Strengths of Plasmon Satellites in XPS: Real-time cumulant Approach

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Plasmon satellites observed in x-ray photoemission spectra reflect many-body effects beyond the one-electron approximation. However, theoretical calculations are challenging, and simplified theories based on electron gas models are not always satisfactory. Here a cumulant Green's function approach with a real-time TDDFT calculation of the cumulant is described for calculations of these effects, without the need for adjustable parameters. The approach yields good agreement with experimental XPS results, as illustrated for Ge and Al. Corrections due to extrinsic losses and interference are also briefly discussed.

I. INTRODUCTION

The behavior of satellites in x-ray photoemission spectra (XPS) has long been of interest.[1,2] These "satellite" features are pure many-body effects that characterize the excitations in the system, and show up as additional peaks in the XPS beyond the quasi-particle peak. Their treatment has been a favorite topic of Fadley and colleagues, in work ranging from plasmon-satellites to satellite band-structures.[3–5] Although electron gas models have been used to treat plasmon excitations in nearly free-electron systems like Al and Na,[4] first principles treatments have been challenging, especially in systems with stronger correlations. Remarkably, plasmon satellites in core-level XPS can be treated exactly in models with bosonic-couplings using cumulant Green's function techniques.[1,6,7] This approach has proved to be quantitative in weakly correlated systems, with a cumulant calculated using the GW approximation of Hedin,[8,9] and is referred to as $GW+C$. A recent review of cumulant Green's function methods is given in Ref. 10. Subsequently, an alternative formulation has been derived, using a real-time, time-dependent density functional theory (TDDFT) approach for the cumulant.[11] This approach is equivalent to the linear response theory of Langreth,[1] but is carried out in the time-domain. For deep core-levels, the approach is also nearly equivalent to $GW+C$, except that the real-time approach uses TDDFT for the screened coulomb interaction, while standard $GW+C$ uses the random phase approximation (RPA). Remarkably, the method has also explained the position and strengths of charge-transfer excitations in more correlated systems, such as transition metal oxides, without the need for arbitrary parameters.[11,12] The method also provides a physical interpretation of the satellites in real space, in terms of induced charge-density fluctuations.[11] However, non-linear corrections to the cumulant can be important in systems with stronger correlations.[13] Our goals in this paper are to explain this method and its physical interpretation, and to illustrate the approach for the treatment of plasmon-excitations in sample systems also studied by Fadley and collaborators.[4] Besides intrinsic excitations,[2,11] we also briefly discuss the effects of extrinsic and interference terms as in Ref. 14.

II. THEORY

Our description of the real-time TDDFT cumulant approach for calculations of intrinsic satellite excitations is adapted from that described in detail by Kas et al.[11] Briefly the XPS photocurrent $J_{\mathbf{k}}(\omega)$ in a given direction $\mathbf{k}$ is directly related to the intrinsic core-level spectral function $A_c(\omega)$, since for deep core electrons and high energy photoelectrons ($k \gg k_F$), the dipole matrix elements are roughly constant

$$J_{\boldsymbol{k}}(\omega) = \sum_j |\Delta_{\boldsymbol{k}j}|^2 A_j(\omega) \propto A_c(\omega). \tag{1}$$

The one-particle spectral function $A_c(\omega)$ characterizes the excitation spectrum associated with a given core level c and is defined by the imaginary part of the core-hole Green's function $G_c(\omega)$. Using the cumulant representation of $G_c(t)$

$$A_c(\omega) = -\frac{1}{\pi}\mathrm{Im}\left[G_c(\omega)\right] \tag{2}$$

$$G_c(\omega) = \int dt e^{i\omega t} G_c(t),$$

$$G_c(t) = G_c^0(t) e^{C(t)}, \tag{3}$$

where $G_c^0(t) = -\theta(-t)\exp(-i\varepsilon_c t)$, $C(t)$ is the cumulant, and $\theta(t)$ the unit step function; and atomic units $e = \hbar = m = 1$ are implicit.

As noted in the introduction, our treatment of the cumulant $C(t)$ is based on a transformation to real-space and real-time of the Langreth linear response formulation.[1] This treatment also facilitates the physical interpretation of the satellites, as discussed below.

$$C(t) = \int_0^\infty d\omega\, \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}, \tag{4}$$

$$\beta(\omega) = \int d^3r d^3r' V(\boldsymbol{r}) \mathrm{Im}\left[\chi(\boldsymbol{r},\boldsymbol{r}',\omega)\right] V(\boldsymbol{r}'). \tag{5}$$

Physically the cumulant kernel $\beta(\omega)$ describes the spectrum of *effective* or charge-neutral "quasi-boson" excitations[2] of

the system, which correspond to the satellites observed in the spectral function at frequency ω. The calculation of the linear density response function $\chi = \delta\rho/\delta v$ is then carried out using the real-time TDDFT approach, similar to that of Yabana and Bertsch,[15] for the electron density response $\delta\rho(\mathbf{r},t)$ due to a suddenly turned on core-hole potential $V(\mathbf{r}')\theta(t')$,

$$\begin{aligned}\delta\rho(\boldsymbol{r},t) &= \int dt' d^3r'\, \chi(\boldsymbol{r},\boldsymbol{r}';t-t')V(\boldsymbol{r}')\theta(t'),\\ \Delta_c(t) &= \int d^3r V(\boldsymbol{r})\delta\rho(\boldsymbol{r},t),\\ \frac{\beta(\omega)}{\omega} &= \mathrm{Re}\left[\int dt\, e^{-i\omega t}\Delta_c(t)\right]. \end{aligned} \tag{6}$$

Here $\Delta_c(t)$ characterizes the oscillatory density response of the system to the suddenly turned on core-hole. Consequently, the real-time cumulant approach provides a direct physical connection between the density fluctuations induced by the creation of the core-hole and the satellites in the spectral function observed in XPS. In contrast to optical response, the density response to a core-hole is monopole in character. Interestingly, as shown by Hedin,[2] the intrinsic excitation spectrum $\beta(\omega)$ is also related to the GW self-energy $\Sigma^{GW} = iGW$ of the core-hole, (as in the $GW+C$ approach), i.e., $\beta(\omega) = (-1/\pi)\mathrm{Im}\Sigma^{GW}(\omega-\varepsilon_c)$. Since $W = v\varepsilon^{-1}$, $\beta(\omega)$ is also proportional to the loss function $L(\omega) = -(1/\pi)\mathrm{Im}\,\varepsilon^{-1}(\omega)$, so the intrinsic spectral function exhibits satellites at peaks of the loss function, as one expects physically. From Eq. (4) it is easy to see that $C(0) = C'(0) = 0$, so the spectral function is normalized, and the integral $\Delta = \int d\omega\,\beta(\omega)/\omega$ is the quasiparticle energy shift or "relaxation energy."

One of the limitations of the above treatment is that it only accounts for intrinsic losses. However additional "extrinsic" losses are encountered during propagation of the outgoing photoelectron, and it is necessary first to add the intrinsic and extrinsic amplitudes and then square to obtain the XPS intensity distribution. The treatment of this problem has a long history. For example, early treatments[16] were based on the coupling of plasmons to electron gas models, and were used by Fadley and coworkers to investigate intrinsic losses from adsorbates.[17] A more detailed study by Hedin et al.[14,18] was carried out using a careful treatment of fluctuation potentials and the cumulant representation. Their treatment of extrinsic losses takes into account contributions from various depths in a material. Since the mean-free-path increases with energy, the extrinsic losses in solids tend to grow with increasing energy.[19] Due to the opposite signs of the electron and hole, the amplitudes of the extrinsic and intrinsic losses tend to cancel. A detailed summary of these developments, including their application to XPS, is given in the recent cumulant review.[10] In particular, it is found to be computationally convenient to use the jellium model to calculate the ratio $R(\omega_p)$ between the total weight of the first satellite $a_{\mathrm{tot}}(\omega_p)$ (including extrinsic and interference) and the intrinsic contribution $a_{\mathrm{int}}(\omega_p)$, as a function of plasmon frequency ω_p. This function is then used to correct the intrinsic spectrum $\beta(\omega)$ for extrinsic and interference effects,

$$\gamma(\omega) = R(\omega)\beta(\omega). \tag{7}$$

We find that to a good approximation, the extrinsic + interference weight is proportional to the plasmon frequency, so that we can write $R(\omega) \approx 1+\alpha\omega$, where $\alpha = a_{\mathrm{total}}/a_{\mathrm{int}}$, and the weights a_{total} and a_{int} only need to be calculated at the plasmon excitation energy for the material. This approach is used here to achieve an efficient approximation for adding extrinsic and interference corrections to our RT-TDDFT intrinsic cumulant, i.e., by replacing the intrinsic cumulant kernel $\beta(\omega)$ by a total cumulant kernel $\gamma(\omega)$ including all losses given by[10]

$$\gamma(\omega) = R(\omega)\beta(\omega) \approx (1+\alpha\omega)\beta(\omega). \tag{8}$$

We note also that the treatment of extrinsic, intrinsic and interference terms in x-ray absorption spectra is rather similar, and can be calculated in terms of quasi-bosonic excitations induced by the sudden appearance of a particle-hole state. A detailed treatment is given in Ref. 12. The net result can again be expressed in cumulant form, where the intrinsic cumulant $\beta(\omega)$ is replaced by a particle-hole cumulant $\gamma(\omega)$ which (neglecting recoil) is a perfect square. As a result both γ_K and the cumulant can be partitioned into intrinsic (c), extrinsic (k), and interference terms (ck), respectively,

$$\gamma_K(\omega) = \gamma_c(\omega) + \gamma_k(\omega) + \gamma_{ck}(\omega), \tag{9}$$

$$\tilde{C}_K(t) = C_c(t) + C_k(t) + C_{ck}. \tag{10}$$

III. DETAILS OF THE CALCULATIONS

Here we provide details of the real-time TDDFT calculations for the Al 3*s* and Ge 3*d* XPS. For both materials, we took the structure from experimental results found in the literature.[20,21] The calculations were performed with the real-time SIESTA code,[22,23] using a 4x5x6 supercell with the default DZP basis set. The $k-$point grid was Γ-point only. Comparison to results using a smaller 4x4x4 supercell ensured that the supercell size was adequate for convergence. Both the ground-state and TDDFT calculations were performed with PBE GGA exchange correlation functionals.[24] The time-step was set to 0.2 a.u. for 1000 time-steps, while for Al, the time-step was 0.4 with 2000 time-steps. To take the small spin orbit splitting of the Ge-3*d* states into account, we summed the spectral function with that shifted by 0.6 eV, with intensity ratio $6:4$ corresponding to the ratio of occupations $3d_{5/2}:3d_{3/2}$. Extrinsic and interference effects were taken into account by increasing the intrinsic satellite signal by a linear function as in Eq. (8). In our calculations the parameter α is calculated with the theory of Ref. 14, and given by 0.17 eV^{-1} for Ge, and 0.25 eV^{-1} for Al. Voigt functions were used to broaden the calculated results to match the high energy tail in the experiment, with 0.4 eV full-width at half-max (FWHM) Gaussian broadening applied to both materials and 0.2 eV and 0.3 eV FWHM Lorentzian broadening applied for Ge and Al respectively. Non-relativistic Troullier-Martins pseudopotentials were used for both calculations,[25] with non-linear core-correction included for Ge.

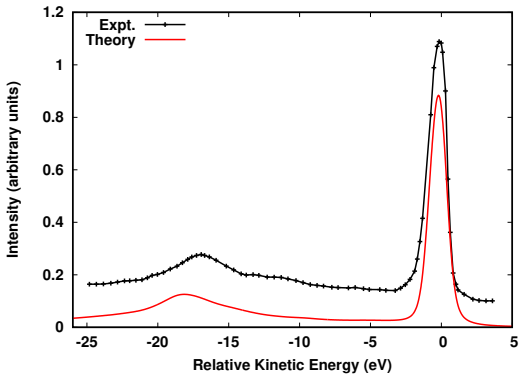

FIG. 1. Calculated 3*d* XPS intensity of Ge vs relative photoelectron energy using the RT-TDDFT cumulant Green's function approach compared to the experimental result of Herman and Fadley, as digitally reproduced from Ref. 4.

IV. RESULTS

As illustrative examples, the XPS intensity of Ge 3*d* and Al 3*s* were calculated using the real time cumulant approach.[11] Fig. 1. shows the calculated results using the real-time cumulant approach compared to the experimental Ge 3*d* XPS of Herman and Fadley taken with Al $K-\alpha$ radiation.[4] Note that our RT-TDDFT theory yields good agreement in both the position and strength of the plasmon satellite, although the position is overestimated by approximately 1 eV. An analysis of the weights of intrinsic, extrinsic, and interference terms shows that the extrinsic contribution dominates with the intrinsic:total satellite weight ratio given by 1 : 3.5.

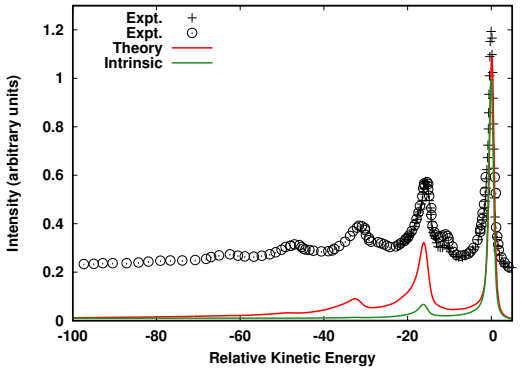

FIG. 2. Calculated 3*s* XPS intensity of Al using the RT-TDDFT cumulant Green's function approach (Theory) and with only intrinsic losses (Intrinsic), compared to the experimental results as digitally reproduced from Figs. 1. and 7. of Ref. 26

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As a second example, Fig. 2 shows the calculated XPS of Al including extrinsic losses and interference compared to experimental results for the Al 3*s* XPS taken with Mg $K-\alpha$ radiation.[26] Note that the cumulant approach reproduces the multiple satellite series observed in the experiment for this system. However, while the predicted amplitude of the first plasmon satellite is nearly correct, the amplitudes of the second and further satellites are too small. This discrepancy is likely due to our exponential approximation for the extrinsic amplitudes, which produces smaller multiple boson satellites than that observed in experiment.[26] In addition, the surface plasmon satellite at $\omega_s = \omega_p/\sqrt{2} \approx -11$ eV can clearly be seen in the experimental results, but is missing in the theoretical results. This is because we did not attempt to model it in this case, although we have found that it is possible to model the surface plasmon by adding a contribution proportional to $\beta(\sqrt{2}\omega)$,[10] where the constant of proportionality depends on both the photon energy and the angle of exit of the photoelectron.[14] A comparison of the individual contributions from intrinsic, extrinsic, and interference terms can also be made. We find that the ratio of these effects for the first satellite is $1 : 2.7 : -0.32$, in good agreement with previously measured and calculated values of Biswas et al.[26]

V. SUMMARY

We have discussed how a real-time cumulant Green's function approach with a real-time TDDFT calculation of the cumulant can be used to calculate plasmon-satellites in XPS, without the need for adjustable parameters. The approach also facilitates a physical interpretation of the satellites in terms of the transient density fluctuations created in response to a suddenly turned-on core-hole. The approach yields results that are in good agreement with XPS experiment, and consequently, has the potential for quantitative interpretations. Many other applications are possible, as illustrated in several recent works.[27–29] Moreover, as discussed in Ref. 30, the cumulant approach may also be useful in treating satellites in systems with multiplets.[31,32]

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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FIG. 2. Calculated 3*s* XPS intensity of Al using the RT-TDDFT cumulant Green's function approach (Theory) and with only intrinsic losses (Intrinsic), compared to the experimental results as digitally reproduced from figures 1 and 7 of Ref. 26.