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#### First-principles Wannier functions of silicon and gallium arsenide

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We present a self-consistent, real-space calculation of the Wannier functions of Si and GaAs within density-functional theory. We minimize the total-energy functional with respect to orbitals which behave as Wannier functions under crystal translations and, at the minimum, are orthogonal. The Wannier functions are used to calculate the total energy, lattice constant, bulk modulus, and the frequency of the zone-center TO phonon of the two semiconductors with the accuracy required in *ab initio* calculations. Furthermore, the centers of the Wannier functions are used to compute the macroscopic polarization of Si and GaAs in zero electric field. The effective charges of GaAs, obtained by finite differentiation of the polarization, agree with the results of linear-response theory. [S0163-1829(97)51504-9]

Since their introduction in 1937, the Wannier functions<sup>1</sup> (WF's) have played an important role in the theoretical study of the properties of periodic solids.<sup>2</sup> Very recently they have been one of the main ingredients of a novel theory of the electronic polarization in terms of a Berry phase.<sup>3</sup> Notwithstanding, in computational applications, the representation of the electronic wave functions with Bloch orbitals is the method of choice. In fact, for periodic systems, the Bloch theorem allows us to exploit the translational invariance of the solid, and to restrict the problem to one unit cell. The properties of the infinite solid are recovered with an integral over the Brillouin zone, which can be approximated with a finite sum.

The WF's extend in principle all over the solid, and it is possible to compute only approximate WF's which are constrained to be zero outside a localization region (LR). In recent years, these approximate WF's turned out to be a key concept in the development of electronic-structure methods whose computational cost scales linearly with the system size.<sup>4,5</sup> Furthermore these Wannier-like functions provide a

very promising way to study the electronic properties of a solid in the presence of a macroscopic electric field.<sup>6</sup>

For these reasons, it is now important to develop *ab initio* methods to compute the approximate WF's of a crystal, to study their properties as a function of the LR, and to show in practice that using WF's it is possible to extract structural and electronic properties of materials as accurate as those obtained with Bloch functions.

The WF's are related to the Bloch functions by a unitary transformation. However, this transformation is highly non-unique because the Bloch functions are determined only up to a multiplicative phase factor which introduces a large ambiguity in the localization properties of the resulting WF's. For one-dimensional periodic solids, with a finite gap, it has been shown analytically that an appropriate choice of the phases of the Bloch functions leads to WF's which decay exponentially in space.<sup>7</sup> In a real solid, band crossing and phase freedom make the problem of localization particularly hard. A possible approach in this direction has been recently discussed by Sporkman *et al.*<sup>8</sup> Although they obtained reasonably localized WF's also for fcc transition metals, they

did not test the accuracy of their functions against any physical properties.

Several years ago, W. Kohn proposed to compute the WF's of solids by minimizing the total energy in a variational scheme where the trial functions were localized.<sup>9</sup> However, from a computational point of view the orthogonality constraint was a major problem and a few numerical experiments have been performed along these lines.<sup>10</sup> Nowadays, after several advances towards an order- $N$  method for electronic structure calculations, it is simpler to build an electronic structure code entirely based on WF's. One example is presented in this work.

In the framework of density-functional theory (DFT), Galli and Parrinello<sup>4</sup> introduced nonorthogonal localized orbitals to minimize the total energy and to obtain the electronic ground state. In Ref. 5, a total-energy functional was proposed, which is minimized by orthogonal orbitals and has the same minimum as the standard total-energy functional. Within a tight-binding formalism, this energy functional has been used to obtain almost orthogonal localized orbitals which reproduce the ground-state properties of silicon and carbon.

In this work we implement this functional in a self-consistent scheme and we test extensively the practical possibility to describe with Wannier functions the structural, electronic, and dielectric properties of materials at the level of accuracy obtained with Bloch wave functions. Focusing on small unit cell systems we can use very large LR and check the convergence of the physical properties to the exact ground state. At variance with the approach of Refs. 4 and 5 we use explicitly the translational properties of the WF's during the minimization of the total-energy functional.<sup>6</sup> At the minimum, the orbitals are almost orthogonal and are a good approximation of a set of WF's for the system. We study two crystals: silicon and gallium arsenide. We use DFT in the local-density approximation (LDA), and describe the atoms with norm-conserving pseudopotentials. For each system we obtain the total energy, the lattice constant, the bulk modulus, and the frequency of the zone-center transverse optical phonon and we study their dependence on the size of the LR. LR's containing up to 342 atoms for Si and 216 atoms GaAs are considered, and our results are compared with converged values obtained with a plane-wave (PW) pseudopotential code based on Bloch orbitals. We show that the error associated to the localization can be made lower than the errors usually associated to the use of LDA or pseudopotentials. We also address the ability of the approximate WF's to describe the macroscopic polarization of semiconductors in zero electric field by computing the Born effective charges of GaAs. We show that the effective charges extracted from our approximate WF's are in good agreement with those obtained with a linear-response approach based on Bloch functions.

A system of  $N$  interacting electrons described in the framework of DFT-LDA, can be studied by introducing  $N/2$  orbitals which describe an auxiliary system of noninteracting electrons.<sup>11</sup> In a periodic solid, the Bloch theorem allows to label these states with a  $\mathbf{k}$  vector in the first Brillouin zone and a band index  $n$ . In insulators the number of occupied bands is one half the number of electrons  $N_{\text{el}}$  contained in one unit cell. An equivalent representation can be

obtained using a set of WF's  $|w_{l,n}\rangle$ , where  $n$  is the band index, and  $l$  indicates the Bravais lattice vector  $\mathbf{R}_l$ . The WF's are orthonormal and  $|w_{l,n}\rangle$  is obtained by translating the function centered at the origin by  $\mathbf{R}_l$ , i.e.,  $|w_{l,n}\rangle = \hat{T}_{\mathbf{R}_l}|w_{0,n}\rangle$ .

The WF's are not unique: their shape and localization in real space are arbitrary. However the physical quantities computed from WF's do not depend on their shape. In particular the electronic contribution to the macroscopic polarization per unit cell has a very compact expression in terms of WF's,<sup>3</sup> i.e.,  $\mathbf{P}_{\text{el}} = -2\sum_n \langle w_{0,n}|\mathbf{r}|w_{0,n}\rangle$ . This expression can be used to compute the Born effective charges which are the derivative of the polarization with respect to atomic displacements in zero electric field. Using WF's this quantity is immediately available from a finite numerical differentiation.

In Refs. 5 and 6 it has been shown that WF's for a solid can be obtained directly by minimizing the following functional:

$$E_{\text{tot}}[\{v\}, \eta] = \sum_n \sum_{l,m} 2Q_{n,m}^{0,l} \langle v_{0,n} | -\frac{1}{2}\nabla^2 + \hat{V}_{\text{NL}} | v_{l,m} \rangle + F[\tilde{n}] + \eta(N_{\text{el}} - \tilde{N}), \quad (1)$$

where  $Q_{n,m}^{0,l} = 2\delta_{l,0}\delta_{n,m} - \langle v_{0,n} | v_{l,m} \rangle$ ,  $\tilde{N}$  is the integral over one unit cell of the charge density  $\tilde{n}(\mathbf{r})$  defined as

$$\tilde{n}(\mathbf{r}) = \sum_{k,n} \sum_{l,m} 2Q_{n,m}^{k,l} \langle v_{k,n} | \mathbf{r} \rangle \langle \mathbf{r} | v_{l,m} \rangle, \quad (2)$$

$\hat{V}_{\text{NL}}$  is the nonlocal part of the pseudopotential and  $F[\tilde{n}]$  is the sum of the local, Hartree and exchange-correlation energies.  $\eta$  is an energy parameter which is fixed in such a way to be higher of the highest occupied eigenvalue. The functions  $|v_{l,n}\rangle$  are obtained by translating  $|v_{0,n}\rangle$ , i.e.,  $|v_{l,n}\rangle = \hat{T}_{\mathbf{R}_l}|v_{0,n}\rangle$  and therefore they do not add any additional degrees of freedom. The charge  $\tilde{n}(\mathbf{r})$  is periodic in the unit cell. Although no orthogonality constraint is explicitly imposed on the  $|v_{l,n}\rangle$ , at the minimum, the  $|v_{l,n}\rangle$  are orthonormal and form a set of WF's for the solid.<sup>5</sup>

In our calculation, we represent the functions  $|v_{l,n}\rangle$  on a uniform cubic real-space mesh with spacing  $h$  in each direction  $\mathbf{r}_{ijk} = (ih, jh, kh)$ , where  $i, j, k$  are integers. Since it has been shown that the WF's of insulators can be chosen exponentially localized, we impose  $\langle \mathbf{r}_{ijk} | v_{0,n} \rangle$  to be zero if  $\mathbf{r}_{ijk}$  is outside a cubic region of size  $2a_{\text{LR}}$ . The nonzero coefficients  $\langle \mathbf{r}_{ijk} | v_{0,n} \rangle$  are obtained by minimizing the total energy Eq. (1). The imposition of localization is a variational approximation for the total energy which, at the minimum, gives orbitals which are not exactly orthonormal.<sup>5</sup> By increasing the size of the localization region the variational estimate of the energy improves and the deviation of the orbitals from orthonormality is reduced. Therefore the orbitals converge to a set of WF's for the system. Note that, if localization is imposed, the sums over  $l$  appearing in Eq. (1) and  $(k, l)$  in Eq. (2) become finite and determined by the set  $(l, m)$  of LR that overlap with all the LR  $(0, n)$  of the first unit cell.

In order to compute  $E_{\text{tot}}[\{v\}, \eta]$  we need to apply  $-\frac{1}{2}\nabla^2 + \hat{V}_{\text{NL}}$  to  $|v_{0,n}\rangle$ . We evaluate these operators directly

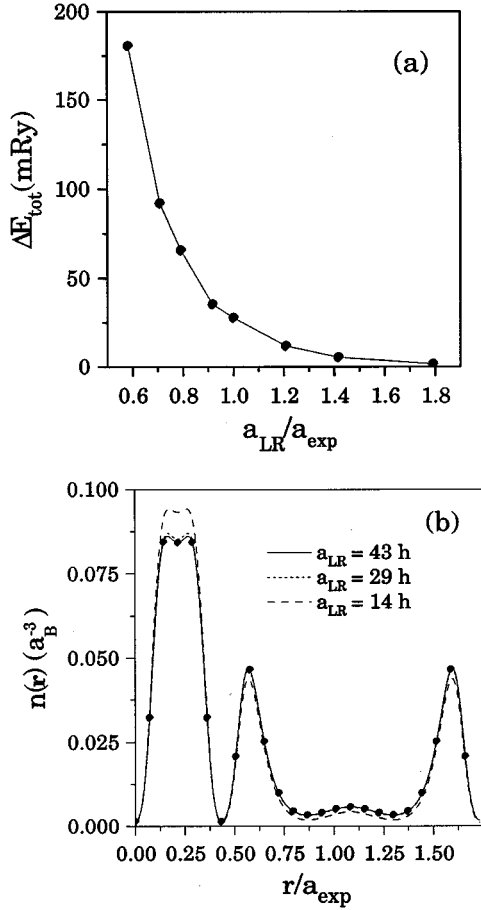


FIG. 1. Si: (a): Total energy versus the size  $a_{\text{LR}}$  of the LR's. (b): Convergence of the charge density along the (111) direction. The lines correspond to a Fourier Transform interpolation of the values of the charge density on the nodes of the real-space mesh inside the eight-atom cell (full circles).  $a_{\text{exp}}$  indicates the experimental lattice constant ( $a_{\text{exp}} = 10.26$  a.u.).

on the real-space grid. For the nonlocal part of the Hamiltonian, we used the technique proposed by King-Smith *et al.*<sup>12</sup> to optimize the Kleinman-Bylander projectors<sup>13</sup> for a real-space evaluation of matrix elements. Thus, for each atom in the position  $\tau_s$ , the Kleinman-Bylander projector is nonzero only on the mesh points contained in a sphere with radius  $R_{\text{cut}}^s$  (core region). For the kinetic-energy operator we evaluate the Laplacian with a finite differences formula as Chelikowsky *et al.*<sup>14</sup> which delocalizes the orbital only up to  $M$  points in each direction, where  $M$  is the degree of the expansion. Once the size of the LR's  $a_{\text{LR}}$  and of the core regions  $R_{\text{cut}}^s$  have been fixed,  $\langle \mathbf{r} | -\frac{1}{2}\nabla^2 + \hat{V}_{\text{NL}} | v_{0,n} \rangle$  will be zero outside a cube with size  $2(a_{\text{LR}} + \max\{Mh, 2R_{\text{cut}}^s\})$ . Since the charge  $\tilde{n}(\mathbf{r})$  is periodic we evaluate it on all the nodes of the real-space mesh within one unit cell and we compute the Hartree energy by solving the Poisson equation in the unit cell with a fast fourier transform (FFT).

We applied our approach to crystalline Si and GaAs. The Bravais lattice is fcc and the unit cell contains two atoms. The electronic structure is described by four occupied orbitals. We considered four LR's centered on the bonds connecting one atom with its four nearest neighbors. We use norm-conserving nonlocal pseudopotentials which have been

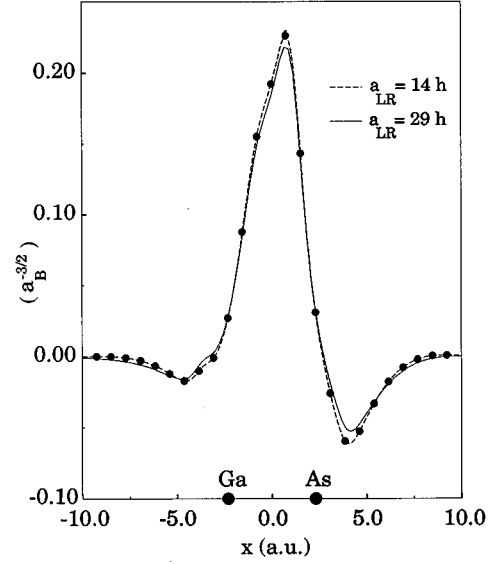


FIG. 2. GaAs: Wannier function  $\langle \mathbf{r} | w_{0,1} \rangle$  centered on  $\mathbf{b}_{0,1} = a/8(1,1,1)$  along the  $\mathbf{r} = x(1,1,1)$  direction. Full circles correspond to the values of this WF on the nodes of the real-space mesh in this direction. The lines correspond to a Fourier interpolation.

optimized with  $R_{\text{cut}} = 4$  a.u.<sup>15</sup> Exchange and correlation effects are treated using the Perdew and Zunger's parametrization.<sup>16</sup> The grid spacing has been chosen as  $h = a/24$ , where  $a$  is the size of the conventional cubic cell. This grid corresponds to a PW cutoff of 54.0 Ry and 49.8 Ry for the density in the case of Si and GaAs, respectively, if one uses the experimental lattice constant. For the kinetic energy we used a very conservative choice of  $M$ , which was set equal to 14. The free parameter  $\eta$  was fixed to 3.0 Ry and 4.0 Ry for Si and GaAs, respectively. The values of these parameters are sufficient to give energies converged within a few mRy for a given size of the LR. We compare the results obtained with WF with those obtained using Bloch orbitals. In this case we expand the Bloch orbitals in a PW basis with cutoff of 48 Ry for Si and 56 Ry for GaAs, and we use 28 special  $\mathbf{k}$  points in the irreducible Brillouin zone. With these parameters the error in the total energy is lower than 0.5 mRy.

In Fig. 1 we show the convergence of the total energy of

TABLE I. Si: Error [ $\Delta E_{\text{tot}} = E_{\text{tot}}(a_{\text{LR}}) - E_{\text{tot}}(\infty)$ ] in the total energy, lattice constant ( $a_0$ ), bulk modulus ( $B_0$ ), and frequency of the zone-center transverse optical phonon ( $\omega_{\text{TO}}$ ) for different sizes of localization ( $a_{\text{LR}}$ ). The numbers in square brackets in the column for ( $a_{\text{LR}}$ ) correspond to the number of atoms inside each LR. The data for  $a_{\text{LR}} = \infty$  are the results obtained with a standard PW code using Bloch orbitals.

$a_{\text{LR}}$ (h)	$\Delta E_{\text{tot}}$ (mRy)	$a_0$ (a.u.)	$B_0$ (kbar)	$\omega_{\text{TO}}$ ( $\text{cm}^{-1}$ )
14 [8]	180.7	10.47	921	594
19 [26]	65.7	10.29	944	543
24 [64]	27.8	10.24	953	520
34 [216]	5.4	10.21	951	
43 [342]	1.5			
$\infty$	0	10.20	941	517

TABLE II. GaAs: Error [ $\Delta E_{\text{tot}} = E_{\text{tot}}(a_{\text{LR}}) - E_{\text{tot}}(\infty)$ ] in the total energy, lattice constant ( $a_0$ ), bulk modulus ( $B_0$ ), and frequency of the zone-center optical phonon ( $\omega_{\text{TO}}$ ) for different sizes of LR's  $a_{\text{LR}}$ . The numbers in square brackets in the column for ( $a_{\text{LR}}$ ) correspond to the number of atoms inside each LR. Born effective charges ( $Z_{\text{As}}^*$ ), ( $Z_{\text{Ga}}^*$ ) for As and Ga atoms, respectively. The data for  $a_{\text{LR}} = \infty$  are the results obtained with a standard PW code using Bloch orbitals, and a linear-response approach for the effective charges.

$a_{\text{LR}}$ ( $h$ )	$\Delta E_{\text{tot}}$ (mRy)	$a_0$ (a.u.)	$B_0$ (kbar)	$\omega_{\text{TO}}$ ( $\text{cm}^{-1}$ )	$Z_{\text{As}}^*$	$Z_{\text{Ga}}^*$
19 [26]	63.4	10.55	792	277	2.08	-2.28
24 [64]	26.7	10.50	807	269	1.96	-2.21
29 [126]	11.9	10.48	804	260	2.02	-2.20
34 [216]	4.7	10.48	794	259		
$\infty$	0	10.48	760	268	2.17	-2.34

Si computed with our method for different sizes of localization  $a_{\text{LR}}$  and compare the results with the exact value obtained by the conventional diagonalization of the Hamiltonian using Bloch orbitals. The figure shows that the error in the localization is 5 mRy if the LR contains more than 216 atoms. In this case the error due to the localization is comparable to the error introduced by the use of a real-space grid.

In order to measure the deviation of the approximate WF's from orthonormality, we can consider the quantity  $\Delta N = N_{\text{el}} - \tilde{N} = 2 \sum_{l,m,n} (\delta_{l,0} \delta_{n,m} - \langle v_{0,n} | v_{l,m} \rangle)^2$ . In silicon, increasing the size of the LR's from  $a_{\text{LR}} = 14h$  to  $a_{\text{LR}} = 43h$ ,  $\Delta N$  decreases from  $2.7 \times 10^{-3}$  to  $6.3 \times 10^{-5}$ . In Fig. 2 we show the electronic charge density of silicon computed along the (111) direction. The charge is converged within 0.1% with  $a_{\text{LR}} = 29h$ .

In Table I we show the total energy, the lattice constant, the bulk modulus and the frequency of the zone-center optical phonon as a function  $a_{\text{LR}}$  for silicon. The convergence of the theoretical lattice constant is very rapid, the error being less than 1% with  $a_{\text{LR}} = 19h$ . With this size of the LR the computed bulk modulus is within 10 kbar from the converged value. The frequency of the zone-center transverse optical phonon is converged to 0.6% for  $a_{\text{LR}} = 24h$  (we used here the experimental lattice constant  $a = 10.26$  a.u.).

In silicon the macroscopic polarization and its derivative with respect to the atomic displacements, the Born effective charges are both zero. We computed this polarization per unit cell using the equation:

$$\mathbf{P}_{\text{tot}} = -2 \sum_n \sum_{l,m} Q_{n,m}^{0,l} \langle v_{0,n} | \mathbf{r} | v_{l,m} \rangle + \mathbf{P}_{\text{ions}}, \quad (3)$$

where the presence of the matrix  $Q_{n,m}^{0,l}$  accounts for the approximate orthogonality of the orbitals.<sup>6</sup> Here  $\mathbf{P}_{\text{ions}}$  is the ionic contribution to the macroscopic polarization. We have verified that the total polarization of Si is zero (modulus a quantum equal to  $\mathbf{R}_i$ ). The accuracy of this zero depends on the degree of orthogonality of the WF's. With our parameters, we find a value of  $|\mathbf{P}_{\text{tot}}| = 1.2 \times 10^{-2}$  a.u. for  $a_{\text{LR}} = 14h$  and  $3.6 \times 10^{-4}$  a.u. for  $a_{\text{LR}} = 43h$ .

The results for GaAs are reported in Table II. Table II shows a convergence with respect to  $a_{\text{LR}}$  of the computed

physical properties similar to that of Si. GaAs is a polar semiconductor with nonzero effective charges. Using the WF we computed the effective charges by finite differentiation of the macroscopic polarization with respect to the atomic displacements. The convergence of the effective charges with respect to the sizes of the LR's is shown in Table II, where for comparison we also report the results obtained with Bloch orbitals and linear response.<sup>17</sup> We note that when the size of the LR's is equal to  $29h$  the effective charges obtained by displacing As or Ga are equal and opposite in sign within 0.18, and, in a linear-response calculation, this accuracy is reached with a Brillouin zone sampling of 10  $\mathbf{k}$  points.

Finally, in Fig. 2 we show one example of Wannier-like orbitals for GaAs along the (1,1,1) direction. The WF's corresponding to two different LR's are displayed. In both cases the Wannier-like orbitals are well localized around the bond center, and the center of each WF is displaced towards the arsenic atom.

In conclusion, we have presented a real-space, self-consistent computation of the WF's of Si and GaAs. The scheme provides approximate WF's which are constrained to be zero outside a cubic region. We showed that it is possible, by using sufficiently large LR, to extract from these WF's the structural and dynamical properties of Si and GaAs, with an accuracy comparable to the standard *ab initio* methods. These results can have important implications in the future developments of *ab initio*, order- $N$  methods based on Wannier orbitals. Furthermore, we showed that the approximate WF's can give a good estimate of the electronic polarization in zero electric field and of its derivatives with respect to atomic displacements. The ability of these approximate WF's to describe the electronic structure of a solid in an external electric field is currently investigated.

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