Research Report

# Electronic State Calculation for Hydrogen Atom under Inhomogeneous Field

Shunsuke Yamakawa and Shi-aki Hyodo

## Abstract

We discuss herein the effectiveness of the Gaussian-finite element (FE) mixed basis method for the purpose of calculating the electronic state under an inhomogeneous electrostatic field. FE basis functions, which possess high degrees of freedom, are combined with Gaussian basis functions in order to describe the steeply varying electron distribution near the nuclei. First, this method was applied to the electronic state calculation for a hydrogen atom without external fields. It was shown that FE basis functions automatically expressed the part of the wave function which can not be expressed using only Gaussian basis functions. Secondly, the model, in which a hydrogen atom was positioned between two conductors, was applied in order to discuss the electronic state of hydrogen in the grain boundary of the polycrystalline metal. The spherical conductors and the crystal grains were adopted as conductors of nanometer scale. The crystal grains were extracted from the polycrystalline structure by 3-D Phase Field simulation. The eigenvalue of the hydrogen atom was found to depend on the diameter of the spherical conductors when the diameter was less than 5 nm. The wave function of the hydrogen atom was distorted due to the complicated grain configuration. The FE basis functions effectively represented the wave function distorted by the existence of inhomogeneous electrostatic fields.

Keywords: Electronic state, Hydrogen, Finite element method, Gaussian function, Polycrystalline, Phase Field method

## 1. Introduction

Hydrogen diffusion in metals is influenced by short-range disorders, such as lattice defects, and long-range disorders, such as the geometry of grain boundaries, especially for nano-polycrystalline.[1, 2] Therefore, the energy dispersion of the hydrogen occupying site arises due to the external electrostatic field induced by the disorders.

Finite element method (FEM) has been regarded as one of the possible techniques for electronic state calculation taking into account this type of inhomogeneous field, because of the high applicability to arbitrary boundary conditions and high degrees of freedom of the basis functions. The FEM has already been applied to the electronic state calculations.[3, 4, 5] However, in order to achieve high accuracy using only FEM, the required number of basis functions is extremely large. The sharp variation in a wave function near nuclei makes this problem more serious. This situation indicates that FEM has a high computational cost. A number of improved techniques, such as the adoptive mesh[5] and pseudopotential[6] techniques, have been proposed. However a difficulty still remains in the case of the electronic state with the large electron density gradient near the nucleus such as metal atom. Therefore, we attempted to reinforce FE basis functions by combining Gaussian basis functions. We think that the high applicability of FE basis functions to an arbitrary inhomogeneous field can be kept in this mixed basis method by using appropriate Gaussian basis components, which have finite amplitude only near the nucleus. Moreover, it is possible to combine this method and the above technique, adoptive mesh or pseudopotential.

**Section 2** outlines this method. **Section 3. 1** presents, as an example of the efficiency of this technique, the electronic state calculation of a hydrogen atom without external fields. **Sections 3. 2** and **3. 3** demonstrate the electronic state of a hydrogen atom under the external electrostatic potential that originated from inhomogeneous structures on the nanometer scale. In these sections, the electronic state of hydrogen in the grain boundary of the nano-polycrystalline metals is discussed. Through the use of plane waves, a supercell model has been used for the electronic structure calculation of the grain boundary with impurities.[7] However, the actual grain boundary with limited curvature appears to differ from a 2-D-plane-like boundary which has been adopted by supercell model under the mesoscale structure. In the present paper, the spherical conductor model or the crystal grains, extracted from polycrystalline structure by 3-D Phase Field simulation, are examined as inhomogeneous structures of nanometer scale.

## 2. Gaussian-FE mixed basis method

We expand the wave function as the linear combination of Gaussian basis functions $\psi_G = (S_{g1},...,S_{gn})$ and FE basis functions $\psi_F = (S_{f1},...,S_{fm})$ in the form:

$$\psi(\boldsymbol{r}) = \boldsymbol{C} \cdot \varphi, \quad \cdots (1)$$

where

$\boldsymbol{C} = (C_{g1},...,C_{gn}, C_{f1},...,C_{fm})$,

$\varphi = (\varphi_1,...,\varphi_{n+m}) = (\psi_G, \psi_F) = (S_{g1},...,S_{gn}, S_{f1},...,S_{fm})$.

The coefficient $\boldsymbol{C}$ is determined by solving the Schrödinger-type equation described later.

First, for simplicity, we explain the FE basis function for the case of a one-dimensional grid. In the present study, we used the first-order basis function in the form:

$$S_f(x) = 1 - |x| \quad \text{with } |x| \le 1. \quad \cdots (2)$$

This is the simplest formulation. **Figure 1** shows the shape of this function in comparison with Gaussian basis functions. In contrast with Gaussian basis functions ranging over an element, this basis function extends only out to the neighboring nodal points.

On a three-dimensional uniform grid, we use the products of the one-dimensional functions in the form:

$$S_f(\boldsymbol{r}) = S_{fx}(x)S_{fy}(y)S_{fz}(z). \quad \cdots (3)$$

Eight FE basis functions are assigned to each element.

As Gaussian basis functions appropriate for hydrogen atom, the following functions[8] have been proposed:

$$\psi_G = C_{g1}S_{g1} + C_{g2}S_{g2}, \quad \cdots (4)$$

where

$$S_{g1} = \sum_{i=1}^{3} \beta_{1i} f_{1i}(\alpha_{1i}, l, m, n), \; S_{g2} = f_{21}(\alpha_{21}, l, m, n),$$

$f_i(\alpha_i, l, m, n) = x^l y^m z^n \exp(-\alpha_i \boldsymbol{r}_H^2)$,
$\alpha_{11} = 18.731088$, $\alpha_{12} = 2.8253952$,
$\alpha_{13} = 0.64012176$, $\alpha_{21} = 0.161277552$,
$\beta_{11} = 0.0334946$, $\beta_{12} = 0.2347270$,
$\beta_{13} = 0.8137570$
$l = m = n = 0$, $\boldsymbol{r}_H$ : position vector relative to nucleus position.

This basis function set is generally referred to as 31G. In order to certify the effectiveness of the contribution of FE basis functions, the following basis functions, which reduced the number of basis functions, were also examined:

3G : $\psi_G = C_{g1} S_{g1} = C_{g1} ( \beta_{11} f_{11} + \beta_{12} f_{12} + \beta_{13} f_{13})$,
2G : $\psi_G = C_{g1} ( \beta_{11} f_{11} + \beta_{12} f_{12} )$.

In the present study, electronic state calculation is carried out using the Hartree approximation.

$$\boldsymbol{H} \cdot \boldsymbol{C} = E\boldsymbol{U} \cdot \boldsymbol{C}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

where

$$\boldsymbol{H}_{ij} = \int d\boldsymbol{r} \varphi_i \left( -\frac{1}{2}\nabla^2 + \frac{-Z_H}{|\boldsymbol{r}_e - \boldsymbol{R}_H|} + V_{ad}(\boldsymbol{r}_e) \right) \varphi_j,$$

$$\boldsymbol{U}_{ij} = \int d\boldsymbol{r} \varphi_i \varphi_j,$$

and $Z_H$ is 1.0. The contributions from all elements are assembled to construct the global matrices $\boldsymbol{H}_{ij}$ and $\boldsymbol{U}_{ij}$. $V_{ad}(\boldsymbol{r}_e)$ is the additional external potential due to the mesoscale inhomogeneous structure. The generalized eigenvalue problem, Eq. (5), was solved by combining the conjugate gradient (CG) method[9] and the inverse iteration method.[10]

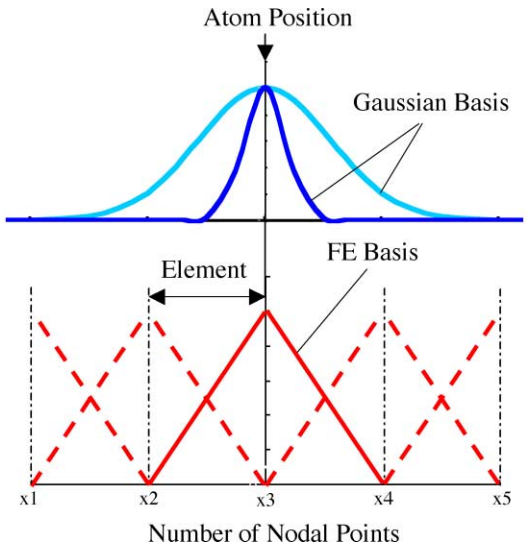


**Fig. 1** Schematic representation of Gaussian and 1-D FE basis functions. FE basis functions on neighboring nodal points are shown by broken lines.

## 3. Results and discussion

### 3. 1 Electronic state of hydrogen atom

The electronic state calculations for a hydrogen atom were performed in order to investigate the contribution of FE basis functions combined with various Gaussian basis functions. The number of nodal points per dimension was 23. The element width was set to 0.5 bohr (1 bohr ≒ 0.05291 nm) for all elements. The shape of this calculation region was cubic at $11 \times 11 \times 11$ bohr$^3$. **Table 1** shows the eigenvalues of the hydrogen atom using various basis functions. **Table 2** shows the contribution of Gaussian basis functions $\psi_G$ and FE basis functions $\psi_F$. The wave function of the hydrogen atom is not completely expressed by 2G alone, because 2G cannot express a spread part of the wave function. Similarly, approximation of only FE basis functions under this calculation condition also has low accuracy, because the basis functions cannot express a steeply varying part of the wave function near the

**Table 1** Eigenvalues (in hartree, 1 hartree ≒ $2.6255 \times 10^6$ J/mol) of the hydrogen atom using various Gaussian basis functions or using the corresponding Gaussian-FE mixed basis functions. The eigenvalue of FE basis functions alone was -0.4826 (hartree).

| | Gaussian | Gaussian -FE |
|---|---|---|
| 2G | ——— | -0.4913 |
| 3G | ——— | -0.4979 |
| 31G | -0.4954 | -0.4994 |
| Exact | -0.5 | |

**Table 2** Contribution of Gaussian basis functions $\psi_G$ and FE basis functions $\psi_F$ to the electron density $\psi^2$ of the hydrogen atom: $\psi^2 = (\psi_G + \psi_F)^2$.

| Basis Function | $\psi_G^2$ | $\psi_F^2$ | $2\psi_G\psi_F$ |
|---|---|---|---|
| 2G-FE | 0.0152 | 0.8872 | 0.0976 |
| 3G-FE | 0.1903 | 0.4352 | 0.3745 |
| 31G-FE | 1.2197 | 0.0151 | -0.2348 |

nucleus. On the other hand, the eigenvalue of 2G-FE mixed basis functions has almost the same accuracy as 31G alone. This is because 2G basis functions express the steeply varying part and FE basis functions express the spread part, as shown in **Fig. 2**(a). Unlike 2G, 31G can express an accurate wave function, as shown in the Fig. 2(b). For 31G-FE mixed basis functions, the contribution of FE basis functions decreases but remains in the spread part.

As a result of these calculations, FE basis functions automatically compensate for the part of the wave function which cannot be expressed by Gaussian basis functions alone.

### 3. 2 Hydrogen atom between two spherical conductors

**Figure 3** shows the schematic representation of the spherical conductor model. This model, in which a hydrogen atom is positioned between the two spherical conductors, is based on the assumption that metal atoms surrounding the hydrogen atom can be treated as a continuous conductive medium. The distance between the conductors (*a* in Fig. 3) was set to 2.5 bohr, roughly corresponding to the covalent bond radius of metal atom. Hydrogen atom is at the center of the line connecting the center of gravity of the conductors. The calculation scheme is as follows.

I. Sources of the electrostatic field are introduced by the charge distribution deduced from the electron and the nucleus charge of the hydrogen atom. Furthermore, the image charge is induced in both conductors to make the potential constant anywhere in the conductor. The electrostatic potential inside conductors and at the boundary were determined by analytical calculation using the abovementioned charges. The potential of the remaining region, $V(\boldsymbol{r})$, was determined by solving the following Poisson equation using the finite differential method (FDM).

$$\nabla^2 V(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r}) / \varepsilon_r \cdots\cdots\cdots\cdots\cdots\cdots (6)$$

$V_{ad}(\boldsymbol{r}_e)$ (in Eq. (5)) is equal to the potential obtained by subtracting the potential due to the electron and the nuclear charge of the hydrogen atom from $V(\boldsymbol{r})$.

II. The electronic state calculation of the hydrogen atom was performed according to Eq. (5). In this section, 3G-FE basis functions were used. The calculation conditions of FE basis functions are the same as those in **Section 3. 1**. In order to compensate the total sum of charges of the conductor, the electron density of the hydrogen atom spreading into the conductor was uniformly

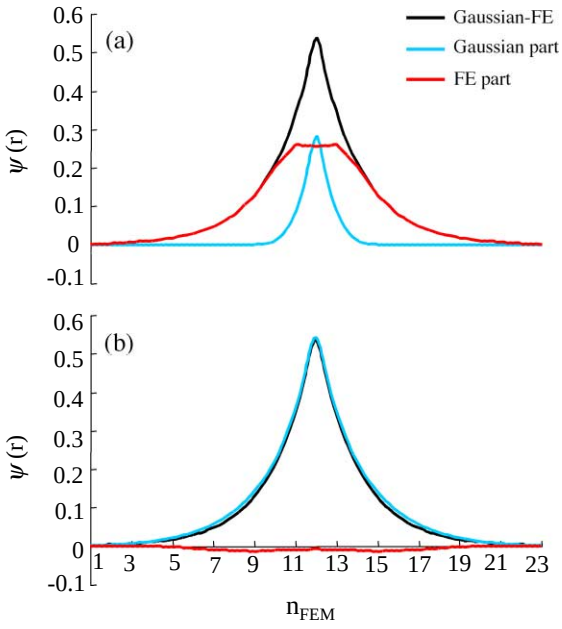


**Fig. 2** Wave function of the hydrogen atom: (a) using 2G-FE mixed basis functions and (b) using 31G-FE mixed basis functions. The abscissa $n_{FEM}$ denotes the number of nodal points.

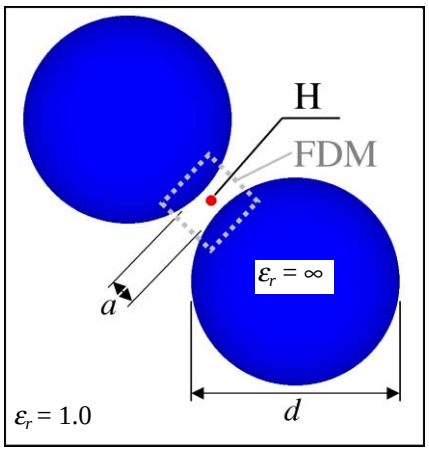


**Fig. 3** Schematic representation of the spherical conductor model. One hydrogen atom is positioned between the two spherical conductors. Relative dielectric constants $\varepsilon_r$ are respectively set to infinity in the conductor regions, and 1.0 in the region surrounding conductors.

redistributed over the conductor surface. This process (from I to II) was iterated until self-consistency was achieved.

**Figure 4** shows the relationship between the eigenvalue of the hydrogen atom and the conductor diameter (*d* in Fig. 3). There is no dependence of the eigenvalue on the diameter of spherical conductors when the diameter is larger than 5 nm. This suggests that 2-D-plane-like boundary using in the supercell model can be used for the problem of a hydrogen atom in the polycrystalline structure composed of grains of diameter larger than 5 nm. On the other hand, the eigenvalue was slightly dependent on the diameter when the diameter was less than 5 nm. Therefore, the electronic state calculation on this scale appears to require explicit consideration for the effect of grain configuration.

**Figure 5** shows the contour map of the wave function of the hydrogen atom inserted between two spherical conductors having a 10 nm diameter. The wave function was distorted by the existence of the spherical conductors. **Figure 6** shows the difference between the contribution of FE basis functions without external field and that in the spherical conductor model having a 10 nm diameter. The contribution increases in the inter-conductor region (red line in Fig. 6) and decreases inside conductors (blue line in Fig. 6). The distortion of the wave function in Fig. 5 is mainly expressed by FE basis functions.

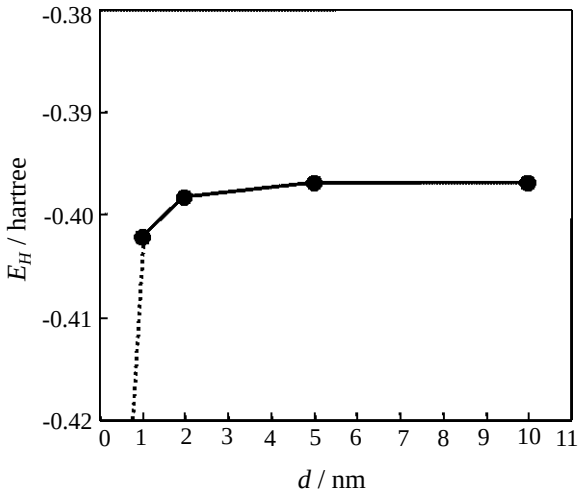


**Fig. 4** Relationship between the eigenvalue of hydrogen atom and the conductor diameter (*d* in Fig. 3).

### 3. 3 Hydrogen atom under polycrystalline-like boundary condition

In this section, an example of the wave function of a hydrogen atom in metallic polycrystalline-like boundaries is depicted. The mesoscopic structure was obtained from the 3-D Phase Field method[11] (PFM), which is based on the numerical evaluation of the time-dependent Ginzburg-Landau equation. The polycrystalline mesoscopic structure adopted

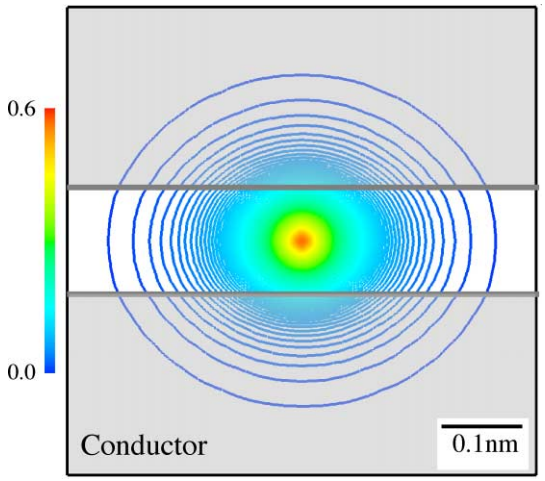


**Fig. 5** Contour map of the wave function of the hydrogen atom inserted between two spherical conductors having 10 nm diameter. The gray region denotes the conductor.

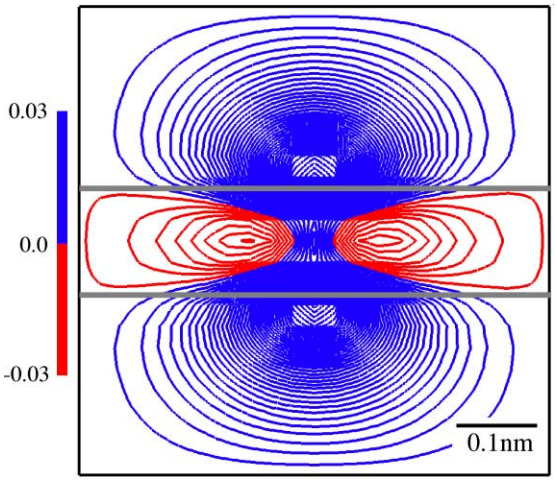


**Fig. 6** Contour map of the wave function difference $\Delta\psi_F$ : $\Delta\psi_F = \psi_F$ (without external field) - $\psi_F$ (in the spherical conductor model having a 10 nm diameter).

here is shown in **Fig. 7**. **Figure 8** shows the configuration of two grains extracted from PFM. Hydrogen atom was inserted into the grain boundary. The electrostatic potential and the corresponding wave function was obtained by the same procedure in **Section 3. 2**.

**Figure 9** shows the difference between the wave function in the spherical conductor model having a 2 nm diameter and that in PFM structure. The wave function was distorted depending on the complicated grain configuration. This result is introduced by the distributed electron charge and the nuclear charge of the hydrogen atom and the mesoscopic metallic boundary condition.

The present study is an introductory study of the electronic state calculation with the complex inhomogeneity of a mesoscopic environment. The wave function is expected to be significantly influenced by the configuration of an inhomogeneous electrostatic field. It was found that FE basis functions, which possess high degrees of freedom, effectively expressed the distortion of the wave function within the present examination. Therefore, this mixed basis method would be available for the electronic state calculation in an inhomogeneous electrostatic field.

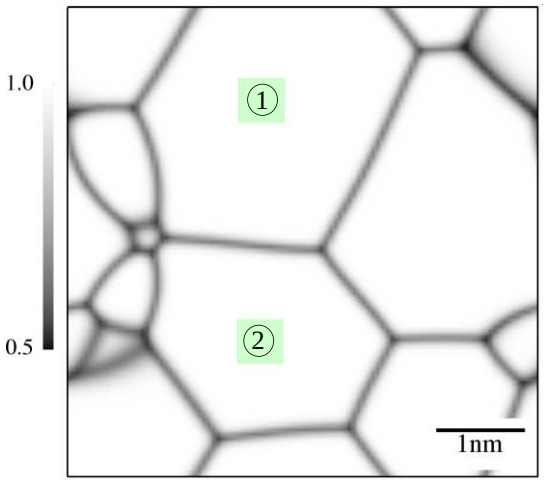


**Fig. 7** Polycrystalline mesoscopic structure obtained from 3-D Phase Field simulation. The grains of 1 and 2 were used as inhomogeneous structure for the electronic state calculation of a hydrogen atom.

## 4. Conclusions

We have examined the effectiveness of the Gaussian-FE mixed basis method for the purpose of calculating the electronic state under an inhomogeneous electrostatic field. Based on the present findings, the following conclusions were obtained. First, this method was applied to the electronic state calculation for a hydrogen atom

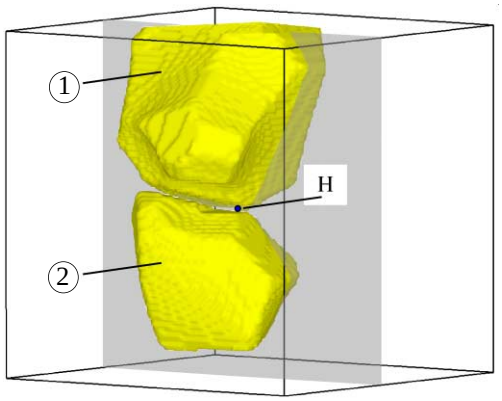


**Fig. 8** Configuration of two grains extracted from the polycrystalline structure. One hydrogen atom was inserted into the grain boundary. The numbers in circles are corresponding to those in Fig. 7.

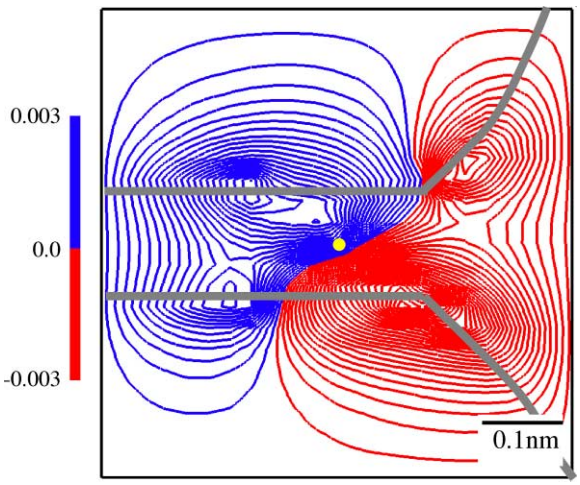


**Fig. 9** Contour map of the wave function difference $\Delta\psi$ : $\Delta\psi = \psi$ (in the spherical conductor model having a 2nm diameter) - $\psi$ (in the Phase Field grain model). Gray lines denote the interface between grain region and grain boundary region, and yellow dot denotes the position of the hydrogen atom.

without external fields. FE basis functions automatically expressed the part of wave function which can not be expressed using only Gaussian basis functions. Second, the model, in which a hydrogen atom was positioned between two conductors, was applied in order to discuss the electronic state of hydrogen in the grain boundary of the polycrystalline metal. The spherical conductors or the crystal grains were adopted as conductors of nanometer scale. The crystal grains were extracted from the polycrystalline structure by 3-D Phase Field simulation. The eigenvalue of the hydrogen atom was found to depend on the diameter of the spherical conductors when the diameter was less than 5 nm. The wave function of the hydrogen atom was distorted due to the complicated grain configuration. FE basis functions effectively represented the wave function distorted by the existence of inhomogeneous electrostatic fields.

## References


1) Hirscher, M., Mössinger, J. and Kronmuller, H. : J. Alloys Comp., **231**(1995), 267
2) Mütschele, T. and Kirchheim, R. : Scr. Met., **21**(1987), 135
3) White, S. R., Wilkins, J. W. and Teter, M. P. : Phys. Rev. B, **39**(1989), 5819
4) Pask, J. E., Klein, B. M., Fong, C. Y. and Sterne, P. A. : Phys. Rev. B, **59**(1999), 12352
5) Tsuchida, E. and Tsukada, M. : J. Phys. Soc. Jpn., **67**(1998), 3844
6) Pickett, W. E. : Comput. Phys. Reports, **9**(1989), 115
7) Krasko, G. L. and Olson, G. B. : Solid State Commun., **79**(1991), 113
8) Binkley, J. S., Pople, J. A. and Hehre, W. J. : J. Am. Chem. Soc., **102**(1980), 939
9) Gan, C. K., Haynes, P. D. and Payne, M. C. : Comput. Phys. Commun., **134**(2001), 33
10) Bathe, K.-J. and Wilson, E. L. : Numerical Methods in Finite Element Analysis, (1976), 417, Prentice-Hall, New Jersey
11) Fan, D. and Chen, L.-Q. : Acta Mater., **45**-2(1997), 611


(Report received on Dec. 26, 2002)


**Shunsuke Yamakawa**
Year of birth : 1969
Division : Organic Materials Lab.
Research fields : Computer simulation for materials design
Academic society : Chem. Soc. Jpn., Jpn. Inst. Metals



**Shi-aki Hyodo**
Year of birth : 1955
Division : Organic Materials Lab.
Research fields : Computational chemistry, Electronic structure theory, Mesoscopic structure theory
Academic degree : Dr. Sci.
Academic society : Chem. Soc. Jpn., Soc. Poly. Sci. Jpn.