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Quasiparticle spectra from molecules to bulk

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(Dated: )

A stochastic cumulant GW method is presented, allowing us to map the evolution of photoemission spectra, quasiparticle energies, lifetimes and emergence of collective excitations from molecules to bulk-like systems with up to thousands of valence electrons, including Si nanocrystals and nanoplatelet. The quasiparticle energies rise due to their coupling with collective shake-up (plasmon) excitations, and this coupling leads to significant spectral weight loss (up to 50% for the low energy states), shortening the lifetimes and shifting the spectral features to lower energy by as much as 0.6 eV. Such features are common to all the systems studied irrespective of their size and shape. For small and low dimensional systems the surface plasmon resonances affect the frequency of the collective excitation and position of the satellites.

Recent developments in Green’s function (GF) techniques have allowed for the description of charge excitations, i.e., quasiparticles (QP) [1, 2], in the bulk, over a wide range of QP energies. Band-edge excitations are well-described by the so called $G_0W_0$ approximation [3–5], while at higher QP energies corrections are required to account for charge-density fluctuations and hole-plasmon coupling [5–8]. Photoemission experiments on solids reveal significant QP lifetime shortening and coupling to other collective excitations, manifested by satellite structures in the photoemission spectra [6, 9, 10]. The satellite structure and the QP lifetime shortening is often captured by the cumulant expansion (CE) ansatz to $G_0W_0$ [6–8, 10–14].

In confined systems, the QP spectrum near the band-edge is governed by the quantum confinement of electrons and holes. Higher energy, satellite-excitations are attributed to simultaneous ionization and excitation of the valence electrons (“shake-up” excitations) [13, 15–18]. Transition and differences between the satellite spectral features of molecules and nanostructures with “shake-up” signatures and bulk with collective plasmon resonances have been difficult to assess, as they require many-body treatment of systems with hundreds and thousands of electrons. In fact, the quantum confinement effect on the satellite transitions has received little attention if any.

In this letter, we address this challenge by combining the well-known cumulant expansion (CE) ansatz [5, 7–9, 11, 19, 20] with the recent stochastic GW approach (sGW [21, 22]), to obtain a nearly linear-scaling algorithm that reveals the changes of the QP spectra from a single molecule to covalently bonded nanocrystals (NCs) of unprecedented size (here up to 5288 valence electrons). The formalism is presented and assessed for the two size extremes (molecule and large bulk-like system), followed by the study of the effects of quantum confinement on the satellite structure in silicon NCs of different size and shape. In small NCs the satellite features are affected by the changes in the plasmon energy. For large NCs, we find observable quantum confinement effects on the satellite features below the exciton Bohr radius, where the position of the satellite peak and the QP lifetime show small dependence on the size of the system.

The central theoretical quantity for quasiparticles is the spectral function, which in the sudden approximation is directly linked to the photoemission current [5, 23, 24]. The spectral function of the $i$th QP state is $A_i(\omega) = \frac{1}{\pi} \text{Im} G_i(\omega)$, where GF fulfills the Dyson equation $G_i(\omega) = G_i^{(0)}(\omega) + G_i^{(0)}(\omega) \Sigma_i(\omega) G_i^{(0)}(\omega) + \cdots$, where $G_i^{(0)}(\omega)$ is the non-interacting GF and $\Sigma_i$ is the self-energy. All the quantities are non-local in space and all the higher terms in the equation represent a convolution integral, but for brevity we omit the spatial dependence in the notation.

As usual, the non-interacting system is described by the Kohn-Sham DFT [25, 26] (see details in [27]) with Troullier-Martins pseudopotentials. The sGW approach is detailed in [21, 22]). The self energy is then given in the diagonal $G_0W_0$ approximation as [3]: $\Sigma_i(t) = i \left\langle \phi_i | \tilde{G}_i^{(0)}(t) W(t^+) | \phi_i \right\rangle$, where $t^+$ is infinitesimally after $t$, $\phi_i$ is the KS eigenstate, $W(\omega) = \epsilon^{-1}(\omega) v_c, v_c$ is the Coulomb kernel and $\epsilon^{-1}(\omega)$ is the inverse dielectric function. Quantities in frequency and time domains (e.g., $G$ and $\Sigma$) are simply related by their Fourier transforms. From the calculated $\Sigma_i(\omega)$ the $G_0W_0$ spectral function is given by:

$$A_i^{GW}(\omega) = \frac{1}{\pi} \frac{\text{Im} \Sigma_i(\omega)}{(\omega - \varepsilon_i - \text{Re} \Sigma_i(\omega) + \nabla_{XC}^2)^2 + (\text{Im} \Sigma_i(\omega))^2},$$

where $\varepsilon_i$ is the KS eigenstate energy and $\nabla_{XC}$ is the expectation value of the mean-field exchange-correlation potential. $A_i^{GW}$ has peaks at the quasi-particle energies,
where the renormalization factor, due to redistribution of $\Sigma$.

We solve for $C_i$ that fulfill the fixed-point equation,

$$\varepsilon_i^{QP} = \varepsilon_i + \text{Re}\Sigma_i (\omega = \varepsilon_i^{QP}) - \tau_{XC}. \quad (2)$$

In this GW approximation, the inverse lifetime of the QP is given by $\text{Im}\Sigma$ at the peak. However, the actual plasmon-coupled excitations are not in general represented by the isolated poles in Eq. (1) and $A_i^{GW}(\omega)$ thus does not yield a proper description of satellite structures. In addition, spurious secondary peaks arise if Eq. (2) has multiple solutions [6, 7, 20].

The CE formulation is required to account for the effect of hole-plasmon coupling. For the $i^{th}$ occupied state, the GF in the CE ansatz reads [5, 9, 19]:

$$\tilde{G}_i(t) = -ie^{i\varepsilon_i t} e^{C_i(t)} \theta(-t) = -ie^{i\varepsilon_i t + C_i^{sp}(t)} e^{C_i(t)} \theta(-t), \quad (3)$$

where $C_i$ is the cumulant, obtained from the Dyson series expansion. Further, following Ref. [6] the cumulant contribution is separated into two components. The first is a QP cumulant, $C_i^{QP}$, derived explicitly in Ref. [6] and associated with a portion of the spectral function describing the main QP peak:

$$A_i^{QP}(\omega) = \frac{Z_i}{\pi} \frac{|\text{Im}\Sigma(\varepsilon_i^{QP})|}{(\omega - \varepsilon_i^{QP})^2 + (\text{Im}\Sigma(\varepsilon_i^{QP}))^2}; \quad (4)$$

where the renormalization factor, due to redistribution of the spectral weight into the satellite peaks, is $Z_i = e^{\alpha_i}$ with $\alpha_i = \frac{\partial \Sigma(\omega)}{\partial \omega} |_{\omega=\varepsilon_i}$. The lifetime of the QP is $1/|\text{Im}\Sigma(\varepsilon_i^{QP})|$.

By itself, $A_i^{QP}(\omega)$ does not include any satellite contributions – it is a single Lorentzian-shaped peak around the QP energy. The satellite peaks stem from resonances identified as poles in $W(\omega)$ (i.e., zeros of $\varepsilon(\omega)$) and appear as strong maxima in the imaginary part of the self-energy; they are introduced by $e^{C_i^s(t)}$ (Eq. (3)) that derives from the spectral representation of $\Sigma_P$ [6, 9, 19]:

$$C_i^s(t) = \frac{1}{\pi} \lim_{\eta \to 0} \int_{-\infty}^{\eta} \frac{\text{Im}\Sigma_P(\omega) e^{-i(\omega - \varepsilon_i + i\eta)t}}{(\omega - \varepsilon_i + i\eta)^2} d\omega. \quad (5)$$

We solve for $C_i^s(t)$ within the stochastic framework using $\Sigma_P$, which is obtained from the stochastic $G_0W_0$ calculation in the time domain. This is distinct from the previous calculations that either employed TDDFT for core-electrons [28] or $G_0W_0$ approximation for the cumulant in the frequency domain. Due to computational cost, the latter is limited to small periodic systems and $C_i^s(t)$ was in many cases further approximated by a single excitation pole in $\Sigma_P$. Here, the self-energy is obtained in a high frequency resolution (<0.01 $E_b$) on a wide range of frequencies ±60$E_b$; no further approximation is introduced.

The computed satellite cumulant, $C_i^s(t)$, is inserted to Eq. (3) which is Fourier transformed to yield $G_i(\omega)$, and thereby $A_i(\omega) = \text{Im}(G_i(\omega))$ [29].

We next verify our approach using a large NC, Si$_{705}$H$_{300}$, that is close to the bulk limit. Fig. 1 shows the spectral function of the bottom valence band (VB - denoted $A_0^{GW}$) with a pronounced QP peak at $-17.5$ eV. If a cumulant expansion is not used, $A_0^{GW}$ shows an additional maximum at $-39.8$ eV. This is in excellent agreement with previous GW calculations for bulk systems, but is not observed experimentally, and is attributed to spurious secondary solutions to Eq. (2) [6–8, 10, 11].

With the cumulant GW (Eq. (3)) the spectrum changes drastically and an additional peak is obtained at $-32.3$ eV in excellent agreement with a result for bulk Si [10]. This peak is physically meaningful as it corresponds to the maximum of $\text{Im}\Sigma(\omega)$ associated with a collective excitation of the valence electrons (plasmon). The appearance of the satellite structure is accompanied by reduction of the intensity of the main QP peak, so that the renormalization factor is $Z = 0.61$, i.e., 39% of the intensity is transferred to the satellites. The additional shoulder in the satellite peak is due to the difference between the effective masses of the QP and the plasmon [12]. The pronounced transfer of the spectral weight to the plasmon satellite for the bottom valence excitations is a consequence of their high energy and spatial extent (leading to large overlaps with other states). An isosurface of the bottom valence orbital of Si$_{705}$H$_{300}$ indeed
exhibits spherical symmetry and lacks nodal planes as seen from the inset of Fig. 1.

To further test our approach on finite systems, we applied (Fig. 2) the stochastic $G_0 W_0$ approximation with CE to a series of small molecules for which experimental photoemission spectra are available. The results in Fig. 2 were further scaled so that the bottom valence state to the satellites is shown above the peak. SAC-CI [30, 31] results are shown by vertical black lines with height proportional to the relative intensities; the colored areas refer to the experimental photoemission spectra for two relative azimuthal angles [31, 32].

(i) the QP energies at the top valence band are captured well by $G_0 W_0$. This is the energy region where DFT is a good starting point. But $G_0 W_0$ fails to reproduce the bottom VB, where it underestimates the position of the peaks by a significant amount of 2 eV. For these states, DFT is not a good starting point and the “single-shot” $G_0 W_0$ procedure is inaccurate.

(ii) Most importantly, the $G_0 W_0$+CE description captures the satellite overall decay, although without the fine structure peaks in the satellite region. The pronounced satellite spectral weight comes at the expense of the QP peaks which transfer up to 51% of their intensity to the satellite tails. The broadening of the satellite peaks observed in $G_0 W_0$+CE is a consequence of an intrinsic decay of the density–density correlation function in time ($\tau$). The peak width is independent of the maximal time used to simulate the screening (varied between 1 and 24 fs without affecting the lifetime) An infinite propagation time would result in presence of many sharp poles due to recurrences in the correlation function. As clearly can be seen in Fig. 2, finite $\tau$ yields a photoelectron spectrum in good agreement with experiment, likely due to other mechanism suppressing the recurrences in photoelectron spectroscopy.

Further, the $G_0 W_0$+CE spectral function has maxima that are shifted with respect to the $G_0 W_0$ QP energies. The shift is large for the bottom VB; e.g., for NH$_3$ the $G_0 W_0$ peak is at $-25.0$ eV while the $G_0 W_0$+CE maximum is at $-25.7$ eV. The 0.7 eV difference is significant as it is 17% of the GW correction to the LDA energy ($-20.8$ eV). Thus, the usual practice where $G_0 W_0$ results are directly compared to photoionization experiment is problematic, especially for low energy states, as it does not include the coupling of these states to the shake-up excitations.

In the next, main, part of this letter we investigate the evolution of the spectral function with system size: the results for a series of Si NCs are shown in Fig. 3. All NCs exhibit a discrete and narrow spectrum near the top of the VB. Due to the quantum confinement effect, the top of the VB shifts to higher energies with increasing size; the highest occupied state has energies of $-8.1$ eV and $-6.4$ eV for for Si$_{35}$H$_{36}$ and for Si$_{201}$H$_{484}$, respectively. For deeper hole excitations, the sharp features merge into a semi-continuous spectral response with significant lifetime shortening. This is accompanied by significant spectral weight transfer ($\sim 50\%$) to the satellites. The bottom of the VB depends weakly on the system size, spanning an energy between $-17.3$ and $-17.7$ eV for the range of NCs studied. The QP peak also overlaps with the emerging satellite, which is already well-developed into its bulk shape for Si$_{35}$H$_{36}$ and found in the range typical for bulk silicon [7]. This result is rather surprising, since both the QP spectrum near the band edge and the plasmonic excitations are sensitive to the system size. We further observe that the dimensionality does not strongly affect the main QP peaks: the silicon platelet has $\sim 60\%$ of the Si atoms on the surface, yet its spectral function is similar to the NCs.

On closer inspection, we observe that the satellite maximum exhibits non-monotonic shifts: First it shows a strong decrease in energy for systems from Si$_{35}$H$_{36}$ to Si$_{705}$H$_{1000}$ (from $-22.5$ to $-26.1$ eV, respectively), which is followed by slight move back to higher energies by
0.6 eV. The initial regime stems from the decrease in the plasmon resonance frequency ($\omega_p$) discussed below in detail. Once $\omega_p$ converges, the satellite maximum follows the changes in the QP DOS of the valence states governed by quantum confinement, i.e. the spectrum moves to higher energies (c.f., Fig. 3).

In Fig. 4 we show $\text{Im}\Sigma_P(\omega)$ together with the graphical solution to Eq. 2 (which also depicts spurious secondary solutions found already for Si$_{35}$H$_{36}$ at $-36$ eV). The plasmon peak in the $\text{Im}\Sigma_P(\omega)$ curve changes till the asymptotic limit is reached; ultimately the curve for NCs with 3120 electrons (Si$_{705}$H$_{300}$) and 5288 electrons (Si$_{1201}$H$_{484}$) have practically identical height, width and position. The distance between the maximum of $\text{Im}\Sigma_P(\omega)$ and the QP energy corresponds to $\omega_p$ coupled to the bottom valence hole; for the largest system $\omega_p = 15.3$ eV. Convergence of $\omega_p$ with system size is shown in the inset for the top and the bottom VBs.

Unlike in solids, the holes in finite systems couple to two types of plasmon resonances: low energy surface plasmon and high energy bulk plasmon. For small NCs, both contribute and lead to a broad peak in $\text{Im}\Sigma_P(\omega)$. The surface plasmon resonances also strongly contribute in low dimensional structures – the plasmon satellite of the platelet has a maximum at $-22.6$ eV which is almost identical to the smallest NC (Si$_{35}$H$_{36}$). Similar strong shift of satellites and enhancement of surface plasmon signatures in low dimensional systems was demonstrated experimentally [34]. For big systems, the hole becomes more localized inside the NC (c.f., inset of Fig. 1) and the coupling to the bulk plasmon dominates, leading to larger $\omega_p$. The distribution of the resonances becomes more narrow and the peak in $\text{Im}\Sigma_P(\omega)$ decreases in width.

In summary, our calculations are the first ab-initio theoretical predictions of the photoemission spectra, quasi-particle energies and lifetimes covering the wide region between molecules and bulk-like systems. The calculations show that the QP energies gradually increase with system size and this is accompanied by changes in the position of the satellite peaks which corresponds to a simultaneous ionization of the system and creation of a collective (shake-up or plasmon) excitation. The characteristic frequency of the plasmon has a narrower energy distribution in comparison to the shake-up but both are similar in nature and significantly alter the spectrum at low energies. Further, we have shown that for small systems the satellite region merges with the QP peak and shifts the apparent photoemission peak maximum to lower energies. The QP energies and photoemission maxima thus differ for the systems studied by as much as 0.6 eV.

The position of the satellite region is dictated by the QP energies and the frequency of the collective excitation. For small and low dimensional systems, surface and bulk plasmon resonances contribute to the satellites. With increasing size the higher energy bulk plasmon coupling dominates. For small and intermediate systems, the maximum of the satellite decreases in energy and is affected by the plasmon resonance energy. For big systems, the maximum shows a slight increase due to changes in the main part of the QP spectrum.
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[27] The LDA DFT calculation used a real-space grid (0.6 a for nanocrystals, 0.4 a for PH₃ and NH₃, 0.5 a for the C₂H₂) with Troullier-Martins pseudopotentials. The sGW approach is detailed in [21, 22].


[29] The quasiparticle energies and the spectral functions vary smoothly with frequency [Vlček et al. 2017, ArXiv:1701.02023] for the extended system studied here. We thus compute the spectral function for several selected states and interpolate the result. The number of states is increased till the interpolation is converged.
to within 0.1 eV. To evaluate $A(\omega)$ in Fig. 3, a single Lorentzian peak was used to describe the satellites, since only one satellite was observed. We found that a third order polynomial fit to the quasiparticle energies and the parameters of the Lorentzian peaks is sufficient to yield QP energies and satellite positions within 0.4 eV, i.e. better than the resolution of the predicted spectral functions. For systems up to Si$_{705}$H$_{300}$, we found that calculations for 5 independent states provide converged results. For Si$_{1201}$H$_{484}$ 3 calculations were performed.


[33] Similar to Ref. [31], the SAC-CI results were convoluted with a Lorentzian peak with 2 eV broadening.


[37] The LDA DFT calculation used a real-space grid (0.6$a_0$ for nanocrystals, 0.4$a_0$ for PH$_3$ and NH$_3$, 0.5$a_0$ for the C$_2$H$_2$) with Troullier-Martins pseudopotentials. The $sGW$ approach is detailed in [21, 22].

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