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CAPACITANCE OF MAGIC Ba_n CLUSTERS

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1. Introduction

The differential capacitance of a cluster is one of the most important quantities for the description of electron transfer at the nanoscale. It plays a central role in many phenomena such as the Coulomb blockade. The first observation on the Coulomb blockade effect in the smallest possible system with a single atom as the central island of double-barrier tunnel junction was reported [1], where the system consists of a single tungsten atom as the central island and a tungsten STM tip and silicon $(100)2 \times 1$ reconstructed surface as the two electrodes. Meanwhile, the linear conductance and current-voltage characteristics in a one-atom point contact are also studied [2], in which the central island is either a single atom or a small atomic cluster. In these kinds of systems, monoelectron conductivity has been realized. Monoelectron conductivity has many advantages, it would help to overcome most of the problems arising from thermal dissipation in very small volumes, or from the smallness of the depletion zones. However, this process is influenced by two factors: thermal energy and electrostatic energy. If the thermal energy is much higher than the electrostatic one, the electron will be expelled, in this case, no single charge controlling is possible. A necessary requirement for the successful trapping of individual charge inside the cluster is that the thermal energy (KT) should be smaller than the electrostatic one ($e^2/2C$, C is the capacitance), this condition can be achieved either by decreasing the temperature or by decreasing the capacitance of the cluster. Therefore, the theoretical calculation of the capacitance is a very important problem for metal cluster, especially for *magic* metal cluster due to its high stability, which makes it possible for a *magic cluster* to be used as a *quantum dot* when embedded in some substrates. In this paper, by using *ab initio* ultrasoft pseudopotential scheme combined with molecular orbitals method, the structures of magic Ba_n clusters are determined, their capacitance are calculated, and the effect of orbitals hybridization on the capacitance is analyzed.

2. Theoretical Method

The differential capacitance (C) of a charged system determines the specific amount of work ($\ddot{a}V$), required to bring a fixed amount of charge ($\ddot{a}Q$), from the vacuum level to the system: $C = \ddot{a}Q/\ddot{a}V$. Macroscopically, capacitance is a system-specific quantity, which can be obtained from Maxwell's equations of classical electrostatics.

From an atomistic viewpoint, the capacitance of the system is determined by [3]

$$e^2/C = \mu(N+1) - \mu(N). \quad (1)$$

Here $\mu(N)$ is the chemical potential of N -electron system, which can be expressed in terms of total energy E

$$\mu(N) = E(N) - E(N - 1). \quad (2)$$

According to the definitions of ionization potential (IP) and electron affinity (EA), we have

$$\begin{aligned} e^2/C &= [E(N + 1) - E(N)] - [E(N) - E(N - 1)] \\ &= [E(N - 1) - E(N)] - [E(N) - E(N + 1)] \\ &= IP - EA. \end{aligned} \quad (3)$$

In the density-functional theory, the difference of IP and EA can be approximated by the gap defined by the eigenvalue difference between the lowest unoccupied $\epsilon^{LUMO}(N)$ and the highest occupied $\epsilon^{HOMO}(N)$ states for an N electron system [4]:

$$IP-EA \approx \epsilon^{LUMO}(N) - \epsilon^{HOMO}(N). \quad (4)$$

In order to get the HOMO-LUMO gap and determine the equilibrium structure of the cluster, we used *ab initio* ultrasoft pseudopotential scheme with plane-wave basis (Vienna *Ab initio* Simulation Program (VASP)) [5], in which the finite-temperature local-density functional theory developed by Mermin [6] is used, and variational quantity is the electronic free energy. Finite-temperature leads to the broadening of the one-electron levels that is very helpful to improve the convergence of Brillouin-zone integrations. The electron-ion interaction is described by a fully nonlocal optimized ultrasoft pseudopotentials [7]. The minimization of the free energy over the electronic and ionic degrees of freedom is performed using the conjugate-gradient iterative minimization technique. In the optimizations, the edge length for the super cubic cell is 33.5 Å. In such a big supercell only the Γ point can be used to represent the Brillouin zone. The exchange-correlation energy of valence electrons is adopted the form of Ceperly and Alder [8] as parameterized by Perdew and Zunger [9]. The structure optimization is symmetry unrestricted, and the optimization is terminated when all the forces acting on the atoms are less than 0.01 eV/Å.

3. Results and Discussions

Due to the closed electronic configuration in divalent atom, the divalent metal (Be, Mg, Ca, Sr, Ba) clusters are specially interesting. They exhibit non-metal-metal transition with increasing their size. Their dimers are weakly bonded and as the cluster size increases, the valence s states hybridize with the unoccupied states which leads to the metallization. Therefore, many studies have been devoted to the divalent metal clusters. Experiments found that magic numbers for Ba_n clusters are 13, 19, 23, 26, 29, and 32 [10]. However, only small clusters ($n \leq 13$) have been theoretically studied, no any information about the structure as well as the behavior of capacitance for these magic clusters has been reported. We have found that among all the possible configurations, icosahedral or polyicosahedral structure is most stable, as shown in Figure 1.

Table 1 gives the average nearest neighbor bond length R (in Å), the average binding energy per atom ϵ (in eV), the HOMO-LUMO gap δ (in eV) and the capacitance C (in aF). The capacitance is in the order of aF ($1aF = 10^{-18}F$). It has been found that many interesting phenomena (such as Coulomb gap, Coulomb staircase and negative differential resistance) would be displayed in small capacitance systems of this order. Therefore, due to the stability and small capacitance, it can be expected that there would be some potential applications for magic Ba_n clusters.

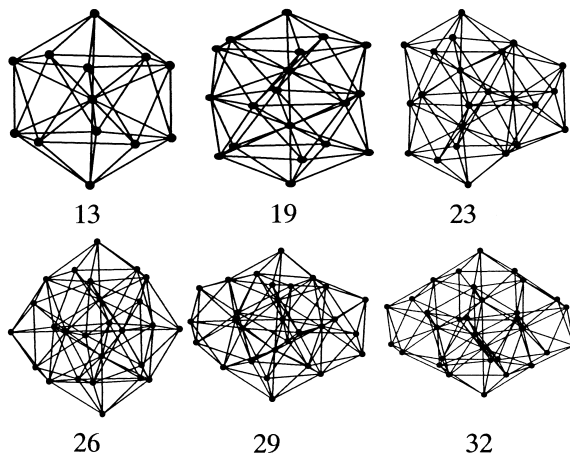
Figure 1. Equilibrium structure of magic Ba_n clusters.

Figure 2 Capacitance changes with cluster size ($N^{1/3}$), which suggests that C nonlinearly increases with $N^{1/3}$, different from the cases in Au_n clusters [11] and Cu_n clusters [12], where a linear behavior has been found. What is the physical origin of the difference in the capacitance between Ba_n and Au_n (or Cu_n) clusters? It can be understood in terms of the bonding feature. In Au_n and Cu_n clusters, the valence electrons are free-like, according to the conducting sphere-droplet model [13], the IP and EA can be expressed as

$$IP = w + \alpha e^2/R \quad EA = w + \beta e^2/R \quad (5)$$

where w stands for the work function, α and β are coefficients, and R is the radius ($N^{1/3}$). Therefore, we have

$$IP - EA = (\alpha + \beta)e^2/R. \quad (6)$$

Comparing Eq.(6) with Eq.(3), we can see that in the free-like electron cluster (e.g. Au, Ag, Cu, and alkali metal clusters), because the valence electrons form jellium sphere, capacitance is a linearly increasing function of cluster radius ($C \propto N^{1/3}$), similar to the classical formula for spherical particle: $C = 2\pi\epsilon R$, ϵ denotes the dielectric constant. However, Ba atom has $6s^2$ closed shell configuration and low-lying empty $5d$ and $6p$ shells, the ground state is $6s^2$ (1S_0), while its first excited state is $6s^1 5d^1$ (1D_1). Therefore, in Ba_n clusters due to the orbital hybridization, d-electrons are expected to contribute

TABLE 1

The Average Nearest Neighbor Bond length R (in Å), the Average Binding Energy per Atom ϵ (in eV), the HOMO-LUMO Gap δ (in eV) and the Capacitance C (in aF) for the Magic Ba_n Clusters with Polyicosahedral Structures

Cluster	R	ϵ	δ	C
Ba ₁₃	4.284	1.2347	0.5885	0.2722
Ba ₁₉	4.320	1.2970	0.2821	0.5678
Ba ₂₃	4.340	1.3310	0.1505	1.0645
Ba ₂₆	4.342	1.3509	0.1497	1.0701
Ba ₂₉	4.345	1.3730	0.1400	1.1443
Ba ₃₂	4.406	1.3500	0.0540	2.9667

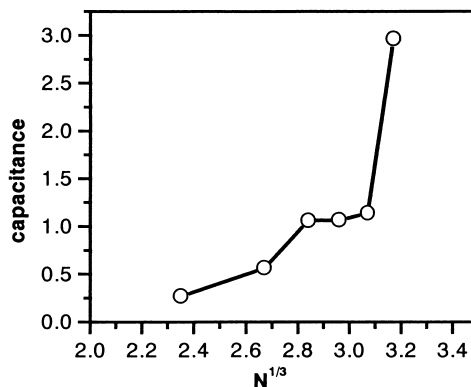


Figure 2. Capacitance changes with cluster size.

to the bonding. In fact, we have found that in Ba_{13} cluster, the average Mulliken populations per atom in 5d, 6s, and 6p orbitals are 0.7794, 0.6865, and 0.5226; while for Ba_{19} cluster, the corresponding numbers are 0.7929, 0.7770, and 0.4300, respectively. Furthermore, the highest occupied molecular orbital (HOMO) in Ba_{13} is composed of 79% 5d, 19% 6s, and 2% 6p orbitals. The HOMO in Ba_{19} is contributed by 71% 5d, 22% 6s, and 7% 6p orbitals. Due to the bonding of 5d electrons, Eq.(6) is not valid for Ba_n cluster, accordingly, nonlinear relation between C and $N^{1/3}$ exists in this system.

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