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Nonadditive Interactions and the Relative Stability of Neutral and Anionic Silver Clusters

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ABSTRACT ▬

We discuss the physical nature of nonadditivity in many-particle systems and the methods of calculations of nonadditive contributions to the interaction energy. For neutral clusters, a 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 general approach for calculation of the nonadditive contribution in the interaction energy of charged systems is developed. The comparative calculation of anionic and neutral silver clusters shows that the geometry of the most stable anionic clusters is established mainly by the additive forces. The stability of neutral silver clusters is determined by the competition of attractive additive forces and repulsive nonadditive ones. © 1995 John Wiley & Sons, Inc.

Introduction: The Nature of Nonadditivity

The interaction of point particles is always additive. A well-known example is the Coulomb law for a system of point charges q_i:

$$V = \sum_{i<j} \frac{q_i q_j}{r_{ij}}. \tag{1}$$

The particles with the pairwise additive law must satisfy two necessary conditions:

1. Their charges must be point or rigid.
2. Particles must be elementary (not composite).

The potential energy of any structureless-point-particle system can be represented as the additive sum of pair potentials g_{ij}:

$$V = \sum_{i<j} g_{ij}. \tag{2}$$

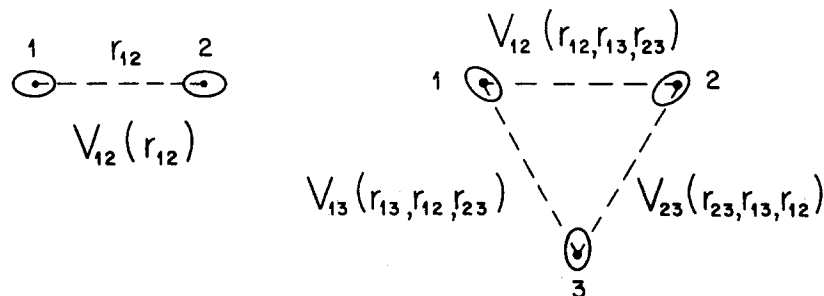*On leave from Karpov Institute of Physical Chemistry, Moscow.

FIGURE 1. The polarization forces. The interaction energy depends upon coordinates of all three particles.

Nonadditivity appears in many-particle systems whose particles satisfy one of the following conditions:

1. They are characterized by a nonrigid spatially distributed charge.
2. The particles have a composite structure and contain subparticles (nonadditivity at short interparticle distances).
3. They interact through transfer particles such as photons (for atomic systems, at large interparticle distances), mesons (for nuclear systems), or gluons (for quarks).

There are two kinds of interparticle forces which can lead to nonadditivity: polarization and exchange forces [1]. As we noted above, rigid point charges are characterized by the pairwise additivity. But in quantum mechanics, charges are spatially distributed and not rigid. The interacting atoms polarize their mutual electronic clouds. The distribution of the electronic density of two interacting atoms depends upon the location of the other atoms. As a result, the interaction energy of two atoms depends not only on their mutual distance but also on the location of surrounding atoms. For three atoms, the interaction energy is equal to (see Fig. 1)

$$V(1,2,3) = V_{12}(r_{12}, r_{13}, r_{23}) + V_{13}(r_{12}, r_{13}, r_{23})$$
$$+ V_{23}(r_{12}, r_{13}, r_{23}). \quad (3)$$

We can always represent it as a sum of the two-body interactions of isolated pairs and a term depending of coordinates of all three atoms:

$$V(1,2,3) = V_{12}(r_{12}) + V_{13}(r_{13}) + V_{23}(r_{23})$$
$$+ V_{123}(r_{12}, r_{13}, r_{23}). \quad (4)$$

This additional term is called the three-body interaction energy.

A second type of interparticle force which leads to nonadditivity comprises exchange forces of two kinds. The Pauli principle requires the antisymmetrization of the many-electron wave function. The exchange of electrons belonging to three or more atoms results in nonadditive terms in the interaction energy. The direct exchange interaction through transfer particles also results in nonadditivity. For atomic and molecular systems, these are electrodynamical interactions through transverse photons. According to the diagram in Figure 2, atom A emits a photon which is scattered by atom B and then absorbed by atom C.

One of the necessary conditions for a many-body description is the validity of the decomposition of the system under consideration on 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
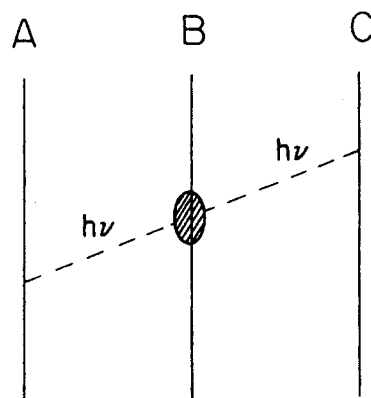

FIGURE 2. The interaction through the tranverse-photon exchange giving rise to the three-body forces.

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 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 semiempirical potentials. We know that there are many empirical and semiempirical pair potentials which describe quite satisfactorily the properties of liquids and solids (see Chap. 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 nonadditive interactions through their parameters. The latter cannot be directly related to the definite physical properties [2]. 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 a good agreement with experimental data, the effective potentials must be constructed with three-body [3,4] and even four-body [5] terms. Empirical potentials with two- and three-body terms satisfactorily describing properties of solid metals and metal surfaces were elaborated in the series of papers by Murrell and collaborators [6–11].

The first study of nonadditive effects in metallic systems was performed by Löwdin [12] in 1948. Since then, many investigations on the role of non-additive interactions in metal cluster stability have been published [13–25]. It was shown that nonadditive forces are crucial for the stability of small Be_n [13,14] and Li_n [20] clusters. For some conformations of these clusters, not only three-body but even four-body forces are greater than the two-body forces. So, in the case of light-metal clusters, the many-body expansion does not converge. This situation is very different from that in nobles gas clusters (see [26] and Chap. 4 in [1]). The nonadditive forces in heavy-metal clusters had been investigated until recently only for trimers: Pd_3 [19], Cu_3 [21], and Ag_3 [22].

In this report, we discuss the methods of calculations of nonadditive contributions in the interaction energy and describe the new approach allowing one to study nonadditive interactions in charged systems. The problem is that in the case of charged clusters we do not know the location of charge in each m-atom part of a charged system. For neutral clusters, a close formula, which express the energy

of the m-body interactions though the energies of $2,3,\ldots(n-1)$-body ones, is presented. We present results of a comparative study of nonadditive contributions in the binding energy of neutral and anionic silver clusters: Ag_n and Ag_n^- ($n = 2-6$).

Methods of Calculation of Nonadditive Interactions

ENERGY DECOMPOSITION IN PERTURBATION THEORY

At distances where the magnitude of interaction between subsystems can be considered small in comparison with the sum of energies of noninteracting subsystems, different types of perturbation theory (PT) can be applied. The interaction energy E_{int} decomposes in a series over various orders of PT:

$$E_{int} = E_{el}^{(1)} + E_{exch}^{(1)} + \sum_{n=2}^{\infty} \left[E_{pol-exch}^{(n)} + E_{pol}^{(n)} \right]. \quad (5)$$

The first order of the PT gives the well-known Heitler–London energy. It is easily calculated if the wave functions ψ_0 of the isolated subsystems are known. For three interacting atoms A, B, and C, the following expressions are valid:

$$E_{el}^{(1)} = \langle \psi_0^A \psi_0^B \psi_0^C | \hat{V} | \psi_0^A \psi_0^B \psi_0^C \rangle, \quad (6)$$

$$E_{exch}^{(1)} = \left\langle \psi_0^A \psi_0^B \psi_0^C | \hat{V} | \sum_{Q \neq 1} (-1)^q Q \psi_0^A \psi_0^B \psi_0^C \right\rangle, \quad (7)$$

where $\hat{V}$ is the interaction operator, Q denotes the permutations of electrons between interacting atoms, and q is the parity of the permutation Q, the normalization factors in Eqs. (6) and (7) are omitted; see subsection 1.2.6 in [1].

$E_{el}^{(1)}$ is the classical electrostatic energy for the interaction of space-distributed charges. Each charge is described by the unperturbed wave function, which means that at this approximation it is rigid. So, the electrostatic energy $E_{el}^{(1)}$ is always additive. The exchange energy $E_{exch}^{(1)}$ is nonadditive for all permutations Q mixing electrons of three atoms. The calculation of $E_{exch}^{(1)}$ for closed-shell many-electron systems in the density matrix formalism was elaborated in [27] and in recent publications [28,29].

As the exchange energy, the polarization–exchange energy $E_{pol-exch}$ is also nonadditive.

Unfortunately, the standard PT cannot be applied to the calculation of the $E_{pol-exch}$. The reason is that the antisymmetrized functions of zeroth order $(\hat{A}\psi_0^A\psi_0^B \ldots)$ are not eigenfunctions of the unperturbed Hamiltonian H_0, as long as the operator H_0 does not commute with the antisymmetrizer operator $\hat{A}$. Many successful approaches for the symmetry-adapted perturbation theory (SAPT) were developed (for a detailed discussion, see Chap. 3 in [1] and, more recent references [30–34]). So, the interaction energy can be calculated at intermediate distances where the magnitude of an interaction is small enough for applying the PT, but overlapping integrals,

$$S^{AB} = \langle \psi_0^A | \psi_0^B \rangle, \tag{8}$$

of interacting atoms cannot be neglected.

At large distances, $S^{AB} \to 0$ and all exchange terms can be neglected. The decomposition (4) transforms into

$$E_{int} = E_{el}^{(1)} + \sum_{n=2}^{\infty} E_{pol}^{(n)}$$
$$= E_{el}^{(1)} + \sum_{n=2}^{\infty} \left[E_{ind}^{(n)} + E_{disp}^{(n)} + E_{ind-disp}^{(n)} \right]. \tag{9}$$

The first two terms in the right-hand sum of Eq. (9) are the well-known induction and dispersion energies [1]; the third one has a mixed nature and appears for $n \geq 3$ (see [34,35]).

In the energy partition, only two terms are additive: $E_{el}^{(1)}$ and $E_{disp}^{(2)}$. All the others have the nonadditive nature. Some of them are discussed in [36]. The relative contributions of different nonadditive terms in the PT and their analytical approximation are very important for building up the model effective potentials, containing three-body or higher-order terms.

VARIATIONAL METHOD

In this method, only the total energy of the n-atom[†] system is found. The interaction energy is computed as the difference between the total energy of a system and the energies of isolated atoms:

$$E_{int}(n) = E(n) - \sum_{a=1}^{n} E(a). \tag{10}$$

[†]Below we use the term "atom" for the brevity; it can denote molecules or any part of the system under consideration.

The total energy can be represented as a finite sum [1]:

$$E(n) = E_1(n) + E_2(n) + E_3(n) + \ldots + E_n(n), \tag{11}$$

where

$$E_1(n) = \sum_{a=1}^{n} E(a), \tag{12}$$

$$E_2(n) = \sum_{a<b}^{\{n\}} \epsilon_{ab}, \tag{13}$$

$$\epsilon_{ab} = E(ab) - E_1(ab) \tag{14}$$

$$E_3(n) = \sum_{a<b<c}^{\{n\}} \epsilon_{abc}, \tag{15}$$

$$\epsilon_{abc} = E(abc) - E_1(abc) - E_2(abc), \tag{16}$$

etc., up to $E_n(n)$. In Eqs. (13)–(16), $E_m(n)$ designates the sum of m-body interactions for all $C_n^m = n!/m!(n - m)!$ combinations of m atoms from a total of n atoms, and $\epsilon_{ab\ldots m}$ designates the interaction energy in the concrete m-atom system.

It should be emphasized that the decomposition of the total energy as the finite sum (11) is exact. The accuracy of the calculation of the many-body contribution is determined only by the accuracy of the variational method used. The relative weights of the many-body contributions in Eq. (11) are method-dependent. If the calculation method is adequate for 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 also calculated by the methods taking into account the electron correlation.

Instead of the algorithm (12)–(16), a more general and convenient one for calculating an expression for the energy of m-body interactions can be obtained (for its derivation see [37]):

$$E_m(n) = \sum_{a<b\ldots<m}^{\{n\}} E(ab\ldots m) - \sum_{k=1}^{m-1} a_{mn}^k E_k(n) \tag{17}$$

$$a_{mn}^k = \frac{(n - k)!}{(n - m)!(m - k)!}. \tag{18}$$

For estimating the convergence of the many-body expansion, it is convenient to express the m-body energy in relative quantities. The decomposition of $E_{int}(n)$ is often expressed as the ratio to the additive two-body energy:

$$E_{int}(n) = E_2(n)[1 + \epsilon_3(2,n) + \epsilon_4(2,n)$$
$$+ \ldots + \epsilon_n(2,n)], \tag{19}$$

where

$$\epsilon_m(2,n) = \frac{E_m(n)}{E_2(n)}. \qquad (20)$$

In charged systems, the main problem is the location of the charge in m-atomic parts of the system. One of the approaches for evaluation of the nonadditive energy is to find it as a difference of the total interaction energy and the additive one. For the latter, we assume that the charge is located on each atom with equal probability. In reality, it is not so. But in this approach all deviations from an equal probability are attributed to nonadditive forces. For symmetric geometries, it must not lead to great errors. This will be seen from the calculation for Ag_n^- and Ag_n presented in the next section. Our approach gives quite reasonable results if we compare neutral and ionic clusters.

Let us consider for definiteness negative-charged homoatomic clusters A_n^- (anions). Then,

$$E_{int}(A_n^-) = E(A_n^-) - (n - 1)E(A) - E(A^-). \qquad (21)$$

The assumption that the charge can be located on each atom with an equal probability means that each interacting pair also can be charged with an equal probability. From this follows that the additive energy can be represented as an average over all possibilities:

$$E_{add}(A_n^-) \equiv \overline{E}_2(A_n^-)$$

$$= \frac{1}{C_n^2}\left[\sum_{a<b}^{\{n\}} \epsilon_{(ab)^-} + (C_n^2 - 1) \sum_{a<b}^{\{n\}} \epsilon_{ab} \right]. \qquad (22)$$

It is convenient to replace the two-body interaction energies on the total two-body energies, because it is the latter that are calculated in variational methods. Instead of Eq. (22), we obtain

$$E_{add}(A_n^-) = \frac{1}{C_n^2}\left[\sum_{a<b}^{\{n\}} E(ab^-) + (C_n^2 - 1) \sum_{a<b}^{\{n\}} E(ab) \right]$$
$$- [E(A^-) + \{n(n - 1) - 1\}E(A)]. \qquad (23)$$

The nonadditive part of the interaction is calculated as a difference:

$$E_{nonadd}(A_n^-) = E_{int}(A_n^-) - E_{add}(A_n^-). \qquad (24)$$

A Comparative Silver Cluster Calculation and Its Discussion

All calculations were performed by the all-electron local spin density method with nonlocal

corrections included (NLSD) [38,39]. We used the DGauss version of NLSD realized in CRAY-YMP4/464. This approach was successfully applied for the calculation of silver cluster properties in our previous studies [40,41]. In [40], we described in detail our calculation method. Here, we concern ourselves only to one aspect.

When an atom is embedded in a cluster, its identity is lost; the same occurs for any m-atom part of the cluster. It can be charged and has not 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 characterized by the minimum value of the total spin (the singlet multiplicity for neutral clusters with an even number of atom and the doublet ones for an odd number of atoms). This is confirmed in the calculations by Bonačić-Koutecký et al. [42,43] of the ground and excited states of Ag_n and Ag_n^- ($n = 2-9$).

For all cases considered (excluding the linear geometries), the many-body decomposition is an alternating series: The two-body forces are attractive, the three-body forces are repulsive, and so on [37]. The convergence of the many-body series is poor or absent entirely. For instance, for the tetragonal pyramidal pentamer, the decomposition (19) is

$$E_{int}(5; C_{2v},3D) = E_2(5)[1 - 1.28 + 0.87 - 0.19], \qquad (25)$$

and for the tripyramidal hexamer,

$$E_{int}(6; C_{2v},3D) = E_2(6)[1 - 1.54 + 1.60 - 0.82 + 0.17]. \qquad (26)$$

According to Eqs. (25) and (26), the energy of three-body interactions for the pantamer and hexamer are larger than the energy of the two-body ones, and for the tripyramidal hexamer, the four-body interactions are stronger than the three-body and two-body ones. The contribution to the interaction energy from the five-body interactions also cannot be neglected. The same behavior has been revealed for lithium [20] and beryllium [13,14] clusters. It means that a good description of some clusters and solids by interatomic potentials including only two- and three-body terms has the single explanation that these potentials are not realistic but effective ones. Their parameters (after fitting)

TABLE I _____

Comparative data on additive and nonadditive interaction energies for Ag_n^- and Ag_n clusters, in au.[a]

$n(G,kD)$	Ag_n^-				Ag_n			
	E_{int}	E_{add}	E_{nonadd}	$\left\|\frac{E_{nonadd}}{E_{add}}\right\|\%$	E_{int}	E_{add}	E_{nonadd}	$\left\|\frac{E_{nonadd}}{E_{add}}\right\|\%$
4 $(D_{2h},2D)$	−0.1585	−0.2585	0.1000	38.7	−0.1409	−0.2566	0.1156	45.0
4 $(D_{\infty h},1D)$	−0.1574	−0.1400	−0.0174	12.4	−0.1233	−0.1280	0.0047	3.7
4 $(C_{2v},2D)$	−0.1551	−0.2027	0.0476	23.5	−0.1338	−0.1936	0.0598	30.8
5 $(C_{2v},2D)$	−0.2220	−0.3521	0.1301	36.9	−0.1941	−0.3507	0.1567	44.7
5 $(D_{\infty h},1D)$	−0.2110	−0.1598	−0.0512	32.0	−0.1539	−0.1423	−0.0116	8.1
6 $(C_{2v},3D)$	−0.2757	−0.6110	0.3353	54.9	−0.2448	−0.6018	0.3569	59.3
6 $(C_{2v},2D)$	−0.2734	−0.4379	0.1645	37.6	−0.2660	−0.4355	0.1695	38.9
6 $(C_{5v},3D)$	−0.2699	−0.5353	0.2654	49.6	−0.2606	−0.5135	0.2529	49.2

[a]The notation used for geometries: G is the point symmetry group and kD is the dimension of a cluster. The parameters for the geometries considered are taken from [40,41].

depend implicitly upon the m-body interactions of higher orders.

The results of our calculations of additive and nonadditive energies for anionic and neutral silver clusters are presented in Table I. As follows from the data presented, the ratio of nonadditive to additive energies for anions in most cases is not far from that for neutral clusters with the same geometry. For larger clusters, the difference in their respective ratios is smaller; according to Table I, in the case of hexamers, these ratios are rather close. They differ to a considerable extent only for the linear geometry of tetramers and pentamers. The reason can be in the not-full-applicability of our approach to linear charged structures. For all conformations considered, the additive energy is negative, so it stabilizes silver clusters, both charged and neutral. The nonadditive energy is positive (except for linear geometries) and plays the destabilization role.

The same situation was observed for Li_n clusters [20] and Cu_3 clusters [21]. We may therefore conclude that this situation is typical for clusters composed of atoms with one valence electron. For clusters containing atoms with closed valence shells (inert gas atoms [26]) or a closed subshell (Be_n clusters [13,14]), the additive energy is positive and destabilizes the clusters. The nonadditive energy can be both negative and positive depending upon the cluster geometry. For Be_n, the total nonadditive energy is negative and plays the stabilization role.

For neutral silver clusters, the relative contribution of the nonadditive energy is small for linear conformations and is about half of the additive

energy for planar and spatial conformations. For these last two types of neutral conformations, the competition of E_{nonadd} and E_{add} determines the relative stability of different isomers. For neutral hexamers, the relative contribution of E_{nonadd} is much greater in 3D-conformations than in the 2D-one. As a result, in spite of the greater values of the additive attractive energy, the spatial conformations of Ag_n are less stable than is the planar one.

Another situation is in the cases of charged silver clusters. The geometry of the most stable anionic isomers for $n = 4-6$ is established mainly by the additive forces. This becomes evident if we compare the magnitude of the nonadditive energy for different isomers. The values of the repulsive nonadditive interactions are the greatest for the most stable anionic conformations. So, the stability of these conformations is established by the great magnitude of the attractive additive energy.

On the other hand, the relative stability of the less stable isomers is determined by competition of additive and nonadditive forces [compare the energies for anionic geometries 4 $(D_{\infty h},1D)$ and 4 $(C_{2v},2D)$, 6 $(C_{2v},2D)$ and 6 $(C_{5v},3D)$ in Table I]. The nonadditive energy is negative only for linear anionic conformations. But for $n = 4$ and 5, these conformations are not the most stable because of the relatively small magnitude of the additive energy.

We can also try to answer the question which rose in our previous article [41]: Why is the most stable geometry for neutral silver hexamers the planar one while for anionic hexamers it is spatial?

According to Table I, for the tripyramidal geometry, 6 $(C_{2v}, 3D)$, we have the larger value of the additive attraction energy and the smaller value of the nonadditive repulsive energy for the anionic hexamer in comparison with the neutral one. This is the reason for the transition 2D → 3D when we pass from neutral to anionic hexamers.

ACKNOWLEDGMENTS

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