

Quantum-chemical approach to cohesive properties of metallic beryllium

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Abstract. Calculations based upon the incremental approach, i.e. an expansion of the correlation energy in terms of one-body, two-body, and higher-order contributions from localized orbital groups, have been performed for metallic beryllium. We apply an embedding scheme which has been successfully applied recently to ground-state properties of magnesium and group 12 elements. This scheme forces localization in metallic-like model systems and allows for a gradual delocalization within the incremental approach. Quantum-chemical methods of the coupled-cluster and multi-reference configuration interaction type are used for evaluating individual increments. Results are given for the cohesive energy and lattice constants of beryllium, and it is shown that further development of the approach is needed for this difficult case.

1. Introduction

Ab initio Hartree-Fock (HF) and post-HF electron correlation methods are standard tools in computational chemistry nowadays and various program packages are available for accurate calculations of properties of atoms and molecules. For solids, HF calculations have become possible with the advent of the program package CRYSTAL [1]. However, the problem of an accurate treatment of electron correlation is not fully settled.

When applying quantum-chemical correlation methods to extended systems one can make use of the property that the correlation hole is fairly local. For a solid it is useful, therefore, to switch from the description with delocalized Bloch states to localized Wannier orbitals. This is the starting-point for the so-called local correlation methods [2, 3, 4]. One method of this type, the method of increments [5], combines HF calculations for periodic systems with correlation calculations for finite embedded clusters, and the total correlation energy per unit cell of a solid is written as a cumulant expansion in terms of contributions from localized orbital groups of increasing size. Calculations based upon the method of increments have been performed on a variety of solids [6]. Among them are insulators and semiconductors, rare-gas crystals, and polymers.

In the past few years the method of increments was also extended to metallic systems. Metals require a special treatment because of two distinct features. Since the conduction bands are only partially filled, one cannot construct well localized orbitals. Furthermore, the vanishing gap leads

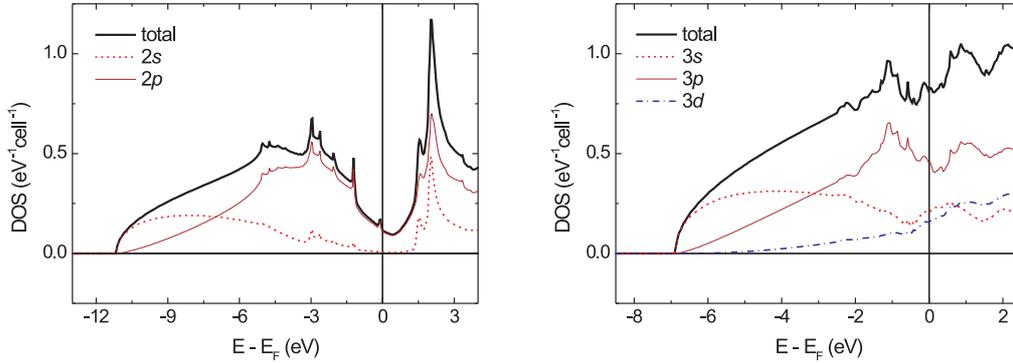


Figure 1. Total and partial density of states of Be (left panel) and Mg (right panel) from DFT calculations, using the FPLO code [7].

to difficulties in the application of single-reference wavefunction-based correlation methods. Via a specially designed embedding scheme, we can force the localization in metallic-like model systems and thus can generate a band structure with gap for finite fragments of the solid [8]. The cumulant expansion is then based on the model systems rather than on the Wannier orbitals of the infinite solid. Up to now we successfully applied the method of increments to magnesium [9] and group 12 elements (zinc, cadmium, and mercury)[10, 11] where in all cases the ground-state properties agree very well with experiment.

The beryllium crystal has the same *hcp* structure as magnesium (they differ in their *c/a* ratio with respect to the ideal one); the free atoms are characterized by closed ns^2 shells. At the same time, Mg is almost free-electron-like whereas beryllium, although in general metallic, shows a lower density of states of almost exclusively *p* character at the Fermi energy (Fig. 1). The reason may be due to the quasi-degeneracy of *s* and *p* orbitals in Be. HF calculations for Be have been described, as one of the first applications of the CRYSTAL program, in a classical paper by Dovesi, Pisani and co-workers [12].

2. Method of increments

Quantum-chemical correlation methods, developed for finite systems, can be applied to periodic systems using the method of increments. In this approach, the total energy is written as $E = E^{\text{HF}} + E^{\text{corr}}$, where E^{HF} is the HF energy of the system, and E^{corr} is the contribution of correlation effects to the total energy per unit cell. The correlation contribution is computed using the aforesaid incremental expansion:

$$E^{\text{corr}} = \sum_A \varepsilon_A + \frac{1}{2!} \sum_{A \neq B} \Delta\varepsilon_{AB} + \frac{1}{3!} \sum_{A \neq B \neq C} \Delta\varepsilon_{ABC} + \dots ,$$

where the summation over *A* involves orbital groups located in the reference cell, while those over *B* and *C* include localized orbital groups from all the centers of the crystal. The ε_A (one-body increment) is computed by considering excitations only from the *A*-orbitals, freezing the rest of the solid at the HF level. The two-body increment is defined as $\Delta\varepsilon_{AB} = \varepsilon_{AB} - [\varepsilon_A + \varepsilon_B]$, where ε_{AB} is the correlation energy of the joint orbital system *AB*. Higher-order increments are defined in an analogous way. Thus, for the three-body term we get: $\Delta\varepsilon_{ABC} = \varepsilon_{ABC} - [\varepsilon_A + \varepsilon_B + \varepsilon_C] - [\Delta\varepsilon_{AB} + \Delta\varepsilon_{BC} + \Delta\varepsilon_{AC}]$. Finally, summing up all increments, with the proper weight factors (according to their occurrence in the solid), one obtains the correlation energy per unit

cell of the infinite system. In order to get reliable results a size-extensive correlation method must be used. Of course, the incremental expansion only makes sense if it is well convergent, i.e., if $\Delta\varepsilon_{AB}$ rapidly decreases with increasing distance between the positions A and B and if the three-body terms are significantly smaller than the two-body ones. This means that only a few increments need to be calculated, yet a full account of the short range correlations is achieved this way.

A direct transfer of this approach to metallic systems is not possible since localized orbitals become very long-range entities. Therefore, a many-body expansion in terms of such orbitals cannot be expected to have useful convergence characteristics. In this case we suggest to start from a system where long-range orbital tails are absent, and to allow for delocalization only successively in the course of the incremental expansion. More specifically, when calculating a pair contribution for a given orbital group combination (A,B), we allow for delocalization $A \rightarrow B$ and $B \rightarrow A$, and similarly with the higher-order terms we allow for delocalization over the triples, quadruples, etc. It is clear, that the final result is not affected, only the convergence properties of the many-body expansion are changed. This way, we can calculate individual terms of the expansion from suitably embedded finite clusters of reasonable size.

The quasi-degenerate bands existing in some metals render questionable a single-reference approach like the coupled-cluster (CC) [13] one which we used in many of our previous applications. We have to check here whether it is necessary to treat the electrons within a multi-reference (MR) approach. In such an approach, the correlation energy is partitioned into a complete active space self-consistent field (CASSCF) part which describes the static correlations and a MR configuration interaction part for the dynamic correlations. In the case of metals we select an active space for the CASSCF calculation including the important bands around the Fermi level, e.g. we use the four $2sp$ orbitals as active orbitals for Be. The dynamic correlations are treated on top of the CASSCF wavefunction with an approximately size-extensive MR correlation method, i.e. an MR averaged coupled pair functional (MR-ACPF) [14].

3. Results and discussion

3.1. Mean-field results

As starting point for the systematic inclusion of electron correlation effects a reliable HF treatment for the periodic system is necessary. To obtain the HF ground-state properties for solid Be we performed calculations with the CRYSTAL06 suite of programs [15]. For application in the CRYSTAL calculations Dunning's cc-pVDZ basis set [16] had to be modified, since very diffuse exponents which are necessary to properly describe the tails of the free-atom wavefunctions cause numerical problems for the solid. We left out the outermost sp exponents, decontracted the sp exponents in the range between 0.1 and 1, and reoptimized two sp exponents as well as one d exponent in this range [17]. This defines a $(9s3p1d)/[4s3p1d]$ basis set.

The following tolerances were employed in the evaluation of the infinite Coulomb and HF exchange series: 10^{-9} for the Coulomb overlap and penetration, 10^{-11} for exchange overlap and the first exchange pseudo-overlap, 10^{-17} for the second exchange pseudo-overlap. The Fock matrix was diagonalized at 133 k-points within the irreducible Brillouin zone of the hcp lattice corresponding to a shrinking factor of 12 in the Monkhorst net. The energy difference with respect to calculations performed with a denser net of k-points (270 k-points corresponding to a shrinking factor of 16) is smaller than 0.002 eV. The convergence thresholds for the total energy were set to $10^{-7} E_h$.

The cohesive energy is defined as $E_{\text{coh}} = E_{\text{total}} - \sum^N E_a$, where E_a is the atomic energy for each atom belonging to the crystal unit cell and N is the number of atoms in the unit cell. The choice of an atomic reference energy is an important point in the evaluation of the cohesive energy. As the basis set is not complete, two different basis sets must be used for isolated atoms and for bulk. Extra functions must be added to the bulk basis set for an accurate description of

the tails of the wavefunction for the isolated atoms. Another possibility is to add 'ghost' basis sets at neighbouring atoms as in the counterpoise (CP) method [18]. HF atomic energies differ only slightly when turning from 18 to 32 ghost atoms used for evaluating the CP-correction ($-14.572114 E_h$ vs. $-14.572369 E_h$). For comparison, E_a^{HF} calculated with the (unmodified) cc-pVDZ basis set is equal to $-14.572338 E_h$. The quantum-chemical *ab initio* program system MOLPRO 2006 [19] was used in the atomic calculations (as well as for the calculations of the next subsection).

With our basis set we get 63% of the experimental binding energy per atom (2.21 eV vs. 3.47 eV [A zero-point energy of 0.15 eV has been added to the experimental cohesive energy [20] to facilitate comparison]). A previously published HF value is 1.87 eV [12]. To compare various representations of exchange and correlation, we also performed DFT investigations with various functionals: LDA (Dirac-Slater exchange, Vosko-Wilk-Nusair correlation [21]) yields 4.20 eV, GGA (Perdew-Wang [22]) gives 3.67 eV, and two hybrid functionals (B3PW [22, 23] and B3LYP [24, 23]) lead to 3.48 eV and 3.04 eV, respectively. The obtained cohesive energies are in very good agreement with values published in Refs. [25, 26].

In addition, we calculated geometrical and mechanical properties with the HF approach. Both lattice constants are slightly too large compared with experiment: $a^{\text{HF}} = 2.32 \text{ \AA}$ vs. $a^{\text{expt}} = 2.2858 \text{ \AA}$ [27] and $c^{\text{HF}} = 3.61 \text{ \AA}$ vs. $c^{\text{expt}} = 3.5843 \text{ \AA}$ [27]. The bulk modulus obtained (117 GPa) agrees well with experiment ($B^{\text{expt}} = 110 \text{ GPa}$ [27]).

3.2. Correlation treatment

The correlation-energy increments are calculated for selected fragments which reflect the geometry of the crystal. These fragments have two components, firstly the atoms A, B, C to be correlated (in the center of the fragment) and secondly the embedding atoms. The embedding scheme has to guarantee that the increments calculated in the finite clusters are in good agreement with the ones in the solid. One of the checks one should perform to confirm this statement is a transferability test: the same increment is calculated in different clusters and the values of the increment should differ only slightly. Usually for embedding atoms we use a minimal valence basis set (for a detailed description see Ref. [8]); for Be, we apply the minimal [2s] part of the cc-pVDZ set [16]. Such an embedding simulates the environment of an atom of the infinite solid, without allowing the electronic charge to diffuse towards the surface of the cluster and enables localization of the orbitals. For the central part, we use the full cc-pVTZ basis set [16]. This allows for a flexible treatment of delocalization of the orbitals over the central region. We can even improve this flexibility by applying better basis sets than minimal ones on the nearest neighbour atoms of the central region. These basis functions are only used for orbital optimization of the central part, they will not affect the occupied embedding orbitals. It was shown in Refs. [8, 9] for Mg that such an additional flexibility has nearly no influence on cohesive properties and is desirable only from a conceptual point of view. However, the importance of *p*-orbitals in the embedding for a correct description of metallic Be is clearly seen when looking at Fig. 2 (left graph). We gradually increase the number of atoms of the first shell, where we either add a [1*p*] contraction from the cc-pVDZ basis set (denoted [*sp*] in the figure) or even supply the full cc-pVTZ basis set. The decrease of the magnitude of the one-body correlation energy ε_A with more and more atoms in the first shell can be explained by the delocalization of the central orbital, which results in less correlation energy. This effect is stronger than the competing effect of the increase of the virtual space, which would increase the correlation contributions. If not indicated otherwise, we use first-shell [2*s*1*p*] embedding in the following.

As a further test, we checked the convergence of the one-body increment and the nearest-neighbor two-body increment with respect to the size of the embedding cluster, applying the [2*s*]- or [2*s*1*p*]-type embedding for the nearest neighbours of the central region. One can see good convergence starting from a cut-off for the embedding of about 1.9 times the nearest-neighbour

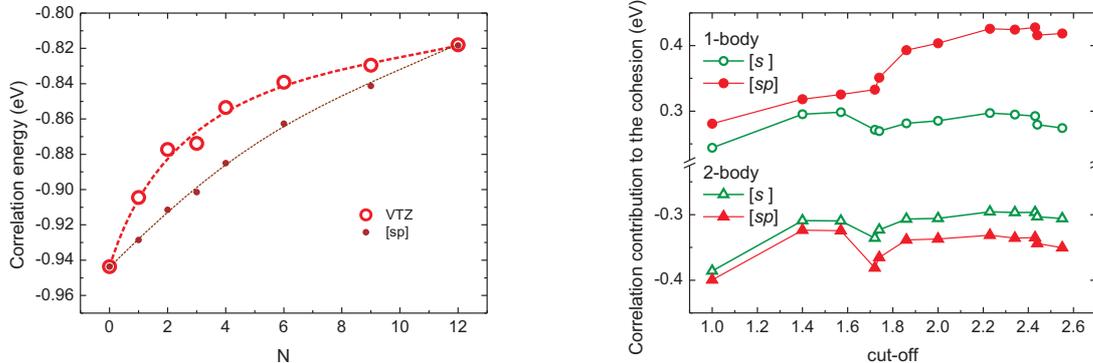


Figure 2. Left panel: Convergence of the one-body increment with respect to the number of neighbors (N) where a cc-pVTZ basis set is used for optimizing the wavefunction of the central region (instead of the minimal-basis set description which is used for generating the frozen embedding). The total number of embedding atoms is 75. For comparison, the data obtained when using a $[2s1p]$ basis set for the nearest neighbours of the central region are also presented (cf. text). Right panel: Convergence of the one-body increment (top) and nearest-neighbour two-body increment (bottom) with the number of embedding atoms (described by cut-off in terms of nearest-neighbour distance). For the first shell around the central region a minimal basis set with $[sp]$ and without $[s]$ p function is used.

distance for $\Delta\varepsilon_A$ (the difference of ε_A and the correlation energy of the free atom) and much faster convergence for the two-body energies in both cases [Fig. 2 (right graph)]. Therefore, to be on the safe side we decided to use a cut-off value of $1.9a_0$ (which corresponds to a 50-atom embedding in the case of the one-body increment) for calculating the cohesive properties of metallic beryllium.

In Tab. 1 we list selected correlation-energy increments for Be obtained with different methods (CCSD(T) [13] and MR-ACPF [14]) and in comparison again between $[2s]$ - or $[2s1p]$ -type embedding for the nearest neighbours of the central region (and a $[2s]$ basis for the rest of the embedding atoms). Concerning the one-body increment ε_A , which is subtracted in all higher order increments, we see changes of up to 11% with $[2s]$ embedding only, whereas with $[2s1p]$ embedding the one-body increment ε_A is well transferable with changes of only about

Table 1. Selected local increments in eV obtained for Be with different methods, cf. text.

Embedding Method	$[s]$		$[sp]$	
	CCSD(T)	MRACPF	CCSD(T)	MRACPF
ε_A	-0.96029	-0.96028	-0.85106	-0.85106
$\Delta\varepsilon_A$	+0.28150	+0.28151	+0.39309	+0.39309
ε_{AB} ($r = a_0$)	-2.09173	-2.10414	-1.95534	-1.96810
ε_A ($\times 2$)	-0.90845	-0.90846	-0.82502	-0.82503
$\Delta\varepsilon_{AB}$	-0.27483	-0.28722	-0.30530	-0.31804
ε_{ABC} ($r = a_0$)	-3.48511	-3.52249	-3.33247	-3.36639
ε_A ($\times 3$)	-0.87982	-0.87983	-0.80898	-0.80898
$\Delta\varepsilon_{AB}$ ($\times 3$)	-0.28948	-0.30216	-0.31125	-0.32399
$\Delta\varepsilon_{ABC}$	+0.02279	+0.02348	+0.02824	+0.03254

Table 2. Local increments (in eV) obtained for Be with the CCSD(T) method. A cut-off of $1.9a_0$ was used for embedding, with an $[2s1p]$ basis on the first-shell embedding atoms, cf. text.

	Correlation energy (eV)	Weight factor	Dist. (Å)		Correlation energy (eV)	Weight factor	Distances (Å)		
ε_A	-0.85106	1		3.1 ^b	+0.02647	6	2.23	2.23	2.29
$\Delta\varepsilon_A$	+0.39309			3.2	+0.02824	2	2.29	2.29	2.29
1-2 ^a	-0.33393	3	2.23	3.3	+0.00671	8	2.23	2.29	3.19
1-3	-0.30531	3	2.29	3.4	-0.02074	3	2.23	2.23	3.58
1-4	-0.08044	3	3.19	3.5	-0.00803	8	2.23	2.29	3.92
1-5	-0.06596	1	3.58	3.6	-0.00297	6	2.29	2.29	3.96
1-6	-0.05200	6	3.92	3.7	-0.00359	6	2.23	2.23	4.25
1-7	-0.04338	3	3.96	3.8	-0.00190	3	2.29	2.29	4.57
1-8	-0.03240	6	4.25	$\Sigma\Delta\varepsilon_{ABC}$	+0.09746				
1-9	-0.02558	3	4.57						
$\Sigma\Delta\varepsilon_{AB}$	-2.93828								

^a see Fig. 3

^b see Fig. 4

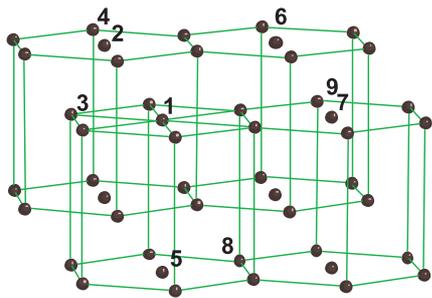


Figure 3. The 2-body increments considered are shown relative to the central atom (number 1). Other atoms are ordered by their distance from the central atom.

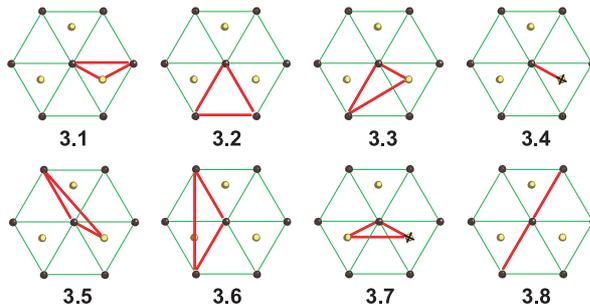


Figure 4. The 3-body increments considered are shown, drawn on the background of a hexagon in the *hcp* plane. Light spheres correspond to atoms below the plane, and crosses to atoms above the plane.

4%. Comparing the single-reference CCSD(T) approach with the MR approach, we see that the CCSD(T) results agree well with the MRACPF results at all orders of the incremental expansion. The correlation part of the CASSCF treatment is small, about 20% of the full value. Therefore we can conclude, that the correlations in beryllium are dominated by dynamical contributions and the CCSD(T) treatment yields reasonable results.

For obtaining the cohesive energy, we need all non-negligible contributions of the one-, two-, and three-body increments to the total correlation energy. These are listed in Tab. 2 and Figs. 3 and 4. For the four-body contributions we selected six different compact geometries, with the aim to prove that these are small enough to merit exclusion. These are shown in Fig. 5. When looking at values for different correlation-energy increments listed in Tab. 2 and in Fig. 5 the good convergence behaviour of the incremental scheme can be observed. The two-body correlation energy is clearly the dominant part. The sum of the compact three-body increments brings only about 4% to the correlation piece of the cohesive energy. Although some individual 4-body terms are comparable to the three-body ones [e.g. **4.6** (Fig. 5)], due to different signs the sum

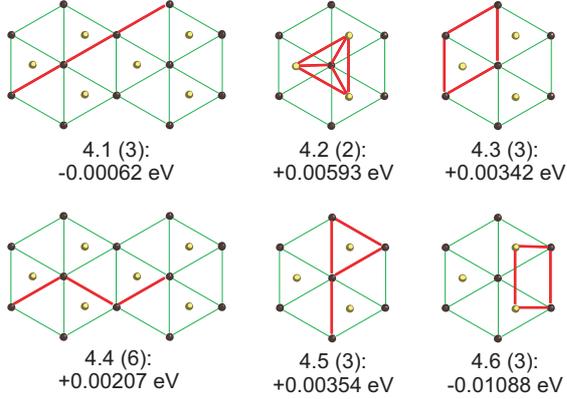


Figure 5. The 4-body increments considered are shown, drawn on the background of a hexagon in the *hcp* plane. Light spheres correspond to atoms below the plane. Numbers in parentheses are the weight factors. Correlation energies of the unweighted increments calculated at the CCSD(T) level for the experimental lattice parameters are shown below each graph.

over the $\Delta\varepsilon_{ABCD}$ amounts to only 11 % of the sum of the 3-body increments. In total, we obtain a correlation contribution to the cohesive energy per atom of 2.45 eV from the weighted sum of increments. Adding this to the HF cohesive energy per atom of 2.21 eV (cf. above), we get a value of 4.66 eV, which is to be compared to the experimental value of 3.47 eV. Apparently, with our approach we overestimate the cohesive energy of metallic beryllium by 34 %. This is in contrast to the case of Mg where we found excellent agreement with experiment. A notable difference to the Mg case is the fact 2-body increments beyond nearest neighbours are very important for Be: their contribution to the cohesive energy per atom is around 1 eV, i.e. more than 50% of the contribution from the 12 nearest neighbours. (For Mg, the corresponding contribution is only 0.3 eV.) This might mean that the coupling of the 2-body increments beyond nearest neighbours and those for nearest neighbours should be more fully taken into account (and not restricted to compact clusters involving at least two nearest-neighbour pairs, as in Fig. 4).

Let us now discuss the influence of correlation contributions on lattice constants, cf. Fig. 6. As was observed in the case of Mg [9], a is mainly affected by $\Delta\varepsilon_{1-3}$ which results in $a^{\text{HF+corr.}} = 2.24 \text{ \AA}$ (deviation of 2 % from experiment). Due to the competition between two effects, coming from the interaction between planes (i.e. from $\Delta\varepsilon_{12}$ and $\Delta\varepsilon_{ABC}^I$) changes in c are insignificant ($c^{\text{HF+corr.}} = 3.63 \text{ \AA}$). The bulk modulus calculated taking into account correlation effects also remains nearly unchanged as compared with the HF value ($B^{\text{HF+corr.}} = 128 \text{ GPa}$ vs. $B^{\text{HF}} = 117 \text{ GPa}$). The value obtained is the outcome of two different effects: On the one hand, as correlations yield a smaller unit cell volume one might expect enlarging of the bulk modulus. On the other hand, the decrease of unit cell volume yields higher correlation energy.

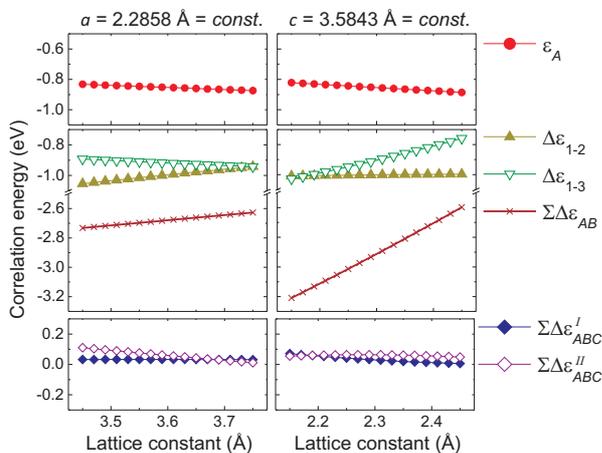


Figure 6. Different type of correlation-energy increments as functions of lattice constants a (right) and c (left): Closed circles are one-body results; triangles correspond to 2-body terms (the open ones are $\Delta\varepsilon_{1-2}$ whereas the closed ones are $\Delta\varepsilon_{1-3}$); open rhombi represent the 3-body data of the group I (includes all 3-body terms, where A , B , and C are in basal plane) and the closed ones correspond to $\Delta\varepsilon_{ABC}^{II}$ (consists of the rest of $\Delta\varepsilon_{ABC}$). The energies are weighted for the total contribution to the lattice of each increment.

4. Conclusion

We applied quantum-chemical correlation methods within an incremental scheme to determine cohesive energy and lattice constants of metallic beryllium. Although Be seems to be a multi-reference case due to the $2s - 2p$ near-degeneracy, the static part only contributes by about 20 % to the correlation energy, and therefore even a single-reference treatment can be reasonable. At the same time, significant admixture of p -orbitals leads to a strong covalent character of the binding in Be. We have tried to model this picture within our embedding scheme, using additional p -functions for the atoms of the outer region, as supplement to the usual minimal [s] basis set. Apparently, with our approach we overestimate the cohesive energy of metallic beryllium by 34 %. Also, the correlation contribution to the lattice constant a comes out too large. The reason for this disagreement is not fully clear currently but may indicate a slower convergence of the incremental expansion than for other group 2 and 12 metals.

Acknowledgments

E.V. acknowledges gratefully financial support by DFG Priority Program 1145 ("Modern and universal first-principles methods for many-electron systems in chemistry and physics").

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