All-electron mixed-basis calculation to optimize structures of vanadium clusters

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All-Electron Mixed-Basis Calculation to Optimize Structures of Vanadium Clusters*1

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As a powerful *ab initio* method for systems with transition metal elements, all-electron mixed-basis approach which uses both plane waves and atomic orbitals as basis functions is tested to optimize structures of vanadium clusters. A good agreement with several previous calculations is obtained for V_2 and V_4.

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1. Introduction

Ab initio total energy calculations[1,2] based on the local density approximation (LDA)[3] and the adiabatic approximation[4,5] has attracted considerable attention as a conceptually new method, which is capable to describe dynamically the stability and reactivity of any objects including clusters, surfaces and bulk materials at finite temperatures, in principle, without using any parameters. Consequentially, Ohno *et al.* have developed the all-electron mixed-basis approach which is applicable to the molecular dynamics of objects in any atomic environments.[6–8]

The mixed-basis means that the combination of both plane waves (PWs) and atomic orbitals (AOs) is used as basis functions. The introduction of AOs reduces considerably the computational load of the PW-expansion method.[9] In particular, in the all-electron mixed-basis method, not only valence AOs but also core AOs are incorporated to describe all-electrons without using pseudopotentials. Historically, all-electron mixed basis method was first formulated by Bendt and Zunger,[10] who incorporated just core AOs in the PW-expansion method. However, the method[6,11] used in the present study is independent and different from Bendt and Zunger's, because ours incorporates also valence AOs in the basis set.

The present paper deals, for the first time, with the structural optimization of transition metal clusters in the all-electron mixed-basis approach. Here, as an example we consider vanadium clusters, which may be the simplest nontrivial transition-metal cluster and can be treated with a spin-unpolarized calculation according to the small size of them.

2. All-Electron Mixed-Basis Method

The all-electron mixed-basis method, that is offered an accurate technique for the electronic states calculation. We solve the Kohn-Sham equation[3]

$$H\psi_i(r) = \varepsilon_i \psi_i(r) \tag{1}$$

for electronic states self-consistently by expanding wave functions simultaneously as a linear combination of both plane waves (PW) and atomic orbitals (AO) as follows:

$$\psi_i(r) = \frac{1}{\sqrt{\Omega}} \sum_G \chi_i(G) e^{iG\cdot r} + \sum_n \sum_\nu \tau_i(n, \nu)\varphi_\nu(r - R_n) \tag{2}$$

where the φ_ν are the atomic orbitals. Here, core AO are computed using the Herman-Skillman atomic code[12] with a logarithmic mesh. Valence AO are generated in the same way but their tail is truncated smoothly inside the non-overlapping sphere of radius r_c prescribed at the outset. The same Coulomb and exchange-correlation potentials are evaluated separately for PW and for AO, respectively, in reciprocal space and in real space (along the radial direction in the atomic spheres), as accurately as possible. In other words, PW-PW, AO-PW and AO-AO contributions to the charge density and the potential are calculated separately.

To achieve self-consistency of electronic states and to orthogonalize different electronic levels, we adopt a simple steepest descent (SD) method combined with the Gram-Schmidt orthogonalization method.[13] The SD method is to move the electronic states toward the SD direction in the energy surface. The SD method has a weak point, slow convergence.

3. Results

We assume that vanadium clusters have no spin magnetic moment, *i.e.*, we calculate the electronic structure of vanadium cluster with LDA. Here we did not use MD method but instead calculated the total energy of vanadium cluster for each bond length.

First, we calculate vanadium dimer. The unit cell is chosen as a cube of 0.7 nm width. The number of PWs is 925. The cutoff energy for PWs is chosen as 8.7 Ry. The result of calculation for vanadium dimer is shown in Fig. 1. Here, the abscissa is the bond length and the ordinate is the force and the total energy. In this figure, the location of the minimum of total energy coincides with the zero of the force at about

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Table 1 Comparison between our result and previous results.

	This study	Exp.[14]	GGA[15]	LSDA[15]	GAUSSIAN[16]
V_2	0.169 nm	0.1774 nm	0.173 nm	0.171 nm	—
V_4	0.221 nm	—	0.216/0.233 nm	0.211/0.227 nm	0.2206 nm

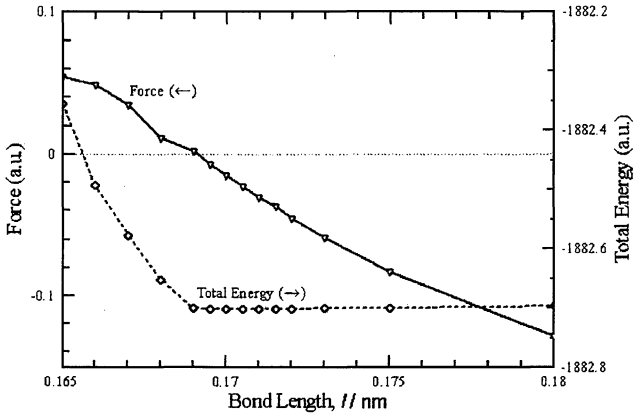

Fig. 1 Total energy (broken curve) and force (solid curve) vs bond length of vanadium dimer.

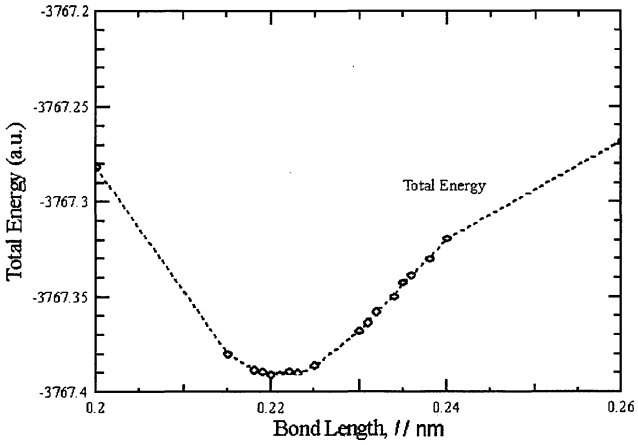

Fig. 2 Total energy (broken curve) vs bond length of V_4.

0.169 nm bond length, but the curvature of the total energy is very different between both sides of the minimum of total energy.

Next, we calculate V_4. The unit cell is chosen as a cube of 0.7 nm width. The number of PWs is 1419, corresponding to the cutoff energy of 11.8 Ry. The result of the V_4 calculation is shown in Fig. 2. We know that V_4 is stable for an equilateral tetrahedron. The result of total energy calculation has the minimum at about 0.221 nm bond length.

Optimized structures are shown in Fig. 3. We compare these results with previous results. Optimized bond length of vanadium dimer is 5% shorter than the experiment[14] and the calculation by *ab initio* GGA or LSDA.[15] This small discrepancy and the difference of the curvatures of the total energy are attributed to ignorance of spin magnetic moment in our calculation. In the case of V_4, the optimized bond length is in good agreement with the result of previous calculations by *ab initio* GGA or LSDA[15] and by GAUSSIAN.[16] V_4 that was calculated by GGA or LSDA[15] is a tetrahedron with spin

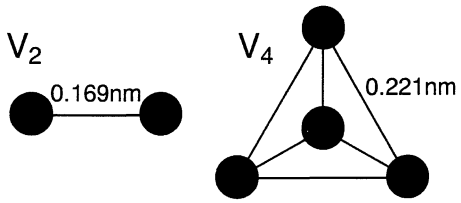

Fig. 3 Optimized structures of V_2 and V_4.

magnetic moment, is not an equilateral tetrahedron with 2 different bond lengths. On the other hand, V_4 that was calculated in detail by GAUSSIAN[16] is an equilateral tetrahedron with no spin magnetic moment. Our result is in better agreement with the result by GAUSSIAN[16] than by GGA or LSDA.[15] We believe that the assumption that V_4 has no spin magnetic moment is a reasonable one. We show these comparison in Table 1.

4. Summary

In summary, we have applied our all-electron mixed basis approach to the vanadium dimer and tetramer. The result agrees reasonably with available experimental data and previous calculations. The method is basically applicable to *ab initio* molecular dynamics simulations. We are now planning to perform *ab initio* molecular dynamics simulations of vanadium clusters by incorporating the conjugate gradient technique in place of the steepest descent technique for the electronic states.

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