Hamiltonian Decomposition for Bulk and Surface States

Ken-ichi Sasaki,[1,*] Yuji Shimomura,[1] Yositake Takane,[1] and Katsunori Wakabayashi[1,2]

[1]*Department of Quantum Matter, Graduate School of Advanced Sciences of Matter, Hiroshima University,
Higashi-Hiroshima 739-8530, Japan*
[2]*PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*

We demonstrate that a tight-binding Hamiltonian with nearest- and next-nearest-neighbor hopping integrals can be decomposed into bulk and boundary parts for honeycomb lattice systems. The Hamiltonian decomposition reveals that next-nearest-neighbor hopping causes sizable changes in the energy spectrum of surface states even if the correction to the energy spectrum of bulk states is negligible. By applying the Hamiltonian decomposition to edge states in graphene systems, we show that the next-nearest-neighbor hopping stabilizes the edge states. The application of Hamiltonian decomposition to a general lattice system is discussed.

PACS numbers: 73.20.-r, 73.21.-b

The energy band structure is of central importance in understanding the electronic properties of material. A tight-binding (TB) model is a versatile approach to study the electronic, magnetic and transport properties of a solid since the TB model describes the qualitative features of the energy band structure [1]. The long-range hopping terms such as next-nearest-neighbor (NNN) hopping are often added to the TB model with nearest-neighbor (NN) hopping to improve the energy band structure. In many cases, the NNN correction to the energy band structure is not a matter of particular importance. In this Letter, we show that the NNN hopping can change appreciably the energy spectrum of surface states which appear near the boundary of a system even when the correction to the energy spectrum of bulk states is negligible. We explain this by decomposing the NNN TB Hamiltonian into two parts: bulk and boundary parts. This Hamiltonian decomposition is essential to understanding the stability of surface states.

We use graphene systems to demonstrate the Hamiltonian decomposition for the following reasons. (1) Graphene is known to have both bulk and surface states. The bulk states exhibit a "relativistic" energy band structure called the Dirac cone [2,3], and the surface states called the edge states appear near the zigzag edge [4]. (2) The edge states have been observed by several experimental groups [5–8], and a theoretical understanding of the experimental results is called for. In fact, the NNN hopping is important to explain the experimental results [9]. (3) The edge states have a large density of states (DOS) near the Fermi energy, which is responsible for the Fermi instabilities. Since the DOS depends on the energy spectrum or bandwidth of the edge states, the NNN hopping is important for the appearance of many-body effects of the edge states [10,11]. Thus, graphene is a good testing system for the Hamiltonian decomposition not only from a theoretical but also from an experimental point of view.

We study the NN (NNN) TB Hamiltonian, H_{NN} (H_{NNN}), which is defined as

$$\left(\frac{H_{NN}}{-\gamma_0}\right) = \sum_{i,j \in \text{all}} c_i^\dagger [\mathcal{H}_{NN}]_{ij} c_j,$$

$$\left(\frac{H_{NNN}}{-\gamma_n}\right) = \sum_{i,j \in \text{all}} c_i^\dagger [\mathcal{H}_{NNN}]_{ij} c_j, \tag{1}$$

where c_i ($c_i^\dagger$) is the annihilation (creation) operator of an electron at the ith site, γ_0 (γ_n) is the NN (NNN) hopping integral, and the matrix element $[\mathcal{H}_{NN}]_{ij}$ ($[\mathcal{H}_{NNN}]_{ij}$) is 1 when the ith site is a (next) NN site of jth site and is zero otherwise. In the following, we will show that H_{NNN} can be decomposed into bulk and boundary (edge) parts for a graphene with zigzag edge.

Suppose that we put an electron on the central site denoted by the empty circle in Fig. 1(a). The initial state is labeled as $|\Psi_0\rangle = c_0^\dagger|0\rangle$. We operate on $|\Psi_0\rangle$ with $H_{NN}/(-\gamma_0)$, then $\mathcal{H}_{NN}$ transfers the electron to three NN sites denoted by the solid circles in Fig. 1(a). This state is written as $|\Psi_0'\rangle = \sum_{i \in \text{all}}[\mathcal{H}_{NN}]_{i0} c_i^\dagger|0\rangle$. The numbers associated with the solid circles in Fig. 1(a) indicate the matrix element of $\mathcal{H}_{NN}$. The successive operation of
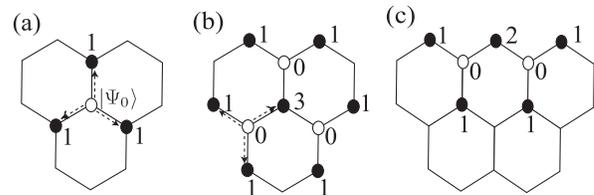

FIG. 1.   (a) An electron at the central site, $|\Psi_0\rangle = c_0^\dagger|0\rangle$, is transferred to three NN sites by $H_{NN}/(-\gamma_0)$. The resultant state is $|\Psi_0'\rangle = \sum_{i \in \text{all}}[\mathcal{H}_{NN}]_{i0} c_i^\dagger|0\rangle$. (b) $\mathcal{H}_{NN}^2$ transfers the electron to the NNN sites. At the same time, $\mathcal{H}_{NN}^2$ returns the electron to the original site. The matrix element of $[\mathcal{H}_{NN}^2]_{ij}$ that returns the electron to the original site is given by 3 because there are three NN sites around the central site. (c) The matrix element for the return process $[\mathcal{H}_{NN}^2]_{ii}$ depends on whether the site is a bulk site ($[\mathcal{H}_{NN}^2]_{ii} = 3$) or a zigzag edge site ($[\mathcal{H}_{NN}^2]_{jj} = 2$).

$H_{\mathrm{NN}}/(-\gamma_0)$ on $|\Psi_0'\rangle$ gives

$$|\Psi_0''\rangle = \sum_{i,j\in\text{all}} [\mathcal{H}_{\mathrm{NN}}]_{ji}[\mathcal{H}_{\mathrm{NN}}]_{i0} c_j^\dagger |0\rangle. \qquad (2)$$

Starting from the initial site, the electron reaches the NNN sites as shown in Fig. 1(b). Thus, the two successive NN hopping processes relate to the NNN hopping process. This indicates that $\mathcal{H}_{\mathrm{NN}}^2$ includes $\mathcal{H}_{\mathrm{NNN}}$. However $\mathcal{H}_{\mathrm{NN}}^2$ and $\mathcal{H}_{\mathrm{NNN}}$ are not identical because in $\mathcal{H}_{\mathrm{NN}}^2$ there is a diagonal matrix element that returns the electron to the original site, that is, $|\Psi_0''\rangle$ of Eq. (2) contains the term with $j = 0$. Since there are three NN sites around the original site, the amplitude of this return process is 3 as shown in Fig. 1(b). $\mathcal{H}_{\mathrm{NN}}^2$ and $\mathcal{H}_{\mathrm{NNN}}$ become identical if we subtract the corresponding diagonal matrix element from $\mathcal{H}_{\mathrm{NN}}^2$. This matrix is proportional to the unit matrix, $[I]_{ij} = \delta_{ij}$.

For a periodic system, since the number of bonds of every site is three, we have $\mathcal{H}_{\mathrm{NNN}} = \mathcal{H}_{\mathrm{NN}}^2 - 3I$. Putting this into Eq. (1), we see that H_{NNN} can be rewritten as

$$H_{\mathrm{NNN}} = -\gamma_n \sum_{i,j\in\text{all}} c_i^\dagger [\mathcal{H}_{\mathrm{NN}}^2 - 3I]_{ij} c_j. \qquad (3)$$

The matrix $\mathcal{H}_{\mathrm{NN}}$ can be diagonalized by a unitary matrix as $[U\mathcal{H}_{\mathrm{NN}}U^\dagger]_{pq} = E_p/(-\gamma_0)\delta_{pq}$, where E_p is the energy eigenvalue of an eigenstate $|E_p\rangle$. Then, from Eq. (3) we see that H_{NN} and H_{NNN} can be diagonalized simultaneously by the basis of $|E_p\rangle$, and the energy eigenvalue of the total Hamiltonian, $H_{\mathrm{NN}} + H_{\mathrm{NNN}}$, is given by

$$E_p - \gamma_n\left(\frac{E_p}{-\gamma_0}\right)^2 + 3\gamma_n, \qquad (4)$$

for $|E_p\rangle$. In Eq. (3), H_{NNN} contains the on-site potential part, $3\gamma_n\sum_{i\in\text{all}}c_i^\dagger c_i$. This on-site potential can be ignored since it changes only the origin of the energy band structure, as shown by $3\gamma_n$ in Eq. (4) [2]. This statement is correct for a periodic system without boundary, but is not approved for a system with boundary. It is because of that the number of bonds of the edge sites is different from that of a bulk site and the corresponding on-site potentials at the edge sites are different from those at the bulk sites.

To show this explicitly, we put an electron on the zigzag edge site labeled as 2 in Fig. 1(c). The electron is transferred to the NNN sites by $\mathcal{H}_{\mathrm{NN}}^2$. For this time, however, the matrix element of the on-site potential term that we need to subtract from $\mathcal{H}_{\mathrm{NN}}^2$ in order to get $\mathcal{H}_{\mathrm{NNN}}$ is 2 because the number of bonds is 2 for the edge site. It is different from 3 for a nonedge (bulk) site. Thus, we obtain the formula for H_{NNN} as

$$H_{\mathrm{NNN}} = -\gamma_n \sum_{i,j\in\text{all}} c_i^\dagger\{[\mathcal{H}_{\mathrm{NN}}^2]_{ij} - g_i[I]_{ij}\}c_j, \qquad (5)$$

where g_i is the number of bonds of the ith site. Since we can shift the origin of the energy by $3\gamma_n$ without a loss of generality, Eq. (5) can be written as

$$H_{\mathrm{NNN}} = -\gamma_n \sum_{i,j\in\text{all}} c_i^\dagger [\mathcal{H}_{\mathrm{NN}}^2]_{ij} c_j + \gamma_n \sum_{i\in\text{all}} (g_i - 3)\hat{n}_i, \qquad (6)$$

where $\hat{n}_i = c_i^\dagger c_i$ is the number operator of the ith site. The first term in Eq. (6) [or the second term of Eq. (4)] shows that H_{NNN} breaks the particle-hole symmetry of H_{NN} because $\mathcal{H}_{\mathrm{NNN}}$ contains the square of $\mathcal{H}_{\mathrm{NN}}$. The second term in Eq. (6) represents quantum well potentials at the edge sites with potential depth of $-\gamma_n$ because $g_i = 2$ for a zigzag edge site. The quantum well potential appears only at an edge site whose number of bonds is different from those of a bulk site. Therefore, a surface state appearing near the boundary is strongly affected by this potential. For bulk states, only the first term of the right-hand side of Eq. (6) is important. In fact, if a system has no boundary (if a system is periodic), the second term of Eq. (6) disappears and the NNN Hamiltonian is given only by the first term. Therefore, the first term can be considered as the bulk part and the second term is as the edge part of the NNN Hamiltonian, i.e., $H_{\mathrm{NNN}} = H_{\mathrm{NNN}}^{\mathrm{bulk}} + H_{\mathrm{NNN}}^{\mathrm{edge}}$, where

$$H_{\mathrm{NNN}}^{\mathrm{bulk}} \equiv -\gamma_n \sum_{i,j\in\text{all}} c_i^\dagger [\mathcal{H}_{\mathrm{NN}}^2]_{ij} c_j,$$
$$H_{\mathrm{NNN}}^{\mathrm{edge}} \equiv \gamma_n \sum_{i\in\text{all}} (g_i - 3)\hat{n}_i. \qquad (7)$$

The edge state is labeled by the wave vector along the zigzag edge, k, as $|E(k)\rangle$. Here $E(k)$ denotes the energy eigenvalue of H_{NN}. Since $E(k)$ of the edge state is very close to zero [4], the energy shift due to $H_{\mathrm{NNN}}^{\mathrm{bulk}}$, $-(\gamma_n/\gamma_0^2)E(k)^2$, is negligible. Thus, the energy correction to the edge state arises from H_{NNN} as

$$\Delta E(k) = -\gamma_n \sum_{i\in\text{edge}} \langle E(k)|\hat{n}_i|E(k)\rangle. \qquad (8)$$

It is only the density at the edge sites that determines $\Delta E(k)$. The energy bandwidth (W) of the edge states can be calculated in the following way. As k approaches the Fermi point, i.e., $ka \to 2\pi/3$ or $4\pi/3$ (a is lattice constant), the edge state changes into a bulk state since the localization length $\xi(k) \to \infty$ [4,12]. Then $\sum_{i\in\text{edge}}\langle E(k)|\hat{n}_i|E(k)\rangle$ is negligible and $\Delta E(2\pi/3a) = \Delta E(4\pi/3a) = 0$. On the other hand, the $k = \pi/a$ state is the most localized state satisfying $\xi(\pi/a) = 0$. For this state, we have $\sum_{i\in\text{edge}}\langle E(k)|\hat{n}_i|E(k)\rangle = 1$ and $\Delta E(\pi/a) = -\gamma_n$. It shows that the $k = \pi/a$ state (the Fermi point) is located at the bottom (top) of the energy band and $W = \gamma_n$ for the edge state. This result of $W = \gamma_n$ reproduces the energy bandwidth that is numerically calculated for the zigzag edge shown in Fig. 2(a) [9]. The quantum well potential of $H_{\mathrm{NNN}}^{\mathrm{edge}}$ lowers the edge state's energy if γ_n is a positive value. We adopt $\gamma_n = 0.3$ eV. A similar value is obtained by a first-principles calculation with the local density approximation [13].

It should be mentioned that Eqs. (5) and (6) include NNN hopping between sites which are connected by two
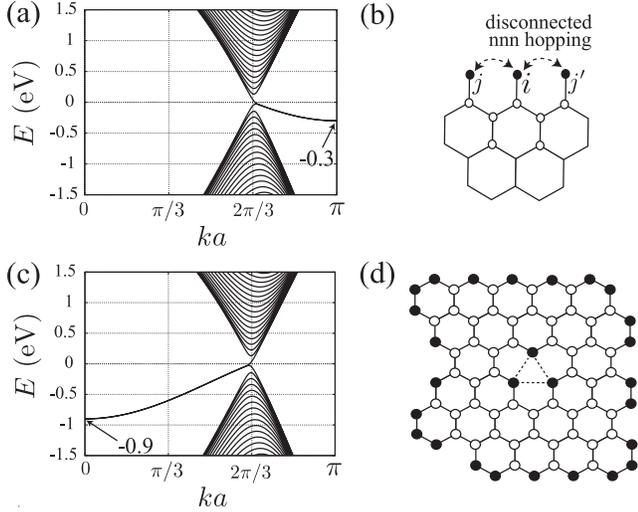
FIG. 2. (a) The energy band structure of graphene system with the zigzag edge. This plot is obtained by diagonalizing $H_{NN} + H_{NNN} - 3\gamma_n$ numerically. We adopt $\gamma_0 = 3.0$ eV and $\gamma_n = 0.3$ eV. The horizontal axis is a wave vector along the zigzag edge (k) multiplied by the lattice constant (a). (b) The lattice structure of the Klein edge. The NNN hopping between NNN edge sites (i and j or i and j') is not represented by the double of the NN hopping. (c) The energy band structure of a graphene system with the Klein edge. (d) A graphene system with a boundary and a lattice vacancy. H_{NNN}^{edge} gives an on-site potential energy shift of $-\gamma_n$ at carbon atoms denoted by solid circles. There is a disconnected NNN Hamiltonian at the dotted lines around the lattice vacancy.

successive NN hopping processes. Two successive NN hopping processes do not include *disconnected* NNN hopping process. The disconnected NNN process is relevant to the Klein edge as shown in Fig. 2(b) [14]. Because $\mathcal{H}_{NN}^2$ cannot transfer an electron at the edge site (i) to the NNN edge site (j or j'), we have to add $\mathcal{H}_{NNN}^{dc}$, which represents the NNN hopping between disconnected sites, to the matrix of the right-hand side of Eq. (5) in order to get a complete $\mathcal{H}_{NNN}$. Thus we have

$$H_{NNN} = -\gamma_n \sum_{i,j \in \text{all}} c_i^\dagger \{[\mathcal{H}_{NN}^2]_{ij} - g_i[I]_{ij} + [\mathcal{H}_{NNN}^{dc}]_{ij}\} c_j.$$

(9)

Since $[\mathcal{H}_{NNN}^{dc}]_{ij}$ is not zero only when i and j are both the edge sites, the disconnected NNN Hamiltonian is written as

$$H_{NNN}^{dc} \equiv -\gamma_n \sum_{i,j \in \text{all}} c_i[\mathcal{H}_{NNN}^{dc}]_{ij} c_j = -\gamma_n \sum_{i,j \in \text{edge}}^{NNN} c_i^\dagger c_j.$$

(10)

H_{NNN}^{dc} can be classified into the edge part of the NNN Hamiltonian since H_{NNN}^{dc} is given by the creation and annihilation operators at the edge sites. If we represent the wave function using the density n and phase θ as $|\Psi\rangle =$

$\sum_{i \in \text{all}} \sqrt{n_i}\, e^{i\theta_i} c_i^\dagger |0\rangle$, then we have

$$\langle\Psi|H_{NNN}^{dc}|\Psi\rangle = -\gamma_n \sum_{i,j \in \text{edge}}^{NNN} \sqrt{n_i n_j}\, e^{i(\theta_i - \theta_j)}.$$

(11)

This result shows that not only the density ($\sqrt{n_i n_j}$) but also the relative phase ($\theta_i - \theta_j$) of the localized wave function is important for the energy shift. This is contrasted to the fact that the quantum well potential couples only to the density of a quantum state. If there is a lattice periodicity along the edge, we can set $\theta_i = (ka)i$ and $n_j = n_i$. Then Eq. (11) becomes

$$\langle\Psi|H_{NNN}^{dc}|\Psi\rangle = -2\gamma_n \cos(ka) \sum_{i \in \text{edge}} n_i.$$

(12)

Since $g_i = 1$ for the Klein edge sites, the edge part of the NNN Hamiltonian is written as

$$H_{NNN}^{edge} = -2\gamma_n \sum_{i \in \text{edge}} \hat{n}_i - \gamma_n \sum_{i,j \in \text{edge}}^{NNN} c_i^\dagger c_j.$$

(13)

Using Eq. (12), we get $\Delta E(k)$ ($\equiv \langle E(k)|H_{NNN}^{edge}|E(k)\rangle$) for the Klein edge as

$$\Delta E(k) = -2\gamma_n[1 + \cos(ka)] \sum_{i \in \text{edge}} n_i(k),$$

(14)

where $n_i(k) \equiv \langle E(k)|\hat{n}_i|E(k)\rangle$. The energy bandwidth for the Klein edge states is calculated as follows. Near the Klein edges, the edge states appear for $0 \le k < 2\pi/3a$ and $4\pi/3a < k \le 2\pi/a$ [see Fig. 2(c)]. It can be shown that the wave function of the most localized state is given by $k = 0$ state, and the sum of the densities at the Klein edge sites is given by $\sum_{i \in \text{edge}} n_i(0) = 3/4$ [12]. Then, by putting $k = 0$ into Eq. (14), we have $\Delta E(0) = -3\gamma_n$. Thus, W for the Klein edge is $3\gamma_n$ (=0.9 eV). This result also reproduces the energy bandwidth that is numerically calculated for the Klein edge shown in Fig. 2(c). Half of W comes from the quantum well potential and the other half of W is due to the disconnected NNN hopping process.

Here let us summarize the formula for the NNN Hamiltonian: H_{NNN} can be decomposed into bulk and edge parts as $H_{NNN} = H_{NNN}^{bulk} + H_{NNN}^{edge}$ with

$$H_{NNN}^{bulk} \equiv -\gamma_n \sum_{i,j \in \text{all}} c_i^\dagger [\mathcal{H}_{NN}^2]_{ij} c_j,$$

$$H_{NNN}^{edge} \equiv \gamma_n \sum_{i \in \text{edge}} (g_i - g)\hat{n}_i - \gamma_n \sum_{i,j \in \text{edge}} c_i^\dagger [\mathcal{H}_{NNN}^{dc}]_{ij} c_j.$$

(15)

g is the number of bonds of a bulk site. The first term of the right-hand side of H_{NNN}^{edge} in Eq. (15) represents quantum well potentials at the edge sites. It is only the number of bonds at the edge site which determines the depth of the quantum well potential. As a result, the quantum well

potential appears at the edge sites, regardless of the edge shape. For example, in the case of graphene, $g_i \neq g(= 3)$ not only for the zigzag (or Klein) edge sites but also for the armchair edge sites. Thus, for a finite system of graphene shown in Fig. 2(d), the quantum well potentials of $-\gamma_n$ are denoted by the solid circles. The quantum well potential at the armchair edge may not be of as much importance as the zigzag edge because the edge state of a graphene is absent from the armchair edge [4–6]. It is also interesting to note that $g_i \neq g$ for the three sites around a lattice vacancy. In addition to the quantum well potentials at the three sites, the disconnected NNN hopping appears between them.

We remark on other effects that can modify the energy spectrum of the edge states. First, it is naively expected that the orbital energy at an edge carbon atom is different from that at a bulk atom when a functional group attaches to the edge atom. The attachment of a functional group gives rise to an additional change of the energy bandwidth of the edge states. However, this energy shift may be a positive or negative value depending on the type of functional group. This can be distinguished from the energy shift due to the NNN Hamiltonian because it is always a negative value. Second, W can be modified by the electron-electron or electron-phonon interactions because they give rise to a self-energy correction to the edge states. A theoretical calculation of the self energy for the edge states is given in Refs. [10,15].

We note that Eq. (15) is not restricted to graphene systems but is applicable to other two-dimensional systems like the square lattice, and three-dimensional systems. Let us consider the application of Hamiltonian decomposition to a square lattice system. On a square lattice, two applications of a NN hopping produces hopping not just to NNN, but even to the 3rd NN sites. Thus we need to subtract hopping between 3rd NN sites ($\mathcal{H}_{3rd}$) from $\mathcal{H}_{NN}^2$ in order to get $\mathcal{H}_{NNN}$. This modifies H_{NNN}^{bulk} in Eq. (15) as

$$H_{NNN}^{bulk} \equiv -\gamma_n \sum_{i,j \in \text{all}} c_i^\dagger \{ [\mathcal{H}_{NN}^2]_{ij} - [\mathcal{H}_{3rd}]_{ij} \} c_j. \quad (16)$$

On the other hand, H_{NNN}^{edge} does not change even for the square lattice system. The NNN Hamiltonian stabilizes surface states in a general system through the quantum well potentials. The energy dispersion relation of surface states is observed below the Fermi level by high-resolution photoemission studies of the (111) surfaces of copper, silver, and gold [16]. We speculate that the observed stability of the surface states is due to the edge part of the NNN Hamiltonian.

In conclusion, H_{NNN} can be decomposed into the bulk and edge parts as shown in Eq. (15). If the energy spectrum of H_{NN} is symmetric with respect to $E = 0$, then H_{NNN}^{bulk} breaks this symmetry. If H_{NN} has a localized energy eigenstate near the edge of a system, then H_{NNN}^{edge} is relevant to shifting the energy eigenvalue through the quantum well potential and the disconnected NNN edge Hamiltonian. The quantum well potential couples only to the density, whereas the disconnected NNN edge Hamiltonian couples to the phase of the localized wave function. Although the Hamiltonian decomposition is proved for two-dimensional graphene systems, it works for other systems like a one-dimensional chain of atoms and a three-dimensional lattice system as well.

*sasaki@hiroshima-u.ac.jp
[1] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 2004).
[2] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
[3] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).
[4] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).
[5] Y. Niimi, T. Matsui, H. Kambara, K. Tagami, M. Tsukada, and H. Fukuyama, Appl. Surf. Sci. **241**, 43 (2005).
[6] Y. Kobayashi, K. Fukui, T. Enoki, K. Kusakabe, and Y. Kaburagi, Phys. Rev. B **71**, 193406 (2005).
[7] Z. Klusek, Z. Waqar, E. A. Denisov, T. N. Kompaniets, I. V. Makarenko, A. N. Titkov, and A. S. Bhatti, Appl. Surf. Sci. **161**, 508 (2000).
[8] K. Sugawara, T. Sato, S. Souma, T. Takahashi, and H. Suematsu, Phys. Rev. B **73**, 045124 (2006).
[9] K. Sasaki, S. Murakami, and R. Saito, Appl. Phys. Lett. **88**, 113110 (2006).
[10] K. Sasaki and R. Saito, J. Phys. Soc. Jpn. **77**, 054703 (2008).
[11] K. Sasaki, J. Jiang, R. Saito, S. Onari, and Y. Tanaka, J. Phys. Soc. Jpn. **76**, 033702 (2007).
[12] K. Sasaki, S. Murakami, R. Saito, and Y. Kawazoe, Phys. Rev. B **71**, 195401 (2005).
[13] D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, Phys. Rev. B **51**, 12 947 (1995).
[14] D. J. Klein, Chem. Phys. Lett. **217**, 261 (1994).
[15] K. Sasaki, K. Sato, R. Saito, J. Jiang, S. Onari, and Y. Tanaka, Phys. Rev. B **75**, 235430 (2007).
[16] S. D. Kevan and R. H. Gaylord, Phys. Rev. B **36**, 5809 (1987).