

# An ‘order-N’ quantum theory for electronic structures and its application to dynamical brittle fractures

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A brief introduction is given for the order-N electronic-structure theory with localized states. Their locality is systematically investigated among the diamond-structure solids. The method is applied to molecular-dynamics algorithms. Test calculations with million atoms are done using a standard PC and parallel computers. The dynamical fractures of Si crystal are simulated using the above order-N method. Their brittle property is analyzed from the quantum mechanical view of the electronic structure.

*Keywords* Large-scale atomistic simulation, electronic structure, brittle fracture, silicon, Wannier states

## I. INTRODUCTION

Large-scale electronic-structure calculations are of great importance in nano materials. Recently, the ‘order-N’ methods have been proposed for calculating such large-scale systems. The computational cost in the order-N method is  $O(N)$ , or linearly proportional to the system size  $N$  [1]. The present theory is one of such order-N theories, based on the localized one-electron states [2,3]. The present article describes the order-N theory with localized states and some molecular-dynamics applications of Si brittle fracture.

## II. LOCALIZED STATES FROM THE FIRST PRINCIPLES

The density-functional theory and the Hartree-Fock theory are modern quantum theories for electronic structures. These theories define one-electron states  $\{\phi_k^{(\text{eig})}\}_k$  and effective one-body Hamiltonians  $H_{\text{eff}}$  that include the electron-electron interaction. Such one-electron states can be regarded as eigen states of the Hamiltonian

$$H_{\text{eff}}\phi_k^{(\text{eig})} = \varepsilon_k^{(\text{eig})}\phi_k^{(\text{eig})}. \quad (1)$$

Usually an eigen-value problem requires a  $O(N^3)$  computational cost. This fact severely limits the system size of electronic-structure calculations to, typically, one hundred of atoms. Even with simpler theories like tight-binding approximations, it is impractical to calculate all the eigen states for systems with thousands of atoms or more.

The present concept of localized states can be generally defined within the first-principle electronic structure theories. These states can be defined as localized one-electron states that satisfy

$$H_{\text{eff}}\phi_i = \sum_{j=1}^N \varepsilon_{ij}\phi_j, \quad (2)$$

where  $N$  is the number of occupied states. Equation (2) is derived from a variational procedure within a single Slater determinant, as is in the Hartree-Fock theory and the density-functional theory. The parameters  $\varepsilon_{ij}$  are the Lagrange multipliers for the orthogonality constraints

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \quad (3)$$

and satisfy  $\varepsilon_{ji} = \langle\phi_i|H|\phi_j\rangle$ . Such states can be formally equivalent to unitary transforms of the eigen states

$$|\phi_j\rangle \equiv \sum_k^N U_{jk}|\phi_k^{(\text{eig})}\rangle, \quad (4)$$

where  $U_{ij}$  is a unitary matrix. These localized states *exactly* reproduce any physical quantity  $\langle\hat{X}\rangle$  as

$$\langle\hat{X}\rangle \equiv \sum_k^N \langle\phi_k^{(\text{eig})}|\hat{X}|\phi_k^{(\text{eig})}\rangle = \sum_j^N \langle\phi_j|\hat{X}|\phi_j\rangle, \quad (5)$$

because of Eq. (4). Especially, the sum of the one-electron energies of the localized states gives the correct band-structure energy

$$E_{\text{bs}} \equiv \sum_{k=1}^N \varepsilon_k^{(\text{eig})} = \sum_{j=1}^N \varepsilon_{jj}, \quad (6)$$

though the Hamiltonian matrix  $\varepsilon_{ij}$  is not diagonal. One example of the localized states is the Wannier state in the solid state physics. Their locality has studied in some cases [5,6]. Wannier states  $W_{\nu l}(\mathbf{r})$  can be written in a form of

$$W_{\nu l}(\mathbf{r}) \equiv \int e^{i\mathbf{k}l} \phi_{\nu \mathbf{k}}^{(\text{eig})}(\mathbf{r}) d\mathbf{k}. \quad (7)$$

Here the eigen states  $\phi_{\nu \mathbf{k}}^{(\text{eig})}$ , or Bloch states, have the suffices of  $\nu$  for the band index and  $\mathbf{k}$  for the wave vector in the Brillouin zone. Wannier states have a suffix  $l$  for the

lattice vector that indicates their localization centers. [4] Eq. (7) can be regarded as one of the unitary transforms (4), where the corresponding unitary matrix

$$U_{\nu\mathbf{l},\nu'\mathbf{k}} \equiv \delta_{\nu,\nu'} e^{i\mathbf{k}\mathbf{l}} \quad (8)$$

is diagonal with respect to the band suffix. In other words, the present concept of localized states is a generalization of the Wannier state to composite-band systems and/or non-periodic systems. Such localized states can be called ‘generalized Wannier states’ [7–9].

For covalent-bonded systems, the simplest physical picture of a localized state  $\phi_j$  is the bonding orbital located at the  $j$ -th bond site. Realistic applications to condensed matters, such as silicon crystal, can be found in Ref. [9] with the density functional theory, where the localized states are constructed using explicit unitary transforms (4). The resultant localized states are exact, but are not constructed with an  $O(N)$  cost, because this procedure requires the eigen states. The localized states in the present order- $N$  calculations correspond to approximate wavefunctions of the above exact wavefunctions, within the framework of the variational procedure.

Hereafter, for simplicity, we discuss the theories within a tight-binding Hamiltonian  $H$ . Equation (2) is closely related to the order- $N$  formulation [2], where an energy functional

$$E_{O(N)} \equiv \sum_{i,j}^N (2\delta_{ij} - \langle \phi_i | \phi_j \rangle) \langle \phi_i | \Omega | \phi_j \rangle \quad (9)$$

is minimized. The operator  $\Omega$  is defined as  $\Omega \equiv H - \eta$  and the energy parameter  $\eta$  must be chosen to be sufficiently high ( $\eta > \varepsilon_N^{(\text{eig})}$ ). Without any localization constraint, the variational procedure leads us to Eq.(2) and the orthogonality ( $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ ). The practical order- $N$  procedure is to minimize  $E_{O(N)}$  iteratively with respect to localized states  $\{\phi_j\}$  under localization constraints. The resultant equation can be written in an eigen-value equation [3] as

$$H_{\text{loc}}^{(j)} |\phi_j\rangle = \varepsilon_{jj} |\phi_j\rangle, \quad (10)$$

where

$$H_{\text{loc}}^{(j)} \equiv H - \bar{\rho}_j \Omega - \Omega \bar{\rho}_j$$

$$\bar{\rho}_j \equiv \sum_{i(\neq j)}^N |\phi_i\rangle \langle \phi_i|. \quad (11)$$

This equation corresponds to the variational problem of one localized state ( $\phi_j$ ), where all the other localized states are fixed. The localized states are not eigen states of  $H$ , but are eigen states of  $H_{\text{loc}}$ . Equation (10) gives a general theory of the locality of the localized states [3].

### III. LOCALIZED STATES IN DIAMOND-STRUCTURE SOLIDS

The structures of the localized states are directly related to the electronic structure. We systematically investigate those among the group IV elements: C, Si, Ge,  $\alpha$ -Sn. The ground states of these materials are the diamond structure. For these materials, a universal theory can be constructed within tight-binding Hamiltonians [10]. A minimal sp tight-binding Hamiltonian is constructed on the atomic s-, p<sub>x</sub>-, p<sub>y</sub>- and p<sub>z</sub>- orbitals, which are equivalent to four sp<sup>3</sup> orbitals. Bonding and antibonding orbitals can be defined from a pair of sp<sup>3</sup> orbitals on each bond site and are denoted by  $\{b_j, a_j\}_j$ , respectively. Here  $j$  indicates the bond site. The corresponding energy levels are denoted as  $\varepsilon_b \equiv \langle b_j | H | b_j \rangle$  and  $\varepsilon_a \equiv \langle a_j | H | a_j \rangle$ , respectively. Since all the bond sites are symmetrically equivalent in the diamond structure, the above energy levels are the unique values ( $\varepsilon_b, \varepsilon_a$ ) among all the bond sites. We also denote the difference between them as  $\Delta_{ab} \equiv \varepsilon_a - \varepsilon_b$ . The energy  $\Delta_{ab}$  describes the order of the energy gain in a bond formation. A sp tight-binding Hamiltonian of single-element materials contains the following *five* energy parameters; One is the difference  $\Delta_{ps}$  between the atomic p-level  $\varepsilon_p$  and the s-level  $\varepsilon_s$  ( $\Delta_{ps} \equiv \varepsilon_p - \varepsilon_s$ ). The other four parameters are the nearest-neighbor hopping integrals in the Slater-Koster forms, which gives  $\Delta_{ab}$ . In general, these four inter-atomic hoppings are independent, but, the ratio among them is almost the same for the group IV elements [10]. Therefore, the system has essentially only two energy scales; the intra-atomic energy-difference  $\Delta_{ps}$ , and the inter-atomic hoppings, mainly characterized by  $\Delta_{ab}$ . To classify real solids, the ratio  $\alpha_m \equiv \Delta_{ps}/\Delta_{ab}$  is calculated from some sets of the tight-binding parameters. The resultant values are  $\alpha_m = 0.44$  for C [11],  $\alpha_m = 0.78$  for Si [12,13], and  $\alpha_m = 0.75$  for Ge [11]. The parameter  $\alpha_m$  may be called ‘metallicity’, because the bandgap would go to zero at  $\alpha_m \rightarrow 1$  [10].

We construct localized states, using an iterative order- $N$  algorithm with the Hamiltonian  $H_{\text{loc}}$  with a periodic cell with 4096 atoms [3]. We also construct the *exact* localized states from the eigen states with a smaller system size (512 atoms) [14]. The simplest approximation of the localized states can be given by the sp<sup>3</sup> bonding orbital on each bondsite ( $|\phi_j\rangle \approx |b_j\rangle$ ). In the present order- $N$  algorithm, such sp<sup>3</sup> bonding orbitals are chosen to be the initial states of the iterative algorithm. To investigate common features of the above solids, we use the nearest-neighbor tight-binding Hamiltonians  $H$  for Si, whose parameters are from Ref. [13]. Here the inter-atomic hopping parameters are functions of the nearest neighbor atomic distance  $d$  and the intra-atomic hopping parameter  $\Delta_{ps}$  is fixed to be 6.75eV. We tune the value of  $d$  for the variety of  $\alpha_m$ .

Here we show some of our results with the order-N calculations. Figure 1 shows the norm distributions  $|C_{j\chi}|^2$  of some resultant localized states, where  $\{\chi\} \equiv \{b_j, a_j\}$  indicates the basis orbital. The case (a) is the case with a low metallicity ( $\alpha_m = 0.47$ ), which might corresponds to the Carbon case. The case (b) is the Si case ( $\alpha_m = 0.78$ ). For both cases, the localized states are contributed mainly by the central bonding orbital and the neighboring antibonding orbitals

$$|\phi_j\rangle \approx C^{(0)}|b_j\rangle + \sum_{i(\neq j)} C^{(\nu(i))}|a_i\rangle. \quad (12)$$

Here the suffix  $\nu$  specifies the bond step and the inequivalent bond sites. The neighboring *bonding* orbitals  $\{|b_i\rangle\}_{i\neq j}$  have quite small contributions, because these are occupied by the other localized states  $\{|\phi_i\rangle\}_{i\neq j}$ . The norm of the central bond  $|C^{(0)}|^2$  is about 96 % in (a) or 94 % in (b). The summation of the norms up to the second bondstep is about 99.8 or 99.7 % in both cases.

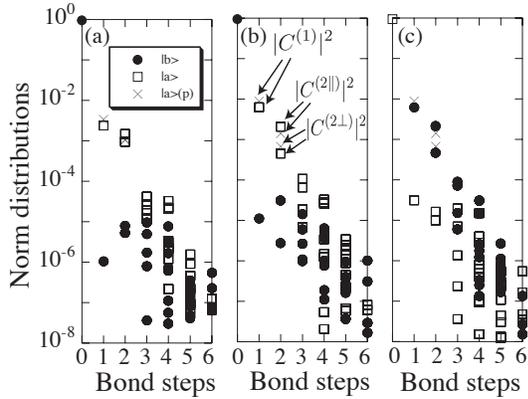


FIG. 1. Norm distributions of localized states  $|C^{(\nu)}|^2$ , as a function of the bondstep from the central bond. [3] The case (a) and (b) correspond to Carbon and Si systems, respectively. The case (c) is the conduction localized states in the Si case. The closed circles and the open squares denote the norms on bonding and anti-bonding orbitals, respectively. The crosses denote the values from the perturbation theory.

The contribution of the neighboring antibonding orbitals can be estimated by the first-order perturbation of Eq.(10) [3,14]. The resultant perturbative coefficients are given by

$$\frac{C^{(\nu)}}{C^{(0)}} = \frac{\langle a^{(\nu)} | H | b_k \rangle}{\varepsilon_b - \varepsilon_a}. \quad (13)$$

The range of non-zero perturbative coefficients  $C^{(\nu)}$  is determined by the interaction range of Hamiltonians. In nearest neighbor tight-binding Hamiltonians  $H$ , the interactions are limited to nearest neighbor atoms. In terms of bond sites, this turns out to be *second* nearest neighbor interactions, which is essential for the diamond

structure. In the diamond structure, each bond site has six first-nearest-neighbor bond sites and eighteen second-nearest-neighbor bond sites. The first-nearest neighbor bond sites are geometrically equivalent and the corresponding perturbative coefficients are denoted as  $C^{(1)}$ . The second-nearest-neighbor bond sites are classified into two geometrically inequivalent bond sites. The corresponding coefficients are denoted as  $C^{(2||)}$  and  $C^{(2\perp)}$ , respectively [15]. The resultant perturbative coefficients are also shown in Fig. 1 and reproduce the more accurate values quite well. The energy of the localized states  $\langle \psi_j | H | \psi_j \rangle$  is also estimated from the perturbation theory [15]. The estimated value has only a small deviation, 0.06 eV or 1 %, from the correct value. This energy corresponds to the average of the occupied eigen levels, or the weighted center of the valence band. Here we can see that the present tight-binding Hamiltonian is a short-range operator and its matrix element  $\langle \psi_j | H | \psi_j \rangle$  can be well explained within a quite local area.

The concept of the localized states can be defined also for the conduction bands within the sp Hamiltonian [3,14]. Such a conduction localized state in the Si case is also plotted in Fig.1(c). The resultant state shows the similar decay property as in the valence state (b), but the role of bonding and antibonding orbitals exchange with each other.

#### IV. MOLECULAR DYNAMICS SIMULATION FOR THE FRACTURE OF SI CRYSTALS

We have developed an order-N molecular-dynamics algorithm based on the above variational and/or perturbative theories. The test calculations were done in systems of up to about 1.4 million atoms, using a standard PC with single Pentium 4 processor and 2GB RAMs. Parallel computations are also tested [16]. Here, we show several results of the dynamical fracture simulations of silicon with external loads as shown in Fig. 2 [17]. We use a sp tight-binding Hamiltonian [13]. The systems are isolated clusters with orientation-fixed  $sp^3$  states at their boundaries. In smaller systems, satisfactory agreements are obtained for the values of elastic constants and the crack-propagating velocity among the order-N calculations, the exact diagonalization, and experimental observations. For example, the order-N calculation gives the Young modulus  $E_{100} = 105$  GPa that is comparable with the experimental value  $E_{100} = 130$  GPa and the crack-propagating velocity 2 km/s in comparison with the observed value  $\leq 3.8$  km/s. The fracture occurs when the band-gap goes to be zero. This is microscopically interpreted as bond-breaking processes or as vanishing the gap between bonding and antibonding states in some local region. The occupation ratio of s-orbital for each localized state  $f_s^{(j)} \equiv |\langle s | \phi_j \rangle|^2$  can be a good physical quantity for investigating the fracture

process. This quantity describes the extent of the  $sp$  hybridization and, for instance, is  $1/4$  for the ideal  $sp^3$  state and  $1/2$  for the ideal  $s^2p^2$  state. Drastic change can be seen also in the projected density of states of the localized states in the bond-breaking processes. After bond-breaking processes, the localized states on the broken bonds are stabilized with a high value of  $f_s^{(j)}$ . This means that such states are similar to an atomic  $s$ -state, rather than a  $sp^3$  dangling-bond state. These ‘ $s$ -rich’ states seem to be transitional and tend to re-bond somewhere later in the simulation.

We can present the quantum mechanical view of the brittle fracture of Si crystals. The energies of atomic  $s$  and  $p$  states are  $\varepsilon_s = -5.45\text{eV}$  and  $\varepsilon_p = 1.2\text{eV}$ , respectively, in the ideal tetrahedrally-bonded environment. Since an isolated silicon atom has the  $s^2p^2$  configuration, the averaged occupation ratio of  $s$ -orbital is the half ( $f_s = 1/2$ ) and the electronic energy is  $\varepsilon_{\text{atom}} \equiv (\varepsilon_s + \varepsilon_p)/2 = -2.13\text{eV}$  per electron. In perfect crystals, all the states are localized, constructed from the  $sp^3$  bonds and the corresponding energy level is  $\varepsilon_{\text{bulk}} = -5.2\text{eV}$ . Therefore the stabilization energy (the cohesive energy) of the bulk electron system per electron is about  $3\text{eV}$ . In crack tips, the  $sp^3$ -bonded network is *locally* broken and the existence of the low  $s$  level stabilizes the transitional *s-rich* states. Therefore the bonds near the crack tips tend to be broken much easier than those at the bulk regions. This can be interpreted as the microscopic origin of the brittle fracture.

## V. SUMMARY

The localized states can be defined from the first principles and give a foundation of an order-N method for large-scale atomistic simulations. The localized states for the diamond-structure solids are systematically investigated with a universal tight-binding theory. The order-N method has been applied to the dynamical process of the brittle fracture in Si crystals. The quantum mechanical view of brittle fracture is presented.

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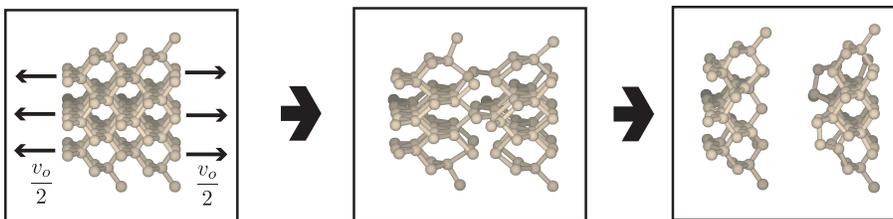


FIG. 2. Example of the present dynamical fracture simulation, where the atoms on the left and right edges are under an external load so as to keep the (001)-component of the velocity to be constant  $v_0/2$ .