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Method of increments for the halogen molecular crystals: Cl, Br, and I

Krista G. Steenbergen,^{1,2} Nicola Gaston,² Carsten Müller,¹ and Beate Paulus¹

¹*Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany*

²*MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, P.O. Box 600, Wellington 6012, New Zealand*

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Method of increments (MI) calculations reveal the n -body correlation contributions to binding in solid chlorine, bromine, and iodine. Secondary binding contributions as well as d -correlation energies are estimated and compared between each solid halogen. We illustrate that binding is entirely determined by two-body correlation effects, which account for >80% of the total correlation energy. One-body, three-body, and exchange contributions are repulsive. Using density-fitting (DF) local coupled-cluster singles, doubles, and perturbative triples for incremental calculations, we obtain excellent agreement with the experimental cohesive energies. MI results from DF local second-order Møller-Plesset perturbation (LMP2) yield considerably over-bound cohesive energies. Comparative calculations with density functional theory and periodic LMP2 method are also shown to be less accurate for the solid halogens. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4896230>]

I. INTRODUCTION

Solid chlorine, bromine, and iodine represent an interesting class of dimeric structures. Although they are crystallographic isomorphs, each has a different state of matter at standard pressure and temperature: chlorine as a gas, bromine as a liquid, and iodine as a solid. Comprised of halogen dimers arranged in a face-centered orthorhombic pattern with $Cmca$ space group symmetry, each plane of molecules exhibits a mirrored tilt, as illustrated in Fig. 1. The solid halogens are generally considered to be van der Waals bound, while the atoms in each halogen molecule are covalently bound. Intriguingly, beyond this covalent neighbor, the next atomic nearest neighbor lies within the van der Waals diameter. This and other key structural parameters are given in Table I.

The nature of these secondary interactions, which arise from overlapping van der Waals radii of two atoms from distinct molecules (r_{2NN} in Fig. 1), can be defined as neither covalent nor purely van der Waals. Despite extensive theoretical interest in the halogen crystal structure,^{1–12} the role of secondary interactions remains largely a mystery. Theoretical methods exploring this topic would require an accurate description of the various contributions to binding in these molecular solids, which would be difficult to achieve with methods such as density functional theory (DFT).

The method of increments (MI)^{13–17} is perfectly suited for such a problem. Verified through previous application to a variety of molecular crystals and van der Waals-bound solids,^{18–22} MI yields highly-accurate wavefunction-based correlation energies for various n -body interactions that contribute to the cohesive properties of a system. Exemplified in recently published work on crystalline benzene, MI yielded exceptional accuracy in capturing the lattice energy to better than an 1 kJ/mol.²³ Through MI, we can directly compare the relative n -body correlation energies, as well as the role of d -correlation and secondary interactions, between each of the solid halogens.

Here, we present the results of MI calculations for solid Cl, Br, and I. We also complete bulk periodic calculations to obtain the exchange Hartree-Fock (HF) contributions to binding, as well as DFT and periodic local second-order Møller-Plesset perturbation (LMP2) results for comparison with the incremental expansion. In Sec. II, we give an overview of the method of increments, followed by a description of our computational methods in Sec. III. We present the results for bulk periodic calculations in Sec. IV. Section V outlines the testing completed for the incremental scheme, with incremental results discussed and compared in Sec. VI. We end with a brief summary of the research in Sec. VII.

II. INCREMENTAL CALCULATIONS

The MI was initially presented as a method extending SCF calculations for electron correlation to crystalline solids and graphite layers.^{13–15} An in-depth review of MI can be found in previous literature,^{16,17} while only a general overview as the method applies to bulk periodic systems is included here. MI is a local correlation method based on the many-body expansion of the bulk correlation energy,

$$E_{\text{u.c.}}^{\text{corr}} = \sum_{i \in \text{u.c.}} \epsilon_i + \sum_{\substack{i \in \text{u.c.} \\ j > i}} \Delta \epsilon_{ij} + \sum_{\substack{i \in \text{u.c.} \\ j > i \\ k > j}} \Delta \epsilon_{ijk} + \dots, \quad (1)$$

where “u.c.” designates the crystal unit cell. A single increment is defined by a subset of localized orbitals (i, j, k), typically referred to as a “center” or “body.” The optimal choice of an incremental center is system dependent, but is normally selected as the group of valence orbitals belonging to a single atom or molecule.

In this work, the incremental center is set to the valence orbitals surrounding a single halogen molecule (Cl_2 , Br_2 , I_2), which are localized within the Foster-Boys scheme²⁷ to form

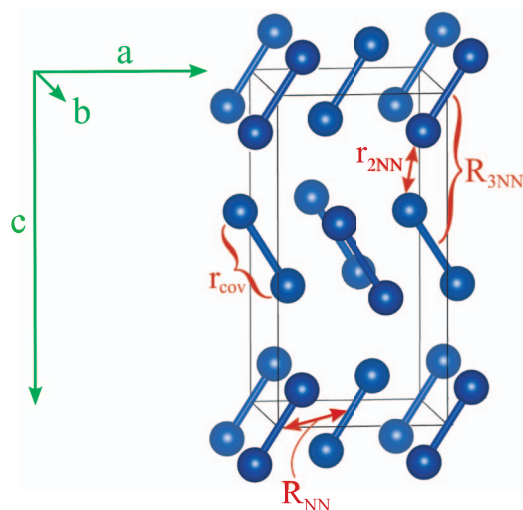


FIG. 1. The solid structures of chlorine, bromine, and iodine have covalently bonded dimers arranged in a fcc-like pattern. Each structure differs only in unit cell lattice parameters and covalent bond distances. The direction of the unit cell parameters, **a**, **b**, and **c** are shown to the left of the structure. The covalent bond (r_{cov}), second atomic nearest neighbor ($r_{2\text{NN}}$), nearest molecular neighbor (R_{NN}), and nearest out-of-plane molecular neighbor (third nearest molecular neighbor, $R_{3\text{NN}}$) are also illustrated.

an orbital group. In order to mimic the infinite periodic crystal, each incremental center is embedded in a finite fragment of the crystal with frozen HF orbitals. Due to the local nature of the correlation energy, this approximation introduces minimal errors so long as the embedding fragment gives reasonably converged correlation energies with increasing size.

The one-center *molecular* energy (E_i) is simply the correlation energy of the individual halogen molecule embedded in a finite fragment of the crystal. However, the one-center *incremental* energy (ϵ_i) must account for both the basis set superposition error (BSSE) as well as the molecular relaxation energy. The BSSE correction is completed through a counterpoise calculation with all embedding atoms replaced by ghosts, to yield E_i^{CP} . The molecular relaxation energy accounts for the energy difference between the free halogen molecule compared to the molecule in the crystal. The

TABLE I. A summary of the key unit cell (u.c.) and crystallographic parameters for solid chlorine,²⁴ bromine,²⁴ and iodine.²⁵ The values corresponding to each label in Fig. 1 (given in Å): the covalent bond length (r_{cov}), the shortest intermolecular separation measured between dimeric centers (R_{NN}), the atomic 2nd NN distance ($r_{2\text{NN}}$), and the van der Waals diameter (D_{vdW}). Also included are the molecular polarizabilities²⁶ (α), in units of Å³.

	u.c.	r_{cov}	R_{NN}	$r_{2\text{NN}}$	D_{vdW}	α
Cl	6.145 (a)					3.6 (α_{xx})
	4.395 (b)	1.99	3.78	3.26	3.50	3.6 (α_{yy})
	8.154 (c)					6.2 (α_{zz})
Br	6.567					5.2
	4.468	2.30	3.97	3.29	3.70	5.2
	8.694					9.4
I	7.255					9.4
	4.795	2.70	4.35	3.54	3.96	9.4
	9.780					16.2

one-center incremental energy is therefore given by

$$\epsilon_i = E_i - E_i^{\text{CP}} - (E_i^{\text{free}} - E_i^{\text{solid}}), \quad (2)$$

where E_i^{solid} is the energy of a bare (non-embedded) molecule at the crystal bond length, while E_i^{free} is the energy of the bare molecule at the non-crystalline (free) bond length.

The two-center increment ($\Delta\epsilon_{ij}$) is the non-additive interaction energy between two molecules, represented as

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (E_i + E_j). \quad (3)$$

The correlation energy of two (embedded) halogen molecules is given by ϵ_{ij} , from which the energies of the embedded one-centers, E_i and E_j , are subtracted. We note that the one-center molecular energy, E_i , differs from that of Eq. (2) due to the increased embedding set, which now includes molecule j and the embedding molecules for both the i and j centers.

By extension, the three-center increment ($\Delta\epsilon_{ijk}$) is the non-additive interaction energy between molecules i , j , and k ,

$$\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\Delta\epsilon_{ij} + \Delta\epsilon_{ik} + \Delta\epsilon_{jk}) - (E_i + E_j + E_k). \quad (4)$$

Once again, the one- and two-centers in Eq. (4) differ from those in Eqs. (2) and (3) due to the larger embedding set, which includes all molecules surrounding the i , j , and k centers. We note that these differences give rise to some *transferability error*,^{13–16,21} which can be approximated at $\ll 1\%$ of the total correlation contribution to the cohesive energy of each solid halogen. Although our incremental series converged at the three-centers, four-center and larger increments can also be calculated by extending the pattern demonstrated in Eqs. (3) and (4).

The index i is constrained to all molecules in the primitive unit cell. In theory, the indices $\{j, k\}$ will extend over the entire periodic crystal. In practice, however, the incremental expansion is helpful only if the increments converge with increasing center-center distance (R). Since we calculate correlation energy per unit cell, the number of one-center increments is independent of R ; the number of two-center and three-center increments increases proportionally to R^2 and R^5 , respectively. However, two-center increments are dominated by London dispersion, while the three-centers are dominated by Axilrod-Teller dispersion, leading to correlation energy decay of R^{-6} and R^{-9} , respectively. Combining the two effects, the cohesive energy contributions from both two- and three-center increments will decay as $\sim R^{-4}$. For the solid halogens, the second and third molecules in the two- and three-center calculations (j and k) include all molecular units up to a defined cut-off distance, which changed between each solid halogen in order to ensure that all calculations were completed for the same subset of the halogen crystal.

III. COMPUTATIONAL DETAILS

MI calculations were completed using density-fitting local coupled-cluster singles, doubles, and perturbative triples (DF-LCCSD(T)) as well as density-fitting local second-order Møller-Plesset perturbation method (DF-LMP2),^{28–31} as im-

plemented in MOLPRO.³² Initial testing revealed that the use of linear scaling approximations (local and density-fitting) changed the incremental energy by less than 0.3%. We note that care must be taken in defining the local domains for each incremental center. MOLPRO assumes a default Boughton-Pulay threshold of 0.985, which leads to inconsistent domain definitions for the solid halogens. In order to obtain consistent localized domains, we instead utilize a structure-based domain definition which includes all projected atomic orbitals (PAOs) from both atoms in a single halogen molecule, to give a Wannier function localized on the incremental center.

All pseudopotentials (PPs) and basis sets were obtained from the Stuttgart-Cologne group. Calculations were completed for two model valence sets: a large-core (LC) model, treating all *d*-electrons as part of the chemically inactive core, with only the 7 outermost s^2p^5 electrons as valence; and a semi-core (SC) model estimating the relative contribution of *d*-correlation, as described in more detail below. The LC model was utilized for all three halogens, while the SC model was implemented only for solid bromine and iodine.

Each of the LC models utilized an energy-consistent, multi-electron fit, quasi-relativistic PP, with a chemically inactive [Ne] core for chlorine, [Ar]3*d*¹⁰ core for bromine, and [Kr]4*d*¹⁰ core for iodine.³³ The valence electrons were represented by contracted Gaussian type orbital (CGTO) sets optimized for the Stuttgart-Cologne PPs,³⁴ where *d*- and *f*-functions are included only for the correlated molecules (excluded from the embedding basis set). As the Stuttgart library does not have a standard triple- ζ basis set for chlorine, we derived an augmented triple zeta basis set from a (6*s*6*p*)/[3*s*3*p*] basis set published by Dolg.³⁵ This derivation included: (1) adding one additional, diffuse *s*- and *p*-function;³⁶ (2) adding *d* and *f* polarization functions from Dunning's aug-cc-pVTZ basis set for Cl;³⁷ and (3) re-optimizing the contraction coefficients in a Hartree-Fock calculation for an isolated Cl atom.

For bromine and iodine, the SC model used an energy-consistent, multi-electron fit, fully relativistic PP with a core of [Ne] and [Ar],³⁸ respectively. Augmented triple- ζ correlation-consistent basis sets (aug-cc-pwCVTZ), which account for molecular semi-core-valence interactions, were used to describe the valence set.³⁹ Two calculations were completed for each increment in the SC model: the first correlated the outermost 25 electrons per atom, while the second utilized the same basis set but correlated only the outermost 7 electrons per atom. In subtracting the second calculation from the first, we are able to quantify the *spd*-semi-core correlation which comes primarily from the *d*-orbitals. The *d*-, *f*-, and *g*-functions were taken into account for the correlated centers, but were excluded from the embedding basis. All basis sets are given in the supplementary material.⁴⁰

In addition to the incremental calculations, we also completed a set of bulk HF and LMP2 periodic calculations using a combination of CRYSTAL09^{41,42} and CRYSCOR.^{43,44} For periodic calculations, we employ the dual basis set scheme.^{42,43} The smaller, HF basis sets removed the most diffuse basis functions, while the full LMP2 basis set was the same as that used in the triple- ζ LC incremental calcu-

lations outlined above. Minor modifications were required in order to accommodate CRYSTAL's limit of 10 primitives per contraction,⁴⁵ as the Stuttgart triple- ζ basis contains a contracted *s* function of 14 primitives for the bromine and iodine basis sets. Each of the modified basis sets are given in the supplementary material.⁴⁰

For comparison and completeness, a set of DFT periodic calculations were also completed using the same basis sets as the LC incremental calculations. DFT was performed with the functionals PW91,⁴⁶ PBE,⁴⁷ B3LYP,⁴⁸ and PBE0.⁴⁹ Both D2⁵⁰ and D3^{51,52} dispersion corrections were included for PBE and B3LYP.

IV. PERIODIC RESULTS

A summary of the periodic results is given in Fig. 2. DFT yielded a wide-range of cohesive energies, depending on the functional. Here, we illustrate only the results for PBE and PBE+D3; however, results for other functionals and dispersion corrections are given in the supplementary material.⁴⁰ As illustrated in Fig. 2, PBE is dramatically under-binding. Of all tested functionals, PBE+D3 performed most consistently for all three solid halogens, with overbinding errors of 5% (Cl), 15% (Br), and 7% (I) in comparison to the experimental cohesive energies⁵³ extrapolated to 0 K and corrected for zero-point energy.⁶ These results agree well with previous DFT research predicting the crystal properties of condensed astatine,⁵⁴ which clearly illustrates the importance of dispersion in predicting the structural properties of crystalline chlorine, bromine, and iodine.

The periodic HF and the singles energy give the total exchange contribution, which is repulsive for all three halogens. Periodic LMP2 results are combined with an extrapolated long-range (8–12 Å) correlation energy, which is calculated by a R^{-6} fit to the LMP2 pair-energy contributions, but is labeled Lennard-Jones (LJ) within CRYSCOR. At ~ 2.5 times the magnitude of the exchange energy, the correlation energies entirely determine binding in the solid halogens. This result is somewhat intuitive for van der Waals bound

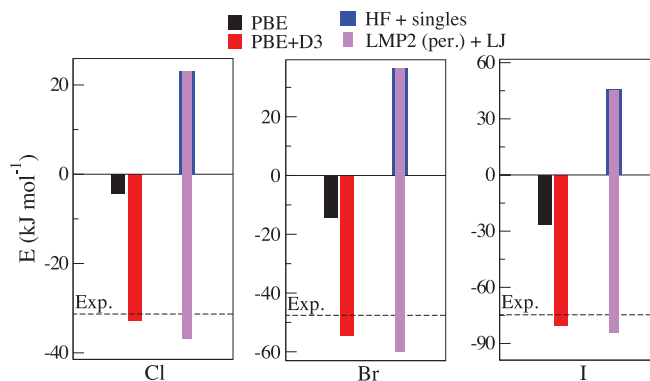


FIG. 2. The results of periodic DFT (PBE and PBE+D3) compared to the results of periodic exchange (HF+singles) and correlation (LMP2+LJ) calculations for the cohesive energy of chlorine, bromine, and iodine. The experimental cohesive energies (Exp., dashed-black line) include zero-point corrections.^{6,53} Note that the plots are scaled differently, so that the experimental cohesive energies for each halogen are of the same dimension. All energies are given in kJ/mol.

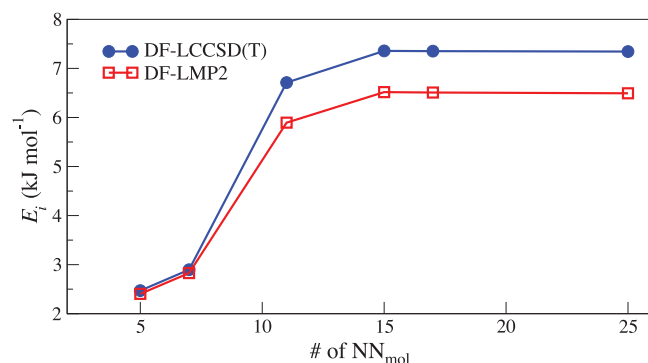


FIG. 3. Summary of one-center incremental convergence with number of NN_{mol} for DF-LCCSD(T) and DF-LMP2 for solid chlorine. The data points represent the 1st–6th groups of NN_{mol} . Note: Due to crystal symmetry, each incremental NN group adds more than one molecule.

systems, although this same correlation-dominated binding has also been noted in metallic solid mercury.^{55–57}

The LMP2+LJ correlation energy added to the HF+single exchange energy yields an estimate of the cohesive energy for each periodic system. As illustrated in Fig. 2, the cohesive energy is significantly overestimated for chlorine (18%), bromine (26%), and iodine (13%). It is clear that in order to accurately model the cohesive energy of all three solid halogens consistently, we require the additional accuracy of coupled-cluster correlation calculations, which are only computationally feasible within an incremental scheme for systems of this size. This approach also allows for direct comparison of secondary effects, *d*-correlation, and various *n*-body correlation contributions between each solid halogen.

V. INCREMENTAL TESTING

The size of the embedding set was determined by the number of nearest neighbor molecules (NN_{mol}) required to achieve convergence. Using the one-center energy (E_i) as the convergence test, incremental calculations were completed for increasing numbers of NN_{mol} groups, with results summarized in Fig. 3. We use the first six NN_{mol} groups for the embedding set of the one-center incremental calculations. The first four NN_{mol} groups (as illustrated in the supplementary material⁴⁰) are utilized for each center in the two- and three-center increments.⁵⁸

For the two- and three-center calculations, the total number of increments was determined by testing convergence with increasing intermolecular separation. In chlorine, the individual incremental energies decreased to ~ 0.03 kJ/mol between 10 and 11 Å (molecular center-to-center), leading to a two-center cutoff of 11 Å. The three-center increments also decreased quickly with increasing average intermolecular separation, similar to the results for argon and CO_2 .^{21,22} The three-center increments in chlorine were calculated up to an average intermolecular separation of 7.0 Å,⁵⁹ where the increments had decreased to < 0.01 kJ/mol. In bromine and iodine, the cutoff distances were defined so that the number of molecules and relative molecular geometries remained consistent for all halogens: two-centers up to 11.6 and 12.7 Å,

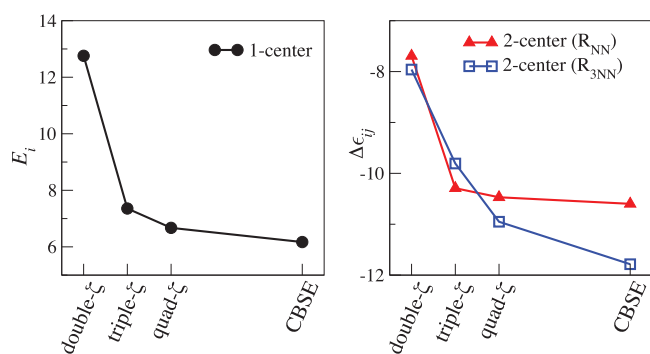


FIG. 4. The DF-LCCSD(T) one-center and two largest two-center increments for solid chlorine using double, triple, and quadruple- ζ basis sets. The two largest two-center increments are given by molecular nearest neighbor, labeled R_{NN} and third nearest neighbor, labeled $R_{3\text{NN}}$. The CBSE energy is calculated using the triple and quadruple- ζ results. Energies are given in kJ/mol.

and three-center up to an average of 7.5 and 7.95 Å, respectively.

In order to approximate errors arising from the basis set limit, we calculated one- and two-center increments using the double- ζ , triple- ζ , and quadruple- ζ basis for the LC models. The double and quadruple- ζ basis for chlorine were obtained as previously described,³⁶ while bromine and iodine utilized the Stuttgart-Cologne CGTO basis sets.³³ The *d*-, *f*-, and *g*-functions are included for the correlated molecules but excluded from the embedding basis. As illustrated in Fig. 4, the double- ζ basis yielded anomalously high energies in comparison with the trends established for the triple and quadruple- ζ . For the two-center calculations, we illustrate the basis set convergence with only the largest two increments: the nearest molecular neighbor and the 3rd molecular NN, illustrated in Fig. 1 by the intermolecular separation labels R_{NN} and $R_{3\text{NN}}$, respectively. In calculating the complete basis set extrapolation (CBSE),⁶⁰ we utilize the more accurate triple and quadruple- ζ results.

As a check on the incremental extent and embedding set, we compared our incremental DF-LMP2 correlation energies to the periodic LMP2 results. Incremental DF-LMP2 yields excellent agreement for each solid halogen as illustrated in Table II, with differences of 0.2%–3%.⁶¹

TABLE II. A comparison of the total pair correlation energy as calculated by the periodic LMP2 method and the incremental method. Periodic LMP2 was calculated by the dual basis set scheme, while the incremental calculations employed DF-LMP2 in order to calculate the one-, two-, and three-center correlation contributions, as previously described. Both calculations were completed with the same triple- ζ basis sets. The percent difference is calculated as $\% \Delta = ((\text{Periodic}-\text{Incremental})/\text{Periodic}) \cdot 100\%$. Energies are given in kJ/mol.

	Cl	Br	I
Periodic LMP2	-58.69	-95.34	-124.60
Incremental DF-LMP2	-59.94	-95.42	-128.57
$\% \Delta$	2%	0%	3%

TABLE III. A table summarizing the incremental correlation energies combined with long-range and exchange (HF+singles) contributions, yielding the simulated cohesive energy (Sim. E_{coh}). The correlation energies were obtained by DF-LCCSD(T) for the one- and two-center energies, while the three centers and semi-core contributions are calculated by DF-LCCSD(TO). The one-center includes the free molecule correlation contribution. For bromine and iodine, the one-center (ϵ_i), two-center ($\Sigma(\Delta\epsilon_{ij})$), and total incremental energies (ΣE_{inc}) include the semi-core correlation which is noted in the parentheses. We add the LJ long-range correlation correction (8–12 Å), as well as the exchange energy (E_{ex} , HF+singles). The simulated cohesive energy for each halogen is compared to the zero-point corrected experimental value (Exp. E_{coh}),^{6,53} with all energies given in kJ/mol.

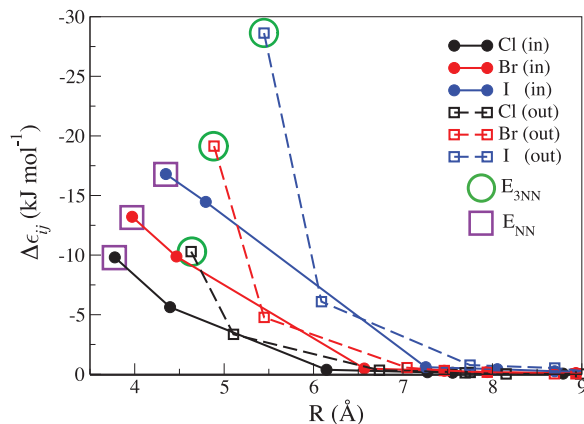
	Cl	Br	I
ϵ_i	6.42	14.40 (1.72)	22.95 (3.15)
$\Sigma(\Delta\epsilon_{ij})$	-62.51	-102.50 (-2.68)	-143.31 (-8.38)
$\Sigma(\Delta\epsilon_{ijk})$	2.12	3.64	5.60
ΣE_{inc}	-53.97	-84.46 (-0.96)	-114.77 (-5.23)
LJ	-1.29	-1.23	-5.14
E_{ex}	23.10	36.43	45.43
Sim. E_{coh}	-32.15	-49.26	-74.48
Exp. E_{coh}	-31.31	-47.57	-74.67
% Δ	-2%	-3%	0%

VI. INCREMENTAL RESULTS

Table III summarizes the incremental results for DF-LCCSD(T). HF+singles exchange energy (obtained by the dual basis set scheme) and LJ long-range correlation corrections are also added, in order to obtain a total cohesive energy for each solid halogen. The results are in excellent agreement with the experimental cohesive energies,^{6,53} yielding only 0.2%–3% error. This significantly outperforms incremental DF-LMP2, which overestimates binding by 18%–26%, as well as PBE+D3 yielding 5%–15% errors.

The one-center energy includes the molecular relaxation energy, as shown in Eq. (2). The energy of the free molecule was calculated using both the experimental bond length as well as an optimized (calculated) free molecule bond length, with both calculations yielding a molecular free energy contribution of less than 0.5% of the total correlation energy. The one- and two-center energies include CBSE corrections; however, the correlation contribution from the semi-cores (SC model) was calculated only at the triple- ζ level, which may account for some part of the minimal error.

Relative semi-core correlation contributions to the one-center, two-center, and total incremental energy are included in parentheses. The semi-core correlation contribution to the one-center is substantial and proportionally similar between Br and I, at 12% and 13%, respectively. The semi-core correlation energy accounts for only 3% of the two-center contribution in bromine and 6% in iodine. The total semi-core correlation contribution is diminished by the opposing signs between the one- and two-centers. As expected, there is a notable increase in the total semi-core correlation for iodine (5%) compared to bromine (1%). However, contrasting with previous studies which have shown that d -correlation is essential for accurate lattice prediction in metals such as zinc and cadmium,⁶² the d -orbitals appear to contribute minimally to the cohesive energy even for metallic iodine.⁶³



	Cl	Br	I
$E_{3\text{NN}} / E_{\text{NN}}$	1.05 / 1	1.45 / 1	1.70 / 1

FIG. 5. The DF-LCCSD(T) two-center increments separated by in-plane and out-of-plane molecular contributions, illustrating the decreasing individual increments with increasing intermolecular separation, R , as well as the difference between in and out-of-plane contributions to binding in solid halogens. The semi-core correlation is included for bromine and iodine. The two largest two-center contributions are noted by the square and circle values, illustrating the increasing ratio of the third molecular nearest neighbor energy ($E_{3\text{NN}}$) to that of the nearest neighbor energy (E_{NN}). The table beneath the plot gives these ratios.

The two-center correlation energies entirely determine binding for all three solid halogens. Fig. 5 breaks down the two-center correlation energy by considering geometric planes of dimers: molecular in-plane contributions, similar to R_{NN} and other planar neighbors as shown in Fig. 1, and out-of-plane contributions from all other molecules. In order to differentiate the effect of van der Waals and secondary contributions to binding, it is useful to compare the correlation energies of the two largest two-center increments: the molecular nearest neighbor and third-nearest neighbor increments. In Fig. 1, we note that the third-nearest neighbor molecule pair (separated by $R_{3\text{NN}}$) contains the 2nd atomic nearest neighbors ($r_{2\text{NN}}$). Secondary effects in the solid halogens arise from $r_{2\text{NN}}$ being less than the van der Waals diameter, D_{vdW} (Table I). As illustrated in Fig. 5, the correlation contribution from the nearest out-of-plane molecular neighbor ($E_{3\text{NN}}$) is larger than that of the nearest-neighbor (E_{NN}), despite the larger inter-molecular separation of $R_{3\text{NN}}$. This result may indicate that the larger $E_{3\text{NN}}$ arises due to the overlapping van der Waals radii for the atomic 2nd NN.

The table at the bottom of Fig. 5 gives the ratio of the $E_{3\text{NN}}$ to E_{NN} , illustrating that secondary effects increase significantly from chlorine to bromine to iodine. In addition to the effect of overlapping van der Waals radii, this increased ratio could also arise from the increasing polarizability of the halogen molecule when moving down the group in the periodic table (see Table I). It is interesting to note that secondary effects contribute significantly to binding in all three solid halogens, with $E_{3\text{NN}}$ accounting for 16%–20% of the two-center correlation energies. Comparing only magnitudes, $E_{3\text{NN}}$ far exceeds the one-center correlation contribution (ϵ_i) for all three halogens, indicating that intermolecular sec-

ondary effects are more important than even the intramolecular correlation contribution.

VII. SUMMARY

In summary, method of increments calculations with DF-LCCSD(T) yield excellent agreement with experimental cohesive energies, with errors ranging between 0.2% and 3%. For each solid, the one-center increment is repulsive. The three-center increments are small, contributing minimally to the overall correlation energy of the solids. Binding is entirely determined by the large two-center correlation contribution, which accounts for >80% of the total correlation energies. The *d*-orbitals contributed only minimally, at 1% for bromine and 5% for iodine. Secondary effects play a significant role in all three solid halogens, although the contribution is greatly enhanced in iodine.

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