

## Nonlocal-density approximation to exchange and correlation: Effect on the silicon band structure

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We present the results of a self-consistent pseudopotential band-structure calculation for silicon using a nonlocal-density approximation for the exchange and correlation potential. The valence bands are very close to the corresponding local-density results; however, the conduction bands are shifted to higher energies with respect to the valence-band edge. Thus the agreement with experiment is substantially improved. In particular, the indirect band gap is reproduced.

### I. INTRODUCTION

A variety of band-structure calculations for silicon have been performed in recent years. The best agreement with the experimental spectra is obtained by using empirical pseudopotentials.<sup>1</sup> These potentials are parametrized one-electron potentials which are designed to reproduce the observed interband transitions. However, such a procedure cannot be made self-consistent because the charge density giving rise to the potentials is not known.

The calculations which have been carried out to self-consistency within the density functional framework used the orthogonalized-plane-wave (OPW) method,<sup>2</sup> the first-principles pseudopotential method,<sup>3</sup> the augmented-plane-wave (APW) method<sup>4</sup> and its linearized version (LAPW),<sup>5</sup> and the linearized-muffin-tin-orbital (LMTO) method.<sup>6</sup> Apart from minor differences the results of these calculations agree with each other, yet the agreement with experimental data is only moderate. In particular, the energy separation between the valence bands and the conduction bands is too small in all these approaches. It is generally believed that this deficiency is related to the insufficient knowledge of the exchange-correlation potential which enters the self-consistent one-electron Hamiltonian. The local-density approximation, which is usually made to obtain an expression for this potential, assumes that the electrons behave locally as a homogeneous electron gas. The resulting exchange-correlation potential is then essentially proportional to the cube root of the local charge density.

The aim of the present work is to show that it is possible to improve agreement with observed interband transitions by going beyond the local-density approximation. We adopt a nonlocal approxima-

tion to exchange and correlation which has been suggested by Gunnarsson *et al.*<sup>7,8</sup> and also by Alonso and Girifalco.<sup>9,10</sup> These authors start with the exact expression for the exchange and correlation energy in terms of the charge density and the pair-correlation function. The latter is then approximated by an analytic function<sup>8</sup> which is exact in several limiting cases. It conserves the total exchange-correlation charge, it reduces to the homogeneous gas form when the electron density is constant, it provides exact cancellation of the electron self-interaction in the case of an hydrogen atom, and it yields the image potential outside a surface. In contrast to the local-density approximation it is not assumed that the electron density varies only weakly in the range of the correlation hole. The exchange and correlation potential derived from this approach has a nonlocal dependence on the entire electron density distribution. Gunnarsson and Jones have shown that these nonlocal modifications lead to a considerable improvement of the exchange-correlation energy in atomic systems when compared with the local-density approximation.<sup>8</sup> Recently Borstel and Neumann used the functional form of a homogeneous electron gas to describe the pair correlation. With this ansatz they performed a relativistic but non-self-consistent APW calculation for rhodium.<sup>11</sup> Even though only the exchange interaction is taken into account they obtained good agreement between the calculated bands and the photoemission data. It is, however, unclear how self-consistency would influence these results.

In the present work we use the nonlocal modification to exchange and correlation proposed by Gunnarsson and Jones<sup>8</sup> to calculate the band structure of silicon self-consistently within the pseudopotential method. In Sec. II the theoretical develop-

ment of the nonlocal approximations to exchange and correlation is given. In Sec. III we present the self-consistent results in terms of the band structure, charge densities, and potentials. In Sec. IV we discuss how the method can be further improved. A summary is given in Sec. V.

## II. NONLOCAL EXCHANGE-CORRELATION POTENTIAL

Following Gunnarsson and Jones<sup>8</sup> we start with the formally exact expression for the exchange-correlation energy

$$E_{xc}[n] = \frac{1}{2} \int d^3r n(\vec{r}) \times \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} n_{xc}(\vec{r}, \vec{r}') . \quad (1)$$

It can be viewed as the interaction energy between the electron distribution  $n(\vec{r})$  and a charge density  $n_{xc}(\vec{r}, \vec{r}')$  of its exchange-correlation hole. The hole describes how the probability of finding an electron at  $\vec{r}'$ , given an electron at  $\vec{r}$ , is suppressed because of the Pauli principle and the Coulomb interaction. We write

$$n_{xc}(\vec{r}, \vec{r}') = n(\vec{r}') G(\vec{r}, \vec{r}') , \quad (2)$$

where  $G(\vec{r}, \vec{r}')$  is related to the pair-correlation function of the system. We choose for  $G$  a convenient analytic form such that certain limits are reproduced, for example,<sup>8</sup>

$$G(\vec{r}, \vec{r}') = C(1 - e^{-\lambda/|\vec{r} - \vec{r}'|^5}) . \quad (3)$$

This ansatz implies that the pair correlation depends only on the distance between two electrons. Because the xc hole corresponds to the removal of one

electron, the following sum rule should be satisfied:

$$\int d^3r' n_{xc}(\vec{r}, \vec{r}') = -1 , \quad (4)$$

which leads to the condition

$$\int d^3r' n(\vec{r}') G(|\vec{r} - \vec{r}'|) = -1 . \quad (5)$$

We require that the energy functional (1) is correct in the homogeneous limit, i.e.,

$$\bar{n} \int G(|\vec{r} - \vec{r}'|) d^3r' = -1 , \quad (6)$$

$$\frac{1}{2} \bar{n} \int \frac{G(|\vec{r}|)}{|\vec{r}|} d^3r = \epsilon_{xc}[\bar{n}] , \quad (7)$$

where  $\epsilon_{xc}[\bar{n}]$  is the exchange-correlation energy per particle of a homogeneous system with density  $\bar{n}$ . Inserting the ansatz (3) into the Eqs. (6) and (7) yields two equations to determine the coefficients  $C$  and  $\lambda$  as a functional of  $\bar{n}$ . For an inhomogeneous system  $\bar{n}$  is determined at each point  $\vec{r}$  by using the sum rule (5). Thus  $\bar{n}$  becomes space dependent. This procedure guarantees that the energy functional (1) gives not only the homogeneous limit but it also yields  $\epsilon_{xc}(\vec{r}) = -e^2/2r$  for large  $r$  in atoms which is the exact result. Finally, outside a surface, it gives the image potential. The hope is that this ansatz can be used to interpolate between the different limits.

The exchange-correlation potential  $V_{xc}$  is defined by

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n} = V_1(\vec{r}) + V_2(\vec{r}) , \quad (8)$$

where

$$V_1(\vec{r}) = \frac{1}{2} \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} n(\vec{r}') [G(|\vec{r} - \vec{r}'|; \bar{n}(\vec{r})) + G(|\vec{r} - \vec{r}'|; \bar{n}(\vec{r}'))] , \quad (9)$$

$$V_2(\vec{r}) = \frac{1}{2} \int d^3r' n(\vec{r}') \int d^3r'' \frac{n(\vec{r}'')}{|\vec{r}' - \vec{r}''|} \frac{\delta G(|\vec{r}' - \vec{r}''|; \bar{n}(\vec{r}'))}{\delta n(\vec{r})} . \quad (10)$$

For systems with slowly varying electron density  $\bar{n}(\vec{r})$  is a weak function of the space variable.<sup>7</sup> It is therefore reasonable to replace the argument  $\bar{n}(\vec{r}')$  of  $G$  in  $V_1(\vec{r})$  by  $\bar{n}(\vec{r})$ .  $V_1(\vec{r})$  is then formally equal to the nonlocal quantum-number-independent exchange potential derived by Alonso and Girifalco using Hartree-Fock theory.<sup>10</sup> The potential  $V_2(\vec{r})$  is

a result of the density functional theory. The functional derivative in Eq. (10) is known and can be calculated once  $\bar{n}(\vec{r})$  is given. Because the computation of  $V_2$  is rather tedious we follow Alonso and Girifalco<sup>10</sup> and also Borstel and Neumann<sup>11</sup> and omit this contribution. A first nonlocal approximation to the exact-correlation potential is then

$$V_{xc}(\vec{r}) \simeq \int d^3r' n(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \times G(|\vec{r} - \vec{r}'|; \bar{n}(\vec{r})), \quad (11)$$

which is used to calculate the band structure of silicon self-consistently. The rhs of Eq. (11) may be rewritten by using the Fourier transform of the charge density  $n(\vec{r})$ ,

$$V_{xc}(\vec{r}) = 4\pi C \lambda^2 \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} F_1(q) |_{q=\lambda G}, \quad (12)$$

where

$$F_1(q) = \frac{1}{q} \int_0^\infty (1 - e^{-(1/r)^5}) \sin(qr) dr. \quad (13)$$

$\vec{G}$  is a reciprocal space vector,  $n_{\vec{G}}$  is the corresponding Fourier component of the charge density. The function  $F_1$  is calculated once and tabulated on a  $q$  grid. The value of  $F_1$  for a  $q$  value, which is not a grid point, is found by interpolation. The coefficients  $C$  and  $\lambda$  are functions of  $\bar{n}(\vec{r})$ , which are determined from the sum rule (5) rewritten in the form

$$4\pi\lambda^3 \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} F_2(q) |_{q=\lambda G} = -1, \quad (14)$$

where

$$F_2(q) = \frac{1}{q} \int_0^\infty (1 - e^{-(1/r)^5}) r \sin(qr) dr. \quad (15)$$

Again  $F_2$  is calculated once and tabulated on a grid. As one can see from Eq. (12)  $V_{xc}$  has to be calculated on a spatial grid throughout the unit cell which should be dense enough to properly include the physical relevant variations in the exchange-correlation potential. If the symmetry of the lattice is taken into account, the numerical effort can be substantially reduced.

### III. RESULTS AND DISCUSSION

To obtain the band structure of silicon the self-consistent pseudopotential method is employed. We construct an effective one-electron pseudo-Hamiltonian for the valence band electrons, which has the form

$$H = p^2/2m + V_{ps} + V_{Coul} + V_{xc}. \quad (16)$$

$V_{ps}$  is a superposition of  $\text{Si}^{4+}$  ionic pseudopotentials. The pseudopotential is generated by using a method described in Ref. 12. It has a soft core but acts differently on the various angular momentum components of the wave function. It yields normalized

pseudowave functions which are smooth and nodeless inside the core region and converge identically to the atomic valence wave functions outside the core. It should be kept in mind, however, that the local-density approximation for exchange and correlation is used to generate the pseudopotential.

The ionic pseudopotential is screened by a Coulomb potential  $V_{Coul}$  which is obtained from the pseudovalence charge density  $\rho(\vec{r})$ :

$$V_{Coul}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' \quad (17)$$

and by the nonlocal exchange-correlation potential  $V_{xc}$  of Eq. (12) where  $n$  is replaced by  $\rho$ . We will denote the sum of  $V_{Coul}$  and  $V_{xc}$  by  $V_{scr}$ . The Schrödinger equation for the Hamiltonian Eq. (16) is solved iteratively in a plane-wave representation until the input and output screening potentials are equal.

The resulting band structure is presented in Fig. 1 and compared with the results of an analogous calculation using a local-density approximation for  $V_{xc}$  suggested by Hedin and Lundqvist.<sup>13</sup> In both cases the energy zero is taken to be the upper valence-band edge at  $\Gamma$ . Obviously the unoccupied conduction bands are shifted upward by 0.3 to 0.5 eV except around  $\Gamma_{2'c}$ , whereas the changes in the valence bands are only minor. In particular, the experimentally measured value of 1.12 eV for the fundamental gap is reproduced in contrast to many other first-principles self-consistent calculations. The agreement with the measured interband transitions  $\Gamma_{15,c} - \Gamma_{25',v}$  and  $\Gamma_{2',c} - \Gamma_{25',v}$  quoted in Table I is only partially improved. The calculated

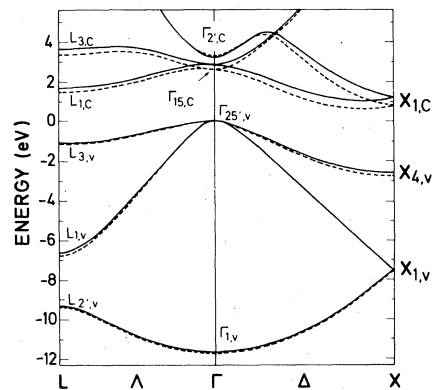


FIG. 1. Self-consistent band structure of Si. The solid lines refer to the results of the present approach using a nonlocal approximation to exchange and correlation. The dashed lines are the corresponding bands obtained from Barth-Hedin's local exchange-correlation potential.

TABLE I. Comparison of some Si-band eigenvalues (in eV) of the present pseudopotential nonlocal exchange and correlation study (NLDA) with the local-density approximation (LDA) using the Barth-Hedin xc functional. The experimental values are quoted from Ref. 4. The "experimental" values for  $\Gamma_{15,c}$  and  $X_{1,v}$  are taken from the empirical pseudopotential results of Ref. 1.

Level	LDA	NLDA	EXPT.
$\Gamma_{1,v}$	-11.80	-11.75	$-12.4 \pm 0.6$
$\Gamma_{25',v}$	0	0	
$\Gamma_{15,c}$	2.60	2.90	(3.42)
$\Gamma_{2',c}$	3.30	3.25	$4.15 \pm 0.05$ $4.21 \pm 0.02$
$X_{1,v}$	-7.55	-7.55	(-7.69)
$X_{4,v}$	-2.70	-2.60	-2.9 $-2.5 \pm 0.3$
$X_{1,c}$	0.75	1.20	1.13
$L_{2',v}$	-9.35	-9.30	$-9.3 \pm 0.4$
$L_{1,v}$	-6.80	-6.60	$-6.4 \pm 0.4$ $-6.8 \pm 0.2$
$L_{3,v}$	-1.10	-1.05	$-1.2 \pm 0.2$
$L_{1,c}$	1.50	1.70	$2.04 \pm 0.06$
$L_{3,c}$	3.35	3.70	$3.9 \pm 0.1$
band gap	0.70	1.10	1.12

values remain too small with respect to experiment.

It is interesting to analyze why the low-lying antibonding state at  $X$  is energetically correct, whereas the corresponding states at  $\Gamma$  are still too tightly bound. Figure 2 shows a contour plot of the difference in the screening potentials  $\Delta V_{scr}$  of the local-density approximation and the present nonlocal approach in the (110) plane. The hatched area where  $\Delta V_{scr}$  is negative refers to the region where the screening potential obtained by the nonlocal xc approximation is larger than the corresponding potential in the local approximation. This region mainly comprises the empty interstitial region of the unit cell. As a consequence states having large amplitudes in this region will be shifted to higher energies. This is indeed the case for states around  $X_{1,c}$  as shown for the  $X_{1,c}$  state in the contour plot of Fig. 3. It is a typical nonbonding state with a fairly high charge density in the interstitial and a low density in the bonding region. From Fig. 4 one can see that the  $\Gamma_{15,c}$  state has a similar charge distribution,

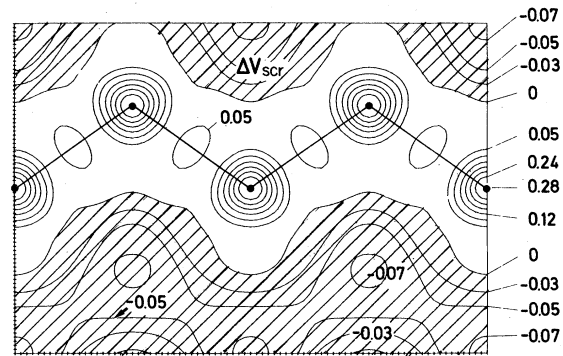


FIG. 2. Difference in the screening potentials of the local-density approximation and the present nonlocal approach in the (110) plane. The contour values are in Ry. The dots indicate the Si atomic positions. Nearest-neighbor sites are connected by a straight line. Also see text.

but it is more localized near the Si sites with much smaller density values in the interstitial. It partially "feels" the reduced screening in the bonding region introduced by the nonlocal xc approach, therefore the upward shift in energy remains moderate.

Figure 2 also shows that by going from the local to the nonlocal-density approximation for exchange and correlation the screening potential is strongly decreased in the Si core region. We will, however, see below that this is an unphysical result which is due to the approximations made in our present nonlocal approach. It implies that the  $\Gamma_{2',c}$  state which is, according to Fig. 5, strongly localized around the

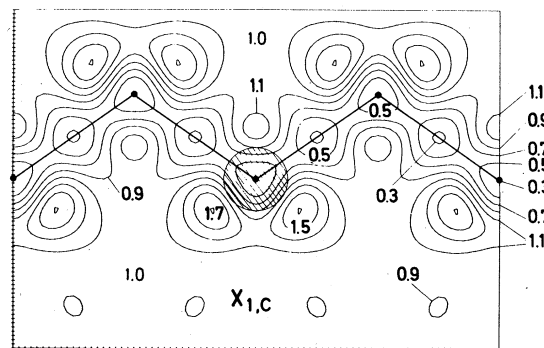


FIG. 3. Symmetrized pseudocharge density of the  $X_{1,c}$  state in the (110) plane of Si as obtained by the present nonlocal exchange and correlation approach. The dots indicate the atomic position, nearest-neighbor sites are connected by straight lines. The charge density is normalized to one electron per unit cell. The extent of the core region is indicated by a hatched circular area around a Si position.

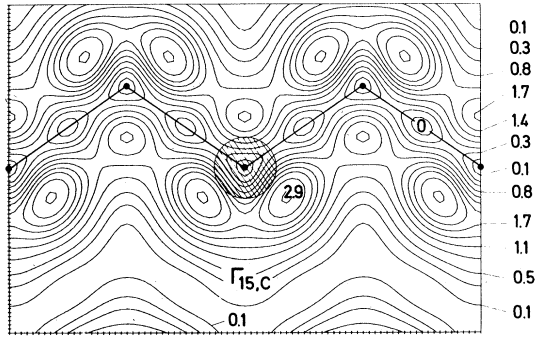


FIG. 4. Symmetrized pseudocharge density of the  $\Gamma_{15,c}$  state in the (110) plane. Conventions as in Fig. 3.

Si sites is even more tightly bound than in the local-density approximation.

#### IV. IMPROVEMENTS

Although the proposed method seems to give an improved description of exchange and correlation in bulk silicon, we have ignored a few inconsistencies which are possibly responsible for the incomplete agreement with experiment. First we recall that the  $\text{Si}^{4+}$  pseudopotential  $V_{\text{ps}}$  is obtained within the local-density approximation for the exchange-correlation part. To be consistent with the bulk calculation the same nonlocal approach should be used for the atom. This means that the pseudopotential as used for the calculation of the Si bulk band structure has to be corrected by adding the term  $V_{\text{ps}}^{NL} - V_{\text{ps}}^L$ , where the superscripts  $NL, L$  should remind us that either the nonlocal or the local-density approximation to exchange and correlation is applied. Gunnarsson *et al.* showed that the xc energy in the proposed nonlocal approach is overestimated in the region between valence and core electron shells in an atom due to intershell effects.<sup>7</sup> To

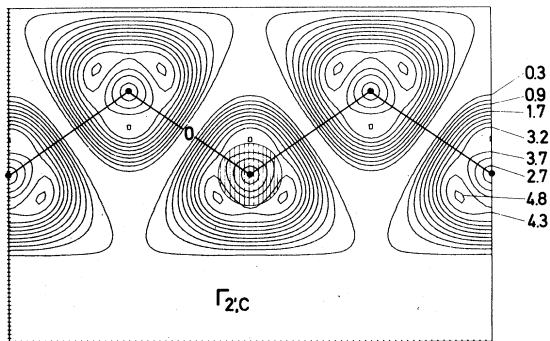


FIG. 5. Symmetrized pseudocharge density of the  $\Gamma_{2,c}$  state in the (110) plane. Conventions as in Fig. 3.

reduce the errors they proposed a partitioning of the atomic charge density  $n_{\text{at}}$  into shell contributions. Neglecting the term  $V_2(\vec{r})$  [Eq. (10)], this scheme means that  $V_{\text{xc}}^{NL}[n_{\text{at}}^{NL}]$  is replaced by  $V_{\text{xc}}^L[n_{\text{at},c}^{NL}] + V_{\text{xc}}^{NL}[n_{\text{at},v}^{NL}]$  if the potential acts on a valence state and by  $V_{\text{xc}}^{NL}[n_{\text{at},c}^{NL}] + V_{\text{xc}}^L[n_{\text{at},v}^{NL}]$  if the potential acts on a core state. The subscripts  $c$  and  $v$  denote core and valence states. The sum rule Eq. (5) for the valence charge density then takes the form

$$\int d^3r' n_{\text{at},v}^{NL}(\vec{r}') G(\vec{r}, \vec{r}'; \bar{n}_{\text{at},v}^{NL}(\vec{r})) d^3r' = - \left[ 1 - \frac{n_{\text{at},c}^{NL}(\vec{r})}{n_{\text{at}}^{NL}(\vec{r})} \right] \quad (18)$$

and similarly for the core charge density. As a consequence the nonlocal exchange-correlation potential due to the charge density  $\rho_{\text{at}}^{NL}$  of the “pseudoatom” is

$$V_{\text{xc}}^{NL}[\rho_{\text{at}}^{NL}] = \int \frac{d^3r'}{|\vec{r} - \vec{r}'|} \rho_{\text{at}}^{NL}(\vec{r}') \times G(\vec{r}, \vec{r}'; \bar{\rho}_{\text{at}}^{NL}(\vec{r})) \quad (19)$$

where  $\bar{\rho}_{\text{at}}^{NL}(\vec{r})$  is determined from Eq. (18) with  $n_{\text{at},v}^{NL}$  replaced by  $\rho_{\text{at}}^{NL}$ . The generalization for a bulk pseudopotential calculation is straightforward. The xc potential is given by Eq. (19) with  $\rho_{\text{at}}^{NL}$  replaced by the bulk pseudocharge density  $\rho$  which mimics the true valence charge density outside the core region of the Si atoms. The density argument  $\bar{\rho}$  in the correlation function  $G$  is calculated from the sum rule Eq. (18), where  $n_{\text{at},v}^{NL}$ ,  $n_{\text{at},c}^{NL}$ , and  $n_{\text{at}}^{NL}$  are replaced by  $\rho$ ,  $n_c$ , and  $\rho + n_c$ .  $n_c$  represents the bulk core charge density. It is obvious that the suggested modifications can only be carried out at the cost of heavier computations. A first estimate showed, however, that the corrected pseudopotential and the modified sum rule yield a considerable repulsive contribution to the effective potential in the core region which would very likely further shift the antibonding states at  $\Gamma$  to higher energies. The potential modification outside the core region turns out to be negligible.

#### V. SUMMARY

We have applied a nonlocal approximation to exchange and correlation to calculate the band structure of silicon self-consistently within the pseudopotential framework. Even though we have neglected in a first step certain features of the method which

are essential to describe the potential in the core region properly, we find that the lowest unoccupied bands are shifted to higher energies with respect to the upper valence-band edge. In contrast to first-principles calculations which make use of the local-density approximation, the agreement with the observed interband transitions is substantially improved. The calculated indirect gap which is usually underestimated by 50% in the local-density approximation agrees with the experimental value.

No attempt is made to test the efficiency of our nonlocal approach at ground-state equilibrium properties like the lattice constant, the bulk modulus, and the cohesive energy. This will be done in a forthcoming publication.

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