Embedding procedure for *ab initio* correlation calculations in group II metals

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Abstract

In order to apply *ab initio* wavefunction-based correlation methods to metals, it is desirable to split the calculation into a mean-field part and a correlation part. Whereas the mean-field part (here Hartree-Fock) is performed in the extended periodic system, it is necessary to use for the correlation part local wave-function based correlation methods in finite fragments of the solid. For these finite entities it is necessary to construct an embedding. We suggest an embedding scheme which has itself no metallic character but can mimic the metal in the internal region, where the atoms are correlated. With this embedding it is also possible to localize the metallic orbitals in the central part. The long range non-additive contributions of metallicity and correlation are treated with the method of increments. In this paper we present different ways to construct such an embedding and discuss the influence of the embedding on the correlation energy of the solid.

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I. INTRODUCTION

Ab initio wavefunction-based correlation methods are desirable for extended systems, because they yield a systematically improvable method for the many-body ground-state properties. One of these methods which can be applied to extended systems is the method of increments. It has been applied to a variety of systems, including ionic solids, semiconductors, and noble gas solids, and is now established as a reliable method for the application of wavefunction based correlation methods to extended systems (for a review see Ref. [1]). The method of increments relies on a many-body expansion of the correlation energy of the infinite system in terms of localized orbitals or localized orbital groups.

If we want to use wavefunction-based correlation methods such as coupled-cluster, we have the problem that to date there are no existing program codes which combine such procedures with periodic boundary conditions in three dimensions. Therefore we would like to use standard quantum chemical program packages and perform our correlation calculations in finite fragments of the solid. The Hartree-Fock (HF) part of the calculation which we rely on to treat the long-range interactions properly is always performed in the infinite periodic system.

For the extension of the method of increments to metals two conceptually new problems occur. The localization of the orbitals in a metal is the first issue to be dealt with. Standard procedures used for non-metallic finite systems such as the Foster-Boys criterion [2] or that of Pipek-Mezey [3] are problematic in metals. One reason is the diminishing HOMO-LUMO gap, which causes very long tails in the localized orbitals, but additionally the minimiziation of the localization functionals can yield different solutions due to degeneracy of the orbitals, which are sometimes not consistent with the symmetry of the lattice.

The second issue is the difference between bulk metals and metal clusters. Within an infinite metal there is a homogeneous distribution of the conduction electrons, whereas in a cluster the charge will move to the surface [4]. Keeping this in mind, we have to construct our embedding so that the central part of the cluster where the correlation calculation will be performed remains neutral. The proper embedding models not only the occupied orbital space of a metal, but can also change the excitation space, i.e. it should mimic the vanishing gap in the metal. Recent results for barium [5] have shown that only in the presence of a properly constructed embedding is it possible to obtain a virtual space, which is similar to the band structure of the extended system.

Although in a first application of the method of increments to bulk mercury [6–8] the calculated ground-state properties agree very well with experiment, we will discuss the problem of the construction of the embedding in this paper in more detail, in order to compare the influence of the embedding for different group II metals. We select magnesium, where no closed d-shells are present, and zinc and cadmium which have a closed, but easily polarizable d-shell. All three materials crystallize in the hexagonal close-packed (hcp) structure, whereas mercury, which we include for comparison, crystallizes in a rhombohedral structure.

The paper is organized as follows: in the first part of the next section we shortly introduce the method of increments in its general form and in the second part we discuss in detail the modifications which are necessary for metals. In Sec. III we discuss necessary properties of the embedding, before giving in Sec. IV a first approximation for the cohesive energy of the group II metals. In the main part of the paper, Sec. V, we discuss in detail the influence of the embedding on the calculated correlation energy of the metals. The conclusion follows in Sec. VI.

II. METHOD OF INCREMENTS FOR METALS

A. General formalism

For metallic systems the general formalism for the method of increments [9] is no different than for insulating sytems. The many-body expansion for the correlation energy is set up in the usual way as

$$E_{\rm corr}^{\rm solid} = \sum_{i\in {\rm u.c.}} \epsilon_i + \frac{1}{2} \sum_{\substack{i\neq j \\ i\in {\rm u.c.} \\ j\in {\rm solid}}} \Delta\epsilon_{ij} + \frac{1}{6} \sum_{\substack{i\neq j\neq k \\ i\in {\rm u.c.} \\ j,k\in {\rm solid}}} \Delta\epsilon_{ijk} + \cdots . \tag{1}$$

For a group II metal it is natural to choose a numbering i, j, k in terms of individual atoms. Thus our one-body increment ϵ_i is analogous to the atomic energy. However this atom must be treated in an appropriate environment, and this environment can still influence the correlation energy. Subtracting the correlation energy of the free atom from ϵ_i, we get the one-body correlation contributions to the cohesive energy. The $\Delta\epsilon_{ij}$ are the non-additive parts of the correlation energies ϵ_{ij} for pairs of atoms i, j:

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j); \tag{2}$$

and higher order increments are defined analogously. For the three-body energy increment we get

$$\Delta\epsilon_{ijk} := \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ik}). \tag{3}$$

The usual criteria for the convergence of the incremental scheme has to be fulfilled also for metals, namely that it must firstly converge with respect to the order of increments

$$\sum_{i<j} \Delta\epsilon_{ij} >> \sum_{i<j<k} \Delta\epsilon_{ijk} >> \sum_{i<j<k<l} \Delta\epsilon_{ijkl}, \tag{4}$$

and secondly converge with increasing distance between the atoms involved:

$$\Delta\epsilon_{ij} > \Delta\epsilon_{ik} > \Delta\epsilon_{il}; \quad r_{ij} > r_{ik} > r_{il}. \tag{5}$$

Due to the need to calculate the correlation energy increments in finite embedded clusters, we have an additional requirement that the energy must converge with the size of the embedding. The construction of the embedding and the convergence of the correlation energy with its size are described in detail in the following text.

B. Modification for applying the method of increments to metals

To deal with the two distinct problems that occur in metals, the difficulty of localization of the orbitals and the generation of clusters with neutral atoms in the center, we suggest the following procedure:

1. **Selection of fragments of the solid:**

   The correlation increments are calculated for selected fragments which reflect the geometry of the crystal. These fragments have two components, firstly the atoms to be correlated (in the center of the fragment) and secondly the embedding atoms. We select the positions of the atoms to be correlated and surround each of these atoms by embedding shells of various sizes. This corresponds to a spherical cut-off, which best simulates the Madelung forces in the center.

2. **Calculation of the cluster with a minimal valence basis set:**

   The embedding atoms are required to simulate the environment of an atom of the infinite solid, without allowing the electronic charge to diffuse towards the surface of the cluster. Additionally the basis set should be chosen in such a way to enable localisation of the orbitals. Both requirements can be satisfied, if we supply only *s*-basis functions for the valence electrons. This way, delocalisation due to *sp*-mixing or *spd*-mixing (possible in the case of magnesium) is avoided and no metallic character

can be described. But each atom still has its correct crystal surroundings with respect to the electrostatic interaction. A description of the embedding atoms by large-core pseudopotentials (LCPP) seems reasonable, although we will test this choice with respect to the pseudopotential. The atoms to be correlated must be described with a small-core pseudopotential (SCPP), because of the quasi-valence character of the d shells in the group IIb metals. An advantage of the use of pseudopotentials is that for the heavier elements they also account for scalar-relativistic effects.

3. **Localization of the orbitals:**

   Within the initial description of only valence s-basis functions, we perform a HF calculation of the cluster and due to the neglect of any metallic character we can use standard procedures to localize the orbitals. This set of localized orbitals contains both the embedding orbitals which are centred at the embedding atoms and also the orbitals located at the atoms, which are to be correlated.

4. **Allowing for delocalization in the central part:**

   While the embedding orbitals are kept frozen, we supply on the atoms to be correlated an extended basis set of at least double zeta quality with polarization functions, recalculate the integrals and perform an HF calculation for the orbitals to be correlated. During this HF calculation the central orbitals are reoptimized and can develop a metallic character. But the long-range tails are nearly absent, because the embedding region is kept frozen and no p-functions are supplied. This procedure is quite critical for metals and has to be tested carefully. Sec. V A and V C will deal with this problem in detail.

5. **Correlation calculation of the central part:**

The reoptimized orbital set may be correlated with any size-extensive method. Within this correlation calculation it is possible to freeze part of the semi-core orbitals, (e.g. the *d*- or underlying *sp*-shell in the case of the group IIb metals) to analyze the influence of the valence only correlations.

For the two-body and higher order increments we have an additional subtlety to consider. The calculation of the one-body increment that we subtract should take place in an environment as close as possible to the one used for the two-body energy ϵ_{ij}. Thus this is not exactly the same one-body increment as considered in the incremental expansion, but rather the one-body increment calculated in the two-body cluster. Then we must decide how to treat atom j while we calculate ϵ_i. Two different possibilities can be thought of:

(a) The second (not correlated) atom is described equivalently to the atom to be correlated, but only the orbitals on the atom to be correlated are reoptimized, the orbitals on the atom not being correlated are kept frozen. The additional basis functions on the second atom can be used for reoptimizing the orbitals on the atom to be correlated.

(b) The second (not correlated) atom is described like an embedding atom.

Option (a) keeps the environment exactly the same as for the two-body calculation, but it may break the symmetry of the atom in such a way as to perturb the atomic orbitals. Additionally the one-body increment in the incremental expansion and the one-body increment for calculating the non-additive two-body energy differ conceptually. The second choice (b) corresponds to making the one-body energy as close

as possible to the original one-body term in the incremental expansion, by replacing the original atom with an embedding-type atom. In this case we also test the effect of different pseudopotentials on the second atom. We will test these ideas for the nearest-neighbour two-body increment, to see whether they yield a significant change in the two-body increments for the different materials.

6. **Determination of the correlation energy of the solid:**

   After evaluating the individual increments and checking their convergence with increasing distance of the atoms involved, we have to determine the weight factors with which the individual increments occur in the solid state structure and sum them up for the correlation energy of the solid per unit cell (or per atom) as described in eqn. 1.

C. Technical details

In this work we have made use of both LCPP (2 valence-electron) and SCPP (20 valence-electron) pseudopotentials for Zn, Cd, and Hg, and the LCPP, as well as an all-electron description in the case of Mg [10–14]. The Dunning-type series of corresponding basis sets has been used, in particular the correlation consistent valence triple-zeta (cc-pVTZ) sets for the correlation calculations [15, 16]. The LCPPs have been used with the corresponding basis sets as described in more detail in the text where modifications have been made to the original basis sets [10–14]. The localization schemes of Foster and Boys [2], or of Pipek and Mezey [3], have been used as implemented in the program package MOLPRO [17]. No difference has been found between the two choices in the results presented here. For all correlation calculations we use the coupled cluster procedure with single and double excitations and triples included perturbatively [CCSD(T)] [18, 19].

III. PROPERTIES OF THE EMBEDDING

The embedding is not only required for the localization of the orbitals in a metal, it must also simulate the bulk metal and not a finite metallic cluster. In metallic clusters it is observed that even for cluster sizes up to 1000 atoms the electrons move to the surface of the cluster yielding a negative surface charge [4]. This charge is compensated by a positive charge in the center of the cluster. If we want to simulate the bulk, it is important to guarantee that each atom is neutral as in the solid. This property is achieved by our embedding. For the embedding atoms large-core pseudopotentials and minimal s basis sets are used. (The influence of different basis sets is discussed in Sec. V A.). Therefore the embedding atoms have to be neutral and their neutrality avoids a positive charge in the center. The results for free metallic clusters (for testing we select magnesium) of different sizes in comparison to embedded clusters are listed in Tab. I. In this case a bare cluster of 13 atoms cut from the solid state structure will develop surface charges of around -0.15 per surface atom, leaving a positive charge of 1.6 electrons on the central atom. Increasing the size of the free cluster does not prohibit the charge transfer from one shell to another. But embedding the individual atom or the 13-atom cluster with respectively 12 or 62 atoms described by a minimal s-basis yields nearly neutral atoms in the centre.

The second important characteristic of a metal is the vanishing gap at the Fermi-level, which means in the language of finite systems, that the HOMO-LUMO gap has to approach zero. We have tested this property while calculating the HOMO-LUMO gap of the Mg atom and the Mg dimer, both with and without embedding at the LDA (SVWN functional [20]) level. In free clusters the HOMO-LUMO gap closes slowly with increasing size of the cluster, whereas in the embedded case, the gap is drastically reduced. For the atom, the HOMO-

LUMO gap is reduced from 0.125 Hartree to 0.024 Hartree by the embedding. For the nearest-neighbour Mg-Mg distance taken from the solid, the HOMO-LUMO gap is 0.076 Hartree for the free dimer, but with an embedding the gap is closed completely. Even though the gap can be underestimated by the LDA treatment, the trend is clear: The metallic character can be much better described with the embedding than in free clusters.

IV. CONTRIBUTION TO THE COHESIVE ENERGY

The HF energy of the metal is calculated for the infinite periodic system using existing codes such as CRYSTAL [22]. For details of the CRYSTAL calculations see Ref. [7, 8] for Hg and Ref. [23] for Mg, Zn, and Cd. The HF energy of the free atom is corrected for the basis set superposition error (BSSE) by a counterpoise correction [24]. The atomic energy is calculated with the optimized crystal basis set in the presence of the same basis sets placed at the positions of neighbouring atoms in the solid (convergence required 12 nearest neighbours for Hg and Mg, 18 for Zn and Cd). In the case of magnesium, the HF cohesive energy of the solid is $-0.366\,\mathrm{eV}$ [23] (another basis set yields $-0.27\,\mathrm{eV}$ [25]), significantly underestimated with respect to the experimental value of $-1.51\,\mathrm{eV}$ [26]. Here we use negative numbers to indicate cohesion. In the case of zinc and cadmium the HF energy is slightly repulsive, whereas in mercury it is as strongly repulsive as the experimental cohesive energy is attractive. Although in these cases we start from repulsive cohesive energies, the HF treatment nevertheless provides a reliable starting point for the inclusion of correlation in a systematic way.

Table II shows the relative contributions to the total correlation energy of the one-body and nearest neighbour two-body increments, and compares this to the correlation energy obtained by subtracting the HF energy from the experimental cohesive energy. The one-

body correlation energy is in all cases very small. One can expect to obtain at least 80 % of the correlation energy from the nearest-neighbour (NN) interaction only (if one assumes ideal hcp or fcc structures, where there are 12 nearest neighbours). For Zn, Cd, and Hg, the assumption of 12 nearest-neighbours results in an over-estimation of the correlation energy due to the non-ideal structures (the 6 next-nearest-neighbours are at 10-15 % longer distances than the 6 nearest neighbours). However it is clear that the convergence of the method of increments is quite reasonable when already with only one pair-interaction we obtain around 90 % of the correlation energy. A second reason for the higher proportions obtained for the group IIB metals is the local nature of the *d*-shell, such that the correlation energy converges more quickly with distance than for the *s*-shell. For pair interactions at distances greater than 4 Å the *s*-correlation is the only non-additive contribution. Therefore the total correlation energy does converge more quickly for Zn, Cd, and Hg than for Mg.

As the nearest-neighbour interaction is the most important for the final cohesive energy of the solid, we test our embedding procedure with respect to this energy as well as with respect to the one-body energy which contributes much less to cohesion, but is very important with regard to the convergence of the incremental expansion due to the subtraction of this increment in all higher-body terms.

V. INFLUENCE OF THE EMBEDDING ON THE CORRELATION ENERGY

A. Dependence of the correlation energy with the *s* basis set on the embedding

In order to test the effect of the basis set used for the embedding atoms on the correlation energy of the central atoms, we fix the size of the embedding (cutoff at $1.5a_0$) and the description of the central atom (SCPP and cc-pVTZ basis set). For the localization we have

to omit valence p functions on the embedding atoms, but the choice of the s basis set can still influence the value of the correlation energy. The embedding basis set [12–14] can be minimal or of better quality for the s shells, i.e. we test also a non-minimal [2s] basis set [12–14]. In the case of a minimal basis different constructions are possible, e.g. the contraction coefficients obtained from the free atom or the contraction optimized in the cluster (in which case the contraction coefficients are iteratively optimized at the central atom until they are converged with the embedding.) The results for the cohesive part of the one-body increment (we account for the BSSE due to the embedding atoms with the counterpoise correction, i.e. the free atom is surrounded by the same basis functions as would be supplied in the cluster modelling the solid) and the nearest neighbour two-body increment are listed in Tab. III.

The final result concerning the cohesive energy does not appear to be particularly sensitive to the contraction used for the minimal basis set. Although the cohesive part of the one-body increment may differ by a factor of up to 1.5, this difference corresponds only to 2 % of the correlation contribution to the cohesive energy due to their small magnitude. Moreover it is partially compensated by the opposite trend in the nearest neighbour two-body term. The underlying physical effect can be understood as follows; the cluster optimised contraction is more compact than the contraction optimised for the atom, and thus the embedding atoms are more compact, allowing the central atom to become more diffuse. More diffuse orbitals mean that less correlation energy can be obtained in the one-body part, and this in turn leads to an increase in correlation energy in the two-body increment.

The use of a [2s]-basis on the embedding atoms has the largest effect, increasing the repulsive energy of the one-body increment by roughly 0.2-0.3 mHartree for Zn and Cd, 1.5 mHartree for Mg, and increasing the binding energy of the NN-two-body increment by a slightly smaller amount to compensate. This can be understood due to two separate

changes: in the one-body case the atomic orbitals become more diffuse due to the use of the available s-functions on the embedding atoms. Thus there is less correlation energy recovered. In particular for Mg the difference is seen most strongly in the correlation of the valence shell. However in the two-body case there is stronger overlap between orbitals possible which makes the non-additive part of the correlation energy stronger, such that we obtain a larger correlation contribution. The net effect for Zn, Cd, and Mg is an overall increase in the total correlation energy due to the [2s]-basis on the embedding atoms, due to the higher weight factor of the NN-two-body increment relative to the one-body increment. However this effect is small (ca. 1-3 % of the cohesive energy) and does not change the overall properties of the method of increments. Only in the case of Hg is the effect of the [2s]-basis non-negligible, increasing the repulsive energy of the one-body increment by 3 mHartree, which is an order of magnitude larger than for Zn or Cd. The NN-two-body increment changes only by about 0.4 mHartree, leaving a net repulsive amount if we consider as a first estimate the 12 nearest neighbours which give a weight of 6 to the NN-two-body increment (6×0.4 mHartree $= 2.4$ mHartree) giving a net repulsive amount of 0.7 mHartree. This is however still only 1 % of the cohesive energy, although a correction with the opposite sign to that found for Zn, Cd, and Mg. However we can account for this since most of this repulsion in the 1-body part occurs when the d-orbitals are correlated, indicating that most of the extra contribution comes from the excitations from the d-orbitals into the expanded virtual s-space. Thus we understand why this effect is much more important for Hg since the d-orbitals are particularly diffuse and therefore excitations from the d-orbitals into the expanded virtual s-space are particularly important.

To test the influence of the pseudopotential (for the embedding atoms of Mg, Zn, Cd, and Hg we selected a 2-valence-electron PP) we have also designed an embedding for Mg with an

all-electron minimal basis set. In this case values of +0.0054 Hartree (valence correlation) and +0.0038 Hartree (core-valence correlation) are obtained regardless of whether we use a Huzinaga-mini or a cc-p-vTZ-type minimal basis set for the embedding. The use of a pseudopotential on the embedding (for Mg) has very little effect on the final energy. This is not surprising due to the requirement for minimal basis sets and freezing of the embedding during the correlation calculation.

In summary, a minimal [1s]-basis set in combination with a LCPP is an adequate and computationally efficient description of the embedding atoms, and both the one-body and two-body increments are relatively insensitive to the exact choice of this [1s]-basis set. However for Hg a [2s]-basis yields an improved description of many-body effects already at the one-body level, and therefore slightly quicker convergence of the incremental expansion.

B. Dependence of the correlation energy with size of the embedding cluster

The embedding clusters are designed as approximate spherical surroundings of the central atom or atom group to be correlated. In all group II metals we consider, the first shell consists of 12 atoms, for magnesium all 12 have nearly the same distance from the center, because of the almost ideal hcp structure. For the other materials these two distances differ by up to 15 %. Then a large gap occurs in the shell structure between $1.15a_0$ and about $1.4a_0$. This next group of atoms consists of 6 atoms and we can speak of a second shell. From around $1.6a_0$ the shells have very small changes in distance, so we can not speak anymore of real shells, the influence of these outer atoms should be negligible for the central part.

We tested the convergence of the 1-body increment and the nearest-neighbour 2-body increment with respect to the size of the embedding cluster. Surprisingly, for the valence-only correlations of the group IIb metals the changes with the size of the cluster are small and

monotonic, whereas the inclusion of d-correlations in the group IIb metals leads to a non-monotonic behaviour. For Mg we see a non-monotonic behaviour in the valence correlations, which is reasonable, because the metal character is much more pronounced in magnesium than in the group IIb metals. A summary of this behaviour is shown in Fig. 1. On the one hand, the non-monotonic behavior continues until rather large sizes of the embedding. On the other hand, so long as one chooses a symmetric cluster of sufficient size (with a cutoff for the embedding of about 1.5 times the nearest neighbour distance for example) then there is little deviation from the final converged value. The non-monotonic behaviour is observed only for the metals with a d-shell, and demonstrates the particularly sensitive nature of the d-shells in these metals. This demonstrates that the d-orbitals can not be treated as core or semi-core. We note that this non-monotonicity is largest for Zn, followed by Cd and then Hg, which correlates approximately to the van der Waals radii of the atoms, or bond lengths of the dimers, rather than to the bond distances in the solids. This therefore implies that it depends on the extent of the valence s-orbital, and not the d-orbitals only. If we compare the distance expectation values for the valence s- and d-orbitals in the atoms, we see that the mean radius of the valence s-shell is relatively constant at 2.9, 3.1, and 2.8 Å, for Zn, Cd, and Hg respectively, whereas the mean radius of the d-shell increases rapidly from 0.9 to 1.3 to 1.5 Å. Thus we conclude that the non-monotonic behaviour comes from the d-to-s correlation, not the d-correlation alone. Indeed, if we correlate only the d-orbitals for Zn, keeping the valence s-orbitals frozen, we obtain less than a fifth of the total sd-correlation. Moreover, a monotonic behaviour is observed in the d-only correlation. Thus the observed 'hump' is due to an increased amount of sd-correlation due to the diffuse s-orbital interacting with the embedding, as embedding atoms are added at distances of 1.9-2.3a_0, i.e between 4.9 Å and 6.0 Å for Zn which compares to the distance expectation value $< r(s) >= 2.9$ Å.

This feature of the convergence of the 1-body increment is no barrier to taking an embedding with a smaller cutoff, so long as we use a minimum value of $1.5a_0$ for which we already have good agreement with the final converged value. In any case, for the one-body increment we are dealing with very small numbers such that this non-monotonicity has very little effect on the final value of the cohesive energy. It would be a much bigger problem if this non-monotonicity were observed for the two-body energies also, however here we see much quicker convergence, as shown in the lower part of Fig. 1.

Because the two-body increment is so important with regard to the cohesive energy, we test for Mg the atomic contraction and the cluster-optimised contraction of the $[1s]$-basis with the size of the embedding (Fig. 2). For the first three shells of neighbours there is a small difference between the two approaches, but from the fourth shell on the two different choices are effectively indistinguishable.

C. Different basis sets for reoptimizing the central orbitals

So far we have only tested s-basis sets on the atoms neighbouring the central cluster. But if we want to have in the central part orbitals which are as much metal-like as possible, it would be desirable to supply also a better basis set on the atoms next to the central part for the reoptimization procedure in the central part. The atoms far away from the atoms to be correlated have to be embedding atoms with a mininal basis to guarantee the localization in the central part. The basis functions in the intermediate part can not modify the occupied orbitals in the intermediate part, because these orbitals are kept frozen. They can only provide a basis for the orbital tails in the central part.

In a first step we test the influence of an improved basis set for the reoptimization for the one-body increment. We increas steadily the numbers of atoms of the first shell, where we

supply the full cc-p-vTZ basis set. The size of the embedding is fixed to a cut-off of about $1.5a_0$ and a LCPP with a minimal (cluster optimised) s-basis is used at the embedding atoms. The results are shown in Fig. 3.

By increasing the number of neighbours which have a better basis set for the reoptimization of the central orbitals the magnitude of the one-body increment for all 4 materials decreases monotonically. We have supplied the improved basis sets on up to 6 nearest neighbours for Zn, Cd and Hg and for Mg even up to 9 nearest neighbours. Good convergence is seen over this range to the final value, changes between 6 neighbours and 9 neighbours are small, about 1 mHartree. If a maximum error of 5 mHartree (for Hg) is acceptable then even the reoptimized orbitals without any p functions in the surrounding are usable. To check the influence of the BSSE correction on the behaviour of cohesive part of the one-body increment with better basis functions in the intermediate part, we include in Fig. 3 the one-body contribution to the cohesion for Mg. This shows the same trend as the total correlation increment.

The decrease of the magnitude of the one-body increments 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 correlations. For illustrating the change of the central orbital due to the extra basis functions for the reoptimization, we show the central orbitals for Mg with no additional basis functions on the surrounding atoms (Fig. 4 A), with basis functions on 6 neighbouring atoms (Fig. 4 B) and on 9 atoms (Fig. 4 C). In the plot the extent of the orbitals looks nearly the same, but there is a tiny delocalization of the orbital. The spherical symmetry is only slightly lost. The hybridisation to the neighbouring p-orbitals is not seen on the HF level, it is a correlation effect. Or, in other words, the

admixture of covalent binding in the group IIb metals is small at the HF level.

Overall, we can conclude, that a better basis set for the reoptimization of the central orbital is desirable from a conceptual point of view. For the actual calculations these basis sets yield a maximum change in the cohesive part of the correlation energy of 8 % for Hg and much less for the other metals. On the other hand a related question occurs when we calculate the two-body part of the incremental expansion, of which one-body increment we should subtract. This topic is addressed in the next part.

D. Different ways to define higher order increments

To determine the 2-body increment or higher order increments it is important that the subtracted one- and lower-order body increments are calculated in the same cluster under the same conditions as the total n-body energy. We will test the different approaches as described in Sec. II B 5 on the nearest neighbour two-body increment, because it is the most important one.

To achieve as much equality as possible the two- and one-body increments are calculated in the same embedding, i.e., the number of the embedding atoms and the basis sets on the embedding atoms is unchanged. The question arises of how one should treat the second atom, which is correlated in the two-body increment, when calculating the corresponding one-body increment. We have tested the two possiblities as described in Sec. II B 5 for Mg, Zn, Cd and Hg. To achieve a better insight into the origin of correlations we have even separated the influence of the valence-shell correlation and the valence-core correlation. To illustrate the shape of the orbitals, we plotted for magnesium the reoptimized valence *s*-orbitals on the atom to be correlated (Fig. 5). The picture labelled (a), corresponds to reoptimisation with the full basis set on the second atom. Clearly a distortion of the orbital

in the direction of the second atom is seen. Approach (b) corresponds to the minimal basis on the second atom. No difference is seen if we replace the second atom with a LCPP and minimal basis set.

The results for Mg, Zn, Cd and Hg are summarized in Tab. IV. We first focus on the approach (a), where the orbitals of the one-body increments are not spherical. For all materials the contribution of the core-valence correlation (correlating the underlying *sp* shell) on the two-body increment is small (less than 2 % for Mg, Zn, Cd, and about 4 % for Hg) This is expected because the core shells in the two-body increment and the coresponding one-body increments should be nearly the same. The *d*-shell of Zn, Cd, and Hg can not be considered as core, their correlation contribution to the two-body increment is about 22 % for Zn and increasing to 29 % for Cd and up to 52 % for Hg.

If we now compare the effect of the description of the second atom, in approach (b), where we have for the calculation of the one-body term on the second atom only a minimal basis, we see that this description has some deficiencies for valence only contributions especially in Mg and Hg. Whereas the difference between (a) and (b) is tolerable in Zn and Cd, for Hg higher order terms in the incremental expansion have to correct for the deficiencies on the two-body level with approach (b). For this reason we have calculated one three-body increment (nearest neighbour one, triangle with distances a_0, a_0 and $1.15a_0$) with approaches (a) and (b) (see Tab. IV). In approach (a) the contribution of this special three-body increment is repulsive and 97 % due to the valence *s*-correlations. In approach (b) this is quite different, as shown in Ref. [7], where this increment has a weak cohesive contribution with stronger *d*-contributions. Whereas in this case the valence *s*-correlations are still repulsive, the *d* correlations become attractive and compensate for the missing correlation at the two-body level.

The effect of the pseudopotential has been considered in two ways. First, we consider the effect in approach (b) of using only a LCPP and minimal basis set on the second atom. In effect, this means replacing the second atom with an embedding atom for the calculation of the one-body correlation energy. This leads to slighly less correlation energy than in the SCPP case, but the overall conclusions remain exactly the same with respect to the division of the correlation energy into core-valence and valence-only. For Mg only we have also tested the use of a LCPP with a polarisation basis set ($2s2p2d1f$) which is therefore the LCPP version of (a). This results in behavior that is very similar to (a), and we can conclude that the choice of pseudopotential is much less important than the basis set used on the neighbour.

Overall we can conclude, that approach (a) is more appropriate for an incremental expansion than approach (b); it can describe the corrected excitations in the one-body increment, which are also present in the two-body calculation, yielding the corrected partitioning into valence s-, d-shell and core correlation.

VI. CONCLUSION

We have presented an embedding scheme, which enables us to use finite fragments of the solid for calculating the correlation energy of a metal with quantum-chemical correlation methods. The focus of this paper was the construction and optimization of the embedding for the group II metals, within the constraint that it must mimic the metal character of the solid in the central part of the selected finite 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. We have tested the size and the basis set of the

embedding in detail, and found only small changes between different choices so long as the size of the embedding is at least larger than 1.5 times the nearest neighbour distance. As long as the basis set on the embedding stays minimal, the effect on the correlation energy of the solid of different contractions is very small. Slightly more critical is the basis set used for the reoptimization of the localized orbitals in the central part. To achieve the most metallic orbitals possible it is desirable to have a non-s basis set also on the first shell of embedding atoms. But even the cheapest computational version with no additional functions on the embedding yield in the worst case for Hg only an error less than 8 % of the cohesive energy of the solid. An important role in the performance of the incremental expansion plays the description of the second atom in the calculation of the one-body increment, which is subtracted for the calculation of the two-body increment which has to be subtracted. The best convergence is achieved if this atom is described with the same basis set as in the two-body caclulation, but only the orbitals on one atom are reoptimized. This description yield a small, but conceptual error in the method of increments, because the one-body increment as first term of the expansion is conceptually not the same as the one subtracted in the higher-body terms. A desirable description would be to partition our embedding into two regions, a true embedding region, where the atoms are described with a minimal basis, and an intermediate region, where the occupied orbitals are kept frozen, but basis sets are supplied for the reoptimization of the orbitals in the central cluster. If the same large intermediate region could be used for all increments considered in the expansion, the differences in the two-body increment which depend on the choice of basis set for calculating the corresponding one-body increment would diminish. This would guarantee convergence of the incremental expansion. Work is underway in our laboratory to test this approach.

Overall we have shown that the method of increments is a robust method for the calcu-

lation of correlation energies in metals. Already with only the one-body increment and the nearest-neighbour two-body increment we achieve between 85 and 93 % of the correlation contribution to the cohesive energy.

Acknowledgments

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List of figure captions:

FIG. 1: Convergence of the one-body increment (top), and nearest-neighbour two-body increment (bottom), with the number of embedding atoms (described by a cut-off in terms of the nearest-neighbor distance). (Open circles: only ns^2-valence electrons are included in the correlation space; triangles: correlation space extended by semi-core $(n-1)d$-orbitals; closed circles: $(n-1)s^2p^6$ are also included). For zinc only we have additionally calculated the d-only correlation (stars) to show that the non-monotonic behaviour is due to ds-correlation.

FIG. 2: Comparison of the convergence of the two-body increment with respect to the size of the embedding for Mg: solid circles are the results obtained with a contraction of the $[1s]$-basis optimised for the atom; open circles are the results when the contraction is optimised in a large cluster.

FIG. 3: Convergence of the one-body increment with respect to the number of neighbours (N) where an LCPP-type embedding atom is replaced by an atom described with a SCPP and cc-VTZ basis for Mg (circle), Zn (triangle down), Cd (triangle up), and Hg (square). Rombii represent contribution to the cohesion of Mg one-body increment. The lines are shown for eyeguides of the corresponding series of points.

FIG. 4: The geometries used for selected points in Fig. 3, for magnesium. Central atom in the cluster **A** has no neighbours described by an improved basis set, the one in the **B** has 6 such neighbours (the nearest neighbours). In the cluster **C** the central atom has 9 (6 nearest neighbours in the hexagonal plane and 3 in the underlying plane). The addition of such neighbours leads to small distortions in the localized occupied orbital in the center, but these are quite small once one has more than three such neighbours.

FIG. 5: Mg 3s-orbitals obtained for the one-body increment in two-site cluster, when the two different approaches are used. Large dark balls are Mg described with all-electron full basis, small dark balls are all-electron Mg with minimal basis, white balls are LCPPs together with minimal basis.

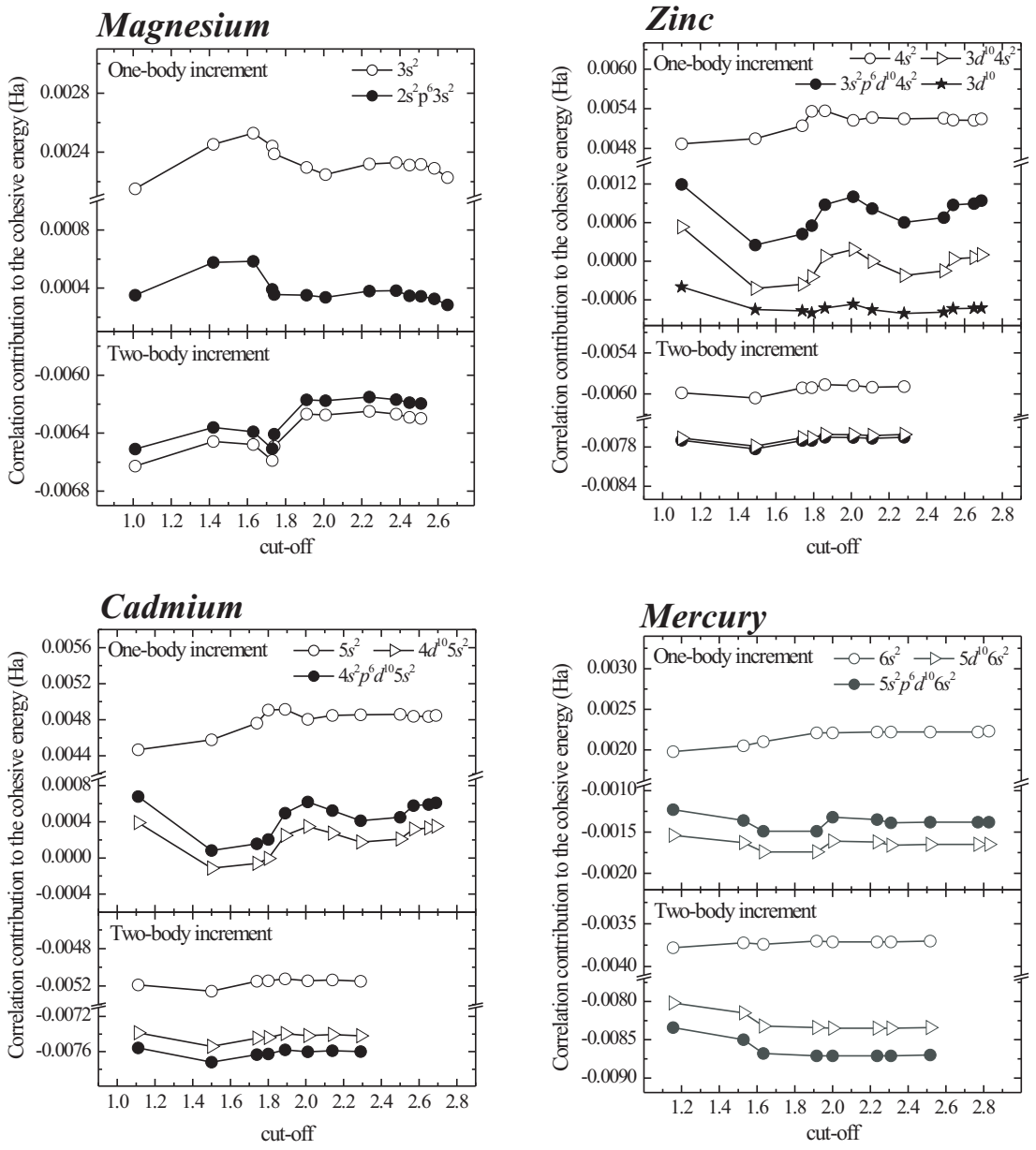
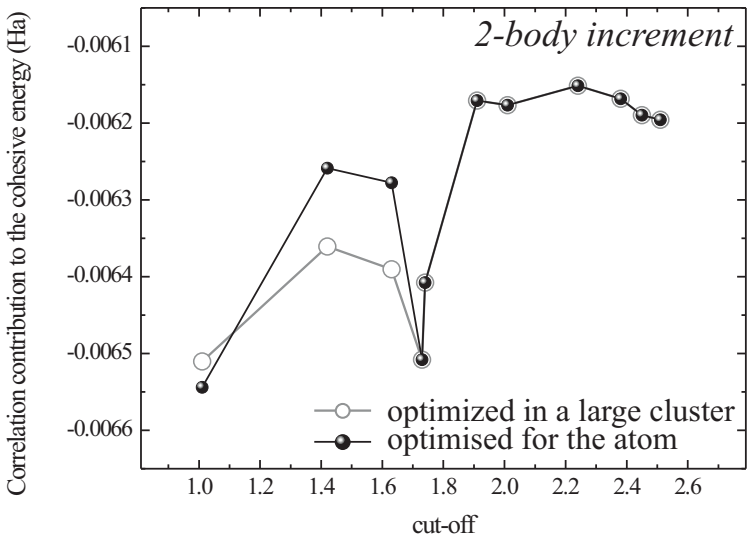


Figure 1, Voloshina *et. al*, Journal of Chemical Physics.



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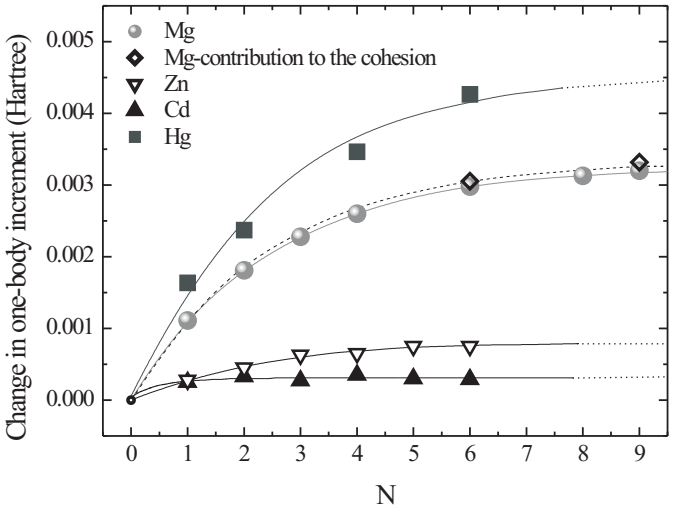

Figure 3, Voloshina *et. al*, Journal of Chemical Physics.

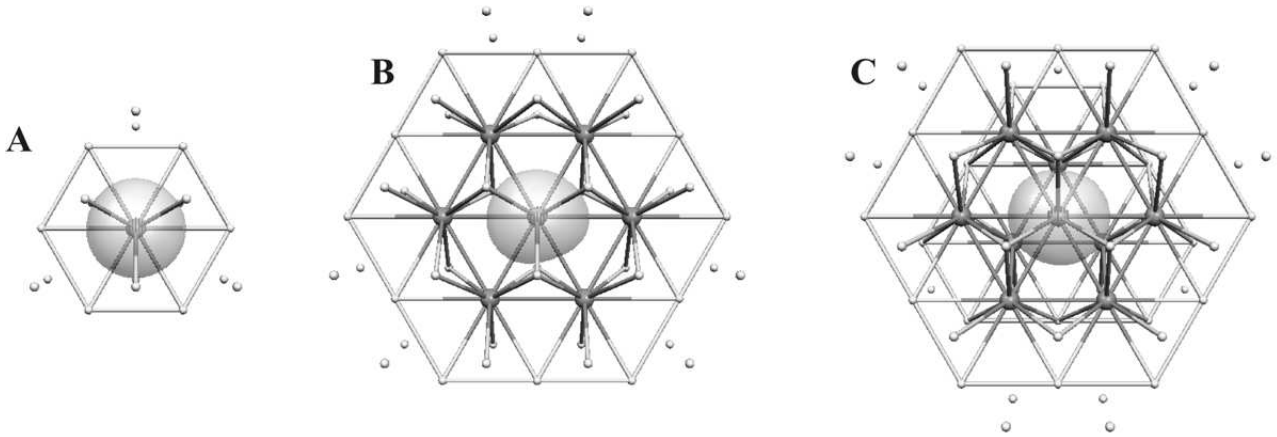

Figure 4, Voloshina *et. al*, Journal of Chemical Physics.

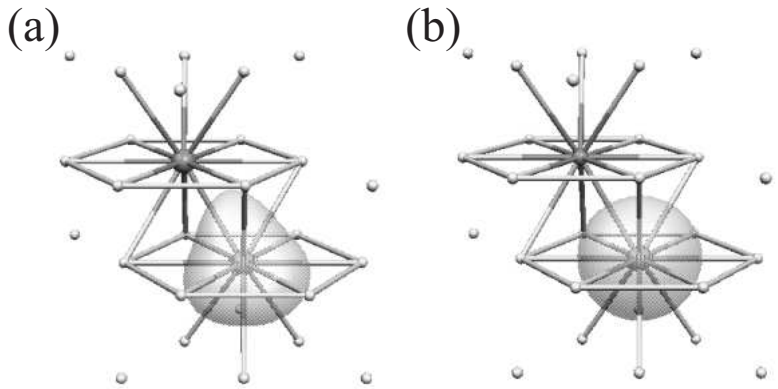

Figure 5, Voloshina *et. al*, Journal of Chemical Physics.

TABLE I: Charge characteristics of symmetric Mg clusters of 13 and 19 atoms compared with an embedded cluster of 13 atoms (embedding cutoff $1.5a_0$) as obtained with a Mulliken population analysis [21]. All atoms are described by a large-core pseudopotential and corresponding basis set [10].

Size of cluster (atoms)	13	19	1	13
Size of embedding (atoms)	—	—	12	62
Charge on central atom	+1.59	+1.82	−0.21	−0.001
Averaged charge on the first shell	−0.15	−0.18	—	+0.026
Charge on embedding			+0.02	−0.008

TABLE II: Correlation contribution to the cohesive energy in Hartree. Results are with correlated $2s^2p^63s^2$ (Mg), $3s^2p^6d^{10}4s^2$ (Zn), $4s^2p^6d^{10}5s^2$ (Cd), $5d^{10}6s^2$ (Hg) electrons, as obtained with cc-pVTZ basis sets, in Hartree. Here the embedding is LCPP+s-basis, minimal s-basis for Mg, Zn, and Cd, [2s]-basis for Hg. We assume for a first estimate of the importance of the nearest neighbour interaction ideal fcc or hcp structures, with 12 nearest neighbours.

	Mg	Zn	Cd	Hg
HF energy	−0.0134	+0.0029	+0.0063	+0.0362
Cohesive energy (expt) [26]	−0.0552	−0.0496	−0.0426	−0.0246
Correlation energy ('expt')	−0.0418	−0.0525	−0.0489	−0.0608
Method of increments				
1-body	+0.0019	+0.0003	+0.0001	+0.0042
2-body (NN)	−0.0063	−0.0077	−0.0076	−0.0098
Total (1 + 6×NN-2-body)	−0.0357	−0.0459	−0.0453	−0.0548
% of 'expt' correlation	85 %	87 %	93 %	90 %

TABLE III: Effect of different s basis set on the embedding atoms on the 1-body correlation contribution to the cohesive energy and on the two-body increment for Mg, Zn, Cd, and Hg, in Hartree. The atomic contraction is the one optimised for the free atom, while the cluster contraction is the one optimised for the central atom in a cluster of 111 atoms. The $[2s]$ basis in Hg is the $(4s)/[2s]$ basis with the most diffuse function left uncontracted. In the one-body cases, 18 embedding atoms are used, and the same cutoff (about $1.5a_0$) is used for the two-body.

basis		min s	min s	$[2s]$
contraction		atomic	cluster	cluster
$\Delta\epsilon_1$	Mg			
$3s$		+0.003743	+0.002453	+0.005069
$2sp3s$		+0.001883	+0.000578	+0.003399
$\Delta\epsilon_{12}$				
$3s$		−0.006342	−0.006458	−0.006695
$2sp3s$		−0.006259	−0.006361	−0.006526
$\Delta\epsilon_1$	Zn			
$4s$		+0.005409	+0.004946	+0.005502
$3d4s$		−0.000461	−0.000422	−0.000127
$3spd4s$		+0.000236	+0.000252	+0.000454
$\Delta\epsilon_{12}$				
$4s$		−0.005861	−0.005985	−0.006153
$3d4s$		−0.007579	−0.007665	−0.007770
$3spd4s$		−0.007616	−0.007698	−0.007795
$\Delta\epsilon_1$	Cd			
$5s$		+0.005195	+0.004578	+0.005316
$4d5s$		+0.000103	−0.000112	+0.000684
$4spd5s$		+0.000274	+0.000084	+0.000576
$\Delta\epsilon_{12}$				
$5s$		−0.005034	−0.005189	−0.005395
$4d5s$		−0.007322	−0.007385	−0.007546
$4spd5s$		−0.007502	−0.007558	−0.007707
$\Delta\epsilon_1$	Hg			
$6s$		+0.002796	+0.002047	+0.003862
$5d6s$		−0.000253	−0.001643	+0.002922
$5spd6s$		+0.000114	−0.001373	+0.003323
$\Delta\epsilon_{12}$				
$6s$		−0.003562	−0.003734	−0.003889
$5d6s$		−0.008019	−0.008125	−0.008398
$5spd6s$		−0.008362	−0.008461	−0.008736

TABLE IV: The nearest-neighbour two-body increment and one selected three-body increment for Hg [in Hartree] obtained with different approaches. (a) corresponds to treating the second atom with the same PP and basis set as for the 2-atom correlation energy, i.e. SCPP and cc-pVTZ basis set (or all-electron basis set for Mg). (b) means using only a minimal basis set on the second atom.

	valence-s^2	+semi-core-d^{10}	+core-s^2p^6
		Magnesium	
(a)	−0.006274		−0.006177
(b)	−0.004029		−0.006502
		Zinc	
(a)	−0.005985	−0.007665	−0.007698
(b)	−0.005259	−0.007339	−0.007505
		Cadmium	
(a)	−0.005189	−0.007385	−0.007558
(b)	−0.004329	−0.006824	−0.007189
		Mercury	
(a)	−0.003719	−0.008155	−0.008495
(b)	−0.002329	−0.005422	−0.005799
		three-body	
(a)	+0.000258	+0.000267	+0.000268
(b)	+0.000083	−0.000092	—