

Total Energy Method from Many-Body Formulation

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The fruitfulness of traditional many-body Green's function theory for calculating the total energy of real systems is demonstrated using the random phase approximation in the Luttinger-Ward formulation. As the first application to a real system, the total energy of H₂ is calculated as a function of nuclear separation and compared with the configuration interaction and the local density approximation results. While the local density result is in large error for large separations, the present approach gives satisfactory agreement with the configuration interaction results. The method is promising as an alternative to the quantum Monte Carlo technique.

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Total energies of electronic systems are undoubtedly one of the most important quantities in material science since total energies determine the structural properties of materials. The most widely used total energy method is the density functional theory [1] within the local density approximation (LDA) [2] or the generalized gradient approximation (GGA) [3]. These approximations have proven to be highly successful for many materials. However, there is evidence that these methods are not sufficiently accurate for a number of cases. A serious problem is revealed in the case of strongly correlated materials involving the presence of *3d* elements where LDA (or GGA) *qualitatively* fails in predicting the structure of many of these materials. To cite some examples, LaMnO₃, a material famous for its colossal magnetoresistance, and La₂CuO₄, a well-known high temperature superconducting parent compound, are predicted to be metals by LDA, whereas experimentally they are antiferromagnetic insulators [4]. In addition, there are systematic errors of quantitative nature. For example, cohesive energy is overestimated and the activation barrier of chemical reactions is usually underestimated. Thus there is a strong need for an improved practical total energy method. Quantum Monte Carlo (QMC) technique is one such method. This method is accurate but computationally demanding.

In this paper, a scheme based on the traditional many-body Green's function technique is introduced. It is not meant as a replacement for LDA, but rather it is intended as an alternative to QMC. This type of approach has remained dormant for several decades due to the lack of computational tools. With the rapid progress in computer technology, it is now timely to reconsider this more traditional approach. Interest in this approach was rejuvenated recently by a pioneering work of von Barth *et al.* [5] for the electron gas. They discovered that, in the *GW* approximation [6,7], the total energy of the electron gas is of comparable accuracy to that of the QMC. Equally important, Almladh *et al.* [8] have also reconsidered a total energy formulation due to Luttinger and Ward (LW) [9] and made a generalization of it.

A scheme based on the original LW formulation is developed, which can be applied to both molecular and solid systems. An important feature of the LW functional is that it is variational with respect to the Green's function under certain conditions. As the first application of our scheme to real systems the total energies of H₂ as a function of nuclear separation have been calculated. H₂ is a suitable test case because there are accurate results from configuration interaction (CI) calculations [10] which may be considered as exact. Besides, H₂ is well known as a problematic case for LDA. Thus, it provides a stringent test for the new scheme. In addition, a two-site Hubbard model has been studied to gain insights into the properties of the LW functional.

The LW energy functional in the zero temperature formulation can be written as [9,11]

$$E_{LW}[G] = T[G] + \Phi[G], \quad (1)$$

where

$$T[G] = E_0 + \text{tr}[G_0^{-1}G - 1] - \text{tr}[\ln G - \ln G_0], \quad (2)$$

$$\Phi[G] = -\frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n} \text{tr} M_n G. \quad (3)$$

G_0 is the Green's function of the noninteracting system with energy E_0 corresponding to the Hamiltonian with the Coulomb interaction switched off. M_n represents self-energy diagrams containing $(2n - 1)$ Green's function lines. The mass operator, i.e., the self-energy including the Hartree potential, is given by

$$M = -\frac{\delta\Phi}{\delta G} = \sum_{n=1}^{\infty} M_n. \quad (4)$$

The tr operator is defined by $\text{tr} = \frac{i}{2\pi} \int dr dr' d\omega e^{i\omega\delta}$. The quantity T may be interpreted as the kinetic energy and the interaction energy with the external field, whereas Φ contains the Hartree, exchange, and correlation energies. An important feature of the LW energy functional is that it is variational with respect to G , i.e., $\delta E_{LW}/\delta G = 0$ provided the Dyson equation

$$G = G_0 + G_0 M G \quad (5)$$

is satisfied. Thus, E_{LW} achieves its extremum at the exact

or self-consistent G . Because of this variational property, the total energy corresponding to an approximate Φ may remain close to its self-consistent value even with a non-self-consistent Green's function. This is in contrast to the Galitskii-Migdal formula [12,13].

For practical applications, it is inevitable to resort to approximations. As a realistic and practical approximation the random phase approximation (RPA) [13,14] is em-

ployed for the correlation part of Φ :

$$\Phi_c^{\text{RPA}} = -\frac{1}{4} \text{tr}[\ln(1 - Pv)(1 - vP) + Pv + vP]. \quad (6)$$

This Hermitian form is convenient for calculations since the eigenvalues are real. The polarization P in imaginary frequency is given by

$$P(r, r'; i\omega) = -\sum_{\sigma} \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \phi_{n\sigma}^*(r) \phi_{m\sigma}(r) \phi_{n\sigma}(r') \phi_{m\sigma}^*(r') \frac{2(\varepsilon_{m\sigma} - \varepsilon_{n\sigma})}{\omega^2 + (\varepsilon_{m\sigma} - \varepsilon_{n\sigma})^2}, \quad (7)$$

where $\{\phi_{n\sigma}\}$ and $\{\varepsilon_{n\sigma}\}$ are single-particle orbitals and energies, respectively. To calculate Φ_c in Eq. (6) we consider

$$\text{tr} \ln(1 - Pv)(1 - vP) = -\int_0^{\infty} \frac{d\omega}{\pi} \sum_{\alpha} \ln Q_{\alpha}(i\omega) = -\int_0^{\infty} \frac{d\omega}{\pi} \ln \det[1 - P(i\omega)v][1 - vP(i\omega)], \quad (8)$$

where $\{Q_{\alpha}\}$ are the eigenvalues of $(1 - Pv)(1 - vP)$. The choice of the contour integration along the imaginary axis is very desirable from a computational point of view because the function $P(i\omega)$ is smooth along this axis and therefore a Gaussian quadrature with only a few points, typically 10, can be used for performing the frequency integral [15]. The other term in Eq. (6), $-\text{tr}Pv/2$, is easily calculated:

$$-\text{tr}Pv/2 = -\frac{1}{2} \int dr dr' \sum_{\sigma} \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \phi_{n\sigma}^*(r) \phi_{m\sigma}(r) v(r - r') \phi_{n\sigma}(r') \phi_{m\sigma}^*(r'). \quad (9)$$

which is not the same as the exchange energy Φ_x

$$\Phi_x = -\frac{1}{2} \int dr dr' \sum_{\sigma} \sum_n^{\text{occ}} \sum_m^{\text{occ}} \phi_{n\sigma}^*(r) \phi_{m\sigma}(r) v(r - r') \phi_{n\sigma}(r') \phi_{m\sigma}^*(r'). \quad (10)$$

As a simple approximation for the total energy in Eq. (1), the exact Green's function is replaced by the LDA one. From the Dyson equation (5) this leads to

$$\begin{aligned} \text{tr}[G_0^{-1}G_{\text{LDA}} - 1] &= \text{tr}(V_{\text{H}} + v_{\text{xc}})G_{\text{LDA}} \\ &= -2E_{\text{H}} - \int v_{\text{xc}}\rho, \end{aligned} \quad (11)$$

where V_{H} and E_{H} are the Hartree potential and energy, respectively, and v_{xc} is the LDA exchange-correlation potential. Furthermore, it is straightforward to show that

$$-\text{tr}[\ln G_{\text{LDA}} - \ln G_0] = \sum_{n\sigma}^{\text{occ}} \varepsilon_{n\sigma}^{\text{LDA}} - E_0. \quad (12)$$

The LW energy functional can then be written as

$$E_{\text{LW}}[G_{\text{LDA}}] = E_{\text{LDA}} - E_{\text{xc}}^{\text{LDA}} + \Phi_x + \Phi_c^{\text{RPA}}, \quad (13)$$

where Φ_x and Φ_c are calculated using G_{LDA} . The last three terms represent the RPA correction to the LDA exchange-correlation energy.

The scheme is now applied to H_2 . The calculations are performed in real space using a nonuniform grid [16]. Figure 1 shows the total energy result for the nonspin-polarized case, which is the proper case to consider since H_2 is a closed shell molecule. The LDA parametrization of Gunnarsson and Lundqvist [17] has been used in this paper. The total energies around the equilibrium separation may depend significantly on which energy functional

is used. Using the von Barth–Hedin LDA parametrization [18], for example, lowers the energy by 0.4 eV. However, at large separations ($>3.5a_0$), which is the focus of this paper, commonly used functionals suffer from the well-known problem of seriously underestimating the total energy, which is associated with the contamination of the LDA ground-state wave function by ionic terms [20]. The LW scheme $E_{\text{LW}}[G_{\text{LDA}}]$ clearly improves substantially the LDA results at large separations. The LW results do not depend significantly on which G_{LDA} is used, reflecting to a certain extent the variational property of the LW functional. For example, the result at the equilibrium separation using the Green's function from the von Barth–Hedin LDA parametrization [18] is essentially the same. Most of the difference in the LDA results arises from E_{xc} .

In Table I we list the equilibrium separation and the energy difference at nuclear separation $4.5a_0$ and equilibrium separation, the latter can give some indication of the accuracy of the binding energy. Both LDA and $E_{\text{LW}}[G_{\text{LDA}}]$ reproduce accurately the equilibrium separation. The LDA energy difference, however, is in large error, whereas the LW one is quite close to the CI result. We note that the LW absolute energies are somewhat lower than the CI values (Fig. 1), but, in many practical applications, it is the energy difference that matters. For example, binding energies and chemical potential barriers involve energy differences.

It is interesting to also calculate the total energy for the spin-polarized LDA (LSDA) solution which can be

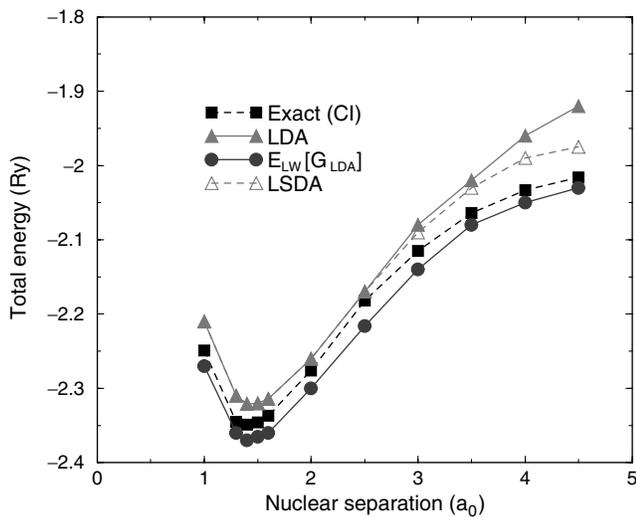


FIG. 1. The total energy of nonspin-polarized H_2 as a function of nuclear separation calculated using LDA and the LW formulation according to Eq. (13) with $G = G_{LDA}$. The exact (CI) result is from Ref. [10]. For nuclear separation $\geq 3a_0$, a spin-polarized solution can also be found. While the LSDA total energy is lower than the LDA one, the LW total energy using G_{LSDA} is found to be almost identical to the unpolarized case. Within the scale of the curves, $E_{LW}[G_{LDA}]$ and $E_{LW}[G_{LSDA}]$ are indistinguishable.

found for nuclear separation $> 3.0a_0$. Although the LSDA solution does not correspond to the proper solution of the ground state (not a pure singlet) it lowers the unpolarized LDA result since it describes the correlation better, with one electron localized on each hydrogen site, as in the correct solution [17]. Still, the LSDA is in significant error at large separations. $E_{LW}[G_{LSDA}]$, on the other hand, improves significantly the LSDA result in this region. It is interesting to observe that $E[G_{LSDA}]$ gives essentially the same result as $E[G_{LDA}]$, supporting the variational property of the LW functional. These encouraging results are expected to improve further when the Green's function from the GW approximation [6,7], is used in $T[G]$ in Eq. (2) but with G_{LDA} in $\Phi[G]$ in Eq. (3). Some evidence and rationale for this will be given later in the case of a two-site model.

To gain some insights into the properties of the LW functional, it is instructive to consider a two-site Hubbard model defined by the following Hamiltonian:

$$\hat{H} = -t \sum_{\langle RR'\rangle\sigma} \hat{c}_{R\sigma}^\dagger \hat{c}_{R'\sigma} + U \sum_R \hat{n}_R \hat{n}_{R'} \quad (14)$$

By utilizing the Dyson equation $G = G_0 + G_0MG$, the LW formula can take several different forms. For example,

TABLE I. The equilibrium separation, d_0 , and the energy difference, ΔE , at $d = 4.5a_0$ and d_0 . The GGA data is from Ref. [19].

	LDA	GGA	LW[G_{LDA}]	Exact (CI)
d_0 (a_0)	1.40	1.40	1.40	1.40
ΔE (Ry)	0.40	...	0.34	0.33

the second term on the right-hand side of Eq. (2) may be replaced by $\text{tr}MG$. These different forms are equivalent when the exact or a self-consistent G is used. In practice, however, one would like to use some approximate non-self-consistent G and to avoid performing self-consistent calculations since they are computationally very demanding. It is therefore interesting to investigate which form is most suitable for practical calculations.

Figure 2 displays the results of a number of approximations which are compared with the exact result. All curves can be calculated analytically with the exception of curve 5 (self-consistent GW). All approximations appear to work well for $U/2t < 1.5$. However, for larger $U/2t$ different approximations lead to substantially different errors. In this regime, the self-consistent GW result (curve 5), obtained by using the Galitskii-Migdal formula [12,13], performs poorly. This result has already been pointed out before by Schindlmayr *et al.* [21] who suggested that the excellent self-consistent GW results for the electron gas might be fortuitous. In some way this is more consistent with the fact that the self-consistent GW quasiparticle energies for the electron gas have been found to be unsatisfactory [5]. Similarly, self-consistent GW has been found to overestimate the band gap in Si [22]. Self-consistent GW appears to be nonphysical, as reflected by the violation of the f sum rule for the polarization function [5], which can be shown explicitly in the present two-site model.

A significantly better result than the self-consistent one is obtained by simply using G_{HF} in Eq. (1) (curve 4), which is theoretically equivalent to the approach taken for the total energy calculations of H_2 described earlier.

From Fig. 2 it is clear that the best result, achieving good agreement with the exact result extending to a strong correlation regime, is obtained by using the Hartree-Fock Green's function G_{HF} in $\Phi[G]$ and the one iteration G_{GW}

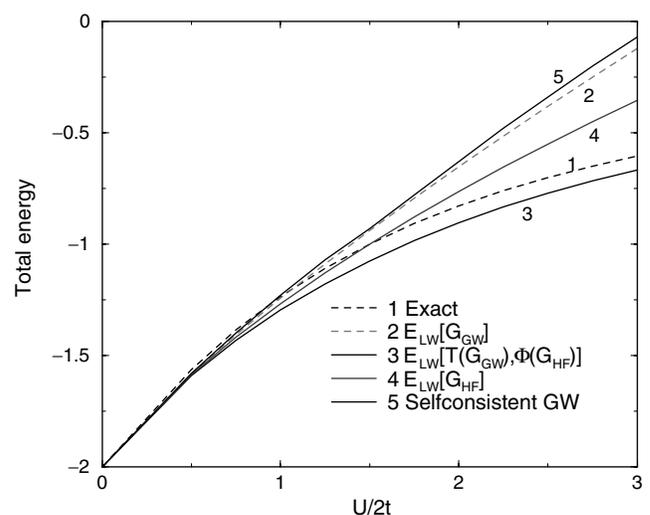


FIG. 2. The total energy of the two-site Hubbard model as a function of $U/2t$ using different approximations. The result from the Galitskii-Migdal formula (not shown) is almost the same as curve 2.

in $T[G]$ (curve 3). This might appear a bit puzzling at first sight. Closer examination of the theory reveals that this way of calculating the total energy has merit. From curves 2 and 3 it can be concluded that the major part of the error arises from $\Phi[G_{GW}]$ which supports the view that the polarization function constructed from G_{GW} entering Φ_c is nonphysical. From curves 3 and 4 it is evident that the main error comes from $T[G_{HF}]$. This is also reasonable since the one iteration G_{GW} presumably describes the kinetic energy of the real system better than does G_{HF} . A further rationale is that by inserting G_{HF} in Φ the term $\delta\Phi/\delta G = -M[G_{HF}]$ cancels $\delta T/\delta G = G_0^{-1} - G^{-1}$ calculated at $G = G_{GW}$, i.e., the Dyson equation is fulfilled. This cancellation does not occur if $M[G_{GW}]$ is used. Thus, it is very important which form of the LW functional should be employed in actual calculations when approximate or nonself-consistent G is used. It is not inconceivable that self-consistent GW is good for weakly or moderately correlated systems such as the electron gas [5] but not for strongly correlated systems. It could also be that the good self-consistent GW result is due to accidental cancellation of errors in T and Φ , which does not occur in the two-site model.

From the foregoing consideration, the total energy may improve when the following formula is used in practical calculation of real systems:

$$E[G] = T[G_{GW}(G)] + \Phi^{\text{RPA}}[G], \quad (15)$$

where G is some (noninteracting) Green's function, e.g., G_{LDA} and G_{GW} are here the one iteration GW Green's function obtained from $G_{GW} = G + G(\Sigma_{GW} - v_{xc})G_{GW}$, where v_{xc} is the exchange-correlation potential corresponding to G and $\Sigma_{GW} = iGW$ with a screened Coulomb interaction W [6,7]. The one iteration G_{GW} is preferred over the self-consistent one since the former is physically sound and much easier to calculate than the latter. Physically, Eq. (15) means that the kinetic energy is described by G_{GW} and the Hartree energy contained in Φ is determined by the LDA density through G_{LDA} . Since the LDA density is known to be accurate, so is the Hartree energy. The correlation energy is determined within the RPA by the polarization function of the LDA, which as argued before is more physical than that of G_{GW} . Equation (15) goes over to the original LW functional in Eq. (1) (within the RPA) if G is the self-consistent G_{GW}^{sc} since $G_{GW}(G_{GW}^{\text{sc}}) = G_{GW}^{\text{sc}}$. It is interesting to note that $T[G_{GW} + \Delta G] + \Phi^{\text{RPA}}[G + \Delta G]$ is quadratic in ΔG since $\delta T/\delta G$, calculated at $G = G_{GW}$, cancels $\delta\Phi^{\text{RPA}}/\delta G$, as discussed previously. Applications of Eq. (15), however, require further numerical development and will be carried out in the near future.

In summary, the feasibility of calculating total energies from the traditional many-body Green's function theory has been demonstrated by calculating the total energies of H_2 using the variational formulation of Luttinger and Ward. H_2 is a difficult case for LDA, in particular for large separations. This problem is remedied by our scheme. A

practical scheme for calculating the difficult correlation part is presented in Eq. (8). At the simplest level of approximation (RPA), shown in Eq. (13), the calculated total energies are already in rather satisfactory agreement with the exact results for H_2 . A functional which incorporates the Dyson equation and uses a nonself-consistent G is constructed, as described in Eq. (15). Further improvement is anticipated when this higher level approximation is used. The present method is promising as an alternative to the more expensive QMC approach.

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