Combined multiplet and cumulant Green’s function treatment of correlation effects in x-ray photoelectron spectroscopy

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The treatment of electronic correlations in open-shell systems is among the most challenging problems of condensed matter theory. Current approximations are only partly successful. Ligand field multiplet theory (LFMT) has been widely successful in describing intra-atomic correlation effects in x-ray spectra, but typically ignores itinerant states. The cumulant expansion for the one electron Green’s function successfully describes shake-up effects but ignores atomic multiplets. More complete methods are computationally problematic. Here we show that separating the dynamic Coulomb interactions into local and longer-range parts yields an efficient, nearly ab initio multiplet + cumulant approach that accounts for both local atomic multiplet-splittings and charge-transfer shake-up satellites. An application to α-Fe2O3 (hematite) yields very good agreement with XPS experiment, including the broad 9 eV satellites and distributed background features missing from previous approaches.

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The frontier of an in-silico description of complex functional behavior of materials lies in a consistent description of their physics and chemistry over many length and time scales. Achieving such a description has been a major challenge of computational materials science, whose success is ultimately assessed by the ability to describe both ground and excited states, including non-equilibrium conditions. Computational methods typically focus on delocalized band-like descriptions, as in Kohn-Sham density functional theory (DFT), or highly localized descriptions, as in ligand-field multiplet theory (LFMT) and quantum chemistry. However, more elaborate approaches such as dynamical mean field theory (DMFT) and embedding methods extended to clusters have been used to move away from purely local or delocalized points of view. Both aspects are important in x-ray spectroscopy, which can provide atom-specific information about local coordination, valency, and excited states that is well captured by multiplet approaches for deep core states. Computational schemes that combine these aspects are highly desirable for strongly correlated materials such as transition metal oxides (TMOs). This is the main goal of this work, where a local LFMT model is combined with the non-linear cumulant Green's function approach to treat both local- and longer-range correlated behavior.

Core-level x-ray photoemission spectroscopy (XPS) is a sensitive probe of correlation effects in excited state electronic structure. In particular, the XPS signal is directly related to the core-level spectral function \( \mathcal{A}_c(\omega) \), which describes the distribution of excitations in a material. The main peak in the XPS corresponds to the quasiparticle, while secondary features, i.e., satellites, correspond to many-body excitations. These satellite features are pure many-body correlation effects which have proved difficult to calculate from first principles in strongly correlated materials. They can also have considerable spectral weight, comparable to that in the main peak and spread over a broad range of energies. Many-body perturbation theory within the GW approximation is inadequate to treat these effects. While GW can give reasonably accurate core-level binding energies (quasiparticle energies), the satellite positions and amplitudes are not well reproduced, even in relatively weakly correlated systems such as sodium and silicon. On the other hand, the cumulant expansion of the one-electron Green’s function has shown notable success in predicting the quasi-bosonic satellite progressions seen in those systems, as well as the charge-transfer satellites observed in some TMOs. Nevertheless an accurate treatment of the excitation spectrum of strongly correlated materials typically demands more elaborate theories, such as CI, coupled-cluster techniques, or by mapping electronic structure from DFT or GW calculations onto model Hamiltonians, as in ab initio LFMT. These approaches can yield impressive results for multiplet splittings from localized states as seen in XPS; however, they generally lack an adequate Hilbert space to fully account for extended states and collective excitations. While dynamical processes such as charge-transfer excitations can be treated with model Hamiltonians as in cluster LFMT, or LDA+DMFT, the inclusion of high energy excitations is numerically challenging.
In an effort to address these limitations, we introduce here an approach that combines a simplified local multiplet model that ignores charge transfer effects, with the cumulant approximation for the core-Green’s function. We dub the approach \textit{Multiplet+C}, in analogy with other methods where the cumulant Green’s function is added to treat satellite excitations. As a consequence, this combined method treats both local electronic correlations and dynamical excitations of the extended system. The approach is also advantageous computationally and simplifies the physical interpretation. For simplicity, we focus our attention on the 2p XPS of TMOS, where the number of 2p electrons changes from 6 to 5 upon photo-excitation. Using a separation of the short- and long-ranged Coulomb interactions, the method yields an expression for the core spectral function \(A_{2p}(\omega) = -(1/\pi) \text{Im} G_{2p}(\omega)\) given by a convolution of the 2p local spectral function with the cumulant spectral function for the extended system,

\[
A_{2p}(\omega) = A_{2p}^{\text{loc}}(\omega) * A_{2p}^{C}(\omega). \tag{1}
\]

As a consequence, each discrete local level is broadened by the cumulant spectral function \(A_{2p}^{C}(\omega)\), which also produces shake satellites. Our calculations are carried out in the time-domain\cite{12}, where the Green’s function is given by the cumulant ansatz,

\[
G_{2p}(t) = G_{2p}^{\text{loc}}(t)e^{C_{2p}(t)}, \tag{2}
\]

where \(G_{2p}^{\text{loc}}(t)\) is the trace over 2p single particle states of the atomic multiplet Green’s function for our simplified model, and \(C_{2p}(t)\) is the cumulant, which builds in dynamic correlation effects. The above approximation was inspired by the work in Refs.\cite{13,14} where a similar product of an atomic Green’s function and cumulant form was used to treat plasmon excitations in DMFT. To justify our approach we define a separable model Hamiltonian \(H = H^{\text{loc}} + H^{\text{box}}\) in which the simplified localized (atomic, ligand field, or cluster) system consists of a limited number of electrons (the 2p and 3d shells for example) interacting with the extended system via quasibosons that characterize the excitations.\cite{13,14} In the results presented here, the local system is defined by a short-range many-body Hamiltonian,

\[
H^{\text{loc}} = \sum_i \varepsilon_i n_i + \sum_{i,j} [V_{ij}^{\text{xf}} c_i^\dagger c_j + c.c.] + \sum_{i,j,k,l} v_{ijkl} c_i^\dagger c_j^\dagger c_k c_l, \tag{3}
\]

where \(V_{ij}^{\text{xf}}\) denotes the crystal field potential, \(v\) the Coulomb interaction, and the electron levels \(\{i,j\}\) are limited to the 2p and 3d shells of a single atom. In general, this Hamiltonian can be extended to include ligands as in \textit{ab initio} LFMT or cluster CI calculations. However, we find that for the results presented here (XPS of \(\text{Fe}_2\text{O}_3\)), it is sufficient to simply scale the Slater-Condon parameters to match the \textit{ab initio} cluster CI results of Bagus et al.\cite{15,16} (see supplementary information for comparison), which did not include shake satellites. Thus \(H^{\text{loc}}\) accounts for covalency effects on the multiplet levels, but does not treat charge transfer satellites which are included via the cumulant. This approximation allows a simple solution of the problem, although it does not include the effects of charge transfer on the local configuration, and instead keeps a fixed number of \(d\)-electrons within the local Hamiltonian. The quasi-boson Hamiltonian for the extended system including the coupling to the localized system is defined as

\[
H^{\text{bos}} = \sum_q \omega_q a_q^\dagger a_q + \sum_{qi} n_i V_i^q(a_i^\dagger + a_q), \tag{4}
\]

where \(V_i^q\) are fluctuation potentials,\cite{16} and \(n_i\) is the occupation of the hole-state \(i\) in 2p. If we now make the approximation that the couplings \(V_i^q\) are independent of the hole state \(i\) of the localized system, the net coupling depends only on the total number of holes \(N_h = \sum n_i\) in the 2p shell, which is equal to 1 in the XPS final state. Then the Hamiltonian \(H^{\text{bos}}\) is equivalent to that of Langreth,\cite{17} which describes a system of bosons interacting with an isolated core-electron. Notably, this model can be solved using a cumulant Green’s function, with a cumulant proportional to the density-density correlation function \(\chi(q,q',\omega)\). This yields a spectral function with a series of satellites corresponding to bosonic excitations. The difference in our treatment is that the localized system has its own set of eigenstates (the atomic-multiplet levels) once the 2p hole appears, each with its own bosonic satellites from the convolution with \(A_{2p}^{C}(\omega)\). In our calculations the cumulant \(C_{2p}(t)\) is obtained using real-time TDDFT approach analogous to the Langreth formulation,\cite{24} and can be expressed in Landau form\cite{28},

\[
C_{2p}(t) = \int d\omega \frac{\beta(\omega)}{\omega^2} [e^{-i\omega t} + i\omega t - 1],
\]

\[
\beta(\omega) = \omega \int d^2r \text{Re}[V(r)\delta p(r,\omega)]\] \tag{5}

Here \(\delta p(r,\omega)\) is the time-Fourier transform of the density fluctuations \(\delta p(r, t)\) induced by the sudden appearance of the core-hole, and \(V(r)\) is the 2p core-hole potential. In order to treat the strong core-hole effects in correlated systems, we also include non-linear corrections to the cumulant, following the approach of Tzavala et al.\cite{18}.

As an illustrative example, we apply this approach to the 2p XPS of \(\alpha-\text{Fe}_2\text{O}_3\) (hematite). The localized system is treated with an atomic multiplet approach using modified Slater-Condon parameters \(F\) and \(G\) scaled by 0.8 to simulate the effects of covalency and ignoring charge-transfer coupling. These parameters are calculated using a modified version of Desclaux’s Dirac-Fock atomic code\cite{11,12} available within the FEFF10 software package.\cite{10,11} We used a crystal field strength \(10Dq = 0.5\ e\)\cite{16} and spin-orbit couplings from the literature.\cite{13} The multiplet spectra obtained with this effective atomic model is found to be in quantitative agreement with the cluster CI calculations of Bagus et al.\cite{15,16} that also ignore the charge-transfer coupling. Further details are reported in the Supplemental Material at
approaches (red).

FIG. 2: Comparison of the area normalized $2p$ XPS of $\alpha$–Fe$_2$O$_3$ from experiment (black crosses) with that calculated using the CI-LFMT (green) and the Multiplet+C approaches (red).
we calculate the fluctuations in the Mulliken charges (Fig. 4) vs time on the central Fe atom (red), the 6 O-ligand atoms (blue), as well as the sum of Fe and O-ligands (green). Within a fraction of a femtosecond, the electron count on the Fe increases by 1, then oscillates between 1 and 1.5 at a frequency $\omega_{CT} \sim 9$ eV, corresponding to charge-transfer fluctuations. In contrast, the oscillations in the O-ligand count are 180° out of phase, indicating a substantial charge transfer between metal and ligand. Note, however, that the sum of ligand and metal counts (green) contains sizable residual oscillations, indicating additional charge transfer from outer shells. In addition, the sum retains most of the initial increase seen in the Fe atom, suggesting that the transient screening in the first fraction of a femtosecond is collective in nature. Finally, although not shown, the oscillations are dominated by the minority spin channel on the Fe atom. This is not surprising, as the majority spin channel has only a small number of unoccupied d-states.

In conclusion, we have developed a combined Multiplet+C approach that treats the complementary short- and longer-ranged excited state correlation effects in open-shell systems. The method is based on the separation of the many-body Hamiltonian into that for a local many-body atomic system coupled to an extended system in terms of quasi-bosonic excitations as in the Langreth cumulant, that characterize the density fluctuations of the extended system. The approach yields a spectral function for the full system as a convolution of the local multiplet spectral function and the non-linear cumulant spectral function for the extended system. Thus each multiplet level of the local system is treated as a quasi-particle with it’s own spectral function and series of quasi-bosonic satellites. In this sense, the Multiplet+C approach is doubly dynamic, as in the DMFT+cumulant approach\[12]. An application to hematite, a prototypical correlated TMO, yields 1s and 2p XPS spectra in very good agreement with experiment. In contrast to CI-based LFMT, Cluster-LFMT, or LDA+DMFT\[13], our approach simplifies the calculations and physical interpretation of the spectra, yet accounts quantitatively for the large shake excitations, double-excitations, and the broad background, with a weight comparable to that in the quasi-particle peak. Many extensions are possible; for example, the local model used here can be improved to treat clusters of atoms; the convolution with the cumulant spectral function can be applied ex post facto to treat collective excitations in other theoretical approaches; and the method can be applied to other x-ray spectra. Finally, we note that the results presented here provide proof of principle for an efficient ab initio approach to charge-transfer LFMT, since the only free parameters in the calculation (other than broadening) were used to match cluster calculations that did not include any shake or charge-transfer excitations.

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Appendix: Derivation of the Multiplet + C Green’s function

The 2p XPS is given by the partial trace over the states of the 2p shell of the Green’s function, i.e., $I_{2p}^{XPS}(\omega) \propto -\frac{i}{\pi} \text{Im} G_{2p}(\omega) = -\frac{i}{\pi} \sum_{i \in 2p} \text{Im} G_{ii}(\omega)$, where $G_{ii}(\omega)$ is the Fourier transform of the real-time Green’s function,

$$G_{ii}(t) = -ie^{-iE_0 t} |0\rangle c_i^\dagger e^{iHt} c_i |0\rangle . \quad (A.1)$$

Here $|0\rangle$ is the ground state with associated energy $E_0$, and the Hamiltonian we take as,

$$H = H_{\text{loc}} + H_{\text{bos}}, \quad (A.2)$$

where $H_{\text{loc}}$ describes a limited set of localized electronic states, and $H_{\text{bos}}$ describes bosonic or quasi-bosonic excitations, i.e., plasmons, charge-transfer excitations, phonons, etc.,

$$H_{\text{loc}} = \sum_i \epsilon_i n_i + \sum_{i,j} V_{ij}^d c_i^\dagger c_j + c.c. + \sum_{i,j,k,l} v_{ijkl} c_i^\dagger c_j^\dagger c_k c_l,$$

$$H_{\text{bos}} = \sum_q \omega_q a_q^\dagger a_q + \sum_{q,i \in 2p} n_i V_q^a (a_q^\dagger + a_q). \quad (A.3)$$

In the above, $V_q^a$ are the fluctuation potentials, which couple the 2p hole $i$ to the bosons $q$, $c_i^\dagger / c_i$ are electron creation/annihilation operators, and $a_q^\dagger / a_q$ are boson creation/annihilation operators. If we assume that $V_q^a = V_q^q$ is independent of the hole state, the boson Hamiltonian becomes,

$$H_{\text{bos}} = \sum_q \omega_q a_q^\dagger a_q + \sum_q N_h V_q^a (a_q^\dagger + a_q), \quad (A.4)$$

where $N_h$ is the total number of 2p holes, equal to 0 in the ground state, and 1 in the XPS final state. Now the entire problem simplifies since $H_{\text{loc}}$ and $H_{\text{bos}}$ commute in the XPS final state, and the Green’s function is given by,

$$G_{2p}(t) = -ie^{-iE_0 t} \sum_{i \in 2p} \langle 0 | c_i^\dagger e^{-iH_{\text{loc}} t} e^{-iH_{\text{bos}} t} c_i | 0 \rangle . \quad (A.5)$$

In addition, the ground state is the zero hole, zero boson state, and can be written $|\Psi_0\rangle |\nu_0\rangle$. Thus the Green’s function becomes separable,

$$G_{2p}(t) = iG_{2p}^{\text{loc}}(t)G_{2p}^{\text{bos}}(t),$$

$$G_{2p}^{\text{loc}}(t) = -ie^{-iE_0 t} \sum_{i \in 2p} \langle \Psi_0 | c_i^\dagger e^{-iH_{\text{loc}} t} c_i | \Psi_0 \rangle ,$$

$$G_{2p}^{\text{bos}}(t) = -i (\nu_0 | e^{-iH_{\text{bos}} t} | \nu_0 \rangle = -i e^{C(t)}. \quad (A.6)$$

The local Green’s function can be calculated via exact diagonalization or iterative inversion schemes such as Lanczos. The Green’s function of the bosons is identical to that of Langreth for an isolated core-electron interacting with bosons, and can be found analytically.\cite{Langreth} Finally, taking the Fourier transform, the XPS intensity can be written,

$$I_{2p}^{XPS}(\omega) \propto A_{2p}(\omega) = A_{\text{loc}}(\omega) \ast A_{\text{bos}}(\omega). \quad (A.7)$$

Appendix: Multiplet Calculations

Ligand-field multiplet theory (LFMT) calculations were carried out with the WebXRS code.\cite{Bagus} The Slater-Condon parameters were calculated based on a Fe$^{3+}$ atom with using the Dirac-Fock atomic code available within the FEFF10 package. In order to take covalency into account, the Slater-Condon parameters were reduced to 85% of the value as calculated for the Fe$^{3+}$ ion, which produces a spectrum that closely matches that for an FeO$_6$ cluster calculated by Bagus et al.\cite{Bagus} as shown in Fig. 5. The values of all parameters necessary to define the local atomic multiplet Hamiltonian are shown in table I.

FIG. 5: Comparison of the LFMT spectral functions calculated using the CI-LFMT calculations of Bagus et al. (red)\cite{Bagus} and the atomic LFMT calculations using the Slater-Condon parameters of this work (green).

| Parameter | Value |
|-----------|-------|
| $D_{pq}$ | 0.5 |
| $D_{d}$ | 8.2 |
| $C_{sd}$ | 0.06 |
| $F_{dd}$ | 10.4 |
| $F_{dd}$ | 6.5 |
| $F_{dd}$ | 5.9 |
| $G_{pd}$ | 4.52431 |
| $G_{pd}$ | 2.4 |

TABLE I: Parameters used in LFMT calculations for Fe$^{3+}$ from this work.

Appendix: Real-Time TDDFT calculations

The real-time TDDFT calculations were performed with the real-time version of the SIESTA code,\cite{Soler} using the PBE generalized gradient functional.\cite{Perdew} The default
double-zeta plus polarization (DZP) basis set was used for both Fe and O atoms. In order to limit the interaction of the core-holes, a 3x3x3 supercell consisting of 270 atoms was used, which was found to produce converged spectra. The pseudopotentials were calculated using the ATOM code with parameters taken from Rivero et al.\textsuperscript{[47]}

Appendix: Separation of the cumulant spectral function

In order to separate the cumulant spectral function into quasiparticle and satellite parts we assume a simple separation of the quasi-boson excitation spectrum, i.e.,

\[
\beta(\omega) = \beta_{\text{sat}}(\omega) + \beta_{\text{QP}}(\omega),
\]

\[
\beta_{\text{QP}}(\omega) = \alpha \omega e^{-\omega^2/\omega_0^2},
\]

where \(\alpha\) is set to match the linear portion of \(\beta(\omega)\) near the origin, and \(\omega_0\) was set to the energy of the charge-transfer peak at 8.5 eV. The quasiparticle portion \(\beta_{\text{QP}}\) contains all of the low frequency weight which produces the asymmetry in the main peak of the spectral function, while the satellite portion, \(\beta_{\text{sat}}\) contains the majority of the weight related to the main quasi-bosonic (charge-transfer) excitation. Note that this separation is not unique, but does not effect the total spectrum, and only effects the definition of shake up weight in the satellite, and the quasiparticle properties such as the renormalization.

Appendix: Broadening of the spectra

All spectra were broadened with Voigt functions using a Gaussian full-width full-max (FWFM) of 1.2 eV to account for experimental broadening and coupling to phonons. The Lorentzian broadening was set to 0.41 eV FWFM for the 2\(p_{3/2}\) portion of the spectrum, above \(\approx -10\) eV, and increased to 1.14 eV below that to account for the larger lifetime width of the 2\(p_{1/2}\) states.

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