

Variational energy functionals of the Green function and of the density tested on molecules

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We have calculated total energies of atoms and diatomic molecules from the Luttinger-Ward functional, using self-energy approximations to second order as well as the *GW* approximation. In order to assess the variational quality of this functional, we have also solved the Dyson equation self-consistently. The Luttinger-Ward functional is compared to the variational functional due to Klein, and we demonstrate that the variational property of the latter functional is inferior to that of the Luttinger-Ward functional. We also show how to obtain variational density functionals from the functionals of the Green function. These orbital functional schemes are important for systems where density-functional theory using local functionals of the density necessarily fails. We derive an optimized effective potential (OEP) scheme that is based on the Luttinger-Ward functional and, unlike the conventional OEP schemes, produces energies in good agreement with the values obtained from the self-consistent Green function. Our calculations show that, when applied to molecules, the Luttinger-Ward functional is more sensitive to the quality of the input Green function than when applied to atoms, but the energies are remarkably close to the self-consistent values when the Hartree-Fock Green function is used as input. This Luttinger-Ward functional is therefore a simple and efficient method for studying the merits of various self-energy approximations while avoiding the computationally demanding task of solving the Dyson equation self-consistently.

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I. INTRODUCTION

Due to the development in recent years of generalized gradient approximations (GGA's) [1–3], density-functional theory (DFT) has become a remarkably versatile and reliable computational method. There are, however, several well-known cases where density-functional methods based on local functionals of the density will necessarily be inadequate. Examples of this are systematic errors in cohesive energies, the inability to describe negative ions, and no hint as to how to calculate band gaps. A scheme based on local functionals of the density will necessarily also fail at describing van der Waals forces. Within density-functional theory, these problems can be overcome by resorting to orbital functionals [4–7], where the Kohn-Sham potentials are implicit functionals of the density.

A different approach is the use of many-body perturbation theory (MBPT) [8], where the central ingredient is the one-particle Green function, rather than the one-electron density. While MBPT prescribes several methods for calculating the total energy from the Green function, these various expressions are not equivalent unless two conditions are satisfied: (1) The Green function G must be a self-consistent solution of the Dyson equation $G = G_0 + G_0 M G$, where the self-energy $M[G]$ is a functional of the Green function. The Green function G_0 is the solution corresponding to a noninteracting system. (2) The self-energy functional $M[G]$ must correspond to a conserving approximation, as explained by Baym and Kadanoff [9,10]. For any conserving self-energy approximation beyond the Hartree-Fock approximation, calculating the self-consistent Green function is a computationally demand-

ing task even for systems such as the homogenous electron gas [11]. Calculations on real systems have only recently appeared [12–14]. The necessity of solving the Dyson equation self-consistently has been an impediment to total-energy calculations and has made it difficult to assess which physical mechanisms must be taken into account when constructing self-energy approximations.

For calculating total energies, the difficult task of solving the Dyson equation can be avoided by using variational energy functionals. These can be put in two main categories: First, there are the functionals of the one-particle Green function G : e.g., the Luttinger-Ward (LW) functional [15]. The second kind of functionals, which was introduced by Almladh, von Barth, and van Leeuwen [16,17], has two input arguments: namely, G and the dynamically screened Coulomb interaction W . The variational functionals are such that if they are evaluated using crude approximations to their input variables, the result will be very close to the energies obtained using the self-consistent G , or G and W . This simplification of the computational effort enables us to investigate which diagrammatic approximations in MBPT will give accurate total energies, and we consequently have a systematic route toward improving the results. We have recently [18] developed a similar method for systematically improved approximations in density-functional theory.

Because there is a direct connection between DFT and the diagrammatic techniques of MBPT, the variational functionals can serve as excellent starting points for deriving orbital functional schemes in DFT. One example of this is the optimized effective potential (OEP) method [4,5], which in the exchange-only approximation is known to produce energies very close to those of the Hartree-Fock approximation. To

assess whether there is such a good agreement also for more advanced self-energy approximations—e.g., the *GW* approximation (GWA) [19]—one in principle needs self-consistent solutions to both the Dyson equation and OEP equation. Fortunately, the variational property of the functionals of the Green function and of the density allows us to make this assessment without self-consistent calculations. It is here important to stress that, while the self-consistent Green function energies depend only on the chosen diagrammatic approximation, the DFT energies will depend both on the diagrammatic approximation and on the form of the functional itself. We will in this paper illustrate this point in detail. The variational functionals can also be generalized to time-dependent systems, in which case we are dealing with action functionals rather than energies. These action functionals are suitable for deriving response functions in time-dependent DFT [18].

There are, therefore, three main issues that need to be addressed. First, we need to investigate the quality of the variational energy functionals of the Green function in order to verify that they actually produce energies in agreement with the self-consistent values. Since we want to rely on the assumption that the functionals are stable with respect to the input Green function, it is useful to check how sensitive the functionals actually are. This has previously been done for the homogenous electron gas [16,20] and for closed-shell atoms [21,22], where the LW functional was shown to give very similar results when evaluated on different approximate Green functions. While this stability indicates that the results are close to the self-consistent result, this can only be verified by calculating the actual self-consistent energies that the LW functional is intended to reproduce.

The second topic of this paper is the relation between the variational functionals of the Green function and the corresponding orbital functionals in DFT. In other words, we want to know whether an orbital functional based on a certain diagrammatic self-energy approximation will produce total energies similar to those obtained from a self-consistent solution of the Dyson equation. Some of these orbital functional schemes have recently been used successfully for calculating the binding energies of molecules [23–26]. In order to understand these results better and to be able to improve upon the DFT methods, it is necessary to compare these results to the Green-function calculations they correspond to.

Finally, the third topic that should be considered is whether a method that produces inaccurate total energies can still produce accurate energy differences and, for this reason, be suitable for calculating properties like binding energies, vibrational frequencies, bond distances, removal energies, etc. We have earlier shown [21] that self-energy approximations to second order give much better results than the commonly used *GW* approximations when applied to systems of strongly localized electrons. This is in contrast to the results obtained for the homogenous electron gas, where the GWA gives total energies in excellent agreement with results of Monte Carlo calculations [11]. But despite producing rather poor total energies, the GWA did indeed give accurate atomic removal energies. We have, therefore, carried out similar calculations on molecules in order to see whether the GWA gives the correct *shape* of the binding energy curve, albeit

with a relatively large offset from the exact curve.

In the following, we will start by giving a brief presentation of the variational functionals of the Green function, stressing the difference between the LW functional and a similar functional defined by Klein [27]. We argue that the LW functional is less sensitive than the Klein functional to the quality of the input Green function, a point which we have demonstrated also in earlier work [21,22]. We also show how a new OEP scheme can be derived from the LW functional in the same manner as the conventional OEP equations can be derived from the Klein functional [28]. In Sec. III we demonstrate the stability of the LW functional by calculating total energies of some diatomic molecules, using both the GWA and the second-order self-energy approximation. We also present total energies of atoms and molecules obtained from self-consistent solutions of the Dyson equation with the second-order self-energy. Finally, we have calculated the binding energies of diatomic molecules using the LW and Klein functionals, and discussed the dissociation problem in more detail by calculating the energy curve of the H_2 molecule for a range of interatomic distances.

II. VARIATIONAL ENERGY FUNCTIONALS

A. Conserving approximation

For notational simplicity, we use the finite-temperature formalism [8] and let $T \rightarrow 0$ at the end of our calculations. The Green function $G(\mathbf{x}_1, \mathbf{x}_2; i\tau)$ is then defined on the imaginary-time axis for τ in the range $-1/k_B T \leq \tau \leq 1/k_B T \equiv \beta$. Due to the antiperiodicity of the Green function over the interval β , the Fourier-transformed Green function $G(\mathbf{x}_1, \mathbf{x}_2; i\omega_n)$ is defined for the discrete frequencies $\omega_n = (2n+1)\pi/\beta$ and is the solution to the Dyson equation

$$[i\omega - \hat{t} - w - v_H + \mu]G = 1 + \Sigma G, \quad (1)$$

where we consider G and Σ to be frequency-dependent matrices, with the combined space and spin variable $\mathbf{x} = (\mathbf{r}, \sigma)$ as indices. Here, $\hat{t} = -\nabla^2/2$ is the kinetic energy operator, $w(\mathbf{x})$ is the external potential, $v_H(\mathbf{x})$ is the Hartree potential, and μ is the chemical potential. We use atomic units throughout this paper. The exchange and correlation effects are included in the self-energy $\Sigma[G]$, which is a functional of the Green function. The Dyson equation should be solved to self-consistency, which is a very demanding problem for approximations beyond the Hartree-Fock (HF) approximation.

It is important that approximate self-energy functionals lead to results that agree with the conservation laws of the underlying Hamiltonian. Baym and Kadanoff [9,10] showed that such *conserving approximations* are automatically generated when the self-energy is obtained as the functional derivative of a functional $\Phi[G]$,

$$\Sigma[G] = \frac{\delta\Phi[G]}{\delta G}. \quad (2)$$

One particularly interesting feature of the conserving approximations is that the total energy calculated from the resulting self-consistent G will be independent of the method

$$\begin{aligned}
 \Phi^{GW} &= -\frac{1}{2} \text{diagram} - \frac{1}{4} \text{diagram} - \frac{1}{6} \text{diagram} + \dots \\
 \Sigma^{GW} &= \text{diagram} + \text{diagram} + \text{diagram} + \dots \\
 \Phi^{(2)} &= -\frac{1}{2} \text{diagram} - \frac{1}{4} \text{diagram} - \frac{1}{4} \text{diagram} \\
 \Sigma^{(2)} &= \text{diagram} + \text{diagram} + \text{diagram}
 \end{aligned}$$

FIG. 1. The Φ diagrams and self-energies $\Sigma = \delta\Phi / \delta G$ corresponding to the two approximations discussed in this paper.

that is used for the computation [10]. There are many ways of obtaining the total energy from a given Green function, and if the self-energy approximation is not conserving or if G is not a self-consistent solution, the result will depend on the chosen method. These points are illustrated in more detail in Appendix A. There have been several attempts at calculating the total energies of atoms and molecules from non-self-consistent Green functions [29,30], but the energy then necessarily depends on the method used for calculating it. Another important point regarding total-energy ground-state calculations is that the kinetic and potential energies will be in agreement with the virial theorem when calculated within a conserving approximation [14].

We will discuss two different conserving approximations in this paper, as illustrated in Fig. 1: the GW approximation and the second-order approximation. The GWA is a natural choice for calculations on extended systems, since this approximation accounts for the screening of the long-range Coulomb potential. The homogenous electron gas is a system where it is essential to account for this effect, and calculations show that self-consistent GW calculations actually produce total energies in excellent agreement with results of Monte Carlo calculations [11,31]. We can, on the other hand, assume that physical processes other than screening may be more important in systems with strongly localized electrons. The relevance of the different self-energy approximations can only be assessed by means of self-consistent calculations, since the results will otherwise depend on a reference state. We have earlier used the variational functionals to estimate the self-consistent energies of closed-shell atoms, within both the GWA [22] and the second-order approximation [21]. Our calculations verified that, in general, the GWA does not give very accurate total energies for systems with strongly localized electrons. This does not, however, exclude the possibility that the GWA can produce good energy differences, and our calculations of atomic removal energies indicated that these can be accurately produced by the GWA.

The relation between Green-function methods and density-functional theory is obvious when noting that the density is given by the Green function according to $n(\mathbf{x}) = \lim_{\eta \rightarrow 0} \sum_n e^{i\omega_n \eta} G(\mathbf{x}, \mathbf{x}; i\omega_n)$. Replacing the self-energy $\Sigma[G]$ in the Dyson equation (1) with the exchange-correlation potential $v_{xc}[n]$ results in a noninteracting Kohn-Sham Green function when solved to self-consistency. The Kohn-Sham Green function G_{KS} is given in terms of the orbitals and eigenvalues of the corresponding Kohn-Sham equation, and the calculation is equivalent to solving the Kohn-Sham equations self-consistently, since $v_{xc}[n] = v_{xc}[G_{KS}]$. Given the ex-

act $v_{xc}[n]$, the resulting G_{KS} will give the exact electron density, but will otherwise differ from the exact Green function. We will in this paper address the question of how to approximate the functional $v_{xc}[n]$ by using diagrammatic self-energy expressions $\Sigma[G_{KS}]$ of the Kohn-Sham Green function rather than the self-consistent, interacting G .

B. Luttinger-Ward functional

For a given $\Phi[G]$ and corresponding $\Sigma[G]$, the Luttinger-Ward functional [15] gives the grand potential Ω according to

$$\begin{aligned}
 \Omega_{LW}[G] &= \Phi[G] - U_0 - \text{Tr}[\Sigma G] - \text{Tr} \ln[-i\omega + \hat{t} + w + v_H \\
 &\quad + \Sigma - \mu].
 \end{aligned} \tag{3}$$

The Hartree potential v_H and the self-energy Σ are functionals of G , and $U_0 = \frac{1}{2} \int n v_H$ is the classical part of the interaction energy. The trace indicates integration over all space variables as well as summation over all frequencies. The total energy in the zero-temperature limit is a functional of G given by $E = \Omega(T \rightarrow 0) + \mu N$. We will in this paper only be interested in the $T \rightarrow 0$ limit and will occasionally refer to Ω as the “energy” rather than the grand potential. The Luttinger-Ward functional is variational in the sense that

$$\frac{\delta \Omega_{LW}[G]}{\delta G} = 0 \tag{4}$$

when G is a self-consistent solution to the Dyson equation. This leads to the presumption that, if the functional is evaluated using an approximate G , the result will be close to the self-consistent energy. If this is true, then the quality of this result will ultimately depend on the chosen Φ approximation. Both these points have earlier been studied in calculations on the homogenous electron gas within the GWA [16,32] and for atoms within the GWA [22] and the second-order approximation [21]. In all these cases, the LW functional was remarkably insensitive to the quality of the input G . Until now, a comparison between energies obtained from the LW functional and self-consistent results has only been done for the electron gas (where the LW results were indeed in very good agreement with the self-consistent values). In the atomic calculations, we did not have self-consistent results to compare with, but the remarkable stability of the LW functional when evaluated on different noninteracting Green functions indicated that the results were indeed close to the self-consistent values.

We have made a point out of testing the functional using both HF and Kohn-Sham Green functions. This is because, while the Green functions obtained from, e.g., local density approximation (LDA) or GGA calculations can differ significantly, they both correspond to a system of noninteracting electrons in a local potential. The HF Green function is obtained from a nonlocal potential and has a spectrum of unoccupied eigenvalues which differs significantly from that of a DFT calculation.

The variational property of the LW functional can also be exploited for creating orbital functionals in DFT. This is done by restricting the input to only noninteracting Green

functions obtained from a local external potential. Due to the 1-1 correspondence between the external potential of the noninteracting system and its ground-state density, we can consider this (arbitrary) local potential to be a functional of the density. Defining this potential as $v_{\text{KS}}(\mathbf{r})$, the Green function G_{KS} which solves the Dyson equation $(i\omega - \hat{t} - v_{\text{KS}} + \mu)G_{\text{KS}} = 1$ is also a functional of the density. This means that when evaluating the LW functional only on Green functions from a local potential, the 1-1 correspondence between the potential and density means that we have also the energy as a functional of the density [18],

$$E_{\text{LW}}^{\text{KS}}[n] \equiv \Omega_{\text{LW}}[G_{\text{KS}}] + \mu N. \quad (5)$$

We can now obtain an OEP scheme for the potential $v_{\text{KS}}[n]$ by finding the density for which $E_{\text{LW}}^{\text{KS}}[n]$ is stationary. Whereas the LW functional (3) is stationary at the G that solves the Dyson equation, $\Omega_{\text{LW}}^{\text{KS}}[n]$ is stationary at the density corresponding to the Kohn-Sham potential v_{KS} such that $\delta E_{\text{LW}}^{\text{KS}}/\delta n = 0$. Using the 1-1 correspondence between the density and Kohn-Sham potential, it is straightforward to derive the equation [18]

$$0 = \text{Tr} \left[(\bar{G} - G_{\text{KS}}) \frac{\delta M}{\delta v_{\text{KS}}(\mathbf{x}_1)} \right], \quad (6)$$

where $M = v_H + \Sigma$ and the Green function

$$\bar{G} = G_{\text{KS}} + G_{\text{KS}}(\Sigma[G_{\text{KS}}] - v_{\text{xc}}[G_{\text{KS}}])\bar{G} \quad (7)$$

is a non-self-consistent solution to the Dyson equation. Equation (6), which we will refer to as the LW-OEP equation, bears a clear resemblance to the ordinary OEP equation, but is somewhat more complicated. Not only does it involve the function \bar{G} , but also the three-point vertex function $\delta M(\mathbf{x}_1, \mathbf{x}_2; i\omega)/\delta v_{\text{KS}}(\mathbf{x}_3)$. Fortunately, it is not necessary to solve this equation as long as we are only interested in the total energy. The variational properties of the energy functional $E_{\text{LW}}^{\text{KS}}[n]$ mean that the energy obtained at a non-self-consistent density (from, e.g., an LDA calculation) will differ only little from the result obtained using the LW-OEP density.

It is important to note that the stationary value of the functional $E_{\text{LW}}^{\text{KS}}[n]$ (obtained by varying over a restricted set of Green functions) is *not* equal to the stationary value of $E_{\text{LW}}[G]$. The stability of the LW functional with respect to the input Green function does, however, indicate that the Dyson equation and the LW-OEP equation should produce similar results. This assumption is further backed up by our earlier calculations [21,22] and the results presented in the following sections.

C. Klein functional and OEP equation

The Luttinger-Ward functional is only one example of a variational energy functional of G . Another such functional encountered in the literature [10,25,33,34] is that used by Klein [27],

$$\Omega_K[G] = \Phi[G] + U_0 + \text{Tr}(1 - G_0^{-1}G) - \text{Tr} \ln(-G^{-1}), \quad (8)$$

where $G_0^{-1} = i\omega - \hat{t} - w + \mu$. This functional is also variational in the sense that $\delta \Omega_K[G]/\delta G = 0$ when G is the self-consistent solution of the Dyson equation. The functionals Ω_K and Ω_{LW} have the same value (and the same functional derivative) at the self-consistent G , but will otherwise give different results. The distinction between the LW and Klein functionals is unfortunately not always noticed, but it is easy to demonstrate that the variational qualities of the Klein functional are inferior to those of the LW functional [22].

The functional (8) takes a particularly simple form when evaluated at a noninteracting Green function G_s , corresponding to some noninteracting Hamiltonian \hat{H}_s with a (possibly nonlocal) single-particle potential w_s . The corresponding Slater determinant $|\Psi_s\rangle$ and eigenvalues $\{\epsilon_i\}$ are related through $\langle \Psi_s | \hat{H}_s | \Psi_s \rangle = \sum_{i=1}^N \epsilon_i$. We now use the relation $G_0^{-1} = G_s^{-1} + w_s - w$ and the fact [15] that $-\text{Tr} \ln(-G_s^{-1}) = \sum_{i=1}^N \epsilon_i - \mu N$ to write the Klein energy functional $E_K = \Omega_K + \mu N$ in the form

$$\begin{aligned} E_K[G_s] &= \Phi[G_s] + U_0 + \text{Tr}\{(w - w_s)G_s\} + \langle \Psi_s | \hat{H}_s | \Psi_s \rangle \\ &= \langle \Psi_s | \hat{H} | \Psi_s \rangle + \Phi_c[G_s]. \end{aligned} \quad (9)$$

The first term in the last line is the HF energy functional, while the correlation energy is given by the correlation part of Φ , defined as $\Phi_c = \Phi - \Phi_x$. The GW approximation to Φ means that $\Phi_c[G_s]$ is the ordinary random phase approximation (RPA) correlation energy,

$$\Phi_c^{GW} = \frac{1}{2} \text{Tr}[v P_0 + \ln(1 - v P_0)], \quad (10)$$

where $P_0 = GG$. The second-order Φ is given by

$$\Phi_c^{(2)} = \frac{1}{4} \text{Tr}[G \Sigma_c^{(2)}], \quad (11)$$

where $\Sigma_c^{(2)}$ refers to the correlation part of the self-energy, $\Sigma = \Sigma_x + \Sigma_c$. The term $\Phi_c^{(2)}$ equals the correlation energy obtained from perturbation theory to second order in $\hat{V} = \hat{H} - \hat{H}_s$ [35,36]. When the zeroth-order Hamiltonian \hat{H}_s is taken to be the HF Hamiltonian, this is referred to as Møller-Plesset (MP) perturbation theory and the second-order approximation is denoted MP2.

In the same way we constructed a density functional from $E_{\text{LW}}[G]$, we can define a density functional from the Klein functional by restricting the input to be only Kohn-Sham (KS) Green functions—i.e., Green functions that result from a local potential v_{KS} . Equation (9) then becomes

$$E_K^{\text{KS}}[n] \equiv T_0[n] + \int n w + U_0 + \Phi[G_{\text{KS}}]. \quad (12)$$

Here, $T_0[n]$ is the noninteracting kinetic energy and the exchange and correlation energy is given by $\Phi[G_{\text{KS}}]$. As shown by Casida [28], this density functional is stationary, $\delta E_K^{\text{KS}}[n]/\delta v_{\text{KS}}(\mathbf{x}_1) = 0$, at the $v_{\text{xc}} = v_{\text{KS}} - w - v_H$ which solves the OEP equation

$$\begin{aligned} & \int \frac{d\omega}{2\pi} \int dx_1 dx_2 G_{\text{KS}}(\mathbf{x}, \mathbf{x}_1; i\omega) \Sigma(\mathbf{x}_1, \mathbf{x}_2; i\omega) G_{\text{KS}}(\mathbf{x}_2, \mathbf{x}; i\omega) \\ &= \int \frac{d\omega}{2\pi} \int dx_1 G_{\text{KS}}(\mathbf{x}, \mathbf{x}_1; i\omega) G_{\text{KS}}(\mathbf{x}_1, \mathbf{x}; i\omega) v_{xc}(\mathbf{x}_1). \end{aligned} \quad (13)$$

This equation has been solved for the second-order approximation $\Phi^{(2)}$ by Facco Bonetti *et al.* [37] and by Grabowski *et al.* [38]. The calculations in Refs. [23–25] amount to evaluating the functional $E_K^{\text{KS}}[n]$ for Φ^{GW} . We will in the following refer to these calculations as DFT-RPA calculations. While the OEP equation gives the density for which the energy is stationary, it is not obvious that the energy is also a minimum at this solution. We show in Appendix C that, under certain conditions, the solution to the OEP equation does indeed correspond to a minimum. It has been demonstrated that the functional $E_K^{\text{KS}}[n]$ is not very sensitive to the input density, but this does not mean that the Klein functional $E_K[G]$ is insensitive to the quality of the input G . There is, in fact, no reason to believe that the energy at the stationary point of $E_K^{\text{KS}}[n]$ should be close to the energy of $E_K[G]$ at the self-consistent G . While the stationary values of $E_{\text{LW}}[G]$ and $E_K[G]$ are the same, the stationary values of the two density functionals $E_K^{\text{KS}}[n]$ and $E_{\text{LW}}^{\text{KS}}[n]$ will differ considerably [22], but the results of the latter functional will in general be closer to the self-consistent energies.

III. CALCULATIONS

We have performed a number of calculations in order to test the different energy functionals mentioned in the previous section. We have addressed four main questions: (1) How reliable is the variational property of the LW functional? In other words, are the energies obtained from this functional when evaluated at a noninteracting Green function really close to the self-consistent energies and is the LW functional stable with respect to the quality of the input Green function? (2) Are the energies obtained from the two density functionals mentioned in the previous section in agreement with the self-consistent energies? (3) For which approximations to Φ does the self-consistent G give accurate total energies. And (4) Can a method which produces rather poor total energies give accurate energy differences?

All the calculations were carried out using Slater basis functions [39]. The evaluation of the Klein functional is relatively straightforward, using Eqs. (10) and (11), but the frequency integral in the logarithmic term of the LW functional requires some extra manipulation since the integrand goes to a constant value as $\omega \rightarrow \infty$. There are several possible ways of calculating this term. Details of the evaluation are given in Appendix B.

A. Self-consistent solutions

In our earlier calculations on atoms [21,22], we showed that the LW functional is highly insensitive to the input Green function when applied to atoms. While this indicates that the results are close to the self-consistent results, this could not be proved since no such energies were available.

To verify this claim, we have solved the Dyson equation self-consistently for some atoms and diatomic molecules. Our earlier work has indicated that the second-order approximation to Σ , as illustrated in Fig. 1(b), is more relevant than the GW approximation when considering systems of localized electrons, and hence we have chosen to solve the Dyson equation within this approximation. In these calculations, we have used the imaginary-time Green function $G(\mathbf{x}, \mathbf{x}'; i\tau)$ to avoid the slowly converging frequency summations that appear when using the Fourier-transformed quantities. A further advantage is that the imaginary-time calculations can easily be extended to calculations on nonequilibrium systems, where the Green function is calculated on a time contour [40]. The Green function is represented in basis sets of Slater functions and hence becomes a time-dependent matrix $G_{ij}(i\tau)$. Since the Green function is quite sharply peaked around $\tau=0$ and $\tau=\pm\beta$, it is inconvenient to use an even-spaced time grid. Instead, the time coordinates are located on a power mesh, as described by Ku and Eguluz in Ref. [12]. More details of the computation can be found in Ref. [14].

From the self-consistent Green function, it is straightforward to obtain the total energy, as explained in Appendix A. The second-order self-energy approximation has been used in earlier Green-function calculations on atoms and molecules, although the Dyson equation has never been solved self-consistently. In Refs. [29,30], the Green function was calculated from the first iteration of the Dyson equation,

$$G^{(2)} = G_{\text{HF}} + G_{\text{HF}} \Sigma_c^{(2)} [G_{\text{HF}}] G^{(2)}. \quad (14)$$

In this case, the value of the total energy depends on the method used for calculating it. This is well illustrated by the calculations in Ref. [30], where it was shown that when calculating the total energy from $G^{(2)}$, using the Galitskii-Migdal formula, the total energy of an H_2 molecule does not diverge when the interatomic separation increases. This is in contrast to the MP2 result and also to higher-order levels of MP perturbation theory which diverge even more strongly. But it is important to point out that since the Green function in Eq. (14) is not self-consistent, calculating the energy from any of the variational functionals discussed in this paper, Eqs. (3) and (8), would give results very different from the Galitskii-Migdal formula. The larger the interatomic separation R , the bigger the deviations would be. A related problem is that, for $R \rightarrow \infty$, one obtains a significant error in the particle number calculated from $G^{(2)}$ due to the lack of self-consistency [30].

In the present work, we have solved the Dyson equation self-consistently; i.e., the self-energy is evaluated using the self-consistent G rather than G_{HF} , such that

$$G = G_{\text{HF}} + G_{\text{HF}} (M[G] - v_H[G_{\text{HF}}] - \Sigma_x[G_{\text{HF}}]) G, \quad (15)$$

where $M = v_H + \Sigma_x + \Sigma_c$. The Green function is in this way calculated to infinite order for a given second-order self-energy functional, in the same way that the Hartree-Fock approximation is the self-consistent solution corresponding to the first-order self-energy. We stress that while the HF Green function appears in Eq. (15), the self-consistent Green function is independent of this. We could equally well use a

TABLE I. Total energies calculated from the self-consistent Green function and from the Luttinger-Ward functional evaluated at the HF and LDA Green functions. All energies are in hartrees.

	$E_{\text{LW}}^{(2)}[G_{\text{LDA}}]$	$E_{\text{LW}}^{(2)}[G_{\text{HF}}]$	SC
He	-2.8937	-2.8969	-2.8969
Be	-14.5953	-14.6405	-14.6409
Ne	-128.8068	-128.8332	-128.8339
Mg	-199.8933	-199.9093	-199.9097
Mg ²⁺	-199.0918	-199.1025	-199.1027
H ₂	-1.1595	-1.1658	-1.1659
LiH	-8.0394	-8.0526	-8.0528

KS system as a starting point, as long as the resulting G satisfies the Dyson equation

$$[-\partial_\tau - \hat{t} - w - v_H + \mu]G = 1 + \Sigma G. \quad (16)$$

In Table I, we have listed the self-consistent energies of a number of atoms and diatomic molecules. We have also included LW results obtained from the second-order Φ , using the same basis sets as the self-consistent calculations. The self-consistent energies agree remarkably well with the energies obtained from the LW functional, in particular those obtained when HF Green functions are used as input. The LW values for the atoms differ slightly from those published in Ref. [21] due to the use of smaller basis sets in the present work. The spectacular agreement between $E_{\text{LW}}^{(2)}[G_{\text{HF}}]$ and the self-consistent results is, however, independent of the size of the basis sets. An important feature of these results is that the MP2 energies of the systems included in Table I differ very little from the $E_{\text{LW}}^{(2)}[G_{\text{HF}}]$ results, as discussed also in Ref. [21]. This is highly interesting as it explains why second-order perturbation theory gives such accurate results to low order, in spite of the fact that the perturbation series is divergent [41]. In Appendix A, we indicated why the values of $E_K[G_{\text{HF}}]$ and $E_{\text{LW}}[G_{\text{HF}}]$ are usually very similar, also for the GW approximation. This agreement turns out to be true not only for atoms and diatomic molecules, but also for the homogenous electron gas [42].

B. Variational functionals applied to diatomic molecules

We have calculated the total energies of several diatomic molecules in order to check the stability of the LW functional and the adequacy of the GWA and second-order approxima-

tion for calculations on atoms and small molecules. All calculations were carried out at the experimentally determined bond lengths. Total energies of H₂, Li₂, LiH, and N₂ are shown in Table II. In addition to the results of the LW functional using Φ^{GW} and $\Phi^{(2)}$, we have also included the energies obtained from the Klein functional within the same two approximations. Since the latter functional gives results almost identical to the LW functional when evaluated on the HF Green function, we have only included the results of the Klein functional with G_{LDA} as input. The results with G_{GGA} as input are practically the same. For the LW functional, we used DFT Green functions from the LDA and GGA [1], as well as the HF Green function.

The LW functional is seen to be more sensitive to the input than when applied to closed-shell atoms, a fact which could cast some doubt on the claim that the LW energies are similar to the self-consistent values. The reduced stability of the functional may partly be caused by using smaller basis sets, as discussed in Appendix B. We have, however, verified that the LW functional when evaluated on the HF Green function does indeed give an excellent estimate for the self-consistent energies, as shown in Table I. When the input is restricted to DFT Green functions, the energy is somewhat farther away from the self-consistent values. The functional is much less sensitive to the choice of Kohn-Sham potential. This reflects the stability of the density functional $E_{\text{LW}}^{\text{KS}}[n]$, defined by restricting the variational freedom of the input G in the LW functional. The results in Table II then indicate that for these diatomic molecules, the stationary point of $E_{\text{LW}}^{\text{KS}}[n]$ is somewhat above the stationary point of $E_{\text{LW}}[G]$ (i.e., the self-consistent energy).

Nevertheless, the LW functional is seen to be much less sensitive than the Klein functional to the quality of the input Green function. While the Klein functional yields results in good agreement with the self-consistent values when a HF Green function is used as input, inserting a DFT Green function results in much too low energies. This reflects the fact that the stationary point of the density functional $E_K^{\text{KS}}[n]$ is significantly below the stationary point of $E_K[G]$, as a consequence of the poorer variational quality of the Klein functional. It should be pointed out that it depends on the choice of self-energy approximation whether the Klein functional overestimates or underestimates the self-consistent energy. For Φ^{GW} and $\Phi^{(2)}$, the functional $E_K^{\text{KS}}[n]$ produces results much lower than the self-consistent values, as shown in Table II, while the functional necessarily overestimates the

TABLE II. Total energies (in Hartrees) of some diatomic molecules, calculated from the LW functional using the GW and the second-order approximations (denoted by E_{LW}^{GW} and $E_{\text{LW}}^{(2)}$, respectively) with the LDA, GGA, and HF Green functions as input. The total energies obtained from the Klein functional within the same two approximations, with G_{LDA} as input, are included in the columns labelled $E_K^{GW}[G_{\text{LDA}}]$ and $E_K^{(2)}[G_{\text{LDA}}]$.

Molecule	$E_K^{GW}[G_{\text{LDA}}]$	$E_{\text{LW}}^{GW}[G_{\text{LDA}}]$	$E_{\text{LW}}^{GW}[G_{\text{GGA}}]$	$E_{\text{LW}}^{GW}[G_{\text{HF}}]$	$E_K^{(2)}[G_{\text{LDA}}]$	$E_{\text{LW}}^{(2)}[G_{\text{LDA}}]$	$E_{\text{LW}}^{(2)}[G_{\text{GGA}}]$	$E_{\text{LW}}^{(2)}[G_{\text{HF}}]$
H ₂	-1.2095	-1.1755	-1.1777	-1.1887	-1.1815	-1.1594	-1.1593	-1.1658
LiH	-8.1338	-8.0750	-8.0835	-8.1015	-8.0772	-8.0386	-8.0396	-8.0526
Li ₂	-15.084	-14.995	-15.002	-15.035	-15.008	-14.925	-14.927	-14.964
N ₂ ^a	-109.720	-109.514	-109.526	-109.575	-109.734	-109.320	-109.317	-109.472

^aUsing the basis set CVB2 from Ref. [43].

TABLE III. Binding energies (in Hartrees) of some diatomic molecules, calculated from the LW and Klein functionals and using the HF, LDA, and GGA Green functions as input.

Molecule	$E_K^{GW}[G_{LDA}]$	$E_{LW}^{GW}[G_{LDA}]$	$E_{LW}^{GW}[G_{GGA}]$	$E_{LW}^{GW}[G_{HF}]$	$E_K^{(2)}[G_{LDA}]$	$E_{LW}^{(2)}[G_{LDA}]$	$E_{LW}^{(2)}[G_{GGA}]$	$E_{LW}^{(2)}[G_{HF}]$	Expt. ^a
H ₂	0.173 ^b	0.158	0.165	0.162	0.184 ^c	0.160	0.160	0.166	0.175
Li ₂	0.027	0.029	0.029	0.020	0.061 ^c	-0.009	-0.007	0.026	0.039
LiH	0.087	0.083	0.091	0.081	0.105 ^c	0.072	0.073	0.084	0.092
N ₂ ^d	0.350 ^e	0.313	0.386	0.311	0.542 ^c	0.253	0.248	0.369	0.364

^aFrom Ref. [45].

^bTo be compared with the value 0.174 from Refs. [46,23].

^cTo be compared with the values 0.182, 0.062, 0.11 and 0.545 from Ref. [26], obtained from GGA orbitals.

^dUsing the basis set CVB2 from Ref. [43].

^eTo be compared with the value 0.355 calculated from the RPA valence electron correlation energy in Ref. [23].

Hartree-Fock energy (corresponding to $\Phi_c=0$.)

While these calculations have been carried out on small systems, several features of these results seem to be quite general. The remarkable similarity between the $E_{LW}[G_{HF}]$, $E_K[G_{HF}]$ and the self-consistent results is highly interesting, as we have found these results to agree for all systems we have studied so far and for both the second-order approximation (shown in Table I) and the GWA [44]. The only other system where the variational functionals have been tested is the homogenous electron gas, where the LW functional has been shown to produce results in excellent agreement with self-consistent GW calculations [11,16,20]. The energy given by $E_K^{GW}[G_{HF}]$, equal to the HF-RPA energy, is also close to the self-consistent GW values [42]. This implies that the relation $E_K[G_{HF}] \approx E_{LW}[G_{HF}] \approx E[G_{SC}]$ is true also for the homogenous electron gas. This should be put in contrast to the functional $E_K^{KS}[n]$ which gives the well-known RPA energies, also here significantly lower than the self-consistent values.

C. Binding energies

The total-energy calculations suggest that the second-order approximation is more relevant than the GWA approximation for calculations on small systems, but we are primarily interested in an accurate description of total-energy differences, such as molecular binding energies. We have calculated binding energies from both $\Phi^{(2)}$ and Φ^{GW} , as shown in Table III. What is particularly noticeable in these results is the high quality of the DFT-RPA binding energies, denoted by $E_K^{GW}[G_{LDA}]$ (almost identical results are obtained using G_{GGA}). The agreement with the experimental numbers, which has earlier been demonstrated by Furche [23] and Fuchs and Gonze [24], is spectacular since DFT-RPA is the method that gives the worst total energies of all the methods considered here. While these energies correspond to the E_K^{GW} functional, this does not mean that we can attribute the high quality of the binding energies to the GWA in itself, since the stationary point of the density functional $E_K^{KS}[n]$ is not close to the self-consistent energy.

For an accurate estimate of the self-consistent GW energy, we should rather look to the $E_{LW}^{GW}[G_{HF}]$ results, which are much better estimates for these. The LW results indicate that while self-consistent GW will produce better total energies

than DFT-RPA, the binding energies will be slightly worse. The second-order approximation, on the other hand, seems to give binding energies of the same quality as DFT-RPA, although the DFT-RPA result for the H₂ molecule is considerably better. As can be seen from Table III, the binding energies obtained from the LW functional are unfortunately rather sensitive to the input Green function. This reflects the fact that we have a variational expression for total energies but not for total-energy differences. For the second-order approximation the results calculated from the DFT Green functions are much closer to each other than to the $E_{LW}[G_{HF}]$ results, but this pattern is not seen for the GW approximation. The situation is not too bad, however, since the $E_{LW}^{(2)}[G_{HF}]$ total energies, and consequently also the binding energies, are almost identical to the self-consistent values in all cases we have considered so far.

The binding energies in Table III were calculated by subtracting the total energies of the isolated fragments from the total energy of the molecule. The result does not necessarily say how well the bonding curves of the molecules are described, and it has indeed been shown that while DFT-RPA can give highly accurate binding energies, the shape of the binding curve is, however, not accurately given by DFT-RPA [46,47]. The main problem associated with calculating binding energies from DFT-RPA is that the method is not size consistent. In other words, when pulling the molecular fragments apart, the total energy will not equal the total energies calculated from the separate fragments. Furthermore, DFT-RPA produces highly accurate binding energies only when the energy of the molecular fragments is calculated separately, but not when it is obtained from the $R \rightarrow \infty$ limit of the binding curve.

This point is illustrated in Fig. 2, where we have plotted the RPA total energy for the H₂ molecule at a range of internuclear separations R . We have used DFT orbitals from both LDA and exchange-only OEP (which for two-electron systems amounts to $v_{KS}=w+\frac{1}{2}v_H$) calculations, in order to illustrate the stability of the DFT-RPA functional, Eq. (12). For comparison, we have also included RPA calculations using HF orbitals and from spin-unrestricted LSDA calculations. The numerical values are given in Table II. Our results agree with those of Fuchs *et al.* [46], except at large separations where the DFT-RPA energies are more sensitive to the input DFT orbitals. The calculations in Ref. [46] used densities

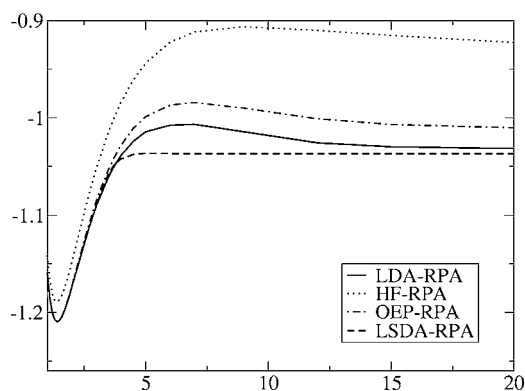


FIG. 2. The total energy of H_2 as a function of the internuclear separation. The figure shows that the RPA energy $E_K^{GW}[n]$ does not converge to the atomic value when the input orbitals come from spin-restricted calculations. The local spin density approximation (LSDA) RPA curve is the RPA energy obtained from spin-unrestricted LSDA calculations, which quickly converge to the atomic value.

from spin-unrestricted exact exchange calculations (which are exact in the $R \rightarrow \infty$ limit), while we have used densities from the spin-restricted LDA. Using the exact density does not, however, mean that the dissociation is correctly described by DFT-RPA. While it has been shown [48] that the RPA total energy of two electrically neutral subsystems, separated by a distance R , goes as $\Delta E = -C/R^6$, this assumes that the noninteracting response function can be written as $\chi^0 = \chi_A^0 + \chi_B^0$ for large R . Here, A and B label the two fragments with densities that do not overlap in the $R \rightarrow \infty$ limit. The noninteracting response function takes this form if the fragments are closed-shell systems. For the H_2 molecule, the noninteracting response function corresponding to spin-restricted HF or DFT calculations cannot be divided, since this would require breaking the spin symmetry. The RPA total energy will therefore approach a constant value slower than $-C/R^6$. We have discussed this point in Appendix D by calculating the RPA energy of a H_2 molecule in a minimum basis.

It has recently been claimed [49] that the DFT-RPA method is size consistent when the input orbitals correspond to the density of spin-unrestricted exact exchange (note that the input orbitals still correspond to a spin-restricted calculation), which is exact when $R \rightarrow \infty$. In Ref. [46], this method has been used to calculate the RPA energy for R as large as 7 a.u., but the energy curve is yet to converge at this point. We have calculated the RPA energy using orbitals corresponding to the bare H nuclei—i.e., $v_{KS}(\mathbf{r}) = -1/r - 1/|\mathbf{r} - \mathbf{R}|$ —for internuclear distances up to $R = 25$ where this should be a very reasonable approximation to the exact v_{KS} . But even at these large separations, the RPA energy is still above the atomic values and has not converged. If the RPA reaches the atomic values from below as $-C/R^6$, as claimed in Ref. [49], then this could only happen for extremely large separations. Since the exact energy curve converges long before $R = 10$, as seen from Fig. 2, the DFT-RPA energy can therefore hardly be said to converge correctly.

Figure 2 shows quite clearly how the RPA energy converges slowly from above, although the asymptotic values are difficult to estimate since the energies have not converged even at $R = 20$ a.u. The situation is quite different if we break the spin symmetry and use orbitals from spin-unrestricted HF and LSDA calculations. As $R \rightarrow \infty$, the two occupied orbitals will then be localized on separate sites, with opposite spins. In this case, the noninteracting response function can be written as a sum of two atomic response functions and the energy converges correctly as $\sim -C/R^6$. In Fig. 2, we have plotted the DFT-RPA energies obtained from LSDA orbitals [50]. We are now faced with a rather awkward situation if we want to calculate binding energies from the RPA. To be consistent, the H_2 molecule should always be described as a $^1\Sigma_g$ state, and one should consequently calculate the binding energy from the asymptotic value of the spin-restricted RPA energy. This is, however, rather difficult since we would have to go to very large separations before the energy converges. Calculating the binding energy as the difference between the RPA energy at equilibrium separation and the energy of the fragments amounts to a spin-unrestricted calculation and can therefore be considered unphysical. The latter approach does nevertheless give binding energies in very good agreement with experiment. Also the shape of the total energy curve, shown in Fig. 5, below, agrees well with that of CI calculations, except around $R \approx 4$.

As is evident from Fig. 2, the RPA energy calculated from HF orbitals differs considerably from the DFT-RPA results. This reflects the fact that the RPA energy is equivalent to the Klein functional $E_K[G]$ with $\Phi = \Phi^{GW}$ and that this functional is rather sensitive to the input Green function. The DFT-RPA energy (equivalent to the density functional $E_K^{KS}[n]$) is stable with respect to the input density, and the energy is therefore relatively independent of the chosen Kohn-Sham potential, as demonstrated in Fig. 2. Due to the large difference between the HF-RPA and DFT-RPA results, the DFT energy can, however, not be expected to be close to the self-consistent Green function value.

The LW functional, on the other hand, is much more stable with respect to the input Green function, and the DFT energy should in this case be closer to the self-consistent result. The LW-GW energy of an H_2 molecule is shown in Fig. 3. Similar to the RPA calculations in Fig. 2, we have used both DFT and HF Green functions as input. The LW functional is clearly much less sensitive to the input G than the Klein functional (as plotted in Fig. 2), though not as stable as when applied to closed shell atoms [21,22]. The LW functional becomes considerably less stable for large values of R , which indicates that the HF Green function and, in particular, the KS Green functions then become too crude approximations. There is still only a very small difference between the $E_{LW}[G_{LDA}]$ and $E_{LW}[G_{OEP}]$ results (except for at large R), which reflects the fact that the density functional $E_{LW}^{KS}[n]$ is not sensitive to the input density. Increasing the variational freedom by allowing the input Green functions to correspond also to nonlocal potentials (i.e., G_{HF}) lowers the total energy to a value which is closer to the self-consistent result. While the HF-RPA curve is not included in Fig. 3, the

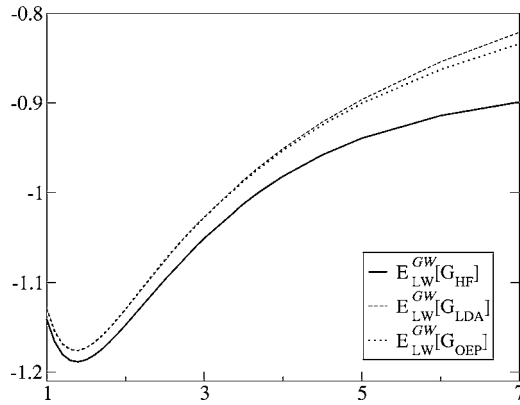


FIG. 3. The figure shows the LW-GW energy of the H_2 molecule as a function of interatomic separation R , using LDA, exchange-only OEP, and HF Green functions as input.

difference between this energy and the $E_{LW}^{GW}[G_{HF}]$ result is minimal ($\sim 0.1-0.2$ mhartree) except for at large values of R . The difference between $E_{LW}^{GW}[G_{LDA}]$ and the LDA-RPA results is much bigger, being ~ 5 mhartree.

In Fig. 4, we have plotted the LW energies for the second-order approximation to Φ , using G_{HF} and G_{LDA} as input. Using a different KS Green function would produce a curve similar to that of $E_{LW}^{(2)}[G_{LDA}]$. In the figure, we have also included the energies obtained from the self-consistent Green function and conventional MP2 energies (equivalent to $E_K^{(2)}[G_{HF}]$). The two latter curves differ very little from the $E_{LW}[G_{HF}]$ results for interatomic separations up to $R \leq 6.0$. The three curves will, however, differ considerably at larger separations when the narrowing of the HF highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gap causes terms like $\Phi_c^{(2)}$ to diverge. The terms in the LW functional that should compensate for the divergence in $\Phi_c^{(2)}$ will necessarily also diverge, but since this cancellation is only approximate. As a consequence, both the $E_{LW}[G_{HF}]$ and $E_K[G_{HF}]$ will diverge. The divergence of the LW functional is even more severe when G_{LDA} is given as input, which is obvious from Fig. 4. While we have not been able to carry

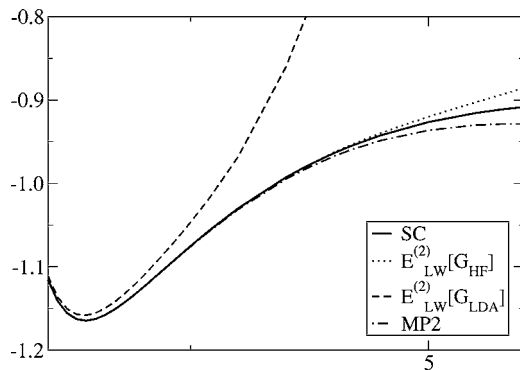


FIG. 4. The LW energy of the H_2 molecule as a function of interatomic separation R , using the second-order approximation $\Phi^{(2)}$ and LDA and HF Green functions as input. We have also included the self-consistent Green function energies and the MP2 energies, equivalent to $E_K^{(2)}[G_{HF}]$.

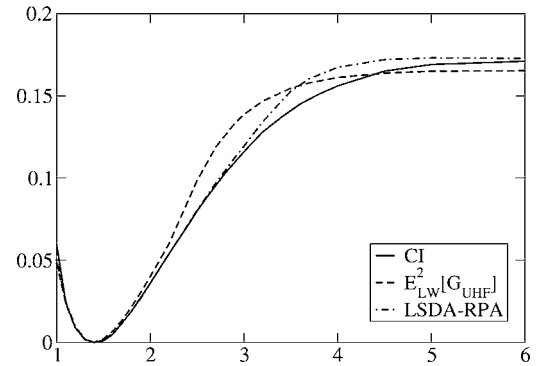


FIG. 5. The energy difference $\Delta E(R) = E(R) - E(R_0)$ of the H_2 molecule, calculated using LSDA-RPA and $E_{LW}^{(2)}[G_{UHF}]$ and compared to CI results.

out self-consistent calculations for large values of R , it has been shown in Ref. [30] that the Green function (14) calculated from the first iteration of the Dyson equation gives a total energy that converges to a constant value for $R \rightarrow \infty$, and we expect this to be the case also for the fully self-consistent energies. The failure of the LW and Klein functionals for large separations then shows that the G_{HF} is a much too crude approximation for large values of R .

In conclusion, since both G_{HF} and G_{LDA} are too far from the self-consistent Green function as $R \rightarrow \infty$, it is better to use Green functions from spin-unrestricted calculations as input in order to produce meaningful binding energy curves. In Fig. 5, we have plotted the binding energy curves of $E_{LW}^{(2)}[G_{UHF}]$, where G_{UHF} is the spin-unrestricted HF Green function, and LSDA-RPA together with results of CI calculations. To compare the shape of the curves, we have subtracted the energies at equilibrium separation. Both curves deviate somewhat from the CI results at intermediate values of R , but the shape of the LSDA-RPA curve shows a striking agreement with the CI results around the equilibrium separation.

IV. CONCLUSIONS

We have in this paper been able to verify that the LW functional evaluated at a noninteracting Green function can produce total energies close to the self-consistent Green-function values. The LW functional is more sensitive to the input Green function when applied to molecules than when applied to atoms, but the functional is still much more stable than the Klein functional. Despite this increased sensitivity, we have been able to show that with a HF Green function the LW functional gives results in excellent agreement with the self-consistent results. The larger deviation between the LW energies and the self-consistent results appears when we restrict the input to DFT Green functions, which apparently are too crude approximations to the self-consistent molecular Green functions. While we have only compared to self-consistent solutions within the second-order self-energy approximation, preliminary results indicate that the excellent agreement between the self-consistent energies and $E_{LW}[G_{HF}]$ is true also for the GWA and other conserving

approximation as well [44]. This means that the LW functional allows us to study the merits of various self-energy approximations without having to solve the Dyson equation.

The larger deviations from the self-consistent values when DFT Green functions are given as input reflects the fact that the restriction in the variational freedom results in an energy functional of the density, $E_{\text{LW}}[n]$. This functional has a stationary point different from the self-consistent result. For atoms, this deviation is rather small, but for molecules the error is more significant. As a consequence, the binding energies calculated from the variational functionals with DFT Green functions as input are not necessarily good approximations to the self-consistent binding energies.

From our calculations, we have seen that the second-order approximation produces better total energies than the GWA for atoms and small molecules. This could be expected since the most important feature of the GWA is the screening of the long-range potential of the Coulomb interaction. In a system with strongly localized electrons, it is not surprising that other physical processes are equally important. For extended systems, the situation is different since screening the electron interaction is essential. The natural formalism for calculations on such systems is then the Ψ formalism, as developed in Refs. [16,17]. This formalism has not yet been applied to molecules, but works very well for atoms [22] and the homogenous electron gas [16,20].

We have also been able to demonstrate that the LW functional is useful also for constructing orbital functionals in DFT. By restricting the input to the variational functionals to be noninteracting Green functions from a local potential, we obtain an energy functional which is stationary at the potential referred to as the OEP potential. It is obviously rather difficult to find v_{xc} from the LW-OEP equation (6), but this is in practice not necessary if we only want to calculate the energy. As we have shown, the energy functional $E_{\text{LW}}^{\text{KS}}[n]$ is insensitive to which DFT orbitals are used as input. The LW functional has the further advantage over the conventional OEP schemes in that the energies are much closer to the self-consistent values. This means that we understand what physical mechanisms are taken into account in our DFT scheme and puts us in a position to systematically improve upon our approximations. Given the importance of orbital functionals for systems where local functionals of the density fail, it will be essential to explore these topics further. This work will not only lead to improved methods for total-energy calculations, but also to improved DFT response functions [18].

ACKNOWLEDGMENTS

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APPENDIX A: OBTAINING THE TOTAL ENERGY FROM THE GREEN FUNCTION

For a given $G(\mathbf{x}, \mathbf{x}'; i\tau)$ there are many ways to obtain the total energy. The most straightforward method would be to use the very definition of the Green function and the property

that, in the limit $\tau \rightarrow 0^-$, the Green function equals the one-particle density matrix. This means that

$$\langle \hat{T} + \hat{W} \rangle = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left\{ \left[-\frac{\nabla^2}{2} + w(\mathbf{x}) \right] G(\mathbf{x}, \mathbf{x}'; 0^-) \right\}. \quad (\text{A1})$$

The electron interaction energy is similarly obtained from

$$\begin{aligned} \langle \hat{V} \rangle &= \frac{1}{2} \int_0^\beta d\tau \int \int d\mathbf{x} d\mathbf{x}' M(\mathbf{x}, \mathbf{x}'; -i\tau) G(\mathbf{x}', \mathbf{x}; i\tau) \\ &= \frac{1}{2} \text{Tr}[MG]. \end{aligned} \quad (\text{A2})$$

Note that this definition of the trace is slightly different from the one used elsewhere in this paper, since we here consider the τ -dependent functions rather than the Fourier-transformed quantities. When G is a solution to the Dyson equation (but not necessarily a self-consistent one), the sum

$$E = \langle \hat{T} + \hat{W} \rangle + \langle \hat{V} \rangle \quad (\text{A3})$$

is equivalent to the Galitskii-Migdal formula [51]

$$E = \frac{1}{2} \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left[-\partial_\tau + \frac{\nabla^2}{2} - w(\mathbf{x}) \right] G(\mathbf{x}, \mathbf{x}'; i\tau). \quad (\text{A4})$$

If the Green function is also a *self-consistent* solution of the Dyson equation corresponding to a conserving Σ , the energy is equal to that obtained from the variational functionals discussed in this paper. An example of this is the case of $\Phi = \Phi_{\text{x}}$, in which G_{HF} is the self-consistent solution to the Dyson equation and all expressions give the HF energy.

That these three methods can give different results is easily seen by considering the second-order approximation of Fig. 1. If we calculate the total energy from the HF Green function, then the Klein functional (9) will give the MP2 energy

$$\begin{aligned} E_K[G_{\text{HF}}] &= \sum_{i=1}^N \epsilon_i^{\text{HF}} - U_0 - \Phi_{\text{x}} + \frac{1}{4} \text{Tr}\{\Sigma^{(2)}[G_{\text{HF}}]G_{\text{HF}}\} \\ &= E_{\text{HF}} + E_c^{\text{MP2}}. \end{aligned} \quad (\text{A5})$$

If we evaluate Eq. (A3), we instead obtain

$$E = E_{\text{HF}} + 2E_c^{\text{MP2}}, \quad (\text{A6})$$

while the Galitskii-Migdal formula (A4) will just give the HF energy E_{HF} .

APPENDIX B: EVALUATING THE LOGARITHMIC TERM IN THE LW FUNCTIONAL

The logarithmic term in the LW functional (3) cannot be evaluated without some further manipulation, since the integrand goes to a constant value for large frequencies. There are several ways of doing this, but we have in these calculations (and in Refs. [21,22,47]) chosen to use an auxiliary Green function \tilde{G} , defined according to

$$\tilde{G}^{-1} = G^{-1} - \Sigma_x + \Sigma_0. \quad (\text{B1})$$

The Green function G is here the Green function that is given as input to the LW functional. In our calculations G is a noninteracting Green function corresponding to a Dyson equation

$$[i\omega - \hat{t} - w - v_H - \Sigma_0 + \mu]G = 1. \quad (\text{B2})$$

The self-energy Σ_0 is v_{xc} or Σ_x , and the corresponding Green function is either a KS or a HF Green function. The auxiliary noninteracting Green function \tilde{G} corresponds to the first iteration towards HF, which means that if $G = G_{\text{HF}}$, then $\tilde{G} = G = G_{\text{HF}}$. We can now write the logarithmic term in the LW functional as

$$\begin{aligned} -\text{Tr} \ln[-G^{-1} + \Sigma - \Sigma_0] &= -\text{Tr} \ln[-\tilde{G}^{-1} + \Sigma_c] \\ &= -\text{Tr} \ln[-\tilde{G}^{-1}] \\ &\quad -\text{Tr} \ln[1 - \tilde{G}\Sigma_c] \\ &= \sum_{i=1}^N \tilde{\epsilon}_i - \mu N - \text{Tr} \ln[1 - \tilde{G}\Sigma_c]. \end{aligned} \quad (\text{B3})$$

The eigenvalues $\tilde{\epsilon}_i$ correspond to \tilde{G} . It is important to note that when we represent the Green functions in terms of one-particle basis functions, the manipulations in this equation assume that we have a complete basis. While the procedure described here is only one of several possible methods for evaluating the logarithmic term, the use of an inadequate basis set could cause the results to depend on the chosen method.

The frequency integral in the last term can now be performed, as it goes as $1/\omega^2$ for large frequencies. It is advantageous to extract the linear term of the logarithm, such that

$$-\text{Tr} \ln[1 - \tilde{G}\Sigma_c] = \text{Tr}\{\tilde{G}\Sigma_c\} - \text{Tr}\{\tilde{G}\Sigma_c + \ln[1 - \tilde{G}\Sigma_c]\}. \quad (\text{B4})$$

The frequency integral in the last term now converges as $1/\omega^4$. Inserted in the LW functional, we now have to calculate

$$\begin{aligned} E_{\text{LW}}[G] &= \sum_{i=1}^N \tilde{\epsilon}_i - U_0 - \text{Tr}\{\Sigma_x G\} + \Phi + \text{Tr}\{(\tilde{G} - G)\Sigma_c\} \\ &\quad - \text{Tr}\{\tilde{G}\Sigma_c + \ln[1 - \tilde{G}\Sigma_c]\}. \end{aligned} \quad (\text{B5})$$

From this expression it is clearly seen that if we evaluate the LW functional on $G = G_{\text{HF}}$, the energy becomes

$$E_{\text{LW}}[G_{\text{HF}}] = E_{\text{HF}} + \Phi_c - \text{Tr}\{G\Sigma_c + \ln[1 - G\Sigma_c]\}. \quad (\text{B6})$$

The last term provides a correction to the correlation energy Φ_c and is quadratic in Σ_c . We found this correction to be almost negligible for most atoms and molecules. The term appears, perhaps surprisingly, to be small also for the homogenous electron gas [42].

When evaluating the logarithm, further manipulation is necessary since the frequency dependent matrix $\tilde{\Sigma}_c$ is not Hermitian. The frequency integral is

$$\begin{aligned} \text{Tr} \ln[1 - \tilde{G}\Sigma_c] &= \text{Tr} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \ln[1 - \tilde{G}(\omega)\Sigma_c(\omega)] \\ &= \text{Tr} \int_0^{\infty} \frac{d\omega}{2\pi} \{\ln[1 - \tilde{G}(\omega)\Sigma_c(\omega)] \\ &\quad + \ln[1 - \tilde{G}(-\omega)\Sigma_c(-\omega)]\} \\ &= \text{Tr} \int_0^{\infty} \frac{d\omega}{2\pi} \{\ln[1 - \tilde{G}(\omega)\Sigma_c(\omega)] \\ &\quad + \ln[1 - (\Sigma_c(\omega)\tilde{G}(\omega))^\dagger]\} \\ &= \text{Tr} \int_0^{\infty} \frac{d\omega}{2\pi} \ln|1 - \tilde{G}(\omega)\Sigma_c(\omega)|^2. \end{aligned} \quad (\text{B7})$$

The last step is valid because we take the trace over the matrices. In order to calculate the logarithm we now need to diagonalize the Hermitian matrix $\tilde{G}\Sigma_c + (\tilde{G}\Sigma_c)^\dagger - \tilde{G}\Sigma_c(\tilde{G}\Sigma_c)^\dagger$ for each frequency. From the eigenvalues of this matrix, the trace is then readily obtained.

APPENDIX C: MINIMUM OF THE OEP ENERGY

The OEP equation follows from finding the density for which the energy functional (12) is stationary,

$$\frac{\delta E}{\delta n(\mathbf{r})} = \frac{T_0}{\delta n(\mathbf{r})} + w(\mathbf{r}) + v_H(\mathbf{r}) + \frac{\delta \Phi}{\delta n(\mathbf{r})} = 0. \quad (\text{C1})$$

At the OEP density, we have

$$\frac{\delta T_0}{\delta n(\mathbf{r})} = -v_s(\mathbf{r}). \quad (\text{C2})$$

The local potential $v_s(\mathbf{r})$ is a functional of the density and can be written in the form $v_s(\mathbf{r}) = w(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$, where v_{xc} is the solution to the OEP equation (13). The obvious question is now whether this stationary point of the energy functional is also a minimum, and to answer this we have to calculate the second derivative of the energy functional. Using the fact that $v_{xc}(\mathbf{r}) = \delta \Phi / \delta n(\mathbf{r})$ and defining the static exchange-correlation response kernel $K_{xc} = \delta v_{xc}(\mathbf{r}) / \delta n(\mathbf{r}')$ the second derivative can be written

$$\begin{aligned} \frac{\delta^2 E}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} &= \frac{\delta^2 T_0}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + v(\mathbf{r} - \mathbf{r}') + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} = -\frac{\delta v_s(\mathbf{r})}{\delta n(\mathbf{r}')} \\ &\quad + v(\mathbf{r} - \mathbf{r}') + K_{xc}(\mathbf{r}, \mathbf{r}') = -\chi^{-1}(\mathbf{r}, \mathbf{r}'), \end{aligned} \quad (\text{C3})$$

where we have used the property $\delta^2 T_0 / \delta n(\mathbf{r}) \delta n(\mathbf{r}') = -\chi_0^{-1}(\mathbf{r}, \mathbf{r}')$ and the fact that $\chi_0^{-1} = \chi^{-1} + v + K_{xc}$. As a consequence, the second derivative of the energy functional is positive, meaning that the OEP energy corresponds to a minimum, as long as the response function χ has negative eigenvalues. We know this to be true for the noninteracting response function χ_0 as well as for the exact response function obtained from the exact K_{xc} . It is also true for the response functions obtained from the approximation $K=0$ and from the exchange kernel $K=K_x$. To strictly prove that the OEP energy is a minimum also for other approximations to

Φ , one should calculate the response function χ from $K(\mathbf{r}, \mathbf{r}') = \delta^2 \Phi / \delta n(\mathbf{r}) \delta n(\mathbf{r}')$. In the case of the RPA energy, there is no indication of singularities that could overshadow the strong Coulomb interaction. In fact, this response function has been used by Langreth and Perdew [52] to obtain gradient corrections and also by Richardson and Ashcroft [53] at finite frequencies, without any sign of such singularities. It is important to keep in mind that if χ should happen to have positive eigenvalues, this would imply an instability in the OEP ground state [54]. In conclusion, the OEP energy is a minimum under the assumption that the static response function $\chi = \chi_0 + \chi_0(v + K_{xc})\chi$ does not have unphysical positive eigenvalues.

APPENDIX D: DISSOCIATION OF H₂ IN A MINIMUM BASIS

We use a minimum basis consisting of the gerade and ungerade orbitals

$$\phi_{gu}(\mathbf{r}) = \frac{1}{\sqrt{2(1 \pm S)}} [A(\mathbf{r}) \pm B(\mathbf{r})], \quad (\text{D1})$$

molecular orbitals, where $A(\mathbf{r})$ and $B(\mathbf{r})$ are the $1s$ hydrogen orbital located on atoms A and B , respectively, and S is their overlap. The noninteracting response function is then given by

$$\chi_0(\mathbf{r}, \mathbf{r}'; i\omega) = -a(i\omega) f(\mathbf{r}) f(\mathbf{r}'), \quad (\text{D2})$$

where $a(i\omega) = 4\epsilon / (\omega^2 + \epsilon^2)$, $f(\mathbf{r}) = \phi_g(\mathbf{r}) \phi_u(\mathbf{r})$, and $\epsilon = \epsilon_u - \epsilon_g$ is the HOMO-LUMO gap. The RPA response function is

$$\chi(\mathbf{r}, \mathbf{r}'; i\omega) = -\frac{a(i\omega)}{1 + a(i\omega)K} f(\mathbf{r}) f(\mathbf{r}'), \quad (\text{D3})$$

where $K = \int \int d^3r d^3r' f(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') f(\mathbf{r}')$. To obtain the interaction energy for the electron interaction $\lambda v(\mathbf{r} - \mathbf{r}')$, we calculate

$$\begin{aligned} -\frac{1}{2} \text{Tr}[\chi^\lambda \lambda v] &= \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\lambda K a(i\omega)}{1 + \lambda K a(i\omega)} \\ &= \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{4\lambda K \epsilon}{\omega^2 + \epsilon^2 + 4\lambda K \epsilon} = \lambda K \sqrt{\frac{\epsilon}{\epsilon + 4\lambda K}}. \end{aligned} \quad (\text{D4})$$

Integrating over the interaction strength gives

$$\begin{aligned} \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda V \rangle_\lambda &= \int_0^1 \frac{d\lambda}{\lambda} \text{Tr}[\chi^\lambda \lambda v] = K \int_0^1 d\lambda \sqrt{\frac{\epsilon}{\epsilon + 4\lambda K}} \\ &= \frac{\epsilon}{2} \left[\sqrt{1 + \frac{4K}{\epsilon}} - 1 \right]. \end{aligned} \quad (\text{D5})$$

From this it follows that the RPA correlation energy [8] is

$$E_{\text{RPA}}^c = \frac{\epsilon}{2} \left[\sqrt{1 + \frac{4K}{\epsilon}} - 1 \right] - K. \quad (\text{D6})$$

The RPA total energy, defined according to Eq. (9), is $E_{\text{RPA}} = E_{\text{HF}} + E_{\text{RPA}}^c$. Assuming that the molecular orbitals are obtained from HF calculations, then in the limit $R \rightarrow \infty$, $E_{\text{HF}} = -1 + J/2 - 1/(2R) + O(1/R^2)$, where

$$J = \int \int d^3r d^3r' |A(\mathbf{r})|^2 v(\mathbf{r} - \mathbf{r}') |A(\mathbf{r}')|^2. \quad (\text{D7})$$

Since the RPA correlation energy goes to $E_{\text{RPA}}^c \rightarrow \sqrt{\epsilon K} - K$, then $\lim_{R \rightarrow \infty} \epsilon = 1/R + O(1/R^2)$ and

$$E_{\text{RPA}} = -1 + \sqrt{\frac{J}{2R}} + O(1/R). \quad (\text{D8})$$

From this expression, we see that the HF-RPA energy approaches a constant value from above, in agreement with our calculations using larger basis sets.

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