Correlation effects in ionic crystals: The cohesive energy of MgO

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High-level quantum-chemical calculations, using the coupled-cluster approach and extended one-particle basis sets, have been performed for $(Mg^{2+})_n(O^{2-})_m$ clusters embedded in a Madelung potential. The results of these calculations are used for setting up an incremental expansion for the correlation energy of bulk MgO. This way approximately 96% of the experimental cohesive energy of the MgO crystal is recovered. It is shown that only about 60% of the correlation contribution to the cohesive energy is of intraionic origin, the remaining part being caused by van der Waals–like interionic excitations.

I. INTRODUCTION

While density-functional theory (DFT), with its long tradition in solid-state physics, is getting wide acceptance in the field of quantum chemistry nowadays, there are also attempts to the reverse, i.e., making use of the traditional quantum-chemical Hartree-Fock (HF) and configuration-interaction (CI) methods not only for molecular but also for solid-state applications. Pisani and co-workers, e.g., devised an *ab initio* HF scheme for solids,[1] which has successfully been applied to a broad range of (mostly) covalently bonded and ionic solids, within the past five years. A main asset of the HF scheme is the availability of a well-defined wave function, which may be used not only for extracting properties but also as a starting point for systematically including electron-correlation effects. Such effects, which are only implicitly accounted for in density-functional methods, often have a strong influence on physical observables, in molecules as well as in solids. Several suggestions have been made as to how to explicitly include electron correlation in solids, among them the quantum Monte Carlo (QMC) approach,[2] the local ansatz (LA),[3] and the method of local increments[4] (which may be considered as a variant of the LA); in QMC the HF wave function is globally corrected for electron-correlation effects by multiplying it by a factor containing interelectronic coordinates (Jastrow factor); the latter two methods rely on applying selected local excitation operators to the HF wave function and thus have a rather close connection to traditional quantum-chemical post-HF methods.

The number of test examples is still rather limited with all three solid-state correlation schemes, and is mainly restricted to semiconductors so far. For ionic insulators where quantum-chemical methods would seem to be most suitable and easily advocated, much work indeed has been devoted to correlation effects on band structures [cf. e.g., Refs. 5(a) and 5(b)], but only a few studies refer to cohesive energies [cf. e.g., Ref. 5(c)], and only

a single application of the post-HF schemes mentioned in the last paragraph exists to our knowledge[5(d)] (NiO with QMC). This does not mean that such applications to ground-state correlation effects are without challenge. For MgO, the system to be dealt with in this paper, HF calculations[6] yield a lattice constant which is in agreement with experiment to ~ 0.01 Å, but the correlation contribution to the cohesive energy is significant (~ 3 eV, nearly half as large as the HF value). The local-density approximation (LDA) of DFT does not do a good job here either: an overbinding results which is more than twice as large as the correlation contribution to the lattice energy,[7] and invocation of gradient-corrected functionals is indispensable for obtaining reasonable results;[6(b)] cf. Sec. III E below. The situation would not seem too complicated, nevertheless, if the effect could be explained just by adding correlation contributions of individual ions; in fact, such a suggestion has repeatedly been made in the literature; cf. Refs. 6(a) and 17(c). However, the O^{2-} ion, one of the building blocks of the MgO crystal, is not stable as a free entity, and an accurate determination of the correlation energy of this highly fluctuating and easily polarizable ion in its crystal surroundings is not expected to be an easy task; the more so, since already for the determination of the electron affinity of the free O atom high-level quantum-chemical correlation methods are required.[8] Moreover, as we shall show below, intraionic interactions contribute only $\sim 60\%$ to the total correlation effect on the bulk cohesive energy, and van der Waals–like interionic excitations play an important role here.

This paper is the first in a series devoted to the application of the method of local increments to ionic solids; it shows, for the example of MgO, how to set up an incremental expansion of the bulk correlation energy using information from quantum-chemical calculations on finite clusters only. The organization of the paper is as follows. In Sec. II, computational details are given for the applied quantum-chemical methods, and test calculations are performed for the first two ionization potentials of

the Mg atom, for the electron affinity of the O atom, and for spectroscopic properties of the MgO molecule. The method of local increments is briefly described in Sec. III; correlation-energy increments are evaluated from calculations on $(Mg^{2+})_n(O^{2-})_m$ clusters, and the incremental expansion for the total correlation energy of bulk MgO is discussed. Conclusions follow in Sec. IV.

II. TEST CALCULATIONS

Our first test concerns the electron affinity (EA) of the oxygen atom. We performed separate calculations for the ground states of O and O^-, respectively, using various single- and multireference quantum-chemical configuration-interaction methods for treating many-body correlation effects.[9] The one-particle basis sets employed have been taken from the series of correlation-consistent (augmented) polarized Gaussian basis sets of Dunning and co-workers.[10,8(a)] The ab initio program package MOLPRO (Ref. 11) has been used in these and all of the following calculations of the present paper. The results for EA(O) are collected in Table I. It is seen that the best single- and multireference methods [coupled-cluster with single and double excitations and perturbative inclusion of triples [CCSD(T)] and 2s-2p active space; multireference averaged coupled pair functional with single and double excitations (MR-ACPF) and 2s-3p active space] yield quite similar results (1.40 eV), which differ from the experimental value by only 0.06 eV. Effects of the one-particle basis set are significant, even at the stage of including g functions, and probably are responsible for the major part of the remaining deviation from experiment. In the $(Mg^{2+})_n(O^{2-})_m$ cluster calculations to be described in Sec. III, we could only afford the valence triple-ζ $[5s4p3d2f]$ basis set, at the single-reference level; the concomitant differential errors can be estimated to about 0.1 eV per O atom and (added) electron.

TABLE I. Electron affinity (eV) for the O atom at various theoretical levels [RHF: restricted Hartree-Fock self-consistent field, CASSCF: complete active space self-consistent field, (MR)CI: (multireference) configuration interaction, (MR)ACPF: (multireference) averaged coupled pair functional, CCSD(T) coupled-cluster with single and double substitutions (and perturbative correction for triples)]; the reference configurations comprise all possible distributions of electrons within the space of active orbitals.

Basis set active space	$[5s4p3d2f]^a$ 2s-2p	$[6s5p4d3f2g]^a$ 2s-2p	$[6s5p4d3f2g]^a$ 2s-3p
RHF	-0.53	-0.54	-0.54
CASSCF	-0.53	-0.53	0.77
(MR)CI	1.02	1.07	1.36
(MR)ACPF	1.23	1.28	1.40
CCSD	1.18	1.24	
CCSD(T)	1.33	1.40	
expt.		1.46	

^{a}Correlation-consistent augmented polarized valence triple- and quadruple-ζ basis sets from Refs. 10 and 8(a) contracted from $(11s6p3d2f)$ and $(13s7p4d3f2g)$ Gaussian primitives, respectively.

TABLE II. Ionization potentials $Mg \rightarrow Mg^+/Mg^+ \rightarrow Mg^{2+}$ of the magnesium atom (in eV), from calculations using a two-valence-electron pseudopotential (PP); in the (single-reference) ACPF calculations a core-polarization potential accounts for core-valence correlation.

Basis set^a	$(4s4p)$	$(4s4p1d)$
RHF^b	6.63/14.75	6.63/14.75
ACPF^b	7.63/15.02	7.65/15.02
expt.	7.65/15.04	

^{a}Valence basis set optimized for the PP; exponents of Gaussian primitives are s: 2.425 719 3, 0.822 625 0, 0.107 749 0, 0.039 485 0; p: 0.769 047 0, 0.188 675 0, 0.075 101 0, 0.029 497 0; d: 0.2; the basis set is used without contraction.
^{b}For explanation of acronyms, cf. Table I.

The next test deals with the ionization potentials (IP) of the magnesium atom ($Mg \rightarrow Mg^+$, $Mg^+ \rightarrow Mg^{2+}$). A difficulty is encountered here, since not only the correlation energy of the valence ($3s^2$) electron pair has to be accounted for but also core-valence correlation effects are non-negligible: the latter contribute with 0.3 eV to the $Mg^+ \rightarrow Mg^{2+}$ IP, e.g. For accurately describing these effects explicitly, a high computational effort is needed in quantum-chemical ab initio calculations. In (all-electron) calculations with a basis set of medium quality $((12s9p1d)/[5s4p1d])$,[12] errors of 0.12 and 0.21 eV remain for the two IP's, and even a very large uncontracted $(20s15p6d3f)$ basis[13] still yields deviations from experiment of 0.03 and 0.04 eV in CCSD(T) calculations. Without loss of accuracy, however, the computational effort can be effectively reduced[14,15] by simulating the Mg^{2+} core by a pseudopotential (PP) which describes core-valence interaction at the HF level, in conjunction with a core-polarization potential (CPP) which accounts for core-valence correlation effects. Using these methods, very good agreement with experiment is obtained, at the correlated level; cf. the results of Table II. [Only ACPF data are given in the table since for a two-electron system all the correlation methods of Table I (CI, ACPF, CCSD) coincide.] For the cluster calculations of Sec. III, we adopt the PP+CPP description, together with the energy-optimized $(4s4p)$ valence basis set; the concomi-

TABLE III. Bond length R_e (Å), dissociation energy D_e (eV), and vibrational frequency ω_e (cm^{-1}) of the MgO molecule, evaluated at various theoretical levels. A Mg^{2+} pseudopotential was used, and, at the correlated levels, a core-polarization potential was added. In the multireference calculations, a five-orbital (Mg 3s, O 2s,2p) active space was chosen.

	R_e	D_e	ω_e
RHF^a	1.715		794
MRCI^a	1.750	2.01	751
MRACPF^a	1.751	2.29	755
CCSD^a	1.744	1.96	746
CCSD(T)^a	1.731	2.49	792
expt.^{b}	1.749	2.61±0.22	785

^{a}For explanation of the acronyms, cf. Table I. Basis sets: O $[5s4p3d2f]$; Mg $(4s4p)$.
^{b}Reference 16.

tant differential errors can be estimated to about 0.02 eV per Mg atom and (removed) electron.

The last test of our quantum-chemical arsenal of methods was performed for the MgO molecule. The basis sets applied here are the same as those used in the next section for $(Mg^{2+})_n(O^{2-})_m$ clusters. The results for bond length, dissociation energy, and vibrational frequency are compiled in Table III. It is seen that excellent agreement with experiment [to 0.02 Å, 0.1 eV, 10 cm^{-1} (1%)] is obtained at the (single-reference) CCSD(T) level. At the multireference level (without triples), the agreement is slightly less good, but this could certainly be improved upon by enlarging the reference space which was chosen in our calculations.

III. LOCAL INCREMENTS

A. Methodological aspects

The main idea to be discussed here is the possibility to extract information from calculations on finite clusters and to transfer it to the infinite crystal. Such a transfer would certainly *not* be a good idea for *global* cluster properties (cohesive energy, ionization potential, etc.)—it only makes sense for *local* quantities. Now, localized orbitals are entities which can be defined within ionic crystals as well as within clusters of these materials. Moreover, electron correlation in or between such orbitals is a local effect. Therefore, if we prepare localized orbitals in the interior of a cluster (in a sufficiently solid-like environment) and if we calculate correlation energies involving these orbitals, we can hope to obtain transferable quantities.

Of course, there is no reason to expect that these quantities would be additive in the solid. If we separately calculate, e.g., the pieces of correlation energy due to orbitals localized at ionic positions A, B, C,...,

$$\epsilon(A), \epsilon(B), \epsilon(C), ..., \qquad (1)$$

the correlation energy of the common orbital system of AB (or AC, BC, ...) will deviate in general from the sum of constituents, due to interionic interactions, and we can define nonadditivity corrections such as

$$\Delta\epsilon(AB) = \epsilon(AB) - \epsilon(A) - \epsilon(B). \qquad (2)$$

Again, the next larger systems of three ions, ABC, ..., will have correlation energies slightly different from the sum of the constituents plus the two-body nonadditivity corrections, and this gives rise to three-body increments

$$\Delta\epsilon(ABC) = \epsilon(ABC) - [\epsilon(A) + \epsilon(B) + \epsilon(C)]$$
$$-[\Delta\epsilon(AB) + \Delta\epsilon(AC) + \Delta\epsilon(BC)]. \qquad (3)$$

Similar definitions apply, in principle, to higher-body increments.

If we now make use of all these quantities, i.e., the intraionic correlation energies and the various interionic correction terms, and multiply them by weight factors appropriate for the solid, we can hope to get a meaningful

incremental expansion of the correlation energy per unit cell of the infinite crystal:

$$\epsilon_{\text{bulk}} = \sum_A \epsilon(A) + \frac{1}{2} \sum_{A,B} \Delta\epsilon(AB)$$
$$+ \frac{1}{3!} \sum_{A,B,C} \Delta\epsilon(ABC) + \cdots . \qquad (4)$$

In Ref. 4(d) we have shown that this equation can be formally derived, under appropriate approximations, from an expression for the correlation energy of an infinite system.

Let us discuss now the assumptions implicit in this approach more closely for the case of the MgO crystal. MgO is generally considered as a nearly perfect ionic crystal consisting of Mg^{2+} and O^{2-} ions;[17] the question of a quantitative measure for the ionicity of MgO has been addressed only recently by Bagus and co-workers,[17(c),17(d)] and in careful studies using various criteria the ionic charges have been shown to deviate from ±2 by <0.1 only. Thus the attribution of localized orbitals to ionic positions made above seems to be a valid assumption. But even if there were some degree of covalency and/or some tendency for delocalization in MgO, this would not invalidate our approach. In fact, the first applications of the method of local increments were made for covalently bonded crystals (diamond, silicon,[4(a),4(b)]) and even for the π system of graphite which according to usual classifications is considered as completely delocalized the method has been shown to yield meaningful results.[4(c)]

Secondly, the determination of increments for nonadditive interionic correlation contributions in Eqs. (2) and (3) makes sense only if the number of non-negligible increments is small, i.e., if the $\Delta\epsilon(AB)$ rapidly decrease with increasing distance of the ions and if the three-body terms $\Delta\epsilon(ABC)$ are significantly smaller than the two-body ones, making the use of four-body contributions obsolete. A necessary prerequisite for satisfying these conditions is the use of a size-extensive correlation method for calculating the increments. This excludes, for instance, the (variational) configuration-interaction method with single and double excitations (CISD), since it does not scale linearly with n for a system of non-interacting atoms A_n. On the other hand, correlation methods of the coupled-cluster variety such as those discussed in the last section [ACPF, CCSD, CCSD(T)] do have this property. (These are benchmark methods of increasing complexity widely used in quantum chemistry; we display results derived from all of them in the following tables, in order to monitor convergence with respect to the many-particle basis set used.) When applying such a method, $\Delta\epsilon(AB)$ should indeed rapidly decrease with increasing AB distance, since for nonoverlapping pairs of ions only van der Waals–like correlation effects ($\sim 1/r^6$) become effective. Furthermore, three-body terms can be expected to be significantly smaller than two-body terms, since two-electron excitations, involving a pair of orbitals at most, are known to dominate correlation effects.

A final assumption underlying our approach is that of the transferability of localized orbitals from clusters to

the bulk which was mentioned right at the beginning of this subsection. Its fulfillment depends, of course, on the preparation of the clusters. A free O^{2-} ion, e.g., would be unstable, and it is essential, therefore, to put this ion in a cage of Mg^{2+} ions in order to stabilize it, and to simulate the Madelung potential of the surrounding ions in order to provide the correct field near the O nucleus. More details on cluster preparation and transferability tests will be given in the following subsections, where the determination of individual increments is discussed.

B. Intraionic correlation

The first increment to be calculated is the correlation energy which can be locally attributed to an O^{2-} ion in crystal surroundings of Mg^{2+} and other O^{2-} ions. As already mentioned, a realistic modeling of the crystal surroundings is essential, since otherwise the O^{2-} ion would not be stable at all. Fortunately, stabilization can be achieved in both a very simple and efficient way, by simulating the Pauli repulsion of the six nearest-neighbor Mg^{2+} ions by means of pseudopotentials; we used the same energy-consistent pseudopotentials here as were used for the treatment of the Mg atom in the calculations of Sec. II. For representing the crystal environment of the resulting seven-atom cluster, a Madelung approximation was made: 336 ions surrounding this cluster in a cube of $7 \times 7 \times 7$ ions were simulated by point charges ± 2 (with charges at the surface planes/edges/corners reduced by factors 2/4/8, respectively). Here and in the following, the experimental bulk lattice constant ($r_{MgO} = 2.105$ Å) was adopted. Employing the $[5s4p3d2f]$ basis set, which was already used for O and O^-, for the description of the O^{2-} orbitals, too, we obtain the differential correlation-energy contributions, $\Delta\epsilon(O^{2-}) = \epsilon(O^{2-}) - \epsilon(O)$, to the affinity of the extra electrons in crystal O^{2-} which are listed in Table IV.

A first point to make is that at all levels of approximation $\Delta\epsilon(O^{2-})$ comes out considerably smaller than one would expect from a simple linear scaling of $\Delta\epsilon(O^-)$ values [2.77 vs 1.86 eV, at the CCSD(T) level, cf. Table I]; such a linear scaling, which approximately works for the isoelectronic systems $\Delta\epsilon(Ne)$ and $\Delta\epsilon(Ne^+)$,[18] probably fails for O^{2-} due to the increased spacing of excited-state levels, when compressing the O^{2-} charge density in the $(Mg^{2+})_6$ cage. When comparing individual $\Delta\epsilon(O^{2-})$ values in Table IV, we observe that in our single-reference calculations (active space $2s$-$2p$), the effect of single and double excitations is quite similar for ACPF and CCSD, while the inclusion of triples in CCSD(T) yields an increase by another 5%. Thus the effect of triples is of less (relative) importance than in free O^- but is still non-negligible. As in the case of O^-, we checked that enlarging the active space (to $2s$-$3p$) in the ACPF calculations (MRACPF) leads to a result numerically nearly identical to CCSD(T). Moreover, we tested the influence of an increase of the basis set ($[5s4p3d2f] \rightarrow [6s5p4d3f2g]$, cf. Table I); at the CCSD(T) level, the correlation-energy increment changes by -0.008 a.u. (-0.2 eV), in line with our estimate given in Sec. II. We also tried in-

TABLE IV. Intraionic correlation-energy increments and total contribution, $\Delta E_{coh}(MgO)$, of these increments to the cohesive energy of bulk MgO (in atomic units, 1 a.u. = 27.2114 eV).

	ACPF	CCSD	CCSD(T)	Weight[a]
$Mg \rightarrow Mg^{2+}$ [b]	0.04690	0.04690	0.04690	1
$O \rightarrow O^{2-}$ [c]	-0.09548	-0.09646	-0.10162	1
$\Delta E_{coh}(MgO)$[d]	0.04858	0.04956	0.05472	

[a]Weight factor in the incremental expansion of the bulk correlation energy (per primitive unit cell) of MgO.
[b]$(4s4p)$ valence basis set, cf. Table II. PP+CPP description of Mg^{2+}.
[c]$[5s4p3d2f]$ basis set, cf. Table I. Stabilization of O^{2-} by means of six Mg^{2+} pseudopotentials at the nearest-neighbor positions of the MgO crystal ($r_{MgO}=2.105$ Å). Madelung field of outer ions in $7\times7\times7$ cube represented by point charges ± 2.
[d]Correlation-energy change per primitive unit cell, for separation into neutral ground-state atoms.

creasing the $[5s4p3d2f]$ basis set by adding off-center functions [the $(4s4p)$ sets of Sec. II at the positions of the Mg^{2+} ions]; the correlation-energy change of -0.005 a.u. is somewhat smaller here because not all components of the higher polarization functions (f, g) at the oxygen site can be simulated this way. A last test concerns the influence of the Madelung field. Leaving out all of the point charges and performing the calculation with the bare $(O^{2-})(Mg^{2+})_6$ cluster leads to quite negligible correlation-energy changes of $\leq 4 \times 10^{-5}$ a.u. only, at all theoretical levels; this underlines the notion of electron correlation being a local effect. Summarizing, lack of completeness of the one-particle basis set seems to be the largest source of error in the O^{2-} results listed in Table IV, and the order of magnitude of the resulting error for the MgO cohesive energy per unit cell (with respect to separated neutral atoms) can be assessed to 0.2–0.3 eV.

Let us next consider the $Mg \rightarrow Mg^{2+}$ correlation-energy increment. This increment can be evaluated directly using the atomic calculations described in Sec. 2. This is so, since the Madelung effect identically vanishes here, when Mg^{2+} is described by a bare pseudopotential. We checked this point by performing all-electron calculations for Mg^{2+} with and without Madelung field: the non-frozen-core effect obtained thereby is of the order of 1×10^{-6} a.u. with our largest basis set. Thus the pseudopotential approximation is certainly valid here.

Adding the Mg^{2+} and O^{2-} correlation-energy increments of Table IV, we get, at the highest theoretical level [CCSD(T)], a correlation contribution of 0.0547 a.u. to the bulk cohesive energy E_{coh} per (primitive) unit cell of the MgO crystal. The experimental cohesive energy corrected for zero-point energy is known to be 0.3841 a.u.;[19] the most recent (and probably best) HF value is 0.2762 a.u.[6(c)] This yields an "experimental" correlation contribution to E_{coh} of 0.108 a.u. which is just about double the intraionic value calculated so far. Thus it is clear that interionic contributions to be dealt with in the next subsection play an important role.

C. Two-body corrections

In this subsection, nonadditivity corrections are determined, which arise when simultaneously correlating two ions in a cluster.

Let us first consider here the interaction of ions with charges of opposite sign, i.e., Mg^{2+} and O^{2-}, which are next neighbors in the crystal. Using the same cluster as in the previous subsection when determining the intraionic correlation energy of O^{2-} (O^{2-} plus six surrounding Mg^{2+} plus 336 point charges) and adding a core-polarization potential at one of the Mg^{2+} neighbors of the central O^{2-} ion, we obtain an interionic core-valence correlation contribution (cf. Table V) which is due to the dynamic polarization of the Mg^{2+} core by the O^{2-} valence electrons and which was clearly absent in the free Mg^{2+} ion. Although the resulting value for the increment turns out to be considerably smaller than the intraionic correlation contributions of Table IV, its effect on the cohesive energy of MgO is by no means negligible, due to the large weight factor.

In order to study the convergence of the correlation-energy increments with increasing distance of the ions,

TABLE V. Interionic two-body correlation-energy increments and total contribution, $\Delta E_{coh}(MgO)$, of these increments to the cohesive energy of bulk MgO (in a.u.). The notation A-$B \to n$ means that the increment describes an nth-nearest-neighbor pair of A and B ions in the crystal.

	ACPF[a,b]	CCSD[a,b]	CCSD(T)[a,b]	Weight[c]
Mg-O $\to$ 1 [d]	-0.003031	-0.003040	-0.003037	6
Mg-O $\to$ 2 [e]	-0.000082	-0.000083	-0.000084	8
Mg-O $\to$ 3 [f]	-0.000014	-0.000013	-0.000014	24
O-O $\to$ 1 [g]	-0.002740	-0.002538	-0.002973	6
O-O $\to$ 2 [h]	-0.000238	-0.000225	-0.000264	3
O-O $\to$ 3 [i]	-0.000066	-0.000061	-0.000072	12
O-O $\to$ 4 [j]	-0.000027	-0.000024	-0.000029	6
O-O $\to$ 5 [k]	-0.000014	-0.000012	-0.000014	12
$\Delta E_{coh}(MgO)$	0.037454	0.036139	0.039066	

[a]For the definition of the increments, see Eq. (2).
[b]The $(4s4p)$ valence basis set was used for Mg (Table II) and the $[5s4p3d2f]$ basis for O (Table I).
[c]Weight factor in the incremental expansion of the bulk correlation energy (per primitive unit cell) of MgO.
[d]O^{2-} at $(0,0,0)$ with six surrounding Mg^{2+} carrying a PP (one of them an additional CPP) in a $7 \times 7 \times 7$ cube of point charges.
[e]Mg^{2+} carrying a PP+CPP at $(0,0,0)$, O^{2-} at $(1,1,1)$ with a cage of six surrounding Mg^{2+} PP, in a $7 \times 7 \times 7$ cube of point charges.
[f]Same as e, but Mg^{2+} at $(-1,0,0)$ and O^{2-} at $(1,1,0)$.
[g]O^{2-} ions at $(0,0,0)$ and $(0,1,1)$, 10 neighboring Mg^{2+} carrying a PP, remaining ions of a $7 \times 8 \times 8$ cube represented by point charges.
[h]O^{2-} ions at $(\pm 1,0,0)$, 11 Mg^{2+} PP, in a cube of $9 \times 9 \times 9$ ions.
[i]O^{2-} ions at $(0,0,0)$ and $(2,1,1)$, 12 Mg^{2+} PP, in a cube of $9 \times 9 \times 9$ ions.
[j]O^{2-} ions at $(-1,-1,0)$ and $(1,1,0)$, 12 Mg^{2+} PP, in a cube of $9 \times 9 \times 9$ ions.
[k]O^{2-} ions at $(-2,0,0)$ and $(1,1,0)$, 12 Mg^{2+} PP, in a cube of $9 \times 9 \times 9$ ions.

we replaced, in the cluster described above, one of the Madelung charges (at positions of Mg^{2+} ions successively more distant from the central O^{2-} ion) by a pseudopotential and evaluated the influence of core polarization. A rapid decrease with r_{MgO} is observed, with the fourth-nearest-neighbor MgO increment already approaching the numerical noise in our calculations.

Turning now to the increments related to pairs of ions of the same kind, we can safely neglect Mg^{2+}-Mg^{2+} interactions. The correlation-energy contributions are exactly zero, at the pseudopotential plus core-polarization level. All-electron test calculations yield very small values around $\sim 2 \times 10^{-5}$ a.u. for a nearest-neighbor pair of Mg^{2+} ions in the crystal.

Far more important are interactions between O^{2-} ions with their diffuse, fluctuating charge distributions. For the increment between nearest-neighboring O^{2-} ions, we used a cluster with 448 ions, where two central O^{2-} ions were treated explicitly, while the ten next Mg^{2+} neighbors of these ions were simulated by pseudopotentials and the remaining ions were represented by point charges. The nonadditivity correction with respect to two single O^{2-} ions (cf. Table V) turns out to be of the same order of magnitude as the MgO increment. The greater strength of interaction in the O-O case compared to the Mg-O one (larger polarizability of O^{2-} compared to Mg^{2+}) is effectively compensated by the enhanced ion distance.

Results for O^{2-}-O^{2-} increments between 2nd through 5th neighbors are also given in Table V. The decrease with increasing ion distance is not quite as rapid as that for the Mg-O increments. By multiplying the O-O increments by r^{-6}, one can easily check that a van der Waals-like behavior is approached for large r, and one can use the resulting van der Waals constant to obtain an estimate of the neglected increments beyond 5th neighbors; this estimate which is $\sim 3 \times 10^{-4}$ a.u. (including appropriate weight factors) should be considered as an error bar for the truncation of the incremental expansion of the MgO cohesive energy in our calculations.

Adding up all the two-body increments which have been determined in this work, we find (cf. the last row in Table V) that the interionic two-body correlation contribution to the cohesive energy of MgO is of comparable magnitude to the intraionic one. Thus the important conclusion may be drawn that even in a (nearly purely) ionic crystal a mean-field description of interionic interactions (electrostatic attraction, closed-shell repulsion) is not sufficient.

D. Three-body corrections

Let us complete now the information necessary for setting up the incremental expansion of the correlation energy of bulk MgO, by evaluating the most important nonadditivity corrections involving three ions. These corrections are obtained for triples with at least two pairs of ions being nearest neighbors of their respective species, using Eq. (3) (cf. Sec. III A). The numerical results are listed in Table VI. It is seen that the largest three-body corrections are smaller by nearly two orders of magnitude

TABLE VI. Interionic three-body correlation-energy increments and total contribution, $\Delta E_{\mathrm{coh}}(\mathrm{MgO})$, of these increments to the cohesive energy of bulk MgO (in a.u.). The notation A-B-$C \to n$ means that AB and BC are nearest neighbors of their species, while AC are nth neighbors.

	ACPF [a,b]	CCSD[a,b]	CCSD(T)[a,b]	Weight[c]
O-O-O $\to$ 1 [d]	0.000069	0.000063	0.000067	8
O-O-O $\to$ 2 [e]	0.000014	0.000016	0.000013	12
O-Mg-O $\to$ 1 [f]	0.000013	0.000014	0.000016	12
O-Mg-O $\to$ 2 [g]	-0.000023	-0.000022	-0.000026	3
$\Delta E_{\mathrm{coh}}(\mathrm{MgO})$	-0.000807	-0.000798	-0.000806	

[a]For the definition of the increments, see Eq. (3).
[b]The $(4s4p)$ valence basis set was used for Mg (Table II) and the $[5s4p3d2f]$ basis for O (Table I).
[c]Weight factor in the incremental expansion of the bulk correlation energy (per primitive unit cell) of MgO.
[d]O^{2-} ions at positions (1,0,0), (0,1,0), (0,0,1), surrounded by a cage of Mg^{2+} PP each, within a cube of $7 \times 7 \times 7$ ions, with point charges ± 2 simulating the outer ions.
[e]Same as d, but O^{2-} positions (1,0,0), (−1,0,0), (0,0,1).
[f]Mg^{2+} PP+CPP at (0,1,0), O^{2-} ions surrounded by Mg^{2+} cage at (0,0,0) and (0,1,1) in a $7 \times 8 \times 8$ cube of point charges.
[g]Mg^{2+} PP+CPP at (0,0,0), O^{2-} ions surrounded by Mg^{2+} cage at (1,0,0) and (−1,0,0) in a $7 \times 7 \times 7$ cube of point charges.

compared to the leading two-body ones, thus indicating a rapid convergency of the many-body expansion with respect to the number of atoms included; the total three-body contribution to the correlation piece of the bulk cohesive energy E_{coh} is $\sim 2\%$ of the two-body part and of opposite sign.

E. Incremental expansion

In Table VII, the sum of local correlation-energy increments to the cohesive energy E_{coh} of MgO (with respect to separated neutral atoms) is compared to the difference of experimental and HF values for E_{coh}. Our calculated values amount to between $\sim 80\%$ and $\sim 85\%$, depending on the correlation method applied, of the experimental value. The inclusion of triple excitations in the correlation method seems to be significant for describing the large fluctuating O^{2-} ions. A major part of the remaining discrepancy with experiment is probably due to deficiencies of the one-particle basis set: as discussed in Sec. III B, extension of the O^{2-} basis set to include g functions, for the evaluation of the intraionic contribution, already reduces the error by a factor of 2.

A comparison to related theoretical results is possible at the density-functional level. A correlation-energy functional including gradient corrections (Perdew 91) yields a ΔE_{coh} value of 0.087 a.u.,[6(b)] only slightly inferior to our CCSD(T) one. Further density-functional results for lattice energies have been reported in Ref. 7; these results have been determined for fixed HF densities, and the reference of the lattice energies is to Mg^{2+} + O^- + e^-. As already mentioned in Sec. I, the LDA value is much too high (by 0.069 a.u.); the result with the Perdew 91 correlation-energy functional on top of the HF

TABLE VII. Total correlation contribution, $\Delta E_{\mathrm{coh}}(\mathrm{MgO})$, to the bulk cohesive energy per primitive unit cell of MgO with respect to separated neutral atoms, from an expansion using the local increments of Tables IV through VI, compared to the "experimental" value. All data in a.u.

	$\Delta E_{\mathrm{coh}}(\mathrm{MgO})$	
ACPF	0.0852	(79%)
CCSD	0.0849	(79%)
CCSD(T)	0.0930	(86%)
expt.[a]	0.1079	
c-DFT[b]	0.087	

[a]Difference of the experimental (Ref. 19) and the HF value [Ref. 6(c)] of the MgO cohesive energy; the experimental value has been corrected for zero-point energy.
[b]Gradient-corrected correlation-energy density functional, Ref. 6(b).

exchange is much better (error 0.014 a.u.), and the same may be said for an exchange-correlation (xc) DFT treatment with the Becke and Perdew 91 gradient corrections for exchange and correlation, respectively (error 0.011 a.u.). Using the Mg^{2+} and O^- data of Tables I and II, our present calculations lead, at the CCSD(T) level, to a value of 0.071 a.u. for the correlation contribution to the lattice energy; adding this value to the HF result of Ref. 7, a deviation from experiment of 0.009 a.u. is obtained, which is similar to that of the gradient-corrected DFT ones. Note, however, that this comparison must be taken with a grain of salt: the HF calculation of Ref. 7 is certainly not too accurate, since a relatively small basis set was used. Otherwise it would be difficult to explain why our correlation contribution to the lattice energy should be too *large*, although all possible sources of errors (discussed in Secs. III B and III C) point in the opposite direction.

IV. CONCLUSION

The correlation energy of the MgO crystal can be cast into a rapidly convergent expansion in terms of local increments which may be derived from finite-cluster calculations. One-particle basis sets of triple-ζ quality with up to f functions at the positions of the O atoms and high-level quantum-chemical correlation methods [CCSD(T)] are necessary for obtaining $\sim 85\%$ of the correlation contribution to the bulk cohesive energy. About one half of this contribution can be attributed to intraionic interactions; the rest is due—in about equal parts—to dynamic polarization of the Mg^{2+} cores by the O^{2-} ions and to van der Waals–like O^{2-}-O^{2-} interactions.

Although numerical results from quantum-chemical calculations of this type are not necessarily superior to DFT ones, they provide additional physical insight into the sources of correlation contributions to solid-state properties.

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