Electronic Structure Calculations of Various Graphite Sheets

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Electronic structures of the graphite sheets including π -orbital exited states are investigated using the recursion methods. A new recursion method is introduced for calculating large size electronic systems. Several results are compared with the known experimental data clearing the conduction band. These results should give a foundation of a molecular orbital theory for calculating electronic states in various materials. Key words: electronic structures, graphite, recursion method, π -orbital exited states.

1. INTRODUCTION

A new clustered recursion method based on the Lanczos algorithm is introduced in this study. It is shown that this method is very easy and useful for calculating electronic structures including valence bands and conduction bands in various complex materials. The electronic structures of a carbon nanotube are calculated as an example for investigating the various graphite sheets and diamond like materials. The comparisons between two clustered recursion methods of previous one using the Householder method [1]-[3] and this work are briefly explained in this paper. Most of them are to be reported in another work. The Lanczos method can save computer memories in use of some techniques.

The graphite-sheet electronic structures have been variously investigated in recent works including the world scientific topics. One of these is the carbon nanotube found by S. Iijima in 1991. In this work, one dimensionally arrayed π -orbital structure is adapted to the graphite sheet construction, and the LCVB (linear combination of valence bonds) method [2][3] is applied for determining the basis set and the interaction energies between state vectors. This method is based on the chemical bonds and the covalent bonds composed of paired spins (singlet spin states), and the interaction energies are semi-empirically determined using the overlap integrals and the absolute value overlap integrals. As new trial calculations, π orbital exited states composed of resonating pair spins on filled sites and empty sites are included in the LCVB basis set, which states are similar to the Hubbard model [4]. The calculated results of the electronic structures in a graphite sheet are compared with the experimental data represented by Hosokawa et al. [5] in good agreements.

The band matrix transformation processes as the clustered recursion method using Lanczos algorithm are formulated in § 2. The carbon sheet is represented using a model system adjusted with the STM picture [6] in § 3. The conduction band construction is discussed as exited states of the π bonds. The results are compared with experimental data of XAS (x-ray absorption spectroscopy) including both of the valence and conduction bands [5] in § 4. The basis orbitals are constructed from the atomic orbitals, which are equated

in § 5 briefly as additional contents for realizing the theory.

2. CLUSTERD RECURSION METHOD USING LANCZOS ALGOLITHM

The molecular orbital system of size N is represented with the secular equation X using the energy parameter E, the overlap integral S and the Hamiltonian H:

$$X = ES - H = \sum_{i}^{N} \sum_{j}^{N} |i > x_{i,j} < j| = 0(1)$$

The transformation from Eq. (1) to a (2l+1)-component band matrix X_b of the elements $b_{n,m}$,

$$X \Rightarrow X_{b} = \sum_{n}^{N} \sum_{i=-l}^{l} |P_{n}| > b_{n,n+i} < P_{n+i} |, \dots (2)$$

is performed using the Lanczos algorithm as like usual matrix tri-diagonalization. The projected vectors of the (2l+1) band matrix at *n*th line

$$|P_n\rangle = \sum_{i}^{N} p_{n,i} |i\rangle$$
 (3)

 $p_{n,i} = p_{l,n}$ (4) are determined in the relations

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where the Schmidt diagonalization for a vector set is analytically included in these processes. With Eq.(6), the norm of the transformed terms are expanded as

$$< P_n \mid X \cdot X \mid P_n > = \sum_{r=-l}^{l} b_{n,n+r}^2$$
 (8)

In this equation, the highest terms of the vector and the coefficient are determined from the lower step terms as the projection to the new basis of the band matrix;

$$b_{n,n+l}^{2} = \sum_{i,j}^{N,N} (\sum_{k}^{N} p_{n,i} x_{i,k} x_{k,j} p_{n,j}) - \sum_{r=-l}^{l-1} b_{n,n+r}^{2} , \quad \dots (9)$$

$$|P_{n+l}\rangle = \frac{1}{b_{n,n+l}} \{ X | P_n \rangle - \sum_{r=-l}^{l-1} b_{n,n+r} | P_{n+r} \rangle \}$$

= $\frac{1}{b_{n,n+l}} \{ \sum_{i}^{N} \sum_{j}^{N} x_{i,j} p_{n,j} | i \rangle - \sum_{r=-l}^{l-1} \sum_{i}^{N} b_{n,n+r} p_{n+r,i} | i \rangle \}$
= $\sum_{i}^{N} p_{n+l,i} | i \rangle$. (10)

Thus, the *l*th-diagonal (band edge) terms $p_{n+l,i}$ of n line for the basis set $|i\rangle$ are calculated from this equation:

$$p_{n+l,i} = \frac{1}{b_{n,n+l}} \{ \sum_{j}^{N} x_{ij} p_{n,j} - \sum_{r=-l}^{l-1} b_{n,n+r} p_{n+r,i} \}(11)$$

Inner band terms from the vector $|P_{n+l}\rangle$ are determined with the previously calculated vectors $|P_{n+l}\rangle$ as

b,,

$$\sum_{i=1}^{N} \sum_{j=1}^{N} p_{n+r,i} x_{i,j} p_{n+l,j} : 1 \le r \le l . \dots (12)$$

Alternating these processes, we can continue the (2l+1) band matrix transformation with the projection expansion of the n+l term at the *n* line.

The first stage transformations are represented as follows. The clustered $l \times l$ terms reserved the original quantities are given by the original terms directly:

$$|P_{n}\rangle = |n\rangle$$
; $1 \le n \le l$,(14)
 $|P_{n}\rangle = |n\rangle$

The first step projection is performed using these terms:

$$b_{l,l+l}^{2} = \sum_{k=1}^{N} x_{l,k} x_{k,l} - \sum_{r=0}^{l-1} b_{l,l+r}^{2} = \sum_{i=l+l}^{N} x_{l,i}^{2}, \dots (15)$$
$$|P_{l+l}\rangle = \frac{1}{b_{l,l+l}} \{\sum_{i=1}^{N} x_{l,i} \mid i > -\sum_{r=1}^{l} b_{l,r} \mid r > \}, \dots (16)$$

$$p_{1+l,i} = \frac{1}{b_{1,1+l}} x_{1,i} ; \ 1+l \le i . \tag{17}$$

The second step is constructed from these terms and the inner band term obtained as

$$b_{2,1+l} = \langle P_2 | X | P_{1+l} \rangle = \frac{1}{b_{1,1+l}} \sum_{i=1+l}^N x_{2,i} x_{i,1+l}$$
 (18)

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The second projection terms become as follows:

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$$b_{2,2+l}^{2} = \sum_{i,j}^{M} (\sum_{k}^{n} p_{2,i} x_{i,k} x_{k,j} p_{2,j}) - \sum_{r=1}^{M} b_{2,r}^{2}$$

$$= \sum_{k=l+l}^{N} x_{2,k}^{2} - b_{2,l+l}^{2}, \qquad (19)$$

$$|P_{2+l} >= \frac{1}{b_{2,2+l}} \{\sum_{i=1}^{N} x_{2,i} \mid i > -\sum_{r=1}^{l+l} \sum_{i=1}^{N} b_{2,r} p_{r,i} \mid i > \}.$$

$$(20)$$

$$p_{2+l,i} = \frac{1}{b_{2,2+l}} \{ x_{2,i} - \frac{b_{2,1+l}}{b_{1,1+l}} x_{1,i} \} ; 1+l \le i . \dots (21)$$

The particular trace of r from 1 to n+l-1 concerned with the clustered elements $x_{n,m}$ and the band elements $b_{n,n+r}$ are performed by continuing the first stage transformations from n=1 to n=l as shown in Eqs. (13)-(20). After finishing the first stage, the projection for the n+l term $|P_{n+l}\rangle$ at *n* line just becomes the trace of n+r from n-l to n+l-1 ($-l \le r < l$), which are formulated in Eqs. (9)~(12). Finally, the 2l+1 line band matrix based on the secular matrix is created at *n*th step as like



In this equation, the projected terms in each line are colored with a gray bar.

3. STRUCTURES OF CARBON SHEETS

The carbon sheets have various structures e.g. graphite, single and several layer graphite sheets, single and several wall nanotubes, and fullerenes. In recent studies, honeycomb lattice cubes are created in graphic images where cross points and lines are composed of diamond bonds [7]. The edges of the graphite sheets also have various structures as like zigzag, armchair and hydrocarbon etc.

As a basic step, the electronic structures of a pure



Fig.1. STM picture of carbon nanotube produced by C. Dekker et al. [6].



Fig. 2. Square lattice structure of a graphite sheet. Bonds and sites are numbered as $m=1\sim40$ and $\{n\}=\{1\}\sim\{23\}$ respectively in four unit cells.

mono-layer graphite sheet same as a large size carbon nanotube as shown in Fig. 1 characterized from a result of C. Dekker et al. [6] are calculated for preparing the parameter foundation in the LCVB theory. The basis set of σ and π orbitals composing spin pair bonds are arrayed using a square lattice shown in Fig. 2, where the basic σ bonds are numbered from 1 to 6, and the π bonds are from 7 to 10 in the first unit cell. The last two are set to the exited states of the π bonds. The carbon atoms are numbered as $\{6\},\{7\},\{11\}$ and $\{12\}$ in this cell, and all of the bond-bond interactions and the overlap integrals in four unit cells in Fig. 2 are taken into accounts in the secular equation. The lattice structure is assumed to fit with the STM structure that the two π bond lines (from $\{6\}=\{7\}$ and $\{8\}=\{9\}$ to $\{11\}=\{12\}$) are crossed in two directions, which is adjusted with Fig. 1 by nearly 45° rotation.

4. CALCULATIONS

The important algorithm is devised in the conduction band calculations for these materials, but such states have not been cleared theoretically. Some types of the conduction bands have been studied based on the anti-bonding states of π and σ orbitals using ab *initio* theories or tight binding theories. These anti-bonding states with triplet-spins show the phosphorescence phenomena, which are observed in the various non-metallic nanotubes. On the other hand, conduction bands in metallic nanotubes or graphite are not so clear, and another types of exited states have been discussed. The electric current is a cooperative phenomena of electrons and phonons, which states are difficult to reserve the triplet spin states of electrons.

In this work, a trial treatment of the conduction band is proposed based on the Hubbard-like model [6] concerned with graphite. The results are compared with the experimental data in Fig.4 produced by Hosokawa et al. [5]. In this figure, The XAS data realized as the conduction band overlap with the SXES data (soft x-ray emission spectroscopy) realized as the valence band. These exited states are treated as the resonated two occupation states of full filed p_z orbitals and empty state as shown in Fig. 5(a). Thus the upper band states in Fig.4 should be composed of superposition of the conductive states and localized phosphorescence states.



Fig. 4. XAS intensity in carbon materials represented by Hosokawa et al. [5].



(a) The ground π bonds and the resonated states composed of p_z orbitals.



(b) Averaged field of the resonated states.



The transition energy from the π states to the resonated p_z states is set to $E_T = 9.0$ eV in this work. The resonated states spread uniformly as the singlet spin states with some occupied rate in the averaged structure as shown in Fig. 5 (b). The full excitation of the π orbitals becomes the half filled state of these. Such exited state model might correspond to the layer-layer interactions of π orbitals in graphite. If the exited states are composed of the anti-bonding states, these are the triplet spin states involving the magnetic phenomena in high magnetic field. This question has to be checked with the experimental data as for Ref. [8].



Fig. 6. The calculated DOS in nanotube. The anti-bonding states are not included.





As an important treatment, the overlap integral between exited state orbitals and ground state orbitals at a same atom are set to be 0 for avoiding the overlaps of a same orbital with a same spin state.

Calculated results are shown in Fig.6. Bold lines indicate the total DOS including the overlap effects. The full total state number is 10 in the unit cell. Thin lines show diagonal terms of the basis orbitals. The vacuum level is 0 eV, and the DOS in near here should include hybrid states composed of 2s, 2p and 3s orbitals that are not discussed in this paper. An important result is that the π bonding states in the ground states and the exited states composed of resonated p_z states are mixed through the transfer interactions, and the Fermi level E_F shifts into the conduction band at -3.5 eV. This level is determined with the total number 8 of the state summation n_T shown in Fig. 7. Thus, for investigating the electronic structures in various graphite sheets, the exited state treatment is very important to determine the ground state it self. This problem should be cleared through various fundamental experiments.

5. BASIS SET

The parameters in molecular orbital interactions are determines semi-empirically in the LCVB method (see the reference [3]), where atomic orbital bonding states are defined as the basis of molecular orbitals. The hybrid orbitals χ in a carbon atom are represented using atomic orbitals ϕ , for sp^2 ;

$$\chi_1 = \frac{1}{\sqrt{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_x$$
,(23)

$$\chi_{3} = \frac{-\phi_{s}}{2\phi_{s}} - \frac{-\phi_{z}}{2\sqrt{3}}\phi_{z} - \frac{-\phi_{z}}{\sqrt{6}}\phi_{x} + i\frac{-\phi_{z}}{\sqrt{2}}\phi_{y}, \quad (29)$$

$$\chi_{4} = \frac{1}{2}\phi_{s} - \frac{1}{2\sqrt{3}}\phi_{z} - \frac{1}{\sqrt{6}}\phi_{x} - i\frac{1}{\sqrt{2}}\phi_{y}. \quad (30)$$

Table I. Parameter setting of K and L.

Κ _{σ,σ} Κ _{σ,π}	Κ _{ex,σ π}	Κσπ	Κ _{π,π}	$L_{\sigma,\sigma}$	$L_{\pi,\pi}$
0.4	-0.4	0.4	2.0	1.2	0

1	Table II. E	Energy levels of basis bonds. [eV]					Energy levels of basis b	
	$E_{\sigma 1}$	$E_{\sigma 2}$	E_{π}	E _{ex}				
1	-38 5	-38.2	-25.6	-76				

The functions of the basis valence bonds are equated as

$$\Psi_{k,l}(r_1, r_2) = \frac{1}{\sqrt{2(1\pm |s_{k,l}|^2)}} \{\chi_k(r_1)\chi_l(r_2) \pm \chi_k(r_2)\chi_l(r_1)\}$$

; + singlet, -triplet,(31)

$$s_{k,l} = \int \chi_k(r) \chi_l^*(r) dr . \quad (32)$$

The basis vector $|\Psi_{k,l}\rangle$ is equated using this Ψ :

$$<\Psi_{k,l} | \Psi_{k,l} >= \iint \Psi_{k,l}(r_1, r_2) \Psi_{k,l}^*(r_1, r_2) dr_1 dr_2 \dots (33)$$

$$S_{kl,mn} = \langle \Psi_{k,l} | \Psi_{m,n} \rangle$$
(34)

Adding this overlap integral in Eq. (34), the absolute value integral

$$D_{kl,mn} = \iint |\Psi_{k,l}(r_1, r_2) \Psi^*_{m,n}(r_1, r_2)| dr_1 dr_2 \dots (35)$$

is defined for determining the interaction energy:

$$V_{kl,mn} = \frac{1}{2} (E_{kl} + E_{mn}) (K_{kl,mn} D_{kl,mn} + L_{kl,mn} S_{kl,mn}), \quad \dots (36)$$

where K and L are the semi-empirical parameters. As for the exited states, the function of the resonated state is defined as

$$\Psi_{kkl}^{e}(r_{1},r_{2}) = \frac{1}{\sqrt{2(1 + \operatorname{Re}(s_{k,l}^{2}))}} \{\chi_{k}(r_{1})\chi_{k}(r_{2}) + \chi_{l}(r_{2})\chi_{l}(r_{1})\}.(37)$$

Using the known data of atomic orbitals (bond lengths, energy levels, binding energies etc.), the basic data of the bonding states can be defined. In this work, the parameters K and L in Table I are adjusted with the energy levels of benzene within 0.5 eV accuracy. The energies of bonding states are determined as Table II.

6. CONCLUSION

In this study, using a new recursion method, the graphite sheet electronic structures are calculated and a treatment of the singlet spin exited states is proposed in good agreements of the experimental data. These results and the treatment should be important for investigating the various carbon materials.

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