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Journal of Alloys and Compounds 356–357 (2003) 231–235

Journal of ALLOYS AND COMPOUNDS

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Electronic state calculation of hydrogen in metal clusters based on Gaussian–FEM mixed basis function

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Received 1 June 2002; received in revised form 21 January 2003; accepted 1 February 2003

Abstract

The electronic state calculation combining Gaussian basis functions with finite element method (FEM) basis functions is presented. The electronic state calculation explicitly accounting for the effect of grain boundaries reproduces well the characteristics of hydrogen in metal materials. FEM is one possible technique because of the high applicability to arbitrary boundary conditions. However, since the wave function of an electron significantly changes near the nucleus, a large number of nodal points of FEM must be taken. This fact means that FEM is expected to require high computational costs. We expect that Gaussian–FEM mixed basis function method simultaneously satisfies the applicability to arbitrary boundary conditions and describes the steeply changing electron distribution. Results are presented for the electronic state calculation of H_2, AlH and Al_2 diatomic molecules and Al_4H cluster without external fields.

Keywords: Electronic structure; Metal cluster; Hydrogen

1. Introduction

Hydrogen diffusion in a nanocrystalline metal is strongly influenced by the grain boundaries [1]. At the grain boundary, the configuration of the metal atoms is disordered. Therefore, it is thought that the electrostatic field according to the grain-boundary configuration is formed and dispersion also arises in the energy level of the site which the hydrogen occupies [2]. The electronic state calculation explicitly accounting for the effect of the grain boundaries then reproduces the characteristics of hydrogen in the nanocrystalline metal.

The electrostatic potential is distributed over a microscopic region for the electronic state calculation, because it originates from the inhomogeneous grain-boundary configuration. The conventional molecular orbital (MO) method uses analytical basis functions and the analytical formulation of the integrals for solving the eigenvalue problem [3]. In such processes, the external potential should be analytically given for the calculations within a realistic computation time. The existence of a boundary in a mesoscopic structure forces the matrix element integration to be developed by complicated calculation routines. In the conventional MO method [4], the integral routines are generally the most time-consuming processes. Therefore, another procedure should be adopted for our purpose. It can be easily seen that the numerical calculation in the spatial grid technique is applicable for the inhomogeneously distributed potentials. As a possible technique, we adopted the finite element method (FEM) [5] as is well known in the structural analysis (i.e., for elastic materials) research field.

FEM has already been applied to the electronic state calculation [6–8]. The calculation results from this approach have been increasingly appearing. However, to achieve a high accuracy using FEM, the required number of nodal points is extremely large. The very sharp variation in the wave function near the nucleus forces this problem to become more serious. This fact means that FEM is expected to also require high computational costs.

We expect that Gaussian–FEM mixed basis function method simultaneously satisfies the applicability to arbitrary boundary conditions and describes the steeply changing electron distribution. In this paper, a certification of the

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doi:10.1016/S0925-8388(03)00353-0

efficiency of this calculation technique is shown upon the electronic state calculation of H_2, AlH and Al_2 diatomic molecules and Al_4H cluster without external fields.

2. Calculation method

We developed this program based on the calculation scheme for the MO method. In this section, a different point from the ordinary MO method is mainly explained.

2.1. Basis functions

First, an FEM basis function is explained. The case of a one-dimensional grid is considered for simplification. We used first order basis function in the form

$$S_{fx}(x) = 1 - |x| \quad \text{with } |x| \leq 1 \tag{1}$$

This is the simplest formulation. Fig. 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

$$S_f(r) = S_{fx}(x)S_{fy}(y)S_{fz}(z) \tag{2}$$

Eight FEM basis functions are assigned to each element.

We then expand the wave function as the linear combination of Gaussian basis functions $S_{g1}, \cdots, S_{gn}$ and FEM basis functions $S_{f1}, \cdots, S_{fm}$ in the form

$$\psi(r) = C \cdot \phi \tag{3}$$

where

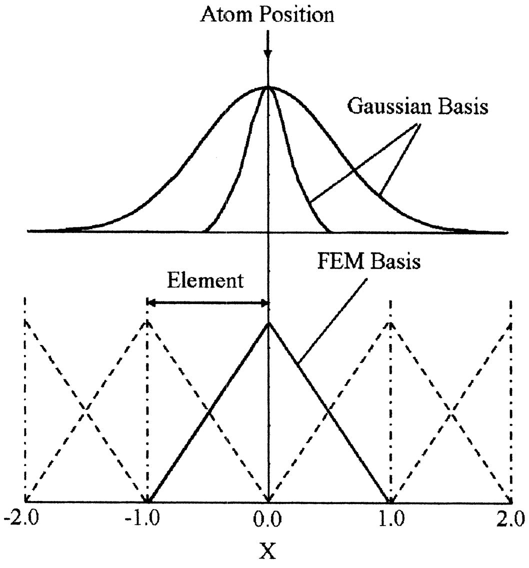

Fig. 1. Schematic representation of Gaussian and FEM basis functions. FEM basis functions on neighboring nodal points are represented by the dashed line.

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

$\phi = (S_{g1}, \cdots, S_{gn}, S_{f1}, \cdots, S_{fm})$. The coefficient C is determined according to a variational principle.

2.2. Coulomb integral

The contribution of the electron–electron coulomb integration to a Fock matrix element F_{ij} is expressed in the form

$$\begin{aligned} F_{ij}^{(kl)} &= \langle S_i(1)|V_{kl}|S_j(1)\rangle \\ &= \int S_i(1)S_j(1)\int a_k a_l \frac{S_k(2)S_l(2)}{r_{12}} \mathrm{d}\tau_1 \mathrm{d}\tau_2 \end{aligned} \tag{4}$$

with $i, j, k, l = g1, \cdots, gn, f1, \cdots, fm$. For calculating $F_{gg}^{(ff)}$, $F_{gg}^{(gf)}$ or $F_{gg}^{(gg)}$, we used the integration method from the MO method [9]. As for $F_{ff}^{(ff)}$, $F_{ff}^{(gf)}$ or $F_{gf}^{(gf)}$, the calculation scale is significantly expanded since the combination number of the element is huge. When two electrons do not locate in the same element, we transform Eq. (4) with respect to $F_{ff}^{(ff)}$, $F_{ff}^{(gf)}$ or $F_{gf}^{(gf)}$ into the following form using the multipole expansion [10]

$$\begin{aligned} F_{ij}^{(kl)} = a_k a_l \bigg\{ & \frac{q_{ij} q_{kl}}{r_{12}} + (q_{ij}\mu_{kl} - q_{kl}\mu_{ij}) \cdot \nabla \frac{1}{r_{12}} \\ & + (q_{ij}\Theta_{kl} - \mu_{kl}\mu_{ij} + q_{kl}\Theta_{ij}) : \nabla\nabla \frac{1}{r_{12}} + \cdots \bigg\} \end{aligned} \tag{5}$$

with

$$q_{ij} = \int S_i(p)S_j(p)\mathrm{d}\tau_p,$$

$$\mu_{ij} = \int r_p S_i(p)S_j(p)\mathrm{d}\tau_p,$$

$$\Theta_{ij} = \int r_p r_p S_i(p)S_j(p)\mathrm{d}\tau_p.$$

We take into account the term of the secondary nabla operator in the present study. In Eq. (5), since the explicit double integration disappeared, the computational cost is expected to be reduced. When two electrons are located within the same element, the direct integration of Eq. (4) is numerically performed.

2.3. Other conditions

The Kohn–Sham equation was self-consistently solved. The exchange potential by Becke and the correlation potential by Lee, Yang, and Parr, which took account of the generalized gradient approximation, were used [11,12]. Gauss–Legendre integration were adopted to numerically evaluate the exchange–correlation potential. At each SCF step, the values of charge density and density gradients were calculated on the Gauss–Legendre grid in each FEM element. For calculating the aluminum atom, only the valence 3s and 3p electrons were explicitly treated, and the remaining electrons were replaced by the model potential (MP) [13]. The equilibrium bond lengths and the harmonic frequencies of diatomic molecules were calculated by using the total energies evaluated for several bond lengths.

3. Results of the test calculations

First, we did calculations for H_2 and examined whether Gaussian basis functions and FEM basis functions would effectively contribute. The number of nodal points per dimension was 23. The element width was set to 0.7 bohr (1 bohr≒0.05291 nm) for all elements. This calculating region was cubic with size of 15.4×15.4×15.4 bohr^3. The H–H distance was 1.4 bohr. Table 1 shows the total electron energies of H_2. The contribution of FEM basis functions to various Gaussian basis functions is investigated. Since only the 3G basis functions cannot express the spread portion of a wave function, the molecular orbital of H_2 is not completely expressed. Therefore, the electron energy of only the 3G basis functions is significantly shifted from the exact value. Similarly, approximation of only FEM basis functions under this calculation condition also has a low accuracy, since the basis functions cannot express the steep wave function near the nucleus. On the other hand, the electron energy of the 3G-FEM mixed basis functions is equivalent to that of only the 311G** basis functions. This is because the 3G basis functions express a steep portion and FEM basis functions express a spread portion, as shown in Fig. 2(a).

Contrary to the 3G basis functions, the 311G** basis functions can independently almost express the molecular orbital, as shown in Fig. 2(b). For the 311G**-FEM mixed basis functions, the contribution of FEM basis functions then decreases, but it still remains in the region between the two protons where the linear combination of atomic orbital (LCAO) cannot express with accuracy. Furthermore, the equilibrium bond length and the harmonic frequency of H_2 were calculated using various Gaussian–FEM mixed basis functions. Following values were obtained: 3G-FEM (0.0736 nm and 4272 cm^{-1}), 31G-FEM (0.0742 nm and 4365 cm^{-1}), and 311G**-FEM (0.0743 nm and 4377 cm^{-1}). These values are in agreement with the reference value (0.0748 nm and 4373 cm^{-1}) using 31G** under the same exchange-correlation potential as that in Section 2.3. [14].

Table 1
Total electron energies (in hartree, 1 hartree≒2.6255×10^6 J/mol) of H_2 using various Gaussian basis functions or using corresponding Gaussian–FEM mixed basis functions

CGTO	Gaussian	Gaussian–FEM	$\|\Delta E\|$
3G	−0.8474	−1.8821	1.0347
31G	−1.8484	−1.8846	0.0362
31G**	−1.8497	−1.8853	0.0356
311G	−1.8809	−1.8847	0.0038
311G**	−1.8837	−1.8853	0.0016
Exact	−1.8888[a]		

Differences in the energies between the two basis functions are listed in the right column of the table. The total electron energy only using FEM basis functions was −1.8173.

[a] Reference [17].

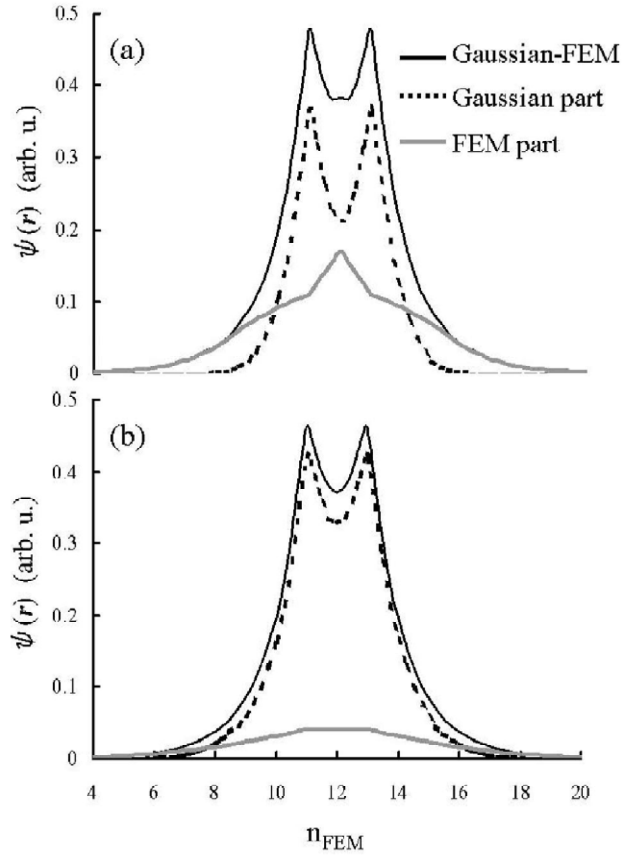

Fig. 2. Molecular orbital $\psi(r)$ (in arbitrary unit) on a molecular axis of H_2: (a) using 3G-FEM mixed basis functions, and (b) using 311G*-FEM mixed basis functions. The abscissa n_{FEM} denotes the number of nodal points.

Next, AlH, Al_2 and Al_4H were calculated. The number of grid points per dimension was the same as that for H_2. The element width was set to 1.2 bohr for all elements. This calculating region was cubic with size of 26.4×26.4×26.4 bohr^3. Gaussian basis functions [15], corresponding to the MP, were assigned to an aluminum atom and the 31G basis functions were assigned to a hydrogen atom. For Gaussian–FEM calculation, Gaussian basis functions with an exponent greater than one were adopted. The Al–Al and Al–H distances were about 5.41 and 3.31 bohr respectively, assuming that hydrogen occupied the tetrahedral site in FCC Al. Table 2 shows the orbital energies of AlH and Al_2 in the triplet state and Al_4H in the doublet state. In each molecule, the orbital energies of Gaussian–FEM mixed basis functions correspond to that of only Gaussian basis functions. Also, Gaussian basis functions express the steep portion and FEM basis functions express the spread portion like the calculations for

Table 2
Orbital energies (in hartree) of AlH, Al_2 and Al_4H using Gaussian–FEM basis functions. These energies are compared with that only using Gaussian (Al: 6-31G* + diffuse, H: 31G) basis functions for all electrons

	AlH			Al_2			Al_4H	
MO	Gaussian	Gaussian –FEM	MO	Gaussian	Gaussian –FEM	MO	Gaussian	Gaussian –FEM
1	−0.3527	−0.3496	1	−0.3280	−0.3296	1	−0.5215	−0.5440
2	−0.2282	−0.2263	2	−0.2500	−0.2476	2	−0.2766	−0.2781
3	−0.1148	−0.1179	3	−0.1340	−0.1386	3	−0.2759	−0.2758
			4	−0.1266	−0.1290	4	−0.2710	−0.2717
						5	−0.2258	−0.2256
						6	−0.1422	−0.1461
						7	−0.1418	−0.1441

α-Spin–orbital energies are only displayed here.

H_2, as shown in Fig. 3. The discrepancy of the molecular orbital in an aluminum atom position is caused by replacing core electrons by effective potential. The equilibrium bond length and the harmonic frequency of Al_2 were respectively calculated as 0.273 nm, 274 cm^{-1} using this mixed basis function. These values are in agreement with the reference value (0.273 nm, 256 cm^{-1}) using Gauss functions and MP [16].

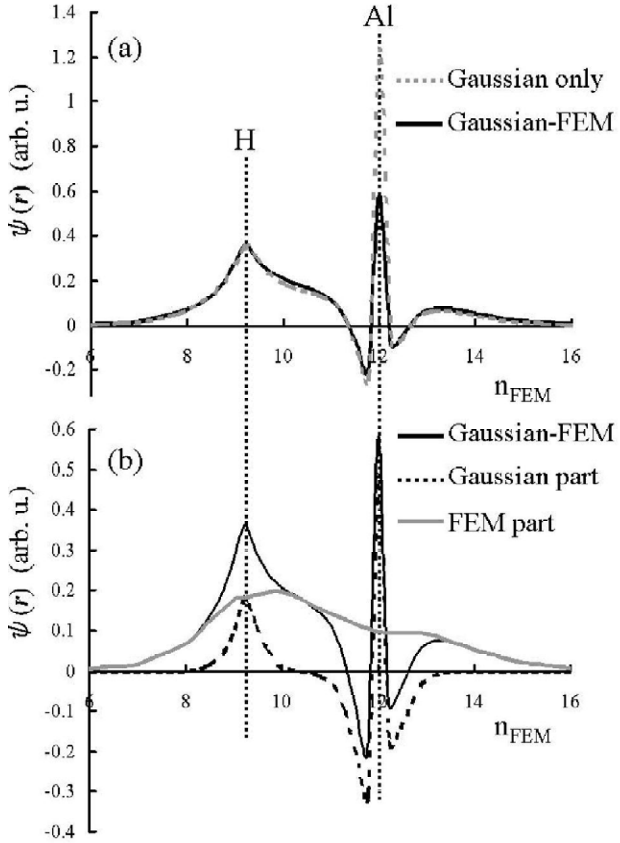

Fig. 3. Molecular orbital ψ(r) (MO-1 cf. Table 2 in arbitrary unit) on a molecular axis of AlH: (a) comparison of the molecular orbital between only using Gaussian basis functions and using Gaussian–FEM basis functions, and (b) contribution of Gaussian and FEM basis functions to the molecular orbital expressed by Gaussian–FEM basis functions.

As a result of these test calculations, FEM basis functions are automatically compensating for the wave function's portion, which cannot be expressed only with Gaussian basis functions. The molecular orbital widely spread in the calculation space is expected to be significantly influenced by the configuration of the inhomogeneous electrostatic field. In this method, FEM basis functions, which possess the applicability to arbitrary boundary conditions, express the spread portion of the molecular orbital and Gaussian basis functions, which can describe the steeply changing electron distribution, express the steep portion. This mixed basis method would be available for the electrostatic calculation in the inhomogeneous electrostatic field.

4. Conclusions

We have examined Gaussian–FEM mixed-basis function method as an electronic-state calculation technique. This method was applied to the H_2, AlH and Al_2 diatomic molecules and the Al_4H cluster. Gaussian basis functions express the steep portion and FEM basis functions express the spread portion of a molecular orbital. Furthermore, we certify that FEM basis functions are automatically compensating for the wave function's portion, which cannot be only expressed by Gaussian basis functions. The applicability of FEM to arbitrary boundary conditions can be kept in Gaussian–FEM mixed basis technique by selecting suitable Gaussian basis components. This method would be available for the electrostatic calculation in the inhomogeneous electrostatic field.

Acknowledgements

We would like to thank Prof. Y. Sakai and Prof. E. Miyoshi at Kyushu University for providing the MP data.

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