

Total energy from the Galitskii-Migdal formula using realistic spectral functions

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Although many-body perturbation theory (MBPT) for quite some time has been used to determine quasi-particle energies and optical properties of solids, traditionally the issue of ground-state energy has not been addressed with this method. Rather, most efforts in that direction have been concentrating on various mean-field theories. The success of density-functional theory (DFT) has enhanced this evolution. However, there are certain systems for which known approximations for the so-called exchange-correlation potential within DFT cannot correctly reproduce the observed ground states or the calculated ground-state properties deviate significantly from experiment. In situations like these, an alternative is to have a theory that does not depend on such approximations, but rather is derived from first principles within MBPT, albeit with some other form of approximation. We here investigate two such schemes, rather closely related to each other, in order to highlight the essential properties of a MBPT that correctly describes spectral properties *and* ground-state energies. As a first step, we have investigated the case of the electron gas that provides a starting point for more general cases of real materials.

I. INTRODUCTION

The total energy of a many-electron system can be calculated in several ways within the Green-function formalism. One approach follows the well-known formulation due to Galitskii and Migdal (GM).¹ In general, only expectation values of single-particle operators can be obtained from the one-particle Green function. The total energy contains two-particle operators arising from the Coulomb interaction. However, from the equation-of-motion of the field operator, the expectation value of the Coulomb operator in the ground state can be related to the one-particle operator and the total energy can then be expressed in terms of the one-particle Green function. The GM formula is very simple but it has a disadvantage of being nonvariational.

A different approach of calculating total energies uses the less well-known energy functional due to Luttinger and Ward (LW).² The energy is derived from a diagrammatic expansion and expressed as a functional of the Green function. The functional is constructed in such a way that the first derivative with respect to the Green function is zero at the self-consistent Green function of a given approximation. This variational property is very desirable. However, one disadvantage of the LW approach is that the energy functional is not easily calculated for real systems. Also, the functional is not explicit, in the sense that an approximation must always be employed. This is in contrast to the GM formula where only the Green function is required as an input. Given the exact Green function, the total energy can be calculated exactly whereas in the LW approach, an approximation is always used in practice so that even with the exact Green function, the exact energy cannot be calculated easily.

The simplicity of the GM formula is very appealing. Recently, applications of the GM formula to the electron gas

were made within the GW approximation (GWA). For this case, it was shown that self-consistency in the GW calculations was a key ingredient for the success of total-energy calculations.^{3,4} Thus, a fully self-consistent GW calculation perfectly reproduces the exchange-correlation energy of the electron gas. On the other hand, however, the resulting spectral function is rather unphysical.³ Spectral weight is transferred from the main quasiparticle peak to the side of the spectrum, the renormalization factor approaches the value of one, indicating that the system is driven towards a noninteracting one, and the screened interaction becomes unphysical with the disappearance of the plasmon excitations. To maintain the plasmon excitations, a partial self-consistent scheme that keeps the screened interaction fixed within the self-consistency procedure can also be used to obtain good energies, not directly from the GM theorem, but from an integration of interaction strength over a range of densities. The application of this scheme to real systems is yet unclear since the question of how to parameterize the interaction with varying densities has to be resolved first.

Clearly, fully self-consistent GW calculations in real systems are computationally demanding. Here we propose two approaches for calculating the total energy using the GM formula. In the first approach, we consider a model spectral function for the Green function from which the total energy can be easily calculated. We make use of the empirically known property of the local-density approximation (LDA) Ref. 5 wave functions which almost diagonalize the spectral function.⁶ The model has two parameters, the renormalization factor of the quasiparticle and the quasiparticle energy that are obtained from a standard GW calculation.⁶⁻¹⁰ In the second approach we use the cumulant expansion (CE) theory¹¹⁻¹⁵ to calculate the spectral function. The input to the CE calculations is the one-iteration GW self-energy. The CE theory has been shown to give spectral functions for Na and

Al^{15,16} in good agreement with the photoemission spectra. The two approaches are tested by applying them to the electron gas.

II. THEORY

A. The Galitskii-Migdal total energy

The Hamiltonian of an electronic system is given by

$$\begin{aligned} \hat{H} = & \int d^3r \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) \\ & + \frac{1}{2} \int d^3r d^3r' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}'), \end{aligned} \quad (1)$$

where

$$h(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}). \quad (2)$$

V_{ext} is the sum of external potentials such as those from the nuclear charges. The field operator in the Heisenberg representation is given by $\hat{\psi}(\mathbf{r}, t) = \exp(i\hat{H}t) \hat{\psi}(\mathbf{r}) \exp(-i\hat{H}t)$ and from the Heisenberg equation-of-motion $i\partial_t \hat{\psi}(\mathbf{r}, t) = [\hat{\psi}(\mathbf{r}, t), \hat{H}]$ we obtain

$$i\partial_t \hat{\psi}(\mathbf{r}, t) = \left[h(\mathbf{r}) + \int d^3r'' v(\mathbf{r}-\mathbf{r}'') \hat{\psi}^\dagger(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}'', t) \right] \hat{\psi}(\mathbf{r}, t). \quad (3)$$

Multiplying from the left with $\hat{\psi}^\dagger(\mathbf{r}', t')$ and taking expectation value in the ground state we find

$$\begin{aligned} i\partial_t \langle 0 | \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) | 0 \rangle \\ = h(\mathbf{r}) \langle 0 | \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) | 0 \rangle + \int d^3r'' v(\mathbf{r}-\mathbf{r}'') \\ \times \langle 0 | \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}^\dagger(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}, t) | 0 \rangle. \end{aligned} \quad (4)$$

From the definition of the one-particle Green function

$$iG(\mathbf{r}t, \mathbf{r}'t') = \langle 0 | T[\hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t')] | 0 \rangle \quad (5)$$

it follows that the total electronic energy $\langle 0 | \hat{H} | 0 \rangle$ is

$$E = \frac{1}{2} \int d^3r \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \lim_{t' \rightarrow t^+} [\partial_t - ih(\mathbf{r})] \text{tr}_\sigma G(\mathbf{r}t, \mathbf{r}'t') \quad (6)$$

which is the well-known Galitskii-Migdal formula.^{1,17}

B. The Galitskii-Migdal formula in the LDA basis

The spectral representation of the Green function is

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \int_{-\infty}^{\mu} d\omega' \frac{A(\mathbf{r}, \mathbf{r}'; \omega')}{\omega - \omega' - i\delta} + \int_{\mu}^{\infty} d\omega' \frac{A(\mathbf{r}, \mathbf{r}'; \omega')}{\omega - \omega' + i\delta}. \quad (7)$$

Writing the Green function in its Fourier representation and using the spectral representation we obtain

$$E = \frac{1}{2} \int d^3r \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \int_{-\infty}^{\mu} d\omega [\omega + h(\mathbf{r})] \text{tr}_\sigma A(\mathbf{r}, \mathbf{r}'; \omega). \quad (8)$$

For solids, let us expand the spectral function in the LDA basis:

$$A(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\mathbf{k}n n'} \psi_{\mathbf{k}n}(\mathbf{r}) A_{nn'}(\mathbf{k}, \omega) \psi_{\mathbf{k}n'}^*(\mathbf{r}'). \quad (9)$$

The LDA wave functions satisfy the Kohn-Sham equation:⁵

$$(h + U + v_{\text{xc}}) \psi_{\mathbf{k}n} = \varepsilon_{\mathbf{k}n} \psi_{\mathbf{k}n}, \quad (10)$$

where U is the Hartree potential arising from the electrons only since the corresponding contribution from the nuclear charges is included in h . Inserting the spin label explicitly, the ground-state energy may then be rewritten as

$$\begin{aligned} E &= \frac{1}{2} \text{tr}_\sigma \int d^3r \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \int_{-\infty}^{\mu} d\omega [\omega + h(\mathbf{r})] \sum_{\mathbf{k}n n'} \psi_{\mathbf{k}n\sigma}(\mathbf{r}) A_{nn'}^\sigma(\mathbf{k}, \omega) \psi_{\mathbf{k}n'\sigma}^*(\mathbf{r}') \\ &= \frac{1}{2} \text{tr}_\sigma \int d^3r \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \int_{-\infty}^{\mu} d\omega [\omega + h(\mathbf{r}) + U(\mathbf{r}) + v_{\text{xc}}^\sigma(\mathbf{r}) - U(\mathbf{r}) - v_{\text{xc}}^\sigma(\mathbf{r})] \sum_{\mathbf{k}n n'} \psi_{\mathbf{k}n\sigma}(\mathbf{r}) A_{nn'}^\sigma(\mathbf{k}, \omega) \psi_{\mathbf{k}n'\sigma}^*(\mathbf{r}') \\ &= \frac{1}{2} \text{tr}_\sigma \sum_{\mathbf{k}n n'} \int d^3r \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \int_{-\infty}^{\mu} d\omega [\omega + \varepsilon_{\mathbf{k}n\sigma} - U(\mathbf{r}) - v_{\text{xc}}^\sigma(\mathbf{r})] \psi_{\mathbf{k}n\sigma}(\mathbf{r}) A_{nn'}^\sigma(\mathbf{k}, \omega) \psi_{\mathbf{k}n'\sigma}^*(\mathbf{r}') \\ &= \frac{1}{2} \text{tr}_\sigma \sum_{\mathbf{k}n} \int_{-\infty}^{\mu} d\omega [\omega + \varepsilon_{\mathbf{k}n\sigma}] A_{nn}^\sigma(\mathbf{k}, \omega) - \frac{1}{2} \text{tr}_\sigma \sum_{\mathbf{k}n n'} \int_{-\infty}^{\mu} d\omega A_{nn'}^\sigma(\mathbf{k}, \omega) \int d^3r \psi_{\mathbf{k}n\sigma} [U + v_{\text{xc}}^\sigma] \psi_{\mathbf{k}n'\sigma}^*. \end{aligned} \quad (11)$$

This formula is so far exact. It is known from GW calculations in semiconductors that the spectral function is practically diagonal in the LDA basis.⁶ This also appears to be the case even in Ni.¹⁸ Some years ago Hedin¹⁹ qualitatively

explained this useful property of the LDA wave functions by using a random-phaselike argument. We will now make an assumption that the spectral function is diagonal in the LDA basis:

$$\int_{-\infty}^{\mu} d\omega A_{nn'}^{\sigma}(\mathbf{k}, \omega) = n_{\mathbf{k}n\sigma} \delta_{nn'}. \quad (12)$$

With this assumption we then have

$$E = \frac{1}{2} \text{tr}_{\sigma} \left\{ \int_{-\infty}^{\mu} d\omega \omega A^{\sigma}(\omega) + \sum_{\mathbf{k}n} n_{\mathbf{k}n\sigma} \varepsilon_{\mathbf{k}n\sigma} - \int d^3r (U + v_{xc}^{\sigma}) \rho^{\sigma} \right\}, \quad (13)$$

where

$$A^{\sigma}(\omega) = \sum_{\mathbf{k}n} A_{nn}^{\sigma}(\mathbf{k}, \omega) \quad (14)$$

and

$$\rho^{\sigma} = \sum_{\mathbf{k}n} n_{\mathbf{k}n\sigma} |\psi_{\mathbf{k}n\sigma}|^2. \quad (15)$$

Numerical evidence shows that the off-diagonal elements of A are very small.^{6,18} Moreover, they may change sign so that the integral over the frequency results in cancellation and make their contribution to the total energy even smaller. This argument is rather similar to the one used by Hedin¹⁹ to explain the reason for the small value of the off-diagonal elements of A .

The correction to the LDA energy can be calculated straightforwardly. The total electronic energy in the LDA is given by

$$E_{\text{LDA}} = \text{tr}_{\sigma} \left\{ \sum_{\mathbf{k}n} n_{\mathbf{k}n\sigma} \varepsilon_{\mathbf{k}n\sigma} - \frac{1}{2} \int d^3r U \rho^{\sigma} - \int d^3r v_{xc}^{\sigma} \rho^{\sigma} + E_{xc}^{\sigma} \right\}. \quad (16)$$

The correction to the LDA total energy is then

$$\begin{aligned} E - E_{\text{LDA}} &= \frac{1}{2} \text{tr}_{\sigma} \left\{ \int_{-\infty}^{\mu} d\omega \omega A^{\sigma}(\omega) - \sum_{\mathbf{k}n} n_{\mathbf{k}n\sigma} \varepsilon_{\mathbf{k}n\sigma} + \int d^3r v_{xc}^{\sigma} \rho^{\sigma} - 2E_{xc}^{\sigma} \right\} \\ &= \frac{1}{2} \text{tr}_{\sigma} \left\{ \int_{-\infty}^{\mu} d\omega \omega [A^{\sigma}(\omega) - A_0^{\sigma}(\omega)] + \int d^3r v_{xc}^{\sigma} \rho^{\sigma} - 2E_{xc}^{\sigma} \right\}, \quad (17) \end{aligned}$$

where A_0^{σ} is the LDA density-of-states. The only unknown input is the spectral function A^{σ} . Other quantities can be obtained from the standard LDA calculations.

C. A model spectral function

While the exact spectral function is difficult to calculate, the general structure is well known. In s - p systems, the spectrum consists of a quasiparticle peak and a series of plasmon satellites located at multiple of the plasmon energy below the quasiparticle peak. In strongly correlated systems, additional

satellites due to short-range correlation may arise but they generally have a small weight.

A physically motivated model spectral function can be derived from a model Hamiltonian describing an electron interacting with a plasmon, a familiar model in the core-electron problem:

$$\hat{H} = \varepsilon \hat{c}^{\dagger} \hat{c} + \omega_p \hat{b}^{\dagger} \hat{b} + g \hat{c} \hat{c}^{\dagger} (\hat{b}^{\dagger} + \hat{b}), \quad (18)$$

where \hat{c} and \hat{b} correspond to the electron and plasmon, respectively, ω_p is the plasmon energy, and the last term is the coupling term describing the interaction between the electron and the plasmon with a coupling strength g . Although this Hamiltonian is very simple, it captures the basic physics of the interaction between an electron and the rest of a solid. The spectral function corresponding to the above Hamiltonian can be obtained analytically:¹¹

$$A(\omega) = e^{-(g/\omega_p)^2} \sum_{m=0}^{\infty} \frac{(g/\omega_p)^{2m}}{m!} \delta(\omega - \varepsilon - \Delta\varepsilon + m\omega_p). \quad (19)$$

$\Delta\varepsilon = g^2/\omega_p$ is the shift due to the self-energy correction. It is straightforward to show that the spectral function integrates to unity. The factor $\exp[-(g/\omega_p)^2]$ may be identified as the quasiparticle renormalization factor Z . Thus, the spectrum consists of a quasiparticle peak and a series of plasmon satellites located at multiples of plasmon energy below the quasiparticle peak, in agreement with our physical picture. X-ray photoemission spectroscopy (XPS) experiments in Na and Al and other s - p metals also show the same spectral structure.²⁰ First-principles calculations for Na and Al using the CE theory also yield a similar result.^{15,16}

We propose now the following model spectral function for an occupied state $\mathbf{k}n\sigma$:

$$A_{nn}^{\sigma}(\mathbf{k}, \omega) = n_{\mathbf{k}n\sigma} Z_{\mathbf{k}n\sigma} \sum_{m=0}^M \frac{|\ln Z_{\mathbf{k}n\sigma}|^m}{m!} \delta(\omega - E_{\mathbf{k}n\sigma} + m\omega_p) \quad (20)$$

where $Z_{\mathbf{k}n}$ is the quasiparticle renormalization factor and $E_{\mathbf{k}n}$ is the quasiparticle energy, both can be obtained from a standard GW calculation. M is the maximum number of plasmons. In reality, the spectral function has weight above the chemical potential. To take this possibility into account we have introduced the occupation number $n_{\mathbf{k}n\sigma}$. The plasmon energy in atomic units (a.u. = 27.2 eV) is given by

$$\omega_p = \sqrt{4\pi\bar{\rho}}, \quad (21)$$

where $\bar{\rho}$ is the average (valence) electron density consisting of those states that contribute to the plasmon. Since only the center of gravity is important in the GM formula, it is clear that it would make no difference to the total energy if we replace the delta functions with, say, Gaussians. This means that the total energy is not sensitive to the detail structure of the spectral function, but only to its center of gravity. This might explain the very good agreement achieved in self-consistent GW calculations for the electron gas although the spectral functions are of little resemblance to the expected true spectra.³ This can only give a partial explanation though since the total energy depends also on the chemical potential.

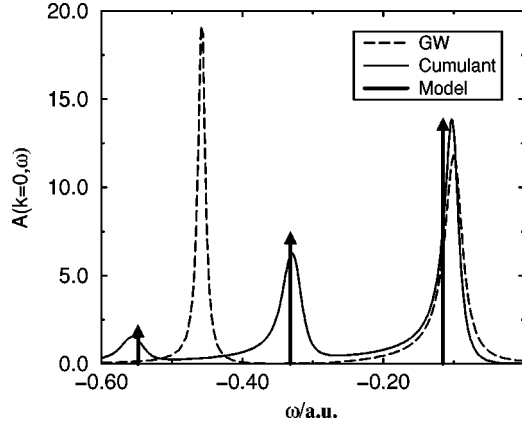


FIG. 1. Spectral functions used in the total-energy calculation. The one of the GW calculation (dashed) has only one plasmon satellite, and the distance between it and the quasiparticle peak is too large. The one of the CE (solid) has multiple plasmon peaks at more appropriate energies. The delta peaks of the model are here indicated by arrows. Note that the arrows only represent relative weight of the peaks within the model. Further, note that the difference of position of the quasiparticle peak of the model and of the other schemes stems from the fact that the change of quasiparticle dispersion has been taken into account for the latter.

An interesting work in this context was recently performed by Schindlmayr *et al.*²¹ where they calculated the spectra and total energies of a Hubbard model using self-consistent GWA. Their conclusion is that the very good results for the total energy in self-consistent GWA may well be spurious. The relevance of this work to real systems, however, remains unclear.

Using the model spectral function in Eq. (13) we find

$$\begin{aligned}
 E &= \frac{1}{2} \text{tr}_\sigma \left\{ \int_{-\infty}^{\mu} d\omega \omega \sum_{\mathbf{kn}\sigma} n_{\mathbf{kn}\sigma} Z_{\mathbf{kn}\sigma} \sum_{m=0}^M \frac{|\ln Z_{\mathbf{kn}\sigma}|^m}{m!} \right. \\
 &\quad \times \delta(\omega - E_{\mathbf{kn}\sigma} + m\omega_p) + \sum_{\mathbf{kn}} n_{\mathbf{kn}\sigma} \varepsilon_{\mathbf{kn}\sigma} \\
 &\quad \left. - \int d^3r (U + v_{xc}^\sigma) \rho^\sigma \right\} \\
 &= \frac{1}{2} \text{tr}_\sigma \left\{ \sum_{\mathbf{kn}} n_{\mathbf{kn}\sigma} Z_{\mathbf{kn}\sigma} \sum_{m=0}^M \frac{|\ln Z_{\mathbf{kn}\sigma}|^m}{m!} (E_{\mathbf{kn}\sigma} - m\omega_p) \right. \\
 &\quad \left. + \sum_{\mathbf{kn}} n_{\mathbf{kn}\sigma} \varepsilon_{\mathbf{kn}\sigma} - \int d^3r (U + v_{xc}^\sigma) \rho^\sigma \right\} \\
 &= \frac{1}{2} \text{tr}_\sigma \left\{ \sum_{\mathbf{kn}} n_{\mathbf{kn}\sigma} \left[-Z_{\mathbf{kn}\sigma} \sum_{m=1}^M \frac{|\ln Z_{\mathbf{kn}\sigma}|^m}{(m-1)!} m\omega_p \right. \right. \\
 &\quad \left. \left. + (E_{\mathbf{kn}\sigma} + \varepsilon_{\mathbf{kn}\sigma}) \right] - \int d^3r (U + v_{xc}^\sigma) \rho^\sigma \right\}. \quad (22)
 \end{aligned}$$

Using Eq. (16) the correction to the LDA total energy is

$$\begin{aligned}
 E - E_{\text{LDA}} &= \frac{1}{2} \text{tr} \left\{ \sum_{\mathbf{kn}} n_{\mathbf{kn}\sigma} \left[-Z_{\mathbf{kn}\sigma} \sum_{m=1}^M \frac{|\ln Z_{\mathbf{kn}\sigma}|^m}{(m-1)!} m\omega_p \right. \right. \\
 &\quad \left. \left. + (E_{\mathbf{kn}\sigma} - \varepsilon_{\mathbf{kn}\sigma}) \right] + \int d^3r v_{xc}^\sigma \rho^\sigma - 2E_{xc}^\sigma \right\}. \quad (23)
 \end{aligned}$$

D. Electron gas test

To test the quality of the model spectral function we use it in the formula in Eq. (13) to calculate the total energy of the electron gas. For the paramagnetic electron gas, the total energy formula in Eq. (13) becomes

$$E = \sum_k \int_{-\infty}^{\mu} d\omega \left[\frac{1}{2} k^2 + \omega \right] A(k, \omega) \quad (24)$$

and the model spectral function is (see Fig. 1)

$$A(k, \omega) = n_k Z_k \sum_{m=0}^M \frac{|\ln Z_k|^m}{m!} \delta(\omega - E_k + m\omega_p). \quad (25)$$

The quasiparticle energy corresponds to its absolute value, not measured with respect to the chemical potential.

To simplify the calculation and to have an analytic expression for the total energy we replace the quasiparticle energy measured with respect to the chemical potential with the free-electron one since they are rather close to each other. The occupation number n_k has been set to unity for occupied states. We also replace the renormalization factor by its average value

$$\bar{Z} = \frac{\sum_k^{k_F} Z_k}{\sum_k^{k_F} 1} = \frac{2}{N} \sum_k^{k_F} Z_k. \quad (26)$$

The last equation is obtained from

$$\sum_k^{k_F} \rightarrow \frac{\Omega}{(2\pi)^3} \int_0^{k_F} d^3k = \frac{N}{2}. \quad (27)$$

This approximation becomes exact if there is only one plasmon. Using the model spectral function, the total energy can be calculated as a function of Z_k and E_k :

$$\begin{aligned}
 E &= \sum_k \int_{-\infty}^{\mu} d\omega \left[\frac{1}{2} k^2 + \omega \right] A(k, \omega) \\
 &= \sum_k^{k_F} \left[\frac{1}{2} k^2 + \int_{-\infty}^{\mu} d\omega \omega A(k, \omega) \right] \\
 &= \sum_k^{k_F} \left[\frac{1}{2} k^2 + \int_{-\infty}^{\mu} d\omega \omega n_k Z_k \right. \\
 &\quad \left. \times \sum_{m=0}^M \frac{|\ln Z_k|^m}{m!} \delta(\omega - E_k + m\omega_p) \right]
 \end{aligned}$$

TABLE I. Correlation energy per electron in a.u. (1 a.u. = 27.2 eV) of the paramagnetic electron gas for different r_s obtained in the present paper. The results under model are obtained from Eq. (31) and those under cumulant are calculated from Eq. (24) using the spectral function given in Eq. (34). QMC is the Ceperley and Alder (Ref. 22) data parametrized by Vosko *et al.* (Ref. 27) which may be regarded as “exact.”

r_s	Model	Cumulant	QMC
1		-0.057	-0.0600
2	-0.045	-0.046	-0.0448
3	-0.036	-0.037	-0.0369
4	-0.032	-0.033	-0.0318
5		-0.030	-0.0281

$$\begin{aligned}
&= \sum_k^{k_F} \left[\frac{1}{2} k^2 + n_k Z_k \sum_{m=0}^M \frac{|\ln Z_k|^m}{m!} (E_k - m \omega_p) \right] \\
&= \sum_k^{k_F} \left[\frac{1}{2} k^2 + n_k E_k - n_k Z_k \sum_{m=1}^M \frac{|\ln Z_k|^m}{(m-1)!} \omega_p \right]. \quad (28)
\end{aligned}$$

Replacing E_k by $(k^2/2 + \mu_{xc})$, Z_k by \bar{Z} , and setting $n_k = 1$, the total energy per electron in a.u. can be readily shown to be

$$E/N = 0.3 \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} - \frac{\bar{Z}}{2} \sum_{m=1}^M \frac{|\ln \bar{Z}|^m}{(m-1)!} \frac{\sqrt{3}}{r_s^{3/2}} + \frac{1}{2} \mu_{xc}. \quad (29)$$

The first term is the kinetic energy of the free electrons, the second term and third term constitute the exchange and correlation energy. μ_{xc} is the exchange-correlation correction to the chemical potential from its noninteracting value:

$$\mu = \varepsilon_F + \mu_{xc}. \quad (30)$$

The correlation energy per electron is therefore

$$\varepsilon_c = -\frac{\bar{Z}}{2} \sum_{m=1}^M \frac{|\ln \bar{Z}|^m}{(m-1)!} \frac{\sqrt{3}}{r_s^{3/2}} + \frac{1}{2} \mu_{xc} + \frac{3}{4\pi} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s}, \quad (31)$$

where the last term is the negative of the well-known exchange energy. For a model with an infinite number of plasmons, the sum over m in the first term can be carried out analytically:

$$\sum_{m=1}^{\infty} \frac{|\ln \bar{Z}|^m}{(m-1)!} = -\frac{\ln \bar{Z}}{\bar{Z}}. \quad (32)$$

We have used the fact that $\exp x = \sum_{m=0}^{\infty} x^m/m!$ and

$$0 \leq \bar{Z} \leq 1. \quad (33)$$

We use this formula to calculate the correlation energy per electron of the paramagnetic electron gas. The average renormalization factor \bar{Z} has been estimated from the data in Ref. 3. The exchange-correlation correction to the chemical potential μ_{xc} , is obtained from the quantum Monte Carlo (QMC) data.²² The result of the test is shown in Table I. For

TABLE II. For comparison, the results for the correlation energy of the electron gas obtained by other authors using different methods are listed. The data are taken from Hindgren’s thesis (Ref. 25), all in a.u. (27.2 eV). RPA corresponds to the Gell-Mann and Brueckner result (Ref. 26) but with the constant term equal to -0.071 a.u. (Ref. 25) instead of the standard value of -0.048 a.u. $\text{GM}(G_0W_0)$ is obtained from the GM formula using the Green function resulting from one-iteration GW calculations (Ref. 28) whereas $\text{GM}(\text{GW})$ is obtained from fully self-consistent GW calculations (Ref. 4). $\text{LW}(G_0)$ is calculated from the LW functional using the noninteracting Green function (Ref. 25). $\text{ABL}(G_0, W^{\text{PP}})$ corresponds to a generalization of the LW functional where both the Green function and the screened interaction W are regarded as variables (Refs. 23 and 25).

r_s	RPA	$\text{GM}(G_0W_0)$	$\text{GM}(\text{GW})$	$\text{LW}(G_0)$	$\text{ABL}(G_0, W^{\text{PP}})$
1	-0.0788	-0.0722		-0.0658	-0.0669
2	-0.0618	-0.0539	-0.045	-0.0455	-0.0468
3	-0.0528	-0.0448	-0.037	-0.0350	-0.0363
4	-0.0468	-0.0382	-0.032	-0.0286	-0.0299
5	-0.0425	-0.0335		-0.0248	-0.0258

comparison, results obtained by other authors using different methods are listed in Table II. As can be seen from Table I, the model spectral function reproduces the QMC result very well. It is quite feasible that the good agreement extends to real systems with a possibility of improving the present accuracy achieved in density-functional theory. For comparison, we have listed in Table II the correlation energy obtained by other authors using different methods. For more details we refer to the given references.

We have calculated the total energies without adjusting the renormalization factor that is obtained from the one-iteration GW calculation. For applications in real systems, we may adjust the form of the spectral weight so that the scheme exactly reproduces the QMC data for the electron gas and the total energies of some atoms and molecules (Table III).

III. TOTAL ENERGY IN THE CUMULANT EXPANSION THEORY

As discussed in the introduction, the GWA yields very good total energies for the electron gas provided the calculations are performed self-consistently. However, self-consistent GW calculations for real systems are computationally very demanding. In fact, the usefulness of the GWA originates from the fact that no attempt of self-consistency is at all invoked in calculations that lead to a remedy of the

TABLE III. Different contributions to the total energy for different methods of obtaining total energies through the GM theorem. The case of $r_s = 4$.

Method	$\frac{1}{2}\mu$	Kinetic	Spectral	Total	Correlation
Cumulant	-0.045	-0.068	0.035 ^a	-0.078	-0.033
G_0W_0	-0.045	-0.081	0.044	-0.0816	-0.036
GW (sc)	-0.034	-0.086	0.042	-0.078	-0.032
QMC					-0.032

^a $\frac{3}{10} \varepsilon_F$.

classical failure of DFT to reproduce, e.g., proper band gaps, conduction bands, and optical properties, where the correct description of excited states is also required. Instead, only one iteration is performed on the cycle of coupled equations, leading to a simplification of the numerical procedure while simultaneously preserving the physical appearance of the properties involved. The spectral function from one-iteration GW calculation, however, has some well-known shortcomings in the description of the plasmon satellite structure. The multiple plasmon satellite structure is not reproduced. Instead, there is only one peak in the hole part (below the chemical potential) and one in the particle part (above the chemical potential) of the spectrum. Further, the difference in energy between this satellite and the main peak does not correspond to the anticipated plasma frequency, but is typically overestimated by a factor 1.5. It can be interpreted as an average of the energies of the multiple plasmon satellites. Albeit this factor is diminished as a consequence of self-consistency, it does not approach 1. This shortcoming partially explains the too low-total energy (Table II) obtained from the GM formula using one-iteration GW spectral functions since the plasmon satellite with too low energy gives more contribution than it should.

A more realistic spectrum is provided by the CE theory using a one-iteration GW self-energy. The spectral function in the CE for a state below the Fermi level is expressed as^{13–15}

$$A(k, \omega) = \frac{n_k}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} e^{-i\varepsilon_k t + C(k, t)}, \quad (34)$$

where n_k is the occupation number of state k , ε_k is the free-electron energy, and $C(k, t)$ is the cumulant. In this approach, the Green function for an occupied state (hole, $t < 0$) is written as

$$G(k, t) = i e^{-i\varepsilon_k t + C(k, t)} \\ = G_0(k, t) [1 + C(k, t) + \frac{1}{2} C^2(k, t) + \dots], \quad (35)$$

where $G_0(k, t) = i e^{-i\varepsilon_k t}$. In terms of the self-energy, the Green function for the hole can be expanded as

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots \quad (36)$$

To first order in the screened interaction W , the cumulant is obtained by equating

$$G_0 C = G_0 \Sigma_{GW} G_0 \quad (37)$$

so that

$$C(k, t) = -i \int_0^t dt' \int_{t'}^{\infty} d\tau \Sigma_{GW}(k, \tau) e^{i\varepsilon_k \tau}, \quad (38)$$

where G_0 refers to the hole Green function. This cumulant is then put back into Eq. (35) which yields an infinite series of diagrams in powers of W . Similar consideration applies also to a state above the Fermi level (particle, $t > 0$). The self-energy appearing in the cumulant $C(k, t)$ is taken to be the GW self-energy.

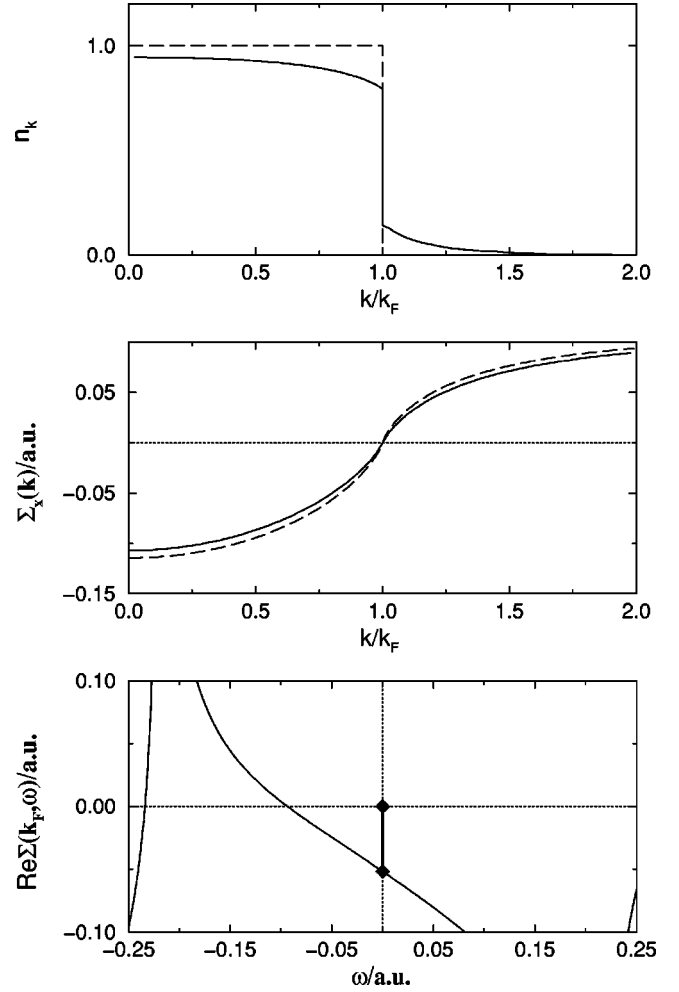


FIG. 2. These plots are aimed to guide the reader through the calculations. In all the examples, $r_s = 4$. Top: The momentum distribution function resulting from a GW calculation (solid) is altered from that of a noninteracting electron gas (dashed), but that of the CE, and of the proposed model, is not. Middle: As a result of different momentum distributions, the exchange energy is altered. The noninteracting exchange (dashed), which is the same as that of the CE, is larger in magnitude, and gives a larger contribution to the chemical potential, than the one resulting from the GW momentum distribution (solid). Bottom: The real part of the self-energy also contributes to the chemical potential through its value at Fermi level and energy.

The resulting spectrum proves to correspond very well to experimental data for the two free-electronlike metals Na and Al.^{15,16} As the CE does not change the quasiparticle properties,²⁴ any modification of a property depending on the spectral function is strictly due to an improvement on the plasmon part of the spectrum.

Thus there are several reasons for using the CE. First, the resulting spectral function will have some similar essential properties in common with that of the model, such as positions and weight of the quasiparticle and plasmon peaks. However, it is physically more appealing since the peaks are broadened and it corresponds better to experimental spectra. The success of the proposed model for the electron gas encourages us to apply the CE. Second, the CE only relies on the one-iteration rather than the self-consistent GW self-

energy as input data. Self-consistent CE has been found to have little effect on the spectra.²⁴ Further advantages are that the spectral function in the CE can be easily calculated once the GW self-energy is available and no modeling of quasi-particle parameters is required. There are, however, some shortcomings. The CE works well for describing long-range correlations manifested in the coupling of electrons to bosonic excitations such as plasmons. In fact, the CE gives the exact solution to the Hamiltonian in Eq. (18). In f systems or in strongly correlated materials, additional satellite features in the range of the valence bandwidth may appear. These satellites are atomic in origin and due mainly to short-range correlations. These are not well accounted for by the CE. However, as mentioned before, the total energy depends on the center of gravity of the spectral function so that the CE could still perform well although the details of the spectral function is not entirely correct.

We have calculated the total energy of the electron gas for several r_s values corresponding to the metallic range using the CE theory and the result is displayed in Table I. As can be seen, the results are comparable in accuracy to the QMC results. To gain insights into the different contributions to the total energy we analyze the results calculated from two spectra obtained from a one-iteration GW calculation and from the CE. The GM total energy expression can be decomposed into three components: One part stemming from the sum of kinetic energies, another part containing spectral energy, arising from the first moment of the spectral function,

$$\int_{-\infty}^{\mu} d\omega \omega A(\omega),$$

and finally a term $\frac{1}{2}\mu$ originating from the upper limit of the integral over energy.

Let us begin with the kinetic-energy term. First it has to be noted that in the CE as well as in the model previously described, for momenta inside the Fermi sphere, the hole part of the spectrum is fully occupied. This is because the CE is only defined for either the hole or particle Green function. This is in contrast to the GW spectrum, which has weight transferred from the hole part to the particle part as illustrated in Fig. 2 (top). The implication of this is that the momentum distribution

$$n_{\mathbf{k}} = \int_{-\infty}^{\mu} A(\mathbf{k}, \omega) d\omega,$$

for the CE is essentially the same as that of the noninteracting electron gas, whereas the GW one is modified, typically reflecting the many-body interaction of the system. A consequence of this is that in the sum over \mathbf{k} , the CE only contributes for occupied \mathbf{k} values, whereas in the GWA, contributions also arise from higher values. Thus, as for the sum over kinetic energies,

$$\sum_{\mathbf{k}} \epsilon_{\mathbf{k}} n_{\mathbf{k}},$$

the CE result is the same as for the noninteracting gas, half of the value of the average kinetic energy or $\frac{3}{10}\epsilon_F$. The GW result is higher because of the modification of momentum distribution. The reason for this is that when evaluating the integral over \mathbf{k} , the k^2 weighting in the integrand results in the unoccupied states giving a larger contribution than the loss due to the reduction of spectral weight in the occupied part.

We now consider the spectral part. Assuming that the CE spectrum below μ has the same weight as that of the GW spectrum, it is clear from Fig. 1 that the GW spectral contribution is more negative than that of the CE since the position of the plasmon satellite is lower than the middle of the two plasmon satellites in the CE. The situation is actually not so simple because as discussed in the previous paragraph, the GW spectrum has some transfer of weight from the hole to the particle part. Numerical calculations, however, show that the GW spectral contribution is still more negative than that of the CE when the reduction of GW spectral weight in the hole (occupied) part is taken into account.

Finally, as for the chemical potential μ , it has three contributions. One is the evident Fermi energy of the noninteracting gas ϵ_F . The second part comes from the exchange contribution, in the case of the electron gas given by the usual expression,

$$\Sigma_x = -\frac{1}{\Omega} \sum_{\mathbf{q}} v_{\mathbf{q}} n_{\mathbf{k}+\mathbf{q}}.$$

Thus, for the CE, the exchange contribution is again the same as for the non-interacting case. For the one-iteration GW scheme there is an ambiguity here. In calculating the exchange energy, should the momentum distribution of the ingoing (i.e., noninteracting) or the outgoing spectrum be used? (cf. Fig. 2, middle) It turns out that the former case underestimates the total-energy, the latter overestimates it. Our investigations show that for the CE total-energy calculation (keeping in mind that the QP parameters are given by the input self-energy, and the position of the QP peak affects the result of the ω integration in the GM theorem), the momentum distribution of the outgoing spectrum is to be preferred for the input GW self-energy when its exchange contribution is evaluated. The third comes from the correlation part of the self-energy, when evaluated at \mathbf{k}_F and ϵ_F (see Fig. 2, bottom). In Table III the different contributions to the total energy are displayed and in Table I we see that we have successfully reproduced the total electron gas energies when using the CE in the prescribed way.

IV. SUMMARY AND CONCLUSIONS

In summary, we have shown that at least for the electron gas, total energies can be obtained in an appealing way by combining the CE with the simple and physically appealing one-iteration GW approximation. We have also proposed a model spectral function from which the total energy can be easily calculated. The parameters in the model are obtained from standard GW calculations. Thus we have at our hands a computational scheme derived from first principles which for the electron gas yields good total energies through the simple

GM formula. This raises hopes to use the GWA for less conventional purposes, e.g., the calculation of ground-state energies of real systems and might give clues for the construction of an improved exchange-correlation energy within DFT. Applications of the scheme to real systems would be desirable.

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