

QUANTUM-CHEMICAL ANALYSIS OF SMALL SILVER CLUSTERS

Grigorii V. GADIYAK^a, Yurii N. MOROKOV^a and Mojmír TOMÁŠEK^b

^a Institute of Theoretical and Applied Mechanics,
Siberian Section, Academy of Sciences of U.S.S.R.,
630090 Novosibirsk 90, U.S.S.R. and

^b The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2, Czechoslovakia

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Total energy calculations of three- and four-atomic silver clusters have been performed by the spin-polarized version of the CNDO/2 method to get the most stable equilibrium geometries, atomization energies, and charge and spin distribution on the atoms for three different basis sets: $\{s\}$, $\{sp\}$, and $\{spd\}$. When viewed from the equilateral triangle and square geometries, the last electronic configuration, *i.e.* the $\{spd\}$ one, appears to be most stable with respect to the geometrical deformations considered. In this case, the behaviour of the atoms of both clusters resembles that of hard spheres (*i.e.* close-packing).

In the last years, the interest in the calculation of small metallic clusters¹⁻³ increased considerably in connection with the possibility to prepare them experimentally (*e.g.*, in the noble-gas matrix^{3,4}). As an example, and by means of finding the extremum of the total energy, it is interesting to consider the possible geometries of silver clusters Ag₂, Ag₃, and Ag₄.

RESULTS AND DISCUSSION

The calculation has been performed using the CNDO/2 method⁵. Three sets of basis functions, namely $\{s\}$, $\{sp\}$, and $\{spd\}$ have been used. In each basis, its own parametrization has been used. When choosing the parameters, the Slater exponents and the parameter β , appearing in the off-diagonal matrix elements, have been varied so as to reproduce the bond energy and bond length of the ground state of the Ag₂ molecule. The respective parameters are given in Table I. To simplify the finding of a stable three-atomic configuration, the following procedure has been used. For each fixed bond length, the minimum of the total energy has been searched for through the variation of the angle Θ of the possible geometrical configurations. The calculations have shown (Figs 1, 2) that closest to the equilateral triangle configuration is the case of the $\{spd\}$ basis: the equilibrium bond length and bond angle are $l = 2.78 \text{ \AA}$ and $\Theta \approx 65^\circ$, respectively; for the $\{sp\}$ basis one

has $l = 2.94 \text{ \AA}$ and $\Theta \approx 75^\circ$ and for the $\{s\}$ basis $l = 3 \text{ \AA}$, $\Theta \approx 97^\circ$. Table II shows the data on charges and spins for the cluster Ag_3 . A strong asymmetry arises in the spin distribution. The spin concentrates on the two equivalent corners of an isosceles triangle, a fact in agreement with experiment^{6,7}. An asymmetry in the distribution of atomic charges also appears, however, its quantity is much smaller. Due to the Coulomb interaction, the double degeneracy of the highest (partly)

TABLE I
Parameters for silver^a

	Basis	q , a.u.	η , eV	β , eV
	s	1.192	4.23	2.776
	sp	1.272	4.23	2.520
	p	1.272	1.34	1.310
	spd	1.800	4.23	4.65
	p	1.800	1.34	2.42
	d	3.050	8.50	7.63

^a 1 eV = $1.6021892 \cdot 10^{-19}$ J; 1 a.u. = $4.359814 \cdot 10^{-18}$ J.

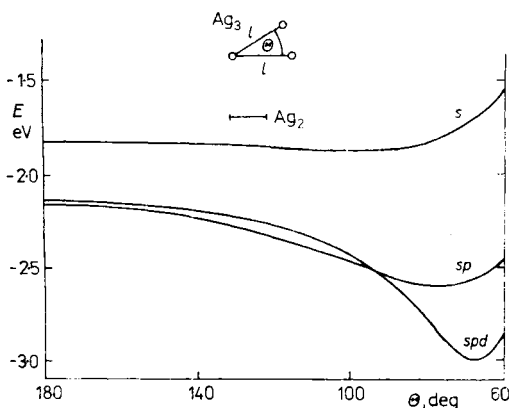


FIG. 1
Total energy of the isosceles triangle Ag_3 cluster as a function of the angle Θ , for the three basis sets $\{s\}$, $\{sp\}$, and $\{spd\}$, (in the minimum with respect to l)

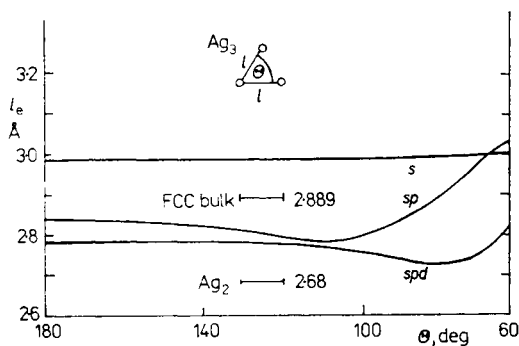


FIG. 2
The equilibrium length l_e of the interatomic bond in Ag_3 as a function of the angle Θ , for the three investigated basis sets

occupied ea_2 state of the equilateral triangle Ag_3 is lifted. The lower state α_2^+ is occupied and the higher α_2^- empty, the shift between them amounting to the value of the Coulomb integral γ (Fig. 3). It is worth noticing that in the CNDO/2 method, the first iteration of the self-consistent procedure is the "Hückel" one. In the Hückel method, the Coulomb interaction parameters are equal to zero and so the first CNDO/2 iteration leads to a coincidence of the α_2^+ and α_2^- states. This degeneracy

TABLE II
Results of calculations for the Ag_3 and Ag_4 clusters

Cluster		E , eV	D_{at}/n^a	l , Å	q_{in}^b	q_{out}	S_{in}^b	S_{out}
Ag_3	C_{2v}	0.000	0.99	2.78	0.13	-0.07	-0.07	0.53
	D_{3h}	0.091	—	2.83	0.17	-0.08	0.11	0.45
	$D_{\infty h}$	0.810	—	2.79	-0.12	0.06	0.23	0.38
Ag_4	D_{2h}	0.000	1.34	2.82	0.13	-0.13	0.00	0.00
	T_d	0.979	—	2.89	± 0.06	—	± 0.46	—
	D_{4h}	1.473	—	2.83	0.00	—	± 0.52	—

^a $D_{at}/n = (E(Ag_n) - nE(Ag))/n$, (i.e. the atomization energy per atom); ^b q (or S) = charge (or spin) on the inner (in) or outer (out) atom.

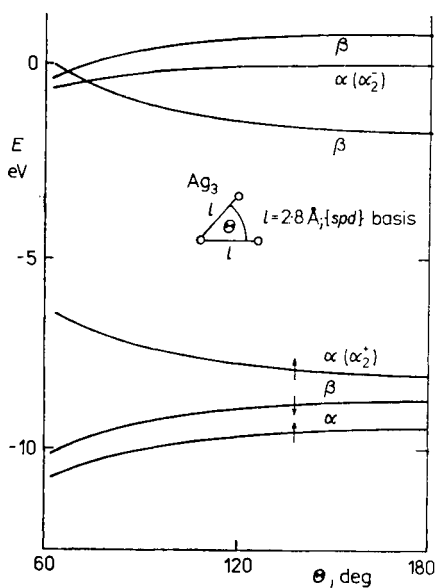


FIG. 3

One-electron energies of Ag_3 in the $\{spd\}$ basis as functions of the angle θ for a fixed value $l = 2.8 \text{ \AA}$ of the bond length. Only highest occupied and lowest unoccupied states of sp -character are shown. α and β denote states with up and down spin, respectively

is lifted in higher iterations, when during the filling of the states there arises an asymmetry in the spin distribution and consequently also in the Hamiltonian. In^{7,8}, an analogous behaviour of three-atomic clusters has been observed for copper.

Figs 4, 5 present the results of the calculation of the total energy of the planar Ag_4 cluster in the $\{s\}$, $\{sp\}$, and $\{spd\}$ bases both for the singlet and the triplet states. As follows from these figures, only for the $\{spd\}$ basis there exists a well pronounced minimum. For that basis, also the triplet state appears to be stable, although with a little bit smaller energy. The calculation has shown the three-dimensional configuration (tetrahedron) to be less favourable than the planar one.

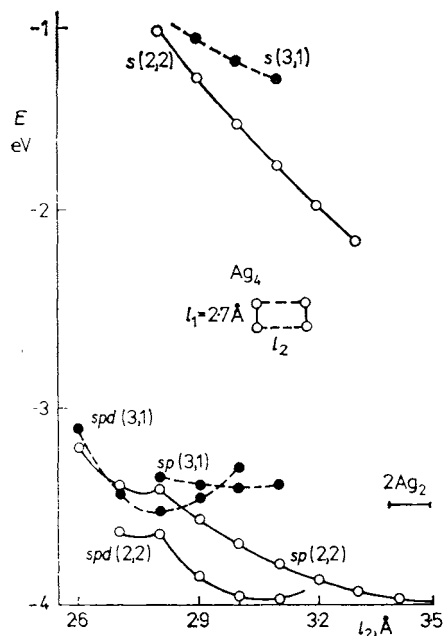


FIG. 4

Total energies of the rectangular Ag_4 cluster as functions of the length of one side (l_2) for the fixed length ($l_1 = 2.7 \text{ \AA}$) of the other side. The singlet (—) and triplet (---) states are drawn for the three investigated basis sets. To describe the two spin configurations, following short-hand notation has been used: $(\alpha^2\beta^2) \rightarrow (2, 2)$ and $(\alpha^3\beta^1) \rightarrow (3, 1)$, respectively

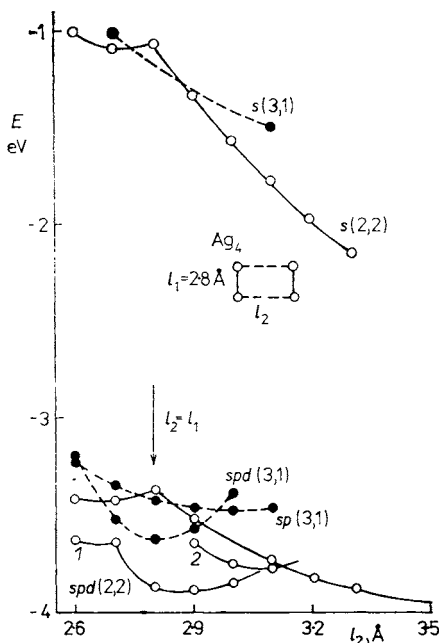


FIG. 5

Same as in Fig. 4, this time for $l_1 = 2.8 \text{ \AA}$. In the $\{spd\}$ basis, two singlet states (1 and 2) have been obtained

Similarly as with the equilateral triangle cluster, even for the quadrate cluster the first iteration of the CNDO/2 method (corresponding to the Hückel method) gives a degenerate highest (partly) occupied level. The Jahn–Teller splitting leads to a structure differing from the quadrate. Notice in this connection that within the Hückel method, equilateral triangle and quadrate shaped molecules represent examples of the so-called Jahn–Teller molecules. For the quadrate geometries, a certain anomaly occurs in the behaviour of the total energy (Fig. 5). The reason of this anomaly consists in the fact that for the quadrate configuration, the highest occupied state is degenerate and according to the Hund's rule, the most favourable is the state with maximum multiplicity ($\alpha^3\beta^1$). A deviation from quadrate geometry removes the above degeneracy (Fig. 6) and the ground state appears to be a singlet ($\alpha^2\beta^2$ – a spin paired configuration). One faces here a typical example of the well known competition, namely the Hund's rule *versus* the Jahn–Teller (electron pairing) effect.

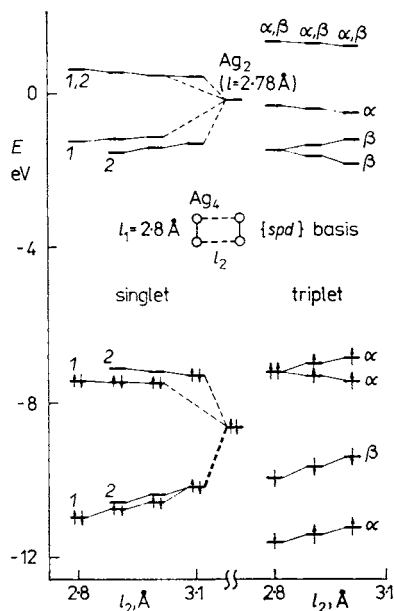


FIG. 6

One-electron energies of the rectangular Ag_4 cluster as functions of l_1 with the fixed value $l_2 = 2.8 \text{ \AA}$, for the $\{spd\}$ basis. The energy levels on the left side correspond to the singlet states 1 and 2, on the right side to the triplet state

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