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Variational second-order Møller–Plesset theory based on the Luttinger–Ward functional

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In recent years there have been some rather successful applications of a new variational technique for calculating the total energies of electronic systems. The new method is based on many-body perturbation theory and uses the one-electron Green function as the basic "variable" rather than the wave function of traditional variational calculations. It is the purpose of the present work to promote the new methods within the realm of traditional theoretical chemistry by demonstrating their utility for calculating the correlation energies of a number of atoms at a level corresponding to second-order Møller–Plesset perturbation theory. The generalization to any desired order of perturbation theory is not hard to accomplish.
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I. INTRODUCTION

The last several years have seen several attempts to calculate the total energies of electronic systems from variational functionals constructed from many-body perturbation theory. Within these methods, the quantity which is varied is not the traditional wave function but rather the one-electron Green function and, sometimes, the dynamically screened Coulomb interaction. The ideas behind these new techniques were put forth in the 1960s[1] when field theory moved into the area of many-electron physics. The originators of the methods did, however, not appreciate the computational advantages of the variational techniques and the latter remained unused until some seven years ago. In 1996/97 our group[2,3] proposed and demonstrated the feasibility of an improved version of these variational techniques particularly suited to large molecules and solids. The essence of these "second generation" functionals consists in using the dynamically screened interaction as an independent variable in addition to the one-electron Green function. After all, in any more extended system the singularities associated with the infinite range of the Coulomb interaction has to be removed by proper screening—a necessity arising already in larger molecules.

Shortly after, the new techniques were tested by some of us[4] in a calculation of the total energy of the interacting electron gas. From a very limited computational effort, they obtained correlation energies for this model system, which were very close to those of very elaborate Monte Carlo simulations. There are two major issues of concern in the construction of the functionals. One is the level of perturbation theory on which they are based. This choice governs which physical processes are allowed to influence the results and to which order in perturbation theory the corresponding effects are accounted for. In the calculation on the gas just mentioned, Hindgren and Almbladh[4] only included effects associated with a linear but dynamic screening of the usual Hartree–Fock (HF) exchange [known as the GW approximation[5] (GWA)]. Their very accurate results are, therefore, somewhat surprising in view of the knowledge that second-order exchange effects give a substantial contribution to the correlation energy also of the gas—especially at the lower densities. The second important issue in connection with the new functionals is their variational quality. The simplest version of the functionals have only one independent variable, the one-electron Green function, and they are stationary at the Green function which solves Dyson's equation. The latter solution is computationally very demanding to obtain in a larger system and the whole idea behind the variational functionals is to evaluate them at an approximate and perhaps noninteracting Green function and still obtain an energy not far from the stationary value. The latter is then assumed to be a very accurate total energy, which, as we just mentioned, depends on the chosen level of perturbation theory. In atomic and molecular calculations, the approximate noninteracting Green function is conveniently described in terms of a basis set, which, in view of the stationary property, could be of a rather poor quality without compromising the results.

The very accurate correlation energies obtained from the new functionals applied to the homogeneous electron gas led to a desire to test the functionals also in very inhomogeneous systems. Thus, we recently[6,7] applied these techniques to a series of atoms. To summarize our results, we found, not surprisingly, that the inclusion of only first-order screened exchange (GW) was inadequate in these systems with very localized electrons. For that case, the calculated correlation energies were approximately halfway between the correct results and the results of the random phase approximation (RPA) which, in turn, are almost a factor 2 too large, at least for the smaller atoms like He and Be. In this context, the term RPA refers to the time-dependent Hartree approximation in the same way as RPAE refers to a time-dependent

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Hartree–Fock (HF) calculation. The total energies are then obtained by integrating over the strength of the Coulomb interaction. The inclusion also of second-order exchange effects led to a marked improvement of the correlation energies. Except for the lightest atoms, the accuracy of our calculated correlation energies were of the order of 10%. We also found a somewhat larger sensitivity of the calculated energies to the choice of approximate Green function used in their evaluation, i.e., in comparison to the case of the gas.

Compared to the energies routinely obtained for these systems from a variety of methods within theoretical chemistry, our results were not that impressive. In the mentioned work we were, however, interested primarily in extended systems, mainly solids, and in the energies associated with the rearrangements of valence charge. Thus, our calculations also for the atoms were carried out using the dynamically screened Coulomb interaction although we sometimes approximated this quantity using a statically screened interaction. This also means that our accurate calculations were carried out within the framework of the ''second generation functionals'' using also the screened interaction as an independent variable. In this perspective, we consider our previously obtained results as very promising for quantities like, e.g., the binding energies of molecules adsorbed on metal surfaces. We are already continuing along this road toward molecular binding energies but this is not the topic or the purpose of the present article. It is well known that within perturbation theory there are large cancellations between the diagrams which can be considered as responsible for the physical process of screening, and those which describe the particle–hole interactions, i.e., the vertex diagrams. In an extended system like the electron gas, the screening of the Coulomb interaction is by far the most dominant correlation effect and must, in fact, be treated to infinite order in order to yield reasonable results (see the following). The vertex effects are not negligible but can be treated to low order—provided very localized electrons are not involved in the problem of interest. In systems with mainly localized electrons such as atoms and smaller molecules that one has to rely on the cancellations between screening and vertex effects to obtain good results. Thus, it becomes advantageous to treat these major effects to the same order in perturbation theory. For the reasons discussed earlier, this principle was violated in our tests on atoms. In the present work we will adhere to this principle in an attempt to introduce the concept of variational energy functionals into the realm of quantum chemistry. We will thus work to a particular order in the bare Coulomb interaction and actually not go beyond second order. Consequently, the physical content of the theory presented here will be similar to that which in the quantum chemistry literature is known as second-order Møller–Plesset (MP2) perturbation theory.[8] The difference is that our variational scheme is a perturbation expansion in terms of the Coulomb interaction and the self-consistent Green function, while the conventional MP2 scheme is based on an expansion in terms of the Coulomb interaction and the HF Green function. The variational scheme allows us to obtain the second-order results at a smaller computational cost, and the principles laid down here are readily extended to any desired order of perturbation theory, e.g., to fourth-order Møller–Plesset theory.

In Sec. II we will present the basic formalism without giving too many details. For a more comprehensive treatment we refer to our previous articles on this topic.[2,3,6] We then present our MP2-like correlation energies for a number of atoms calculated from different approximate noninteracting Green functions. Finally, we will discuss our results and how the variational techniques can be generalized to higher order of perturbation theory. We will also discuss possible ways of improving the variational quality of the functionals in order to further reduce the computational labor.

II. BASIC THEORY

The basic variable of the original variational functional due to Luttinger and Ward (LW) is the one-electron Green function, which from the basic equation of motion for the field operators can be shown to obey Dyson's equation,

$$[i\omega-\hat{t}-w-V_H+\mu]G=1+\Sigma G. \tag{1}$$

While Green functions have been used extensively in quantum chemistry,[9–11] the formalism has, with some exceptions,[12–15] mainly been used to compute excitation energies rather than total ground state energies, a fact which is reflected in these authors' choice of approximations to Σ. The variational energy functionals, which is the topic of this paper, have not been used before and we will therefore start by presenting them briefly. The formulas presented here are mainly meant as illustrations to the basic line of thought and are not intended as exact derivations. Thus, in Eq. (1), all quantities are matrices with rows and columns labeled by space and spin coordinates, they all depend on the imaginary frequency $i\omega$ as well as the temperature T, which eventually will be allowed to go to zero. On the left-hand side, the quantity $\hat{t}$ is the usual operator $-\nabla^2/2$ for the kinetic energy, w is the external potential which, for an atom or molecule, is just the sum of the Coulomb potentials from the nuclei, $V_H(\mathbf{r})=\int d^3r' n(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')$ is the Hartree-potential meaning the classical Coulomb potential $[v(\mathbf{r})=1/r]$ from the all-electron charge density $n(\mathbf{r})$ and, finally, μ is the chemical potential of the system which ensures that it has the correct number of electrons as calculated from the Green function G. On the right-hand side, the quantity Σ is known as the irreducible self-energy of the system. From the rules of the Feynman diagrams, Σ is a functional of the Green function G and the bare Coulomb interaction v to arbitrary orders in perturbation theory.

In the present work we restrict ourselves to a discussion of the original LW energy functional mainly for two reasons: (1) this functional is defined in terms of the bare Coulomb interaction as opposed to the screened interaction, a property consistent with the treatment of physical effects to a particular order in the bare interaction, and (2) in previous calculations[4,6] we have found this functional to be relatively stable with respect to the choice of Green function used for its evaluation. We should, however, mention already here that there is nothing unique about this functional. It is relatively easy to invent other functionals with different varia-

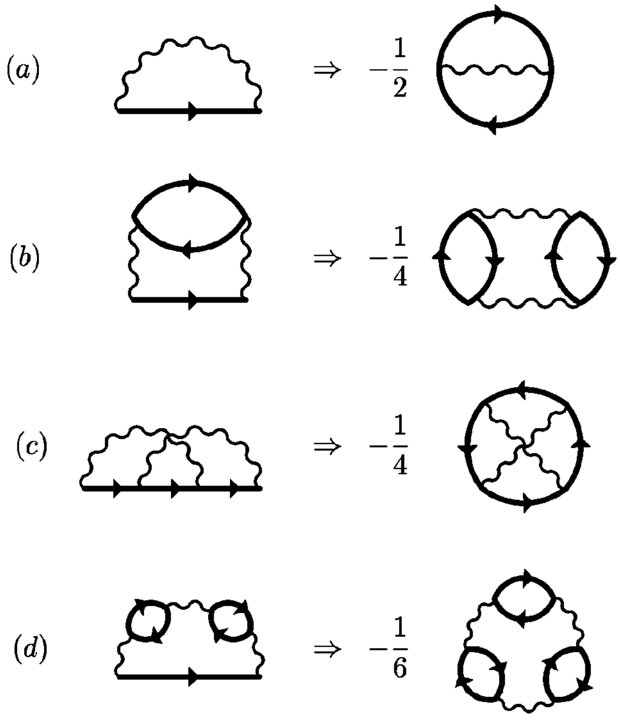

FIG. 1. It is shown how the Φ functional is constructed by closing irreducible self-energy diagrams with a Green function line and multiplying with an appropriate prefactor. All of the first- and second-order diagrams and one of the many third-order diagrams are shown.

tional qualities and it would be an interesting topic for future research to find more optimal choices. We will return to this point in the last section.

The basic quantity of the LW functional is the functional $\Phi[G]$ giving the self-energy $\Sigma[G]$ from the relation

$$\Sigma=\frac{\delta\Phi}{\delta G}. \tag{2}$$

The rule for obtaining this quantity was given in the original paper by LW and can be stated as follows. Take all skeleton self-energy diagrams $\Sigma_k^{(n)}$ of a particular order n in v, close each diagram with a Green function G and integrate over all variables (we will here designate the latter operation with the symbol Tr for trace in keeping with earlier works). Divide each thus obtained diagram by the factor $2n$ and sum all contributions to infinite order. Formally,

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

The construction is illustrated in Fig. 1 for the lowest orders. Examples of Φ-derivable approximations include the Hartree ($\Phi=0$) and the Hartree–Fock approximation [Fig. 1(a)]. In this paper we study the second-order approximation obtained by including all first- and second-order diagrams [Figs. 1(a)–(c)]. The GW approximation[5] is also Φ-derivable and is obtained from the sum of the diagram in Fig. 1(a) and all of the ring diagrams [Figs. 1(b) and 1(d), etc.] to infinite order. Note that in these diagrams, the Green function lines represent the self-consistent solution to the Dyson equation for the corresponding Φ. This procedure for obtaining self-energy approximations differs from those commonly used in quantum chemistry where Σ is frequently obtained from response functions,[9,10,14] or diagrammatic expansions using a three-particle propagator.[16] As mentioned earlier, it appears that for systems of very localized electrons it is necessary to treat screening and vertex effects to the same order. The second-order approximation is therefore more appropriate than the GWA for calculations on atoms.

Using the functional Φ we here directly write down the resulting LW functional $\Omega_{\mathrm{LW}}[G]$, which reads

$$\Omega_{\mathrm{LW}}[G]=\Phi[G]-U_0-\mathrm{Tr}\{G\Sigma[G]\}$$
$$-\mathrm{Tr}\ln\{\hat{t}+w+V_H+\Sigma[G]-\mu-i\omega\}, \tag{4}$$

where the term $U_0=\frac{1}{2}\int nV_H$ is the classical part of the interaction energy. The quantity Ω_{LW} is actually the grand canonical potential which might appear as the use of excessive force in an atom or a molecule with a fixed number of particles at zero temperature. The full formalism of equilibrium statistical many-body physics is, however, often much easier to handle and the formalism looks more appealing as compared to, e.g., the zero-temperature technique. When the temperature tends to zero, Ω becomes the ordinary total energy except for an additive constant equal to $-\mu N$ where N is the total number of electrons.

We can rather easily see this [Eq. (4)] from the Hellman–Feynman theorem applied to a multiplicative factor λ in front of the Coulomb interaction v, $v\rightarrow\lambda v$. Let us differentiate Φ with respect to λ. In each diagram making up Φ, there is an explicit power-law dependence on λ plus an implicit dependence through the Green function G. Differentiating with respect to the explicit dependence removes the $1/n$ factors in front of the diagrams resulting in a sum equal to the full self-energy divided by 2λ. Thus,

$$\frac{d\Phi}{d\lambda}=\frac{1}{2\lambda}\mathrm{Tr}[G\Sigma]+\mathrm{Tr}\left[\Sigma\frac{dG}{d\lambda}\right], \tag{5}$$

where we have also used Eq. (2). Now, differentiating also the logarithm in Eq. (4), we can use Dyson's equation [Eq. (1)] to obtain

$$-\frac{d}{d\lambda}\mathrm{Tr}\ln\{\hat{t}+w+V_H+\Sigma[G]-\mu-i\omega\}$$
$$=\mathrm{Tr}\left\{G\left[\frac{d\Sigma}{d\lambda}+\frac{dV_H}{d\lambda}\right]\right\} \tag{6}$$

from this term. Finally we see that the λ derivative of U_0 is just $\mathrm{Tr}[n\,dV_H/d\lambda]-U_0/\lambda$ and, adding everything up, we obtain

$$\frac{d\Omega_{\mathrm{LW}}}{d\lambda}=\frac{1}{2\lambda}\mathrm{Tr}[G\Sigma]+\frac{1}{\lambda}U_0, \tag{7}$$

where we have also used the fact that the Green function gives the electron density according to $n(\mathbf{r})=\int(d\omega/2\pi)e^{i\omega\delta}\sum_{\sigma,\sigma'}G(\mathbf{r}\sigma,\mathbf{r}\sigma',i\omega)$. Now, the right-hand side of this equation is just the ground-state expectation value of the interaction energy divided by λ, i.e., the expectation value of the λ derivative of the Hamiltonian and, thus, the λ derivative of the ground-state energy according to the

Hellman–Feynman theorem. Consequently, except for some λ-independent constant to be determined when $\lambda=0$, Ω_{LW} is the λ-dependent total energy. When $\lambda=0$, Ω_{LW} from Eq. (4) reduces to

$$\Omega_{\mathrm{LW}}(\lambda=0)=-\mathrm{Tr}\ln[\hat{t}+w-\mu-i\omega]. \tag{8}$$

This expression can, after some manipulations, be shown[1] to be the total energy minus μN of N noninteracting electrons all moving in the external potential w. This completes the demonstration that the functional given by Eq. (4) actually represents the total ground-state energy of the many-electron system.

It is also not difficult to see the variational property of the LW functional. If we evaluate the LW expression at some approximate Green function, we can study the resulting error in the energy. We must then, certainly, account for the fact that all of the quantities appearing in Eq. (4) are functionals of the Green function, like the self-energy Σ or the density n. We obtain

$$\begin{aligned}\delta\Omega_{\mathrm{LW}}=\mathrm{Tr}\Bigg\{&\frac{\delta\Phi}{\delta G}\,\delta G-\Sigma\,\delta G-G\,\delta\Sigma-V_H\delta G-[\hat{t}+w\\&+V_H+\Sigma-\mu-i\omega]^{-1}[\delta\Sigma+v\,\delta G]\Bigg\}.\end{aligned} \tag{9}$$

Using the fact that $\Sigma=\delta\Phi/\delta G$ we can see that $\delta\Omega_{\mathrm{LW}}=0$ whenever

$$G=[i\omega-\hat{t}-w-V_H-\Sigma+\mu]^{-1}, \tag{10}$$

i.e., whenever G is a solution to Dyson's equation. Thus, first-order errors in the Green function produce second-order errors in the energy. While Green functions have earlier been used in total-energy calculations for atoms and molecules, the energies have been obtained from them through the use of the Galitskii–Migdal formula.[17] There are, however, many other ways of calculating the total energy from a given G which could give different results unless this G was a self-consistent solution of the Dyson equation for a Φ-derivable self-energy.[18] In the mentioned earlier work,[12–15] the Green function was not calculated self-consistently and the resulting energies therefore depended on the choice of reference state. There is no such ambiguity in our variational approach, and the energies should only depend on the choice of Φ diagrams.

At this stage, the whole procedure should be transparent. Guided by physical intuition concerning which processes are important for the system under study, one decides to include a set of skeleton self-energy diagrams. From these, one constructs the Φ functional according to the LW recipe. We remark that this process might lead to additional self-energy diagrams according to Eq. (2). Should this be the case, these diagrams must, of course, be included in the total self-energy. Then all occurrences of the Green function G are replaced by some approximate and easy-to-calculate Green function—preferably a noninteracting one like a Hartree–Fock or a density-functional Green function—and the LW expression is evaluated. We note that it is important not to, e.g., use Dyson's equation to remove the self-energy in favor of the Green function G before the evaluation is carried out. This will destroy the nice variational property of the LW expression.

III. SECOND-ORDER THEORY

We here present total energies calculated using the LW-functional (4), including the diagrams up to second order in the Φ functional. These are the diagrams (a–c) in Fig. 1. The first-order Φ diagram is just the exchange energy, and we therefore write $\Phi=\Phi_x+\Phi_c$ to single out the correlation part of the Φ functional. Evaluating the functional at a set of noninteracting Green functions gives an indication of the stability of the LW functional, as well as suggesting the value of the self-consistent second-order correlation energy. When evaluating the logarithmic term in the LW functional, it is necessary to take care of the terms that are static and will cause the frequency integral to diverge. For this purpose, it is convenient to define a new Green function $\tilde{G}$ according to

$$\tilde{G}^{-1}=i\omega-\hat{t}-w-V_H-\Sigma_x[G]+\mu, \tag{11}$$

where V_H and $\Sigma_x[G]$ are the Hartree-potential and the exchange self-energy [shown in Fig. 1(a)]. Using $\tilde{G}$, the logarithm can be written

$$\begin{aligned}-\mathrm{Tr}\ln\{&\hat{t}+w+V_H+\Sigma[G]-\mu-i\omega\}\\&=-\mathrm{Tr}\ln\{-\tilde{G}^{-1}+\Sigma_p[G]\},\end{aligned} \tag{12}$$

where Σ_p is defined as the dynamic part of the self-energy, $\Sigma_p=\Sigma-\Sigma_x$. When the LW functional is evaluated at a noninteracting G, $\tilde{G}$ represents the first iteration toward the Hartree–Fock Green function. Using $\tilde{G}$, the functional can be rewritten as

$$\begin{aligned}\Omega_{\mathrm{LW}}[G]=&\Phi_x[G]+\Phi_c[G]-U_0\\&-\mathrm{Tr}\{G\Sigma[G]\}-\mathrm{Tr}\ln\{-\tilde{G}^{-1}+\Sigma_p[G]\}\\=&\Phi_c[G]-U_0-\Phi_x[G]-\mathrm{Tr}\{(G-\tilde{G})\Sigma_p[G]\}\\&-\mathrm{Tr}\ln\{-\tilde{G}^{-1}\}-\mathrm{Tr}\{\tilde{G}\Sigma_p[G]\\&+\ln[1-\tilde{G}\Sigma_p[G]]\},\end{aligned} \tag{13}$$

where we, in the last step, have also used the fact that $\Phi_x[G]=\frac{1}{2}\mathrm{Tr}[\Sigma_x G]$. When this expression is evaluated at a noninteracting Green function, the term $-\mathrm{Tr}\ln\{-\tilde{G}^{-1}\}$ is just the sum over the occupied eigenvalues of $\tilde{G}$, and an additional constant term, $-\mu N$.

While the LW functional is stationary when evaluated at a self-consistent G, it is not obvious that it has a minimum at this point. It is therefore interesting to see how the results differ when the functional is evaluated at various approximate Green functions. As a particular example, we can consider evaluating the functional at the Hartree–Fock Green function G_{HF}. In this case $\tilde{G}$ becomes $G=G_{\mathrm{HF}}$, and the energy functional $(E=\Omega+\mu N)$ simplifies to

$$\begin{aligned}E_{\mathrm{LW}}[G_{\mathrm{HF}}]=&E_{\mathrm{HF}}+\Phi_c[G_{\mathrm{HF}}]-\mathrm{Tr}\{G_{\mathrm{HF}}\Sigma_p[G_{\mathrm{HF}}]+\ln(1\\&-G_{\mathrm{HF}}\Sigma_p[G_{\mathrm{HF}}])\}.\end{aligned} \tag{14}$$

Here, the term E_{HF} is the usual HF energy given by

TABLE I. Correlation energies for some spherically symmetric atoms and ions. The energies are in hartrees. The results of conventional MP2 calculations differ with less than a millihartree from the numbers in the column labeled $E_c^{\mathrm{LW}}[G_{\mathrm{HF}}]$ and are therefore not included.

	$E_c^{\mathrm{LW}}[G_{\mathrm{OEP}}]$	$E_c^{\mathrm{LW}}[G_{\mathrm{LDA}}]$	$E_c^{\mathrm{LW}}[G_{\mathrm{HF}}]$	CI[a]
He	−0.035	−0.034	−0.037	−0.042
Be^{2+}	−0.041	−0.040	−0.041	−0.044
Be	−0.038	−0.028	−0.074	−0.094
Ne	−0.363	−0.348	−0.378	−0.390
Mg^{2+}	−0.365	−0.361	−0.372	−0.390
Mg	−0.379	−0.373	−0.410	−0.438
Ar	−0.650	−0.641	−0.685	−0.722

[a] Taken from Ref. 22.

$$E_{\mathrm{HF}} = \mu N - \mathrm{Tr}\ln[-G_{\mathrm{HF}}^{-1}] - \Phi_x[G_{\mathrm{HF}}] - U_0 . \tag{15}$$

If the logarithmic term in Eq. (14) can be neglected, then this expression reduces to evaluating the term Φ_c at the HF Green function. This is equivalent to evaluating the second-order Møller–Plesset correlation energy.[8,9] This connection can be made only if the last term of Eq. (14) can be neglected, which is not true in general. For the atomic systems in our calculations, however, this term is quite small, usually less than a millihartree.

In Table I, we show the correlation energies calculated from the LW functional for a few spherically symmetric atoms. The functional was evaluated using HF and density functional Green functions, where the orbitals were expanded in a set of Slater functions.[19] The DFT Green functions were calculated using both the local density approximation (LDA) and the exchange-only optimized effective potential (OEP) method.[20] We see that, with an exception for Be, the energies are relatively insensitive to the choice of input G. For all atoms, the lowest value is obtained when the functional is evaluated at G_{HF}. The results for G_{HF} are (as could be expected) quite close to results obtained from MP2 calculations, and also close to the exact correlation energies obtained from configuration interaction calculations. If the LW functional has a minimum at the self-consistent G, this indicates that the MP2 results are in fact close to the self-consistent second-order correlation energies.

Since our main interest was to study the LW functional and its relation to MP2 calculations, the stability of the functional was tested by changing the one-particle Green function, rather than varying the basis sets. The HF and DFT orbitals are expanded in the same basis set, and the Green functions differ only in the one-particle Hamiltonians they are generated from. It would, however, be possible to study the variational properties of the LW functional also with respect to the size of the basis set. In this case, the above-mentioned manipulations involving $\tilde{G}$ are not valid, since the definition of $\tilde{G}$ in Eq. (11) assumes that it is expanded in an infinite basis. When the input single-particle Green function is given in a limited basis set, it is no longer true that $\tilde{G} = G$ when the energy is evaluated at G_{HF}.

IV. CONCLUSION

The purpose of the present work is to suggest an alternative way of calculating correlation energies in atoms and smaller molecules. As an illustration, we have here chosen to obtain correlation energies of atoms to second order in the bare Coulomb interaction. This level of accuracy is usually referred to as MP2 theory in the quantum chemistry literature. In contrast to this theory, the scheme we propose involves an infinite number of additional Feynman diagrams which are not intended to add to the physical quality of the results but rather to render the theory variational, i.e., to make it much less sensitive to the choice of basis set or to the underlying zeroth order Hamiltonian. From the ideas presented here it is not difficult to invent a variety of variational schemes of different quality with regard to accuracy and stability. In the present work we, however, limit ourselves to the study of the variational functional due to Luttinger and Ward from 1960—and we take this functional to the MP2 level. This does not mean that we will reproduce the ‘‘proper’’ MP2 results of previous workers. Instead, the functional is designed to yield the total energy produced by the self-consistent Green function obtained from a Dyson equation in which the self-energy is calculated to second order in the bare Coulomb interaction using that same Green function. And it is understood that the total energy produced by a particular one-electron Green function is that which obtains from applying the Galitskii–Migdal[17] formula to it. Including, as we do here, all skeleton self-energy diagrams of second order, it seems appropriate to label the resulting energy the ‘‘self-consistent MP2’’ energy. This could be either above or below the ‘‘proper’’ MP2 energy obtained from straightforward perturbation theory starting from HF. Assuming for a moment the good variational properties of the LW functional (small second functional derivative with respect to the Green function G), we can obtain the self-consistent MP2 energy by evaluating the LW functional at the HF Green function. (Notice that the latter only differs from the self-consistent Green function by terms of second order in the Coulomb interaction and that thus the error we make in this procedure is of fourth order.) But, as seen from Eq. (14), we then obtain an energy which is a negligible amount (less than 1 mhartree) above the traditional MP2 energy. This is actually a strong argument for expecting a very high quality of the MP2 energies, much higher than one has any right to expect from a simple perturbation expansion. Self-consistent total energies tend to be very accurate although they might leave out important physical effects. This is due to a cancellation of errors occurring because of the conserving properties of self-consistent theories. The latter property implies that many physically different ways of calculating the total energy, (the GM formula, integration over the strength of the Coulomb interaction, integration with respect to the number of particles, etc.) all produce the same total energy, leaving very little room for errors.

Although we have not yet been able to prove in a strict sense that the stationary point of the LW functional is actually a minimum, our present and previous experience suggests that it is. Should this conjecture be correct, our discussion above based on Eq. (14) suggests that the self-consistent

MP2 energies should be slightly below the traditional ones but not by much. In fact, the difference should be of fourth order in the Coulomb interaction.

As mentioned earlier, our actual LW-MP2 energies displayed in Table I are some millihartrees above the traditional MP2 results. And due to the very small contribution of the last term in Eq. (14), the ‘‘conventional MP2’’ energies differ by less than a millihartree from the LW results obtained using a HF Green function. Due to the use of a less sophisticated basis set, these results are slightly above the MP2 results found in the literature.[21] We have actually not attempted to optimize our basis sets. Instead we have here studied the variational quality of the LW expression by evaluating the total energy using several noninteracting Green functions including two from density-functional theory. We find again (see Table I) that the LW functional is remarkably stable with respect to the choice of input Green function. The fact that our results are rather close to the very carefully obtained traditional MP2 energies, strongly support the use of our variational procedures in these systems.

The stability of the LW functional with regard to the quality of the basis set is an interesting topic for further investigations. In this context, we stress the importance of formulating the use of a limited basis set in terms of an approximate Green function in order to be protected by the variational property when evaluating the functional. It would, e.g., be impermissible to implicitly consider the basis to be complete in some parts of the variational expression and to be of poorer quality in other parts of the expression. We hope to be able to sort out these intricacies in a later publication in which we would also like to address the binding energies of smaller molecules. It is, e.g., known that traditional MP2 theory fails for the standard test problem of the hydrogen molecule at large separation. There are, however, some indications[15] that a self-consistent treatment will give reasonable results for this famous case, and that, therefore, the LW functional would be both accurate and easy to apply to calculations of the energy surfaces of molecules.

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