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Convergence of multibody expansions for alkaline earth metals. Contrast between magnesium and beryllium clusters[a]

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An *ab anitio* SCF–LCAO–MO study of nonadditive three- and four-body interaction energies in Mg_3 (equilateral and linear) and Mg_4 (tetrahedral) clusters is presented. The relative importance of these few-body terms to the interaction energy is at most 39% for three- and 8% for four-body terms. This lies in marked contrast with the case of Be clusters where these terms can have a relative weight of up to 76%, and 31.6%, respectively. The reason for such radically different nonadditive effects is discussed. Some new results for Be_3, Be_4, and Be_5 clusters are presented confirming this is a case where multibody expansions are expected to be very slowly convergent. Finally these results provide an explanation for the poor convergence of the chemisorption energy of an H atom as a function of the size of Be_n clusters.

I. INTRODUCTION

A series of studies of the departure from pairwise additivity for intermolecular interactions through SCF–LCAO–MO calculations of small clusters already exists.[1–5] Rare gas and alkaline earth atoms, with their closed shell or closed subshell electronic structures, have been used as models for molecular dimers, trimers, etc. The rare gas and alkaline earth "dimer" ground states generally present shallow van der Waals wells. Little information exists about the hardest to detect molecules He_2 and Be_2 while Ne_2, Mg_2, and Ar_2 are much better characterized experimentally. In spite of these and other similarities, the few-body nonadditive contributions to the Be_n system differ dramatically from those of equivalent rare gas clusters. For instance, the SCF results for He_3 show that the three-body terms are only of the order of 10% relative to the pairwise additive terms at short distances ($3a_0$) and regularly decrease, henceforth becoming quite negligible in the region of the van der Waals well.[2] The cases of Ne and Ar show an even smaller nonadditivity.[3,4] For Be clusters, however, a very different situation arises. The three-body term is much larger, over 70% of two-body terms for equilateral Be_3, and has been shown to be directly related[1] to the stability of Be_4 tetrahedral clusters of side $4a_0$ first reported by Bender, Schaefer, and coworkers.[6,7] One is naturally led to the question whether such enormous nonadditive terms are typical of all alkaline earth atom clusters. In an attempt to answer this question, we here present some calculations on magnesium clusters to see if the nonadditive effects are actually as large and structure determining as in the case of beryllium. At the same time, we shall report some new results on beryllium clusters to clarify further the question whether multibody expansions converge rapidly beyond the three-body term or not.[1,8]

In Sec. II, we describe the calculations for the ground electronic state of Mg_2, together with the basis functions we have used throughout. Section III contains an analysis of the nonadditive effects in small magnesium clusters. A preliminary comparison with beryllium clusters is included. We look more closely into this question in Sec. IV, where we propose a decomposition of the SCF nonadditive contributions to the energy, in terms of more physical interactions. In Sec. V, we make some remarks regarding previously reported chemisorptive properties[6] of beryllium clusters. Finally, Sec. VI gives a qualitative discussion of the difference between the two alkaline earth elements studied.

II. DETAILS OF THE METHOD AND THE Mg_2 CURVE

The present study consists of SCF–LCAO–MO calculations using the following sets: set I is the $12s6p$ Gaussian type basis set of Veillard[9(a)] in a (531111/42) contraction without any polarization functions. Set II is a double-zeta quality set $12s7p2d$ proposed by Purvis and Bartlett[9(b)] with a (6111111/511/11) contraction, thus leaving two p-type and two d-type functions to account for polarization; set III is essentially the same as set II but without the d functions, thus having only p-type polarization. The total energy for a single Mg atom is, respectively, (in a.u.) -199.59312, -199.600489, and -199.600369 for sets I, II, and III. We first study the Mg_2 interaction curve, the results of which are given in Table I and plotted in Fig. 1. A purely repulsive curve is observed, as a direct consequence of the Hartree–Fock approximation. This closed shell–closed shell repulsion had been already shown for the Mg_2[10] systems. In Fig. 1, we compare with the values of Stevens and Krauss[10] which are near the Hartree–Fock limit. It is evident that sets II and III adequately represent the two-body interactions, giving a potential curve which is very close to the Hartree–Fock limit curve. The lack of polarization functions in set I makes it slightly poorer for Mg_2. One must consider moreover that nonadditive effects for Mg clusters are certainly more sensitive to distances and geometries. We therefore decided to test the basis set effects through the counterpoise method.[11] In Table II, we report the energies of a Mg atom when one or two ghost orbital sets are located around empty

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TABLE I. Comparison of sets I, II, and III (see text) for the Mg_2 interaction energy and for the nonadditive effects in an equilateral Mg_3 cluster with an internuclear distance of $6.052a_0$. Energies are in atomic units.

Mg_2	R	Set I $E(2)$	Set II $E(2)$	Set III $E(2)$
	4.	0.137811		0.120988
	5.	0.052312	0.035436	0.036729
	6.028	0.020074		0.011695
	6.052	0.019654	0.010497	0.011539
	7.	0.007971	0.003918	0.004483
	8.	0.002955		0.001741
Mg_3 (equilateral $R = 6.052a_0$)		Set I	Set II	Set III
Interaction energy $E(3)$		+0.049921	+0.017776	+0.021124
Pairwise energy $E(2,3)$		+0.058962	+0.031491	+0.034617
Nonadditive energy $E(3,3)$		−0.009042	−0.013715	−0.013493
Percent nonadditivity $\epsilon(3,3)$		15%	43%	39%

centers at a distance of $6.052 a_0$. A Mg_2 calculation placing a ghost orbital set to form an equilateral triangle of side $6.052 a_0$ is reported as well. The basis set extension effect for Mg and Mg_2 is quite small indeed and furthermore roughly additive ($\sim 18\times10^{-6}$ a.u. per "ghost orbital" set[11] per Mg atom) so we may feel confident that these effects will be negligible in the present calculations.

Another question which arises is whether the addition of extra p or d functions to account for the polarization of the charge cloud in Mg_2, Mg_3, and Mg_4 systems is crucial. Evidently complete neglect of polarization functions as in set I is not adequate even for Mg_2 repulsions as seen in Fig. 1. In Table I, nonadditive results for a Mg_3 (equilateral triangle geometry) cluster with internuclear distances equal to $R = 6.052 a_0$ are reported for all three sets. The definitions of the energy terms are given in the following section. It is clear that set I is not adequate, due to the lack of polarization functions, to reproduce three-body terms. The difference between sets II and III are much smaller, i.e., the inclusion of d-type polarization functions is not really determinant. Considering also that we shall compare with Be clusters for which a basis set with only two p-type polarization functions was used,[1,6] it seems more rational to do so with set III than the larger set II. We shall therefore essentially base our conclusions on basis set III. From Table I, we see that the use of set II would only make a small difference, predicting that the nonadditive to additive ratio $E(3,3)$ amounts to 43% instead of the set III ratio of 39%. Such a small difference would not change the following conclusions at all.

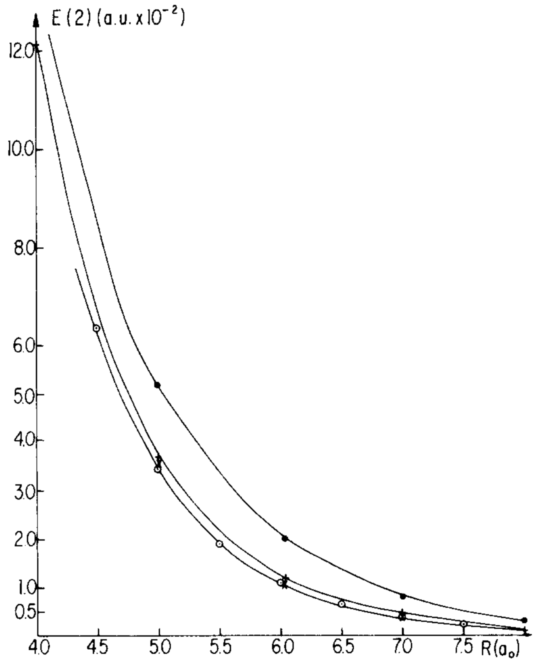

FIG. 1. Repulsive interaction curves for Mg_2 as obtained with basis sets I, II, and III (symbols ●, x, and + respectively) compared to the HF limit results (symbol ○) of Stevens and Krauss.[10]

III. NONADDITIVE TERMS FOR Mg_3 and Mg_4 CLUSTERS

The results for Mg_3 and Mg_4 clusters are reported in Table III, where the usual notation for the analysis of the multibody expansion for the energy of a cluster of n atoms is used:

$$E(n) = E(2,n)[1 + \epsilon(3,n) + \cdots + \epsilon(n,n)] , \tag{1}$$

where $E(m,n)$ is the m-body contribution and $\epsilon(m,n) = E(m,n)/E(2,n)$.

Two different configurations for the magnesium trimer are given in Table III, the symmetric linear and the equilateral of varying side lengths starting at $4 a_0$ and including the value $6.052 a_0$, which corresponds to the nearest neighbor intralayer distance for solid magnesium.[12] A single isosceles structure of sides 6.028 and $6.052 a_0$ is reported to represent a triangle formed from one atom in one layer and the other two in the next layer ($6.028 a_0$ being the nearest neighbor interlayer distance). The single Mg_4 cluster is a "quasitetra-

TABLE II. Basis set extension effect for some typical geometrical situations. X is an empty center with the same basis set as the Mg atom. All distances are equal to $6.052a_0$. E is the total energy of the system depicted in the first column and ΔE is the basis set extension effect. All energies are in atomic units and were obtained using set I.

	E	ΔE
Mg	−199.593116	
Mg···X	−199.593135	19×10^{-6}
·X Mg·: ·X	−199.593152	36×10^{-6}
Mg···Mg	−399.166577	
Mg···Mg ·. .· X	−399.166613	36×10^{-6}

TABLE III. Nonadditive terms for several Mg_3 clusters and one Mg_4 cluster. E(3) is the total interaction energy in the Mg_3 clusters, $E(3,3)$ is the nonadditive three-body contribution, and $\epsilon(3,3)=E(3,3)/E(2,3)$ is the relative weight of nonadditive versus additive contribution. $E(4)$, $E(4,4)$, and $\epsilon(4,4)$ are defined correspondingly for the tetramer. These results were obtained using set III and are in atomic units.

	$E(3)$	$E(3,3)$	$\epsilon(3,3)\times 10^2$
Symmetric linear trimers			
$R=4a_0$	0.243827	+0.000110	+0.04
$R=5a_0$	0.074217	−0.000674	−0.9
$R=6.052a_0$	0.022753	−0.000346	−1.4
$R=7.0a_0$	0.008784	−0.000183	−2.0
$R=8a_0$	0.005824	−0.000085	−1.5
$R=10a_0$	0.000719	−0.000005	−0.5
Equilateral triangles			
$a=b=c=4.0a_0$	0.266228	−0.096736	−26.6
$5.0a_0$	0.070597	−0.039590	−35.9
$6.052a_0$	0.021124	−0.013493	−39.0
$7.0a_0$	0.008957	−0.004492	−33.4
Isosceles triangles			
$a=b=6.028a_0$ $c=6.052a_0$	0.021469	−0.013460	−38.0
	$E(4)$	$E(4,4)$	$\epsilon(4,4)$
Quasitetrahedral tetramer	+0.021211	+0.005703	+8.0

hedral" structure of the type first studied by Bauschlicher *et al.*[6] for the case of Be. The two nearest neighbor interlayer and intralayer distances for Mg differ only by a tenth of an Å, which makes Mg_4 to be very close indeed to a perfect tetrahedron.

From Table III, we arrive at the following picture: Nonadditive effects are substantially smaller than for beryllium clusters[1] for which three-body terms $\epsilon(3,3)$ reach values as large as -0.764 (equilateral Be_3) and -0.248 (linear Be_3). Thus, the considerations which apply to Be clusters[1,5] are not valid for Mg. In particular, the Mg_4 tetrahedron is *not* bounded, in contrast to Be_4.[6,7] The convergence of multibody expansions, quite doubtful for Be, seems better for Mg because four-body effects $\epsilon(4,4)$ are also much smaller in Mg_4. Compare the value for Be_4 (31.6%) with the value 8% in Table III. The contrast between results for Mg and Be is so striking that a detailed analysis is required, in order to understand the reasons and consequences of this difference. Let us first note, however, that some similarities exist which distinguish the two alkaline earth systems from rare gas systems.

Firstly, $\epsilon(3,3)$ terms in absolute value go through a maximum at intermediate distances. This is depicted in Fig. 2, where $\epsilon(3,3)$ for equilateral Mg_3 is plotted, as well as for other trimers (Be_3, He_3, Ar_3, Ne_3). The differences between rare gas and alkaline earth systems are quite evident. $\epsilon(3,3)$ decreases always in absolute value with the distance for the former while for equilateral Be_3 and Mg_3 it increases, reaching a maximum before starting to decrease (much more slowly than for the noble gas trimers). From Fig. 2, the three-body attraction well for Be_3 is deep and narrow, and approximately located at the solid's internuclear distance. It is flatter, shallower, and more extended for Mg_3, for which it is probably not structure determining. For Mg_3, it also has a minimum at the solid's distance ($6.052a_0$ in this case) but the curve is flatter, shallower, and more extended. The $E(3,3)$ value is much smaller than for Be; this seems the cause of Be_4 being bound[1] and not Mg_4. A last point to be noted is that linear Mg_3 clusters (see Table III) present, as for Be,[1] *attractive* nonadditive effects in contrast to noble gas clusters. This has been discussed elsewhere.[18]

IV. DECOMPOSITION OF TRIMER ENERGIES

In the preceding section, it was shown that the multibody energy expansion terms for Be and Mg are quite different in spite of a qualitatively similar behavior. The most striking difference lies in the values of $\epsilon(3,3)$ for equilateral triangles with side equal to the solid nearest neighbor distance. This seems quite surprising in view of the equivalent electronic structures of Be and Mg. A way of explaining this discrepancy is to break down the total interaction energy into components which might be related to some specific aspect of the electronic structure, and to examine the nonadditivity of each component.

Several methods[13-15] have been proposed to decompose the SCF interaction energies into various contributions, usually in terms of classical components such as electrostatic and polarization, plus exchange components as repulsion and delocalization. These schemes have been up to now only applied to dimer interaction analysis. Since we are interested in the nonadditivity of the individual components of the interaction energy, one of us[16] has extended the Morokuma[15] method to cases with more than two subsystems.

The extension is in fact straightforward, and we shall only recall the decomposition scheme in order to introduce the notation. Let us denote by ψ^A, H^A, and E^A (or ψ^B, H^B, E^B and ψ^C, H^C, E^C) the wave function, Hamiltonian, and energy, respectively, of the isolated subsystem A (or B or C), ψ^{ABC} the Hartree product,

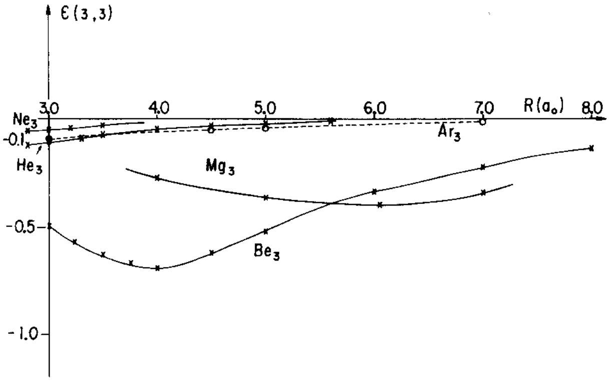

FIG. 2. Three-body nonadditive ratio for Mg_3 equilateral triangle clusters of varying sides R obtained using set III (see text). The nonadditive ratios for other rare gas and alkaline earth trimers are also plotted for comparison.

TABLE IV. Components (in kcal/mol) of the interaction energy of beryllium and magnesium dimers at the nearest neighbor solid equilibrium distance. The definition of the components is given in the text. Set I was used for Mg.

	Be_2 $R = 4.32a_0$	Mg_2 $R = 6.052a_0$
$E_{\mathrm{el}}(2,2)$	−24.62	−13.16
$E_{\mathrm{rep}}(2,2)$	63.18	27.36
$E_{\mathrm{pol}}(2,2)$	−19.36	−0.86
$E_{\mathrm{del}}(2,2)$	−5.49	−1.03
$E_{\mathrm{SCF}}(2,2)$	13.72	12.32

and $\mathcal{A}\psi^{ABC}$ the antisymmetrized product of the wave functions ψ^A and ψ^B, and $\psi^C - H^{AB}H^{BC}$ and H^{CA} are the interaction Hamiltonians, and H the total Hamiltonian, i.e., $H = H^A + H^B + H^C + H^{AB} + H^{BC} + H^{CA}$. The electrostatic energy is defined as $E_{\mathrm{el}}(3) = \langle\psi^{ABC}|H^{AB} + H^{BC} + H^{CA}|\psi^{ABC}\rangle$ and is clearly pairwise additive. The first order interaction $E_1(3)$ is defined as

$$E_1(3) = \langle\mathcal{A}\psi^{ABC}|H|\mathcal{A}\psi^{ABC}\rangle - (E^A + E^B + E^C)$$

contains both electrostatic and repulsive effects.

We can see that $E_1(3) = E_{\mathrm{el}}(3) + E_{\mathrm{rep}}(3)$. When the energy of the Hartree product ψ^{ABC} is optimized without exchange between the subsystem, the monomer wave functions are polarized by the other monomers and the resulting energy $E_2(3)$ contains the sum of the energies of the isolated subsystems, the electrostatic contribution, and the polarization energy:

$$E_2(3) = E^A + E^B + E^C + E_{\mathrm{el}}(3) + E_{\mathrm{pol}}(3) .$$

Finally, the delocalization component $E_{\mathrm{del}}(3)$ appears when the electron exchange is included in the optimization of the antisymmetrized $\mathcal{A}\psi^{ABC}$. Thus, if we call $E_{\mathrm{SCF}}(3)$ the total SCF interaction energy, $E_{\mathrm{del}}(3)$ is defined by

$$E_{\mathrm{del}}(3) = E_{\mathrm{SCF}}(3) - E_{\mathrm{el}}(3) - E_{\mathrm{rep}}(3) - E_{\mathrm{pol}}(3).$$

For each component, the multibody expansion is defined in the same way as for the total energy [see Eq. (1)].

The discussion of the magnitude of E_{pol} and E_{del} in terms of the electronic structure can be made by relating these two quantities to their counterpart—in a second-order perturbation expansion—for interatomic interactions, namely, the energy contributions due to singly excited configurations[17]:

$$E^{PT} = \sum_{i,a} F_{ia}^2/\epsilon_{ia} , \tag{2}$$

where i labels occupied atomic orbitals and a unoccupied ones. If i and a both belong to the same atom, we have a polarization term. Otherwise, it is a delocalization term. F_{ia} is the matrix element of the Fock operator for orbitals i and a. ϵ_{ia}, which is the difference between the orbital energies of i and a ($\epsilon_{ia} = \epsilon_a - \epsilon_i$), plays an important role in the magnitude of the polarization and delocalization energy. The smallest ϵ_{ia}'s arise obviously from the first single excitation. Hence, the smaller this excitation is, the larger will the polarization–delocalization contribution to the interaction energy be.

TABLE V. Analysis of the nonadditive effect for each component of the interaction energy of beryllium and magnesium trimers in an equilateral configuration corresponding to the solid equilibrium distances. All energies are in kcal/mol. The definition of the components is given in the text.

	Be_3			Mg_3		
	$E(3)$	$E(3,3)$	$\epsilon(3,3)$	$E(3)$	$E(3,3)$	$\epsilon(3,3)$
E_{el}	−73.86	0	0	−39.47	0	0
E_{rep}	168.60	−20.94	11%	74.92	−7.16	9%
E_{pol}	−81.79	−23.71	40%	−3.75	−1.17	45%
E_{del}	−3.23	13.24	80%	−0.37	2.72	88%
E_{SCF}	9.72	−31.41		31.33	−5.61	

TABLE VI. Same as Table V for the symmetric linear configuration.

	Be_3			Mg_3		
	$E(3)$	$E(3,3)$	$\epsilon(3,3)$	$E(3)$	$E(3,3)$	$\epsilon(3,3)$
E_{el}	−49.40	0	0	−26.34	0	0
E_{rep}	128.23	1.43	1%	54.86	0.10	0.2%
E_{pol}	−31.34	7.38	19%	−1.24	0.48	27%
E_{del}	−26.53	−15.44	139%	−2.95	−0.89	43%
E_{SCF}	20.96	−6.65		24.33	−0.31	

The above decomposition was made for Be_3 and Mg_3 equilateral triangles at the solid internuclear distance ($R = 6.052a_0$ for Mg and $R = 4.32a_0$ for Be) as well as for symmetric linear trimers using the same distances. For the nonadditive analysis, two pairs—at distances R and $2R$ apart—are needed. Table IV shows the decomposition of the interaction energy for the dimers at distance R. The interaction energy is not reported at distance $2R$ since it is almost zero. The most noticeable feature is that, in spite of having similar total SCF interaction energies (12.32 kcal/mol for Mg_2, 13.72 kcal/mol for Be_2), the balance between the various components is quite different. The absolute values for Be_2 are at least twice as large as those of Mg_2. The importance of this fact is clearly illustrated in Table V, which contains the decomposition results for the equilateral triangles. The relative weight of nonadditive contributions is similar in both cases, but their absolute values are much larger for Be_3. The case of symmetric linear trimers is again different (see Table VI). We first notice that all nonadditive contributions have opposite signs with respect to the equilateral triangles. For the polarization component $E_{\mathrm{pol}}(3,3)$, this is a trivial consequence of geometric addition of electric fields.[18] From Table VI, we see that $E_{\mathrm{del}}(3,3)$ is substantially larger than $E_{\mathrm{pol}}(3,3) + E_{\mathrm{rep}}(3,3)$, producing an overall attractive $E(3,3)$. This of course would not be true for shorter distances, where $E_{\mathrm{rep}}(3,3)$ grows very rapidly, and this appears to be the reason for the repulsive $E(3,3)$ value for linear Mg_3 at $R = 4a_0$ (see Table III).

Before we compare the Be_3 and Mg_3 results in Tables IV–VI, we should point out that for Mg the results were obtained using set I, which lacks polarization functions. Consequently, the smallish Mg polarizability as compared to Be may be due *partly* (although certainly not *only*) to such a deficiency. Firstly, if we look at the relative weight of each component with respect to the total interaction energy, we see that it is roughly the same for the dimer, the trimer, and also for the nonadditive three-body contribution, in both Mg and Be cases (the only exception being the symmetric linear trimer of Mg, where the repulsive component is negligible due to the large distance between the extreme atoms). If we compare now each component in magnesium and beryllium cases, E_{el} and E_{rep} are not too different, but E_{pol} and E_{del} are much smaller for Mg than for Be. As we mentioned above, the two terms are inversely proportional to the orbital energy difference ϵ_{ia} [Eq. (2)]. Similarly, around the equilibrium distances, the HOMO–LUMO SCF energy gap is 1.5 times larger in Mg_3 than in Be_3. In other words, the small energy gap between the MO's corresponding to the 2*s* occupied states and the 2*p* unoccupied states of Be makes the trimer highly polarizable, particularly at the short distances of neighboring atoms in solid beryllium. We shall focus our attention once more on these features of beryllium, namely, the large polarizability and shorter equilibrium distances of the solid, in the following section.

V. FEW BODY CONTRIBUTIONS TO THE STABILITY AND CHEMISORPTIVE PROPERTIES OF Be_n CLUSTERS

The results presented in the previous sections comply us to consider Be as having exceptionally large three- and four-body terms. The role played by nonadditive effects is decisive in determining which clusters are bound and which are not. Besides, the multibody expansion is not expected to converge rapidly at all for beryllium. To supplement further these statements, we shall now report some new results obtained for small Be clusters.

In Ref. 6, Bauschlicher *et al.* sampled a five-body structure corresponding essentially to the said quasitetrahedral quartet plus a fifth atom lying on the plane formed by three members of the quartet. However, this is not expected to be the most stable geometry. In fact, the total binding energy is -0.013 a.u., and the fifth Be atom does not attach to the quasitetrahedral quartet. A more symmetric candidate for Be_5 would be the trigonal bipyramidal structure as depicted in Table VII. We have studied it as well as all the inscribed substructures, with the large basis set of Ref. 6. The results presented in Table VII show that the total binding energy $E(5) = -0.0177$ a. u. is not much larger than the one reported in Ref. 6. The fifth atom is again unattached to the other four in spite of the important three-body attractions. The five-body term $E(5,5) = +0.0318$ a. u. is very large and repulsive, contrary to the other Be_5 structure where it was found to be attractive (see Ref. 1). The comparison of $E(5)$ and $E(5,5)$ indicates that the multibody expansion does not converge rapidly. Using the notation of Eq. (1) in fact, we have

$$E(5) = E(2,5)(1 - 2.029 + 0.801 + 0.146) = -0.082E(2,5). \quad (3)$$

TABLE VII. Nonadditive terms for the Be_3 cluster and all inscribed dimers, trimers, and tetramers. All energies and distances are in atomic units. The structure of the pentamer is trigonal–bipyramidal as described below. There are two different inscribed tetramers, the first one being the quasitetrahedral structure of sides $4.3211a_0$ and $4.28a_0$. The second one contains one intralayer pair, four interlayer pairs, and one alternate plane pair distance. The trigonal bipyramid consists of an equilateral array of three Mg atoms with the other two located in neighboring layers (one above and one below).

Beryllium			
Dimers	$E(2)$		
$a = 4.3211a_0$	0.021864		
$4.2036a_0$	0.025023		
$6.77a_0$	0.002140		
Trimers	$E(3)$	$E(3,3)$	
$a = b = c = 4.3211a_0$	0.015499	-0.050093	
$a = 4.32a_0$; $b = c = 4.2036a_0$	0.016727	-0.005183	
$a = 6.77a_0$; $b = c = 4.20a_0$	0.031910	-0.020276	
Tetramers	$E(4)$	$E(4,4)$	
	-0.030819	0.044162	
	0.022211	0.028757	
Pentamer	$E(5)$	$E(5,5)$	$\epsilon(5,5)$
	-0.017702	0.031852	14%

More generally, in all cases studied here and in Ref. 1, $E(n,n)$ is larger (in absolute value) than $E(n)$. Therefore, the stability of beryllium clusters could not be predicted from the calculation of the first terms of the multibody expansion of the energy.

In the same spirit as in the above sections, we would now like to extend the comparison between the two alkaline earths studied and try to understand further the dual nature of beryllium. Let us first recall that it forms one of the weakest bound ground states as a van der Waals molecule whose estimated equilibrium distance[19] ($8.59 a_0$) is unusually large, even in comparison with rare gas atoms (~ 5–$6 a_0$) or compared with magnesium[20] ($7.35 a_0$). Nevertheless, the structure of solid beryllium is hexagonal closed packed, with a small nearest neighbor distance ($4.2 a_0$) in particular much smaller than that of solid magnesium ($6.0 a_0$). In the second place, three-body nonadditive effects (see Fig. 2) present a minimum precisely in the region of $4.2 a_0$ for beryllium. For magnesium, we have the same effect but it is smaller and quite constant over a large range of distances, running from the van der Waals minimum up to the solid equilibrium distance. The contrast between these two extreme behaviors leads us to ask whether these large and distance dependent few-body effects are responsible for the switching from a loosely bound van der Waals pair to the very compact metal structure for beryllium. Tempting as this hypothesis might sound, in order to provide a thorough answer, it would require a systematic analysis of nonadditive interactions, out of the scope[21] of the studies developed for larger clusters. Furthermore, it is not evident at this stage that correlation effects could be disregarded. We shall therefore not pursue this important question here.

Another question closely related to the many-body effects refers to the chemisorptive properties of beryllium clusters. In the light of the very peculiar properties of beryllium, we would like to advance some speculations on some reported results for H–Be_n interactions. In their interesting analysis of a hydrogen atom adsorbed on a beryllium cluster, Bauschlicher *et al.*[6] asked the very relevant question of how many surface atoms participate in the bond with the adsorbate. An important implicit assumption is that, by adding more and more Be atoms to the cluster, the solid itself would finally be well represented, and the chemisorption energy would converge to a reasonable value. In spite of the fact that we have not done any calculations on the H–Be_n cluster as yet, we are convinced that the few-body analysis of Be_n clusters as such sheds some light on some of the peculiar results reported in Ref. 6. It was found[6] that when the hydrogen atom is chemisorbed on a beryllium layer of seven atoms forming an hexagonal cluster, with the incoming H atom placed overhead the central Be atom, an important "chemisorption energy" of 71.3 kcal/mol was obtained. However, if three or more Be atoms are added, placed in a layer immediately below (i.e., opposite to the H atom), the chemisorption energy collapses to 27.3 kcal/mol.

Still another conspicuous case is that of Be_4 clusters, where the chemisorption energy (65.4 kcal/mol) is very large when H lies on the planar Be_4 structure, while for the quasitetrahedral Be_4 it is only 33 kcal/mol. In order to understand these anomalies, let us compare the total nonadditive energy ΔE [defined as the total interaction energy minus the pairwise additive term $E(2,4)$]. These quantities can be easily extracted from Ref. 1, and we have that for the planar Be_4 it is $\Delta E = -20.77$ kcal/mol, while the quasitetrahedron has $\Delta E = -107.62$ kcal/mol. We tend to believe that the presence of the H atom induces a stabilization of the planar cluster through nonadditive effects (i.e., changing the Be–Be interactions). This would however not occur for the "nonadditivewise saturated" quasitetrahedron. In the same manner, the cases of Be_7 and Be_{10} clusters mentioned above can be rationalized. Thus, the central Be atom is the vertex of planar quartets exclusively in the former structure, while for the latter, it is shared by three tetrahedral quartets as well. Consequently, the high "chemisorption energy" of Be_7 would represent a measure of its small nonadditive terms. We are not in a position to give any values for the Be_7 and Be_{10} clusters unfortunately. Instead, we can study a further example from Ref. 1, namely, Be_5 with a large value of $\Delta E = -127.26$ kcal/mol. Once more, this yields an interaction energy with the H atom reasonable enough (20 to 30 kcal/mol), as in the case of tetrahedral Be_4. What we are stating here, of course, was briefly pointed out by Bauschlicher *et al.*[6] in a different language, e.g., when they say that their planar Be_7 is not a good model for chemisorption because it uses the approaching H atom as a means of "alleviating its discomfort."

From the discussion above, it follows that a clear distinction between spurious effects, such as cluster stabilization, and real chemisorption energies is needed. We would finally like to add that, to our minds, Be clusters are particularly unsuited in this, as well as other respects, due to the large nonadditive effects they present.

VI. CONCLUDING REMARKS

The nonadditive effects for magnesium show the same general trends as for beryllium. Nevertheless, their order of magnitude is smaller, especially four-body terms. Contrary to the case of beryllium, the convergence of the interaction energy in a multibody expansion series is expected to be fast.

All alkaline earth dimers exhibit a weakly bound (or repulsive) ground state and, at the same time, strongly bound excited states. For Mg_2, there exists reliable experimental information[20] on the ${}^1\Sigma_g^+$ ground state and the ${}^1\Sigma_u^+$ excited state. Multiconfigurational SCF studies[10] have provided reasonable theoretical predictions both for the ground and lowest excited states. The equilibrium distance for the ground state is $7.35\,a_0$[20] and around 5.5–$6.0\,a_0$ for these excited states.[10]

The situation for Be_2 is more uncertain both experimentally and theoretically. There do exist calculations including electron correlation which exhibit a very shallow van der Waals minimum at $8.5\,a_0$ for the ${}^1\Sigma_g^+$ ground state,[19] and extensive configuration interaction results for various excited bound states, all with equilibrium distances at around $4a_0$.[22] So the common characteristic shared by magnesium and beryllium is to have a pure van der Waals ground state, and excimer states which can be accounted for using simple qualitative molecular orbital arguments.[10] As a consequence, the dimer in its ground state is highly polarizable, due to the small gap between the ground state and the excited states and this polarizability enhances as the distance decreases up to the excimer's equilibrium distance. In the case of beryllium, the situation is extreme, since the equilibrium distances for the ground state and the excited states differ by $4.5\,a_0$ (i.e., more than half the ground state equilibrium distance). The polarizability of the beryllium dimer at $4.2\,a_0$ must hence be very large. Let us emphasize that this is also the nearest neighbor distance for solid Be and it lies in the region where nonadditive effects become very large. For Mg_2, the same effects are present, but in a milder scale; The ground state and the excited states differ be some $1.5a_0$ only. This is apparently due to the fact that the $Mg(3s^2)+Mg(3s3p)$ resonance effect (i.e., the energy curve repulsion) is relatively smaller than the one for $Be(2s^2)+Be(2s2p)$. Hence, the energy gap is expected to be smaller for Be_2 than for Mg_2. We therefore infer that the magnesium dimer is less polarizable, and consequently the nonadditive terms turn out to be less important than for beryllium.

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