Ab Initio Multiplet-Plus-Cumulant Approach for 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 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 has been successful in describing shake-up effects but ignores atomic multiplets. More complete methods, such as dynamic mean-field theory can be computationally demanding. Here, we show that separating the dynamic Coulomb interactions into local and longer-range parts with *ab initio* parameters yields a combined multiplet-plus-cumulant approach that accounts for both local atomic multiplets and satellite excitations. The approach is illustrated in transition metal oxides and explains the multiplet peaks, charge-transfer satellites, and distributed background features observed in XPS experiment.

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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 nonequilibrium conditions [1]. Computational methods typically focus on delocalized bandlike descriptions, as in Kohn-Sham density functional theory (DFT), or highly localized descriptions, as in ligand-field multiplet theory (LFMT) [2,3] and quantum chemistry [4,5]. However, more elaborate approaches such as dynamical mean-field theory (DMFT) [6,7] and embedding methods extended to clusters [8,9] 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. Quantitative approaches that treat both aspects without adjustable parameters are highly desirable. This is the main goal of this work, where an *ab initio* approach combining a local LFMT model with the nonlinear cumulant Green's function [10–13] is developed to treat both local and longer-range correlations.

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 $A_c(\omega)$, 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 that have proved difficult to calculate from first principles in highly 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 and quasiparticle energies [14,15], 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 [16–18] has had notable success in predicting the quasibosonic satellite progressions [10,19–23], as well as the charge-transfer satellites observed in some correlated materials [24,25]. Nevertheless a quantitative treatment of the excitation spectrum of strongly correlated materials demands more elaborate theories. Theories like CI [4], coupled cluster [26,27], or model Hamiltonian methods fit to DFT or GW calculations as in *ab initio* LFMT [28–31] can yield impressive results for the multiplet splittings seen in XPS. However, they usually lack an adequate Hilbert space to account for extended states and collective excitations. Moreover, these theories typically include some adjustable parameters that may obscure the underlying physics. Although dynamical processes such as charge-transfer excitations can be treated with cluster LFMT or local-density approximation plus DMFT (LDA + DMFT) [8,32], the inclusion of higher energy excitations has remained computationally challenging [7].

In an effort to address these limitations, we introduce here an *ab initio* approach that combines a local multiplet model that ignores charge-transfer excitations, with a nonlinear cumulant approximation for the core Green's function. We dub the approach $Multiplet + C$ in analogy to other methods where the cumulant Green's function is added to treat satellite excitations [10,19,21,24,33]. Our approach is advantageous computationally, both for its simplicity in implementation and its physical interpretation. For definiteness, we focus here on the $2p$ XPS of transition metal oxides. By separating the short- and long-ranged Coulomb interactions, the method yields an expression for the core spectral function $A_{2p}(\omega) = -(1/\pi)\mathrm{Im}G_{2p}(\omega)$ given by a convolution of the local model and cumulant spectral functions:

$$A_{2p}(\omega) = A_{2p}^{\mathrm{loc}}(\omega) * A_{2p}^{C}(\omega). \tag{1}$$

Thus, each discrete local multiplet level is broadened by $A_{2p}^{C}(\omega)$, which accounts for shake satellites and an extended tail. As a consequence, our combined method treats both local correlations and dynamical, more extended excitations. Similar convolutions have been used to add many-body excitations to correlated systems [34,35]. In the time domain, the cumulant ansatz gives the Green's function as a product of the local Green's function and an exponential of the cumulant $C_{2p}(t)$:

$$G_{2p}(t) = G_{2p}^{\mathrm{loc}}(t)e^{C_{2p}(t)}. \tag{2}$$

Here, $G_{2p}^{\mathrm{loc}}(t)$ is the trace over $2p$ single particle states of the atomic multiplet Green's function for our local atomic model, and $C_{2p}(t)$ is the cumulant, which is calculated in real time [12], and builds in dynamic correlation effects. The above approximation was inspired by the work in Refs. [7,36], where a similar product of an atomic Green's function and cumulant spectral function was used to treat plasmon excitations in DMFT.

To formalize this approach, we define a separable model Hamiltonian $H = H^{\mathrm{loc}} + H^{\mathrm{bos}}$ in which the localized 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 many-body excitations [10]. Here, the local system is defined by a many-body Hamiltonian:

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

where V^{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. Although charge transfer is ignored, this model is otherwise similar to that used in LFMT fits of multiplet structure. More generally, this Hamiltonian could be extended to include ligands, as in cluster LFMT and CI calculations. Thus, H^{loc} accounts for covalency effects on the multiplet levels but ignores charge-transfer satellites that are included via the cumulant. Additional details are given in the Supplemental Material [37]. Although this approximation yields a simple solution of the full problem, it ignores possible final-state effects of charge transfer on the local configuration, and instead keeps a fixed number of d electrons in the local Hamiltonian.

The quasiboson Hamiltonian for the extended system, including the coupling to the localized system, is

$$H^{\mathrm{bos}} = \sum_{q}\omega_q a_q^{\dagger}a_q + \sum_{qi}n_i V_i^q(a_q^{\dagger} + a_q), \tag{4}$$

where V_i^q are fluctuation potentials [10], and n_i is the occupation of the hole state $i \in 2p$. If we now approximate the couplings V_i^q to be independent of the multiplet hole state i of the localized system, the net coupling depends only on the total number of holes $N_h = \sum_i n_i$ in the $2p$ shell, which is equal to 1 in the XPS final state. Then the Hamiltonian H^{bos} becomes equivalent to that of Langreth [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 $\chi(q, q', \omega)$ and 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 $A_{2p}^{C}(\omega)$.

Our *ab initio* calculations of the local LFMT model include extensions to account for strong correlation effects. The local multiplet system defined by H^{loc} depends on several parameters. The Slater-Condon parameters F and G are calculated using self-consistent radial wave functions that take covalency into account, averaged over the occupied $3d$ states, and $2p$ core-level states from the modified Dirac-Fock atomic code of Desclaux [11,44,45] available within FEFF10 [38]. We find that the calculated F and G values are typically reduced from free-atom values by a factor of about 0.7 to 0.8 due to covalency effects, consistent with other studies [28,46]. The crystal field strengths $10Dq$ were estimated from the $T_{2g} - E_g$ splitting in the angular momentum projected densities of states from FEFF10, and are given by 0.8 and 1.3 eV for Fe_2O_3 and MnO, respectively, although the spectra are not particularly sensitive to these values. Spin-orbit couplings were taken to be the atomic values [47], which can also be obtained from the Dirac-Fock code in FEFF10. We have verified that the resulting multiplet spectra for hematite obtained with this model agrees well with the accurate cluster CI calculations of Bagus *et al.* [48], which also ignore charge-transfer coupling (i.e., shake satellites). Further details are reported in the Supplemental Material [37].

The cumulant Green's function is calculated with $C_{2p}(t)$ analogous to that in the Langreth formulation, but obtained using a modified real-time time-dependent DFT (TDDFT) approach [24]. Within the Landau representation [49],

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

$$\beta(\omega) = \omega \int d^3r \mathrm{Re}[V(r)\delta\rho(\mathbf{r},\omega)]. \qquad (5)$$

Here, $\delta\rho(\mathbf{r},\omega)$ is the time-Fourier transform of the density fluctuations $\delta\rho(r,t)$ 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 include nonlinear corrections to the cumulant, following Tzavala *et al.* [13]. A measure of correlation strength is given by the dimensionless satellite amplitude $a = \int d\omega\beta(\omega)/\omega^2 = -\ln Z$ where Z is the renormalization constant. Note that a is sensitive to the behavior of $\beta(\omega)$ near $\omega = 0$. To account for the energy gap in transition metal oxides, which is not well treated in TDDFT and affects the asymmetry of the quasiparticle peak, we set the linear part of the cumulant kernel $\beta(\omega)$ at low ω to zero. This is in contrast with the use of the scissor operator, which shifts unoccupied states uniformly to higher energies by the gap correction; however, recent calculations show that the shake-up satellite energies are not affected by the gap correction [8].

As illustrative examples, we apply the $Multiplet + C$ approach to the $2p$ XPS of α-Fe_2O_3 (hematite) and MnO. Both the Fe and Mn sites in these systems are octahedrally coordinated by O, although there is distortion from octahedral symmetry in Fe_2O_3. In addition, the nominal oxidation state is different in the two materials, i.e., Fe^{3+} and Mn^{2+} in the ground state. Nevertheless, their multiplet structure is similar, since both metal atoms are nominally d^5. At room temperature, MnO is paramagnetic, while Fe_2O_3 is antiferromagnetic, but the magnetic structure seems to have little affect on the shake satellites in Fe_2O_3 [9].

Our results for the cumulant kernel $\beta(\omega)$ for $\alpha - Fe_2O_3$ (hematite) are shown in Fig. 1. Note that the nonlinear corrections further broaden and redshift the main satellite in the direction of the -9 eV peak in the experimental XPS. Thus, our calculation of $\beta(\omega)$ differs from the conventional treatment based on linear response and the GW approximation, $\beta^{GW}(\omega) = (1/\pi)|\mathrm{Im}\Sigma^{GW}(\omega + \epsilon_c)|$ [10]. Within our simplified model Hilbert space, there are no excitations due to charge transfer from the localized system to the surroundings or vice versa. Consequently, the spherical contributions to the direct interactions F^0_{pd} and F^0_{dd} only contribute to overall static shifts in the spectrum but not satellite structure. Thus, in order to minimize double counting in the calculation of shake-up or charge-transfer satellites, we only use the spherical part of the Coulomb interaction when calculating the density response $\delta\rho(t)$ to the suddenly created core hole at $t = 0$. The spectral function associated with the cumulant $A^C_{1s}(\omega) \approx A^C_{2p}(\omega) = (-1/\pi)\mathrm{Im}\mathcal{F}\{\exp[C(t)]\}$, where $\mathcal{F}$ denotes a Fourier transform, is directly related to the 1s XPS, which does not have atomic multiplet splitting, as shown in Fig. 2. To better characterize the nature of the satellite excitations,

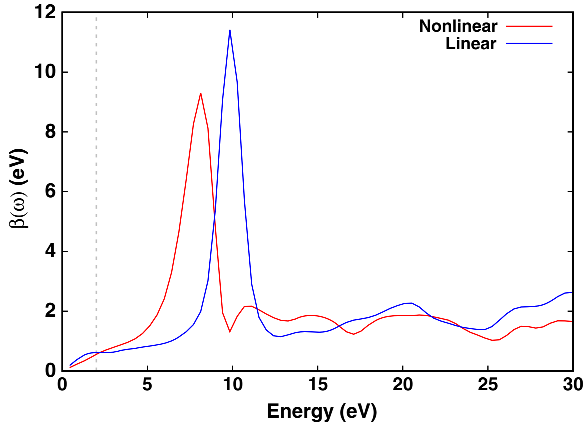

FIG. 1. Quasiboson excitation spectrum $\beta(\omega)$ of Eq. (5) for hematite calculated within linear (blue) and nonlinear (red) response using the real-time TDDFT approach [12]. The main peak corresponds to the charge-transfer excitation energy, which is redshifted by nonlinear response, and the tail corresponds to a broad background. The gray dashed line shows the energy below which the spectrum was set to zero to correct the gap.

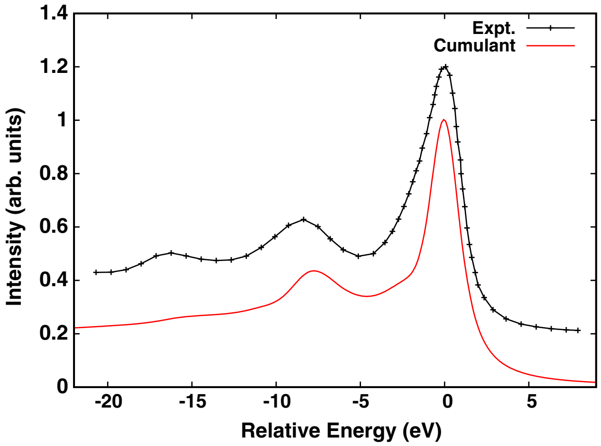

FIG. 2. Spectral function $A_{1s}(\omega)$ for Fe_2O_3 compared with the 1s XPS [50], both normalized by the main peak height. Although the position and strength of the main satellite calculated with the nonlinear cumulant spectral function are in reasonable agreement with experiment, the calculated satellite at -16 eV is too weak.

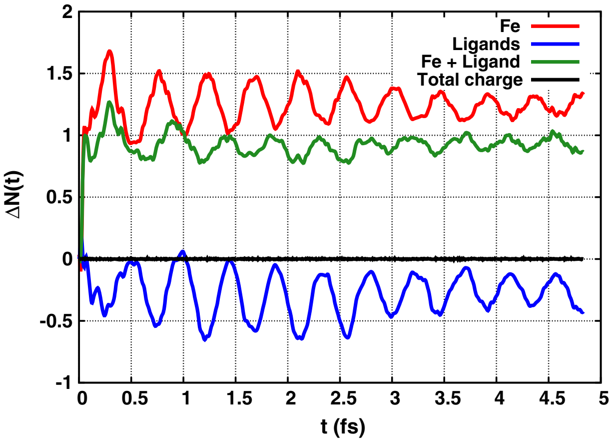

FIG. 3. Fluctuation in Mulliken counts $\Delta N(t)$ on the central Fe atom (red), the 6 O ligands (blue), the sum of Fe and O ligands (green), and the total (black) (which is zero to high accuracy) in hematite. Note that these counts oscillate with period ~0.46 fs, corresponding to the charge-transfer frequency $\omega_{CT} \sim 9$ eV.

it is useful to analyze the induced charge associated with the main shake satellite at −9 eV, following creation of the $2p$ core hole. Figure 3 shows our calculations of the fluctuations in the Mulliken charges (Fig. 3) vs time for hematite on the central Fe atom (red), on 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 substantial charge transfer between metal and ligand. Note, however, that the sum of ligand and metal counts (green) contains sizable residual oscillations, indicating some charge transfer from outer shells. This 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.

Finally, Fig. 4 shows our results for the $2p$ XPS spectra from our *ab initio* $Multiplet + C$ approach; our *ab initio* local atomic multiplet-only model; and experiment for both hematite and MnO. The most noticeable differences between the spectra with and without the cumulant spectral function are the broad satellites roughly 7 eV and 9 eV below each of the main ($2p_{1/2}$ and $2p_{3/2}$) peaks in MnO and Fe_2O_3, respectively. Upon convolution with the multiplet spectral function, they yield replicas of the local spectra at lower energies, with an energy splitting corresponding to the peak in the bosonic excitation spectrum $\beta(\omega)$. In contrast the multiplet-only spectra have weak multiplet features at about −6 eV and no satellite below the $2p_{1/2}$ peak or any substantial background intensity.

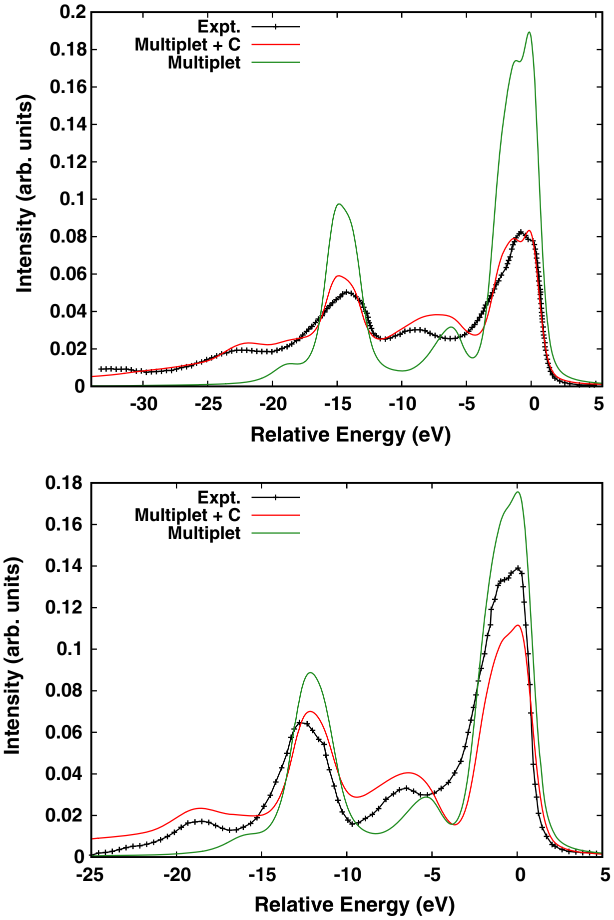

FIG. 4. Comparison of the area normalized $2p$ XPS of (top) $\alpha - Fe_2O_3$ from experiment digitally reproduced from Ref. [48] (black crosses) with the $Multiplet + C$ approach (red), and atomic multiplet only (green), and (bottom) similar results for the XPS of MnO compared to experiment (black crosses) [9]. Note that the multiplet-only calculations have relatively weak multiplet features ~6 eV below the $2p_{3/2}$ main line that are not at the correct energy to explain the shake peaks.

While LDA + DMFT calculations [9] also yield comparable agreement for the main satellite, those results used some adjustable parameters. Moreover, there is a long tail extending well beyond the satellites that contributes substantial intensity underneath the $2p_{1/2}$ main peaks, consistent with the background structure in $\beta(\omega)$ in Fig. 1 and in experiment. These properties reflect the different timescales and dynamic correlation effects involved in the local and shake-up processes that are missing in conventional atomic multiplet models.

In conclusion, we have developed an *ab initio* $Multiplet + C$ approach that treats both short- and longer-ranged excited state correlation effects in open-shell systems. The approach yields XPS spectra for the full system as a convolution of the local multiplet spectrum and the nonlinear cumulant spectral function for the extended system. In this sense, the $Multiplet + C$

approach is *doubly dynamic*, as in the DMFT + cumulant approach [7] and provides an attractive alternative to such methods. Applications to Fe_2O_3 and MnO yield XPS spectra that agree reasonably well with experiment. In contrast to CI-based LFMT [48], cluster LFMT, or LDA + DMFT [8], our approach simplifies both the calculations and physical interpretation of the large-shake excitations and double excitations in terms of density fluctuations induced by the suddenly turned on core hole. As a consequence, the $Multiplet + C$ approach yields an *ab initio* treatment of the atomic multiplet spectra that improves on that in typical LFMT fits by including both charge-transfer excitations and the broad background observed in experiment. However, the *ab initio* character and minimization of double counting within our approach neglects some of the physics of correlated systems and will likely need correction in some cases. For example, strongly correlated systems such as NiO may require a treatment of the quasibosonic excitation spectrum beyond TDDFT. An additional simplification is the representation of all shake satellites as quasibosonic. This reduces the local model to that of a single configuration, an approximation that may need to be improved in the future. Finally, the use of a spherical core-hole potential and the reduction of the local Hamiltonian minimizes double counting, since the core-hole potential creates only monopole excitations, which are excluded in the multiplet coupling. Nevertheless, double counting may not be completely avoided. This approximation also neglects nonspherical effects on the shake satellites, but we expect these effects to be small in most cases. Given the simplicity of the nonlinear TDDFT approach and the approximate bosonic coupling, various improvements are desirable, especially for more strongly correlated systems like NiO. For example, better treatments of the density response and nonlocal screening corrections, as well as the effect of charge transfer on the local model will likely be necessary for these systems [8,9].

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