

Variational energy functionals tested on atoms

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It was recently proposed to use variational functionals based on many-body perturbation theory for the calculation of the total energies of many-electron systems. The accuracy of such functionals depends on the degree of sophistication of the underlying perturbation expansions. An older such functional and a recently constructed functional, both at the level of the *GW* approximation (GWA), were tested on the electron gas with indeed very encouraging results. In the present work we test the older of these functionals on atoms and find correlation energies much better than those of the random-phase approximation but still definitely worse as compared to the case of the gas. Using the recent functional of two independent variables it becomes relatively easy to include second-order exchange effects not present in the GWA. In the atomic limit we find this to be very important and the correlation energies improve to an accuracy of 10–20 % when obtained from calculations much less demanding than those of, e.g., configuration-interaction expansions.

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I. INTRODUCTION

Over the past 15 years, the calculation of the total energies of many-electron systems has become a widespread and important activity in physics and chemistry. The activity, which involves an increasing number of practitioners, could have consequences for a large number of potential applications. One is, for instance, interested in the position, orientation, and binding energies of molecules adsorbed at surfaces, in the energy required to move a particular radical from one side of a large molecule to another, in the enthalpy of the formation of a particular alloy, in the energy involved in the formation of a particular defect in a solid, in the energy barrier for a certain molecular reaction, or in vibrational frequencies. The list can be continued indefinitely.

The overwhelming majority of all such calculations is carried out within the framework of density-functional theory (DFT).¹ This is due to the simplicity of the resulting one-electron equations and the accuracy one can achieve from the use of modern so-called generalized gradient approximations (GGA's).^{2,3} Binding distances between constituent atoms are usually correct to within a tenth of an Ångström and the binding energies of metallic systems are, on the average, correct to within 0.3 eV/atom. For more open systems and particularly for finite and small systems the errors in binding energies can easily exceed 1 eV/atom and reaction barriers can be several factors off the mark. There is thus a clear need for better approximations within DFT. The impressive progress which has been achieved so far is, however, the result of tedious and painstaking work over a long period of time and there is no obvious route toward systematic improvements within DFT.

An additional reason for the popularity of DF methods is of course the lack of alternative methods applicable to real systems of practical interest. For atoms and smaller molecules there are certainly very accurate *ab initio* methods like, e.g., the coupled cluster (CC) method or ordinary configuration-interaction (CI) expansions. For larger molecules and particularly in extended systems the calculational effort required for such *ab initio* methods becomes prohibi-

tively large. The CC method has been applied to extended systems^{4,5} and there is also a *local* version of the CI expansion⁶ but neither has, so far, been able to compete with DF methods with regard to simplicity, versatility, or applicability.

Total energies can also be obtained from the one-electron or the two-electron Green functions of many-body perturbation theory (MBPT).⁷ Except for the initial and very successful calculations of the total energy of the infinite electron gas,⁸ this approach has had little to offer in systems of practical interest. A few atoms and a number of small molecules have been treated by MBPT (Ref. 9) but, to our knowledge, no large molecules or solids. There have been several reasons for this dismal record. Although there are systematic rules for carrying the perturbation expansion to higher order in the Coulomb interaction, the expansion is, in principle, divergent and physical intuition must be allowed to guide the choice of Feynman diagrams to be included. The statement “more diagrams are better than fewer” is certainly not true. Another reason is the fact that the diagrammatic expressions quickly become prohibitively difficult to calculate with increasing order.

Two major developments have made us reconsider the use of MBPT as a tool for obtaining total energies of many-electron systems. In an attempt to find the limitations and also possible improvements of the so-called *GW* approximation (GWA) (Ref. 10) for the quasiparticle energies of solids, Holm and von Barth¹¹ carried out self-consistent *GW* calculations for the interacting but homogeneous electron gas. The calculations were self-consistent in the sense that the Green function used to calculate the electronic self-energy within the GWA was identical to that which was obtained from Dyson's equation using, as a potential, the calculated self-energy. As a byproduct of these calculations, it was discovered that the total energy obtained from the self-consistent Green function of the gas was as accurate as that obtained from very elaborate Monte Carlo simulations—to within the computational accuracy. Stimulated by these results Almladh, von Barth, and van Leeuwen (ABL)^{12,13} reexamined a variational expression for the total energy due to Luttinger

and Ward (LW).¹⁴ This expression was not used by the latter authors for obtaining total energies. It was rather used for deriving certain exact properties of the expansions within MBPT. The same expression has later been used by Langreth¹⁵ for “deriving” DFT from MBPT and by Sham and Schlüter¹⁶ for obtaining an expression for the so-called derivative discontinuity of the effective potential for exchange and correlation within DFT. The central quantity of the LW variational expression is the functional $\Phi[G]$ whose variational derivative with respect to the Green function G yields the electronic self-energy Σ . If the functional Φ is chosen to yield the GWA for Σ , the LW functional is stationary at the Green function of the self-consistent GWA and the resulting total energy is that of the GWA. The stationary property of the LW functional at the solution to Dyson’s equation can now be used for obtaining a close approximation to the self-consistent total energy by evaluating the functional at, e.g., a noninteracting Green function, a task much easier than iterating to self-consistency. In 1996, it was shown by Hindgren¹⁷ that only a few millihartrees were lost in this procedure when it was applied to the electron gas at the level of the GWA.

The next development, also from 1996, was our (ABL) discovery that one can easily replace the bare Coulomb interaction v with the screened interaction W by means of a simple Legendre-like transformation of the original Φ functional. In this way, the central quantity becomes $\Psi[G, W]$ which is a functional of two independent variables, G and W . As before, the functional derivative of Ψ with respect to the Green function G yields the electronic self-energy, whereas the functional derivative with respect to W now yields the irreducible polarizability P of the system. From the basic functional Ψ it is a rather trivial matter to invent expressions for the total energy which are stationary with respect to variations of both the Green function G and the screened interaction W when G is a solution to Dyson’s equation and W a solution to the *contracted Bethe-Salpeter* equation. The latter equation is simply defined as the exact relation which expresses the screened interaction W in terms of the irreducible polarizability P and the bare Coulomb potential v . The expression for the total energy is, by no means, unique and the investigation of different choices would be an interesting task for future research. In 1996, Hindgren¹⁷ tested a rather straight-forward choice by evaluating the total energy of the electron gas at a simple plasmon-pole approximation to the screened interaction W . They again found that this very simple and fast procedure gave energies which deviated little from those of the fully self-consistent GWA.

When attempts are made to go beyond simple one-electron or mean-field theories in realistic systems, present-day computational facilities do rarely allow the use of interacting Green functions and the calculation of the screened interaction is usually a bottleneck of such calculations (as, e.g., in GW calculations). If the variational principle would allow for the use of noninteracting Green functions and simple models of the screened interaction, it might become feasible to evaluate rather complicated but, hopefully, accurate expressions for the total energy of real systems. This is the reason behind our newly found interest in the possible

use of MBPT as a tool for calculating the total energies of real electronic systems.

Given the success of the variational methods as applied to the total energy of the electron gas, the assessment of the quality and feasibility of these methods in inhomogeneous systems is an obvious continuation of our research. Two major questions need to be answered: (1) Is the GW level of approximation adequate also in strongly inhomogeneous systems? (2) Does the variational property of the new functionals alleviate the necessity for self-consistency? Anticipating the results of the present work on atomic systems, we could answer the first question in the negative and the second question by “yes, provided certain conditions are met.” It is the purpose of the present work to qualify these answers and to provide suggestions for future approximations which are both accurate and feasible to apply to real systems.

Concerning the first question above, a lot can be said already from the vast experience pertinent to finite systems accumulated within the community of quantum chemists. For atoms and molecules it is well known that the second-order exchange diagrams have to be included in order to obtain reasonable values for the correlation energies.¹⁸ At the GW level, however, the LW functional does not include these important physical effects. The LW functional does include an infinite number of Feynman diagrams above the normal random-phase approximation (RPA), the latter approximation being essential for cutting down the long range of the Coulomb interaction. The additional diagrams are of high orders in the screened interaction and are probably responsible for modifying the screening effects. But they do not include the second-order exchange effects so important in systems with localized electrons. The latter effects are known to be important also in the electron gas especially at low densities. Thus, in retrospect, the accurate results previously obtained for that system might have been fortuitous.

A further indication on the importance of the effects beyond the GWA can be found in the work by Schindlmayr *et al.*¹⁹ After learning about the results of our group, they performed self-consistent GW calculations on a model system consisting of a finite two-dimensional lattice of model atoms with on-site Hubbard interactions. For this system the total energy could be obtained by direct diagonalization and compared to that of the GWA. They found a rather large deviation between the two sets of energies—especially at the larger Coulomb repulsions. True enough, the model appears somewhat remote from real systems but some of the effects illuminated by the work of Schindlmayr *et al.* are indeed present also in our atomic systems.

With regard to the second question about the quality of the variational procedure, there is no previous experience to draw from. Neither have we here performed any self-consistent calculations. Our investigations of this issue rely on evaluating the functionals at different reasonable Green functions and screened interactions, and monitoring how results change. As already mentioned above, in these very inhomogeneous systems results are much more sensitive to the choice of noninteracting Green function and also to the choice of screened interaction. We argue that certain choices are to be preferred to others.

With regard to the very essential question on how to proceed beyond the less satisfactory GWA without jeopardizing the possibility of applying our variational methods to realistic systems, we propose and test the inclusion of exchange effects which are second order in the screened interaction. In order to make the calculation tractable also in extended systems, we then find it essential to make use of the variational property of the energy functional based on our Ψ formulation.

We will conclude this introduction by a quick résumé of the short history of the variational procedures based on MBPT plus an outline of the present paper. The history goes back to the construction of the LW functional in 1960. This functional, although discussed in several later papers, was never used for calculating total energies. It was first used by Hindgren and Almladh at the level of the GWA to calculate the energy of the gas. Suggestions and precursors toward the Ψ formulation can be found in several older papers by, e.g., Hedin,¹⁰ Klein,²⁰ and De Dominicis.²¹ Again, these authors never found any practical use for their theories. The complete theory of the Ψ functionals was first presented in 1997 at the conference *Recent Progress in Many-Body Theories* in Sydney. The ensuing papers^{12,17} presented the main ideas illustrated by an application to the electron gas with numerical results by Hindgren and Almladh. A longer paper giving details of the new theory including complete derivations as well as instructions for the application of the theory to inhomogeneous systems was written in 1997.¹³ After 1996, the new theory has been presented at many international conferences.³⁹ A simplified version of the variational theory was recently used by a former member of our group and his collaborators²² to calculate the binding energy of the hydrogen molecule at different separations. The latter authors employed a simpler functional,^{20,23,24} also at the *GW* level. This functional is, however, inferior to the LW functional in the sense that it yields an inaccurate RPA energy, whereas the LW functional gives almost the exact answer when both functionals are evaluated for the electron gas at a noninteracting Green function. Finally we should mention the results of the self-consistent calculations by Holm and von Barth,¹¹ Schindlmayr *et al.*,¹⁹ García-González and Godby,²⁵ and Gould *et al.*,²⁶ which the variational procedures are designed to reproduce and which thus serve as benchmarks for these procedures.²⁵

In the following section of this paper we will give some basic formulas for the application of the theory to inhomogeneous systems plus some details on how the theory connects to the exact DF formulation. In Sec. III we will discuss the calculations of the total energies of atoms using the LW functional and in Sec. IV we will include second-order exchange effects within the Ψ formulation. Finally, in Sec. V we state our conclusions and discuss the way to proceed toward obtaining more accurate results without any substantial increase of the computational effort.

II. GREEN FUNCTIONS AND CONSERVING APPROXIMATIONS

We will in this paper only consider ground-state energies, but will for notational simplicity use the finite temperature

formalism, letting $T \rightarrow 0$ at the end of the calculations. All quantities are given on the imaginary frequency axis, and the Green function $G(\mathbf{r}\sigma, \mathbf{r}'\sigma'; i\omega)$ satisfies the equation of motion (leaving out coordinates and indices)

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

where $\hat{t} = -\nabla^2/2$, $w(\mathbf{r})$ is the external potential, $V_H(\mathbf{r}) = \int d^3r' n(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')$ is the Hartree potential, and μ is the chemical potential. We use atomic units throughout this paper. The self-energy $\Sigma(\mathbf{r}\sigma, \mathbf{r}'\sigma'; i\omega)$ includes the exchange and correlation effects of the electron interaction, and will have to be approximated at some level in perturbation theory. We will in the following skip the coordinates, and treat G and Σ as matrices with (\mathbf{r}, σ) and (\mathbf{r}', σ') as indices. The ground-state total energy E is, at $T=0$, related to the grand potential Ω according to $\Omega(T \rightarrow 0) = E - \mu N$, where N is the total number of particles.

Since both V_H and Σ are functionals of the Green function G , Eq. (1) should be solved to self-consistency within the chosen approximate scheme for Σ . While a knowledge of the Green function provides us with the ground-state expectation values of one-particle operators, as well as the total energy, these values will necessarily depend on the choice of approximation for Σ . Baym and Kadanoff^{24,27} showed that a conserving approximation for Σ , i.e., an approximation for which the resulting Green function obeys the same conservation laws as the underlying Hamiltonian, is obtained when Σ is derived from a functional $\Phi[G]$ according to

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

A recipe for how to construct such a functional was developed in an earlier paper by Luttinger and Ward (LW),¹⁴ who suggested summing over all irreducible self-energy diagrams closed with an additional Green function and multiplied by specific numerical factors,

$$\Phi[G] = \sum_{n,k} \frac{1}{2n} \text{Tr}[\Sigma_k^{(n)} G]. \quad (3)$$

The index n indicates number of interaction lines and Tr indicates a summation over all indices as well as a frequency integration, $\text{Tr} = \sum_{\sigma} \int d^3r \int (d\omega/2\pi)$. The construction of Φ diagrams is illustrated in Fig. 1 for the lowest orders.

While this was not the main purpose of their work, Luttinger and Ward in the same paper derived a *variational* expression for the total energy. MBPT provides several possibilities for obtaining the ground-state energy. One is, e.g., through the Galitskii-Migdal formula²⁸ which, however, requires an accurate Green function which, in turn, necessitates a self-consistent solution to Dyson's equation. Since the total-energy expression presented by Luttinger and Ward is variational with respect to G , the result will not be very sensitive to the quality of the input Green function.

The original formulation in Ref. 14 takes the Green function corresponding to a completely noninteracting system as a starting point for a perturbation series in terms of the electron-electron interaction. This is inconvenient for calcu-

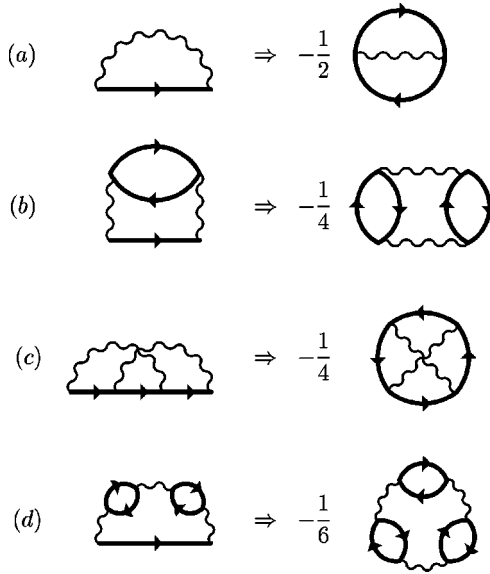


FIG. 1. The figure shows how the Φ functional is constructed by closing irreducible self-energy diagrams with a Green-function line and multiplying with an appropriate prefactor. The figure shows all of the first- and second-order diagrams and one of the many third-order diagrams.

lations on inhomogeneous systems. The strong attractive force of the bare atomic nucleus produces orbitals which are tightly bound, and a more reasonable starting point is a Hamiltonian where the static screening by the other electrons is taken into account. A natural choice of a noninteracting system is given by DFT, which already produces the exact one-electron density. While the variational functionals themselves are not based on DFT, they will be evaluated using noninteracting Green functions which are typically obtained from DFT calculations. To highlight this connection, we will therefore deviate from the original work and sketch a derivation more closely related to the formalism of DFT. We introduce an interaction strength parameter λ , such that $\lambda = 0$ corresponds to a noninteracting system and $\lambda = 1$ corresponds to the fully interacting system. The Hamiltonian can then be written as a function of the interaction strength,

$$\hat{H}^\lambda = \sum_{i=1}^N \hat{t}_i + \sum_{i=1}^N w^\lambda(\mathbf{r}_i) + \frac{\lambda}{2} \sum_{i \neq j}^N v(\mathbf{r}_i - \mathbf{r}_j), \quad (4)$$

where λv is the modified electron interaction and the external potential w^λ is such that the electron density remains constant at all λ . It is thus equal to the exact ground-state density $n^\lambda(\mathbf{r}) = n(\mathbf{r})$. At $\lambda = 0$, the external potential w^0 is equal to the Kohn-Sham potential $v_{\text{KS}}[n](\mathbf{r})$. The Green function then reduces to the Kohn-Sham Green function G_{KS} , which is related to the Green function at a general λ through Dyson's equation

$$G^\lambda = G_{\text{KS}} + G_{\text{KS}}(\Sigma^\lambda + \lambda V_H + w^\lambda - v_{\text{KS}})G^\lambda. \quad (5)$$

Note that both G_{KS} and v_{KS} are functionals of the electron density. The definition of G^λ in Eq. (5) does not therefore

imply any particular dependence on G_{KS} , but is equivalent to Eq. (1).

With this connection between the fully interacting Green function and the Kohn-Sham system, the derivative of the grand potential with respect to the interaction strength is

$$\frac{d\Omega^\lambda}{d\lambda} = \left\langle \frac{d\hat{H}^\lambda}{d\lambda} \right\rangle = \text{Tr} \left[\left[\frac{dw^\lambda}{d\lambda} + \frac{1}{2} V_H + \frac{1}{2\lambda} \Sigma^\lambda \right] G^\lambda \right]. \quad (6)$$

The last two terms in Eq. (6) are related to the interaction energy, conveniently divided into its classical part $U_0 = \frac{1}{2} \text{Tr}[V_H G]$ and the exchange-correlation energy $U_{\text{xc}}^\lambda = \frac{1}{2} \text{Tr}[\Sigma^\lambda G^\lambda]$. The grand potential can then be obtained by integrating Eq. (6) from $\lambda = 0$ to $\lambda = 1$. In the limit $T \rightarrow 0$, the thermodynamic potential at $\lambda = 0$ is just the sum over the difference between the occupied Kohn-Sham eigenvalues and the chemical potential,¹⁴

$$\Omega_0 = -\text{Tr} \ln(-G_{\text{KS}}^{-1}) = \sum_{i=1}^N \epsilon_i - \mu N. \quad (7)$$

In order to relate the total energy to the Φ functional, let us consider Φ defined in Eq. (3) as a functional of the interaction strength. The derivative with respect to λ is

$$\begin{aligned} \frac{d\Phi^\lambda}{d\lambda} &= \sum_{n,k} \frac{1}{2n} \frac{n}{\lambda} \text{Tr}[\Sigma_k^{\lambda(n)} G^\lambda] + \text{Tr} \left[\frac{\delta\Phi^\lambda}{\delta G^\lambda} \frac{dG^\lambda}{d\lambda} \right] \\ &= \frac{1}{2\lambda} \text{Tr}[\Sigma^\lambda G^\lambda] + \text{Tr} \left[\Sigma^\lambda \frac{dG^\lambda}{d\lambda} \right]. \end{aligned} \quad (8)$$

Combining this equation and Eq. (6), we can express the derivative of Φ in terms of the derivative of the grand potential. Using also Dyson's equation (5), we can rewrite this as follows:

$$\begin{aligned} \frac{d\Omega}{d\lambda} &= \frac{d\Phi^\lambda}{d\lambda} - U_0 - \frac{d}{d\lambda} \text{Tr}[\Sigma^\lambda G^\lambda] - \frac{d}{d\lambda} \text{Tr} \ln(\Sigma^\lambda + \lambda V_H + w^\lambda \\ &\quad - v_{\text{KS}} - G_{\text{KS}}^{-1}). \end{aligned} \quad (9)$$

Integrating over the interaction strength, we finally obtain the LW functional,

$$\Omega = \Phi - U_0 - \text{Tr}[\Sigma G] - \text{Tr} \ln(\Sigma - v_{\text{xc}} - G_{\text{KS}}^{-1}), \quad (10)$$

where v_{xc} is the exchange-correlation potential of DFT. This functional is stationary with respect to G , since

$$\frac{\delta\Omega}{\delta G} = 0, \quad (11)$$

when G satisfies Dyson's equation $G = G_{\text{KS}} + G_{\text{KS}}(\Sigma - v_{\text{xc}})G$. This variational property suggests that evaluating Eq. (10) at some approximate Green function should result in a total energy close to the self-consistent result. Note that, while Eq. (11) shows that Ω is stationary at the self-consistent G , it does not say that it is a minimum. The energy will of course depend not only on the quality of the approximate G , but more fundamentally on the approximation scheme for Φ . The accuracy of the total energy obtained

from the LW functional can therefore never exceed the quality of the chosen Φ functional.

Note that the inclusion of $-v_{xc} - G_{KS}^{-1}$ in the logarithm in Eq. (10) is somewhat formal. The LW functional can equally well be written without any reference at all to DFT:

$$\Omega = \Phi - U_0 - \text{Tr}[\Sigma G] - \text{Tr} \ln(\Sigma + V_H + w + \hat{t} - \mu - i\omega). \quad (12)$$

Thus, whereas G_{KS}^{-1} and v_{xc} taken separately are both very complicated functionals of the one-electron Green function G —through the density—their sum is a rather trivial functional of G .

Note also that it is essential that the chemical potential μ_{KS} of G_{KS} is equal to the true chemical potential corresponding to the approximate Σ . For a finite system, as we discuss in the present paper, this is not a serious concern. As long as the total particle number given by $N = -\delta\Omega/\delta\mu$ is correct, the energy is independent of the location of the chemical potential.

It is actually possible to write the energy functional in an infinite number of other ways, but the LW functional has the advantage of being quite stable. For instance, a slightly different functional due to Klein,²⁰

$$\tilde{\Omega} = \Phi - U_0 - \text{Tr}[G(G_{KS}^{-1} + v_{xc}) - 1] - \text{Tr} \ln[-G^{-1}], \quad (13)$$

which has been used by several authors,^{15,20,22,23,29} is also a variational grand potential with exactly the same value as the LW functional when evaluated at the self-consistent G . This functional is, however, much more sensitive to the quality of the Green function, as we will demonstrate in Sec. III (see also Sec. I). Note that when the input to this functional is a Kohn-Sham Green function, the third term on the rhs simplifies to $-\text{Tr}[G_{KS}(G_{KS}^{-1} + v_{xc}) - 1] = -\int n v_{xc}$. The reference to DFT in the Klein functional (13) can, however, be removed in a manner similar to going from Eq. (10) to Eq. (12).

Any choice of Φ diagrams results in a conserving approximation for Σ . For instance, including only the diagram shown in Fig. 1(a) yields the Hartree-Fock (HF) approximation, while other examples of conserving Φ -derivable schemes mentioned in Ref. 27 are the GW approximation¹⁰ and the T -matrix approximation.³⁰ The primary reason why we are interested in calculating the total energy from variational expressions such as the LW functional is that we want to avoid solving Dyson's equation. If the self-consistent solution gives accurate total energies, the LW functional will produce approximations to these energies with much less computational effort. There are, however, no obvious rules for choosing Φ diagrams that will produce good total energies.

Whereas the LW functional is based on a perturbation series in terms of the Green function and the bare Coulomb interaction v , the Hedin equations¹⁰ describe a perturbation expansion in terms of G and the screened interaction W . Almladh, von Barth and van Leeuwen^{12,13} constructed a variational energy functional similar to the LW functional, but where the perturbation expansion is in terms of W rather

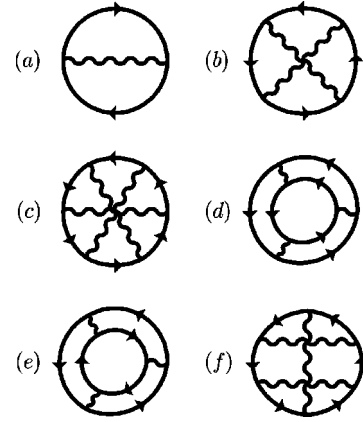


FIG. 2. Some of the low-order Ψ diagrams. These diagrams differ from the diagrams contributing to the Φ functional in that the interaction lines represent the screened interaction W , and the diagrams therefore have no polarization insertions. There is only one first-order and one second-order diagram, shown on the upper line.

than v . Writing the screened interaction in terms of the bare interaction and the irreducible polarizability P according to the contracted Bethe-Salpeter equation

$$W = v + vPW, \quad (14)$$

ABL constructed a functional Ψ of G and W , defined by a Legendre-like transformation of the Φ functional

$$\Psi[G, W] = \Phi[G, v[G, W]] - \frac{1}{2} \text{Tr}[PW - \ln(1 + PW)]. \quad (15)$$

This functional has the properties

$$\frac{\delta\Psi}{\delta G} = \Sigma \quad \text{and} \quad \frac{\delta\Psi}{\delta W} = -\frac{1}{2}P, \quad (16)$$

which we will here present without any further proof. In analogy with the diagrammatic construction of the Φ functional in Eq. (3), the Ψ functional can be constructed by a similar summation over self-energy diagrams,¹³ keeping only the diagrams without any polarization insertions. Labeling these diagrams $\sigma_k^{(n)}$, where n denotes the order in W , the functional is constructed according to

$$\Psi[G, W] = \sum_{n,k} \frac{1}{2n} \text{Tr}[\sigma_k^{(n)} G]. \quad (17)$$

A few of these diagrams are shown in Fig. 2. Even though the expansion (17) involves self-energy diagrams different from those involved in the construction of the Φ functional, any Ψ -derivable scheme (meaning that the self-energy can be obtained as $\Sigma = \delta\Psi/\delta G$) is also Φ derivable.¹³

Employing the Ψ functional, ABL suggested the following form for the grand potential:

$$\Omega = \Psi - U_0 - \text{Tr}[\Sigma G] + \frac{1}{2} \text{Tr}[PW + \ln(1 - Pv)] - \text{Tr} \ln(\Sigma - v_{xc} - G_{KS}^{-1}), \quad (18)$$

where they used Eq. (14) in order to keep a coupling between W and v . As we did also for the LW functional pre-

viously, we can rewrite $G_{\text{KS}}^{-1} + v_{\text{xc}}$ in a way which reveals the rather trivial dependence on the density of the sum of these terms and obtain

$$\Omega = \Psi - U_0 - \text{Tr}[\Sigma G] + \frac{1}{2} \text{Tr}[PW + \ln(1 - Pv)] - \text{Tr} \ln(\Sigma + V_H + w + \hat{t} - \mu - i\omega). \quad (19)$$

This functional is stationary with respect to both G and W , meaning that $\delta\Omega/\delta G = 0$ and $\delta\Omega/\delta W = 0$ if $G^{-1} = G_{\text{KS}}^{-1} - \Sigma + v_{\text{xc}}$ and $W^{-1} = v^{-1} - P$. The form of this functional is not at all unique. It is possible to add any functionals $F[\Sigma - v_{\text{xc}} + G^{-1} - G_{\text{KS}}^{-1}]$ and $H[P + W^{-1} - v^{-1}]$ as long as $F = \delta F = 0$ and $H = \delta H = 0$ at the self-consistent G and W . In this way, we can improve the stationarity of the energy functional, but the quality of the energies is ultimately determined by the choice of approximation to Ψ .

III. ATOMIC CORRELATION ENERGIES FROM THE LW-GW FUNCTIONAL

We will in this section present atomic correlation energies calculated by using the LW functional, Eq. (10). As mentioned in the preceding section, the energies we obtain will be approximations to the self-consistent energies corresponding to the chosen Φ functional. The calculations allow us to test the variational properties of the LW functional, as well as indicating whether the self-consistent GW approximation produces good total energies even for atoms. There are numerous highly accurate results for the total energies of atoms, and our goal is not to produce more accurate results than obtained with quantum chemical methods. Our main interest is rather in finding a simple and accurate method that can be extended to infinite systems, where quantum chemical methods are impractical.

In some simple cases, the variational properties can be tested directly. For instance, keeping only the uppermost diagram in Fig. 1, the self-consistent total energy is equal to the HF energy. In this case, the Klein functional defined by Eq. (13) reduces to the energy functional of the HF approximation, but with the orbitals of the input Green function. If we use the HF Green function G_{HF} , the result will be the HF energy, but at a different noninteracting G , the energy will be higher and not necessarily close to the HF energy. The LW functional has additional terms that reduce this error and make the functional less sensitive to the choice of G . Calculations on some spherical atoms show the difference in stability between the two functionals: Whereas the LW functional evaluated at an LDA Green function deviated from the HF energy by only 1 millihartree for Ne and 2 millihartree for Ca, the HF energies calculated from the functional given in Eq. (13) differed by 17 and 23 millihartree for the same atoms. Due to the poor variational properties of this functional, we might, of course, obtain an accurate total energy using an unphysical choice of functional Φ and a Green function far from self-consistency. But we consider such results to be irrelevant.

To go beyond HF and calculate correlation energies is a significantly more complicated task, and there are not many

$$\Sigma_{\text{GW}} = \text{Exchange} + \text{Ring} + \text{Complex Ring} + \dots$$

$$\Phi_{\text{GW}} = -\frac{1}{2} \text{Ring} - \frac{1}{4} \text{Two Bubbles} - \frac{1}{6} \text{Three Bubbles} + \dots$$

FIG. 3. The figure shows how Φ_{GW} is constructed by summing the exchange diagram and the ring diagrams. The upper diagrams show $\Sigma = -GW$ where W is the screened interaction W_{RPA} . The diagrams on the lower row show the corresponding Φ diagrams.

known self-consistent results. The GW approximation to the Φ functional is obtained by summing the ring diagrams, as shown in Fig. 3. These are the infinite set of diagrams with their corresponding numerical factors such that the electronic self-energy generated by Eq. (2) is that of the GWA. This implies that $\Sigma = -GW_{\text{RPA}}$ where the screened interaction is given by the RPA expression $W_{\text{RPA}} = v/(1 - vP_0)$ in terms of the noninteracting irreducible polarizability $P_0 = GG$. The first of the Φ_{GW} diagrams in Fig. 3 is just the exchange energy $E_x[G] = \frac{1}{2} \text{Tr}[G\Sigma_x]$, where Σ_x is the exchange part of the self-energy. The remaining diagrams can be summed as follows:

$$\begin{aligned} \Phi_{\text{GW}} &= E_x - \text{Tr} \left[\frac{1}{4} (vP_0)^2 + \frac{1}{6} (vP_0)^3 + \dots \right] \\ &= E_x + \frac{1}{2} \text{Tr} [vP_0 + \ln(1 - vP_0)] \\ &= E_x + \Phi_c^{\text{RPA}}. \end{aligned} \quad (20)$$

Without the numerical prefactors in front of the Φ_{GW} diagrams, their sum would just have generated the usual expression for the exchange-correlation part of the electron-electron interaction energy within the RPA. The numerical prefactors actually correspond to integrating each diagram over the strength of the Coulomb interaction. Therefore, the sum of this particular infinite series of Φ diagrams (including the numerical prefactors) is what in DFT is referred to as the exchange-correlation energy within the RPA, i.e., the exchange-correlation part of the interaction energy plus the correlation part of the kinetic energy. Consequently, the term Φ_c^{RPA} is the common formula for the correlation energy of the RPA. Both E_x and Φ_c^{RPA} are functionals of G , and will depend strongly on the input Green function.

The only previous total-energy calculation using the LW functional was one for the electron gas,^{12,17} where the results agreed with the accurate results from self-consistent GW calculations.¹¹ Schindlmayr *et al.*¹⁹ did not study the LW functional, but they obtained self-consistent GW energies for a Hubbard model, in poor agreement with the exact energies. Aryasetiawan *et al.*²² recently observed similar results in a two-site Hubbard model. Given these quite different conclusions from two sets of extreme model systems, a calculation of atomic total energies is highly interesting. If the self-consistent GW approximation gives accurate total energies also for a real system, the LW functional at the GW level (LW- GW) constitutes a simple method for obtaining highly accurate total energies with only a simple noninteracting G as input.

TABLE I. Correlation energies for some spherically symmetric atoms. The RPA correlation energies were calculated using G_{OEP} . The columns indicated by $E_{c,\text{LW}}^{\text{GW}}$ are results from the LW functional at the GW level, calculated using G_{OEP} , G_{LDA} and G_{HF} . All energies are in hartrees.

Atom	$E_c^{\text{RPA}}[G_{\text{OEP}}]$	$E_{c,\text{LW}}^{\text{GW}}[G_{\text{OEP}}]$	$E_{c,\text{LW}}^{\text{GW}}[G_{\text{LDA}}]$	$E_{c,\text{LW}}^{\text{GW}}[G_{\text{HF}}]$	CI ^a
He	-0.083	-0.064	-0.062	-0.066	-0.042
Be	-0.174	-0.110	-0.104	-0.128	-0.094
Ne	-0.579	-0.494	-0.481	-0.498	-0.390
Mg ²⁺	-0.574	-0.510	-0.501	-0.511	-0.390
Mg	-0.651	-0.550	-0.535	-0.560	-0.438
Ar	-1.070	-0.906	-0.891	-0.928	-0.722
Ca ²⁺	-1.104	-0.946	-0.939	-0.967	-0.754
Ca	-1.175	-0.977	-0.972	-1.013	

^aFrom Ref. 32.

We have calculated the total energy for a few spherically symmetric atoms and ions, approximating G with noninteracting HF and DFT Green functions. The DFT Green functions were calculated using both the LDA and the exchange-only optimized effective potential (OEP) method.³¹ The HF and DFT atomic orbitals were calculated using a set of Slater basis functions. The polarizability is represented in a basis of excitation functions f_q , where the index q represents a pair $q=(i,j)$ of an occupied and an unoccupied atomic orbital,

$$f_q(\mathbf{r}) = \phi_i(\mathbf{r})\phi_j(\mathbf{r}), \quad i \leq N < j. \quad (21)$$

We do not want the conclusions of the present paper to be obscured with irrelevant difficulties associated with the use of too limited basis sets. Consequently, care has been taken to use a large enough basis set to, e.g., ensure the convergence of the term Φ_c^{RPA} which is known to be difficult to converge. The accuracy of the results ranges from less than a millihartree for the lighter atoms to a few millihartree for the heavier. Since our theory is variational, the results should, in principle, not be very sensitive either to the choice of Green function or to the choice of basis for the orbitals. In future applications we will exploit this fact in order to make computational shortcuts and to save computational time. But that is not the purpose of the present work.

It is not possible to calculate the frequency integral in Eq. (10) without manipulating the expression somewhat. The logarithm contains terms which are static and will cause the frequency integral to diverge. This problem can be overcome by extracting the static exchange part Σ_x of the self-energy, and introducing a new Green function \tilde{G} defined by $-\tilde{G}^{-1} = \Sigma_x + V_H + w + \hat{t} - \mu - i\omega$. The logarithmic term can then be rewritten according to

$$\begin{aligned} & -\text{Tr} \ln(\Sigma + V_H + w + \hat{t} - \mu - i\omega) \\ & = -\text{Tr} \ln(-\tilde{G}^{-1}) - \text{Tr} \ln(1 - \tilde{G}\Sigma_p), \end{aligned} \quad (22)$$

where Σ_p is defined as $\Sigma_p = \Sigma - \Sigma_x$. The first term on the right-hand side of Eq. (22) is just a sum over the difference between the eigenvalues and the chemical potential of the occupied orbitals of \tilde{G} [as in Eq. (7)]. Note that \tilde{G} is the first iteration towards the HF Green function, and that the sum

over the eigenvalues is close to the sum over the HF eigenvalues. This is of course not the only way of performing this integral, but it is a simple procedure for atomic systems. If the HF Green function is given as an input to the LW functional, then $\tilde{G} = G_{\text{HF}}$. As a consequence, for atoms, the LW functional reduces to

$$E_{\text{LW}}[G_{\text{HF}}] \approx E_{\text{HF}} + \Phi_c[G_{\text{HF}}], \quad (23)$$

if we approximate $-\text{Tr} \ln(1 - \tilde{G}\Sigma_p)$ by $\text{Tr}[\tilde{G}\Sigma_p]$. This is certainly not valid in solids, but is quite reasonable in atoms. By Φ_c we mean the correlation part of the Φ functional [see Eq. (20)].⁴⁰

Calculated correlation energies $E_c \equiv E - E_{\text{HF}}$ are shown in Table I. In addition to the correlation energies obtained from the LW functional, we have included the RPA correlation energies E_c^{RPA} evaluated at G_{OEP} . With the exception of Be, the results clearly show that the LW functional is not very sensitive to the input Green function. This is in contrast to the RPA correlation energies which are much more unstable. While the RPA values in Table I are distinctly lower than the LW energies, they will, according to Eq. (23), be approximately equal to the LW results if they are evaluated at the HF Green function G_{HF} rather than at G_{OEP} .⁴¹

The obtained LW- GW values were, however, not particularly close to the exact results. Beryllium was the only atom for which the LW- GW calculations produced accurate results, but the values for Be were, on the other hand, much more sensitive to the choice of Green function. For the other atoms, the results differ only little when changing G . This confirms the good variational property of the LW functional and indicates that the results are close to the self-consistent GW total energies. Consequently, self-consistent GW calculations do not produce accurate total energies for atoms. In the absence of self-consistent calculations, this conclusion cannot be drawn with absolute certainty. But we know what physical processes are left out at the GW level (second-order exchange effects) and are not surprised by the deviation from the exact results. These conclusions are in agreement with the total-energy results for atoms obtained from a second-order approximation to Φ . The LW functional here showed a similar insensitivity to the input G , but the resulting energies were much closer to the exact values.³³

TABLE II. Removal correlation energies Δ_c [as defined in Eq. (24)] for Be, Mg, and Ca. The energies are calculated using the LW-GW functional evaluated at various approximate Green functions. The experimental result is obtained by subtracting the HF removal energy from the experimental removal energies.

Atoms	$\Phi[G_{\text{OEP}}]$	$\Phi[G_{\text{LDA}}]$	$\Phi[G_{\text{HF}}]$	Expt.
Be \rightarrow Be $^{2+}$	0.032	0.028	0.051	0.050
Mg \rightarrow Mg $^{2+}$	0.040	0.034	0.049	0.049
Ca \rightarrow Ca $^{2+}$	0.031	0.033	0.046	0.056

^aFrom Ref. 34.

It is important to remember that the total energies of the larger atoms such as Ar ($E \approx -527$ hartree) and Ca ($E \approx -678$ hartree) are very large. Most of it comes from the physically less interesting core region and is not very interesting *per se*. It is more relevant to study changes in the total energy as the structure of the system is modified, i.e., changes mainly due to the valence electrons. The simplest way of testing this for the spherically symmetric atoms is to remove two electrons and calculate the removal energy. The correlation part of the removal energies, defined for an atom A as

$$\Delta_c(A) = E_c(A^{2+}) - E_c(A) \quad (24)$$

were calculated for Be, Mg, and Ca using the LW-GW functional and the same Green functions as above. The calculated removal energies are shown in Table II together with experimental values. The removal energies obtained when using G_{OEP} and G_{LDA} are not particularly good, yielding 50–80% of the experimental results. The removal energies calculated from G_{HF} are in excellent agreement for Be and Mg. The removal energy for Ca is less accurate but the relativistic effects are expected to be significant for Ca. This could cause the discrepancy. We should also keep in mind that, while the LW functional is a variational expression for the total energy, we do not have a variational expression for the removal energies. This is evident from Table II, where the removal energies differ significantly depending on the G used in the evaluation. The calculations on the electron gas¹⁷ indicated that the stationary value of the LW functional is indeed a minimum, although we have not yet tried to formally prove this conjecture. Should this be the case, the results of Table I indicate that G_{HF} is closest to the self-consistent Green function in our atomic systems. The results for the removal energies in Table II then suggest that the self-consistent GWA gives a very accurate description of valence electron energies. It should be noted that we have also calculated the removal energies corresponding to the RPA, and have found them to be very different from the experimental numbers.

A more interesting test of the GWA would be to consider a redistribution rather than a removal of valence electrons, e.g., by calculating the total energy of a molecule as a function of the position of the nuclei. Such a calculation has recently been carried out by Aryasetiawan *et al.*²² for a H₂ molecule. As mentioned above, the latter authors employed the Klein functional, Eq. (13), which is quite sensitive to the

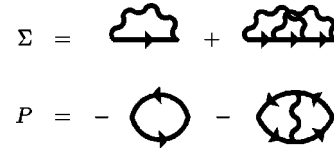


FIG. 4. The figure shows the approximate Σ and P diagrams corresponding to including the first- and second-order diagrams in the Ψ_{2X} functional.

input G . As discussed above, their calculations amount to finding the RPA energy of H₂. It would be interesting to perform similar calculations for that case, using the LW functional and various noninteracting Green functions in order to check the stationarity as well as the quality of the LW-GW energies.

IV. CORRELATION ENERGIES FROM THE ABL FUNCTIONAL

The results of the LW-GW calculations clearly indicate that GW is not sufficient for obtaining accurate total energies for atoms. It is, however, well known that the second-order Møller-Plesset perturbation theory (MP2) gives very accurate atomic total energies.³⁵ The name MP2 designates ordinary second-order perturbation theory, starting from the HF single-particle Hamiltonian. In essence this amounts to adding to the HF energy the contributions from the diagrams in Figs. 1(b) and 1(c). The MP2 scheme is, however, not variational and the total energy is very sensitive to the choice of one-electron Green function used to evaluate the diagrams. It would, however, not be very difficult to incorporate the second-order exchange effects present in MP2 theory into an LW functional. One could construct the Φ functional from just the diagrams in Figs. 1(a–c) in order to obtain a variational energy expression of similar accuracy to MP2 theory but much less sensitive to the choice of Green function and basis set. Such calculations have been carried out by us with rather promising results for the atoms.^{33,36} Unfortunately, MP2 is an expansion in the bare Coulomb interaction which will lose its relevance in larger molecules and solids.

The knowledge of the importance of second-order exchange in systems with localized electrons, and the necessity of screening the electron interaction in extended systems, leads in an obvious way to the ABL functional. As discussed in Ref. 13, any Ψ -derivable scheme is also Φ derivable. And the GW approximation described in Fig. 3 in terms of Φ diagrams is, in the Ψ formalism, represented by only a single Ψ diagram, shown in Fig. 2(a). A further advantage of the Ψ formalism is that the inclusion of second-order exchange effects amounts to adding only one extra diagram, shown in Fig. 2(b). The self-energy diagrams are shown in Fig. 4, together with the corresponding irreducible polarizability $P = -2\delta\Psi/\delta W$. Here, the interaction lines represent the screened interaction W . Another very essential property of the Ψ formulation is the fact that it is stationary with respect also to variations in the screened interaction. This will allow for the use of approximate such interactions, thus reducing the computational labor.

The stationarity properties of the ABL functional is, however, somewhat more complicated because it is a functional of two variables. The functional is stationary only if G satisfies Dyson's equation and W satisfies the contracted Bethe-Salpeter equation. This implies that we cannot really expect the error in Ω to be small if we evaluate at an approximate W , unless G satisfies Dyson's equation. And we cannot expect the error in Ω to be small if we employ an approximate G when W does not satisfy Eq. (14). The problem is illustrated by considering the ABL functional at the GW level, denoted ABL- GW . Setting $W=v$, a choice which clearly does not satisfy the contracted Bethe-Salpeter equation, the energy functional reduces to a sum of two terms, $E[G] = E_{\text{HF}}^{\text{LW}}[G] + \Phi_c^{\text{RPA}}[G]$. The term $E_{\text{HF}}^{\text{LW}}$ is the LW functional for the HF energy and is, as mentioned above, quite accurate and insensitive to the input G . The term Φ_c^{RPA} is on the contrary quite sensitive to G . As a numerical example, the correlation energy of Ne will be 81 millihartree lower (more negative) if it is calculated with G_{OEP} instead of G_{HF} . If we instead evaluate the ABL- GW functional at $W=W_{\text{RPA}}$, which is a solution to the contracted Bethe-Salpeter equation, the ABL- GW functional is equal to the LW- GW functional, and the results are indeed insensitive to G as demonstrated in Sec. III. The difference in the correlation energies for Ne calculated with G_{OEP} and G_{HF} is then only 4 millihartree.

In the present work, we have chosen to calculate atomic total energies using a functional Ψ_{2X} that, in addition to the GW diagram, includes also the second-order Ψ diagram. Keeping in mind our ultimate goal of applying the theory to extended systems, we want to avoid evaluating the energy at some complicated screened interaction which might lead to undue computational labor. The simplest possible model W which does not lead to divergent results in extended systems is a simple Yukawa interaction,

$$W^k(r) = \frac{e^{-kr}}{r}. \quad (25)$$

By varying k , we can actually allow W^k to span the whole range of possible screened interactions, i.e., from a nonexistent interaction at $k \rightarrow \infty$ to an unscreened Coulomb interaction at $k=0$. Our choice of screened interaction clearly lacks the proper analytic properties in frequency space and it would certainly have been interesting to use a plasmon-pole-like model as we did for the electron gas. It should be remembered though that our present simple choice is far from unphysical. In fact, nearly all the very successful calculations of excitonic effects in the optical spectra of semiconductors and insulators are based on this simple choice of particle-hole interaction.³⁷ With this choice we hope to be able to find an intermediate value for the parameter k that could simulate the effects of a dynamically screened interaction. The rationale for this hope is, of course, the variational property of the ABL functional with respect to the screened interaction. It turns out that in all our calculations we do find a particular value for k which renders the total energy stationary. This value of k is different for different atoms.

The self-energy and irreducible polarizability corresponding to our approximation Ψ_{2X} are shown in Fig. 4. The first

self-energy diagram is just the statically screened exchange diagram $\Sigma_1^k = -GW^k$. Considering the last term of Eq. (19), we see that the argument in the logarithm defines a Green function

$$\bar{G}^k = [i\omega - \hat{t} - w - V_H - \Sigma^k + \mu]^{-1}. \quad (26)$$

If the screened interaction entering the self-energy Σ^k is changed according to Eq. (25), we can obviously expect \bar{G}^k to change significantly. In the extreme limit of $W \rightarrow 0$, this Green function will describe the solution to the Hartree equations with the self-interaction included, a system which is physically quite unrealistic since the electrons will be pushed away from the nucleus by the dominating Hartree potential. It is important that the chemical potential in Eq. (26) is located such that \bar{G}_k has the correct number of particles. As the eigenvalues of the Hartree equations are much higher than for instance the HF eigenvalues, this implies that μ should be modified as the screening is switched on, in order to preserve the number of particles.

As mentioned above, the grand potential will be more sensitive to the quality of W if G does not satisfy Dyson's equation, but solving Dyson's equation is exactly what we wanted to avoid by employing the variational energy functionals. In order to make the functional more stable, we have therefore chosen to evaluate the ABL functional at the Green function

$$G_{\text{HF}}^k = [i\omega - \hat{t} - w - V_H - \Sigma_1^k + \mu]^{-1}, \quad (27)$$

which is the HF Green function with a statically screened exchange. This Green function is a solution to an approximate Dyson equation in which we have neglected the second-order exchange part of the self-energy. At $W=v$, G_{HF}^k reduces to the ordinary HF Green function, and when $k \rightarrow \infty$, it approaches the Hartree Green function. As mentioned above, the Green function is, in this limit, not very realistic but, more importantly, it does reduce the magnitude of $\delta\Omega/\delta W$.

At G_{HF}^k , Ψ_{2X} becomes

$$\Psi_{2X} = \frac{1}{2} \text{Tr}[\Sigma_1^k G_{\text{HF}}^k] + \frac{1}{4} \text{Tr}[\Sigma_2^k G_{\text{HF}}^k], \quad (28)$$

where the first term on the right-hand side is just the statically screened exchange energy. In addition to calculating the total energy using the ABL functional with Ψ_{2X} , we also calculated the total energy using only the first-order approximation (Ψ_{GW}), for which G_{HF}^k is a self-consistent solution to Dyson's equation. Unlike the LW- GW calculations presented in the previous section, W here has static screening instead of RPA screening. Furthermore, the ABL- GW functional is evaluated at a Green function which satisfies Dyson's equation, whereas the LW functional was previously evaluated at HF and DFT Green functions.

The calculated total energies turned out to be quite stable when changing the statically screened W . Plotting the total energy as a function of the screening parameter k , the ABL functional yields a minimum in the energy curves for both Ψ_{2X} and Ψ_{GW} . This can be seen in Fig. 5 where the correlation energy curves for Ne and Mg are shown. We will refer

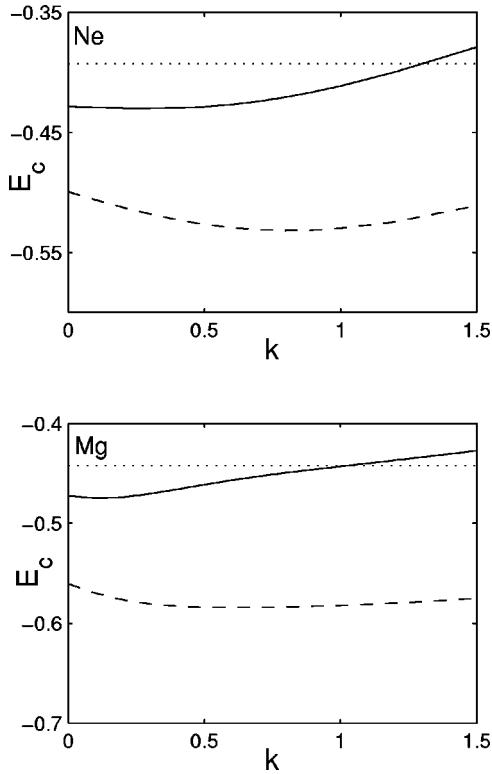


FIG. 5. The sensitivity of the correlation energies for Ne and Mg, to the screening parameter k , calculated using the ABL functional, Eq. (18). The full lines show the energies calculated from the Ψ_{2X} functional, while the dashed lines show the energies from the Ψ_{GW} functional. For comparison, the results from CI calculations (taken from Ref. 32) are also plotted (dotted lines).

to these minimum values as the “true” total energies. Table III contains the minimum values for spherical atoms and ions, together with the results from the LW- GW calculations, results from GGA calculations, and the “exact” correlation energies from CI calculations. The results are now much improved compared to those of the LW- GW functional, although the trend is less dramatic for the smaller atoms.

The insensitivity of the results to the screening at an approximately self-consistent Green function is evident from Fig. 5. It can also be appreciated from the following arguments applied, for simplicity, to the ABL functional taken at the GW level (ABL- GW). If this functional is evaluated at the Green function of the HFA, the difference in the total energies between using a bare Coulomb interaction and one which is dynamically screened within the RPA is, to leading order, an expression of the form

$$E[G_{\text{HF}}, W_{\text{RPA}}] - E[G_{\text{HF}}, v] \approx \frac{1}{2} \text{Tr}[G_{\text{HF}} \Sigma^P G_{\text{HF}} \Sigma^P], \quad (29)$$

where Σ^P is the dynamical part of the self-energy, i.e., that part which vanishes at large frequencies. The numerical value of this term is indeed very small in the atoms we have studied—usually less than 1 millihartree. And it is a manifestly positive quantity meaning that the total energy moves upwards (becomes less negative) when a bare Coulomb interaction is replaced by a dynamically screened one. If in-

TABLE III. Correlation energies for some spherically symmetric atoms and ions. The LW- GW values in the first column are the same as in Table I. The second and third column contains the values from ABL, using Ψ_{GW} and Ψ_{2X} , respectively. The fourth column contains the results from CI calculations. The columns labeled by k_{GW} and k_{2X} are the screening parameters corresponding to the tabulated ABL results. The values of these parameters are those for which the ABL functional is stationary (compare Fig. 5).

Atom	$E_{c,\text{LW}}^{GW}[G_{\text{HF}}]$	$E_{c,\text{ABL}}^{GW}$	k_{GW}	$E_{c,\text{ABL}}^{2X}$	k_{2X}	GGA ^a	CI ^b
He	-0.066	-0.072	0.50	-0.056	0.10	-0.045	-0.042
Be ²⁺	-0.078	-0.081	1.00	-0.053	0.00	-0.039	-0.044
Be	-0.128	-0.144	0.40	-0.120	0.17	-0.088	-0.094
Ne	-0.498	-0.532	0.80	-0.430	0.30	-0.426	-0.390
Mg ²⁺	-0.510	-0.536	1.20	-0.414	0.00	-0.414	-0.390
Mg	-0.560	-0.584	0.60	-0.475	0.11	-0.478	-0.438
Ar	-0.928	-0.963	0.70	-0.779	0.20	-0.734	-0.722
Ca ²⁺	-0.966	-1.020	1.20	-0.807	0.20	-0.766	-0.754

^aUsing the BLYP functional (see Ref. 3).

^bFrom Ref. 32.

stead, the bare Coulomb interaction is replaced by a statically screened one, the energy decreases although the variation with the screening parameter is rather weak as can be seen in Fig. 5. (Note that $k=0$ in Fig. 5 represents a bare, unscreened Coulomb interaction.) Thus, in this respect a statically screened interaction cannot be said to simulate a dynamically screened one.

Note that the expression above [Eq. (29)] is not valid when the energy functional (ABL- GW) is evaluated at, e.g., the Green function of the OEP. The difference in energy between a screened and an unscreened interaction then contains a term which is linear in this difference with a coefficient which is proportional to the difference between G_{OEP} and the self-consistent \bar{G}^k [defined in Eq. (26)]. This difference is large already at $k=0$ and becomes much more pronounced at large screening parameters k corresponding to a negligible exchange interaction. Then \bar{G}^k approaches the Hartree Green function with charge moving away from the nucleus, a situation very different as compared to that described by G_{OEP} . These circumstances will cause a drastic screening dependence when G_{OEP} is used in the evaluation and there is really no natural way of defining a particular value as the proper total energy. The correlation energy at a bare interaction is also rather poor.

Similarly, using G_{OEP} in Ψ_{2X} again results in poor correlation energies and there is then no improvement on the results of the LW- GW functional.

V. SUMMARY AND CONCLUSIONS

Recently proposed variational methods for the total energy of electronic systems were tested a few years ago on the electron gas. The results suggested that very accurate total energies can be obtained at a computational cost so limited

that the application of the methods to systems of practical importance is clearly within reach. Of course, tests on the homogeneous gas say little about the performance of the variational methods in systems with strongly localized electrons. We have, therefore, in the present work, tested these methods in the opposite but realistic case of atoms.

There are two major issues to be discussed in connection with the methods. They are based on MBPT and their accuracy will therefore depend on the set of diagrams one chooses to include in the variational functionals. The diagrams describe different physical processes which might or might not be of importance to the physical system at hand. The second issue is the sensitivity of the variational energy functionals to the use of simple, approximate quantities in their evaluation.

In the homogeneous gas the tests only included terms in the total energy corresponding to a self-consistent GW calculation. Thus, second-order exchange effects were left out of the calculation. Still, the results were very close to those of sophisticated Monte Carlo simulations. This is somewhat surprising in view of the fact that the second-order exchange diagram gives a density independent contribution which is large and quite important at the lower densities. Here, in atoms, we find that the correlation energy of the self-consistent GWA lies about half way between the correct result and the rather poor correlation energies of the RPA. In accordance with the previous work on the gas, we here used what we in the text refer to as the Luttinger-Ward functional as our variational expression. In the gas there was almost no loss of accuracy in evaluating this expression at the very simple noninteracting Green function. We here find, a somewhat larger but still small—less than 10%—variation in the total correlation energies when using a variety of noninteracting Green functions. Based on the vast previous experience of the calculation of atomic and molecular correlation energies we attribute the remaining errors in the atomic correlation energies to the absence of second- and higher-order exchange effects within the GWA.

Total correlation energies of atoms increase rapidly with their size, whereas our main interest lies in an accurate description of correlation effects in binding and reactions. More appropriate tests would thus be the application of the variational methods to, e.g., molecular binding energies. We are presently involved in such investigations which will be reported in due course. In the meanwhile we have here simulated structural changes in calculations of electronic removal energies. These are differences between variational quantities and are thus not themselves variational. Consequently, as our results show, they differ markedly depending on the noninteracting Green function used in their evaluation. The results closest to the experiments—and they are indeed very close—are those obtained from using a HF Green function. It is, however, hard to draw any definite conclusions from this. Are the results good because the LW- GW functional is accurate for the outer valence electrons and the HF Green function is the one which is, in some sense, closest to the self-consistent Green function? Or are they good because the LW- GW functional is inaccurate but the HF Green function is far from the optimal Green function in a way that com-

pensates for the errors in the functional?

In small systems, it would be quite straightforward to include second-order exchange processes based on the bare Coulomb interaction within the framework of the LW functional. We are, however, ultimately interested in extended systems for which an unscreened Coulomb interaction has little relevance. In terms of a dynamically screened interaction within the LW functional, the second-order exchange terms become exceedingly difficult to evaluate in any realistic system. Fortunately, switching to the Ψ formulation of our group, the inclusion of second-order exchange effects comprises adding only one extra diagram. Moreover, already one screened interaction constitutes a difficult problem in, e.g., a solid—let alone the two such factors needed for these effects. Therefore, the variational property of our Ψ formulation with respect also to the screened interaction will be very important because it will allow for the use of model screened interactions such as a plasmon-pole approximation previously and successfully used for the gas. Or even a statically screened interaction which is what we have chosen to test here.

From a simple Taylor expansion of a stationary function of two variables, it is not hard to realize that there will be first-order corrections to the stationary value unless one of the variables lies at or close to the stationary point. In order to be able to use a crude approximation to the dynamically screened Coulomb interaction such as a static Yukawa potential, we have found it essential to use a Green function relatively close to self-consistency. It is, however, adequate to use the HF Green function corresponding to a statically screened nonlocal exchange potential as evidenced by the insensitivity of the resulting correlation energies to the chosen screening parameter of the model interaction. In accordance with our expectations concerning the importance of second-order exchange effects, we obtain substantially better correlation energies when these effects are included.

Seen as *ab initio* calculations of atomic correlation energies, our results are certainly not that impressive. The results are particularly bad for the smaller atoms with errors of the order 10–20 millihartrees amounting to 33% in helium. In particular, they are worse than the atomic correlation energies recently obtained by our group from the exchange-only approximation within time-dependent DFT.³⁸ The latter theory is, however, computationally more demanding in solids and we are, after all, looking for binding energies rather than total energies.

The main results of the present paper can be summarized as follows.

(1) We have demonstrated the feasibility of applying our variational many-body approach to strongly inhomogeneous systems at different levels of approximation with regard to the electron-electron interactions. The computational effort involved is such that the application to real solids is within reach.

(2) We have shown that absolute values for total energies of strongly inhomogeneous systems definitely require the inclusion of second-order exchange effects in the variational functionals.

(3) The results are much more encouraging for valence energies as compared to energies involving also the atomic cores.

(4) The stationary property of the Ψ formalism is not impaired by the use of a simple statically screened electron-electron interaction.

We finally stress once again that our final aim is energy differences, e.g., molecular binding energies, involving mainly valence electrons. This theory is beyond the level of the RPA already at the GW level and can thus clearly describe, e.g., the van der Waals interaction at large interatomic separations. Such results will be reported in a future paper on our variational functionals. We also contemplate using the variational freedom to incorporate hybrid methods in which

beyond RPA effects, i.e., vertex effects, are accounted for through approximate local vertex functions obtained from time-dependent DFT.

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⁴⁰We mention this as an interesting shortcut to the results obtained. The quoted results are evaluated in full.

⁴¹This is likely due to the unphysical eigenenergies of the unoccupied orbitals of the HF approximation.