Theor Chem Acc (2005) 114: 259–264
DOI 10.1007/s00214-005-0689-1

REGULAR ARTICLE

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On the application of the incremental scheme to ionic solids: test of different embeddings

Received: 30 June 2005 / Accepted: 19 July 2005/ Published online: 20 September 2005

Abstract Within the application of the incremental scheme to cerium dioxide high-level quantum chemical calculations, using the coupled-cluster approach, have been performed for $(Ce^{4+})_m(O^{2-})_n$ clusters. Two different approaches were considered. In the first one all increments were obtained from the nearly neutral Ce_4O_7-cluster. In the second approach different clusters were used for the evaluation of increments. Several embeddings were tested: from purely point charges up to pseudopotential-surrounding of oxygens to imitate the Ce-ions. The advantages and disadvantages of applied embedding schemes were discussed.

Keywords ab initio calculations · Electron-correlation calculations · Embedded cluster calculation · Incremental scheme

1 Introduction

Quantum-chemical ab initio calculations including the electronic correlations via a many-body wavefunction ansatz are nowadays possible for finite objects with various program packages. For extended systems, like solids, the most widely used method to include electronic correlations is density functional theory (DFT) [1]. In principle, DFT is able to capture the full correlation energy. In practice, presently available DFT functionals exhibit a number of serious deficiencies and are difficult to improve in a systematic way. On the other hand Hartree-Fock (HF) calculations have become routinely possible for solids with the advent of the program package CRYSTAL [2]. The HF Hamiltonian a priori does not include the effects of electron correlation. This leads to an overestimation of the electron–electron repulsion energy and, as a consequence, very high total energy. For a proper microscopic treatment of electron correlations it is necessary to go beyond the one-particle formulation and to deal with many-body wavefunction. Unfortunately, the problem of accurate treatment of electron correlations in solids (by using configuration interaction (CI) or coupled-cluster (CC) type models) is not fully settled. However, the development of the "method of increments" [3] has made it possible to apply size-consistent standard quantum-chemical correlation methods to periodic systems. The method is based on a many-body expansion of the total correlation energy in terms of local one-body, two-body and higher terms. It allows to obtain the correlation energy of the solid at ab initio level using standard quantum-chemical programs (such as MOLPRO [4]). The bulk correlation energy is obtained using the information from finite cluster. This method has been successfully applied to covalently bonded solids, like diamond [3], graphite [5], and many typical semiconductors [6–8], and to ionic solids, including transition metal oxides and rare earth compounds [9–13].

Since the information obtained from finite cluster is transferred to the properties of the solid, an appropriate embedding procedure simulating the influence of the infinite system surrounding the chosen cluster is of crucial importance. Especially for the materials bonded between ionic and covalent the choice of the embedding is not straightforward. In the covalent case a saturation of the dangling bonds is necessary (usually with hydrogens), whereas in the purely ionic compound an embedding composed of array of point charges is sufficient to model the long range electrostatic forces.

Here, we present the results of testing several embedding schemes for cerium dioxide (CeO_2). CeO_2 is a technologically important material, with remarkable properties, used in a number of applications [14–17]. The CeO_2 is known to exist in the cubic fluorite structure (Fig. 1). Formally the charges are distributed as follows: Ce^{4+} and O^{2-}. Therefore, cerium is in a $4f^0$ configuration and the Ce-ion has no magnetic moment. Different embeddings have been tested: from purely point charges, for each increment individually, up to large clusters with surrounding shells of pseudopotentials to mimic the Ce^{4+}. After presenting the method in the next section (Sect. 2) we discuss the obtained results in Sects. 3 and 4.

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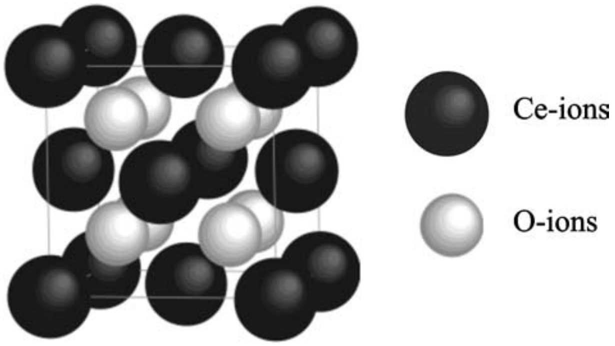

Fig. 1 Structure of cerium dioxide

2 The method of increments

The main ideas of the “method of increments” are:

- Generating suitable clusters from the structure of the solid and selection of the embedding for this cluster.
- Starting from SCF calculations for these clusters localized orbitals are generated which are assumed to be similar to the ones in the solid. Then the localized orbital groups are selected (in the case of CeO_2 the $5s^2p^6$ outer-core shell for Ce^{4+} and the $2s^2p^6$ valence shell of O^{2-}). These two groups define the one-body increments. To be more specific: one-body correlation-energy increments ϵ_A and ϵ_B are calculated by allowing only excitations out of the orbital group A or B individually. The correlation energy can be determined with any size-consistent correlation method.
- Two-body increments are defined as nonadditivity corrections:

  $$\Delta\epsilon_{AB} = \epsilon_{AB} - [\epsilon_A - \epsilon_B],$$

  where ϵ_{AB} is the correlation energy of the joint orbital system of AB.
- Three-body increments are defined as:

  $$\begin{aligned}\Delta\epsilon_{ABC} = \epsilon_{ABC} &- [\epsilon_A + \epsilon_B + \epsilon_C] \\ &-[\Delta\epsilon_{AB} + \Delta\epsilon_{BC} + \Delta\epsilon_{AC}].\end{aligned}$$

  Similar definition can be applied to higher-body increments.
- The correlation energy of the solid can now be expressed as the sum of all possible increments:

$$E^{\text{corr}}_{\text{bulk}} = \sum_A \epsilon_A + \frac{1}{2!}\sum_{AB} \Delta\epsilon_{AB} + \frac{1}{3!}\sum_{ABC} \Delta\epsilon_{ABC} + \cdots$$

Of course, this expansion only makes sense if it is well convergent, i.e., if $\Delta\epsilon_{AB}$ rapidly decreases with increasing distance between the ions at positions A and B and if the three-body terms are significantly smaller than the two-body ones. The embedding scheme has to guarantee that the increments calculated in the finite clusters are in good agreement with the ones in the solids. Because the latter ones can not be calculated, we infer this agreement by performing the so-called transferability tests: the same increment is calculated in different clusters and the values of the increment should differ only slightly.

From a conceptual point of view it would be desirable to take localized periodic orbitals as they become available in the CRYSTAL-code [18]. Also it is possible to obtain Wannier orbitals for periodic systems with the Wannier-code [19]. Although the correlation calculations at full CI level, with such local orbitals, has been performed for LiH [20], some problems still occur. Namely, the long tails of the orbitals obtained in such approaches give rise to very large clusters which are very difficult to treat in correlation calculations. Besides that the basis set used in the codes for periodic systems are too poor for an explicitly correlated many-body correlation method. Therefore, it is still the state of the art to use finite embedded clusters for the application of the method of increments, especially if heavy atoms are involved in the studied compound.

3 Different embedding schemes

The CeO_2 adopts the cubic fluorite structure (Fig. 1) with one Ce^{4+} ion and two O^{2-} ions per unit cell, where Ce^{4+} is surrounded by eight O^{2-}. Because the valence electrons are located at the oxygen, we select an oxygen-centered cluster to calculate the correlation energy increments. A nearly neutral cluster is the Ce_4O_7-cluster: central O-ion with four neighboring ceriums according to the crystal structure and six additional O-ions connecting the ceriums by pairs (Fig. 2). For Ce[1] we used a quasi-relativistic pseudopotential which models the f^0-configuration which is present in Ce^{4+} ($ecp46$) [24] and the corresponding basis set increased by even tempered orbitals up to $[8s7p6d3f2g]$ [25 , E. Voloshina and B. Paulus, Submitted]. Oxygen was treated with the augmented valence triple-ζ ($avtz$) basis set by Dunning [26,27]. This cluster was surrounded by an additional cover consisting of 12 Ce^{4+} described by large-core pseudopotential ($ecp54$, [28]) as shown in Fig. 2. With this pseudopotential a $[1s1p1d1f]$ basis set is supplied to allow a charge transfer from the O-ions to the neighboring ceriums. The obtained structure is further surrounded by a point-charge array simulating the $2\times2\times2$ unit cell construction. The increments obtained for this case are converged to $5\cdot10^{-7}$ a.u. The atomic distances are adopted from the experimental lattice parameter (a=5.41 Å).

This embedding approach has some advantages: (1) the cluster accounts for the proper surrounding of the valence electrons of correlated ions; (2) there is a possibility to get

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[1] For our calculations the traditional picture of the Ce f-occupation was assumed to be unoccupied in CeO_2. Experimental studies on the bulk and surfaces of nearly pure CeO_2 [21] as well as DFT calculations [22], performed for the solid, suggest that this approximation is valid for the stoichiometric CeO_2. To confirm this point we also performed the HF-calculations for CeO_2 with Ce in f^1-subconfiguration [E. Voloshina and B. Paulus, Submitted]. The obtained values are shown not to be in agreement with experimental values when comparing with Ce-f^0-case.

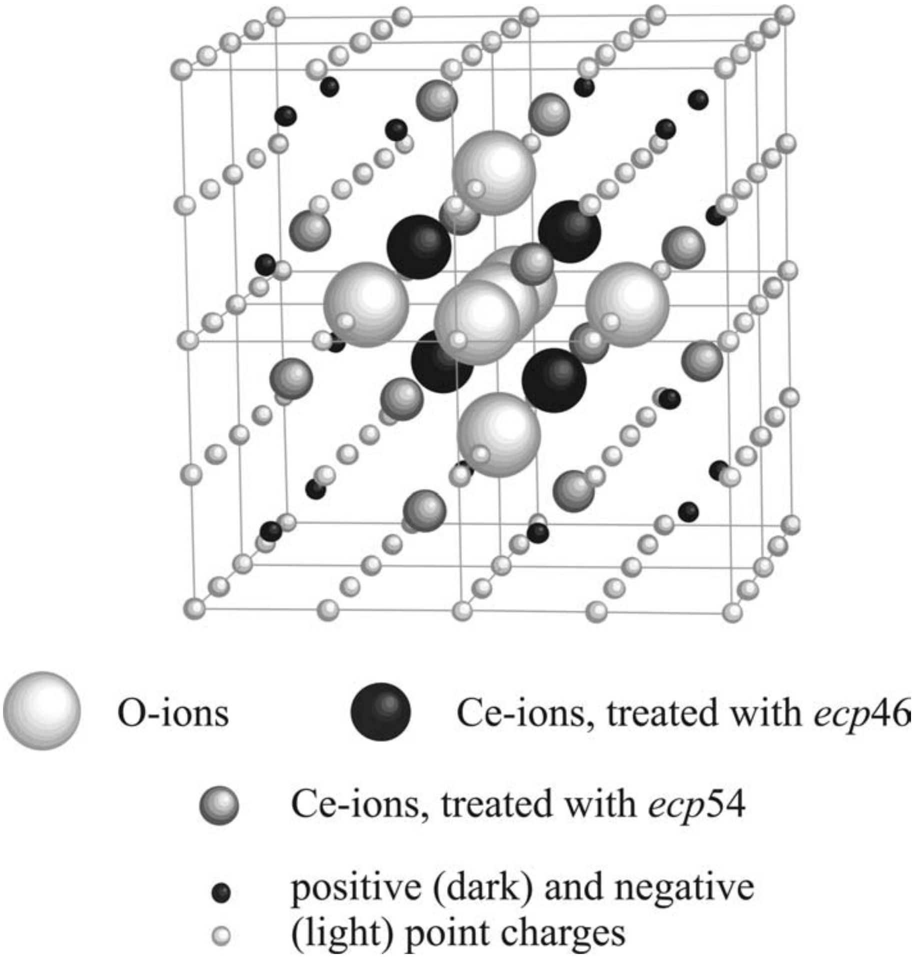

Fig. 2 Embedding of the Ce_4O_7-cluster

large number of increments from the same cluster; (3) ground-state properties obtained with this approach are in good agreement with the experiment [E. Voloshina and B. Paulus, Submitted]. On the other hand, the studied cluster allows to consider only a finite number of increments [E. Voloshina and B. Paulus, Submitted]. Moreover for the studied system it requires a significant amount of computational resources. For these reasons we also decided to test an alternative embedding scheme, where each particular increment can be obtained from corresponding individual cluster. This approach was successfully applied in works [9, 10, 13] for several ionic compounds. In this scheme the individual ions are embedded in different ways: (1) only point charges of value (+4) for Ce and (−2) for O at the positions of the lattice, the point charge embedding is chosen as large as the increments are converged; (2) the negatively charged O-ions are embedded with Ce^{4+} pseudopotentials (*ecp*54) as next neighbors to simulate the Pauli repulsion; (3) to test the quality of the large-core pseudopotential *ecp*54 we used the *ecp*54 instead of the *ecp*46 with eight outer-core electrons in the $5s^2p^2$ shell, which is described with a minimal basis; (4) to allow delocalization of the valence electrons of the O^{2-} we supply together with the pseudopotentials a contracted $[1s1p1d1f]$ basis. The correlation energies are evaluated using the coupled cluster approach with single and double excitations (CCSD) [29, 30] as implemented in MOLPRO 2002. Localized orbitals used in these calculations were obtained according to the Pipek–Mezey criterion [31].

4 Results and discussion

For the studied embedding schemes only the four most important increments (one body ϵ_{Ce} and ϵ_O as well as nearest-neighbor Ce–O and O–O two-body increments) have been determined. With these four increments we obtain 98% of the total correlation energy calculated with a given correlation method and a given basis set. A detailed analysis and convergence study can be found in Ref. [E. Voloshina and B. Paulus, Submitted]. In this work the cohesive energy, lattice constant and bulk modulus of CeO_2 have been determined with the incremental scheme which were found in very good

Table 1 Selected correlation-energy increments obtained at the CCSD level

Cluster		Ce_4O_7		Individual clusters for calculating of each increment				
Embedding	Structure	Full atoms + PP + point charges		PP + point charges				Point charges
	PP	Ce: *ecp*54		Ce: *ecp*46		Ce: *ecp*54		–
	Basis	*spdf*	–	*sp*-minimal	*spdf*	–	*spdf*	–
ϵ (a.u.)	Ce (1)[2]	−0.17418	−0.16781	−0.18048	−0.18048	−0.18048	−0.18048	−0.18048
	O (2)	−0.26155	−0.25917	−0.25799	−0.26681	−0.26512	−0.29413	−0.30242
	Ce–O (8)	−0.01198	−0.01161	−0.01492	−0.01162	−0.01174	−0.00779	−0.00987
	O–O (6)	−0.00691	−0.00764	−0.00337	−0.02100	−0.00326	−0.00472	−0.01832
$\Sigma\epsilon_A + \frac{1}{2}\Sigma\Delta\epsilon_{AB}$		−0.76593	−0.75551	−0.76625	−0.82385	−0.76746	−0.81406	−0.87976

[2] In parenthesis weight factors per primitive unit cell are given

agreement with experiment.[3] The results for the selected one- and two-body increments are shown in Table 1. We regard the results obtained within the Ce_4O_7-cluster as the one most closely to the solid. Changes of the basis set at the embedding ceriums (c.f. first two columns in Table. 1) result in deviations of the correlation energy of the solid only by about 1%. This fact and the population analysis show that the electronic distribution in this cluster is well-balanced and solid-like.

The values obtained for the Ce-increment differ only by 0.0063 a.u. (see the first row of Table 1). The outer-core shell of Ce is not much dependent on the embedding as one may expect. One can clearly see from Fig. 3 that the shape and extension of the localized orbitals is not very different. The Ce-increment in the point charge embedding is somewhat larger in magnitude as in the cluster. Replacing the O^{2-} by point charges results in stronger localizations of electrons at Ce-ion and, accordingly, in an increase of the correlation-energy magnitude.

The analysis of the results obtained for the O-increment leads to the conclusion that we have two main effects which can yield in an increase of correlation energy. The first one is the too strong localization of the electrons at the Hartree-Fock level, that leads to the increase of the electron correlations. The second one is the enlargement of the excitation space, if at the neighboring sites additional basis functions are supplied. At the same time, the orbitals obtained for the second case can be more delocalized so that a decrease of the correlation energy is expected. Turning to the obtained numbers, it is interesting to note, that using both cases for surrounding Ce^{4+} of *ecp*46 ([*ecp*46/minimal basis] and [*ecp*46/*spdf*]) as well as *ecp*54 without any basis ([*ecp*54/point charges]) give good agreement with the Ce_4O_7 results (deviation of about 1%). In the first case (O in [*ecp*46/minimal basis]-embedding) some decrease of the magnitude can be explained by the fact that in the O-cluster without explicitly treated ceriums some excitations to ψ_{Ce} becomes impossible (decrease of the correlation space), that leads to an increase of the total correlation energy. Similar results for ϵ_O obtained for two different embeddings (1: O surrounded by [*ecp*46/*spdf*] and 2: O surrounded by [*ecp*54/point charges]) are explained by two opposite factors. In the case of [*ecp*54/point charges]-embedding the slight increase of the correlation energy can be explained by the localization of electrons at the oxygen (see Fig. 4d). On the other hand, in the first case ([*ecp*46/*spdf*]) the electron-delocalization takes place (see Fig. 4c), which certainly leads to decreasing of correlation effects. At the same time additional basis at the surrounding Ce-ions allows for more excitations to the ψ_{Ce}. The too strong localization of electrons leads to increase of ϵ_O in the case of only point-charge embedding (see Fig. 4f and Table. 1, the rightest column).

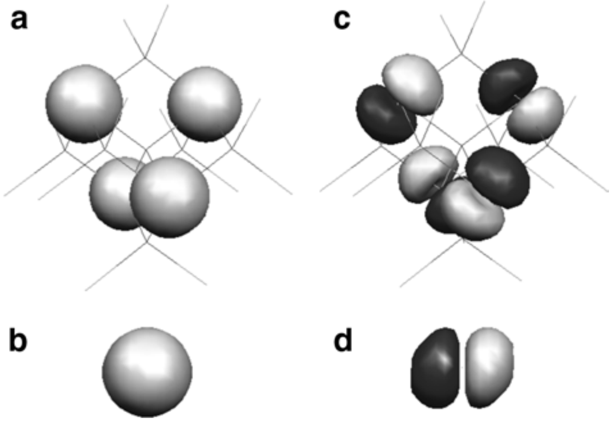

Fig. 3 The Ce-orbitals obtained for different embeddings: **a** one of the four Ce-*s*-orbitals (Ce_4O_7-cluster); **b** Ce-*s*-orbital (Ce^{4+}/point-charge-embedding); **c** one of the 12 Ce-*p*-orbitals (Ce_4O_7-cluster); **d** Ce-*p*-orbital (Ce^{4+}/point-charge-embedding)

Let us now consider the inter-ionic interactions. The obtained values for $\Delta\epsilon_{Ce-O}$ are reduced in magnitude, if we supply a basis set on the Ce surrounding the O-ion (note, not the basis at the Ce-ion which is correlated, but the surrounding of the O-ion is changed). Due to the more delocalized orbitals of the O^{2-}, the overlap and, therefore, the correlation between Ce and O were smaller by about 0.004 a.u. for both pseudopotentials.

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[3] The HF calculations performed for the cerium dioxide give 73% of the experimental cohesive energy. The lattice constant is overestimated by 2.5%, and bulk modulus, evaluated at the experimental lattice constant, is too large as compared with the measured value. After including all correlations we recover about 93% of the cohesive energy. The obtained lattice constant is accurate to 0.4%; bulk modulus is 8% higher compared with the experiment.

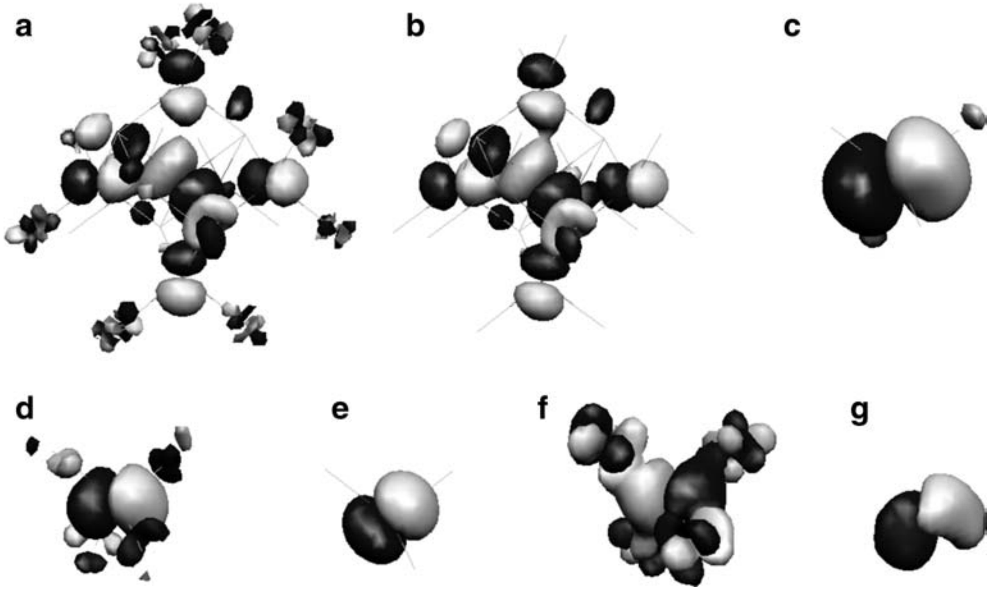

Fig. 4 The O-orbitals obtained for different embeddings: **a** one of the 21 O-p-orbitals (Ce_4O_7-cluster); **b** one of the 21 O-p-orbitals [Ce_4O_7-cluster (ecp54 without basis)]; **c** one of the three O-p-orbitals (O^{2-} surrounded by four Ce^{4+} carrying a *ecp*46 and minimal basis set plus point charges); **d** one of the three O-p-orbitals (O^{2-} surrounded by four Ce^{4+} carrying a *ecp*46 and corresponding [$spdf$] basis set plus point charges); **e** one of the three O-p-orbitals (O^{2-} surrounded by four Ce^{4+} carrying a *ecp*54 plus point charges); **f** one of the three O-p-orbitals (O^{2-} surrounded by four Ce^{4+} carrying a *ecp*54 and corresponding [$spdf$] basis set plus point charges); **g** one of the three O-p-orbitals (O^{2-} surrounded by point charges only)

The O–O-increment strongly depends on the embedding. Regarding the O–O-increment value obtained for the Ce_4O_7-cluster, which can be assumed to be more close to the one in solid, ($\Delta\epsilon_{\mathrm{O-O}}$) calculated with only point-charge embedding is larger by a factor of three. In this case the gain in electron-correlation energy is due to possible excitations of the electrons from one atom to the other. In the case of pseudopotential embedding only the O–O-increment is too small compared with the one obtained for the Ce_4O_7-cluster. This is due to the quite delocalized orbitals together with the absence of excitations at the Ce-positions. If we supply there additional basis functions, the shape of the orbitals changes drastically only for the *ecp*54. The effect of delocalized orbitals dominates in this case over the energy gain due to the additional excitations. For *ecp*46 the orbitals remain quite localized and therefore a significant increase of correlation energy can be achieved due to the larger excitation space.

If we put our attention to the weighted sum of the increments as it occurs in CeO_2, one can notice, that the correlation energy obtained with pseudopotentials only is quite similar to the one obtained for the cluster. The point charge embedding only yields 15% larger correlation energy as the one in the cluster at the chosen level of the incremental expansion. But the incremental expansion is constructed in such a way, that when sufficient number of increments is added, it must converge to a proper value. As a confirmation, in the case of point-charge embedding the three-body increments are repulsive. For example, the largest three-body O–O–O increment is equal to $+0.01293$ a.u., whereas the same correlation-energy increment obtained for the case of [*ecp*46/minimal basis]-embedding is -0.00013 a.u. Moreover, the sum of three-body increments in the last case contributes less than 1% to the correlation part of the bulk cohesive energy [E. Voloshina and B. Paulus, Submitted]. The values obtained with the pseudopotentials and basis sets are somewhat too large compared to the ones obtained for the Ce_4O_7-cluster. The error due to the embedding can be estimated from the difference between the values obtained for the cluster-approach and the [$ecp46/spdf$]-embedding by aproximately 0.06 a.u. which corresponds to 8% of the correlation energy. The use of [$ecp54/spdf$]-embedding yields a too large repulsion between O-electrons at the same atom and, therefore, is not appropriate for the proper description of electron transfer to the environment. In general the use of a basis at the environment yields a larger correlation contribution on the oxygens as compared to the O-increments in the Ce_4O_7-cluster. Whereas in the embedding of Ce_4O_7-cluster the basis sets yield a balanced electron distribution (each of its six O^{2-} have two neighboring Ce^{4+} treated with (*ecp*46+full basis) and two neighboring Ce^{4+} with ($ecp54+spdf$); at the same time one of the oxygen-ions is fully surrounded with such types of Ce^{4+}; all correlated ceriums (Ce^{4+}: *ecp*46+full basis) in the cluster have also appropriate environment, that leads to a more solid-like electron distribution and in the individual cluster approach the basis on the embedding atoms increase the correlation contribution on the one- and two-body level and has to be compensated with repulsive three-body increments. Thus, all embeddings should yield the same correlation energy due to the inclusion of more and more increments. At the same time the best choice for the embedding would be the one that is modeled similar to the solid, i.e., as large as possible, preferably neutral, cluster.

5 Conclusion

Within the application of the method of increments to the ionic solid, several different embedding approaches have been tested using CeO_2 as an example. Embedded large nearly neutral cluster (Ce_4O_7) as well as several individual clusters, each of which consists of only correlated parts of the solid, were used in the calculations. Besides the pure point charges, also the pseudopotential-surrounding of oxygens were used as an embedding. Analysis of obtained results allows us to conclude that all tested embedding-schemes should result in the same value of correlation energy. At the same time a large neutral cluster seems to be the best choice for the embedding. Reasonable results were also obtained by using [*ecp*46/minimal basis] – as well as [ecp54/point charges] – embeddings.

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