

The Many-Body Expansion for Metals: II. Nonadditive Terms in Clusters Composed of Metals with ns¹, ns², and ns²p¹ Configurations

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ABSTRACT: The man homometallic and heter and ns^2p^1 configuratio magnitude and nature (terms and seek an un- different families of clust alkali metals (Li ₃ , Na ₃ , K and LiB ₂), and alkaline e	y-body expansion (MBE) was applied to ometallic trimers of metals with ns^1 , ns^2 , ns to investigate its convergence, the stabilizing/destabilizing) of the individual derstanding of their variation across the ers. In particular, we examined the series of r_3 , Li ₂ Na, LiNa ₂), alkali metal borides (Li ₂ B arth metals (Be ₂ , Be ₂ Mg, BeMg ₂ , and Mg ₂)	Na	2b' 3-B (+) (+) (+) (+) (+) (+) (+) (+)	2b (€ (†) (†) (†) (†) (†) (†) (†) (†)	4a ⁴ ^{3-B} Σ(2-B) = 3x(2-B3)
trimers, as well as sodiu there is no uniform contr the series in the differen	im clusters Na_n , $n = 2-5$. We found that ribution (stabilizing or destabilizing) across t families of trimers. For instance, the 2-B			@ <u>``</u> ⊛`@``© s'.p°	

them; however, the opposite holds for the quartet state of the Li_3 , Li_2Na , $LiNa_2$, and Na_3 clusters (destabilizing 2-B, stabilizing 3-B). Substituting Li with B in the quartet state of Li_3 results in a significant reduction of the 3-B term amounting to 16% (Li_2B) and 5% (LiB_3) of the binding energy. On the contrary, the ground states of the alkaline earth metal clusters (Be_3 , Be_2Mg , $BeMg_3$, and Mg_3) are stabilized by the 3-B term, while the 2-B term destabilizes them. Overall, we find that the 3-B terms significantly stabilize the high-spin multiplicity states of the ns^1 configurations and the low-spin states of the ns^2 configurations. Finally, as the size of the metal increases, the contribution of the 3-B term to the binding energy decreases due to the longer metal–metal bond distances.

1. INTRODUCTION

Small metal clusters are of great interest in physical science due to their unique electronic structure properties¹⁻⁴ and their potential use in catalysis or other industrial applications.⁵⁻⁷ For instance, the binding energies of these clusters can vary drastically with size and geometry, signaling the dominance of nonadditive interaction terms.⁸ The size of the clusters can also affect other properties such as the onset metallicity¹ or the catalytic activity of the clusters due to the changing energetics of adsorbate interactions.⁹ Because of their complex electronic structure, accurate calculations on metal clusters often require highly correlated electronic structure methods that include both dynamic and nondynamic correlation, spin–orbit coupling, scalar relativistic effects, etc.

term stabilizes the ground states of the Na_3 (doublet), Na_4 (singlet), and Na_5 (doublet) clusters, and the 3-B term destabilizes

To understand the interatomic interactions, electronic structure and (non)additivity of such clusters, it is often beneficial to expand the total energy of the system in a manybody decomposition. That is, the total energy is expressed as the sum of 1-, 2-, 3-, 4-body terms, and so on. Ideally, this sum should converge with increasing *n*-body terms, as it does for hydrogen bonded aqueous and ionic clusters^{10–13} but in the case of covalent systems, the convergence is often slow and not

always guaranteed.^{14,15} Moreover, it is not always obvious which term in this expansion will be dominant for any particular system or geometry. The dominance of nonadditive interactions in metallic clusters implies that terms higher than 2-body make up the most stabilizing interactions between atoms.

2-B2

2-B3

In a previous study,¹⁶ we examined the many-body expansion of alkaline earth metals by investigating several isomers of M_n , where M = Be, Mg, Ca and n = 2-6. Regardless of the level of theory used, the calculations suggested that these alkaline earth clusters had negligible 2-body interactions and were primarily bound by 3-body interactions. Higher order interactions (4-, 5body, etc.) were also important in some cases though they slowly converged in an oscillatory fashion for terms above the 3-body. Through quasi-atomic orbital analysis,^{17–21} it was demonstrated

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Figure 1. Calculated minimum structures for Na_n , n = 2-5.

how the nature of the orbitals changes from a dimer to a trimer and how the presence of a third atom was essential to the binding energy of the cluster.

Unlike alkaline earth metals, alkali metals have a valence configuration of ns¹, which translates into a much stronger 2body interactions in their ground states. This is reflected in the binding energy of the individual dimers, as Na2 is bound by almost an order of magnitude more than Mg2.^{22,23} Despite the larger magnitude of the two-body term, alkali metal clusters still exhibit large higher-body terms that often exceed the magnitude of the 2-body interaction. Spin-polarized excited states of alkali metal trimers (e.g., Na3 or Li3) exhibit minimal 2-body interactions and are entirely bound by 3-body interactions.²⁴⁻²⁶ However, this is not uniform down the group, and the role of nonadditive attractive terms decrease from 130% of the total interaction energy in Li to about 49% in Cs.²⁶ Ground state alkali metal clusters, on the other hand, exhibit a more balanced many-body expansion with respect to 2-, 3-, and higher body terms.^{27,28} In a study of Li and Be clusters, Kaplan and coworkers²⁷ reported that electronic correlation, and in particular exchange and dispersion terms, play a significant role in the nonadditive interactions of these metals.

There are surprisingly few studies that examine the manybody expansion of alkaline metal clusters in their ground states.^{26–30} It is evident that many-body terms play a significant role in the stability of both alkaline and alkali-earth metal clusters, even though the differences between these two groups are not well understood. The single valence electron in alkaline metals adds several practical challenges to the computation of the MBE. Odd numbered clusters, or odd intermediate terms of the MBE (3-body, 5-body, etc.) will contain unpaired electrons which complicates the many-body decomposition by multiple "spin-paths" that generate the same total energy.¹⁶ For instance, one can imagine that a sodium dimer with well separated atoms can be in either the singlet or triplet state. This is by no means unique to alkali metals. In our previous paper in this series,¹⁶ we demonstrated for beryllium trimers how different paths on the MBE lead to the same binding energy.

Following our examination of alkali-earth metals,¹⁶ in this study we examine the potential energy surfaces and many-body decomposition of several pure and composite alkaline systems. In order to obtain a comprehensive picture of the MBE of these systems, several geometries are examined for various cluster sizes.

2. COMPUTATIONAL DETAILS

The conformational analysis of the Na_n clusters, n = 2-5, for various spin multiplicities was carried out at the coupled-cluster singles and doubles (CCSD) level of theory³¹ using the aug-cc-pVTZ (AVTZ) basis set.^{32–35} The calculated geometries are shown in Figure 1. Additionally, the Møller–Plesset second order perturbation theory (MP2)^{36,37} and the coupled-cluster singles and doubles with perturbative triples (CCSD(T)) were used.^{31,38} Only valence electrons were correlated with the MP2, CCSD and CCSD(T) methods.

For a series of metal cluster trimers, i.e., the alkali metal clusters (Li₃, Na₃, K₃, Li₂Na, LiNa₂), and the alkali metal borides (Li₂B and LiB₂) the quartet states were calculated at the CCSD/ AVTZ and the MP2/AVDZ levels of theory (except for K for which the Sapporo valence triple- ζ basis set³⁹ was used). Furthermore, the ground state (singlet state) of the alkaline earth metal clusters (Be₃, Be₂Mg, BeMg₃, and Mg₃) were calculated at the CCSD/AVTZ level of theory. Finally, for the homometallic alkali metal clusters (Li₃, Na₃, K₃) potential energy surfaces were computed at the multireference MP2 (MRMP2) level of theory, except for potassium which was modeled at the complete active space self-consistent field (CASSCF).^{40,41} The active space for the CASSCF calculations included all the valence *s* and *p* orbitals, totaling one electron in four orbitals per atom (e.g., 3 electrons in 12 orbitals).

The cluster binding energies of a cluster of *n* atoms with respect to the ground atomic state products (ΔE_{atomiz}) were decomposed based on the many body analysis as described previously^{12,13} in one-body (1-B), two-body (2-B), three-body (3-B), four-body (4-B), and up to five-body (5-B) terms for clusters with up to 5 atoms according to eqs 1–6,

$$\Delta E_{atomiz} = E(12345) - \sum_{i=1}^{5} E(X_i^{gs})$$

$$\approx \Delta E(1\text{-B}) + \Delta E(2\text{-B}) + \Delta E(3\text{-B}) + \Delta E(4\text{-B})$$

$$+ \Delta E(5\text{-B})$$
(1)

$$\Delta E(1-B) = \sum_{i}^{5} \left[E(X_{i}^{is}) - E(X_{i}^{gs}) \right]$$
(2)

$$\Delta E(2-B) = \sum_{i < j}^{5} \Delta^{2} E_{ij}$$
(3)

$$\Delta^2 E_{ij} = E(X_i X_j) - E(X_i) - E(X_j)$$
(4)

$$\Delta E(3-B) = \sum_{i < j < k}^{5} \Delta^{3} E_{ijk}$$
(5)

$$\Delta^{3} E_{ijK} = E(X_{i}X_{j}X_{k}) - E(X_{i}) - E(X_{j}) - E(X_{k}) - \Delta^{2} E_{ij} - \Delta^{2} E_{ik} - \Delta^{2} E_{jk}$$
(6)

etc.

where $E(X_i^{is})$ is the *in situ* (ground or excited) atomic state and $E(X_i^{gs})$ is the ground atomic state of atom X_i . It is obvious that if the *in situ* atomic state is the ground state, then the 1-B term is zero.

Additionally, the binding energies and the many body terms were corrected for basis set superposition error $(BSSE)^{42-44}$ as described in references.^{12,13,45} An additional notation is introduced to denote the identity of fragments held at the cluster geometry (subscripts) and the basis set used (superscripts). In this notation $E_g^b(F)$ refers to the energy of fragment $F = X_i \cup X_j \cup X_k \cup \cdots \cup X_m$ computed at the cluster geometry $g = (x_i \cup x_j \cup x_j \cup \cdots \cup x_m)$ with basis set $b = b_i \cup b_j \cup b_k \cup \cdots \cup b_k$ where $m \leq n$. The BSSE-corrected interaction energies $(\Delta E'_{atomiz})$, the BSSE-corrected $\Delta E'(2-B)$, $\Delta E'(3-B)$, etc. terms are given in eqs 7–12

$$\Delta E'_{atomiz} = E^{b_1 b_2 b_3 \cdots b_n}_{x_i x_2 x_3 \cdots x_n} (X_i X_j X_k \cdots X_n) - \sum_{i=1}^n E^{b_1 b_2 b_3 \cdots b_n}_{x_i} (X_i^{gs})$$
(7)

$$\Delta E'(1-B) = \Delta E(1-B) \tag{8}$$

$$\Delta E'(2-B) = \sum_{i < j}^{n} \Delta^{2} E'_{ij}$$
(9)

$$\Delta^{2} E_{ij}' = E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}X_{j}) - [E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}) + E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{j})]$$
(10)

$$\Delta E'(3-B) = \sum_{i < j < k}^{n} \Delta^{3} E'_{ijk}$$
(11)

$$\begin{split} \mathbf{A}^{3}E_{ijk}' &= E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}X_{j}X_{k}) - [E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}) \\ &+ E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{j}) + E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{k})] \\ &- [\Delta^{2}E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}X_{j}) + \Delta^{2}E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{i}X_{k}) \\ &+ \Delta^{2}E_{x_{1}x_{2}x_{3}\cdots x_{n}}^{b_{1}b_{2}b_{3}\cdots b_{n}}(X_{j}X_{k})] \end{split}$$
(12)

etc.

Δ

The CCSD and MP2 calculations were performed with the GAUSSIAN16 program,⁴⁶ the CCSD(T) calculations with the MOLPRO program⁴⁷⁻⁴⁹ and finally the CASSCF(3,12) calculations were carried out using the General Atomic and Molecular Electronic Structure System (GAMESS) program.⁵⁰

3. RESULTS AND DISCUSSION

3.1. Na_n, n = 2-5 Clusters. The low-lying isomers of the Na_n clusters, where n = 2-5, were calculated for various spin multiplicities at the CCSD/aug-cc-pVTZ level of theory.

Na₃: All five structures shown in Figure 1 were investigated in both the doublet and quartet spin multiplicities. Minimum structures were obtained for the **a**, **b**, and **d** structures of Figure 1, whereas the geometry optimization of the **c**, and **e** structures collapsed to the **b** or **d** structures. The 2b' and 2b are both isosceles; the equal sides of 2b' are shorter that the third side, while in 2b the opposite occurs. The clusters are named as **nx**, where n = 2S + 1 and x = type of structure of Figure 1 and S is the total spin. The geometries and the MBE of their binding energies are given in Tables 1 and 2. The global minimum structure is the

Table 1. Geometry of the Na₂ and Na₃ Clusters, R (Å) and φ (Degrees), and Their Relative Energy T_e (kcal/mol) at the CCSD/aug-cc-pVTZ Level of Theory

Species	Structure ^a	State	R_1 (Å)	R_2 (Å)	φ (deg.)	$T_{ m e}$ (kcal/mol)
Na ₂		${}^{1}\Sigma_{g}^{+}$	3.178			
		${}^{3}\Sigma_{u}^{+}$	5.171			
Na ₃	2b′	${}^{2}B_{2}$	3.314	4.253	79.83	0.00
	2b	${}^{2}A_{1}$	3.787	3.192	49.85	0.47
	2d	${}^{2}\Sigma_{u}^{+}$	3.400	6.800	180.0	2.08
	2a	² E'	3.499	3.499	60.00	2.15
	4a	⁴ A ₁ '	4.340	4.340	60.00	19.38
	4b	${}^{4}B_{2}$	5.046	9.829	153.77	21.04
	4d	${}^{4}\Sigma_{\rm u}$	5.042	10.084	180.00	21.04

^{*a*}**nx**: n = 2S + 1 and x = type of structure of Figure 1. *S* is the total spin.

Table 2. MBE of the Binding Energies (kcal/mol) of the Na ₃
Clusters at the MP2, CCSD, and CCSD(T) /aug-cc-pVTZ
Levels of Theory

Level of theory	Structure	ΔE	Total (2-B)	3-B
MP2	4a ^{<i>a</i>}	-0.59	-0.07	-0.52
CCSD		-2.95	-0.42	-2.53
CCSD(T)		-3.07	-0.32	-2.74
CCSD	2b'	-22.40	-44.08^{b}	21.68 ^b
			-27.55°	5.15 [°]
CCSD	2b	-21.93	-42.79^{b}	20.86 ^b
CCSD	2a	-20.25	-46.91 ^b	26.66 ^b

^{*a*}MBE with respect to Na₂ (${}^{3}\Sigma_{u}$). ^{*b*}MBE with respect to Na₂ (${}^{1}\Sigma_{g}^{+}$). ^{*c*}MBE with respect to two Na₂ (${}^{1}\Sigma_{e}^{+}$) and one Na₂ (${}^{3}\Sigma_{u}$).



Figure 2. (i) Analysis of the *n*-B terms and (ii) molecular valence orbitals of the Na₃ cluster.

2b'(²B₂), while the 2b(²A₁) and 2d(² Σ_u^+) are lying 0.47 and 2.08 kcal/mol above the global minimum. This agrees with the first theoretical study of Martin and Davidson in 1978,³ who reported the 2b and 2d structures to be 0.60 and 2.99 kcal/mol above the 2b' structure at the CISD/(6s4p1d) level of theory. The atomization energy of the 2b'(²B₂) is calculated at -22.40 kcal/mol, while the lowest quartet minimum structure 4a(⁴A₁') is calculated to lie 19.38 kcal/mol above the 2b'(²B₂) minimum, i.e., the minimum of the quartet state is bound by 3.02 kcal/mol with respect to the atomization products. This state has been observed experimentally using laser-induced emission spectroscopy.¹⁸ Recently, the quantum dynamics of the Na + Na₂⁵¹ and Li + Na₂ reactions⁵² have been reported using the fundamental invariant neural network method, showing that the 2b' structure of the Na₃ is also stable and it has a lifetime of 3.9 ns.

By comparing the geometries the of the Na₂ and Na₃ clusters, it is evident that both the **4b** (⁴B₂) and **4d** (⁴\Sigma_u) clusters of Na₃ contain two Na₂(³Σ_u⁺), i.e., the Na–Na bond distances of the Na₃ are 5.046 Å and 5.042 Å and the corresponding Na–Na bond distance of the Na₂(³Σ_u⁺) is 5.171 Å, see Table 1. On the contrary, the **2b**'(²B₂) minimum has two Na–Na bonds (3.314 Å) that correspond to the Na₂(¹Σ_g⁺) minimum with a Na–Na bond distance of 3.178 Å, while the **2b** (²A₁) minimum has one Na–Na bond (3.192 Å) that corresponds to the Na₂(¹Σ_g⁺) state.

The MBE of the binding (atomization) energy is given in Table 2. In the case of the 4a minimum the 3-B term stabilizes the cluster, i.e., for a total atomization energy of $\Delta E = -1073$ cm^{-1} the 3-B term amounts to $-960 cm^{-1}$, while the sum of the 2-B terms to -113 cm^{-1} at the CCSD(T) level of theory. Therefore, the 3-B term corresponds to 89.5% of the total binding energy. When compared to the CCSD(T) benchmark, the CCSD level of theory was found to predict both the total binding energy and the magnitude of the MBE terms quite well, in contrast to MP2, which significantly underestimates all energetics. However, MP2 also predicts that the 4a minimum structure is stabilized mainly due to the 3-B term, which amounts to 87.7% of the MP2 atomization energy. Note that the MBE has been performed with respect the in situ atoms, i.e., three Na(²S), and the *in situ* diatomic molecule in the Na₂(${}^{3}\Sigma_{u}^{+}$) state. The importance of the 3-body interaction has also been previously reported by Higgins et al.²⁴ who studied the lowest

quartet state of Na_{3} , both experimentally and theoretically at the CCSD(T) level and they concluded that the 3-B interaction indeed stabilizes the trimer in agreement with the present work.

The 2-B terms, the 3-B term and the valence molecular orbitals of the 2b', 2b, and 4a structures are visualized in Figure 2. In the **4a** trimer, there is an *sp* hybridization and the molecule is stabilized by three σ bonds that form a ring. The Na₃ can be characterized as a σ -aromatic compound, i.e., it is a cyclic compound in which the three Na atoms are conjugated, and the σ -electrons are delocalized in the molecule. The σ -aromaticity, which was proposed by Dewar in 1979,⁵³ is less common than the π -aromaticity. In general, σ -aromaticity stabilizes fully saturated rings,⁵⁴ resulting to shorter bond lengths, however, even though the system here is unsaturated, the bond distance of 5.171 Å in Na₂(${}^{3}\Sigma_{n}^{+}$) is reduced by 0.8 Å in Na₃ (4a, ${}^{4}A'_{1}$) to 4.340 Å and thus the molecule is stabilized. To sum up, the Na_3 (4a, ⁴A'₁) minimum corresponds to an unsaturated molecule, which is stabilized by the 3-body term or in other words via a σ aromaticity.

The 2b' and 2b cluster minima are stabilized via the 2-B terms, while the 3-B term is destabilizing. Pictorially, the 2-B and 3-B terms and the bonding of both the 2b' and 2b trimers are shown in Figure 2. In the case of the 2b' structure, the top Na(²S) atom forms two σ -bonds with each of the bottom Na(²S) atoms forming two Na₂($X^{1}\Sigma_{g}^{+}$), see the discussion regarding the bond distances above, while these two bottom Na atoms are connected via a σ_u bond, see Figure 2. In the case of the 2b structure, the two bottom Na atoms are connected via a σ bond forming a Na₂(X¹ Σ_{g}^{+}) dimer, while the top Na(²S) atom forms one π^{1} bond $(sp_{z}^{1} \rightarrow \sigma^{0})$, see Figure 2. The MBE has been evaluated with respect to the in situ Na(2S) atoms, and the diatomic $Na_2(X^1\Sigma_g^{+})$ molecule. Additionally, for the 2b'minimum the 2-B terms have been calculated with respect to two Na₂(X¹ Σ_{g}^{+}) and one Na₂(³ Σ_{u}^{+}), (Table 2) which is the most accurate description since two $Na_2(X^1\Sigma_g^+)$ and one $Na_2(^3\Sigma_u^+)$ are formed, see Figure 2. Its corresponding ΔE is -7835 cm⁻¹ (-22.40 kcal/mol) with the sum of the 2-B terms amounting to -27.55 kcal/mol and the 3-B 5.15 kcal/mol. Note that in the paramagnetic metallic clusters, the MBE is associated with the location of the unpaired spins and it can be used to identify their location, since the interaction of metal atoms with unpaired

Table 3. Geometry of the Na₄ Clusters, R (Å) and φ (Degrees), Dissociation Energy ΔE (kcal/mol), and Relative Energy T_e (kcal/mol) at the CCSD/aug-cc-pVTZ[CCSD(T)/aug-cc-pVTZ] Method^a

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Structure	State	R_1 (Å)	R_2 (Å)	φ_1 (deg.)	$\varphi_2 ~({\rm deg.})$	ΔE (kcal/mol)	$T_{\rm e}$ (kcal/mol)
1c	${}^{1}A_{g}$	3.608	3.229	53.15	63.42	-41.50 (-41.47)	0.00
						[-42.82 (-42.79)]	
1e	¹ A'	3.234	3.983	47.59		-37.22	4.29
1h	^{1}A	3.172	5.418	34.04	72.97	-33.76	7.75
1g	${}^{1}\Sigma_{g}$	4.398	3.191	180.00	180.00	-33.30	8.20
1b	${}^{1}A_{g}$	3.176	6.760	90.00	90.00	-33.15	8.35
1a	A _{1g}	3.483		90.00	90.00	-28.02	13.48
3h	${}^{3}A_{1}$	3.472	4.460	50.04	79.92	-33.21 (-33.19)	8.19
						[-35.16 (-35.13)]	
3c	${}^{3}B_{3g}$	3.491	4.337	76.79	103.21	-32.87	8.63
3a	${}^{3}A_{1g}$	3.479		90.00	90.00	-32.81	8.70
3e	³ A ₁ '	3.447	3.447	120.00		-25.25	16.26
3g	${}^{3}\Sigma_{u}$	3.277	3.850	180.00	180.00	-21.30	20.21
5d	⁵ A ₁	3.947		60.00		-10.74 (-10.73)	30.77
						[-11.31 (-11.29)]	
5c	⁵ B _{3g}	4.723	4.291			-4.33	37.18
5a	⁵ B _{1g}	5.073		90.00	90.00	-2.72	38.79
5e	⁵ A ₁ '	4.854	4.854			-2.29	39.22
5g	${}^{5}\Sigma_{g}$	4.895	4.994	180.00	180.00	-2.17	39.34
^a The BSSE corr	ected values a	re listed in pare	ntheses.				

Table 4. Geometry of the Na₅ Clusters, R (Å) and φ (Degrees), Dissociation Energy ΔE (kcal/mol), and Relative Energy T_e (kcal/mol) at the CCSD/aug-cc-pVTZ[CCSD(T)/aug-cc-pVTZ] Method^a

Structure	State	R_1 (Å)	R_2 (Å)	R_3 (Å)	φ_1 (deg.)	φ_2 (deg.)	ΔE (kcal/mol)	$T_{\rm e}$ (kcal/mol)			
2i	${}^{2}A_{1}$	3.5177	3.6331	3.5478	61.87	60.45	-54.40 (-54.36)	0.00			
							[-56.38 (-56.34)]				
2a'	${}^{2}B_{2}$	3.4962	3.5080	3.5018	90.46	60.96	-51.84	2.56			
2c	^{2}A	3.871	3.866	3.416, 3.357	67.26	90.48	-49.07	5.33			
2d	${}^{2}A_{2}''$	3.463	3.582		60.00	62.28	-47.05	7.34			
2e	${}^{2}A_{1}$	3.5560	4.6030	3.5630	80.48	130.67	-41.75	12.65			
2f	$^{2}\Sigma_{g}$	3.4185			180.00	180.00	-37.34	17.05			
2g	$^{2}\Sigma_{g}$	3.2760	3.5370		180.00	180.00	-37.91	16.48			
4d	${}^{4}A_{2}''$	3.5455	3.9312		60.00	67.34	-46.03 (-46.00)	8.36			
							[-49.76 (-49.73)]				
4c	${}^{4}A_{1}$	3.4750	3.4750	3.7711	54.87	81.32	-45.10	9.29			
4b	${}^{4}A_{1}$	3.9728	3.4260	3.5774	60.00	70.87	-34.61	19.79			
4i	${}^{4}B_{2}$	3.6139	3.7668	4.0183	58.86	54.27	-33.68	20.72			
4a	${}^{4}A_{1}$	3.686	3.5283	3.6060	100.97	88.43	-28.27	26.12			
4e	${}^{4}A_{1}$	3.3542	4.1973	4.4686	77.46	156.52	-24.49	29.91			
4g	${}^{4}\Sigma_{g}$	3.4261	4.4219		180.00	180.00	-22.65	31.75			
4f	$4\Sigma_{g}$	3.7135			180.00	180.00	-20.24	34.15			
6d	⁶ A ₂ "	4.3856	3.9113		60.00	52.96	-12.17 (-12.14)	42.22			
							[-13.11 (-13.08)]				
6b	⁶ A ₁	3.9251	3.9560	4.5565	60.00	59.48	-11.68	42.72			
6a	⁴ A ₁ '	4.0362	4.0362	4.0362	108.00	108.0	-7.90	46.50			
6c	⁶ B ₂	4.6460	4.6460	4.3925	63.86	96.82	-7.55	46.85			
6 i	⁶ A ₂	3.6181	3.8412	4.1620	58.67	54.36	-1.59	52.81			
6e	⁶ A ₁	4.2891	4.2842	4.7972	59.92	142.54	-4.75	49.65			
6f	$^{6}\Sigma_{g}$	4.8948			180.00	180.00	-2.87	51.53			
6g	$^{6}\Sigma_{g}$	4.8203	4.9639		180.00	180.00	-6.05	48.35			
6i′	⁶ A ₁	4.6978	4.4302	4.514	59.18	86.31	-2.88	51.51			
^a The BSSE co	^a The BSSE corrected values are listed in parentheses.										

parallel spins is typically associated with a small or positive 2-B

 Na_4 and Na_5 : The geometries of the calculated minima structures of the Na_4 and Na_5 clusters and their dissociation energies are given in Tables 3 and 4. For both clusters the

Article

Species	Structure	ΔE	2-B	3-B	4-B	5-B
Na ₄	1c	-41.50 (-41.47)	$-77.42(-77.52)^{bb}$	71.20 (71.41)	-35.29 (-35.38)	
			-22.40°	-38.83	19.73	
	5d	$-10.74(-10.73)^{dd}$	4.20 (4.13)	-18.47(-18.38)	3.53 (3.52)	
Na ₅	2i	-54.40 (-54.36)	-108.38(-108.53)	101.87 (102.18)	-59.40 (-59.56)	11.51 (11.55)
	6d	-12.17 (-12.14)	1.09 (1.40)	-23.69 (-24.14)	11.88 (12.12)	-1.46 (-1.52)

Table 5. MBE of the Binding Energies (kcal/mol) of the Na₄ and Na₅ Clusters at the CCSD/aug-cc-pVTZ Level of Theory^a

^dMBE with respect to Na₂ (${}^{3}\Sigma_{u}$).



Figure 3. Molecular valence orbitals of selected Na4 and Na5 clusters.

ground states are the low spin states, i.e., a singlet for Na_4 and a doublet state for Na_5 . The MBE of the binding energies and the molecular valence orbitals for selected minima are given in Table 5 and are shown in Figures 3 and 4.

For the Na₄ cluster the lowest minimum structure singlet state is the 1c (${}^{1}A_{g}$), which is formed by adding the fourth Na (${}^{2}S$) interacting with the 2b (${}^{2}A_{1}$) of the Na₃ trimer resulting in the



Figure 4. Magnitude of the MBE terms for the (**2b**', **4a**) minima of Na₃, the (**1c**, **5d**) minima of Na₄, and the (**2i**, **6d**) minima of the Na₅ clusters. The shaded patterns trace the magnitude of the MBE terms for the (**2b**') minimum of Na₃ and the (**1c**) minimum of Na₄ when a specific spin orientation of the Na atoms is retained, i.e., two or three (${}^{1}\Sigma_{g}^{+}$) Na₂ and two or three (${}^{3}\Sigma_{u}$) Na₂ are formed.

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formation of the 1c rhombus isomer, i.e., two triangular 2b Na₃ structures sharing the same base. The R_2 bond distance of the **2b** $({}^{2}A_{1})$ minimum of the Na₃ trimer is 3.787 Å, a value that is reduced by ~ 0.18 Å to 3.608 Å in the 1c $({}^{1}A_{g})$ minimum of Na₄. In contrast, the R_1 distance of the **2b** (2A_1) minimum of Na₃ is increased by ~0.04 Å in the 1c $({}^{1}A_{g})$ minimum of Na₄. The lowest in energy triplet state 3h (${}^{3}A_{1}$) can be regarded as a combination of two triangular 2b Na3 structures having the same base while an elongation is observed in the tetramer's bond distances by about ~0.2 Å compared to the bond distances of the triangular 2b minimum in Na₃. The lowest energy high spin quintet state $5d({}^{5}A_{1})$ of Na₄ forms a tetrahedron with a Na–Na bond distance of 3.947 Å. The corresponding lowest energy high spin state quartet state 4a ($^{1}A_{1}$) of Na₃ forms an equilateral triangle with a Na-Na bond distance of 4.340 Å. It is interesting to note that even though the **5d** $({}^{5}A_{1})$ minimum of Na₄ is a high spin state, the addition of the fourth Na atom results in a shorter Na–Na distance by 0.4 Å compared to the $4a (^{1}A_{1})$ minimum of Na₃. Furthermore, the binding energy of the 4a $({}^{1}A_{1})$ minimum of Na₃ with respect to the atomic ground state products is -3.02kcal/mol, i.e., 1.0 kcal/mol/atom, while the binding energy in the 5d (${}^{5}A_{1}$) minimum of Na₄ is significantly larger at -10.64kcal/mol, i.e., 2.66 kcal/mol/atom. The increase of the binding energy is consistent with the shortening of the Na-Na bond distance.

For the Na₅ pentamer the lowest doublet state minimum structure is the **2i** $({}^{2}A_{1})$, which consists of two joint Na₃ triangles. Both the lowest energy quartet state **4d** $({}^{4}A_{2}")$ and the lowest energy sextet state **6d** $({}^{6}A_{2}")$ are triangular bipyramids. It appears that they are formed from the high spin tetrahedral quintet state **5d** $({}^{5}A_{1})$ with the addition of the fifth



Figure 5. Potential energy surfaces of the dimers and trimers of Li (first row), Na (second row), and K (third row). The Li and Na clusters were computed at the MRMP2/aug-cc-pVDZ level of theory, while the K clusters were computed at the CASSCF/SPK-ATZP level of theory. "D" and "Q" refer to the various doublet and quartet states, respectively.

Na atom, which interacts with three Na atoms resulting in the formation of a triangular bipyramid. The triangle in the center of the triangular bipyramid has Na–Na bond distances of 3.931 Å (4d) and 3.911 Å (6d), which are similar to the Na–Na bond distance of 3.947 Å in the 5d (${}^{5}A_{1}$) minimum of the Na₄ tetramer. On the contrary, the other Na–Na bond distances of the pentamer are 3.545 Å (4d) and 4.386 Å (6d), i.e., they are significantly shorter by ~0.4 Å in 4d and significantly longer by ~0.4 Å in 6d compared to the Na–Na distances in the 5d (${}^{5}A_{1}$) minimum of the Na₄ tetramer. The binding energies per atom with respect to the atomic ground state products are –9.21 kcal/mol (4d) and –2.43 kcal/mol (6d), respectively.

For the Na₅ pentamer the lowest doublet state minimum structure is the **2i** (²A₁), which consists of two joint Na₃ triangles. Both the lowest energy quartet state **4d** (⁴A₂") and the lowest energy sextet state **6d** (⁶A₂") are triangular bipyramids. It appears that they are formed from the high spin tetrahedral quintet state **5d** (⁵A₁) with the addition of the fifth

Na atom, which interacts with three Na atoms resulting in the formation of a triangular bipyramid. The triangle in the center of the triangular bipyramid has Na–Na bond distances of 3.931 Å (4d) and 3.911 Å (6d), which are similar to the Na–Na bond distance of 3.947 Å in the 5d (${}^{5}A_{1}$) minimum of the Na₄ tetramer. On the contrary, the other Na–Na bond distances of the pentamer are 3.545 Å (4d) and 4.386 Å (6d), i.e., they are significantly shorter by ~0.4 Å in 4d and significantly longer by ~0.4 Å in 6d compared to the Na–Na distances in the 5d (${}^{5}A_{1}$) minimum of the Na₄ tetramer. The binding energies per atom with respect to the atomic ground state products are –9.21 kcal/mol (4d) and –2.43 kcal/mol (6d), respectively.

The MBE of the dissociation energies (including the BSSE corrected values) for the global minimum structures are given in Table 5. For both the Na₄ (1c; ¹A_g) and the Na₅ (2i; ²A_i) minima, the sum of the *n*-body terms oscillates between negative and positive values. This oscillating behavior is quite commonly observed in the analysis of the MBE especially for covalent



Figure 6. Distribution of 2-B, 3-B, and 4-B terms of all homometallic clusters investigated in this study, computed at the MP2/aug-cc-pVDZ level of theory. The thick horizontal lines inside the boxes represent the median energy, while the dashed red lines represent the average energies. The whiskers of the boxplot extend to 1.5 the interquartile range (75% of the data); points outside the boxes are considered outliers.

bonds,¹⁶ but the normally observed trend of the overall decrease of the absolute value of the *n*-body terms as *n* increases,^{12,13,55,56} is not the case here. While the total 2-B term stabilizes and the

total 3-B term destabilizes the cluster, these two are very close (albeit with different signs). Specifically, the absolute value of the total 2-B energy is larger than the absolute value of the total 3-B energy by about 6 kcal/mol. Additionally, it is interesting that the total 4-B term significantly stabilizes both the tetramer and pentamer clusters, demonstrating the importance of the simultaneous existence of the four atoms with the lowest spin multiplicity forming tetramers. The values of the 3- and 4-body terms are about half of the total 2-B term. Finally, the 5-B term destabilizes the (2i) minimum of Na₅. In the case of the (1c)minimum of Na₄, appropriate spin orientations of the fragments to produce the tetramer singlet state can be considered by the formation of two Na₂ $({}^{1}\Sigma_{g}^{+})$ and four Na₂ $({}^{3}\Sigma_{u})$. Note that the total binding energy of -41.50 kcal/mol for the (1c) minimum of Na4 in Table 5 can be attained via two different paths, denoted by superscripts "a" and "b" in that table, the first with respect to $Na_2({}^{1}\Sigma_{g})^{+}$ and the other with respect to two $Na_2({}^{1}\Sigma_{g})^{+}$ and four $Na_2({}^{3}\Sigma_{u})$. These two paths have very different 2-, 3- and 4-body terms, viz. -77.42, 71.20 and -35.29 kcal/mol for the first path and -22.40, -38.83 and 19.73 kcal/mol for the second path, respectively, both summing up to the total binding energy of -41.50 kcal/mol. For the high spin state isomers (5d) of Na₄ and (6d) of Na₅, the sum of *n*-body terms again oscillates between negative and positive values, but the 2-B term is quite small and destabilizing, while the binding is almost exclusively due to the 3-B term. The 3-B term is therefore the reason that drives the formation of triangles that stabilize the Na_4 (5d) and Na_{5} (6d) isomers. The molecular valence orbitals for the lowest energy Na4 and Na5 clusters for different spin multiplicities are shown in Figure 3. As in the case of the (4a) quartet state of Na₃, the onset of *sp* hybridization assists the stabilization of the high spin states of Na₃, as seen in Figure 3.

The magnitude of the MBE terms at the minimum energy structures with the lowest and the highest spin multiplicities for Na_3 (2b', 4a), Na_4 (1c, 5d), and Na_5 (2i, 6d) clusters is summarized in Figure 4. The minimum structures of the low

spin states of Na₃, Na₄ and Na₅ are stabilized mainly via the 2-B term, while their corresponding structures of the high spin states are destabilized by the 2-B term. The 3-B term significantly stabilizes them and this is the reason why triangles of Na atoms are formed in the most stable structures of the Na₃, Na₄ and Na₅ clusters. Furthermore, it is found that most (96%) of the correlation energy in the binding is described at the CCSD level compared to the CCSD (T) benchmark, see Figure 4 and Tables 2–4. Finally, the BSSE corrections are negligible, amounting to <0.3% of the total binding and can be neglected.

3.2. Li_n, Na_n, and K_n Clusters, n = 2-4. The potential energy surfaces (PESs) of the alkali metal dimers (Figure 5, first column) show a minimum that is considerably deeper than that of alkali-earth metals,¹⁶ emphasizing the effect of the ns^1 vs the ns² configurations. The binding energy becomes smaller moving down the periodic table. Specifically, the binding energies are -22.6 kcal/mol, -15.8 kcal/mol, -9.9 kcal/mol for Li₂, Na₂, and K₂, respectively. It should be noted that the CASSCF calculations for potassium were quite difficult to converge. This may be attributed to the effect of the *d* orbitals, which were not included in the active space. In the case of alkali metal trimers (Figure 5, columns 2–4), the minima for all 3 metals have C_{2v} symmetry due to the Jahn-Teller effect in the D_{3h} symmetry. The binding energies of the trimers at their minimum geometries are -35.2 kcal/mol, -21.2 kcal/mol, and -10.5 kcal/mol for Li₃, Na₃, and K₃, respectively. Avoided crossings are observed (Figure 5, columns 2 and 3) at the PESs of the doublet states. Specifically, at the PES of the C_{2v} angle scan, i.e., along the bending coordinate of the trimer, the avoided crossing is observed around 60 degrees while at the PES of the C_{2y} linear scan, i.e., along the bond stretching, at $\sim 3 \text{ Å}$ (Li₃), $\sim 3.5 \text{ Å}$ (Na₃), and ~ 5 Å (K₃). This crossing corresponds to the alteration of the **2b**' to the **2b** trimer.

Figure 6 shows the distribution of the 2-B, 3-B, and 4-B energies for several homometallic alkali metal clusters computed at the MP2/aug-cc-pVTZ levels of theory. As expected, the ground states (doublet states) of these clusters are stabilized by their 2-B and 4-B interactions and are destabilized by their 3-B interactions. The magnitude of the many-body terms decreases

from Li to Na to K, the last of which exhibits the smallest (in magnitude) 2-, 3-, and 4-B terms with averages close to 0 kcal/ mol. Generally, the magnitude of the 2-, 3-, and 4-B terms is found to be proportional to each other. Figure 7 shows the



Figure 7. Relationship between the energy differences $\delta_1 = E(3-B) - E(2-B)$, $\delta_2 = E(4-B) - E(2-B)$ and the E(3-B) term.

clearly linear correlation between the energy differences $\delta_1 = E(3-B) - E(2-B)$ and $\delta_2 = E(4-B) - E(2-B)$ and the E(3-B) term. From the fits displayed in Figure 7, it can be deduced that

$$\delta_1 = E(3-B) - E(2-B) = 1.683 \times E(3-B), \quad R^2 = 0.98$$
(13)

$$\delta_2 = E(4-B) - E(3-B) = -1.983 \times E(3-B), \quad R^2 = 0.93$$
(14)

leading to the following scaling of the higher order 3- and 4-B terms with respect to the pairwise additive 2-B term

$$E(3-B) = -1.464 \times E(2-B) \tag{15}$$

$$E(4-B) = 1.439 \times E(2-B) \tag{16}$$

The dependence of the higher order E(3-B) and E(4-B) on the pairwise term E(2-B) is captivating, especially given the proximity in the values of the proportionality coefficients (albeit of different signs) in eqs 15 and 16. These relations hold for the MBE analysis at the respective minima, and it remains to be seen whether they hold for other trimer and tetramer geometries. Nevertheless, it would be intriguing to perform a Monte Carlo simulation of a small metal cluster based on the premise of eqs 15 and 16, while obtaining the 2-B term from a highly accurate PES obtained from electronic structure and compare the MBEbased results to the ones obtained with the full cluster potential.

3.3. Li_nNa_m and Li_nB_m, n + m = 3. The lowest in energy quartet state of the Li₃ and Na₃ and the mixed Li₂Na and LiNa₂ trimers were calculated at the CCSD level, while in the case of Na₃ the MP2 and CCSD(T) levels of theory were also used. Additionally, the substitution of the Li atoms in the Li₃ trimer with B, which also has a singlet electron but in a p orbital, is investigated for the LiB₂, Li₂B and B₃ clusters to examine the effect of the ns¹ and ns²p¹ configurations on the magnitude of the 3-B term. The geometries of these trimers are given in Table 6, their binding energies and n-body terms are listed in Table 7 and schematically plotted in Figure 8.

The M–M bond distances in the quartet states of the metal trimers are significantly shorter by 0.83–1.14 Å than the ones in the triplet states of the corresponding diatomic metal molecules. However, the difference of the B–B and Li–B bond distances in the trimers and in the diatomic molecules is up to 0.29 Å, see

Table 6. M–M Bond Distances R_1 and R_2 (See Figure 1) in Å, Corresponding φ Angles in Degrees, Binding and Relative Energies T_e in kcal/mol for Various Homometallic and Heterometallic Diatomic and Triatomic Metal Clusters at the CCSD/aug-cc-pVTZ Level of Theory

	Diatomic metal clusters										
Species	State	R (Å)	ΔE (kcal/mol)	State	R (Å)	$T_{\rm e}$ (kcal/mol)	ΔE (kcal/mol)				
Li ₂	$X {}^{1}\Sigma_{g}^{+}$	2.700	-23.81	${}^{3}\Sigma_{u}^{+}$	4.210	22.86	-0.95				
LiNa	$X^{1}\Sigma^{+}$	2.951	-19.72	$^{3}\Sigma^{+}$	4.718	19.00	-0.72				
Na ₂	$X {}^{1}\Sigma_{g}^{+}$	3.178	-16.53	${}^{3}\Sigma_{u}^{+}$	5.171	22.86	-0.58				
LiB	$^{1}\Sigma^{+}$	2.408	-19.79	$X^3\Pi$	2.147	-16.51	-26.50				
B_2	${}^{1}\Sigma_{g}^{+}$	1.636	-37.33	$X^{3}\Sigma_{g}^{-}$	1.603	-6.70	-53.84				
	Triatomic metal clusters										
Species	Structure	State	R_1 (Å) ^{<i>a</i>}	<i>R</i> ₂	(Å)	φ (deg.)					
Li ₃	2b′	² B ₂	2.788	3.2	88	72.25					
	4a	⁴ A ₁ '	3.139	3.1	39	60.00					
Li ₂ Na	2b	² A ₁	3.389	2.6	88	46.73					
	4b	⁴ B ₂	3.581	3.2	57	54.10					
LiNa ₂	4b′	${}^{4}B_{2}$	3.755	4.0	87	65.94					
Na ₃	2b'	² B ₂	3.314	4.2	53	79.83					
	4a	⁴ A ₁ '	4.340	4.3	40	60.00					
			5.169 ^b	5.1	69 ^b	60.00 ^b					
Li ₂ B	4b′	⁴ A ₂	2.082	3.2	20	101.30					
LiB_2	4b	${}^{4}B_{1}$	2.206	1.6	35	43.51					
B ₃	4b′	⁴ A ₂	1.582	1.8	93	73.47					
	4a		1.820 ^b	1.8	20 ^b	60.00 ^b					

^aIn the mixed trimers, atom M' in Figure 1 corresponds to a metal atom with different identity than M. ^bMP2/aug-cc-pVTZ.

Table 7. Binding Energies ΔE , Individual 2-B Terms, Total 2-B (Total 2-B), and 3-B Term in kcal/mol at the CCSD and CCSD(T) (in Italics)/aug-cc-pVTZ Levels of Theory for the Quartet States of the Various Triatomic Mixed Clusters^a

Species	Structure	ΔE	2-B (M–M)	2-B $(M-M')^{b}$	Total 2-B	3-B
Li ₃	4a	-10.94 (-10.93)	1.13 (1.13)	1.13 (1.13)	3.40 (3.39)	-14.34 (-14.32)
Li ₂ Na	4b	-7.07 (-7.06)	0.51 (0.50)	0.80 (0.80)	2.10 (2.10)	-9.17 (-9.16)
LiNa ₂	4b	-4.47 (-4.46)	0.35 (0.35)	0.20 (0.20)	0.75 (0.75)	-5.22 (-5.21)
Na ₃	4a	-2.95 (-2.94)	-0.14 (-0.14)	-0.14 (-0.14)	-0.42 (-0.42)	-2.53 (-2.52)
		-3.07 (-3.06)	-0.11 (-0.11)	-0.11 (-0.11)	-0.32 (-0.32)	-2.74 (-2.74)
Li ₂ B	4b'	-61.39 (-61.10)	0.68 (0.67)	-26.25 (-26.13)	-51.82 (-51.60)	-9.57 (-9.50)
LiB ₂	4b	-112.1 (-111.3)	-53.60 (-53.09)	-26.32 (-26.29)	-106.3 (-105.7)	-5.88(-5.62)
B ₃	4b′	-147.1 (-145.6)	-41.19 (-40.94)	-53.73 (-53.35)	-148.7 (-147.6)	1.56 (2.01)

"The BSSE corrected values are given in parentheses. b In the mixed trimers, atom M' in Figure 1 corresponds to a metal atom with different identity than M.



Figure 8. BSSE corrected *n*-body analysis of the quartet states of the M₃ clusters with respect to the *in situ* products: (a) $\text{Li}_n \text{Na}_m$, n + m = 3 with respect to $M(^2\text{S})$ and $\text{MM}'(^3\Sigma^+)$, where M, M' = Li, Na and (b) $\text{Li}_n \text{B}_m$, n + m = 3 with respect to $\text{Li}(^2\text{S})$, $B(^2\text{P})$, and $\text{Li}_2(^3\Sigma^+)$, $B_2(^3\Sigma_g^-)$ and $\text{LiB}(^3\Pi)$.



Figure 9. Molecular valence orbitals of the $\text{Li}_n \text{Na}_m$ and $\text{Li}_n B_m$ trimers, where n + m = 3.

Table 6. It should be noted that the ground states of the diatomic LiB and B_2 are triplets, i.e., $X^3\Pi$ and $X^3\Sigma_g^-$, respectively.

The Li_3 , Li_2Na , and $LiNa_2$ trimers are stabilized by the 3-B term, as in the case of the quartet state of the Na_3 trimer.

However, the 2-B terms for the Na_3 trimer is quite small and stabilizing, whereas for the Li_3 , Li_2Na , and $LiNa_2$ trimers the three 2-B terms are destabilizing (cf. Table 7), because the M–M bond distance in the trimers is at the repulsive part (positive

energies) of the potential energy curve of the triplet state of the diatomic molecule. For the quartet state of the Li_3 , Li_2Na , $LiNa_2$ and Na_3 clusters, the 3-B term is the one that stabilizes the cluster as it corresponds to 131%, 130%, 117% and 86 (89)% of the binding energy at the CCSD(CCSD(T))/AVTZ level of theory. The BSSE corrections have negligible effect on the 2-B and 3-B terms, as seen in Table 7.

To further examine the effect of the ns^1 and ns^2p^1 configurations on the value of the 3-B term and generally on the stabilization of the trimers, the $Li(^{2}S, 2s^{1})$ atoms of the quartet state of the Li3 cluster were substituted gradually with $B(^{2}P, 2s^{2}2p^{1})$ atoms, since boron has an unpaired valence electron as the alkali metals and the lowest energy quartet states of the $\text{Li}_n \text{B}_m$ trimers (n + m = 3) were calculated. In the case of the Li₂B, LiB₂, and B₃ trimers, the binding energy is mainly equal to the sum of the 2-B terms, see Table 7 and Figure 8. The 3-B term further stabilizes the Li_2B and LiB_2 trimers, while in the case of the B₃ molecule, the 3-B term destabilizes it. Specifically, the 3-B term of the quartet state of the Li₃ trimer corresponds to the 131% of its binding energy, while the substitution of Li with B results in a significant reduction of the 3-B term amounting to 16% (Li₂B) and 5% (LiB₂) of the binding energy. In contrast, for the B₃ cluster the 3-B term is small and destabilizing as it amounts to -1% of the binding energy. It should be noted that in the cases of the quartet states of the Li₂B, LiB₂ and B₃ trimers, the 2-B in LiB and B₂ are significant because they correspond to the ground states of the corresponding diatomic molecules, which have a triplet spin multiplicity, i.e., X ${}^{3}\Pi$ (LiB) and $X^{3}\Sigma_{g}^{-}(B_{2}).$

The three single occupied MO of the Li_nNa_m and Li_nB_m trimers are shown in Figure 9. The valence MO of the four Li_nNa_m trimers have the same shape suggesting the existence of an *sp* hybridization and the trimer molecules are stabilized by three σ bonds that form a ring, see discussion above and Figure 2. In the case of Li_2B , and LiB_2 trimers, there is an *sp* hybridization for both the Li and B atoms, however, the atoms are in their ground states. On the contrary, for the B₃ trimer the single occupied orbitals are mainly *p* orbitals, see Figure 9.

To summarize, the quartet states of the trimers of the ns¹ atoms are stabilized by the 3-B term, the M–M bond distances are significantly ($\gtrsim 1$ Å) shorter compared to the corresponding *in situ* diatomic molecules and they exhibit a σ aromaticity. This is not the case, i.e., there is no aromaticity for the Li₂B, LiB₂, and B₃ molecules, in which the ns¹ atoms are replaced by the ns²np¹ atoms, and these trimers are species are mainly stabilized by the LiB and B₂ 2-B terms, which correspond to the ground states of the corresponding diatomic molecules. The 3-B term was found to stabilize the Li₂B and LiB₂ trimers, whereas it slightly destabilizes the B₃ trimer.

3.4. Be_nMg_m, n + m = 3. In our previous study¹⁶ of the metal clusters of alkaline earth metals (Be, Mg and Ca) the many-body interactions in alkaline earth metals trimers were analyzed using quasi-atomic molecular orbitals (QUAO). The QUAO analysis revealed that the *sp* hybridization is crucial in obtaining a strong, stabilizing 3-B term for beryllium. This was absent in Mg₃ and Ca₃ at the equilibrium distances due to the large core—core repulsion forces that extend the average bond length compared to beryllium. However, in the case of Ca₃ the presence of *d*-orbitals (in the form of hybridized s-p-d orbitals) facilitate stronger interactions in the Ca clusters.¹⁶ Here we extend this study to the mixed metal trimer clusters and the effect of the gradual replacement of Be atoms with Mg in the magnitude of the MBE terms.

The geometries, dissociation energies and MBE of the ground state of the Be_nMg_m, n + m = 3, trimers calculated at the CCSD/ aug-cc-pVTZ level of theory are given in Tables 8 and 9. As seen

Table 8. M–M Bond Distances (R_1 and R_2 of Figure 1) in Å and Corresponding φ Angles in Degrees for the Be_nMg_m, n + m = 3 Trimers at the CCSD/aug-cc-pVTZ Level of Theory

	Species	Structure	State	R_1 (Å) ^{<i>a</i>}	R_2 (Å)	$\varphi \; (\mathrm{deg.})$
	Be ₃	1a	${}^{1}A_{1}{}^{\prime}$	2.235		60.00
	Be_2Mg	1b	${}^{1}A_{1}$	2.771	2.298	48.99
	BeMg ₂	1b′	${}^{1}A_{1}$	2.906	3.389	71.33
	Mg ₃	1a	${}^{1}A_{1}{}^{\prime}$	3.666		60.00
a	In the mixed	trimers.	atom M' in	Figure 1	corresponds t	o a meta

atom with different identity than M.

earlier, the effect of the BSSE correction on the binding energy and the MBE is negligible, see Table 9. The MBE of the dissociation energy with respect to different possible channels is listed in Table 9 and plotted in Figure 10a–c. It should be noted that the sum of the total n-B terms obtained via different fragmentation pathways is always equal to the total interaction energy between atoms. The only change is the way that the overall interaction energy in partitioned into the various terms. The MBE of the ground state $({}^{1}A_{1})$ of the Be_nMg_m, n + m = 3species is calculated with respect to the Be (^{1}S) , Mg (^{1}S) , Be₂ $(X^1\Sigma_g^+)$, Mg₂ $(X^1\Sigma_g^+)$, and BeMg $(X^1\Sigma^+)$ channels. These trimers are stabilized mainly by the 3-B term, which is significantly reduced as the Be atoms are replaced with the Mg atoms. Specifically, for the Be3, Be2Mg, BeMg3, and Mg3 trimers the 3-B term corresponds to 178%, 222%, 253% and 132% of their binding energies, suggesting that the total 2-B term destabilizes the clusters, whereas the 3-B term stabilizes them.

Regarding the Be₃ trimer, the QUAO analysis¹⁰ had shown that the sp hybridization is crucial at stabilizing the three-body term. Significant hybridization¹⁶ can be regarded in bond formation terms as equivalent to the excitation of Be to the ³P states,⁵⁷ since either via hybridization or via excitation, the occupation of the 2s orbital of the Be in the Be₃ trimer is about 1 e^{-} . The potential energy surfaces of a Be $({}^{1}S)$ atom approaching a $\operatorname{Be}_2(X^1\Sigma_{\sigma}^{+})$ diatomic, calculated at the MRCISD/aug-cc-pVTZ level of theory, show that the occupation of the 2s orbital of the approaching $Be({}^{1}S)$ atom is reduced from 2 at infinity to about 1 e⁻, see Figure 10e,f. The MBE for the case of Be₃ trimer with respect to different channels is plotted in Figure 10c. Different channels or different characterizations of the atomic states result in rendering a different picture regarding the MBE, see also ref.¹⁶ In general, we regard that the MBE should be calculated with respect to either the ground state(s) of the correlated products or the appropriate exited state products with respect to spin or angular momentum multiplicities.

Finally, it should be noted that for heterometallic clusters the differences in the various electronegativities should be considered because this may result in different channels that include metal anions and cations. However, this is not the case here, because the population analysis shows that the atoms, rather than their ions, are present in the clusters.

4. SUMMARY AND CONCLUSIONS

We have examined the nonadditive many-body terms for various mixed metal trimer clusters in order to investigate how the electronic structure of the constituent metals affects both the

Table 9. Dissociation Channels, Energy ΔE , 1-B, Individual 2-B, Total 2-B, and 3-B Terms in kcal/mol for the Ground State of the Be_nMg_m, n + m = 3 Clusters at the CCSD/aug-cc-pVTZ Levels of Theory^{*a*}

Species	Channel	ΔE	1-B	2-B (MM)	2-B (MM') ^b	2-B (total)	3-B
Be ₃	$3 \times \text{Be}(^{1}\text{S})^{c}$	12.56	0.00	3.28	3.28	9.85	-22.42
	$2 \times \text{Be}(^{1}\text{S}) + \text{Be}(^{3}\text{P})^{d}$		63.00	3.28	-33.70	-64.11	-11.46
	$Be(^{1}S) + 2 \times Be(^{3}P)^{d}$		126.01	-96.70	-59.72	-216.14	77.57
	$3 \times \text{Be}(^{3}\text{P})^{e}$		189.01	-96.70	-96.70	-290.11	88.53
	$3 \times \text{Be}(^{3}\text{P})^{f}$		189.01	-122.72	-122.72	-368.17	166.60
Be ₂ Mg	$2 \times Be(^{1}S) + Mg(^{1}S)^{c}$	-6.75	0.00	2.43	2.89	8.21	-14.97
	$2 \times \text{Be}(^{1}\text{S}) + \text{Mg}(^{3}\text{P})^{d}$		59.87	2.43	-21.43	-40.42	-26.20
	$2 \times \text{Be}(^{1}\text{S}) + \text{Mg}(^{3}\text{P})^{d}$		126.01	-95.05	-60.11	-215.27	82.51
	$2 \times \text{Be}(^{3}\text{P}) + \text{Mg}(^{3}\text{P})^{e}$		185.87	-95.05	-84.43	-263.91	71.29
BeMg ₂	$Be(^{1}S) + 2 \times Mg(^{1}S)^{c}$	-3.13	0.00	1.21	1.79	4.79	-7.93
	$Be(^{3}P) + 2 \times Be(^{1}S)^{d}$		63.00	1.21	-21.36	-41.51	-24.63
	$Be({}^{1}S) + 2 \times Mg({}^{3}P)^{d}$		119.73	-74.23	-58.07	-190.37	67.51
	$Be(^{3}P) + 2 \times Mg(^{3}P)^{e}$		182.73	-74.23	-81.22	-236.68	50.81
Mg ₃	$3 \times Mg(^{1}S)^{c}$	-2.17	0.00	0.23	0.23	0.70	-2.87
	$2 \times Mg(^{1}S) + Mg(^{3}P)^{d}$		59.87	0.23	-14.01	-27.79	-34.25
	$Mg(^{1}S) + 2 \times Mg(^{3}P)^{d}$		119.73	-73.88	-59.63	-193.14	71.24
	$3 \times Mg(^{3}P)^{e}$		179.60	-73.88	-73.88	-221.63	39.86
BSSE							
Be ₃	$3 \times Be(^{1}S)$	-12.27	0.00	3.33	3.33	9.99	-22.25
	$2 \times Be(^{1}S) + Be(^{3}P)$		62.98	3.33	-33.72	-64.11	-11.14
	$Be(^{1}S) + 2 \times Be(^{3}P)$		125.96	-96.70	-59.65	-216.01	77.78
	$3 \times Be(^{3}P)$		188.95	-96.70	-96.70	-290.10	88.89
	$3 \times Be(^{3}P)$		188.95	-122.64	-122.64	-367.91	166.69
Be ₂ Mg	$2 \times Be(^{1}S) + Mg(^{1}S)$	-6.53	0.00	2.50	2.91	8.33	-14.86
	$2 \times Be(^{1}S) + Mg(^{3}P)$		59.75	2.52	-21.40	-40.28	-26.00
	$2 \times Be(^{1}S) + Mg(^{3}P)$		125.95	-94.99	-60.06	-215.10	82.62
	$2 \times Be(^{3}P) + Mg(^{3}P)$		185.72	-94.99	-84.39	-263.76	71.51
BeMg ₂	$Be(^{1}S) + 2 \times Mg(^{1}S)$	-2.99	0.00	1.20	1.83	4.87	-7.85
	$Be(^{3}P) + 2 \times Be(^{1}S)$		62.97	1.20	-21.36	-41.52	-24.44
	$Be(^{1}S) + 2 \times Mg(^{3}P)$		119.56	-74.21	-57.95	-190.10	67.56
	$Be(^{3}P) + 2 \times Mg(^{3}P)$		182.53	-74.21	-81.14	-236.49	50.98
Mg ₃	$3 \times Mg(^{1}S)$	-2.09	0.00	0.24	0.24	0.73	-2.82
	$2 \times Mg(^{1}S) + Mg(^{3}P)$		59.79	0.24	-13.95	-27.66	-34.21
	$Mg(^{1}S) + 2 \times Mg(^{3}P)$		119.58	-73.74	-59.54	-192.83	71.17
	$3 \times Mg(^{3}P)$		179.37	-73.74	-73.74	-221.23	39.78

^{*a*}The BSSE Corrected values are also listed. ^{*b*}In the mixed trimers, atom M' in Figure 1 corresponds to a metal atom with different identity than M. ^{*c*}MBE with respect to Be₂ ($X^{1}\Sigma_{g}^{+}$), Mg₂ ($X^{1}\Sigma_{g}^{+}$), and BeMg ($X^{1}\Sigma^{+}$). ^{*d*}MBE with respect to Be₂ ($X^{1}\Sigma_{g}^{+}$), Mg₂ ($X^{1}\Sigma_{g}^{+}$), BeMg ($X^{1}\Sigma^{+}$), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$). ^{*d*}MBE with respect to Be(^{3}P), Mg(^{3}P), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$). ^{*f*}MBE with respect to Be(^{3}P), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$). ^{*f*}MBE with respect to Be(^{3}P), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$). ^{*f*}MBE with respect to Be(^{3}P), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$). ^{*f*}MBE with respect to Be(^{3}P), Be₂($^{3}\Sigma_{u}^{+}$), Mg₂($^{3}\Sigma_{u}^{+}$), and BeMg ($^{3}\Sigma^{+}$).

nature (negative or stabilizing/positive or destabilizing) as well as the magnitude of the 2- and 3-B terms. Our goal was to examine how constituent metals comprising of the ns^1 , ns^2 and ns^2p^1 configurations in pure homometallic or mixed heterometallic clusters affect the value and nature of the MBE terms. The calculations were performed at various levels of theory, including MP2, CCSD, CCSD(T), CASSCF, and MRCISD. For all systems considered here the effect of BSSE was found to be negligible and this correction can therefore be ignored. We found that the MBE is not uniform, since it does not follow any trends either across the series or even for the different states of the same cluster. Below, we attempt to group the trends by metal identity, size or electronic state to the best possible. In particular, we have investigated the variation of the MBE terms for:

The series of *homometallic* alkali metal clusters with metals of similar electronic structures (ns^1) and progressing n from 2 to 4, viz. from $[He]2s^1 \rightarrow [Ne]3s^1 \rightarrow [Ar]4s^1$ in the Li₃, Na₃, K₃ trimers: for this series the MBE oscillates from negative (stabilizing) 2- and 4-B terms and positive (destabilizing) 3-B term, with the magnitude of the manybody term decreasing across the series. A remarkable correlation between the higher (3- and 4-B) terms and the pairwise additive 2-B term was found at the cluster minima, paving the way for a fast scheme for performing Monte Carlo simulations with an *ab initio* derived 2-B potential if this relationship continues to hold for geometries away from the minimum energy structures.

The series of *heterometallic* alkali metal clusters mixing metals with similar electronic structures (ns^1) but varying n from 2 to 3 in the Li₃, Li₂Na, LiNa₂, Na₃ trimers: when mixing s^1 metals in the cluster, the quartet states are stabilized exclusively by the 3-B term, which amounts to 131%, 130%, 117% and 86% of the binding energy at the CCSD/AVTZ level of theory, suggesting that the 2-B terms destabilize these clusters. Very little change in the percentage contribution of the 3-B terms was observed when including additional correlation, for example the 3-



Figure 10. BSSE corrected MBE of the ground state $({}^{1}A_{1})$ of the $Be_{n}Mg_{m}$, n + m = 3 clusters at the CCSD/aug-cc-pVTZ levels of theory. (a) MBE with respect to Be $({}^{1}S)$, Mg $({}^{1}S)$, Be₂ $(X^{1}\Sigma_{g}^{+})$, Mg₂ $(X^{1}\Sigma_{g}^{+})$, and BeMg $(X^{1}\Sigma^{+})$ channels, (b) MBE with respect to the Be $({}^{3}P)$, Mg $({}^{3}P)$, Be₂ $({}^{3}\Sigma_{u}^{+})$, Mg₂ $(X^{1}\Sigma_{g}^{+})$, and BeMg $(X^{1}\Sigma^{+})$ channels, (b) MBE with respect to the Be $({}^{3}P)$, Mg $({}^{3}P)$, Be₂ $({}^{3}\Sigma_{u}^{+})$, Mg₂ $(X^{1}\Sigma_{g}^{+})$, and BeMg $(X^{1}\Sigma^{+})$ channels, (b) MBE with respect to the Be $({}^{3}P)$, Mg $({}^{3}P)$, Be₂ $({}^{3}\Sigma_{u}^{+})$, Mg₂ $(X^{1}\Sigma_{g}^{+})$, and BeMg $({}^{3}\Sigma^{+})$ channels, (c) MBE of Be₃ with respect to different channels; **1**: M₃ $\rightarrow 3 \times M({}^{1}S)$; **2**: M₃ $\rightarrow 2 \times M({}^{1}S) + M({}^{3}P)$; **3**: ${}^{c}M_{3} \rightarrow M({}^{1}S) + 2 \times M({}^{3}P)$; **4**: M₃ $\rightarrow 3 \times M({}^{3}P)$. (d) PEC of the Be₃ cluster at the MRCISD/aug-cc-pVTZ method. (e) Occupation of the 2s orbital of a Be ({}^{1}S) atom approaching Be₂ $(X^{1}\Sigma_{g}^{+})$. (f) Occupation of the 2s orbital of the Be atoms in Be₂ $(X^{1}\Sigma_{g}^{+})$ when a Be (${}^{1}S$) atom is approaching it.

B term for Na₃ amounts to 89% of the binding energy at the CCSD(T), compared to 86% at the CCSD levels. Larger *homometallic* clusters at their ground and excited electronic states comprising of metals with the $[Ne]3s^1$ electronic structure, viz. Na_n, n = 2-5: In the pure s^1 alkali metal clusters, the ground states of the Na₃ (doublet), Na₄ (singlet) and Na₅ (doublet) are stabilized by the 2-B term, while the 3-B term destabilizes them. In contrast, the high

spin states of the Na₄ (quintet) and Na₅ (sextet) clusters are stabilized by the 3-B and destabilized by the 2-B terms, i.e., the opposite trend is observed. The latter, however, explains why the minimum energy structures for the Na₄ and Na₅ clusters are built up from trimer subunits.

The series of *heterometallic* alkali metal boride clusters mixing metals with dissimilar electronic structures, viz. $[He]2s^1$ with $[He]2s^22p^1$ in the Li₃, Li₂B, LiB₂, B₃ trimers:

the substitution of Li atoms in the quartet state of Li₃ with B results in a significant reduction of the three-body term corresponding to 16% (Li₂B) and 5% (LiB₃) of the binding energy, while for the B₃ cluster the three-body term slightly destabilizes the cluster as it amounts to -1% of the binding energy.

The series of *heterometallic* alkaline earth clusters mixing metals with similar electronic structures (ns^2) but varying n from 2 to 3 in the Be₃, Be₂Mg, BeMg₂, Mg₃ trimers: for the ground states of these clusters, the 3-B term corresponds to 178%, 222%, 253% and 132% of their binding energies, suggesting that the 2-B term destabilizes the clusters, while the binding is provided mainly by the 3-B term.

Replacing metal atoms of ns^1 configurations with atoms of ns^2p^1 configurations results in the weakening of the 3-B term, while the cluster is stabilized via the 2-B terms. Finally, as the atom size is increased the contribution of 3-B term to the binding energy is decreased due to enlarged bond distances. The described approach for metal clusters can be easily extended to the area of coordination chemistry, where the MBE analysis can add physical insight in the metal–ligand interaction energies.

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Notes

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