

## Investigating Exact Density-Functional Theory of a Model Semiconductor

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Using the diffusion quantum Monte Carlo method, we calculate the ground-state density and energy, and the quasiparticle band gap, of a model semiconductor. The exchange-correlation potential of density-functional theory (DFT),  $V_{xc}(\mathbf{r})$ , is obtained using optimization techniques. From this we calculate the DFT functionals  $E_{xc}$  and  $T_x$  and the DFT band gap for various external potentials and compare the results with the local-density approximation (LDA). Whereas energies are found to be very accurate in the LDA, and the density reasonably good, we find large differences in the shape of  $V_{xc}(\mathbf{r})$ .

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In the Kohn-Sham formulation of density-functional theory (DFT) [1,2], the main computational tool for investigating ground-state properties of solids, the full interacting Schrödinger equation is replaced by a fictitious system of noninteracting electrons moving in an effective potential  $V_{\text{eff}}(\mathbf{r})$ , reproducing the true ground-state density  $n(\mathbf{r})$ . These so-called Kohn-Sham (KS) equations involve a universal functional, the exchange-correlation energy  $E_{xc}[n]$ , and its functional derivative  $V_{xc}(\mathbf{r})$ , which are not known exactly. Instead, the local-density approximation (LDA) is generally used, in which the contribution to  $E_{xc}$  from each volume element is taken to be the same as that of a homogeneous electron gas. Despite its crudeness, the LDA has been remarkably successful, although binding energies of molecules and solids are typically overestimated [3]. Also, the band gap of semiconductors is much too small, for example, by 50% for Si [4] and 100% for Ge [5]. It has been shown [6-8] that the band gap  $E_g^{\text{DFT}}$ , even in exact DFT, differs from the true band gap  $E_g$  by an amount  $\Delta$ , which is the discontinuity in  $V_{xc}(\mathbf{r})$  on addition of an electron, reflecting the importance of nonanalyticities in the DFT functionals. In this paper we investigate aspects of the functionals of exact DFT (as estimated using our Monte Carlo calculations) and compare them with the LDA.

Our model system is a semiconducting wire with a strong lateral potential  $v_{\perp}(\mathbf{r}_{\perp}) = \frac{1}{2} \alpha^4 r_{\perp}^2$  confining the electrons to a line. We take  $\alpha$  sufficiently large that excited one-particle states in the lateral direction are suppressed, which leads to an effective one-dimensional Schrödinger equation with an electron-electron interaction of  $v_{e-e}(x) = (\pi/2)^{1/2} \alpha \exp(\xi^2) \text{erfc}(\xi)$ , where  $\xi = \alpha x / \sqrt{2}$ . (A similar system was used in Refs. [6], [9], and [10].) The external potential in the  $x$  direction is taken to be  $V_{\text{ext}}(x) = a \cos(Qx)$ , with the reciprocal-lattice constant  $Q = 2\pi/5$  a.u.<sup>-1</sup>. We choose  $\alpha = 2Q$  and restrict ourselves to systems with one valence band, i.e., with two electrons per primitive cell of length 5 a.u. We simulate systems of  $N=8$  and 12 electrons (with very similar results) in a supercell with periodic boundary conditions for the many-body wave function. In order to avoid "surface" effects, this supercell is repeated 1000 times and the

interaction with the images in the other supercells is taken into account in the electron-electron interaction. The values taken for  $a$  are 0.1, 0.15, 0.25, and 1.0 hartree, taking us from a near-homogeneous semiconducting wire to effectively isolated subsystems.

Our method is based on the calculation of the ground-state energy and electron density of the interacting system using the diffusion quantum Monte Carlo (DQMC) method in its fixed-node approximation, which has been found previously to be very accurate [11,12]. In this method the evaluation of integrals involving the ground-state many-body wave function is reduced to the sampling of a population of random walkers in Hilbert space. The density is approximated as  $n(x) = 2n_f(x) - n_T(x)$ , where  $n_f$  is sampled from  $f = \psi_0 \psi_T$  and  $n_T$  from  $\psi_T^2$ , in which  $\psi_0$  is the many-body ground state and  $\psi_T$  a trial wave function (both of which are real). Since the error in the density is then proportional to  $[\psi_0 - \psi_T]^2$ , we found it necessary to go beyond a simple Slater determinant for  $\psi_T$  by using a Jastrow wave function:  $\psi_T(\mathbf{R}) = D(\mathbf{R}) \exp\{-\sum u(x_{ij})\}$ , where  $D(\mathbf{R})$  is the Slater determinant of self-consistent LDA wave functions obtained as the first step, and  $u(x)$  is a Jastrow pseudopotential whose amplitude is determined variationally [12,13]. We found that the energy, density, and DFT effective potential calculated directly from our optimized trial wave function were very close to our final DQMC results. This gives us confidence in the accuracy of our calculations and leads us to believe that the error involved is not substantially larger than the DQMC noise (indicated in Fig. 1).

In inhomogeneous systems the Jastrow factor has sometimes been modified by the addition of a one-body term [14] which has the effect of constraining the density. However, we found that such a term failed to reduce the total energy in our systems when the density was constrained to be similar to the LDA density, presumably reflecting the error in the LDA density.

The effective potential  $V_{\text{eff}}(x)$  is then calculated. Standard numerical optimization techniques are used to determine the potential which, when occupied with noninteracting electrons, reproduces the density  $n(x)$ . We use

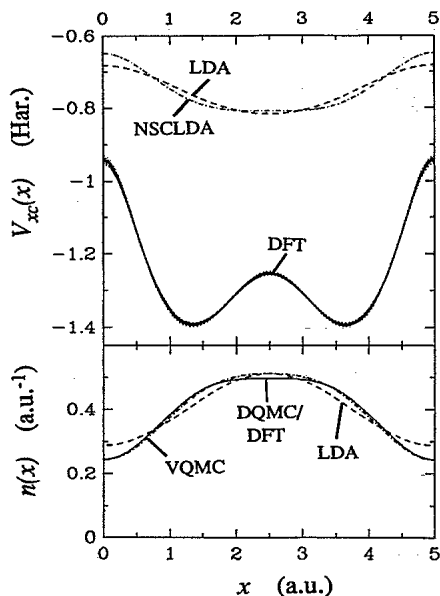


FIG. 1. Top: The exchange-correlation potential  $V_{xc}(x)$  for  $N=8$  electrons and  $a=0.15$  hartree. The exact  $V_{xc}$  lies within the range of the family of dotted curves, indicating the effect of the Monte Carlo noise in the density. The LDA and non-self-consistent LDA potentials are shown for comparison. Bottom: The DFT (calculated using the diffusion quantum Monte Carlo method) and LDA densities  $n(x)$  together with the trial (variational quantum Monte Carlo method) density  $n_T(x)$ . A representation of the Monte Carlo noise in  $n(x)$  (less than 1%) would be almost invisible on the graph.

the first twenty Fourier components of  $V_{\text{eff}}$  as parameters, and an essentially exact fit of  $n(x)$  is possible. This procedure only determines  $V_{\text{eff}}(x)$  within an additive constant, which is adjusted in such a way that the highest occupied KS eigenvalue is equal to the ionization potential calculated directly in DQMC, a property of exact DFT proved earlier [15].  $V_{xc}(x)$  is obtained by subtracting  $V_{\text{ext}}(x)$  and the Hartree potential. Once  $V_{xc}(x)$  is determined, it is possible to decompose the DQMC total energy into its DFT components:  $T_s$  (kinetic energy of the noninteracting electrons),  $E_{\text{ext}}$  (electrostatic energy in  $V_{\text{ext}}$ ),  $E_H$  (Hartree energy), and the remainder  $E_{xc}$  (exchange-correlation energy). Additionally, we obtain the DFT band gap  $E_g^{\text{DFT}}$  from  $V_{\text{eff}}$ , and the true (quasi-particle) band gap  $E_g$  by calculating the ground-state energy upon addition and subtraction of one electron using DQMC:  $E_g = (E_{N+1} - E_N) - (E_N - E_{N-1})$ . This allows us to determine  $\Delta$ , the discontinuity in  $V_{xc}$ . We compare our results (denoted DFT) with the self-consistent LDA (denoted LDA), and also with the non-self-consistent LDA (NSCLDA) in which the DQMC ground-state density is used to determine  $E_{xc}$  and  $V_{xc}$  in the LDA. The LDA exchange-correlation potential used throughout is the Ceperley-Alder LDA [16]:

$$V_{xc}^{\text{LDA}}(x) = \int V_{xc}^{\text{LDA}}(n(\mathbf{r})) |\chi_{\perp}(r_{\perp})|^2 d^2 r_{\perp},$$

where  $\chi_{\perp}(r_{\perp})$  is the lateral part of the wave function and  $V_{xc}^{\text{LDA}}(n)$  is the Ceperley-Alder LDA potential.

The most striking feature of  $V_{xc}^{\text{DFT}}$  is its large difference in shape compared to the LDA result, despite the fact that the density is quite well represented in the LDA (see Fig. 1).  $V_{xc}^{\text{LDA}}(x)$  also lies significantly above  $V_{xc}^{\text{DFT}}(x)$  (Fig. 1). The same was found in all our calculations [13] and agrees with previous results for small atoms [17].  $V_{\text{eff}}^{\text{DFT}}$  has a similar appearance to  $V_{xc}^{\text{DFT}}$ , whereas  $V_{\text{eff}}^{\text{LDA}}$  is rather flat. The density in Fig. 1 has a flat region in the center of the unit cell which coincides with a considerable rise in  $V_{xc}^{\text{DFT}}$  in the same region. Both are absent in the LDA. This illustrates the constraint resulting from locality in the LDA, because a local formulation of  $E_{xc}[n]$  will certainly not be able to reproduce the complex shape of  $V_{xc}(x)$ . In fact, the results suggest that no local or near-local approximation for  $V_{xc}$  could yield the correct density; for example, no gradient expansion could be expected to reproduce the rapid variation of  $V_{xc}(x)$  in the region where the density is almost flat. Using the exact density in NSCLDA leads to other problems. For the system shown in Fig. 1,  $V_{\text{eff}}^{\text{NSCLDA}}$  is not only flat, but also its maxima lie roughly where  $V_{\text{eff}}^{\text{DFT}}$  has its minima. This appears for small  $a$  and leads to a qualitatively wrong KS band structure.

In Ref. [18] an exchange-correlation potential was obtained for silicon by inserting a self-energy operator obtained from many-body perturbation theory into an exact expression for  $V_{xc}$ . In that case the potential determined was rather close to  $V_{xc}^{\text{LDA}}$ , in contrast to the present system. We interpret the difference as arising from two sources. First, our semiconducting wire contains a rapid variation in density perpendicular to the wire, which takes it further than silicon from the homogeneous limit in which the LDA is exactly correct. Second, all occupied Kohn-Sham eigenstates in our semiconducting wire have relatively long wavelengths along the wire, so that the wave functions are somewhat insensitive to the variations in  $V_{\text{eff}}$  on the length scale of 1 a.u. shown in Fig. 1, and it is necessary for the variations to be large to obtain a smaller change in the density. In silicon, the presence of short-wavelength components in the occupied Kohn-Sham wave functions means that a small change in potential is required to change the LDA density to the exact form.

In contrast to the exchange-correlation potential, the LDA yields a reasonably accurate density (average error around 10%) and very accurate results for the total energy (error typically 0.4%) and its components (typical error in  $T_s$  is 6%, but only 0.004 hartree; in  $E_H$ , 0.3%; in  $E_{xc}$ , 1% to 2%; full results to be published [13]): See Table I. This astonishing accuracy underlines how powerful a tool the LDA is for ground-state energy calculations. However, we find that for  $a=1$  hartree, where the primitive cells represent effectively isolated two-electron subsystems, the LDA slightly overestimates the total energy by 0.3 eV per electron, whereas for the

TABLE I. The total energy and its components, in hartrees per electron, in DFT and in the LDA, for the case of  $N=8$  electrons. Results are shown for the two external potentials  $a=0.15$  and 1.0 hartree. The error from the Monte Carlo noise is generally below  $10^{-3}$  hartree. (1 hartree=27.21 eV.)

$a$ (hartree)		$E_{\text{tot}}$	$T_s$	$E_H$	$E_{\text{ext}}$	$E_{\text{xc}}$
0.15	DFT	3.684	0.077	4.203	-0.024	-0.572
	LDA	3.670	0.074	4.198	-0.021	-0.581
1.0	DFT	3.358	0.170	4.418	-0.561	-0.669
	LDA	3.369	0.153	4.394	-0.531	-0.647

near-homogeneous case of  $a=0.15$  hartree it gives an *underestimate* of 0.4 eV (see Table I), with a smooth variation for intermediate values of  $a$ . If we regard the isolated subsystems as "atoms," this would correspond to a cohesive energy too high by 0.7 eV per electron in the LDA, which is roughly the amount that has been observed in molecules and solids [3]. It is remarkable that the error in the LDA total energy is not restricted to  $E_{\text{xc}}$  itself, especially for large  $a$ . For example, the LDA always underestimates the charge inhomogeneity, which results in values for  $T_s$  and  $E_H$  which are too small, and for  $E_{\text{ext}}$  which are too large. For  $a=1$  hartree, the LDA exchange-correlation energy is too high by 0.02 hartree or 3%, which is of the same order as the relative error found by Almladh and Pedroza [17] for two-electron atoms.

In examining the band gaps it is necessary to extrapolate to infinite systems. We find a very weak  $N$  dependence of the DFT band gap  $E_g^{\text{DFT}}$  which is similar to that of  $E_g^{\text{LDA}}$ , allowing a reliable finite-size scaling based on the LDA result. In contrast, the  $N$  dependence of  $E_g$  is very strong, but nearly fully accommodated by using a simple electrostatic model [13]. The results, shown in Fig. 2, reveal that  $E_g^{\text{DFT}}$  is larger than  $E_g^{\text{LDA}}$ , but only about a third of  $E_g$ ; in fact, approximately 85% of the LDA band-gap error is still present in exact DFT (the discontinuity  $\Delta$  in  $V_{\text{xc}}$  on addition of an electron). This agrees with predictions made for Si (over 80%) from Green's-function many-body calculations [18] and also in a two-plane-wave model [6,9]. These results indicate strongly that the main source of the LDA's failure to predict the correct band gap is in fact inherent in exact DFT, emphasizing that one should be cautious when attaching any physical meaning to the eigenvalue spectrum of the KS equations, and showing the role of nonanalyticities in  $E_{\text{xc}}[n]$ .

In conclusion, diffusion quantum Monte Carlo calculations have allowed us to investigate the components of the DFT energy functional, and their functional derivatives, for systems varying from effectively isolated "atoms" to a small-band-gap semiconductor. The small error in the functional  $E_{\text{xc}}$  in the LDA is in striking contrast to the error in its functional derivative  $V_{\text{xc}}$ , while illuminating the known tendency of the LDA to exaggerate cohesive energies. The large discontinuity  $\Delta$  accounts for most of

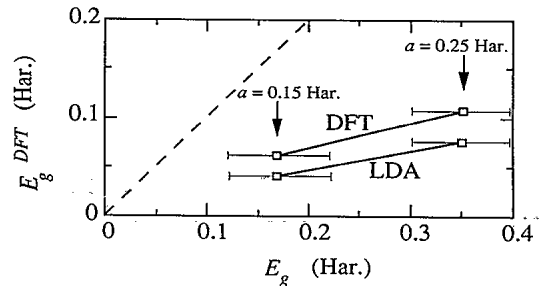


FIG. 2. The DFT band gap  $E_g^{\text{DFT}}$  and the LDA band gap  $E_g^{\text{LDA}}$  vs the true band gap  $E_g$ , obtained from finite-size scaling. The dashed line corresponds to  $E_g^{\text{DFT}}=E_g$ ; the shaded lines are linear extrapolations. The estimated error bars from finite-size scaling are shown.

the LDA band-gap error.

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