Cohesive properties of alkali halides

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We calculate cohesive properties of LiF, NaF, KF, LiCl, NaCl, and KCl with \textit{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.

I. INTRODUCTION

One of the earliest methods for a quantitative treatment of the cohesion of ionic solids was the Born-Mayer theory. L"owdin 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. However, there has also been progress in the development of wavefunction based methods. Hartree-Fock (HF) calculations can be done routinely nowadays with the help of the program package CRYSTAL, and it is even possible to include electron correlations. One way of achieving that is by multiplying the HF wavefunction with a Jastrow factor containing several parameters; these parameters can be optimized with the help of Monte-Carlo methods. A first attempt to include correlations by means of quantum chemical methods was made using the Local Ansatz, here local excitation operators are applied for modifying the HF wavefunction. In the last 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. This method has been extended to ionic solids and applied to several oxides (MgO, CaO, NiO). Alkali halides are model examples of ionic solids and have recently been carefully investigated at the HF level. 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)

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

$\epsilon(A)$ is the correlation energy of a group of localized orbitals (a so-called one-body increment), the non-additivity $\Delta \epsilon(AB) = \epsilon(AB) - \epsilon(A) - \epsilon(B)$ 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 pseudopotentials 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 (CCSD) with an exponential ansatz for the correlated wavefunction:

$$
|\Psi_{\text{CCSD}}| = \exp \left( \sum_r c_r a_r^+ a_r + \sum_{a<b} c_{ab} a_r^+ a_s^+ a_r a_s \right) |\Psi_{\text{SCF}}|.
$$

In addition, we applied the CCSD(T) scheme including triple excitations in a perturbative way. All the calculations were done with the \textit{ab-initio} program package MOLPRO. Localization was done by the Foster-Boys
method\textsuperscript{25} and all of the \textit{ns, np} valence and outer-core orbitals of the halide and alkali ions, respectively, (\textit{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\textsuperscript{+} 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 \pm 1 in the interior and reduced by factors of 2, 4 and 8 at the surface planes, edges and corners, respectively). The description of the explicitly treated ions is as follows. We used a [5s4p3d2f] basis\textsuperscript{5} for F and a [6s5p3d2f] basis\textsuperscript{4} for Cl. For Li, we used a [5s4p3d2f] basis\textsuperscript{4} for Na a [7s6p5d4f] basis (Ref. \textsuperscript{23}, with \textit{d} and \textit{f} functions uncontracted). Finally, for K we used a 9-valence-electron pseudopotential\textsuperscript{25} with the corresponding \textit{sp} basis set (uncontracted) and augmented with 5 \textit{d} and 3 \textit{f} functions\textsuperscript{26}, 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 \(< 0.02\) \AA\ (1\%) for bond lengths, 24 cm\textsuperscript{-1} (4\%) for vibrational frequencies, and 0.1 eV for dissociation energies \(D_c\). Note that we calculated \(D_c\) as the difference \(E_{\text{atom}1} + E_{\text{atom}2} - E_{\text{diatomic}}\), in contrast to Ref. \textsuperscript{24}, 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. \textsuperscript{22} is probably too high, the experimental value given in Ref. \textsuperscript{24} (\(D_c = 4.97\) eV) and the theoretical value from Ref. \textsuperscript{24} are closer to our calculated value.

B. Results for the solid

1. Hartree-Fock calculations

We repeated the CRYSTAL calculations from Ref. \textsuperscript{11} with essentially the same basis sets\textsuperscript{11}. 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 \pm 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\textsuperscript{12}. 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.

2. One-body increments

Results for the crystal correlation energies are given in Tables III, IV, V, 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\textsuperscript{−} and Cl\textsuperscript{−}, 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\textsuperscript{4} 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 VII. 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 inter-atomic correlations is similar for X = F and X = Cl, but for given X increases from Li to K (i.e. with increasing polarizability \(\alpha\) 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 VII, VIII). The X-X increments in turn are larger in magnitude for Cl than for F, in agreement with the trend of the respective \(\alpha\) values but in contrast to the situation for the intra-atomic difference in correlation energies \(\epsilon\) (free ion)\textsuperscript{−} \(\epsilon\) (embedded ion). Quantitatively 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\textsuperscript{28}). The result for \(C_6 = \Delta E \times r^6\) obtained this
An estimate of the van der Waals interaction can be obtained using the London formula for dispersion interactions:

\[
E = -\frac{3}{2} \eta \frac{IP_1 IP_2}{r^{1+\alpha}}
\]

with the ionization potentials (IP) as characteristic excitation energies and polarizabilities (\(\alpha\)) of the two interacting systems (\(\eta\) 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 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. 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 II) 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 (\(\alpha\), excitation energies), but is not able to predict results quantitatively. Van der Waals interactions in extended systems have also been considered for H₂O (see also a recent review). We calculated three-body increments only for KCl (Tables III and IV). 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 to 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 at high force 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).

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 turn out to be slightly superior to CCSD(T).

At fixed lattice constant, 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 \(\epsilon(\text{embedded } \text{Cl}^-) - \epsilon(\text{free } \text{Cl}^-)\) 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, the correlation energy \(\epsilon(\text{embedded } \text{Cl}^-)\) 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 pass 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 IV, 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 literature for the systems considered. A KKR calculation (combined with a local exchange-correlation potential) and more recently a full-potential xc-LDA calculations have been performed. In Refs. 38, 39 correlation-only density functionals with gradient corrections have been included a posteriori (i.e. using the
density and non-local 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. [44] 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 \( E_{\text{lat}} \) 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 \( |E_{\text{lat}}| \) of \( \sim 0.003 \) H is reported, we find \( \sim 0.013 \) H at the CCSD level) and KCl (\( |E_{\text{lat}}| \) \( \sim -0.011 \) 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 inter-ionic 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 to 98 % of the lattice energies. Bulk moduli exhibit satisfactory agreement with experiment, with a maximum deviation of \( \sim 8 \% \).

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1 see, e.g., M. P. Tosi: *Solid State Physics*, Vol. 16, edited by F. Seitz and D. Turnbull (Academic, New York, 1964).
For KF, we optimized one \( d \)-exponent for K (0.54), for KCl we optimized one \( d \)-exponent for K (0.44) and one \( d \)-exponent for Cl (0.5, a more diffuse exponent led to numerical instabilities). The misprints of the original paper (Ref. [9], +0.1222 instead of -0.1222 in the F basis set, and +0.0082 instead of -0.082 in the Cl basis set) have been corrected. To calculate the energies of the neutral Li, Na, and K atoms, enhanced basis sets have to be used, we enlarged the basis sets by one more \( sp \) exponent.

As already pointed out in Ref. [9], the triples correction within CCSD(T) is only exact for canonical orbitals. Since we have to used localized orbitals, we estimated the error as described in previous work and did not find it to be a significant error.

| System | HF      | CCSD    | CCSD(T) | exp. [9] |
|--------|---------|---------|---------|---------|
| 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 difference in correlation energies free Na\(^{+}\) → embedded Na\(^{+}\) is relatively large compared to Li and K. This changes when the Na basis set is taken uncontracted. Of course, the error for the total energy is negligibly small. We did not find any other artifact of the contraction.
TABLE II. Bond lengths $R_e$ (Å), dissociation energies $D_e$ (eV) and vibrational frequencies $\omega_e$ (cm$^{-1}$) of diatomic molecules. The values taken from literature are CI(SD) calculations.

|           | RHF  | CCSD | CCSD(T) | literature | expt  |
|-----------|------|------|---------|------------|-------|
| **LiF**   |      |      |         |            |       |
| $R_e$     | 1.555| 1.561| 1.565   | 1.571      | 1.564 |
| $\omega_e$| 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 |
| $\omega_e$| 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 |
| $\omega_e$| 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 |
| $\omega_e$| 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 |
| $\omega_e$| 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 |
| $\omega_e$| 266  | 276  | 276     | 273        | 281   |
| $D_e$     | 3.48 | 4.21 | 4.29    | 4.33       | 4.36  |
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 |
|--------|-------|------|---------|------|------|
| LiF    |       |      |         |      |      |
| $E_{lat}$ | 0.3975 | 0.3976 | 0.3961 | 0.417$^d$, 0.400$^b$, 0.365$^c$ | 0.404 |
| $a$    | 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 |
| $a$    | 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 |
| $a$    | 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 |
| $a$    | 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 |
| $a$    | 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 |
| $a$    | 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 |

$^a$Ref. 38, Hartree-Fock exchange, Perdew and Wang 91 correlation functional
$^b$Ref. 38, LDA exchange and correlation
$^c$Ref. 38, Becke exchange$^{39}$ and Perdew and Wang 91 correlation functionality
$^d$Ref. 36, KKR calculation with local exchange and correlation
$^e$Ref. 34, LDA exchange and correlation
$^f$Ref. 39, Hartree-Fock exchange, Colle and Salvetti correlation functional
$^g$Ref. 39, Hartree-Fock exchange, Perdew 1986 correlation functional
$^h$Ref. 39, Hartree-Fock exchange, Perdew and Wang 91 correlation functional

For further density functional results for NaCl, see also Ref. 39.
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⁺ → embedded X⁺ | -0.000021 | -0.000021     | -0.000165*  | -0.000179*     | -0.000013 | -0.000016     |
| free F⁻ → 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     | -0.00198   | -0.002015     | -0.001422 | -0.001605     |
| sum             | -0.000159 | +0.001348     | -0.002195  | -0.000869     | -0.007861 | -0.007702     |

*See footnote (Ref. 48).

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⁺ → embedded X⁺ | -0.000013 | -0.000013     | -0.000101*  | -0.000109*     | -0.000005 | -0.000005     |
| free Cl⁻ → 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             | -0.014597 | -0.016132     | -0.012943  | -0.013995     | -0.016359 | -0.018157     |

*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 2 and 3 ions are non-additivity corrections (increments).

|                  | weight | CCSD   | CCSD(T)  |
|------------------|--------|--------|----------|
| free K⁺ → embedded K⁺ | 1      | -0.000004 | -0.000004 |
| free Cl⁻ → 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 |
TABLE VII. Comparison of CCSD two-body increments $\Delta E$ 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 | $\Delta E$ | $\Delta E \times r^6$ | $IP_{\text{cat}}$ | $IP_{\text{an}}$ | $\alpha_{\text{cat}}$ | $\alpha_{\text{an}}$ | $-\frac{2}{3} \frac{r^2}{\alpha_{\text{cat}} \alpha_{\text{an}}} IP_{\text{cat}}^2 IP_{\text{an}}^2 \times \Delta E$ |
|-----------------|---------------------------|-------------|-------------------------|-------------------|-------------------|--------------------|--------------------|---------------------------------|
| 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               | 3.4               | 3.3                | 3.3                | 3.3                             |
| Na-F            | 4.60                      | -0.001351   | -9.11                   | 3.4               | 3.4               | 3.4                | 3.4                | 3.4                             |
| K-F             | 5.34                      | -0.002382   | -39.3                   | 3.3               | 3.3               | 3.3                | 3.3                | 3.3                             |
| Li-Cl           | 5.14                      | -0.000440   | -5.77                   | 2.8               | 2.8               | 2.8                | 2.8                | 2.8                             |
| Na-Cl           | 5.65                      | -0.001132   | -26.2                   | 2.9               | 2.9               | 2.9                | 2.9                | 2.9                             |
| K-Cl            | 6.30                      | -0.002392   | -106                    | 2.7               | 2.7               | 2.7                | 2.7                | 2.7                             |
| Mg-O$^a$        | 4.18                      | -0.003129   | -11.9                   | 5.3               | 5.3               | 5.3                | 5.3                | 5.3                             |
| Ca-O$^a$        | 4.81                      | -0.005906   | -52.0                   | 5.2               | 5.2               | 5.2                | 5.2                | 5.2                             |
| Ni-O$^a$        | 4.17                      | -0.009958   | -37.3                   | 3.8               | 3.8               | 3.8                | 3.8                | 3.8                             |

$^a$ Ref. 9