



Performance of modified Lennard–Jones potential to seed *ab initio* calculations of small cadmium clusters



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ARTICLE INFO

Article history:

Received 17 May 2013

Received in revised form 26 July 2013

Accepted 27 July 2013

Available online 6 August 2013

Keywords:

Cadmium clusters

Lennard–Jones

Isomers

Seed

Ab initio calculations

ABSTRACT

Weakly bonded Cadmium clusters have, even for small number of atoms, many isomers that are stable structures. Before any attempt to use *ab initio* calculations on these clusters, a limited set of good possible stable isomers (seeds) has to be defined. It is customary to use Lennard–Jones isomers as seeds in weakly bonded clusters. Here we show how a simple extended Lennard–Jones (ELJ) potential performs better than Lennard–Jones potential. We find that ELJ clearly decreases the size of possible stable isomers and increases its fitness. We also assess the capability of ELJ potential to predict isomers of Cd₃ to Cd₁₀ that coincide or are close to actual *ab initio* structural-optimized isomers.

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1. Introduction

Searching stable isomers (local minima) on potential energy surface (PES) of van der Waals (vdW) atomic clusters has been and is an active area of research [1,2]. In classical mechanics dynamic simulations it is customary to describe vdW interactions with a Lennard–Jones (LJ) potential. Although the Lennard–Jones potential only includes interactions between pairs of atoms, the structural optimization problem becomes quite complex as the number of critical points on the PES increases rapidly with the number of atoms [3,4]. Optimization of LJ clusters is far beyond an academic optimization problem. Finding vdW minima is important in practical terms because it is believed that these structures are good candidates for stable structures on the PES [5–8] that results from computationally expensive *ab initio* calculations, which are, ultimately, the suitable methods to determine actual stable structures of clusters. In this work we test the suitability of a modified Lennard–Jones potential to seed *ab initio* calculations with good candidates to stable structures.

Although the LJ potential performs well in fitting to the dissociation energy curve of atoms that are bonded with London dispersion forces [9], as it is the case of the noble gases, is not completely suitable to describe systems in which the dispersion

forces and the tendency to form covalent bonds compete together [10]. Good examples of this are Cd and Hg clusters. The dimers of both metals atoms are weakly bonded and show a vdW character [11–15]. In principle one can say that dispersive-bonding character of these elements is evident from their “low” melting points (235 K for Hg and 594 K for Cd) [16]. However, if one compares Hg and Cd with the noble gases, it is clear that in the solid state these transition metals are not held together only by dispersion forces but by metallic bonds. Therefore, there should be a transition in the bonding pattern of Cd ranging from vdW bonds for few atoms, some degree of covalent bond as the number of atoms increases and metallic bond in the bulk. In a recent work, Schwerdtfeger et al. [11,12] have proposed extended Lennard–Jones potentials (ELJ) [17–20] for Zn, Cd and Hg of the form

$$V_{ELJ}(r_{ij}) = \sum_{k=6}^{14} a_k r_{ij}^{-k} \quad (1)$$

where r_{ij} is the interatomic distance between atoms i and j and a_k are parameters fitted to dissociation energy curves computed with high-precision *ab initio* methods. To our best knowledge these are the most reliable calculations of these systems reported in literature [13–15,21–23]. So, it is interesting to investigate the possible differences in the stable structures of clusters of Cd when ELJ potential, instead of a LJ, is used to describe the pair-only interatomic potential. In this work, we are particularly interested in (i) look for the differences of Cd isomers corresponding to ELJ and LJ potentials, and (ii) assess the performance of ELJ Cd isomers as potential local

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minima on the *ab initio* PES. Finding *ab initio* minima of metallic clusters and weakly bonded clusters is a challenging task, as chemical intuition usually it is not sufficient to guide the search of potential isomers (seeds).

2. Computational methods

2.1. Optimization of LJ and ELJ structures

To find critical points on the PES of LJ and ELJ clusters of Cd we used a non-energy conservative molecular dynamic that aims a rapid convergence of the system to critical points on the PES. Namely, we used the *Fast Inertial Relaxation Engine* (FIRE) [24]. FIRE is a conventional molecular dynamics with modifications in the instantaneous velocity and adaptive time step. The main ingredient of FIRE is that it corrects trajectories that deviate the system from local critical points. Specifically, if the velocity of an atom in a step of simulation is opposite to the force acting on it, the velocity is restored to its value in the previous iteration and the time step is substantially reduced so that velocity vectors are reoriented in a convenient direction, i.e., until the force is not opposed to the velocity.

First, the $3N$ coordinates corresponding to N atoms are assigned randomly. Atoms are confined inside a small box of volume 1 \AA^3 , so that all atoms repel each other. Then the system is free of evolution following a FIRE dynamics. In order to assure diversity in the set of structures 10^6 trajectories are computed for every set of clusters. A structure is considered converged to a local minimum when the maximum force on an atom is less than 10^{-9} eV/\AA . The size of the confining box and the maximum force have been systematically studied, and the value chosen here assures that all reported LJ structures of up to 15 atoms of Hg and Cd are found. As many trajectories could yield to the same isomer, each new structure has to be compared to the ones previously found. To compare similarity between structures we used the second-moment-distribution-like distance (SMDL) [25–27]

$$d(\alpha, \beta) = \left[\frac{2}{N(N-1)} \sum_{n=1}^{N(N-1)/2} (d_n^\alpha - d_n^\beta)^2 \right]^{\frac{1}{2}} \quad (2)$$

where d_n^α are all interatomic distances of the cluster α sorted in increasing order. d_n^β is the same set of distances of the cluster β and N is the number of atoms. If two clusters are exactly the same, then SMDL distance is necessary null. It is important to mention that SMDL is invariant to rotation and translation, but cannot differentiate enantiomers. Although the second moment distribution of atomic positions could be, in general, a limited descriptor, we ought to emphasize that Eq. (2) has more information than the regular second moment distribution because it includes “all pairs” of relative interatomic distances ($N(N-1)/2$) and not merely individual (N) distances with respect to an anchor point [21]. Besides, one of the authors have shown that SMDL successfully identify identical structures of small to medium size homoatomic clusters (see details in paper “How relevant is the choice of classical potentials in finding minimal energy cluster conformations?” in this same issue) We use a threshold of $d = 10^{-4} \text{ \AA}$ to consider that two isomers are the same. These calculations were done in a local version of the computing environment ASE (Atomic Simulation Environment) [28] adapted to our needs.

2.2. Ab initio calculations

As is well known in DFT, “standard” GGA and hybrid exchange correlation functionals fail to include dispersion forces [29]. However, nowadays there are available functionals that include

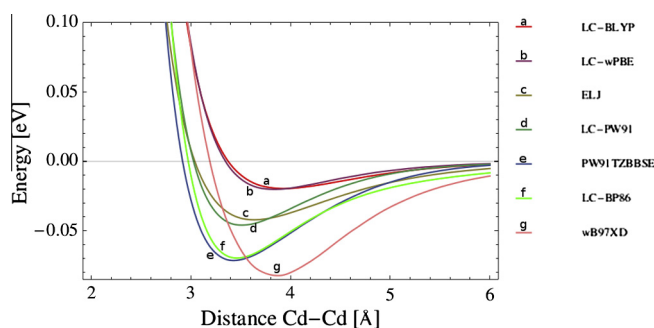


Fig. 1. Dissociation curves of Cd_2 computed with five different functionals and ELJ potential.

long-range corrections. To choose a functional that is suitable to describe Cd clusters we have used as selection criterion the fitness of a functional, within a set of *long-range-corrected* functional, to describe the dissociation curve of the dimer. The functionals tested were LC-wPBE [30,31], LC-BP86 [31–33], LC-BLYP [31,34], LC-PW91 [31,35], wB97XD [36]. Basis set superposition error (BSSE) was also checked within the PW91 functional. We found no significant BSSE effects. 28 innermost core electrons were described with as small-core Stuttgart effective core potential that includes relativistic effects [37]. To represent the “valence” electrons an augmented-triple-zeta basis set with polarization and diffuse functions (aug-cc-pVTZ) was used [38].

In the optimization of the geometry an extremely tight convergence criterion was needed as the PES of these clusters is very flat. A structure was considered converged when the maximum force on an atom was less than 0.005 eV/\AA . In all optimized structures it was checked that all vibrational frequencies were real. All DFT calculations were done using Gaussian 09 [39].

Fig. 1 shows the dissociation curves of Cd dimer found by Schwerdtfeger et al. along with the five functionals mentioned above. It can be seen that the functional that performs better, compared with Schwerdtfeger et al. results, is LC-PW91. This functional underestimates the value of the bond distance (3.459 \AA vs. experiments: $3.78 \pm 0.03 \text{ \AA}$), but the binding energy (-0.043 eV) is quite close to the experimental values available in the literature ($-0.041 \pm 0.001 \text{ eV}$) [40–42]. Thus, LC-PW91 functional is used in all further DFT calculations.

3. Results and discussion

3.1. The number of ELJ and LJ isomers

Fig. 2 shows the logarithm of the number of isomers found with ELJ and LJ potentials as a function of the size of the cluster. It is to note the tremendous difference in the number of structures as the number of atoms in the cluster increases. In the limit of only 20 atoms there is a difference of about two orders of magnitude between both sets. This represents a first desirable advantage of the ELJ because it enormously reduces the size of the set of possible actual stable structures that can be explored with *ab initio* methods. This is obviously true if one accepts the hypothesis that ELJ performs better than LJ potential. A simple explanation of why the number of structures is reduced it is in the shape of the ELJ potential around the minimum. ELJ potential is wider than LJ potential at distances as large as 6 \AA . As a result of this, the coupling between atoms that are not first neighbors increases and the cluster becomes more tight. As counter example, note that if the potential is infinitely narrow (a Dirac-delta function), any configuration is stable. The same characteristic of the ELJ potential explains why the minimum distance between atoms in ELJ clusters is always less

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