

Theory of generalized Wannier functions for nearly periodic potentials

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There is a great interest in the properties of electrons in nanostructures with superposed potentials varying slowly in space, or with slowly graded composition, or both. The quantum mechanics of these electrons, moving in *nearly periodic potentials*, is conveniently described in a basis of localized generalized Wannier functions, similar to the conventional Wannier functions for strictly periodic potentials. This has led us to consider generalized Wannier functions for (i) weakly perturbed and (ii) compositionally graded crystals. We first construct generalized Wannier functions for uniform crystals with an everywhere weak perturbation. The corrections to an unperturbed Wannier function of a given band may be chosen to involve only the unperturbed Wannier functions from other bands. We then consider crystals with slowly varying composition, and construct generalized Wannier functions from the Wannier functions of uniform crystals.

I. INTRODUCTION

In contemporary nanostructures, electrons frequently move in crystals with superposed potentials varying slowly in space (for example, from gates), or with slowly graded composition c (for example, $\text{Al}_{c(r)}\text{Ga}_{1-c(r)}\text{As}$), or both. The quantum mechanics of these electrons, moving in *nearly periodic potentials*, is conveniently described in a basis of localized generalized Wannier functions, similar to the conventional Wannier functions for strictly periodic potentials. In this note, we show how to construct generalized Wannier functions for nearly periodic potentials. In a separate publication,¹ we have used these generalized Wannier functions to construct an effective Hamiltonian for electrons in compositionally graded crystals.

In a uniform crystal, the Wannier functions of a given energy band are related to the Bloch functions of the same band by a unitary transformation, and thus they span the same Hilbert space. The idea of a generalized Wannier function basis was introduced by Kohn and Onffroy² to extend the Wannier function concept to nonperiodic potentials. In nearly periodic potentials, where the concept of a band is still meaningful, the generalized Wannier functions $|a_{n\nu l}\rangle$ for a given perturbed band may be defined as any orthonormal and band-diagonal set of localized functions spanning the Hilbert space of the perturbed band:

$$\langle a_{n\nu l} | a_{n'\nu' l'} \rangle = \delta_{nn'} \delta_{\nu\nu'} \delta_{ll'} \quad (1.1)$$

$$\langle a_{n\nu l} | H | a_{n'\nu' l'} \rangle = \langle a_{n\nu l} | H | a_{n\nu' l'} \rangle \delta_{nn'} \quad (1.2)$$

Here l is a lattice vector about which the generalized Wannier function is localized, n is a band index, and ν labels the branches of the band if it is composite. H is the Hamiltonian for an electron in the nearly periodic potential. Like Wannier functions for uniform crystals, generalized Wannier functions are not unique. Generalized Wannier functions have been constructed for a one-dimensional lattice with a point defect² and for a one-dimensional lattice with a surface.³ Recently, the ex-

istence of exponentially localized generalized Wannier functions has been proven for a large class of nonperiodic three-dimensional potentials.⁴ Generalized Wannier functions have also been used recently in a new formulation of density functional theory.⁵

In this note, generalized Wannier functions are constructed for simple and composite bands in three-dimensional nearly periodic potentials. We consider two types of nearly periodic potentials, the first type arising from a uniform crystal in a weak applied potential, and the second from a crystal with a slowly graded composition. Our analysis is restricted to monatomic Bravais lattices $l = \sum_{\alpha=1}^3 l_{\alpha} \mathbf{b}^{\alpha}$, where the \mathbf{b}^{α} are the three smallest primitive lattice vectors, the lattice constants assumed to be the same throughout the crystal.

We first review some properties of Wannier functions associated with uniform crystals.⁶⁻¹⁰ Let H_0 be the Hamiltonian for an electron in a uniform crystal, and let $|\varphi_{n\nu\mathbf{k}}\rangle$ be the corresponding normalized Bloch states: $H_0|\varphi_{n\nu\mathbf{k}}\rangle = E_n^{\nu}(\mathbf{k})|\varphi_{n\nu\mathbf{k}}\rangle$. Then we define the Wannier functions for a simple band as

$$|a_{nl}^0\rangle \equiv v^{-(1/2)} \int_{\text{BZ}} d^3k e^{-i\mathbf{k}\cdot\mathbf{l}} A_n(\mathbf{k}) |\varphi_{n\mathbf{k}}\rangle, \quad (1.3)$$

where v is the volume of a Brillouin zone (BZ) and $A_n(\mathbf{k})$ is a pure phase [$|A_n(\mathbf{k})|=1$]. The arbitrary phase for each Bloch function has been made explicit by including the factor $A_n(\mathbf{k})$, and by requiring each Bloch function to satisfy some phase-fixing condition, for example, $\varphi_{n\mathbf{k}}(0) = \text{real and positive}$. The Wannier functions are not unique—each choice of $A_n(\mathbf{k})$ corresponds to a different set, which may or may not be exponentially localized. For a simple band with s -like symmetry, there does exist a unique $A_n(\mathbf{k})$ yielding Wannier functions that are real, symmetric, and exponentially localized.¹⁰ While the Wannier functions are in general complex, the matrix elements of the Hamiltonian are real and are independent of the phases of the Bloch functions:

$$\begin{aligned} \langle a_{nl}^0 | H_0 | a_{n'l'}^0 \rangle &= \int d^3r a_n^*(\mathbf{r}-l) H_0 a_n(\mathbf{r}-l') \\ &= \frac{1}{v} \int d^3k E_n(\mathbf{k}) e^{i\mathbf{k}\cdot(l-l')}, \end{aligned}$$

which are real since $E_n(\mathbf{k}) = E_n(-\mathbf{k})$.

The Wannier functions for a composite band are defined as

$$|a_{nvl}^0\rangle \equiv v^{-(1/2)} \sum_{\nu'} \int_{\text{BZ}} d^3k e^{-i\mathbf{k}\cdot l} A_n^{\nu\nu'}(\mathbf{k}) |\varphi_{n\nu\mathbf{k}}\rangle, \quad (1.4)$$

where $A_n^{\nu\nu'}(\mathbf{k})$ is a matrix (in branch indices) satisfying

$$A_n(\mathbf{k}) A_n^\dagger(\mathbf{k}) = I. \quad (1.5)$$

Here I is the identity matrix. The condition (1.5) follows from the requirement of unitarity,

$$(1/v) \int d^3k A_n(\mathbf{k}) A_n^\dagger(\mathbf{k}) = I \delta_{nn'},$$

and the requirement that $\langle \mathbf{r}+l | a_{nvl}^0 \rangle = \langle \mathbf{r} | a_{n\nu 0}^0 \rangle$ for all l . In each unit cell of the (monatomic) crystal, there is one Wannier function for each branch of each band. Any $A_n^{\nu\nu'}(\mathbf{k})$ satisfying (1.5) will yield a complete set of band-diagonal orthonormal functions, but the existence of a unique $A_n^{\nu\nu'}(\mathbf{k})$ giving exponentially localized Wannier functions is a more delicate matter.

Once a particular set of Wannier functions is chosen, through the use of the above relations, or variational methods,¹⁰⁻¹² or otherwise, their relation to the Bloch functions is uniquely determined. If (1.4) is used to obtain the Wannier functions then

$$|\varphi_{n\nu\mathbf{k}}\rangle = v^{-(1/2)} \sum_{\nu'} \int A_n^{\nu\nu'}(\mathbf{k}) e^{i\mathbf{k}\cdot l} |a_{n\nu l}^0\rangle. \quad (1.6)$$

More generally, suppose we start with some set of Wannier functions, and write

$$|\varphi_{n\nu\mathbf{k}}\rangle = \sum_{\nu'} \sum_l B_n^{\nu\nu'}(\mathbf{k}) e^{i\mathbf{k}\cdot l} |a_{n\nu l}^0\rangle. \quad (1.7)$$

Then, $\langle a_{n\nu l}^0 | H_0 | \varphi_{n\nu\mathbf{k}}\rangle = E_n^{\nu}(\mathbf{k}) \langle a_{n\nu l}^0 | \varphi_{n\nu\mathbf{k}}\rangle$ yields the eigenvalue problem

$$\sum_{\nu'} \sum_l \langle a_{n\nu l}^0 | H_0 | a_{n\nu' l'}^0 \rangle e^{i\mathbf{k}\cdot(l-l')} B_n^{\nu'\nu''}(\mathbf{k}) = E_n^{\nu}(\mathbf{k}) B_n^{\nu\nu'}(\mathbf{k}), \quad (1.8)$$

which determines both $B_n^{\nu\nu'}(\mathbf{k})$ and $E_n^{\nu}(\mathbf{k})$.

As a final remark, we note that the Wannier functions for a periodic potential are related to a set of orthonormal *wavelets*, the latter drawing recent attention from scientists and engineers.¹³ The set of wavelets obtained by the translation and dilation of a single square-integrable function (the "basic wavelet") forms an orthonormal basis for L^2 . Similarly, the set of Wannier functions for a simple band are obtained by translating a single Wannier function to each unit cell, and the resulting set forms an orthonormal basis for the Hilbert space of the band.

II. GENERALIZED WANNIER FUNCTIONS FOR WEAKLY PERTURBED CRYSTALS

We now construct a set of generalized Wannier functions for a *uniform* crystal with an everywhere weak per-

turbation. Let the Hamiltonian be $H = H_0 + \lambda H_1$, where H_0 is periodic and $\lambda \ll 1$. We may construct these generalized Wannier functions in two steps. First choose a complete set of band-diagonal functions. Then make a unitary transformation to localized functions. We show how to construct the generalized Wannier functions to order λ .

Step 1. Choose a complete set of band-diagonal basis functions for the perturbed Hamiltonian $H = H_0 + \lambda H_1$. The perturbed eigenfunctions $|\varphi_{n\nu\mathbf{k}}^1\rangle$ given by first-order perturbation theory are an obvious choice:

$$|\varphi_{n\nu\mathbf{k}}^1\rangle = |\varphi_{n\nu\mathbf{k}}\rangle + \lambda \sum_{n'\nu'} \frac{\langle \varphi_{n'\nu'\mathbf{k}} | H_1 | \varphi_{n\nu\mathbf{k}} \rangle}{E_n^{\nu}(\mathbf{k}) - E_{n'}^{\nu'}(\mathbf{k}')} |\varphi_{n'\nu'\mathbf{k}}\rangle, \quad (2.1)$$

where the primed summation excludes $n\nu\mathbf{k}$ and any Bloch states degenerate with $|\varphi_{n\nu\mathbf{k}}\rangle$. The perturbed states $|\varphi_{n\nu\mathbf{k}}^1\rangle$ are obviously band diagonal, in fact completely diagonal, to order λ . However, equally sufficient is the simpler choice,

$$\begin{aligned} |\psi_{n\nu\mathbf{k}}\rangle &\equiv |\varphi_{n\nu\mathbf{k}}\rangle \\ &+ \lambda \sum_{n' \neq n} \sum_{\nu'} \int d^3k' \frac{\langle \varphi_{n'\nu'\mathbf{k}'} | H_1 | \varphi_{n\nu\mathbf{k}} \rangle}{E_n^{\nu}(\mathbf{k}) - E_{n'}^{\nu'}(\mathbf{k}')} |\varphi_{n'\nu'\mathbf{k}'}\rangle. \end{aligned} \quad (2.2)$$

That is, as far as the completeness and band-diagonality properties are concerned, we may eliminate the intraband contribution in the order λ term of (2.1), since the n th band has already been spanned by the first term. We have now obtained a basis of band-diagonal functions to order λ . The $|\psi\rangle$ basis is not exactly complete; if U denotes the transformation from the Bloch basis to the $|\psi\rangle$ basis, then $U^\dagger U = I + O(\lambda^2)$.

Step 2. Make a unitary transformation to localized functions. Motivated by the relation (1.4) between the Bloch functions and the Wannier functions for a *uniform* crystal, we define

$$|a_{n\nu l}\rangle \equiv v^{-(1/2)} \sum_{\nu'} \int d^3k e^{-i\mathbf{k}\cdot l} A_n^{\nu\nu'}(\mathbf{k}) |\psi_{n\nu\mathbf{k}}\rangle, \quad (2.3)$$

where the $A_n^{\nu\nu'}(\mathbf{k})$ are the same coefficients used to define the unperturbed Wannier functions $|a_{n\nu l}^0\rangle$. Then,

$$|a_{n\nu l}\rangle = |a_{n\nu l}^0\rangle + \lambda \sum_{n' \neq n} \sum_{\nu'} \int d^3k C_l^{n\nu\nu'}(\mathbf{k}) |\varphi_{n'\nu'\mathbf{k}}\rangle, \quad (2.4)$$

where

$$\begin{aligned} C_l^{n\nu\nu'}(\mathbf{k}) &\equiv v^{-(1/2)} \sum_{\nu''} \int d^3k' e^{-i\mathbf{k}'\cdot l} A_n^{\nu\nu''}(\mathbf{k}') \\ &\times \frac{\langle \varphi_{n'\nu'\mathbf{k}} | H_1 | \varphi_{n\nu\mathbf{k}} \rangle}{E_n^{\nu'}(\mathbf{k}') - E_n^{\nu}(\mathbf{k})}. \end{aligned} \quad (2.5)$$

It is simple to verify that these generalized Wannier functions are orthonormal to order λ :

$$\langle a_{n\nu l} | a_{n'\nu' l'} \rangle = \delta_{nn'} \delta_{\nu\nu'} \delta_{ll'} + O(\lambda^2).$$

Furthermore, the generalized Wannier functions will be exponentially localized provided the quantity

$$F_{nn'}^v(\mathbf{k}, \mathbf{k}', \mathbf{r}) \equiv \sum_{v''} A_n^{vv''}(\mathbf{k}') \frac{\langle \varphi_{n'v''\mathbf{k}'} | H_1 | \varphi_{nv''\mathbf{k}} \rangle}{E_n^{v''}(\mathbf{k}') - E_n^{v''}(\mathbf{k})} \varphi_{nv''\mathbf{k}}(\mathbf{r}), \quad (2.6)$$

which is periodic in \mathbf{k} and \mathbf{k}' , is analytic in \mathbf{k} and \mathbf{k}' . We believe that the *branch summations*, which makes F a single-valued function of \mathbf{k} and \mathbf{k}' throughout any Brillouin zone (unlike, for example, $\varphi_{n\mathbf{k}}$), also makes F ana-

$$D_{ll'}^{nvn''v'} \equiv v^{-(1/2)} \sum_{v''} \int d^3k e^{i\mathbf{k}\cdot\mathbf{l}'} C_l^{nvn''v''}(\mathbf{k}) [A_n^\dagger(\mathbf{k})]^{v''v'} \\ = \frac{1}{v} \sum_{v''} \int d^3k d^3k' e^{i(\mathbf{k}\cdot\mathbf{l}' - \mathbf{k}'\cdot\mathbf{l})} A_n^{v''v''}(\mathbf{k}') [A_n^\dagger(\mathbf{k})]^{v''v'} \frac{\langle \varphi_{n'v''\mathbf{k}'} | H_1 | \varphi_{nv''\mathbf{k}} \rangle}{E_n^{v''}(\mathbf{k}') - E_n^{v''}(\mathbf{k})} \quad (2.8)$$

The generalized Wannier functions (2.4) and (2.7) are valid for an everywhere weak perturbation. Our method may be used to extend these expansions to higher orders in λ as well.

III. GENERALIZED WANNIER FUNCTIONS FOR GRADED CRYSTALS

The results of Sec. II are now used to construct generalized Wannier functions for compositionally graded crystals. Let $c(\mathbf{r})$ characterize the spatially varying composition of the crystal, c defined as an atomic fraction ranging from zero to unity. For example, $c(\mathbf{r})$ might be the local fraction of type A atoms in the graded alloy $A_c B_{1-c}$. We define a dimensionless small parameter $\epsilon(\mathbf{r})$ characterizing the small composition gradients by $b\nabla c = \epsilon \mathbf{n}$, where \mathbf{n} is a unit vector in the direction of the composition gradient and b is the average magnitude of the three \mathbf{b}^α . In this section, we construct a generalized Wannier function basis to order ϵ . The local composition determines the generalized Wannier functions to zeroth order, and the perturbation due to the local composition gradient determines the order ϵ correction.

Let $V(\mathbf{r}, c)$ be the periodic potential in a crystal with uniform composition c . The nearly periodic potential in the graded crystal is taken to be $V[\mathbf{r}, c(\mathbf{r})]$. We assume that the primitive lattice vectors \mathbf{b}^α are independent of c . The perturbation near site l due to a gradient in $c(\mathbf{r})$ is

$$V[\mathbf{r}, c(l) + (\mathbf{r}-l) \cdot \nabla c(l)] - V[\mathbf{r}, c(l)] \\ = \epsilon \frac{\mathbf{n} \cdot (\mathbf{r}-l)}{b} \left[\frac{\partial V(\mathbf{r}, c)}{\partial c} \right]_{c(l)}. \quad (3.1)$$

We write this as a limit of a function that is everywhere finite, and equivalent to (3.1) near $\mathbf{r}=l$. The Hamiltonian near site l may then be written as

$$H = H_0 + \epsilon(l)H_1 + O(\epsilon^2),$$

where

$$H_1(\mathbf{r}) = \lim_{\delta \rightarrow 0} \frac{\sin[\mathbf{n} \cdot (\mathbf{r}-l)b^{-1}\delta]}{\delta} \left[\frac{\partial V(\mathbf{r}, c)}{\partial c} \right]_{c(l)}. \quad (3.2)$$

lytic in the six complex variables $k_x, k_y, k_z, k'_x, k'_y,$ and k'_z for real values of these variables. However, we have no proof of this. (In systems in which there are no singularities of the Bloch waves and energies, such as one-dimensional or low symmetry two-dimensional and three-dimensional periodic lattices, this problem does not arise.)

Equation (1.6) allows (2.4) to be written as

$$|a_{nvl}\rangle = |a_{nvl}^0\rangle + \lambda \sum_{n' \neq n} \sum_{v'} \sum_{l'} D_{ll'}^{nvn''v'} |a_{n'v'l'}^0\rangle, \quad (2.7)$$

where

For finite δ there is no linear divergence as $|\mathbf{r}-l| \rightarrow \infty$. Let $|a_{nvl}^0\rangle$ be a set of Wannier functions for a uniform crystal with composition c . For a crystal with a small composition gradient ϵ , the expansion (2.7) yields

$$|\bar{a}_{nvl}\rangle = |a_{nvl}^0; c(l)\rangle \\ + \epsilon(l) \sum_{n' \neq n} \sum_{v'} \sum_{l'} \Gamma_{ll'}^{nvn''v'}[c(l)] |a_{n'v'l'}^0; c(l)\rangle \\ + O(\epsilon^2), \quad (3.3)$$

where the $\Gamma_{ll'}^{nvn''v'}(c)$ are c -dependent coefficients that follow from (2.8) with the perturbation (3.2):

$$\Gamma_{ll'}^{nvn''v'}(c) \equiv \frac{1}{v} \sum_{v''} \int d^3k d^3k' e^{i(\mathbf{k}\cdot\mathbf{l}' - \mathbf{k}'\cdot\mathbf{l})} A_n^{v''v''}(\mathbf{k}'; c) \\ \times [A_n^\dagger(\mathbf{k}; c)]^{v''v'} \\ \times \frac{\langle \varphi_{n'v''\mathbf{k}'} | H_1 | \varphi_{nv''\mathbf{k}} \rangle}{E_n^{v''}(\mathbf{k}'; c) - E_n^{v''}(\mathbf{k}; c)}. \quad (3.4)$$

Hence, the matrix elements of H_1 are calculated in the local Bloch state basis $|\varphi_{n\mathbf{k}}; c(l)\rangle$, and the energy denominator refers to the local band structure $E_n^v[\mathbf{k}; c(l)]$.

To evaluate the matrix element

$$\langle \varphi_{n\mathbf{k}}; c(l) | H_1 | \varphi_{n'\mathbf{k}'}; c(l) \rangle,$$

note that $(\partial V(\mathbf{r}, c)/\partial c)_c$ is spatially periodic, and therefore may be written as

$$\left[\frac{\partial V(\mathbf{r}, c)}{\partial c} \right]_c = \sum_{\mathbf{K}} L_{\mathbf{K}}(c) e^{i\mathbf{K}\cdot\mathbf{r}}$$

where

$$L_{\mathbf{K}}(c) \equiv \frac{1}{v_r} \int_{v_r} d^3r e^{-i\mathbf{K}\cdot\mathbf{r}} \left[\frac{\partial V(\mathbf{r}, c)}{\partial c} \right]_c.$$

Here \mathbf{K} is a reciprocal lattice vector and v_r is the real space unit-cell volume. Then,

$$\langle \varphi_{n\nu\mathbf{k}}; c(I) | H_1 | \varphi_{n'\nu'\mathbf{k}'}; c(I') \rangle = b^{-1} \sum_{\mathbf{K}} L_{\mathbf{K}}[c(I)] \mathbf{n} \cdot \langle \varphi_{n\nu\mathbf{k}}; c(I) | (\mathbf{r}-I) e^{i\mathbf{K}\cdot\mathbf{r}} | \varphi_{n'\nu'\mathbf{k}'}; c(I') \rangle .$$

The localized functions $|\tilde{a}_{n\nu l}\rangle$ given in (3.3) are not yet orthonormal to order ϵ because the states $|a_{n\nu l}^0; c(I)\rangle$ are *not* orthogonal: $\langle a_{n\nu l}^0; c(I) | a_{n'\nu' l'}^0; c(I') \rangle = O(\epsilon)$ for $l \neq l'$. We orthonormalize the functions (3.3) by the method of Löwdin.¹⁴ Let $|a_{nJ}\rangle = \sum_{J'} M_{JJ'} |\tilde{a}_{nJ'}\rangle$ where $J \equiv \nu l$ is a composite index; we seek the coefficients $M_{JJ'}$ that yield orthonormal $|a_{nJ}\rangle$. The requirement $\langle a_{nJ} | a_{nJ'} \rangle = \delta_{JJ'}$ implies

$$MS^* M^\dagger = I, \quad (3.5)$$

where $S_{JJ'} \equiv \langle \tilde{a}_{nJ} | \tilde{a}_{nJ'} \rangle$ and I is the identity matrix. Since S is equal to I plus off-diagonal terms of order ϵ terms that we want to “remove”, write $S = I + \epsilon S_1$. Then a solution of (3.5) is

$$M = (I + \epsilon S_1^*)^{-1/2} = I - \frac{1}{2} \epsilon S_1^* + O(\epsilon^2),$$

which is Hermitian since S is Hermitian. This yields the generalized Wannier functions

$$\begin{aligned} |a_{n\nu l}\rangle &= |a_{n\nu l}^0; c(I)\rangle \\ &+ \epsilon(I) \sum_{n' \neq n} \sum_{\nu'} \sum_{l'} \Gamma_{ll'}^{n\nu\nu'} [c(I)] |a_{n'\nu' l'}^0; c(I)\rangle \\ &+ \epsilon(I) \sum_{\nu' \neq \nu} \sum_{l' \neq l} \Omega_{ll'}^{n\nu\nu'} |a_{n\nu' l'}^0; c(I)\rangle + O(\epsilon^2), \end{aligned} \quad (3.6)$$

where

$$\epsilon \Omega_{ll'}^{n\nu\nu'} \equiv -\frac{1}{2} \langle a_{n\nu l}^0; c(I) | a_{n\nu' l'}^0; c(I') \rangle .$$

It is straightforward to show that $\langle a_{n\nu l} | a_{n\nu' l'} \rangle = \delta_{\nu\nu'} \delta_{ll'} + O(\epsilon^2)$. This completes our construction of generalized Wannier functions for graded crystals.

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¹M. R. Geller and W. Kohn, Phys. Rev. Lett. **70**, 3103 (1993).

²W. Kohn and J. R. Onffroy, Phys. Rev. B **8**, 2485 (1973).

³J. J. Rehr and W. Kohn, Phys. Rev. B **10**, 448 (1974).

⁴A. Nenciu and G. Nenciu, Phys. Rev. B **47**, 10 112 (1993).

⁵W. Kohn, Chem. Phys. Lett. **208**, 167 (1993).

⁶W. Kohn, Phys. Rev. **115**, 809 (1959).

⁷J. Des Cloizeaux, Phys. Rev. **129**, 554 (1963).

⁸J. Des Cloizeaux, Phys. Rev. **135**, A685 (1964).

⁹J. Des Cloizeaux, Phys. Rev. **135**, A698 (1964).

¹⁰W. Kohn, Phys. Rev. B **7**, 4388 (1973).

¹¹G. F. Koster, Phys. Rev. **89**, 67 (1953).

¹²G. Parzen, Phys. Rev. **89**, 237 (1953).

¹³C. K. Chui, *An Introduction to Wavelets* (Academic, San Diego, 1992).

¹⁴P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).