Hydrogen bonding in infinite hydrogen fluoride and hydrogen chloride chains

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Hydrogen bonding in infinite (HF)$_\infty$ and (HCl)$_\infty$ bent (zigzag) chains is studied using the \textit{ab initio} coupled-cluster singles and doubles (CCSD) correlation method. The correlation contribution to the binding energy is decomposed in terms of nonadditive many-body interactions between the monomers in the chains, the so-called energy increments. Van der Waals constants for the two-body dispersion interaction between distant monomers in the infinite chains are extracted from this decomposition. They allow a partitioning of the correlation contribution to the binding energy into short- and long-range terms. This finding affords a significant reduction in the computational effort of \textit{ab initio} calculations for solids as only the short-range part requires a sophisticated treatment whereas the long-range part can be summed immediately to infinite distances.

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I. INTRODUCTION

Hydrogen fluoride\textsuperscript{1,2,3,4,5,6} and hydrogen chloride\textsuperscript{7,8,9} are representatives of molecular crystals; the electronic structure of the constituent HF or HCl monomers is essentially preserved upon crystallization. The monomers in both crystals are hydrogen bonded\textsuperscript{10,11,12,13,14} it is a directional and anisotropic bonding of the hydrogen in a HF and HCl monomer to the fluorine or chlorine atom, respectively, of a neighboring monomer. The bonding is caused by a partial withdrawal of charge from the hydrogen atom due to the high electronegativity of the fluorine or chlorine atoms\textsuperscript{10,11,12,13,14}. Hydrogen bonds are intermediates between ionic bonding and van der Waals bonding and are of great importance for the physical and chemical properties of many organic and inorganic crystals. Moreover, they turn out to be crucial for the structural chemistry of many biopolymers such as proteins and nucleic acids\textsuperscript{10,11,12,13,14}.

At low temperature, HF and HCl crystals are structurally very similar. While HF forms strong hydrogen bonds, HCl forms weak hydrogen bonds. Therefore, HF and HCl represent good candidates for a thorough analysis of this special type of bonding in crystals. The monomers in both compounds are found to be arranged in terms of parallel zigzag chains with a large interchain distance and, hence, a weak interchain interaction [see Sec. III for details]. Frequently, a single infinite chain is considered as a simple but realistic model of the crystals. The isolated (HF)$_\infty$ chain has fascinated many theoreticians and much work has been carried out dealing with it; namely, model studies\textsuperscript{15,16} semiempirical (intermediate neglect of differential overlap) examinations of (HF)$_\infty$ by Zunger\textsuperscript{17} density functional theory calculations [local density approximation] of Springborg\textsuperscript{18} and \textit{ab initio} investigations\textsuperscript{19,20,21,22,23,24,25,26,27,28,29,30,31,32,33}. In contrast, the (HCl)$_\infty$ chain has not been investigated very extensively; there are only a few \textit{ab initio} examinations\textsuperscript{20,21,34,35}. For both isolated chains the zigzag geometry of Fig. 1 is the energetically favored arrangement in comparison with the linear geometry. For (HF)$_\infty$ chains this has been shown in early studies of Karpfen \textit{et al.}\textsuperscript{19,23} and Beyer and Karpfen\textsuperscript{25}. The structure of isolated (HCl)$_\infty$ chains is investigated in Ref. 33.

The large number of \textit{ab initio} studies that have been carried out for the chains also exhibits how challenging hydrogen-bonded systems are. An accurate treatment of hydrogen bonds requires both a good electron correlation method and a large one-particle basis set\textsuperscript{32,33,35}. Hence, in Refs. 32,33,35 we applied basis set extrapolation schemes—which are powerful methods to improve the accuracy of both Hartree-Fock and correlation energies for small molecules—to extended systems, showing their validity and usefulness also in this situation. Thereby, a periodic Hartree-Fock treatment was accompanied by correlation calculations.

We use the coupled-cluster singles and doubles (CCSD) correlation method\textsuperscript{36} in conjunction with the incremental scheme\textsuperscript{38,39,40,41,42} which has been used in many applications and yields a physically meaningful many-body decomposition of the correlation energy. It has been applied to a few one-dimensional systems before: the trans-polyacetylene polymer\textsuperscript{43} the infinite lithium hydride chain\textsuperscript{44} the beryllium hydride polymer\textsuperscript{44} and poly(para-phenylene)\textsuperscript{45} In the context of the present paper, the contributions of Doll \textit{et al.}\textsuperscript{46,47,48,49} who studied ionic solids, as well as the investigations of rare-gas...
crystals by Rościszewski et al.\textsuperscript{50,51} are worth mentioning because hydrogen-bonded crystals fall in between these two types of bonding.

This paper is structured as follows. The CCSD electron correlation method and the incremental scheme are introduced in Sec. II whereas Sec. III describes geometries, basis sets, and the computer programs employed. In Sec. IV, we discuss electron correlation effects and their implications. The contributions to the binding energy of the \((\text{HF})_\infty\) and \((\text{HCl})_\infty\) chains are evaluated in Sec. V and conclusions are drawn in Sec. VI.

II. THEORY

We choose the Hartree-Fock approximation as a starting point to study electron correlations, employing the full non-relativistic Hamiltonian of the chains within the fixed-nuclei approximation.\textsuperscript{33,41,42,52,53} The resulting Hartree-Fock Bloch orbitals are transformed to Wannier orbitals because the latter provide a more appropriate, local representation of the Hamiltonian for a subsequent treatment of electron correlations.\textsuperscript{31,42,54} The ground-state wave function is modeled by the coupled-cluster ansatz:\textsuperscript{42}

\[
|\Psi_0^N\rangle = e^T |\Phi_0^N\rangle
\]  

which relates the \(N\)-electron Hartree-Fock ground-state wave function \(\Phi_0^N\) to the correlated ground-state wave function \(\Psi_0^N\) employing the cluster operator \(T\). For the calculations in this study, it is sufficient to restrict \(T\) to single and double excitations, resulting in the coupled-cluster singles and doubles (CCSD) scheme\textsuperscript{37,55}

\[
\hat{T} = \sum_{\bar{R}_{\kappa_1} \subset \bar{R}_{\kappa_2}} t_{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}}^{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}} \hat{c}_{\bar{R}_{\kappa_1}} \hat{c}_{\bar{R}_{\kappa_2}}
\]  

The coefficients \(t_{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}}^{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}}\) and \(t_{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}}^{\bar{R}_{\kappa_1} \bar{R}_{\kappa_2}}\) are referred to as excitation amplitudes. Let \(r\) and \(s\) denote spatial and spin coordinates; then \(\hat{c}_{\bar{R}_{\kappa_1}}\) creates electrons in virtual spin Wannier orbitals \(w_{\bar{R}_{\kappa_1}}(\bar{r}s)\) whereas \(\hat{c}_{\bar{R}_{\kappa_1}}\) annihilates electrons from occupied spin Wannier orbitals \(w_{\bar{R}_{\kappa_1}}(\bar{r}s)\). Here \(\bar{R}_1\) and \(\bar{R}_2\) denote the unit cell in which the Wannier orbital is located and \(\alpha_1\) and \(\kappa_1\) refer to Wannier orbital indices. Assuming Born-von Kármán boundary conditions, the correlation energy per unit cell \(E_{\text{corr}}\) is given by

\[
N_0 E_{\text{corr}} = \langle \Psi_0^N \mid \hat{H} \mid \Psi_0^N \rangle - \langle \Phi_0^N \mid \hat{H} \mid \Phi_0^N \rangle,
\]

where \(N_0\) is the number of unit cells in the chains.

Occupied Wannier orbitals are grouped in terms of \(n_{\text{one}}\) pairwise disjunct one-body orbital sets which are defined by

\[
\bar{R}_l \in \{w_{\bar{R}_\alpha}(\bar{r}s) \mid \alpha \in I_l\}
\]

for \(l = 1, \ldots, n_{\text{one}}\).

The expression for the correlation energy of a crystal is rearranged and decomposed in terms of correlation energies \(\varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K}\) of the electrons from the one-body orbital sets \(\bar{R}_1 I_1 \cdots \bar{R}_K I_K\). The resulting formula for the correlation energy of the chains per unit cell \(E_{\text{corr}}\) reads\textsuperscript{33,38,39,40,41,42,43,44,45}

\[
N_0 E_{\text{corr}} = \frac{1}{N_0} \sum_{\bar{R}_1 I_1} \Delta \varepsilon_{\bar{R}_1 I_1} + \frac{1}{N_0^2} \sum_{\bar{R}_1 I_1 \neq \bar{R}_2 I_2} \Delta \varepsilon_{\bar{R}_1 I_1 \bar{R}_2 I_2} + \cdots + \frac{1}{N_0^K} \sum_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K} \Delta \varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K} + \cdots
\]

The one-body \(\Delta \varepsilon_{\bar{R}_1 I_1}\), the two-body \(\Delta \varepsilon_{\bar{R}_1 I_1 \bar{R}_2 I_2}\), \ldots, up to the \(K\)-body \(\Delta \varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K}\), \ldots energy increments are defined recursively by\textsuperscript{33,38,39,40,41,42,43,44,45}

\[
\Delta \varepsilon_{\bar{R}_1 I_1} = \varepsilon_{\bar{R}_1 I_1},
\]

\[
\Delta \varepsilon_{\bar{R}_1 I_1 \bar{R}_2 I_2} = \varepsilon_{\bar{R}_1 I_1 \bar{R}_2 I_2} - \Delta \varepsilon_{\bar{R}_1 I_1} - \Delta \varepsilon_{\bar{R}_2 I_2},
\]

\[
\vdots
\]

\[
\Delta \varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K} = \varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K} - \sum_{n=1}^{K-1} \frac{1}{n!} \sum_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K} \Delta \varepsilon_{\bar{R}_1 I_1 \cdots \bar{R}_K I_K}.
\]
The factors $\frac{1}{\beta_1}, \frac{1}{\beta_2}, \ldots, \frac{1}{\beta_n}$ in front of the sums on the right-hand side of Eq. (5) account for permutations among the one-body orbital sets of a certain $K$-body energy increment ($K \geq 2$). One can eliminate all permutations that lead to the same energy increment by letting the sums in Eq. (5) run only over distinct sets of one-body orbital sets.

The translational relation of the Wannier orbitals leads to the translational symmetry of the energy increments, i.e., $\Delta \varepsilon_{\beta_1 t_1 \ldots \beta_k t_k} = \Delta \varepsilon_{\beta_1 t_1 \ldots \beta_k t_k}$. This can be exploited in Eq. (5) to make the right-hand side of Eq. (5) independent of the first lattice sum $\sum_{\beta_1}$, which for this reason, is $N_0$ times the sum of the translational symmetry-adapted energy increments. It allows us to eliminate the factor $N_0$ in front of the left-hand side of Eq. (5) and enormously reduces the number of energy increments that need to be calculated to describe the chains with a given accuracy.

The localized occupied molecular orbitals of oligomers, comprising a few monomers arranged in the geometry of the infinite chains, are found to be a good approximation to the Wannier orbitals of infinite chains and crystals.38,39,40,41,42,43,44,45 This facilitates the determination of the correlation contribution to the binding energy of infinite chains from the energy increments in oligomers using Eq. (5). Yet the virtual Wannier orbitals involved in the determination of the energy increments, and implicitly contained in Eq. (6), are replaced by all the virtual canonical molecular orbitals of the oligomers. The procedure outlined in this paragraph is termed the incremental scheme.38,39,40,41,42

III. COMPUTATIONAL DETAILS

Hydrogen fluoride and hydrogen chloride crystallize in an orthorhombic low-temperature phase described by the space groups $Bm\bar{2}a$ for HF12 and $Bb\bar{2}1m$ for HCl.7,8,9 The unit cells of both crystals contain four monomers which are arranged in terms of weakly interacting parallel zigzag chains [Fig. 1]. The chains are described by a unit cell which comprises two monomers and are considered as an excellent one-dimensional model for HF and HCl crystals.15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35

The structure of a single chain is determined by three parameters, the $\mathbf{H} \cdots \mathbf{X}$ distance $r$, the $\mathbf{X} \cdots \mathbf{X}$ distance $R$, and the angle $\alpha = \angle (\mathbf{H}X\mathbf{X})$, $\mathbf{X} = \mathbf{F}, \mathbf{Cl}$. Experimental values for the parameters are $r = 0.92$ Å, $R = 2.50$ Å, and $\alpha = 120^\circ$ for (HF)$_\infty$9,56 and $r = 1.25$ Å, $R = 3.688$ Å, and $\alpha = 93.3^\circ$ for (DCl)$_\infty$.7 HCl and deuterated DCl crystals have very similar lattice constants and are considered to be isomorphous.7 Unfortunately, further structural information for HCl crystals is unavailable.

To calculate the energy increments in Eq. (5), we perform molecular calculations on oligomers (HF)$_n$ and (HCl)$_n$, respectively, i.e., short fragments of the chains. We utilize the program package MOLPRO57 employing Foster-Boys localization58,59 of the molecular orbitals and the coupled-cluster singles and doubles (CCSD) correlation method.77,78,79 Thereby, we are consistent with Refs. 32,33 where also the CCSD method was employed. We use the aug-cc-pVDZ basis set61,62,63,64 which yields somewhat less accurate total binding energies than those obtained in Refs. 32,33. Yet we are mainly interested in the long-range behavior of electron correlations in the hydrogen-bonded chains; it is well described by the aug-cc-pVDZ basis set due to vanishingly small geometrical orbital overlaps among the one-body orbital sets in the $K$-body energy increments considered. In fact, the modulus of the two-body energy increment involving the third-nearest-neighbor monomer $|\varepsilon_{\beta_3}|$, as obtained with the aug-cc-pVDZ basis set $61,62,63,64$ is smaller by 2% for (HF)$_\infty$ and by 4% for (HCl)$_\infty$ than $|\varepsilon_{\beta_3}|$ obtained with the larger aug-cc-pVTZ basis set61,62,63,64 [Sec. IV]. Similarly, $K$-body energy increments for $K \geq 3$ agree well as soon as the geometrical orbital overlaps between the one-body orbital sets become negligible.

In Tab. III below, reference is made to periodic Hartree-Fock calculations of (HF)$_\infty$ and (HCl)$_\infty$ chains, described in Refs. 32,33, which were carried out with the CRYSTAL program.65,66,67 For these calculations, the $f$, $g$, $h$, $i$ functions were removed from the basis sets. To estimate the influence of the neglected basis functions on the total binding energy of the chains, we use MOLPRO57 to calculate the Hartree-Fock binding energy per monomer for (HF)$_9$ and (HCl)$_9$ both with and without $f$, $g$, $h$ functions using the cc-pV5Z basis set $61,63,64$ at the Hartree-Fock level it is close to completeness with respect to basis functions with the angular momenta $s$, $p$, $d$. The binding energies of both chains obtained with $f$, $g$, $h$ functions are smaller by $\approx 13 \mu$E$_h$ than those determined without them. This deviation turns out to be sufficiently small to be neglected in the subsequent calculation of total binding energies in Sec. VI. However, note that for the correlation calculations the $f$, $g$, $h$ functions are fully considered.

The calculated binding energies reported here account for the basis set superposition error (BSSE) by the counterpoise correction (CP); it is determined by surrounding an isolated HF or HCl monomer by sufficiently many ghost atoms positioned in the geometry of the infinite chains.68,69
FIG. 2: (Color online) One-body energy increments $\Delta \varepsilon_0$ of $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$ chains as determined in oligomers of varying length reduced by the CP-corrected correlation energy $E_{\text{corr mon}}$ of the corresponding isolated monomer. The mean value of the two innermost energy increments of the oligomers is taken. Circles stand for $(\text{HF})_{\infty}$ and squares for $(\text{HCl})_{\infty}$ data. Open symbols refer to oligomers surrounded by point charges whereas closed symbols denote isolated oligomers.

IV. ELECTRON CORRELATIONS

A. Transferability

We have to ensure that the Foster-Boys-localized molecular orbitals, which are extracted from oligomers are a good approximation to the Wannier orbitals of the infinite $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$ chains. They have to be approximately translationally related within a certain oligomer and must not differ substantially among oligomers of varying length. These two properties of the localized occupied molecular orbitals are termed transferability. In order to achieve transferability for moderately sized molecular clusters, one is frequently obliged to account for the omitted monomers in terms of an appropriate substitute. In the case of $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$, two options offer themselves. On the one hand, both chains are cut out from a molecular crystal, implying no substitutes as in rare-gas crystals; on the other hand, particularly $(\text{HF})_{\infty}$ is rather ionic and a surrounding by point charges can be envisaged to create the embedding which adequately models the infinite chains.

I explore both possibilities to elucidate what kind of procedure is adequate for hydrogen-bonded solids. The virtual orbitals of the oligomers are not altered and remain canonical molecular orbitals in the calculation of the individual energy increments. The oligomer approximation thus corresponds to a sort of domain decomposition of the virtual space which also is applied in other local correlation methods.

In the case of $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$, the outer and inner valence orbitals, i.e., eight electrons, are assigned to the one-body orbital set representing a particular HF or HCl monomer. To test the transferability, we calculate all one-body energy increments and all two-body energy increments between two adjacent monomers, the so-called connected two-body energy increments, in isolated oligomers $(\text{HF})_n$ and $(\text{HCl})_n$ for $n = 2, 4, 6, 10$. They are compared with the energy increments from the oligomers which were surrounded by point charges up to twentieth-nearest neighbors. The hydrogen atoms are represented by $q = +1$; fluorine and chlorine atoms are described by $q = -1$ with the exception of the terminal charges which are set to $q = -\frac{1}{2}$.

Comparing the one-body and the connected two-body energy increments obtained in oligomers of varying length in Figs. 2 and 3, we observe a rapid convergence of their values toward the limit of the infinite chains where the values determined for the isolated oligomers and the values resulting from the point-charge-embedded oligomers approach each other quickly. The energy increments taken from the isolated oligomers increase (decrease) in Fig. 2 (Fig. 3) monotonically with the oligomer length whereas the embedding with point charges causes an unsystematic but quicker convergence. The convergence behavior of the individual curves in Figs. 2 and 3 is governed by a small variation in the localized orbitals and, predominantly, by the improvement of the electronic structure which approaches rapidly the electronic structure of the infinite chains with increasing length of the oligomers. Obviously, the decision whether to employ point charges or not has only a small impact on the values of the energy increments. The one-body (two-body) energy increments differ by $67 \mu E_h$ ($14 \mu E_h$) in $(\text{HF})_{\infty}$ and by $22 \mu E_h$ ($31 \mu E_h$) in $(\text{HCl})_{\infty}$. In what follows only energy increments taken from isolated oligomers are considered, as in Refs. 32, 33.
and at most by 11
and (HCl)∞ to represent the electronic structure of infinite (HF)∞ of the HCl monomer, ∞ first. The most relevant energy increments of (HF)∞ relative energy of the HF monomer, (HCl)∞ magnitude by 1
(Fig. 4) with either odd or even cardinal numbers n, respectively, to Eq. (7). All data are given in millihartrees.

| Increment | (HF)∞ | (HCl)∞ |
|-----------|-------|--------|
| ∆ε0      | −223.3632 | −175.0985 |
| ∆ε01     | −4.0879  | −2.8213 |
| ∆ε02     | −0.0861  | −0.1347 |
| ∆ε012    | −0.0163  | 0.0014 |
| ∆ε03     | −0.0063  | −0.0092 |
| ∆ε013    | −0.0015  | −0.0016 |
| ∆ε0123   | 0.0003   | 0.0006 |

TABLE I: Exemplary energy increments of (HF)∞ and (HCl)∞ chains taken from (HF)10 and (HCl)10 oligomers. The energy increments are computed using the one-body orbital sets of the innermost monomers in the oligomers. All data are given in millihartrees.

The error on the binding energy due to the approximate translational relation of the Wannier orbitals taken from the finite-length oligomers can be estimated by investigating the numerical differences between energy increments whose values should be identical due to (translational) symmetry. The connected two-body increments, for example, vary at most by 40 μEh in (HF)10 and at most by 11 μEh in (HCl)10.78 We conclude that the transferability prerequisite of the energy increments is satisfied within good accuracy. The agreement between the results obtained in the two different ways described before corroborates the applicability of oligomers to represent the electronic structure of infinite (HF)∞ and (HCl)∞ chains.

### B. Short-range correlations

Let us discuss the short-range correlation contributions first. The most relevant energy increments of (HF)∞ and (HCl)∞ are summarized in Tab. I. The CP-corrected correlation energy of the HF monomer, −227.3406 mEh, and of the HCl monomer, −176.2151 mEh, are only larger in magnitude by 1.8% and 0.6%, respectively, than the corresponding one-body energy increments ∆ε0. They are a bit larger because the electrons of a monomer in the chains experience Pauli repulsion exerted by the neighboring monomers. However, these effects are small in our case and the electronic structure of the HF and HCl monomers is essentially preserved in the (HF)∞ and (HCl)∞ chains.

The K-body energy increments, K ≥ 2, describe the mutual correlation of the valence electrons of several monomers. They give rise to a pronounced nonlinear increase of the binding energy of small clusters and short oligomers which is termed bond cooperativity (Ref. 17 and references therein). The modulus of the connected two-body energy increment of (HCl)∞, |∆ε01HCl|, is 31% smaller than the modulus of the corresponding energy increment of (HF)∞, |∆ε01HF|. The connected three-body energy increment ∆ε012HCl is repulsive, i.e., greater than zero, but ∆ε012HF is again attractive, i.e., smaller than zero. The reverse trend is observed for the remaining energy increments. The modulus of the energy increment ∆ε012HF is 57% larger than |∆ε012HCl|. The connected four-body increment ∆ε0123HCl is 100% larger than ∆ε0123HF and both are repulsive. These two trends of the energy increments can be explained by two effects. First, short-range correlation is effective for nearest neighbors [see also the ensuing Sec. IV C]; it is apparently stronger in (HF)∞ than in (HCl)∞ due to the tighter packing of the monomers in (HF)∞ and the higher compactness of the HF monomer itself. Second, chlorine atoms have a higher polarizability than fluorine atoms because their valence electrons are more diffuse than those of the latter atom. This causes the van der Waals interaction to be stronger in (HCl)∞ than in (HF)∞, leading to the more distant energy increments being larger in (HCl)∞ when compared with (HF)∞: all this despite the larger intermonomer distances in (HCl)∞ than in (HF)∞.

However, note that one should not associate too much physics with the particular values of energy increments; namely, they depend on the specific unitary transformation used to localize the occupied orbitals (here the one of Foster and Boys58). Only the binding energy, which involves the sum of all the energy increments [Eqs. (9) and (10)], is a physical observable and thus invariant under orbital transformations. When an analysis of the individual energy increments is to be meaningful, their value should be fairly independent of the localization procedure which is well satisfied in our case.

### C. Long-range correlations

At a separation of two isolated monomers where the geometrical overlap between the orbitals from distinct one-body orbital sets of the monomers becomes negligible, only van der Waals dispersion interactions remain. This is also the case for the interaction between two monomers in the infinite chains which is correspondingly described by the two-body energy increments. Their absolute values in (HF)∞ and (HCl)∞ for two monomers at a distance up to seventh nearest neighbors are displayed in Fig. 1; the curves drop off rapidly with distance.

The monomers in Fig. 1 that are labeled by odd cardi-
nal numbers are tilted with respect to monomer 0. Likewise, monomers with even cardinal numbers are arranged parallel to the monomer 0. We will refer to the two types of two-body energy increments that result from a parallel or tilted setting of monomers as even or odd energy increments, respectively. The long-range interaction between two monomers is approximated by the leading term of the two-body van der Waals dispersion interaction:

\[ \varepsilon_{0n}^{vdW} = \begin{cases} -\frac{C_6^{odd}}{(\tilde{r}_{0n})^6}, & n \text{ odd} \\ -\frac{C_6^{even}}{(\tilde{r}_{0n})^6}, & n \text{ even} \end{cases}, \quad (7) \]

where individual van der Waals constants \( C_6^{odd} \) and \( C_6^{even} \), respectively, are affixed for odd and even energy increments. Here \( a \) represents the lattice constant of the chains. The van der Waals constants are obtained by a weighted nonlinear curve fit of the data in Fig. 4 for either the odd or the even energy increments. The weights are chosen such that the fit reproduces the energy increments with large \( n \) best, as for them the geometrical orbital overlaps between the orbitals from two different one-body orbital sets are negligible. The van der Waals constants for the fits of the two sets of translationally equivalent monomers are given in Tab. II. Our theoretical data compare satisfactorily with the experimental data for the dispersion interaction between two isolated monomers also given in the table.

Having identified the van der Waals contribution to the two-body energy increments in the chains, we can subtract it from the two-body energy increments to obtain van der Waals-reduced energy increments

\[ \Delta \varepsilon_{0n} = \Delta \varepsilon_{0n} - \varepsilon_{0n}^{vdW}. \quad (8) \]

Their absolute values \( |\Delta \varepsilon_{0n}^{vdW}| \) is shown next to the absolute value of the two-body energy increments \( |\Delta \varepsilon_{0n}| \) in Fig. 4.

Two regions can be identified in Fig. 4. First, from the nearest to the third-nearest neighbors, there is the local correlation zone, where, due to geometrical orbital overlaps, short-range electron correlations are effective. There, the decay of two-body energy increments with the distance between the two monomers is faster than the one that would result from a pure van der Waals interaction, following Eq. (7). We observe that the van der Waals contribution to \( |\Delta \varepsilon_{0n}^{vdW}| \) of (HCl)\(_\infty\) is appreciably larger than in (HF)\(_\infty\) as the curves for \( |\Delta \varepsilon_{01}| \) and \( |\Delta \varepsilon_{01}^{vdW}| \) are much closer for (HCl)\(_\infty\) than for (HF)\(_\infty\). Second, there is the van der Waals zone reaching from the third- up to the seventh-nearest neighbor. Here a typical \( r^{-6} \) decay is observed, leading to van der Waals-reduced energy increments that are essentially zero. A slight deviation of the two-body energy increments from an \( r^{-6} \) behavior is perceived beyond fifth-nearest neighbors which likely can be attributed to inaccuracies caused by the oligomer approximation. The translational relation of the Wannier orbitals is better satisfied in (HCl)\(_\infty\) compared with (HF)\(_\infty\) [Sec. IV A] which leads to a lower absolute value of the fourth to seventh van der Waals-reduced energy increments. The low absolute value of \( \Delta \varepsilon_{06}^{vdW} \) for both chains is an artifact of the fitting process. Figure 4 also reveals that the two-body energy increments are of satisfactory accuracy even beyond the estimates given in Sec. IV A of \( 40 \mu E_h \) for (HF)\(_\infty\) and \( 11 \mu E_h \) for (HCl)\(_\infty\) due to a considerable error cancellation.

Given the van der Waals constants in Tab. II we can use Eq. (7) to sum up the van der Waals contribution of the two-body energy increments to the binding energy to infinite distance \( \sum_{n=3}^{\infty} \varepsilon_{0n}^{vdW} \) which yields \(-8 \mu E_h \) for (HF)\(_\infty\) and \(-12 \mu E_h \) for (HCl)\(_\infty\). The bigger polarizability of chlorine atoms compared with fluorine atoms leads to the larger contribution in (HCl)\(_\infty\) when compared with (HF)\(_\infty\) as can be expected from the analysis of the energy increments in Sec. IV A. The contribution of two-body energy increments beyond third-nearest neighbors is in both cases \( \approx 30\% \) of \( \Delta \varepsilon_{03} \).

Generally, once a good estimate of the van der Waals constants of a crystal is available, the decomposition of the energy increments into a short- and a long-range van der Waals contribution can be made. This allows one to focus on the short-range part. Thereby, the required number of energy increments to be calculated to reach a certain accuracy of the correlation energy is reduced considerably. Therefore, the computational demand of its determination is also significantly decreased.

V. BINDING ENERGY

Having understood the impact of electron correlations in (HF)\(_\infty\) and (HCl)\(_\infty\) chains, we are now in a position to examine the total binding energy per monomer \( \Delta E \) of
the chains; it is given by

$$\Delta E = \Delta E_{\text{SCF}} + \Delta E_{\text{corr}}$$

$$= \frac{1}{2} \left( \varepsilon_{\text{SCF}} - \varepsilon_{\text{corr}} \right) - \varepsilon_{\text{SCF monomer}} - \varepsilon_{\text{corr monomer}}.$$  

(9)

It consists of the Hartree-Fock and the correlation contributions $\Delta E_{\text{SCF}}$ and $\Delta E_{\text{corr}}$, respectively, where $\varepsilon_{\text{SCF}}$ and $\varepsilon_{\text{corr}}$ denote the Hartree-Fock and correlation energies per unit cell of the chains. Furthermore, $\varepsilon_{\text{SCF monomer}}$ and $\varepsilon_{\text{corr monomer}}$ are the corresponding energies for the monomers. The Hartree-Fock energies are readily available from molecular and periodic calculations, but electron correlations are more involved and were discussed in the previous Sec. IV.

In Tab. III we communicate basis-set-extrapolated Hartree-Fock binding energies $\Delta E_{\text{SCF}}(\infty)$ for the chains taken from Refs. 32, 33. At the Hartree-Fock equilibrium geometry of ($HF$)$_{\infty}$, Bayer and Karpfen give $-10.360$ mE$_h$ for basis set 3 in Ref. 25 while Hirata and Iwata find $-10.585$ mE$_h$ for the 6-311++G(d,p) basis set. Both numbers are in good agreement with our result which is $-10.202$ mE$_h$. Yet Berski and Latajka report $-9.696$ mE$_h$ for ($HF$)$_{\infty}$, when using the 6-311G(d,p) basis set and $-2.073$ mE$_h$ for ($HCl$)$_{\infty}$, harnessing the DZ(d,p) basis set. The latter number in particular deviates considerably from our result, $-0.586$ mE$_h$, which is most likely due to the fact that they did not remove the BSSE.

To determine the correlation energy per monomer of the infinite chains $\varepsilon_{\text{corr}}$, we inspect the energy increments in Tab. I. They converge rapidly with increasing distance among the monomers involved and with increasing order of the many-body expansion, i.e., with the maximum number of monomers correlated in a specific energy increment. In order to obtain an accuracy $\varepsilon_{\text{corr}}$ of $\approx 50$ mE$_h$ for ($HF$)$_{\infty}$ and of $\approx 11$ mE$_h$ for ($HCl$)$_{\infty}$, we see from Tab. I that it is enough to include the following energy increments:

$$\varepsilon_{\text{corr}} \approx \Delta \varepsilon_0 + \Delta \varepsilon_{01} + \Delta \varepsilon_{02}.$$  

(10)

Hence, it is sufficient to correlate the electrons in the Wannier orbitals of only two monomers at a time for ($HF$)$_{\infty}$ and ($HCl$)$_{\infty}$ chains in which more distant two-body energy increments contribute only $-8$ mE$_h$ for ($HF$)$_{\infty}$ and $-12$ mE$_h$ for ($HCl$)$_{\infty}$ as shown in Sec. IV. In three-dimensional crystals, three-body terms become more important according to the analyses in Refs. 51, 77 and the much larger number of three-body energy increments compared with the number of two-body energy increments.

We report $\Delta E$ based on the approximation of Eq. (10) as obtained by basis-set extrapolation in Tab. III. Using density functional theory, Hirata and Iwata find at optimized geometries for the total binding energy of ($HF$)$_{\infty} -13.521$ mE$_h$ (BLYP) and $-13.864$ mE$_h$ (B3LYP) [utilizing the 6-311++G(d,p) basis set] which are larger in magnitude by 14% and 17%, respectively, than our result for the experimental geometry. The observed differences can be partially ascribed to the different geometries used; our experimental geometry leads to a binding energy that is somewhat smaller in magnitude than the binding energy in the optimized geometry. The 6-311++G(d,p) basis set of Iwata and Hirata also differs substantially from our choices in Refs. 32, 33. Above all, we do not consider the impact of triple excitations in our study; they increase the absolute value of the short-range correlation contributions and, consequently, also the absolute value of the binding energies.

|          | ($HF$)$_{\infty}$ | ($HCl$)$_{\infty}$ |
|----------|------------------|-------------------|
| $\Delta E_{\text{SCF}}(\infty)$ | $-10.202$ | $-0.586$ |
| $\Delta E_{\text{corr}}(\infty)$ | $-1.623$ | $-2.764$ |
| $\Delta E(\infty)$ | $-11.826$ | $-3.350$ |

TABLE III: Basis-set-extrapolated total binding energies per monomer $\Delta E(\infty)$ of ($HF$)$_{\infty}$ and ($HCl$)$_{\infty}$ chains and their decomposition into basis-set-extrapolated Hartree-Fock $\Delta E_{\text{SCF}}(\infty)$ and electron correlation $\Delta E_{\text{corr}}(\infty)$ contributions. All data are taken from Refs. 32, 33 and are given in millihartrees.

VI. CONCLUSION

We study hydrogen bonding in infinite ($HF$)$_{\infty}$ and ($HCl$)$_{\infty}$ chains. Whereas in ($HF$)$_{\infty}$ the Hartree-Fock contribution dominates the total binding energy by 86% due to the electrostatic contribution of the rather ionic HF monomers, in the much more weakly bound ($HCl$)$_{\infty}$, the Hartree-Fock calculation yields only 18% of the binding energy (Tab. III). The transitional character of hydrogen-bonded crystals between the ionic and van der Waals regimes is reflected in these numbers. The very weak hydrogen bonds in the ($HCl$)$_{\infty}$ chains bear a close resemblance to purely van der Waals-bonded systems, like rare-gas solids, where bonding is entirely caused by electron correlations. In fact only the inclusion of electron correlations puts the binding energy per monomer of the ($HCl$)$_{\infty}$ chain into the range conventionally ascribed to hydrogen bonding, namely $\approx 3$–16 mE$_h$.

The incremental scheme, which provides a decomposition of the contribution of electron correlations to the binding energy of the chains in terms of nonadditive many-body energy increments, is shown to converge rapidly with respect to the number of monomers, i.e., bodies, involved in the energy increments and the distance among them, thus providing a good tool to study hydrogen bonding in crystals. In contrast to three-dimensional crystals, the dominant contribution of electron correlations to the binding energies of the infinite chains is, in the present investigation, already given by pair interactions between the valence electrons of a monomer and its nearest and next-nearest neighbors. The $K$-body energy increments represent a general framework to describe van der Waals dispersion in-
teraction among the electrons from \( K \) one-body orbital sets. The decay of the two-body energy increments, i.e., the electron correlations between two monomers in the chains, with the intermonomer distance is investigated and van der Waals constants are determined, which affords a partition of the energy increments into a short-range, van der Waals-reduced part and a long-range part that can be summed analytically to infinite distances.

This partitioning affords a methodological advancement; if the van der Waals constants of a crystal are available from other sources, then the number of energy increments in the incremental expansion can be reduced by considering only van der Waals-reduced energy increments; they typically need to comprise only the nearest- and next-nearest-neighbor energy increments. The small number of van der Waals-reduced energy increments permits one to significantly decrease the number of energy increments which have actually to be calculated to reach a certain accuracy of the correlation energy compared with the conventional incremental series. Furthermore, the long-range part turns out to be well described using small (double-\( \zeta \)) basis sets—contrast to the short-range part where basis-set extrapolation is required for an accurate description—thus facilitating further computational savings.

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