

A priori Wannier functions from modified Hartree-Fock and Kohn-Sham equations

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The Hartree-Fock equations are modified to directly yield Wannier functions following a proposal of Shukla *et al.* [Chem. Phys. Lett. **262**, 213 (1996)]. This approach circumvents the *a posteriori* application of the Wannier transformation to Bloch functions. I give a rigorous derivation of the relevant equations by introducing an orthogonalizing potential to ensure the orthogonality among the resulting functions. The properties of these, so-called *a priori* Wannier functions, are analyzed and the relation of the modified Hartree-Fock equations to the conventional, Bloch-function-based equations is elucidated. It is pointed out that the modified equations offer a different route to maximally localized Wannier functions. Their computational solution is found to involve an effort that is comparable to the effort for the solution of the conventional equations. Above all, I show how *a priori* Wannier functions can be obtained by a modification of the Kohn-Sham equations of density-functional theory.

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I. INTRODUCTION

Ever since the introduction of Wannier functions in 1937,¹ they have been used as an alternative representation to Bloch functions in the study of crystalline solids.¹⁻⁸ They provide a local, atomic-orbital-like view on one-particle states of crystals, which is the direct generalization to periodic systems of the concept of localized molecular orbitals used by chemists to study bonding in molecules and clusters. In such a way, they come much closer to the intuitively accessible concepts of chemical bonding than the conventional, plane-wave-like Bloch orbitals which are completely delocalized over the whole crystal.¹⁻⁸ Wannier functions have been used frequently in formal deductions. However, only recently do they become practically important, e.g., they are used to achieve linear scaling with the system size of the tight-binding or Kohn-Sham method.^{9,10} Moreover, as soon as electron correlations in the ground state and in excited states are regarded, a local representation offers big advantages.^{5,8,11-18}

Conventionally, Wannier functions are determined *a posteriori* from Bloch functions utilizing the Wannier transformation.^{1-4,6,7} It is unique up to a unitary matrix, which can be chosen freely to obtain a certain set of Wannier functions, e.g., those which are maximally localized with respect to a given criterion. Marzari and Vanderbilt⁶ and Zicovich-Wilson *et al.*⁷ advocate the Foster-Boys functional.¹⁹⁻²¹ However, there are a number of other localization criteria such as the method of Edmiston and Ruedenberg²² or the recipe of Pipek and Mezey²³ which can be used, too.

Instead, Shukla *et al.*²⁴ proposed an embedded-cluster model that facilitates solving modified Hartree-Fock equations, which directly yield Wannier-type functions. The theory has been implemented in terms of the computer program WANNIER,^{24,25} which has been used in a series of studies of polymers and crystals.^{11,24-27} It was found, empirically, to provide accurate Hartree-Fock energies and band structures.^{24,25,27,28} The program has also been used as a starting point for post Hartree-Fock calculations; the correlation energy of the ground state^{11,29} and the quasiparticle band structure of several polymers and crystals have been

investigated.^{12,14,15,17} The idea to directly solve for Wannier-type functions has also been discussed, e.g., in Refs. 9, 10, and 30 (and references therein).

The paper is structured as follows. In Sec. II, I devise a rigorous proof of the modified Hartree-Fock equations of Shukla *et al.*²⁴ and give the corresponding modified Roothaan-Hall equations. The functions that result from these equations are termed *a priori* Wannier functions. The relation of the modified equations to the canonical, Bloch-function-based equations and a comparison of the computational effort of both approaches can be found in Sec. III. Conclusions are drawn in Sec. IV; specifically, I show that the Kohn-Sham equations of density-functional theory can be modified in the same way as the Hartree-Fock equations to obtain *a priori* Wannier functions.

Atomic units are used throughout the article.

II. A PRIORI WANNIER FUNCTIONS**A. Definitions**

The sets of functions $\{w_{\vec{R}\varrho}(\vec{r}s), \varrho=1, \dots, K\}$ are associated with each unit cell \vec{R} of a crystal; they depend on the spatial and spin coordinates \vec{r} and s , respectively. The sets are translationally related; i.e., two such sets can be brought into coincidence by displacing the functions in one of them by a suitable lattice vector \vec{R}' ,

$$w_{\vec{R}+\vec{R}'\varrho}(\vec{r}s) \equiv \langle \vec{r}s | \vec{R} + \vec{R}' \varrho \rangle = w_{\vec{R}\varrho}(\vec{r} - \vec{R}'s) = \hat{T}_{\vec{R}'} w_{\vec{R}\varrho}(\vec{r}s). \quad (1)$$

Here, $\hat{T}_{\vec{R}'}$ denotes the translation operator for a passive translation by \vec{R}' . Furthermore, the functions are assumed to be orthonormal with respect to an integration over the entire space,

$$\langle w_{\vec{R}\sigma} | w_{\vec{R}'\varrho} \rangle = \sum_{s=-1/2}^{1/2} \int_{\mathbb{R}^3} w_{\vec{R}\sigma}^*(\vec{r}s) w_{\vec{R}'\varrho}(\vec{r}s) d^3r = \delta_{\vec{R}\vec{R}'} \delta_{\sigma\varrho}. \quad (2)$$

The two properties (1) and (2) characterize (spin) Wannier functions,¹⁻⁴ which are frequently termed (spin) Wannier or-

bitals, if they are Hartree-Fock or Kohn-Sham (spin) orbitals.

I describe the crystal by a nonrelativistic Hamiltonian^{5,31}

$$\hat{H} = \sum_{n=1}^N \hat{h}_n + \frac{1}{2} \sum_{\substack{m,n=1 \\ m \neq n}}^N \frac{1}{|\vec{r}_m - \vec{r}_n|} + \hat{E}_{\text{nucl}}, \quad (3a)$$

$$\hat{h}_n = -\frac{1}{2} \vec{\nabla}_n^2 - \sum_{i=1}^{N_0} \sum_{A=1}^M \frac{Z_{R_i A}}{|\vec{r}_n - \vec{r}_{R_i A}|}, \quad (3b)$$

$$\hat{E}_{\text{nucl}} = \frac{1}{2} \sum_{i,j=1}^{N_0} \sum_{\substack{A,B=1 \\ i \neq j \vee A \neq B}}^M \frac{Z_{R_i A} Z_{R_j B}}{|\vec{r}_{R_i A} - \vec{r}_{R_j B}|}, \quad (3c)$$

assuming fixed nuclei. Here, N denotes the number of electrons in the crystal which is represented by a parallelepiped that consists of N_0 unit cells. The distance between the m th and the n th electron is represented by $|\vec{r}_m - \vec{r}_n|$. The number of nuclei per unit cell is indicated by M and $Z_{R_i A} \equiv Z_A$ stands for the charge of nucleus A in unit cell \vec{R}_i . Then, $|\vec{r}_n - \vec{r}_{R_i A}|$ is the distance between the n th electron and the A th nucleus in unit cell \vec{R}_i . Finally, $|\vec{r}_{R_i A} - \vec{r}_{R_j B}|$ denotes the distance between nuclei A and B of charge $Z_{R_i A} \equiv Z_A$ and $Z_{R_j B} \equiv Z_B$ in unit cells \vec{R}_i and \vec{R}_j , respectively.

B. Wannier-Hartree-Fock equations

The ansatz for the Hartree-Fock wave function is given by the Slater determinant in terms of the occupied Wannier orbitals,

$$\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N) = \hat{A} \prod_{i=1}^{N_0} \prod_{j=1}^{N'} w_{\vec{R}_i \kappa_j}(\vec{r}_{j+(i-1)N'} s_{j+(i-1)N'}), \quad (4)$$

where $N' = \frac{N}{N_0}$ is the number of occupied orbitals per unit cell and \hat{A} stands for the antisymmetrizer.³² The energy expectation value of the Slater determinant (4) with the Hamiltonian (3) reads^{24,32,33}

$$\begin{aligned} E[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)] &= \sum_{\vec{R}} \sum_{\kappa=1}^{N'} \langle w_{\vec{R}\kappa} | \hat{h}_1 | w_{\vec{R}\kappa} \rangle + \frac{1}{2} \sum_{\vec{R}, \vec{R}'} \sum_{\kappa, \xi=1}^{N'} \\ &\times \left[\left\langle w_{\vec{R}\kappa}(1) w_{\vec{R}'\xi}(2) \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| w_{\vec{R}\kappa}(1) w_{\vec{R}'\xi}(2) \right\rangle \right. \\ &\left. - \left\langle w_{\vec{R}\kappa}(1) w_{\vec{R}'\xi}(2) \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| w_{\vec{R}'\xi}(1) w_{\vec{R}\kappa}(2) \right\rangle \right] \\ &+ E_{\text{nucl}}; \end{aligned} \quad (5)$$

it is a functional of the Wannier orbitals.

In order to minimize the energy expectation value to obtain the best description of the ground state by a single Slater determinant in terms of Ritz' variational principle, functional

variation with respect to the orbitals in Eq. (5) is carried out.^{14,32,33} In doing so, I subtract the constraints

$$\sum_{\vec{R}, \vec{R}'} \sum_{\kappa, \xi=1}^{N'} \Lambda_{\vec{R}' \xi \vec{R} \kappa} (\langle w_{\vec{R}\kappa} | w_{\vec{R}'\xi} \rangle - \delta_{\vec{R}\vec{R}'} \delta_{\kappa\xi}) \quad (6)$$

from $E[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)]$, employing the Lagrangian multipliers $\Lambda_{\vec{R}' \xi \vec{R} \kappa}$; this ensures the orthonormality of the orbitals. One arrives at the Hartree-Fock equations in terms of Wannier orbitals,

$$\hat{f} |w_{\vec{R}\kappa}\rangle = \sum_{\xi=1}^{N'} \Lambda_{\vec{R} \xi \vec{R} \kappa} |w_{\vec{R}\xi}\rangle + \sum_{\vec{R}' \neq \vec{R}} \sum_{\xi=1}^{N'} \Lambda_{\vec{R}' \xi \vec{R} \kappa} |w_{\vec{R}'\xi}\rangle, \quad (7)$$

with \hat{f} denoting the Fock operator. Expression (7) forms a set of N equations which couple the occupied Wannier orbitals in a unit cell to the occupied Wannier orbitals in all other cells of the crystal. Above all, the Hartree-Fock equations (7) do not have the form of an eigenvalue equation. For these reasons, their practical application is cumbersome.

To make progress towards a more favorable, modified form of Hartree-Fock equations for Wannier orbitals, I omit the intercell Lagrangian multipliers in Eq. (6) and thus arrive at the new energy functional

$$\begin{aligned} \mathcal{L}[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)] &= E[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)] - \sum_{\vec{R}} \sum_{\kappa, \xi=1}^{N'} \Lambda_{\vec{R} \xi \vec{R} \kappa} (\langle w_{\vec{R}\kappa} | w_{\vec{R}\xi} \rangle - \delta_{\kappa\xi}). \end{aligned} \quad (8)$$

Here, the translational symmetry of Λ is exploited, i.e., $\Lambda_{\xi\kappa} \equiv \Lambda_{\vec{0}\xi\vec{0}\kappa} = \Lambda_{\vec{R}\xi\vec{R}\kappa}$ for all lattice vectors \vec{R} and orbital indices ξ, κ . This symmetry, however, will be broken again in the next paragraph. Minimizing \mathcal{L} leads to orthonormal spin orbitals in each unit cell. However, by this simplification of Eq. (6), one does not enforce the mutual intercell orthogonality of the orbitals. Starting from a properly orthonormalized initial guess for the Wannier orbitals in the origin cell may lead to overlapping orbitals.

In order to nonetheless achieve orthogonality of the occupied orbitals in the origin cell to all other orbitals, i.e., their periodic images in all the other unit cells, I modify the energy functional \mathcal{L} in Eq. (8) once more by adding an artificial orthogonalizing potential,

$$\mathcal{L}'[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)] = \mathcal{L}[\Phi_0^N(\vec{r}_1 s_1, \dots, \vec{r}_N s_N)] + V_{\text{Orth}}, \quad (9)$$

which is defined by

$$V_{\text{Orth}} = \frac{\lambda}{2} \sum_{\substack{\vec{R}, \vec{R}' \\ \vec{R} \neq \vec{R}'}} \sum_{\kappa, \xi=1}^{N'} \langle w_{\vec{R}\kappa} | w_{\vec{R}'\xi} \rangle \langle w_{\vec{R}'\xi} | w_{\vec{R}\kappa} \rangle, \quad (10)$$

where $\lambda > 0$ is called the orthogonalizing potential strength or shift parameter. All terms in definition (10) are real and non-negative, causing an increase of energy proportional to

the square of the modulus of the overlap between a pair of orbitals in different unit cells \vec{R} and \vec{R}' . Minimizing \mathcal{L}' , in the limit $\lambda \rightarrow \infty$, both preserves the orthogonality among the Wannier orbitals in all cells of the crystal and minimizes the Hartree-Fock energy functional E in Eq. (5). It has been shown in practical computations that a finite orthogonalization potential strength λ in the range of 10^3 – 10^5 hartrees causes the resulting Hartree-Fock energies not to show a noticeable dependence on λ .²⁶

Expression (10) can be rewritten compactly by recognizing that the orbitals within a particular unit cell are orthonormal by construction (8). Therefore, the constraint $\vec{R}\kappa \neq \vec{R}'\xi$ can be used instead for the summation in Eq. (10). Consequently, the potential V_{Orth} can be expressed in terms of the off-diagonal elements of the overlap matrix between the orbitals,

$$\mathfrak{S}_{\vec{R}\kappa\vec{R}'\xi} = (1 - \delta_{\vec{R}\vec{R}'}\delta_{\kappa\xi})\langle w_{\vec{R}\kappa} | w_{\vec{R}'\xi} \rangle. \quad (11)$$

By taking the trace of \mathfrak{S}^2 , I arrive at

$$V_{\text{Orth}} = \frac{\lambda}{2} \text{Tr} \mathfrak{S}^2, \quad (12)$$

which is an alternate form for Eq. (10).

To minimize the functional \mathcal{L}' in Eq. (9), I carry out functional variation with respect to the N' occupied orbitals in unit cell \vec{R} ;⁴⁴ I arrive at modified Hartree-Fock equations

$$(\hat{f} + \lambda \hat{\mathcal{P}}_{\vec{R}}) | w_{\vec{R}\kappa} \rangle = \sum_{\xi=1}^{N'} \Lambda_{\vec{R}\xi\vec{R}\kappa} | w_{\vec{R}\xi} \rangle, \quad (13)$$

which I term *Wannier-Hartree-Fock equations*. The penalty projection operator⁴⁵ therein is defined by

$$\hat{\mathcal{P}}_{\vec{R}} = \sum_{\vec{R}' \neq \vec{R}} \sum_{\xi=1}^{N'} | w_{\vec{R}'\xi} \rangle \langle w_{\vec{R}'\xi} |. \quad (14)$$

It is not translationally symmetric; instead, the relation $\hat{T}_{\vec{g}} \hat{\mathcal{P}}_{\vec{R}} = \hat{\mathcal{P}}_{\vec{R}-\vec{g}}$ holds. This property of the projector $\hat{\mathcal{P}}_{\vec{R}}$ distinguishes the Wannier orbitals in unit cell \vec{R} in the Wannier-Hartree-Fock equations (13) from their periodic images in other unit cells because it breaks the translational symmetry of the Fock operator \hat{f} .

The translational relation of the Wannier function (1) implies that it is sufficient to formulate and solve Eq. (13) only in the origin cell. For orthogonal orbitals, the Lagrangian multipliers $\Lambda_{\vec{0}\kappa\vec{0}\xi}$ constitute a Hermitian matrix,^{32,33} which is diagonalizable by a unitary transformation $X^\dagger \Lambda X = \epsilon$. Both \hat{f} and $\hat{\mathcal{P}}_{\vec{0}}$ are invariant under such a transformation which mixes the orbitals within every unit cell including, particularly, the origin cell. Therefore, I formally get a Hermitian $N' \times N'$ eigenvalue problem

$$(\hat{f} + \lambda \hat{\mathcal{P}}_{\vec{0}}) | \check{w}_{\vec{0}\kappa} \rangle = \epsilon_{\vec{0}\kappa} | \check{w}_{\vec{0}\kappa} \rangle, \quad (15)$$

which resembles the canonical Hartree-Fock equations^{31–35} and is thus named pseudocanonical Wannier-Hartree-Fock equations. The transformation of the orbitals is indicated by

affixing a check accent. They are referred to as pseudocanonical Wannier orbitals. Due to the fact that these orbitals diagonalize the Fock matrix in the origin cell, they are uniquely determined, apart from degeneracies, in analogy to canonical orbitals.^{32,33} Once a self-consistent solution of Eq. (15) has been found, the parametrical dependence on λ of the orbitals and eigenvalues therein vanishes because they are equal to the orthonormal orbitals from the previous iteration that have been used to construct \hat{f} and $\hat{\mathcal{P}}_{\vec{0}}$ to begin with.

The pseudocanonical Wannier orbitals are delocalized over the entire origin cell and thus implicate a similar disadvantageous nonlocality associated with Bloch orbitals when applying cutoff criteria to the Fock matrix and to the two-electron integrals.^{14,15,17} However, this form of the Wannier-Hartree-Fock equations is a good starting point for further improvements by means of an additional localizing potential that can be introduced in the expression for \mathcal{L}' in Eq. (9). Established forms of localizing potentials are the one of Edmiston and Ruedenberg²² for their localization criterion and the one of Gilbert³⁶ for the Foster-Boys criterion.^{19–21}

The functional dependence of $\hat{f} + \lambda \hat{\mathcal{P}}_{\vec{0}}$ on the occupied Wannier orbitals can be disregarded.^{32,33} Then, the Fock operator becomes a conventional Hermitian operator and the restriction of the penalty projection operator, to act only on occupied orbitals, can be released, i.e., N' in Eq. (14) is replaced by the total number of orbitals per unit cell K . Now, Eq. (15) holds also for virtual Wannier orbitals.

C. Wannier-Roothaan-Hall equations

Spin Wannier orbitals have been employed so far. Let me assume a restricted, closed-shell Hartree-Fock point of view to remove the spin dependence.^{32,33} In this case, the spin orbitals are expressed as the product of a spatial orbital $\tilde{w}_{\vec{R}\varrho}(\vec{r})$ with the spinor for spin up $\alpha(s)$ and spin down $\beta(s)$, respectively. The spatial orbitals, $\tilde{w}_{\vec{R}\varrho}(\vec{r})$, $\varrho = 1, \dots, K$, are expanded in terms of one-particle basis functions,^{7,24} $\chi_\mu(\vec{r})$, $\mu = 1, \dots, K$,

$$\begin{aligned} \tilde{w}_{\vec{R}\varrho}(\vec{r}) &= \hat{T}_{\vec{R}} \sum_{\vec{g}} \sum_{\mu=1}^K C_{\vec{g}\mu\vec{0}\varrho} \hat{T}_{\vec{g}+\vec{d}_\mu} \chi_\mu(\vec{r}) \\ &= \sum_{\vec{g}} \sum_{\mu=1}^K C_{\vec{g}+\vec{R}\mu\vec{R}\varrho} \chi_\mu(\vec{r} - \vec{d}_\mu - \vec{g} - \vec{R}). \end{aligned} \quad (16)$$

The number of basis functions K determines the number of orbitals per unit cell. In Eq. (16), I exploit the fact that both the spatial Wannier orbitals and the basis functions $\hat{T}_{\vec{g}+\vec{d}_\mu} \chi_\mu(\vec{r})$ form sets of functions whose members are related by lattice translations (1). The expansion coefficients, hence, are translationally symmetric $C_{\vec{g}+\vec{R}\mu\vec{R}\varrho} = C_{\vec{g}\mu\vec{0}\varrho} \equiv C_{\mu\varrho}(\vec{g})$. The displacement \vec{d}_μ of the μ th basis function in a unit cell accounts for the fact that a basis function is frequently centered on atoms which, in turn, are displaced somewhat from the origin of the unit cell.

The basis-set representation of the Fock operator \hat{f} is $F_{\vec{g}\mu\vec{g}'\nu} = \langle \chi_{\vec{g}\mu} | \hat{f} | \chi_{\vec{g}'\nu} \rangle$, the overlap matrix is $S_{\vec{g}\mu\vec{g}'\nu}$

$=\langle\chi_{\vec{g}\mu}|\chi_{\vec{g}'\nu}\rangle$, and the matrix of the penalty projection operator (14)—with N' replaced by K —reads²⁴

$$\begin{aligned} (\mathcal{P}_{\vec{R}})_{\vec{g}\mu\vec{g}'\nu} &= \langle\chi_{\vec{g}\mu}|\hat{\mathcal{P}}_{\vec{R}}|\chi_{\vec{g}'\nu}\rangle \\ &= \sum_{\substack{\vec{R}',\vec{g}_1,\vec{g}_2 \\ \vec{R}'\neq\vec{R}}} \sum_{\kappa,\xi,\varrho=1}^K S_{\vec{g}\mu\vec{g}_1\kappa} C_{\vec{g}_1\kappa\vec{R}'\varrho} C_{\vec{g}_2\xi\vec{R}'\varrho}^* S_{\vec{g}'\nu\vec{g}_2\xi}^*. \end{aligned} \quad (17)$$

Representing Eq. (15) in the basis set, I obtain modified Roothaan-Hall equations²⁴

$$(\mathbf{F} + \lambda\mathcal{P}_{\vec{0}})\vec{C}_{\varrho} = \varepsilon_{\vec{0}\varrho}\mathbf{S}\vec{C}_{\varrho} \quad (18)$$

to which I refer as Wannier-Roothaan-Hall equations. Formula (18) yields the occupied and virtual Wannier orbitals in the origin cell $\tilde{w}_{\vec{0}\varrho}(\vec{r})$ with $\varrho=1,\dots,K$ and expansion coefficients $(\vec{C}_{\varrho})_{\vec{g}\mu} \equiv C_{\vec{g}\mu\vec{0}\varrho}$ for all KN_0 indices $\vec{g}\mu$. In expression (18), the coupling of the Wannier orbitals in the origin cell to the Wannier orbitals in neighboring unit cells reappears by means of the basis-set representation (16) which could be avoided by omitting the Lagrangian multipliers in Eq. (8). Consequently, the dimension of the matrices in Eq. (18) scales both with the number of basis functions in the origin cell and with the number of unit cells utilized to support the Wannier orbitals. Note that only a subset of K eigenvectors out of the KN_0 eigenvectors of Eq. (18) is required. The Wannier orbitals in other but the origin cell are simply given by lattice translations (1), exploiting that the expansion coefficients $C_{\mu\varrho}(\vec{g})$ are translationally symmetric. Therewith, all Wannier orbitals of the crystal are determined. The energy bands are not given by the $\varepsilon_{\vec{0}\varrho}$ in Eq. (18). Instead, they are found by diagonalizing the Hermitian matrix $\mathbf{F}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \mathbf{F}_{\vec{0}\vec{R}}$ for a number of \vec{k} points, where $(\mathbf{F}_{\vec{0}\vec{R}})_{\sigma\varrho} = \langle w_{\vec{0}\sigma} | \hat{f} | w_{\vec{R}\varrho} \rangle$ are blocks of the Fock matrix in Wannier representation.

The solution of the Wannier-Roothaan-Hall equations (18) has been implemented in the WANNIER program^{24,25} and its accuracy was tested in a series of studies. Systematic comparisons were made of ground-state properties and band structures of crystals^{25,27} and infinite chains.²⁸ The basis-set expansion (16) is found to provide a satisfactory accuracy using up to third-nearest-neighbor cells for ionic three-dimensional crystals^{14,15,24-27} as well as covalently bonded and hydrogen-bonded infinite chains.^{13,14,16,17,28} Note, however, that despite the fact that variation of the expansion coefficients in Eq. (16) is allowed only in a small cluster of unit cells, a sophisticated treatment of the very long range electrostatic interactions in the Fock operator is required, accounting for a large number of unit cells. Therefore, one uses the Ewald summation technique for the Coulomb matrix elements and an extended summation for the exchange matrix elements.²⁵ The occupied pseudocanonical *a priori* Wannier orbitals are found to reach a few angstroms from the atom they are centered on.^{25,26}

III. PROPERTIES

A. Relation to canonical Hartree-Fock equations

The connection of the Wannier-Hartree-Fock equations (15) to the corresponding equations of a Bloch-orbital-based formalism—the canonical Hartree-Fock equations^{32,33}—can be achieved readily. To this end, the orthogonalizing potential (12) is replaced by an expression which comprises the full overlap matrix, i.e., $\frac{\lambda}{2}\text{Tr}\mathbf{S}^2$. As the Wannier functions are normalized to unity, one obtains $\text{Tr}\mathbf{S}^2 = \text{Tr}\mathbf{S}^2 + KN_0$. This amounts to a meaningless overall energetic shift of \mathcal{L}' in Eq. (9) upon replacing V_{Orth} . Functional variation of the new \mathcal{L}' yields that the summation in the penalty projector of Eqs. (14) and (17) is no longer restricted to the unit cells in the neighborhood but also contains the origin cell, i.e., the operator $\sum_{\vec{R}'\neq\vec{R}}$ is exchanged by $\sum_{\vec{R}'}$. The new projector $\hat{\mathcal{P}}$ becomes translationally symmetric and actually the identity operator $\hat{1}$. This transformation of the Hartree-Fock equations is equivalent to the addition of $\sum_{\xi=1}^{N'} |w_{R\xi}\rangle\langle w_{R\xi}|$ on both sides of Eq. (13), which causes the eigenvalues $\varepsilon_{\vec{0}\kappa}$ [cf. Eq. (15)] to shift by λ , i.e., they become $\varepsilon_{\vec{0}\kappa} + \lambda$. The modification undoes the orthogonalizing potential and reverts the equations to the modified Hartree-Fock equations which result from Eq. (8) with its eigenvalues shifted by λ . Expression (7) is obtained again by realizing that the matrix representation of $\hat{f} + \lambda\hat{\mathcal{P}}$ in terms of Wannier orbitals also contains off-diagonal terms with respect to the lattice vectors, thus reintroducing off-diagonal Lagrangian multipliers.

The arguments of the previous paragraph can be expressed more clearly by changing the Wannier-Roothaan-Hall equations (18) because their dimensionality and formal structure are preserved under the replacement of the projector. Due to the translational symmetry of $\hat{f} + \lambda\hat{\mathcal{P}}$, Born-von Kármán boundary conditions become beneficial.^{3,4} With the matrix representation of $\hat{\mathcal{P}} = \hat{1}$, which is $\mathcal{P} = \mathbf{S}$, the modified Roothaan-Hall equations (18) are changed to¹⁴

$$(\mathbf{F} + \lambda\mathcal{P})\mathbf{C}' = \mathbf{S}\mathbf{C}'\boldsymbol{\varepsilon}'. \quad (19)$$

The $N_0K \times N_0K$ matrices \mathbf{F} , \mathbf{S} , and \mathcal{P} are cyclic matrices which can be block diagonalized employing the unitary transformation^{31,37} $\mathcal{W}_{R\varrho\vec{k}p} = \frac{1}{\sqrt{N_0}}\delta_{\varrho p}e^{i\vec{k}\vec{R}}$. Multiplying with \mathcal{W}^\dagger from the left and inserting $\mathcal{W}\mathcal{W}^\dagger$ before \mathbf{C}' , the eigenvalue problem (19) breaks down into N_0 independent $K \times K$ eigenvalue problems,

$$[\mathbf{F}(\vec{k}) + \lambda\mathcal{P}(\vec{k})]\mathbf{C}'(\vec{k}) = \mathbf{S}(\vec{k})\mathbf{C}'(\vec{k})\boldsymbol{\varepsilon}'(\vec{k}). \quad (20)$$

Solving these equations yields orthonormal Bloch orbitals and energy bands which are shifted by λ .

B. Computational efficiency

To compare the computational effort of the canonical Hartree-Fock method to the modified Hartree-Fock method, I analyze the corresponding Roothaan-Hall equations, Eqs. (20) and (18), respectively. Without regarding space group symmetry, both sets of equations have the same dimensionality because the number of orbitals (or basis functions) is

the same, namely, KN_0 . The effort to compute the matrix elements is clearly the same for the basis-set overlap matrix; it is also equal for the Fock matrix because the Fock operator is invariant under unitary transformations of the orbitals. The support of the basis-set expansion is the same for Bloch and Wannier orbitals: the basis functions in the parallelepiped of N_0 unit cells. Only the expansion coefficients differ. Consequently, the number of floating point operations necessary to determine the Fock operator is the same, if no further approximations are made. Yet the projection operator, which is only required for the modified Hartree-Fock equations, requires an extra effort.

In a next step, the modified and canonical Roothaan-Hall equations need to be diagonalized. In both cases, a full diagonalization requires the same effort. However, in practice a selective computation is carried out. The canonical equations are block diagonalized first, Eq. (20), and the subblocks are independently diagonalized fully afterwards for a grid of \vec{k} points.³⁸ The Wannier-Roothaan-Hall equations have to be treated differently. The spectrum of $F + \lambda \mathcal{P}_0^\dagger$ in Eq. (18) has a very favorable property: the lower K eigenvalues correspond to the Wannier orbitals in the origin cell. The other eigenvalues are well separated from the former ones because they are shifted to high values by the shift parameter λ .²⁵ Iterative eigenvalue solvers, particularly the one of Davidson,³⁹ can be employed to reduce the numerical effort to determine the lowest K eigenpairs of $F + \lambda \mathcal{P}_0^\dagger$. Their effort is predominantly determined by the matrix times vector product. As the summation expression for this product and the summations for the block diagonalization and subsequent \vec{k} space integration are similar, the overall computational effort of both methods, to determine crystal orbitals with a certain accuracy, should be comparable. In fact, the Bloch-orbital-based equations can be solved more efficiently for crystals with a small number of atoms per unit cell; the solution of the Wannier-orbital-based equations is more efficient for crystals with a large unit cell because cutoff criteria can be established to lower the actual effort.

IV. CONCLUSION

In this paper, I derive modified Hartree-Fock equations, which directly yield Wannier orbitals. An orthogonalizing potential is added to the Hartree-Fock energy functional to ensure the proper orthonormality of the resulting orbitals. It

serves to replace the Lagrangian multipliers between unit cells needed otherwise. The equations necessarily break the translational symmetry as Wannier functions are translationally related, in contrast to Bloch functions which are translationally symmetric. I show how the conventional Bloch-orbital-based Hartree-Fock equations can be recovered by restoring the translational symmetry of the modified equations. Analyzing the spectral properties of the modified Fock matrix, I find the numerical effort of the method to be comparable to the effort of the Bloch-orbital-based approach.

The orbitals which result from the modified Hartree-Fock equations are referred to as pseudocanonical Wannier functions as they are delocalized over the entire unit cell. However, they can be localized additionally within unit cells by adding a suitable localizing potential to the energy expression. Particularly, the potential of Gilbert³⁶ is to be mentioned here, which minimizes the Foster-Boys functional.¹⁹⁻²¹ It thus offers a different route to Refs. 6 and 7 to determine maximally localized Wannier functions. Alternatively, the potential of Edmiston and Ruedenberg can be used as a localizing potential.²²

This study is based on the Hartree-Fock theory. However, the extension of the ideas to density-functional theory⁴⁰⁻⁴² is straightforward. To this end, one exchanges the Hartree-Fock energy functional (5) by the Hohenberg-Kohn energy functional in terms of the Kohn-Sham orbitals.^{41,42} The Hohenberg-Kohn variational theorem^{40,42} ensures that minimizing this functional with respect to the orbitals provides the exact ground-state energy, if one uses the exact exchange-correlation energy functional. The minimization is carried out under the constraint that the orbitals remain orthonormal using Eq. (6). In other words, we can essentially follow the line of argument that leads from Eq. (5) to Eq. (15). I term the latter equation—with the Fock operator replaced by the Kohn-Sham operator—pseudocanonical Wannier-Kohn-Sham equations. All subsequent arguments and expressions carry over analogously.

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- ⁴⁵Note that Eq. (14) only describes a projection operator for orthonormal orbitals $w_{R'\xi}(\vec{r}_s)$.