

Incrementally Corrected Periodic Local MP2 Calculations: I. The Cohesive Energy of Molecular Crystals

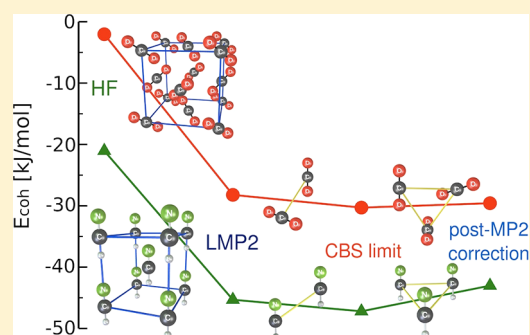
Carsten Müller^{*,†} and Denis Usvyat^{*,‡}

[†]Institut für Chemie und Biochemie, Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

[‡]Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Universitätsstraße 31, 93040 Regensburg, Germany

S Supporting Information

ABSTRACT: A method for accurate calculations of the cohesive energy of molecular crystals is presented. The cohesive energy is evaluated as a sum of several components. The major contribution is captured by periodic Hartree–Fock (HF) coupled with the local Møller–Plesset perturbation theory of second order (LMP2) with a triple- ζ basis set. Post-MP2 corrections and corrections for the basis set incompleteness are calculated from inexpensive incremental calculations with finite clusters. This is an essential improvement with respect to the periodic LMP2 method and allows for results of benchmark quality for crystalline systems. The proposed technique is superior to the standard incremental scheme as concerns the cluster size and basis set convergence of the results. In contrast to the total energy or electron correlation energy, which are evaluated in standard incremental calculations, post-MP2 and basis set corrections are rather insensitive to approximations and converge quickly both in terms of the order of the increments and the number of terms at a given order. Evaluation of the incremental corrections within the sub-kJ/mol precision requires computing very few of the most compact two-center and three-center non-embedded clusters, making the whole correction scheme computationally inexpensive. This method as well as alternative routes to compute the cohesive energy via the incremental scheme are tested on two molecular crystals: carbon dioxide (CO₂) and hydrogen cyanide (HCN).



1. INTRODUCTION

An accurate description of long-range electron correlation in solids remains challenging. This might be considered of little importance for ionic or covalent systems. However, even for such systems, it becomes decisive when small energy differences, such as relative stabilities of crystalline polymorphs, are under consideration.^{1,2} In van der Waals-bound solids, long-range correlation (dispersion) is the main binding contribution. A proper account of dispersion alone, however, might not guarantee high accuracy of the overall interaction energy because in molecular crystals it is governed by a delicate balance between different repulsive and attractive components.

The standard Kohn–Sham density functional theory (DFT), which is widely used for solids, does not capture van der Waals dispersion and, hence, is unfit for molecular crystals. An inexpensive way to include dispersive effects a posteriori within the DFT framework is, for example, Grimme’s empirical D-correction,³ which adds long-range atomic-pair C_6/R^{-6} energy-terms damped at small interatomic distances by an appropriate function. Although a correct qualitative description is achieved with this scheme, the underlying empiricism limits the predictive power of this approach (for examples, see refs 4 and 5). A DFT-based random-phase approximation (RPA)^{6–9} allows for a more rigorous treatment of electron dispersion but at the price of increased computational cost.

A hierarchy of post-Hartree–Fock (post-HF) methods allows for a balanced and accurate treatment of both long- and short-range electron correlation. However, even for molecules, post-HF techniques are rather expensive, and their application to extended periodic systems is far from trivial. Correlated treatment at a relatively high level is available for polymers.^{10–13} For 3D solids, there exist several implementations of the second-order Møller–Plesset perturbation theory (MP2)^{14–17} or RPA,^{7,18} but methods beyond that are hardly available. Only very recently the first 3D periodic coupled cluster plane-wave-based implementation has been reported.^{19,20} A common problem of purely periodic approaches is basis-set convergence. If nonorthogonal atomic orbitals are used as basis functions, mutual quasi-linear dependencies hinder employing high-quality basis sets (e.g., beyond triple- ζ) in periodic calculations. Plane waves are advantageous in this respect because they are mutually orthogonal, and the quality of the corresponding basis set is controlled by just one parameter. However, for a proper description of the wave function, a large number of plane waves might be required, making the corresponding calculations expensive. Up to now, basis set-converged post-HF results have been reported only for

Received: September 9, 2013

Published: November 14, 2013

relatively simple 3D crystals^{15,17,21–29} or the uniform electron gas.^{30,31}

A number of finite cluster-based strategies have been developed as alternatives to purely periodic techniques.^{21,23,25,32–36} The advantage of these approaches is that the molecular quantum chemical *machinery* can readily be utilized for solids to obtain high-quality results both in terms of the order of the correlated treatment and the basis set. In fact, such techniques had been proposed³² and used (for reviews, see refs 34 and 37) well before any 3d-periodic correlation method had been developed. In principle, a finite cluster-based many-body expansion converges to the correct periodic result, but the convergence rate strongly depends on the character of the property that is expanded, the nature of the interactions in the system, and the embedding model used for the clusters.

In this article, we describe a method where periodic and incremental correlated calculations are used in a complementary way to yield highly accurate results at a moderate cost. We start off with the periodic local MP2 (LMP2) cohesive energy calculated with a triple- ζ basis set. Corrections for the limited basis set size and post-MP2 contribution to the cohesive energy are evaluated from a small number of inexpensive finite cluster calculations. This method in a pragmatic way circumvents the above-mentioned individual deficiencies of the finite cluster and periodic treatment and allows a very good level of accuracy. In this paper, we will focus on molecular crystals and investigate the performance of this methodology on two examples: crystalline carbon dioxide (CO₂), which is mainly dispersively bound, and hydrogen cyanide (HCN), which has a significant electrostatic contribution from intermolecular dipole–dipole interactions. These systems are more complex than the previously studied noble gas solids^{28,38,39} but still sufficiently simple to study the general properties of our methodology. Furthermore, there exist several theoretical benchmarks,^{15,23–25,36,40,40} which can be used in the present study as references. With small customizations, the method can be applied to other material classes, which will be the topic of follow-up publications.

2. COMPUTATIONAL MODELS

In the traditional method of increments,³² the electron correlation energy is calculated on a series of finite clusters, while the Hartree–Fock (HF) energy is obtained from periodic calculations. However, in the past decade, periodic MP2 has become feasible and can serve as a new baseline for a combined periodic and incremental scheme. In this section, we describe both individual methods and how they are combined for a new complementary scheme.

2.1. Periodic Local MP2 Method. The local MP2 method (LMP2), which is used below in both the periodic and some of the finite cluster calculations, is based on an Ansatz by Pulay and Saebø,⁴¹ which was implemented first for molecules (MOLPRO program)^{42–44} and later for periodic systems (CRYSCOR program).^{2,16,45–48} In this scheme, the occupied space is spanned by orthonormal localized orbitals [also referred to as Wannier functions (WFs)] and the virtual space by local but mutually nonorthogonal (and even redundant) projected atomic orbitals (PAOs). Two types of local approximations are introduced. The first is the domain approximation, which restricts the virtual space of an orbital pair to a domain spanned by PAOs centered in the vicinity of either of the two occupied orbitals. This approximation significantly reduces the number of excitation amplitudes and

thus the computational cost, with just a very slight decrease in accuracy, provided that reasonably large domains are used. The second approximation exploits the locality of electron correlation and truncates the list of correlated electron pairs at some distance. In periodic systems, this approximation is essential because an untruncated list of pairs would be infinite. Nevertheless, contributions from the excluded pairs are added a posteriori by C_6R^{-6} -type pair-energy extrapolation.⁴⁶ The corresponding pair-type-specific C_6 coefficients are fitted to the decay of the actual pair energies beyond a certain distance.

2.2. Method of Increments. The idea of the incremental method is based on a many-body expansion of the energy of a solid

$$E^{\text{incr}} = \sum_L \varepsilon_L + \sum_{LM} \Delta\varepsilon_{LM} + \sum_{LMN} \Delta\varepsilon_{LMN} + \dots \quad (1)$$

The convergence of the incremental expansion relies partially on the choice of “bodies” or “centers”, i.e., the selection of orbitals that are treated as one increment. For crystals of small molecules, all valence orbitals at one molecule are considered as one center, denoted by the indices L, M, \dots . The sums over L in eq 1 run over all molecules in one unit cell, while the range for the other sums is, in principle, not restricted. In practice, however, a cutoff radius is used to restrict these sums, similar to the truncation of the pair-list in periodic LMP2. The “one-center” terms, ε_L , are the energies of single molecules, and the “many-center” terms, $\Delta\varepsilon_{LM}$, $\Delta\varepsilon_{LMN}$, etc., represent the two-body, three-body, etc. interactions between molecules:

$$\begin{aligned} \Delta\varepsilon_{LM} &= \varepsilon_{LM} - (\varepsilon_L + \varepsilon_M) \\ \Delta\varepsilon_{LMN} &= \varepsilon_{LMN} - (\Delta\varepsilon_{LM} + \Delta\varepsilon_{LN} + \Delta\varepsilon_{MN} + \varepsilon_L + \varepsilon_M + \varepsilon_N) \\ &\dots \end{aligned} \quad (2)$$

For the incremental expansion of the cohesive energy of a molecular crystal,

$$\Delta E = E^{\text{incr}} - \sum_L E_L^{\text{mol}} \quad (3)$$

it is convenient to absorb the (counterpoise-corrected) energies of isolated molecules, E_L^{mol} , in the corresponding one-center terms,

$$\Delta\varepsilon_L = \varepsilon_L - E_L^{\text{mol}} \quad (4)$$

which have then the meaning of the one-body terms of the cohesive-energy incremental series.

Incremental expansions of the total cohesive energy in solids usually converge very slowly due to the long-range and many-body electrostatic and induction contributions. Therefore, the leading orders of these interactions are usually evaluated either within a fully periodic HF^{34,37} or DFT^{49,50} treatment, or embedding is introduced to mimic the periodic environment.^{23,25,36,51–53} An incremental expansion of the total energy with nonembedded clusters (*bare* clusters)^{35,38} is reliable only if the molecules in the crystal are nonpolar and possess small or zero quadrupole moments.

The correlation energy, representing the difference between total and HF energy, converges substantially faster than the total or HF energy alone, both in terms of the order of increments and distance between active molecules. We note, however, that without proper embedding even the correlation energy might not converge to appreciable accuracy after three-

body terms (vide infra), which is a desirable cutoff in practical calculations.

2.3. Embedded Cluster Models for Many-Body Expansions of the Correlation Energy. Embedding schemes can significantly accelerate the convergence of incremental expansions. The fastest convergence of an incremental expansion of the MP2 energy would be achieved with a periodic self-consistent MP2 embedding, which trivially reduces the incremental expansion to one-body terms only. Obviously, such an embedding is impractical for the MP2 energy method itself but potentially useful for higher-order treatment. Bare clusters without any embedding are the opposite extreme, yielding the slowest possible convergence rate. Indeed, incremental expansions of the cohesive energy with bare clusters start only from two-body terms (one-body terms vanish, see eq 4) and can exhibit a sign alternating convergence pattern.⁵⁴

A periodic HF⁵⁵ or DFT⁵⁶ embedding incorporates the influence of the low-order long-range and many-body effects on the correlation energy. In molecular crystals, the three-body correlation energy contribution mainly represents Axilrod–Teller dispersion,⁵⁷ which is not captured at MP2 level.^{28,58} Hence, with such an embedding, the MP2 cohesive energy expansion is expected to converge after two-body terms. In higher-order methods, starting from MP3, Axilrod–Teller dispersion and related effects are captured.⁵⁸ Hence, even with HF-embedded clusters, three-center correlation contributions are generally non-zero.

Because fully periodic HF embedding is yet not available in standard quantum chemical programs, here we test a finite cluster HF embedding with point charges (HFPC).^{59,60} In this scheme, the nearest neighbor molecules surrounding the “active” (one, two, or three) centers are treated at the HF level, and more distant molecules within 21 Å are represented by point charges. The values for these point charges are obtained from an isolated molecule in vacuum as described in the Supporting Information.⁶¹ On the sphere’s surface, the charges are modified to mimic the Madelung potential of an infinite array of point-charge molecules. This embedding is expected to be a reasonably good approximation to the real periodic HF embedding for crystals of unpolar molecules, as far as only the correlation energy is concerned. It explicitly takes into account the influence of the short- and medium-range HF effects on the correlation energy of the active centers, and the influence of the long-range electrostatics via the point charges. For polar molecules, however, this approach can lead to substantial errors if the dipole moment of a molecule in the crystal deviates much from that of an isolated molecule. For other approximate embedding schemes for molecular crystals we refer to refs 25, 36, and 52.

For the practical use of an incremental expansion, the computational cost becomes a key issue, especially in the context of the rivalry with the recently developed purely periodic high-order techniques.²⁰ The accelerated convergence within sophisticated embedding models is usually achieved at the price of an excessive cost for the calculations. Indeed, bare cluster calculations of two-center contributions are relatively inexpensive even at the CCSD(T) or LCCSD(T0) level (for large molecules where the incremental scheme can be based on submolecular fragments). In principle, individual three-center bare cluster terms are usually also affordable. However, the overall bare cluster three-center calculation can be somewhat costly due to a large number of clusters. Therefore, three-body

contributions are sometimes a priori neglected^{25,36,49,50,62} or evaluated by alternative means.^{23,25} Computation of four-body and higher contributions is, in most systems, prohibitively expensive even with bare clusters and is, therefore, commonly avoided. With HFPC-embedded clusters, computational costs are already large for two-body terms, which for bulky systems can become hardly feasible without local correlation treatment, due to the substantial increase of the virtual space.

2.4. Common Problems in Finite Cluster Expansions. Formally, an infinite incremental expansion converges to the periodic result. However, this equivalence holds only if the virtual space and occupied orbitals do not depend on the shape, size, or structure of the clusters from which the increments are calculated. A fully periodic embedding would ensure this requirement, as would a scheme in which all increments are calculated from the same cluster. However, with individual bare or HFPC-embedded clusters for each increment, this cannot be guaranteed.

For canonical electron correlation methods employing atom-centered basis sets, the virtual space depends on the size of the cluster, which progressively grows with the order of the increment. Consequently, the magnitude of the one-body correlation energy is greater in a cluster with two active molecules than in a cluster with just one, etc.^{38,39} Local correlation methods are more stable in this respect because the virtual domains are independent of the clusters’ shape or size. However, incremental schemes utilizing local-correlation methods are prone to errors of a different kind. When localized occupied orbitals change from one cluster to another, the compatibility of the increments in the expansion (1) and of the energies in the individual increments (2) can get lost. This is especially critical for the orbital-variant LCCSD(T0) method,⁶³ which is the computationally most efficient local approximation to CCSD(T). The Pipek–Mezey localization method⁶⁴ is known to be rather sensitive to the form and symmetry of the cluster. Therefore, in finite cluster incremental calculations, the Foster–Boys localization method⁶⁵ is preferable.

Another potential hassle in incremental calculations with local correlation methods is a mismatch of the virtual spaces in the evaluation of individual increments according to eq 2. The obvious prerequisite for a balanced local correlation treatment is the use of identical virtual domains in all finite cluster calculations. With the default Boughton–Pulay scheme⁶⁶ of setting the domains, this is not automatically guaranteed; hence, special attention should be given to this issue. However, even with the consistently defined domains, the size of the virtual space might remain slightly nonuniform for different clusters. Because PAOs form a redundant basis set, the pair-specific orthogonalized virtual space is subject to additional truncation according to the eigenvalues of the pair-specific PAO overlap matrix.⁶⁷ Eigenvalues that drop below a predefined threshold are considered to flag quasi-redundant orbitals among the pair-specific orthogonalized virtual set, and the corresponding eigenvectors are disregarded. This truncation has usually only a negligible effect on the interaction energy in a conventional supermolecular or periodic calculation. However, in incremental calculations, where the overall energy is a sum of a large number of independently evaluated terms, errors of this kind can accumulate. This problem becomes especially pronounced in the case of highly symmetric crystals, for which symmetry unique increments are multiplied by large weight factors.

Finally, we note that because the correct description of the intermolecular interaction is crucial in molecular crystals, incremental calculations should avoid additional pair approximations⁶⁸ inside the local correlation treatment, i.e., in the local correlation language, all active pairs within a given increment, should be considered as strong. If this is not feasible due to the size of the clusters (e.g., for crystals of large molecules), an approximate coupled cluster treatment of weak pairs⁶⁹ should be preferred to simple MP2, which is presently the default.

2.5. Incrementally Corrected Periodic LMP2 Scheme.

The periodic correlation treatment and the finite cluster incremental scheme are two alternative methods for evaluating the cohesive energy, both having advantages and deficiencies with respect to each other. The periodic LMP2 method is rather inexpensive, at least for small- and medium-sized unit cells. At the same time, calculations with the CRYSCOR code cannot go beyond the LMP2 level and moderate basis sets (triple- ζ), which not only limits the accuracy of CRYSCOR calculations but—more severely—limits the range of materials for which calculations are credible due to the well-known deficiencies in the Møller–Plesset perturbation theory. For example, MP2 notoriously overestimates the interaction in highly polarizable systems (for examples, see refs 70 and 71) but at the same time underestimates them in weakly polarizable ones.^{5,72–74} In case of metals, for which MP2 simply diverges,^{72,75} periodic RPA,^{7,18} which can be seen as an inexpensive approximation to CCD,⁷⁶ can be used instead. It is, however, not implemented in CRYSCOR, yet.

The incremental scheme can utilize accurate models, for example, CCSD or CCSD(T), and large basis sets but with the challenge of accurately representing a solid with finite clusters. We note in passing that for metals, however, the perturbative triples correction (T) diverges as well.⁷⁵ As explained above, a bare cluster incremental expansion might converge rather slowly, demanding substantial, sometimes even prohibitive, computational efforts for the desired accuracy. Expansion with embedded clusters converges faster, but the computational cost of the individual calculations grows considerably, which can again prevent one from obtaining highly accurate results. Below, we formulate a combined periodic/finite cluster scheme that uses both approaches in a complementary way, allowing for a level of accuracy not feasible by a separate application of the periodic LMP2 method or the method of increments.

2.5.1. Periodic Treatment. When the incremental scheme is applied to periodic systems, the HF part of the interaction energy usually is evaluated in a fully periodic way. Because an efficient periodic LMP2 code is now available, we extend the fully periodic treatment to this level. It allows for the correct calculations of the long-range and many-body effects, which in addition to electrostatics and induction now also include dispersion.

For a reasonable description of weakly bound systems, at least triple- ζ basis sets augmented with polarization and diffuse functions are required. In periodic HF calculations, diffuse orbitals lead to convergence problems but can be added at the LMP2 stage only by means of the dual basis set technique.^{2,77} In our approach, the Hartree–Fock energy is calculated with the cc-pVTZ basis set⁷⁸ (abbreviated as VTZ) and the LMP2 energy using the aug(d,f)-cc-pVTZ basis set^{24,79} (abbreviated as (A)_{DB}VTZ, where “DB” refers to the dual basis-set scheme).^{24,79} The counterpoise-corrected interaction energy

per molecule (for a monomolecular crystal) obtained within the periodic part of the calculation is

$$\Delta E_{\text{HF+LMP2/(A)}_{\text{DB}}\text{VTZ}} = \frac{1}{N_{\text{mol}}} [E_{\text{HF+LMP2/(A)}_{\text{DB}}\text{VTZ}}^{\text{bulk}}] - E_{\text{HF+LMP2/(A)}_{\text{DB}}\text{VTZ}}^{\text{mol}} \quad (5)$$

Here, $E_{\text{HF+LMP2/(A)}_{\text{DB}}\text{VTZ}}^{\text{bulk}}$ and $E_{\text{HF+LMP2/(A)}_{\text{DB}}\text{VTZ}}^{\text{mol}}$ are the total periodic energy per cell, and the total energy of an isolated molecule surrounded by ghost atoms, respectively, and N_{mol} is the number of molecules per cell. Obviously, the energy for the single molecule has to be calculated with the same basis set and domains as the energy of the bulk.

2.5.2. Incremental Corrections to Periodic LMP2 Interaction Energy. The periodic HF + MP2/(A)_{DB}VTZ treatment is expected to provide the main fraction of the cohesive energy for molecular crystals. The corrections for the method and basis set deficiencies of the periodic calculations are substantially smaller. Hence, a larger relative error can be tolerated for the corrections than for the whole interaction energy. This argument has been utilized in several hierarchical schemes,^{5,21,80,81} where corrections of progressively smaller magnitude were evaluated with a progressively lower precision, or in purely periodic approaches,^{10,11,19,20} which employ a progressive down-sampling technique for higher-order treatment. In a similar fashion, we suggest the use of the method of increments only for these corrections rather than for the whole correlation energy. This will imply a much faster convergence of the incremental expansion (1), both in terms of the size of the clusters and the orders of the increments, and allows for the use of inexpensive bare clusters.

Although the Hartree–Fock interaction energy with a triple- ζ basis set is usually sufficiently close to the basis set limit, the correlation contribution is not expected to converge with this basis set. The basis set correction, δE_{BSC} , is here defined as the difference between the basis set extrapolated energy and the energy obtained with the basis set of the periodic calculations [in our case (A)VTZ],

$$\delta E_{\text{BSC}} = \Delta E_{\text{LMP2/BSL}}^{\text{incr}} - \Delta E_{\text{LMP2/(A)}\text{VTZ}}^{\text{incr}} \quad (6)$$

both calculated by incremental expansions. The value for $\Delta E_{\text{LMP2/BSL}}^{\text{incr}}$ can be obtained by the standard inverse cubic extrapolation⁸² of the correlation energy calculated with the aug-cc-pVTZ and aug-cc-pVQZ basis sets as in this study or via an alternative route using the MP2-F12 method.^{83,84} Fortunately, long-range correlation is not as prone to basis set deficiencies as short-range correlation effects. This means that for the incremental calculation of δE_{BSC} quite a small number of two-center bare clusters will be sufficient.

Next, the post-MP2 energy contribution, $\delta E_{\text{post-MP2}}$, is defined here as the incrementally calculated difference between the CCSD(T) and MP2 [or LCCSD(T0) and LMP2] energies

$$\delta E_{\text{post-MP2}} = \Delta E_{\text{CCSD(T)}}^{\text{incr}} - \Delta E_{\text{MP2}}^{\text{incr}} \quad (7)$$

Other approaches, employing a CCSD(T)-MP2 energy correction in a related context can be found in refs 5, 21, 23, 81, and 85. The energy correction $\delta E_{\text{post-MP2}}$ is much less sensitive to approximations than the correlation energy and can be to a good accuracy evaluated using the bare cluster model with a modest basis set. For $\delta E_{\text{post-MP2}}$, the three-center calculations, which capture Axilrod–Teller dispersion and other

three-body effects, become essential, but fourth and higher-center terms can be disregarded.

The bottleneck of the whole scheme is the evaluation of the three-center CCSD(T) or LCCSD(T0) bare cluster energies. The number of such calculations should be reduced as much as possible, yielding only the essential incremental energy differences. In order to do this, an initial larger set of two- and three-center clusters could be treated with less accurate but cheaper high-order methods, for example, MP3 (or LMP3). This prescreening allows for selecting only those increments for treatment at the coupled cluster level that show significant LMP3–LMP2 energy differences.

3. RESULTS AND DISCUSSION

The calculations discussed below were carried out using the CRYSTAL^{86–88} (periodic HF), CRYSCOR^{2,16,46,89} (periodic LMP2), and MOLPRO^{42,63,68,90} (incremental calculations) programs. Specifications of the computational parameters can be found in the Supporting Information.⁶¹

Both systems have been studied already with the periodic LMP2 method,^{24,40,45} and the energies benchmarked there could be used for the periodic HF/LMP2 part. Here, we additionally investigate the effect of the local approximations on the results by progressively expanding the domains. These results are presented in the Supporting Information.⁶¹ As shown in Table 1 of the Supporting Information, the dependence of the LMP2 cohesive energy is weak, and the virtual space, truncated to three-atom (i.e., molecular) domains, provides essentially converged results.

3.1. CO₂. Before discussing the corrections, we note that periodic LMP2 results could be used to check the quality of the finite cluster incremental results for the HF and correlation energy. Recently, it was shown that, for the argon crystal, the periodic and finite cluster calculations yield virtually identical interaction energies.³⁸ In our case, the bare cluster incremental expansion of the HF energy in Table 1 does not match the periodic HF result,⁶¹ indicating that quadrupole–quadrupole interactions do not appear to converge after three body terms. Incremental correlation energies at the LMP2/aug(d,f)-cc-pVTZ level, however, are quite close to the periodic value for both bare and HFPC-embedded clusters. As expected, the HFPC embedding indeed accelerates the convergence rate of the incremental expansion, such that the three-center LMP2 energy is negligibly small. In bare clusters, three-body contributions are sizable, but the computational time for all two- and three-body bare clusters is still smaller than for just one- and two-body HFPC-embedded clusters.

For CO₂, the final LCCSD(T0) energy is rather close to that of LMP2 due to fortuitous cancellation of the higher-order energy contributions. The difference between MP3 and MP2 energies is, however, substantial. It is evident from Table 1 that the incremental correlation energy noticeably depends on the approximation and the basis set. It is furthermore prone to errors discussed in section 2.4. In particular, the imbalance in the virtual space in three-body bare cluster calculations, caused by elimination of quasi-redundancies of the virtuals in the local correlation scheme^{46,67} with the tolerance of 10^{−5}, can lead to deviations of a few kJ/mol in the correlation energy. Tightening this threshold to 10^{−6}, corrects the unrealistic three-body increments in the aug-cc-VTZ calculations. However, the three-body aug-cc-VQZ energy remains unreliable even with such a threshold, as with this basis set the LMP2 or LCCSD(T0)

Table 1. Cohesive Energy Contributions for CO₂ from Increments Calculated with Bare and HFPC-Embedded Clusters^a

	one-body (kJ/mol)	two-body (kJ/mol)	three-body (kJ/mol)	total (kJ/mol)
HFPC-embedded incremental calculations				
aug(d,f)-cc-pVTZ				
LMP2 ^b	+12.99	−38.47	+0.02	−25.47
aug-cc-pVTZ				
LMP2 ^b	+12.04	−38.54	+0.04	−26.47
LMP3 ^b	+7.93	−29.76	+2.08	−19.74
LMP3–LMP2^b	−4.11	+8.78	+2.04	+6.71
LCCSD(T0) ^b	+10.20	−37.54	+0.71	−26.63
LCCSD(T0)–LMP2^b	−1.84	+1.00	+0.67	−0.16
Bare cluster incremental calculations				
aug(d,f)-cc-pVTZ				
HF	—	−1.67	−2.64	−4.31
LMP2	—	−26.59	+0.72	−25.87
MP2	—	−26.51	+1.62	−24.89
aug-cc-pVTZ				
LMP2 ^b	—	−26.79	+3.58	−23.21
LMP3 ^b	—	−22.00	+5.09	−16.91
LMP3–LMP2^b	—	+4.73	+1.56	+6.29
LCCSD(T0) ^b	—	−27.04	+4.25	−22.79
LCCSD(T0)–LMP2^b	—	−0.25	+0.67	+0.42
LMP2 ^c	—	−26.65	+0.39	−26.37
LMP3 ^c	—	−21.89	+2.01	−19.88
LMP3–LMP2^c	—	+4.76	+1.62	+6.39
LCCSD(T0) ^c	—	−27.11	+1.27	−25.84
LCCSD(T0)–LMP2^c	—	−0.45	+0.88	+0.43
MP2	—	−26.71	+1.59	−25.12
MP3	—	−21.90	+3.19	−18.71
MP3–MP2	—	+4.81	+1.53	+6.34
CCSD(T)	—	−27.36	+2.96	−24.40
CCSD(T)–MP2	—	−0.65	+1.36	+0.72
aug-cc-pVQZ				
LMP2 ^c	—	−27.57	+1.52	−26.05
LCCSD(T0) ^c	—	−28.37	+2.68	−25.69
LCCSD(T0)–LMP2^c	—	−0.79	+1.15	+0.36
MP2	—	−27.85	+1.66	−26.19

^aBold font indicates post-MP2 energy corrections. ^b10^{−5} tolerance for the quasi-redundancy of the virtuals. ^c10^{−6} tolerance for the quasi-redundancy of the virtuals.

correlation interaction energy is above that of the triple- ζ basis, in disagreement with the canonical result.

Importantly, the deviations of the incremental correlation energies virtually disappear in the post-MP2 corrections, as concerns the basis set, embedding, or local approximation effects. This stability is especially apparent in the MP3–MP2 energies, which are of larger magnitude than the CCSD(T)–MP2 ones. This shows that the post-MP2 correction is indeed a more suitable quantity for an incremental treatment than the correlation energy. The sub-kJ/mol deviations remaining in $\delta E_{\text{post-MP2}}$ are acceptable within the desired precision (see below).

Moreover, the incremental expansion of $\delta E_{\text{post-MP2}}$ converges with the cutoff interatomic distance of the clusters included in the calculations much faster than that for the complete correlation energy. Figure 1 shows the accumulated sum of the two-center and three-center contributions. In the standard bare cluster incremental calculations of the correlation energy added to the periodic HF value, the convergence of the two-

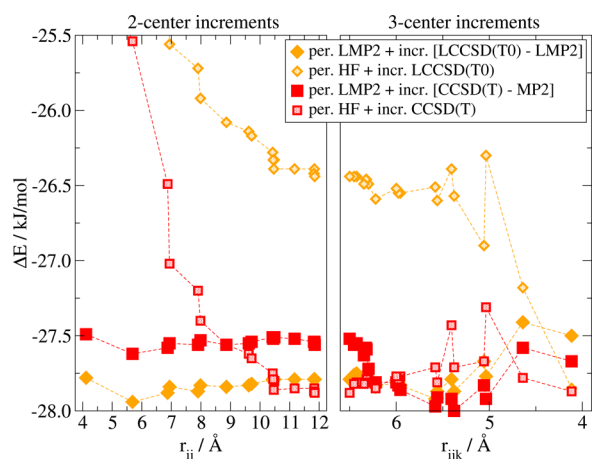


Figure 1. Convergence of two- and three-center incremental CCSD(T) and LCCSD(T0) cohesive energies for CO₂ added to the periodic HF result, and CCSD(T)–MP2 and LCCSD(T0)–LMP2 corrections added to the periodic HF + LMP2 result, as functions of the maximal averaged distance between atoms belonging to different molecular units in bare (CO₂)₂ or (CO₂)₃ clusters. The incremental LMP2 and LCCSD(T0) energies were obtained with the pair-specific virtual space redundancy threshold of 10^{−5}. The two-center curves contain the corresponding complete three-center contributions and vice versa. The direction of the *x*-axis for the three-center terms is reversed.

center terms with the interatomic distances exhibits a slow r^{-6} pattern. The three-center contributions converge faster, but the number of three-center clusters grows excessively with the averaged intercenter distance. This usually requires a large number of clusters to be included in standard incremental calculations, especially for crystals of low point-group symmetry, making this method relatively expensive. As expected, the post-MP2 correction is much smaller than the correlation energy itself and converges very rapidly. For CO₂, sub-kJ/mol accuracy is reached already with the most compact two-center and three-center cluster. Figure 1 also illustrates how an error in the correlation energy of a few three-center clusters due to the unbalanced truncation of the virtual space redundancies in LMP2 or LCCSD(T0) shifts the final result by several kJ/mol [cf. the difference between “per. HF + incr. LCCSD(T0)” and “per. HF + incr. CCSD(T)”]. For $\delta E_{\text{post-MP2}}$, this error, which would be quite difficult to detect without canonical incremental calculations for reference, is systematic and disappears.

The basis set correction is to be evaluated at the MP2 (or LMP2) level. The canonical MP2/aug-cc-pVQZ results (Table 1) demonstrate that the three-center energy remains virtually unaffected when improving the basis set, and hence, it is sufficient to consider only two-center increments. The local quadruple- ζ three-center energies are not entirely reliable (see above), but the two-center component of the LMP2 incremental calculation is quite regular and can, therefore, be used for basis set extrapolation.

Figure 2 shows the HF + LMP2 cohesive energy calculated (i) with the incremental MP2 and LMP2 energies extrapolated to the basis set limit and (ii) with the periodic LMP2 (A_{DB})VTZ energies plus the incremental basis set correction, both as functions of the intercenter cutoff for the two-body clusters. As discussed above, the correlation energy itself converges relatively slow, but the incremental basis set correction, similar to the method error correction, exhibits

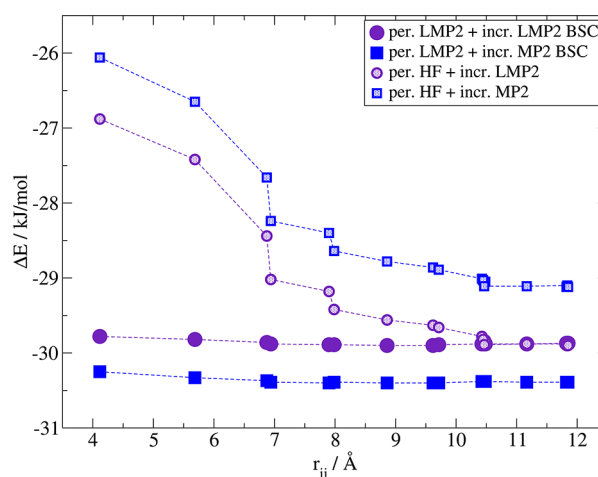


Figure 2. Convergence of the two-center incremental MP2 and LMP2 cohesive energies for CO₂ extrapolated to the basis set limit and added to the periodic HF result, along with the basis set corrections added to the periodic HF + LMP2 result as functions of the maximal averaged distance between atoms belonging to different molecular units in bare (CO₂)₂ clusters. The inverse cubic aug-cc-pVT/QZ extrapolation was used to obtain the basis set limit values. The correction was calculated as the energy difference between the MP2 or LMP2 basis set limit estimate and the energy obtained with the (A)VTZ basis, which was used in the periodic calculations. The curves contain the corresponding complete three-center contributions at the aug-cc-pVTZ level.

extremely rapid convergence. In CO₂, even the most compact two-center cluster is enough to reproduce it to the required precision.

Our LMP2 basis set limit estimate for the cohesive energy of CO₂ (−29.9 to −30.4 kJ/mol) agrees very well with other MP2 results reported in the literature. In CO₂, the monomer structure relaxation contribution (at the B3LYP level) is tiny (+0.1 kJ/mol) and can be neglected. The pure periodic LMP2 calculations with the aug(d)-cc-pVDZ/aug(d,f)-cc-pVTZ and aug(d,f)-cc-pVT/QZ basis set extrapolation give −30.1 and −29.8 kJ/mol,²⁴ respectively. With a recent periodic canonical MP2 implementation,¹⁵ a basis set limit extrapolated cohesive energy for CO₂ of −26.09 kJ/mol was obtained. The discrepancy could be attributed to the relatively small supercell used to obtain this value, which in our approach would relate to a stronger pair-list restriction, leaving out some fraction of the dispersive interaction. Besides, in ref 15, the basis sets extrapolation was done with standard rather than augmented basis sets.

The CO₂ crystal has been also investigated with several embedding models, yielding values of −29.5,²³ −29.1,²⁵ and −28.0 kJ/mol,³⁶ all in line with our results. The CCSD(T) correction is small (a few tenth of a kJ/mol) and positive, giving a final result of around −29.5 kJ/mol. Our calculations show that the repulsiveness of the CCSD(T) correction originates from the three-body correlation effects, while the two-center term alone is slightly attractive (Table 1), which also agrees with the other studies.^{23,25}

The largest discrepancy between different incremental correction models is slightly above 1 kJ/mol, which is substantially smaller than the experimental precision of the sublimation enthalpy measurements, which can be as much as 4.9 kJ/mol.⁹¹ To compare the experimental and calculated energies, one needs to correct the sublimation enthalpies for

zero-point vibrational energies and for finite temperature thermodynamic effects. Commonly, a value of $2 RT$ (or $3/2 RT$ for linear molecules) is taken for this correction,^{4,91,92} which is the high-temperature limit for the intermolecular vibrational energy, i.e., $6 RT$ (or $5 RT$ for linear molecules) minus the rotational and translational energy and the $PV = RT$ term of the ideal gas. This approach relies on two assumptions: (i) The relaxation of the intramolecular vibrations is negligible. (ii) The error in the vibrational high-temperature limit and the unaccounted energy of the zero-point intermolecular vibrations to a large extent compensate each other. Although, this is quite a rough estimate, it provides acceptable accuracy, as its error, in most cases, is smaller than the error bar of experimental energies.⁹¹ For CO_2 , such an approach yields the corrected experimental value of around -28.5 kJ/mol .⁹³ In a more elaborate study of the thermodynamic contributions,⁹¹ a similar result of -27.8 kJ/mol was obtained. Our calculated results are in very good agreement with these experimental estimates.

3.2. HCN. The incremental results for the second system in this study, HCN, are compiled in Table 2. For this crystal, there

Table 2. Bare Cluster Incremental Cohesive Energies of the HCN Crystal Calculated at Different Levels of Theory with and without Local Approximation, as Well as Post-MP2 Corrections to the Cohesive Energies^a

	two-body (kJ/mol)	three-body (kJ/mol)	total (kJ/mol)
	aug(d,f)-cc-pVTZ		
HF	+15.29	+0.91	+16.20
MP2	-29.36	+0.62	-28.74
	aug-cc-pVTZ		
MP2	-29.38	+0.62	-28.76
CCSD(T)	-25.64	+1.17	-24.58
CCSD(T)-MP2	+3.63	+0.56	+4.18
LMP2	-29.84	+0.25	-29.23
LCCSD(T0)	-25.75	+0.75	-24.90
LCCSD(T0)-LMP2	+3.83	+0.50	+4.33
	aug-cc-pVQZ		
MP2	-30.50	+0.66	-29.84

^aBold font indicates post-MP2 energy corrections.

is considerably less theoretical benchmark data available in the literature, and the present work is, to our knowledge, the first study of HCN beyond the LMP2/aug-cc-pVTZ level. More importantly, due to the large dipole-dipole interactions in the crystal, HCN represents a more challenging test case for any method relying at least partially on finite clusters.

Not surprisingly, an incremental expansion of the HF energy completely fails for this crystal. With a two- and three-center bare cluster expansion truncated at 12 and 5 Å of averaged intercenter distances, respectively, even the correct sign of the HF interaction energy is not reproduced. Unlike in CO_2 , the incremental expansion for the correlation energy of HCN does not reproduce the periodic result either. The error here is noticeably smaller than for HF but is still about -5 kJ/mol (or slightly less than 20% of the correlation energy contribution to the cohesive energy). Furthermore, the HFPC embedding scheme for this system appears to be a too crude approximation to the actual periodic HF embedding. It shifts the correlation energy by a few kJ/mol but in the wrong direction.

Omission of higher than three-center terms is vital for the feasibility of incremental calculations. Although, in HCN this

turns out to be not possible for the correlation energy, such terms are, indeed, unimportant for the post-MP2 and basis set corrections. The problematic long-range electrostatic and induction components have less effect on the post-MP2 cohesive energy than on the second-order one. Therefore, for the former, the corresponding relative error in the bare cluster expansion, which lacks these contributions, is expected to be smaller than for the latter. However, even if it remains at 20%, as for the correlation energy, the small value of the post-MP2 energy correction alleviates this error such that it becomes acceptable within the required precision. The same argument holds for the basis set incompleteness correction. Similar to CO_2 , only few clusters are sufficient to provide essentially converged values for both the post-MP2 (Figure 3) and basis set incompleteness (Figure 4) corrections.

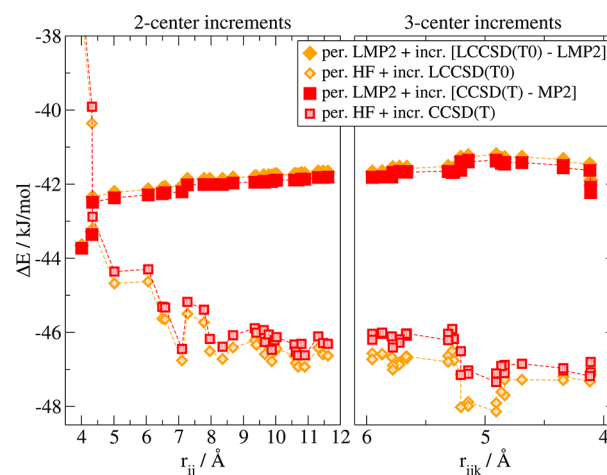


Figure 3. Convergence of two- and three-center incremental CCSD(T) and LCCSD(T) cohesive energies for HCN added to the periodic HF result, as well as CCSD(T)-MP2 and LCCSD(T0)-LMP2 corrections added to the periodic HF + LMP2 result, as functions of the maximal averaged distance between atoms belonging to different molecular units in bare $(\text{HCN})_2$ or $(\text{HCN})_3$ clusters. The two-center curves contain the corresponding complete three-center contributions and vice versa. The direction of the x-axis for the three-center terms is reversed.

The contribution due to structure relaxation of the monomer in HCN is again very small ($+0.3 \text{ kJ/mol}$). Adding up the corrections to the periodic LMP2 results,⁶¹ one obtains a cohesive energy of -43.5 kJ/mol . The experimental values,⁹³ corrected for thermodynamic effects by adding $-1.5 RT$ (vide supra) are -38.7 to -40.5 kJ/mol , which agrees with our calculated result within the experimental error bar. A deficiency may remain in the incremental correction due to the neglect of four-body and higher-order terms. However, it is more likely, that the main sources of the remaining discrepancy are the experimental error and the crudeness of the thermodynamic correction.

It is important to point out that for HCN neither periodic LMP2 calculations nor incremental CCSD(T) calculations are able to reach the accuracy, provided by the here-proposed combined scheme. Both individual schemes overestimate the binding in HCN but for different reasons. Periodic LMP2 notoriously overestimates dispersive interaction; incremental calculations lack long-range effects and contributions beyond three-body increments.

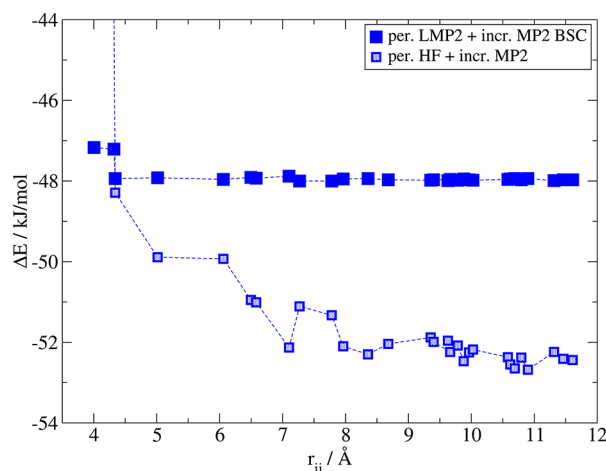


Figure 4. Convergence of the two-center incremental MP2 cohesive energies for HCN extrapolated to the basis set limit and added to the periodic HF result, as well as the basis set correction added to the periodic HF + LMP2 result, as functions of the maximal averaged distance between atoms belonging to different molecular units in bare $(\text{HCN})_2$ clusters. The inverse-cubic aug-cc-pVT/QZ extrapolation was used to obtain the basis set limit values. The correction was calculated as the energy difference between the MP2 basis set limit estimate and the energy obtained with the (A)VTZ basis, which was used in the periodic calculations. The curves contain the corresponding complete three-center contributions at the aug-cc-pVTZ level.

4. CONCLUSIONS

In combining two well-established schemes for calculating electron correlation effects in solids, periodic local MP2 calculations and the method of increments, we have constructed a pragmatic method that allows for a coupled cluster level of accuracy and mitigates the effects of finite basis set. The new scheme consists of a two-level hierarchical scheme: (i) The HF + LMP2 part of the cohesive energy is evaluated via periodic HF and local MP2 treatment using a basis set of triple- ζ quality [(A)VTZ]. (ii) The post-MP2 energy correction and basis set incompleteness correction are evaluated as incremental CCSD(T)–MP2 [or LCCSD(T0)–LMP2 for large molecules] and MP2_{BSL}–MP2_{(A)VTZ} [or LMP2_{BSL}–LMP2_{(A)VTZ} for large molecules] energy differences, respectively. The incremental expansion can be truncated after three-center terms for the higher-order energy correction and after two-center terms for the basis set correction.

In such a scheme, the periodic part naturally captures many-body and long-range effects (including dispersion) up to second order. The remaining higher-order energy contribution and basis set incompleteness error correction are quite insensitive to approximations and can be evaluated, to a good accuracy, with bare clusters. Furthermore, the corrections are of very short range and require only a few compact clusters to be processed. The MP3–MP2 energy can be evaluated to prescreen the essential clusters, subject to subsequent CCSD(T) treatment. The basis set dependence of the post-MP2 correction, in contrast to that of the full correlation energy, is mild. Because the principle features of the electron cusp, which requires large basis sets in conventional correlated calculations, are described well at the MP2 level, post-MP2 corrections are in this respect less demanding. This allows for avoiding expensive large basis-set calculations with the CCSD(T) method without compromising the accuracy.

The proposed technique provides an improved accuracy with respect to both methods that it is based upon, as demonstrated for the HCN crystal. Applications to more complex molecular crystals as well as other material classes require only slight modifications and are underway. In particular, we plan to use this technique for ionic and even covalent crystals, where the low sensitivity of the incremental corrections to the embedding scheme becomes crucial. A project on the periodic LMP2–F12 method, which will allow us to include the basis set correction in the periodic framework, is also in progress.²⁹

■ ASSOCIATED CONTENT

Supporting Information

Details on the HFPC-embedding procedure, exact specifications of the computational parameters, and the effect of different domain definitions on the periodic LMP2 results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: carsten.mueller@fu-berlin.de (C.M.).

*E-mail: denis.usvyat@chemie.uni-regensburg.de (D.U.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We express our gratitude to Beate Paulus, Martin Schütz, and Hermann Stoll for valuable discussions and Krista Steenbergen for her help in preparing the manuscript. This project was supported by the Zentraleinrichtung für Datenverarbeitung (ZEDAT) at the Freie Universität Berlin. Denis Usvyat acknowledges financial support from the Deutsche Forschungsgemeinschaft (DFG) (Grant US 103/1-1).

■ REFERENCES

- (1) Halo, M.; Pisani, C.; Maschio, L.; Casassa, S.; Schütz, M.; Usvyat, D. *Phys. Rev. B* **2011**, 83, 035117.
- (2) Usvyat, D.; Maschio, L.; Pisani, C.; Schütz, M. *Z. Phys. Chem.* **2010**, 224, 441.
- (3) (a) Grimme, S. *J. Comput. Chem.* **2004**, 25, 1463. (b) Grimme, S. *J. Comput. Chem.* **2006**, 27, 1787.
- (4) Civalieri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. *Cryst. Eng. Comm.* **2008**, 10, 405.
- (5) Tosoni, S.; Sauer, J. *Phys. Chem. Chem. Phys.* **2010**, 12, 14330.
- (6) Furche, F. *J. Chem. Phys.* **2008**, 129, 114105.
- (7) Harl, J.; Kresse, G. *Phys. Rev. Lett.* **2009**, 103, 056401.
- (8) Paier, J.; Janesko, B. G.; Henderson, T. M.; Scuseria, G. E.; Grüneis, A.; Kresse, G. *J. Chem. Phys.* **2010**, 132, 094103.
- (9) Heßelmann, A.; Görling, A. *Mol. Phys.* **2011**, 109, 2473.
- (10) Ohnishi, Y.; Hirata, S. *J. Chem. Phys.* **2010**, 133, 034106.
- (11) Ohnishi, Y.; Hirata, S. *J. Chem. Phys.* **2011**, 135, 094108.
- (12) Katagiri, H. *J. Chem. Phys.* **2005**, 122, 224901.
- (13) Shiozaki, T.; Hirata, S. *J. Chem. Phys.* **2010**, 132, 151101.
- (14) Ayala, P. Y.; Kudin, K. N.; Scuseria, G. E. *J. Chem. Phys.* **2001**, 115, 9698.
- (15) Ben, M. D.; Hutter, J.; VandeVondele, J. *J. Chem. Theory Comput.* **2012**, 8, 4177.
- (16) Pisani, C.; Schütz, M.; Casassa, S.; Usvyat, D.; Maschio, L.; Lorenz, M.; Erba, A. *Phys. Chem. Chem. Phys.* **2012**, 14, 7615.
- (17) Marsman, M.; Grüneis, A.; Paier, J.; Kresse, G. *J. Chem. Phys.* **2009**, 130, 184103.
- (18) Ben, M. D.; Hutter, J.; VandeVondele, J. *J. Chem. Theory Comput.* **2013**, 9, 2654.

- (19) Grüneis, A.; Booth, G. H.; Marsman, M.; Spencer, J.; Alavi, A.; Kresse, G. *J. Chem. Theory Comput.* **2011**, *7*, 2780.
- (20) Booth, G.; Grüneis, A.; Kresse, G.; Alavi, A. *Nature* **2012**, *493*, 365.
- (21) Nolan, S. J.; Gillan, M. J.; Alfè, D.; Allan, N. L.; Manby, F. R. *Phys. Rev. B* **2009**, *80*, 165109.
- (22) Usvyat, D.; Civalieri, B.; Maschio, L.; Dovesi, R.; Pisani, C.; Schütz, M. *J. Chem. Phys.* **2011**, *134*, 214105.
- (23) Wen, S.; Beran, G. J. O. *J. Chem. Theory Comput.* **2011**, *7*, 3733.
- (24) Maschio, L.; Usvyat, D.; Schütz, M.; Civalieri, B. *J. Chem. Phys.* **2010**, *132*, 134706.
- (25) Bygrave, P. J.; Allan, N. L.; Manby, F. R. *J. Chem. Phys.* **2012**, *137*, 164102.
- (26) Rościszewski, K.; Paulus, B.; Fulde, P.; Stoll, H. *Phys. Rev. B* **1999**, *60*, 7905.
- (27) Rościszewski, K.; Paulus, B.; Fulde, P.; Stoll, H. *Phys. Rev. B* **2000**, *62*, 5482.
- (28) Schwerdtfeger, P.; Assadollahzadeh, B.; Hermann, A. *Phys. Rev. B* **2010**, *82*, 205111.
- (29) Usvyat, D. *J. Chem. Phys.* **2013**, *139*, 194101.
- (30) Shepherd, J. J.; Grüneis, A.; Booth, G.; Marsman, M.; Kresse, G.; Alavi, A. *Phys. Rev. B* **2012**, *86*, 035111.
- (31) Grüneis, A.; Shepherd, J. J.; Alavi, A.; Tew, D. P.; Booth, G. H. *J. Chem. Phys.* **2013**, *139*, 084112.
- (32) (a) Stoll, H. *Phys. Rev. B* **1992**, *46*, 6700. (b) Stoll, H. *Chem. Phys. Lett.* **1992**, *191*, 548. (c) Stoll, H. *J. Chem. Phys.* **1992**, *97*, 8449.
- (33) Ayala, P. Y.; Scuseria, G. E. *J. Comput. Chem.* **2000**, *21*, 1524.
- (34) Paulus, B. *Phys. Rep.* **2006**, *428*, 1.
- (35) Podeszwa, R.; Rice, B. M.; Szalewicz, K. *Phys. Rev. Lett.* **2008**, *101*, 115503.
- (36) Sode, O.; Keçili, M.; Hirata, S. *J. Chem. Phys.* **2013**, *138*, 074501.
- (37) Müller, C.; Paulus, B. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7605.
- (38) Müller, C.; Usvyat, D.; Stoll, H. *Phys. Rev. B* **2011**, *83*, 245136.
- (39) Nolan, S. J.; Bygrave, P. J.; Allan, N. L.; Manby, F. R. *J. Phys.: Condens. Matter* **2010**, *22*, 074201.
- (40) Maschio, L.; Usvyat, D.; Civalieri, B. *Cryst. Eng. Comm.* **2010**, *12*, 2429.
- (41) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 151.
- (42) Schütz, M.; Hetzer, G.; Werner, H.-J. *J. Chem. Phys.* **1999**, *111*, 5691.
- (43) Schütz, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3941.
- (44) Werner, H.-J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149.
- (45) Usvyat, D.; Maschio, L.; Manby, F. R.; Casassa, S.; Schütz, M.; Pisani, C. *Phys. Rev. B* **2007**, *76*, 075102.
- (46) Pisani, C.; Maschio, L.; Casassa, S.; Halo, M.; Schütz, M.; Usvyat, D. *J. Comput. Chem.* **2008**, *29*, 2113.
- (47) Maschio, L. *J. Chem. Theory Comput.* **2011**, *7*, 2818.
- (48) Maschio, L.; Civalieri, B.; Ugliengo, P.; Gavezzotti, A. *J. Phys. Chem. A* **2011**, *115*, 11179.
- (49) Rubes, M.; Bludsky, O. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2611.
- (50) Taylor, C. R.; Bygrave, P. J.; Hart, J. N.; Allan, N. L.; Manby, F. R. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7739.
- (51) Beran, G. J. O.; Nanda, K. *J. Phys. Chem. Lett.* **2010**, *1*, 3480.
- (52) Wen, S.; Nanda, K.; Huang, Y.; Beran, G. J. O. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7578.
- (53) Hirata, S.; Sode, O.; Keçili, M.; Shimazaki, T. Electron Correlation in Solids: Delocalized and Localized Orbital Approaches. In *Accurate Condensed-Phase Quantum Chemistry*; Computation in Chemistry Series; CRC Press: Boca Raton, FL, 2010; Chapter 6.
- (54) Hermann, A.; Krawczuk, R.; Lein, M.; Schwerdtfeger, P.; Hamilton, I. P.; Stewart, J. P. *Phys. Rev. B* **2007**, *76*, 013202.
- (55) Birkenheuer, U.; Fulde, P.; Stoll, H. *Theor. Chem. Acc.* **2006**, *116*, 398.
- (56) Huang, C.; Pavone, M.; Carter, E. A. *J. Chem. Phys.* **2011**, *134*, 154110.
- (57) Axilrod, B. M.; Teller, E. *J. Chem. Phys.* **1943**, *11*, 299.
- (58) Chalasinski, G.; Szczesniak, M. *Chem. Rev.* **1994**, *94*, 1723.
- (59) Herschend, B.; Baudin, M.; Hermansson, K. *J. Chem. Phys.* **2004**, *120*, 4939.
- (60) Müller, C.; Hermansson, K. *Surf. Sci.* **2009**, *603*, 3329.
- (61) See Supporting Information for the specification of the structural and computational parameters and the results of the periodic HF/LMP2 calculations.
- (62) Hermann, A.; Schwerdtfeger, P. *Phys. Rev. Lett.* **2008**, *101*, 183005.
- (63) Schütz, M. *J. Chem. Phys.* **2000**, *113*, 9986.
- (64) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.
- (65) (a) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300. (b) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 306.
- (66) Boughton, J. W.; Pulay, P. *J. Comput. Chem.* **1993**, *14*, 736.
- (67) Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1996**, *104*, 6286.
- (68) Werner, H.-J.; Schütz, M. *J. Chem. Phys.* **2011**, *135*, 144116.
- (69) Masur, O.; Usvyat, D.; Schütz, M. *J. Chem. Phys.* **2013**, *139*, 164116.
- (70) Hesselmann, A.; Korona, T. *Phys. Chem. Chem. Phys.* **2011**, *13*, 732.
- (71) Heßelmann, A. *J. Chem. Phys.* **2008**, *128*, 144112.
- (72) Grüneis, A.; Marsman, M.; Kresse, G. *J. Chem. Phys.* **2010**, *133*, 074107.
- (73) Martinez-Casado, R.; Mallia, G.; Usvyat, D.; Maschio, L.; Casassa, S.; Schütz, M.; Harrison, N. M. *J. Chem. Phys.* **2011**, *134*, 014706.
- (74) Usvyat, D.; Sadeghian, K.; Maschio, L.; Schütz, M. *Phys. Rev. B* **2011**, *86*, 045412.
- (75) Shepherd, J. J.; Grüneis, A. *Phys. Rev. Lett.* **2013**, *110*, 226401.
- (76) Scuseria, G. E.; Henderson, T. M.; Sorensen, D. C. *J. Chem. Phys.* **2008**, *129*, 231101.
- (77) Wolinski, K.; Pulay, P. *J. Chem. Phys.* **2003**, *118*, 9497.
- (78) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (79) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (80) Manby, F. R.; Alfè, D.; Gillan, M. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5178.
- (81) Boese, A. D.; Sauer, J. *Phys. Chem. Chem. Phys.* **2013**, *15*, 16481.
- (82) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; John Wiley and Sons: Chichester, U.K., 2000.
- (83) Bachorz, R. A.; Bischoff, F. A.; Glöck, A.; Hättig, C.; Höffener, S.; Klopper, W.; Tew, D. *J. Comput. Chem.* **2011**, *32*, 2492.
- (84) Adler, T. B.; Werner, H.-J.; Manby, F. R. *J. Chem. Phys.* **2009**, *130*, 054106.
- (85) Friedrich, J. *J. Chem. Theory Comput.* **2012**, *8*, 1597.
- (86) Dovesi, R.; Saunders, V. R.; Roetti, R.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalieri, B.; Doll, K.; Harrison, N. M.; Bush, I. J.; Arco, P. D.; Llunell, M. *CRYSTAL09 User's Manual*; University of Torino: Turin, Italy, 2009.
- (87) Zicovich-Wilson, C. M.; Dovesi, R.; Saunders, V. R. *J. Chem. Phys.* **2001**, *115*, 9708.
- (88) Casassa, S.; Zicovich-Wilson, C. M.; Pisani, C. *Theor. Chem. Acc.* **2006**, *116*, 726.
- (89) Schütz, M.; Usvyat, D.; Lorenz, M.; Pisani, C.; Maschio, L.; Casassa, S.; Halo, M. Density Fitting for Correlated Calculations in Periodic Systems. In *Accurate Condensed-Phase Quantum Chemistry*; Computation in Chemistry Series; CRC Press: Boca Raton, FL, 2010; Chapter 2.
- (90) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. *WIREs Comput. Mol. Sci.* **2012**, *2*, 242.
- (91) Otero-de-la-Roza, A.; Johnson, E. R. *J. Chem. Phys.* **2012**, *137*, 054103.
- (92) Gavezzotti, A. *Theoretical Aspects and Computer Modeling of the Molecular Solid State*; John Wiley & Sons: New York, 1997.
- (93) Chickos, J. S.; Acree, W. E. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537.