Cumulant expansion of the retarded one-electron Green function

J. J. Kas, J. J. Rehr, and L. Reining

Phys. Rev. B **90**, 085112 — Published 11 August 2014

DOI: 10.1103/PhysRevB.90.085112

Cumulant expansion of the retarded one electron Green's function

J. J. Kas,[1,*] J. J. Rehr,[1,2,†] and L. Reining[3,2,‡]
[1] *Department of Physics, University of Washington Seattle, WA 98195*
[2] *European Theoretical Spectroscopy Facility (ETSF)*
[3] *Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France*

(Dated: July 28, 2014)

The cumulant expansion is a powerful approach for including correlation effects in electronic structure calculations beyond the GW approximation. However, the expansion is not generally valid, as current implementations ignore terms that mix particle- and hole-states and lead to partial occupation numbers of one-electron states. These limitations are corrected here using a cumulant expansion of the retarded one electron Green's function that includes both particle and hole contributions. The approach provides a consistent framework that improves on the GW approximation to the spectral function without additional computational effort. The method is illustrated with results for the homogeneous electron gas and comparisons to experiment and other methods.

PACS numbers: 02.70.0c,31.10.+z,71.10.-w,71.15.-m
Keywords: Green's function, GW, spectral function, cumulant, cumulant expansion, correlation energy

I. INTRODUCTION

One of the major challenges in condensed matter theory is to capture the effects of electron-electron interactions. Such many-body effects are responsible for the renormalization of energies and redistribution of spectral weight, but they also lead to new features such as satellite structures in the spectral function and partial occupation numbers, e.g., as observed in XPS.[1–4] These features arise from the coupling of electrons to excitations (e.g., plasmons) and cannot be captured by any independent-particle description. While this coupling can be treated formally, e.g., using many-body perturbation theory for the electron Green's function G, such expansions often converge poorly. Thus it is often preferable to introduce some auxiliary quantity from which G is obtained. This is a general strategy in many-body theory, a prominent example being the Dyson equation $G = G^0 + G^0 \Sigma G$, where the auxiliary quantity is the electron self-energy Σ. The self-energy is then expanded to low order, commonly via the GW approximation of Hedin,[5–7] while the Green's function contains contributions from diagrams of all orders. The GW approximation achieves its efficiency by expanding Σ in the screened – rather than the bare – Coulomb interaction W, and retaining only the leading term. This is accomplished by summing certain classes of diagrams, e.g., the "bubble-diagrams" in the random phase approximation (RPA). However, while the GW approximation generally yields good quasi-particle properties, it often gives a poor description of the spectral function,[2,3] and in particular the satellite structure beyond the quasi-particle peak. One of the primary objectives of the present paper is to describe an approach that overcomes this limitation.

An attractive alternative to the GW approximation is the so-called cumulant expansion,[8] which is the primary theoretical tool in our approach. This expansion is usually based on an exponential ansatz for the time ordered Green's function $G = G^0 e^C$, where the cumulant C is now the auxiliary quantity and practical calculations are carried out with a low order approximation for C. Surprisingly, however, this ansatz is not generally valid so both approaches have limitations. To make progress, one must answer three questions: (i) What is the best fundamental quantity to calculate; (ii) What is the best ansatz, e.g., what auxiliary quantity should be used?; and (iii) What is the optimal approximation for that quantity? It is desirable that the development be exact *in principle*, and that even a simple approximation gives good results.

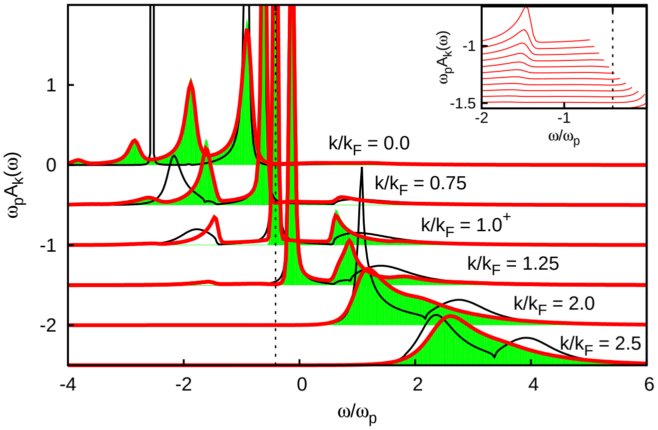

FIG. 1: (Color online) Spectral function $A_k(\omega)$ of an electron gas at zero-temperature for $r_s = 4.0$ in units of the plasmon energy ω_p, for a range of k from the retarded cumulant (RC) approach of this work (thick red lines); the time-ordered (TC) cumulant (filled green curves); and the G^0W^0 approximation (thin black lines). G^0W^0 fails to produce multiple satellites while TC cumulants only exhibit satellites on one side of the Fermi energy. The largest discrepancy between RC and TC is near k_F. The inset shows the existence of a dispersionless satellite below the Fermi energy with increasing k from $k/k_F = 1.0+$ (top) to 1.45 (bottom) in steps of 0.025, as predicted by RC. The dashed vertical line in both plots is set at the chemical potential μ.

The usual procedure to address the above difficulties, is to try to improve (iii), i.e., search for higher order approximations such as vertex corrections. However, as yet, no practical direct approximation for the vertex has been found. In addition, physical properties such as positive spectral weight and normalization are violated at 2nd order in W.[9–11] These shortcomings have led to the development of an exponential ansatz, i.e., with the cumulant C instead of Σ as the auxilliary quantity in (ii).[6,10–13] The exponential representation is motivated by analogy to the case of core-electrons coupled to bosonic excitations,[12,14] where the cumulant expansion is exact. This representation is physically appealing as it systematically includes higher order diagrams that serve implicitly as dynamical vertex corrections.[3] This strategy is advantageous in many cases, e.g., systems of electrons coupled to plasmons and phonons,[6] multiple plasmon-satellites in photoemission,[2,3,13,15–18] the time-evolution of excitations,[19] correlation energies,[20] and dynamical mean field theory.[21] Exponential forms are also found in a wider context, e.g. summations over vacuum bubbles based on the linked cluster theorem,[22] coupled cluster methods,[23] the Thouless theorem for determinantal wave functions,[24] and the Landau formula for electron energy loss.[25]

Despite these successes, many difficulties remain. Formal proofs of the validity of the cumulant expansion are lacking,[26] and indeed, none of the formulations proposed for valence spectra[1–3,9,13] is fully satisfactory. Neither is the method appropriate for interactions that cannot be treated in terms of bosonic excitations.[13]

The remainder of the paper is organized as follows. In Sec. II, the time-ordered cumulant approach is briefly reviewed, and a derivation of the retarded cumulant formalism given. Sec. III presents our results, and finally Sec. IV contains a summary and conclusions.

II. THEORY

In this section, we summarize the application of the cumulant expansion to the one electron Green's function. Here and elsewhere, unless specifically stated, we use Hartree atomic units ($e = \hbar = m = 1$) with energies in Hartrees = 27.2 eV. For simplicity we illustrate the theory for the case of the homogeneous electron gas, where G and G^0 (the non-interacting Green's function) are diagonal in the same independent particle states k. This case is well defined and illustrates the difficulties of conventional cumulant approaches. This case is also used in our numerical tests and comparisons presented in Sec. III. To be clear, the non-interacting Green's function $G^0(t)$ is defined by the single particle Hamiltonian $h = \mathbf{p}^2/2 + V^{ext} + V^H + V^{xc}$, where V^H is the Hartree potential, and V^{xc} is an appropriate exchange correlation potential. In the case of the homogeneous electron gas, $V^{ext} + V^H = 0$, and we choose $V^{xc} = 0$ as well, so that the single particle eigenstates $|\mathbf{k}\rangle$ have energy eigenvalues $\epsilon_k = k^2/2$. The generalization to more realistic systems is reasonably straightforward, as discussed in the Appendix.

A. Time-ordered cumulant

To illustrate the difficulties posed by previous cumulant expansions, we briefly describe the standard time-ordered approach for the cumulant (TC). The cumulant ansatz for the zero-temperature TC Green's function $G_k^T(t) = -i\langle N|Ta_k(t)a_k^\dagger|N\rangle$ is given by

$$G_k^T(t) = G_k^{T,0}(t)e^{C_k^T(t)}, \qquad (1)$$

where $a_k^\dagger$ and a_k are Fermionic creation and destruction operators, T is the time ordering operator, and $C_k^T(t)$ is the TC cumulant. A serious problem with Eq. (1) is that $G_k^{T,0}(t)$ (and thus $G_k^T(t)$) vanishes for negative (positive) times for particles (holes), but this is not the case for the exact (or even GW) Green's functions. Thus Eq. (1) cannot be exact for all times, even in principle. Moreover, the resulting Green's functions have no spectral weight below (above) the Fermi energy, and the occupation numbers n_k remain unchanged from their non-interacting values.[20] This unphysical behavior follows from the form of the non-interacting part $G_k^{T,0}(t) = \mp i\theta(\pm t)\theta(\pm(\epsilon_k - \epsilon_{k_F}))e^{-i\epsilon_k t}$, where the upper (lower) sign refers to particles with $k > k_F$ (holes $k < k_F$), and θ is the unit step function. Physically these defects can be traced to the neglect of diagrams with negatively propagating intermediate states;[27] e.g., recoil effects that mix particle and hole-states.[9] The missing terms account for partial occupation numbers n_k, which are a general property of interacting Fermi systems, as observed e.g., in Compton scattering. Such terms are crucial to understanding correlation effects since n_k is typically $0.1 - 0.4$ above k_F in condensed matter.[6]

B. Retarded cumulant

To overcome these difficulties, a different strategy for question (i) is needed. Instead of $G_k^T(t)$, we take the fundamental quantity of interest to be the *retarded* Green's function,[28] $G_k^R(t) = -i\theta(t)\langle N|\{a_k(t), a_k^\dagger\}|N\rangle$, where $\{,\}$ denotes the anti-commutator. The cumulant representation analogous to Eq. (1) is,

$$G_k^R(t) = G_k^{R,0}(t)e^{C_k^R(t)}, \qquad (2)$$

with a cumulant $C_k^R(t)$ that includes particle and hole branches on an equal footing. The above equation gives a relation between the Green's function and the cumulant valid for all relevant times provided that $G^{0,R}$ and G^R are invertible for $t > 0$. $G_k^{0,R}(t > 0)$ is invertible for any retarded Green's function defined by a Hermitian single-particle Hamiltonian and we conjecture that this is also true for the exact Green's function, although we have no formal proof. Here and below we refer to this representation as the retarded cumulant expansion (RC). Remarkably, many of the difficulties with the TC form disappear with this formulation, yet the *approximate* expression for $C_k^R(t)$ remains *simple*. Thus a seemingly small change in the starting point has dramatic *quantitative* and *qualitative* consequences. In particular, the RC permits calculations of electronic properties that depend on both branches, including occupation numbers, density matrices, and correlation energies. To achieve a practical method, we follow Ref. 13, and approximate $C_k^R(t)$ by expanding to first order in W and matching to the diagrammatic expansion, which gives

$$C_k^R(t) = ie^{i\epsilon_k t}\int \frac{d\omega}{2\pi} e^{-i\omega t}[G_k^{0,R}(\omega)]^2\Sigma_k^R(\omega). \tag{3}$$

Note that in the above equation and in the remainder of this paper (unless specifically stated) we use the symbol Σ to denote the G^0W approximation to the self-energy for a given W. The approximation of Eq. (3) can be related to a quasi-boson treatment of the excitations of the system. The integral in Eq. (3) can be evaluated exactly by contour integration over the poles in the lower-half frequency plane with $G_k^{0,R}(\omega) = [\omega - \epsilon_k + i\delta]^{-1}$ and the spectral representation of the G^0W self-energy

$$\Sigma_k^R(\omega) = \Sigma_k^x + \int \frac{d\omega'}{\pi}\frac{\left|\mathrm{Im}\Sigma_k^R(\omega')\right|}{\omega - \omega' + i\delta}, \tag{4}$$

where the static $\Sigma_k^x = iG^0 v$ exchange self-energy is separated out. Carrying out the integrations then yields

$$\begin{aligned} G_k^R(t) &= -i\theta(t)e^{-i\epsilon_k^x t}e^{\tilde{C}_k^R(t)}, \qquad (5)\\ \tilde{C}_k^R(t) &= \int d\omega \frac{\beta_k(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1),\\ \beta_k(\omega) &= \frac{1}{\pi}\left|\mathrm{Im}\,\Sigma_k^R(\omega + \epsilon_k)\right|, \end{aligned}$$

where $\epsilon_k^x = \epsilon_k + \Sigma_k^x$, and $\tilde{C}_k^R$ is the dynamic part of C_k^R, which is found by replacing Σ_k^R with $\Sigma_k^R - \Sigma_k^x$ in Eq. (3). Note that altough the integrand in the expression for the cumulant above appears to be singular with a double pole at $\omega = 0$, this singularity is cancelled by the factor $[\exp(-i\omega t) + i\omega t - 1]$ so that $\tilde{C}_k$ is well defined even in cases where $\beta(0) = 0$. Finally, the spectral function is

$$A_k(\omega) = -\frac{1}{\pi}\mathrm{Im}\,G_k^R(\omega). \tag{6}$$

While the above equations are similar to the TC formulae,[2] a major difference lies in the excitation spectrum $\beta_k(\omega) = \beta_k^+(\omega) + \beta_k^-(\omega)$, where $\beta_k^\pm(\omega) = \left|\mathrm{Im}\,\Sigma_k^R(\omega + \epsilon_k)\right|\theta(\pm(\epsilon_{k_F} - \epsilon_k - \omega))$. While the RC contains all frequencies and builds in particle-hole symmetry, the TC forms only contain β_k^+ or β_k^- for particles or holes, respectively. For particles (+) or holes (−) for example, the TC formalism gives

$$\tilde{C}_k^T(t) = \int d\omega \frac{\beta_k^\pm(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1). \tag{7}$$

Consequently the spectral functions are substantially different (see Fig. 1). The simplicity of the RC allows one to check that the basic requirements and sum-rules are fulfilled. Thus $C_k(t=0) = 0$, so that $A_k(\omega)$ is normalized to unity. In addition, $C_k'(t=0) = 0$ so the spectral function has a centroid at the unperturbed (non-self consistent) Hartree-Fock energy ϵ_k^x, consistent with a one-shot calculation of $A_k(\omega)$. One also easily obtains the renormalization constant Z_k, quasi-particle energy shift Δ_k, and occupation numbers n_k,

$$\begin{aligned} Z_k &= e^{-a_k}, \qquad (8)\\ a_k &= \int d\omega\, \frac{\beta_k(\omega)}{(\omega - i\delta)^2},\\ \Delta_k &= \int d\omega\, \frac{\beta_k(\omega)}{(\omega - i\delta)},\\ n_k &= \int_{-\infty}^{\mu} d\omega\, A_k(\omega), \end{aligned}$$

where the chemical potential μ is fixed by enforcing total occupation $\Sigma_k n_k = N$. This definition of the chemical potential is reasonable for the electron gas, although enforcing the occupations in this manner can cause problems in semiconductors, where μ may not lie in the band gap. In any case, this problem occurs with the G^0W^0 approximation as well.[29] These quantities permit a separation of the quasiparticle and satellite parts of the Green's function;[2] however, this separation may not always be reasonable, e.g., in cases when the real part of the renormalization constant is negative (see Fig. 2). Nevertheless, the total cumulant and related Green's function as given by Eq. 5 are always well defined within either the RC or TC methods. Note also, that when $\beta_k(0) > 0$, a_k and thus Z_k are complex. For the electron gas, this is the case for all $k \neq k_F$. One can also express a_k in terms of the derivative of the self-energy, i.e.,

$$a_k = -\left.\frac{d\Sigma_k(\omega)}{d\omega}\right|_{\omega=\epsilon_k}, \tag{9}$$

which leads to the familiar GW form of the renormalization constant $Z_k = 1/(1 - \Sigma_k'(\epsilon_k)$. The primary many-body ingredient in the RC is $\beta_k(\omega)$, the imaginary part of the retarded G^0W self energy Σ_k^R, where W is defined by a given screening approximation and has a structure that reflects peaks in the loss function $|\mathrm{Im}\,\epsilon^{-1}(\omega)|$. Thus the computational effort in the RC is comparable to that in G^0W^0 if we also use the RPA $W = W^0$. Going to higher order is technically difficult and not necessarily an improvement, since higher order terms can lead to non-physical behavior in $A_k(\omega)$.[9,13] The complex renormalization constant Z_k describes the reduction in strength, and assymetry of the quasi-particle peak and agrees to 1st order in W with that for G^0W^0 where $Z_k^{GW} = 1/(1 + a_k)$. Physically the behavior of the RC in Eq. (5) can be interpreted as a transfer of spectral weight away from the quasi-particle peak by quasi-boson excitations at frequency ω, with coupling constants

$g^2 \sim \beta(\omega)$. The "shake-up" counts $a_k = a_k^+ + a_k^-$ correspond to the mean number of bosons coupled to the electron (or hole), and account for the satellite strengths $a_k^{\pm} = \int d\omega\, \beta_k^{\pm}(\omega)/(\omega - i\delta)^2$ in $A_k(\omega)$ above $(+)$ and below $(-)$ the quasi-particle peak. To further interpret the RC and compare to previous approaches, it is useful to examine various limits. Due to the separation $\beta_k = \beta_k^+ + \beta_k^-$, a complete calculation of $A_k(\omega)$ requires a Fourier transform of the product $e^{C_k^+(t)} e^{C_k^-(t)}$, where $C_k^{\pm}$ are the TC cumulants which contain $\beta_k^{\pm}$ instead of β_k. Since one of the branches is always small (except close to $k = k_F$), and vanishes far from k_F, one can estimate the contributions separately using the identity $e^{C_k^R(t)} \equiv e^{C_k^-(t)} + e^{C_k^+(t)} - 1 + (e^{C_k^+(t)} - 1)(e^{C_k^-(t)} - 1)$. For example, for hole spectra ($k < k_F$), the leading term $e^{C_k^-(t)}$ corresponds to the TC cumulant,[2,6] to which the RC reduces when $k \ll k_F$ (Fig. 1). Interestingly, the cumulant $C_k^-(t)$ is identical to that obtained with the recoil approximation of Hedin.[9] The next terms $e^{C_k^+(t)} - 1$ correspond to the minor branch of Ref. 13. However, that approximation does not conserve spectral weight, and the remaining terms that mix particles and holes are needed to preserve normalization.

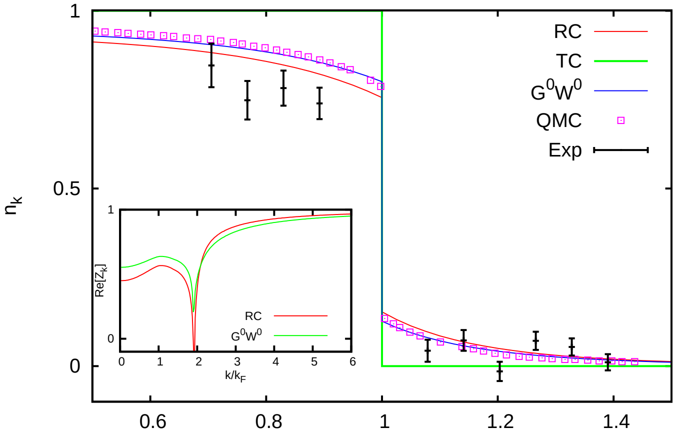

FIG. 2: (Color online) Occupation number n_k vs k calculated for an electron gas with $r_s = 4.0$ from RC (red) compared to TC (green), G^0W^0 (blue), Compton experiment for Na[32] (black error bars), and QMC (pink squares).[32] Inset: Re[Z_k] vs k from RC (red) and G^0W^0 (green).

III. RESULTS AND DISCUSSION

Below we illustrate the RC with explicit results for the homogeneous electron gas at zero temperature. This model is often used as a standard for quantitative theoretical approaches. The case with $r_s = 4.0$ corresponds to bcc Na, which is also a widely used prototype material for treatments of plasmon-satellites.[2,7,14,20] For consistency we use the same RPA approximation for W as in Ref. 7, and we checked that our results agree to high accuracy with previous G^0W^0 calculations.[14,30] The integrations involved in the cumulants, occupation numbers, and total energies were performed using the trapezoidal rule, except near $\omega = 0$ where the integrand was expanded to avoid the singular point. Fourier transforms from time to frequency were performed with minimal Gaussian broadening. Integrals were converged with respect to range and spacing of points to sufficient accuracy for all values reported here. Fig. 1 shows $A_k(\omega)$ from the RC for a range of k compared to the standard TC and G^0W^0 (thin solid line) approximations. The largest discrepancy between the RC and TC forms is near $k = k_F$, where the RC exhibits a nearly symmetrical particle-hole spectrum, consistent with a reduction of the jump in n_k at the Fermi surface from its non-interacting value. As expected, the TC $A_k(\omega)$ agrees with the RC far from k_F, so that previous cumulant treatments are preserved in that limit. Note too that the quasiparticle peak has substantial broadening at large k due to the onset of particle-hole and plasmon excitations. In all cases, $A_k(\omega)$ differs markedly from the G^0W^0 approximation, thus demonstrating the importance of vertex corrections. The differences are especially noticable at $k = 0$, where RC and TC exhibit multiple plasmon peaks; in contrast G^0W^0 has only one sharp "plasmaron" peak, shown previously to be in qualitative disagreement with experimental photoemission spectra in metals and semiconductors.[2,3,16] The inset in Fig. 1 shows a nearly dispersionless satellite at $\mu - \omega_p$, not predicted by TC and ill-described by G^{0}W^0, where $\omega_p = \sqrt{4\pi n_e}$ is the plasma frequency. This feature may be experimentally observable, e.g., via ARPES, and would provide an additional measure of correlation effects. Values of n_k and Z_k are important diagnostics of the quality of a given many-body approximation.[14,30,31] Also n_k are central ingredients in the one-body density matrix. Fig. 2 shows n_k from RC compared to G^{0}W^0 for an electron gas with $r_s = 4.0$, together with values extracted from Compton scattering data for Na[32] and QMC.[32] The RC gives n_k in reasonable agreement with G^{0}W^0 and quantum Monte Carlo (QMC) though slightly lower for $k < k_F$. They are also consistent with, though somewhat higher than, Compton data below $k = k_F$. The real part of the calculated renormalization constant Re[Z_k] is shown in the inset to Fig. 2, and Table I summarizes results at $k = k_F$ compared to G^0W^0, GW,

TABLE I: Quasiparticle renormalization factor Z_F at $k = k_F$ from RC, TC, G^0W^0, self-consistent GW,[33] and QMC.[30] No imaginary part is reported since Z_k is real at the Fermi momentum. Note that within the TC formalism, Z_k is discontinuous at the Fermi momentum, thus we have reported both values as $Z_{k_F-\delta}$,$Z_{k_F+\delta}$.

r_s	RC	TC	G^0W^0	GW	QMC
1	0.85	0.91,0.90	0.86	-	0.84
2	0.73	0.85,0.81	0.76	0.85	0.77
4	0.57	0.76,0.68	0.64	0.79	0.64
5	0.50	0.73,0.63	0.59	-	0.58
10	0.29	0.63,0.42	0.45	-	0.40

and QMC for a range of r_s.[30,33] Note that within the TC approach, Z_k is discontinuous at the Fermi momentum. This unphysical behaviour is due to the fact that within the TC approximation, particles contain only particle sattelites, and holes contain only hole sattelites. The weight of these sattelites is related directly to the imaginary part of the self-energy, thus Z_k is continuous only if $\mathrm{Im}[\Sigma_{k_F}(\omega)]$ is symmetric about $\omega = \mu$, which is not the case for the electron gas. We find reasonable agreement between the RC and QMC at higher densities and a larger discrepancy at smaller values. Interestingly, G^0W^0 results compare well with QMC, while those for self consistent GW are too large, confirming that some correlation effects are underestimated by self-consistent GW.[33]

Finally we present a RC calculation of electron correlation energies using the Galitskii-Migdal formula. This formula was previously applied to the TC cumulant approximation in Ref. 20. Other formulations, such as the variational Luttinger-Ward functional may give improved energies but do not appear straightforward to implement with the cumulant representation. Assuming a paramagnetic system the total energy E is given by

$$\begin{aligned} E &= \frac{1}{2}\sum_{k\sigma}\lim_{t\to 0^-}[\partial_t - i\epsilon_k]G_k(t) \qquad (10)\\ &= \sum_k \int d\omega\ [\epsilon_k + \omega]\, A_k(\omega). \end{aligned}$$

The correlation energy per particle is defined as $\epsilon_{corr} = (E - E_{HF})/N$, where the total Hartree-Fock energy is

$$E_{HF} = \sum_k [\epsilon_k + \epsilon_k^x]\, \theta(k_F - k). \qquad (11)$$

For example, for the electron gas at $r_s = 4.0$, $\epsilon_k = (1/2)k^2$ and $E_{HF}/N = -0.0445$. Note that the above formula for the Hartree-Fock energy is only correct in the homogeneous electron gas where the eigenfunctions are not modified by the exchange potential. In a real system, the energies would be defined by the self-consistent Hartree-Fock energy. Table II presents correlation energies calculated from Eq. (10) and (11) for r_s from 1 to 5, and for comparison, results for TC, G^0W^0, GW,[33,34] and QMC.[20] For all cases RC yields some improvement in correlation energies compared to G^0W^0, while improvement in comparison to TC is seen only for $r_s > 3$. While some correlation energies reported in Ref. 20 are also close to QMC, their prescription uses some approximations that go beyond TC.

TABLE II: Homogeneous electron gas correlation energies as a function of r_s calculated using RC (Eq. (10) and compared to TC, G^0W^0, self-consistent GW[33,34] and QMC calculations[20].

r_s	RC	TC	G^0W^0	GW	QMC
1	-0.070	-0.064	-0.074	-0.058	-0.0600
2	-0.051	-0.049	-0.055	-0.044	-0.0448
3	-0.041	-0.041	-0.044	-0.037	-0.0369
4	-0.035	-0.036	-0.038	-0.031	-0.0318
5	-0.030	-0.033	-0.033	-0.027	-0.0281

IV. SUMMARY AND CONCLUSIONS

In conclusion, we have presented a cumulant approximation based on a retarded one-particle Green's function formalism with a cumulant expanded to first order in W. The RC provides a unifying framework for the electron Green's function that yields partial occupations, multiple satellites in the spectral function on both sides of the Fermi energy, and total energies, all in reasonable agreement with available theoretical and experimental data. In contrast, the GW approximation and previous TC cumulant approximations fail to account for one or more of these properties. Differences between the RC and TC Green's functions are especially significant near k_F. These differences are important in many contexts, e.g., cases with particle-hole symmetry such as phonons and other low energy excitations. Moreover, the approach can be straightforwardly extended to finite temperature, whereas the TC cannot. Also, differences with respect to the GW approximation provide insights into the nature of vertex corrections. Results for the homogeneous electron gas show that this level of theory gives correlation energies that quantitatively improve on G^0W^0 compared to QMC. But they are still slightly low, and the renormalization constants Z_k too small. However, the RC permits some freedom in the choice of initial one-particle states and the screened interaction W. Thus based on differences between self-consistent GW and G^0W^0, it is plausible that part of the remaining discrepancy can be explained by some form of self-consistency.[33,35–37] For these reasons the RC provides an attractive approach for going beyond the GW approximation without additional computational complexity, and with a simplicity that points to its utility for real systems.

Acknowledgments

We thank F. Aryasetiawan, G. Bertsch, S. Biermann, M. Casula, M. Gatti, E.K.U. Gross, M. Guzzo, V. Pavlyukh, E. Shirley, D.J. Thouless, and others in the European Theoretical Spectroscopy Facility, for useful comments, and S. Huotari for providing experimental data. This work was supported by DOE Grant DE-FG03-97ER45623 (JJR,JJK), by the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement n. 320971 (LR,JJR), and was facilitated by the DOE Computational Materials Science Network. One of us (JJR) thanks the Laboratories des Solides Irradíes at the École Polytechnique, Palaiseau for hospitality during part of this work.

Appendix: Generalization to inhomogeneous systems

For a general inhomogeneous system, G^0, G, and Σ may not all be diagonal in the same single particle states, so the the exponential ansatz must be generalized, i.e.,

$$G^R_{kk'}(t) = G^{0,R}_k(t)e^{C^R_{kk'}(t)}, \tag{A.1}$$

where k denotes the eigenstates of the initial one-particle Hamiltonian, and $G^{0,R}$ is the related Green's function. It is desirable to choose our single particle states such that the starting Green's function $G^{0,R}$ is as close as possible to the full Green's function, without making the calculations impractical. For example, the choice of Kohn-Sham states with a density functional Hamiltonian is appropriate for many systems. Alternatively one could start with a quasiparticle Green's function, in which case ϵ_k refers to the quasiparticle energies. As the derivation of the full, off diagonal cumulant expansion is somewhat more complicated, we limit our attention here to the diagonal approximation. With Kohn-Sham initial states, this amounts to the assumption that the operator $\Sigma - V^{xc}$ is nearly diagonal in the same states as G^0. Within this approximation, the derivation of the RC now largely parallels that given in Sec. II. For example, Eq. (3) becomes

$$\begin{aligned} C^R_k(t) &= ie^{i\epsilon_k t}\int \frac{d\omega}{2\pi} e^{-i\omega t} G^{0,R}_k(\omega) \\ &\quad \times \left[\Sigma^R_k(\omega) - V^{xc}_k\right] G^{0,R}_k(\omega), \end{aligned} \tag{A.2}$$

where ϵ_k are the Kohn-Sham energies, V^{xc} the associated exchange correlation potential, and $G^0(\omega) = [\omega - (h^0 + V^{xc}]^{-1}$. The leading cumulant C^R_k can again be found by contour integration, which gives

$$\begin{aligned} G^R_k(t) &= -i\theta(t)e^{-i\tilde{\epsilon}_k t}e^{\tilde{C}^R_k(t)}, \\ \tilde{C}^R_k(t) &= \int d\omega \frac{\beta_k(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1), \\ \beta_k(\omega) &= \frac{1}{\pi}\left|\mathrm{Im}\,\Sigma^R_k(\omega + \epsilon_k)\right|, \end{aligned} \tag{A.3}$$

where $\tilde{\epsilon}_k = \epsilon_k + \Sigma^x_k - V^{xc}_k$. While the diagonal approximation is not always reliable (e.g. transition metal oxides), the self-energy is nearly diagonal in many systems, and has been used with much success within the GW approximation.[6,38–40] The diagonal approximation has also been used previously for the TC cumulant expansion for a variety of materials.[2,3,15,16]

---

[*] `joshua.j.kas@gmail.com`

[†] `jjr@uw.edu`

[‡] `lucia.reining@polytechnique.fr`

[1] C.-O. Almbladh and L. Hedin, Handbook on Synchroton Radiation **1**, 686 (1983).

[2] F. Aryasetiawan, L. Hedin, and K. Karlsson, Phys. Rev. Lett. **77**, 2268 (1996).

[3] M. Guzzo, G. Lani, F. Sottile, P. Romaniello, M. Gatti, J. J. Kas, J. J. Rehr, M. G. Silly, F. Sirotti, and L. Reining, Phys. Rev. Lett. **107**, 166401 (2011).

[4] A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. **75**, 473 (2003).

[5] L. Hedin, Phys. Rev. **139**, A796 (1965).

[6] L. Hedin, Journal of Physics: Condensed Matter **11**, R489 (1999).

[7] B. I. Lundqvist, Phys. kondens. Materie **6**, 206 (1967).

[8] R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).

[9] L. Hedin, Physica Scripta **21**, 477 (1980).

[10] B. Bergersen, F. W. Kus, and C. Blomberg, Can. J. Phys. **51**, 102 (1972).

[11] P. Minnhagen, J. Phys. C **8**, 1535 (1975).

[12] D. C. Langreth, Phys. Rev. B **1**, 471 (1970).

[13] O. Gunnarsson, V. Meden, and K. Schönhammer, Phys. Rev. B **50**, 10462 (1994).

[14] H. Ness, L. K. Dash, M. Stankovski, and R. W. Godby, Phys. Rev. B **84**, 195114 (2011).

[15] M. Guzzo, J. Kas, F. Sottile, M. Silly, F. Sirotti, J. Rehr, and L. Reining, Eur. Phys. J. B **87**, 324 (2012).

[16] J. Lischner, D. Vigil-Fowler, and S. G. Louie, Phys. Rev. Lett. **110**, 146801 (2013).

[17] T. Fujikawa, M. Kazama, and H. Shinotsuka, e-J. Surf. Sci. Nanotech. **6**, 263 (2008).

[18] M. Gatti and M. Guzzo, Phys. Rev. B **87**, 155147 (2013).

[19] Y. Pavlyukh, J. Berakdar, and A. Rubio, Phys. Rev. B **87**, 125101 (2013).

[20] B. Holm and F. Aryasetiawan, Phys. Rev. B **62**, 4858 (2000).

[21] M. Casula, A. Rubtsov, and S. Biermann, Phys. Rev. B **85**, 035115 (2012).

[22] P. Nozières and C. T. de Dominicis, Phys. Rev. **178**, 1097 (1969).

[23] I. Shavitt and R. J. Bartlett, Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory (2009).

[24] D. J. Thouless, The Quantum Mechanics of Many-body Systems, 2nd Edition (1972).

[25] L. Landau, J. Phys. USSR **8**, 201 (1944).

[26] G. D. Mahan, Many-particle Physics, 3^{rd} edition (2000).

[27] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

[28] R. D. Mattuck, A Guide to Feynman Diagrams in the Many-Body Problem, 2^{nd} edition (1976).

[29] A. Schindlmayr, P. García-González, and R. W. Godby, Phys. Rev. B **64**, 235106 (2001).

[30] M. Holzmann, B. Bernu, C. Pierleoni, J. McMinis, D. M.

Ceperley, V. Olevano, and L. Delle Site, Phys. Rev. Lett. **107**, 110402 (2011).

[31] M. Vogt, R. Zimmermann, and R. J. Needs, Phys. Rev. B **69**, 045113 (2004).

[32] S. Huotari, J. A. Soininen, T. Pylkkänen, K. Hämäläinen, A. Issolah, A. Titov, J. McMinis, J. Kim, K. Esler, D. M. Ceperley, et al., Phys. Rev. Lett. **105**, 086403 (2010).

[33] B. Holm and U. von Barth, Phys. Rev. B **57**, 2108 (1998).

[34] P. García-González and R. W. Godby, Phys. Rev. B **63**, 075112 (2001).

[35] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).

[36] U. von Barth and B. Holm, Phys. Rev. B **54**, 8411 (1996).

[37] E. L. Shirley, Phys. Rev. B **54**, 7758 (1996).

[38] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).

[39] F. Aryasetiawan, Phys. Rev. B **46**, 13051 (1992).

[40] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).