

Ab initio correlation calculations for the ground state properties of the group 12 metals zinc and cadmium

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The unusual hexagonal close-packed (hcp) structures of the group 12 metals zinc and cadmium which have easily polarizable closed d shells, are not described by density functional calculations. We perform a wavefunction-based correlation treatment on top of periodic Hartree-Fock calculations for these materials. This treatment corresponds to a many-body expansion of the correlation energy of the extended system in term of localized orbital groups. This ansatz is the method of increments, which uses an embedding scheme for metals to model the metallic character. Although the Hartree-Fock treatment yields no binding and no equilibrium geometry for zinc and cadmium, the binding of the ground-state structure is fully described by electronic correlations. Our values of the cohesive energy agree within 5% with the experimental value and within 2% for the lattice parameters.

I. INTRODUCTION

In the last decade considerable theoretical work has been done on the calculation of the ground-state properties and the electronic structure of zinc and cadmium [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] However all of these calculations are performed within the framework of density functional theory (DFT) treating the electronic correlations implicitly with various functionals. A recent publication[12] proved that none of the functionals including the recent hybrid functionals give entirely satisfactory results, although certain functionals reproduce a few properties. The lack of systematic improvability within the DFT framework means that a wavefunction based correlation treatment would be desirable, although this is not standard treatment for extended metallic systems.

In previous studies[13, 14, 15, 16] it was shown that an *ab initio* incremental energy decomposition scheme, which corresponds to a many-body expansion of the correlation energy of the solid in terms of local entities, can accurately describe the binding and the ground state structure of mercury[13, 14, 15] and magnesium[16]. The so-called “method of increments” was initially developed by Stoll[17] in order to facilitate the use of standard quantum chemical post-Hartree-Fock correlation methods for solids. A recent review of this approach describes the successful application to such systems as van der Waals (vdW) solids, insulators and metals[18]. A general many-body expansion for the correlation energy may be written in the form

$$E_{corr} = \sum_i \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots \quad , \quad (1)$$

where i, j, k numbers localized orbital groups. To mimic the metallic character for the correlated orbital groups we employ a special embedding scheme[19]. In fact, if we attempted a many-body expansion of the correlation energy without a properly modelled metallic embedding we would have poor convergence of the many-body series[20]. For the incremental expansion of the correlation energy in principle all size-extensive quantum chemical correlation treatments are appropriate. We employ a highly accurate coupled-cluster treatment with single and double excitations and perturbative treatment of triple excitations (CCSD(T)).

As a prerequisite for the application of the method of increments to solids we need a Hartree-Fock treatment of the periodic system. Therefore the paper is organized as follows. First the Hartree-Fock (HF) results are presented, with particular emphasis on the need to be able to vary lattice parameters over a reasonable range in order to study the structure. In section III, the correlation contributions are calculated explicitly within the method of increments, and these are discussed with respect to their position and orientation within the hcp structure in section IIIB. We then

present in section IIIC results for the optimization of the lattice. The conclusions follow in Section IV.

II. MEAN-FIELD RESULTS

We performed periodic mean-field calculations for bulk Zn and Cd using the program package CRYSTAL06[21]. In order to obtain converged results for the HF binding energy, we changed the default parameters, i.e. we set the integral threshold to $\leq 10^{-8}$ a.u. and convergence criteria for the total energy to 10^{-5} a.u.; our k -mesh involved 1200 k -points in a Gilat net. We use the keyword `fixindex` to ensure equivalent cut-off tolerances when changing the lattice parameters. The chemically inactive [Ne] or [Ar]3d¹⁰ cores of the Zn and Cd atoms respectively were simulated by an energy-consistent scalar-relativistic pseudopotential (PP)[22].

The basis sets used are contracted Gaussian type orbital (CGTO) sets obtained from the Dunning-type cc-p-vTZ basis sets optimized for the Stuttgart pseudopotentials[23]. In order to construct a basis set suitable for the periodic metal, we remove exponents below a threshold of 0.1, and optimize the remaining most diffuse exponent. In this work we require convergence of the SCF procedure down to distances at least 5% shorter than the experimental lattice parameters, in order to enable a geometry optimisation. This leads to additional constraints on the most diffuse functions in our basis set. In this way we obtain most diffuse exponents for the s -, p -, and d -parts of the basis set of 0.15, 0.15, and 0.20 for Zn and 0.12, 0.16, and 0.17 for Cd. The use of f -polarisation functions has recently become possible in CRYSTAL06, we take the f -exponent from the cc-p-vDZ basis set with no further optimisation.

The crystal basis set is rather compact and not optimally suited for calculating the energy of the free atom. Especially for metals it has been shown that an improper treatment of the free atom can influence the cohesive energy by as much as 1 eV[18]. We perform a counterpoise (cp) correction[24] by placing basis functions at the positions of the neighboring atoms in the solid. For metals, this correction may require more than a single shell of neighboring atoms in order to be properly converged, which we have tested for the basis sets used for both Zn and Cd. The counterpoise correction is larger at shorter lattice constants, such that it may change the position of the minimum energy structure; therefore we always calculate the optimized geometry with the inclusion of the counterpoise correction. A summary of the effect of the cp correction is given in Tab. I. The counterpoise correction with 18 neighbors is 0.70 eV at the experimental lattice parameters for Zn, and a similar magnitude, 0.95 eV, for Cd. The effect of the next shell (24 neighbors) is relatively small, at less than 0.017 eV for Zn and 0.005 eV for Cd.

Hartree-Fock calculations find a relatively weakly interacting nonbound lattice, with 0.09 eV and 0.25 eV for Zn and Cd respectively, at the experimental lattice parameters with the 24 atom counterpoise correction. In this paper

Cohesive energy [eV]		Zn	Cd
Hartree-Fock	no cp	-0.630	-0.705
	18 cp	0.072	0.250
	24 cp	0.089	0.255
	atom basis from [23]	0.331	0.555
DFT[12]	LDA (S-VWN)	-1.650	-1.520
	GGA (PBE)	-0.970	-0.770
exp.[25]		-1.370	-1.160

TABLE I: Results for the HF energy of Zn and Cd, at the experimental lattice parameters. The counterpoise (cp) corrected cohesive energies are calculated with basis functions at the positions of zero, 18 or 24 neighbors in the solid, for the atomic energy calculation. Alternatively the binding energy was calculated with atomic energies which are determined with different (atomic) basis sets. For comparison two DFT values with different functionals and the experimental value is listed.

we will systematically use negative values for the cohesive energy, to indicate that positive interaction energies are repulsive.

III. EXPLICIT TREATMENT OF ELECTRONIC CORRELATION

A. Method of increments for metals

We apply the method of increments with a CCSD(T)[26, 27] treatment for the correlation energy of the group 2 or 12 metals in the following way. For closed shell atoms 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 :

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

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

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

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;

$$\sum_{i<j} \Delta\epsilon_{ij} \gg \sum_{i<j<k} \Delta\epsilon_{ijk} \gg \sum_{i<j<k<l} \Delta\epsilon_{ijkl}, \quad (4)$$

and secondly converge with increasing distance of the atoms involved:

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

The second convergence criteria can be violated slightly depending on the shape and direction of the localized orbital groups at the centres i, j, k , which can lead to slightly non-monotonic behavior, but an overall convergence with respect to distance should be retained.

Due to the need to calculate the correlation energy increments in finite fragments of the solid, we have to design an embedding which models the metallic character of the periodic system, in the part which is correlated. 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 have suggested an embedding with atoms where only minimal s basis sets are supplied, for group 2 or 12 metals. We have tested this embedding for magnesium, zinc, cadmium and mercury[19] and in all cases it fulfills the requirements of the method of increments. Specifically, in our embedding scheme we add a shell of atoms defined by a spherical cut-off. We test also the convergence of our correlation increments with respect to this cutoff. These embedding atoms are described by 2-valence-electron scalar relativistic pseudopotentials[28] which simulate a large definition of the atomic core, in which even the semi-core d -electrons are included. Thus only the valence s -shell is explicitly treated in the embedding region. In order to be able to separate the embedding region from the atoms to be correlated, we need to be able to localize the metallic orbitals calculated in the embedding region. This localization is done in our approach by a unitary transformation of the occupied canonical orbitals within the Foster-Boys scheme[29] as implemented in Molpro[30]. In order to obtain well localized orbitals, we supply only a minimal (4s)/[1s] basis on the embedding atoms, where the contraction coefficients are reoptimized for the solid within a cluster of 111 atoms by using the freely optimized coefficients of the central atom for the embedding atoms and iterating until convergence is achieved.

The use of a minimal basis on the embedding atoms has the additional advantage of preventing the movement of charge to the surface of the fragment, as would be natural in a metal cluster but absolutely unphysical for a description

of the bulk solid. We have discussed in more detail the construction of this embedding for metallic systems in a recent paper[19].

Within this properly localized environment we must then describe the atoms to be correlated in a way which will allow the inclusion of metallic delocalization in an incremental fashion.

Thus after the localisation procedure, for which we also provide only a minimal basis at the atoms to be correlated, we supply a $(11s10p9d3f2g)/[8s7p6d3f2g]$ basis set based on the augmented correlation consistent valence triple zeta (aug-cc-pvTZ) basis sets of Peterson[23] but with further decontraction of the inner functions. This was done, because the Zn and Cd atoms in the solid are compressed to a distance about 35% smaller than the dimer distance. With this basis set we recalculate the integrals, reoptimize the orbitals of the atoms to be correlated in an SCF step, and then perform the correlation calculation on these orbitals only, though they are still contained within the frozen embedding environment. The correlation calculation is done with a standard coupled cluster calculation with inclusion of single, double, and perturbative triple excitations (CCSD(T))[26, 27], as implemented in the code Molpro[30]. We can do this with different definitions of the core in order to see the different contributions of the valence ns and $(n-1)d$, and core $(n-1)sp$ electrons.

The increments must be calculated in selected fragments of the hcp lattice. The neighbors of an atom in the hcp structure are arranged in shells. In ideal hcp we would have 12 nearest neighbors, however for Zn and Cd in the experimental structure we have actually 6 nearest neighbors at a distance n_1 , in a hexagonal arrangement in the hcp plane. The 6 next nearest neighbors (n_2) are at a distance about ten percent longer, above and below the plane. Then the next six neighbors are at distances n_3 , 30% longer again, before the next 20 atoms occur at distances between $1.7a$ and $1.9a$. Therefore a natural cut off for the definition of our embedding is at a distance of $1.5a$ (i.e. for the one-body increment we have 18 embedding atoms), which we use for all subsequent increments.

The two-body increments may in principle be simply defined by a distance cutoff, without need for topological considerations. This implies that the 2-body energies will decrease monotonically with distance, which is not necessarily the case as we will show. However so long as the energy is dominated by a rapid decay with distance then the use of a simple cutoff is well justified. The 2-body increments are shown in Tab. II, ordered by distance within the hcp lattice.

For the three-body increments the choice of cut-off criteria is rather more complicated. For the experimental geometry we have divided the 3-body increments into those situated purely in the basal (hexagonal) plane, those between two planes (out-of-plane) and those that connect 3 planes: (pictured in Fig. 2). All pictured increments were

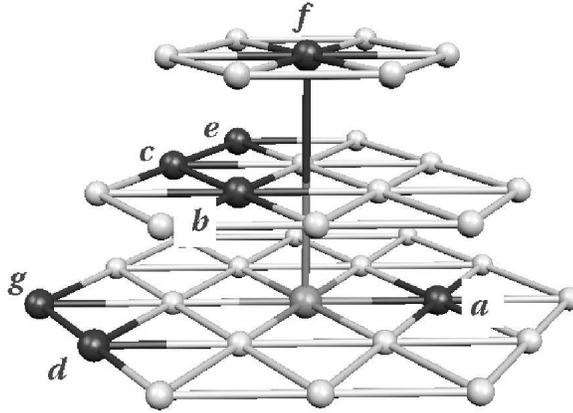


FIG. 1: The 2-body increments considered are shown relative to the central atom at the bottom of the figure (in light grey) as atoms in dark grey ordered by their distance from the central atom. Only bonds of distance a are shown, and the distance c which is the length of the two-body increment f .

	zinc		cadmium			
label	r (\AA)	r (a)	r (\AA)	r (a)	weight	planes
a	2.665	1.00	2.979	1.00	3	1
b	2.913	1.09	3.294	1.11	3	2
c	3.948	1.48	4.442	1.49	3	2
d	4.616	1.73	5.160	1.73	3	1
e	4.763	1.79	5.348	1.80	6	2
f	4.947	1.86	5.619	1.89	1	3
g	5.330	2.00	5.959	2.00	3	1

TABLE II: Definition of the 2-body increments for Zn and Cd, at the expt lattice parameters. The distances are given both in \AA ngström and in units of a , the lattice parameter. Also given are the number of hexagonal planes connected by this increment; for example the the increment (f) connects atoms in plane 1 and plane 3 at a distance of the lattice parameter c .

included for the cohesive energy at the experimental lattice parameters.

We have then ordered these according to increasing bond length from left to right. This grouping does not by itself indicate the relative importance of these increments for the total bulk energy, as the weight factors will here play a very important role. However this is a useful tool for comparing the contributions of different geometries within the

solid.

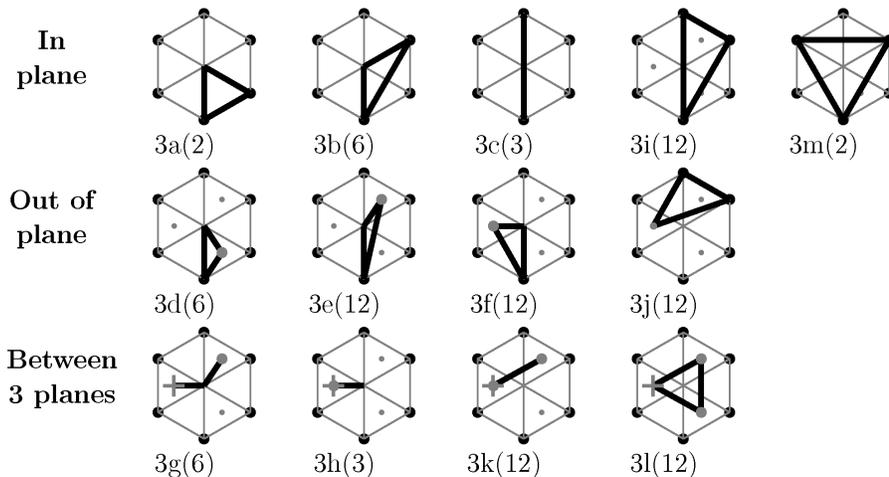


FIG. 2: The 3-body increments considered are shown, drawn on the background of a hexagon in the hcp plane. Grey dots correspond to atoms above the plane, and crosses to atoms below the plane. The numbers in parantheses are the weight factors of these increments in the hcp structure.

The fourth order increments are of course much more numerous and we have not attempted to classify them in such a rigorous manner. Instead we have restricted our examination of 4-body increments to a selected number of quite different geometries, with the aim of assuring ourselves that these are small enough to merit exclusion, and thereby confirming the convergence of the many-body expansion. The chosen geometries are shown in Fig. 3. For this purpose we use the cc-pvTZ basis set without the additional diffuse functions used for all smaller-order increments.

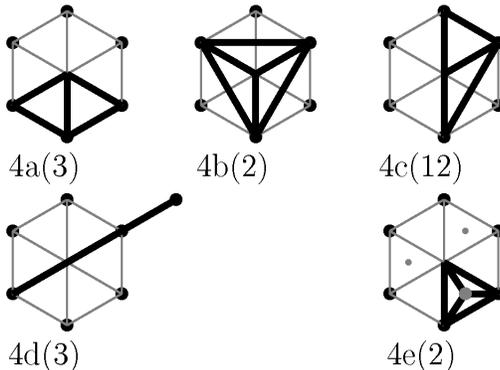


FIG. 3: The 4-body increments considered are shown, drawn on the background of a hexagon in the hcp plane. Grey dots correspond to atoms above the plane. The numbers in parantheses are the weight factors of these increments in the hcp structure.

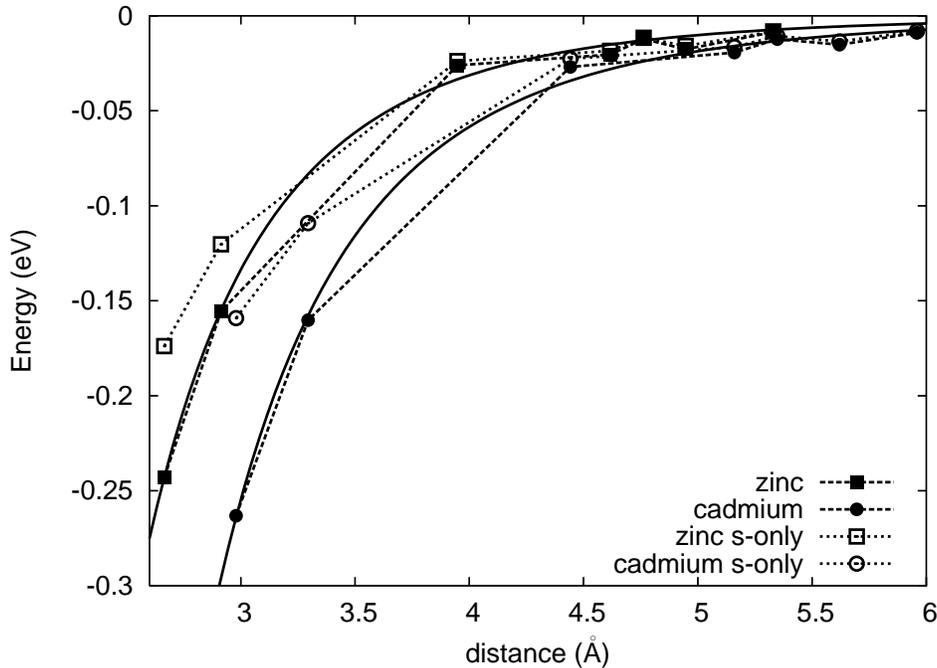


FIG. 4: The 2-body correlation increments are plotted as a function of distance, for both zinc and cadmium. The solid lines are the results of a fit to a vdW like function with $E = ar^{-\alpha}$, giving exponents $\alpha = 5.04$ (Zn) and 5.11 (Cd).

The calculated correlation energies for all increments for Zn and Cd at the experimental lattice parameters are given in Tab. III.

B. Results at the experimental lattice parameters

The first point to note is that the 2-body energies do not decrease purely monotonically with distance, as might have been expected. This is certainly the general trend, but at the longer distances the difference between in-plane and out-of-plane energies is noticeable. This is clear from examining Fig. 4, where the total correlation energies are plotted as a function of distance.

In particular, the unweighted contribution of (2f) (connecting 3 planes perpendicular) is considerably larger in magnitude than that of (2e) (connecting 2 planes), despite the longer distance. Thus the correlation contribution to the binding along the c-axis, at 90 degrees to the basal plane, is greater than that along a line that is about 30 degrees between two planes. This is a first indication of a preferred directionality in these systems. Also the decrease in energy going from (2d) to (2e), a reduction of almost a factor of two can not really be justified by the decrease in bond length (a mere 0.1 \AA). Thus correlation contributions in the basal plane (such as (2d)) seem to be stronger than the contributions coming from interactions between two planes (2e). Therefore we can conclude, that the correlation

Increment	Zinc		Cadmium		
	s^2	$d^{10}s^2$	s^2	$d^{10}s^2$	weight factor
One-body increment					
1a	0.13631	-0.04597	0.13071	-0.00664	1
Two-body clusters					
2a	-0.17384	-0.24093	-0.15914	-0.25644	3
2b	-0.12031	-0.15449	-0.10917	-0.15758	3
2c	-0.02387	-0.02618	-0.02262	-0.02699	3
2d	-0.01844	-0.02069	-0.01642	-0.01936	3
2e	-0.01156	-0.01232	-0.01061	-0.01235	6
2f	-0.01588	-0.01781	-0.01348	-0.01523	1
2g	-0.00819	-0.00862	-0.00806	-0.00902	3
Three-body clusters					
3a	0.02883	0.01847	0.02366	0.01490	2
3b	-0.00467	-0.00236	-0.00499	-0.00090	6
3c	-0.00605	-0.00236	-0.00765	-0.00181	3
3d	0.01251	0.00911	0.01022	0.00808	6
3e	-0.00274	-0.00133	-0.00303	-0.00127	12
3f	0.00194	0.00171	0.00158	0.00202	12
3g	-0.00317	-0.00188	-0.00333	-0.00171	6
3h	-0.00291	-0.00128	-0.00284	-0.00088	3
3i	0.00084	0.00091	0.00066	0.00083	12
3j	0.00095	0.00093	0.00062	0.00069	12
3k	0.00042	0.00037	0.00036	0.00038	12
3l	0.00047	0.00037	0.00045	0.00035	12
3m	-0.00013	0.00019	0.00010	0.00031	2
Four-body clusters					
4a	0.00051	-0.00170	0.00062	-0.00103	3
4b	-0.00306	-0.00189	-0.00249	-0.00184	2
4c	0.00202	0.00252	0.00147	0.00167	12
4d	-0.00072	-0.00020	-0.00084	0.00010	3
4e	0.00065	0.00063	0.00078	0.00137	2

TABLE III: Correlation (CCSD(T)) energies of the unweighted increments calculated for Zn and Cd at the experimental lattice parameters, in eV. The four-body results are using the cc-pvTZ basis set only, all smaller increments are calculated using the aug-cc-pvTZ basis set. The importance of each cluster for the ground-state properties of the solid depends on the weight factor which describes how often each geometry occurs in the solid.

contribution to binding is weaker between the AB planes of the hexagonal structure than between the second nearest AA planes within the ABA stacking.

The effect of screening within the metal can be estimated by a fit to the decay of the 2-body energy correlation contributions with distance. Without screening we would expect a decay proportional to r^{-6} at long range. Due to screening this exponent is reduced to 5.05 for zinc, and 5.12 for cadmium.

The effects of orientation, which were discussed at the 2-body level are even more evident in the 3-body contributions. The analysis is made rather more complicated by the fact that the 3-body contributions may be either attractive, or repulsive. As general trend we found that general acute angled triangles (3a,3d,3f,3i,3j,3k,3l,3m) are repulsive, whereas obtuse triangles (3b,3c,3e,3g,3h) are attractive. Here we include the linear cluster (3c) as an obtuse triangle, whereas the right-angled triangles are included in the group of acute triangles. The obtuse angled triangles have one pair of atoms at a relatively long distance, therefore the correlation energy of the long-distance pair is overestimated in magnitude at the two-body level (excitations to the virtual space of the bridging atom and the three-body term allow corrections to give an attractive contribution). Acute angled triangles do not have pairs with bridging atoms in between. Therefore there is nearly no overestimation at the two-body level and thus at the three-body level the correlation energy increment yields a contribution to binding since the 2-body energy decays rather quickly with distance.

As expected, the individual 3-body increments are smaller than the corresponding 2-body increments in the incremental expansion. Even the sum of all 3-body increments is smaller by an order of magnitude than the sum of the 2-body, due to the cancellation of attractive and repulsive terms. The 4-body terms are subsequently even another order of magnitude smaller than the corresponding 3-body terms, and also can be both attractive and repulsive: therefore neglecting the 4-body terms is well-justified. Far away three-body terms can be estimated with an induced dipole-dipole-dipole potential such as the Axilrod-Teller potential[31], which contains the cosine of the angle between the three atoms and therefore yields in a nearly isotropic 3-dimensional solid an equal amount of positive and negative contributions. However the short-range 3-body terms must be included in an optimisation of the lattice parameters due to this complicated dependence on both shape and orientation within the lattice. The division of the 3-body terms into shells is an attempt to include the 3-body terms in a well-balanced way, since for a geometry optimisation we would like to avoid calculating any more terms than necessary. For example, if we only include the increments that sit in the basal plane we can clearly not hope to describe the effect of changing the lattice parameter c properly.

The equilateral triangle (3a) is twice as repulsive as (3d), the out-of-plane equivalent which would have the same

distances in the ideal lattice. At the equilibrium structure this is partly due to the two bonds that are 10% longer, but there is also a strong effect of orientation. In total, if we sum up all the in-plane 3-body increments (3a,3b,3c,3i,3m) and the out of plane increments (3d,3e,3f,3g,3h,3j,3k,3l), the in-plane repulsion for Zn is 30 meV, more than a factor of two smaller than the out-of-plane repulsion (67 meV). For Cd, the in-plane repulsion totals 32 meV, and the out-of-plane 56 meV. In order to try to explain the hcp anisotropy in Zn and Cd as opposed to Mg, which has no d -orbitals, it is interesting to examine the different contributions of s - and d -correlation in the increments.

In the one-body increment the s -correlation is repulsive, whereas correlating the d -orbitals yields an attractive contribution larger in magnitude, and consequently a net attractive contribution. The d -correlation is about 30% larger than the s -correlation, while the core sp -correlation is an order of magnitude smaller.

In the 2-body increments, all orbitals produce an attractive correlation contribution, the d -component varying between nearly 30% of the total for the nearest-neighbor term, and decreasing to 5% for (2g), the largest distance considered. This quick decay of the d -contribution is clearly explicable in terms of the greater compactness of the d -orbitals relative to the valence s -orbitals.

The situation is naturally more complicated for the 3-body increments. Overall, the attractive contributions of the 3-body increments are more greatly reduced by d -correlation than are the repulsive contributions, such that the total 3-body contribution is more repulsive due to d -correlation. This effect is much stronger for cadmium than for zinc; of the total 3-body energy only 10 meV (11%) is due to the d -correlation for zinc, whereas for cadmium this reaches 56 meV (57%). Despite the varying magnitudes and signs of the d -correlation energy, the extreme dependence of the d -correlation contribution on both geometry and orientation is a clear indication of the importance of the d -orbitals in determining the structure of the lattice.

In terms of the final cohesive energy, if d -correlation were neglected for zinc we would obtain only 0.90 eV correlation energy instead of the total correlation contribution to binding of 1.44 eV at the experimental lattice constant, which would lead to a cohesive energy only 63% of the experimental value. Similarly, for cadmium, we would only get 0.86 eV correlation energy and so 60% of the experimental correlation contribution to the cohesive energy. If we compare the contribution of the core s^2p^6 correlation energy to binding, this amounts to only 14 meV (1%) for zinc and 25 meV (2%) for cadmium.

The performance of the method of increments for Zn and Cd at the experimental lattice parameters is summarized in Fig. 5. The 2-body correlation energy is clearly the dominant part of the total binding energy. It is interesting to note that the 2-body correlation energy of cadmium is larger than that of zinc, and the decreased binding energy of

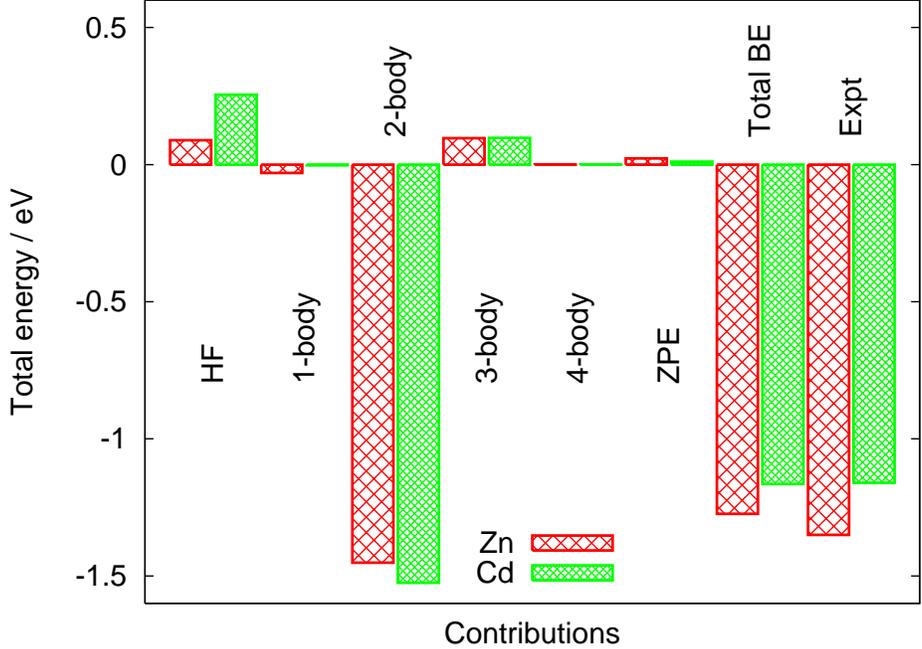


FIG. 5: The different contributions to the total binding energy from the method of increments are plotted, for the experimental lattice parameters, and compared to the experimental value. The zero-point energy (ZPE) correction is estimated from the Debye temperature[25].

cadmium relative to zinc is due to the increased repulsion in the solid at the HF level. Overall we reach a very good agreement with the experimental values. The largest error in determining the cohesive energy is not in the correlation part (neglected far-away two- and three-body terms and four-body terms are of the order of the zero-point vibrational energy) but in the Hartree-Fock part due to the difficult balance between the basis sets describing the crystal and the free atom. We think the most balanced treatment involves calculating the atom with the crystal basis set and applying the cp correction with 24 neighboring atoms.

C. Geometry optimisation

In order to discuss the dependence of the energy of the lattice on its structure, we vary the lattice parameters of the structure around the experimental lattice parameters. We produced a 4x4 array of lattice points to determine the optimized lattice parameters at the CCSD(T) level. The results with the c/a ratios, and cohesive energies are summarized in Tab. IV. The calculated points varying a at the fixed experimental lattice parameter c and varying c at fixed experimental a are shown in Figs 6 and 7.

For both zinc and cadmium, the HF energy is generally repulsive, and thus decreases with increasing a or c as

	$a/\text{\AA}$	$c/\text{\AA}$	c/a	E_{coh}/eV minimum	E_{coh}/eV expt. a, c
Zn calc.	2.62	4.96	1.89	1.40	1.31
expt	2.66	4.95	1.86	1.35	
Cd calc.	3.04	5.65	1.86	1.26	1.16
expt	2.98	5.62	1.89	1.16	

TABLE IV: The optimized values of a , c , and c/a are given, along with the cohesive energy at the optimized lattice parameters (minimum), and the cohesive energy at the experimental lattice parameters. Lattice parameters are in \AA , and energies in eV.

is normal for a purely repulsive potential. At the longest value of a , the HF energy for zinc becomes very slightly attractive. The 1-body correlation energy has almost no dependence on the lattice parameter. Correlating the s -shell only leads to a more repulsive curve, while the d -correlation essentially cancels with the s -shell correlation leading to a final HF+1-body curve similar to the original counterpoise corrected HF curve.

The first term in the expansion to examine closely with respect to the effect of the lattice parameter are therefore the two-body increments. Their contributions are always attractive. The s -only correlation is only about two thirds of the total two body correlation energy, and leads to longer lattice parameters than experiment; including d -correlation leads to a slight overbinding at the 2-body level and therefore shorter lattice constants. Both the valence-only contributions and the correlation energies including d correlations increase in magnitude for shorter values of a and c . But the effect at the valence-only correlations is not strong enough to provide a decisive minimum near the experimental lattice parameters. Only the inclusion of the d correlations leads to shorter values of both a and c .

We have chosen to truncate the expansion of the three-body correlation after the first ten increments described above for the experimental lattice parameters. This is because we wish to treat the different shells as equally as possible, i.e include equivalently increments which lie in the hexagonal plane and their out-of-plane counterparts. This is very important for a reliable description of the c/a dependence. The first 10 geometries include an equal number of repulsive and attractive contributions, which have a net repulsive contribution. The sum of the far-away 3-body increments k - m have contributions a factor of two smaller than the next smallest even despite relatively high weights for k and l , when compared at the experimental lattice parameters. This demonstrates that we have reasonable convergence with respect to the number of increments from this point. The three-body correlations are generally repulsive, although as c/a is increased the three-body terms become smaller, and the s -only correlations may become weakly attractive.

This minimum formed by the d -shell correlation is made much more pronounced by the 3-body terms, leading to optimized values of $a = 2.62 \text{ \AA}$ and $c = 4.96$ for zinc, and $a = 3.04 \text{ \AA}$ and $c = 5.65 \text{ \AA}$ for cadmium. Therefore

we have excellent agreement with experiment for the lattice parameters of zinc and small deviations of less than 2% for cadmium. At the experimental value of a we obtain an optimum value of $c = 4.83 \text{ \AA}$ for zinc, i.e. enlarging the lattice parameter in plane leads to a reduction in the out-of plane lattice constant. The volume of the unit cell stays thereby nearly unchanged. In particular, for zinc, we see very clearly that the position of the minimum with respect to a is already established by the s -correlations at the three-body level. The non-monotonic behaviour of the 3-body s -correlations for zinc is clearly observed in individual increments, where as a decreases the out-of-plane increments with angles less than 90 degrees become less repulsive, and the attractive out of plane increments become more attractive. As we go below the observed minimum the repulsion of the in plane increments begins to dominate again, and the total three-body contribution once again becomes repulsive. However the d -correlations are needed to include the repulsion for longer values of a . For cadmium, in contrast, already at the two-body level the s correlations have made a local minimum, which is shifted to shorter distances by the d -correlations.

Also in contrast to zinc we obtain a slightly longer value of the lattice parameter a for cadmium, and also a slightly longer c value. Finally we arrive at a value of c/a that is close to the experimental value, and although our calculated values of c/a are greater for zinc than for cadmium, in contrast to experiment, this error of 0.03 in the c/a ratio is well within the error of the optimisation we have performed in this work.

IV. CONCLUDING REMARKS

Whereas the Hartree-Fock treatment of zinc and cadmium does not yield binding, with an explicit inclusion of correlations on the coupled-cluster level we achieve a very good agreement with the experimental cohesive energy and the experimental lattice parameters. The correlation energy was divided up in terms of one-atom increments, which are small. The two-body contributions yield about 105% of the total correlation part to the cohesive energy. The three-body terms are small again (8% of the correlation part to the cohesive energy) and repulsive. d correlation is 42% of the total correlation for zinc and 48% for cadmium. Therefore an improper treatment of the d shell will yield unrealistic results. Whereas the 2-body terms determine the cohesive energy, for the lattice parameters the three-body terms are essential. The minimum at the experimental lattice constants is only achieved with 3-body terms. The potential surface is very flat with respect to variation of the lattice parameter c , whereas the variation of the in plane-parameter a , which determines the nearest-neighbor distance between two atoms, leads to a steeper potential. With this analysis we have proven, that we have now a systematically improvable method at hand, which reproduces accurately the experimental ground state properties of zinc and cadmium. Work is underway in our laboratory to vary

the lattice parameters towards the ideal hcp structure in order to compare with magnesium, which experimentally has the ideal structure, and to understand the highly anisotropic c/a ratio found for the hcp structure of zinc and cadmium.

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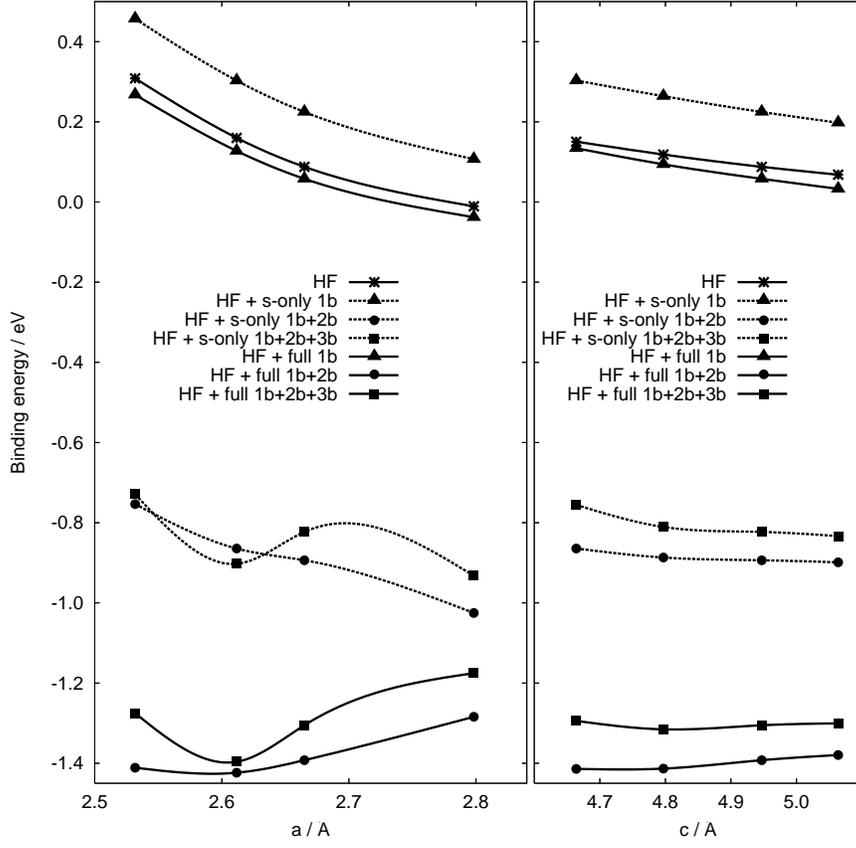


FIG. 6: The binding energy of zinc upon variation of the lattice parameters a (left) at the fixed experimental lattice parameter c and c (right) at fixed experimental a .

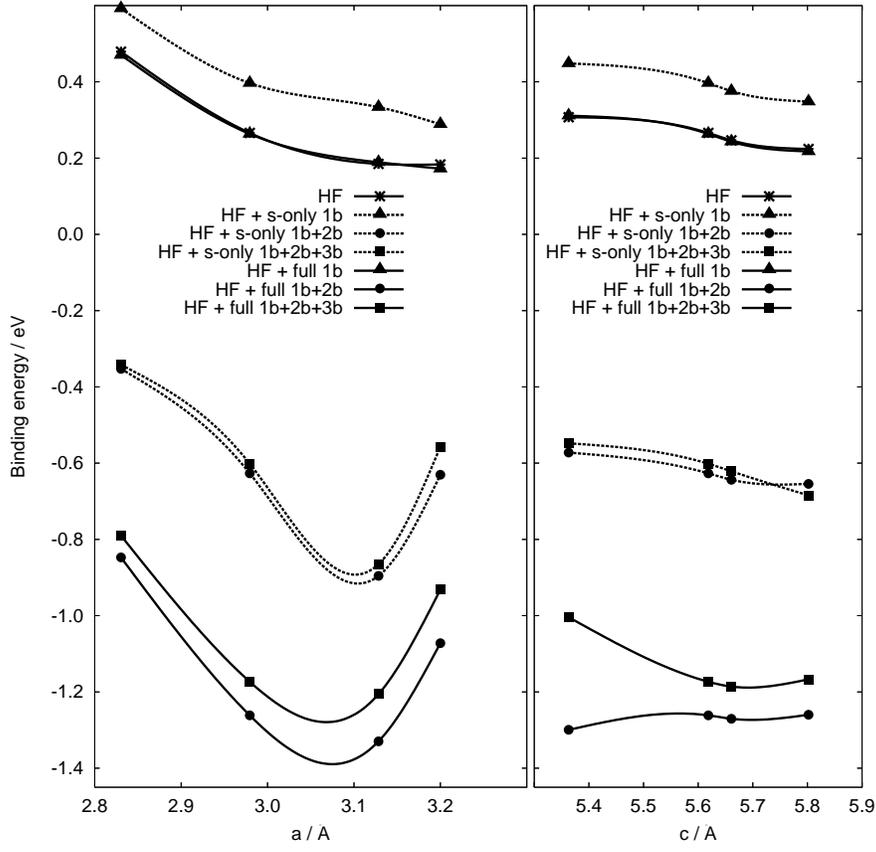


FIG. 7: The binding energy of cadmium upon variation of the lattice parameters a (left) at the fixed experimental lattice parameter c and c (right) at fixed experimental a .