



Research paper

Influence of the potential model parameters on the structures and potential energy surface of cobalt clusters

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ABSTRACT

Potential energy surfaces (PES) of Co clusters with Gupta potential using four parameter sets are characterized in terms of conformational analysis. Their structures are obtained using three optimization algorithms. Three new structures with lower energies for one of these parameter sets are found. For all parameter sets, the structural variation from icosahedron to decahedron to close-packed face centered cubic (FCC) or stacking fault FCC and amorphous motifs is related to the potential range of the parameters. The difference between the PES is investigated, and for a long potential-range parameter, the number of local minima on the PES is extremely large.

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1. Introduction

In recent years there have been growing interest and significant research developments in the experimental and theoretical studies of the nanoclusters, owing to their peculiar physical and chemical properties compared with bulk matters [1–3]. Metallic or alloyed multi-metallic clusters have been widely studied because of their special electrical, optical and catalytic properties [4,5]. The magnetic properties of cobalt clusters were investigated by Stern-Gerlach molecular beam deflection experiment [6,7] and from first-principles calculations [8,9]. To understand the unique chemical, electronic, optical, and magnetic properties of metallic clusters, the fundamental research problem is to locate their stable structures.

Empirical potential played an important role in computer simulation of the thermodynamic and structural properties of atomic clusters. For instance, Gupta potential [10], Murrell-Mottram (MM) potential [11], embedded atom model (EAM) potential [12], and Sutton-Chen (SC) potential were adopted to study gold clusters, and another glue potential [13] was also utilized for aluminum clusters. In order to study the effect of potentials on the geometrical structure of a cluster, He clusters were investigated by Lennard-Jones (LJ), Pirani, and Hartree-Fock-dispersion individual damping (HFD-ID) potential [14]. It was concluded that the differences between structures depended upon the disagreements of

the potentials. Furthermore, the impact of potential function parameters was also studied [15]. Experimental-fitted parameters and density-functional-theory (DFT)-fitted parameters were used to determine the lowest energy structures of Ag-Pd clusters with Gupta potential [16]. In the calculation on Pd-Pt clusters with the Gupta potential, homonuclear Pd-Pd and Pt-Pt parameters were fitted by bulk properties of Pd and Pt metals, and three heteronuclear Pd-Pt parameter sets were used. The first Pd-Pt parameter set was defined as the mean of the homonuclear, i.e., Pd-Pd and Pt-Pt parameters. The second and third parameter sets for the heteronuclear Pd-Pt interaction used the values of the first one, but making the repulsive pair energy scaling parameter (A) and the attractive many-body energy scaling parameter (ξ) larger than the corresponding parameters for the homonuclear interactions [17]. Research results showed that by tuning the potential parameters, structural and chemical ordering patterns could be qualitatively reproduced.

The Gupta potential has been widely adopted to study Co clusters and other transition metal clusters. However, after searching the related literatures on Co clusters with Gupta potential, we found that different parameters were adopted in various research areas, e.g., Co adsorption on Au(111) and Pt deposit onto a Co (0001) substrate [18–21]. Therefore, the aim of this paper is to discuss the influence of four representative parameter sets on the geometrical structures, energies, and the potential energy surface of Co clusters with the same Gupta potential. The potentials with these parameter sets were compared, and the geometrical optimization is performed by using three high efficient algorithms to

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determine the stable structures. The minimal structures of Co clusters with one of these parameter sets were reported previously, but three new structures with lower energies were found in this work. Furthermore, the structural distribution and average bond length of Co clusters for all parameter sets were summarized and compared. The difference between the potential energy surfaces (PES) with these parameter sets was investigated by conformational analysis using a dynamic lattice searching (DLS) method [22,23].

2. Method

2.1. Gupta potential with four parameter sets

The Gupta potential is one of the most commonly used interatomic potentials for metallic and alloy clusters, which is based on the second moment approximation of a tight-binding Hamiltonian. It is written in terms of repulsive pair $V^r(i)$ and attractive pair $V^m(i)$ term, and potential V_N with N atoms can be depicted in the following form:

$$V_N = \frac{1}{2} \sum_{i=1}^N \{V^r(i) - V^m(i)\} \quad (1)$$

$$V^r(i) = \sum_{j=1(j \neq i)}^N A_{ij} \exp\left(-p_{ij} \left(\frac{r_{ij}}{r_{ij}^{(0)}} - 1\right)\right) \quad (2)$$

$$V^m(i) = \left[\sum_{j=1(j \neq i)}^N \xi_{ij}^2 \exp\left(-2q_{ij} \left(\frac{r_{ij}}{r_{ij}^{(0)}} - 1\right)\right) \right]^{1/2} \quad (3)$$

where r_{ij} is the distance between atom i and j and $r_{ij}^{(0)}$ is the equilibrium first-neighbor distance. A_{ij} is the coefficient of repulsive term, ξ_{ij} is an effective hopping integral between atoms at site i and j , and p_{ij} and q_{ij} describe their dependence on the repulsive and attractive interatomic interactions, respectively.

In general, the parameters of A , ξ , p and q , are fitted to experimental values of the cohesive energy, lattice parameters and independent elastic constants for the reference crystal structure at 0 K temperature. Table 1 lists the parameter sets I, II, III and IV taken from references. The parameter set I is derived by Cleri and Rosato [18], and it is utilized to study the stable structures [24] and the melting behaviors [25]. The parameter sets II and IV are proposed by Goyhenex and Bulou, and they are designed for studying the Co adsorption on Au(111) substrate [19] and Pt deposit onto a Co (0001) substrate, respectively [20]. It is noted that to deal with bimetallic surface problems (segregation, deposition), the difference between the surface energies of the materials has to be preserved, and in their corresponding fitting procedure, an additional constraint was introduced. Furthermore, the parameter IV of Co clusters was also applied to study thermal properties of Co/Au alloys with core-shell structure [21]. On the other hand, the parameter set III was taken from Ref. [26], which was also applied in the theoretical study of cobalt-palladium clusters [27].

To distinguish the four parameter sets I, II, III and IV, their Gupta potential energies with the variation of $r_{ij}/r_{ij}^{(0)}$ are plotted in Fig. 1.

Table 1
Gupta potential parameters for cobalt clusters with parameter sets I, II, III and IV used in this study.

Metal	A_{ij} (eV)	ξ_{ij} (eV)	p_{ij}	q_{ij}
Co (I)	0.095	1.488	11.604	2.286
Co (II)	0.106	1.597	10.87	2.36
Co (III)	0.1757	1.843	9.21	2.975
Co (IV)	0.189	1.907	8.80	2.96

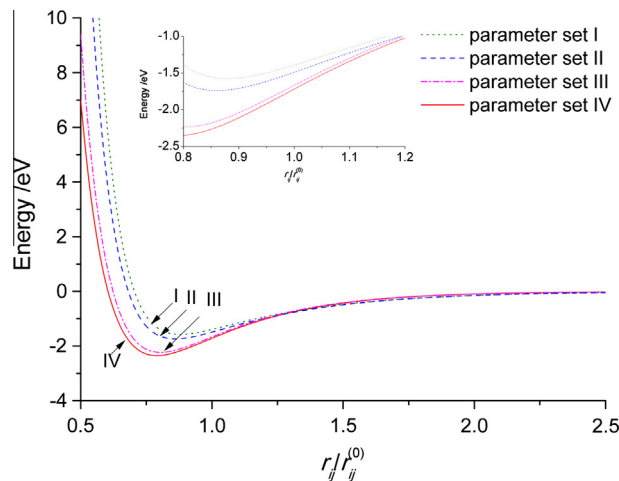


Fig. 1. Plots of Gupta potential energies with parameter sets I, II, III, and IV for cobalt clusters as a function of $r_{ij}/r_{ij}^{(0)}$. The subfigure shows the enlarged comparison of the range 0.8–1.2.

It can be seen that the bottom curve for set IV corresponds to the longest potential range, and the sequence of the potential range is set IV > III > II > I. Furthermore, the potential range of set I is close to that of set II, and the potential ranges of sets III and IV are very close. It is because the parameter values A , ξ , p and q of sets I and II are close to each other as listed in Table 1, and the same situation occurs for sets III and IV. On the other hand, as plotted in Fig. 1, the sequence of the potential minimum energies is set IV < III < II < I.

2.2. Optimization algorithms for cluster geometry optimization

For atomic clusters, the number of local minima on the PES is believed to rise exponentially with the cluster size N [28]. Finding the global minimum of the PES is a difficult problem, and the extensive search of the PES should be performed to locate the most stable structure [29]. Lots of global optimization techniques have been applied to the problem, e.g., genetic algorithm (GA) [30], basin-hopping (BH) method [31], simulated annealing (SA) [32], adaptive immune optimization algorithm (AIOA) [33,34], DLS method and its variant with constructed cores (DLSc) [22,35], and heuristic algorithm combined with the surface and interior operation (HA-SIO) [36]. In this work, DLS, DLSc and AIOA-DLS methods are adopted to locate the stable structures.

2.2.1. DLS and DLSc methods

Taking the advantages of the modeling strategy and stochastic optimization, a DLS method was developed for the fast optimization of atomic clusters [37]. The basic steps of the DLS can be summarized as follows: (1) Randomly generate a starting configuration of a cluster, which is locally minimized by limited memory quasi-Newton algorithm (LBFGS) [38]. (2) The vacant dynamic lattice (DL) sites are constructed around the starting configuration, and new configurations are generated by iteratively moving the atoms with higher energy to the vacant DL sites with lower energies. The former operation is ‘lattice construction’, and the latter one is the ‘lattice searching’. (3) If the new solution has lower energy than the starting configuration, it will be taken as the starting configuration and return to step (2), otherwise, the current solution will be taken as the result of the run of DLS. This method has been successfully used for the optimization of LJ clusters up to 500 atoms [22] and Morse₂₁₀ clusters [39].

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