Quasiparticle spectra from molecules to bulk

Vojtěch Vlček,†* Eran Rabani,‡,§,∥ and Daniel Neuhauser‡,¶

1Department of Chemistry and Biochemistry, University of California, Los Angeles California 90095, USA
2Department of Chemistry, University of California and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
3The Raymond and Beverly Sackler Center for Computational Molecular and Materials Science, Tel Aviv University, Tel Aviv 69978, Israel

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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 bulklike systems with up to thousands of valence electrons, including Si nanocrystals and nanoplatelets. 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 energies by as much as 0.6 eV. Such features are common to all the systems studied irrespective of their sizes and shapes. For small and low-dimensional systems the surface plasmon resonances affect the frequency of the collective excitation and position of the satellites.

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Recent developments in Green’s function (GF) techniques have allowed for the description of charge excitations, i.e., quasiparticles (QPs) [1,2], in the bulk over a wide range of QP energies. Band edge excitations are well described by the so-called $G_0 W_0$ approximation [3–5], whereas 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 $G_0 W_0$ [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 Rapid Communication, we address this challenge by combining the well-known CE ansatz [5,7–9,11,19,20] with the recent stochastic $GW$ approach (s$GW$ [21,22]) to obtain a nearly linear-scaling algorithm that reveals the changes in 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 (molecules and large bulklike systems), followed by the study of the effects of quantum confinement on the satellite structure in silicon NCs of different sizes and shapes. 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 $A_i^\text{FW}(\omega) = \frac{1}{\pi} \text{Im} G_i(\omega)$ where the 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 noninteracting GF and $\Sigma_i$ is the self-energy. All the quantities are nonlocal 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 noninteracting system is described by the Kohn–Sham (KS) density functional theory (DFT) [25,26] (see the details in Ref. [27]) with Troullier-Martins pseudopotentials. The s$GW$ approach is detailed in Refs. [21,22]). The self-energy is then given in the diagonal $G_0 W_0$ approximation as [3]: $\Sigma(t) = i \langle \phi_i | G_i^{(0)}(t) W(t^+) | \phi_i \rangle$, 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 $\tilde{G}$) are simply related by their Fourier transforms. From the calculated $\Sigma(\omega)$ the $G_0 W_0$ spectral function is given by

$$ A_i^{\text{FW}}(\omega) = \frac{1}{\pi} \frac{\text{Im} \Sigma_i(\omega)}{[\omega - \epsilon_i - \text{Re} \Sigma_i(\omega) + \Pi_{xc}]^2 + [\text{Im} \Sigma_i(\omega)]^2}. $$

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*vojtech@chem.ucla.edu
‡eran.rabani@berkeley.edu
§dxn@ucla.edu

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where $\epsilon_i$ is the KS eigenstate energy and $\Sigma_{XC}$ is the expectation value of the mean-field exchange-correlation potential. $A_i^{GW}$ has peaks at the quasiparticle energies $\epsilon_i^{qp}$ that fulfill the fixed-point equation,

$$\epsilon_i^{qp} = \epsilon_i + \text{Re} \Sigma_i(\omega = \epsilon_i^{qp}) - \Sigma_{XC}. \quad (2)$$

In this $GW$ approximation, the inverse lifetime of the QP is given by $\text{Im} \Sigma$ at the peak. However, the actual plasmon-hole 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]

$$\hat{G}_i(t) = -i e^{i\epsilon_i t} e^{\Sigma_i(t)} \hat{\theta}(-t) = -i e^{i\epsilon_i t + C_i^{\text{Q}}(t)} e^{\Sigma_i(t)} \hat{\theta}(-t), \quad (3)$$

where $C_i$ is the cumulant, obtained from the Dyson series expansion. Furthermore, 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,

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

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

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 $\epsilon(\omega)$] and appear as strong maxima in the imaginary part of the self-energy; they are introduced by $e^{C_i^{\text{Q}}}$ [Eq. (3)] that derives from the spectral representation of $\Sigma_p$ [6,9,19],

$$C_i^{\text{Q}}(t) = \frac{1}{\pi} \lim_{\eta \rightarrow 0} \int_{-\infty}^{\infty} \frac{\text{Im} \Sigma_p(\omega)e^{-i(\omega - \epsilon_i + i\eta)t}}{(\omega - \epsilon_i + i\eta)^2} d\omega. \quad (5)$$

We solve for $C_i^{\text{Q}}(t)$ 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 employed time-dependent DFT for core electrons [28] or employed the $G_0W_0$ approximation for the cumulant in the frequency domain. Due to computational cost, the latter is limited to small periodic systems, and $C_i^{\text{Q}}(t)$ 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 ($<0.01E_F$) on a wide range of frequencies $\pm60E_F$; no further approximation is introduced.

The computed satellite cumulant $C_i^{\text{Q}}(t)$ is inserted into 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. Figure 1 shows the spectral function of the bottom of the valence band (VB)—denoted $A_{b}^{GW}$ with a pronounced QP peak at $-17.5$ eV. If a cumulant expansion is not used, $A_{b}^{GW}$ 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 a 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 in Fig. 1.
FIG. 2. Spectral functions (the red line) from stochastic $G_0W_0+CE$ for C$_2$H$_2$, PH$_3$, and NH$_3$. The spectral weight loss from the bottom valence state to the satellites is shown above the peak. Symmetry-adapted-cluster configuration-interaction (SAC-CI) [30,31] results are shown by the 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].

To further test our approach on finite systems, we applied (Fig. 2) the stochastic $G_0W_0$ 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 peak has the same intensity as the $G_0W_0+CE$ curve. The $G_0W_0+CE$ description relies on the concept of a plasmon associated with charge excitations in extended systems. Yet, Eq. (5) is applicable to small systems and yields good results. The stochastic $GW$ with damped real-time propagation of the excited state [21,22] is in qualitative agreement with experiment and with high level SAC-CI calculations, computationally feasible for small molecules [33]. We note that:

(i) The QP energies at the top valence band are captured well by $G_0W_0$. This is the energy region where DFT is a good starting point. But $G_0W_0$ 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” $G_0W_0$ procedure is inaccurate.

(ii) Most importantly, the $G_0W_0+CE$ 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 $G_0W_0+CE$ is a consequence of an intrinsic decay of the density-density correlation function in time (τ). 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 the presence of many sharp poles due to recurrences in the correlation function. As clearly can be seen in Fig. 2, finite τ yields a photoelectron spectrum in good agreement with experiment, likely due to other mechanisms suppressing the recurrences in photoelectron spectroscopy.

Furthermore, the $G_0W_0+CE$ spectral function has maxima that are shifted with respect to the $G_0W_0$ QP energies. The shift is large for the bottom VB; e.g., for NH$_3$ the $G_0W_0$ peak is at $-25.0$ eV, whereas the $G_0W_0+CE$ 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 $G_0W_0$ results are directly compared to the 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 Rapid Communication 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 $-8.1$ and $-6.4$ eV for Si$_{35}$H$_{36}$ and for Si$_{1201}$H$_{484}$, respectively. For deeper hole excitations, the sharp features merge into a semicontinuous spectral response with significant lifetime shortening. This is accompanied by significant spectral weight transfer (∼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.
from the decrease in the plasmon resonance frequency (ωp) back to higher energies by 0.6 eV. The initial regime stems from the maximum of Im Σp(ωp), which is almost identical to the smallest NC (Si35H36). A similar strong shift of satellites and enhancement of surface plasmon signatures in low-dimensional systems were demonstrated experimentally [34]. For big systems, the hole becomes more localized inside the NC (cf., the inset of Fig. 1), and the coupling to the bulk plasmon dominates, leading to larger ωp’s. The distribution of the resonances becomes narrower, and the peak in Im Σp(ω) decreases in width.

To summarize, our work presents first principle theoretical predictions of the photoemission spectra, quasiparticle energies, and lifetimes covering the wide region between molecules and bulklike 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 correspond 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. Furthermore, 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 local density approximation (LDA) DFT calculation used a real-space grid (0.6a0 for nanocrystals, 0.4a0 for PH3, and NH3, 0.5a0 for the C2H2) with Troullier-Martins pseudopotentials. The sGW approach is detailed in Refs. [21,22].
[29] The quasiparticle energies and the spectral functions vary smoothly with frequency [V. Vlček et al., 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 until the interpolation is converged to within 0.1 eV. To evaluate A(ω) 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 are 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 Si30H600, we found that calculations for five independent states provide converged results. For Si120H44 three calculations were performed.
[33] Similar to Ref. [31], the SAC-CI results were convoluted with a Lorentzian peak with 2-eV broadening.