

# Tight-binding Calcium Clusters from Adaptive Tempering Monte Carlo Simulation

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*Abstract:* The most stable structure of calcium clusters with 14 to 32 atoms is optimized by the Adaptive Tempering Monte Carlo method. The binding energy of the clusters is obtained within the tight-binding approach parameterized in a previous work. The optimization process is started at about 800 K and the tempering brings the structure to the global minimum ending the process at 1 K. It is found that six cluster sizes, 15, 16, 18, 21, 23 and 25 have a global minimum structure not reported in the literature. In this size range,  $\text{Ca}_{15}$ ,  $\text{Ca}_{21}$  and  $\text{Ca}_{23}$  are the preferred geometries that can be identified as magic numbers. The tight-binding one-electron levels in the valence band display a large energy gap of 0.5 eV between the last occupied and first unoccupied levels for the magic number clusters. This band gap is 5 to 10 times smaller for other cluster sizes.

*Keywords:* calcium clusters, multicanonical, tempering, adaptive tempering Monte Carlo

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## 1 Introduction

The structure and electronic properties of metallic clusters have long been subject of interest giving rise to several popular approaches such as the jellium model for alkaline metals, in which electron sub-shell closings occur when the number of electrons in the valence band is 2, 8, 18, 20, 34, 40, 58, 68, 90, etc. On the other hand, the alkaline earths metals such as calcium have a different electronic behavior due to the s-p-d character of the conduction band of bulk calcium. Recently an important computational effort led to the discovery of the preferred structures of calcium clusters from  $\text{Ca}_{32}$  to  $\text{Ca}_{85}$  within the tight-binding (TB) approach [1]. These clusters do not satisfy the jellium model shell closings. Additionally, small clusters of up to 13 atoms were investigated with the all-electron density-functional approach [2]. Calcium clusters with hundreds of atoms have been studied with empirical classical potentials based on parameterization of bulk properties [3]. This approach, though, is not suitable for smaller clusters since it overestimates the binding energy [2]. However, the structure, energetics and electronic properties of clusters in the range 14-32 have not been reported from quantum mechanical approaches. This is the subject of the present letter. The optimization of the best structure from quantum mechanical methods is a difficult task because clusters present many isomer geometries that are stable. The process of finding the structure with lowest binding energy is more computationally eager than the quantum calculation of the electronic energy of one given geometry. In this letter we propose a simulation

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method that permits to optimize cluster structures, and that we have linked to a quantum tight-binding approach. The process is the Adaptive Tempering Monte Carlo (ATMC) [4] which is here combined with the TB model from Ref. [1] parameterized for calcium nanoclusters. The ATMC belongs to a family of algorithms named multicanonical and/or parallel tempering that initiated with the work of Marinari and Parisi [5] and that of Lyubartsev et. al. [6]. This letter is organized as follows. In section 2 we describe the ATMC method. In section 3 we describe the energetics and structural results for  $\text{Ca}_{14}$  through  $\text{Ca}_{32}$  and show details on the valence band eigenvalues. In Section 4 we present our conclusions.

## 2 Adaptive Tempering Monte Carlo linked to Tight-Binding

In the ATMC method [4] the system accesses a multitude of canonical ensembles, each with constant  $T_i N V$ , where each  $T_i$  characterizes a different canonical ensemble within a predetermined temperature range. Each canonical ensemble is simulated with the usual Metropolis Monte Carlo algorithm, and the various ensembles are connected along the simulation by a super-Markov chain in which the temperature is allowed to hop adaptively according to the following acceptance probability

$$acc = \min [1, \exp[-(E - \langle E \rangle_{T_{old}}) (\frac{1}{k_B T_{new}} - \frac{1}{k_B T_{old}})]] \quad (1)$$

Here,  $E$  is the instantaneous cluster binding energy,  $k_B$  is Boltzmann's constant, and  $\langle E \rangle_T$  is the average cluster binding energy at temperature  $T$ . Both  $T_{old}$  and  $T_{new}$  are considered to have hopping probabilities  $q$  and  $p = 1 - q$ . The probability  $p$  is the normalized Boltzmann factor  $\exp(-\delta E/k_B T_{new})/Z$  and  $q = \exp(-\delta E/k_B T_{old})/Z$  where we replaced  $E - \langle E \rangle_T$  by  $\delta E$ , the standard deviation of the binding energy at temperature  $T_{old}$ . Here  $Z$  is the normalizing configuration integral. We introduce one parameter  $a$  in terms of which  $p = 1/(1+a)$  and  $q = a/(1+a)$ . In this example of calcium clusters, the optimal value is  $a = 0.135$ . Therefore the selection of one temperature over the other satisfies the following relation:

$$T_{new} = \frac{\ln(a) \delta E T_{old}}{\delta E + \ln(a) k_B T_{old}} \quad (2)$$

This algorithm enables the system to visit a wide range of temperatures. Every time that the temperature *hops* to a new temperature with probability  $p$ , we say that a tempering event took place. Subsequently, the system evolves at the new temperature  $T_{new}$  under the new canonical MC in which the step size is also adapted to yield a run in which roughly 50% of configuration changes are accepted, and 50% are rejected. In all simulations, the cluster was started from an arbitrary initial configuration at high temperatures close to the upper limit of the allowed temperature range. For calcium clusters, the upper limit for the temperature is set at  $T = 1000$  K. The total binding energy  $E$  is calculated with the TB model from Ref. [1]. The TB model and parameters adopted to obtain the binding energy  $E$  were previously used by the authors in Ref. [1] where readers are referred for details. The model is based on the Slater-Koster (SK) approach [7] in which  $s$ ,  $p$  and  $d$  orbitals span a  $9 \times 9$  matrix representation of the TB Hamiltonian for each atom in the cluster. The basis set is non-orthogonal and the model has 97 parameters associated to the analytical representation of on-site and hopping integrals. These parameters were fitted to the energy bands and cohesive energy of bulk fcc and bcc calcium [8] and to the *ab initio* energy surfaces of  $\text{Ca}_7$  through  $\text{Ca}_{13}$  [2] and are reported in Ref. [1]. The starting cluster configurations are spherical cuts from a simple cubic lattice. Before the tempering starts, any given cluster is warmed up for 10,000 iterations of a regular canonical ensemble MC at temperature  $T = 800$  K. At this point the adaptive tempering starts, and the system adaptively changes temperature until the  $T_{new}$  reaches the desired lower limit, which was  $\sim 1$  K in the case of the calcium clusters.

A typical example of the temperature evolution as the ATMC progresses is given in Fig. 1 for a cluster with 23 atoms. Fig. 1a shows the evolution of the temperature over approximately 10,000 ATMC iterations. Fig. 1b depicts the corresponding changes in the average binding energy as the tempering process evolves. In this specific example, the temperature changed 247 times.

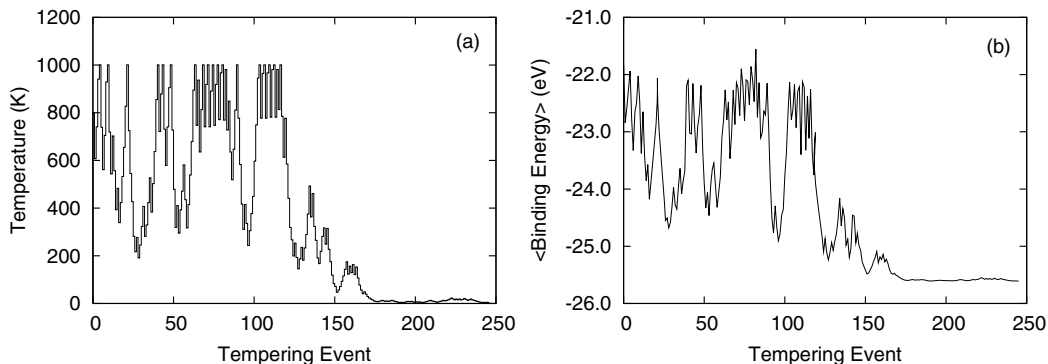


Figure 1: Temperature and average binding energy of  $\text{Ca}_{23}$  along the ATMC simulation

For some of the clusters studied, the system evolves for a certain number of iterations, reaches a relatively low temperature where it seems to be trapped in a local minimum. Then the ATMC allows the system to overcome barriers and escape from such local minimum leading the system to excursion again to high temperature regions. Finally after more tempering events the system lands in the global minimum. One of such cases is shown in Fig. 2 for a  $\text{Ca}_{14}$  cluster. As seen in Fig. 2a, at about 100 K the cluster remains quite some time in regions of configuration space with low binding energy (Fig. 2b). However, the cluster is able to hop out of that region and excursion to other regions consistent with high temperatures. After about an extra 10,000 MC iterations the cluster finally finds the global minimum, and the temperature collapses fast to 1 K. For this example, the temperature changed about 1866 times before ending the process.

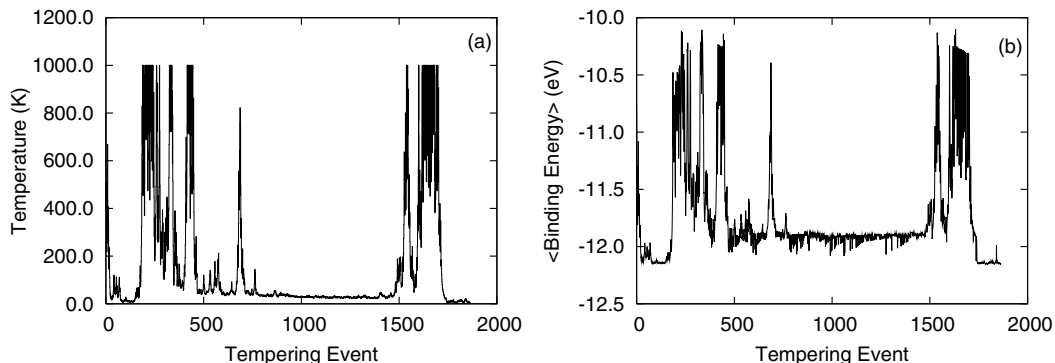


Figure 2: Temperature and average binding energy of  $\text{Ca}_{23}$  along the ATMC simulation

### 3 Energetics and Structural Changes

The ATMC method was applied to all calcium cluster sizes containing 13 to 32 atoms. The electronic energy of these clusters was in all cases calculated within the TB model described above. In Fig. 3a we have gathered results of the binding energy  $E_N$  per atom. The binding energy is defined as the TB electronic energy of a cluster of  $N$  calcium atoms minus  $N$  times the TB energy of one calcium atom. In Fig. 3a, the TB results correspond to the empty triangles. For comparison, black triangles in the figure are the TB energies of clusters with geometries borrowed from the Morse potential (parameter  $\rho = 3.6$ ) [9], which have been scaled consistently with the TB energy. It is clear that none of those geometries is preferred over the configurations obtained with the ATMC. Figure 3b shows the second difference of the TB energies obtained by our calculation. Peaks correspond to energetically preferred sizes because a size associated with a peak is more stable than both nearest sizes. It is interesting to note that there is an even-odd alternation where odd sizes are preferred over even sizes. Three of these sizes, 15, 21 and 23 show the most abrupt drop of peak height towards larger sizes. Because of that, these sizes can be called magic numbers. In this TB approach, the core electrons of Ca are frozen, and only the 2 valence electrons are considered. Therefore, the number of electrons corresponding to these magic number clusters is 30, 42 and 46, which are not consistent with shell closings of the jellium model (20, 40, 58, etc). When analyzing closely the preferred cluster geometries, we find that all of them except for six are

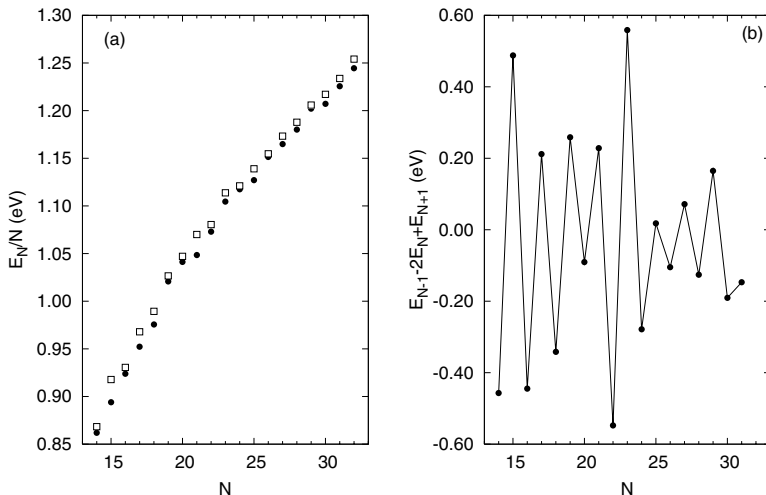


Figure 3: Binding energy and magic numbers of calcium clusters versus size

relaxed Morse structures in which bond lengths and angles accommodate somehow to adjust for the large surface to volume ratio. These six clusters,  $\text{Ca}_{15}$ ,  $\text{Ca}_{16}$ ,  $\text{Ca}_{18}$ ,  $\text{Ca}_{21}$ ,  $\text{Ca}_{23}$  and  $\text{Ca}_{25}$  depicted in Fig. 4, have a preferred structure not previously reported in the literature as the most stable under any model potential (Lennard Jones[10], Morse[11], Sutton-Chen [12], TB-second-moment many body [13, 14], Murrell Mottram [15], Dzugutov[16]). The three  $C_{2v}$  magic number clusters are among the six new structures. The  $\text{Ca}_{15}$  cluster is a pentagonal bipyramid with apex vertexes capped by two parallel squares. The  $\text{Ca}_{23}$  cluster has a structure built on the elongated 19-atom icosahedron capped with one pentagonal pyramid to which two symmetrically opposed sides are decorated by dimers. The  $\text{Ca}_{21}$  cluster is an incomplete 23-atom cluster in which two atoms are missing, the apex vertex atom and one from the pentagonal pyramid underneath.

TB also provides the one-electron quantum levels of the cluster valence band. It is interesting

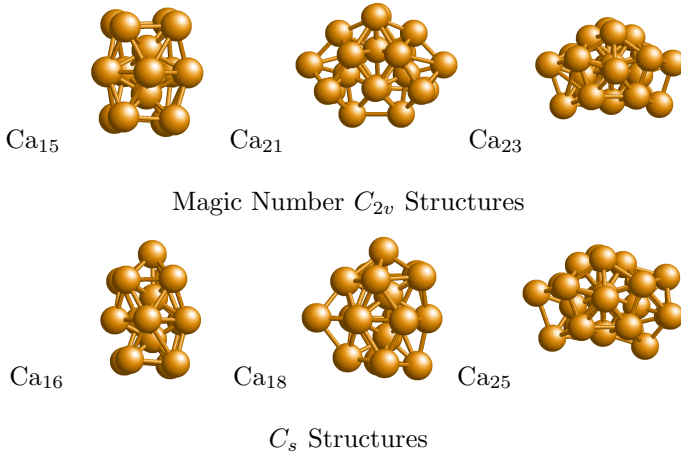


Figure 4: Six new calcium cluster structures.  $\text{Ca}_{15}$ ,  $\text{Ca}_{21}$  and  $\text{Ca}_{23}$  are magic numbers

to note that these eigenvalues present a large energy gap between the highest occupied state and lowest unoccupied state of 0.63, 0.47 and 0.48 eV for the magic number clusters  $\text{Ca}_{15}$ ,  $\text{Ca}_{21}$  and  $\text{Ca}_{23}$ , respectively. However, the energy gap for all other sizes in the range studied is smaller, i. e. on the order of 0.05 to 0.1 eV. Fig. 5 illustrates this effect. Eigenvalues are sorted by energy and numbered in increasing order from the bottom of the band. Fig. 5 shows the distribution of TB eigenvalues in a  $\pm 1$  eV band around the Fermi energy. Black circles identify occupied states whereas white squares indicate the unoccupied states. Visually one sees that whereas the energy gap for  $\text{Ca}_{15}$  is large, it is considerably smaller for  $\text{Ca}_{16}$ . The same effect is shown in Fig. 5 for  $\text{Ca}_{23}$  and  $\text{Ca}_{21}$  has a behavior very similar to  $\text{Ca}_{23}$ . Therefore, electronic effects are fundamental in the determination of the magic numbers in calcium clusters.

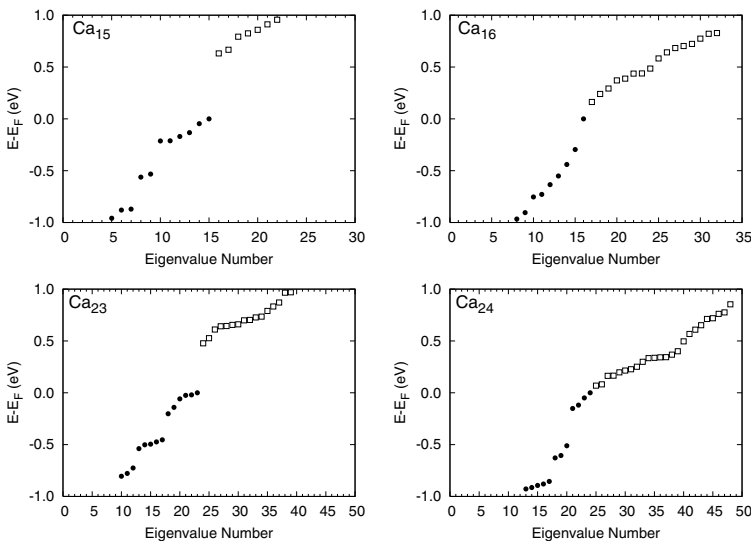


Figure 5: Eigenvalues of  $\text{Ca}_{15}$ ,  $\text{Ca}_{16}$ ,  $\text{Ca}_{23}$ ,  $\text{Ca}_{24}$

## 4 Conclusions

In this letter we have combined the Adaptive Tempering Monte Carlo method to optimize the calculation of the binding energies of calcium clusters within the tight-binding quantum approach. The ATMC is very efficient, optimizes structures in a fraction of the time the simulated annealing method requires, and can easily be coupled to quantum approaches. The cluster sizes studied spanned from  $\text{Ca}_{13}$  to  $\text{Ca}_{32}$ . Within this size range, three magic numbers  $\text{Ca}_{15}$ ,  $\text{Ca}_{21}$  and  $\text{Ca}_{23}$  were revealed. The structure of these magic number clusters, as well as the structure of three other sizes (16, 18, 25), is new to the literature. It is also observed that a large energy gap of about 0.5 eV exists between the highest occupied TB-eigenstate and the lowest unoccupied TB-eigenstate for the magic number clusters. The corresponding energy gap for all other sizes studied drops to about 0.05-0.1 eV. This correlation is indicative that at these three magic sizes there is an electronic shell closing which is not consistent with that predicted by the jellium model.

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