CoO_{3-y} on the oxidation of CO is determined by the degree of nonstoichiometry due to the incorporation of foreign atom such as Sr.

Acknowledgement. The financial support of the Korea Science and Engineering Foundation is greatly acknowledged. The authors are grateful to Drs. H. J. Won, S. K. Cho, and T. J. Kim for helpful assistances of the experiments.

References

1. E. G. Derouane, *Ind. Chim. Belg.*, **36**, 359 (1971).
2. R. J. H. Voorhoeve, "Advanced Materials in Catalysis", p. 129. Academic Press, New York, 1977.
3. R. J. H. Voorhoeve, D. W. Johnson, J. P. Remeika, Jr., and P. K. Gallagher, *Science*, **195**, 827 (1977).
4. R. J. H. Voorhoeve, D. P. Remeika, and L. E. Trimble, *Ann N. Y. Acad. Sci.*, **272**, 3 (1976).
5. K. M. Choi, K. H. Kim, and J. S. Choi, *J. Phys. Chem. Solids*, **49**, 1027 (1988).
6. P. V. Huong, E. Oh-Kim, K. H. Kim, D. Kim, and J. S. Choi, *J. Less-Common Met.*, **151**, 133 (1989).
7. K. H. Kim, D. Y. Yim, K. M. Choi, J. S. Choi, and R. G. Sauer, *J. Phys, Chem. Solids*, **50**, 1027 (1989).
8. D. Kim, K. M. Choi, K. H. Kim, and J. S. Choi, *ibid.*, **50**, 821 (1989).
9. K. H. Kim, S. H. Park, J. S. Choi, and K. W. Hyung, *ibid.*, **49**, 1019 (1988).
10. H. J. Won, S. H., Park, K. H. Kim, and J. S. Choi, *ibid.*, **48**, 383 (1987).
11. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* (Lond.), **57**, 160 (1945).
12. Y. Y. Kim, K. H. Kim, and J. S. Choi, *J. Phys. Chem. Solids*, **50**, 903 (1989).
13. B. E. Gushee, L. Katz, and R. Ward. *J. Am. Chem. Soc.*, **79**, 5601 (1957).
14. H. A. Laitenen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

The Approximate Electronic Solutions in A Closed Form, for f.c.c., b.c.c. and h.c.p. Clusters

Gean-Ha Ryu and Hojing Kim*

Department of Chemistry, Seoul National University, Seoul 151-742. *Received August 1, 1990*

A cluster made of N_A, N_B and N_C atoms in the x, y and z directions respectively, is treated with Hückel method. We obtain the approximate expressions for the eigenvalues and eigenvectors of f.c.c., b.c.c. and h.c.p. clusters in closed forms. The maximum and minimum values of the band so obtained converge to those derived from the Bloch sum in the limit of infinite extension. For a small cluster (of $9\times9\times5$ atoms, for instance), LDOS from the analytical (approximate) solution manifests better agreement at the surface, than inside the bulk.

Introduction

There are two main streams in assessing the interaction between an adsorbate and a solid substrate. The methods of solid state physics[1-3] treat the substrate as a semi-infinite solid, which has infinite extent in the $\pm x$, $\pm y$, and $-z$ direction and has surface at $z=0$, or as *slab*, which is a solid of finite thickness Δz but has infinite extent in the $\pm x$ and $\pm y$ directions. On the other hand, the methods of molecular quantum theory[4-6] approximate the metal substrate as a cluster of finite number of atoms.

One question which immediately comes to mind with regard to cluster representing a metal substrate is: how many atoms are needed in the cluster to *describe the metal* ? The answer to this question will obviously depend upon which properties of metal one wishes to describe. Empirically,[7-9] it is known that localized effects, such as metal-adsorbate bonding, can be treated successfully with a moderate size of cluster which is within a computational reach through most molecular orbital methods. However a cluster of 50 atoms or less, which is already quite a computational feat, would be sorely inadequate for the discussion of a number of solid state aspects of the substrate, such as bulk cohesive energies and work functions. In practice, therefore, one should investigate and justify the convergence of results as a function of cluster size. It would be very convenient, if one has an analytical measure, to treat a cluster of an arbitrary size, in a consistent way. In a limit of infinite size, the method should reproduce the results derived from bulk solid.

Using simple Hückel theory, Messmer[10] had shown that for a simple cubic (s.c.) array of atoms, the eigenvalues and eigenvectors can be obtained in a closed form for any size of cluster up to the infinite solid.

Here an extension of this to other lattices is intended. That is, the solution of closed form is persued, within a framework of Hückel theory. The major obstacle is a large coordination number (12 for face centered cubic, while 6 for simple cubic) which leads to an unfavorable form of the secular matrix. A cluster of average configuration is thus conjectured, and there results energy matrix of manageable form. Analytic (Hückel type) solutions for face centered cubic

(f.c.c.), body centered cubic (b.c.c.) and hexagonal close-packed (h.c.p.) lattices are derived. In the limitting case of an infinite extension, the maximum and minimum eigenvalues from the present method can be identified with those from the Bloch function[11] describing the infinite lattice.

Theory

It is started with a simple one-electron Hamiltonian $\hat{H}$, within a tight-binding linear combination of atomic orbital approximation. If one chooses a cluster with one atomic *s*-orbital x per site for simplicity and only interactions from the nearest neighbors are taken into account, then the system is completely characterized by its Hamiltonian matrix elements given by

$$\langle\chi_\mu \mid \hat{H} \mid \chi_\mu\rangle = \varepsilon_0 \tag{1}$$

$$\langle\chi_\mu \mid \hat{H} \mid \chi_\nu\rangle = \begin{cases} t & \text{(if } \mu \text{ and } \nu \text{ are the nearest neighbors)} \\ 0 & \text{(otherwise)} \end{cases} \tag{2}$$

The subscript is a label for the site of atomic orbitals. As it is common in the tight-binding approximation, the overlap integrals are neglected, *i.e.*,

$$\langle\chi_\mu \mid \chi_\nu\rangle = \delta_{\mu\nu} \tag{3}$$

Assuming that the cluster consists of N_A, N_B and N_C atoms in the x, y, and z directions, respectively, one can arrive at a secular equation

$$(H-\underline{\varepsilon})D=0 \tag{4}$$

of dimension $N_AN_BN_C \times N_AN_BN_C$. The matrix H contains the matrix elements of Eqs.(1) and (2), the matrix $\underline{\varepsilon}$ is the unit matrix multiplied with ε; D is the eigenvector matrix (column vector), which is made of the linear coefficients $d_{\alpha\beta}$ of the atomic orbitals such that

$$\Psi_\beta = \sum_\alpha d_{\alpha\beta}\chi_\alpha \quad \beta = 1, 2, \cdots, N_AN_BN_C \tag{5}$$

Then the eigenvalues are obtained by the solution of

$$\mid C \mid = \mid H-\underline{\varepsilon} \mid = 0. \tag{6}$$

The index l of each atom in the cluster is given by

$$l=(i, j, k) \tag{7}$$

where $i=1,\cdots N_A$, $j=1,\cdots N_B$, $k=1,\cdots N_C$, and i, j and k provide a sequential label for the positions along the x, y and z axes, respectively. The serial number of the atom is

$$\alpha=(k-1)\ N_BN_A+(j-1)\ N_A+i \tag{8}$$

The f.c.c. cluster stacked with (1, 0, 0) planes (Figure 1) is considered.

The matrix C of Eq.(6) for the cluster is

$$C=\begin{bmatrix} B & tJ_B & 0_B & 0_B & 0_B & \cdots\cdots \\ \tilde{tJ}_B & B & \tilde{tJ}_B & 0_B & 0_B & \cdots\cdots \\ 0_B & tJ_B & B & tJ_B & 0_B & \cdots\cdots \\ 0_B & 0_B & \tilde{tJ}_B & B & \tilde{tJ}_B & \cdots\cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{9}$$

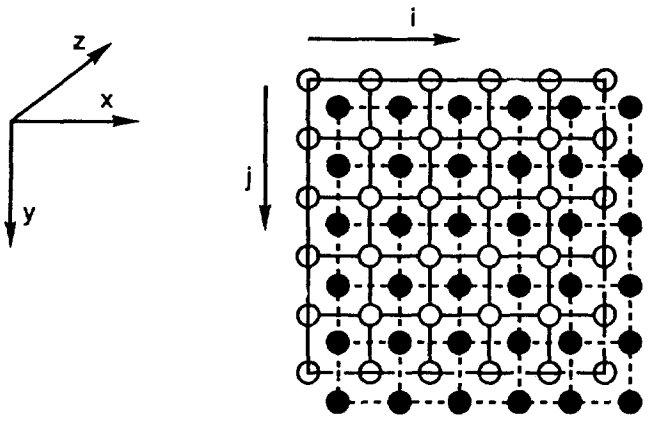

Figure 1. The f.c.c. cluster. The open circles denote atoms at first, third, ...layers and the shaded are for second, fourth, ...planes of (1, 0, 0).

where the matrix $\tilde{J}_B$ is the transpose of the matrix J_B, and the matrix O_B is a null matrix with the dimension of the matrix B. The C is an $N_C \times N_C$ matrix when written in terms of these B, J_B, $\tilde{J}_B$ and O_B matrices of the identical dimension. The matrices B and J_B are

$$B=\begin{bmatrix} A & tI_A & 0_A & 0_A & \cdots\cdots \\ tI_A & A & tI_A & 0_A & \cdots\cdots \\ 0_A & tI_A & A & tI_A & \cdots\cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{10}$$

and

$$J_B=\begin{bmatrix} J_A & 0_A & 0_A & \cdots\cdots \\ J_A & J_A & 0_A & \cdots\cdots \\ 0_A & J_A & J_A & \cdots\cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{11}$$

which again have elements which are themselves matrices. In terms of A, J_A, I_A and O_A, the matrices B, J_B and $\tilde{J}_B$ are of dimension $N_B \times N_B$. The matrices I_A and O_A are the unit and null matrices, respectively, with the dimension of A. The matrices A and J_A are

$$A=\begin{bmatrix} \varepsilon_0-\varepsilon & t & 0 & 0 & \cdots\cdots \\ t & \varepsilon_0-\varepsilon & t & 0 & \cdots\cdots \\ 0 & t & \varepsilon_0-\varepsilon & t & \cdots\cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{12}$$

and

$$J_A=\begin{bmatrix} 1 & 0 & 0 & \cdots\cdots \\ 1 & 1 & 0 & \cdots\cdots \\ 0 & 1 & 1 & \cdots\cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} \tag{13}$$

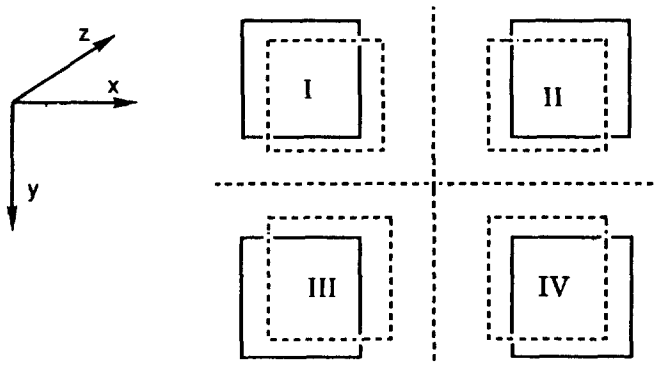

Figure 2. The f.c.c. clusters with four different configurations. The solid line depicts the odd-numbered layers and the broken line represents the even-numbered layers.

which have dimension of $N_A \times N_A$. The matrix C, of a single configuration, has overall dimension of $N_A N_B N_C \times N_A N_B N_C$.

Here, the matrix C is not a very convenient form for analytic diagonalization. Four clusters ($N_A = N_B$) are taken, which are created by rotation of 90 degrees about the z-axis from previous one successively, (Figure 2).

Labeling of the atoms, and atomic orbitals, in each layer starts from the upper left corner to the lower right corner (see Figure 1). The four configurations, which are physically equivalent, then give slightly different forms of secular matrices. The arithmetical mean of the four matrices is a fairly simple form as follows.

$$C' = \begin{bmatrix} B & \frac{t}{4}K_B & 0_A & 0_B & \cdots \\ \frac{t}{4}K_B & B & \frac{t}{4}K_B & 0_B & \cdots \\ 0_B & \frac{t}{4}K_B & B & \frac{t}{4}K_B & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{14}$$

In terms of the element B and $\frac{t}{4}K_B$, the matrix C' is of dimension $N_C \times N_C$. The matrix K_B is

$$K_B = \begin{bmatrix} 2K_A & K_A & 0_A & 0_A & \cdots \\ K_A & 2K_A & K_A & 0_A & \cdots \\ 0_A & K_A & 2K_A & K_A & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{15}$$

The matrix K_B is of dimension $N_A \times N_A$, with each element being itself a matrix. The matrix K_A is

$$K_A = \begin{bmatrix} 2 & 1 & 0 & 0 & \cdots \\ 1 & 2 & 1 & 0 & \cdots \\ 0 & 1 & 2 & 1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{16}$$

with the dimension of $N_A \times N_A$. Thus the matrix C' has overall dimension of $N_A N_A N_C \times N_A N_A N_C$.

The procedure one will adopt to obtain the solution of $|C'| = 0$, may not be the most elegant derivation, but it has an advantage of being straightforward. To solve the problem, it is only necessary to obtain the eigenvalues and the eigenvectors of the following type of $n \times n$ matrix:

$$\begin{bmatrix} a & b & 0 & 0 & \cdots \\ b & a & b & 0 & \cdots \\ 0 & b & a & b & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{17}$$

They are given as follows[12]:

$$\lambda_k = a + 2b \cos\frac{k\pi}{n+1} \tag{18}$$

and

$$\chi^{(k)} = \begin{bmatrix} \chi_1^{(k)} \\ \chi_2^{(k)} \\ \vdots \\ \chi_n^{(k)} \end{bmatrix} \tag{19}$$

where $$\chi_j^{(k)} = \left(\frac{2}{n+1}\right)^{1/2} \sin\frac{kj\pi}{n+1} \tag{20}$$

$j = 1, 2, \cdots, n$

$k = 1, 2, \cdots, n.$

Now, one can obtain the eigenvalues and the eigenvectors of the matrix C':

$$B_n = B + \frac{1}{2}tK_B \cos\frac{n\pi}{N_c+1} \tag{21}$$

$$u_c(k, n) = \left(\frac{2}{N_c+1}\right)^{1/2} \sin\frac{kn\pi}{N_c+1} \tag{22}$$

$k = 1, 2, \cdots, N_c$

$n = 1, 2, \cdots, N_c.$

To represent B_n, one should revisit Eq.(17) with $n = N_A$

$$B_n = \begin{bmatrix} a & b & 0 & 0 & \cdots \\ b & a & b & 0 & \cdots \\ 0 & b & a & b & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{23}$$

where $$a = A + tK_A \cos\frac{n\pi}{N_c+1} \tag{24}$$

$$b = tI_A + \frac{1}{2}tK_A \cos\frac{n\pi}{N_c+1} \tag{25}$$

The eigenvalues and eigenvectors are

$$A_{mn}=A+t(K_A\cos\frac{n\pi}{N_c+1}+\cos\frac{m\pi}{N_A+1}\times(2I_A+K_A\cos\frac{n\pi}{N_c+1})) \quad (26)$$

$$u_B(j,\ m)=(\frac{2}{N_A+1})^{1/2}\sin\frac{jm\pi}{N_a+1} \quad (27)$$

$$j=1,\ 2,\ \cdots,\ N_A$$

$$m=1,\ 2,\ \cdots,\ N_A$$

respectively.
A_{mn} is an $N_A\times N_B$ matrix of the form,

$$A_{mn}=\begin{bmatrix} c & d & 0 & 0 & \cdots\cdots \\ d & c & d & 0 & \cdots\cdots \\ 0 & d & c & d & \cdots\cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \quad (28)$$

where

$$c=\varepsilon_0+2t(\cos\frac{m\pi}{N_A+1}+\cos\frac{n\pi}{N_c+1}+\cos\frac{m\pi}{N_A+1}\cos\frac{n\pi}{N_c+1}) \quad (29)$$

$$d=t(1+\cos\frac{n\pi}{N_c+1}+\cos\frac{m\pi}{N_A+1}\cos\frac{n\pi}{N_c+1}) \quad (30)$$

Therefore the eigenvalues and eigenvectors of the matrix A are given by:

$$\varepsilon_{lmn}=\varepsilon_0+2t(\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_A+1}+\cos\frac{n\pi}{N_c+1}\times(1+\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_A+1}+\cos\frac{l\pi}{N_A+1}\cos\frac{m\pi}{N_A+1})) \quad (31)$$

$$u_A(i,l)=(\frac{2}{N_A+1})^{1/2}\sin\frac{il\pi}{N_A+1} \quad (32)$$

$$i,\ l=1,\ 2,\ \cdots,\ N_A$$

The label β of the state is given similarly to α:

$$\beta=(n-1)N_AN_A+(m-1)N_A+1 \quad (33)$$

where $l,\ m,\ n=1,\ 2,\ ...,\ N_A$

Then the final results of an eigenvalue problem for f.c.c. cluster of arbitrary size are given by:

$$\varepsilon_\beta=\varepsilon_0+2t(\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_A+1}+\cos\frac{n\pi}{N_c+1}\times(1+\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_A+1}+\cos\frac{l\pi}{N_A+1}\cos\frac{m\pi}{N_A+1})) \quad (34)$$

$$d_{\alpha\beta}=u_c(k,\ n)\ u_B(j,\ m)\ u_A(i,\ l) \quad (35)$$

where $$u_A(i,\ l)=(\frac{2}{N_A+1})^{1/2}\sin(\frac{il\pi}{N_A+1}) \quad (36)$$

$$u_B(j,\ m)=(\frac{2}{N_A+1})^{1/2}\sin(\frac{jm\pi}{N_A+1}) \quad (37)$$

$$u_C(k,\ n)=(\frac{2}{N_C+1})^{1/2}\sin\frac{kn\pi}{N_C+1}) \quad (38)$$

Due to the averaging process of the four secular matrices, as stated earlier, the center of the atomic orbital x_α located at an atom of even-numbered layer is not well defined. The shortcoming is nothing but a price one has to pay to obtain an analytical form of eigenvalues. The matter is taken up later at the section of discussion.

One can derive the eigenvalues and the eigenvectors of b.c.c. and h.c.p. cluster, similarly to the case of f.c.c. cluster. The eigenvalues are:

$$\varepsilon_\beta=\varepsilon_0+2t\cos\frac{n\pi}{N_C+1}(1+\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_A+1}+\cos\frac{l\pi}{N_A+1}\cos\frac{m\pi}{N_A+1}) \quad (39)$$

for b.c.c. cluster;

$$\varepsilon_\beta=\varepsilon_0+2t(\cos\frac{l\pi}{N_A+1}+\cos\frac{m\pi}{N_B+1}+\cos\frac{n\pi}{N_C+1}+\cos\frac{l\pi}{N_A+1}\cos\frac{m\pi}{N_B+1}+\cos\frac{m\pi}{N_B+1}\cos\frac{n\pi}{N_C+1}+\cos\frac{l\pi}{N_A+1}\cos\frac{n\pi}{N_C+1}) \quad (40)$$

for h.c.p. cluster.
The eigenvectors are of the same forms as those of f.c.c. cluster (Eqs. 35-38). However, the molecular functions ψ_β are quite different since the positions of *s*-orbitals are characteristic of each lattice.

Discussion

In infinite solid, Bloch functions which are periodic in *k*-space satisfy the relation,

$$\Psi_n(\vec{k},\ \vec{r})=\Psi_n(\vec{k}+\vec{k}_m,\ \vec{r}) \quad (41)$$

where $\vec{r}$, $\vec{k}$ and $\vec{k}_m$ are a displacement in the real spece, a wave vector and a primitive translation in the reciprocal space, respectively. The Bloch functions can therefore be represented as a Fourier series

$$\Psi_m(\vec{k},\ \vec{r})=\frac{1}{\sqrt{N}}\sum_n a_m(\vec{R}_n,\ \vec{r})\ \exp(i\vec{k}\cdot\vec{R}_n) \quad (42)$$

where N and $\vec{R}_n$ are the number of unit cell and the primitive translation in real lattice. The functiion $a_m(\vec{R}_n,\ \vec{r})$ in the expansion is the Wannier function. With the tight-bonding model, the Wannier function $a_m(\vec{r}\text{-}\vec{R}_n)$ can be approximated by the atomic orbital $x(\vec{r}\text{-}\vec{R}_n)$. Taking only nearest neighbor interaction into account, one can show that[11]

$$E_m(\vec{k})=E_m^{at}+\int\chi_m^*(\vec{r})[V(\vec{r})-V^{at}(\vec{r})]\ \chi_m(\vec{r})d\tau$$

$$+ \sum_{\substack{\text{nearest}\\ \text{neighbors}}} \exp(i\vec{k}\cdot\vec{R}_n)\int\chi_m^*(\vec{r})[V(\vec{r})-V(\vec{r}-\vec{R}_n)]\ \chi_m(\vec{r}-\vec{R}_n)d\tau. \quad (43)$$

If *s*-orbital is exclusively considered as an atomic function, the integrals in the sum on the right-hand side are equal. If a is the lattice constant, Eq.(43) can be written with further abbreviations,[13]

$$E_m(k)=E_m^{at}+C_m+4t(\cos\frac{a}{2}k_x\ \cos\frac{a}{2}k_y + \cos\frac{a}{2}k_y\cos\frac{a}{2}k_z\ +\cos\frac{a}{2}k_z\ \cos\frac{a}{2}k_x) \quad (44)$$

for f.c.c.;

$$E(k)=E_m^{at}+C_m+8t\ \cos\frac{a}{2}k_x\ \cos\frac{a}{2}k_y\ \cos\frac{a}{2}k_z \quad (45)$$

for b.c.c., where

$$C_m=\int\chi_m^*(\vec{r})[V(\vec{r})-V^{at}(\vec{r})]\chi_m(\vec{r})d\tau. \quad (46)$$

Table 1. Convergence of f.c.c. Cluster Analytical Solution (in units of-t)

N	No. of atoms	E_{min}	E_{max}	Band Width	Fraction of surface atoms
3	27	−6.949747	2.949748	9.899495	.962963
4	64	−8.531153	3.295085	11.826238	.875000
5	125	−9.495190	3.495191	12.990381	.784000
6	216	−10.115506	3.621547	13.737054	.703704
7	343	−10.534652	3.706225	14.240876	.635569
8	512	−10.829783	3.765606	14.595389	.578125
9	729	−11.044850	3.808783	14.853633	.529492
10	1000	−11.206135	3.841121	15.047255	.488000
11	1331	−11.330048	3.865946	15.195994	.452292
12	1728	−11.427231	3.885407	15.312638	.421296
13	2197	−11.504813	3.900937	15.405750	.394174
14	2744	−11.567706	3.913525	15.481231	.370262
15	3375	−11.619383	3.923865	15.543249	.349037
16	4096	−11.662351	3.932462	15.594814	.330078
17	4913	−11.698456	3.939686	15.638142	.313047
18	5832	−11.729081	3.945812	15.674893	.297668
19	6859	−11.755279	3.951053	15.706332	.283715
20	8000	−11.777861	3.955570	15.733431	.271000
21	9261	−11.797463	3.959491	15.756954	.259367
22	10648	−11.814585	3.962916	15.777501	.248685
23	12167	−11.829628	3.965925	15.795552	.238843
24	13824	−11.842915	3.968582	15.811497	.229745
25	15625	−11.854708	3.970941	15.825649	.221312
26	17576	−11.865224	3.973044	15.838268	.213473
27	19683	−11.874639	3.974927	15.849567	.206168
28	21952	−11.883102	3.976620	15.859723	.199344
29	24389	−11.890738	3.978147	15.868885	.192956
30	27000	−11.897649	3.979530	15.877179	.186963
40	64000	−11.941402	3.988280	15.929682	.142625
50	125000	−11.962103	3.992421	15.954523	.115264
60	216000	−11.973499	3.994700	15.968199	.096704
70	343000	−11.980434	3.996087	15.976521	.083289
80	512000	−11.984965	3.996993	15.981958	.073141
90	729000	−11.988086	3.997617	15.985704	.065196
100	1000000	−11.990328	3.998066	15.988394	.058808

Table 2. Convergence of b.c.c. Cluster Analytical Solution (in units of-t)

N	No. of atoms	E_{min}	E_{max}	Band Width	Fraction of surface atoms
3	27	−4.121320	4.121321	8.242641	.962963
4	64	−5.295085	5.295085	10.590170	.875000
5	125	−6.031089	6.031089	12.062178	.784000
6	216	−6.511631	6.511631	13.023262	.703704
7	343	−6.839134	6.839134	13.678267	.635569
8	512	−7.071013	7.071013	14.142026	.578125
9	729	−7.240624	7.240625	14.481249	.529492
10	1000	−7.368163	7.368163	14.736326	.488000
11	1331	−7.466345	7.466345	14.932689	.452292
12	1728	−7.543464	7.543464	15.086928	.421296
13	2197	−7.605101	7.605101	15.210202	.394174
14	2744	−7.655116	7.655116	15.310232	.370262
15	3375	−7.696242	7.696242	15.392485	.349037
16	4096	−7.730459	7.730459	15.460918	.330078
17	4913	−7.759225	7.759225	15.518450	.313047
18	5832	−7.783636	7.783636	15.567272	.297668
19	6859	−7.804525	7.804526	15.609051	.283715
20	8000	−7.822538	7.822538	15.645076	.271000
21	9261	−7.838177	7.838177	15.676354	.259367
22	10648	−7.851841	7.851841	15.703682	.248685
23	12167	−7.863848	7.863849	15.727697	.238843
24	13824	−7.874456	7.874456	15.748912	.229745
25	15625	−7.883873	7.883873	15.767746	.221312
26	17576	−7.892270	7.892270	15.784541	.213473
27	19683	−7.899790	7.899790	15.799581	.206168
28	21952	−7.906551	7.906551	15.813101	.199344
29	24389	−7.912650	7.912650	15.825300	.192956
30	27000	−7.918172	7.918172	15.836344	.186963
40	64000	−7.953139	7.953139	15.906278	.142625
50	125000	−7.969689	7.969689	15.939378	.115264
60	216000	−7.978803	7.978803	15.957606	.096704
70	343000	−7.984349	7.984349	15.968698	.083289
80	512000	−7.987973	7.987973	15.975946	.073141
90	729000	−7.990470	7.990470	15.980940	.065196
100	1000000	−7.992263	7.992263	15.984526	.058808

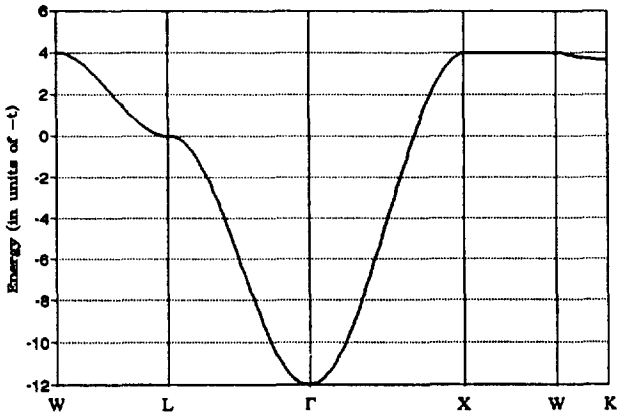

Figure 3. S-type band structure of the face centered cubic (f.c.c.) lattice, computed by Eq.(44).

and the wave vector k is limited to Brillouin zone.

The analytic solutions of finite clusters(Table 1, 2) conver-

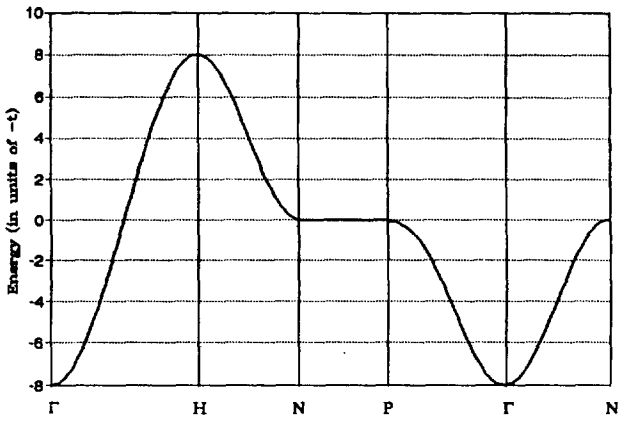

Figure 4. S-type band structure of the body centered cubic (b.c.c.) lattice, computed by Eq.(45).

ge to the results of Eqs.(44) and (45) of infinite lattice cases (Figure 3, 4), in the minimum and maximum of the energy (band width).

Now, the last but the most important question to be answered is: how well the analytic solution based on the "average configuration" does represent the real lattice? Since the density of states, especially the local one, depends on both the set of eigenvalues and eigenvectors, it would be logical to compare those(DOS and LDOS) from the numerical solution of the lattice of the configuration I of Figure 2, with those from the analytical solution obtained by the "average" configuration, for the moderate size of the cluster. The DOS and LDOS at the atom with index α is given by[14]

$$\rho(E)=\sum_{\beta}\delta(E-\varepsilon_{\beta}) \quad \text{(for DOS)} \tag{47}$$

$$\rho_{\alpha}(E)=\sum_{\beta}|d_{\alpha\beta}|^2\,\delta(E-\varepsilon_{\beta}) \quad \text{(for LDOS)} \tag{48}$$

For finite clusters, one can replace the delta function by a Gaussian of the width parameter σ. Thus Eqs.(47) and (48) become

$$\rho^{c}(E)=(2\pi\sigma^2)^{-1/2}\sum_{\beta}\exp[-(E-\varepsilon_{\beta})/2\sigma^2] \quad \text{(for DOS)} \tag{49}$$

$$\rho^{c}_{\alpha}(E)=(2\pi\sigma^2)^{-1/2}\sum_{\beta}|d_{\alpha\beta}|^2\ \exp[-(E-\varepsilon_{\beta})/2\sigma^2] \quad \text{(for LDOS)} \tag{50}$$

The $\varepsilon_o=0$ and $\sigma=0.075$ (in units of t) are taken in the present work.

Figure 5 compares the DOS's obtained by numerical solution with the analytical one, for the f.c.c. cluster of 5×5×5, 7×7×5 and 9×9×5 respectively. In the case of 100×100×100 cluster, the energy eigenvalues derived from Eq.(44) are used instead of the numerical solutions, *i.e.* the Brillouin zone is divided into 10^6 segments, and at center of each segment $E_m(k)$ of Eq.(44) is computed. For small clusters (up to 9×9×5 atoms), DOS's of the analytical solution agree with those of the numerical one. Since, for those clusters, the fractions of the surface atoms are relatively large (more than 50%), DOS may not be too different from LDOS at a surface atom. Consequently, one may interpret the close agreement

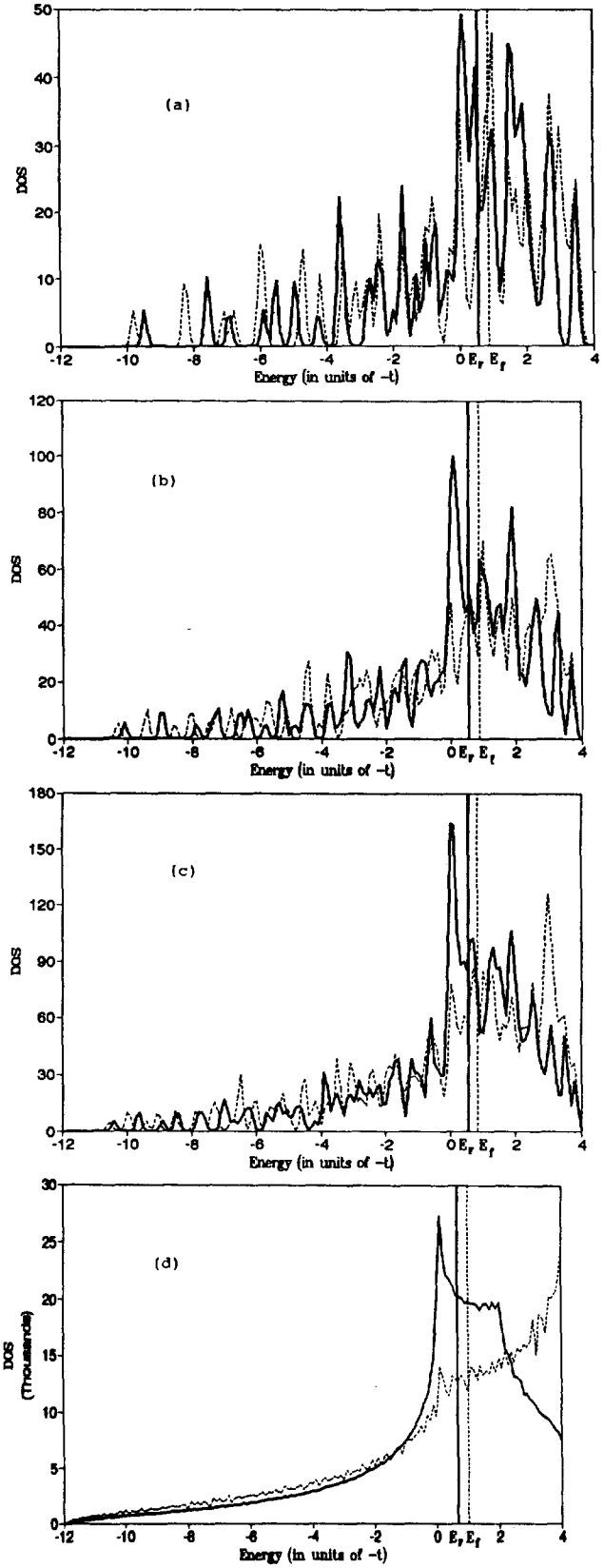

Figure 5. Density of states (DOS) of the face centered cubic (f.c.c.) clusters of (a) 5×5×5, (b) 7×7×5, (c) 9×9×5, (d) 100×100×100, atoms respectively. The solid line denotes the DOS from the analytical solution and the dashed line corresponds to the one from the numerical solutions for (a), (b) and (c), and Bloch sum for (d). E_f and E_f are Fermi levels.

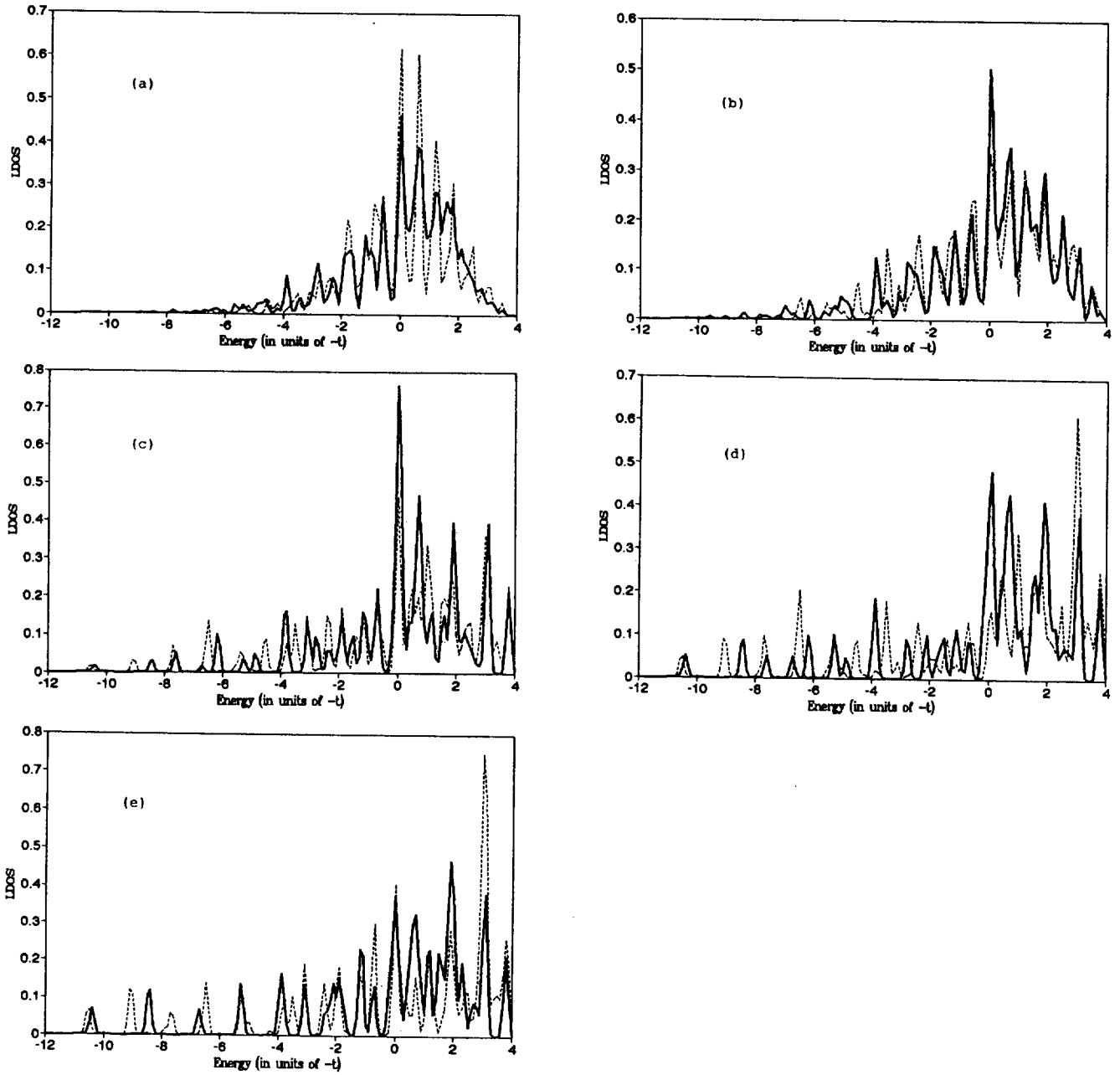

Figure 6. The local density of states (LDOS) of 9×9×5 f.c.c. cluster at (a) (1, 1, 1), (b) (5, 1, 1), (c) (5, 5, 1), (d) (5, 5, 2) and (e) (5, 5, 3). The position index is defined by Eq.(7) of the text. The solid line denotes the analytical solution and the dashed line corresponds to the numerical solution (See text).

between DOS's as the agreement between LDOS at a surface atom. On the other hand for a large cluster of 100×100×100, where the fraction of surface atoms is mere 6 percent DOS from the analytical solution poorly copies the result from the Bloch sum, especially in the region of near and above the Fermi level. It means that the analytical solution is inadequate to describe the bulk properties which may depend sensitively on the DOS profile near the Fermi level.

The above observation of Figure 5 also is consistent with the fact, which Figure 6 will show shortly, that the LDOS from the analytical solution agrees with that from the numerical one better at surface than inside.

The advantage of the present work lies in the simplicity of calculation: the computation of eigenvalues for 10^6-atomic cluster, which is nearly impossible by the numerical method, requires only a few hours in PC. LDOS's (see Figure 6) from the analytic solution shows relatively good fit for that from the numerical solution at the region of the surface.

The work, however, has problems too. First, the analytically-obtained DOS agrees fairly well, for the cluster of atoms with singly occupied s-orbital, with numerical one nearly up to Fermi level, but doesn't around above Fermi level (see Figure 5). Therefore the solution may not be useful for treating bulk properties (cohesive energy, work function *etc*) and any effects associated with Fermi surface. Secondly, because the cubium cluster model used here is based on (1, 0, 0)

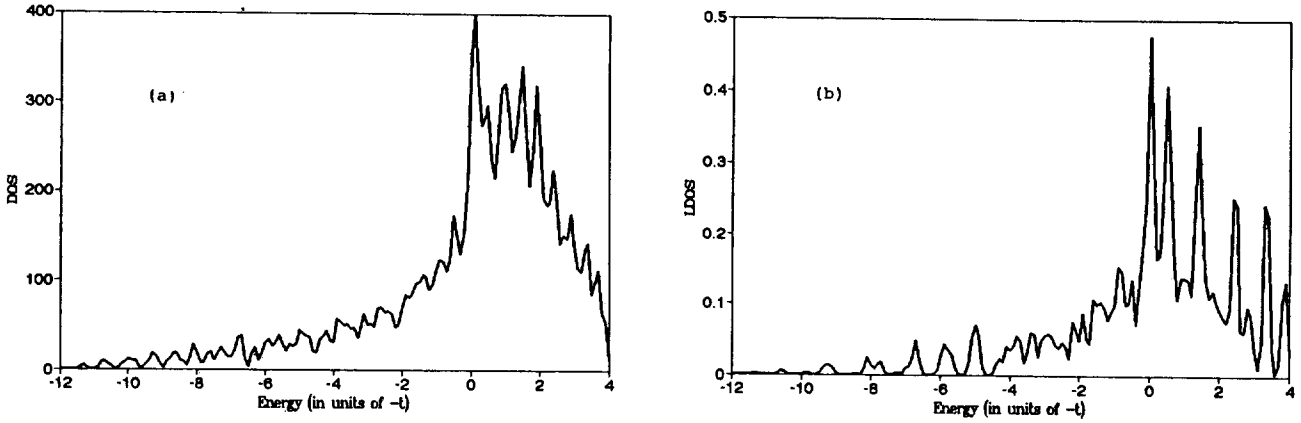

Figure 7. (a) The density of states (DOS) and (b) the local density of states (LDOS) at (6, 6, 1), of 11×11×11 f.c.c. cluster, computed with Eqs.(34) and (35) (See text.).

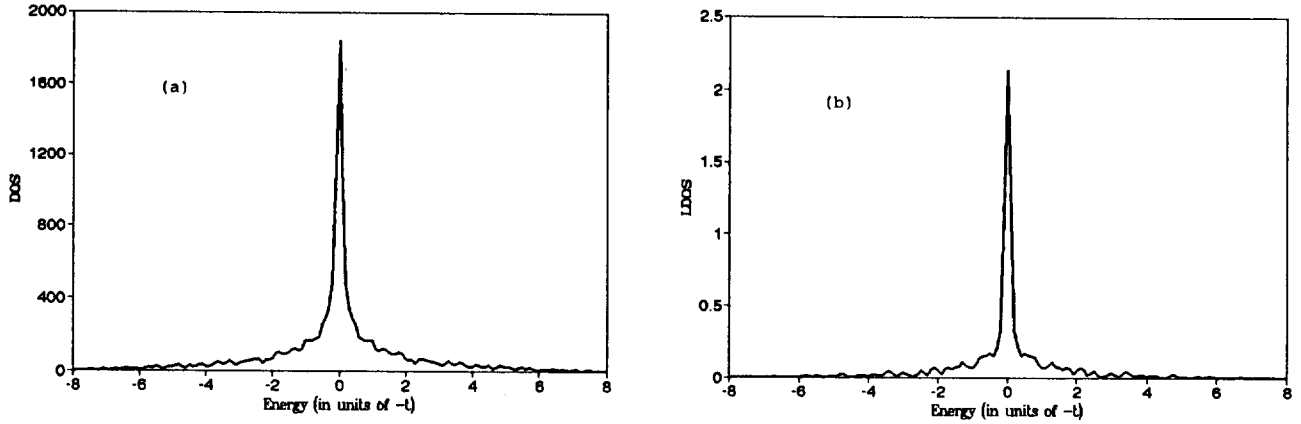

Figure 8. (a) DOS and (b) LDOS at (6, 6, 1), of 11×11×11 b.c.c. cluster, computed with Eqs.(35) and (39) (See text).

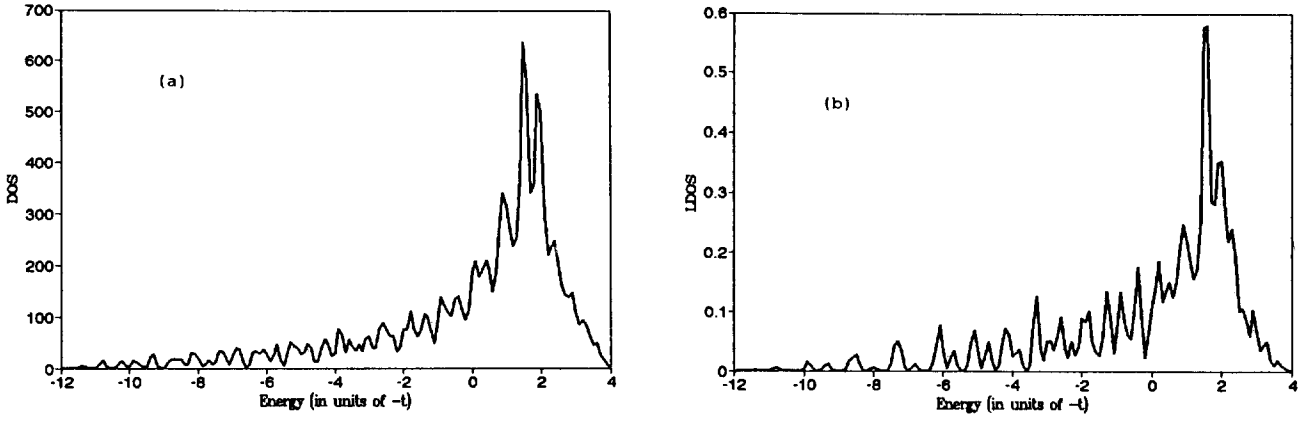

Figure 9. (a) DOS and (b) LDOS at (6, 6, 1), of 11×11×11 h.c.p. cluster, computed with Eqs.(35) and (40) (See text).

Miller index plane, it is not feasible to represent diverse surface other than this plane.

With the analytic cluster solution, The density of states (DOS) and local density of states (LDOS) for the clusters of 1331 atoms, which is a 11×11×11 array, have been computed. The DOS's of f.c.c. (Figure 7a) and h.c.p. (Figure 9a) seem to be unsymmetric; the minimum energy is farther apart than the maximum one from the origin, but the states are more densely distributed at high energy than at low energy. But the DOS of b.c.c. (Figure 8a) appears to be symmetric to the origin. In the b.c.c. lattice, the present model is rather inadequate since the nearest neighbors don't exist in a layer and so the off-diagonal elements of the matrix are far apart from the diagonal elements. The LDOS (Figure 7, 9) of each lattice has a general profile which is qualitatively similar to the DOS of itself, but the deviation, of each LDOS computed with analytic solution, from the one with numerical means becomes greater from surface to the inside of the bulk. Therefore, the analytic solution may be adequate for problems of adsorbate-substrate interactions, but may not

be so for bulk properties.

Acknowledgement. This work has been supported by the Korea Science and Engineering Foundation. Considerable thanks are given to Miss Eun-hee Suh for her typing.

References

1. O. Gunnarsson, H. Hjelmberg, and B. I. Lundgvist, *Phys. Rev. Lett.*, **37**, 292 (1976).
2. T. L. Einstein and J. R. Schrieffer, *Phys. Rev.*, **B7**, 3629 (1973).
3. T. B. Grimley and C. Pisani, *J. Phys. C: Solid State Phys.*, **7**, 2831 (1974).
4. D. J. M. Fassarert and A. von der Avoird, *Surface Sci.*, **55**, 291 (1976).
5. I. P. Batra and O. Robaux, *Surface Sci.* **49**, 653 (1975).
6. C. W. Jr., Bauschlicher, D. H. Liskow, C. F. Bender and H. F. Schaefer, *J. Chem. Phys.*, **62**, 4815 (1975).
7. T. H. Upton, P. Stevens, and R. J. Madix, *J. Chem. Phys.*, **88**, 3988 (1988).
8. K. Hermann, P. S. Bagus, and C. J. Nelin, *Phys. Rev.*, **B35**, 9467 (1987).
9. R. P. Messmer and D. R. Salahub, *Phys. Rev.*, **B16**, 3415 (1977).
10. R. P. Messmer, *Phys. Rev.*, **B15**, 1811 (1977).
11. O. Madelung, *Introduction to Solid-State Theory* (Springer Verlag Berlin) pp. 53-55 (1981).
12. R. T. Gregory and D. L. Karny, *Collection of matrices for testing computational algorithms* (Wiley-Interscience) p.137 (1969).
13. C. Kittel, *Introduction to Solid State Physics* (John Willy and Sons, Inc, New York) p. 232 (1986).
14. R. P Messmer, in *The Nature of the Surface Chemical Bond* (North-Holland Amsterdam) Ed., T. N. Rhodin and G. Ertl pp. 60-63 (1979).

A Study on Spin-Lattice Relaxation of Methyl Protons in 2,6-Dichlorotoluene and N-Methyl Phthalimide

Jo Woong Lee*, Man-Ho Lim, and Jung-Rae Rho

Department of Chemistry, Seoul National University, Seoul 151-742. *Received August 10, 1990*

Spin-lattice relaxation of methyl protons in 2,6-dichlorotoluene and N-methyl phthalimide, each dissolved in $CDCl_3$, has been studied at 34℃ and the contribution from spin-rotation interaction to the relaxation process has been separated from that due to dipole-dipole interactions among methyl protons. The results show that the spin-rotational contributions to the initial rate of relaxation in 2,6-dichlorotoluene and N-methyl phthalimide amount to 18 and 31%, respectively, of the total relaxation rate at 34℃. The method of separating the spin-rotational contribution from that of dipolar interactions adopted in this paper is based on the well known fact that in an A_3 spin system such as methyl protons in liquid phase dipolar relaxation mechanism gives non-exponential decay of the z-component of total magnetization of protons while the random field fluctuation such as spin-rotational mechanism causes exponential decay.

Introduction

It is nowadays a well-established fact that the study of nuclear magnetic relaxation can provide valuable informations regarding inter- and intramolecular interactions and their dynamical characters in bulk materials.[1] Relaxation of nuclear spins in a molecule is known to be caused by randomly fluctuating magnetic fields produced at the nuclear sites by various inter- and intramolecular interactions. Among these the most pronounced are (inter- and/or intramolecular) nuclear magnetic dipole-dipole interactions, spin-rotation interactions, nuclear electric quadrupole-electric field gradient interactions, chemical shift anisotropy interactions, scalar couplings of the first and second kind, and interactions due to the presence of paramagnetic molecular species.[2]

For protons in small organic molecules dissolved in a deuterated solvent such as $CDCl_3$, it is known that only inter- and intramolecular dipole-dipole interactions and the spin-rotation interactions are the two major relaxation mechanisms to be considered and the contributions from other causes can safely be ignored.[3,4] The dipolar interactions are usually a dominating factor; however, if the molecule is of highly symmetrical shape and can undergo easy rotational motions in bulk phase, the spin-rotational contribution may be appreciable in magnitude.[5] Such seems to be the case also for protons located on a methyl group which can undergo rapid internal rotation about its own axis of symmetry with respect to the molecular frame.

Since dipolar and spin-rotational contributions are known to provide different kinds of molecular motional informations between them, it is of great importance to distinguish one from the other.[6] Many NMR investigators have probably had more or less frustrating experiences that for protons on a methyl group they did not have an easy and legitimate means at hand by which they could separate dipolar contributions from those due to spin-rotation interactions in their

* To whom correspondence should be addressed