Wavefunction-based *ab initio* method for metals: application of the incremental scheme to magnesium

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We apply *ab initio* quantum-chemical methods to calculate correlation effects on cohesive properties of Mg, thereby extending the method of increments to metallic systems. Metals require special treatment because of two distinct features. Since the conduction bands are only partially filled, we cannot construct well localized orbitals from them. Furthermore we must deal properly with charge screening which obviously is a correlation effect. A starting point for treatment of the many-body correlation effects in solids is a reliable Hartree-Fock self-consistent-field (HF SCF) result for the infinite system. In the case of Mg the HF cohesive energy of the solid is significantly underestimated with respect to the experimental value. Summing up all correlation contributions, we obtain nearly 100 % of the difference between the experimental and HF cohesive energies. Ignoring the correlations, HF model gives rather good agreement with experiment of one lattice parameter (c), but incorrect value for c/a ratio because of too large lattice constant a. Application of the method of increments allows us not only to improve the HF values, giving deviation by about 1 % from experimental values, but also to explain the reason for these changes.

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I. INTRODUCTION

The field of many-body theory has been developing at high speed in recent years. A significant amount of effort is directed toward affordable descriptions of electronic correlation in infinite periodic systems. The most widely used approach here is density-functional theory (DFT) [1, 2]. Within a DFT-based formalism 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 the Hohenberg-Kohn theorem is unknown and, therefore, approximations are required. One of the most important, local-density approximation (LDA), developed by Kohn and Sham [2], works successfully for the ground-state properties of weakly correlated systems. At the same time, for strongly correlated systems it is far from satisfactory. There have been many improvements proposed to the LDA (e.g. taking into account the on-site Coulomb interaction U (LDA+U) [3] or random phase approximation (RPA-LDA) [4]), but their applicability depends on the system involved. Generally, the present DFT-based approaches are not amenable to systematic improvements, although they have seen more and more refinements [5–9].

The alternative approach to the problem of electron correlations tries to obtain the many particle wavefunction of the system by approximately solving the corresponding Schrödinger equation. One can systematically improve this approach by enlarging the basis set and by including more terms in the expansion of the wavefunction of the system. However such wavefunction-based approaches scale quite unfavorably with the size of the system. Therefore in their *ab initio* form they have been applied mainly in the quantum chemistry of small molecules. In condensed-matter physics, wavefunction-based many-body approaches are generally used in conjugation with model Hamiltonians. Usually various approximations have to be made, and the extension of *ab initio* quantum-chemistry-type methods to infinite systems did not seem feasible for a long time. Recently, using the idea of local excitations in the electronic structure theory of solids, Stoll developed the so-called "method of increments" [10]. This method combines Hartree-Fock (HF) 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 [11]. Among them are insulators and semiconductors, rare-gas crystals, polymers, and graphite.

Metals require special treatment because of two distinct features. Since the conduction bands are only partially filled, we cannot construct well localized orbitals from them. Furthermore we must deal properly with charge screening which obviously is a correlation effect. One would expect that the metallic solid should be well described within DFT. Unfortunately, this seems to be not the case. For instance, in the case of solid mercury the method of increments was successfully applied, whereas various DFT-functionals fail. The obtained ground-state properties agree well with the experimental values [12].

Here we present the results for magnesium. It is an

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important alkaline-earth element. Mg has the *hcp* structure with a c/a ratio equal to 1.624, which is very close to the ideal one ($c/a = \sqrt{8/3} \simeq 1.633$). It is a typical metal and characterized by closed a $3s^2$ shell. We select magnesium because there are no occupied *d*-shells present, whose correlation contributes about half to the cohesion of mercury, and the calculation can be expected to demand less computing time. From another side, there is a big contribution of $3p$ partial density of states (DOS) to a total DOS at the Fermi level (Fig. 1), that can lead to strong influence of correlation on $3p$ orbitals. Ground-state properties of Mg have been previously studied by means of HF as well as DFT calculations [13, 14]. The HF model, ignoring correlations, yields a too small value for the cohesive energy ($-0.27\,\text{eV}$ [13] vs. experimental $-1.51\,\text{eV}$). It gives rather good agreement with experiment for one lattice constant ($c = 5.13\,\text{Å}$ vs. measured $5.21\,\text{Å}$), but underestimated value of c/a ratio (1.553) because of a too long value of a. As was shown in Refs. [15–17], where band structures calculated with the LDA-functional for simple metals were compared with measurements made with angle-resolved photoemission spectroscopy, LDA can obviously not account properly for the correlation effects in such systems. This can also be confirmed by LDA-calculated ground-state properties of magnesium: strong underestimation of both lattice constants, that gives by accident rather good agreement with the ideal c/a ratio, but a too high cohesive energy [13, 14]. The choice of functional leads to sometimes good or sometimes bad agreement with experiment, giving in the case of the gradient generalized approximation (GGA: the Perdew-Wang form [18]) excellent coincidence with the measurements for a, c/a, bulk modulus, and cohesive energy [14]. However, it is well known, that a
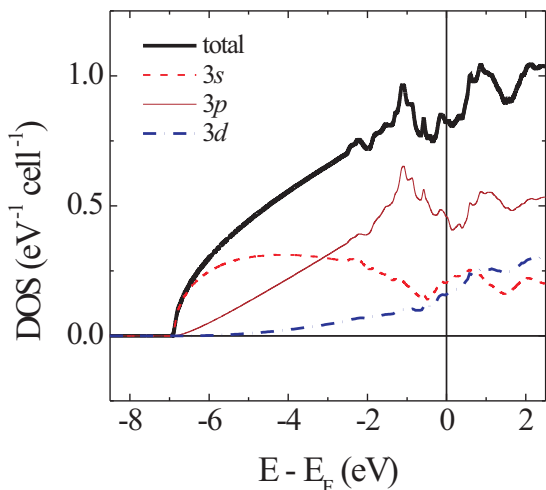

FIG. 1: (Color online) The calculated (FPLO [19]) total and partial density of states of Mg.

systematic improvement towards the exact results is currently not possible with DFT. Wavefunction-based methods are more suitable for this purpose. Application of the method of increments allows us not only to improve the HF values, but also to explain the reason for these changes.

The paper is organized as follows: Next section (Sec. II) is devoted to presentation of the obtained results and their discussion. There the main ideas concerning the application of the method of increments to metals are presented (Sec. II A). The embedding procedure as well as some important features of correlation calculations are outlined in Sec. II B using magnesium as an example. Thermodynamic (Sec. II C) and mechanical (Sec. II D) properties of Mg are discussed in the next two subsections. Conclusion follows in Sec. III.

II. RESULTS AND DISCUSSION

A. Method of increments for metals

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:

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

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 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, the expansion 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.

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 [20] 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 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, tetraples, etc. It is clear, that the final result is not affected, only the convergence properties of the many-body expansion are changed. As an additional advantage, we can calculate individual terms of the expansion from suitable embedded finite clusters of reasonable size (for details see Ref. [21]). In the next section (Sec. II B) we provide the results of a more extensive study of the method for magnesium.

B. Incremental expansion

Within the incremental scheme the energy increments are obtained from finite cluster calculations. Mg-clusters can be built on the basis of the *hcp* structure where the central atom is surrounded by various-size shells of atoms. There the first shell contains 12 atoms, which have nearly the same distance ($3.197\,\text{Å}$ and $3.209\,\text{Å}$) from the central one (ideal structure). The next group of atoms (second shell) is at $4.529\,\text{Å}$ (about $1.4a$) from the center. Further away the shells have very small changes in distance, so we can not speak anymore of real shells. We have tested the convergence of the 1-body increment and the nearest-neighbor 2-body increment with respect to the size of the embedding cluster for group II metals [21]. For magnesium it was found out that the correlation-energy changes with the number of embedding atoms are small and monotonic: all calculated one-body and two-body increments differ by at most $0.2 \div 0.3$ mHartree. Therefore, in order to avoid excessive computational effort, for the embedding we selected a reasonable size of two shells (18 atoms) (Fig. 2).

The generatin of an embedding for metallic systems is a difficult task. Clusters of metal atoms have not the same electronic structure as the three-dimensional bulk metal. In the cluster the delocalized electrons move to the surface of the cluster and the central atoms remain positively charged. In our case the embedding must simulate the bulk metal (where each atom is neutral) and not a finite metallic cluster. In order to achieve neutrality of the central (correlated) atoms, the embedding atoms are described with Mg^{2+}-pseudopotential (PP) [22] and minimal ([1s]) basis set (Basis **E1**), that was shown to be both adequate and computationally efficient [21]. This small basis set prevents the electrons from moving onto the surface of the cluster (see [21]), but still mimics the

Pauli repulsion of the neighbors sufficiently well. Moreover, this type of embedding (without virtual orbitals in the embedding region) enables an easy localization of the central part of the cluster.

Another important characteristic of the bulk metal is the vanishing gap at the Fermi level, that means in the language of finite systems, that the HOMO-LUMO gap has to approach zero. LDA-calculations of HOMO-LUMO gap of the Mg atom as well as Mg dimer, both with and without embedding, show that the metallic character can be much better described with the embedding than in free clusters [21].

Within the initial description of only valence *s*-basis functions also for the central atoms we perform a HF calculation [23] of the cluster and due to the neglect of any metallic character we can use the standard Foster-Boys criterion [24] to localize the orbitals. This set of localized orbitals contains both the embedding orbitals which are centered at the embedding atoms and also the orbitals located at the atoms, which are to be correlated.

In the next step, we improve the description of the atoms to be correlated while keeping frozen the localized orbitals attributed to the atoms of the embedding region. At the same time, the basis set of the atom to be correlated has to be enlarged to a reasonable quality (Basis **C1**: cc-pVTZ basis set [25]). Using this basis set in a HF calculation, we recalculate the integrals and re-optimize the orbitals of the atoms to be correlated. This provides us with orbitals which are still fairly local, but are more or less delocalized (metallic) over the atoms A, B, etc. to be correlated. On top of this HF calculations, we perform a coupled-cluster calculations with single and double excitations and perturbative treatment of the triples [CCSD(T)] [23, 26, 27].
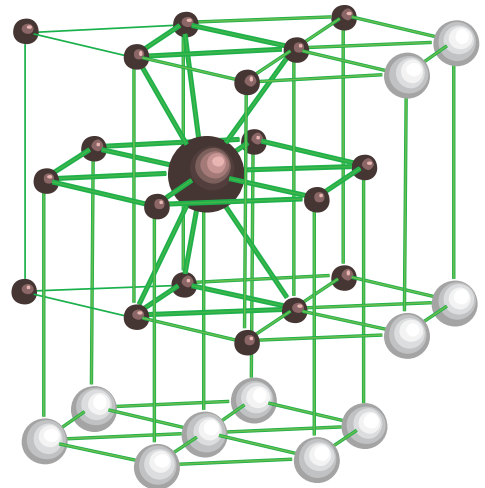

FIG. 2: (Color online) Crystallographic structure of *hcp* Mg. Dark balls show the studied one-body cluster: Large dark ball is the central atom and small dark balls are 18 embedding atoms. Light atoms are shown in order to complete the *hcp* cells of Mg.

The two-body $[(\Delta\varepsilon_{AB} = \varepsilon_{AB} - (\varepsilon_A + \varepsilon_B)]$ and higher order increments are calculated as follows: while calculating ε_A atom B is described equivalently to the atom to be correlated (A), but only the orbitals on the atom A are reoptimized, the orbitals on the atom B are kept frozen. The additional basis functions on the second atom can be used for reoptimizing the orbitals on the atom to be correlated. Thus, the calculation of the one-body increment that we subtract is made in an environment as close as possible to the one used for the two-body energy ε_{AB}.

Contributions of the one-, two-, and three-body increments to the total correlation energy are shown in Tab. I.

As was already mentioned above, there is a rather big contribution of $3p$-PDOS to a total DOS at the Fermi level (Fig. 1), that can lead to strong influence of correlation on the $3p$ orbitals. It can seem, therefore, reasonable to discuss the influence of $[p]$ basis on the embedding for reoptimization of the central orbitals. So, we have performed correlation calculations using Basis **E2** (**E1** where polarization p-exponent was added) at the positions of embedding atoms. The derived changes have only insignificant differences from the **C1**/**E1**-combination.

As might be expected, using a 2-valence-electron PP for correlated Mg yields also nearly no changes in energy (see Tab. I): The cohesive part of the correlation contribution is almost uneffected by the core-valence correlations. Therefore, Mg^{2+}-PP together with a sufficient basis set (Basis **C2**: **E1** augmented by set $[2s2p2d1f]$ of polarization functions) can be applied for the further more time-consuming calculations, such as the optimization of the lattice constants and the calculation of 4-body terms.

To test the influence of the quality of basis set on the correlated atoms on the computed cohesive energy we compared the sums of the relative contributions to the total correlation energy of the 1-body and nearest neighbor as well as second next neighbor 2-body increments obtained with different basis sets. $E_{\mathrm{coh}}^{\mathrm{corr}} = \Delta\varepsilon_1 + \Delta\varepsilon_{12} \times 3 + \Delta\varepsilon_{13} \times 3$ are equal to $-0.034438\,\mathrm{Ha}$ and $-0.036312\,\mathrm{Ha}$ (i. e. differ by about $5\,\%$) for cc-pVTZ and cc-pVQZ [25] basis sets, respectively.

Looking at the results concerning the two-body correlation-energy increments presented in Tab. I, one can be surprised by the fact that sometimes the correlation energy between atoms located at larger distance between each other (e.g. $r_{13} = 3.209\,\text{Å}$), than previous ($r_{12} = 3.197\,\text{Å}$), is higher in magnitude ($\Delta\varepsilon_{13} = -0.006428\,\mathrm{Ha}$), than in previous case ($\Delta\varepsilon_{12} = -0.006381\,\mathrm{Ha}$). It can be easily explained when looking at depicted orbitals involved in the calculation of increments under discussion (Fig. 3). While in the case of $r_{12} = 3.197\,\text{Å}$ [Fig. 3 (a)] electrons finding themselves in the $3p$-levels can avoid each other, the structure of the cluster with $r_{13} = 3.209\,\text{Å}$ [Fig. 3 (b)] provides for better interaction of $3p$-orbitals. This makes correlation effects in the last case stronger. The effect might be seen more clearly if one were to consider Mg with an ideal hcp structure (with $a = 3.2089\,\text{Å}$ and $c = 5.2401\,\text{Å}$, then $r_{12} = r_{13}$). For such a case $\Delta\varepsilon_{AB}$ are $-0.006298\,\mathrm{Ha}$ and $-0.006772\,\mathrm{Ha}$ for structures in Fig. 3 (a) and (b), respectively (i.e. $\Delta\varepsilon_{13}$ is by $7\,\%$ higher in magnitude than $\Delta\varepsilon_{12}$). The same situation can be observed when r_{AB} is equal to $5.551\,\text{Å}$ and $5.558\,\text{Å}$. For all other cases $\Delta\varepsilon_{AB}$ rapidly decreases with increasing interatomic distance.

We have calculated all three-body increments where at least two distances are within the first-neighbor shell. It is interesting that the three-site cluster forming acute triangle yield positive correlation energy, whereas those with obtuse angles correspond to attractive $\Delta\epsilon_{ABC}$. Since the largest contributions arise for the compact geometries, the total sum of three-body terms is repulsive and consists about $4\,\%$ of $\sum\Delta\varepsilon_{AB}$. The largest three-body correlation-energy increment is 7 times smaller than $\Delta\varepsilon_{AB}$ first in the row.

There are rather a large number of tetramers where all four distances are within the first-neighbor shell to be found in hexagonal structure. We have calculated correlation energies for 47 four-body embedded clusters. The
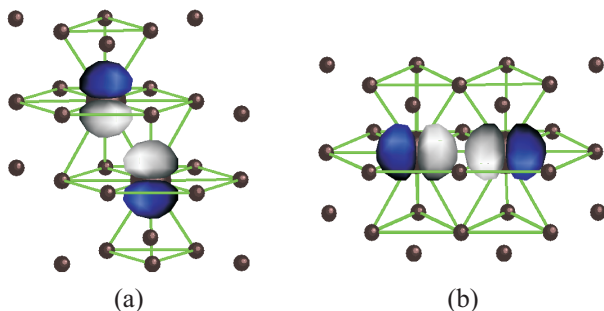

FIG. 3: (Color online) Structures of the two 2-atom clusters with schematic view of p-orbitals at central atoms. (a) Corresponds to the correlation-energy increment for $r_{\mathrm{Mg-Mg}} = 3.197\,\text{Å}$, while the structure (b) was used for the calculation of $\Delta\varepsilon_{\mathrm{Mg-Mg}}$ with $r_{\mathrm{Mg-Mg}} = 3.209\,\text{Å}$.
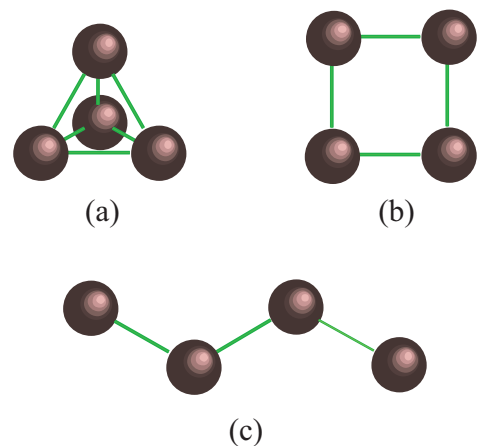

FIG. 4: (Color online) The four-body structures making the largest [(a) and (b)] and the smallest (c) contributions to the cohesion of magnesium. The embedding atoms are not presented.

TABLE I: Local increments in Hartree obtained for Mg with CCSD(T) method.

Basis:	Correlation energy (Ha) C1/E1	C2/E1	Weight factor	Distances Å
One-body increments (ε_A)				
ε_A	−0.030038	−0.029959	1	
$\Delta\varepsilon_A$ [a]	+0.003743	+0.004740		
Two-body increments ($\Delta\varepsilon_{AB}$)				
	−0.006342	−0.006381	3	3.197
	−0.006385	−0.006428	3	3.209
	−0.000929	−0.001089	3	4.529
	−0.000776	−0.000820	1	5.210
	−0.000544	−0.000561	6	5.551
	−0.000543	−0.000571	3	5.558
	−0.000296	−0.000305	6	6.119
	−0.000234	−0.000239	3	6.418
$\sum \Delta\varepsilon_{AB}$	−0.050140	−0.049115		
Three-body increments ($\Delta\varepsilon_{ABC}$)				
	+0.000571	+0.000356	6	3.197 3.197 3.209
	+0.001050	+0.000846	2	3.209 3.209 3.209
	+0.000055	+0.000037	8	3.197 3.209 4.529
	−0.000139	−0.000113	3	3.197 3.197 5.210
	−0.000129	−0.000078	8	3.197 3.209 5.551
	−0.000111	−0.000074	6	3.209 3.209 5.558
	−0.000183	−0.000097	6	3.197 3.197 6.119
	−0.000207	−0.000104	3	3.209 3.209 6.418
$\sum \Delta\varepsilon_{ABC}$	+0.002132	+0.001823		
$E_{\text{total}}^{\text{corr}}$	−0.073278	−0.073536		
$E_{\text{coh}}^{\text{corr}}$	−0.043240	−0.043577		

[a]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 $E_{\text{free}}^{\text{corr}}$: $\Delta\varepsilon_A = \varepsilon_A - E_{\text{free}}^{\text{corr}}$.

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. So, the largest contribution is from the pyramidal [Fig. 4 (a)] and square-like [Fig. 4 (b)] tetramers. They are opposite in sign, but similar in magnitude and consist ~ 0.2 mHa (5 times smaller than the largest $\Delta\varepsilon_{ABC}$). The smallest contribution belongs to the one of the zig-zag clusters [Fig. 4 (c)], which is 45 times smaller than the largest $\Delta\varepsilon_{ABCD}$. The total sum of the four-body terms is attractive and consists 0.564 mHa, that is about 30 % of $\sum \Delta\varepsilon_{ABC}$.

TABLE II: Experimental and calculated lattice constant (a), c/a ratio, bulk modulus (B), and cohesive energy (E_{coh}) of Mg.

	a (Å)	c/a	B (GPa)	E_{coh} (Ha)	
expt. [29]	3.209	1.624	36.90	−0.0552	
HF	3.310[a]	1.550[a]	36.99[a]	−0.0099[a]	−0.0134[b]
HF+corr.	3.205	1.604	35.13	−0.0529	−0.0564

[a]Ref. [13]
[b]Ref. [28]

C. Contribution to the cohesion

A starting point for 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 [13, 28] and are presented in Tab. II. The HF cohesive energy of solid Mg is −0.01345 Ha [28] (another basis set yields −0.00992 Ha [13]), significantly underestimated with respect to the experimental value −0.05549 Ha [29], which indicates the importance of taking into account electron correlations.

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 [30]: the free atom, described with Basis C1 (or C2) was surrounded by two shells of ghost atoms (i.e., E1 was placed at the position of these atoms, but no nuclear charge or electrons were supplied). As can be seen from Tab. I the one-body contribution is small and repulsive.

In Fig. 5 the various contribution to the cohesive energy of magnesium are presented. One can clearly see the good convergence behavior of the incremental scheme: 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.

Summing up all correlation contributions we obtain −0.0430 Ha. Therefore, after improving HF-value (−0.0134 Ha or −0.0099 Ha) by the obtained correlation-energy increments the calculated cohesive energy is −0.0564 Ha or −0.0529 Ha depending on which reference HF energy we used (Tab. II). Both obtained values are

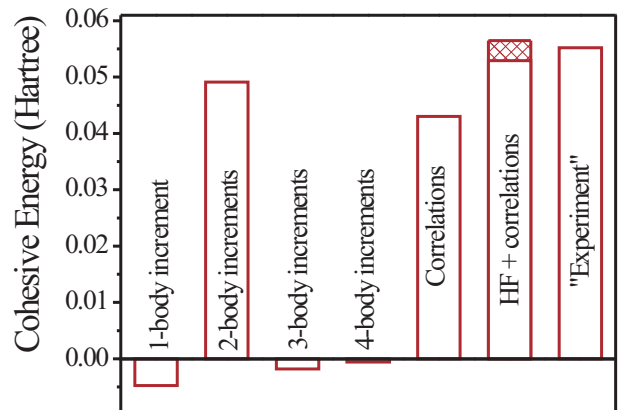
FIG. 5: (Color online) Cohesive energy of Mg: contribution to the cohesive energy of 1-,2-,3-,and 4-body increments and calculated cohesive energy as compared with "experimental" value. The shading of the final result (HF + correlations) indicates the uncertainty in the HF value.

very close to the experimental one ($-0.0552\,\text{Ha}$).

D. Lattice constant and bulk modulus

As was already mentioned in Sec. I the HF lattice constant a is by about $4\,\%$ too large compared with the experimental value. Another lattice constant, c, is in rather good agreement with experiment ($c^{\text{HF}} = 5.13\,\text{Å}$ vs. $c^{\text{expt.}} = 5.21\,\text{Å}$). That leads to the underestimation of c/a ratio by about $5\,\%$. It is interesting, therefore, to study the influence of electron correlation effects on mechanical properties.

Looking at Fig. 6 one can realize that correlations reduce a giving excellent agreement with the experimental value ($a^{\text{expt.}} = 3.209\,\text{Å}$ vs. $a^{\text{HF+corr.}} = 3.205\,\text{Å}$). Another lattice constant, c, remains nearly unchanged after inclusion of correlations ($a^{\text{HF}} = 5.13\,\text{Å}$ vs. $a^{\text{HF+corr.}} = 5.14\,\text{Å}$), but tends towards for a larger value.

From the first view it may seem that this fact has a very simple qualitative explanation: As was already mentioned above, Mg-Mg with $r_{13} = 3.209\,\text{Å}$ in the basal plane provides for a strong correlation between $3p_x$-orbitals. Looking for such a structure allowing good interaction between p_z-orbitals, that will contain the principal axis, leads to Mg-dimer with $r_{14} = 5.210\,\text{Å}$. This is a rather long distance and the related correlation energy is expected to be relatively low. Thus, the equilibrium lattice constant a should be strongly influenced by the correlations, whereas the effect on equilibrium c could be very small (if any). An asset of the incremental scheme is the possibility to get a quantitative confirmation or refutation of this idea, since various contributions to the correlation energy can be analyzed.

The one-body terms of the correlation energy influence the lattice constants only slightly (Fig. 7). Two-body increments make both lattice constants smaller. Among them the largest effects on mechanical properties are due to the nearest- and second-nearest-neighbor increments ($\Delta\varepsilon_{12}$ and $\Delta\varepsilon_{13}$, respectively). $\Delta\varepsilon_{12}$ yield smaller a and c: The less the distance between Mg-atoms, the more difficult for electrons to avoid each other and, therefore, the higher the correlation energy. likewise, c is more affected by this increment than a (Fig. 7) due to the smaller distance between the layers in z-direction containing c. $\Delta\varepsilon_{13}$ has nearly no influence on c, but significantly changes a (Fig. 7), that is determined by the structure [Fig. 3 (b): both atoms are in basal plane]. To study the importance of 3-body terms, they have been divided into two groups: I includes all 3-body terms, where A, B, and C are in basal plane; II consists the rest of $\Delta\varepsilon_{ABC}$. As in the case of 2-body increment with $r_{AB} = 3.209\,\text{Å}$ [Fig. 3 (b)] $\Delta\varepsilon^I_{ABC}$ affects only a, keeping c nearly constant (Fig. 7). Group II has influence of a comparable strength and increases both lattice constants in equal degree (Fig. 7).

Summing up all mentioned above, one can note, that at equilibrium a is mainly effected by $\Delta\varepsilon_{13}$, which addition to E^{HF} makes $a = 3.15\,\text{Å}$. The 3-body terms overcome
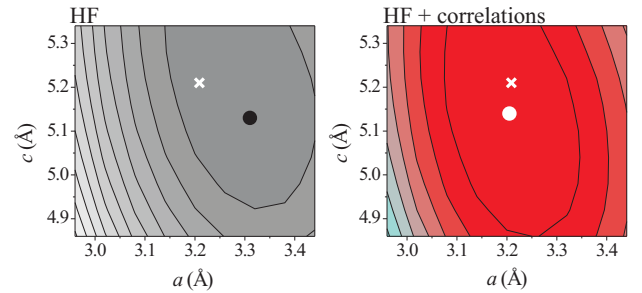

FIG. 6: (Color online) The total energy per unit cell as a function of lattice constants a and c. Isoelectronic lines show every $2\,\text{mHa}$ energy change. White cross shows the experimental a and c. Black circle ($E^{\text{HF}} = -399.234\,\text{Ha}$) corresponds to the HF equilibrium lattice constants, while the white one ($E^{\text{HF}} = -399.312\,\text{Ha}$) is the value obtained accounting correlation effects.

this significant underestimation giving $a = 3.205\,\text{Å}$. The nearly unchanged (as compared with HF-data) c is the result of competition between two effects, coming from the interaction between planes: $\Delta\varepsilon_{12}$ and $\Delta\varepsilon^{II}_{ABC}$ which work in opposite directions. Note, however, that since c is less affected by correlations than a in this case also small contributions from ε_A and $\Delta\varepsilon_{13}$ can not be completely neglected.

The bulk modulus, B, is a material property that relates the change in volume with a change in pressure: $B = -V(\partial P/\partial V)_T$. It can be calculated by distorting
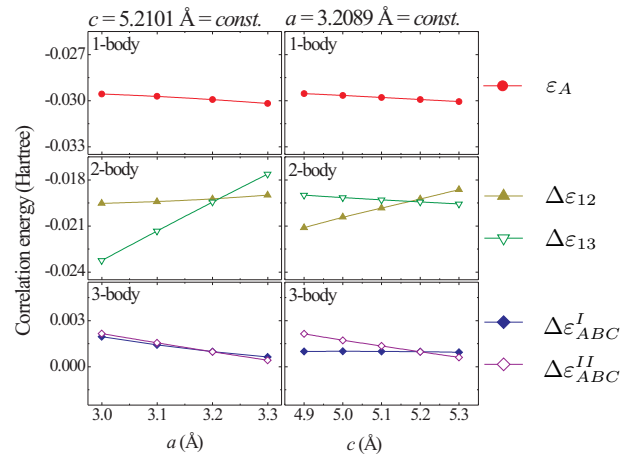

FIG. 7: (Color online) Different type of correlation-energy increments as functions of lattice constants a (left) and c (right): Closed circles are one-body results; triangles correspond to 2-body terms (the closed ones are $\Delta\varepsilon_{12}$ whereas the opened ones are $\Delta\varepsilon_{13}$); closed rombii represent the 3-body data of the group I and the opened ones correspond to $\Delta\varepsilon^{II}_{ABC}$. The energies are weighted for the total contribution to the lattice of each increment. The scale is the same in each subplot.

all of the dimensions of the unit cell and calculating the energy as a function of the change in volume. This procedure uses the fact that the pressure is $P = -(\partial E/\partial V)_T$ and so: $B = V(\partial^2 E/\partial^2 V)_T$, where $V = a^2 \cdot c \cdot sin(\pi/3)$ is the volume of the unit cell. The Mg bulk modulus calculated at the HF level agrees very well with experimental results and differs slightly from the one calculated taking into account correlation effects (see Tab. II). It does not mean that correlations have no influence on this property. The obtained value is the outcome of two different effects: On one hand, as correlations yield smaller unit cell volume one may expect enlarging of bulk modulus. On another hand, the decrease of unit cell volume yields higher correlation energy (then electrons can easier avoid each other).

III. CONCLUSION

We have shown that the incremental scheme using quantum-chemical methods is capable of accurately treating metallic systems with closed shell atoms. We obtained approximately $100\,\%$ of the cohesive energy for magnesium. Our calculated values for the lattice constants slightly (by about $1\,\%$) underestimate the experimental parameters. Although it is possible to select a DFT-functional that will yield good agreement of experimental and calculated properties, it is well known, that the present DFT-based approaches are not amenable to systematic improvements. Application of the method of increments allow us not only to obtain values closed to experimntal data, but also to understand influence of individual correlation-energy increments on the cohesive properties of magnesium.

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