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Assessing electronic structure methods for long-range three-body dispersion interactions: Analysis and calculations on well-separated metal atom trimers.

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Abstract

Three-body dispersion interactions are much weaker than their two-body counterpart. However, their importance grows quickly as the number of interacting monomers rises. To explore the numerical performance of correlation methods for long-range three-body dispersion, we performed calculations on eight very simple dispersion-dominated model metal trimers: Na_3, Mg_3, Zn_3, Cd_3, Hg_3, Cu_3, Ag_3, and Au_3. One encouraging aspect is that relatively small basis sets of augmented triple zeta size appear to be adequate for three-body dispersion in the long-range. Coupled cluster calculations were performed at high levels to assess MP3, CCSD, CCSD(T), empirical density functional theory dispersion (D3) and the many-body dispersion (MBD) approach. We found that

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the accuracy of CCSD(T) was generally significantly lower than for two-body interactions, with errors sometimes reaching 20% in the investigated systems, while CCSD and particularly MP3 were generally more erratic. MBD is found to perform better than D3 at large distances, whereas the opposite is true at shorter distances. When computing reference numbers for three-body dispersion, care should be taken to appropriately represent the effect of the connected triple excitations, which are significant in most cases and incompletely approximated by CCSD(T).

1 Introduction

Non-covalent interactions are omnipresent in molecular systems. They influence crucial processes like protein folding, enantioselective reactions or molecular crystallization. The pairwise contributions between two molecules or two molecular fragments generally dominate the total non-covalent energy, since three- and higher-body non-additive contributions decay quickly with distance and individually represent smaller energies. However, as the number of involved monomers per unit volume increases like in large biopolymers, in liquids or in the solid phase, the effect of many-body interactions accumulates quickly and becomes non-negligible.[1–5] Since electrostatic energies are strictly pairwise additive, the main components of many-body interaction energies are many-body polarization and many-body dispersion. Many-body polarization arises from the wavefunction response to permanent electrostatic moments and Pauli repulsion between more than two monomers. Mean-field methods already qualitatively take into account both phenomena. By contrast, many-body dispersion purely arises from electronic correlation and requires methods including appropriate electronic correlation effects. The relative importance of polarization and dispersion obviously depends on the system under study but dispersion cannot *a priori* be neglected.

Different contexts call for different definitions for many-body effects, depending on the problem at hand: a body can be a single electron, a single atom or a molecular monomer. Recent work on the benzene crystal lattice energy by Kennedy *et al.*[6] and by Yang *et al.*,[7]

defining a body as a single molecule, found that many-body effects contributed about 10% of the lattice energy. This is in line with results from Tkatchenko and coworkers who approximated many-body dispersion contributions for 23 molecular crystal lattice energies, defining this time each body as a single atom.[8] While benchmarking dispersion-corrected Density Functional Theory (DFT) methods on the S12L set of very large molecular complexes, Grimme and coworkers found that three-body dispersion contributed 2 to 15% of the total interaction energy.[9] Approximate estimations of three-body interatomic dispersion in even larger systems pointed to extremely large contributions, reaching 51% in the case of graphene bilayers.[10] These last two examples also define an atom as a single body, which yields larger three-body contributions than defining a molecule as a single body since the number of contributing trimers increase. Solvation energies and in particular aggregation phenomena are also very sensitive to the inclusion of many-body dispersion.[11]

Since many-body dispersion effects only become important in large systems where the necessary high-level electron correlation treatments are impractical, empirical expressions have been developed and used for most of the estimates mentioned above. In particular, the D3 method[12,13] includes a correction for three-body dispersion based on the Axilrod-Teller-Muto formula.[14–16] D3 approximates the necessary C_9 coefficients from monomer's C_6 coefficients, however other methods exist to directly compute C_9 *ab initio*.[10,17] Recently, Tkatchenko *et al.* developed the Many-Body Dispersion (MBD) method that treats atoms as coupled quantum harmonic oscillators. MBD takes into account three- and higher-body dispersion (for atomic bodies) while damping the Coulomb potential in the short range to avoid double counting when combined with density functional approximations.[18,19]

Naturally, the accuracy of these empirical expressions for dispersion should be assessed. Unfortunately, many-body interactions were the subject of much less attention than two-body interactions and in particular reliable benchmarks for many-body dispersion are scarce. Recently, the 3B-69 set partly remedied the situation by providing accurate CCSD(T) interaction energies for trimers of 23 organic molecules, each in three different geometries

extracted from various crystal structures.[20] Other examples of highly accurate three- and higher-body interaction energy computations include a study of nucleic acid tetramers,[21] accurate computations of several lattice energies[22] and high-level potential energy surfaces of the trimers of Ne,[23] water[24,25] and CO_2.[26,27] The existing data has in our opinion two shortcomings for benchmarking three-body dispersion: the systems considered are bound by a mixture of many-body dispersion and polarization, and CCSD(T) is the highest level of theory employed. The accuracy of CCSD(T) has been studied in detail for dimer interactions[28,29] where it reaches an accuracy of 1-2% with respect to Full Configuration Interaction (FCI) for typical closed-shell molecules. Computations of three-body interactions beyond CCSD(T) only exist for a few systems, specifically $(H_2)_3$,[30] He_3[31] and Ar_3.[32,33] In the He_3 case, the difference between FCI and CCSD(T) is significant and mostly originates from the neglect of the full triples effect present in CCSDT. Similar results were also found for Ar_3 where the difference between CCSD(T) and CCSDT reaches 7% of the three-body energy for an equilateral triangular geometry at 7.0 Bohrs interatomic separation.[33] We note that reference lattice energies including many-body effects can also be extracted from experimental data, but only after correcting for vibrational contributions, which introduces an additional source of uncertainty.[8,34] The data from noble gas studies indicate that CCSD(T) may not be sufficient to reach benchmark accuracy for three-body interactions. Since Hartree-Fock models three-body repulsion and polarization reasonably well (for example in water),[24] most of the challenge arises in describing three-body dispersion. It would thus be highly desirable to obtain high-level reference interaction energies for different models of dispersion-bound trimers, to explore and quantify the generality of CCSD(T) errors in the long range where only three-body dispersion is expected to contribute.

Since two-body dispersion can be viewed as simultaneous electronic excitations on two monomers,[14] it seems that three-body dispersion should arise from simultaneous electronic excitations on three monomers. In Section 2, we will clarify which three-body dispersion contributions exist at different levels of Møller-Plesset perturbation theory through an alge-

braic analysis instead of a previous diagrammatic analysis.[35] In Section 3, we will present very simple model systems bound purely by dispersion and detail the electronic structure methods used to quantify the three-body part of their interaction. The results are presented and discussed in Section 4, and Section 5 contains our conclusions.

2 Theory of 3-body dispersion

In the present paper, we define the non-additive three-body interaction energy $\Delta E^{\text{3-body}}$ for three monomers A, B and C through the usual many-body expansion:

$$\Delta E^{\text{3-body}} = \Delta E^{ABC} - \Delta E^{AB} - \Delta E^{AC} - \Delta E^{BC} \tag{1}$$

where ΔE^{XY} is the interaction energy of monomer X with monomer Y and is defined as:

$$\Delta E^{XY} = E_{tot}^{XY} - E_{tot}^{X} - E_{tot}^{Y} \tag{2}$$

where E_{tot}^{Z} is the total energy of system Z. The trimer interaction energy ΔE^{ABC} is

$$\Delta E^{ABC} = E_{tot}^{ABC} - E_{tot}^{A} - E_{tot}^{B} - E_{tot}^{C} \tag{3}$$

All total energies for monomers, dimers and trimers are computed in the trimer basis set to mitigate the effects of Basis Set Superposition Error (BSSE), following recommendations from previous work.[36,37] Here, monomers A, B and C are pairwise long-ranged, and thus $\Delta E^{\text{3-body}}$ is associated with long-range three-electron processes. In the next Section, we introduce our benchmark systems that have been chosen so that $\Delta E^{\text{3-body}}$ is largely dominated by the dispersion component $\Delta E_{\text{disp}}^{\text{3-body}}$.

The emergence of many-body interactions in intermolecular perturbation theory and supermolecular perturbation theory has been studied in detail previously,[38–40] including using

diagrammatic analysis of the various perturbation orders.[35] We present here an alternative algebraic analysis of Møller-Plesset perturbation theory that contributes to building an intuitive understanding of the emergence of three-body dispersion in electronic structure methods. By analogy with long-range perturbation theory expressions for two-body dispersion,[14] we could expect three-body dispersion to involve simultaneous electron excitations on three monomers. Naively, we may expect that three-body dispersion only arises in electronic structure methods including triply excited determinants, which first enter at the fourth order of Møller-Plesset perturbation theory. This would make three-body dispersion considerably more difficult to treat than two-body dispersion. We start our analysis with the simplest contribution to the correlation energy, MP2.

It is easy to verify that MP2 contains exactly no three-body dispersion:

$$
E_{MP2}^{corr} = \left\langle \Psi^{(0)} \left| \hat{V} \right| \Psi^{(1)} \right\rangle \tag{4}
$$

$$
= \frac{1}{2} \sum_{ijab} \frac{\langle ij|ab \rangle \left(\langle ij|ab \rangle - \langle ji|ab \rangle \right)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{5}
$$

where $\left\langle \Psi^{(0)} \right|$ is the unperturbed Hartree-Fock wavefunction, $\left| \Psi^{(1)} \right\rangle$ the first-order correction to the wavefunction, $\hat{V}$ the electron correlation operator, ϵ_p the energy of orbital p, i and j label occupied orbitals whereas a and b label virtual orbitals. In the long range, the exchange integral $\langle ji|ab \rangle$ vanishes. The Coulomb integrals $\langle ij|ab \rangle$ where both i and j are on the same monomer give rise to intramonomer correlation, as excitations from one monomer to the other also vanish exponentially. Thus, the non-vanishing integrals corresponding to dispersion have indices i and a on the first monomer and indices j and b on the second monomer. Each term in the MP2 correlation energy involves at most two monomers and the long-range interaction energy of the trimer ΔE^{ABC} is strictly pairwise additive, i.e. $\Delta E^{ABC} = \Delta E^{AB} + \Delta E^{AC} + \Delta E^{BC}$. The non-additive three-body energy $\Delta E^{\text{3-body}}$ vanishes. We emphasize that this analysis is only valid when the non-additive polarization of the SCF orbitals is negligible, i.e. in the long range and in the absence of permanent electrostatic

moments.

Turning to MP3, we can write the corresponding correlation energy in two ways:

$$E_{MP3}^{corr} = \left\langle \Psi^{(0)} \left| \hat{V} \right| \Psi^{(2)} \right\rangle \tag{6}$$

$$= \left\langle \Psi^{(1)} \left| \hat{V} \right| \Psi^{(1)} \right\rangle - E^{(1)} \left\langle \Psi^{(1)} | \Psi^{(1)} \right\rangle \tag{7}$$

where $E^{(1)}$ is the first-order Møller-Plesset energy which is already included in Hartree-Fock and $\left| \Psi^{(2)} \right\rangle$ is the second-order correction to the wavefunction. $\left| \Psi^{(2)} \right\rangle$ can also be interpreted as a first-order correction to $\left| \Psi^{(1)} \right\rangle$. Since $\left| \Psi^{(1)} \right\rangle$ can be written as a linear combination of doubly excited Slater determinants weighted by amplitudes t_{ij}^{ab}, Equation (6) represents the relaxation of these amplitudes from their MP2 values. Alternatively, Equation (7) expresses the MP3 energy as a coupling between all the doubly excited configurations in $\left| \Psi^{(1)} \right\rangle$ mediated by the correlation operator $\hat{V}$.

In any case, the MP3 energy still only involves doubly excited Slater determinants.[41–43] However, this energy does contain a three-body term, as previously shown diagramatically.[35] Starting from the fully expanded unrestricted MP3 energy, as presented for example by Szabo and Ostlund,[43] we neglect all terms that are pairwise additive (those involving only one or two monomers) and all terms that decay exponentially with distance. This effectively imposes the constraint that occupied orbitals i, j and k must be on three different monomers, and they must be excited to a virtual orbital on the same monomer. We are then left with the following term:

$$E_{MP3}^{\text{3-body,disp}} = \sum_{ia \in A} \sum_{jb \in B} \sum_{kc \in C} \mathcal{P}_{ABC} \frac{\langle ij|ab \rangle \langle jk|bc \rangle \langle ik|ac \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)(\epsilon_a + \epsilon_c - \epsilon_i - \epsilon_k)} \tag{8}$$

where a, b and c label virtual orbitals in which electrons are excited from orbitals i, j and k respectively in the above formula. The permutation operator $\mathcal{P}_{ABC}$ sums over all permutations of index pairs ia, jb and kc while preserving ordering within each pair. Thus MP3 does contain a non-additive three-body contribution, that will be purely dispersive in

the limit of negligible non-additive SCF polarization of the orbitals and vanishing permanent electrostatic moments. Note that the three-body dispersion in this equation can be both repulsive and attractive, as found by previous numerical studies.[44] Rewriting it in terms of MP2 doubles amplitudes we have:

$$E_{MP3}^{\text{3-body,disp}} = \sum_{ia \in A} \sum_{jb \in B} \sum_{kc \in C} \mathcal{P}_{ABC} t_{ij}^{ab} t_{ik}^{ac} \langle jk|bc \rangle \tag{9}$$

which reveals the coupling between doubles amplitudes evoked by Equation (7). We can interpret the MP3 three-body dispersion as an interaction between pairwise correlations that introduces a correction to the MP2 doubles amplitudes. Finally, since the long-range integrals and first order amplitudes decay no slower than R^{-3} with inter-monomer separation (e.g. arising from the dipole of the charge-less $(ia|$ product interacting with the $|jb)$ dipole), we see from Equation (8) that three-body dispersion decays as R^{-9} with separation. Three-body dispersion will also be present in CCSD through two different effects: the infinite-order relaxation of the doubles amplitudes, and the appearance of disconnected triples in the residual equations which indirectly contribute to the total energy.

The above analysis demonstrates that doubles amplitude relaxation and disconnected triples contribute to three-body dispersion. However, two-body dispersion is exclusively associated with connected doubles, thus the role of connected triples in three-body dispersion should be elucidated. The first order of Møller-Plesset perturbation theory to contain connected triples is MP4. In that case, the non-additive triples term that survives in the long-range interaction of three monomers is:

$$E_{MP4,T}^{\text{3-body,disp}} = -\frac{1}{36} \sum_{ia \in A} \sum_{jb \in B} \sum_{kc \in C} \mathcal{P}_{ABC} \frac{\left| w_{ijk}^{abc} \right|^2}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k} \tag{10}$$

where w_{ijk}^{abc} was defined by Krishnan at $al.$[45] and is not further explicated here. Equation (10) shows that the perturbative connected triples contribution is strictly attractive. However, once coupling and relaxation effects on the doubles and singles amplitudes are fully included

as in CCSDT, the sign of the total three-body connected triples contribution can change.

In conclusion, three-body dispersion first arises as a recoupling of double excitation amplitudes, and not as triple excitations.[35] However, three-body dispersion still arises at a higher order of Møller-Plesset perturbation theory than two-body dispersion, and thus we expect higher-order methods to be necessary for an accurate description. We will explore in this work the relative importance of connected triples in three-body dispersion and examine the performance of MP3, CCSD, and the most popular perturbative approximation to full triples, CCSD(T), on small model systems.

3   Systems and methods

Our model systems need to satisfy several constraints: (i) only dispersion should contribute to interaction energies in the long range ; (ii) our models should be small enough to be treated by (very) high-level correlated wavefunction methods ; (iii) our models should be very polarizable to maximize the magnitude of dispersion interactions and hence three-body dispersion. To satisfy constraints (i) and (ii), we choose to study trimers of atoms with a spherically symmetric ground state. Constraint (iii) led us to consider eight different atomic trimers: Na_3, Mg_3, Zn_3, Cd_3, Hg_3, Cu_3, Ag_3, Au_3. These elements display very large static polarizabilities,[46] which are connected to large dispersion energies through the frequency-dependent polarizabilities.[14] Moreover, they all have a filled or half-filled outer s shell which ensures that only dispersion contributes in the non-overlapping regime. In all cases, we only considered trimers in an equilateral triangular geometry to facilitate our interpretation and reduce the total number of necessary monomer and dimer computations to extract three-body dispersion energies.

To reduce computational expenses further and gain insight into one-, two- and many-electron intramonomer processes in dispersion, we froze a number of core electrons in each trimer. Initially, trimers of Na, Cu, Ag and Au only have one active electron per atom in

the correlation treatment while trimers of Mg, Zn, Cd and Hg have two active electrons per atom. In all these cases, the active electrons are in s shells. The use of such large cores precludes us from obtaining accurate total interaction energies for these trimers, yielding instead models for three-body dispersion interactions of very polarizable s electrons in various effective potentials. To probe the generality of our conclusions, we also performed selected computations with smaller frozen cores: Na and Mg trimers with a [He] core, Cu with an [Ar] core and Cd with a [Kr] core. We chose a triplet spin state for dimers of open-shell monomers and a quartet spin state for trimers of open-shell monomers. In these cases, the underlying SCF computations were unrestricted. Dimers of metals near their equilibrium distance tend to display significant multireference character, which in turn degrades the quality of CCSD(T) energies. For example, CCSD(T) error varies between 17 and 20% in a recent study of Mg_2 using large basis sets.[47] However, as the interatomic separation increases the CCSD(T) errors on the dimer decrease significantly. In our case, they vary between 7 and 9% for both large and small cores in the case of Mg (see Supporting Information Tables S13-S15, S21 and S22). Only Zn has similar errors while all other systems have lower errors. Thus, at the distances examined in this work, the trimers do not exhibit strong multireference character, and CCSD(T) offers a quantitatively reasonable description of the corresponding dimer interactions in most cases. Noble gas trimers were not considered as their lower polarizability reduces the magnitude of dispersion interactions, especially in the long range. Moreover, very accurate data for He_3[31] and Ar_3[32,33] already exist in the literature.

Even though the considered models are very polarizable, the associated three-body dispersion energies are still extremely small and the default numerical thresholds in quantum chemistry softwares are insufficient to obtain total energies to the needed numerical accuracy. In the present work, we generally set integral sieving thresholds to 10^{-14} and converged all energies to an accuracy of 10^{-12} Hartrees. In some cases, SCF convergence was still difficult with these thresholds and it was necessary to increase the integral sieving threshold to 10^{-16}.

Computations were performed using Psi4,[48] Q-Chem[49] and MRCC.[50-52] In the case of

Q-Chem, we noticed that the use of symmetry would sometimes make the results deviate from what was obtained with the other programs, and we thus deactivated symmetry in these electronic structure computations. We believe this originated in minute adjustments to either the orbitals or the integrals that affected the very small three-body dispersion energies. No such behavior seemed to occur in Psi4 or MRCC.

We computed all trimers, dimers and monomers in the basis set of the trimer to correct for BSSE.[36,37] We did not consider any of the more refined schemes to correct for BSSE[37,53] for two reasons: we believe our chosen basis set to be of a sufficient quality as supported by data presented later in this study, and the large distance between monomers limits the magnitude of the BSSE since basis functions on distant centers have a small influence on a monomer energy. All systems were computed with MP2, MP3,[41,54] CCSD,[55] CCSD(T)[56] and CCSDT,[57] which becomes equivalent to Full Configuration Interaction (FCI) for trimers with only three active electrons. Additional computations were performed for the two-electron monomer systems at the CCSDT(Q)[58] level to assess the performance of CCSDT. In the case of Mg_3 with two active electrons per monomer we pushed further to CCSDTQ[59,60] and CCSDTQ(P)[52] to assess the convergence of the excitation level. Computations were performed with triple zeta diffuse basis sets, namely aug-cc-pVTZ[61–63] (AVTZ) for Na_3 and Mg_3, def2-TZVPPD[64,65] without Effective Core Potential (ECP) for Cu_3 and Zn_3 and with the appropriate def2-ECP[66] for Ag_3, Au_3, Cd_3 and Hg_3. The basis set convergence was estimated by comparison with aug-cc-pVQZ (AVQZ) results for Mg_3 and Na_3 with large frozen cores, leaving respectively one and two active electrons per monomer.

Finally, we examined empirical methods correcting for three-body dispersion on the trimers for which we performed small-core computations (Na_3, Mg_3, Cu_3 and Cd_3). In particular, we computed the D3 dispersion term[12] that is based on the Axilrod-Teller-Muto expression[14–16] with a zero-damping function. The parameters of the three-body dispersion damping function do not depend on the functional used in conjunction with D3. We also tested MBD which obtains screened dispersion energies from the solution to the Schrödinger

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equation for a system of coupled quantum harmonic oscillators.[18] MBD does not include a damping function, but instead modifies the Coulomb potential to avoid double counting of the correlation energy at short distances. Here we use the parametrization of MBD for PBE0, however in the long-range regime the results should be identical with other existing parametrizations. The appropriate stand-alone programs were used to obtain MBD[67] and D3[68] numbers.

4   Results and discussion

We organize the discussion of our results in three sections, correlating an increasing number of electrons. In Section 4.1 we present our results for trimers with only one active electron per monomer in the correlation treatment. For these, reference CCSDT energies correspond to FCI. In Section 4.2 we add intramonomer correlation effects since two electrons are active per monomer. In these cases, we chose CCSDT(Q) to provide reference energetics, after performing some test calculations at the CCSDTQ and CCSDTQ(P) levels. Finally we consider fully many-body intramonomer correlation effects in Section 4.3 on the basis of CCSDT reference results. We emphasize that our goal here is not to obtain benchmarks for the true interaction energies of these trimers, but rather to examine the accuracy of various methods in reproducing high-level energies for three-body dispersion between highly polarizable model systems.

4.1   One-electron monomers

In this section, we examine trimers of Na, Cu, Ag and Au where all electrons are frozen except for the outermost s shell for each monomer, which contains one electron. The spherical electronic structure ensures that the only contribution to long-range interaction energies is dispersion. In addition, there is no intramonomer correlation effect, thus ensuring that the correlation energy directly corresponds to dispersion in the long range. This allows us to

examine directly the effect of various correlation treatments on pure three-body dispersion.

Table 1: Percent relative errors for three-body dispersion energies computed with AVTZ compared to an AVQZ reference for the Na_3 equilateral triangle at 6.0, 10.0 and 15.0 Å distance.

Method	6.00 Å	10.0 Å	15.0 Å
MP3	-0.58%	-0.40%	0.34%
CCSD	-1.11%	0.63%	0.24%
CCSD(T)	-2.05%	1.67%	0.34%
CCSDT	-1.95%	2.80%	0.47%

We first provide data supporting our basis set choice, since AVTZ is usually not sufficient to converge intermolecular interactions at the coupled-cluster level.[47] In Table 1, we report the percent relative error of our AVTZ results with respect to AVQZ computations for Na_3. At all distances and for all methods, the error is at most 3% and often significantly lower. Dispersion energies are in general expected to converge faster than total correlation energies with respect to the basis set angular momentum since recent work showed that low angular momentum virtual orbitals describe dispersion energies accurately.[69] Indeed, in the long range the basis set need not describe the sharp electron-electron cusp. Moreover, the distances examined in this work are significantly larger than the ones considered in most basis set convergence studies. Hence, the remainder of this section relies on AVTZ and def2-TZVPPD as detailed in Section 3.

As highlighted in Section 2, MP2 does not contain any three-body dispersion. Hence, we expect MP2 three-body interaction energies to be effectively vanishing as we approach the long-range limit. In the shorter range both MP2 and Hartree-Fock will give a non-negligible contribution to the three-body energy due to orbital deformation caused by either electrostatic charge penetration effects or Pauli repulsion effects. We observe that at a distance of 6.0 Å, the MP2 and HF three-body energies are non-negligible (see Supporting Information Tables S7-S24). Although 6.0 Å is a relatively large distance, we emphasize again that three-body interaction energies are extremely small, ranging from a few tenths of cal·mol^{-1} to a few cal·mol^{-1}. Thus, very small overlaps between the monomer's wavefunctions signif-

icantly affect them. At 10.0 Å and beyond, such effects do not appear: the MP2 and HF three-body energies are effectively zero and we are confident that our systems are into the long-range regime at this point. The range of distance under study gives us access to both the long-range regime that is purely dispersive and a slightly overlapping regime where other contributions emerge.

Relative percent errors for three-body interaction energies with respect to CCSDT are reported in Figure 1 for trimers with three correlated electrons. Although MP3 has a rather large relative percent error of about 80%, it does describe some three-body dispersion in the long-range as predicted by our algebraic analysis in Section 2 and a previous diagrammatic analysis.[35] Thus a description of three-body dispersion purely in terms of doubly excited determinants, taking into account the first-order relaxation of doubles amplitudes, only recovers about 20% of the energy in the long range. Clearly, this is not sufficient to reach quantitative accuracy. We also note that, in the particular geometry studied, three-body dispersion is repulsive.

We then consider a more sophisticated electron correlation treatment, CCSD. Here, singles and doubles amplitudes enter the energy expression, and they are fully relaxed by repeatedly solving the residual equations. In addition, the exponential nature of the coupled-cluster excitation operator includes disconnected triple excitations which are products of singles and doubles excitations. Both these effects contribute to significantly improve the description of three-body dispersion as observed on Figure 1. For the three noble metals considered here, the error is always below 4% at 10.0 Å and longer distances. Thus CCSD suffices to describe long-range three-body dispersion quantitatively in these cases. Whereas MP3 three-body dispersion energies were not repulsive enough, the full amplitude relaxation introduced by CCSD becomes slightly too repulsive. In Na_3, the CCSD error is larger and reaches 20% at 10.0 Å.

The missing terms with respect to the CCSDT reference computations are the connected triples, acting on the energy through their effect on the doubles and singles amplitudes. The

CCSD(T) perturbative approximation to the full triples only recovers about half of their effect in Na_3, which is less than the typical two-body case.[28] Considering both Na_3 and the noble metals examined here, CCSD(T) always compensates for the over-repulsion of CCSD. This is consistent with the algebraic analysis of Section 2 which showed that the leading triples contribution is attractive. However, the quantitative aspect of the perturbative triples is somewhat unsatisfactory: it is either negligible for the case of the noble metals, or relatively far from the full triples effect in the case of Na_3.

Finally, the errors at 6.0 Å are much larger than at longer distances. Since this effect appears in the overlapping regime, it might contain contributions beyond pure three-body dispersion and it is outside the scope of this paper to completely elucidate it. Table 1 seems to exclude a basis set effect, since the overall difference between AVTZ and AVQZ is quite small. We note however that this difference does tend to increase with decreasing inter-monomer distance. We also examined the multireference character of the FCI wavefunction for Cu_3 and Na_3 but found that the leading determinant's coefficient was larger than 0.99. It is however possible that on the scale of the very small energies examined here, a minor multireference character causes large relative errors. We also noticed that the weight of the leading determinant was decreasing with distance, indicating once again that the studied systems are better behaved in the long range than in the short range. Indeed, the study from Patkowski et al. of alkaline earth metal dimers near their equilibrium distance point to inadequacies of single-reference methods at these distances.[47]

4.2 Two-electron monomers

We now turn to trimers of Mg, Zn, Cd and Hg where all electrons are frozen except in the outermost s shell. This shell now contains two electrons, thus intramonomer correlation contributions enter the computed energies. We start by examining again the effect of extending the basis set from AVTZ to AVQZ for Mg_3, reporting the relative percent error of AVTZ in Table 2. In the long range (10.0 Å and beyond), the relative error is below 3%, similar
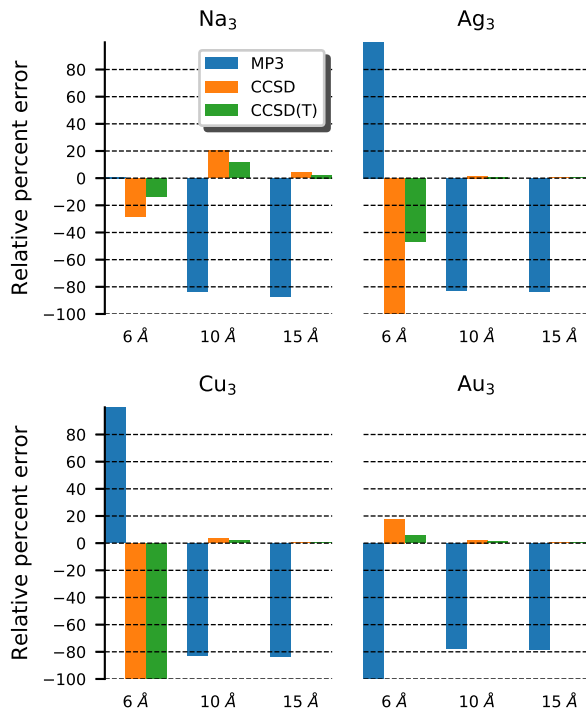
Figure 1: Relative percent errors in the three-body interaction energy for Na_3, Cu_3, Ag_3 and Au_3 for MP3 (blue), CCSD (orange) and CCSD(T) (green) relative to CCSDT.

to what we observed in the previous section. The exception is MP3 which has a relative error of 7% at 15.0 Å, however this is still significantly lower than the error due to neglect of higher-order correlation effects as we will see below. At 6.0 Å, the basis set error becomes more important, indicating a distance dependence of the basis set requirements. Since our main interest lies in the long-range region, we perform our computations with AVTZ for Mg and def2-TZVPPD for Zn, Cd and Hg as detailed in Section 3.

Table 2: Percent relative errors for three-body dispersion energies computed with AVTZ compared to an AVQZ reference for the Mg_3 equilateral triangle at 6.0, 10.0 and 15.0 Å distance.

Method	6.00 Å	10.0 Å	15.0 Å
MP3	-1.15%	-0.14 %	7.09%
CCSD	-22.81%	1.91%	0.24%
CCSD(T)	11.93%	0.74%	-0.83%
CCSDT	6.52%	0.76%	0.18%
CCSDT(Q)	9.57%	0.67%	2.98%

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In the trimers examined in this section, there are 6 active electrons in the correlation treatment and CCSDT does not correspond to FCI. To assess the effect of higher-order clusters, we ran computations up to CCSDTQ(P) on the Mg trimer with the AVTZ basis set. The relative percent error for various methods with respect to these reference three-body interaction energies are reported in Table 3. Overall, CCSDT(Q) approximates the reference numbers pretty well with errors below 2% except at the shortest distance examined in this work. Even then, the error of 3.4% is not excessively large when compared to the performance of more approximate methods, and thus we choose CCSDT(Q)/AVTZ as our reference method in this section. Our observations are also consistent with the intuition that once connected triples are fully included in the treatment of three-body dispersion at the CCSDT level, only minor errors remain.

Table 3: Percent relative errors for three-body dispersion energies computed with various methods with respect to CCSDTQ(P) for the Mg_3 equilateral triangle at 6.0, 10.0 and 15.0 Å distance.[a]

Method	6.00 Å	10.0 Å	15.0 Å
MP3	63.6%	-21.5%	-25.6%
CCSD	-106.4%	-44.2%	-45.3%
CCSD(T)	-60.9%	-25.3%	-25.3%
CCSDT	6.6%	-1.4%	-1.8%
CCSDT(Q)	-3.4%	-0.90%	2.0%
CCSDTQ	-2.3%	0.16%	0.26%
CCSDTQ(P)[b]	[4.11]	[0.113]	[$2.89 \cdot 10^{-3}$]

[a] All computations are performed with the AVTZ basis set. [b] CCSDTQ(P) total three-body interaction energies in cal/mol.

The three-body dispersion relative percent errors for MP3, CCSD, CCSD(T) and CCSDT with respect to CCSDT(Q) are reported in Figure 2 for Mg_3, Zn_3, Cd_3 and Hg_3. In all cases, only the two outermost s electrons for each atom are active in the correlation treatment. For all four of these trimers, MP3 reproduces three-body dispersion energies surprisingly well, being superior to CCSD in most cases and even to CCSD(T) in some cases. This is unexpected since CCSD contains higher-order perturbation terms than MP3 and is thus expected to be more accurate. Indeed, the good performance of MP3 originates in a fortuitous

error compensation that occurs only in specific cases as we will see in the next section. Similarly to the previous section, MP3 is not repulsive enough and underestimates the three-body dispersion correction. However, the full amplitude relaxation in CCSD worsens the error and makes three-body dispersion even less repulsive in most cases.

The CCSD(T) perturbative triple contribution makes three-body dispersion more repulsive, bringing it closer to reference values. Our analysis in Section 2 indicated that the leading triples correction should be attractive. This is however not a contradiction: in the present case the triples also contribute to the two-body energies since they involve four electrons. Thus, the difference between the effect of the triples on the dimer energies and their effect on the trimer energy may be of either sign, and happens to be repulsive in the present case. Unfortunately, the CCSD(T) perturbative triples only account for about half of the difference between CCSD and CCSDT. Thus, CCSD(T) three-body dispersion energies still contain significant errors (in a percentage sense) that range between 10 and 25% at 10.0 Å and further.

Finally, in all cases the CCSDT numbers are accurate to within 4%, except for Mg_3 at the shortest distance examined here. This is consistent with observations by Patkowski et al. on Mg_2 who showed that the convergence of the perturbation series is slower than what is usually observed for closed-shell systems.[47] We believe however that this is less of a problem at the intermonomer distances examined in this work, as supported by Tables 1, 2 and 3 that all show improved convergence behavior of the basis set and the cluster expansion at larger distances.

To explore the possibility of correcting CCSD(T) errors, we computed a composite CCSDT three-body dispersion energy $\Delta \tilde{E}_{CCSDT}^{\text{3-body}}$:

$$\Delta \tilde{E}_{CCSDT}^{\text{3-body}} = \Delta E_{CCSD(T)/AVTZ}^{\text{3-body}} + \Delta E_{CCSDT/AVDZ}^{\text{3-body}} - \Delta E_{CCSD(T)/AVDZ}^{\text{3-body}} \qquad (11)$$

where $\Delta E_{CCSD(T)/AVTZ}^{\text{3-body}}$ is the three-body energy computed at the CCSD(T)/AVTZ level,
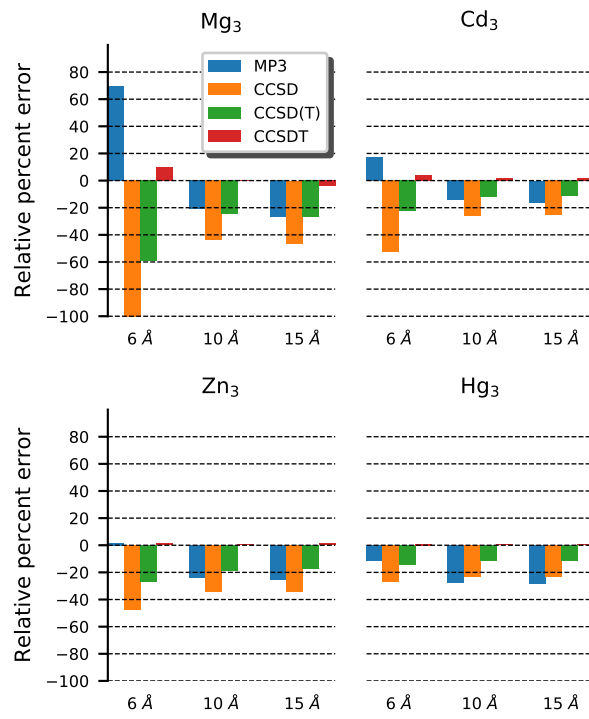
Figure 2: Relative percent errors in the three-body interaction energy for Mg_3, Zn_3, Cd_3 and Hg_3 for MP3 (blue), CCSD (orange), CCSD(T) (green) and CCSDT (red) relative to CCSDT(Q).

and the other energies are defined similarly for CCSD(T) and CCSDT where ADVZ is short for the aug-cc-pVDZ basis. In spite of the small size of the basis set used for this correction, we see an improvement in the three-body dispersion energies for both Na_3 and Mg_3 at all distances, as reported in Table 4. In the worst case, our correction scheme reduces the CCSD(T)/AVTZ relative percent errors by a factor of two but the improvement is usually more substantial. Whether such a correction is more generally applicable will require more testing that is outside the scope of the current work. AVDZ is usually considered too small a basis set to give useful results for electron correlation, however we would expect three-body dispersion in the long range to converge relatively fast with angular momentum. In the shorter range the situation will of course be different.

Table 4: Percent relative errors for three-body energies $\Delta E^{\text{3-body}}_{CCSD(T)/AVTZ}$ and $\Delta \tilde{E}^{\text{3-body}}_{CCSDT}$ for Na_3 and Mg_3.[a]

	Method	6.00 Å	10.0 Å	15.0 Å
Na_3[b]	CCSD(T)	-13.9%	11.3%	2.32%
	composite CCSDT	-2.08%	2.72%	0.45%
Mg_3[c]	CCSD(T)	-59.5%	-24.6%	-26.7%
	composite CCSDT	14.0%	1.20%	-17.4%

[a] All electrons are frozen except those in the outermost s shell. The calculations used equilateral triangle geometries at 6.0, 10.0 and 15.0 Å atom-atom distances. [b] Reference energies CCSDT/AVTZ. [c] Reference energies CCSDT(Q)/AVTZ.

4.3 Small core benchmarks

In this section, we investigate three-body dispersion for selected systems with a smaller frozen core. This allows us to assess the robustness of the previous results and to examine the accuracy of D3 and MBD three-body dispersion energies. We computed Na and Mg with *2s2p3s* electrons included in the correlation treatment ([He] core), Cu with *4s3d* electrons active ([Ar] core) and Cd with *5s4d* electrons active ([Kr] core) using CCSDT with AVTZ for Na and Mg and with def2-TZVPPD for Cu and Cd as reference for three-body dispersion. Looking at the total trimer binding energies (see Supporting Information Tables S1-S6), we

see that they become more attractive for MP2 as the number of active electrons is increased. This is expected since the MP2 correlation energy is strictly additive in the long range for non-polar monomers. However, for coupled-cluster methods the binding energies become a little less attractive for smaller cores, as more electrons are correlated. This seems to indicate that the use of a large core tends to over-correlate the remaining electrons in the active space, giving rise to some partial error compensation between the overestimated correlation of the active electrons and the neglected correlation of the frozen core electrons.

Turning to three-body interaction energies, the results displayed in Figure 3 show errors between 40 and 80% for MP3, except for the Mg trimer. The fortuitous error cancellation observed in the previous section disappears for Cd when switching from a large to a small frozen core, confirming that it is not robust. For Mg_3, the favorable error cancellation remains even with a smaller frozen core, which may indicate that the outer s electrons dominate the three-body dispersion term. MP3 underestimates three-body repulsion for Na_3, Mg_3 and Cu_3 but overestimates it for Cd_3. Overall, we should thus expect generally large errors for MP3 three-body dispersion energies.

CCSD three-body interaction energies have very significant errors, reaching 20 to 40% in the long range, that correspond to both over- and undercorrections of the MP3 results. More importantly though, the inclusion of perturbative triples in CCSD(T) only partially corrects the deficiencies of CCSD. In most cases, the (T) correction only recovers about half of the effect of the full triples, although the situation is a bit better for Cd trimer. The CCSD(T) errors are still around 10% of the CCSDT reference in most cases but reach 20% in the Mg trimer.

Turning to empirical methods for three-body dispersion, our results show that MBD performs reasonably well at long range, especially given its negligible cost compared to the high-level wavefunction methods applied here. For Cd_3 and Mg_3 in particular, MBD relative error is below 20%, thus performing better than CCSD. Here we emphasize again that we believe our results to be reasonably well-converged in the long-range, as the effect of higher-

order clusters and larger basis sets is at most a few percent. D3 generally performs worse than MBD at long range. This seems to indicate that the effective C_9 coefficients in MBD are more accurate than in D3, however the exact origin of this difference should be pinpointed by further investigations. At the shortest distance examined here however, the trend is reversed and the D3 error is lower than MBD. We believe that the damping used in MBD is at the origin of this difference. Issues with MBD damping at shorter distances have been pointed out in previous work.[70]
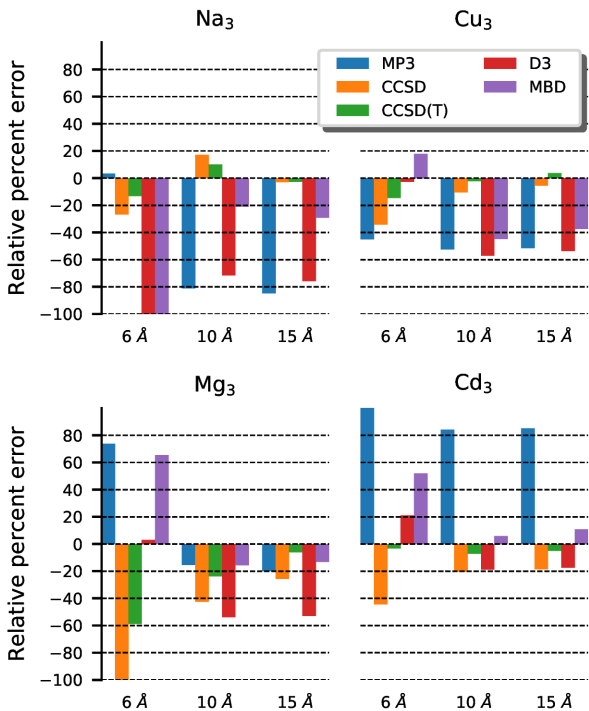

Figure 3: Relative percent errors in the three-body interaction energy for Na_3, Mg_3, Cu_3 and Cd_3 for MP3 (blue), CCSD (orange), CCSD(T) (green), D3 (red) and MBD (purple) relative to CCSDT. Small frozen cores were employed as described in the text.

4.4 Discussion

The atoms we examined in the present work offer the advantage of having a spherical outer shell of s electrons and high polarizabilities, ensuring a significant dispersion contribution in the long range. However, they also appear to be generally more difficult to treat than typical

closed-shell systems. The larger errors observed at 6.0 Å are symptomatic of this difficulty, where the convergence of the basis set and cluster expansions become slower than at longer range. This is consistent with previous observations by Patkowski et al. who showed that CCSD(T) yields large errors of about 20% for Zn_2 and Mg_2 at their equilibrium distance.[47] Our work demonstrates numerically that at larger distances the CCSD(T) error decreases significantly. Specifically, we observe errors of 7-10% for Zn_2 and Mg_2 with triple zeta basis set, 5-7% for Cd_2 and Hg_2, less than 1% for Na_2, Cu_2, Ag_2, Au_2. These results are valid in both the large and small core cases, except for Cu_2 where the small core error reaches 3-4%. Thus, at the distances considered in this work, most of our systems do not exhibit strong multireference character, and CCSD(T) is suitable for a quantitative description of the dimer interaction. This is further confirmed in the case of Cu_3 and Na_3 with a large core where the weight of the Hartree-Fock determinant for the FCI wavefunction is larger than 0.99. The difficulty in treating Mg_2 and Zn_2 near equilibrium is thought to be linked to the proximity of their ground and excited states.[47] Based on the sum-over-state formula, we would expect the proximity of ground and excited states to be linked to larger polarizabilities, and hence to larger dispersion energies. Thus, we believe our trimers model the behaviour of very polarizable systems with limited or no multireference character. The large errors observed in the above analysis for CCSD and CCSD(T) might be relevant to other highly polarizable systems, which are precisely the systems where three-body dispersion becomes more significant. In the Supporting Information, we compare the relative errors obtained for three-body and two-body dispersion (see Tables S7-S24). We observe that the relative percent error of three-body dispersion is generally larger than that of two-body dispersion in the trimers studied. We also believe this trend to be robust, since three-body dispersion first appears at a higher perturbation order than two-body dispersion and is thus intrinsically more difficult to describe. This is further supported by previous results on noble gas trimers, which highlight the importance of including full triples excitations beyond CCSD(T) to reach accurate results.[31–33]

Since three-body dispersion becomes important in large systems, we need efficient approximate methods to account for it. Often, such methods are tested first on small systems using highly correlated wavefunctions. Although CCSD(T) is usually considered the gold standard of quantum chemistry and provides accurate reference energetics for intermolecular interactions, our computations indicate that for three-body dispersion higher level methods might be necessary. Other perturbative corrections to CCSD may provide more accurate energetics, in particular those taking into account the relaxation of the singles and doubles amplitudes.[71] This will be the object of future work.

5 Conclusions

In this work, we investigated three-body dispersion and assessed the accuracy of various computational methods on model systems. Careful algebraic analysis revealed that MP3 already contains a three-body dispersion contribution, in line with previous diagramatic work.[35] Our analysis showed that the MP3 contribution can be both repulsive or attractive, whereas the first contribution involving triply excited determinants at the MP4 level should always be attractive. However, in coupled-cluster wavefunctions amplitudes are allowed to relax and so does the constraint on the sign of the triply excited term.

To obtain quantitative insight into the accuracy of various methods, we computed three-body interaction energies for carefully chosen atomic trimers of high polarizability and spherical valence electronic structure. This allowed us to identify the three-body interaction energy with three-body dispersion in the long range. We divided our systems in three classes: monomers with one active electron, two active electrons, and many active electrons. We computed reference energies with triple zeta diffuse basis sets, at the CCSDT(Q) level for the monomers with two active electrons and at the CCSDT level for the other ones, and ensured both basis set and cluster excitation levels were reasonably converged. Overall, our results show that MP3 indeed contains three-body dispersion contributions, however with a

very significant error of about 80% in most cases. Fortuitous error cancellation reduces this relative error to about 20% for systems where two valence electrons dominate the dispersion description. The MP3 contribution can both over- and underestimate the reference results.

CCSD generally improves upon MP3 results by fully relaxing singles and doubles amplitudes and introducing disconnected triple excitations. For monomers with one active electrons, where there is no intramonomer correlation, the remaining error is low and CCSD even reached quantitative accuracy for Cu_3, Ag_3 and Au_3 in the long-range regime. For Na_3, CCSD is still in error by about 20% at 10.0 Å intermonomer separation. As intramonomer correlation is introduced in the Mg_3, Zn_3, Cd_3 and Hg_3 systems, the CCSD errors rise significantly to range between 20 to 40% in the long range. CCSD(T) always improves the energetics, unfortunately in a number of cases only half of the full triples effect is recovered and significant errors of around 20% remain at relatively large distances. Finally, inclusion of the full triples with the CCSDT method accurately reproduces our reference results to within a few percent. Our results on monomers with one active electron seem to suggest that full triples are especially important when intramonomer correlation is present.

We investigated the accuracy of D3 and MBD for three-body dispersion. In the long range, MBD errors are at most 20% to 40% and usually lower, a very good result given that this method is considerably faster than CCSD and reaches higher accuracy. D3 surpasses MBD for short-range results, a behavior that could originate from the different damping in the two methods.

Some model systems we have chosen are more difficult to describe than typical closed-shell molecules since their excited states are in close energetic proximity to their ground state. This is however, also true for highly polarizable molecules, for which dispersion interactions become dominant. Moreover, our data reveals that relative errors for three-body dispersion are systematically larger than for two-body dispersion. Thus, we believe caution should be applied when using CCSD(T) to obtain reference numbers for three-body dispersion.

Acknowledgement

Supporting Information Available

Description of the geometries employed; comparison of total trimer binding energies for small and large core computations; all total energies, interaction energies and percent relative errors.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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