# Ab initio self-consistent calculation of silicon electronic structure by means of Wannier functions

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The Kohn variational method to study Wannier functions has been rewritten in a new form that makes it suitable for numerical calculations. Thus, using a Wannier-function scheme, we have been able to perform an *ab initio* self-consistent calculation of the charge density and band structure of silicon. The interactions between the Wannier functions are calculated as well. The Hamiltonian has been built up with a local approximation for the screening potential and a bare ionic potential taken from a fit to atomic properties. Our charge density and band structure are in good agreement with previously reported pseudopotential results. This is the first time that the Wannier functions for connected bands have been calculated. We have verified that satisfactory results are obtained when starting with a simple trial set of localized orbitals.

## I. INTRODUCTION

Localized-orbital schemes seem to be the most convenient way to deal with the electronic properties of semiconductors. Nevertheless, the most precise self-consistent calculations have been done in terms of extended Bloch waves within the pseudopotential framework.<sup>1,2</sup> Some interesting attempts have been made<sup>3-5</sup> to describe the covalent semiconductors by means of localized orbitals, but they do not provide a self-consistent picture.

Conceptually, the most useful set of localized functions for studying the electronic states of a crystal is made of Wannier functions (WF). The direct calculation of the WF from the Bloch functions presents two main difficulties: (i) The integration in the Brillouin zone gives a correct decay of the WF only when several  $\vec{k}$  points are used; (ii) in the case of connected bands a complex computation is necessary to obtain the WF.<sup>6</sup> Although the general theory for obtaining this basis without previous knowledge of the Bloch functions is well established,<sup>7</sup> the serious calculational difficulties have precluded its use in problems where the WF should be very adequate.<sup>8</sup> The WF are determined by a variational procedure. The main obstacle arises because the computation of the necessary spatial integrals is very difficult. This has constrained their use to cases with oversimplified band structures.<sup>9</sup> We have used the variational method by doing the minimization of magnitudes in  $\vec{k}$  space. We so elude the spatial integration as it was done by Mauger and Lanoo<sup>10</sup> in a different framework. The treatment is applied to covalent semiconductors in a self-consistent form by introducing in the Hamiltonian the Hartree, exchange, and correlation potentials produced by the charge in the valence bands. The procedure automatically includes the self-consistency within the minimization, avoiding iterative loops which are time consuming. Thus, the method becomes useful and has allowed us to perform the first self-consistent calculation for silicon based on a description of localized orbitals. As an indication of the power of the method, the calculations reported here were not time consuming (a minimization with two parameters took about three minutes with a UNIVAC 1110).

In Sec. II we briefly sketch the method. The selfconsistent scheme for covalent semiconductors is presented in Sec. III. We apply this scheme to silicon. The results for the bands, charge density, Wannier functions, and the interaction between them are given in Sec. IV. Section V contains the conclusions and a discussion of some forthcoming applications of this work.

# II. FORMALISM

The WF have been invoked in many theoretical discussions, but the difficulty of their calculation, already outlined in Sec. I has precluded the use of this basis in quantitative computations. The bands of actual solids are composite and, therefore, to arrive at the WF from the Bloch states is a substantial endeavor.<sup>6</sup> Nevertheless, a localized set of WF can be obtained in an easier way by a variational procedure as has been shown by Kohn.<sup>7</sup> The method is based on the equivalence between the resolution of the monoelectronic Schrödinger equations for a system of N electrons and the calculation of the stationary value of the functional

$$\epsilon(\Psi) = \frac{1}{N} \langle \Psi \mid \sum_{i=1}^{N} H_{i} \mid \Psi \rangle / \langle \Psi \mid \Psi \rangle , \qquad (2.1)$$

where  $\Psi$  is an arbitrary antisymmetric function and

19

2283

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2284

the  $H_i$  are the N monoelectronic Hamiltonians. By means of the unitary transformation between the Bloch and Wannier functions, Kohn has shown that, in the case of simple bands, the WF  $a(\vec{\mathbf{r}})$  must make stationary the following functional:

$$\langle a(\vec{\mathbf{r}}) | H | a(\vec{\mathbf{r}}) \rangle$$
 (2.2)

When the bands are composite the result must be generalized to include the  $\overline{m}$  WF  $a_m(\vec{\mathbf{r}})$ ,  $\overline{m}$  being the number of connected bands. In this case, the extremum of the functional

$$\epsilon(\Psi) = \sum_{m=1}^{\overline{m}} \langle a_m(\vec{\mathbf{r}}) | H | a_m(\vec{\mathbf{r}}) \rangle$$
(2.3)

must be obtained.

The application of this scheme requires the calculation in real space of the integrals contained in (2.3). In actual crystals, the spatial configuration of the WF makes this computation very difficult. Moreover, the use of a variational procedure implies integration for many values of the variational parameters. This problem can be avoided by writing  $\epsilon(\Psi)$  in the reciprocal space. We are going to sketch briefly the construction of  $a_m(\mathbf{r})$  proposed by Kohn<sup>7</sup> in order to clarify this point. One begins with a set of localized functions, which are normalized but nonorthogonal, depending on a set  $\beta$  of variational parameters

$$f_m(\vec{\mathbf{r}}) = f_m(\vec{\mathbf{r}},\beta), \quad m = 1, \dots, \overline{m} .$$
(2.4)

These functions  $f_m$  must have the adequate spatial symmetry. Usually, physical applications almost never deal with the lowest band of a solid. By orthogonalizing each  $f_m$  to all core states, Eq. (2.3) can be converted from an extremum to a minimum. We must emphasize that this does not mean a minimization of the total electronic energy. In order to orthogonalize the functions  $f_m$ , while maintaining their symmetry, one constructs a set of Bloch functions having the translational symmetry of the lattice.

$$\chi_{m,\vec{k}}(\vec{r},\beta) = \frac{1}{\sqrt{N}} \sum_{\vec{n}} f_m(\vec{r}-\vec{n}) e^{i\vec{k}\cdot\vec{n}}, \qquad (2.5)$$

 $\vec{n}$  being the lattice vectors, and N the number of cells in the crystal. By means of the inner-product matrix

$$G(\vec{\mathbf{k}},\beta)_{m'm} = \langle \chi_{m'\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) | \chi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) \rangle$$
(2.6)

it is possible to build up a second set of Bloch orthogonalized functions

$$\psi_{m,\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) = \sum_{m'} \chi_{m'\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) G^{-1/2}(\vec{\mathbf{k}},\beta)_{m'm}.$$
 (2.7)

At this stage Kohn proposes to obtain the trial WF,

$$a_m^t(\vec{\mathbf{r}}) = \frac{1}{\sqrt{N}} \sum_{\vec{\mathbf{r}}} \psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) , \qquad (2.8)$$

which are exponentially localized and orthonormalized. Hereafter, all the summations in  $\vec{k}$  are over the Brillouin zone. Substitution of  $a_m^t(\vec{r})$  in (2.3) and minimization with respect to  $\beta$  allows one to calculate rather accurately the actual WF. Nevertheless, in order to simplify the numerical computation, it is preferable to make the minimization with the set  $\psi_{m\vec{k}}(\vec{r},\beta)$ . Substituting in (2.3) from (2.8) and using the translational invariance of the Hamiltonian yields

$$\epsilon(\Psi) = \frac{1}{N} \sum_{m=1}^{m} \sum_{\vec{\mathbf{k}},\vec{\mathbf{k}}} \langle \psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) \left| H \left| \psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) \right\rangle \right.$$
$$= \frac{1}{N} \sum_{m=1}^{\bar{m}} \sum_{\vec{\mathbf{k}}} \langle \psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) \left| H \left| \psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta) \right\rangle.$$
(2.9)

The translational symmetry of the functions  $\psi_{m \vec{k}} \left( {\bf r}, \beta \right)$  enables us to write

$$\psi_{j\vec{k}}(\vec{r},\beta) = \sum_{i} \sum_{\vec{g}} c_{i}(\vec{k}+\vec{g},\beta)G^{-1/2}(\vec{k},\beta)_{ij}$$
$$\times e^{i(\vec{k}+\vec{g})\cdot\vec{r}}/\sqrt{N\Omega} , \qquad (2.10)$$

where  $\Omega$  is the volume of the unit cell,  $\vec{g}$  is a reciprocal-lattice vector, and

$$c_{i}(\vec{\mathbf{k}}+\vec{\mathbf{g}},\beta) = \frac{1}{\sqrt{\Omega}} \int_{\Omega} d\vec{\mathbf{r}} e^{-i(\vec{\mathbf{k}}+\vec{\mathbf{g}})\cdot\vec{\mathbf{r}}} f_{i(\vec{\mathbf{r}})}.$$
(2.11)

Then, the inner-product matrix can be rewritten

$$G(\vec{\mathbf{k}},\beta)_{m',m} = \sum_{\vec{\mathbf{g}}} c_{m'}^* (\vec{\mathbf{k}}+\vec{\mathbf{g}},\beta) c_m (\vec{\mathbf{k}}+\vec{\mathbf{g}},\beta). \qquad (2.12)$$

Defining

$$\psi_{j}(\vec{k} + \vec{g}, \beta) = \sum_{i} c_{i}(\vec{k} + \vec{g}, \beta) G^{-1/2}(\vec{k}, \beta)_{ij}, \qquad (2.13)$$

we finally express the functional as

$$\epsilon(\Psi) = \frac{1}{N} \sum_{m=1}^{\overline{m}} \sum_{\vec{k}} \sum_{\vec{g}, \vec{g}'} \psi_m^*(\vec{k} + \vec{g}, \beta) \psi_m(\vec{k} + \vec{g}', \beta)$$

$$\times \langle \vec{k} + \vec{g} | H | \vec{k} + \vec{g}' \rangle$$

$$= \frac{1}{N} \sum_{m=1}^{\overline{m}} \sum_{\vec{k}} \sum_{\vec{g}, \vec{g}'} \psi_m^*(\vec{k} + \vec{g}, \beta) \psi_m(\vec{k} + \vec{g}', \beta)$$

$$\times [\frac{1}{2} (\vec{k} + \vec{g}) \delta_{\vec{g}, \vec{g}'} + V(\vec{k} + \vec{g}, \vec{k} + \vec{g}')]$$
(2.14)

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The cumbersome spatial integrals in (2.3) are

now replaced with the much easier summations in reciprocal space and the integration in the Brillouin zone; the last summation can be done satisfactorily by means of sets of special points.<sup>11,12</sup> In a local approximation only the Fourier components  $V(\vec{g} - \vec{g}')$  of the potential are required. In such an approximation  $V(\vec{g} - \vec{g}')$  is a function of the electronic charge density  $\rho$ . Generally the calculation of  $\rho$  needs a previous resolution of the Schrödinger equations. Therefore, we can only get self-consistency by an iterative procedure. In some cases this can be avoided, as we shall show in Sec. III.

#### **III. COVALENT SEMICONDUCTORS**

The method developed in Sec. II takes its simplest form when we are interested in the calculation of WF for the valence bands of covalent semiconductors. We shall include the core electrons through an ionic pseudopotential, which is equivalent to making the valence states orthogonal to the core states. As a consequence, the whole charge in the system is in the valence bands. Since there is a unitary transformation between the set of functions  $\psi_{m,\vec{k}}(\vec{r},\beta)$  and the valence eigenstates, and the bands are fully occupied, we can write the charge as

$$\rho(\vec{\mathbf{r}},\beta) = 2 \sum_{\vec{\mathbf{k}}} \sum_{m=1}^{4} \psi_{m\vec{\mathbf{k}}}^{*}(\vec{\mathbf{r}},\beta)\psi_{m\vec{\mathbf{k}}}(\vec{\mathbf{r}},\beta)$$
$$= 2 \sum_{\vec{\mathbf{k}}} \sum_{m=1}^{4} \sum_{\vec{\mathbf{g}},\vec{\mathbf{g}}'} \psi_{m}^{*}(\vec{\mathbf{k}}+\vec{\mathbf{g}},\beta)\psi_{m}(\vec{\mathbf{k}}+\vec{\mathbf{g}}',\beta)$$
$$\times e^{i(\vec{\mathbf{g}}'-\vec{\mathbf{g}})\cdot\vec{\mathbf{r}}}/\Omega N.$$
(3.1)

The local potential is a function of the ionic pseudopotential and the variational parameters  $\beta$  through the charge density (3.1). Therefore, the parameters  $\beta$  in  $\epsilon(\Psi)$  are contained both in  $\psi_m(\vec{k} + \vec{g}, \beta)$  and in the Hamiltonian. Nevertheless, the variational procedure enables us to obtain the eigenfunctions of a fixed Hamiltonian, and so it must not vary in the process, though it must be self-consistent with the resulting charge. In other words, the variational equations can be expressed as

$$\delta_{\beta_{1}}\left(\frac{1}{N}\sum_{m,\vec{k}}\sum_{\vec{k},\vec{g}}\psi_{m}^{*}(\vec{k}+\vec{g},\beta_{1})\psi_{m}(\vec{k}+\vec{g}',\beta_{1})\right) \times \langle \vec{k}+\vec{g} | H(\beta_{2}) | \vec{k}+\vec{g}' \rangle \right)|_{\beta_{2}=\beta_{1}}=0, \quad (3.2)$$

or better,

$$\sum_{m,\vec{k}} \sum_{\vec{e},\vec{e}'} \langle \vec{k} + \vec{g} | H(\beta) | \vec{k} + \vec{g}' \rangle$$
$$\times \left| \delta_{g} \left[ \psi_{m}^{*}(\mathbf{k} + \mathbf{g}, \beta) \psi_{m}(\vec{k} + \vec{g}', \beta) \right] = 0.$$
(3.3)



FIG. 1. Atoms in the diamond structure. The first neighbors are labeled according to the  $\vec{\nu}_m$  vectors (see text).

It must be emphasized that this equation represents a cleaner and more elegant way of doing self-consistent calculations than the traditional procedure of iterative resolution of the monoelectronic Schrödinger equations with effective potentials obtained from the charge of the previous solution.

In the diamond structure, the existence of two atoms in the unit cell allows a choice of the WF centered in the bond.<sup>6,7</sup> With this origin, the four WF  $a_m^v(r)$  belong to the identity representation of the point group  $C_{3i}$ . Therefore, in order to build up the trial function we start with functions  $f_m$  which are symmetrical combinations of the  $sp^3$  orbitals on each atom (see Fig. 1):

$$f_m(\mathbf{\tilde{r}}) = (1/\sqrt{2}) \left[ \phi_{\vec{\nu}_m}(\mathbf{\tilde{r}}) + \phi_{-\vec{\nu}_m}(\mathbf{\tilde{r}} - \frac{1}{4}a\vec{\nu}_m) \right], \quad m = 1, \dots, 4$$
(3.4)

where a is the lattice parameter and the  $sp^3$  orbitals are

$$\phi_{\vec{\nu}_{m}}(\vec{\mathbf{r}}) = (1/4\sqrt{\pi}) \left[ F_{s}(\vec{\mathbf{r}},\beta) + \sqrt{3} \left( \vec{\nu}_{m} \cdot \vec{\mathbf{r}}/r \right) F_{\rho}(\vec{\mathbf{r}},\beta) \right],$$
(3.5)

 $\vec{\nu}_m$  being the tetrahedral vectors (1,1,1),  $(\overline{\Gamma},\overline{\Gamma},1)$ ,  $(\overline{\Gamma},1,\overline{\Gamma})$ ,  $(1,\overline{\Gamma},\overline{\Gamma})$ , and  $F_s(\vec{r},\beta)$  and  $F_p(\vec{r},\beta)$  localized orbitals with symmetry s and p, respectively.

It is interesting to point out that the WF associated with the valence bands must be symmetric with respect to the midbond<sup>6,7</sup> and then, in (3.4), there cannot exist a term containing an antisymmetric combination of the functions  $\phi$ —the only restriction on our trial functions consisting of the form taken for the orbitals  $F_s$  and  $F_{\phi}$ .

The angular part of the integrals contained in (2.11) can be easily performed, leading to

2285

6

$$\begin{split} c_{m}(\vec{\mathbf{k}}+\vec{\mathbf{g}}) &= \left(\frac{\pi}{2\Omega}\right)^{1/2} \bigg[ \left( P_{s}(\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|) - iP_{p}(\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|)\sqrt{3} - \frac{\vec{\mathbf{v}}_{m} \cdot (\vec{\mathbf{k}}+\vec{\mathbf{g}})}{\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|} \right) + e^{-i(\vec{\mathbf{k}}+\vec{\mathbf{g}})\cdot\vec{\mathbf{p}}_{m}a/t} \\ &\times \left( P_{s}(\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|) + iP_{p}(\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|)\sqrt{3} - \frac{\vec{\mathbf{v}}_{m} \cdot (\vec{\mathbf{k}}+\vec{\mathbf{g}})}{\left|\vec{\mathbf{k}}+\vec{\mathbf{g}}\right|} \right) \bigg] \end{split}$$

where

$$P_{s}(q) = \int_{0}^{\infty} dr \, r^{2} j_{0}(qr) F_{s}(r), \qquad (3.7)$$

$$P_{p}(q) = \int_{0}^{\infty} dr \, r^{2} j_{1}(qr) F_{p}(r) , \qquad (3.8)$$

 $j_0$  and  $j_1$  being spherical Bessel functions.

In order to solve the variational equations, the first step is to obtain G by substituting (3.6) in (2.12). We calculate  $G^{-1/2}$  by bringing G to diagonal form. Then Eq. (2.13) straightforwardly gives the functions  $\psi_m(\vec{k} + \vec{g}, \beta)$ . The other element necessary in the variational equation is the Hamiltonian. The ionic term of the Hamiltonian can be treated by means of a pseudopotential for the ion  $X^{4+}$  as we shall specify in Sec. IV. The Hartree potential is directly obtained from the Fourier components of the charge:

$$\rho(\vec{\mathbf{G}},\beta) = \frac{2}{N\Omega} \sum_{m=1}^{4} \sum_{\vec{\mathbf{k}}} \sum_{\vec{g},\vec{g}'} \psi_m^*(\vec{\mathbf{k}}+\vec{g},\beta)\psi_m(\vec{\mathbf{k}}+\vec{g}',\beta)\delta_{\vec{\mathbf{G}}+\vec{g}-\vec{g}'}$$
(3.9)

The exchange and correlation potential is usually<sup>1,2</sup> calculated using the Slater approximation for the exchange potential with a coefficient fitted to agree with the Wigner interpolation formula at the average valence-electron density. This term is proportional to  $[\rho(\vec{\mathbf{r}},\beta)]^{1/3}$ . To obtain the Fourier components of this potential requires a troublesome integration in real space. In order to avoid this difficulty we have adopted an approximation which has given very good results for many semiconductors.<sup>13</sup> The charge density in covalent semiconductors varies spatially between 1 and 30 electrons per cell. Within this range  $[\rho(\vec{\mathbf{r}})]^{1/3}$  can be approximated by

$$\rho^{1/3} \simeq 0.1676 + 5.0782 \rho - 21.2564 \rho^2$$
 in a.u. (3.10)

This expansion is easily Fourier transformed using

$$\rho^{2}(\vec{\mathbf{G}}) = \sum_{\vec{\mathbf{g}}, \vec{\mathbf{g}}'} \rho(\vec{\mathbf{g}}) \rho(\vec{\mathbf{g}}') \delta(\vec{\mathbf{g}} + \vec{\mathbf{g}}' - \vec{\mathbf{G}}) . \qquad (3.11)$$

With these approximations the electronic term of the Hamiltonian can be expressed as a function of  $\rho(\vec{G},\beta)$ .

We have now all the ingredients to solve the fundamental Eq. (3.3) and obtain the variational parameters. Once we have determined  $\beta$ , the Wannier functions and a number of interesting magnitudes can be calculated.

4

Finally, let us see the explicit form of the WF. A tractable representation of these functions is their expression in terms of the localized orbitals  $f_m(\vec{\mathbf{r}} - \vec{\mathbf{n}})$  because this gives a picture of their shape and extension. Substituting (2.5)-(2.7) in (2.8) yields

$$a_{m}(\vec{\mathbf{r}}) = \sum_{m'=1}^{4} \sum_{\vec{\mathbf{n}}} f_{m'}(\vec{\mathbf{r}} - \vec{\mathbf{n}}) \alpha_{m'm}(\vec{\mathbf{n}}) , \qquad (3.12)$$

where

$$\alpha_{m'm}(\vec{n}) = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{n}} G^{-1/2}(\vec{k})_{m',m}.$$
(3.13)

If the orbitals  $f_m$  are exponentially localized functions, the matrix  $G^{-1/2}(\vec{k})$  is a smoothly varying function of the wave vector. The spatial dependence of  $\alpha_{m'm}(\vec{n})$  is given by the factor  $\exp(i\vec{k}\cdot\vec{n})$  in the integrand. The fast oscillations of this factor for large  $\vec{n}$  show that  $\alpha_{m'm}(\vec{n})$  must vanish for highorder neighbors. In the case of near neighbors the smoothness of the integrand allows an integration using special points.

#### **IV. APPLICATION TO SILICON**

Silicon has been widely studied both by linear combination of localized orbitals<sup>3-5</sup> and pseudopotential<sup>1,2</sup> approaches. Nevertheless, the selfconsistency has only been reached in delocalized schemes. We are going to apply to silicon the method developed above for two main reasons: First, the existence of self-consistent calculations allows us to test the method. Second, in order to have a self-consistent description of this semiconductor in terms of localized functions.

In self-consistent-field atomic calculations the Slater-type orbitals (STO) have given the best results for minimal basis.<sup>14</sup> Therefore, to start the calculation we choose the STO as a functional form for  $F_s(\vec{r},\beta)$  and  $F_p(\vec{r},\beta)$  which has the radial dependence

$$F_{s}(r) = c_{s} r^{2} e^{-\beta_{s} r}, \quad F_{p}(r) = c_{p} r^{2} e^{-\beta_{p} r} \quad (4.1)$$

(3.6)

where

$$c_s = (2\beta_s)^{7/2} / \sqrt{6!}, \ c_p = (2\beta_p)^{7/2} / \sqrt{6!}, \ (4.2)$$

 $\beta_s$  and  $\beta_b$  being the variational parameters.

All the results presented below have been obtained with the trial functions (4.1), but we have solved the self-consistent Eq. (3.3) with a better description of the p orbitals,

$$F_{a}(r) = cr^{2}(e^{-\beta_{1}r} + \alpha e^{-\beta_{2}r}), \qquad (4.3)$$

where  $\beta_1$ ,  $\beta_2$ , and  $\alpha$  are variational parameters. The numerical value of the minimum calculated for the functional  $\epsilon(\Psi)$  does not change significatively (<2%) from that obtained for the simpler set (4.1).

The simplicity of the choice (4.1) allows one to perform analytically the integrals in (3.7) and (3.8), giving

$$P_{s} = \frac{24c_{s}(\beta_{s}^{3} - \beta_{s}q^{2})}{(\beta_{s}^{2} + q^{2})^{4}}, \quad P_{p}(q) = \frac{8c_{p}(5\beta_{p}^{2}q - q^{3})}{(\beta_{p}^{2} + q^{2})^{4}}.$$
 (4.4)

Hereafter, our calculation must be done numerically. In the equations, two types of sums are involved: the sums which run over the reciprocallattice vectors  $\vec{g}$  and those over the wave vector  $\vec{k}$ . For the former, we have studied the convergence by doing the computations successively with 27, 59, and 169  $\vec{g}$  vectors. The results show good convergence for the approximation with 59 vectors which-includes the sets  $\{(0,0,0)\}$ ,  $\{(1,1,1)\}$ ,  $\{(2,0,0)\}$ ,  $\{(2,2,0)\}$ ,  $\{(3,1,1)\}$ , and  $\{(2,2,2)\}$ . The sums in which  $\vec{k}$  runs over the whole Brillouin zone have been calculated satisfactorily by means of sets of special points.<sup>12</sup> In particular, for simplicity, we have worked with the mean-value point proposed by Baldereschi.<sup>11</sup>

The last point to discuss is the ionic pseudopotential for Si<sup>4+</sup>. Very good ionic pseudopotentials have been used in previous computations of the silicon band structure.<sup>1,2</sup> They contain parameters adjusted to the bulk crystal properties within a specific calculation. Perhaps their use in other schemes is not well justified. Recently, Simunek<sup>15</sup> has obtained a pseudopotential for Si<sup>4+</sup> which is fitted to reproduce the spectroscopic energy levels and the outer part of the wave function in the atom. Therefore, we have used this ion<sup>16</sup> which is the most interesting for the analysis presented here. However, in order to test the accuracy of our approach, we shall show as well the results obtained by using the pseudopotential of Schlüter *et al.*<sup>2</sup>

The existence of two parameters in our trial functions transforms the fundamental Eq. (3.3) in a system of two nonlinear coupled equations where the unknown quantities are  $\beta_s$  and  $\beta_p$ . By solving

TABLE I. Fourier components of the valence charge density (in electrons per cell) and form factors of the pseudopotential (in a.u.).

$\dot{\bar{g}}(a/2\pi)$	$\rho^{a}$	v <sup>a</sup>	ρ <sup>b</sup>	v <sup>b</sup>
(1,1,1)(2,2,0)(3,1,1)(2,2,2)(4,0,0)(3,3,1)(4,2,0)	-1.419 0.191 0.259 0.162 0.183 -0.044	-0.1134 0.0290 0.0417 0.0 0.0353 0.0283	$-1.376 \\ 0.195 \\ 0.249 \\ 0.153 \\ 0.171 \\ -0.040 \\ 0.0$	$\begin{array}{c} -0.1037\\ 0.0243\\ 0.0391\\ 0.0\\ 0.0341\\ 0.0268\\ 0.0\\ \end{array}$
(4,2,0) (4,2,2) (3,3,3) (5,1,1) (4,4,0)	$-0.037 \\ -0.016 \\ -0.016 \\ -0.003$	0.0180	$\begin{array}{c} 0.0 \\ -0.034 \\ -0.014 \\ -0.014 \\ -0.001 \end{array}$	0.0152

<sup>a</sup>Results for the ion of Simunek (Ref. 15).

<sup>b</sup>Results for the ion of Schlüter et al. (Ref. 2).

the system we have obtained  $\beta_s = 1.711$  and  $\beta_p = 1.269$ for the Simunek's ion and  $\beta_s = 1.714$  and  $\beta_p = 1.231$ for the ion of Schlüter *et al.* A self-consistentfield calculation<sup>14</sup> for atomic silicon with a minimal STO basis gives  $\beta_s = 1.634$  and  $\beta_p = 1.428$ . From these values it is straightforward to obtain the form of the  $sp^3$  orbitals noticing a spreading of these orbitals when they are in the crystal. This result can be physically understood. The overlap between ions lowers the potential in the orbital tails region, expanding the "atomic" wave functions.

In Table I the Fourier components of the charge density obtained from Eq. (3.9) are given in a system where the origin is placed in the midbond. The results with different ions are very similar and compare satisfactorily with previous calculations.<sup>17,18</sup> The spatial distribution along the direction which joins two nearest neighbors is shown in Fig. 2 for the Simunek ion. The other calculation gives nearly the same result, the small differences being the



FIG. 2. Valence charge density in silicon along the bond direction. The dots represent the ions. Units are electron per cell. The values of the extrema are 10.8, 6.3, and 18.9.



FIG. 3. Band structure of Si obtained from the ionic pseudopotential of Schlüter *et al.* (Ref. 2). The origin of the energy scale is taken at the mean value of the crystal potential.

values of the two maxima and the minimum which are 10.7, 6.4, and 18.5. In Table I the pseudopotential form factors are also shown, where, in consistency with our approximation (59  $\tilde{g}$  vectors), the components with  $g^2 > 24(a^2/4\pi^2)$  are not included. There is a nonzero (2,2,2) Fourier component in the potential, caused by a corresponding component in the charge. Nevertheless, the Hartree potential produced by it is much smaller than the other components of the pseudopotential form factors. The numerical values obtained for v(g) are similar to those given in the literature.<sup>1,2</sup> The meaning of this result is that we have a good screening of the bare ions by means of the simple functions (4.1). The small differences appearing with respect to previous work must be clarified by means of a band-structure calculation. Such a calculation is very easy in our scheme, where we have a basis formed by four Bloch functions, and so the computation is reduced to the diagonalization of a  $4 \times 4$  matrix. Hitherto we have studied the valence bands, but for a band structure it would be interesting to have information about the conduction bands. If the conduction bands were an isolated set of four bands, one could build up a set of four WF  $a_m^{(c)}(\mathbf{r})$  belonging to the one-dimensional antisymmetric representation of the group  $C_{3i}$ . Nevertheless, these bands are connected with higher bands and the application of the variational method is somewhat questionable. Still, in order to calculate a more complete band structure we shall construct, as an approximation to the conduction bands, a set of four "antisymmetric" functions in a manner similar to our handling of the valence bands. So we have a basis of eight localized functions per cell in terms of the parameters  $\beta_s$ ,  $\beta_p$ previously determined. The diagonalization of the  $8 \times 8$  Hamiltonian in the corresponding Bloch basis gives us the band structure which is shown in Figs. 3 and 4 for the different ions. The results are satisfactory, not only for the valence bands but also for the conduction bands.<sup>19</sup> We must emphasize that only the valence bands are included in the variational procedure. Therefore, the good result obtained for these bands was expected. On the contrary, the good agreement of the conduction bands is somehow surprising.

The WF  $a_m(\vec{\mathbf{r}})$  for the valence bands are the most important result of the method. As we have pointed out in Sec. III, the WF can be expressed in terms of the atomic orbitals. The results for  $\alpha_{m'm}(\vec{\mathbf{n}})$  are given in Table II. They do not depend significatively on the ion, and decrease rapidly, being almost zero beyond the third-bond neighbors.

As an application of the WF we have studied the interaction of the WF through the self-consistent Hamiltonian

$$\epsilon_{m'm''}(\vec{\mathbf{n}}) = \langle a_{m'}(\vec{\mathbf{r}}) | H | a_{m''}(\vec{\mathbf{r}} - \vec{\mathbf{n}}) \rangle , \qquad (4.5)$$

by using (2.8)

$$\epsilon_{m'm''}(\vec{n}) = \frac{1}{N} \sum_{\vec{k}} \sum_{\vec{k},\vec{k}'} e^{-i\vec{k}\cdot\vec{n}} \psi_{m'}^*(\vec{k}+\vec{g})\psi_{m''}(\vec{k}+\vec{g}') \times \langle \vec{k}+\vec{g} | H | \vec{k}+\vec{g}' \rangle.$$
(4.6)

The results are shown in Table II (in a.u.). It is important to notice that the third-bond-neighbor interactions are not negligible. This is a conse-



FIG. 4. Band structure of Si obtained from the Simunek ionic pseudopotential (Ref. 15). The scale is taken as in Fig. 3.

Bond neighbors	α <sup>a</sup>	α <sup>b</sup>	ۻ	€b	
First: parallel	0.8072	0.8125	0.1846	0.1979	
nonparallel	-0.0355	-0.0387	-0.0460	-0.0462	
Second: parallel	0.0186	0.0205	0.0055	0.0060	
nonparallel	-0.0136	-0.0145	-0.0031	-0.0035	
Third: parallel	-0.0186	-0.0205	-0.0055	-0.0060	
nonparallel	0.0160	0.0173	0.0104	0.0108	
	0.0173	0.0183	0.0135	0.0138	
	0.0043	0.0046	0.0015	0.0015	
	-0.0043	-0.0046	-0.0077	-0.0077	
	-0.0075	-0.0082	-0.0011	-0.0014	

TABLE II. Coefficients  $\alpha$  of the expansion of a WF in terms of the localized orbitals  $f_m$  and interactions  $\epsilon$  (in a.u.) between WF through the self-consistent Hamiltonian (see text).

<sup>a</sup>Results for the ion of Simunek (Ref. 15).

<sup>b</sup>Results for the ion of Schlüter et al. (Ref. 2).

quence of the overlap between atomic orbitals. From the integrals (4.5) general information about the behavior of the Koster-Slater parameters could be obtained.

## V. CONCLUDING REMARKS

In this work the method developed by Kohn<sup>7</sup> to build up the Wannier functions of connected bands has been reformulated in such a way that it can be used in numerical computations. We want to stress the two innovations introduced here: First, is the minimization of magnitudes in  $\vec{k}$  space avoiding the cumbersome integrations in real space; The second is the possibility of obtaining, in the case of fully occupied bands, a self-consistent solution by means of the fundamental Eq. (3.3), which is a more elegant way than the usual iterative procedure. The method has been applied to the calculation of WF for the valence bands of silicon. As a previous test, both the charge and band structure have been calculated for a well-known ionic crystal potential<sup>2</sup> with satisfactory results even for the lower conduction bands, although they are connected with higher bands. On these grounds we have done the first ab initio self-consistent computation of the charge density and band structure of silicon by using a localized basis and an ionic noncrystalline pseudopotential.<sup>15</sup> The WF have been invoked in many papers but they have only been obtained in simple cases.<sup>9</sup> Therefore, our more important result is a set of WF for the valence bands of silicon. Moreover, we have calculated their interactions through a self-consistent Hamiltonian.

We are working on the extension of the scheme in three directions: (i) The application of the results here obtained to the study of problems in covalent semiconductors such as the dielectric function, optical absorption, etc. (ii) The study of other materials where a localized scheme is the most adequate, such as the *d* bands of noble and transition metals. Two main difficulties must be solved: the nonexistence of an ionic pseudopotential and the charge-density calculation when the bands are not fully occupied. (iii) The use of variational methods for a quantitative study of localized problems such as impurities, vacancies, surfaces, etc., where generalized Wannier functions must be introduced.<sup>20</sup>

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