS) including excitons, resonances and continuum excitations obtained with the script language ***Quanty***. A basic introduction to the script language is presented.

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