Theory of composite-band Wannier states and order-N electronic-structure calculations

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(March 24, 2022)

From the order-N electronic-structure formulation, a Hamiltonian is derived, of which lowest eigen state is the generalized or composite-band Wannier state. This Hamiltonian maps the locality of the Wannier state to that of a virtual impurity state and to a perturbation from a bonding orbital. These theories are demonstrated in the diamond-structure solids, where the Wannier states are constructed by a practical order-N algorithm with the Hamiltonian. The results give a prototypical picture of the Wannier states in covalent-bonded systems.

PACS number: 71.15.-m, 71.20.-b, 71.23.An

Recently, Wannier state (WS) has been re-focused as a foundation of the order-N methods, linear-scaling methods for large-scale electronic-structure calculations. The original concept of WS’s is defined within a single isolated band under the periodic boundary, but now is generalized to systems with composite bands and/or non-periodic boundaries. This letter is devoted to the fundamental theories of WS’s in composite-band systems.

The generalized WS’s can be defined, in insulators, as localized one-electron states that satisfy

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

where \(N\) is the number of occupied states. Equation (1) is derived from a variational procedure within a single Slater determinant. The parameters \(\varepsilon_{ij}\) are the Lagrange multipliers for the orthogonality constraints \(\langle \psi_i | \psi_j \rangle = \delta_{ij}\) and satisfy \(\varepsilon_{ji} = \langle \psi_j | H | \psi_j \rangle\). The above definition does not uniquely determine the wavefunctions. The resultant set of one-electron states \(\{\psi_i\}\) has a ‘gauge’ freedom in the sense that any physical quantity is invariant under the unitary transforms with respect to the occupied states \(\psi_i \rightarrow \psi'_i \equiv \sum_{j=1}^{N} U_{ij} \psi_j\), where \(U\) is a unitary matrix. If this ‘gauge’ is fixed so as to diagonalize the matrix \(\varepsilon_{ij}\), we obtain the set of the eigen states \(\{\psi_k^{(eig)}\}\), or the Bloch states in the periodic boundary; \(H \psi_k^{(eig)} = \varepsilon_k^{(eig)} \psi_k^{(eig)}\), where \(\{\varepsilon_k^{(eig)}\}\) are the eigen energies. With WS’s, the matrix \(\varepsilon_{ij}\) is not diagonal, but its trace gives the correct band-structure energy

$$E_0 \equiv \sum_{k=1}^{N} \varepsilon_k^{(eig)} = \sum_{k=1}^{N} \varepsilon_{kk}. \quad (2)$$

The diamond-structure solids, C, Si, Ge and α-Sn, are typical composite-band systems. For such materials, nearest-neighbor tight-binding (TB) Hamiltonians can be constructed within sp³-hybridized orbitals, where the hopping along a bond is dominant. The corresponding hopping integral is the half of the difference between the energy level of an antibonding orbital \(\varepsilon_a\) and that of a bonding orbital \(\varepsilon_b\); \(\Delta_{ab} \equiv \varepsilon_a - \varepsilon_b\). If all the other hoppings are ignored, the TB Hamiltonian is diagonal with respect to bonding and antibonding orbitals;

$$H_0 = \sum_{k=1}^{N} (|b_k\rangle \varepsilon_b \langle b_k| + |a_k\rangle \varepsilon_a \langle a_k|). \quad (2)$$

Here the \(k\)-th bonding and antibonding orbitals \(|b_k\rangle\), \(|a_k\rangle\) are defined by the pair of sp³ orbitals on the \(k\)-th bond. The WS’s for \(H_0\) are just the bonding orbitals \(|\{b_k\}\rangle\), and this simple picture is the starting point of the present theory. In the present iterative calculations of the WS’s, the bonding orbitals are chosen as the initial states. Since all the bonds are symmetrically equivalent in the diamond structure, the resultant energy levels of the WS’s \(\{\varepsilon_k\}\) have the unique value \(\varepsilon_{WS} \equiv (1/N) \sum_{j=1}^{N} \varepsilon_j^{(eig)}\), which is the weighted center of the valence band.

Another important hopping in the diamond structure is the hopping within an atom, whose energy is one fourth of the energy difference between the atomic p-level (\(\varepsilon_p\)) and the s-level (\(\varepsilon_s\)); \(\Delta_{ps} \equiv \varepsilon_p - \varepsilon_s\). Within the present TB parameterizations, the electronic structures of the diamond-structure solids can be scaled with the unique parameter, \(\alpha_m \equiv \Delta_{ps}/\Delta_{ab}\), called ‘metallicity’ and a system would be metallic, when \(\alpha_m \rightarrow 1\). For classification of group IV elements, some TB parameterizations were picked out and we obtained \(\alpha_m = 0.44\) for C, \(\alpha_m = 0.75\) for Si, and \(\alpha_m = 0.77\) for Ge. In the present numerical demonstrations, we use the nearest-neighbor TB Hamiltonians \(H\) for Si whose parameters are from Ref. \[3\]. Here \(\Delta_{ps}\) is fixed to be 6.45 eV, \(\Delta_{ab}\) and all the other interatomic hoppings are functions of the bond length \(d\). In the equilibrium case \((d = d_0 \equiv 4.44\text{a.u.})\), \(\Delta_{ab} = 8.25\text{eV}\) and \(\alpha_m = 0.78\).

Equation (1) is closely related to the localized-orbital order-N formulation \[2\], where an energy functional \(E_{\Omega(N)} = \sum_{j=1}^{N} (2\delta_{ij} - \langle \psi_j | \psi_i \rangle \langle \psi_i | \Omega | \psi_j \rangle) = \text{Tr}(\langle 2\rho - \rho^2 \rangle \Omega)\) is iteratively minimized. Here \(\Omega \equiv H - \eta\), and \(\rho \equiv \sum_{k=1}^{N} |\psi_k\rangle \langle \psi_k|\), \(\rho\) is the one-body density matrix and the energy parameter \(\eta\) must be chosen to be sufficiently high \((\eta > \varepsilon_N)\). The WS wavefunctions satisfy
Due to the large energy shift of the variational freedom of the WS space of the other WS's is automatically 'excluded' in the eigen states of $H$, from the relation $H_{\text{occ}} \approx (H - H_{\text{occ}}) \psi_k = 0$. This eigen-value problem corresponds to the variational properties; (a) The 'central' WS of $H$ and $H_{\text{WS}}^{(k)}$ is reduced to Eq. (1). (b) The eigen states in the conduction band of $H_{\text{WS}}^{(k)}$ with the same energies $\epsilon_{kk}^{(\text{eig})} = H_{\text{WS}}^{(k)} \psi_i^{(\text{eig})} = H \psi_i^{(\text{eig})} = \epsilon_i^{(\text{eig})} \psi_i^{(\text{eig})}$.

$$ H_{\text{WS}}^{(k)} \psi_k = \epsilon_{kk} \psi_k, \quad (5) $$

where

$$ H_{\text{WS}}^{(k)} \equiv H - \bar{\rho}_k \Omega - \Omega \bar{\rho}_k \quad (6) $$

$$ \bar{\rho}_k = \rho - \psi_k \langle \psi_k | \sum_{j \neq k} N \psi_j \rangle \langle \psi_j | \psi_j \rangle. \quad (7) $$

This eigen-value problem corresponds to the variational procedure of a specified WS ($\psi_k$), while all the other WS's ($\{\psi_j\}_{j \neq k}$) are fixed. If $\bar{\rho}_k \psi_k = 0$ is satisfied, Eq. (5) is reduced to Eq. (1). A WS is not an eigen state of $H$, but an eigen state of $H_{\text{WS}}^{(k)}$. We call the specified state ($\psi_k$) as 'central' WS.

Figure 1 shows the density of state (DOS) of $H$ and $H_{\text{WS}}^{(k)}$ in the Si case ($d = d_0$). We see the following properties; (a) The 'central' WS $|\psi_k\rangle$ is the non-degenerate ground state of $H_{\text{WS}}^{(k)}$ with the eigen value of $\epsilon_{kk} = \epsilon_{\text{WS}}$. (b) The eigen states in the conduction band of $H_{\text{WS}}^{(k)}$ with the same energies $\epsilon_{i\text{eig}} = \epsilon_{j\text{eig}}$, $N + 1 \leq i \leq 2N$, are also the eigen states of $H_{\text{WS}}^{(k)}$.

(c) All the other $(N - 1)$ occupied WS's of $H$ are not eigen states of $H_{\text{WS}}^{(k)}$. They form a high-energy band, located at $\epsilon \geq 2\eta = \epsilon_N \approx 272$ eV. The corresponding DOS profile is $D_{\text{high}}(\epsilon) \approx D_{\text{val}}(2\eta - \epsilon)$, where $D_{\text{val}}(\epsilon)$ is the DOS profile of the valence band of $H$. This property rises from the relation

$$ \langle \psi_i | H_{\text{WS}}^{(k)} | \psi_j \rangle = 2\eta - \langle \psi_i | H_{\text{occ}} | \psi_j \rangle, \quad i, j \neq k. \quad (9) $$

Due to the large energy shift of $D_{\text{high}}(\epsilon)$, the Hilbert space of the other WS's is automatically 'excluded' in the variational freedom of the WS $\psi_k$.

To construct WS's, we used an iterative order-N algorithm with the Hamiltonian $H_{\text{WS}}$. The periodic cell contains 4096 atoms and $N = 8192$ doubly-occupied WS's. For each WS $\psi_k$, the localization center was chosen at the center of the initial bonding orbital $|b_k\rangle$ and each WS was expanded into 614 sp$^3$ orbitals with a spherical cutoff from the localization center. The resultant energy per WS ($\epsilon_{\text{WS}}$) has a deviation of about 0.006 eV (0.1%) from the correct value, where the correct value is obtained by a standard diagonalization method with the primitive cell and many k-points. The actual procedures are followings; (i) With proper initial states of WS's, the density matrix $\rho$ and the Hamiltonians $\{H_{\text{WS}}^{(k)}\}$ are constructed. (ii) For each WS $|\psi_k\rangle$, the one-body energy $\langle \psi_k | H_{\text{WS}}^{(k)} | \psi_k \rangle$ is minimized under the localization constraint on $|\psi_k\rangle$ with the fixed Hamiltonian $H_{\text{WS}}^{(k)}$. (iii) The updated WS's $\{\psi_k\}_k$ are orthogonalized using the Löwdin symmetric orthogonalization $\|\|$. Then the procedure goes back to (i), until converges. Since the present TB Hamiltonians are upper-bounded, WS's can be also defined for the unoccupied or conduction band. The resultant WS's satisfy Eq. (1), where the $N$ one-electron states should be those in the unoccupied band. Such conduction WS's can be formulated within the energy maximization procedure of $E_{\text{WS}}(|\psi_k|)$, where the initial WS's is chosen as the antibonding orbitals $\{|a_k\rangle\}_{k=1,N}$ and the energy parameter $\eta$ is chosen to be enough low.

Figure 2 shows the norm distributions $|C_{kk}|^2$ of some
WS’s, where \( \{ \phi \} \equiv \{ b_k, a_k \} \). Figure 3 contains all the 614 orbitals of the resultant WS’s. The case (a) is the WS with \( d = 0.8d_0 \), whose metallicity \( \alpha_m \) = 0.47 might corresponds to the Carbon case. The case (b) is the equilibrium Si case \( (d = d_0) \). For both cases, the norm distributions on bonding orbitals are very small except the central one, because they are occupied mainly by the other WS’s. The conduction WS’s in the Si case is also plotted in Fig. 2(c), which shows the similar decay property as in the valence WS (b), but the role of bonding and antibonding orbitals exchange with each other. The norm of the central bond is about 96 % in (a) or 94 % in (b) and (c). The summation of the norms upto the bondstep of \( n = 2 \) is about 99.8 or 99.7 % in all the cases.

The most important issue for the practical order-N calculations is to reproduce physical quantities under localization constraints on WS’s. With the exact WS’s \( \{ \psi \} \), the physical quantity of a one-body operator \( \hat{X} \) can be described as \( \langle \hat{X} \rangle \equiv \sum_k \langle \psi_k | \hat{X} | \psi_k \rangle \). In a practical order-N calculation with a localization constraint, the strict orthogonality constraint is modified to an approximate one \( \langle \psi_j | \psi_i \rangle \approx \delta_{ij} \) and the expression of a physical quantity is replaced by \( \langle \hat{X} \rangle = \sum_{i,j} \langle 2\delta_{ij} - \langle \psi_j | \psi_i \rangle \rangle \langle \psi_i | \hat{X} | \psi_j \rangle \), which is mainly contributed by the diagonal elements \( \langle \psi_k | \hat{X} | \psi_k \rangle \). If an operator \( \hat{X} \) is short-ranged, like the present TB Hamiltonian, its matrix element \( \langle \psi_k | \hat{X} | \psi_k \rangle \) should be determined dominantly by a ‘central’ region of WS, but little by the ‘tail’ or the asymptotic long-distance behavior. From this point of view, we analyse the present WS’s through the matrix elements \( \langle \psi_k | \hat{X} | \psi_k \rangle \) of some operators, not through the asymptotic long-distance behavior. Notice that the asymptotic long-distance behavior of WS is discussed in Refs. 1.

If we apply the above discussion to the operator \( (\hat{r} - r_k)^2 \), where \( r_k \) is the center of the central bond \( (|b_k|) \), an effective spatial spread of WS can be defined as \( r_{WS} \equiv (\langle \psi_k | (\hat{r} - r_k)^2 | \psi_k \rangle)^{1/2} \). The values were actually calculated with the assumption that each sp³ orbital is localized at the atom that the orbital belongs to. For a bonding orbital, this parameter is \( r_{\alpha} \equiv d/2 \) from its definition. For the WS in the Si case \( (d = d_0) \), we obtained \( r_{WS} = 1.16 \bar{r}_b \). To see the effect of the boundary condition, we also calculated the system with 512 atoms without localization constraint and found \( r_{WS} = 1.19 \bar{r}_b \). Since the operator \( (\hat{r} - r_k)^2 \) is not short-ranged, the value of \( r_{WS} \) might be sensitive to the boundary conditions.

Another definition of the spatial spread of WS can be derived from the Hamiltonian \( H_{WS}^{(k)} \). The Hamiltonian \( H_{WS}^{(k)} \) has one localized eigen state \( \psi_k \) and the conduction band, and so \( H_{WS}^{(k)} \) maps the WS formally to an impurity state, where the corresponding ionization energy is defined as \( \Delta_{WS} \equiv \varepsilon^{(eig)}_e - \varepsilon_{WS} \). A simplest case is the Hamiltonian in Eq.(3), where the WS’s are reduced to bonding orbitals and the corresponding gap \( \Delta_{WS} \) is to \( \Delta_{ab} \). Using the uncertainty relation, a spatial spread is defined as \( \xi_b \equiv \hbar/\sqrt{2m_e \Delta_{ab}} \), where \( m_e \equiv 1.a.u. \). Using the value in the Si case \( \Delta_{ab} = 8.25 eV \), we obtain \( \xi_b = 0.29d_0 \), which is consistent to the fact that the spread of a bonding orbital should be less than or about equal to the bond length \( d_0 \). Such parameters can be also defined for WS’s as \( \xi_{WS} \equiv \hbar/\sqrt{2m_e \Delta_{WS}} = \xi_b \sqrt{\Delta_{ab}/\Delta_{WS}} \). For the WS in the Si case, we obtained \( \Delta_{WS} = 6.49 eV \) and \( \xi_{WS}/\xi_b = 1.13 \), which agrees, in the order, to the another definition of the spatial spread \( r_{WS}/\bar{r}_b = 1.16 \) or 1.19. This agreement shows that the mapping theory to a virtual impurity state is consistent to the resultant WS’s. The resultant values of the spatial spread lead us to the conclusion that the WS in the Si case is so localized that its spatial spread is in the same order as that of a bonding orbital.

To see a limiting case with vanishing the bandgap, we also calculated an artificial case with \( \Delta_{ps} = 0 \), where the system is a direct-gap insulator and the bandgap \( \Delta = 8E_{xx} \) is located at \( \Gamma \) point \( [2] \). We modified the parameter \( E_{xx} \) from the value in the Si case \( E_{xx} = 0.20 eV \) to an almost vanishing one \( (E_{xx} = 0.0005 eV) \). This modification was done by the tuning of \( V_{ppr} \) and \( V_{pp}, \) so as to keep \( E_{xy} \) unchanged \( [2] \). This modification changes the value of \( \Delta_{ab} \) as well. The resultant WS still shows a localized property with the spatial spread of \( r_{WS}/\bar{r}_b = 1.15 \) or 1.20, where the latter value is from the calculation with 512 atoms without localization constraint. From the gap parameters \( \Delta_{ab} = 7.95 eV, \Delta_{WS} = 4.23 eV \), we obtained \( \xi_{WS}/\xi_b = 1.37 \). These resultant values of the spatial
spread lead us to the same conclusions as those in the above Si case.

The first-order perturbation of Eq. (2) can be constructed using $H_0$ in Eq. (4) as the non-perturbative Hamiltonian;

$$ |\psi_k⟩ = C^{(0)}|b_k⟩ + \sum_{j(≠k)} C^{(ν(j))}|a_j⟩ $$

where $C^{(0)} ≈ 1$. The suffix $ν$ specifies the bond step and the inequivalent bond sites from the central bond $|b_k⟩$. In the perturbation terms, bonding orbitals $\{|b_j⟩\}_{j≠k}$ are ‘excluded’, because these are the other WS in the non-perturbative terms and are in the high-energy band in Fig. 3. Because the Hamiltonian $H$ is a short-range operator, the perturbation series in Eq. (10) contain only the 6 first-nearest-neighbor (FNN) antibonding orbitals $\{|a^{(1)}⟩\}$ and the 18 second-nearest-neighbor (SNN) antibonding orbitals $\{|a^{(2)}⟩\}$. For the FNN antibonding orbitals, the perturbative coefficients are given [5] by

$$ C^{(1)}_{C} ≈ \frac{⟨a^{(1)}|H|b_k⟩}{−Δ_{ab}} = \frac{Δ_{ps}}{8Δ_{ab}} = \frac{α_m}{8} $$

Here the factor $1/8$ stems from the four atomic coordination of the diamond structure, which is a three dimensional effect. On the other hand, the SNN antibonding orbitals are classified into two geometrically inequivalent bond sites: The 6 SNN bonds are parallel to the central bond. The other 12 SNN bonds exist, in a rough sense, within the plane perpendicular to the central bond. We denote the corresponding coefficients $C^{(2)}_C$ and $C^{(2,⊥)}_C$, respectively, and propose the estimations of

$$ C^{(2λ)}_{C} ≈ \frac{⟨a^{(2λ)}|H|b_k⟩}{−Δ_{ab}} + \left(\frac{α_m}{8}\right)^2 $$

where $2λ$ indicates $2||$ or $2⊥$. The first term is the first-order perturbation and its value is about $1/34$ for $C^{(2||)}_C$ or $−1/27$ for $C^{(2⊥)}_C$. Since this term is reduced to the ratio between two inter-atomic hoppings, its value is almost unchanged within the diamond-structure solids 2. The second term in Eq. (2) is responsible for the successive hopping of the FNN hoppings, where $C^{(0)}_C = 1$ is assumed. This term varies with $α_m$ and is essential to the distinction between the cases in Fig. 2(a) and (b). Notice that, in the realistic cases ($α_m ≤ 1$), the second term $(α_m/8)^2 ≤ 1/64$ is smaller than the first term, though not negligible. The above coefficients can be determined by Eqs. (11), (12) and the normalization condition $[|C^{(0)}|^2 + 6|C^{(1)}|^2 + 6|C^{(2||)}|^2 + 12|C^{(2⊥)}|^2 = 1]$. For the conduction WS’s, the same perturbation theory can be constructed, where the role of bonding and antibonding orbitals exchange with each other. The resultant norm distributions $|C^{(1)}|^2, |C^{(2||)}|^2$ and $|C^{(2⊥)}|^2$ are shown as crosses in Fig. 2. The energy of the WS $ε_{WS} = ⟨ψ_k|H|ψ_k⟩$ was also estimated from the perturbation results and the deviation from the correct value was about 0.06 eV in the Si case, which corresponds to 1% of the energy ($ε_{WS}$) and to 10% of the energy difference from a bonding orbital ($ε_b − ε_{WS}$). Here we can see that the present TB Hamiltonian is a short-range operator and the value of its matrix element $⟨ψ_k|H|ψ_k⟩$ can be well explained within a quite local area.

In conclusion, the concept of composite-band WS’s connects the picture of ‘chemical bond’ with the modern variational theory of electronic structures. In this letter, we have shown how a WS is similar to and different from a bonding orbital within the diamond-structure solids, where the Hamiltonian $H_{WS}$ plays a crucial role both for the construction and the analysis of WS’s. These theories are derived from the variational order-N formulation and so are applicable to other WS’s in covalent-bonded systems and/or ab initio Hamiltonians. Results of these theories give microscopic pictures for practical order-N calculations of large-scale systems.

This work is supported by a Grant-in-Aid for COE Research ‘Spin-Charge-Photon’ and by a Grant-in-Aid from the Japan Ministry of Education, Science, and Culture. The numerical calculation was partly carried out by the computer facilities at the Institute of Molecular Science at Okazaki and at the Institute for Solid State Physics at the University of Tokyo.

[1] For review articles of the order-N methods, P. Ordejón, Comp. Mat. Sci. 12, 157 (1998); S. Goedecker, Rev. Mod. Phys 71, 1085 (1999).
[2] F. Mauri and G. Galli, Phys. Rev. B 50, 4316 (1994); P. Ordejón, D. A. Drabold, R. M. Martin, and M. P. Grumbach, Phys. Rev. B 51, 1456 (1995).
[3] W. Kohn, Chem. Phys. Lett. 208, 167 (1993).
[4] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
[5] W. A. Harrison, Electronic structure and the properties of solids, W.H. Freeman and Company (1980).
[6] The present definition of the metallicity is different from Ref. 2 by a factor 1.11.
[7] D. J. Chadi and M. L. Cohen, Phys. Status. Solidi (b) 68, 405 (1975).
[8] D. J. Chadi, J. Vac. Sci. Technol. 16, 1290 (1979).
[9] I. Kwon, R. Biswas, C. Z. Wang, K. M. Ho, and C. M. Soukoulis, Phys. Rev. B 49, 7242 (1994).
[10] P. Löwdin, J. Chem. Phys. 18, 365, (1950).
[11] From the general theory of impurity states, one might think that the mass for $ξ_{WS}$ should be an effective mass. In general, this might be true, but the analysis of this letter shows that the WS for the diamond-structure solids is very similar to a bonding orbital and such an effective mass should be that of a bare electron (1 a.u.).
[12] The definitions and relations of the present TB parameters are given in Ref. 3 or other standard textbooks.