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Violation of particle number conservation in the GW approximation

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We present a nontrivial model system of interacting electrons that can be solved analytically in the GW approximation. We obtain the particle number from the GW Green's function strictly analytically, and prove that there is a genuine violation of particle number conservation if the self-energy is calculated non-self-consistently from a zeroth order Green's function, as done in virtually all practical implementations. We also show that a simple shift of the self-energy that partially restores self-consistency reduces the numerical deviation significantly.

INTRODUCTION

Many-body perturbation theory for condensed-matter physics allows the Green's function of a system of interacting electrons to be formulated in a picture of independent quasiparticles moving in an effective potential. The key quantity that incorporates the contributions of dynamic exchange and correlation to this effective potential is the self-energy operator Σ, which in general is both nonlocal and energy dependent. It is itself a functional of the Green's function that can formally be expressed through an infinite series of Feynman diagrams. In practice, however, approximations for the functional form are required, of which the most popular is the GW approximation introduced by Hedin.[1] This approach replaces the infinite series of Feynman diagrams for the self-energy operator by a single Fock-like diagram that is the product of the Green's function G and the dynamically screened Coulomb interaction W, hence the name of the scheme. Originally the GW approximation was devised to be applied self-consistently on an equal footing with the Hartree and Hartree-Fock approximations, in the sense that the Green's function used to generate the self-energy be identical to that obtained from it, but the computational cost proved prohibitive. Thus GW self-energies are traditionally calculated from a zeroth order Hartree or LDA Green's function, although a small degree of self-consistency is sometimes introduced by rigidly shifting the zeroth order Green's function on the energy axis in such a way that its chemical potential agrees with that of the GW Green's function derived from it. It is in this fashion that the GW approximation has in the past been successfully applied to a wide range of materials including semiconductors,[2,3] simple metals,[4] and transition metals.[5] The first fully self-consistent GW calculations for model systems were reported only recently,[6,7] but these consistently showed an undesired loss of structural features in the Green's function in disagreement with experiment.[8]

As future GW calculations for realistic materials are therefore unlikely to adopt a fully self-consistent approach, the question of particle number conservation, long since a subject of debate in this context, has gained renewed significance. Since the imaginary part of the Green's function is directly related to the density of states as well as to the real-space charge density, it must integrate to the correct number of electrons contained in the system, a condition frequently used to determine the numerical accuracy in practical implementations. However, while the fully self-consistent GW scheme is known to conserve the exact particle number,[9] the same, while tacitly assumed, has never actually been proven for the approximation used in practice, in which the self-energy is calculated from a zeroth order Green's function. Numerical simulations appeared to corroborate this positive assumption, with deviations below one percent fully within the range expected due to systematic numerical errors, and this has already prompted occasional confirmative conjectures in the literature.[5] However, in this paper we shall show that upon elimination of these errors, which arise from numerical integration, transformation to Fourier space with a finite broadening of the quasiparticle peaks, alignment of the chemical potentials only within second order perturbation theory, etc., there still remains a genuine albeit numerically small violation of particle number conservation, as was previously demonstrated by accurate molecular calculations for the analogous scheme based on time-dependent Hartree-Fock rather than Hartree theory that is frequently employed in quantum chemistry.[10] We also demonstrate that restoring a degree of self-consistency by means of an appropriate shift in the zeroth order Green's function, which in practice is often omitted because of its negligible influence on the band structure, further significantly reduces the deviation. The significance of this result is that it provides a way to minimize the fundamental limit on the accuracy with which quantities such as the charge density or the total energy can be calculated in the GW approximation.

DESCRIPTION OF MODEL SYSTEM

For our proof we consider as an analytically solvable counter-example a four-site Hubbard cluster with tetrahedral symmetry, populated by two electrons. To the best of our knowledge this is in fact the first model system forwarded in the literature for which the Green's function and particle number in the GW approximation can be calculated strictly analytically, without any numerical errors. Its significance for theoretical investigations therefore stretches beyond the objective of this paper, and for the benefit of the reader we will thus present all derivations in sufficient detail. The Hamiltonian is

$$\mathcal{H} = \left(\epsilon - \frac{U}{2}\right) \sum_{\mathbf{R},\sigma} \hat{n}_{\mathbf{R}\sigma} - t \sum_{\mathbf{R},\mathbf{R}',\sigma} c^{\dagger}_{\mathbf{R}\sigma} c_{\mathbf{R}'\sigma} + U \sum_{\mathbf{R}} \hat{n}_{\mathbf{R}\uparrow} \hat{n}_{\mathbf{R}\downarrow}, \tag{1}$$

where $c^{\dagger}_{\mathbf{R}\sigma}$ and $c_{\mathbf{R}\sigma}$ are the creation and annihilation operators for an electron at site $\mathbf{R}$ with spin σ, and $\hat{n}_{\mathbf{R}\sigma} = c^{\dagger}_{\mathbf{R}\sigma} c_{\mathbf{R}\sigma}$. We set $\epsilon = 4t$ and $t = 1$ while leaving the onsite interaction strength U variable. To construct the GW self-energy we start from a zeroth order Green's function in the Hartree approximation, noting that the exchange-correlation potential in a corresponding density-functional treatment is a mere constant due to spatial symmetries and would not affect the following arguments. Spatial symmetries and degeneracy in σ also require a uniform fractional site occupation of one half and accordingly a Hartree potential of $U/2$ on all sites. Analytic diagonalization of the Hartree 4×4 Hamiltonian matrix $\mathcal{H}^{\mathrm{H}}_{\mathbf{R}\mathbf{R}'} = \epsilon \delta_{\mathbf{R}\mathbf{R}'} - t$ for each spin orientation then yields a nondegenerate ground state at zero energy and a threefold degenerate excited state at energy ϵ. With the electrons in the ground state $|0\rangle$ the zeroth order Green's function becomes

$$G^{\mathrm{H}}_{\mathbf{R}\mathbf{R}'}(\omega) = \frac{\langle \mathbf{R}|0\rangle\langle 0|\mathbf{R}'\rangle}{\omega - i\eta} + \sum_{\nu=1}^{3} \frac{\langle \mathbf{R}|\nu\rangle\langle \nu|\mathbf{R}'\rangle}{\omega - \epsilon + i\eta}, \tag{2}$$

where we have omitted the spin index. η denotes a positive infinitesimal. Using the relation $\langle \mathbf{R}|0\rangle\langle 0|\mathbf{R}'\rangle = 1/4$ for the components of the ground-state vector we proceed to calculating the polarization propagator in the random-phase approximation (RPA), defined through

$$\begin{aligned} P^{\mathrm{RPA}}_{\mathbf{R}\mathbf{R}'}(\omega) &= -2 \frac{i}{2\pi} \int G^{\mathrm{H}}_{\mathbf{R}\mathbf{R}'}(\omega + \omega') G^{\mathrm{H}}_{\mathbf{R}'\mathbf{R}}(\omega)\, d\omega' \\ &= \frac{1}{2} \sum_{\nu=1}^{3} \langle \mathbf{R}|\nu\rangle\langle \nu|\mathbf{R}'\rangle \left\{ \frac{1}{\omega - \epsilon + i\eta} - \frac{1}{\omega + \epsilon - i\eta} \right\}, \end{aligned} \tag{3}$$

including a factor 2 for the spin summation. The polarization propagator is diagonal in eigenvector space, and can thus be analytically inverted to yield the screened interaction

$$\begin{aligned} W^{\mathrm{RPA}}_{\mathbf{R}\mathbf{R}'}(\omega) &= U \delta_{\mathbf{R}\mathbf{R}'} + U \sum_{\mathbf{R}''} P^{\mathrm{RPA}}_{\mathbf{R}\mathbf{R}''}(\omega) W^{\mathrm{RPA}}_{\mathbf{R}''\mathbf{R}'}(\omega) \\ &= U \delta_{\mathbf{R}\mathbf{R}'} + \frac{\epsilon U^2}{2z} \sum_{\nu=1}^{3} \langle \mathbf{R}|\nu\rangle\langle \nu|\mathbf{R}'\rangle \\ &\quad \times \left\{ \frac{1}{\omega - z + i\eta} - \frac{1}{\omega + z - i\eta} \right\}, \end{aligned} \tag{4}$$

with $z = [\epsilon(\epsilon + U)]^{1/2}$. A similar analytic expression for the screening in a related model system was previously given in Ref. 11. The self-energy in the GW approximation is a convolution of the zeroth order Green's function and the RPA screened interaction,

$$\begin{aligned} \Sigma^{GW}_{\mathbf{R}\mathbf{R}'}(\omega) &= \frac{i}{2\pi} \int G^{\mathrm{H}}_{\mathbf{R}\mathbf{R}'}(\omega - \omega') W^{\mathrm{RPA}}_{\mathbf{R}\mathbf{R}'}(\omega') e^{i\delta\omega'}\, d\omega' \\ &= -\frac{U}{4} \delta_{\mathbf{R}\mathbf{R}'} + \frac{3\epsilon U^2}{8z} \frac{\langle \mathbf{R}|0\rangle\langle 0|\mathbf{R}'\rangle}{\omega - z - \epsilon + i\eta} \\ &\quad + \frac{\epsilon U^2}{8z} \sum_{\nu=1}^{3} \langle \mathbf{R}|\nu\rangle\langle \nu|\mathbf{R}'\rangle \\ &\quad \times \left\{ \frac{2}{\omega - z - \epsilon + i\eta} + \frac{1}{\omega + z - i\eta} \right\}, \end{aligned} \tag{5}$$

where δ denotes a positive infinitesimal. We have written Σ^{GW} in such a way as to emphasize that it is diagonal in the eigenvectors $|\nu\rangle$ of the initial Hartree system. On the other hand, diagonalization of the full Hamiltonian including the self-energy yields the quasiparticle states of the interacting electron system, so for our model the two are in fact identical, although the corresponding energy eigenvalues are not. In this way we can calculate the chemical potential μ of the interacting electron system exactly from its true quasiparticle properties. By definition the chemical potential is identical to the energy eigenvalue of the highest occupied quasiparticle state, which is zero for the original Hartree system, and at the GW level is given implicitly through the self-energy correction,

$$\mu = 0 + \Sigma^{GW}_{\nu=0}(\mu - \tilde{\omega}). \tag{6}$$

Here we have allowed for the possibility of using a self-energy derived from a zeroth order Green's function whose chemical potential has been shifted by $\tilde{\omega}$ on the energy axis. To simulate the effect of a self-consistent calculation we determine the shift by requiring the chemical potentials of the shifted zeroth order Green's function and the GW Green's function obtained from it to be identical. While this equation is usually solved within second order perturbation theory, the simple form of the self-energy for our model (5) allows us to derive the exact analytic solution

$$\tilde{\omega} = -\frac{U}{4} - \frac{3\epsilon U^2}{8z(z + \epsilon)}, \tag{7}$$

which correctly approaches zero as $U \to 0$. Accordingly we solve Dyson's equation

$$G^{GW}_{\nu}(\omega) = G^{\mathrm{H}}_{\nu}(\omega) + G^{\mathrm{H}}_{\nu}(\omega) \Sigma^{GW}_{\nu}(\omega - \tilde{\omega}) G^{GW}_{\nu}(\omega) \tag{8}$$

in eigenvector space both for $\tilde{\omega} = 0$ and $\tilde{\omega}$ as in Eq. (7), and compare the results. In this diagonal form Dyson's equation is analytically solvable. For $\nu = 0$ the self-energy (5) contains one pole, which adds a satellite to the quasiparticle peak of the Hartree Green's function and yields a quadratic equation for the positions of the poles of G^{GW}. Similarly the quasiparticle and satellite structure of the $\nu > 0$ matrix elements is obtained from the zeroes of a third order polynomial, reflecting the richer spectrum in the self-energy. The GW Green's function therefore takes the analytic form

$$\begin{aligned}
&G^{GW}_{\mathbf{RR}'}(\omega + \tilde{\omega}) \\
&= \langle \mathbf{R}|0\rangle\langle 0|\mathbf{R}'\rangle \frac{\omega - z - \epsilon}{(\omega - x_1 - i\eta)(\omega - x_2 + i\eta)} \\
&\quad + \sum_{\nu=1}^{3} \langle \mathbf{R}|\nu\rangle\langle \nu|\mathbf{R}'\rangle \\
&\quad \times \frac{(\omega - z - \epsilon)(\omega + z)}{(\omega - y_1 - i\eta)(\omega - y_2 + i\eta)(\omega - y_3 + i\eta)},
\end{aligned} \tag{9}$$

where we have defined the symbols

$$x_{1,2} = \frac{z + \epsilon - \tilde{\omega} - \dfrac{U}{4}}{2} \mp \sqrt{\left(\frac{z + \epsilon + \tilde{\omega} + \dfrac{U}{4}}{2}\right)^2 + \frac{3\epsilon U^2}{8z}} \tag{10}$$

together with $y_1 = -(b/3) - 2r\cos(\phi/3)$ and $y_{2,3} = -(b/3) + 2r\cos[(\pi \mp \phi)/3]$ as well as the auxiliary quantities $r = \pm\sqrt{|p|}$, $\phi = \arccos(q/r^3)$, $q = b^3/27 - bc/6 + d/2$, $p = (3c - b^2)/9$, and the polynomial coefficients

$$b = -2\epsilon + \tilde{\omega} + \frac{U}{4}, \tag{11a}$$

$$c = -z(z + \epsilon) + \epsilon\left(\epsilon - \tilde{\omega} - \frac{U}{4}\right) - \frac{3\epsilon U^2}{8z}, \tag{11b}$$

$$d = z(z + \epsilon)\left(\epsilon - \tilde{\omega} - \frac{U}{4}\right) + \frac{(\epsilon - z)\epsilon U^2}{8z}. \tag{11c}$$

RESULTS

From the Green's function in the GW approximation (9) the particle number may be obtained by an analytic contour integration along a path closed across the upper half plane, to sample all occupied states below the chemical potential. By inspection we note that these are the states at x_1 and y_1. For the total particle number we thus obtain

$$\begin{aligned}
N &= 2\sum_{\mathbf{R}} \frac{1}{2\pi i} \int G^{GW}_{\mathbf{RR}}(\omega) e^{i\delta\omega}\, d\omega \\
&= \frac{2(x_1 - z - \epsilon)}{x_1 - x_2} + \frac{6(y_1 - z - \epsilon)(y_1 + z)}{(y_1 - y_2)(y_1 - y_3)},
\end{aligned} \tag{12}$$

including a factor 2 for spin summation. If the particle number in the GW approximation was conserved, N would have to be a constant with a value of two. In particular, it would also have to be independent of the interaction strength U, which so far we have not specified, but an analysis of the expression (12) confirms that this is not the case. In Fig. 1 we show the calculated particle number as a function of U, both with and without applying the shift $\tilde{\omega}$ in the zeroth order Green's function. In either case the growing deviation from the true value as U increases is clearly visible, evidence of a genuine and fundamental violation of particle number conservation in the GW approximation as usually applied. In absolute terms, however, we find that the discrepancy is much reduced when the chemical potentials are aligned in the prescribed way, and that it depends only very weakly on the interaction strength up to high values of U. For a medium correlation of $U = 4$ the numerical deviation amounts to an underestimation of merely 0.21% of the true particle number.

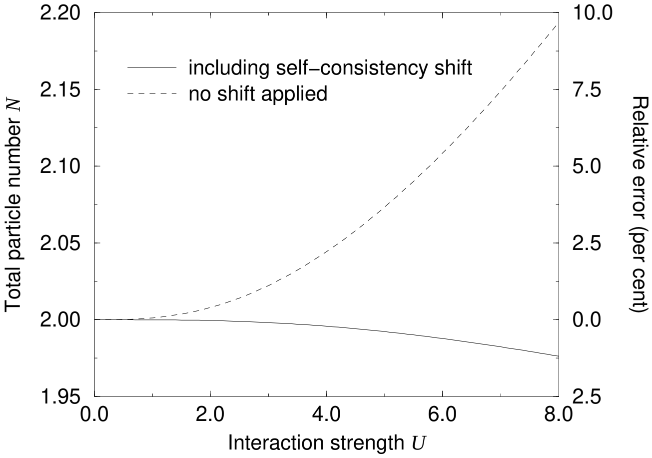

FIG. 1. Analytically calculated particle number in the GW approximation for our two-electron model system as a function of the interaction strength U. Applying a rigid shift to the zeroth order Green's function such as to align its chemical potential self-consistently with that of the GW Green's function significantly reduces the violation of particle number conservation, but fails to remove it completely.

A comparison of the weight factors of G^{GW} with those of the exact Green's function, calculated by numerical diagonalization of the Hamiltonian matrix, shows that in the absence of the self-consistency shift $\tilde{\omega}$ the main error in N stems from a serious overestimation of the satellite spectrum, while the weight of the quasiparticle peak at x_1 deviates relatively little from the correct value up to high correlation strength. When the self-consistency shift is applied the satellites are also overestimated, although by a lesser amount. In this case, however, this is the result of a balanced weight transfer from the quasiparticle peaks that has little influence on the integrated spectral weight and yields a total particle number in much better agreement with the correct value.

SUMMARY

In summary, we have presented a two-electron model system for which the particle number from the Green's function in the *GW* approximation can be derived strictly analytically, without any additional inaccuracies that have previously beset numerical calculations. Through an analysis of this model system we have demonstrated that there is a genuine violation of particle number conservation in the *GW* approximation as it is usually applied, i.e., with the self-energy calculated non-self-consistently from a zeroth order Green's function. However, we also find that the numerical deviation from the exact particle number can be kept low even for an extremely strong correlation by introducing a small degree of self-consistency in the form of a simple rigid shift of the zeroth order Green's function on the energy axis in such a way as to align its chemical potential with that of the *GW* Green's function, which is calculated from it through Dyson's equation. While the effect of this shift on the quasiparticle band structure may be small, our results clearly indicate its significance for the calculation of quantities such as the particle number and charge density that are derived through integration over the complete spectral function.

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