

## Many-body forces and electron correlation in small metal clusters

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The many-body decomposition of the interaction energy for  $\text{Be}_N$  and  $\text{Li}_N$  ( $N=2$  to 4) clusters is calculated in two approximations: the self-consistent-field method and the Møller-Plesset perturbation theory up to the fourth order. This allows us to estimate the electron-correlation contributions to the many-body forces. The explicit expressions for these contributions in the perturbation theory formalism are obtained. We present a comparative analysis of the role of electron correlations in the  $\text{Be}_N$  and  $\text{Li}_N$  cluster formations and in the many-body interactions in these clusters. As follows from our results, the contribution of electron correlation to many-body interactions is essential for both the  $\text{Be}_N$  and  $\text{Li}_N$  clusters, especially for the latter ones, where nonadditivities are surprisingly large.

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### I. INTRODUCTION

Small metal clusters are a fruitful field to study the dependence of calculated physical properties on the accuracy of the calculation method applied. In this paper we study the dependence of cluster stability and many-body forces of small metal clusters when allowing for the inclusion of electron correlation.

The first study of many-body effects in atomic systems was performed by Löwdin [1] in 1948. Since then, many investigations of the role of many-body interactions in clusters and the solid state have been published; see Refs. [2,3], and references therein.

The beryllium clusters were the first metal system in which the role of many-body forces was investigated [4–6]. The calculations were based on the self-consistent-field (SCF) method. It was shown that while  $\text{Be}_2$  and  $\text{Be}_3$  clusters are not bound at the SCF level,  $\text{Be}_4$  is a stable cluster with a tetrahedral geometry [5]. For the stability of the latter the attractive three-body forces are decisive, since the two- and four-body forces are repulsive.

The many-body decomposition of the interaction energy in lithium clusters was studied for  $\text{Li}_3$  [7] and later on for  $\text{Li}_N$  ( $N=2$  to 9) [8] in the framework of the configuration-interaction (CI) method. According to the results obtained, for some conformations of lithium clusters not only the three-body, but even the four-body interaction energies are greater than the two-body ones [8] (as previously found for beryllium clusters [4,5]).

Thus, in these investigated metal systems the convergence of the many-body decomposition of the interaction energy of an  $N$ -atom cluster

$$E_{\text{int}}(N) \equiv E(N) - E_1(N) = E_2(N) + E_3(N) + \cdots + E_N(N), \quad (1)$$

is poor. In Eq. (1),  $E(N)$  is the total energy and  $E_1(N)$  is the energy of the noninteracting  $N$ -atom system,

$$E_1(N) = \sum_{a=1}^N E_a, \quad (2)$$

$E_m(N)$  ( $m \geq 2$ ) denotes the sum of  $m$ -body interaction energies in an  $N$ -atom system, as will be defined in the following section.

However, we know of many empirical and semiempirical pair potentials that describe quite satisfactorily the properties of liquids and solids; see chapter 5 in Ref. [3]. 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. However, in some cases, in order to obtain a good agreement with experimental or theoretical data, the effective potentials must be constructed with three-body [9–11] and even four-body [12] terms. The knowledge of the analytical form of many-body interaction energy is very useful for constructing such effective potentials.

The physical nature of  $m$ -body interactions and the concept of nonadditivity are discussed in Refs. [13–15]. Here we want to stress that the representation of the interaction energy as the finite sum (1) is exact and can be performed for arbitrary configurations and distances between atoms. But the relative weights of the many-body contributions in Eq. (1) are method dependent. In order to find the dependence upon electron correlation, it is necessary to make a comparative calculation at two levels: with the SCF approach and with one of the methods allowing for the electron correlation. We took up the Møller-Plesset perturbation-theory approach and compared the many-body decompositions obtained in this approach for  $\text{Be}_N$  and  $\text{Li}_N$  ( $N=2$  to 4) clusters with the corresponding SCF calculation.

There are a lot of precise calculations of small beryllium and lithium clusters incorporating the correlation effects [16–26]. But in all these works only the total interaction energy was investigated. In the present study, which has the accuracy of the best calculations (see Tables I and II), we obtained the  $m$ -body decomposition of  $E_{\text{int}}$  and studied the influence of electron correlation on it.

Although the importance of electron correlation for the stability of beryllium clusters is well known [17] and it is customary to suppose that the same situation takes place in

TABLE I. Comparison of our calculation of  $\text{Be}_N$  with literature data.

$\text{Be}_N$		$r_0$ (a.u.)	$-E^{\text{SCF}}(N)$ (a.u.)	$-E^{\text{SCF+corr}}(N)$ (a.u.)	$-E_{\text{int}}(N)$ (kcal/mol)	Method of electron correlation account
$\text{Be}_2$	[16]	4.72			2.12	ICF2H
	[17]	4.75			1.86	Full CI(CAS SCF)
	[20]		29.137 64	29.301 25	2.36 <sup>a</sup>	MP2-R12
	This work	4.91	29.134 85	29.229 29	1.81	MP4[6-311+ $G(3df)$ ]
	[33]	4.63			$2.36 \pm 0.08$	Experiment
$\text{Be}_3^{\text{b}}$	[17]	4.20			17.9	Full CI(CAS SCF)
	[19]	4.20		43.891 968	22.4	MR CI
	[18]	4.23	43.714 40	43.873 64	21.6	MP4 (6-311+ $G^*$ )
	[20]	4.20	43.718 25	43.998 97	31.75 <sup>a</sup>	MP2-R12
	This work	4.23	43.714 94	43.881 26	25.8	MP4[6-311+ $G(3df)$ ]
$\text{Be}_4^{\text{c}}$	[17]	3.92			64.8	CEPA-1
	[19]	3.90		58.595 343	73.3	MR CI
	[18]	3.94	58.353 58	58.585 27	83.4	MP4 (6-311+ $G^*$ )
	[20]	3.93	58.359 46	58.774 47	110.94 <sup>a</sup>	MP2-R12
	This work	3.93	58.354 69	58.600 40	92.0	MP4[6-311+ $G(3df)$ ]

<sup>a</sup>Estimated value.<sup>b</sup>Equilateral triangle ( $D_{3h}$ ).<sup>c</sup>Tetrahedron ( $T_d$ ).

the case of lithium clusters, the correlation contributions to many-body forces in these clusters have not been studied. Water clusters are the only investigated system in this respect. According to calculations of Habitz *et al.* [27], it is enough to perform calculations at the SCF level for finding nonadditive contributions to the interaction energy of water clusters. This statement was confirmed in recent studies [28,29]. As follows from our results presented in this paper (see Tables IV and V), in the case of metal clusters the situation is quite opposite. For beryllium and, especially, for lithium clusters the many-body interactions cannot be studied without taking into account the electron correlation.

In the recent interesting paper by Jellinek *et al.* [30], the molecular dynamics study of the cluster  $\text{Li}_8$  is performed at the SCF level. The authors [30] discuss the possibility of taking into account the electron correlation in *ab initio* molecular dynamics simulations in future studies. According to our results, the contribution of the electron correlation to the total interaction energy of lithium clusters at equilibrium distances is extremely large; for  $\text{Li}_4$  the magnitude of the electron correlation contribution is more than twice as large as the SCF binding energy (see Table III). It cannot be excluded that the same situation takes place at some other points of the potential surface. In the last case, it is necessary to carry out the molecular dynamics study of lithium clusters on the level that incorporates the correlation effects.

The plan of this paper is as follows: In Sec. II we describe the computing method and present the basic formulas for the  $m$ -body interaction energies. The correlation corrections to the  $m$ -body energies are expressed in Sec. III in the perturbation-theory formalism. In Sec. IV we analyze the numerical results obtained for the many-body decomposition and the correlation corrections in the case of beryllium and lithium clusters.

## II. COMPUTING METHOD AND BASIC FORMULAS FOR $m$ -BODY INTERACTION ENERGIES

All calculations were carried out using the GAUSSIAN-92 program [31] on a CRAY-YMP4/464. We performed an all-electron SCF calculation using the triply split valence basis set [6-311+ $G(3df)$ ], having one diffuse  $p$  function, three  $5d$  functions, and one  $7f$  function. The electron correlation calculations are performed by means of the Møller-Plesset perturbation theory up to the fourth order (MP4) in the frozen-core approximation.

The geometries were optimized at the MP4 level (for the  $\text{Be}_4$  cluster, the equilibrium geometry was taken from Ref. [18]). The final calculated energies were corrected for the basis set superposition error (BSSE) with the counterpoise method (see Ref. [32] and references therein). Because of the large basis set used, the BSSE corrections are small.

As we mentioned in the Introduction, the relative weights of the many-body contributions in Eq. (1) are method dependent. In order to obtain reliable results, we must be sure of the precision of the method used. The results of our geometry and energy calculations of  $\text{Be}_N$  and  $\text{Li}_N$  clusters are presented in Tables I and II together with literature data. The comparison of our results with previously published ones indicates a quite satisfactory agreement.

For  $\text{Be}_3$  and  $\text{Be}_4$  all calculations predict almost the same equilibrium distances. The total energies are very close at the SCF level, where the precision depends upon the size of the basis set used. Note the closeness of our SCF results to those of Klopper and Almlöf [20], who used a very large basis set:  $16s12p8d4f$  primitive functions. The predicted interaction energies calculated at electron correlation level are more divergent because of the different precision of the methods used to account for the electron correlation.

TABLE II. Comparison of our calculation of  $\text{Li}_N$  with literature data.

$\text{Li}_N$		$r_1, r_2$ (a.u.)	$-E^{\text{SCF}}(N)$ (a.u.)	$-E^{\text{SCF}+\text{corr}}(N)$ (a.u.)	$-E^{\text{int}}(N)$ (kcal/mol)	Method of electron correlation account
$\text{Li}_2$	[24]	5.08			20.45	CI
	[25]	5.05			22.70	OMC
	[23]				17.32	CI-Dav
	[21]	5.27	14.864 52	14.893 24	20.63	CEPA
	This work	5.15	14.870 28	14.899 16	22.02	MP4[6-311+G(3df )]
	[34]	5.05			24.66±0.3	Experiment
$\text{Li}_3^{\text{a}}$	[23]	5.46, 7.50			24.15	CI-Dav
	[22]	5.22, 6.56			36.89	Pseudo+DFT
		5.50, 6.69			37.29	CI+H <sub>eff</sub>
	[26]					
	This work	5.14, 6.47	22.315 07	22.344 52	30.38	MP4[6-311+G(3df )]
$\text{Li}_4^{\text{b}}$	[23]	5.14, 6.47			51.08	CI-Dav
	[21]	5.97, 10.28	29.745 64	29.810 89		CEPA
	[26]	5.95, 5.00			59.76	CI+H <sub>eff</sub>
	This work	5.74, 5.00	29.759 27	29.829 83	63.8	MP4[6-311+G(3df )]

<sup>a</sup>Isosceles triangle.<sup>b</sup>Rhombic geometry.

For  $\text{Li}_N$  clusters according to Table II, there is a great dispersion of the calculated equilibrium distances, contrary to the beryllium case. Our total energies at the SCF level are the lowest of those presented in Table II. From this follows the good quality of the basis set used. The interaction energy obtained in our calculation for  $\text{Li}_2$  is very close to the experimental value. The interaction energy for  $\text{Li}_3$  and the total and interaction energies obtained for the  $\text{Li}_4$  cluster are in good agreement with previous calculations. Data presented in Tables I and II show that there is a convergence in the total energy prediction and to some extent in the interaction energy. On the whole, we can conclude that the computing method used in our study can be applied with confidence to the calculation of the energy decomposition (1).

In many-body decomposition (1),  $E_2(N)$  is the total energy of the pair interactions  $\varepsilon_{ab}$ , the so-called pairwise additive energy

$$E_2(N) = \sum_{a < b}^{\{N\}} \varepsilon_{ab}, \quad (3)$$

$$\varepsilon_{ab} = E(ab) - E_1(ab) = E(ab) - (E_a + E_b). \quad (4)$$

The sum in Eq. (3) is taken over all  $C_N^2 = N(N-1)/2$  pair interaction energies  $\varepsilon_{ab}$  of the isolated atoms;  $E(ab)$  is the total energy of the isolated system  $ab$ . All other terms in Eq. (1) represent the nonadditive part of the  $N$ -atom interaction energy

$$E_{\text{nonadd}}(N) = \sum_{m=3}^N E_m(N). \quad (5)$$

As for the energy of two-body interactions, similar definitions hold for the total energy  $E_3(N)$  of the three-body interactions  $\varepsilon_{abc}$

$$E_3(N) = \sum_{a < b < c}^{\{N\}} \varepsilon_{abc}, \quad (6)$$

$$\varepsilon_{abc} = E(abc) - E_1(abc) - E_2(abc), \quad (7)$$

etc. up to  $E_N(N)$ . The sum in Eq. (6) is taken over all,  $C_N^3 = N!/(N-3)!3!$ , combinations of three atoms in the cluster of  $N$  atoms.

The total energy of  $m$ -body interactions can be expressed through the total energies of 2-, 3-, ..., and  $(m-1)$ -body interactions (for a derivation see Ref. [14])

$$E_m(N) = \sum_{a < b < \dots < m}^{\{N\}} E(ab \dots m) - \sum_{k=1}^{m-1} a_{mN}^k E_k(N), \quad (8)$$

where

$$a_{mN}^k = \frac{(N-k)!}{(N-m)!(m-k)!}. \quad (9)$$

For  $m=N$  all  $a_{NN}^k=1$ , in full accordance with the decomposition (1). The use of Eqs. (8) and (9) make it possible to perform the calculation of the energy of  $m$ -body interactions by the simple recurrence procedure:

$$E_2(N) = \sum_{a < b}^{\{N\}} E(ab) - a_{2N}^1 E_1(N), \quad (10)$$

$$E_3(N) = \sum_{a<b<c}^{\{N\}} E(abc) - a_{3N}^1 E_1(N) - a_{3N}^2 E_2(N), \quad (11)$$

$$E_4(N) = \sum_{a<b<c<d}^{\{N\}} E(abcd) - a_{4N}^1 E_1(N) - a_{4N}^2 E_2(N) - a_{4N}^3 E_3(N), \quad (12)$$

$$E_N(N) = E(ab\dots N) - E_1(N) - E_2(N) - \dots - E_{N-1}(N). \quad (13)$$

The coefficients in Eqs. (10)–(13) are given by formula (9).

For an estimation of the convergence of the many-body decomposition of the interaction energy, the latter is often expressed as the ratios of  $m$ -body to two-body energies,

$$E_{\text{int}}(N) = E_2(N)[1 + \alpha_3(2,N) + \dots + \alpha_N(2,N)], \quad (14)$$

where

$$\alpha_m(2,N) = \frac{E_m(N)}{E_2(N)}. \quad (15)$$

### III. PERTURBATION THEORY AND ELECTRON CORRELATION CONTRIBUTIONS TO THE MANY-BODY DECOMPOSITION

It is useful to decompose the many-body contributions on different physical parts, as is performed in perturbation theory (PT). At distances where the magnitude of the interaction between subsystems can be considered small in comparison with the sum of the energies of the noninteracting subsystems, the interaction energy  $E_{\text{int}}$  decomposes in a series over various orders of PT,

$$E_{\text{int}} = \varepsilon_{\text{el}}^{(1)} + \varepsilon_{\text{exch}}^{(1)} + \sum_{n=2}^{\infty} [\varepsilon_{\text{pol exch}}^{(n)} + \varepsilon_{\text{pol}}^{(n)}]. \quad (16)$$

The first order of the PT gives the well-known Heitler-London energy. It is easily calculated if the wave functions  $\psi_0$  of the isolated subsystems are known.  $\varepsilon_{\text{el}}^{(1)}$  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  $\varepsilon_{\text{el}}^{(1)}$  is always additive. The exchange energy  $\varepsilon_{\text{exch}}^{(1)}$  is nonadditive for all permutations mixing electrons of three or more atoms. The evaluation of the exchange energy for closed-shell many-electron systems has now become a popular topic; see Refs. [35–38].

As the exchange energy, the polarization-exchange energy  $\varepsilon_{\text{pol exch}}$  is also nonadditive. The standard PT cannot be applied to the calculation of the  $\varepsilon_{\text{pol exch}}$ . The reason is that the antisymmetrized functions of zeroth order ( $A\psi_0^A\psi_0^B\dots$ ) 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) have been developed; for a detailed discussion see chapter 3 in Ref. [3] and more recent Refs. [39–41].

The polarization energy  $\varepsilon_{\text{pol}}^{(n)}$  comprises the induction and dispersion energies. These energies are nonadditive in all orders of PT; the only exception is  $\varepsilon_{\text{disp}}^{(2)}$ , see Ref. [3], chapter 4. Thus, in the energy partition only two terms are additive:  $\varepsilon_{\text{el}}^{(1)}$  and  $\varepsilon_{\text{disp}}^{(2)}$ . If we subtract them from  $E_{\text{int}}$ , the remaining part will contain only nonadditive contributions. Let us denote them  $E_{\text{int}}^{\text{nonadd}}$ ,

$$E_{\text{int}}^{\text{nonadd}} = \varepsilon_{\text{exch}}^{(1)} + E_{\text{pol exch}} + E_{\text{pol}}^{\text{nonadd}}, \quad (17)$$

where

$$E_{\text{pol exch}} = \sum_{n=2}^{\infty} \varepsilon_{\text{pol exch}}^{(n)} E_{\text{pol}}^{\text{nonadd}} = \left( \sum_{n=2}^{\infty} \varepsilon_{\text{pol}}^{(n)} \right) - \varepsilon_{\text{disp}}^{(2)}. \quad (18)$$

Now we can decompose the  $m$ -body interaction energies into the PT series. For the two-body interaction energy the expression follows from Eq. (16):

$$E_2(N) = \sum_{a<b}^{\{N\}} \varepsilon_{ab}; \varepsilon_{ab} = \varepsilon_{\text{el}}^{(1)}(ab) + \varepsilon_{\text{exch}}^{(1)}(ab) + \sum_{n=2}^{\infty} [\varepsilon_{\text{pol exch}}^{(n)}(ab) + \varepsilon_{\text{pol}}^{(n)}(ab)]. \quad (19)$$

The  $m$ -body interaction energy with  $m \geq 3$  is expressed through the nonadditive term (17). For  $E_3(N)$  we have [15]

$$E_3(N) = \sum_{a<b<c}^{\{N\}} \varepsilon_{abc}; \varepsilon_{abc} = E_{\text{int}}^{\text{nonadd}}(abc) - \sum_{a<b}^{\{abc\}} E_{\text{int}}^{\text{nonadd}}(ab). \quad (20)$$

For the energy of  $m$ -body interactions the following recurrence formula is valid [15]:

$$E_m(N) = \sum_{a<b<\dots<m}^{\{N\}} E_{\text{int}}^{\text{nonadd}}(ab\dots m) - a_{mN}^2 \sum_{a<b}^{\{N\}} E_{\text{int}}^{\text{nonadd}}(ab) - \sum_{k=3}^{m-1} a_{mN}^k E_k(N). \quad (21)$$

Let us turn to the electron correlation energy. According to its definition [42], the correlation energy is the difference between the precise value of the energy and the Hartree-Fock value. But except for the smallest systems, we cannot obtain the exact energy. So the definition of the correlation energy is conventional and depends upon the approximation used. For the energy of  $m$ -body interactions, the correlation contribution in our approximation is equal to

$$\Delta E_m^{\text{corr}}(N) = E_m^{\text{MP4}}(N) - E_m^{\text{SCF}}(N). \quad (22)$$

The SCF interaction energy can be decomposed as [43,44]

$$E_{\text{int}}^{\text{SCF}} = \varepsilon_{\text{el}}^{(1)} + \varepsilon_{\text{exch}}^{(1)} + E_{\text{def}}^{\text{SCF}}. \quad (23)$$

On the distances where exchange effects can be neglected,  $E_{\text{def}}^{\text{SCF}}$  is the classical induction energy.

TABLE III. The contributions  $\varepsilon_{\text{MP}}^{(n)}$  is the energy in the  $n$ th order of the Møller-Plesset perturbation theory,  $\Delta E_b^{\text{corr}} = \varepsilon_{\text{MP}}^{(2)} + \varepsilon_{\text{MP}}^{(3)} + \varepsilon_{\text{MP}}^{(4)}$ ,  $E_b^{\text{MP4}} = E_b^{\text{SCF}} + \Delta E_b^{\text{corr}}$ , to the binding energy  $E_b = -E_{\text{int}}$  in  $\text{Be}_N$  and  $\text{Li}_N$  clusters, in kcal/mol.

$N$		$E_b^{\text{SCF}}$	$\varepsilon_b^{(2)}$	$\varepsilon_{\text{MP}}^{(3)}$	$\varepsilon_{\text{MP}}^{(4)}$	$\Delta E_b^{\text{corr}}$	$E_b^{\text{MP4}}$
2	$\text{Be}_2$	-5.7	6.4	0.7	0.4	7.5	1.8
	$\text{Li}_2$	3.9	13.0	3.5	1.6	18.1	22.0
3	$\text{Be}_3$	-0.6	28.1	-2.6	0.9	26.4	25.8
	$\text{Li}_3$	11.9	12.3	3.9	2.2	18.4	30.4
4	$\text{Be}_4$	41.9	59.6	-13.3	3.8	50.1	92.0
	$\text{Li}_4$	19.5	32.4	8.1	3.8	44.3	63.8

For  $\Delta E_2^{\text{corr}}(N)$ , we obtain from Eqs. (19), (22), and (23) the following expression:

$$\Delta E_2^{\text{corr}}(N) = \sum_{a < b}^{\{N\}} \left[ \sum_{n=2}^4 [\varepsilon_{\text{pol}}^{(n)} \text{exch}(ab) + \varepsilon_{\text{pol}}^{(n)}(ab)] - E_{\text{def}}^{\text{SCF}}(ab) \right]. \quad (24)$$

If we use the notations (18) and keep in mind that

$$E_{\text{pol}} = E_{\text{pol}}^{\text{nonadd}} + \varepsilon_{\text{disp}}^{(2)}, \quad (25)$$

Eq. (24) can be written in a more compact form:

$$\Delta E_2^{\text{corr}}(N) = \sum_{a < b}^{\{N\}} [E_{\text{pol}} \text{exch}(ab) + E_{\text{pol}}(ab) - E_{\text{def}}^{\text{SCF}}(ab)]. \quad (26)$$

The contributions of the induction energy to the difference inside the brackets of Eq. (26) are almost canceled. To some degree the same happens to the exchange energy. At the large distances, the exchange terms can be totally neglected and the main contribution to  $\Delta E_2^{\text{corr}}$  will be given by the dispersion energy.

The expression for the correlation contribution to the energy of three-body interactions can be represented as follows:

$$\begin{aligned} \Delta E_3^{\text{corr}}(N) = & \sum_{a < b < c}^{\{N\}} [E_{\text{pol}} \text{exch}(abc) + E_{\text{pol}}^{\text{nonadd}}(abc) \\ & - E_{\text{def}}^{\text{SCF}}(abc)] - (N-2) \sum_{a < b}^{\{N\}} [E_{\text{pol}} \text{exch}(ab) \\ & + E_{\text{pol}}^{\text{nonadd}}(ab) - E_{\text{def}}^{\text{SCF}}(ab)]. \quad (27) \end{aligned}$$

Similar expressions can be obtained for the correlation contribution to the  $m$ -body energy for  $m > 3$ . At large distances, the exchange terms can be neglected and, as in the case of  $\Delta E_2^{\text{corr}}$ , the expression for  $\Delta E_3^{\text{corr}}$  will contain only the dispersion terms, in which the leading term is the Axilrod-Teller III order dispersion energy. The three-body dispersion terms

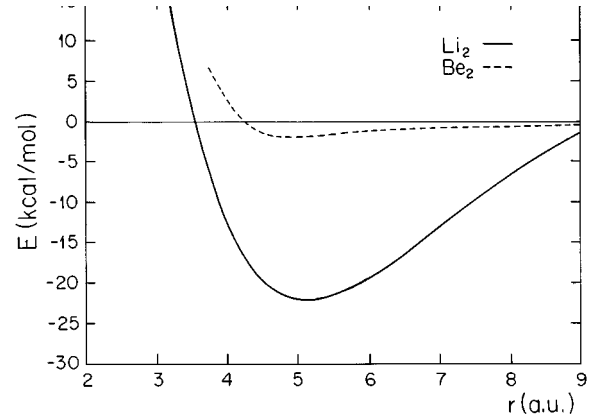


FIG. 1. MP4 potential curves for beryllium and lithium dimers.

appearing in the intermolecular Møller-Plesset perturbation theory approach were studied recently [45] in the noble gas (He, Ne, and Ar) trimers.

#### IV. NUMERICAL RESULTS AND DISCUSSION

In Table III the contribution to the binding energy in  $\text{Be}_N$  and  $\text{Li}_N$  clusters, calculated at different orders of the Møller-Plesset perturbation theory, are presented. It is well known [4,5] that in the SCF approximation the  $\text{Be}_N$  clusters are stable only for  $N \geq 4$ . According to Table III, the corrections to the SCF energy are of great importance for beryllium clusters, to the point of making the unstable  $\text{Be}_2$  and  $\text{Be}_3$  clusters become stable; see also Ref. [17]. What was not so evident is the great importance of the correlation corrections to the binding energy of lithium clusters. The relative magnitude of these corrections is especially large for  $\text{Li}_2$  and  $\text{Li}_4$  clusters: the ratio  $\Delta E_b^{\text{corr}}/E_b^{\text{SCF}}$  equals 4.6 for  $\text{Li}_2$  and 2.3 for  $\text{Li}_4$ . The convergence of the MP series is rather good, although for  $\text{Be}_3$  and  $\text{Be}_4$  clusters we have an alternating series. Note that in the  $\text{Ar}_3$  clusters, according to Chałasiński, Szczesniak, and Cybulski [43], the  $\varepsilon_{\text{MP}}^{(3)}$  and  $\varepsilon_{\text{MP}}^{(4)}$  contributions have also different signs. The binding in the lithium dimer is much tighter than in the beryllium one; see Fig. 1. As follows from Table III, for trimers the difference is not so large and the situation is reversed for tetramers: the binding energy at the MP4 level for the  $\text{Be}_4$  clusters is 1.5 times larger than that for the  $\text{Li}_4$ .

The results of the comparative study of the many-body decomposition for  $\text{Be}_N$  and  $\text{Li}_N$  clusters are presented in Tables IV and V. The poor convergence of the many-body decomposition of the interaction energy obtained for  $\text{Be}_N$  clusters at the SCF level [4–6] becomes even poorer at the MP4 level. The extremely large magnitude of the ratio  $E_{\text{nonadd}}/E_{\text{add}}$  for  $\text{Be}_3$  is due to the almost zero value of  $E_2(3)$  (the equilibrium distance in the  $\text{Be}_3$  triangle is located in the vicinity of the intersection of the  $\text{Be}_2$  potential curve and the abscissa axis). For  $\text{Be}_4$ , we also have a divergent series. According to Eq. (14) and the data presented in Table IV,

$$E_{\text{int}}^{\text{MP4}}(\text{Be}_4) = E_2(4)[1 - 6.69 + 1.03]. \quad (28)$$

A poor convergence is observed in the  $\text{Li}_4$  cluster:

$$E_{\text{int}}^{\text{MP4}}(\text{Li}_4) = E_2(4)[1 - 1.09 + 0.71]. \quad (29)$$

TABLE IV. Influence of the calculation method on the  $m$ -body energy decomposition, in a.u.

(a) $\text{Be}_N$								
$N$		$E(N)$	$E_{\text{int}}(N)$	$E_2(N)$	$E_3(N)$	$E_4(N)$	$E_{\text{nonadd}}$	$\left  \frac{E_{\text{nonadd}}}{E_{\text{add}}} \right $
2	SCF	29.134 86	0.009 05	0.009 05				
	MP4	-29.229 29	-0.002 89	-0.002 89				
3	SCF	-43.714 94	0.000 94	0.057 06	-0.056 12		-0.056 12	0.98
	MP4	-43.881 26	-0.041 15	-0.000 75	-0.040 40		-0.040 40	53.87
4	SCF	-58.354 69	-0.066 81	0.172 44	-0.327 56	0.088 31	-0.239 25	1.39
	MP4	-58.600 40	-0.146 72	0.031 50	-0.210 80	0.032 58	-0.178 22	5.66
(b) $\text{Li}_N$								
$N$		$E(N)$	$E_{\text{int}}(N)$	$E_2(N)$	$E_3(N)$	$E_4(N)$	$E_{\text{nonadd}}$	$\left  \frac{E_{\text{nonadd}}}{E_{\text{add}}} \right $
2	SCF	-14.870 28	-0.006 21	-0.006 21				
	MP4	-14.899 16	-0.035 09	-0.035 09				
3	SCF	-22.315 07	-0.018 98	-0.004 06	-0.014 92			
	MP4	-22.344 52	-0.048 42	-0.088 46	0.040 04		0.040 04	0.45
4	SCF	-29.759 27	-0.031 11	0.017 25	-0.039 86	-0.008 50	-0.048 36	2.80
	MP4	-29.829 83	-0.101 66	-0.163 42	0.178 82	-0.117 06	0.061 76	0.38

A detailed analysis of expansion (14) shows that for  $\text{Be}_3$  and  $\text{Be}_4$ , the three-body forces are not only a factor of stabilization, but the dominant factor of the expansion. So the conclusion that the three-body forces stabilize  $\text{Be}_3$  and  $\text{Be}_4$  clusters at the SCF level [4–6] is retained also at the MP4 level. We can see in Table IV that the two-body contribution is very small for all  $\text{Be}_N$  clusters. This is a consequence of a very shallow two-body potential, as presented in Fig. 1. The four-body term is almost an order of magnitude smaller than the total energy of three-body interactions. But if we divide the latter by the number of three-body terms (for a tetramer there are four different triplets) the difference between three- and four-body terms will not be so large. The total interaction energy of the stable tetramer comes from a three-body attraction and two- and four-body repulsions which together amount to 30% of the three-body attraction energy. The fact that the  $\text{Be}_3$  and  $\text{Be}_4$  clusters are stabilized by the three-body interactions and the flatness of the two-body potential explains the decrement in the interatomic distances as the size of the cluster increases: the attractive three-body forces become larger with decreasing Be-Be distance while the two-body forces undergo small changes until the Be-Be distance becomes smaller than  $4a_0$ .

For lithium clusters the pattern is completely different. The two-body interaction energies are large and stabilizing. In Fig. 1 we see that the Li-Li interaction has, similar to Be a broad well, but deeper and with a steeper repulsive ascent. The three-body forces play a destabilizing role. As a result there is an increase of the equilibrium distances in the se-

quence  $\text{Li}_2$ ,  $\text{Li}_3$ , and  $\text{Li}_4$  in order to reduce the three-body repulsion: the latter diminishes more sharply with increasing the interatomic distance, than the two-body attraction. But the most striking result is the important role of the four-body attraction energy. For  $\text{Li}_4$  the two-body attraction is smaller than the three-body repulsion. So the attractive four-body forces are decisive for the formation of stable lithium tetramers. Here we see that the many-body expansion requires also the four-body term, in the case of  $\text{Li}_4$  in a crucial manner.

Now let us consider the influence of the electron correlation on each term of the energy decomposition (1). For the additive  $E_2(N)$  energy, allowing for the electron correlation results in great changes for both beryllium and lithium clusters.  $E_2(N)$  even changes sign for  $\text{Be}_2$  and  $\text{Be}_3$ , as well as for  $\text{Li}_4$ . The correlation contributions to the many-body energies are not so pronounced in beryllium clusters, but are very essential in lithium clusters. This is evident from Table V, where we present the correlation contributions to the energies of  $m$ -body interactions defined by Eq. (22), the relative contribution of electron correlation to the  $m$ -body energy is denoted by  $\gamma_m(N)$ :

$$\gamma_m(N) = \frac{\Delta E_m^{\text{corr}}(N)}{E_m^{\text{SCF}}(N)}. \quad (30)$$

The absolute and relative magnitudes of correlation energy corrections are much larger for lithium clusters than for the beryllium ones.

TABLE V. Role of electron correlation on the  $m$ -body energy decomposition [ $\Delta E_m^{\text{corr}}(N)$  is defined by Eq. (22),  $\gamma_m(N)$  by Eq. (30); all energies are in atomic units].

(a) $\text{Be}_N$				
$N$	$\Delta E_2^{\text{corr}}(N)$ $\gamma_2(N)$	$\Delta E_3^{\text{corr}}(N)$ $\gamma_3(N)$	$\Delta E_4^{\text{corr}}(N)$ $\gamma_4(N)$	$\Delta E_{\text{nonadd}}^{\text{corr}}(N)$ $\gamma_{\text{nonadd}}(N)$
2	-0.011 94 1.32			
3	-0.057 81 1.01	0.015 72 0.28		0.015 72 0.28
4	-0.140 94 0.82	0.116 76 0.36	-0.055 73 0.63	0.061 03 0.25
(b) $\text{Li}_N$				
$N$	$\Delta E_2^{\text{corr}}(N)$ $\gamma_2(N)$	$\Delta E_3^{\text{corr}}(N)$ $\gamma_3(N)$	$\Delta E_4^{\text{corr}}(N)$ $\gamma_4(N)$	$\Delta E_{\text{nonadd}}^{\text{corr}}(N)$ $\gamma_{\text{nonadd}}(N)$
2	-0.028 88 4.65			
3	-0.084 40 20.79	0.025 12 1.68		0.025 12 1.68
4	-0.180 67 10.5	0.218 68 5.49	-0.108 56 12.8	0.110 12 2.28

According to Table IV, the changes in the magnitude of  $E_m(N)$ , calculated in the SCF and MP4 approximations, have for  $\text{Be}_N$  and  $\text{Li}_N$  clusters the opposite tendency:

$$|E_m^{\text{MP4}}(\text{Be}_N)| < |E_m^{\text{SCF}}(\text{Be}_N)|, \quad (31)$$

$$|E_m^{\text{MP4}}(\text{Li}_N)| > |E_m^{\text{SCF}}(\text{Li}_N)| \quad (32)$$

for all calculated  $N$  and  $m$ . The reason is that  $\Delta E_m^{\text{corr}}$  has the same sign for  $\text{Be}_N$  and  $\text{Li}_N$  clusters (see Table V), while  $E_m^{\text{SCF}}$  has different signs for beryllium and lithium dimers and trimers (in the case of  $E_3^{\text{SCF}}$  the sign is the same, but for lithium the absolute values of the three-body energy are very small). For tetramers the absolute value of  $E_m^{\text{SCF}}(\text{Li}_4)$  is extremely small and the adding of  $\Delta E_m^{\text{corr}}$  increases the absolute value of  $E_m(\text{Li}_4)$  irrespective of the  $E_m^{\text{SCF}}$  sign.

Let us now consider the case of the additive two-body energy in more detail. The analytical expression for the correlation correction to it is given in Sec. III by Eq. (26). At large distances, it contains only dispersion terms  $\epsilon_{\text{disp}}^{(2)}(ab)$ . The second-order dispersion energy is always negative. At intermediate distances, the exchange terms, which are usually positive, must be taken into account. But at the equilibrium distances for lithium and beryllium clusters, their contribution are smaller than those of dispersion and  $\Delta E_2^{\text{corr}}(N)$  remains negative (see Table V).

Thus, in the case of beryllium clusters, the negative correlation corrections are added to the positive SCF two-body energy and reduce, as a result, its value. In the case of lithium clusters, the negative correlation corrections are added to the negative  $E_2^{\text{SCF}}(\text{Li}_2)$  and  $E_2^{\text{SCF}}(\text{Li}_3)$  or to the positive but small  $E_2^{\text{SCF}}(\text{Li}_4)$ . This leads to an increase of the absolute magnitude of the two-body interaction energy.

The contribution of the correlation to the nonadditive energy is essential for both  $\text{Be}_N$  and  $\text{Li}_N$  clusters. In particular for  $\text{Li}_N$  clusters its magnitude is surprisingly large (see Table V). As follows from Eq. (27), see Sec. III, the correlation contribution to the energy of three-body interactions contains the exchange and dispersion terms [the induction terms are almost all cancelled in the differences inside the brackets of Eq. (27)]. At large distances the leading term in the dispersion is the Axilrod-Teller III order energy, which has  $R^{-9}$  dependence. But at intermediate distances dispersion terms depend upon the wave-function overlap and the electron exchange effects [3]. The great contribution of the electron correlation to nonadditive terms indicates that at the equilibrium distances the exchange forces play an essential role. The exchange nonadditivity is very marked in the lithium cluster formation, but it is also important in beryllium clusters.

So, contrary to the situation in water clusters [27–29], in beryllium and especially in lithium clusters, nonadditive interactions cannot be studied without taking into account electron correlation. As we noted in the Introduction, electron correlation must also be incorporated in a molecular dynamics simulation of lithium clusters carried out at the *ab initio* level.

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