

Theory of Composite-Band Wannier States and Order-N Electronic-Structure Calculations

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From the order-N electronic-structure formulation, a Hamiltonian is derived, of which the 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.

KEYWORDS: Wannier state, order-N method, large-scale simulation, ab initio electronic-structure theory, diamond-structure solids

Recently, the Wannier state (WS) has been re-focused as a foundation of the order-N methods, linear-scaling methods for large-scale electronic-structure calculations.^{1,2)} The original concept of WS's is defined within a single isolated band under the periodic boundary, but is now generalized to systems with composite bands and/or non-periodic boundaries.¹⁻⁴⁾ 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 ε_{ij} are the Lagrange multipliers for the orthogonality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ and satisfy $\varepsilon_{ji} = \langle \psi_i | H | \psi_j \rangle$. 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 ε_{ij} , we obtain the set of the eigen states $\{\psi_k^{(\text{eig})}\}$, or the Bloch states in the periodic boundary; $H\psi_k^{(\text{eig})} = \varepsilon_k^{(\text{eig})} \psi_k^{(\text{eig})}$, where $\{\varepsilon_k^{(\text{eig})}\}$ are the eigen energies. With WS's, the matrix ε_{ij} is not diagonal, but its trace gives the correct band-structure energy $E_0 \equiv \sum_{k=1}^N \varepsilon_k^{(\text{eig})} = \sum_{k=1}^N \varepsilon_{kk}$.

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 sp^3 -hybridized orbitals, where the hopping along a bond is dominant. The corresponding hopping integral is half of the difference between the

energy level of an antibonding orbital (ε_a) and that of a bonding orbital (ε_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 sp^3 orbitals on the k -th bond. The WS's for H_0 are just the bonding orbitals $\{|b_k\rangle\}_{k=1, N}$, 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 $\{\varepsilon_{kk}\}$ have the unique value $\varepsilon_{\text{WS}} \equiv (1/N) \sum_{j=1}^N \varepsilon_j^{(\text{eig})}$, which is the weighted center of the valence band.

Another important hopping in the diamond structure is that within an atom, whose energy is one fourth of the energy difference between the atomic p-level (ε_p) and the s-level (ε_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 $\alpha_m \rightarrow 1$.^{5,6)} For classification of group IV elements, some TB parameterizations were picked out and we obtained $\alpha_m = 0.44$ for C,⁷⁾ $\alpha_m = 0.75$ ⁸⁾ for Si, and $\alpha_m = 0.77$, for Ge.⁷⁾ In the present numerical demonstrations, we use the nearest-neighbor TB Hamiltonians H for Si whose parameters are from ref. 9. Here Δ_{ps} is fixed to be 6.45 eV. Δ_{ab} and all the other interatomic hoppings are functions of the bond length d . In the equilibrium case ($d = d_0 \equiv 4.44$ a.u.), $\Delta_{ab} = 8.25$ eV and $\alpha_m = 0.78$.

Equation (1) is closely related to the localized-orbital order-N formulation,²⁾ where an energy functional $E_{\text{O(N)}} = \sum_{i,j}^N (2\delta_{ij} - \langle \psi_j | \psi_i \rangle) \langle \psi_i | \Omega | \psi_j \rangle = \text{Tr}[(2\rho - \rho^2)\Omega]$ is iteratively minimized. Here $\Omega \equiv H - \eta$, and

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$\rho \equiv \sum_{k=1}^N |\psi_k\rangle\langle\psi_k|$. ρ is the one-body density matrix and the energy parameter η must be chosen to be sufficiently high ($\eta > \varepsilon_N$). The WS wavefunctions satisfy

$$\begin{aligned} 0 &= \frac{\delta E_{O(N)}}{\delta \langle\psi_k|} = (2\Omega - \rho\Omega - \Omega\rho)|\psi_k\rangle \\ &= 2(H - H_{\text{occ}})|\psi_k\rangle - 2\eta(1 - \rho)|\psi_k\rangle. \end{aligned} \quad (3)$$

H_{occ} is the Hamiltonian within the valence or occupied Hilbert space

$$\rho H = H\rho = H_{\text{occ}} \equiv \sum_{j=1}^N |\psi_j^{(\text{eig})}\rangle \varepsilon_j^{(\text{eig})} \langle\psi_j^{(\text{eig})}|. \quad (4)$$

On the other hands, eq. (1) and the orthogonality constraint are rewritten as $(H - H_{\text{occ}})|\psi_k\rangle = 0$ and $(1 - \rho)|\psi_k\rangle = 0$, which satisfy eq. (3). In the present numerical calculations, the value $\eta = 5$ a.u. is chosen.

From eq. (3), we derive an eigen-value equation;

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

where

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

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

This eigen-value problem corresponds to the variational procedure of a specified WS (ψ_k), while all the other WS's ($\{\psi_j\}_{j\neq k}$) are fixed. If $\bar{\rho}_k|\psi_k\rangle = 0$ 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 (ψ_k) a 'central' WS.

Figure 1 shows the density of states (DOS) of H and $H_{\text{WS}}^{(k)}$ in the Si case ($d = d_0$). We observe 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 $\varepsilon_{kk} = \varepsilon_{\text{WS}}$. (b) The eigen states in the conduction band of H , ($\psi_i^{(\text{eig})}$, $N+1 \leq i \leq 2N$), are also the eigen states of $H_{\text{WS}}^{(k)}$ with the same eigen energies

$$H_{\text{WS}}^{(k)}|\psi_i^{(\text{eig})}\rangle = H|\psi_i^{(\text{eig})}\rangle = \varepsilon_i^{(\text{eig})}|\psi_i^{(\text{eig})}\rangle. \quad (8)$$

(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 $\varepsilon \geq 2\eta - \varepsilon_N \approx 272$ eV. The corresponding DOS profile is $D_{\text{high}}(\varepsilon) \approx D_{\text{val}}(2\eta - \varepsilon)$, where $D_{\text{val}}(\varepsilon)$ is the DOS profile of the valence band of H . This property arises 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 $D_{\text{high}}(\varepsilon)$, the Hilbert space of the other WS's is automatically 'excluded' in the variational freedom of the WS ψ_k .

To construct WS's, we used an iterative order- N algorithm with the Hamiltonian H_{WS} . The periodic cell contains 4096 atoms and $N = 8192$ doubly-occupied WS's. For each WS ψ_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 cut-off from the localization center. The resultant energy per

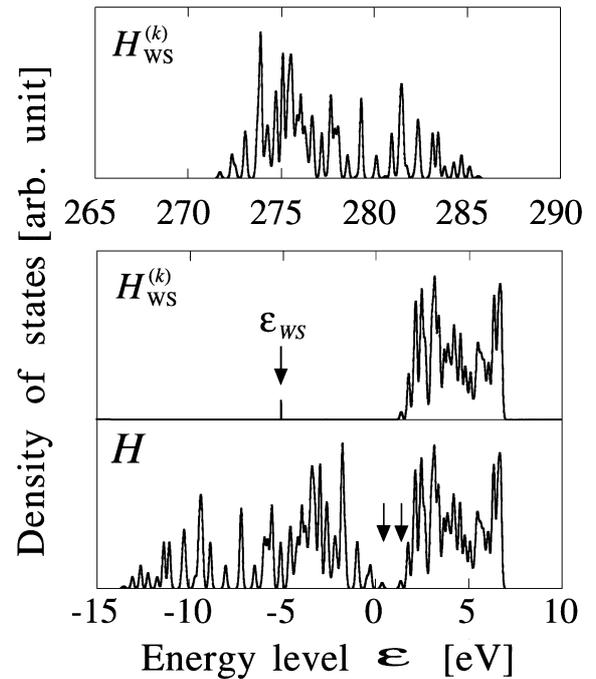


Fig. 1. The DOS of Hamiltonians H and $H_{\text{WS}}^{(k)}$ for the Si case with 512 atoms in the periodic cell. The isolated level ε_{WS} is broadened by a Gaussian with a width 0.01 eV and all the other levels are by that with a width of 0.1 eV. The two parallel arrows in H indicate $\varepsilon_N^{(\text{eig})}$ and $\varepsilon_{N+1}^{(\text{eig})}$.

WS (ε_{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 as follows; (i) With proper initial states of WS's, the density matrix ρ 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.¹⁰ 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 $E_{O(N)}$, where the initial WS's are chosen to be the anti-bonding orbitals $\{|a_k\rangle\}_{k=1,N}$ and the energy parameter η is chosen to be enough *low*.

Figure 2 shows the norm distributions $|C_{k\phi}|^2$ of some WS's, where $\{\phi\} \equiv \{b_k, a_k\}$. Figure 2 contains all the 614 orbitals of the resultant WS's. Case (a) is the WS with $d = 0.8d_0$, whose metallicity $\alpha_m = 0.47$ may correspond to the carbon case. 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 a decay property similar to that in the valence WS (b), but the roles of bonding and anti-bonding orbitals are exchanged. The norm of the central

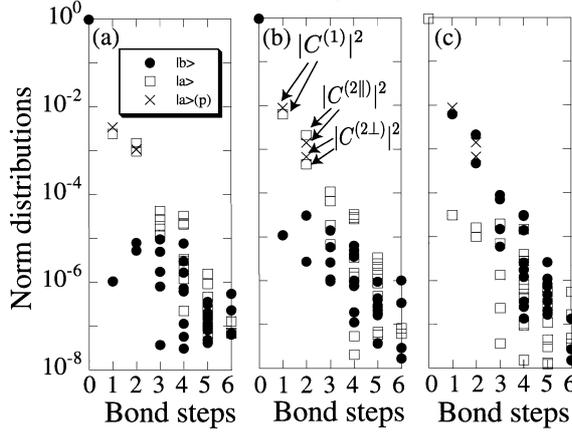


Fig. 2. Norm distributions of WS's $|C_{k\phi}|^2$, as a function of the bondstep from the central bond. The closed circles and the open squares denote the norms on bonding and anti-bonding orbitals, respectively. (a) The valence WS in the case with $d = 0.8d_0$, (b) the valence WS in the Si case ($d = d_0$), (c) the conduction WS in the Si case. The crosses denote the values from the perturbation theory. In (a), the two values $|C^{(2||)}|^2$ and $|C^{(2\perp)}|^2$ from the perturbation theory are almost identical.

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 $\{\psi_k\}$, the physical quantity of a one-body operator \hat{X} can be described as $\langle \hat{X} \rangle \equiv \sum_k^N \langle \psi_k^{(\text{eig})} | \hat{X} | \psi_k^{(\text{eig})} \rangle = \sum_k^N \langle \psi_k | \hat{X} | \psi_k \rangle$. 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 $\langle \hat{X} \rangle = \sum_{i,j}^N (2\delta_{ij} - \langle \psi_j | \psi_i \rangle) \langle \psi_i | \hat{X} | \psi_j \rangle$, 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 the WS, and only slightly by the 'tail' or the asymptotic long-distance behavior. From this point of view, we analyze 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. Note that the asymptotic long-distance behavior of WS is discussed in refs. 1.

If we apply the above discussion to the operator $(\hat{r} - \mathbf{r}_k)^2$, where \mathbf{r}_k is the center of the central bond ($|b_k\rangle$), an effective spatial spread of WS can be defined as $\bar{r}_{\text{WS}} \equiv (\langle \psi_k | (\hat{r} - \mathbf{r}_k)^2 | \psi_k \rangle)^{1/2}$. The values were actually calculated with the assumption that each sp^3 orbital is localized at the atom that the orbital belongs to. For a bonding orbital, this parameter is $\bar{r}_b \equiv d/2$ from its definition. For the WS in the Si case ($d = d_0$), we obtained $\bar{r}_{\text{WS}} = 1.16\bar{r}_b$. To see the effect of the boundary condition, we also calculated the system with 512 atoms *without* localization constraint and found $\bar{r}_{\text{WS}} = 1.19\bar{r}_b$. Since the operator $(\hat{r} - \mathbf{r}_k)^2$ is *not* short-ranged, the value of \bar{r}_{WS} might be sensitive to the boundary conditions.

Another definition of the spatial spread of the WS can be derived from the Hamiltonian $H_{\text{WS}}^{(k)}$. The Hamiltonian $H_{\text{WS}}^{(k)}$ has one localized eigen state ψ_k and the conduction band, and so $H_{\text{WS}}^{(k)}$ maps the WS formally to an impurity state, where the corresponding ionization energy is defined as $\Delta_{\text{WS}} \equiv \varepsilon_{N+1}^{(\text{eig})} - \varepsilon_{\text{WS}}$. A simplest case is the Hamiltonian in eq. (2), where the WS's are reduced to bonding orbitals and the corresponding gap Δ_{WS} is to Δ_{ab} . Using the uncertainty relation, a spatial spread is defined as $\xi_b \equiv \hbar/\sqrt{2m_e\Delta_{\text{ab}}}$, where $m_e \equiv 1$ a.u. Using the value in the Si case ($\Delta_{\text{ab}} = 8.25$ eV), we obtain $\xi_b = 0.29d_0$, which is consistent with 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 also be defined for WS's as $\xi_{\text{WS}} \equiv \hbar/\sqrt{2m_e\Delta_{\text{WS}}} = \xi_b\sqrt{\Delta_{\text{ab}}/\Delta_{\text{WS}}}$.¹¹⁾ For the WS in the Si case, we obtained $\Delta_{\text{WS}} = 6.49$ eV and $\xi_{\text{WS}}/\xi_b = 1.13$, which agrees, in the order, to the other definition of the spatial spread $\bar{r}_{\text{WS}}/\bar{r}_b = 1.16$ or 1.19 . This agreement shows that the mapping theory to a virtual impurity state is consistent with 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 observe a limiting case with vanishing the bandgap, we also calculated an artificial case with $\Delta_{\text{ps}} = 0$, where the system is a direct-gap insulator and the bandgap $\Delta = 8E_{xx}$ is located at Γ point.¹²⁾ 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 $V_{pp\sigma}$ and $V_{pp\pi}$, so as to keep E_{xy} unchanged.¹²⁾ This modification changes the value of Δ_{ab} as well. The resultant WS still shows a localized property with the spatial spread of $\bar{r}_{\text{WS}}/\bar{r}_b = 1.15$ or 1.20 , where the latter value is from the calculation with 512 atoms *without* localization constraint. From the gap parameters ($\Delta_{\text{ab}} = 7.95$ eV, $\Delta_{\text{WS}} = 4.23$ eV), we obtained $\xi_{\text{WS}}/\xi_b = 1.37$. 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. (5) can be constructed using H_0 in eq. (2) as the non-perturbative Hamiltonian;

$$|\psi_k\rangle = C^{(0)}|b_k\rangle + \sum_{j(\neq k)} C^{(\nu(j))}|a_j\rangle, \quad (10)$$

where $C^{(0)} \approx 1$. The suffix ν specifies the bond step and the inequivalent bond sites from the central bond $|b_k\rangle$. In the perturbation terms, bonding orbitals $\{|b_j\rangle\}_{j\neq k}$ are 'excluded', because these are the other WS in the non-perturbative terms and are in the high-energy band in Fig. 1. 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 ($|a^{(1)}\rangle$) and the 18 second-nearest-neighbor (SNN) antibonding orbitals ($|a^{(2)}\rangle$). For the FNN antibonding orbitals, the perturbative coefficients are given⁵⁾ by

$$\frac{C^{(1)}}{C^{(0)}} \approx \frac{\langle a^{(1)} | H | b_k \rangle}{-\Delta_{\text{ab}}} = \frac{\Delta_{\text{ps}}}{8\Delta_{\text{ab}}} = \frac{\alpha_{\text{m}}}{8}. \quad (11)$$

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 anti-bonding 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 $C^{(2\parallel)}$ and $C^{(2\perp)}$, respectively, and propose the estimations of

$$\frac{C^{(2\lambda)}}{C^{(0)}} \approx \frac{\langle a^{(2\lambda)} | H | b_k \rangle}{-\Delta_{ab}} + \left(\frac{\alpha_m}{8} \right)^2, \quad (12)$$

where (2λ) indicates $(2\parallel)$ or $(2\perp)$. The first term is the first-order perturbation and its value is about $+1/34$ for $C^{(2\parallel)}$ or $-1/27$ for $C^{(2\perp)}$. Since this term is reduced to the ratio between two *inter-atomic* hoppings, its value is almost unchanged within the diamond-structure solids.⁵⁾ The second term in eq. (12) is responsible for the successive hopping of the FNN hoppings, where $C^{(0)} = 1$ is assumed. This term varies with α_m and is essential to the distinction between the cases in Figs. 2(a) and 2(b). Note that, in the realistic cases ($\alpha_m \leq 1$), the second term $(\alpha_m/8)^2 \leq 1/64$ is smaller than the first term, though not negligible. The above coefficients can be determined by eqs. (11), (12) and the normalization condition ($|C^{(0)}|^2 + 6|C^{(1)}|^2 + 6|C^{(2\parallel)}|^2 + 12|C^{(2\perp)}|^2 = 1$). For the conduction WS's, the same perturbation theory can be constructed, where the roles of bonding and anti-bonding orbitals are exchanged. The resultant norm distributions $|C^{(1)}|^2$, $|C^{(2\parallel)}|^2$ and $|C^{(2\perp)}|^2$ are indicated by crosses in Fig. 2. The energy of the WS $\varepsilon_{WS} = \langle \psi_k | H | \psi_k \rangle$ 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 ($\varepsilon_b - \varepsilon_{WS}$). Here we can see that the present TB Hamiltonian is a short-range operator and the value of its matrix element $\langle \psi_k | H | \psi_k \rangle$ 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 thus 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.

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 - 12) The definitions and relations of the present TB parameters are given in ref. 5 or other standard textbooks.