

Variational method for the generation of localized Wannier functions on the basis of Bloch functions

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A simple and universal variational method for constructing localized Wannier functions from Bloch functions is proposed. The variational procedure is preceded by a symmetry analysis based on the induced representation theory and succeeded by a suitable orthogonalization procedure. The reliability of the method is demonstrated by computations of localized displacements in a one-dimensional diatomic lattice and a germanium lattice, of localized electronic states in a one-dimensional Kronig-Penney model, for the upper valence bands of Si and MgO crystals.

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I. INTRODUCTION

Since their introduction in 1937,¹ Wannier functions have been often used in many theoretical considerations of electronic properties of crystals. The use of localized functions significantly facilitates the study of local properties (atom charges, active valences, bond orders, and so on) in solids. These quantities calculated in the localized Wannier basis instead of the traditional atomic basis scheme seem to be more physically valid.² The Wannier function approach is also essential in the modern theory of polarization.^{3,4}

The analytical behavior of Bloch functions of energy bands in \mathbf{k} space determines the degree of localization of corresponding Wannier functions in \mathbf{r} space.⁵⁻⁸ A useful concept of band (induced) representations has been introduced in the theory of crystals, according to which the position of symmetry localization and the symmetry properties of Wannier functions for a given energy band define unambiguously the symmetry properties of corresponding Bloch functions.⁹⁻¹² The concept of localized states has also been applied to vibrational problems in perfect crystals.¹³

Practical methods for the calculation of Wannier functions for nondegenerate and degenerate bands in perfect crystals have been elaborated and applied. For the *ab initio* construction of Wannier functions a method based on the variational principle was proposed by Kohn.¹⁴ This technique has been applied to a simple band in hydrogen¹⁵ and to the d bands and the d - s composite bands of copper and nickel.^{16,17} It has proved to be productive, but very complicated in realization. Another approach applies the Fourier transformation of Bloch functions in the Wannier functions' construction. In general, the set of Wannier functions for a given band is not unique. The actual behavior of Wannier functions depends upon the choice of Bloch functions' phase factors in the case of nondegenerate bands or upon a unitary transformation of Bloch functions at every wave vector \mathbf{k} otherwise. Particularly, a variational method for construction of Wannier functions for one-periodical structures and nondegenerate energy bands has been described.¹⁸ The results have coincided with the ones obtained according to Kohn's procedure.⁵ One of the first attempts at dealing with three-periodical systems was a construction of orthogonal and nonorthogonal systems

of Wannier functions for copper.¹⁹ The Wannier functions have turned out to be poorly localized. Apparently, the main reason for this is the nonanalytical behavior of the Bloch functions. Teichler succeeded in generating the best localized symmetry-adapted Wannier functions for a three-dimensional diamond-type lattice,²⁰ where the technique of Ref. 8 has been applied. A different approach was used by Satpathy and Pavlovskaya who constructed the Wannier functions of silicon's valence band with the above-mentioned unitary transformation chosen according to physical considerations.²¹ The functions have appeared to be localized, but the range of application of this method is essentially limited. To avoid the difficulty at points of degeneracy of composite bands, the use of the eigenvectors of a Slater-Koster model Hamiltonian has been proposed.^{22,23} The results for fcc transition metals and for Si and GaAs can be regarded as satisfactory and, besides this approach is interesting for the problem of local properties determination. A different method was developed by Marzary and Vanderbilt.⁴ To determine the maximally localized Wannier functions a functional representing the sum of the second moments of the corresponding Wannier functions is minimized. This procedure has been carried out as a steepest-descent algorithm leading to a particular set of unitary matrices among the occupied Bloch orbitals at every wave vector. The examples of crystalline Si, GaAs, and molecular C_2H_4 and LiCl have illustrated this approach.

The method of the localized Wannier functions construction on the basis of Bloch functions we describe in the present paper can be called variational as well. It consists of three steps: (i) a symmetry analysis based on the band representation theory, (ii) a variational procedure of nonorthogonal localized functions generation, and (iii) a suitable orthogonalization procedure.

II. SYMMETRY ANALYSIS

The background of Wannier functions symmetry analysis is the theory of representations (reps) of a space group G induced from the irreducible representations (irreps) of its site subgroup $M_q \subset G$ called, for brevity, induced representations (indreps). We describe the main principles of this theory related to the examined problem. One can get acquainted with it in detail in Refs. 9, 10 and 12.

The Wannier functions $W_{i1}^{(\beta)}(\mathbf{r}) \equiv W_i^{(\beta)}(\mathbf{r} - \mathbf{q}_1)$ are the basis functions of the irrep β of the site symmetry group $S_{\mathbf{q}} \subset G$ corresponding to their centering point \mathbf{q}_1 :

$$(l|\mathbf{v}_l)W_{i1}^{(\beta)}(\mathbf{r}) = \sum_{i'} d_{i'i}^{(\beta)}(l)W_{i'1}^{(\beta)}(\mathbf{r}), \quad (1)$$

where $(l|\mathbf{v}_l) \in S_{\mathbf{q}}$, $d^{(\beta)}(l)$ is the matrix mapping the element $(l|\mathbf{v}_l)$ in the irrep β . Applying symmetry operations $(g_j|\mathbf{v}_j + \mathbf{a}_n)$ from the decomposition of the group G into left cosets with respect to the site group $S_{\mathbf{q}}$,

$$G = \sum_j (g_j|\mathbf{v}_j + \mathbf{a}_n) \cdot S_{\mathbf{q}}, \quad (2)$$

where \mathbf{a}_n are the lattice translations, on the functions $W_{i1}^{(\beta)}(\mathbf{r})$,

$$W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) \equiv (g_j|\mathbf{v}_j + \mathbf{a}_n)W_{i1}^{(\beta)}(\mathbf{r}), \quad (3)$$

one can obtain the complete basis of the reducible rep of the group G induced from the irrep β of the group $S_{\mathbf{q}}$. The functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) \equiv W_i^{(\beta)}(\mathbf{r} - \mathbf{q}_{j,n} - \mathbf{a}_n)$ are centered at the points $\mathbf{q}_{j,n} \equiv (g_j|\mathbf{v}_j + \mathbf{a}_n)\mathbf{q}_1 = g_j\mathbf{q}_1 + \mathbf{v}_j + \mathbf{a}_n$. Such a basis consisting of the localized functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) \equiv W_{\tau}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) \equiv W_t^{(\beta)}(\mathbf{r})$ (the index τ replaces i , and j and the index t replaces τ and \mathbf{n}) is called \mathbf{q} basis. It is perfectly determined by any of its single representatives [for example, $W_{i1}^{(\beta)}(\mathbf{r}) \equiv W_0^{(\beta)}(\mathbf{r})$]. All the others can be obtained from it by the symmetry operations (1) and (3). An indrep is characterized in \mathbf{q} basis by the site \mathbf{q} [the center of symmetry localization of $W_{i1}^{(\beta)}(\mathbf{r})$] and the irrep β of the site group $S_{\mathbf{q}}$; (\mathbf{q}, β) is a symbol of an indrep in \mathbf{q} basis. Resolving this indrep into irreps of the space group G , one gets the indices of the indrep in \mathbf{k} basis (Bloch basis). The short symbol of an indrep in \mathbf{k} basis contains only the indices of the small irreps for the most symmetrical points of the Brillouin zone (BZ), because the indices for all other irreps contained in the indrep are determined with the help of compatibility relations. There exist simple and composite indreps. An indrep is simple, if it does not consist of two or more indreps of a smaller dimension. All simple indreps for a given space group are generated by site symmetry groups of just a few points in the Wigner-Seitz cell. The tables of indreps for all space groups can be found in Ref. 24 and in Ref. 12 are those of some most important space groups.

From the theory of indreps of space groups it follows that the construction of localized functions corresponding to a given energy band is possible, only if canonical orbitals of this band form the basis of some simple or composite indrep. This analysis permits us not only to establish the principle possibility to construct localized orbitals but also to define the possible positions of their symmetry localization center \mathbf{q} and their symmetry with respect to site symmetry group $S_{\mathbf{q}}$. The latter is not always unambiguous due to the fact that there are the indreps which have different symbols in \mathbf{q} basis, but the same index in \mathbf{k} basis,²⁵ or there are the composite indreps which can be decomposed into simple ones by a few ways (see the details in Ref. 12). Thus, the symmetry analy-

sis consists of a procedure of identifying localized functions symmetry from the symmetry of the canonical orbitals of the considered energy band, or of establishing the fact that the construction of localized functions is impossible for the reasons of symmetry.

III. VARIATIONAL PROCEDURE

When calculating the electronic structure of crystals one uses usually the cyclic model of a crystal. It consists of L primitive unit cells and is defined by translation vectors,^{12,26}

$$\mathbf{A}_j = \sum_{i=1}^3 l_{ij}\mathbf{a}_i, \quad l_{ij} \text{ are integers, } |\det l| = L, \quad j = 1, 2, 3. \quad (4)$$

The transformation (4) is supposed to conserve the point symmetry of the system. The symmetry group of the cyclic model contains L primitive translations \mathbf{a}_n , and the number of wave vectors \mathbf{k} in the BZ also equals L . The integration over the BZ in the model of the infinite crystal is replaced in the cyclic model by the summation over L wave vectors \mathbf{k} . The direct lattice summation is supposed to be limited by L primitive vectors.

Actually, we exploit a well-known algorithm when integration over the BZ is substituted by a summation over a set of special points of the BZ.²⁷ This method allows one to carry out approximate but reliable and well-defined integration of real or complex functions of wave vector \mathbf{k} . A number of procedures for construction of different optimal sets of the special points have been elaborated.^{12,27,28} Any set of the special points corresponds to a certain cyclic model, i.e., when the integration is carried out as a summation over a set of the special points it means that a cyclic model of a certain size is introduced for the crystal. The relations between the symmetry group G of the model of an infinite crystal and the symmetry group $G^{(L)}$ of the corresponding cyclic model and their irreps and indreps have been studied in detail in Ref. 26. Wannier functions of the model of an infinite crystal are well reproduced in the region of their localization by Wannier functions of those cyclic models completely covering this region.²⁹

We assume that the canonical orbitals $\varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r}) \equiv \varphi_{\sigma}(\mathbf{k}, \mathbf{r}) \equiv \varphi_s(\mathbf{r})$ (the index m numbers the basis vectors of irrep γ with wave vector \mathbf{k} , and μ discriminates between the independent bases of equivalent irreps; the index σ replaces γ , m , and μ and s replaces σ, \mathbf{k}) of the energy band under consideration form a basis in the space $\mathcal{Q}_{(\mathbf{q}, \beta)}$ of some indrep of the group $G^{(L)}$ of a crystal. The localized functions are defined by a unitary transformation in the space of the indrep,

$$W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) = L^{-1/2} \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{a}_n) \times \sum_{\gamma m \mu} \tilde{U}_{\gamma m \mu, ij}(\mathbf{k}) \cdot \varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r}), \quad (5a)$$

or

$$W_t(\mathbf{r}) = L^{-1/2} \sum_s U_{st} \cdot \varphi_s(\mathbf{r}) \quad \text{with}$$

$$U_{st} = \tilde{U}_{\gamma m \mu, ij}(\mathbf{k}) \cdot \exp(-i\mathbf{k}\mathbf{a}_n), \quad (5b)$$

where $\tilde{U}_{\gamma m \mu, ij}(\mathbf{k}) \equiv \tilde{U}_{\sigma, \tau}(\mathbf{k})$ is a unitary matrix, which in the case of a nondegenerate band, reduces to a phase factor $\exp[i\alpha(\mathbf{k})]$. The \mathbf{k} summation in Eq. (5) substitutes integration over the BZ and is carried out over a set of the special points. In the present work we have used standard sets of the special points containing the point $\mathbf{k}=0$.¹²

As the functions $\varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r})$ satisfy the conditions of orthonormality

$$(\varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r}), \varphi_{m'\mu'}^{(\gamma')}(\mathbf{k}', \mathbf{r})) = \delta_{mm'} \delta_{\mu\mu'} \delta_{\gamma\gamma'} \delta_{\mathbf{k}\mathbf{k}'}, \quad (6)$$

the functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ form an orthonormal system:

$$(W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n), W_{i'j'}^{(\beta)}(\mathbf{r} - \mathbf{a}_{n'}))$$

$$= \delta_{ii'} \delta_{jj'} \delta_{nn'} \quad \text{or} \quad (W_t(\mathbf{r}), W_{t'}(\mathbf{r})) = \delta_{tt'}. \quad (7)$$

The integrations in Eqs. (6) and (7) are over the volume of the cyclic model.

Let $Q_{(\mathbf{q}, \beta)}$ be the space of a simple irrep (\mathbf{q}, β) (for simplicity). The space $Q_{(\mathbf{q}, \beta)}$ is spanned by both the set of orthonormal functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) \equiv W_t^{(\beta)}(\mathbf{r})$ and the set of Bloch functions $\varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r}) \equiv \varphi_s(\mathbf{r})$. The orthonormal functions $W_t^{(\beta)}(\mathbf{r})$ can be chosen to be real (if irrep β is real) and transform according to the irrep β of the site groups $L_{\mathbf{q}, n}$ of the points $\mathbf{q}_{j, n}$. Their localization depends on the choice of the matrix U_{st} in Eq. (5). The existence of Wannier functions decreasing exponentially at infinity (for the model of an infinite crystal) has been established in many special cases.^{8,30} The uniqueness of these functions has been proved for nondegenerate bands in crystals with centers of inversion.^{5,8} In this case the Wannier functions correspond to a special choice of phase factors $\tilde{U}_{\sigma, \tau}(\mathbf{k}) = \exp[i\alpha(\mathbf{k})]$ of Bloch orbitals $\varphi_\sigma(\mathbf{k}, \mathbf{r})$ in Eq. (5). Any other choice of phase factors destroys either symmetry properties of the Wannier functions, or their reality, or both.^{5,8,31} Obviously these functions are as well localized as possible. If the choice of phase factors is not correct the Wannier functions lose the exponential character of their decreasing and, therefore, cannot be maximally localized according to any reasonable criterion of localization. Unfortunately the uniqueness of Wannier functions is not yet proved for the more general case of the degenerate bands in crystals with centers of inversion where it apparently exists (see Sec. IV).

As a criterion of localization for a localized function $W(\mathbf{r})$ one uses the value of the integral over the whole space of the crystal,¹⁸

$$\mathbf{I} = \int \rho(\mathbf{r}) |W(\mathbf{r})|^2 d\mathbf{r}, \quad (8a)$$

with the weight function $\rho(\mathbf{r}) \geq 0$, which is supposed to be invariant under the operations from the site symmetry group S_q . Particular choices of the weight function are

$$\rho(\mathbf{r}) = (\mathbf{r} - \mathbf{q})^2 \quad (\text{Refs. 6, 22, 23, and 4}), \quad (8b)$$

$$\rho(\mathbf{r}) = \begin{cases} 1, & \text{if } \mathbf{r} \in \Delta, \\ 0, & \text{if } \mathbf{r} \notin \Delta, \end{cases} \quad (8c)$$

where Δ is some region surrounding the point \mathbf{q} of symmetry localization of the function $W_0^{(\beta)}(\mathbf{r})$, or

$$\rho(\mathbf{r}) = (\pi r_0^2)^{-3/2} \exp\left(-\frac{(\mathbf{r} - \mathbf{q})^2}{r_0^2}\right), \quad (8d)$$

which accentuates the contribution of the values of the function $|W_0^{(\beta)}(\mathbf{r})|^2$ inside the sphere of radius r_0 and centered on the point \mathbf{q} into the functional (8). As a special case of Eq. (8d) for $r_0 \rightarrow 0$ one has $\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{q})$.

One searches for the set of nonorthogonal localized functions $V_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ in the form

$$V_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n) = L^{-1/2} \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{a}_n)$$

$$\times \sum_{\gamma m \mu} C_{\gamma m \mu, ij}(\mathbf{k}) \cdot \varphi_{m\mu}^{(\gamma)}(\mathbf{k}, \mathbf{r}), \quad (9a)$$

or

$$V_t^{(\beta)}(\mathbf{r}) = L^{-1/2} \sum_s C_{st} \cdot \varphi_s(\mathbf{r}). \quad (9b)$$

The system of functions $V_{ij}^{(\beta)}(\mathbf{r}) \equiv V_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ can be obtained from the function $V_{11}^{(\beta)}(\mathbf{r}) \equiv V_0^{(\beta)}(\mathbf{r})$ in the same way as the functions $W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$ from the function $W_{11}^{(\beta)}(\mathbf{r})$ (see above). Therefore, it is sufficient to find only one function, for example,

$$V_0^{(\beta)}(\mathbf{r}) = L^{-1/2} \sum_s C_{s0} \cdot \varphi_s(\mathbf{r}). \quad (10)$$

The coefficients C_{s0} can be found from the following variational problem: to find the coefficients C_{s0} in Eq. (10), which maximize (or minimize) the functional (8) and satisfy the supplementary condition

$$\int |V_0^{(\beta)}(\mathbf{r})|^2 d\mathbf{r} = 1. \quad (11)$$

This variational problem is equivalent to the eigenvalues and eigenvectors problem for the matrix:

$$A_{ss'} = \frac{1}{L} \int \rho(\mathbf{r}) \varphi_s^*(\mathbf{r}) \varphi_{s'}(\mathbf{r}) d\mathbf{r}. \quad (12)$$

The eigenvalues of the matrix A are stationary values of the localization criterion \mathbf{I} (8), and the eigenvectors corresponding to these values are the required coefficients of the expansion (10). In our case, it is necessary to search for the eigenvector corresponding to the highest eigenvalue for the choices (8c) and (8d) of the weight function $\rho(\mathbf{r})$ and to the lowest one for the case (8b). Let us note that it is sufficient to use the variational procedure in the subspace of the first basis

vectors of the irrep β of the site group S_q instead of the whole space of the canonical orbitals of the energy band under consideration.

Though the set of the functions $V_i(\mathbf{r})$ is not orthogonal, these functions are close to the accurate localized Wannier functions $W_i^{(\beta)}(\mathbf{r}) \equiv W_{ij}^{(\beta)}(\mathbf{r} - \mathbf{a}_n)$. They can be chosen to be real (for the real irrep β of the site group S_q) and satisfy all the symmetry requirements for the functions $W_i^{(\beta)}(\mathbf{r})$. The orthonormal system $\tilde{W}_i^{(\beta)}(\mathbf{r})$ is generated from the functions $V_i^{(\beta)}(\mathbf{r})$ by a suitable-for-periodic-systems orthogonalization procedure.³² According to Ref. 32,

$$\tilde{W}_i^{(\beta)}(\mathbf{r}) = \sum_{i'} (S^{-1/2})_{i'i} V_{i'}^{(\beta)}(\mathbf{r}), \quad (13)$$

where S is the overlap matrix of the functions $V_i^{(\beta)}(\mathbf{r})$:

$$S_{i'i'} \equiv (V_i^{(\beta)}(\mathbf{r}), V_{i'}^{(\beta)}(\mathbf{r})). \quad (14)$$

Combining Eqs. (9b) and (13) we get

$$\tilde{W}_i^{(\beta)}(\mathbf{r}) = L^{-1/2} \sum_{i's} C_{si'} \cdot (S^{-1/2})_{i'i} \cdot \varphi_s(\mathbf{r}). \quad (15)$$

As the symmetrical orthogonalization procedure³² leaves unchanged the reality and symmetry properties of the functions, the set of orthonormalized functions $\tilde{W}_i^{(\beta)}(\mathbf{r})$ satisfy all the requirements, to the localized Wannier functions (reality, symmetry requirements and orthonormality) and (in the case when this set of the functions is unique) has to coincide with the latter:

$$\tilde{W}_i^{(\beta)}(\mathbf{r}) = W_i^{(\beta)}(\mathbf{r}). \quad (16)$$

The weight function $\rho(\mathbf{r})$ in the functional \mathbf{I} (8) can be varied. In particular, one can choose for the region Δ in Eq. (8c) a muffin-tin sphere, some part of a Wigner-Seitz cell (even very small), etc. The functions $V_i(\mathbf{r})$ depend on the choice of $\rho(\mathbf{r})$, but, according to our calculations, in the case of lattices with centers of inversion after the procedure of symmetric orthogonalization we always have the same result even for degenerate bands in crystals with centers of inversion. Apparently the proposed method gives in these cases the orthonormal set of maximally localized Wannier functions. This is demonstrated in the next section.

Thus the numerical calculations imply constructing matrix $A_{ss'}$ (12), diagonalization of this matrix, then obtaining the overlap matrix $S_{i'i'}$ (14), taking its matrix square root, and, in addition, some elementary operations of linear algebra. For the integration over the BZ we use the method of summation over the special points (5), which is equivalent to the introduction of a cyclic model of the crystal.

The suggested procedure of Wannier functions calculation can be easily extended to an inclusion of the influence of the correlation effects on the chemical bonding in crystalline solids. For example, in the linear combination of atomic orbitals (LCAO)-density functional theory approach³⁷ the self-consistent Bloch functions and the corresponding density matrix are calculated with an inclusion of the exchange-

correlation corrections in the Kohn-Sham Hamiltonian. The correlated Bloch functions lead to correlated Wannier functions, which allow one to determine the correlation corrections to the corresponding local properties of the electronic structure. This possibility is essential for future studies of the correlation effects in solids, the problem being much more complicated than for molecules (in the latter case post-Hartree-Fock approaches are widely used).

IV. CALCULATIONS OF THE LOCALIZED FUNCTIONS

To demonstrate the reliability of the proposed variational method let us consider five examples of its applications. Three of them deal with those types of lattices for which the precise form of localized states is known. These examples are less practically valuable but reveal directly the accuracy of the proposed variational procedure. The fourth example is more practically interesting as it regards the classical case of a covalent bond formed by electrons of the upper valence band of an Si crystal. And the last one is devoted to Wannier functions for valence bands of an MgO crystal. As far as we know, the Wannier functions for MgO haven't been generated before.

A. Localized displacements in a one-dimensional lattice with two atoms per unit cell

Localized displacements are introduced in the same way as localized electron functions, but instead of canonical orbitals one has to consider vectors of normal displacements. At first we study the localized displacements in a one-dimensional lattice with two atoms per unit cell.^{13,29} Such a lattice is characterized by masses of the atoms m_1 and m_2 , force constants of the springs g_1 and g_2 , and the lattice constant $a=1$. Centers of symmetry appear when $m_1=m_2=m$ or $g_1=g_2=g$. The symmetry analysis of such a structure shows that the center of the localized displacements is on the middle of the bonds with the larger g , if $m_1=m_2$. The symmetries of the displacements for the acoustic and optical branches are a_u and a_g , respectively. When $g_1=g_2$, the localized displacements have the a_u symmetry and are centered on the heavier and the lighter atoms for the acoustic and optical branches, respectively.

The calculation shows that the localized displacements constructed by the variational method coincide within the computational error with the correct ones for all values of the parameters (m_1, m_2, g and m, g_1, g_2) and for Δ in Eq. (8c) varying in the range from some part of the unit cell up to several unit cells. The correct, i.e., the most localized Wannier displacements have been found according to the procedure described in Ref. 13. As an example, the localized displacements for $m_1=m_2=1$, $g_1=2$, and $g_2=1$ are given in Table I: n is an atom number, $W_1^{(no)}(n)$ and $W_2^{(no)}(n)$ are nonorthogonal displacements for $\Delta=1$ and $\Delta=2$, respectively, and $W_1(n)=W_2(n)$ are corresponding orthogonal displacements, coinciding with the correct ones $W(n)$. In calculations we have used the cyclic model of a one-dimensional crystal consisting of 10 unit cells (20 atoms).

TABLE I. Localized displacements for a one-dimensional diatomic crystal.

| n | $W_1^{(no)}(n)$ | $W_2^{(no)}(n)$ | $W_1(n) = W_2(n)$ | $W(n)$ |
|-----|-----------------|-----------------|-------------------|---------|
| 0 | 0.6954 | 0.6958 | 0.6954 | 0.6954 |
| 1 | 0.0929 | 0.1717 | 0.0906 | 0.0906 |
| 2 | -0.0810 | 0.0030 | -0.0847 | -0.0847 |
| 3 | -0.0118 | -0.0106 | -0.0171 | -0.0171 |
| 4 | 0.03000 | 0.0092 | 0.0262 | 0.0262 |
| 5 | 0.0025 | 0.0025 | 0.0047 | 0.0047 |
| 6 | -0.0124 | -0.0046 | -0.0097 | -0.0097 |
| 7 | 0.0001 | -0.0004 | -0.0010 | -0.0010 |
| 8 | 0.0053 | 0.0021 | 0.0037 | 0.0037 |
| 9 | -0.0021 | -0.0007 | -0.0010 | -0.0010 |

The displacements of other atoms for the acoustic and optical branches may be obtained by symmetry operations (irreps a_u and a_g , respectively).

B. Electron localized states for the one-dimensional Kronig-Penney model

To construct localized electron functions we used the model of a one-dimensional lattice with a Kronig-Penney potential.^{5,18,29,33} This case is particularly interesting. First, the band structure has nontrivial symmetry properties of Wannier functions corresponding to a different choice of Bloch functions' phase factors and to different bands.^{29,31} Second, the parameters of the model can be chosen in such a way that Wannier functions corresponding to certain bands would have, although exponential, quite a slow decay.⁵ That allows us to examine the method in the cases of slow decrease of Wannier functions. And besides, it is very helpful that the most localized Wannier functions in this case can be generated explicitly because the procedure for choosing the correct phase factors for Bloch functions in one-dimensional crystals is known.⁵

The Bloch one-electron orbitals $\varphi_i(k, x)$, where i is the number of an energy band, are determined from the Schrödinger equation

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + V(x) \right] \varphi_i(k, x) = E \varphi_i(k, x) \quad (17)$$

with the periodic and symmetrical at the lattice sites potential,

$$V(x) = C \sum_n \delta(x - n). \quad (18)$$

There are two inversion centers in the unit cell: $a(x=0), b(x=\frac{1}{2})$. The symmetry analysis of band states shows that if $C < 0$ the lowest-energy band corresponds to the irrep $a(a_g)$. All the other bands have the symmetry $b(a_g)$ or $b(a_u)$, alternatively. In the case when $C > 0$ all the bands are of the $b(a_g)$ or $b(a_u)$ symmetry, alternatively.²⁹

We've considered different bands at different values of C . As an example of functioning of the variational and orthogo-

TABLE II. Localized Wannier functions for a one-dimensional Kronig-Penney model.

| x | $W_1^{(no)}(x)$ | $W_2^{(no)}(x)$ | $W_1(x) = W_2(x) = W(x)$ |
|-----|-----------------|-----------------|--------------------------|
| 0.0 | 1.6521 | 1.6487 | 1.6488 |
| 0.2 | 0.9834 | 0.9847 | 0.9847 |
| 0.4 | 0.5431 | 0.5536 | 0.5534 |
| 0.6 | 0.2401 | 0.2646 | 0.2641 |
| 0.8 | 0.0208 | 0.0655 | 0.0644 |
| 1.0 | -0.1421 | -0.0676 | -0.0699 |
| 1.2 | -0.1184 | -0.0757 | -0.0778 |
| 1.4 | -0.0728 | -0.0527 | -0.0555 |
| 1.6 | -0.0211 | -0.0185 | -0.0229 |
| 1.8 | 0.0282 | 0.0160 | 0.0088 |
| 2.0 | 0.0690 | 0.0435 | 0.0316 |

nalization procedures we give in Table II Wannier functions in some points x for the lowest-energy band when $C = -2.5$. Ninety nine percent of the normalization integral for this function is contained in the "volume" of 1.4 unit cells.²⁹ Functions $W_1^{(no)}(x)$ and $W_2^{(no)}(x)$ are nonorthogonalized ones corresponding to the choice of weight function $\rho(x) = \delta(x)$ and Eq. (8c) with $\Delta = 1$, respectively. The last column represents these functions after the procedure of symmetric orthogonalization coinciding with one another and with the correct one⁵ ($W_1(x) = W_2(x) = W(x)$).

C. Localized displacements for a germanium crystal

We have also constructed the localized displacements in the germanium crystal by the proposed variational method. This crystal has a diamond-type lattice with two atoms per unit cell, atoms occupying the Wyckoff position a with the site group T_d . The symmetry analysis of normal displacements for six vibrational branches shows that all normal displacements form a basis of the simple irrep (a, t_2) : six localized displacements per unit cell, centering at Ge atoms, with three at each. These displacements transform according to the vector rep t_2 of the site group T_d . In the calculations, we have used a cyclic model consisting of $3 \times 3 \times 3 = 27$ unit cells and defined by vectors $\mathbf{A}_i = 3\mathbf{a}_i$ ($i = 1, 2, 3$). The volume Δ (8c) of the region in the variational functional has been chosen to be half of the unit cell, i.e., one Ge atom (so long as displacements in a vibrational problem are defined only at atom positions).

As it was expected, the localized displacements turned out to be the unit displacements of atoms along Cartesian axes. This result can be explained by the fact that the six vibrational branches in the germanium crystal represent one "degenerate band." The normal displacements are linear combinations of the unit displacements, which form the basis in the space of the full vibrational rep and, obviously, are the most localized functions and fulfill the necessary symmetry conditions.

D. Wannier functions for the upper valence band of an Si crystal

At last we have applied the proposed variational procedure to find electron Wannier functions for three-dimensional

TABLE III. Localized states for the upper valence band of an Si crystal along the $[111]$ direction (the origin is taken in the middle of the Si-Si bond, x is in $a\sqrt{3}/96$ units, and a is the conventional lattice constant).

| x | $W_1(x)$ | $W_8(x)$ | $W_{64}(x)$ | $W_{64}^{(no)}(x)$ |
|-----|----------|----------|-------------|--------------------|
| 0 | -0.2300 | -0.2036 | -0.1982 | -0.1988 |
| 3 | -0.2190 | -0.1975 | -0.1926 | -0.1930 |
| 6 | -0.1566 | -0.1465 | -0.1436 | -0.1437 |
| 9 | 0.1204 | 0.1216 | 0.1199 | 0.1196 |
| 11 | 0.4116 | 0.3840 | 0.3725 | 0.3747 |
| 12 | -0.5831 | -0.7333 | -0.7579 | -0.7406 |
| 15 | -0.0596 | -0.0401 | -0.0354 | -0.0373 |
| 18 | 0.0497 | 0.0336 | 0.0288 | 0.0307 |
| 22 | 0.0620 | 0.0501 | 0.0453 | 0.0471 |
| 27 | 0.0250 | 0.0327 | 0.0317 | 0.0321 |
| 33 | -0.0099 | 0.0097 | 0.0127 | 0.0121 |
| 39 | -0.0098 | -0.0002 | 0.0040 | 0.0030 |
| 45 | 0.0045 | -0.0017 | 0.0011 | 0.0004 |
| 51 | 0.0045 | -0.0002 | 0.0006 | 0.0003 |
| 57 | -0.0098 | 0.0005 | 0.0003 | 0.0003 |
| 63 | -0.0099 | 0.0000 | 0.0000 | -0.0001 |
| 69 | 0.0250 | -0.0006 | -0.0002 | -0.0002 |
| 75 | 0.0649 | -0.0015 | -0.0002 | -0.0001 |
| 81 | -0.0596 | 0.0008 | 0.0000 | -0.0001 |
| 84 | -0.5831 | -0.0082 | -0.0005 | 0.0000 |
| 87 | 0.1204 | -0.0001 | 0.0000 | 0.0000 |
| 90 | -0.1566 | -0.0002 | -0.0001 | -0.0002 |
| 93 | -0.2190 | -0.0006 | -0.0002 | -0.0004 |
| 96 | -0.2300 | -0.0008 | -0.0003 | -0.0006 |

crystals, particularly, for the upper valence band of the perfect Si crystal (space group O_h^7 , a diamond-type lattice with two atoms per unit cell). As is well known and in accordance with the theory of induced (band) representations the corresponding Wannier functions (four per unit cell) are centered at the middle of the bonds between the nearest Si atoms (Wyckoff position c with site group $L_c = D_{3d}$) and transform according to the irrep a_g of the site group D_{3d} .

For our variational procedure we have used two sets of electron Bloch functions of an Si crystal obtained with the help of the program CRYSTAL 95.^{34,35} The first set (S_1) corresponds to the full electron restricted Hartree-Fock (RHF) LCAO calculations, and the second one (S_2) to the pseudopotential RHF LCAO method. The first basis consists of 13 s and p atomiclike functions per atom; the “pseudopotential” basis consists of two s , six p , and five d functions per atom. We have taken the weight function $\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{q})$ in Eq. (8).

A cyclic model of the crystal consisting of $4 \times 4 \times 4 = 64$ primitive cells has been adopted. The band structure calculations show that this cyclic model ensures the convergence of the results (for further enlarging of L the changes appeared to be small).² It means that the corresponding Wannier functions are localized inside the volume consisting of $4 \times 4 \times 4 = 64$ primitive cells and defined by vectors $\mathbf{A}_i = 4\mathbf{a}_i$ ($i = 1, 2, 3$).²

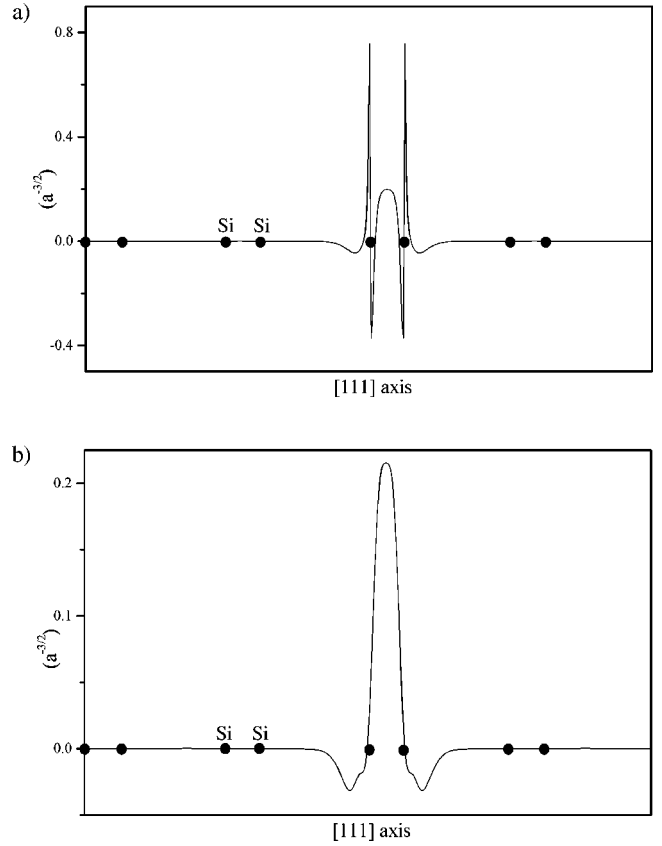


FIG. 1. Wannier functions of the upper valence band of Si in the $[111]$ direction for the $4 \times 4 \times 4$ cyclic model. (a) Wannier function $W_{64}(x)$; (b) “pseudo-wave” Wannier function $W_{64}^{(pp)}(x)$.

The bigger the cyclic model of a crystal, the closer its Wannier functions to the ones of the model of an infinite crystal.²⁹ To study the convergence of the Wannier functions $W(\mathbf{r})$ in cyclic models of different sizes we have calculated Wannier functions $W_1(x)$, $W_8(x)$, and $W_{64}(x)$ from 4 (point Γ ; the supercell coincides with a primitive cell), 32 (points Γ , X , L ; $2 \times 2 \times 2 = 8$ primitive cells in the supercell), and 256 ($4 \times 4 \times 4 = 64$ primitive cells in the supercell) Bloch states, correspondingly (for the set S_1). Table III gives the values of the Wannier functions $W_1(x)$, $W_8(x)$, $W_{64}(x)$, and $W_{64}^{(no)}(x)$ (the latter is nonorthogonalized) in some points along the $[111]$ direction. As is seen from the table, the function $W_{64}^{(no)}(x)$ is very close to $W_{64}(x)$. So the orthogonalization procedure changes the Wannier function insignificantly. When comparing the functions $W_1(x)$, $W_8(x)$, and $W_{64}(x)$ it is necessary to take into account that these functions are normalized differently, in the volume of 1, 8, and 64 primitive cells, respectively. The fact that their values are relatively close to each other from $x=0$ to $x=48$ (in units $a\sqrt{3}/96$, the translational period in the $[111]$ direction is equal to $a\sqrt{3}$) shows a good localization of the Wannier function and, on the other hand, the convergence of the summation (5) over the sets of special points to the corresponding integral over the BZ.

Figure 1 gives the $W_{64}(x)$ and “pseudopotential” Wannier function $W_{64}^{(pp)}(x)$ in the $[111]$ direction. The functions differ significantly at the atoms’ cores. Outside the cores the behav-

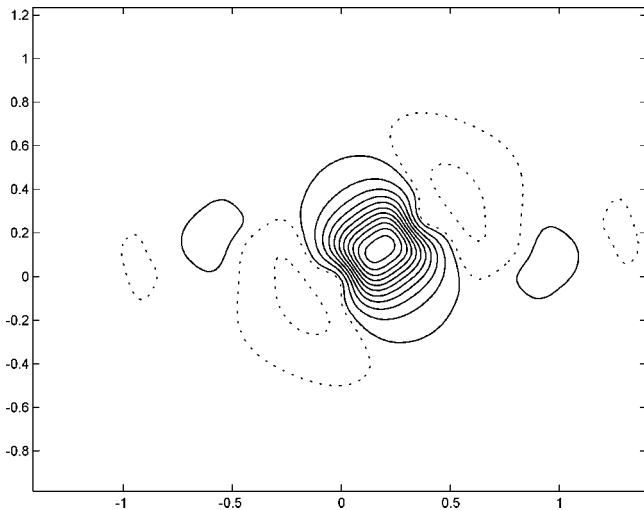


FIG. 2. Contour plot of the “pseudowave” Wannier function for the $4 \times 4 \times 4$ cyclic model of Si in the $(\bar{1}10)$ plane. The origin is taken at one of the Si atoms, and axes are scaled in units of a . The dashed lines correspond to negative values. The lower level of positive values is at 0.005, the upper level of negative values is at -0.005 , and the step is 0.02 (all values are in units of $a^{-3/2}$).

ior of the functions is alike. This is quite natural, since the “pseudopotential” Wannier functions are constructed from smooth pseudowave Bloch functions—nonorthogonal to the core states. Orthogonalization of these smooth Wannier functions to the localized core functions would lead to an uprising of oscillations at the atoms’ cores observed in the Wannier functions $W_{64}(x)$. And the differences between the Wannier functions in the interatomic space are due to the normalization. The contour plot of the “pseudopotential” Wannier function in the $(\bar{1}01)$ plane is presented in Fig. 2.

In this case, just as in the previous examples, the method reveals a very good stability with respect to the choice of the weight function $\rho(\mathbf{r})$ form. The computations give the same resulting orthogonalized Wannier functions whereas the intermediate nonorthogonalized functions $V_i(\mathbf{r})$ turn out to be different. We have found an amazing thing. Even if one uses the weight functions $\rho(\mathbf{r})$ centered at any point in the localization region of the Wannier function and therefore the functions $V_i(\mathbf{r})$ do not have the symmetry compatible with the site group S_q , the same orthogonalized Wannier functions of the needed symmetry arise after the orthogonalization procedure. The latter not only conserves the symmetry of the localized orbitals, but reconstructs it up to an appropriate level. The reason for such flexibility is apparently the fact that the most localized Wannier functions of the silicon valence band are unique and just these functions arise without fail as the result of the proposed variational procedure [see Sec. III and Refs. 5 and 7] succeeded by the symmetrical orthogonalization. This property of uniqueness (to within the linear transformation in the space of rep β of site group S_q), is seemingly a common feature of the most localized Wannier functions corresponding to degenerate or nondegenerate energy bands separated from other bands by band gaps in crystals with centers of inversion (see Refs. 5 and 7).

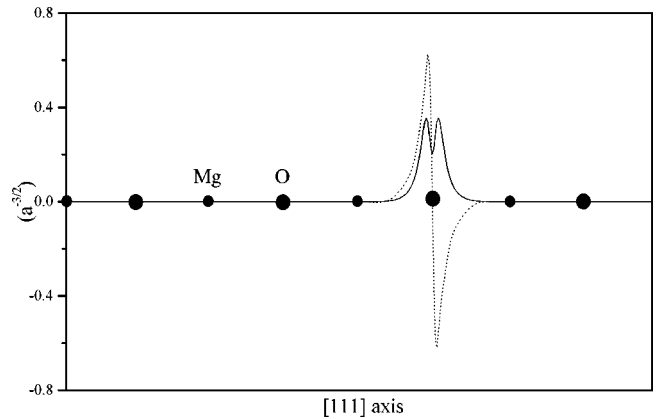


FIG. 3. Wannier functions of the valence bands of MgO in the $[111]$ direction for the $4 \times 4 \times 4$ cyclic model: the solid curve relates to the a_g Wannier function of the lower band, and the dashed one presents one of the three t_{1u} Wannier functions of the upper valence band.

Unfortunately we cannot compare our Wannier functions with those in Ref. 20, because there the decreasing of Wannier functions is demonstrated indirectly, by means of the coefficients in the Fourier expansion of the Hamiltonian. The fact that the main features of Wannier functions’ behavior (Fig. 1 and Fig. 2) are reproduced in our calculations and we have a direct comparison of the form of our Wannier functions with those in Refs. 4, 21, and 36 allow us to conclude that the proposed method is effective in constructing the maximally localized Wannier functions.

E. Wannier functions for the upper valence bands of the MgO crystal

Finally we have constructed the Wannier functions for the upper valence bands of the perfect MgO crystal (space group O_h^5 , with a face-centered lattice with one formula unit per unit cell). As in the above case of silicon we have applied a set of MgO Bloch functions obtained with the help of the program CRYSTAL 95 (Refs. 34 and 35) corresponding to pseudopotential RHF LCAO calculations. For the same reasons as in the case of silicon the $4 \times 4 \times 4$ cyclic model has been used in the calculations. The valence band of MgO represents two separated bands, and thus it is possible to construct two independent sets of Wannier functions (for each of the bands). The method of induced representations gives all the Wannier functions being centered on O atoms (Wyckoff position b with site group $L_c = O_h$) and transforming, according to the irrep a_g of the site group O_h for the lower band (one Wannier function per unit cell) and according to the irrep t_{1u} for the upper band (three Wannier functions per unit cell). We have taken the weight function $\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{q})$ in Eq. (8) located some distance away from the centering point of the corresponding Wannier function, because the Wannier functions of the upper band are anti-symmetric and thus equal zero in their centering points while as stated above the symmetrical centering of the $\rho(\mathbf{r})$ function is not necessarily needed in this case.

Figure 3 shows the Wannier functions for both bands in

the [111] direction. We should mention that the function corresponding to the upper band (dashed curve) is determined up to a linear combination of the three functions transforming via the t_{1u} irrep. One can see that both Wannier functions are almost completely localized around one of the oxygen atoms, which confirms the ionic character of the MgO compound.

V. CONCLUSION

The character of the localization of Wannier functions depends on the analytical properties of Bloch states (as a function of the wave vector) which are essentially determined by the nature of the system under consideration. One can arbitrarily change only the form of a unitary transformation of Bloch functions. It is just this arbitrariness that is used in our

variational approach to assure the best localization of Wannier functions. The accuracy of the Wannier functions obtained by the proposed method is determined solely by the accuracy of the Bloch functions and the size of the supercell used. As the calculations have shown, the proposed method is reliable and useful in the problem of generation of the localized Wannier functions.

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