

Beyond Pairwise Additivity in London Dispersion Interactions

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Published

2014

Journal Title

International Journal of Quantum Chemistry

DOI

[10.1002/qua.24635](https://doi.org/10.1002/qua.24635)

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Non-additivity in London Dispersion interactions

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ABSTRACT

The simplest way to predict London dispersion energies involving complex multi-atom objects is to add separate contributions from each pair of atoms. Semi-empirical, and even certain less empirical, ways to do this can be very efficient computationally and have recently been developed to a high level of sophistication, with considerable success. There are however effects that are not captured in this way, including surprising dependences of the dispersion energy on the number N of atoms and on separation D . Higher level quantum chemical, perturbative and RPA-like theories can capture these beyond-pairwise effects, but at a high computational cost. Very recent simplified RPA-like approaches based on localized oscillators account for the unusual N dependence in a computationally efficient way. In order to proceed further, the present work proposes three physically distinct categories of non-additive effects (Types A, B and C) against which the performance of existing and future theories can be assessed.

Introduction

Second-order perturbation theory¹ shows that the London dispersion interaction energy between two non-overlapping electronically polarizable objects can be written in Generalized Casimir-Polder (GCP) form, **appropriate for widely-separated finite systems:**

$$E^{(2:A,B)} = -\frac{\hbar}{2\pi} \int_0^\infty du \int d\vec{r}_A d\vec{r}_A' d\vec{r}_B d\vec{r}_B' \times \frac{e^2}{|\vec{r}_A - \vec{r}_B|} \frac{e^2}{|\vec{r}_A' - \vec{r}_B'|} \chi^{(A)}(\vec{r}_A, \vec{r}_A', iu) \chi^{(B)}(\vec{r}_B, \vec{r}_B', iu) \quad (1)$$

where $\chi^{(i)}$ is the electronic density-density response of system i . Eq (1) can be pictured as in Fig 1, with dashed lines representing the inter-system Coulomb interaction, and the filled bubbles representing $\chi^{(i)}$, the density response function with all intra-system Coulomb interactions included.

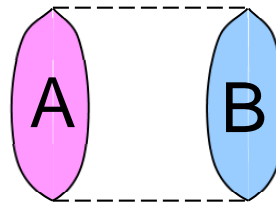


Figure 1: Feynman diagram for GCP interaction

For isotropic systems such as closed-shell atoms and for the case where the intersystem spacing R greatly exceeds the system size a , (1) can be reduced to a dipolar approximation leading to (2):

$$E^{(2:A,B)} = -C_6^{AB} R^{-6},$$

$$C_6^{AB} = \frac{3\hbar}{\pi} \int_0^\infty \alpha^{(A)}(iu) \alpha^{(B)}(iu) du, \quad (2)$$

$$\alpha^{(A)}(iu) = \int x x' \chi^{(A)}(\vec{r}, \vec{r}', iu) d\vec{r} d\vec{r}'$$

Eq (1) however includes other multipolar terms.

The simplest way to account for this London dispersion energy, when many centers labelled i (e.g. atoms) are present, is to add terms like (2) for every pair of centers:

$$E = -\sum_{i,j} f_{ij}(R_{ij}) C_6^{ij} R_{ij}^{-6}. \quad (3)$$

Here the factor f , with $f \rightarrow 1$ as $R \rightarrow \infty$, can be included to deal with short-ranged phenomena. Higher powers R^{-n} are also used.

This form has provided the basis for many calculations² over the years where non-contacting macroscopic objects interact. More recently³, pairwise atom-atom theory as in (3) has been used for correction of the semi-local density-functional interaction between molecular species right down to intimate contact. With carefully chosen short-ranged terms f and atom-atom coefficients C_6 (not the same as the gas-phase ones!) this approach has been having much semi-quantitative success^{4,5} across molecular systems from small chemical species up to biomolecules.

Nevertheless the simple pairwise additive form (3) (including its generalization to higher powers R^{-n}) is not always accurate. We now introduce three categories of dispersive nonadditivity, defined in general as the departure of the dispersion part of the interaction from a sum of gas-phase-based $C_n R^{-n}$ terms between pairs of pre-chosen “centers” (usually atoms). We term these departures Type A, Type B and Type C non-additivity.

Type A non-additivity

This simply refers to the fact that it would not be sensible to use an interaction derived for free isolated atoms (the gas-phase C_6 coefficients) to describe the interaction between the same two atoms when they are bonded in molecules. See Fig. 2. Almost all modern theories allow for this, and it is included here for completeness. The other two types, B and C described below, present more substantial difficulties, however.

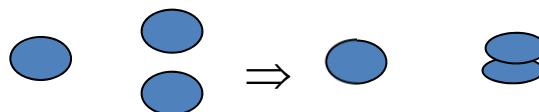


Figure 2 Modification of atom-atom C_6 due to bonding, causing crowding of orbitals (reduction of atomic volume) and consequent reduction of atomic polarizability.

This type-A departure is often dealt with semi-empirically^{3,4}, e.g. by choosing the optimal $C_6^{(ij)}$ for a pair of atoms by minimizing the error of the pairwise calculation relative to accurate molecular binding energies of a dispersion-bonded training set. Of course the success of this approach depends also on an appropriate parametrization of the short-ranged modifier f of the pair interaction. It is remarkable how transferable these optimized $C_6^{(ij)}$ coefficients turn out to be³. The transferability of C_6 coefficients can be further improved by modifying them based (e.g.) on the number of bonds in which an atom participates⁶.

The basic physics that makes the fitted $C_6^{(ij)}$ different from its free-atom or gas-phase value can be understood primarily as the quantum mechanics of compression. If the spatial extent of an orbital is reduced (e.g. by Pauli repulsion or directional bond formation) then by de Broglie’s principle the momentum and consequently energy of an orbital are raised. This tends to increase the energy level separation and hence the energy denominator in the perturbative expression for the atomic polarizability χ , which is thereby reduced. Within simple models (or indeed on dimensional grounds), the polarizability of a fixed number of electrons is approximately proportional to the volume, $\alpha_i \propto V$. Tkatchenko and Scheffler⁵ exploited this by using a density-partitioning scheme to identify the effective volume V_i of each atom in a molecule. Noting that $C_6^{AA} \propto \alpha_A^2$ and starting from accurate high-level quantum chemical calculations of the gas-phase atomic polarizability $\alpha_A^{(\text{free})}$, they wrote the dispersion

coefficient of a pair of atoms of species A in a molecule as

$$C_6^{AA} = \left(V_A / V_A^{(free)} \right)^2 C_6^{AA(free)} \quad (4)$$

where $C_6^{AA(free)}$ is the coefficient calculated from the accurate free-atom polarizability. This gave a high degree of transferability.

Sato and Nakai⁷ have also given a non-empirical density-based way to obtain C_6 coefficients for atoms in molecules.

The Becke-Johnson C_6 scheme⁸ based on the exchange hole may be useful in the present context, and was extended to include multipolar pairwise terms R^{-n} , $n > 6$.

The basic Antony-Grimme⁴, Tkatchenko-Scheffler⁵, Sato-Nakai⁷ and Becke-Johnson⁸ approaches all still make the assumption of additivity of two center interactions only (e.g. atom pairs). Ref⁶ also considers three-center interactions, and the next Sections discuss these and higher effects.

Type B non-additivity

In contrast to type-A non-additivity, which is a quantal but pairwise effect, Type B is an essentially classical electromagnetic effect that goes beyond pairwise additivity.

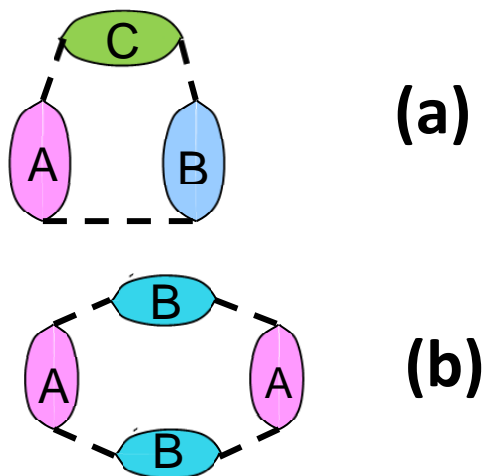


Figure 3

(a) Lowest-order type-B non-additive (*beyond pairwise*) energy: system C screens the Coulomb interaction between systems A and B.

(b) A 4th order dRPA term contributing to pairwise interaction beyond R^{-6} (NOT type B).

Type B non-additivity occurs because an additional polarizable center C can screen the Coulomb interaction between a given pair of centers A,B, thus altering one of the dashed Coulomb lines in Fig 1 and thereby changing the correlation energy (see Fig. 3a).

The lowest-order term shown in Fig 3a leads, in the isotropic case, to an irreducible 3-center angularly dependent interaction energy of form $C_9 f(\theta_1, \theta_2) R_{AB}^{-3} R_{BC}^{-3} R_{AC}^{-3}$, sometimes termed the Axilrod-Teller interaction. Clearly, infinitely many further terms (ring diagrams) like this arise from multiple response function insertions into all possible Coulomb lines, leading to N -center contributions for all positive integers N .

If the shaded bubbles are interpreted as the isolated-center responses within the direct Random Phase Approximation⁹ (dRPA), then¹⁰ the set of ring diagrams like Fig. 3 constitute the part of the total dRPA correlation energy⁹⁻¹² that depends on the subsystem separations R_{ij} . Thus E_c^{dRPA} contains type-B non-additive effects. So does the correlation energy from theories that go beyond dRPA, such as dRPA+SOSEX (second-order screened exchange), Coupled-Cluster theory, ACFD-TDDFT (adiabatic connection, fluctuation dissipation, time dependent density functional) approaches^{13,14} and high-level quantum chemical approaches. In general,

Second-order Moeller-Plesset perturbation theory (MP2) cannot however capture type-B effects because the lowest order Type-B diagram (Fig. 3a) already contains more than two coulomb lines.

The n th-order SAPT (symmetry-adapted perturbation theory) approach also contains n -center Type-B terms.

The dRPA theory is convenient because it captures type-B effects and because its correlation energy is related to a sum of zero-point energies $\sum_j (1/2) \hbar \omega_j$ of interacting modes (Eq (35) of Ref⁹), a fact that helps in understanding some recent simplified models^{11,15,16} to be discussed below.

Note that here the type-B non-pairwise interaction is defined as an interaction between *more than two centers*. This definition does *not* correspond to the number of Coulomb lines¹² but rather to the *number of centers involved*. For example, Figure 3b shows a 4th order coulomb term present in the dRPA correlation energy that is part of the *pair* interaction between centers A and B and falls off faster than R^{-6} . It therefore modifies the R^{-6} pairwise interaction at shorter distances. Such terms are NOT classified as type B in the present scheme because they involve only two centres.

While not appearing explicitly in the pairwise expansion of Eq (3), terms such as that of Fig. 3b may be implicitly included in an averaged way when the shorter-ranged damping factors f_{ij} are optimally fitted to accurate energies for dispersion-dominated molecular test sets. In practice the R^{-12} term from Fig 3b is probably not more important than the R^{-8} , R^{-10} ,... terms that arise by going beyond the dipolar approximation for the response functions χ in Eq 1. Recent works based on pairwise additivity do include these multipolar terms, and have also been extended to 3-centre non-pairwise terms⁶. Jones et al.¹¹ have given a diagrammatic scheme explaining multipole, high order Coulomb and and multi-center terms within an oscillator model.

An example of a pure Type-B effect is the calculation¹⁶ by Kim et al. on chains of non-contacting SiO₂ spheres using a discretized harmonic-oscillator version of the dRPA. Each “center” here is a macroscopic silica sphere, not an atom. Striking dispersion energy dependences were found on the geometrical arrangement of the spheres, quite different from the predictions of Eq (3), and not adequately described by simply adding the three-center Axilrod-Teller term of Fig 3a.

Grimme et al. in their recent work⁶ also included a lowest-order type-B term between 3 atoms, corresponding to Fig. 3a, as did Schwerdtfeger and Hermann¹⁷ in their work on rare-gas crystals. Tkatchenko et al.¹⁵ implemented a more sophisticated “many-body” dRPA-like scheme with atoms as the basic centers, each

also represented as a harmonic oscillator. These schemes include type-B many-center terms as well as modified two-center terms such as that in Fig. 3b.

Sato and Nakai¹⁸ also refined their earlier work⁷ by including some 3- and 4-center terms, but it is not clear that the physical origin of these is the type-B electric screening process.

The “many-body” method of Tkatchenko et al¹⁵ was used to show¹⁹ that the dependence of the dispersion interaction between two molecules on the number of atoms (centers) N in each molecule can be completely different from the pairwise prediction ($E \propto -N^2$) from (3). A similar conclusion was reached²⁰ by Ruzsinszky et al. concerning the N -dependence of the dispersion interaction between N -atom bucky balls. (Their calculation may also include type-C effects: see the next Section below). This type of N -dependence is perhaps the most striking qualitative consequence of type-B non-additivity. Inclusion of the Axilrod-Teller 3-center term is often insufficient¹⁶ to capture these N dependences

All of these type-B effects are missed by pairwise additive theories, even ones in the vdW-DF class that are quite sophisticated, seamless and non-empirical in their treatment of the short-ranged part of the dispersion interaction.

Type C non-additivity

The discrete atom-based approaches described above assume that each electron can be ascribed to a particular center (atom). Type C non-additivity is an intrinsically quantal phenomenon that occurs in cases of degeneracy. This causes zero energy denominators in perturbation theory, which favours large bare electronic response and large electron density fluctuations related to hopping of electrons between neighbouring atoms: see Fig. 4.

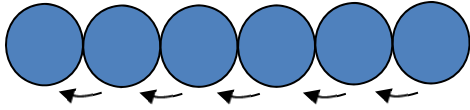


Figure 4. Long Electron paths, type C physics.

A metal is a case in point. The longer electronic motions permit large dipoles to be induced, enhancing the bare electronic susceptibility/polarizability and thereby tending to increase the vdW interaction. This is however strongly suppressed by Type-B screening effects for the case of 3D metals, though less so for 2D or 1D metals. The dRPA is sensitive to energy gaps and metallic screening, so is suitable to describe Type C effects. These were calculated within the dRPA approach for graphene sheets^{21,22}, 2D metals²³ and 1D conductors such as metallic nanotubes^{21,24}. Type C effects were also demonstrated²⁵ to be present for chains of hydrogen atoms with equal spacing (high-symmetry, degenerate case) but not for unequal spacing (lower symmetry, nondegenerate case).

Perhaps the most striking consequence²¹ of Type-C nonadditivity is to cause quite different and slower spatial decay of the asymptotic interaction energy $E(D)$ between gapless extended low-dimensional objects separated by distance D , compared with the pairwise predictions from Eq (3). The type-C predictions from RPA theory are as follows: $E \sim -C_3 D^{-3}$ for parallel graphene sheets²¹ compared with $-C_4 D^{-4}$ from Eq (3); $E \sim -C_{5/2} D^{-5/2}$ for parallel 2D metal sheets²³ compared with $-C_4 D^{-4}$ from Eq. (3); and $E \sim -K_2 D^{-2} \ln(D/D_0)^{-3/2}$ for 1D metallic nanotubes^{21,24,26}, compared with $-C_5 D^{-5}$ from Eq. (3). By contrast, for gapped systems

(including insulators and semiconductors), and for 3D metals, the D dependence of the asymptotic dispersion interaction follows the same power laws in pairwise-additive and RPA-like theories. (Quantitative differences are still present for small-gap systems at intermediate distances^{26,19}, however) The variety of asymptotic power laws exhibited in type-C cases is due to degeneracy, and also partly to the qualitative differences in type-B Coulomb screening in different dimensionalities.

The author and collaborators are currently working on some model small degenerate molecular systems that also exhibit surprising type-C dispersion effects without major influence from type B screening.

Conclusions

To summarise, three distinct physical considerations (labelled type A,B,C) have been identified that cause qualitative departures of the dispersion interactions of complex systems from the pairwise-additive predictions of Eq (3) with gas-phase parameters. Virtually all current modelling methodologies account for Type A, but types B and C are more challenging. The systems used above as examples of Type B and Type C effects should prove useful for benchmarking existing and future theories of the dispersion interaction.

Type A non-additivity refers to the different dispersion coefficients for atoms in molecules, compared with their gas-phase values, a basically quantal orbital-compression effect.

Type-B non-additivity is an electromagnetic effect arising from the screening of the Coulomb interaction between electrons on different centers by the electrons in yet other centres. It is most significant in large collections of highly polarizable centres. Its most dramatic

chemical effects found to date are in the N -dependence of the vdW interaction between two well-separated N -atom molecules¹⁹. However it has distinct effects on other systems as well^{16,19,27}

Type C non-additivity is a quantum mechanical effect arising from electronic degeneracy, with consequent high polarizability and inter-centre electronic hopping. Its most striking effects²¹ found to date are changes in the exponent p of decay with distance, D^{-p} , for the dispersion energy between extended low-dimensional gapless systems. In these systems it may have consequences at shorter separations as well²⁶.

Table I summarizes the expected performance of some popular computational algorithms in treating type A, B and C non-additivity, based on the physics that they contain.

A number of open questions remain. Two examples are:

(i) How important are type-B effects beyond the three-center Axilrod Teller term, in various types of system?

(ii) How can one predict type-C effects in small-gap systems including metals, for all cases and not just in asymptotic geometries, without invoking the computational intensity of microscopic RPA-type approaches?

Acknowledgments

This work was supported Australian Research Council Discovery Grant no. DP1096240. The author benefited from discussions with T. Gould, J.A. Angyan, A. Savin, S. Lebegue, A. Tkatchenko, A. Misquitta and A. Rubio.

Keywords: London dispersion forces, DFT+D, dRPA, non-pairwise interactions, van der Waals forces, non-additivity.

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METHOD	Describes Type A Nonadditivity?	Describes Type B Nonadditivity?	Describes Type C Nonadditivity?	Comments
Yang, Becke-Johnson, DFT+D1, DFT+D2, DFT +D3	Y	N (D3 gets 3-center)	N	Becke-Johnson, D3 also include multipoles (R^{-8})
Tkatchenko et al ⁵	Y	N	N	
Tkatchenko et al ¹⁵	Y	Y	(N?)	
vdW-DF	Y	N	N	Includes multipoles
Lifshitz	N/A (not atom-based)	Y	N/A	Takes dielectric function from experiment
dRPA + extensions	Y (if decomposed by centers such as atoms)	Y	Y	Right answers for right reasons (but short ranged correlation beyond dRPA needed in some cases). Recently becoming computable for real solids
MP2	Y	N	Y (but lacks correct metallic screening)	MP _n describes up to n-centre interactions
DMC, high-order quantum-chemical approaches	Y	Y	Y	Right answers for right reasons. Convergence? Computation time?

Table 1: Expected performance of dispersion theories based on their physical content