PHYSICAL REVIEW B VOLUME 35, NUMBER 5 15 FEBRUARY 1987-I

All-electron self-consistent variational method for Wannier-type functions: Applications to the silicon crystal

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(Received 11 September 1986)

A new iterative algorithm is introduced that enables the direct calculation of Wannier-type functions. These functions are practically identical to the Wannier functions except for a minor difference in the structure of the Lagrange multiplier matrix. With this method, multiband systems are as easy to study as single-band systems. This method is used to carry out fully self-consistent local-spin-density (LSD) calculations on the silicon crystal. The resulting Wannier-type functions are guaranteed to satisfy the site othogonality constraints to the arbitrarily chosen value of 0.000 01. The LSD band centroids and band structures which are obtained within the Wannier-type formulation are in excellent agreement with those obtained using the usual Bloch formulation.

I. INTRODUCTION

During the past decade, there has been a renewed effort on the part of various researchers[1–14] for obtaining *ab initio* methods for the explicit construction of Wannier functions.[15–22] To a large extent, this is due to a series of papers by Kohn *et al.*[1–6] These papers have demonstrated that, within the framework of the linear combination of atomiclike orbitals (LCAO) method, Wannier functions enjoy practical advantages over Bloch functions in the quantum-mechanical description of nonperiodic systems. For example, suppose the Wannier functions for a certain perfect crystal are known. If a defect is introduced at the origin, it is expected that the charge density far from the origin will be unperturbed but that in the vicinity of the origin there will indeed be rather large changes in the electron density. One might then assume that outside a certain shell (Q) of nearest-neighbor atoms, the occupied orbitals may be represented exactly by the perfect-crystal Wannier functions. Inside the shell Q, one might use the perfect-crystal Wannier functions plus some additional basis functions localized about the origin to describe the occupied orbitals near the defect. The key point which is needed to justify this approach is that in the Hartree-Fock[23–25] (HF) theory, local-spin-density (LSD) theory,[26,27] and self-interaction corrected local-spin density theory[28–31] (SIC-LSD), it is not necessary to describe electronic ground states by the canonical orbitals. It is only a question of how many nearest-neighbor shells (Q) of atoms are affected by the defect. In a practical calculation, this may be answered by allowing Q to be an input parameter and monitoring the convergence of the results as a function of Q. Calculations of this nature have been carried out for one-dimensional model defect systems, and it has been demonstrated that a set of "generalized Wannier functions" may be found which, far from the defect center, converge to those of the one-dimensional perfect crystal.[3,4] Likewise, for the description of a surface, it is expected that the interior of the crystal should be well described by the perfect-crystal Wannier functions but that there will be perturbations near the surface. Using techniques analogous to those described for defects, one-dimensional model surface systems have been studied in terms of generalized Wannier functions.[5,7] Methods for carrying out self-consistent calculations on metals, which may have partially filled bands, in terms of Wannier functions have also been discussed.[6] In addition to a description of ground-state properties, it is possible to describe excitonic and particle-hole effects in terms of Wannier functions. Work along these lines has been carried out by various researchers.[32,33]

While there are many practical applications for Wannier functions, an obvious prerequisite to utilizing Wannier functions in studies of real systems are efficient and accurate methods for finding them. Although various researchers[1,17] have discussed variational methods for the direct calculation of Wannier functions, there have been little numerical results on real systems given in the literature. The existing numerical results on real systems include a metallic hydrogen calculation by Andreoni[8] and valence-only calculations on covalent crystals by Kane[9] and others.[10,12] All of these calculations are similar in that the occupied states are all described in terms of symmetry operations on a single function. To the best of our knowledge, there have been no all-electron (multiple-bands) methods discussed which have led to practical and feasible calculations. In our applications of the SIC-LSD theory to electronic systems, we have often found it convenient to carry out our calculations in terms of noncanonical orbitals rather than the usual canonical orbitals.[30,31] These orbitals satisfy Schrödinger-type equations which are coupled together by off-diagonal Lagrange multipliers which (formally) must not be neglected. In a recent paper on the application of SIC-LSD to diatomic lithium,[31] an eigenvalue equation which is satisfied by noncanonical orbitals has been introduced. In this paper, the approach is generalized to enable all-electron variational methods for the explicit calculation of Wannier functions.

In Sec. II an eigenvalue equation which is satisfied by

Wannier functions is presented. This eigenvalue equation suggests a variational procedure for the direct calculation of functions which are essentially the same as the Wannier functions aside from a minor difference in the structure of the Lagrange multiplier matrix. We refer to these functions as Wannier-type functions. In Sec. III the formalism is slightly modified which enables applications within the framework of the LCAO method. In Sec. IV this method is used to generate perfect-silicon-crystal LSD core and valence Wannier-type functions. These Wannier-type functions are guaranteed to satisfy the orthogonality constraints to the chosen value of 0.000 01 and lead to a fully self-consistent variational minimization of the LSD total energy. We have chosen silicon for a test calculation due to the rather large overlaps between the neighboring atoms. This provides a very stringent test of the method. In order to further test the method, the band centroids obtained within the Wannier-type formulation are compared to those obtained within the Bloch formulation using two different schemes of averaging over the Brillouin zone which have been proposed by Heaton[34] and by Chadi and Cohen.[35] The accuracy of the final self-consistent field (SCF) potentials are also monitored by comparing the valence-band structure obtained from the Wannier-type formulation and the Bloch formulation. The two formulations are in excellent agreement with one another. A more detailed account of this work and some group theoretical techniques which are necessary for applications appear in Ref. 36.

II. AN EIGENVALUE EQUATION FOR WANNIER AND WANNIER-TYPE FUNCTIONS

To obtain the Wannier functions directly from the Schrödinger-type equations requires the solution of a set of coupled differential equations. To circumvent this difficulty we derive an eigenvalue equation which is satisfied by Wannier functions. Here, spin-unpolarized LSD-type Hamiltonians are considered. We will start by reviewing the general aspects of Bloch functions and their relation to Wannier functions so as to introduce and clarify some of the notation which we will be using.

Suppose that the Hamiltonian, $H_0=\{-\frac{1}{2}\nabla^2+V_0(\mathbf{r})\}$, is invariant under the translations generated by the group of symmetry operations $\{T_0,\ldots,T_{N-1}\}$ where

$$T_m g(\mathbf{r})=g(\mathbf{r}-\mathbf{R}_m)\ , \tag{1}$$

with T_0 designated as the identity operator ($\mathbf{R}_0=\mathbf{0}$). The canonical orbitals $\{\psi_{pq\mathbf{k}}\}$, labeled by a band index p, a subband index q, and a momentumlike index $\mathbf{k}$ satisfy the following equations:[26]

$$H_0\,|\,\psi_{pq\mathbf{k}}\rangle=\epsilon_{pq\mathbf{k}}\,|\,\psi_{pq\mathbf{k}}\rangle\ , \tag{2}$$

$$\langle\,\psi_{pq\mathbf{k}}\,|\,\psi_{p'q'\mathbf{k}'}\rangle=\delta_{\mathbf{k}\mathbf{k}'}\delta_{pp'}\delta_{qq'}\ , \tag{3}$$

$$T_m\,|\,\psi_{pq\mathbf{k}}\rangle=\exp(-i\mathbf{k}\cdot\mathbf{R}_m)\,|\,\psi_{pq\mathbf{k}}\rangle\ . \tag{4}$$

For each band, a set of symmetry-adapted Wannier functions may be constructed from a unitary transformation on the symmetry-adapted Bloch waves $\{\phi_{p\Gamma l\mathbf{k}}\}$ of that band. The site-zero Wannier functions may be expressed as

$$|\,a_{p\Gamma l}\rangle\equiv\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}|\,\phi_{p\Gamma l\mathbf{k}}\rangle\ , \tag{5}$$

where the set of $\{\phi_{p\Gamma l\mathbf{k}}\}$ are formed from a unitary transformation on the eigenfunctions $\{\psi_{pq\mathbf{k}}\}$ according to

$$|\,\phi_{p\Gamma l\mathbf{k}}\rangle=\sum_{q}U_{\Gamma lq}(\mathbf{k},p)\,|\,\psi_{pq\mathbf{k}}\rangle\ . \tag{6}$$

The method for finding the unitary transformation $U(\mathbf{k},p)$ for a composite band is quite complicated and has been discussed in detail by Des Cloizeaux.[20–22] The indices Γ and l are, respectively, the irreducible representation index and the row index for that irreducible representation. The Wannier functions at other sites are then formed by translating the site-zero Wannier functions. These will be designated as $|\,T_m a_{p\Gamma l}\rangle$ with

$$\begin{aligned}|\,T_m a_{p\Gamma l}\rangle\equiv T_m\,|\,a_{p\Gamma l}\rangle&=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}T_m\,|\,\phi_{p\Gamma l\mathbf{k}}\rangle\\&=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}\exp(-i\mathbf{k}\cdot\mathbf{R}_m)\,|\,\phi_{p\Gamma l\mathbf{k}}\rangle.\end{aligned} \tag{7}$$

Since $\mathbf{R}_0=\mathbf{0}$, the above equation may be taken as the definition for all of the Wannier functions. It can be shown that[26]

$$|\,\phi_{p\Gamma l\mathbf{k}}\rangle=\frac{1}{\sqrt{N}}\sum_{m}\exp(i\mathbf{k}\cdot\mathbf{R}_m)\,|\,T_m a_{p\Gamma l}\rangle\ , \tag{8}$$

$$\langle\,T_m a_{p\Gamma l}\,|\,T_n a_{p'\Gamma'l'}\rangle=\delta_{pp'}\delta_{\Gamma\Gamma'}\delta_{ll'}\delta_{mn}\ . \tag{9}$$

Further, from Eqs. (2), (6), and (7), it follows that the site-zero Wannier functions satisfy the coupled Schrödinger-type equation

$$\begin{aligned}H_0\,|\,a_{p\Gamma l}\rangle=&\lambda^{p}_{\Gamma l\Gamma l}(\mathbf{0})\,|\,a_{p\Gamma l}\rangle\\&+\sum_{m(\neq 0)}\sum_{\Gamma',l'}\lambda^{p}_{\Gamma'l'\Gamma l}(\mathbf{R}_m)\,|\,T_m a_{p\Gamma'l'}\rangle\ ,\end{aligned} \tag{10}$$

$$\lambda^{p}_{\Gamma'l'\Gamma l}(\mathbf{R}_m)=\langle\,T_m a_{p\Gamma'l'}\,|\,H_0\,|\,a_{p\Gamma l}\rangle\ . \tag{11}$$

The off-diagonal Lagrange multipliers between the site-zero Wannier functions of the same band index are guaranteed to vanish due to the point-group symmetry. The equations for the Wannier functions located at other sites may be obtained by operating on the left-hand side of Eq. (10) with the translation operator T_n. However, it is evident that the equations for the Wannier functions located at other sites are satisfied if and only if the equations for the site-zero Wannier functions are satisfied. All the relevant information is contained in Eq. (10).

Now consider the Hermitian operator H_0' which is defined by

$$H_0'=[1-P^a]H_0[1-P^a]\ , \tag{12}$$

$$P^a=\sum_{m(\neq 0)}\sum_{p,\Gamma,l}|\,T_m a_{p\Gamma l}\rangle\langle\,T_m a_{p\Gamma l}\,|\ . \tag{13}$$

It is easily verified that if Eqs. (9) and (10) are satisfied, the site-zero Wannier functions are eigenfunctions of the H_0' Hamiltonian. That is,

$$H_0'\,|\,a_{p\Gamma l}\rangle=\lambda^{p}_{\Gamma l\Gamma l}(\mathbf{0})\,|\,a_{p\Gamma l}\rangle\ . \tag{14}$$

We now wish to address the converse question. Suppose that we are furnished with a set of functions $\{\omega_{p\Gamma l}\}$ which are eigenfunctions of the H_0' Hamiltonian and which satisfy the Wannier-type orthonormality conditions,

$$H_0' \,|\, \omega_{p\Gamma l}\rangle = \lambda^{pp}_{\Gamma l \Gamma l}(\mathbf{0}) \,|\, \omega_{p\Gamma l}\rangle \;, \tag{15}$$

$$\langle T_m \omega_{p\Gamma l} \,|\, T_n \omega_{p'\Gamma' l'}\rangle = \delta_{pp'}\delta_{\Gamma\Gamma'}\delta_{ll'}\delta_{mn} \;. \tag{16}$$

In Eq. (15) the projection operator used in the construction of the H_0' Hamiltonian is due to the translated ω orbitals rather than the a orbitals, i.e., in Eq. (12), the projection operator P^a has been replaced by P^ω which in analogy to Eq. (13) is defined according to

$$P^\omega = \sum_{m(\neq 0)} \sum_{p,\Gamma,l} |\, T_m \omega_{p\Gamma l}\rangle\langle T_m \omega_{p\Gamma l} \,| \;. \tag{17}$$

In a paragraph below, we will show that Eqs. (15) and (16) are sufficient conditions to ensure that

$$H_0 \,|\, \omega_{p\Gamma l}\rangle = \lambda^{pp}_{\Gamma l \Gamma l}(\mathbf{0}) \,|\, \omega_{p\Gamma l}\rangle + \sum_{m(\neq 0)} \sum_{p',\Gamma',l'} \lambda^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m) \,|\, T_m \omega_{p'\Gamma' l'}\rangle \;. \tag{18}$$

However, we first wish to discuss the above equations a bit. For the remainder of the paper, we will refer to the ω functions as Wannier-type functions due to the similarity between these functions and the actual Wannier a functions of Eqs. (9) and (10). The only quantitative difference between the two sets of functions is that we neither guarantee nor require that the Lagrange multipliers between Wannier-type functions of different "bands" on different sites vanish. This is a small difference and will (rigorously) not affect either the total energy or SCF eigenvalue spectrum. That is, from the standpoint of minimizing the total energy, the only requirement on the SCF Lagrange multiplier matrix is that it should be Hermitian. Any set of orbitals which satisfies the equations $H_0 \,|\, u_i\rangle = \sum_j \lambda_{ji} \,|\, u_j\rangle$ minimize the total energy and lead to the same canonical orbitals and associated eigenvalues. The flexibility on the SCF Lagrange multiplier matrix allows us to look for the Wannier-type functions discussed above. However, if one is interested in finding true Wannier functions, a slight modification of the procedure which we are about to discuss is presented in the Appendix. We do not advocate following the procedure of the Appendix since, with less computational effort, one may reap the same benefits from the Wannier-type functions as the Wannier functions. Also, our belief is that the Wannier-type functions come extremely close to coinciding with the Wannier functions since the site-zero Lagrange multipliers between orbitals of different bands vanish.

We now proceed with the proof of Eq. (18). Suppose Eqs. (15) and (16) are satisfied. Using Eqs. (15) and (17), we may write

$$\begin{aligned} H_0' \,|\, \omega_{p\Gamma l}\rangle &= (1-P^\omega) H_0 (1-P^\omega) \,|\, \omega_{p\Gamma l}\rangle \\ &= (1-P^\omega) H_0 \,|\, \omega_{p\Gamma l}\rangle \;, \end{aligned} \tag{19}$$

since due to the orthogonality of the site-zero and translated ω functions, $P^\omega \,|\, \omega_{p\Gamma l}\rangle = 0$. Further, it is always possible to decompose the quantity $H_0 \,|\, \omega_{p\Gamma l}\rangle$ in terms of a linear combination of the site-zero and translated ω functions and a state $|\, \theta_{p\Gamma l}\rangle$ which is orthogonal to all of the ω functions. This may be written as

$$H_0 \,|\, \omega_{p\Gamma l}\rangle = \sum_{m=0}^{N} \sum_{p',\Gamma',l'} L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m) \,|\, T_m \omega_{p'\Gamma' l'}\rangle + |\, \theta_{p\Gamma l}\rangle \;, \tag{20}$$

$$L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m) = \langle T_m \omega_{p'\Gamma' l'} \,|\, H_0 \,|\, \omega_{p\Gamma l}\rangle \;, \tag{21}$$

$$|\, \theta_{p\Gamma l}\rangle = H_0 \,|\, \omega_{p\Gamma l}\rangle - \sum_{m=0}^{N} \sum_{p',\Gamma',l'} L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m) \,|\, T_m \omega_{p'\Gamma' l'}\rangle \;. \tag{22}$$

However, since

$$(1-P^\omega) \,|\, T_m \omega_{p\Gamma l}\rangle = \delta_{m0} \,|\, \omega_{p\Gamma l}\rangle$$

and

$$(1-P^\omega) \,|\, \theta_{p\Gamma l}\rangle = |\, \theta_{p\Gamma l}\rangle \;,$$

Eq. (19) becomes

$$H_0' \,|\, \omega_{p\Gamma l}\rangle = \sum_{p',\Gamma',l'} L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{0}) \,|\, \omega_{p'\Gamma' l'}\rangle + |\, \theta_{p\Gamma l}\rangle \;, \tag{23}$$

but, if Eq. (15) holds, it follows that $|\, \theta_{p\Gamma l}\rangle$ and the off-diagonal numbers $L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{0})$ $(p'\Gamma' l' \neq p\Gamma l)$ must be identically zero. Once this has been established it follows that the numbers $L^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m)$ must coincide with the Lagrange multipliers $\lambda^{p'p}_{\Gamma' l' \Gamma l}(\mathbf{R}_m)$. Hence, we have proved that if the site-zero Wannier-type functions $\{\omega_{p\Gamma l}\}$ are eigenfunctions of the H_0' Hamiltonian and if the $\omega_{p\Gamma l}$ orbitals and their translations form an orthonormal set, Eq. (18) is automatically satisfied. This implies that the $\omega_{p\Gamma l}$-orbitals span the same space as the canonical Bloch functions and the unitary transformation between these two representations may be found by translationally symmetrizing the Wannier-type functions and diagonalizing the resulting Hamiltonian matrix.

The result of the preceding paragraph suggests that it is possible to find an iterative approach which enables one to find Wannier-type functions which satisfy Eqs. (15) through (19). Let us suppose that we are furnished with a zeroth-order set of site zero Wannier-type functions $\{\omega^0_{p\Gamma l}\}$, such as atomic orbitals, where the superscript 0 designates the iteration index. These orbitals do not satisfy the Wannier-type orthogonality constraints [Eq. (16)]. So, for the purposes of discussion, suppose we use Löwdin's[37–39] method of symmetric orthogonalization to find a modified set of site-zero Wannier-type functions $\{(\omega'_{p\Gamma l})^0\}$ which do indeed satisfy the Wannier-type orthogonality constraints. We may now use this set of functions to construct the H_0' Hamiltonian. That is, we construct the zeroth-order projection operator $P_0^{\omega'}$ in terms of the primed zeroth-order Wannier-type functions according to

$$P_0^{\omega'} = \sum_{m(\neq 0)} \sum_{p,\Gamma,l} |\, T_m (\omega'_{p\Gamma l})^0\rangle\langle T_m (\omega'_{p\Gamma l})^0 \,| \;, \tag{24}$$

and with the above projection operator, the zeroth-order H_0' Hamiltonian is constructed according to Eq. (12).

Now, to close the iterative cycle, we define a first-order set of site-zero Wannier-type functions $\{\omega^{1}_{p\Gamma l}\}$ to be the lowest eigenfunctions of the zeroth-order H'_0 Hamiltonian. Once the first-order set of site-zero Wannier-type functions are found, they are used to construct a first-order H'_0 Hamiltonian in an analogous way as was done to construct the zeroth-order H'_0 Hamiltonian. This cycle is repeated over and over with the ith-order site-zero Wannier-type functions used to construct the ith-order H'_0 Hamiltonian which, in turn, yield the $(i+1)$th-order Wannier-type functions.

We wish to show that if this iterative algorithm converges, it converges to a set of Wannier-type functions which satisfy Eqs. (15) through (18). In order to do this, it is necessary to note that the ith-order primed translated Wannier-type functions are themselves eigenfunctions of the ith-order H'_0 Hamiltonian with an eigenvalue of zero,

$$(1-P^{\omega'}_{i})H_0(1-P^{\omega'}_{i})\,|\,T_n(\omega'_{p\Gamma l})^{i}\rangle=0 \text{ for } n\neq 0 \;. \tag{25}$$

Further, since the $(i+1)$th iteration site-zero Wannier-type functions and the ith iteration translated primed Wannier-type functions are eigenstates of the same Hermitian operator, they are guaranteed to be orthogonal to one another. Now, suppose this iterative procedure is repeated over and over, and for some iteration K convergence is reached. By this, we mean

$$(1-P^{\omega'}_{K})H_0(1-P^{\omega'}_{K})\,|\,\omega^{K+1}_{p\Gamma l}\rangle=\lambda^{pp}_{\Gamma l\Gamma l}(\mathbf{0})\,|\,\omega^{K+1}_{p\Gamma l}\rangle \;, \tag{26}$$

$$|\,(\omega'_{p\Gamma l})^{K}\rangle=|\,\omega^{K+1}_{p\Gamma l}\rangle\equiv|\,\omega_{p\Gamma l}\rangle \quad \text{for all } p\Gamma l \;. \tag{27}$$

Under these conditions, it is possible to remove the primes and the iteration indices from Eqs. (26) and simply write

$$H'_0\,|\,\omega_{p\Gamma l}\rangle=\lambda^{pp}_{\Gamma l\Gamma l}(\mathbf{0})\,|\,\omega_{p\Gamma l}\rangle \;, \tag{28}$$

which is the necessary result to ensure that, when convergence is achieved, the ω functions are indeed Wannier-type functions.

While the methods discussed in this section would, in principle, lead to Wannier-type functions, there are several improvements in the formalism which may be made to render this procedure more amenable to applications within the framework of LCAO. For example, in practice it is necessary to find a proper way of truncating the P^{ω} operator at a certain shell Q. In doing so, the site-zero Wannier-type functions are constrained to be orthogonal to only those Wannier-type functions on the first Q nearest-neighbor shells. Since the site-zero Wannier-type functions are assumed to be well localized about the origin, for Q large enough, the overlaps between the site-zero Wannier-type functions and those outside of the Qth nearest-neighbor shell are negligibly small. From a practical standpoint it would be most convenient to express the site-zero Wannier-type functions in terms of symmetry-adapted linear combinations of atomiclike orbitals (SALC's) which are on the first Q nearest-neighbor shells. In this way, the entire procedure depends on a number Q, which when made large enough will reproduce the perfect-crystal Wannier-type functions. This cannot be accomplished by using either Löwdin's method of symmetric orthogonalization[38,39] or Gram-Schmidt orthogonalization. In the next section, an alternative orthogonalization scheme will be introduced so this formalism can be used within the framework of LCAO. This modified method still guarantees Wannier-type functions which, to any desired accuracy, are exact.

III. A WANNIER-TYPE VARIATIONAL PROCEDURE FOR LCAO CALCULATIONS

A. The nontruncated (infinite crystal) case

In this section, several modifications in the formalism are made which enable practical calculations within the framework of the LCAO method. The first step is to define an alternative way of orthogonalizing functions to one another in order to construct the operator $P^{\omega'}_{1}$. This method reduces to Löwdin's method of symmetric orthogonalization under certain conditions but provides a convenient way for truncating the orthogonality constraints at a given shell Q. Let us start by considering the variational minimization of the error functional

$$D\equiv\sum_{n,m,j,k}|\langle T_m\omega_k\,|\,T_n\omega_j\rangle|^2 -(\tau+1)\sum_{m,j,k}|\langle T_m\omega_k\,|\,T_m\omega_j\rangle|^2 \;, \tag{29}$$

subject to the simple orthonormality constraints

$$\langle\omega_k\,|\,\omega_j\rangle=\delta_{kj} \;. \tag{30}$$

In the above equation, the subscripts k and j stand for the indices $p\Gamma l$ and cover $1,2,\ldots,L$. For the time being, τ is an arbitrary positive parameter. If Eq. (30) is satisfied, the expression for D becomes

$$\begin{aligned} D&={\sum_{n,m}}'\sum_{k,j}|\langle T_m\omega_k\,|\,T_n\omega_j\rangle|^2 -\tau\sum_{m,k,j}|\langle T_m\omega_k\,|\,T_m\omega_j\rangle|^2 \;,\\ D&={\sum_{n,m}}'\sum_{k,j}|\langle T_m\omega_k\,|\,T_n\omega_j\rangle|^2-\tau\sum_{m,k,j}\delta_{kj} \;, \qquad (31)\\ D&={\sum_{n,m}}'\sum_{k,j}|\langle T_m\omega_k\,|\,T_n\omega_j\rangle|^2-\tau NL \;, \end{aligned}$$

where the prime on the summation symbol indicates that we are not to sum over the terms where $n=m$. Since the first term of Eq. (31) consists of a sum of non-negative quantities, it is apparent that D is minimized if and only if

$$\langle T_m\omega_k\,|\,T_n\omega_j\rangle=0 \quad \text{for } n\neq m \;. \tag{32}$$

So, minimizing D with the constraints $\langle\omega_k\,|\,\omega_j\rangle=\delta_{kj}$ ensures that the more complicated constraints $\langle T_m\omega_k\,|\,T_n\omega_j\rangle=\delta_{kj}\delta_{nm}$ are satisfied. In other words, D is a functional which takes on its minimum for functions which satisfy the Wannier-type orthonormality relations.

In order for D to be minimized, the first variation of D with respect to orthonorm-conserving variations of the ω orbitals must vanish. Varying Eq. (29) yields

$$\begin{aligned}\delta D&=2\left[\sum_{n,m,k,j}\langle T_m\delta\omega_k\,|\,T_n\omega_j\rangle\langle T_n\omega_j\,|\,T_m\omega_k\rangle-(\tau+1)\sum_{m,k,j}\langle T_m\delta\omega_k\,|\,T_m\omega_j\rangle\langle T_m\omega_j\,|\,T_m\omega_k\rangle\right]+\text{c.c.}\ ,\\ \delta D&=2\sum_m\left[\sum_{k,j,n}\langle\delta\omega_k\,|\,T_m^{-1}T_n\omega_j\rangle\langle T_m^{-1}T_n\omega_j\,|\,\omega_k\rangle-(\tau+1)\sum_{k,j}\langle\delta\omega_k\,|\,\omega_j\rangle\langle\omega_j\,|\,\omega_k\rangle\right]+\text{c.c.}\ ,\end{aligned}\tag{33}$$

where c.c. stands for the complex conjugate of the former quantity. The above equation may be further simplified by making use of the group rearrangement theorem as

$$\begin{aligned}\delta D&=2\sum_m\left[\sum_{k,j,n'}\langle\delta\omega_k\,|\,T_{n'}\omega_j\rangle\langle T_{n'}\omega_j\,|\,\omega_k\rangle-(\tau+1)\sum_{k,j}\langle\delta\omega_k\,|\,\omega_j\rangle\langle\omega_j\,|\,\omega_k\rangle\right]+\text{c.c.}\ ,\\ \delta D&=2\sum_m\sum_k\langle\delta\omega_k\,|\,\Pi\,|\,\omega_k\rangle+\text{c.c.}\end{aligned}\tag{34}$$

In the above equation we have introduced a Hermitian operator Π, which is defined by

$$\Pi=\sum_{m=1}^{N-1}\sum_{j=1}^{L}|\,T_m\omega_j\rangle\langle T_m\omega_j\,|-\tau\sum_{j=1}^{L}|\,\omega_j\rangle\langle\omega_j\,|\ ,\tag{35}$$

with L the total number of site-zero Wannier-type functions. Requiring that Eq. (34) vanish subject to the constraints that $\langle\omega_k\,|\,\omega_j\rangle=\delta_{kj}$ yields the eigenvalue equations

$$\Pi\,|\,\omega_k\rangle=p_{kk}\,|\,\omega_k\rangle\ .\tag{36}$$

We wish to use the Π operator instead of Löwdin's method of symmetric orthogonalization to identify the translated primed Wannier-type functions.

In order to see how this is done, consider the ith iteration's Π operator

$$\Pi(i)=\sum_{m=1}^{N-1}\sum_{j=1}^{L}|\,T_m\omega_j^i\rangle\langle T_m\omega_j^i\,|-\tau\sum_{j=1}^{L}|\,\omega_j^i\rangle\langle\omega_j^i\,|\ .\tag{37}$$

Next, define the space which is spanned by the translated $(\omega')^i$ orbitals to be all those orbitals which coincide with the eigenfunctions of $\Pi(i)$ that have a positive eigenvalue. It is evident that if the ω functions and their translations are indeed orthonormal, the operator $\Pi(i)$ has exactly $(N-1)L$ eigenfunctions with an eigenvalue of unity and exactly L eigenfunctions with an eigenvalue of $-\tau$. The L eigenfunctions with an eigenvalue of $-\tau$ span the space of the site zero ω-functions and the $(N-1)L$ eigenfunctions with an eigenvalue of unity span the space of the translated ω' functions. So, what this method does is provide us with a way to find $(N-1)L$ orthonormal orbitals which, when the process converges, span the same space as the $(N-1)L$ translated ω functions. The advantage of this method is that the translated ω functions so obtained are automatically orthogonal to the ω functions. In the forthcoming discussions, we will refer to the eigenfunctions which have positive eigenvalues as the χ^i functions.

The operator $\Pi(i)$ will be referred to as the χ-finding operator. Due to the fact that the χ^i functions and the translated $(\omega')^i$ functions span the same space, the $P_i^{\omega'}$-projection operator may now be constructed according to

$$P_i^{\omega'}=\sum_{m(\neq 0)}\sum_j|\,T_m(\omega_j')^i\rangle\langle T_m(\omega_j')^i\,|=\sum_k|\,\chi_k^i\rangle\langle\chi_k^i\,|\ .\tag{38}$$

In practice, it is more convenient to use a set of χ orbitals rather than the ω' orbitals since group theory may be used to block diagonalize the projection operator in terms of a set of χ orbitals.

The parameter τ has not been specified. It is in fact a free parameter and does not affect the converged solution. However, the rate of convergence is affected by this parameter. In order to understand this, a perturbative analysis can be made which should be fairly accurate provided that

$$\langle\omega_i^k\,|\,\omega_j^i\rangle=\delta_{kj}\ ,\tag{39}$$

$$|\,\langle T_m\omega_k^i\,|\,\omega_j^i\rangle\,|<\varepsilon\quad(T_m\neq\text{the identity operator})\ ,\tag{40}$$

where ε is a positive number which is small compared to unity. Further, τ should be on the order of unity or greater. Under these circumstances, it can be shown that, to order ε, the site-zero primed Wannier-type functions $\{(\omega_1')^i,\ldots,(\omega_N')^i\}$ are given by

$$\left|(\omega_k')^i\right\rangle=\left[1-\frac{1}{1+\tau}P_i^{\omega}\right]\left|\omega_k^i\right\rangle\ .\tag{41}$$

Equation (41) is easiest to prove by substituting it into Eq. (36). In order to measure the speed of convergence, the corresponding ith-order primed and unprimed overlaps, $\langle T_m(\omega_k')^i\,|\,(\omega_j')^i\rangle$ and $\langle T_m\omega_k^i\,|\,\omega_j^i\rangle$, should be compared. By doing this, and using Eq. (41), it is found with some algebraic reduction

$$\begin{aligned}\langle T_m(\omega_k')^i\,|\,(\omega_j')^i\rangle&=\left\langle T_m\left[1-\frac{1}{1+\tau}P_i^{\omega}\right]\omega_k^i\,\middle|\,\left[1-\frac{1}{1+\tau}P_i^{\omega}\right]\omega_j^i\right\rangle\ ,\\ \langle T_m(\omega_k')^i\,|\,(\omega_j')^i\rangle&=\langle T_m\omega_k^i\,|\,\omega_j^i\rangle\left[\frac{\tau-1}{\tau+1}\right]+O(\varepsilon^2)\ .\end{aligned}\tag{42}$$

From Eq. (42) it is evident that by choosing $\tau=1$, if the overlaps between the ith iteration approximation to the primed Wannier-type functions are of order ε the corresponding overlaps for the ith iteration are of order ε^2. So, from the above analysis, it is apparent that convergence is fastest for $\tau\approx 1$. Further justification for choosing the value of unity for τ is that for a complete basis set and near orthogonality of the ith iteration Wannier-type functions, it corresponds to Löwdin's method of symmetric orthogonalization.[38,39] In practice, a finite dimensional basis set is employed, and although the speed of convergence still depends on τ, the dependence is more complicated and the preceding argument does not apply exactly. In practice, it is found that $\tau=\frac{1}{2}$ is the best value to choose for finite dimensional applications.

B. The truncated $\mathcal{X}$-finding operator

We now turn our attention to carrying out a calculation in terms of a finite fixed basis set. To simplify the analysis (without loss of generality), it is assumed that the site-zero Wannier-type functions are to be expanded in terms of M orthonormal basis functions $\{f_1,\ldots,f_M\}$:

$$|\omega_j\rangle=\sum_p a_{jp}\,|f_p\rangle\ , \tag{43}$$

$$\langle f_p\,|\,f_q\rangle=\delta_{pq}\ . \tag{44}$$

The functions $f_q(\mathbf{r})$ are assumed to be centered in the vicinity of the origin and to vanish quickly far from the origin. In practice, the f functions will be replaced by a set of (nonorthogonal) symmetry-adapted linear combinations[40] (SALC's) of Gaussian-type orbitals lying on the first Q nearest-neighbor shells of atoms. The number Q will be an input parameter and when chosen to be large enough does not affect the solution. Even for a perfect crystal there are only a finite number of orthogonality constraints since the overlap between the function $\omega_j(\mathbf{r})$ and $\omega_k(\mathbf{r}-\mathbf{R}_m)$ will be negligible for $|\mathbf{R}_m|$ large enough.

Let $\{T_1,\ldots,T_{N'}\}$ $(N'\le N-1)$ be the symmetry operators which translate the Wannier functions to the N' sites which are closest to the origin and are expected to lead to a non-negligible overlap if the orthogonality is not strictly enforced. The $\mathcal{X}$-finding operator can now be truncated and is written as

$$\Pi(i)=\sum_{m=1}^{N'}\sum_{j=1}^{L}|T_m\omega_j^i\rangle\langle T_m\omega_j^i|-\tau\sum_{j=1}^{L}|\omega_j^i\rangle\langle\omega_j^i|\ . \tag{45}$$

In the non-truncated case diagonalizing the $\mathcal{X}$-finding operator was justified since it corresponded to minimizing an error functional which took on its minimum for Wannier-type functions. Provided that the set of operators $\{T_1,\ldots,T_{N'}\}$ is chosen so that, as will be done in Sec. IV, its inverse set $\{T_1^{-1},\ldots,T_{N'}^{-1}\}$ is identical to itself, a similar variational principle applies. Under these conditions, diagonalizing the truncated $\mathcal{X}$-finding operator is equivalent to minimizing the error functional D^T given by

$$D^T=\sum_{m,j,i}|\langle\omega_j\,|\,T_m\omega_i\rangle|^2-(\tau+1)\sum_{j,i}|\langle\omega_j\,|\,\omega_i\rangle|^2\ , \tag{46}$$

subject to the orthonormality constraints of the site-zero functions. Earlier, we were interested in forcing $\langle\omega_j^i\,|\,T_m\omega_k^i\rangle$ to vanish. However, now with the constraint that the function $\omega_j^i(\mathbf{r})$ is to be a linear combination of the functions $\{f_1,\ldots,f_M\}$, it becomes apparent that the job has been reduced to forcing the part of the function $|T_m\omega_k^i\rangle$ lying in the space spanned by the functions $\{f_1,\ldots,f_M\}$ to be orthogonal to the function $|\omega_j^i\rangle$. That is, the function $|T_m\omega_k^i\rangle$ may be uniquely decomposed as

$$|T_m\omega_k^i\rangle=|(T_m\omega_k^i)_{\parallel}\rangle+|(T_m\omega_k^i)_{\perp}\rangle\ , \tag{47}$$

$$|(T_m\omega_k^i)_{\parallel}\rangle=\sum_{p=1}^{M}a_{kp}^i(T_m)\,|f_p\rangle\ , \tag{48}$$

$$\langle f_p\,|\,(T_m\omega_k^i)_{\perp}\rangle=0\ . \tag{49}$$

The first and second kets on the right-hand side of Eq. (47) are referred to as the parallel and perpendicular components of $|T_m\omega_k^i\rangle$, respectively. Since the overlap between the perpendicular component of $|T_m\omega_k^i\rangle$ and any ket $|f_p\rangle$ vanishes, it immediately follows that $\langle\omega_j^i\,|\,(T_m\omega_k^i)_{\perp}\rangle$ also vanishes. Thus, it is only necessary to ensure that $\langle\omega_j\,|\,(T_m\omega_k)_{\parallel}\rangle$ vanishes.

The most straightforward way of dealing with this problem would be to modify the way the $\mathcal{X}$-finding operator is constructed. That is, first one would decompose the translated Wannier-type functions into their parallel and perpendicular components. Next, the $\mathcal{X}$-finding operator would be redefined in terms of the parallel components of the translated Wannier-type functions. In practice, this would be quite tedious and fortunately there is a much more elegant way of carrying out this procedure. Note that the $\mathcal{X}$-finding operator may be decomposed using Eq. (47) as

$$\begin{aligned}\Pi(i)=\sum_{m=1}^{N'}\sum_{j=1}^{L}\big[\,&|(T_m\omega_j^i)_{\parallel}\rangle\langle(T_m\omega_j^i)_{\parallel}|+|(T_m\omega_j^i)_{\perp}\rangle\langle(T_m\omega_j^i)_{\parallel}|\\&+|(T_m\omega_j^i)_{\parallel}\rangle\langle(T_m\omega_j^i)_{\perp}|+|(T_m\omega_j^i)_{\perp}\rangle\langle(T_m\omega_j^i)_{\perp}|\,\big]-\tau\sum_{j=1}^{L}|\omega_j^i\rangle\langle\omega_j^i|\ .\end{aligned} \tag{50}$$

From the above expression, it follows that the matrix elements $\langle f_p\,|\,\Pi(i)\,|\,f_q\rangle$ are not affected by the perpendicular contributions to the $\mathcal{X}$-finding operator. Hence, the $\mathcal{X}$-finding operator may be set up and diagonalized in the usual way. The eigenfunctions of the truncated $\mathcal{X}$-finding operator may be divided into three sets. The first set of eigenfunctions have an eigenvalue of $-\tau$ (when convergence is reached) and span the space of the site-zero

Wannier-type functions. The second set of eigenfunctions have positive eigenvalues. These $\mathcal{X}$-functions represent the parts of the translated Wannier-type functions which extend into the space spanned by the f functions. In contrast to the earlier results which assumed a complete basis set, the eigenvalues of the $\mathcal{X}$ functions are not all unity. The magnitude of the eigenvalue corresponds to the probability of finding the translated Wannier-type function within the space spanned by the basis functions. The remaining eigenfunctions have an eigenvalue of zero and are orthogonal to the site-zero Wannier-type functions and the translated Wannier-type functions.

In order to monitor the convergence, it is most convenient to find a single number which is an upper limit on the largest overlap between the site-zero and translated Wannier-type functions. One such number is given by

$$d(i)=\left[\sum_{m=1}^{N'}\sum_{j,k}|\langle\omega_j^i\,|\,T_m\omega_k^i\rangle|^2\right]^{1/2} . \tag{51}$$

It is easy to show that $d(i)>|\langle\omega_j^i\,|\,T_m\omega_k^i\rangle|$. An alternative measure of the error which is computationally much more convenient to calculate is given by

$$d'(i)=\left[\sum_{j=1}^{L}\sum_{k=1}^{N''}p_{kk}^i\,|\langle\omega_j^i\,|\,\mathcal{X}_k^i\rangle|^2\right]^{1/2} , \tag{52}$$

where p_{kk}^i is the eigenvalue corresponding to $\mathcal{X}_k^i$. In the above expression, N'' is the number of $\mathcal{X}$ states with positive eigenvalues obtained by diagonalizing the operator $\Pi(i)$. It can be shown that providing the translated Wannier-type functions are nearly orthogonal to the site-zero Wannier-type functions, $d(i)=(1+\tau)d'(i)$. (Strictly speaking, the proof of this required a complete basis set, but it is found to be true for fixed basis sets also.)

At this point, it is appropriate to note that, in analogy to canonical orbital fixed basis calculations, the modifications discussed in this section still yield Wannier-type functions which are exact to any desired accuracy. For example, for a calculation with a basis set $\{g_1,\ldots,g_M\}$, the SCF canonical orbitals (obtained by such methods as HF and LSD) which extremize the total energy need only satisfy $H_0\,|\,u_i\rangle=\epsilon_i\,|\,u_i\rangle+|\,v_i\rangle$, where $|\,v_i\rangle$ is a function which is orthogonal to all the g-basis functions. Likewise, in the truncated Wannier-type function case, the summation in Eq. (18) should be truncated at N' and a state $|\,\mu_{p\Gamma l}\rangle$ which is orthogonal to all the f functions may be appended to the right-hand side of the equation. It can be shown that, with the modifications of this section, the ω functions satisfy an equation of this type which implies that, within the orthonormality constraints and the imposed finite dimensional space, they extremize the total energy.

IV. A LSD APPLICATION OF THE WANNIER-TYPE FORMULATION ON SILICON

In this section, the variational procedure discussed in the previous sections is utilized to carry out an all electron SCF calculation on the perfect silicon crystal. We start by reviewing the ground-state configuration of the perfect silicon crystal in terms of Wannier-type functions.

It has been customary to represent the valence configuration of the silicon crystal in terms of bond-centered Wannier-type functions which have been proposed by Kohn.[1] The valence-bond-centered Wannier functions are labeled by an fcc site index $\mathbf{R}_\nu$, a bond index $(\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3,\mathbf{t}_4)$, and the letter v for valence. For example, the site-zero valence configuration is represented by

$$a_{v\mathbf{t}_1}^2a_{v\mathbf{t}_2}^2a_{v\mathbf{t}_3}^2a_{v\mathbf{t}_4}^2 , \tag{53}$$

with

$$\mathbf{t}_1=a(1,1,1)/4,\mathbf{t}_2=a(1,-1,-1)/4 ,$$
$$\mathbf{t}_3=a(-1,1,-1)/4,\mathbf{t}_4=a(-1,-1,1)/4 .$$

The above functions form a reducible (permutation) representation of the T_d point group. Because of this, it is only necessary to know the spatial form of one of the site-zero functions and the remaining functions in the crystal may be generated by applying the T_d rotations and the fcc translations. Due to the glide plane symmetry, each valence function is symmetric under inversion through its center. That is,

$$a_{v\mathbf{t}_i}(\mathbf{r})=a_{v\mathbf{t}_i}(\mathbf{t}_i-\mathbf{r}) . \tag{54}$$

Also each bond-centered function exhibits threefold symmetry about its axis.

A way of representing the core Wannier-type functions is in terms of an fcc site index $\mathbf{R}_\nu$, an atom index ($\mathbf{t}_0$ or $\mathbf{t}_1$), and a band index ($p\Gamma l=1s,2s,2p_x,2p_y,2p_z$). For example, the site-zero core states could be taken as the atom-centered functions

$$\omega_{1s\mathbf{t}_0}^2\omega_{2s\mathbf{t}_0}^2\omega_{2p\mathbf{t}_0}^6\omega_{1s\mathbf{t}_1}^2\omega_{2s\mathbf{t}_1}^2\omega_{2p\mathbf{t}_1}^6 , \tag{55}$$

with $\mathbf{t}_0=(0,0,0)$. Strictly speaking, with the notation of Johnson and Smith[41] (Kohn[1]), the symmetry indices should be labeled a_1 (Γ_1) for the s states and t_2 (Γ_{15}) for the p states. For the remainder of this paper, it is understood that when we use the atomiclike symmetry labels (s and p), we really mean their respective T_d counterparts. Due to the glide plane symmetry, the core Wannier-type functions located on the $\mathbf{t}_1$ sites are related to those on the $\mathbf{t}_0$ sites according to

$$\omega_{p\Gamma l\mathbf{t}_1}(\mathbf{r})=\omega_{p\Gamma l\mathbf{t}_0}(\mathbf{t}_1-\mathbf{r}) . \tag{56}$$

From a computational standpoint, it is convenient to unify the treatment of the core and valence Wannier-type functions so that they are either all bond centered or all atom centered. While the former approach is certainly possible, we have chosen to carry out our calculations in terms of atom-centered functions. In order to do this, we note that the valence-bond-centered Wannier-type functions transform like sp^3 hybrids under the T_d symmetry operations. As such, it is possible to find an irreducible set of functions which we refer to as $\omega_{3s\mathbf{t}_0}$, $\omega_{3p_x\mathbf{t}_0}$, $\omega_{3p_y\mathbf{t}_0}$, and $\omega_{3p_z\mathbf{t}_0}$. For example, at the origin we have

$$\begin{bmatrix} \omega_{3s\mathbf{t}_0} \\ \omega_{3p_x\mathbf{t}_0} \\ \omega_{3p_y\mathbf{t}_0} \\ \omega_{3pz\mathbf{t}_0} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix} \begin{bmatrix} a_{v\mathbf{t}_1} \\ a_{v\mathbf{t}_2} \\ a_{v\mathbf{t}_3} \\ a_{v\mathbf{t}_4} \end{bmatrix} . \tag{57}$$

With the above considerations, it is evident that all the Wannier-type functions in the crystal may be generated in terms of the site-zero Wannier-type functions

$$\omega_{1s\mathbf{t}_0}^2 \omega_{2s\mathbf{t}_0}^2 \omega_{2p\mathbf{t}_0}^6 \omega_{3s\mathbf{t}_0}^2 \omega_{3p\mathbf{t}_0}^6 . \tag{58}$$

The core states are translated (or glide plane translated) to all sites in the crystal, and the valence states are translated to only the fcc sites in the crystal. As demonstrated in Ref. 36, with the atom centered Wannier-type functions, it is possible to allow the crystal to dissociate to a lattice of separated ^5S silicon atoms for large lattice constants. From a practical standpoint, we mention that all the information which is necessary for construction of the $\mathcal{X}$-finding operator may be obtained by translating each function to a given atom on each shell. Hence the computational work increases linearly with the number of nearest-neighbor shells as opposed to the number of atoms. The complications due to the glide plane translations require a slightly more general argument to show that the eigenfunctions of the $\mathcal{X}$-finding operator lead to functions which satisfy the Wannier-type orthonormality conditions. It is necessary to note that, for each ω_n, if $\Pi \mid \omega_n \rangle = -\tau \mid \omega_n \rangle$ then $\langle \omega_n \mid P^\omega \mid \omega_n \rangle = 0$. But since $\langle \omega_n \mid P^\omega \mid \omega_n \rangle$ is the sum of the squares of the overlaps between a site-zero Wannier-type function and a translated or glide plane translated Wannier-type function, the truncated error functional is minimized.

To achieve self-consistency, the usual iterative procedure is used in which the kth iterations site-zero Wannier-type functions $\omega_{p\Gamma l}^k(\mathbf{r})$ are used to find the $(k+1)$th iterations Wannier-type functions $\omega_{p\Gamma l}^{k+1}(\mathbf{r})$ through the potential

$$V_{\text{eff}}^k(\mathbf{r}) = \sum_v \left[\frac{-Z}{\mid \mathbf{r} - \mathbf{R}_v \mid} + \int d\mathbf{r}' \frac{\rho_\omega^k(\mathbf{r}' - \mathbf{R}_v)}{\mid \mathbf{r} - \mathbf{r}' \mid} \right] - \left[\frac{3}{\pi} \sum_v \rho_\omega^k(\mathbf{r} - \mathbf{R}_v) \right]^{1/3} , \tag{59}$$

$$\rho_\omega^k(\mathbf{r} - \mathbf{R}_v) \equiv \sum_{p,\Gamma,l,\mathbf{t}_i} f(p\Gamma l \mathbf{t}_i) \mid \omega_{p\Gamma l \mathbf{t}_i}^k(\mathbf{r} - \mathbf{R}_v) \mid^2 , \tag{60}$$

where $\mathbf{R}_v$ is an fcc site lattice. The numbers $f(p\Gamma l \mathbf{t}_i)$ account for the spin multiplicities of each Wannier-type function and are given by

$$f(p\Gamma l \mathbf{t}_i) = \begin{cases} 2 & \text{for } \mathbf{t}_i = \mathbf{t}_0 \text{ or } p\Gamma = 1s, 2s, 2p \\ 0 & \text{for } \mathbf{t}_i = \mathbf{t}_1 \text{ and } p\Gamma = 3s, 3p \ . \end{cases} \tag{61}$$

In Eq. (59), the spin unpolarized version of the Kohn-Sham[42] exchange-only version of LSD is used.

For these silicon calculations, the potential was generated by first fitting the difference between the crystal density and the overlapping atomic density to a linear combination of symmetrized Slater-type functions centered on each atom and then integrating the result. To this, the overlapping atomic Coulomb and nuclear potential and the crystal exchange potential are added to yield the crystal LSD potential. The exchange potential was computed from the crystal electron density for a large number of points in the fundamental wedge. The LSD potential was then fit to a lattice superposition of linear combinations of Gaussian-type functions[43] $[r^{-1}\exp(-\alpha r^2)$ and $\exp(-\alpha r^2)]$ plus a constant. For both fits we have included $l = 0$, 3 and 4 angular fit functions. To obtain high-quality fits, both the linear and nonlinear parameters were optimized. A set of fourteen bare Gaussians was used to construct an optimized contracted basis set of four s-type and three p-type orbitals. The fourteen bare Gaussians were obtained by some modifications of the $12s$-$9p$ set given by Veillard.[44] All the multicenter integrals in the Hamiltonian and overlap matrix elements can be computed exactly by means of the Gaussian technique as explained in Ref. 43. The largest calculation which has been carried out enforced all the orthogonality constraints between the site-zero Wannier-type functions and those translated to the atoms within six nearest neighbors. For this calculation, the basis set consisted of all the SALC's constructed from the $1s$, $2s$, and $2p$ atomic orbitals on the origin and six nearest neighbors, the SALC's from the $3s$ and $3p$ atomic orbitals on the shells (0,0,0), (1,1,1), (2,2,0), $(-1,-1,-3)$, (0,0,4), $(-2,-2,-4)$, and (2,2,4), plus the SALC's constructed from the $4s'$, and $4p'$ (single long-range Gaussian $\alpha = 0.065\,43$) basis functions on the shells (0,0,0), (1,1,1), and (2,2,0). Here we have used units of $a/4$ with $a = 10.26$ a.u.

As noted earlier, since the SCF Wannier-type functions are expected to be well localized about their respective origins, many of the orthogonality constraints are guaranteed to be negligibly small and zero to computational precision.

TABLE I. The dependence of the diagonal Lagrange multipliers $(\langle \omega_{p\Gamma l} \mid H_0 \mid \omega_{p\Gamma l} \rangle)$ for the Wannier-type functions on the number of nearest-neighbor (NN) orthogonality constraints.

	Diagonal Lagrange multiplier (a.u.)				
	0NN	1NN	2NN	4NN	6NN
$1s$	−64.8990	−64.8990	−64.8990	−64.8990	−64.8990
$2s$	−4.8940	−4.8940	−4.8940	−4.8940	−4.8940
$3s$	−0.5081	−0.4074	−0.3942	−0.3943	−0.3953
$2p$	−3.3291	−3.3291	−3.3292	−3.3292	−3.3292
$3p$	−0.4582	−0.2828	−0.2128	−0.2132	−0.2181

TABLE II. Comparison of the band centroids for the silicon crystal obtained from the Wannier functions and from the Bloch functions. The centroids obtained from the Bloch calculation have utilized the same basis set as that used in the Wannier calculations. The columns labeled by Bloch (a) and Bloch (b) correspond to the selection of **k** points according to Refs. 34 and 35, respectively.

	Silicon band centroids (a.u.)		
	Wannier	Bloch (a)	Bloch (b)
1*s*	−64.8990	−64.8990	−64.8990
2*s*	−4.8940	−4.8941	−4.8941
2*p*	−3.3292	−3.3292	−3.3292
3*sp*	−0.2624	−0.2644	−0.2666

Hence, it is only necessary to ensure that the orthogonality constraints between the site-zero Wannier-type functions and those on a "relatively small" number of nearest-neighbor shells are satisfied. Clearly, the number of strict orthogonality constraints which need to be satisfied will be dependent on the system in question. This question is easily addressed by allowing the number of nearest-neighbor shells Q for which the orthogonality constraints are strictly enforced to be an input parameter for the computer program. For a given number of shells Q, the $\mathcal{X}$-finding operator is set up as many times as is necessary to ensure that the overlaps between the site-zero Wannier-type functions and those translated to the sites on and within shell Q are less than 0.000 01 (using d' defined before as a guide). This number has been chosen arbitrarily and could be made smaller if desired. In fact, at SCF most of the overlaps are found to be several orders of magnitude smaller than this. Typically, using $\tau=\frac{1}{2}$, it is necessary to set up the $\mathcal{X}$-finding operator about ten times to achieve this. By steadily increasing Q, it is possible to monitor the convergence of the site-zero diagonal Lagrange multipliers $\lambda^{pp}_{\Gamma l\Gamma l}(\mathbf{0})$ and hence the band centroids as a function of the number of nearest-neighbor orthogonality constraints. A final test is to compare the band centroids obtained from a Bloch-function calculation to those obtained from the Wannier-type function calculation.

In Table I the (LSD) diagonal Lagrange multipliers of the SCF Wannier-type functions are compared as a function of Q. It is apparent that orthogonality to at least two nearest neighbors must be imposed in order to achieve accurate diagonal Lagrange multipliers. On the other hand, comparison of the two nearest-neighbor results to the four and six nearest-neighbor results indicates that for silicon very accurate centroids may be obtained by enforcing orthogonality to two nearest neighbors. In Table II the 1*s*, 2*s*, 2*p*, and 3*sp* centroids obtained using the Wannier-type function formalism are compared to the corresponding band centroids from a Bloch-function calculation which used the same basis set and SCF potential. The Bloch-function calculation was carried out using a program which was supplied by Heaton. Comparison of the two sets of calculations is extremely encouraging. The core bands are in perfect agreement and the valence-band centroids differ by 0.003 a.u. or 1.2%.

Another useful test of convergence is to examine the spatial variation of the site zero Wannier-type functions as additional orthogonality constraints are imposed. Due to the rather complicated decomposition of the Wannier-type functions in terms of SALC's which are themselves constructed from contracted Gaussian-type orbitals, it is convenient to introduce a simple property of the Wannier-type function which enables one to monitor the convergence of the Wannier-type functions as a function of Q. To do this, we introduce the rms radial moment r_{rms} defined by

$$r_{\mathrm{rms}}=\left[\int d\mathbf{r}\,r^2\,|\omega_{p\Gamma l}(\mathbf{r})|^2\right]^{1/2}, \tag{62}$$

which gives an idea of the spatial extent or localization of the Wannier-type functions. In Table III the rms radial moments are presented as a function of nearest-neighbor orthogonality constraints. Again, the convergence is observed to be quite good. It is particularly interesting to note that the effect of the orthogonality constraints for $Q\geq 2$ is to *reduce* the rms radial moments of the valence states and hence lead to states which are more localized than those which would be expected from the crude single-center atomic approximation ($Q=0$). This can be understood by noting that in the absence of any orthogonality constraints, the $Q=0$ approximation to the Wannier-type functions will try to extend onto the bare nuclei surrounding them. When the orthogonality constraints are imposed, the desired vector space is occupied by Wannier functions on other sites which force the valence states to contract.

An alternative way of monitoring the convergence of the Wannier-type functions is to utilize a Mulliken analysis[45] to find the total amount of charge which is associated with the SALC's lying on the first q shells with $q\leq Q$. This number $c(p\Gamma l{:}q)$ is given by

TABLE III. The dependence of the rms radial moments ($\langle\omega_{p\Gamma l}|r^2|\omega_{p\Gamma l}\rangle^{1/2}$) for the Wannier-type functions on the number of nearest neighbor orthogonality constraints.

	rms radial moment (a.u.)				
	0NN	1NN	2NN	4NN	6NN
1*s*	0.1295	0.1295	0.1296	0.1296	0.1296
2*s*	0.6265	0.6265	0.6268	0.6269	0.6270
3*s*	3.7076	2.9976	2.6985	2.7150	2.7759
2*p*	0.6067	0.6067	0.6074	0.6074	0.6077
3*p*	4.5826	4.2849	3.3245	3.3538	3.8703

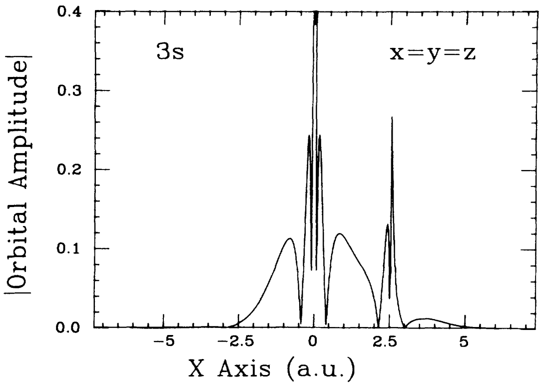

FIG. 1. The orbital amplitude (absolute value) of the silicon 3s Wannier-type function along the [111] direction. These functions were generated with the imposition of orthogonality to four nearest neighbors.

$$c(p\Gamma l{:}q)=\sum_{\lambda=1}^{q}\sum_{\lambda'=1}^{Q}\langle\phi_{p\Gamma l}(\lambda)\,|\,\phi_{p\gamma l}(\lambda')\rangle\ , \tag{63}$$

where $\phi_{p\Gamma l}$ represents the part of the Wannier-type function $\omega_{p\Gamma l}$ which consists of the SALC's on shell λ. When this number is close to one it is an indication that the contributions from the outer shells are negligible. A Mulliken analysis has been carried out for the valence 3s and 3p Wannier-type functions which were obtained by enforcing orthogonality to six nearest neighbors. It was found that the Mulliken charge associated with the origin and first two nearest-neighbor shells is given by 0.998 862 and 0.997 383 for the 3s and 3p Wannier-type functions, respectively. This analysis supports the assertion that the site-zero valence Wannier-type functions are reasonably well localized on the origin and two nearest-neighbor shells of atoms. Actually, by looking at the pictures of the 3s and 3p Wannier-type functions, (Figs. 1 and 2) it is apparent that the resulting Wannier-type functions are well localized on the origin and first nearest-neighbor atoms. A similar analysis for the 1s, 2s, and 2p Wannier-type functions shows that they are extremely well localized at the origin.

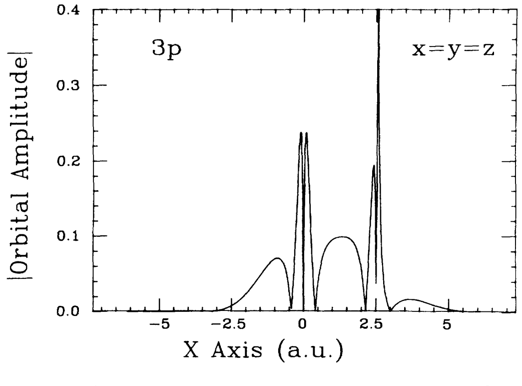

FIG. 2. The orbital amplitude (absolute value) of the silicon 3p Wannier-type function along the [111] direction. These functions were generated with the imposition of orthogonality to four nearest neighbors.

TABLE IV. Some selected band energies obtained from the SCF Wannier-type formulation as compared with the corresponding values which were obtained from the SCF Bloch formulation. The energy of the Γ'_{25} has been taken as zero.

	Energies (eV)	
	Wannier	Bloch
Γ'_{25}	0.00	0.00
Γ_{1v}	−12.40	−12.41
$L_{2'v}$	−9.98	−10.02
$L_{3'v}$	−1.48	−1.48
L_{1v}	−7.48	−7.44
X_{1v}	−8.18	−8.20
X_{4v}	−3.31	−3.29

As a final test on the accuracy of the local orbital formulation, the band structure from the SCF potential obtained within the Wannier-type formulation will be compared to the band structure which was obtained using the SCF Bloch-function formulation by Heaton. For this calculation, a 7s-4p contracted basis set of Heaton was used for both calculations so that any differences in the resulting band structure are entirely due to the input potentials. In Table IV selected valence eigenvalues (Γ,L,X) which were obtained using the Bloch and Wannier-type formulations are compared. The agreement between the two theoretical formulations is excellent. For nine other **k** points which were suggested by Heaton, the valence-band structure obtained using the Wannier-type formulation agrees with that of the Bloch formulation to 0.05 eV. Both formulations lead to an indirect band gap with the bottom of the conduction band at $(2\pi/a)(0.8,0,0)$ in agreement with experiment. However, as is well known for LSD calculations, the resulting band gap of 0.72 eV (both formulations) is found to be significantly smaller than the experimental value of 1.17 eV.[46] It is likely that addition of d-type basis functions would further decrease the calculated band gap, but for our purposes this is irrelevant since we are concerned with a systematic comparison of the two methods.

V. CONCLUSION

In this paper, an iterative algorithm has been introduced which has enabled an all-band self-consistent variational treatment of the perfect silicon crystal in terms of Wannier-type functions. Silicon has been chosen for this study due to the large overlap between the nearest-neighbor valence wave functions. The accuracy of this method has been tested by comparing the band centroids obtained from our Wannier-type formulation to those obtained from the Bloch formulations. The results are in excellent agreement with one another. We believe that, in analogy to the one-dimensional model defect calculations of Refs. 3, 4, and 7, this method may provide an alternative computational scheme for theoretical studies on point defects in crystals. Other problems which could be studied within the Wannier-type formulation include studies on excitonic transistions, and total energy calculations.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. DMR-8500458. The authors wish to thank Dr. R. A. Heaton, S. C. Erwin, and K. A. Jackson for many helpful and interesting discussions. Thanks are also due to Dr. B. M. Klein, Dr. D. A. Papaconstantopoulos, Dr. W. E. Pickett, and Dr. C. S. Wang for discussion on various aspects of the silicon LSD band gap.

APPENDIX

The algorithm which has been described allows one to find Wannier-type functions which are distinguished from actual Wannier functions since the Lagrange multipliers between orbitals of different bands at different sites do not vanish. Since the Wannier-type and Wannier functions are related by a unitary transformation, neither representation is preferred over the other. Nevertheless, we wish to note that a slight modification of the procedure allows one to calculate actual Wannier functions instead of Wannier-type functions.

In order to see this, it is first noted that, if there is only one occupied band, the Wannier-type functions will coincide with the Wannier functions. Suppose that we are interested in finding true Wannier functions for a system containing B bands. Further, suppose that the true Wannier functions for the $b(b<B)$ lowest bands are known. To find the next lowest band of Wannier functions, it is only necessary to replace the Hamiltonian H_0 by

$$H_0 \rightarrow I_b H_0 I_b \ , \tag{A1}$$

$$I_b = 1 - \sum_m \sum_{i=1}^{b} | T_m \omega_i \rangle \langle T_m \omega_i | \ , \tag{A2}$$

where the sum over i indicates a sum over all the Wannier-type functions which are in the lowest b bands. Now, by carrying out the original algorithm for the $(b+1)$th band only with the above definition of H_0, it can be verified that the SCF orbitals will indeed correspond to Wannier functions of band $(b+1)$. But since it is possible to find the Wannier functions for the lowest band by using the original algorithm for this band only, it is clear that one could iterate over each band index and find true Wannier functions with this method.

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