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著者	Taneda Akito, Esfarjani Keivan, Hashi Yuichi, Kawazoe Yoshiyuki
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Tight - binding method for Cu clusters ; Ground state studies of Cu_3 - Cu_{12}

Akito Taneda, Keivan Esfarjani, Yuichi Hashi*
and Yoshiyuki Kawazoe

Institute for Materials Research, Tohoku University, Sendai 980-77, JAPAN
**Hitachi Tohoku Software Ltd., Sendai 980, JAPAN*

abstract. The recently developed tight-binding parametrization of copper by Mehl and Papaconstantopoulos (1) is tested against the ab-initio Discrete Variational Method (DVM). Good agreement is found for the eigenvalues, and total energies. Next, this parametrization is used to perform Molecular Dynamics (MD) and simulated annealing in order to investigate the ground state structure of small copper clusters. In this study, clusters of size up to 12 were considered. Results concering their ground state geometry, binding energy and HOMO-LUMO gap are reported and compared to available theoretical and experimental data.

INTRODUCTION

Study of the ground state of neutral and charge metal clusters has been a subject of increasing interest. Indeed these clusters or so-called nano-particles can be used in different matrix hosts, and can yield interesting physical properties. Studying them by ab-initio methods, even though accurate, is computationally limited. We, therefore, have adopted the tight-binding technique to perform molecular dynamics simulations on these small systems.

METHODS

Among the available parameters for copper, the most recent one by Mehl and Papaconstantopoulos (1) has been able to reproduce rather accurately the ab-initio DVM results. These parameters are found by fits to FLAPW band structure and total energy curves of several bulk structures of copper. Here, they have been, however, used for clusters where the coordination number is usually

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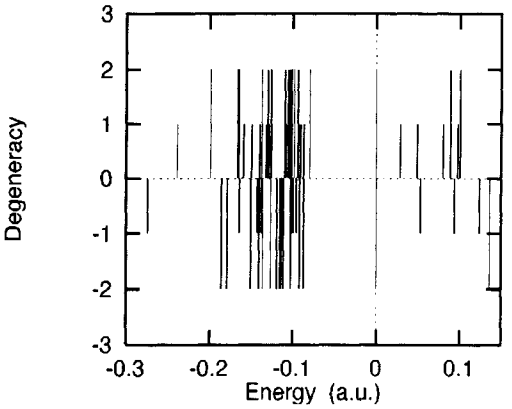

FIGURE 1. Eigenvalues of Cu_7. Upper one is from DVM, lower one is from TB.

smaller than bulk metallic systems. The reason for the success of such parametrization lies in two factors: One is the non-orthogonality, and the other is the dependence of the on-site energy on the coordination number. These factors of course make the computations slightly more complicated, but still the computational time is much smaller than ab-initio methods. In this study, 9 orbitals were used per one copper atom.

For the structural relaxation, we have used a recently developed Adaptive Simulated Annealing (ASA) algorithm (2), in which the temperature is evolved according to:

$$dT / dt = -v\, T / \varepsilon\, C^{1/2} \qquad (1)$$

where v is a velocity scale taken as a constant (v = 0.1 to 1), C is the heat capacity of the system indicating the fluctuations in the average configurational (or potential) energy, and ε represents the relaxation time, and is related to the second highest eigenvalue of the transition matrix by the following relation:

$$\varepsilon = - Log\, (q_{N-1}) \qquad (2)$$

One typically starts at high temperatures (about 2,000 K in the case of copper), and lowers it according to (1) every 500 MD timesteps. After reaching a temperature of about 300 K, we stop the SA algorithm, and minimize the structure by a velocity scaling technique which is very similar to the Steepest Descent (SD) algorithm. It takes typically 50,000 to 100,000 MDsteps to anneal small clusters.

TABLE 1. Binding energy (B. E.), HOMO - LUMO energy gap (Gap), and geometry of the annealed Cu_n clusters.

n	Structure	B. E. (a.u./atom)	Gap (a.u.)
3	Triangle	-.0001	no gap
4	Planar rhombus	-.0505	0.1159
5	3 planer adjacent triangle	-.0461	no gap
6	4 planer adjacent triangle	-.0614	0.1066
7	Hexagon + atom at athe center	-.0600	no gap
8	Capped hexagon + atom at the center	-.0637	0.0719
9	Incomplete pyramid	-.0625	no gap
10	complete pyramid	-.0637	0.0008
11	complete pyramid + atom	-.0703	no gap
12	complete pyramid + 2 atoms	-.0725	0.0256

RESULTS AND DISCUSSION

Eigenvalues of Cu_7 by TB and DVM are shown in Figure 1. Geometry of Cu_7 used here is optimized in present study (see Figure 2). As one can see from Figure 1, TB eigenvalues are good agreement with DVM.

The relaxations were performed for clusters of size 3 to 12. The MD time step was 1 fs ,and the Verlet algorithm has been used to update the atomic coordinates. The annealing was done in a hard-wall spherical box of radius increasing with deceasing temperature. We found the following for the ground state structures (Table 1).

Because of the presence of the *d* orbitals, there is strong tendency for the atoms to align in a plane and form mostly triangular shapes. As the structure gets larger, more compact forms emerge, mostly of capped form. Compared to LCAO - X α calculations of Post and Baerends (3), our result shows different tendency. Binding energy calculated by Post and Baerends monotonicaly decreases as increasing cluster size, but our result shows even - odd oscillation as a function of n. From UPS experiment of Pettiette (4), we found that cluster size dependence of binding energy should oscillate in agreement with our result.

Compared to other calculations (3)(5), binding energy of n = 3 and 4 are too small and too large respectively . This is due to TB parameterization. Because Mehl's TB parameter cannot give accurate eigenvalues of isolated atom, and we have not introduced any correction term to improve them yet. We will try to improve them by fitting to reproduce total energy and eigenvalues of small Cu clusters.

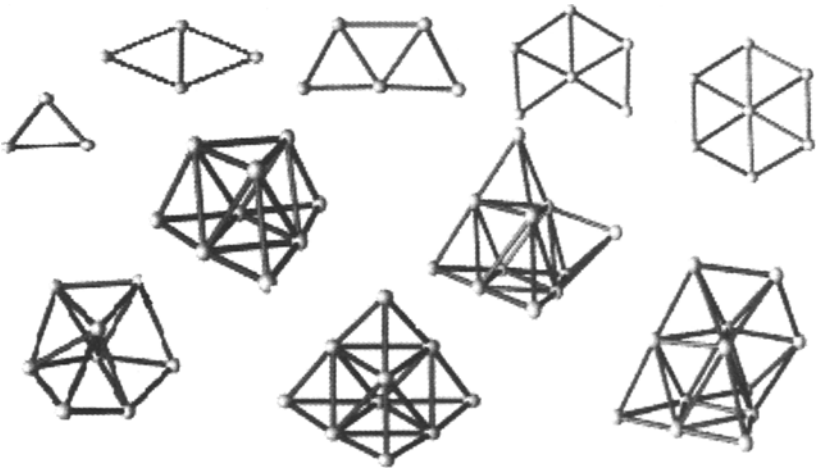

FIGURE 2 . Optimaized structures of Cu_3 - Cu_{12}

In Figure 1, we present structures of Cu clusters obtained by the present simulation. Our results for n = 3, 4, 5 are in good agreement with first-principle all-electron calculations of Jackson (5).

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