

Total energy of solids: An exchange and random-phase approximation correlation studyT. Miyake,¹ F. Aryasetiawan,² T. Kotani,³ M. van Schilfhaarde,⁴ M. Usuda,⁵ and K. Terakura²¹*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan*²*Research Institute for Computational Sciences, AIST, 1-1-1 Umezono, Tsukuba Central 2, Ibaraki 305-8568, Japan*³*Department of Physics, Osaka University, 1-1 Machikane-yama, Toyonaka 560-0043, Japan*⁴*Sandia National Laboratory, Livermore, California 94551*⁵*Department of Physics, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510, Japan*

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Total energies of solids are calculated by an *ab initio* method based on the Green's-function theory. Green's function is constructed from one-body wave functions and eigenvalues obtained in the local-density approximation (LDA) to density-functional theory, and the correlation energy is estimated within the random-phase approximation. The scheme is applied to Na and Si. In both cases, the equilibrium lattice constants are in reasonable agreement with experiments. The role of the exchange-correlation energy in the total-energy curve is discussed in detail in comparison with the LDA.

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The Green's-function theory provides a way to include correlations in many-electron systems. One of the simple approximations for practical application is the random-phase approximation (RPA) for the polarizability,¹ and the *GW* approximation (GWA) for the self-energy.^{2,3} The RPA takes into account dynamical screening of electrons within the time-dependent Hartree approximation. The GWA includes RPA screening and has been successful in describing one-electron excitation spectra in solids.⁴⁻⁹ Optical properties, including the semiconductor band gap are much more accurate than in the LDA.

Although the Green's-function approach has been traditionally used for electronic excitations, energy functionals of Green's function can be used to calculate ground-state properties. This possibility is attracting strong interest, since it can potentially overcome drawbacks in the widely used LDA in density-functional theory.

There have been several papers reporting total-energy calculations based on the Green's-function technique. Electron gas studies have revealed good total energies in the GWA/RPA. In particular, energies from the self-consistent *GW* method are as accurate as the quantum Monte Carlo (QMC) method.¹⁰⁻¹² Applications to the Hubbard model also have shown reasonable results except strong correlation regime where vertex corrections are considered to be important.^{13,14} Related works have been also reported.¹⁵⁻¹⁷ These results suggest that the Green's-function approach at the level of RPA could be an improved tool for the total energies. It may be more accurate than the LDA, and would be less computation demanding than the QMC. However, so far applications to solids have resorted to further simplifications such as a model self-energy¹⁸ and a model spectral function.¹⁹

Recently, we proposed a method for the total energy based on the RPA.¹⁴ We calculated the total energy of the hydrogen molecule as a function of nuclear separation, and obtained encouraging results, particularly at large nuclear separations where the LDA fails. In this work, we report the application of this method to solids. The total-energy curves for Na and Si are presented and the results are compared with experiments and LDA.

The total energy of a many-electron system is obtained by the formula due to Luttinger and Ward,²⁰

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

where the tr operator is defined by $\text{tr} \equiv (i/2\pi) \int d\mathbf{r} d\mathbf{r}' d\omega e^{i\omega\delta}$. E_0 and G_0 are the total energy and Green's function of the noninteracting system in which the Coulomb interaction is switched off. G is Green's function including the electron-correlation effect. The functional Φ is defined as $\Phi[G] \equiv -\sum_n \text{tr}(M_n G)/2n$, with M_n being the n th order contributions to the self-energy. It contains contributions from the Hartree, exchange (Φ_x) and correlation (Φ_c) energies.

In order to carry out calculation in practice, we introduce two approximations. First, we construct Green's function from LDA wave functions $\{\psi_n\}$ and eigenvalues $\{\epsilon_n\}$. Thus $G = G_{\text{LDA}} = \sum_n \psi_n \psi_n^* / (\omega - \epsilon_n)$ is included in Eq. (1). Secondly Φ_c is estimated within the RPA. In terms of a diagrammatic approach, this corresponds to counting closed bubble diagrams only. The total energy E_{RPA} is then rewritten as¹⁴

$$E_{\text{RPA}} = E_{\text{LDA}} - E_{\text{xc}}^{\text{LDA}} + \Phi_x + \Phi_c, \quad (2)$$

where E_{LDA} and $E_{\text{xc}}^{\text{LDA}}$ are the LDA total energy and exchange-correlation energy, respectively. Φ_x is the exchange energy defined by $\Phi_x = -\frac{1}{2} \sum_{n,m}^{\text{occ}} \langle \psi_n \psi_m | 1/r | \psi_m \psi_n \rangle$ and Φ_c is the RPA correlation energy whose explicit expression is given below. We note that both Φ_x and Φ_c are estimated from the LDA wave functions, not from the Hartree-Fock wave functions. Thus, Φ_c is not the difference between the RPA total energy and the Hartree-Fock energy.

The numerical implementation is done as follows. We first solve the LDA Kohn-Sham equation to obtain the band structure. As a numerical check, we use both the full-potential linear-muffin-tin-orbital (FLMTO) method and the full-potential linear-augmented-plane-wave (FLAPW) method. For the LDA exchange-correlation functional, we adopt the von Barth-Hedin formula,²¹ which is based on the RPA cal-

calculation for the electron gas. In the Green's-function approach, we need physical quantities involving the Coulomb interaction $v \equiv \langle \psi_n \psi_m | 1/r | \psi_m' \psi_n' \rangle$. We decompose this by inserting basis $\{|M_I\rangle\}$ such that $\sum_{I,J} \langle \psi_n \psi_m | M_I \rangle \langle M_I | 1/r | M_J \rangle \langle M_J | \psi_m' \psi_n' \rangle$. Here, $\{|M_I\rangle\}$ is required to cover the function space consisting of two one-electron wave functions. We then construct $\{|M_I\rangle\} \equiv \{|B_\alpha\rangle, |P_\beta\rangle\}$ as follows. Within the muffin-tin region, product of two atomic orbitals ϕ_{nlm} is used, namely, $B_\alpha(\mathbf{r}) = \phi_{nlm}(\mathbf{r}) \phi_{n'l'm'}(\mathbf{r})$, which are then optimized to form a minimal orthonormal basis.²² Outside the muffin-tin region, plane wave P_β is used for the basis.⁸ The exchange energy (Φ_x) and the polarizability (χ_0) are computed in this mixed basis. Further numerical techniques will be found elsewhere.^{8,23} The correlation energy is calculated from v and χ_0 as¹⁴

$$\Phi_c = -\frac{1}{4\pi} \int_{\text{BZ}} d\mathbf{k} \int_0^\infty d\omega \sum_I \langle M_I | \ln\{[1 - \chi_0(\mathbf{k}, i\omega)v(\mathbf{k})] \times [1 - v(\mathbf{k})\chi_0(\mathbf{k}, i\omega)]\} + 2\chi_0(\mathbf{k}, i\omega)v(\mathbf{k}) | M_I \rangle. \quad (3)$$

The frequency integration in Eq. (3) is performed along the imaginary axis. This is numerically advantageous, since the polarizability is smooth, in contrast to the real axis where χ_0 has poles at excitation energies. Ten Gaussian points are sufficient for convergence. In this method, the correlation energy is obtained directly from the polarizability, and we need neither the self-energy nor the spectral function of Green's function. This is also preferable for practical calculations, since the polarizability is calculated from LDA wave functions and eigenvalues for which it is easy to obtain numerically accurate values. The Brillouin-zone integration is replaced with summation over 12^3 and 8^3 \mathbf{k} point mesh for Na and Si, respectively. The difference from the LDA total energy, $-E_{xc}^{\text{LDA}} + \Phi_x + \Phi_c$, is estimated by including contributions from valence orbitals only, which are $3s, 3p, 3d$, and $4f$ in both Na and Si. To check the code, we have performed test calculations for the electron gas.

In Fig. 1(a), the exchange energy of Na is plotted by triangles (circles) as a function of the lattice constant a in which the FLMTO (FLAPW) wave function is used. The squares are the LDA exchange energy. For comparison, the analytic value for the electron gas is also presented by a solid line, where the density is set to the average density of valence electrons in Na. The exchange energy is very close to the electron-gas value, reflecting the fact that the valence orbitals of simple metals are nearly free electron. It is interesting to observe that although the Fock exchange Φ_x is electron-gas-like, the LDA exchange energy deviates from the electron-gas line. It is larger in magnitude, and has a slightly steeper slope. The exchange energy from the FLMTO wave function is close to that from FLAPW. This gives us confidence that the calculation has been performed correctly.

The correlation energy is plotted in Fig. 1(b). It is smaller than the exchange energy not only in magnitude but also in variation against a . The variation is, however, sizable on the scale of the total-energy curve described below, so that the correlation energy is crucial for the equilibrium lattice con-

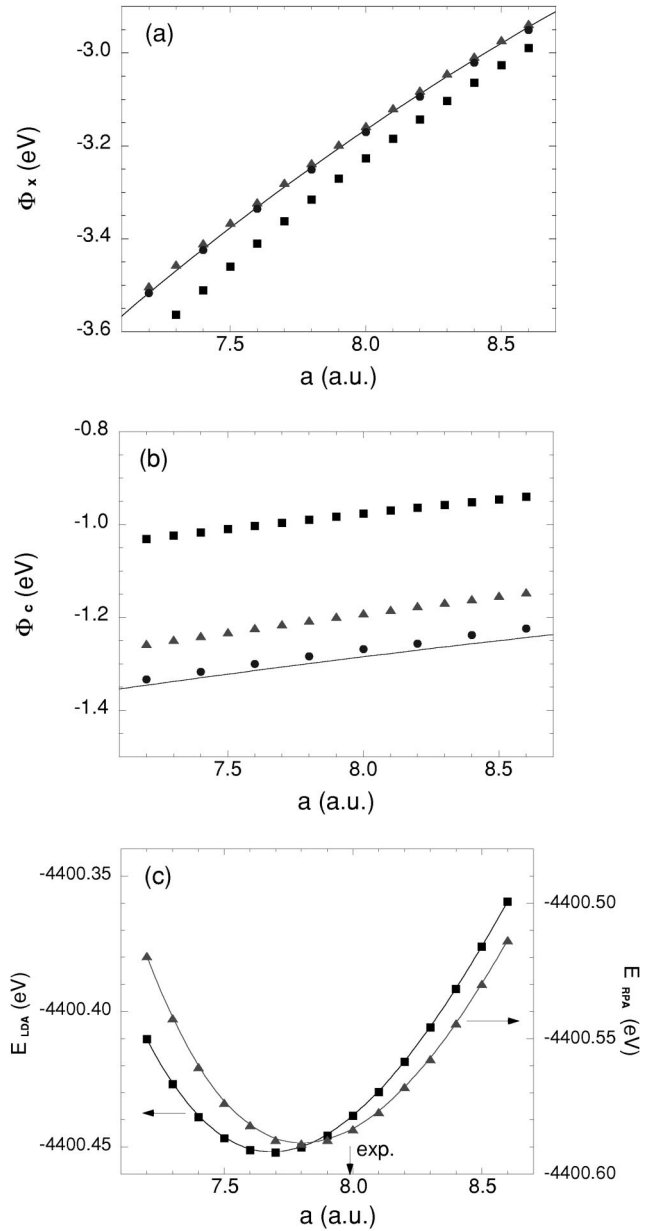


FIG. 1. (a) Exchange energy and (b) correlation energy of Na as a function of the lattice constant. Triangles (circles) are energies computed from the FLMTO (FLAPW) wave functions and eigenvalues. The LDA values are plotted by squares for comparison. The solid line in (a) is the exchange energy of the electron gas, and the solid line in (b) is the electron-gas correlation energy with the von Barth–Hedin formula. (c) Total energy of Na using the LDA (squares) and using the present approach with the RPA correlation (triangles). The experimental lattice constant is also indicated by an arrow.

stant. We see that Φ_c is underestimated by about 10%, when FLMTO wave functions and eigenvalues are used (triangles in the figure). This value is as large as that found in the electron-gas check with the same number of basis, and is attributed to the limited number of unoccupied states in the FLMTO calculation, which includes $3s, 3p, 3d$, and $4f$ orbitals. In any case, the error can be regarded as a constant shift

in the total-energy curve. The solid line is the von Barth–Hedin formula for the RPA correlation of the electron gas.²¹ We see that, as is found in the exchange energy, the correlation energy is also close to the electron-gas line. The LDA correlation energy (squares) is smaller in magnitude than the RPA correlation energy. This partly cancels the overestimation of the exchange energy in the total-energy calculation.

In Fig. 1(c), the total energy by the present approach (triangles) is compared with the LDA energy (squares). Because the exchange energy curve is flatter in the present approach, the total-energy curve leads to a larger equilibrium lattice constant than the LDA case. It is closer to the experimental value, though it is still smaller. The bulk modulus is 0.086 Mbars. It is close to the LDA value, 0.085 Mbars, but is considerably larger than the experimental value 0.077 Mbars (at 0 K). These discrepancies with experiment could be partly due to the effect of $2p$ orbitals. Since they are shallow in energy, their polarization effect will not be negligible. In the present calculation, however, they are treated as core, and the polarization effect is neglected. Further significant development in the numerical calculations is necessary to treat the core.

Now we move to Si. In Fig. 2(a) the exchange energy, (b) the correlation energy, and (c) the total energy are shown. Φ_c is only 1/6 of Φ_x and its variation against a is also small, so that the correlation is not important in structural properties such as the equilibrium lattice constant and the bulk modulus. Actually, even though we neglect the correlation energy, namely, we put $\Phi_c=0$ in Eq. (2), the total-energy curve (not shown here) is reasonable. It shows a minimum at 10.4 bohrs, which is slightly larger than the experimental value 10.26 bohrs. When we include Φ_c , the total energy decreases by about 9 eV and approaches the LDA total energy. The position of the energy minimum is also reduced when Φ_c is included, because Φ_c has a slightly positive slope. To check the convergence, we present two kinds of calculation with different number of muffin-tin orbitals (MTO's). In Fig. 2(b), triangles (crosses) denote a case with 84 (72) MTO's. The difference between the two calculations is rather independent of the lattice constant, and they both show similar behavior with the FLAPW data. Therefore FLMTO with relatively small number of MTO's is quite accurate in describing mechanical properties. The bulk modulus is 0.96 Mbars, which is to be compared with that of the LDA, 0.94 Mbars, and experiment, 0.988 Mbars.

The present approach is based on two approximations. The first one is the approximation of G with G_{LDA} . Hence, the total energy depends on the LDA wave functions and eigenvalues. The GW method starting from the LDA gives an accurate band gap in a wide range of materials. The success implies that the LDA hamiltonian is a good starting point for one-electron excitation spectra. Our results suggest that this is the case also for the total energy. We note here that the Luttinger-Ward formula, on which Eq. (2) is based, satisfies a variational principle; The derivative of the total energy with respect to G is zero, if G is *conserving* in the sense of Baym and Kadanoff.^{24,25} This is an advantage of using the Luttinger-Ward formula over the simpler Galitskii-

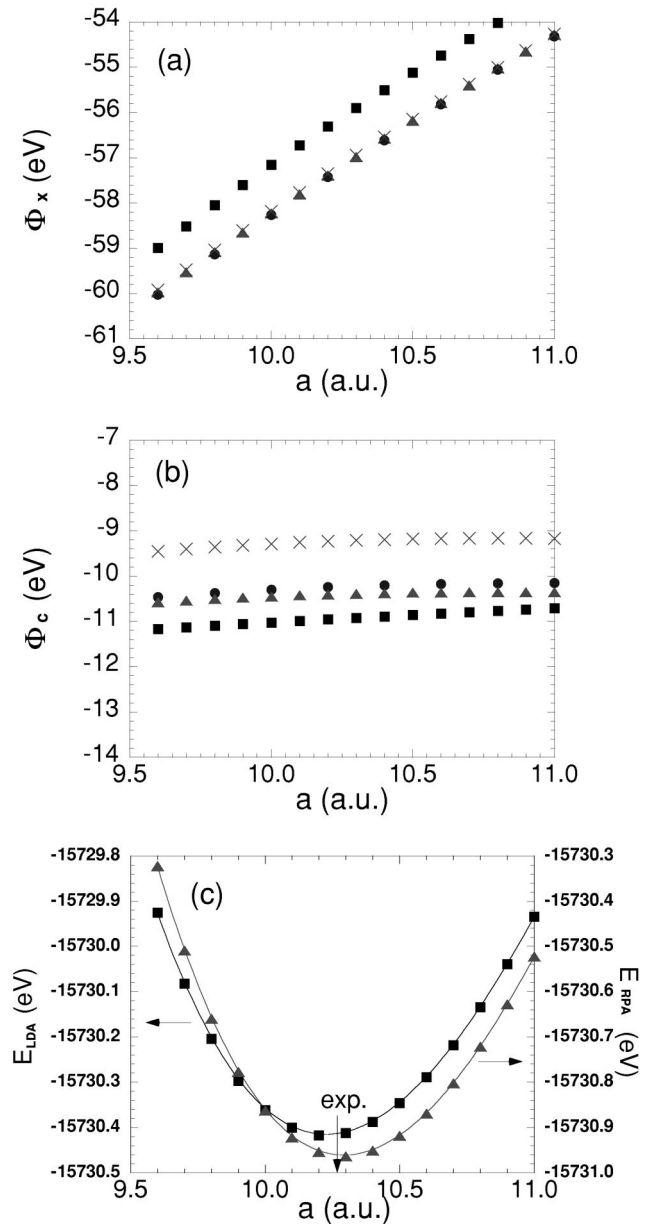


FIG. 2. (a) Exchange energy and (b) correlation energy of Si as a function of the lattice constant. Triangles (circles) are computed from the FLMTO (FLAPW) wave functions and eigenvalues, while squares are LDA values from the FLMTO. Crosses are obtained from the FLMTO with smaller number of basis (see text). (c) Total energy of Si calculated using the LDA (squares) and using the present approach (triangles). The energies are per unit cell which contains two Si atoms. The experimental lattice constant is also indicated by an arrow.

Migdal formula.²⁶ We can expect that the total energy is rather insensitive to the input Green's function.

The other approximation is the RPA for electron correlation. The present two studies suggest that it is valid for describing structural properties of solids. The RPA has a potential to be a powerful tool also for problems for which the LDA fails. An interesting possibility is application to the van der Waals force. It arises from the interaction of virtual di-

poles between distant atoms, and is captured in the RPA as the second-order bubble diagram.^{16,17,27} Neither the LDA nor generalized gradient approximation (GGA) properly describe this interaction.^{28–31,38} Treatment of short-range Coulomb repulsion is another problem in the LDA. Structures and magnetism are qualitatively wrong in some strongly-correlated materials such as LaMnO₃.³² Although the RPA may not be sufficient, it is interesting to apply the present approach to such systems, and see the effect of nonlocality in electron correlations. Comparison with other methods going beyond LDA (GGA,^{33–36} meta-GGA,³⁷ and so on^{38,39}) is also a future problem.

In summary, we have calculated total energies of solids based on the Green's-function approach at the level of RPA. The input Green's function is constructed from LDA wave

functions and eigenvalues, and no adjustable parameters are introduced. As an illustration, total energies of Na and Si are calculated and accurate equilibrium lattice constants are obtained. In particular, the underestimation of lattice constant for Na by the LDA is improved.

The present approach opens a way for deeper understanding of, and going beyond the LDA. In this paper, as a test of the method, we have treated materials for which the performance of LDA is not so bad. Next targets include systems that are difficult to treat with the LDA, such as those with the van der Waals interaction.

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