

Correlation energies for small Mg-clusters in comparison to bulk magnesium

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The method of increments combines Hartree-Fock calculations for periodic systems with correlation calculations on the corresponding finite embedded cluster, where the total correlation energy per unit cell of a solid is written in terms of interactions of increasing complexity among the electrons assigned to localized orbitals comprising the solid under consideration. Calculations based upon the method of increments have been performed on a variety of solids with a band gap. In the last few years the method was also extended to metals and was successfully applied for mercury and magnesium. The correlation effects which influence the ground-state properties in this case are quite local. Therefore the question still arises, whether it is really necessary to embed the clusters for the correlation calculation. In order to answer this question, the correlation contributions extracted from free and embedded fragments of the *hcp*-structure of magnesium have been compared.

Keywords: Method of increments, *Ab initio* calculations, Electron correlations, Metals

I. INTRODUCTION

The description of electronic correlation in metallic systems is a difficult task. The most widely used approach in this field is density functional theory (DFT) [1, 2]. Within a DFT-based models one avoids constructing the many-body wavefunction of the system and instead computes directly ground-state properties from its charge density. However, the exact form of the functional embodied in Hohenberg-Kohn theorem is unknown, which yields difficulties in systematic improvements of the method.

The alternative approach to the problem of electron correlations determines the many particle wavefunction by approximately solving the corresponding Schrödinger equation. One can systematically improve this approach by enlarging the basis set and by including more and more terms in the expansion of the wavefunction of the system. This approach (e.g. the coupled cluster method) is used mainly for small molecules. For extended systems in the last decades local correlation methods [3] have been developed for solids [4], where via transformation of the extended Bloch states into localized Wannier states, the expansion of the wavefunction is performed with localized orbitals. One such local correlation method, the method of increments [5], was successfully applied to ground-state properties of a variety of insulators and semiconductors (for a review see Ref. [6]).

In the last few years the method of increments was also extended to metals. Via an embedding scheme, we can guarantee the localization in metallic systems and can mimic the metallic band structure within finite fragments of the solid (details can be found in Ref. [7]). Up to now we have successfully applied the method of increments for mercury [8–10] and magnesium [11], where in both cases the ground-state properties like cohesive energy, lattice

constants and bulk modulus agree very well with the experimental value. Especially for mercury, where the DFT approaches fail, we have reliable results.

The question still arises, whether it is really necessary to embed the clusters for the correlation calculation. The correlation effects which influence the ground-state properties are quite local. Could we not take the correlation part from free fragments of the metals, i.e. the two-body part from dimers, the three-body parts from trimers and so on. Still the long range Hartree-Fock (HF) part of the ground-state properties would be calculated in the periodic system.

In this paper we want to address this question and compare the correlation contributions for free and embedded fragments of the *hcp*-structure of magnesium (Fig. 1). The paper is organized as follows: In the next part (Sec. II) we shortly present the method of increments and the necessary technical details. In the main part (Sec. III) we present our results for the free and embed-

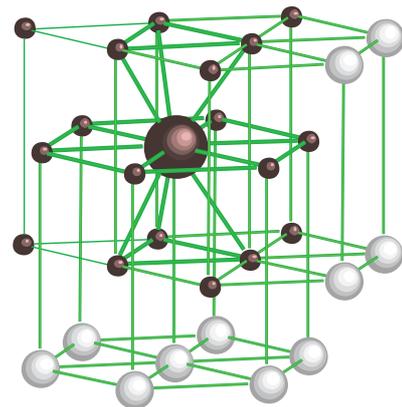


FIG. 1: (Color online) Crystallographic structure of *hcp* Mg. Dark balls show the studied one-body cluster: Large dark ball is the central atom and small dark balls are 18 embedding atoms. Light atoms are shown in order to complete the *hcp* cells of Mg.

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ded clusters and compare the many-body expansion of the incremental scheme in both cases. Conclusion follows in Sec. IV.

II. METHOD OF INCREMENTS

A. Theory

According to the method of increments [5], 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 incremental expansion:

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

where the summation over A involves orbitals located in the reference cell, while those over B and C include 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. So, 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 exact 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, this only makes sense if the incremental expansion 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.

B. Technical details

In this work we have made use of an all-electron description with the Dunning-type basis sets: the correlation consistent valence triple-zeta (cc-pVTZ), valence quadruple zeta (cc-pVQZ), and valence quintuple-zeta (cc-pV5Z) basis sets [12]. The large-core pseudopotential (Mg²⁺-PP) [13] has been used with the corresponding minimal basis set. The localization schemes of Foster and Boys [14] have been used as implemented in the program package MOLPRO [15]. For all correlation calculations we use the coupled cluster procedure with single and double excitations and triples included perturbatively [CCSD(T)] [16, 17].

III. RESULTS AND DISCUSSION

A. Dimer contribution

The two-body contributions in the solid can be labeled due to the distance at which they are occurring in the periodic system. The nearest neighbor distance in the solid magnesium (a_0) is 3.197 Å and therefore $\sim 20\%$ smaller than the equilibrium distance of the free dimer ($r_0 = 3.890$ Å). In Table I we present the correlation contribution of the dimer at the nearest neighbor distance of the solid a_0 and at the equilibrium distance of the free dimer r_0 . Three different approaches are presented: **(I)** In the first one the dimer is surrounded by 26 Mg-atoms in the solid structure, which are described with large-core PP and minimal basis sets and kept frozen during the correlation calculation. This is the approach which was employed for the magnesium and mercury calculations [8–11]. The second approach **(II)** involves removing this embedding, but keeping the second atom of the dimer in its place and freezing its orbitals for the calculation of the one-body increment which is subtracted for the determination of the two-body contribution. This approach shows clearly the influence of the embedding, but is not changing the occupied orbital space in the correlation region. The third approach **(III)** is the usual one used for determining the potential curve of a dimer. For the correlation part of the two-body interaction, the dimer and the free atom are calculated independently. For the basis set superposition error (BSSE) we use the counterpoise (CP) correction [18].

In Fig. 2 we have plotted the dissociation curve of the dimer with the last two approaches for different basis sets. It is well known, that physical contributions to the self-consistent field (SCF) energy can be classified as electrostatic, exchange, induction and some additional interactions not having such clear physical meaning. Mg-atoms, having a closed subshell, have no multipole moments and their electrostatic and induction interactions have a pure overlap origin from which follows their short range character. The exchange interaction between Mg-atoms is repulsive as in noble-gas atom systems. All this

TABLE I: Local increments in eV obtained for Mg with the CCSD(T) method using the three approaches as described in Sec. III A.

	Embed (I)	Free (II)	Free (III)	
	a_0	a_0	a_0	r_0
dimer, $r_{AB} = 3.197$ Å ^a	-0.17252	-0.25394	-0.22464	-0.10503
dimer, $r_{AB} = 3.209$ Å	-0.17367	-0.25108	-0.22183	-0.10503
trimer, $\alpha = 60^\circ$	+0.02879	+0.02526	+0.02403	+0.01078
trimer, $\alpha = 90^\circ$	+0.00151	+0.00667	+0.01448	+0.00016
trimer, $\alpha = 120^\circ$	-0.00346	-0.00737	-0.00101	-0.00230

^aThe one-body increment subtracted from two-body term is -0.78812 eV, -0.903915 eV, -0.91850 eV, and -0.91814 eV, respectively.

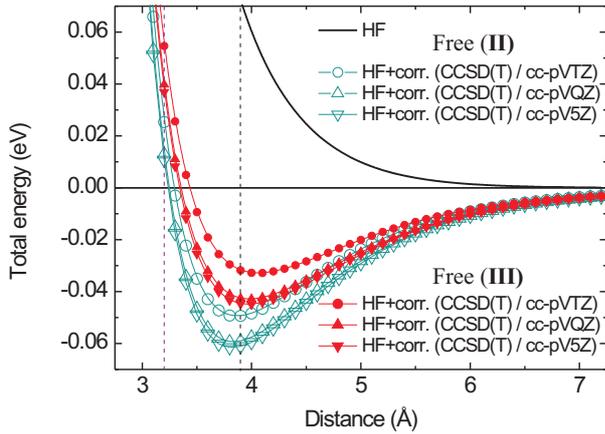


FIG. 2: (Color online) The potential curve of the Mg-dimer is plotted for different basis sets and approaches as described in Sec. III A. The dashed lines correspond to the nearest neighbor distance in the solid Mg ($a_0 = 3.197 \text{ \AA}$) and the equilibrium distance of the free dimer ($r_0 = 3.890 \text{ \AA}$).

leads to the instability of Mg-dimer at the HF SCF approximation: The HF curve is purely repulsive, and the magnesium dimer is stabilized by the electron correlation effects. At large distances ($r \gtrsim 4.5 \text{ \AA}$), the electron correlation energy can be interpreted as a van der Waals interaction ($E \sim r^{-6}$, see Fig. 3). At intermediate distances where the overlap of the atomic valence shells becomes essential, the dispersion forces cannot be defined without allowing for exchange effects. The calculated equilibrium distance is equal to 3.84 \AA (for approach II) or 3.99 \AA (for approach III), that is in good agreement with experimental value (3.89 \AA). The obtained binding energy

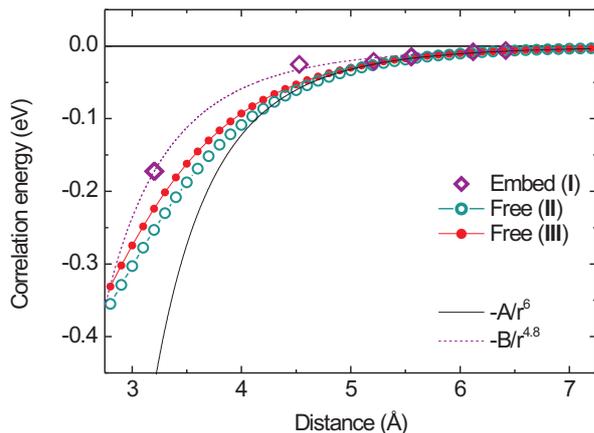


FIG. 3: (Color online) Correlation energy of the Mg-dimer as a function of Mg-Mg distance obtained for the three different approaches as described in Sec. III A

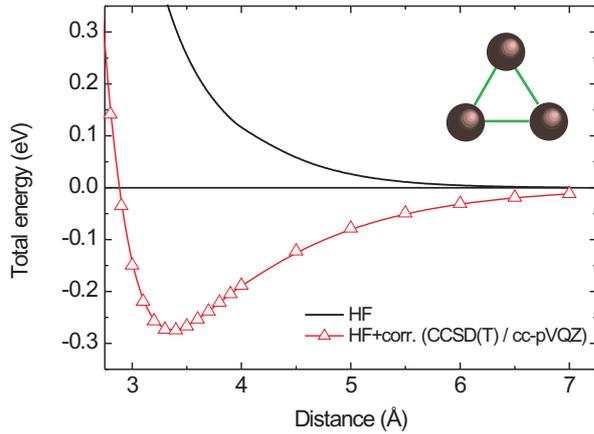
depends on the used basis set and shows the best agreement with experiment in the case of cc-pVTZ when using the II approach (-0.0493 eV vs. -0.0502 eV [19]). At the same time enlargement of the basis set up to cc-pV5Z in this case yields strong overestimation of the binding energy by 20%. That is clear, because the approach II does not describe the proper chemical dissociation process. In the case of approach III using of cc-pV5Z basis set one can get 90% of the binding energy, whereas with cc-pVTZ basis only 66% of the experimental value can be reached.

In Fig. 3, where the correlation energies obtained for the free dimer with cc-pVTZ basis set are plotted, we have added the results for the embedded dimers. One of the requirements of the incremental scheme is a rapid decrease of the two-body correlation-energy terms with increasing distance between the positions A and B: $\Delta\epsilon_{AB} > \Delta\epsilon_{AC}$ if $r_{AB} < r_{AC}$. When considering solid Mg, it might be seemed that the requirement is failed since $\Delta\epsilon_{12} > \Delta\epsilon_{13}$, where $r_{12} = 3.197 \text{ \AA}$ and $r_{12} = 3.209 \text{ \AA} > r_{12}$ (Tab. I). However, as was already mentioned in Ref. [11], this is a consequence of the crystal symmetry and is due to better interaction between $3p$ -orbitals of Mg_1 and Mg_3 as compared with Mg_1 and Mg_2 , that makes the correlation effects stronger in the first case. In general, $\Delta\epsilon_{AB}$ extracted from embedded clusters decrease fast with distance, and can be fitted to $-B/r^{4.8}$ (see Fig. 3). The weaker than r^{-6} decay is due to screening in the metals. As expected, in the free dimer all two-body energies decrease purely monotonically with distance.

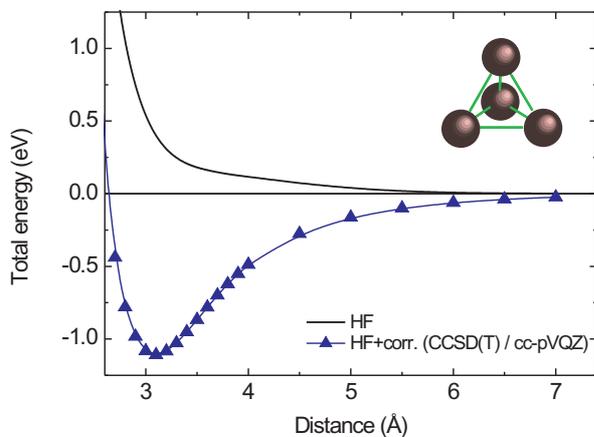
Another interesting point to notice is the difference between the two-body correlation-energy increments obtained from the embedded cluster and the corresponding free one. From Tab. I one can note that in the embedded case the correlation contribution is smaller for the one- and two-body increment. That is due to the fact, that in the embedded case a metal is simulated, the binding can be described better on the HF level as in the free case, where the binding is totally van der Waals-like. Therefore the correlation contribution to binding (two-body increment) is smaller in the embedded approach than in the free one.

B. Higher-body contributions

The calculated dissociation curves for the most stable configurations of the trimer (equilateral triangle) and tetramer (tetrahedron) are presented in Figs. 4 (a) and (b), respectively. The trimers and tetramers as well as dimers are not stable in the SCF approximation: The SCF energy is positive at all calculated distances (Fig. 4, solid lines). On the other hand, the electron correlation corrections are negative and lead to stabilization of Mg_3 (Fig. 4 (a), open-triangle line) and Mg_4 (Fig. 4 (b), close-triangle line). The obtained equilibrium distances ($r_0(\text{Mg}_3) = 3.37 \text{ \AA}$ and $r_0(\text{Mg}_4) = 3.11 \text{ \AA}$)



(a)



(b)

FIG. 4: (Color online) The potential curves of Mg-trimer (a) and Mg-tetramer (b).

and binding energies ($E_b(\text{Mg}_3) = -0.09 \text{ eV/atom}$ and $E_b(\text{Mg}_4) = -0.28 \text{ eV/atom}$) are in good agreement with previously published data [20, 21]. Whereas the equilibrium distance of the dimer is 20% larger than the distance in solid, for Mg_3 the interatomic distance is only 5% larger, and for Mg-tetramer it is even smaller by 3%. Also the binding energy per atom increases drastically from Mg_3 to Mg_4 . That is also seen in a DFT/BP-86 study for Mg clusters up to 22 atoms [21], where the cohesive energy per atom has a bend at $n = 4$, for larger clusters it increases more slowly (Fig. 5). This gives a hint, that for Mg_4 the electronic structure is changed from purely van der Waals-like to binding with metallic contributions.

Using the three approaches described above we have calculated all three-body increments where at least two distances are within the first-neighbor shell (the possible angles are $60^\circ, 90^\circ, 109^\circ, 120^\circ, 146^\circ, 180^\circ$). It is interest-

ing that for all approaches the three-site cluster forming acute triangles yield positive correlation energy, whereas those with obtuse angles correspond to attractive $\Delta\epsilon_{ABC}$. This can be easily explained by the fact, that in obtuse angled triangles there is one pair of atoms at a relatively long distance. The two short range pairs can be well described with the two-body increments, which are subtracted. The two long-distance atoms do not have any overlap, their interaction is purely van der Waals-like and therefore attractive. In the case of acute angles the overlap plays an important role. The individual two-body increments overestimate the correlation part and therefore the three-body increment is slightly repulsive.

There are rather a large number of tetramers where all four distances are within the first-neighbor shell to be found in the hexagonal structure. We have calculated correlation energies for 47 four-body embedded clusters [11]. The general trend is similar with that of the 3-body case: the largest contributions arise for the compact geometries, whereas the longer the distance is between the first and the fourth atom, the smaller is the contribution of the corresponding cluster.

C. Many-body expansion for the solid

Hartree-Fock Result. A starting point for the treatment of the many-body correlation effects in solids is a reliable HF SCF result for the infinite system. Such data for Mg can be found in the literature. The HF cohesive energy of solid Mg is -0.36 eV [22] (another basis set yields -0.27 eV [23]), significantly underestimated with respect to the experimental value -1.50 eV [24], which indicates the importance of taking into account electron correlations.

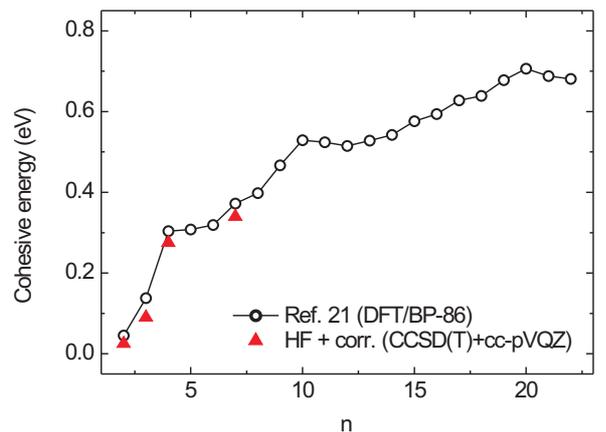


FIG. 5: (Color online) Calculated cohesive energies per one atom. Circles are data obtained for Mg_n ($n=2$ to 22) with DFT [21]. Triangles are the data obtained with the CCSD(T) method.

Correlation contribution. For the embedded cluster the cohesive contribution of the one-body increment is defined as the difference between the correlation energy of the embedded atom (ε_A) and the free atom $E_{\text{free}}^{\text{corr}}$: $\Delta\varepsilon_A = \varepsilon_A - E_{\text{free}}^{\text{corr}}$. The basis set superposition error was corrected applying the counterpoise method: the free atom, described with *cc-pVTZ* was surrounded by two shells of ghost atoms. The one-body contribution is small and repulsive.

In Sec. III A we checked convergence of the incremental expansion with regard to rapid decrease of $\Delta\varepsilon_{AB}$ with increasing Mg-Mg distance. Now we would like to focus on another criterion: Three-body terms should be significantly smaller than the two-body ones, four-site species should give correlation-energy increments smaller than three-body ones, and so on, i.e. $\Delta\varepsilon_{AB} \gg \Delta\varepsilon_{ABC} \gg \Delta\varepsilon_{ABCD}$.

In Fig. 6 the various contribution to the cohesive energy of magnesium are presented. As was shown in Sec. III A, neglecting of embedding leads to increasing of $\sum \Delta\varepsilon_{AB}$ and, as a consequence, the weighted sum of two-body terms in the case of using approach **II** is $\sim 45\%$ higher as compared with $\sum \Delta\varepsilon_{AB}$ extracted from the embedded clusters. The sum of the BSSE-corrected 2-site terms has an intermediate value ($\sim 1/3$ higher than in the case of approach **I**). While the sums of three-body terms obtained for embedded clusters (approach **I**) or free ones with BSSE -correction (approach **III**), are repulsive, simple neglectation of embedding (approach **II**) yields $\sum \Delta\varepsilon_{ABC} < 0$. At the same time the last value is the smallest one in magnitude and consists of less than 1% of the corresponding sum of two-body correlation-energy increments. At this step all three series show rather good convergence ($\Delta\varepsilon_{AB} \gg \Delta\varepsilon_{ABC}$) and can lead to more or less good results. The situation changes

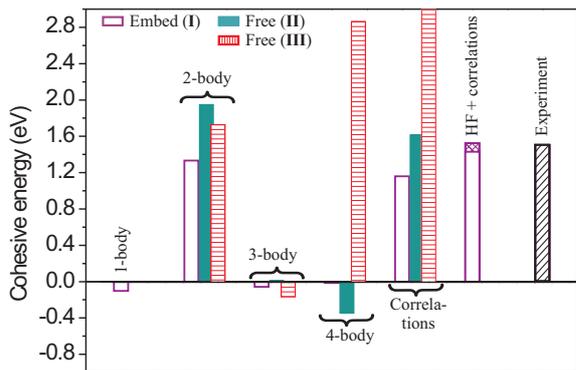


FIG. 6: (Color online) Cohesive energy of the solid magnesium: contribution to the cohesive energy of 1-, 2-, 3-, and 4-body increments as obtained for the three different approaches (see Sec. III A) and calculated cohesive energy as compared with experimental value. The shading of the final result (HF + correlations) indicates the uncertainty in the HF value.

drastically when considering 4-body correlation-energy terms. One can clearly see the good convergence behavior of the incremental scheme when using the embedded clusters: whereas two-body correlation energy increments have large importance, three-body increments are significantly smaller, and the four-body terms give nearly nothing to the total correlation energy, i.e. for approach **I** $\Delta\varepsilon_{AB} \gg \Delta\varepsilon_{ABC} \gg \Delta\varepsilon_{ABCD}$. Neglecting of embedding makes $\sum \Delta\varepsilon_{ABCD}$ 28 times larger than the corresponding sum of three-body increments. BSSE-corrected terms give value which is even 1.5 times higher than corresponding two-body contribution. Of course, such data yield a great overestimation of expected correlation energy (by 30% or 350% for approaches **II** and **III**, respectively). The reason for this problem is the fact, that binding in Mg_4 can no longer be viewed as van der Waals-like (see Sec. III B). Therefore, trying to apply incremental scheme to magnesium, making use of free fragments of *hcp*-solid, we mix species of different natures. This certainly leads to the total crash of our attempt.

Taking into account the total failure of convergence in the case of the free species for further comparison of calculated and experimental cohesive energy we will use only the data obtained for embedded clusters (approach **I**). Summing up all correlation contributions, extracted from the embedded clusters, we obtain -1.17 eV . Therefore, after improving HF-value (-0.36 eV or -0.27 eV) by the obtained correlation-energy increments the calculated cohesive energy is -1.53 eV or -1.44 eV depending on which reference HF energy we used. Both obtained values are very close to the experimental one (-1.50 eV [24]).

IV. CONCLUSION

We have presented our results concerning the application of the method of increments to metallic systems. The method was already successfully applied to such systems as mercury and magnesium, but the question of the necessity of embedding the clusters for the correlated calculations was still open, since the correlation effects influencing the ground-state properties in this case are quite local. In order to answer this question, the correlation contributions extracted from free and embedded fragments of the *hcp*-structure of magnesium were compared. As was shown recently [7], the embedding mimics the metal character of the solid in the central part of the selected fragment of the solid: Due to the embedding the HOMO-LUMO gap in the central part, which is correlated, is very small or even zero as expected in a metal. The other advantage of the embedding is the neutrality of the atoms in the center, as it is in the bulk material. By modifying the nature of binding, embedding influences also the correlation energy, that can be extracted from the corresponding clusters. From the other side, while Mg-dimer and Mg-trimer can be viewed as van der Waals-

like compounds, the interatomic interaction in Mg_4 has also a metallic contribution. Therefore the attempt to get good agreement with experiment for Mg-bulk correlation energy, using the free clusters, fails due to the mixing of species of different nature. At the same time when using the embedded scheme [7] one reaches nearly 100% of the expected value with the method of increments. An analogous study concerning the use of non-embedded species

was performed for mercury [8]. In that case, in contrast to the embedded clusters, the convergence of the incremental scheme also failed, although the result is not so dramatic since the metallic character in solid Hg is less pronounced. Another reason is that approximately half of the cohesion of mercury is due to d -correlation, that has very local character.

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