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Variational Energy Functionals of the Green Function Tested on Molecules

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ABSTRACT: 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. The energy functionals are variational in the sense that they can be evaluated at rather crude approximations to their independent variables, which are the one-electron Green function, or the one-electron Green function and the dynamically screened electron interaction. The functionals were previously applied to the electron gas and shown to be extraordinarily accurate already at the level of the so-called *GW* approximation (GWA). In the current work we have tested the functional due to Luttinger and Ward, which is a functional of the Green function. Using density functional theory (DFT) and Hartree–Fock Green functions as input variables, we have calculated total energies of diatomic molecules at the level of the GWA as well as with second-order exchange effects included. We will also discuss various other variational energy functionals, including DFT orbital functionals based on many-body perturbation theory. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 101: 512–519, 2005

Key words: Green's functions; Luttinger–Ward functional; many-body perturbation theory; orbital functions; variational energy functions

Introduction

The importance and versatility of density functional theory (DFT) due to recent years' progress in the development of powerful computers and more sophisticated energy functionals can hardly be underestimated. Despite this success, there remains a number of well-known problems, most of which can be attributed to the local nature of approximations such as the local density approximation (LDA) and the generalized gradient approximation (GGA). Examples of such shortcomings include systematic errors in cohesive energies and the inability to describe negative ions. In addition, the mentioned methods give no hint as to how to calculate band gaps. It is not obvious how to

overcome these problems, but it seems important to include nonlocality in the approximations. An obvious formalism for including such nonlocal effects is many-body perturbation theory (MBPT), where the central quantity is the one-particle Green function $G(r_1\sigma_1, r_2\sigma_2; i\omega)$, which is a quantity that is more complicated than the electron density. Unlike DFT, MBPT provides a route toward systematic improvement; our approximations can be refined by including additional diagrams. While ab initio methods such as coupled cluster and configuration interaction expansions are also highly accurate methods, the large computational effort involved in these methods make them less interesting for extended systems.

When applying MBPT, either in total energy calculations based on the Green function or as a starting point for constructing orbital-functional schemes in DFT, the most important question is what kind of diagrams to include in our approximations. In other words, which physical processes must be taken into account in order to obtain accurate total energies? The recent interest in the use of variational total energy functionals based on MBPT was triggered by the discovery that self-consistent calculations within the GW approximation [1] give surprisingly accurate total energies for the homogenous electron gas [2, 3]. The computational obstacle in these calculations is to find the Green function by solving the Dyson equation to self-consistency. The appeal of the variational functionals is that they give a possibility to avoid doing this. One example of such variational functionals is the Luttinger-Ward (LW) functional [4], which has the Green function G as input variable. This functional is stationary with respect to variations in G, which means that it can be evaluated at an approximate, simple Green function and produce results that differ little from the self-consistent energies. Applying the LW functional to the homogenous electron gas, giving the noninteracting Green function as input, does indeed work well [5, 6]. After these discoveries, Almbladh, von Barth, and van Leeuwen (ABL) developed a functional of the Green function and the dynamically screened electron interaction W, which would be suitable to use for solids or large molecules [6, 7]. This functional of two variables (G and W) was also tested on the electron gas using a noninteracting Green function and a plasmon pole approximation to W, obtaining results in excellent agreement with the self-consistent GW energies [5].

We recently tested the functionals on atoms, finding results of inferior quality compared with those obtained for the electron gas. By evaluating the LW functional at different DFT and Hartree–Fock (HF) Green functions, we noticed that the results were insensitive to the choice of input G. This could indicate that the results were indeed close to the self-consistent energies. However, the energies obtained at the GW level were significantly too low, typically halfway between the exact energies and the results from random-phase approximation (RPA) calculations. These results indicate that it is necessary to include higher-order exchange contributions. Although the GW approximation may give significant errors in the total energies, this does not imply that the approximation should be discarded. The error in the total energy could be due to the core region, and there is still a possibility of obtaining good binding energies.

Because of the recent interest in variational energy functionals, we start by describing the LW and ABL functionals. In doing this, we stress the difference between the LW functional and other variational energy functionals. We compare these functionals with the frequently used orbital functionals based on MBPT [8–10], which we refer to as the optimized effective potential (OEP) method [11]. The simplest of these orbital functionals is the exchange-only OEP functional [12]. From total energy calculations on the H_2 molecule we demonstrate the difference in the results obtained from the OEP scheme and the results obtained from the LW functional. The RPA total energy curve as a function of the nuclear separation was recently calculated by Aryasetiawan et al. [13] and Fuchs et al. [14], with rather different results.

Finally we compare results of the LW calculations at the GW level with those obtained using a self-energy approximation to second order in the electron interaction, similar to the second-order Møller–Plesset approximation (MP2) [15]. Our calculations on H_2 and LiH confirm our conclusions from calculations on atoms, that higher-order exchange effects must be included in our approximations.

Variational Energy Functionals

The Green function is the solution to the equation of motion (treating G and Σ as matrices with (r, σ) as indices)

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

where $\hat{t} = -\nabla^2/2$, $w(r)$ is the external potential, and μ is the chemical potential. We use atomic units throughout this paper. The effects of the electron interaction are described by the Hartree potential $V_H(r) = \int d^3r' n(r')v(r - r')$ and the self-energy Σ $(r\sigma, r'\sigma'; i\omega)$. The self-energy must then be approximated at some level in perturbation theory. Both V_H and Σ are functionals of G, which means that Eq. (1) must be solved to self-consistency for the given functional $\Sigma[G]$. We use the finite temperature formalism for notational simplicity, letting $T \to 0$ at the end of the calculations. The ground-state total energy E is, at $T = 0$, related to the grand potential Ω according to $\Omega(T \to 0) = E - \mu N$, where N is the total number of particles.

The Green function provides us with the ground-state expectation values of one-particle operators, as well as the total energy, but these values necessarily depend on the choice of approximation for Σ. Baym and Kadanoff [16, 17] showed that a conserving approximation for Σ, that is, 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

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

In an earlier paper, Luttinger and Ward [4] constructed such a functional by summing over all irreducible self-energy diagrams closed with an additional Green function and multiplied by specific numerical factors,

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

The index n indicates number of interaction lines and the index k labels topologically different self-energy diagrams. The trace Tr indices a summation over all indices as well as a frequency integration, $\text{Tr} = \sum_\sigma \int d^3r \int (d\omega/2\pi)$. The simplest examples of conserving approximations are the Hartree ($\Phi = 0$) and the Hartree–Fock approximation. Other examples of Φ-derivable schemes mentioned in Ref. [16] are the GW-approximation [1] and the T-matrix approximation [18]. In the calculations presented here, we have used the GW approximation as illustrated in Figure 1(a) and the second-order approximation shown in Figure 1(b).
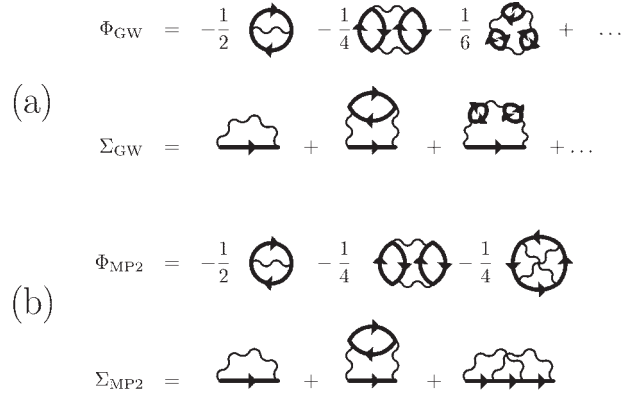

FIGURE 1. The two different approximations to Φ and the corresponding self-energy approximations that we have used in this paper. (a) The GW approximation that corresponds to an infinite sum of bubble diagrams. (b) The approximation where only diagrams to second order are included, labeled "MP2," because these are the diagrams evaluated in MP2 calculations.

The Φ functional was used by Luttinger and Ward for deriving an expression for the total energy. This derivation was based on integration over the interaction strength. A slightly different derivation that relates the functional to DFT is based on the Hamiltonian

$$\hat{H}^\lambda = \sum_{i=1}^{N} \hat{t}_i + \sum_{i=1}^{N} w^\lambda(r_i) + \frac{\lambda}{2} \sum_{i \neq j}^{N} v(r_i - r_j), \qquad (4)$$

where λ is between 0 and 1, v is the electron interaction and the external potential w^λ is such that the electron density remains constant at all λ. At $\lambda = 0$, this potential then corresponds to the Kohn–Sham potential v_{KS}. For a given value of λ, we can define a corresponding Green function G^λ and self-energy Σ^λ. Using the well-known Hellman–Feynman theorem,

$$\frac{d\Omega^\lambda}{d\lambda} = \left\langle \frac{d\hat{H}^\lambda}{d\lambda} \right\rangle = \text{Tr}\left\{\left[\frac{dw^\lambda}{d\lambda} + \frac{1}{2} V_H + \frac{1}{2\lambda} \Sigma^\lambda\right] G^\lambda\right\}, \qquad (5)$$

as well as the relation

$$\frac{d\Phi^\lambda}{d\lambda} = \sum_{n,k} \frac{1}{2n} \frac{n}{\lambda} \text{Tr}[\Sigma_k^{\lambda(n)} G^\lambda] + \text{Tr}\left[\frac{\delta\Phi^\lambda}{\delta G^\lambda} \frac{dG^\lambda}{d\lambda}\right]$$

$$= \frac{1}{2\lambda} \text{Tr}[\Sigma^\lambda G^\lambda] + \text{Tr}\left[\Sigma^\lambda \frac{dG^\lambda}{d\lambda}\right], \qquad (6)$$

we can relate the derivative of Φ to the derivative of the grand potential. Integrating over the interaction strength λ, we obtain the LW functional,

$$\Omega[G] = \Phi - U_0 - \text{Tr}[\Sigma\, G]$$
$$- \text{Tr}\ln(\Sigma - v_{\text{xc}} - G_{\text{KS}}^{-1}), \quad (7)$$

where v_{xc} is the exchange-correlation potential that produces the density $n(\mathbf{r}) = \Sigma_\sigma \int (d\omega/2\pi)G(\mathbf{r}\sigma, \mathbf{r}\sigma, i\omega)$, G_{KS} is the corresponding noninteracting Green function, and $U_0 = (1/2) \int V_H n$ is the classical part of the interaction energy. It is important to realize the difference between the LW functional and other variational functionals that are also sometimes referred to as the LW functional [13, 19]. This difference is discussed below.

The LW functional is stationary with respect to G, because

$$\frac{\delta\Omega[G]}{\delta G} = 0, \quad (8)$$

when G satisfies the Dyson equation $G = G_{\text{KS}} + G_{\text{KS}}(\Sigma - v_{\text{xc}})G$. This suggests that evaluating the functional at some approximate, noninteracting Green function should result in a total energy close to the self-consistent result. The primary reason 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 produce good total energies. The energy of course depends 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. Notice that although Eq. (8) shows that Ω is stationary at the self-consistent G, it does not say that it is a minimum.

The LW functional is based on a perturbation series in terms of the Green function and the bare Coulomb interaction v, but because of the long range of the Coulomb interaction, this is not necessarily the best approach for calculations on solids. Almbladh, von Barth, and van Leeuwen [6, 7] constructed a variational energy functional similar to the LW functional, but where the perturbation expansion is in terms of the screened interaction W

$$\Psi = -\frac{1}{2} \quad -\frac{1}{4}$$

$$-\frac{1}{6} \quad -\frac{1}{6} \quad + \dots$$

FIGURE 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.

rather than v. The screened electron interaction is given by the irreducible polarizability $P[G, W]$ according to the contracted Bethe–Salpeter equation

$$W = v + vPW, \quad (9)$$

which should also be solved to self-consistency. Almbladh, von Barth, and van Leeuwen constructed a functional Φ of G and W, defined by a Legendre-like transformation of the Φ functional

$$\Psi[G, W] = \Phi[G, v[G, W]]$$
$$- \frac{1}{2} \text{Tr}[PW - \ln(1 + PW)]. \quad (10)$$

This functional has the properties

$$\frac{\delta\Psi}{\delta G} = \Sigma \quad \text{and} \quad \frac{\delta\Psi}{\delta W} = -\frac{1}{2} P, \quad (11)$$

which we here present without any further proof. The Ψ functional can also be constructed diagrammatically [7], analogous to the construction of the Φ functional in Eq. (3). The summation is now over skeleton self-energy diagrams (we keep only those diagrams without any polarization insertions). Labeling these diagrams $\tilde{\Sigma}_k^{(n)}$, where n denotes the order in W, the functional is constructed according to

$$\Psi[G, W] = \sum_{n,k} \frac{1}{2n} \text{Tr}[\tilde{\Sigma}_k^{(n)} G]. \quad (12)$$

A few of these diagrams are shown in Figure 2. In this formalism, the GW approximation corresponds to including only the first-order Ψ diagram. Even

though the expansion (12) 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 [7].

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

$$\Omega[G, W] = \Psi - U_0 - \mathrm{Tr}[\Sigma G] + \frac{1}{2}\mathrm{Tr}[PW$$
$$+ \ln(1 - Pv)] - \mathrm{Tr}\ln(\Sigma - v_{\mathrm{xc}} - G_{\mathrm{KS}}^{-1}). \quad (13)$$

This functional is stationary with respect to both G and W, meaning that

$$\frac{\delta\Omega[G, W]}{\delta G} = 0 = \frac{\delta\Omega[G, W]}{\delta W} \quad (14)$$

if $G^{-1} = G_{\mathrm{KS}}^{-1} - \Sigma + v_{\mathrm{xc}}$ and $W^{-1} = v^{-1} - P$.

The form of this functional is not at all unique. It is possible to add any functionals $F[\Sigma - v_{\mathrm{xc}} + G^{-1} - G_{\mathrm{KS}}^{-1}]$ 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. Similar arguments apply to the LW functional. An example of this is the energy functional used by Klein [20], Baym [17], and others [21],

$$\tilde{\Omega}[G] = \Phi - U_0 - \mathrm{Tr}[Gv_{\mathrm{xc}}]$$
$$- \mathrm{Tr}[GG_{\mathrm{KS}}^{-1} - 1] - \mathrm{Tr}\ln(-G^{-1}), \quad (15)$$

which we in the following refer to as the Klein functional. This functional is also stationary

$$\frac{d\tilde{\Omega}[G]}{dG} = 0 \quad (16)$$

when $G^{-1} = G_{\mathrm{KS}}^{-1} - \Sigma + v_{\mathrm{xc}}$. The Klein functional gives the same result as the LW functional if they are both evaluated on the self-consistent G, but for other input G they give quite different results. The Klein functional and the LW functional are thus different functionals of G, and it is unfortunate that this is not always pointed out, for example, in Refs. [13] and [19]. Despite the variational property, Eq. (16), the Klein functional is clearly less stable than the LW functional. For instance, at the GW level, the Klein functional is equal to the RPA energy func-

tional, which has been studied in several papers recently [13, 19, 22, 23]. Approximating Φ as done in Figure 1(b), the Klein functional is equal to the ordinary MP2 energy functional. This functionals is not stable with respect to the input Green function.

It has, however, been noticed that the RPA energies calculated using DFT orbitals are insensitive to the choice of exchange-correlation potential used in the calculation of the input orbitals. It is thus tempting to explain this as a consequence of the stationarity of the Klein functional, but this conclusion is dubious. As shown by Casida [8], the Klein functional is transformed into a density functional by restricting the input Green function to only DFT Green functions. It is then easy to show that this functional is also stationary

$$\frac{\delta\tilde{\Omega}[G_{\mathrm{KS}}]}{\delta v_{\mathrm{KS}}} = 0 \quad (17)$$

when the Kohn–Sham potential is the solution to the OEP equation

$$\mathrm{Tr}[G_{\mathrm{KS}}(\Sigma[G_{\mathrm{KS}}] - v_{\mathrm{xc}})G_{\mathrm{KS}}]=0. \quad (18)$$

This equation should also be solved to self-consistency, because v_{xc} and G_{KS} are functionals of the corresponding density. It is important to keep in mind that the density functional $\tilde{\Omega}[G_{\mathrm{KS}}]$ is not the same as the Klein functional (15) and that the points of stationarity for these two functionals [given by Eqs. (16) and (17), respectively] are not equivalent. We must then ask whether the total energy corresponding to the solution of the OEP equation (18) is similar to the energy obtained from the self-consistent G. In other words, whether $\tilde{\Omega}[G_{\mathrm{KS}}]$ where G_{KS} satisfies the OEP equation (18) is similar to $\tilde{\Omega}[G]$ where G is the self-consistent solution to the Dyson equation. In the exchange-only approximation [12], this is known to be the case, but for other approximations, this is quite questionable. Taking the GW approximation as an example, the DFT–RPA energy corresponding to the solution of the OEP equations can be shown to be a minimum [24]. In all the calculations we have done (on the electron gas, atoms, and a few molecules), this minimum is clearly below the energy obtained from the LW functional. In the case of the electron gas, the RPA energies are well below the self-consistent GW energies (whereas the LW functional gives energies in good agreement with the latter).

Similar to Casida's derivation of the OEP equation, we can derive a DFT scheme by starting from the LW functional rather than from the Klein functional. Defining a density functional by restricting the input G in the LW functional to DFT Green functions, we could search for the Kohn–Sham potential for which this functional is stationary, similar to Eq. (17). The resulting equation for v_{xc} is more complicated than the OEP equation Eq. (18), because it also contains the three-point many-body vertex function and the contracted DFT vertex function. The implementation of such a scheme is deferred to a future publication.

Calculations

In this section we present some of the results obtained for the diatomic molecules H_2 and LiH. These molecules are interesting to study, because their simplicity implies that we can compare our results with several other calculations. In particular, the recent RPA calculations on the H_2 molecule [13, 14] are interesting in this context, because they illustrate some of the properties of the Klein functionals discussed above. The calculations have been performed using a basis set of Slater functions. The convergence of the basis has been checked by performing MP2 calculations and comparing with results from the literature.

The first calculations using the LW and ABL functional were done on the homogenous electron gas within the GW approximation, which gives remarkably accurate total energies. Later, the calculations on atoms indicated that the GW approximation is probably less suitable for a system of localized electrons. Although the total energies were insensitive to the input Green function and the energies improved compared with the RPA values, the energies were not particularly close to the accurate results obtained from CI calculations. Inclusion of second-order exchange effects improved the results considerably. From this experience, we have tested the LW functional on H_2 and LiH using the two approximations shown in Figure 1. As can be seen in Table I, the energies obtained by keeping terms only to second order are better than those obtained from the GW approximation. We also see that the results of using the Klein functional (the RPA and MP2 energies) differ considerably depending on whether they are calculated using the HF or DFT Green function [25].

TABLE I

Total energies of H_2 and LiH at equilibrium separations, calculated from the LW functional, Eq. (7), and the Klein functional, Eq. (15), with LDA and HF Green functions as input.[a]

	H_2	LiH
$E_{LW}^{GW}[G_{HF}]$	−2.379	−16.199
$E_{LW}^{GW}[G_{LDA}]$	−2.357	−16.148
$E_{RPA}[G_{HF}]$	−2.380	−16.201
$E_{RPA}[G_{LDA}]$	−2.421	−16.262
$E_{LW}^{MP2}[G_{HF}]$	−2.332	−16.103
$E_{LW}^{MP2}[G_{LDA}]$	−2.319	−16.078
$E_{MP2}[G_{HF}]$	−2.333	−16.104
$E_{MP2}[G_{LDA}]$	−2.364	−16.151
CI	−2.344	−16.080[b]

[a] The self-energy approximations are illustrated in Figure 1. All energies are in Rydbergs. Accurate results from CI calculations are included for comparison.
[b] Taken from Ref. [25].

In Figure 3, we have plotted the total energies as a function of the nuclear separation. The DFT–RPA curve is in agreement with the results obtained by Fuchs et al. [14] but is lower than the results obtained by Aryasetiawan et al. [13]. In addition to the plotted curve, which is obtained using local density approximation (LDA) orbitals, we have also done calculations using exchange-only OEP orbitals such as those in Ref. [14]. In agreement with the results in the latter paper, we see that this curve differs little from the LDA–RPA curve. This can be explained from the fact that the RPA as a density functional is stationary with respect to changes in the Kohn–Sham potential, Eq. (17). However, if we evaluate the RPA energy using HF orbitals, the figure shows that RPA energies differ considerably from the DFT–RPA results. This reflects the fact that the Klein functional, as a functional of G, is not very stable. Exactly the same features are observed in the RPA calculations on atoms [26, 27]. The fact that the DFT–RPA energy is insensitive to the Kohn–Sham potential of the input orbitals indicates that these results are close to the solution of the OEP equations. It does not mean that we are close to the self-consistent GW energy. The energies obtained from the LW functional are less sensitive to the Green function that is used in the evaluation. The functional is, however, much more sensitive to the input G than we observed in the atomic calculations [26, 27], where we could see only tiny variations in the total energy (for He, the energies differ by less
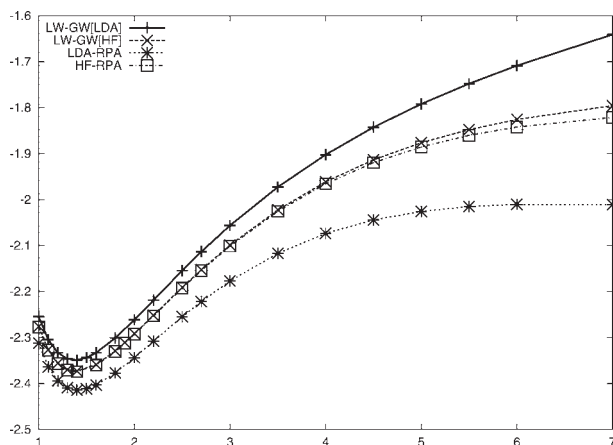
FIGURE 3. Total energy (in Rydbergs) of the H_2 molecule as a function of the nuclear separation. Results of the LW functional with the HF Green function as input differs little from the HF–RPA curve, whereas the LW functional with G_{LDA} as input has a large correction to the RPA energy.

than 4 milli-Hartree, whereas for Ca, the maximum deviation was 40 milli-Hartree). For the molecules, the sensitivity of the LW functional to the input Green function is larger at large separation. This reflects the fact that the chosen form of the input Green function becomes quite unphysical at large separations. It is interesting to note that although the energies obtained using the LW functional and LDA Green functions differ significantly from the LDA–RPA energies, the LW and RPA energies give practically the same result when they are both evaluated on G_{HF}. The same feature was observed in the atomic calculations [26, 27].

Although the calculations on atoms and molecules clearly indicate that GW does not give accurate total energies on systems with localized electrons, it is important to keep in mind that we are mainly interested in total energy differences. It has been noted that while DFT–RPA calculations give poor total energies, the binding energies are quite good [13, 14, 22]. It is, however, not obvious how the binding energies should be calculated. For instance, if the total energy curves shown in Figure 3 would be extended to infinitely large separations, the energy would most likely not converge to the energies obtained from calculations on two separate atoms. If we instead choose to calculate the total energies of an isolated (spin-polarized) H atom, the binding energy defined by $\Delta = 2E(H) - E(H_2)$ is accurately described by DFT–RPA calculations. Using LDA orbitals as input, binding energies

of H_2 are shown in Table II. Clearly, the best binding energies are obtained from DFT–RPA calculations, despite that fact that this is the method that gives the poorest total energies among the four methods considered.

Conclusions

The use of variational energy functionals based on MBPT is still in a pioneering stage, but many things have already been learned. Although the lack of self-consistent calculations on atoms and molecules makes it difficult to draw conclusions with absolute certainty, the results indicate that the GW approximation does not give accurate total energies for systems with localized electrons. The relation between the GW approximation and the DFT–RPA calculations is interesting, because the latter calculations appear to produce worse total energies but better binding energies. However, the minimum of the DFT–RPA energy does not appear to be near the self-consistent GW results. Although LW calculations on the homogenous electron gas and on atoms and small molecules are quite straightforward, there are still technical questions on how to make the implementation as effective as possible. As the calculations on diatomic molecules demonstrate, it is also necessary to have a better understanding of what constraints to put on the Green functions that are used as input to the variational functionals. In future work, the effects of the various self-energy approximations will be studied in detail. We are also developing an OEP scheme based on the LW functional rather than on the Klein functional. Our calculations so far indicate that, unlike traditional OEP calculations, these density functionals will produce total energies close to the self-consistent values.

TABLE II _____

The binding energy (in Rydbergs) of H_2, calculated by using the LDA Green as input to the energy functionals.[a]

$E_{LW}^{GW}[G_{LDA}]$	$E_{RPA}[G_{LDA}]$	$E_{LW}^{MP2}[G_{LDA}]$	$E_{MP2}[G_{LDA}]$
−0.315	−0.347[b]	−0.320	−0.367

[a] The energies should be compared with the exact result of −0.349 Ry.
[b] To be compared with the value 0.347 from Refs. [14] and [22].

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