Non-additive forces in atomic clusters

Ilya G. Kaplan a, Ruben Santamaria a & Octavio Novaro a

a Instituto de Física, UNAM, Apdo. Postal 20-364, México D.F., Mexico

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Non-additive forces in atomic clusters
The case of Agₙ

By ILYA G. KAPLAN,† RUBEN SANTAMARIA and OCTAVIO NOVARO
Instituto de Fisica, UNAM, Apdo. Postal 20-364, 01000 México, D.F., Mexico

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The closed recurrence formula which expresses the energy of m-body interactions through the energies of 2-, 3- and (m - 1)-body ones is obtained. The m-body contributions to the interaction energy of silver clusters are calculated by the all-electron non-local spin density method. The importance of not only 3- but also 4- and 5-body forces for cluster stability has been revealed. The stable geometry of planar and spatial silver clusters is determined by the competition of attractive additive forces and repulsive non-additive forces. The larger magnitude of non-additive forces for three-dimensional conformations in comparison with two-dimensional ones is the reason that for Agₙ with n = 4–6 the most stable geometries are planar.

1. Introduction

The interaction of point charges is always characterized by pair additivity. A well-known example is the Coulomb law:

\[ V = \sum_{i<j} \frac{q_i q_j}{r_{ij}} \]  

(1)

However, atoms and molecules obey quantum mechanics and have spatially distributed charge. The internal structure of the interacting atoms is disturbed by surrounding atoms. So an interacting pair of atoms has different interaction energies in different environments. This results in deviations from a simple pairwise formula (equation (1)), introducing terms called non-additive.

This kind of non-additivity originates from the polarization forces [1]. A second type of interparticle force which leads to non-additivity is the exchange force (of which there are two kinds [2]). One type of exchange force has its origin in the Pauli principle, which requires the antisymmetrization of the many-electron wavefunction. The exchange of electrons belonging to three or more atoms results in non-additive terms in the interaction energy. The direct exchange interaction through transfer particles also results in non-additivity. For atomic and molecular systems these are electrodynamic interactions through transverse photons. The analysis of different types of non-additivity and their physical nature are presented in [1–9].

One of the necessary conditions for separating many-body interactions is the validity of the decomposition of the system under consideration into separate subsystems. Sometimes for the case of very large collective effects we cannot separate the individual parts of the system. In this case only the total energy of the system can be calculated. However, in atomic systems the inner-shell electrons are to a great extent localized. Therefore, even in metals with strong collective valence-electron

† On leave from Karpov Institute of Physical Chemistry, Moscow, Russia.
interactions, atoms can be identified as individuals and we can define many-body interactions.

The knowledge of many-body contributions is important for constructing effective semi-empirical potentials. We know that there are many empirical and semi-empirical pair potentials which describe quite satisfactorily the properties of liquids and solids: see chapter 5 in [1]. The point is that the parameters in these potentials are not the parameters of a true two-body interaction: their values depend upon properties of a medium. So these effective two-body potentials include non-additive interactions through their parameters. The latter cannot be related directly to definite physical properties [10]. For instance, the coefficient of the term $R^{-6}$ in the Buckingham or Lennard-Jones potentials is not equal to the dispersion constant $C_6$. But, in many cases for obtaining good agreement with experimental data the effective potentials must be constructed with 3-body [11, 12] and even 4-body [13] terms. Empirical potentials with 2- and 3-body terms satisfactorily describing properties of solid metals and metal surfaces were elaborated in a series of papers by Murrell and collaborators [14–19].

The first systems in which non-additive effects were investigated were clusters of noble gas atoms, see chapter 4 in [1] and also [20]. Metal clusters are of particular interest, and a lot of precise calculations of their properties have been published [21–30]. The role of non-additive forces in metal cluster stability was studied in a series of papers by Novaro and co-authors [31–38]; see also references [39–42] and chapter 4 in [1]. In other studies [43, 44], the importance of non-additive effects in chemisorption and catalysis was reported.

In particular, it was shown that non-additive forces are crucial for the stability of small $\text{Be}_n$ [31, 32] and $\text{Li}_n$ [35, 36] clusters. For the tetramer $\text{Be}_4$ the non-additivity interaction energy is attractive, and in the region of interatomic distances $r = 4.0–4.5 \, a_0$ it exceeds the additive 2-body repulsion. It is interesting to note that this occurs at distances which are close to experimental nearest-neighbour separations in metallic beryllium. Thus the non-additive forces are responsible for the formation of the beryllium crystal [20].

For some conformations of beryllium and lithium clusters not only 3-body, but even 4-body forces are greater than 2-body ones [32, 35]. So in the case of light metal clusters the many-body expansion does not converge. This situation is different from that in noble gas clusters [20]. As for the role of non-additivity in the formation of heavy-metal clusters, it had been investigated until recently only for trimers: $\text{Pd}_3$ [34], $\text{Cu}_3$ [37] and $\text{Ag}_3$ [38].

In the present paper we study the non-additive contributions to the binding energy of neutral silver clusters: $\text{Ag}_n$ ($n = 2–6$). We have obtained a close formula which expresses the energy of $m$-body interactions through the energies of $2$, $3$, ..., $(m - 1)$-body interactions. All calculations were performed by the all-electron local spin density method with non-local corrections included (NLSD) [45, 46]. We used the DGAuss version of NLSD realized on a Cray-YMP4/464. This approach was applied successfully for the calculation of silver cluster properties in our previous studies [47, 48].

2. The definition of many-body forces and the basic equations

In variational calculations only the total energy of the $n$-particle system is found. The interaction energy is computed as a difference of the total energy of a system
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and the energies of constituent particles

\[ E_{\text{int}}(n) = E(n) - \sum_{a=1}^{n} E(a). \]  

(2)

This energy can be decomposed into the energies of pair, triplet, etc., up to \( n \)-body interactions (see chapter 4 in [1]). In the literature, different notations for \( m \)-body energies are used. We shall now fix our notation and introduce the necessary definitions.

We shall designate the total energy of the \( n \)-particle system and the sum of its \( m \)-body interaction energies by the capital italics letter \( E \). The interaction energy of each separated \( m \)-particle part of the system we will designate by the Greek letter \( \epsilon \).

The total energy of an \( n \)-particle system can be represented as a finite sum

\[ E(n) = E_1(n) + E_2(n) + E_3(n) + \cdots + E_n(n). \]  

(3)

In equation (3)

\[ E_1(n) = \sum_{a=1}^{n} E(a), \]  

(4)

\[ E_2(n) = \sum_{a < b}^{\binom{n}{2}} \epsilon_{ab}, \]  

(5)

\[ \epsilon_{ab} = E(ab) - [E(a) + E(b)] = E(ab) - E_1(ab). \]  

(6)

The sum in equation (5) is taken over all \( \binom{n}{2} = \frac{n(n - 1)}{2} \) 2-body interaction energies \( \epsilon_{ab} \). Similar definitions hold for the energy of 3-body interactions,

\[ E_3(n) = \sum_{a < b < c}^{\binom{n}{3}} \epsilon_{abc}, \]  

(7)

\[ \epsilon_{abc} = E(abc) - E_1(abc) - E_2(abc), \]  

(8)

4-body interactions,

\[ E_4(n) = \sum_{a < b < c < d}^{\binom{n}{4}} \epsilon_{abcd}, \]  

(9)

\[ \epsilon_{abcd} = E(abcd) - E_1(abcd) - E_2(abcd) - E_3(abcd), \]  

(10)

etc., up to \( E_n(n) \). It should be emphasized that the representation of the total energy as the finite sum (3) is exact and can be performed for arbitrary distances between atoms. The accuracy of the calculations of the many-body contributions is determined by the accuracy of the variational method used. The relative weights of the many-body contributions in equation (3) are method dependent. If the calculation method is adequate for the prediction of stable geometries the many-body decomposition based on it is useful for explaining the results obtained. So, for systems in which the electron correlation is important the many-body contributions must be calculated also by methods taking into account the electron correlation.

For large \( n \) the calculation according to algorithm (4)–(10) becomes rather cumbersome. A closed formula for the energy of the \( m \)-body interactions can be obtained. For this we have to express the energy of the \( m \)-body interactions through \( k \)-body \((k \leq m - 1)\) interactions.
According to the definition,

$$E_m(n) = \sum_{a < b < \ldots < m} \epsilon_{ab\ldots m}. \quad (11)$$

This sum contains $C_n^m = n!/(n - m)!m!$ terms. Let us consider one of them,

$$\epsilon_{ab\ldots m} = E(ab\ldots m) - \sum_{k=1}^{m-1} E_k(ab\ldots m). \quad (12)$$

The energy of the $k$-body interactions in an $m$-particle system is equal to

$$E_k(ab\ldots m) = \sum_{a < b < \ldots < k} \epsilon_{ab\ldots k}. \quad (13)$$

Substituting equations (13) and (12) into (11) we obtain

$$E_m(n) = \sum_{a < b < \ldots < m} E(ab\ldots m) + \sum_{k=1}^{m-1} \left( \sum_{a < b < \ldots < m} \sum_{a < b < \ldots < k} \epsilon_{ab\ldots k} \right). \quad (14)$$

The double sum in parentheses in equation (14) contains $C_n^m C_m^k$ terms. Collecting terms on $C_n^k$-membered sets, each corresponding to the energy of $k$-body interactions in an $n$-particle system,

$$E_k(n) = \sum_{a < b < \ldots < k} \epsilon_{ab\ldots k}, \quad (15)$$

we obtain the expression sought:

$$E_m(n) = \sum_{a < b < \ldots < m} E(ab\ldots m) - \sum_{k=1}^{m-1} a_{mn}^k E_k(n), \quad (16)$$

where

$$a_{mn}^k = \frac{C_n^m C_m^k}{C_n^k} = \frac{(n - k)!}{(n - m)!(m - k)!}. \quad (17)$$

For $m = n$ all $a_{mn}^k = 1$ in full accordance with decomposition (3).

Thus the calculation of $m$-body contributions to the interaction energy of an $n$-particle system can be performed by a recurrent procedure:

$$E_2(n) = \sum_{a < b} E(ab) - a_{2n}^1 E_1(n), \quad (18)$$

$$E_3(n) = \sum_{a < b < c} E(abc) - a_{3n}^1 E_1(n) - a_{3n}^2 E_2(n), \quad (19)$$

$$E_4(n) = \sum_{a < b < c < d} E(abcd) - a_{4n}^1 E_1(n) - a_{4n}^2 E_2(n) - a_{4n}^3 E_3(n), \quad (20)$$

$$E_n(n) = E(ab\ldots n) - E_1(n) - E_2(n) - \cdots - E_{n-1}(n). \quad (21)$$

The coefficients in equations (18)–(21) are given by formula (17).
For estimating the convergence of the many-body expansion it is convenient to express the \(m\)-body energy in relative quantities. The rate of decrease of \(m\)-body energy is given by the ratio
\[
\epsilon_m(m - 1, n) = \frac{E_m(n)}{E_{m-1}(n)}.
\] (22)

The decomposition of \(E_{\text{int}}(n)\), from equation (2), is often expressed as the ratio to the additive 2-body energy
\[
E_{\text{int}}(n) = E_2(n)[1 + \epsilon_3(2, n) + \epsilon_4(2, n) + \cdots + \epsilon_n(2, n)] .
\] (23)

If we estimate not the total \(m\)-body energy \(E_m(n)\) but the behaviour of its constituent the \(m\)-body interactions \(E_{ab\cdots m}\), the useful quantity is the average value of the \(m\)-body interaction energy [20],
\[
\bar{\epsilon}_m(n) = \frac{1}{C_n} E_m(n).
\] (24)

The case of a charged system is worthy of special treatment. The main problem is that in a charged system we do not know the location of the charge in its constituent \(m\)-body parts (the only exceptions are the heteroatomic ionic crystals, discussed in [41, 42]). The approximate approach for partition of the total interaction energy of a charged system on its additive and non-additive components will be presented in a following paper [2].

3. Computational method

The computational method used is based on density functional theory. One of the simplest versions of the Kohn–Sham formulation is the local spin density (LSD) approximation [49]. According to this approach, not only the electronic orbitals but also the electron density play a central role. In particular, Coulomb, exchange and correlation energies are represented in terms of the electron density while the kinetic energy is represented in terms of electronic orbitals [46, 50]. Hence, two basis sets are required to expand the electron density and the electronic orbitals. Charge conservation is attained by minimizing the difference between the fitted electron density and that computed from the electronic orbitals. Exchange and correlation energy functionals inside LSD theory are obtained within the uniform electron gas approximation [51, 52]. Such functionals reduce the computing time considerably, leading to three-electron integrals instead of the traditional four-electron integrals. As a result, the method roughly scales as the third power in the number of primitive basis functions.

In this study, we used the DGauss approach [46], which implements the LSD theory described above to solve the LSD Hamiltonian equations with additional non-local terms containing gradients of the electron density. The gradient corrections to the exchange–correlation functional are those proposed by Becke [53] and Perdew [54]. They substantially improve the precision of the LSD approach. As was shown by Andzelm and Wimmer [46], inclusion of non-local corrections lets us predict bond dissociation energies within 0.1 eV.

The DGauss approach was applied successfully to the calculation of energetic characteristic of silver clusters in our recent studies [47, 48]. Therefore we use this...
approach for calculating the $m$-body energies according to the expressions presented in the previous section. More details of the method used can be found in [47]. Below we concern ourselves with only one aspect connected with many-body interactions.

When an atom is embedded in a cluster its identity is lost, and the same occurs for any $m$-atom part of the cluster. It can be charged, and has no definite multiplicity. However, for finding the $m$-body interactions in the neutral $n$-atom cluster we have to consider the isolated neutral dimers, trimers, etc., with the same interatomic distances as in the $n$-cluster studied. The multiplicity of these $m$-atom parts must correspond to their ground state. For silver clusters the ground state is characterized by the minimum value of the total spin (the singlet multiplicity for neutral clusters with an even number of atoms and the doublet for an odd number of atoms). This is confirmed in the calculations by Bonačić-Koutecký et al. [55] of ground and excited states of Ag$_n$ ($n = 2–9$).

4. Results of silver cluster calculations and discussion

In tables 1 and 2 we present the $m$-body interaction energies and their average values for different conformations of neutral silver clusters. We also present the total interaction energy. Its value lets us distinguish the relative stability of the isomers with the same $n$.

Table 1. $m$-Body energy contributions to the binding energy of silver clusters Ag$_n$ (a.u.).

The percentage non-additivity is given in parentheses, and $\epsilon_m(2, n)$ is defined by equation (21).

<table>
<thead>
<tr>
<th>$n(G, kD)^a$</th>
<th>$E_{\text{int}}$</th>
<th>$E_2(n) = E_{\text{add}}$</th>
<th>$E_3(n)$</th>
<th>$E_4(n)$</th>
<th>$E_5(n)$</th>
<th>$E_6(n)$</th>
<th>$F_{\text{non-add}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{add}}$</td>
<td>$</td>
<td>\epsilon_3(2, n)</td>
<td>%$</td>
<td>$</td>
<td>\epsilon_4(2, n)</td>
<td>%$</td>
<td>$</td>
</tr>
<tr>
<td>4 (D$_{2h}$, 2D)</td>
<td>$-0.1409$</td>
<td>$-0.2566$</td>
<td>$0.2006$</td>
<td>$-0.0850$</td>
<td>$0.1156$</td>
<td>$45.0$</td>
<td></td>
</tr>
<tr>
<td>4 (C$_{2v}$, 2D)</td>
<td>$-0.1338$</td>
<td>$-0.1936$</td>
<td>$0.0972$</td>
<td>$-0.0374$</td>
<td>$0.0598$</td>
<td>$30.9$</td>
<td></td>
</tr>
<tr>
<td>4 (D$_{sh}$, 1D)</td>
<td>$-0.1233$</td>
<td>$-0.1280$</td>
<td>$-0.0113$</td>
<td>$0.0159$</td>
<td>$0.0047$</td>
<td>$(3-7)$</td>
<td></td>
</tr>
<tr>
<td>4 (T$_h$, 3D)</td>
<td>$-0.0889$</td>
<td>$-0.3057$</td>
<td>$0.3078$</td>
<td>$-0.0910$</td>
<td>$0.2168$</td>
<td>$(70-9)$</td>
<td></td>
</tr>
<tr>
<td>5 (C$_{2v}$, 2D)</td>
<td>$-0.1941$</td>
<td>$-0.3507$</td>
<td>$0.3263$</td>
<td>$-0.2598$</td>
<td>$0.0902$</td>
<td>$0.1567$</td>
<td>$(44-7)$</td>
</tr>
<tr>
<td>5 (C$_{2v}$, 3D)</td>
<td>$-0.1770$</td>
<td>$-0.4502$</td>
<td>$0.5787$</td>
<td>$-0.3913$</td>
<td>$0.0859$</td>
<td>$0.2733$</td>
<td>$(60-7)$</td>
</tr>
<tr>
<td>5 (D$_{sh}$, 1D)</td>
<td>$-0.1539$</td>
<td>$-0.1423$</td>
<td>$-0.1355$</td>
<td>$0.1992$</td>
<td>$-0.0753$</td>
<td>$0.0116$</td>
<td>$(8-1)$</td>
</tr>
<tr>
<td>6 (C$_{2v}$, 2D)</td>
<td>$-0.2660$</td>
<td>$-0.4355$</td>
<td>$0.4020$</td>
<td>$-0.3432$</td>
<td>$0.1549$</td>
<td>$-0.0442$</td>
<td>$0.1695$</td>
</tr>
<tr>
<td>6 (C$_{3v}$, 3D)</td>
<td>$-0.2606$</td>
<td>$-0.5135$</td>
<td>$0.6324$</td>
<td>$-0.6513$</td>
<td>$0.3802$</td>
<td>$-0.1084$</td>
<td>$0.2529$</td>
</tr>
<tr>
<td>6 (C$_{2v}$, 3D)</td>
<td>$-0.2448$</td>
<td>$-0.6018$</td>
<td>$0.9262$</td>
<td>$-0.9637$</td>
<td>$0.4973$</td>
<td>$-0.1029$</td>
<td>$0.3569$</td>
</tr>
</tbody>
</table>

*Notations used for geometries: $G$ is the point symmetry group, $kD$ is the dimension of a cluster; the conformations and the parameters of the geometries used are given in reference [48].
Table 2. Average values of $m$-body interaction energy $\bar{e}_m(n)$ of Ag$_n$ clusters (a.u.).

<table>
<thead>
<tr>
<th>$n(G, kD)$</th>
<th>$\bar{e}_2(n)$</th>
<th>$\bar{e}_3(n)$</th>
<th>$\bar{e}_4(n)$</th>
<th>$\bar{e}_5(n)$</th>
<th>$\bar{e}_6(n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 (D$_{2h}$, 2D)</td>
<td>-0.0428</td>
<td>0.0501</td>
<td>-0.0850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (C$_{2v}$, 2D)</td>
<td>-0.0323</td>
<td>0.0243</td>
<td>-0.0374</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (D$_{oh}$, 1D)</td>
<td>-0.0213</td>
<td>-0.0028</td>
<td>0.0159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (C$_{2v}$, 2D)</td>
<td>-0.0351</td>
<td>0.0326</td>
<td>-0.0520</td>
<td>0.0902</td>
<td></td>
</tr>
<tr>
<td>5 (C$_{2v}$, 3D)</td>
<td>-0.0450</td>
<td>0.0579</td>
<td>-0.0783</td>
<td>0.0859</td>
<td></td>
</tr>
<tr>
<td>5 (D$_{oh}$, 1D)</td>
<td>-0.0142</td>
<td>0.0135</td>
<td>0.0398</td>
<td>-0.0753</td>
<td></td>
</tr>
<tr>
<td>6 (C$_{2v}$, 2D)</td>
<td>-0.0290</td>
<td>0.0201</td>
<td>-0.0229</td>
<td>0.0258</td>
<td>-0.0442</td>
</tr>
<tr>
<td>6 (C$_{3v}$, 3D)</td>
<td>-0.0342</td>
<td>0.0316</td>
<td>-0.0434</td>
<td>0.0634</td>
<td>-0.1084</td>
</tr>
<tr>
<td>6 (C$_{2v}$, 3D)</td>
<td>-0.0401</td>
<td>0.0463</td>
<td>-0.0642</td>
<td>0.0829</td>
<td>-0.1029</td>
</tr>
</tbody>
</table>

The notations for the geometries are as for table 1.

For all cases considered (excluding the linear geometries), many-body decomposition is an alternating series: the 2-body forces are attractive, the 3-body forces are repulsive, and so on. Convergence of the many-body series is poor or absent entirely. For instance, for the tetragonal pyramidal pentamer the decomposition (23) is

$$E_{\text{int}}(5; C_{2v}, 3D) = E_2(5)[1 - 1.28 + 0.87 - 0.19],$$

and for the tripyramidal hexamer it is

$$E_{\text{int}}(6; C_{2v}, 3D) = E_2(6)[1 - 1.54 + 1.60 - 0.82 + 0.17].$$

The total non-additive energy is positive (the only exception is the linear pentamer). So the non-additive interactions on the whole destabilize silver clusters. On the other hand, the additive interactions stabilize silver clusters because they are attractive.

Let us consider the energy of additive interactions in more detail. Its calculation involves only dimers, in contrast to the non-additive component which involves trimers, tetramers, etc. The values of the additive terms are directly related to the distance between atoms in the dimer. In order to analyse additive interactions in terms of dimer distances we define an 'optimal distance' in such a way that deviations from it diminish the additive energy. A natural definition of optimal distance for a dimer is the equilibrium distance it has in vacuum. In particular, for the silver dimer it is approximately 2.66 Å. When we take into consideration deviations from that distance we observe that, for a given cluster of size $n$, the ordering of additive energies which appear in table 1 can be explained. For example, for tetramers we find that for the linear structure we have three large distances, for the planar we have two of them, for the rhombic we only have one and for the tetrahedron we have none. This specific order is manifested in terms of additive energies in table 1. Similar additive behaviour is observed for the remaining clusters that appear there. In fact, we expect this result to be independent of the method under use, as any reasonably accurate method should distinguish among energies for dimers with different interatomic distances. Hence, as a conclusion to this part, we may say that the lower is the additive energy, the smaller is the number of deviations from the optimal distance we have in the cluster, and vice versa.
Similar considerations hold for the total 3-body interaction energy $E_3(n)$. Its value is usually larger for the structure which has a maximum number of trimers with geometry close to the equilibrium geometry for an isolated trimer. For instance, the tetrahedron ($T_d$) is the conformation which has not only the largest $E_2(4)$ but also the largest $E_3(4)$, because in this case there are 4 equal equilateral triangles. The signs of $E_2(4)$ and $E_3(4)$ are opposite and they almost compensate each other.

Let us now carry out a comparative discussion of the role of non-additive forces (see table 1) in linear, planar, and spatial (1D, 2D and 3D) neutral cluster geometries. For linear geometry (1D case) the 3-body forces become attractive, and the signs of the 2- and 3-body interaction energies coincide. In the linear tetramer the absolute values of 3- and 4-body interaction energies are very small, and in the linear pentamer there is almost full compensation of the non-additive contributions. In consequence, in both cases the contribution of the total non-additive energy to the interaction energy is very small and the binding energy of linear conformations is determined by the pairwise additive interactions. On the other hand, as we have explained above, their magnitude for the linear geometry is small as compared with that for other geometries considered.

For 2D- and 3D-conformations the additive and non-additive energies have the same order of magnitude and opposite signs. It is their competition that determines the relative stability of different isomers. The total non-additive energy is positive (repulsive) for all geometries considered, and its contribution is much greater in 3D conformations than in 2D. So in spite of the greater values of the additive attractive energy the spatial conformations for $n = 4–6$ are less stable than the planar ones.

5. Conclusions

The study of $m$-body contributions to the interactions energy of clusters $Ag_n$ ($n = 4–6$) has revealed the importance of not only 3- but also 4- and 5-body interactions for the cluster formation. The same results have been obtained for $Li_n$ [35] and $Be_n$ [32] clusters. The good description of some clusters and solids by interatomic potentials including only 2- and 3-body terms [14–19, 11, 12] has the single explanation that these potentials are not realistic but effective ones. Their parameters (after fitting) depend upon the $m$-body interactions of higher orders.

From our results on the decompositions of the total interaction energy into the two components: the additive and non-additive ones, the following qualitative conclusions can be made. The stability of linear conformations is determined mainly by 2-body additive interactions. On the other hand, the relative stability of planar and spatial silver clusters is determined by the competition of the additive and non-additive interactions. Although the contributions of the additive interaction energy to the binding energy of the clusters $Ag_n$ with $n = 4–6$ is larger for 3D conformations, the high non-additive repulsion energy made isomers with a 3D geometry less stable than planar ones.

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