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Ground-state properties of simple elements from GW calculations

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A self-consistent implementation of Hedin's GW perturbation theory is introduced. This finite-temperature method uses Hartree-Fock wave functions obtained with full potential linear augmented plane-wave method to represent Green's function. With our approach we are able to calculate total energy as a function of the lattice parameter. Ground-state properties calculated for Na, Al, and Si compare well with experimental data.

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Density-functional theory (DFT) (Ref. 1) in its local-density approximation (LDA) or generalized gradient approximation (GGA) is a widely used method to calculate ground-state properties of solids. But this theory is not always good in situations where electronic correlations are essential. The problem is then arising that existing variants of DFT cannot be improved systematically (or at least it is very difficult to accomplish that). It is therefore very desirable to have a method capable to deal with ground-state properties and at the same time allowing their systematical improvement. This flexibility is obviously present in methods based on diagrammatic expansion and one of them, Hedin's GW approach, is becoming computationally accessible during last years. However, while the GW method has become standard for studying excitation spectra, the possibility of using it for calculating total energies and other ground-state properties is not well established. This question has been addressed only in a few works. Holm and von Barth[2] and Garcia-Gonzalez and Godby[3] performed self-consistent (SC) GW calculations for the homogeneous electron gas (HEG) and concluded that in spite of a bad electronic structure obtained in their SC calculations the total energy was quite close to the result of a quantum Monte Carlo (QMC) (Ref. 4) study. Stan *et al.*[5,6] applied SC GW to calculate total energies of atoms and molecules. They conclude that GW calculations should be done self-consistently in order to obtain physically meaningful and unambiguous energy differences. Miyake *et al.*[7] studied ground-state properties of sodium and aluminum using Galitskii-Migdal formula[8] with a model spectral function. Their equilibrium volumes and bulk modulus appeared to be slightly overestimated as compared to the experiment, but some improvement over LDA results was reported. Also using model self-energy, Sanchez-Friera and Godby[9] successfully studied the structural properties of bulk silicon. Miyake *et al.*[10] applied the total-energy formula due to Luttinger and Ward[11] to the calculation of equilibrium lattice constants in Na and Si. Their one-shot-type results appeared to be very close to the experimental data. However, to our knowledge fully self-consistent GW calculations of the total energy and the ground-state properties for real solids have not yet been carried out.

To address this question we have implemented a variant of GW method which allows us to calculate total energies. The key ingredients of our implementation are the following. First, we use full potential linear augmented plane-wave (FLAPW) method[12] to find the solutions of the Hartree-Fock (HF) equations which serve as a basis for the expansion of one-electron Green's function. Second, we have found it vital to use Matsubara's time τ mesh to calculate correlated part of the self-energy. It appears that it is very difficult to obtain comparable accuracy in total energy using self-energies calculated in frequency domain. Third, our calculations are self-consistent.

In our implementation we use the Galitskii-Migdal formula to calculate exchange-correlation part of total energy, i.e., we convolute the Green's function $\mathcal{G}^{\alpha}_{\lambda'\lambda}(\mathbf{k};\tau)$ and the self-energy $\Sigma^{\alpha}_{\lambda\lambda'}(\mathbf{k};-\tau)$,

$$E_{xc}=\frac{1}{2}\sum_{\alpha\mathbf{k}}\sum_{\lambda\lambda'}\int\Sigma^{\alpha}_{\lambda\lambda'}(\mathbf{k};-\tau)\mathcal{G}^{\alpha}_{\lambda'\lambda}(\mathbf{k};\tau)d\tau, \tag{1}$$

where α is a spin index; $\mathbf{k}$ denotes points in the Brillouin zone, λ and λ' are band indices, and the self-energy is defined by

$$\Sigma^{\alpha}_{\lambda\lambda'}(\mathbf{k};\tau)=-\sum_{\mathbf{q}}\sum_{\lambda''\lambda'''}\sum_{ij}\langle\Psi^{\alpha\mathbf{k}}_{\lambda}|\Psi^{\alpha\mathbf{k}-\mathbf{q}}_{\lambda''}M^{\mathbf{q}}_{i}\rangle\times\mathcal{G}^{\alpha}_{\lambda''\lambda'''}(\mathbf{k}-\mathbf{q};\tau)W_{ij}(\mathbf{q};-\tau^{+})\langle M^{\mathbf{q}}_{j}\Psi^{\alpha\mathbf{k}-\mathbf{q}}_{\lambda'''}|\Psi^{\alpha\mathbf{k}}_{\lambda'}\rangle, \tag{2}$$

where $\Psi^{\alpha\mathbf{k}}_{\lambda}$ are Bloch states, $W_{ij}(\mathbf{q};\tau)$ are screened Coulomb interaction elements, and $M^{\mathbf{q}}_{j}$ are product basis functions. Due to our implementation on top of the Hartree-Fock method, we calculate exactly exchange part of self energy coming from core-core, core-valence, and valence-valence

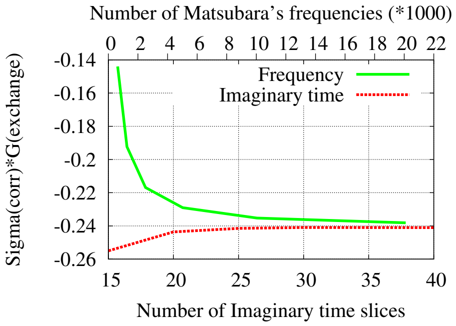

FIG. 1. (Color online) Convergence of the product of correlated part of self-energy and exchange part of Green's function for Na with respect to the number of Matsubara's frequencies and to the number of imaginary time slices.

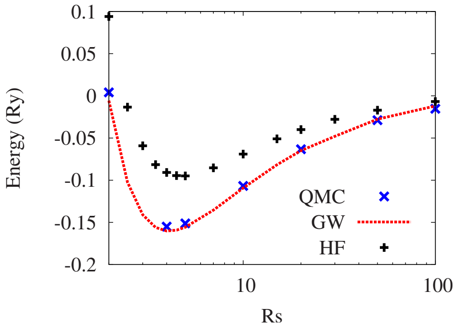

FIG. 2. (Color online) Total energy of HEG with respect to R_s obtained in HF and GW approximations. Comparison is made with QMC results (Ref. 4).

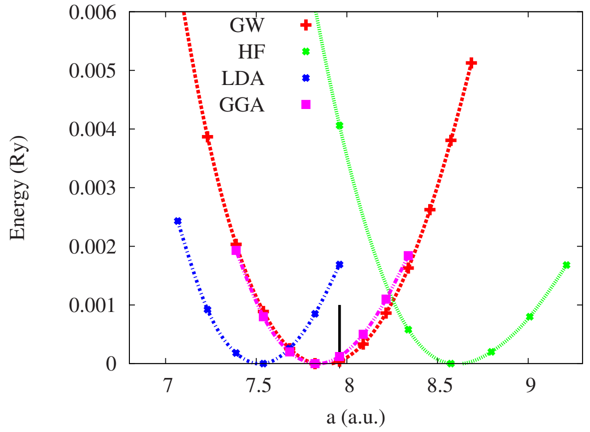

FIG. 4. (Color online) Total energy of Na as a function of lattice parameter. Symbols are calculated values, and lines are fitted curves. Arrow indicates the room-temperature experimental lattice parameter (Ref. 14).

electrons. The effects of correlations in the deep enough core are known to be small,[13] and we neglect them.

The importance of calculating the self-energy using imaginary time formalism instead of frequency summation is evident from the fact that imaginary part of self-energy is slowly convergent $(\sim\frac{1}{\omega})$ function of frequency and this function is not known analytically which prevents direct summation. Figure 1 illustrates this point using Na as an example. As it is seen 25–30 points on imaginary time mesh (we use denser mesh at the boundaries of the interval $[0;\beta]$) give very good absolute convergence of the product of correlated part of self-energy and exchange part of Green's function. On the other hand even more than 20 000 Matsubara's frequencies are not enough to converge. There is also quite practical reason to avoid frequency summation: τ algorithm is just much faster because we only have to multiply Green's function with screened Coulomb interaction. In frequency domain we have to perform a convolution, which is rather time consuming.

As a test of our newly developed code we have applied it to calculate the total energy for the homogeneous electron gas. As we have already mentioned, this was already done previously,[2,3] but in those calculations zero temperature formalism was utilized. In Fig. 2 the result from our finite temperature (300 K) approach is shown in comparison with the accurate quantum Monte Carlo data obtained by Ceperly and Alder.[4] As it is seen, self-consistent-field (SCF) GW total energies are in very good agreement with QMC simulations.

All our calculations for real solids have been performed for temperature $T=2000$ K. For our LDA and GGA studies we used the exchange-correlation functionals from Refs. 15 and 16, respectively. An important question is the convergence of the GW results with respect to the calculational parameters. We have discovered that the most critical of them is the number of k points in Brillouin zone. Figure 3 shows the dependence of GW total energy on the k mesh used (we use Monkhorst-Pack[17] regular meshes of points). As it is seen as the division number increases from 4 to 8, the energy changes by 0.04 Ry. For a comparison the same value changes only by 0.005 Ry in GGA calculations. But as it is

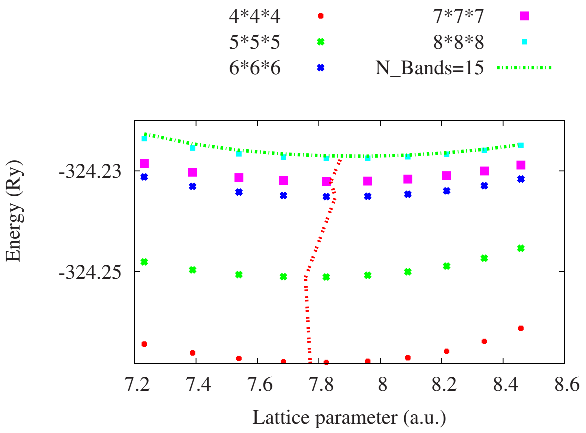

FIG. 3. (Color online) GW total energy of Na as a function of lattice parameter for different k-points samplings. Dot-dashed curve represents the result for $8\times8\times8$ mesh but with decreased number of bands used (15 instead of 23 in other calculations). Broken line drawn from bottom to top shows the positions of minimums of the curves.

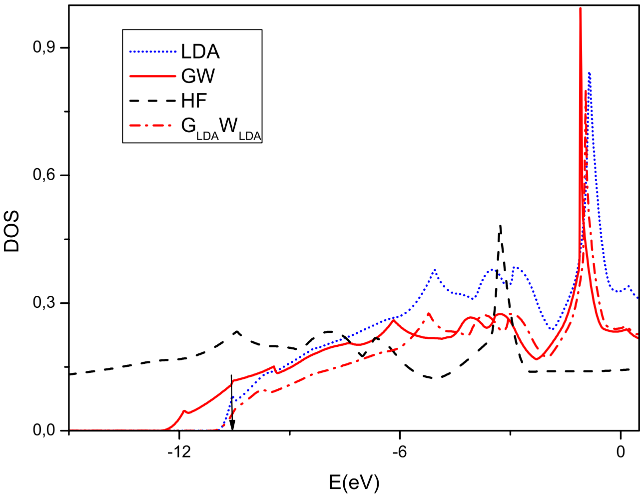

FIG. 5. (Color online) DOS of Al calculated in GGA, HF. and GW approximations. Chemical potential is placed at zero energy. The arrow shows the experimental position of the valence-band bottom.

TABLE I. Equilibrium lattice parameter a_0(a.u.) and bulk modulus B_0(GPa) of Al, Na, and Si compared to room-temperature experimental data (Refs. 14 and 18). The results correspond to Brillouin-zone meshes $8 \times 8 \times 8$ (Na and Al) and $5 \times 5 \times 5$ (Si).

	Na		Al		Si	
	a_0	B_0	a_0	B_0	a_0	B_0
LDA	7.53	87	7.585	82.5	10.01	91.2
GGA	7.83	71.5	7.72	73.3	10.14	93.5
HF	8.62	50	7.82	82.5	10.34	97.0
GW	7.87	69.9	7.64	86.5	10.17	100.7
Expt.	7.96	68.1	7.65	72.16	10.26	99

also seen from Fig. 3 the position of a minimum $E(a)$ is quickly becoming stable, which allows us to study structural properties with GW approach. We also have discovered that the number of bands representing the correlated part of Green's function has little effect on total energy (Fig. 3). We speculate that is the result of using Hartree-Fock basis set.

Figure 4 presents our calculated total energy versus lattice parameter for Na, where we compare the results of the LDA, GGA, HF, and GW approximations. For GW curve we have perform two Birch-Murnaghan fittings for $E(V)$ with the following parameters: for $7.23 < a < 8.46(\text{a.u.}): V_0 = 243.476\,99(\text{a.u.}^3)$, $B_0 = 69.86(\text{kbar})$, $B_0' = 2.529\,75$ and for $6.1 < a < 8.69(\text{a.u.}): V_0 = 241.230\,30(\text{a.u.}^3)$, $B_0 = 72.71(\text{kbar})$, $B_0' = 3.248\,05$.

Table I contains the calculated ground-state properties for all studied elements: Na, Al, and Si. As it is seen GW results are quite good encouraging us to use this approach for ground-state investigations.

As a by-product of our Rapid Communication we have investigated the influence of the self-consistency on the excitation spectra (at experimental equilibrium lattice parameter). Despite it was already noticed long ago[19] that the GW approximation can be quite useful for calculating one-electron spectra, there is still some ambiguity with respect to the effect of self-consistency. Usually, GW calculations are exceedingly demanding and only one-shot variant is used to calculate bandwidths or band gaps. Calculated on top of LDA or GGA such one-shot quasiparticle band structures appeared to be in much better agreement with experimental data when compared to the LDA ones.[2,20–23] Later it was shown that self-consistency within GW gives too large band gaps for semiconductors and insulators.[20,22,24] However this question of self-consistency still remains as a few other works aimed at self-consistent GW calculations used some simplifications.[20,22,23,25–29]

We have performed SC GW calculations and compared the results with the results from the one-shot GW calculations based on DFT self-consistent calculations. As example of calculated density of states (DOS) for metals, we present our calculated electronic structure of Al in Fig. 5. We are especially concerned with the valence-band width for this material. As it is seen, our non SC GW bandwidth for Al is much closer to the LDA result and to the experimental data[30,31] than SC GW result which is about 10% too big. Since Aluminum is a free-electron metal, we think that the above result is similar and consistent with the results[2,32] obtained for the homogeneous electron gas. Based on the work by Shirley[32] and Takada[33] we expect that higher-order vertex corrections will bring the calculated bandwidth in closer agreement with experiment.

In Table II we have collected the calculated fundamental gaps for silicon obtained in earlier works along with our results. Our band gap from non-SC GW calculation is quite close to the results of others. However our band gap from SC GW appears to be a bit wider than it is usually obtained. We would stress however that neither of previous calculations

TABLE II. Band gap (energies in eV) for Si. The values in round brackets were obtained with SC in eigenvalues only. Experimental band gap is 1.17 eV.

	Ref. 20	Ref. 26	Ref. 28	Ref. 23	Ref. 22	Ref. 24	Present work
LDA	0.53	0.52		0.46	0.51		0.46
GGA							0.54
HF							6.27
$G_{\text{LDA}}W_{\text{LDA}}$	1.34	0.85	0.86	0.98	1.14		0.86
$G_{\text{HF}}W_{\text{HF}}$							2.69
$G_{\text{COHSEX}}W_{\text{COHSEX}}$					1.56		
GW_{LDA}						1.28(1.20)	
$QPscGW$				1.25(1.14)	1.47	1.41	
GW	1.91	1.03	1.10				1.55

are approximation free and that partially SC results obtained in the works[22–24] also show a trend in increasing the band gap. In this respect it is important to notice that approximate vertex correction[24] reduces band gaps, partially cancelling the effect of self-consistency. We hope to get more answers to this question in the nearest future.

In summary, we have presented a self-consistent realization of the GW method and its performance for evaluating total energies and ground-state properties of solids. Based on our case study for several simple systems (Na, Al, and Si) we conclude that the GW approach delivers the accuracy in predicting total energy vs volume relations comparable with the state-of-the-art GGA-type calculations of density-functional theory. Obviously this success can be understood as a result of a Φ derivability of the GW total-energy functional.[34] Our results for the electronic structure of the above mentioned materials are in agreement with the earlier works, but in general we should conclude that some deterioration in calculated bandwidths and band gaps is seen when we are trying to do the self-consistency. In this respect our conclusion is the same as the one by Holm and Barth found for homogeneous electron gas:[2] the self-consistency within GW improves total energies but not one-electron spectra.

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