

Wannier states in order-N electronic-structure method

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Brief introductions of Wannier states and the localized-orbital order-N method are given. The following related topics are also presented; (1) real-space methods toward fully-selfconsistent order-N calculations, (2) locality of 'exact' composite-band Wannier states within tight-binding Hamiltonians.

Introduction

The 'order-N' or 'linear-systemsize-scaling' methods¹⁾ are electronic-structure calculations in which the computational cost is ' $O(N)$ ', or linearly proportional to the system-size N . In conventional schemes, the computational cost should be $O(N^3)$, because of the matrix-diagonalization procedures or the orthogonalization constraints of the wavefunctions. The aim of order-N methods is to calculate large systems, for instance, systems containing some thousands of atoms or more, without such operations. So far many order-N methods have been proposed, and one of them is called 'localized-orbital order-N' (LO-O(N)) method,²⁾ which is based on the locality of Wannier states. Here Wannier states are not the conventional ones,^{3,4)} defined by Wannier, but are generalized concepts, applicable to non-periodic and/or composite-band cases.⁵⁾

Generalized Wannier states and order-N method

In general, Wannier states can be derived, from the variational procedure within a single Slater determinant, as

$$H\psi_k = \sum_{j=1}^N \varepsilon_{kj} \psi_j. \quad (1)$$

Now we restrict the discussions to insulating cases and N is the number of occupied states. H is an effective one-body Hamiltonian. The parameters ε_{ij} are the Lagrange multipliers for the orthogonality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ and satisfy $\varepsilon_{ij} = \langle \psi_i | H | \psi_j \rangle$. The resultant one-electron states $\{\psi_i\}$ has a 'gauge' freedom in the sense that physical quantities are invariant under unitary transforms with respect to occupied states

$$\psi_i \rightarrow \psi'_i \equiv \sum_{j=1}^N U_{ij} \psi_j, \quad (2)$$

where U is a unitary matrix. Wannier states can be defined as localized wavefunctions that satisfy Eq. (1) and the orthogonality constraint. Since Wannier states are *not* eigen states, the Hamiltonian matrix $\varepsilon_{ij} \equiv \langle \psi_i | H | \psi_j \rangle$ is not diagonal and has following properties; (1) the trace gives the correct total energy ($E_{\text{tot}} = \sum_{k=1}^N \varepsilon_{kk}$), (2) the offdiagonal elements are expected to be small when Wannier states are localized in real space and the Hamiltonian is shortrange.

Here we derive the conventional or single-band Wannier states. In periodic systems, eigen states are Bloch states

$\{\psi_{\nu\mathbf{k}}\}$ with the suffices of the band ν and the k-point \mathbf{k} . On the other hands, the single-band Wannier states $W_{\nu\mathbf{l}}(\mathbf{r})$ have the suffices of the same band ν and the lattice vector \mathbf{l} . The corresponding unitary matrix U is $U_{\nu\mathbf{k}\nu'\mathbf{l}} \equiv \delta_{\nu\nu'} \exp(-i\mathbf{k}\cdot\mathbf{l})$. Back to the case with general unitary transformations (2), the resultant one-electron states in Eq. (2) are called 'composite-band' Wannier states, in the sense that the unitary transformations (2) mix eigen states $\{\psi_{\nu\mathbf{k}}\}$ with different band suffices ν .

An actual procedure of solving Eq. (1) under the orthogonal constraint is the LO-O(N) formulation,²⁾ based on a new variational procedure without any explicit orthogonalization procedure. Within tight-binding cases, the energy functional is written by

$$E_{O(N)} \equiv 2 \sum_{ij} A_{ij} \langle \psi_i | H | \psi_j \rangle + 2\mu\Delta N, \quad (3)$$

$$\Delta N \equiv N - \sum_{ij} A_{ij} S_{ij} = \sum_{ij} |S_{ij} - \delta_{ij}|^2. \quad (4)$$

where $S_{ij} \equiv \langle \psi_i | \psi_j \rangle$ and $A_{ij} \equiv 2\delta_{ij} - S_{ji}$ and the parameter η should be chosen as $\eta > \varepsilon_N$. See the original papers²⁾ for the cases of the density functional theory (DFT). Note that (1) the minimization of the energy term $2\eta\Delta N$ means an iterative orthogonalization procedure ($S_{ij} \rightarrow \delta_{ij}$), and, (2) when the orthogonality is satisfied, the energy functional $E_{O(N)}$ is reduced to the physical one $E = \sum_i \langle \psi_i | H | \psi_i \rangle$ and the resultant one-electron equation is reduced to Eq. (1). To obtain localized states, we must prepare proper localized initial states, such as simple bonding orbitals, and the minimization procedure must be done under some localization constraints.

Real-space methods toward fully-selfconsistent order-N calculations

Hereafter we present our works related to the order-N method. First one is the methodology toward DFT cases. Our recent works⁶⁾ present a selfconsistent formulation, applicable to the order-N method, where Wannier states $\{\psi_k\}$ are expanded by some localized, possibly non-orthogonal, basis functions, $\psi_k(\mathbf{r}) = \sum_{\phi} C_{k\phi} \phi(\mathbf{r})$, and both the basis functions $\{\phi(\mathbf{r})\}$ and the coefficients $\{C_{k\phi}\}$ are the variational parameters. If we fix the basis functions, the formulation is reduced to a tight-binding one and if we do not impose any localization constraints, the formulation is mathematically equivalent to the plane-wave calculation.

To treat the basis functions $\{\phi(\mathbf{r})\}$ as variational parameters, we propose a real-space method with finite-differences, where the basis functions are described on a real-space square mesh grid. Within this formalism, we proposed (1) an ‘exact’ finite-difference forms of the kinetic-energy (Laplacian) operator to obtain an exact equivalence to the plane-wave formulation, (2) a ‘preconditioning operator’ as a finite-difference form in real space so as to save the computational cost, (3) a ‘window-function technique’ to obtain localized basis functions $\{\phi(\mathbf{r})\}$ on mesh grid.

Locality of Wannier states

Now we turn to the second topic,⁷⁾ the locality of the Wannier states within tight-binding cases, which corresponds to the locality of the coefficients $C_{k\alpha}$ in the previous section.

In a one-dimensional single-band case, Wannier states decay exponentially with a decay parameter proportional to the square root of the bandgap.⁴⁾ In three-dimensional composite-band cases, however, theories have not been well developed. So we study the locality of Wannier states in such cases, especially what governs their locality. We focus on the Wannier states of the diamond-structure solids, corresponding to the elements of group IV, C, Si, Ge and α -Sn. Within minimal tight-binding Hamiltonians, we presented a tractable and general method of the construction and analysis of the ‘exact’ Wannier states. The resultant Wannier states correspond to the wavefunctions in the LO-O(N) formulation *without localization constraints*. The resultant Wannier states are bond-centered and are analyzed by some conventional perturbation theory of Wannier states. Based on the general tendencies of hopping integrals within the diamond-structure solids, we could conclude that the entire decay property of Wannier states are ‘universal’ or is insensitive to the value of the

bandgap, which is very different from the above single-band case. We also discussed a general theory of the direct relations between the Wannier states and the order-N method. All the results imply that the locality of Wannier states directly depends on Hamiltonians and can be insensitive to the value of the bandgap. In other words, Wannier states are not mere ‘byproducts’ of the order-N method, but are fairly useful for understanding the microscopic mechanism of the condensed matters.

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