Efficient Total Energy Calculations from Self-Energy Models

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We propose a new method for calculating total energies of systems of interacting electrons, which requires little more computational resources than standard density-functional theories. The total energy is calculated within the framework of many-body perturbation theory by using an efficient model of the self-energy, that nevertheless retains the main features of the exact operator. The method shows promising performance when tested against quantum Monte Carlo results for the linear response of the homogeneous electron gas and structural properties of bulk silicon.

Density-functional theory (DFT) [1] is a powerful method to calculate ground-state properties of electronic systems. In its standard Kohn-Sham form [2], the system of interacting electrons is mapped onto a system of noninteracting electrons moving in an effective local potential. This potential, however, exhibits some nonanalyticities in its dependence on the electron density, such as the discontinuity on addition of an extra particle to the system, which is reflected in the band gap problem [3] and the failure to correctly describe the response of a macroscopic system to an external electric field [4]. This nonanalytic behavior is missing from the standard approximations to the Kohn-Sham potential, i.e., the local density (LDA) and generalized gradient approximations (GGA), which may explain some of their limitations when applied to complex systems such as catalyzed chemical reactions [5].

One way forward is to avoid the need to describe the nonanalyticities by incorporating the true nonlocal nature of the exchange and correlation. Recently, a new realization of DFT, the generalized Kohn-Sham scheme (GKS) [6,7], has been proposed, in which the electrons move in an effective *nonlocal* potential. Among the GKS approaches, the screened-exchange LDA (sX-LDA) [6] appears to give the best performance, describing structural properties with the same accuracy as the LDA but improving on its description of quasiparticle energies. However, this scheme is numerically as expensive as a standard Hartree-Fock calculation.

In this work we propose a new generalized Kohn-Sham scheme, the Σ-GKS scheme, in which the exchange-correlation potential is intended to mimic the self-energy operator, which in many-body perturbation theory (MBPT) exactly describes exchange and correlation effects and, being truly nonlocal, is expected to be more amenable to approximation than the Kohn-Sham potential.

In the framework of MBPT, the total energy of a system of electrons moving in an external potential V_{ext} can be calculated by means of the Galitskii-Migdal formula:

$$E = \frac{1}{2} \sum_{i,j} \int_{-\infty}^{\mu} d\omega \, (\omega \delta_{ij} + h_{ij}) A_{ji}(\omega), \qquad (1)$$

where i and j are the indices of a suitable complete set of one-particle wave functions, h_{ij} are the matrix elements of $h = -\nabla^2/2 + V_{\text{ext}}$, and A is the spectral function of the Green's function. Atomic units are used through this Letter.

From a particular approximation for the self-energy, a model spectral function A can be obtained and the total energy can be calculated via Eq. (1). Using the GW approximation [8], in its self-consistent formulation, total energies derived from Eq. (1) have recently been shown to be in very good agreement with quantum Monte Carlo data, when applied to 3D [9,10] and 2D [10] homogeneous electron gases. However, this approximation is computationally too expensive to be in competition with methods such as the LDA and GGA in applications to very large systems. The self-energy model that we propose will allow us to calculate total energies within the same order of numerical cost as the LDA.

We start by modeling the self-energy of a homogeneous electron gas (jellium) of density n_0. For occupied states the energy dependence of the self-energy is relatively weak [8], suggesting the approximation [11]

$$\Sigma(|\mathbf{r} - \mathbf{r}'|; \epsilon_i) \approx \Sigma(|\mathbf{r} - \mathbf{r}'|; \mu), \qquad (2)$$

where μ is the chemical potential of the system. The self-energy for jellium at μ can be well reproduced by the following model function:

$$\Sigma^0(\mathbf{r}, \mathbf{r}'; n_0) = f(n_0) g(|\mathbf{r} - \mathbf{r}'|; n_0), \qquad (3)$$

where $f(n_0) = V_{\text{xc}}^{\text{LDA}}(n_0)$ and

$$g(|\mathbf{r} - \mathbf{r}'|; n_0) = C(n_0) \frac{e^{-\alpha(n_0)|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}. \qquad (4)$$

The constant $C(n_0)$ ensures that the chemical potential given by Σ^0 is correct and $1/\alpha(n_0)$ represents the range of the self-energy for a jellium of density n_0.

In Fig. 1 the model function given by Eq. (3) is compared to the GW data of Ref. [12], showing an excellent agreement in the region in which Σ has the largest contribution. The small discrepancy that appears in the long-range region is unimportant for the total energy, owing to
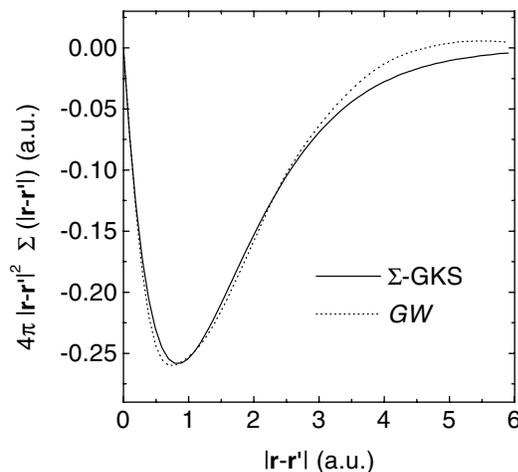
FIG. 1. Comparison between the model self-energy and the *GW* data from Ref. [12] for jellium of $r_s = 2$.

the oscillatory behavior of the wave functions [13]. In addition to its suitability for jellium, the function g defined in Eq. (4) has been shown to have the correct asymptotic decay in semiconducting systems [14].

The key idea of this approach is to use a jelliumlike self-energy to describe the exchange and correlation energy of inhomogeneous systems. This is suggested by the fact that for several semiconductors the self-energy has been shown [15] to be almost spherical and to have the same range as the self-energy of a jellium with the corresponding average density. A natural extension of Eq. (3) to an inhomogeneous system is

$$\Sigma^0(\mathbf{r}, \mathbf{r}'; [n]) = \frac{f(n(\mathbf{r})) + f(n(\mathbf{r}'))}{2} g(|\mathbf{r} - \mathbf{r}'|; n_0),$$
(5)

where here n_0 is the average density. This may be likened to an LDA exchange-correlation potential that has been made nonlocal by including a *spreading function g*.

The self-energy in Eq. (5) is the self-energy of a system of noninteracting electrons, since it is energy independent and real. The method that we propose is equivalent to a mapping between the interacting system and the fictitious noninteracting system represented by Σ^0. If we choose the basis set ϕ_i to be formed by the wave functions of the quasiparticles in this fictitious sytem, then the spectral function A^0 is simply given by

$$A_{ij}^0(\omega) = \delta_{ij}\delta(\omega - \epsilon_i^0),$$
(6)

where ϵ_i^0 are the quasiparticle energies of the noninteracting system.

Using this spectral function A^0 and the Galitskii-Migdal formula [Eq. (1)] the total energy of the model system can be obtained:

$$E^0 = \sum_i^{occ} \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 + V_{ext} + \frac{1}{2}V_H + \frac{1}{2}\Sigma^0 \right| \phi_i \right\rangle$$

$$= T + E_{ext} + E_H + E_{nl},$$
(7)

where, as usual, T is the kinetic energy, E_H is the Hartree energy, E_{ext} is the external energy, and

$$E_{nl} = \frac{1}{2}\sum_i^{occ} \int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \int d\mathbf{r}'\, \Sigma^0(\mathbf{r}, \mathbf{r}', [n])\phi_i(\mathbf{r}').$$
(8)

As in other generalized Kohn-Sham schemes, a correction term E_{ss} is added so that the total energy given by the model is exact in the homogeneous limit. This term can be interpreted in MBPT as the remaining energy associated with the satellite structure of the spectral function [16],

$$E_{ss}[n] = \int d\mathbf{r}\, n(\mathbf{r})[\epsilon_{xc}^{LDA}(n(\mathbf{r})) - \epsilon_l(n(\mathbf{r}))],$$
(9)

where ϵ_l is the energy per particle obtained from Eq. (8) in the limit of homogeneous densities:

$$\epsilon_l(n) = \frac{1}{8\pi^3 n}\int_{|\mathbf{k}|<k_F(n)} d\mathbf{k}\, \Sigma(\mathbf{k}),$$
(10)

where $k_F(n)$ is the Fermi vector of a jellium of density n.

The total energy of the interacting system is thus

$$E = T + E_H + E_{ext} + E_{nl} + E_{ss}.$$
(11)

This functional is minimized with respect to variations in the one-particle wave functions, yielding the following effective Hamiltonian:

$$\hat{h} = -\frac{1}{2}\nabla^2 + V_{ext} + V_H + \left(\frac{1}{2}\Sigma^0 + V_m + V_{ss}\right),$$
(12)

where $V_{ss}(n(\mathbf{r})) = \delta E_{ss}/\delta n(\mathbf{r})$ and

$$V_m(\mathbf{r}) = \frac{1}{2}f'(n(\mathbf{r}))\int d\mathbf{r}'\, \mathrm{Re}\rho(\mathbf{r}, \mathbf{r}')g(|\mathbf{r} - \mathbf{r}'|),$$
(13)

in which ρ is the density matrix of the fictitious noninteracting system:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i^{occ} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}').$$
(14)

In the limiting case of the spreading function g tending to a delta function, the term $\frac{1}{2}\Sigma^0 + V_m + V_{ss}$ reduces to the conventional LDA exchange-correlation potential, so that the LDA can be considered as a particular case of the more general scheme proposed here.

The computational effort involved in solving the variational equations determined by Eq. (12) is not significantly larger than in traditional DFT's. In a plane wave basis set, the matrix elements of the nonlocal potential take the simple form

$$\langle \mathbf{k} + \mathbf{G}|\Sigma^0|\mathbf{k} + \mathbf{G}'\rangle = f(\mathbf{G} - \mathbf{G}')$$
$$\times \frac{g(|\mathbf{k} + \mathbf{G}|) + g(|\mathbf{k} + \mathbf{G}'|)}{2},$$
(15)

i.e., they are just the product of the LDA exchange-correlation potential and an analytical function of the

moduli of the vectors $\mathbf{k} + \mathbf{G}$ and $\mathbf{k} + \mathbf{G}'$. The calculation of Σ^0 scales, as with local potentials, linearly with the number of reciprocal-lattice vectors n_G.

The potential V_m defined by Eq. (13) depends on the density matrix of the system rather than the density itself, but it can be efficiently calculated in reciprocal space, where the action of the nonlocal operator g on the wave functions is simply given by the products $g(\mathbf{G})\phi_i(\mathbf{G})$. The calculation of V_m also scales linearly with n_G. In contrast, in Hartree-Fock or sX-LDA schemes, calculating the exchange-correlation matrix scales with the cube of n_G.

By construction, the Σ-GKS is exact for homogeneous densities. In order to test its performance for inhomogeneous systems, we have used it to calculate the linear response of a homogeneous electron gas to an external perturbation $2\delta V_{ext} \cos(\mathbf{q} \cdot \mathbf{r})$. This is a stringent test since it involves the calculation of total energies for a whole family of systems with different values of the perturbation amplitude δV_{ext} and the wave vector q. The total energy changes with respect to its unperturbed value by an amount $\chi(\mathbf{q})\delta V_{ext}^2$, where $\chi(\mathbf{q})$ is the response function of the system, related to the local field factor $G(\mathbf{q})$ via

$$\chi(\mathbf{q}) = \frac{\chi_0(\mathbf{q})}{1 - w(\mathbf{q})[1 - G(\mathbf{q})]\chi_0(\mathbf{q})}, \qquad (16)$$

where $w(\mathbf{q}) = 4\pi/q^2$ is the Coulomb potential and $\chi_0(\mathbf{q})$ is the noninteracting Lindhard response function. For a given value of $\mathbf{q}$, the total energy is calculated for several values of δV_{ext} and then the set of points $(\delta V_{ext}^2, E)$ are fitted to a polynomial, whose first-order coefficient is $\chi(\mathbf{q})$. In Fig. 2, the local field factor $G(\mathbf{q})$ calculated within the Σ-GKS scheme is plotted against the wave vector of the perturbation and compared to the quantum Monte Carlo (QMC) results of Moroni *et al.* [17], the LDA and the
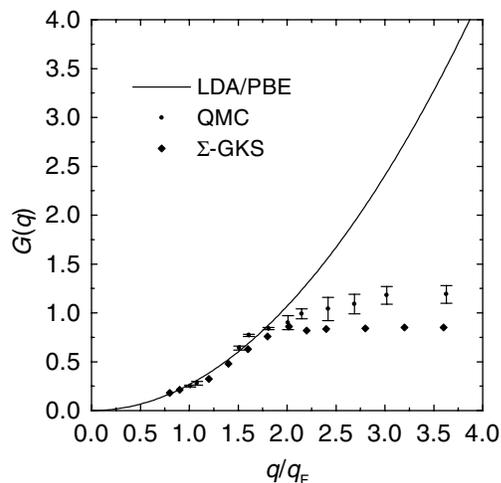
FIG. 2. Local field factor for the linear response of jellium at $r_s = 2$ in the Σ-GKS scheme compared to the QMC results [17], the LDA, and the GGA of Ref. [18] (PBE) (which coincide). The numerical uncertainties in the Σ-GKS results are of the order of 0.05 and are not shown for clarity. The new scheme proposed considerably improves the local field factor for large values of q with respect to the LDA and to PBE.

GGA. For small values of q all methods agree well with QMC. The large q response, however, is not correctly described with the LDA, nor with the best GGA available due to Perdew, Burke, and Ernzerhof (PBE) [18]. The Σ-GKS shows a significant improvement in the local field factor for large values of q.

As a further test, the Σ-GKS scheme was applied to calculate structural properties of a typical semiconductor such as silicon. The bulk total energy was calculated using an LDA pseudopotential [19] due to Kerker [20] and a plane wave basis set, and compared with the QMC results of Ref. [21], calculated with exactly the same pseudopotential. The results are shown in Table I. Both the Σ-GKS and the convential DFT's (LDA and GGA) total energies are in good agreement with the QMC results, although Σ-GKS agrees slightly less well [25]. The lattice parameter and bulk modulus are equally well described in the LDA, the GGA, and the Σ-GKS scheme.

Although describing quasiparticle spectra is not the primary goal of our scheme, we also calculated the quasiparticle energies of Si. The overall tendency is to correctly increase the eigenvalues at the conduction band with respect to the LDA values. The direct band gap at Γ is increased from 2.6 eV in the LDA to 3.0 eV in our scheme, whereas the GW and experimental values are 3.4 eV. Valence band widths in the Σ-GKS are in general overestimated.

In summary, we have proposed a new method for calculating total energies at the same time as quasiparticle energies which is just as efficient as a standard DFT calculation, but that is constructed as a model of the self-energy, thus

TABLE I. Total energy of bulk Si within the Σ-GKS scheme, the LDA and GGA (PW91) [22], calculated with a $4 \times 4 \times 4$ Monkhorst-Pack $\mathbf{k}$ grid, and QMC [21], all with a cutoff of 15 Ry for the $\mathbf{G}$ vectors. A LDA pseudopotential due to Kerker [20] was used in all four cases, which allows a comparison of the exchange-correlation functional under this particular choice of external potential. The lattice parameter and bulk modulus were also calculated, using a cutoff of 22 Ry for the $\mathbf{G}$ points and a Monkhorst-Pack set of 14 special $\mathbf{k}$ points in the Brillouin zone. The use of an LDA pseudopotential does not justify the comparison of our results with experiment, but nevertheless we present also the experimental values, for completeness. In common with the LDA and PW91, the Σ-GKS scheme shows generally good agreement with QMC and experiment. Note that quantities shown in parentheses have not been calculated with the pseudopotential of Ref. [20].

	E (eV/atom)	a ($\mathbf{r}$A)	B (Mbar)
Σ-GKS	−107.65	5.39	1.008
LDA	−107.90	5.39	0.967
PW91	−108.17	(5.46[a])	(0.92[a])
QMC	−108.3[b]	(5.45[c])	(1.03[c])
Expt.	· · ·	(5.43[d])	(0.992[d])

[a]From Ref. [23].
[b]From Ref. [21]; estimated finite-size convergence error ±0.05 eV/atom.
[c]From Ref. [24].
[d]Cited in Ref. [24].

describing the exchange and correlation in a more realistic way than the LDA and GGA. This type of approach holds the prospect of enhanced accuracy of total-energy calculations by avoiding the pathological aspects of the traditional Kohn-Sham exchange-correlation energy functional.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1122 (1965).

[3] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983); L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983); R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[4] X. Gonze, P. Ghosez, and R. W. Godby, Phys. Rev. Lett. **74**, 4035 (1995); P. Ghosez, X. Gonze, and R. W. Godby, Phys. Rev. B **56**, 12 811 (1997).

[5] D. M. Bird and P. A. Gravil, Surf. Sci. **377**, 555 (1997).

[6] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Phys. Rev. B **53**, 3764 (1996); G. E. Engel, Phys. Rev. Lett. **78**, 3515 (1997).

[7] G. E. Engel and W. E. Pickett, Phys. Rev. B **54**, 8420 (1996).

[8] L. Hedin and S. Lundqvist, in *Solid State Physics,* edited by F. Seitz, H. Ehrenreich, and D. Turnbull (Academic Press, New York, 1969), Vol. 23.

[9] U. von Barth and B. Holm, Phys. Rev. B **54**, 8411 (1996); B. Holm and U. von Barth, Phys. Rev. B **57**, 2108 (1998).

[10] P. García-González and R. W. Godby (unpublished); (private communication).

[11] Since the imaginary part of Σ at μ is zero, the model self-energy Σ^0 is real.

[12] I. D. White (private communication).

[13] The products $\phi_i^*(\mathbf{r})\Sigma(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}')$ cancel out when the difference between $\mathbf{r}$ and $\mathbf{r}'$ is large, and thus the two wave functions are not in phase.

[14] A. Schindlmayr (to be published).

[15] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10 159 (1988).

[16] A uniform background structure with a certain cutoff ω_p will yield precisely this correction term if ω_p is chosen using the criterion that the total energy of jellium is exact.

[17] S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] It should be noted that the use of an LDA pseudopotential tends to reproduce LDA structural properties when used with any other exchange-correlation functional: see M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev. B **57**, 2134 (1998). This does not affect, however, the comparison between theoretical methods.

[20] G. Kerker, J. Phys. C **13**, L189 (1980).

[21] P. R. C. Kent, R. Q. Hood, A. J. Williamson, R. J. Needs, W. M. C. Foulkes, and G. Rajagopal, Phys. Rev. B **59**, 1917 (1999); (private communication).

[22] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[23] I.-H. Lee and R. M. Martin, Phys. Rev. B **56**, 7197 (1997).

[24] X.-P. Li, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **44**, 10 929 (1991).

[25] An improved Σ-GKS total energy functional can be built through a simple spectral function model for the energy dependence of Σ. This reduces the correction term of Eq. (9) by 2 orders of magnitude in jellium at $r_s = 2$ and will be the subject of a future publication.