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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

旨

要

不均一静電場中における電子状態計算を目的と してGauss-FE混合基底法の開発を行っている。 有限要素法 (FEM) で用いられる基底関数(以下, FE基底関数)は局所基底のため高い自由度を具 備しており,不均一場によって歪んだ波動関数を 表現するのに適していると考えられる。原子核付 近での波動関数の急峻な変化を表現するため,原 子核近傍に局在したGauss関数をFE基底関数と組 み合わせた。本計算手法の適用対象の一つとして は,ナノ多結晶体中の水素原子の電子状態計算を 想定している。

最初に,Gauss-FE混合基底法を水素原子の電子 状態計算に適用し,Gauss関数とFE基底関数が相 互補完して波動関数を表現することを確認した。 次に,2つの金属結晶粒に挟まれた粒界に水素原 子が位置していることを想定して,2つの導体間 に水素原子を設置した。導体モデルとしては球体 とフェーズフィールド法で作成した多結晶組織か ら抽出した結晶粒を用いた。導体球を用いたモデ ル計算では,球径が5nm以下の場合,水素原子の 電子の固有値に粒径依存性が現れた。結晶粒を用 いたモデル計算では,水素原子の波動関数は結晶 粒の複雑な形状に依存した歪みを示した。FE基 底関数は,不均一静電場による波動関数の歪みを 表現するのに有効であった。

キーワード 電子状態,水素原子,有限要素法,ガウス関数,多結晶体,フェーズフィールド法

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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 mesh⁵⁾ and pseudopotential⁶⁾ 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:

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

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

 $S_f(x) = 1 - |x|$ with $|x| \le 1....(2)$

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:

Eight FE basis functions are assigned to each element.

As Gaussian basis functions appropriate for hydrogen atom, the following functions⁸⁾ have been proposed:

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 $f_i(\alpha_i, l, m, n) = x^l y^m z^n \exp(-\alpha_i r_{\rm H}^2),$ $\alpha_{11} = 18.731088, \ \alpha_{12} = 2.8253952,$ $\alpha_{13} = 0.64012176, \ \alpha_{21} = 0.161277552,$ $\beta_{11} = 0.0334946, \ \beta_{12} = 0.2347270,$ $\beta_{13} = 0.8137570$

l = m = n = 0, $r_{\rm H}$: 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.

$$\boldsymbol{H}_{ij} = \int d\boldsymbol{r} \, \boldsymbol{\varphi}_i \bigg\{ -\frac{1}{2} \, \nabla^2 + \frac{-Z_{\rm H}}{|\boldsymbol{r}_e - \boldsymbol{R}_{\rm H}|} + V_{ad}(\boldsymbol{r}_e) \bigg\} \boldsymbol{\varphi}_j,$$
$$\boldsymbol{U}_{ij} = \int d\boldsymbol{r} \, \boldsymbol{\varphi}_i \boldsymbol{\varphi}_j,$$

and $Z_{\rm H}$ is 1.0. The contributions from all elements are assembled to construct the global matrices H_{ij} and U_{ij} . $V_{ad}(\mathbf{r}_e)$ 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) method⁹⁾ and the inverse iteration method.¹⁰⁾

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 $11 \times 11 \times 11$ bohr³. Table 1 shows the eigenvalues of the hydrogen atom using various basis functions. Table 2 shows the contribution of Gaussian basis functions ψ_G and FE basis functions ψ_{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 = 2.6255×10^6 J/mol) of the hydrogen atom using variousGaussian basis functions or using the
corresponding Gaussian-FE mixed basisfunctions. The eigenvalue of FE basis functions
alone was -0.4826 (hartree).

Gaussian	Gaussian -FE
	-0.4913
	-0.4979
-0.4954	-0.4994
	-0.5
	Gaussian

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

Basis Function	ψ_G^2	ψ_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



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.

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(r), was determined by solving the following Poisson equation using the finite differential method (FDM).

 $V_{ad}(\mathbf{r}_e)$ (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 $V(\mathbf{r})$.

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. 3 Schematic representation of the spherical conductor model. One hydrogen atom is positioned between the two spherical conductors. Relative dielectric constants ε_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. 5). 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 method¹¹ (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 $\Delta \psi_{\rm F} : \Delta \psi_{\rm F} = \psi_{\rm F}$ (without external field) - $\psi_{\rm F}$ (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. 特

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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) - ψ (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. 特

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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.

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