Cohesive properties of alkali halides

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We calculate cohesive properties of LiF, NaF, KF, LiCl, NaCl, and KCl with *ab initio* quantum chemical methods. The coupled-cluster approach is used to correct the Hartree-Fock crystal results for correlations and to systematically improve cohesive energies, lattice constants, and bulk moduli. After inclusion of correlations, we recover 95–98% of the total cohesive energies. The lattice constants deviate from experiment by at most 1.1%, bulk moduli by at most 8%. We also find good agreement for spectroscopic properties of the corresponding diatomic molecules. [S0163-1829(97)00239-7]

I. INTRODUCTION

One of the earliest methods for a quantitative treatment of the cohesion of ionic solids was the Born-Mayer theory.[1] Löwdin[2] made a first quantum-mechanical approach starting from the symmetrically orthogonalized orbitals of the free ions; these orbitals were used to approximate the density matrix and to calculate the Hartree-Fock energy. Since the advent of density-functional theory and especially the local density approximation, the latter methods have become standards in solid state physics.[3] However, there has also been progress in the development of wave function based methods. Hartree-Fock (HF) calculations can be done routinely nowadays with the help of the program package CRYSTAL,[4] and it is even possible to include electron correlations. One way of achieving that is by multiplying the HF wave function with a Jastrow factor containing several parameters; these parameters can be optimized with the help of Monte Carlo methods.[5] A first attempt to include correlations by means of quantum chemical methods was made using the local ansatz;[6,7] here local excitation operators are applied for modifying the HF wave function. In the past years, an ''incremental scheme'' (an expansion of the total correlation energy in terms of one-body, two-body, three-body, and higher contributions, the so-called ''local increments'') has been developed and successfully applied to semiconductors.[8] This method has been extended to ionic solids and applied to several oxides (MgO, CaO, NiO).[9] Alkali halides are model examples of ionic solids and have recently been carefully investigated at the HF level.[10] The major part of the experimental lattice energy is already recovered at this level. However, the lattice constants significantly deviate from the experimental values, especially for the heavier compounds. We want to show that the incremental scheme can explain the deviations of the HF results from experiment.

II. THE METHOD

A. Incremental scheme

The scheme has been explained in earlier work and we only repeat the main ideas. The correlation energy of the solid is expanded into a sum of local contributions (increments),

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

$\epsilon(A)$ is the correlation energy of a group of localized orbitals (a so-called one-body increment), the nonadditivity $\Delta\epsilon(AB) = \epsilon(AB) - \epsilon(A) - \epsilon(B)$ defining a two-body increment, and so on. Usually, this series is evaluated up to three-body increments. The increments are extracted from clusters containing up to three explicitly described ions (i.e., ions with a high-quality basis set) embedded in a set of pseudo-potentials and point charges. They should be well transferable, which means that they should only weakly depend on the specific cluster chosen for their evaluation (e.g., the value of a one-body increment obtained from a cluster with one explicitly described ion only weakly varies when extracted from a cluster with more than one explicitly described ion). As correlation scheme, we chose the coupled-cluster approach with single and double substitutions[11] (CCSD) with an exponential ansatz for the correlated wave function:

$$|\Psi_{\text{CCSD}}\rangle = \exp\left(\sum_{\substack{a \\ r}} c_a^r a_r^+ a_a + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} a_r^+ a_s^+ a_a a_b \right) |\Psi_{\text{SCF}}\rangle.$$

In addition, we applied the CCSD(T) (Ref. 12) scheme including triple excitations in a perturbative way. All the calculations were done with the *ab initio* program package MOLPRO.[13,14] Localization was done by the Foster-Boys method,[15] and all of the ns, np valence and outercore orbitals of the halide and alkali ions, respectively ($n = 2$ for F, Na and 3 for Cl, K, $1s$ in the case of Li), were correlated.

B. Pseudopotentials and basis sets

The increments are taken from cluster calculations. The ions to be correlated are accurately described with extended basis sets. Negatively charged ions are embedded with X^+ pseudopotentials as next neighbors to simulate the Pauli repulsion. Finally, the system is embedded in a set of point charges (typically $7 \times 7 \times 7$ lattice sites with charges ± 1 in

TABLE I. Electron affinities and ionization potentials in Hartrees (1 H = 27.2114 eV).

System	HF	CCSD	CCSD(T)	Expt. (Ref. 41)
F → F⁻	0.05070	0.11612	0.12192	0.12499
Cl → Cl⁻	0.09505	0.12605	0.12919	0.13276
Li → Li⁺	0.19631	0.19731	0.19733	0.19814
Na → Na⁺	0.18195	0.18785	0.18810	0.18886
K → K⁺	0.14679	0.15637	0.15723	0.15952

the interior and reduced by factors of 2, 4, and 8 at the surface planes, edges, and corners, respectively.[16]) The description of the explicitly treated ions is as follows. We used a $[5s4p3d2f]$ basis[17] for F and a $[6s5p3d2f]$ basis[17] for Cl. For Li, we used a $[5s4p3d2f]$ basis,[17] for Na a $[7s6p5d4f]$ basis (Ref. 18, with d and f functions uncontracted). Finally, for K we used a nine-valence-electron pseudopotential[19] with the corresponding sp basis set (uncontracted) and augmented with $5d$ and $3f$ functions,[20] resulting in a $[7s6p5d3f]$ basis.

III. RESULTS

A. Ionization potentials, electron affinities, and results for the diatomic molecules

In Table I, we give results for atomic electron affinities and ionization potentials. At the correlated level, we obtain good agreement with experiment (to <0.1 eV) in all cases. Results for the diatomic molecules are given in Table II. Again, we obtain nice agreement, to ≤ 0.02 Å (1%) for bond lengths, 24 cm^{-1} (4%) for vibrational frequencies, and 0.1 eV for dissociation energies D_e. Note that we calculated D_e as the difference $E_{atom1}+E_{atom2}-E_{diatomic}$, in contrast to Ref. 21, where the dissociation energy was first calculated with respect to the singly charged ions and then corrected with the help of the experimental electron affinities and ionization potentials. The experimental dissociation energy for NaF from Ref. 22 is probably too high, the experimental value given in Ref. 23 ($D_e=4.97$ eV) and the theoretical value from Ref. 21 are closer to our calculated value.

B. Results for the solid

1. Hartree-Fock calculations

We repeated the CRYSTAL calculations from Ref. 10 with essentially the same basis sets.[24] We calculated both the lattice energy (cohesive energy with respect to the ions) as well as the cohesive energy with respect to the neutral atoms. The lattice energy is already in good agreement with experiment. This is what one would expect since in purely ionic solids (the Mulliken population analysis gives a charge transfer very close to ± 1 in all cases) the Madelung energy makes the most important contribution to the lattice energy; the Madelung energy is already in rough agreement with experiment.[25] However, the cohesive energy with respect to the atoms is less well described as a consequence of the missing intra-atomic correlation effects. Moreover, lattice constants are by up to $\sim 5\%$ too large at the HF level, bulk moduli up to $\sim 21\%$ too small.

TABLE II. Bond lengths R_e (Å), dissociation energies D_e (eV), and vibrational frequencies ω_e (cm^{-1}) of diatomic molecules. The values taken from literature are configuration interaction calculations with single and double substitutions [CI(SD)].

	HF	CCSD	CCSD(T)	Literature (Ref. 21)	Expt. (Ref. 22)
LiF					
R_e	1.555	1.561	1.565	1.571	1.564
ω_e	943	923	910	919	910
D_e	4.12	5.85	5.98	6.12	5.97
NaF					
R_e	1.924	1.925	1.929	1.921	1.926
ω_e	549	517	512	538	536
D_e	3.11	4.77	4.91	5.02	5.36
KF					
R_e	2.204	2.189	2.189	2.184	2.171
ω_e	420	422	421	428	428
D_e	3.29	4.89	5.03	5.10	5.10
LiCl					
R_e	2.037	2.026	2.028	2.033	2.021
ω_e	645	645	642	646	643
D_e	3.85	4.76	4.84	4.86	4.88
NaCl					
R_e	2.390	2.344	2.344	2.366	2.361
ω_e	359	368	367	361	366
D_e	3.26	4.12	4.20	4.23	4.25
KCl					
R_e	2.738	2.692	2.688	2.697	2.667
ω_e	266	276	276	273	281
D_e	3.48	4.21	4.29	4.33	4.36

2. One-body increments

Results for the crystal correlation energies are given in Tables III–VI. Concerning the one-body increments, we obtain nearly the same correlation energy for the free alkali ions and the corresponding embedded ions. This is of course a consequence of the small ionic radii of the cations. In the case of the anions F⁻ and Cl⁻, we find that the absolute value of the correlation energy in the solid is smaller than for the free ion, by up to 0.4 eV. Such an effect was already found in the calculations on the oxides[9] and is explained by the lower level spacing of the excited states for the free ion compared to the embedded ion where excitations are higher in energy.

3. Two-body and three-body increments

The two-body correlation-energy increments decrease rapidly. The decay is compatible with a van der Waals law from second nearest neighbors on, cf. Table VI. By far the largest contributions come from next-neighbor metal-halide (M-X) and halide-halide (X-X) interactions. The total effect of the M-X interatomic correlations is similar for $X=$ F and

TABLE III. Hartree-Fock (HF) and correlated results [CCSD, CCSD(T)], in comparison to density-functional (DFT) and experimental values, for the solids. Cohesive energies E (with respect to neutral atoms) and lattice energies E_{lat} (with respect to free ions) are given in Hartree units, lattice constants a in Å, and bulk moduli B in GPa. Zero point energies have been estimated with a Debye approximation (Debye temperatures taken from Ref. 42) and added to the experimental cohesive energies. The experimental bulk moduli are at 4.2 K and have been taken from Ref. 34 and references therein.

	HF	CCSD	CCSD(T)	DFT	Expt. (Refs. 41, 43 and 34)
LiF					
E_{lat}	0.3975	0.3976	0.3961	0.417,[a] 0.400,[b] 0.365[c]	0.404
E	0.2534	0.3179	0.3222	0.352,[d] 0.345[e]	0.331
a	4.011	3.991	3.993	4.035,[d] 4.05,[e] 3.88,[a] 3.96,[b] 4.13[c]	4.010
B	78.9	70.1	74.9	78.3,[d] 70.5,[e] 95,[a] 83,[b] 60[c]	69.9
NaF					
E_{lat}	0.3496	0.3518	0.3504		0.358
E	0.2186	0.2803	0.2845	0.323,[d] 0.294[e]	0.294
a	4.636	4.601	4.603	4.582,[d] 4.76[e]	4.609
B	52.2	55.7	53.9	55.8,[d] 42.3[e]	51.4
KF					
E_{lat}	0.3028	0.3101	0.3100		0.318
E	0.2076	0.2707	0.2755	0.294[e]	0.283
a	5.450	5.331	5.320	5.40[e]	5.311
B	29.9	34.4	34.8	31.3[e]	34.2
LiCl					
E_{lat}	0.3088	0.3225	0.3241		0.331
E	0.2096	0.2533	0.2580	0.251,[d] 0.265[e]	0.266
a	5.281	5.136	5.124	5.32,[d] 5.08[e]	5.106
B	30.1	35.2	34.8	28[d], 35.2[e]	35.4
NaCl					
E_{lat}	0.2839	0.2960	0.2971	0.304,[a] 0.312,[b] 0.285,[c] 0.307,[f] 0.303,[g] 0.300,[h,i]	0.302
E	0.1978	0.2350	0.2390	0.239,[d] 0.232[e,i]	0.246
a	5.791	5.646	5.634	5.737,[d] 5.75,[e] 5.47,[a] 5.49,[b] 5.83,[c] 5.53,[f] 5.51,[g] 5.54[h,i]	5.595
B	24.5	26.6	26.6	25.5,[d] 22.8,[e] 31,[a] 29,[b] 21,[c] 32.5,[f] 32.1,[g] 30.1[h,i]	26.6
KCl					
E_{lat}	0.2538	0.2687	0.2704		0.275
E	0.2035	0.2398	0.2438	0.249,[d] 0.243[e]	0.248
a	6.548	6.314	6.295	6.30,[d] 6.26[e]	6.248
B	15.5	18.4	21.3	19.7,[d] 18.9[e]	19.7

[a]Reference 38, Hartree-Fock exchange, Perdew and Wang 91 correlation functional (Ref. 44).
[b]Reference 38, LDA exchange and correlation.
[c]Reference 38, Becke exchange (Ref. 45) and Perdew and Wang 91 correlation functional (Ref. 44).
[d]Reference 36, KKR calculation with local exchange and correlation (Ref. 37).
[e]Reference 34, LDA exchange and correlation.
[f]Reference 39, Hartree-Fock exchange, Colle and Salvetti correlation functional (Ref. 46).
[g]Reference 39, Hartree-Fock exchange, Perdew 1986 correlation functional (Ref. 47).
[h]Reference 39, Hartree-Fock exchange, Perdew and Wang 91 correlation functional (Ref. 44).
[i]For further density functional results for NaCl, see also Ref. 39.

$X=$Cl, but for given X increases from Li to K (i.e., with increasing polarizability α of the metal ion) in such a way, that the ratio of the M-X contribution to the X-X contribution changes from <1 to >1 (cf. Tables IV and V). The X-X increments in turn are larger in magnitude for Cl than for F, in agreement with the trend of the respective α values but in contrast to the situation for the intra-atomic difference in correlation energies ϵ(free ion) $- \epsilon$(embedded ion). Quanti-

TABLE IV. Local correlation energies per primitive unit cell (in Hartree) for LiF (at a lattice constant of 3.99 Å), NaF (4.60 Å), and KF (5.34 Å).

	LiF		NaF		KF	
	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)
Free $X^+ \rightarrow$ embedded X^+	-0.000021	-0.000021	-0.000165 [a]	-0.000179 [a]	-0.000013	-0.000016
Free $F^- \rightarrow$ embedded F^-	+0.011776	+0.014782	+0.010106	+0.012820	+0.009684	+0.012352
Sum of F-F increments	-0.007926	-0.009141	-0.003384	-0.003954	-0.001170	-0.001359
Sum of X-F increments	-0.003970	-0.004254	-0.008554	-0.009346	-0.014940	-0.017074
Sum of X-X increments	-0.000018	-0.000018	-0.000198	-0.000210	-0.001422	-0.001605
Sum	-0.000159	+0.001348	-0.002195	-0.000869	-0.007861	-0.007702

[a]See footnote (Ref. 48).

tatively comparing the F-F and Cl-Cl next-neighbor increments from different systems (Table VII) and assuming a purely van der Waals interaction, we find that even in that case the van der Waals law holds surprisingly well. The C_6 coefficient can be determined from the two-body increments. For the sake of simplicity, we assume a purely van der Waals interaction already for next neighbors and for all types of correlations (e.g., also spin-flip processes for Ni-O increments.[9]) The result for $C_6 = \Delta E \times r^6$ obtained this way is comparable to results from literature, e.g., Refs. 26, 27 and references therein.

An estimate of the van der Waals interaction can be obtained using the London formula for dispersion interactions:[28] $E = -\frac{3}{2}\eta[IP_1 IP_2/(IP_1 + IP_2)](\alpha_1 \alpha_2/r^6)$ with the ionization potentials (IP) as characteristic excitation energies and polarizabilities (α) of the two interacting systems (η is of order unity, r is the distance). Polarizabilities and ionization potentials were calculated with the same arrangement as the one-body increments: One ion with the extended basis set was embedded in a set of point charges at the experimental lattice constant (and pseudopotentials as next neighbors, in the case of anions). To evaluate the polarizabilities, we applied a small dipolar field and find values in good agreement with values from literature.[29-31] The ionization potential was calculated with the same cluster, which is certainly a crude approximation because effects such as long-range polarization are not included: the IP obtained this way is *not* what would be experimentally measured for the solid. Our CCSD results for the two-body increments are roughly 2

to 5 times larger (see Table VII) than what is predicted from the London formula. This implies that the London formula can give a qualitative understanding of the magnitude of the interionic interaction and the parameters describing it (α, excitation energies), but is not able to predict results quantitatively. van der Waals interactions in extended systems have also been considered for He (Ref. 32) (see, also, a recent review[33]).

We calculated three-body increments only for KCl (Tables V and VI). We find that they are very small indicating a rapid convergence of the incremental expansion. Neglecting three-body increments is not a serious approximation, therefore.

4. Sum of increments and discussion

The sums of the increments are given in Table III. Including correlations, we obtain 95–98 % of the experimental cohesive energies. The relatively good agreement of the HF lattice energies already mentioned above turns out to be due to a partial error cancellation. When the HF cohesive energies are calculated with respect to the free ions, the corrections due to the missing correlation effects have opposite signs: the one-body contributions diminish the cohesive energy since the absolute value for the free anion is higher than that for the embedded ion; on the other hand, the van der Waals interactions which are also missing at the HF level lead to an increase of the cohesive energy (cf. Tables IV and

TABLE V. Local correlation energies per primitive unit cell (in Hartree) for LiCl (at a lattice constant of 5.14 Å), NaCl (5.65 Å), and KCl (6.30 Å).

	LiCl		NaCl		KCl	
	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)
Free $X^+ \rightarrow$ embedded X^+	-0.000013	-0.000013	-0.000101 [a]	-0.000109 [a]	-0.000005	-0.000005
Free $Cl^- \rightarrow$ embedded Cl^-	+0.002567	+0.003572	+0.002448	+0.003415	+0.002426	+0.003411
Sum of Cl-Cl increments	-0.014439	-0.016785	-0.008124	-0.009495	-0.003732	-0.004368
Sum of X-Cl increments	-0.002712	-0.002906	-0.007112	-0.007746	-0.014992	-0.017066
Sum of X-X increments	absolute value $< 10^{-6}$		-0.000054	-0.000060	-0.000444	-0.000501
Sum of three-body increments					+0.000388	+0.000372
Sum	-0.014597	-0.016132	-0.012943	-0.013995	-0.016359	-0.018157

[a]See footnote (Ref. 48).

TABLE VI. Local correlation energies per primitive unit cell (in Hartree) for KCl at a lattice constant of 6.57 Å. The quantities involving two and three ions are nonadditivity corrections (increments).

	Weight	CCSD	CCSD(T)
Free $K^+ \rightarrow$ embedded K^+	1	-0.000004	-0.000004
Free $Cl^- \rightarrow$ embedded Cl^-	1	+0.002059	+0.002911
Cl(0,0,0)-Cl(0,1,1)	6	-0.002736	-0.003228
Cl(0,0,0)-Cl(2,0,0)	3	-0.000138	-0.000162
Cl(0,0,0)-Cl(2,1,1)	12	-0.000144	-0.000168
Cl(0,0,0)-Cl(2,2,0)	6	-0.000030	-0.000036
K(0,0,0)-Cl(1,0,0)	6	-0.011256	-0.012858
K(0,0,0)-Cl(1,1,1)	8	-0.000320	-0.000360
K(0,0,0)-Cl(2,1,0)	24	-0.000192	-0.000216
K(0,0,0)-K(0,1,1)	6	-0.000318	-0.000360
K(0,0,0)-K(2,0,0)	3	-0.000018	-0.000021
Cl(1,0,0)-Cl(0,1,0)-Cl(0,0,1)	8	+0.000064	+0.000080
Cl(0,0,0)-K(0,1,0)-Cl(0,1,1)	12	+0.000204	+0.000204
Sum		-0.012829	-0.014218

V). The compensation is nearly perfect for LiF, but already for KF the interatomic correlation effects overcompensate the intra-atomic ones by nearly a factor of 2, and the weight is still further shifted in favor of the two-body effects for the MCl crystals, so that for KCl, e.g., a factor of ~6 is reached.

After inclusion of correlations, the lattice constants deviate by at most 1.1% from experiment. As already found in the context of the oxides, the one-body increments would enforce larger lattice constants (the absolute value of the correlation energy of an anion increases when the lattice constant increases because of the lower level spacing at larger lattice constant). The large reduction of the lattice constants, on the other hand, is a two-body effect resulting from the van der Waals interaction between the ions. The CCSD(T) results

TABLE VII. Comparison of CCSD two-body increments ΔE between next neighbors (without multiplying with the weight factor). All results are given in atomic units (except for the lattice constant in column 2). r is the distance between the respective ions in bohr.

| System	Lattice constant a in Å	ΔE	$\Delta E \times r^6$	IP_{cat}	IP_{an}	α_{cat}	α_{an}	$-\dfrac{2}{3}\dfrac{r^6}{\alpha_1\alpha_2}\dfrac{IP_1+IP_2}{IP_1IP_2}\times\Delta E$
F-F (LiF)	3.99	-0.001181	-27.1	2.3	0.52	0.19	5.0	2.8
F-F (NaF)	4.60	-0.000502	-27.1	1.3	0.47	0.97	5.4	2.6
F-F (KF)	5.34	-0.000174	-23.0	0.80	0.42	5.4	5.4	2.5
Cl-Cl (LiCl)	5.14	-0.002155	-226	2.4	0.45	0.19	19	1.9
Cl-Cl (NaCl	5.65	-0.001215	-225	1.4	0.42	0.97	19	2.0
Cl-Cl (KCl)	6.30	-0.000558	-199	0.85	0.39	5.4	18	2.1
O-O (MgO) [a]	4.18	-0.002582	-78.4	2.1	0.38	0.48	9.7	2.9
O-O (CaO) [a]	4.81	-0.001067	-75.2	1.2	0.27	3.1	9.7	3.9
O-O (NiO) [a]	4.17	-0.003356	-100	0.42	0.41	2.8	11.4	2.5
Li-F	3.99	-0.000627	-1.80					3.0
Na-F	4.60	-0.001351	-9.11					3.4
K-F	5.34	-0.002382	-39.3					3.3
Li-Cl	5.14	-0.000440	-5.77					2.8
Na-Cl	5.65	-0.001132	-26.2					2.9
K-Cl	6.30	-0.002392	-106					2.7
Mg-O [a]	4.18	-0.003129	-11.9					5.3
Ca-O [a]	4.81	-0.005906	-52.0					5.2
Ni-O [a]	4.17	-0.009958	-37.3					3.8

[a]Reference 9.
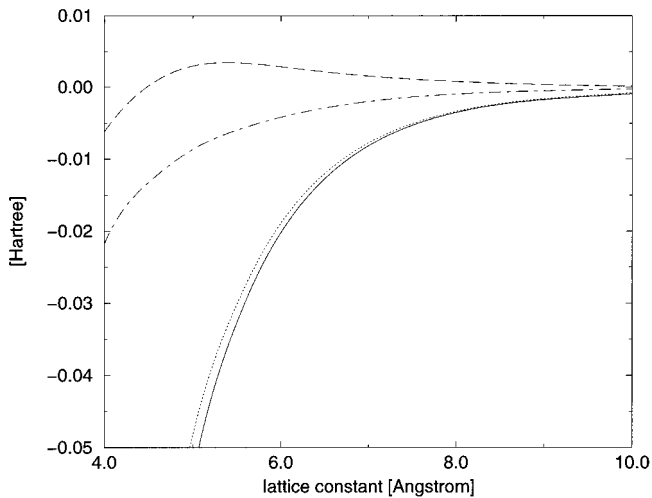
FIG. 1. CCSD correlation energies for KCl as a function of the lattice constant. The two-body increments are already multiplied with the corresponding weight factors. Displayed is the difference of correlation energy ϵ(embedded Cl$^-$) $-\epsilon$(free Cl$^-$) (dashed line, — — —), the two-body increment Cl-Cl for next neighbors (dashed-dotted line, $-\cdot-$), the two-body increment K-Cl for next neighbors (dotted line, $\cdots$), and the sum of these three correlation energies (solid line, ———) which make the most part of the total correlation contribution to the cohesive energy.

turn out to be slightly superior to CCSD.[35]

At a fixed lattice constant, the inclusion of correlations leads to a decrease of the bulk modulus. However, for most of the solids considered here correlations reduce the lattice constant. This means that the HF bulk modulus has to be calculated at a smaller lattice constant where it increases again. As a net result, correlations increase the bulk moduli in most cases. Note that the bulk moduli are more sensitive to the fitting procedure than cohesive energies and lattice constants and that they also have large experimental uncertainties even at room temperature (see the comparison in Ref. 34).

A more detailed account of correlation contributions to the potential-energy surface of KCl is given in Fig. 1, where we display the difference of correlation energies ϵ(embedded Cl$^-$) $-\epsilon$(free Cl$^-$) as a function of the lattice constant, i.e., its variation from free Cl$^-$ to an embedded Cl$^-$ in KCl. Starting from a very small (unrealistic) lattice constant a, the correlation energy ϵ(embedded Cl$^-$) decreases in magnitude with increasing a—excitations into d_{xy}, d_{yz}, d_{xz} orbitals are very important for small a since these orbitals have smaller overlap with the region that is occupied by the K electrons—, then passes through a minimum and increases again because of the argument given earlier (excitations into the diffuse Cl $4p$ orbitals are lower in energy the larger the distance to the K electrons). The next-neighbor K-Cl and Cl-Cl correlation-energy increments also shown in Fig. 1 monotonously decrease with increasing a, for larger distance according to the van der Waals law. The three contributions depicted in Fig. 1 are the most important ones and nearly exhaust the incremental expansion (see Table VI, the remaining increments amount to $\sim$ 1 mH only). The first derivative

of their sum with respect to the lattice constant clearly shows that in total correlations reduce the lattice constant. The second derivative shows that—at fixed lattice constant—correlations reduce the bulk modulus (the one-body increments alone might lead to an increase of lattice constant and bulk modulus, but are outweighed by the two-body increments).

Several density functional calculations are available in the literature for the systems considered. A Korringa-Kohn-Rostoker (KKR) calculation[36] (combined with a local exchange-correlation potential[37]) and more recently a full-potential xc-LDA calculation[34] have been performed. In Refs. 38 and 39 correlation-only density functionals with gradient corrections have been included *a posteriori* (i.e., using the density and nonlocal exchange energy from a Hartree-Fock calculation). The best density functional results are in good agreement with experiment, but it seems to be difficult to choose one single functional as reference method.

In Ref. 40, a large number of alkali halide clusters has been investigated. Bulk properties were extrapolated from cluster calculations by linearly fitting the energy vs $n^{-1/3}$, where n is the number of MX units. The results for the lattice energies E_{lat} are in good agreement with experiment. The predicted correlation corrections are in agreement with our findings for LiF ($\sim$ 0), but different for NaCl (an increase of $|E_{\mathrm{lat}}|$ of $\sim$ 0.003 H is reported, we find $\sim$ 0.013 H at the CCSD level) and KCl ($\Delta|E_{\mathrm{lat}}| \sim -0.011$ H from Ref. 40, we obtain a CCSD value of $\sim$ 0.016 H). The geometries were optimized at the HF level using a $M_{32}N_{32}$ cluster. It was proposed to use the bond length of the interior cube of this cluster as an estimate of the lattice constant of the solid. This leads to a slight underestimation in all cases compared to the HF lattice constants from CRYSTAL calculations. Surface effects are probably the explanation for the differences, since each atom of the interior cube has three next neighbors also residing in the interior cube, but also three next neighbors located at the surface whose charges will be different from interior ions; the Pauli repulsion and the Madelung field are probably not too well reproduced. This is avoided in our approach since a cluster approach is applied at the correlated level only, and even there all explicitly treated ions are surrounded by pseudopotentials (or point charges) simulating bulk cations (or anions).

IV. CONCLUSION

We have shown that the method of local increments can successfully be applied for the determination of bulk electron-correlation effects in alkali halides. The main shortcoming of the Hartree-Fock approximation is the missing interionic van der Waals interaction which results in too large lattice constants (by up to 5%). After including correlations at the coupled-cluster level, the deviations of the lattice constant from the experimental values are reduced to a maximum of 1.1%. We obtain between 95 and 98 % of the cohesive energies with respect to neutral atoms or 97–98 % of the lattice energies. Bulk moduli exhibit satisfactory agreement with experiment, with a maximum deviation of $\sim$ 8%.

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