Electronic Structure Calculations of Diamond in Various Cluster Sizes

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The electronic structures in covalent bond clusters are calculated using a semi-empirical method based on the Heitler-London theory. The method is formulated within linear combination of valence bonds method by means of non-orthogonal basis functions of sin-pair state-vectors. Real space electronic structures in diamond structure (zinc sulfide structure) compounds are calculated variously. The electronic states of bulk diamond are obtained using the Clustered Recursion method and are compared with the experimental data of photo-electron spectroscopy.

1. INTRODUCTON

In this paper, the electronic structures in covalent bond clusters of diamond are calculated for researching new materials concerned with wide energy-gap semiconductors. The clusters are assumed as micro-grains of diamond and zinc sulfide structure compounds. The energy states in grain boundaries are important for investigating hole behaviors, which are discussed in § 4 by changing the boundary energy-parameters.

A linear combination of valence bonds (LCVB) method is applied in this paper, which is formulated as like the linear combination of atomic orbitals (LCAO) method. In this method, the basis functions of the σ bonds are created at first, where the Heitler-London (H.L.) theory is adapted to sp^3 atomic orbital bonds of carbon. The diamond systems are created with the array of the bond units consisting of 4 σ bonds shown in Fig.1.
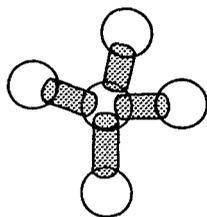

Fig.2 The bond unit arrays in the X, Y and Z axis.

The covalent bond cluster systems are created with the bond unit arrays of the number n, l, m in the X, Y, Z axes.

Fig.1 the bond unit of 4 σ bonds.

The arrays of the X, Y and Z directions are set as shown in Fig.2. Such bond arrays may not be stable in pure carbon, but we can assume the stable structure as in SiC (zinc sulfide structure) under some boundary conditions. Using the covalent bond interactions of diamond, we can suppose the results in the zinc sulfide structure systems similarly.
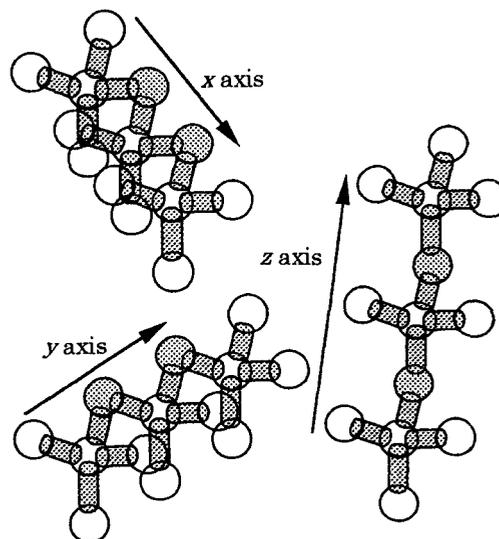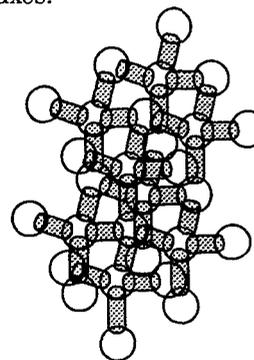

Fig.3 The bond array of the 2,2,2 cluster.

The interactions between the σ bonds are counted from the first to the third nearest

neighbors. In these calculations, the atomic orbitals are treated as complex number functions. The results of the binding energies and the interaction energies become real numbers in the calculation processes.

Different from the k-space calculation methods such as OPW, APW and LMTO[1], our real space method has enough applicability to the electronic structure calculations of the chemical bond systems. For calculating the bulk system, the Clustered Recursion method[2][3] is applied to the LCVB equations. The results are compared with the experimental data of photo-electron spectroscopy, and the calculation reliability is checked in good agreement.

2. FORMULATION

According to the H.L. theory, the two particle state-vectors are calculated from the binding atomic orbitals. The atomic orbitals ϕ_a in the molecules are determined approximately by the hydrogen-like Hamiltonian

$$H_a = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{z_a e^2}{r_{a1}}, \tag{1}$$

with the eigenvalues e_a:

$$H_a \phi_a = e_a \phi_a. \tag{2}$$

We can solve this equation as detailed in educational books of quantum mechanics. The atomic energies e_a are related to effective charges z_a

$$e_a = -13.6\left(\frac{z_a(n,l)}{n}\right)^2 \text{ [eV]}, \tag{3}$$

and obtained empirically from the experimental data. The atomic orbitals ϕ_a can be determined by the principal quantum number n and the azimuthal quantum number l.

The averaged energy level for hybrid orbitals in sp^3 e.g. are calculated such as

$$e_1 = e_2 = e_3 = e_4 = \frac{1}{2}(\varepsilon_s + \varepsilon_p): \tag{4}$$

Based on the concept of the H.L. manipulation, we use the hybrid orbitals (j-th valence orbital at atom i) $\chi_{i,j}(r) = \chi_m(r)$ to create these state-vectors. Following the H.L. equation, the Hamiltonian is similarly formulated as follows:

$$\hat{H}_{mn} = \hat{H}_m + \hat{H}_n + \hat{V}_{mn} \tag{5}$$

The hybrid orbitals $\chi_m(r)$ consisted of atomic orbitals satisfy the Schrödinger equation:

$$\hat{H}_m \chi_m(r) = e_m \chi_m(r). \tag{6}$$

We can calculate the expected values of bond energies E_{mn} using the σ bond wave-functions:

$$\psi_{mn}(1,2) = \frac{1}{\sqrt{2(1+s_{mn}^2)}} \times$$
$$\{\chi_m(1)\chi_n(2) + \chi_m(2)\chi_n(1)\}, \tag{7}$$

$$s_{mn} = \int \chi_m(1)\chi_n(1)dr_1. \tag{8}$$

$$E_{mn} = e_m + e_n + V_{mn}, \tag{9}$$

Here, we use the empirical values of the binding energies V_{mn} which are well known values in chemistry data books. The two-particle wave functions $\psi_{mn}(1,2)$ in Eq.7 are rewritten to the state-vectors $|\psi_{mn}\rangle$ as the LCVB basis, which must satisfy the normalization condition:

$$\langle\psi_{mn}|\psi_{mn}\rangle = \iint \psi_{mn}(1,2)\psi_{mn}^*(1,2)dr_1 dr_2 = 1. \tag{10}$$

When the basis state-vectors are represented as $|\psi_{mn}\rangle = |\psi_f\rangle$, they are not orthogonal and the overlap integrals become finite:

$$S_{fg} = S_{mn,pq} = \langle\psi_f|\psi_g\rangle \tag{11}$$

The suffixes f and g represent the bond orbitals m,n and p,q respectively.

3. ELECTRONIC STRUCTURE CALCULATIONS

The LCVB equations are non-orthogonal by using above state-vectors. For simplicity, let us use orthonormal state-vectors $|f\rangle$ and $|g\rangle$ which are considered as the diagonal part in each bond. Here the following notations are defined; S : the overlap integral matrix, H : the Hamiltonian, E_f: the diagonal energy of the σ bond and U_{fg}: the interaction energy. The LCVB equation is formulated as follows:

$$S = \sum_f \sum_g |f\rangle S_{fg}\langle g|, \tag{12}$$

$$H = \sum_f |f\rangle E_f\langle f| + \sum_{f \neq g}\sum |f\rangle U_{fg}\langle g|. \tag{13}$$

The interaction energies U_{fg} in the Hamiltonian should be determined as:

$$U_{fg} = U_{mn,pq} = \langle\psi_f|U|\psi_g\rangle$$
$$= \text{Coulomb terms + exchange terms +}$$
$$\text{higher order terms.}$$

The absolute value overlap integral is introduced to estimate the direct charge-charge interactions in molecules:

$$D_{fg} = \iint |\psi_{mn}(1,2)\psi_{pq}^*(1,2)|dr_1 dr_2. \tag{14}$$

Using these quantities D and the usual overlap integrals S, the transfer energies U_{fg} are approximated as

$$U_{fg} = \frac{1}{2}(E_f + E_g)(K_{fg}D_{fg} + L_{fg}S_{fg}), \quad (15)$$

where K and L are parameters determined empirically for each type of results. The eigenvector $|\alpha\rangle$ at energy ε_α is expanded by the vectors $|f\rangle$ and the coefficients C_f:

$$|\alpha\rangle = \sum_f C_f(\varepsilon_\alpha)|f\rangle. \quad (16)$$

These matrices satisfy the equations;

$$\langle\alpha|S|\beta\rangle = \delta_{\alpha\beta}, \quad (17)$$

$$H|\alpha\rangle = \varepsilon_\alpha S|\alpha\rangle, \quad (18)$$

$$\det X = \det[ES - H] = 0. \quad (19)$$

The eigenvectors determining the space charge density are given using the same coefficients in Eq.(16):

$$|\Phi_\alpha\rangle = \sum_f C_f(\varepsilon_\alpha)|\psi_f\rangle. \quad (20)$$

Using a well-known block matrix transformation and determinant results,

$$Y(n) = \begin{bmatrix} U(n) & V(n) \\ V(n)^* & W(n) \end{bmatrix} =$$

$$\begin{bmatrix} I & VW^{-1} \\ 0 & I \end{bmatrix}\begin{bmatrix} U - VW^{-1}V^* & 0 \\ 0 & W \end{bmatrix}\begin{bmatrix} I & \\ W^{-1}V^* & I \end{bmatrix}$$

$$Y(n-1) = U(n) - V(n)W^{-1}(n)V(n)^*, \quad (21)$$

the matrix reduction can be performed in reverse order of n. The Green's function concerning orbitals f and g are obtained after repetitive use of the transformation in Eq.(21):

$$G_{fg}(E) = < f|[ES - H]^{-1}|g >$$
$$= 1/(X_{fg} - X_{ff}X_{gg}/X_{gf}) \quad (22)$$

where X_{fg}, X_{ff}, X_{gg} and X_{fg} are the matrix elements of the 2×2 matrix in the last transformation. This Green's function has the relation:

$$G_{fg} = \frac{1}{X_{fg} - X_{ff}X_{gg}/X_{gf}} = \sum_\alpha \frac{C_f(\varepsilon_\alpha)C_g(\varepsilon_\alpha)}{E - E_\alpha}. \quad (23)$$

From this relation, the coefficients are obtained in the differential form of the Green's function:

$$C_f(E_\alpha)C_g(E_\alpha) = \lim_{E\to\varepsilon_\alpha} \frac{E - \varepsilon_\alpha}{X_{fg} - X_{ff}X_{gg}/X_{gf}}. \quad (24)$$

The normalization condition of the coefficients becomes

$$\sum_f \sum_g S_{fg}C_f C_g = 1 \quad (25)$$

at eigenvalue ε_α.

4. ELECTRONIC STRUCTURES

Based on the above formulas, the electronic

structures of covalent bond clusters constructing the diamond (or zinc sulfide) structure are calculated using the σ -bond state-vectors. The DOS in bulk diamond is obtained as in Fig.4 using the constants K=0.38 and L=1.0.
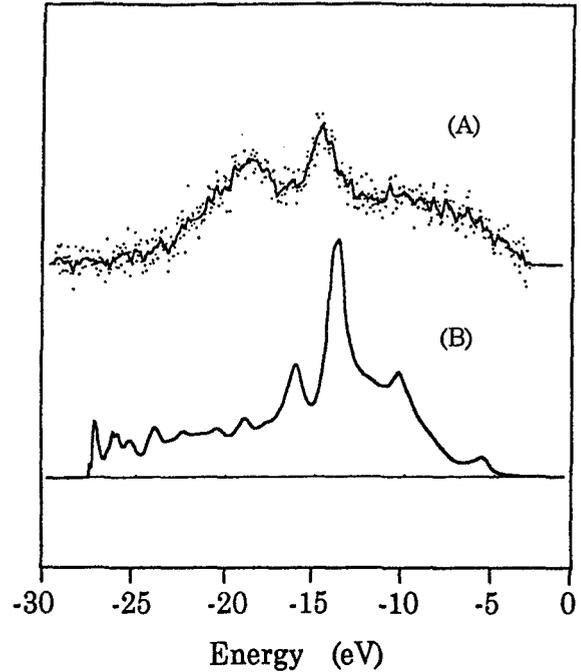

Fig.4 Density of states in bulk diamond.
(A) The photo-electron spectroscopy by K. Yamamoto et al.[4]. (B) The calculated results.

The system consists of 3600 σ -bond orbitals, and the clustered recursion method[2][3] is applied to the DOS calculations. Central 8 bonds are selected for calculating the overlap integral terms of bonds. The states are nicely fit with the XPS data[4] by K. Yamamoto et al.. The another experimental data[5] also represent similar results. Comparing with the above results, it can be said that the energy parameters are evaluated with sufficient accuracy.

The electronic structures in the small σ -bond clusters are investigated using the same parameters with the above bulk diamond calculations. The calculations of the eigenvalues and the eigenvectors involving the overlap integrals are performed using the Eqs.(16)-(25) numerically. The grain boundaries are consisted of modified bonds and hydrogenated bonds. The hydrogenated bonds are arrayed on the x-y plane surface and other surfaces are consisted of modified bonds. The energy of the C-C bond is set to −35.41 eV, and C-H bond is −33.79 eV. The energy of the modified bonds are set to be −30.79 and −33.79 eV as the parameters of (a) and (b) which results are shown in Fig.5 respectively.

The interactions within the covalent bond clusters are taken into account till the third nearest neighbors. The correlation between the clusters is neglected. The cluster sizes l,m,n are

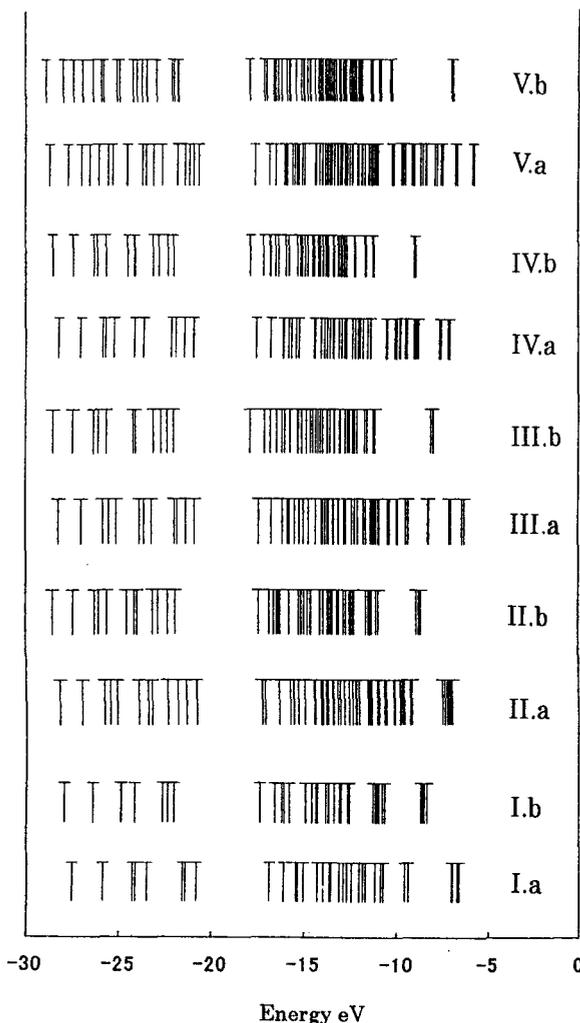changed over I=2,2,2, II=2,2,3, III=2,3,2, IV=3,2,2 and V=3,3,2.

Fig.5 The energy spectra in the covalent bond
clusters. The modified bond energies on the
boundaries are set as a=-30.79 and b=-33.79 eV.
The cluster sizes l,m,n are I=2,2,2, II=2,2,3,
III=2,3,2, IV=3,2,2 and V=3,3,2.

The energy spectra in the range from -5 to -10 eV are particularly disturbed. At this valence band edge, the energy states of the modified bond produce separated four states. The high state energy of the boundary reflects directly the high level edge states.

In these results, we might conclude that the energy states of the grain boundaries are very important to discuss the hole states at the upper valence band edge. It is natural to consider that the boundary structures are complex and the energy states at the valence band edge become random configuration. Under such condition, the band edge states are localized and the hole mobility is not expectable.

The semiconductors of the diamond and the zinc sulfide structure might not have enough state density at the band edge for creating the

conductivity. For discussing more accurate results, it is need to calculate the energy states including the cluster-cluster correlation.

5. CONCLUSION

The LCVB molecular orbital calculation method is introduced. The DOS of the bulk diamond is calculated with enough accuracy. The electronic states of the isolated small covalent bond cluster constructing the diamond structure are calculated. The band edge states from -5 to - 10 eV seem to be disturbed in these results. This condition probably induces the localized states at the upper band edge.

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