

Model potential for beryllium clusters

E. Blaisten-Barojas* and S.N. Khanna

Department of Physics, Virginia Commonwealth University, 1020 West Main Street, Richmond, VA 23284-2000, USA

Received 5 July 1988; final version 30 September 1988

A many-body potential is developed for beryllium based on the electronic information extracted from the total energy surface of clusters with up to 5 atoms. The cluster sequence of growth generated with the potential is in excellent agreement with the quantum mechanical calculations in the literature. The hcp lattice of bulk beryllium is correctly found to be more stable than fcc and bcc lattices.

PACS: 34.20.Gj; 31.20.Sy; 36.40.+d; 61.45.+s

1. Introduction

The last few years have seen research in cluster physics and chemistry develop into an intensively studied area of science [1]. The common approach in simulation studies of cluster structure has been to use potentials developed to fit bulk properties [2, 3, 4] with the hope of bridging between cluster and condensed matter theories. However, recent molecular dynamics studies of Si clusters [3] using bulk potentials have predicted structures in disagreement with ab-initio calculations [5]. A different scheme was proposed by Car and Parrinello [6] where the need to solve the electronic and nuclear dynamics separately is bypassed. In this work we propose another approach. It too, like the Car and Parrinello technique, relies on the local density description (LD) of the electronic structure of the system. We develop a new class of potentials containing two- and three-body functions built simultaneously on the LD energy surface data of the dimer, trimer, tetramer and pentamer.

The binding in Be clusters increases dramatically with size due to the increasing *s-p* hybridization [7]. Namely, the dimer and trimer are weakly bonded [8, 9] whereas beryllium is metallic in the solid phase [7].

Ab-initio CI calculations predict Be_4 to be a stable tetrahedron [9, 10, 11], Be_5 to have a trigonal bipyramid structure [10], Be_6 to be a square bipyramid and Be_7 to acquire the pentagonal bipyramid structure. The fcc and hcp structures of Be_{13} have been analyzed [10, 11, 12] with the prediction that the fcc polyhedron is the most stable. Beryllium bulk calculations yield the hcp lattice [13] as the most stable in agreement with experiment.

2. Many-body potential for beryllium

In order to keep the problem computationally tractable we divide the total potential energy of a cluster into pair potentials and three-body potentials. Next we construct a model $V_2 + V_3$ so as to give a good simultaneous fit to values of the total energy surface of Be_2 up to Be_5 calculated within the local spin density (LSD) approximation. We have considered 23 values for the dimer, 76 points for the trimer in various angular conformations, 19 points for tetramer corresponding to isotropic expansions of the tetrahedron and one point for the pentamer trigonal bipyramid conformation. By so doing 4- and 5-body contributions are partially accounted for in the construction of a scaled 3-body term.

We write the binding energy of a system with *N* atoms as the sum over pairs plus the sum over the

* On sabbatical leave from Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000 México DF, México

orientational 3-body potentials [14] as:

$$E_N = \sum_{i < j}^N (A \exp(-\alpha r_{ij}) - C f_B(r_{ij})/r_{ij}^5) + \sum_{i < j < k}^N \left(-D(N) \exp(-\beta(r_{ij} + r_{ik} + r_{jk})) + \frac{C'}{(r_{ij} r_{ik} r_{jk})^3} \right) \times h(r_{ij}, r_{ik}, r_{jk}) f_B(r_{ij}) f_B(r_{ik}) f_B(r_{jk}) \quad (1)$$

where $f_B(r) = \exp[-B(r_0/r - 1)^5]$ if $r < r_0$ and $f_B(r) = 1$ otherwise. The function $h(r_{ij}, r_{ik}, r_{jk}) = 1 + 3 \cos \theta_{ijk} \cos \theta_{kij} \cos \theta_{jki}$ depends upon the angles θ_{ijk} subtended by any triplet of atoms ijk . The dependence of the s - p binding on cluster size is modelled through the scaled parameter $D(N) = D - G(0.25 - 1/N)$ if $N > 4$ and $D(N) = D$ otherwise. The parameters values are in atomic units: $A = 77.27716$, $\alpha = 1.71169$, $B = 0.6961$, $C = 87.39774$, $D = 9.65426$, $\beta = 0.485767$, $G = 35.945$, $C' = 673.4099$, $B' = 0.333333$, $r_0 = 4.04$. The quality of the fit was excellent leading to a sum of squares less than one thousand.

3. Results and discussion

With this potential we have generated clusters consisting of up to 13 beryllium atoms by a Monte Carlo simulation [15]. The resulting most stable structures of the dimer up to the pentamer are the same as those given by the LSD calculation in what concerns both binding energies and geometries. The structures obtained for the most stable Be_5 , Be_6 and Be_7 are in remarkably good agreement with ab-initio CI results [10]—bond distances differing by only 2–3%. However, the binding energies obtained with the potential for these clusters are lower than those obtained up to now with CI calculations [15]. This was expected since for Be the LSD approximation is known to overestimate the binding [7]. The most stable structures obtained with the potential for clusters with 8 up to 12 atoms are plotted in Fig. 1. A careful inspection shows that the square bipyramid and the pentagonal pyramid are the two building blocks contributing to the aggregation of the larger clusters. The 11-atom cluster is made up of two trigonal bipyramids sharing one atom and rotated 45° with respect to one another. This cluster is the first in the series of growth to have one internal atom (not drawn in the figure) with 10-fold coordination. The 12-atom cluster is an icosahedron with one missing atom. The potential predicts Be_{13} to have the icosahedral structure as the most stable, the hcp and fcc polyhedra following in binding energy. This seems to contradict the CI results stating the fcc structure to be more stable than the hcp structure [11, 12]. However these results do not emphasize the need of geometry optimization at the CI level. Besides, no

quantum mechanical calculation exists for icosahedral Be. If the binding energy of the hcp and fcc structures are calculated with the potential in exactly the geometries given in [12], the energy order is reversed, i.e., -0.897 a.u. (fcc) and -0.889 a.u. (hcp). Thus, geometry optimization is as important as the search of the most significant electronic configurations in the CI calculations.

In Fig. 2a we show that in this series the cluster binding energy (full line and left scale) tends to the bulk value as the cluster increases its size. The dotted line and right scale shows the point derivative of the binding energy. It puts in evidence that the 4-, 6- and 13-atom clusters are the most stable in the series. In Fig. 2b we have plotted the cluster average bond distance as a function of size. It is clearly shown how dramatic a change occurs near 4–5 beryllium atoms. This fact points exactly to the cluster size where s - p hybridization has acquired almost the bulk values. For larger clusters the bond distances change mostly as a result of the increasing number of atoms and evolves with oscillations towards the bulk lattice constants.

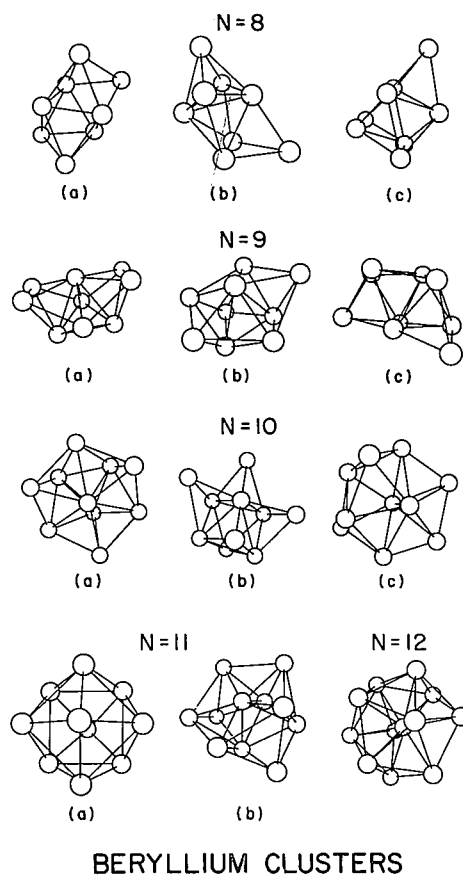


Fig. 1. Cluster configurations

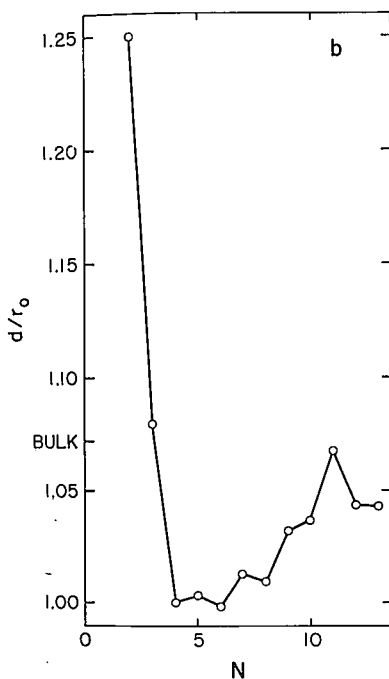
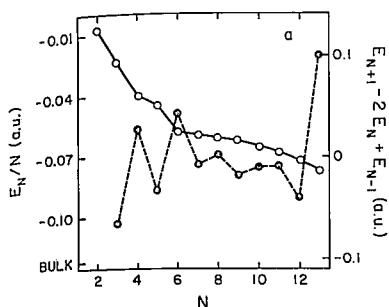


Fig. 2. a Potential energy per atom as a function of cluster size (full line, left scale) and its point derivative (dashed line, right scale); b Average bond distance as a function of cluster size

We have also calculated the cohesive energies E of the hcp, fcc and bcc lattices as a function of density [15]. The hcp lattice is the most stable with $E = -3.597$ eV/atom, lattice constants $a = 2.254$ Å and $c = 3.683$ Å and compressibility $K = 1.001 \cdot 10^{-12}$ cm/dyn. These values are in excellent agreement with experiment ($E = 3.32$ eV/atom, $a = 2.285$ Å, $c = 3.585$ Å) as well as with bulk ab-initio calculations [13]. Besides the potential predicts the fcc lattice to be

the next in stability at the room temperature density, but at low densities it predicts the bcc structure to become more stable than even the hcp lattice. This again is in agreement with experiment since beryllium bcc beryllium is stable at high temperatures.

The calculations we have reported describe a very successful strategy that makes possible to incorporate the information contained in the electronic structure of small clusters to the development a classical force field.

EBB thanks support from the international agreement between CONACyT (Mexico) and the NSF (USA) and from the Army Research Office (DAAG 29-85-K-0244). SNK acknowledges support from the Department of Energy (DE-FG05-87ER45316).

References

1. See for example references in: Benedek, G., Martin, T.P., Pacchioni, G. (eds.) *Elemental and molecular clusters*. Springer Series in Materials Science, Vol. 6. Berlin, Heidelberg, New York: Springer 1988
2. Honeycutt, D., Andersen, H.C.: *J. Phys. Chem.* **91**, 4950 (1987); Blaisten-Barojas, E., Garzon, I. L., Avalos-Borja, M.: *Phys. Rev. B* **36**, 8447 (1987)
3. Blaisten-Barojas, E., Levesque, D.: *Phys. Rev. B* **34**, 3910 (1986); Feuston, B.P., Kalia, R.K., Vashishta, P.: *Phys. Rev. B* **35**, 6222 (1987)
4. Martin, T.P.: *Phys. Rep.* **95**, 167 (1983); Landman, U., Sharf, D., Jortner, J.: *Phys. Rev. Lett.* **54**, 1860 (1985)
5. Ragavachari, K.: *J. Chem. Phys.* **84**, 5672 (1986); Pacchioni, G., Koutecky, J.: *J. Chem. Phys.* **84**, 3301 (1986); Tomanek, D., Schluter, H.: *Phys. Rev. Lett.* **56**, 1055 (1986)
6. Car, R., Parrinello, M.: *Phys. Rev. Lett.* **55**, 2471 (1985); Ballone, P., Andreoni, W., Car, R., Parrinello, M.: *Phys. Rev. Lett.* **60**, 271 (1988)
7. Jones, A.O.: In: *Ab-initio methods in quantum mechanics-I*. Lawley, K.P. (ed.), p. 413. New York: John Wiley 1987
8. Lengsfeld, III, B., McLean, A.D., Yoshimine, M., Liu, B.: *J. Chem. Phys.* **79**, 1891 (1983)
9. Harrison, R.J., Handy, N.C.: *Chem. Phys. Lett.* **123**, 321 (1986)
10. Ermler, W.C., Kern, C.W., Pitzer, R.M., Winter, N.W.: *J. Chem. Phys.* **84**, 3937 (1986); Marino, M., Ermler, W.C.: *J. Chem. Phys.* **86**, 6283 (1987)
11. Rohlfing, C.M., Binkley, J.S.: *Chem. Phys. Lett.* **134**, 110 (1987)
12. Bauschlicher, Jr., C.W., Pettersson, L.G.M.: *J. Chem. Phys.* **84**, 2226 (1986)
13. Chu, M.Y., Lam, P.K., Chen, M.L.: *Phys. Rev. B* **28**, 4179 (1983)
14. Bruch, L.W., Blaisten-Barojas, E., Novaro, O.: *J. Chem. Phys.* **67**, 4701 (1977); Blaisten-Barojas, E., Novaro, O., Bruch, L.W.: *Mol. Phys.* **37**, 599 (1979)
15. Blaisten-Barojas, E., Khanna, S.N.: *Phys. Rev. Lett.* **61**, 1477 (1988)