

Beyond Pairwise Additivity in London Dispersion Interactions

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The simplest way to predict London dispersion energies involving complex multiatom objects is to add separate contributions from each pair of atoms. Semiempirical, 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 random-phase approximation

(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. To proceed further, the present work proposes three physically distinct categories of nonpairwise effects (types A, B, and C) against which the performance of existing and future theories can be assessed. © 2014 Wiley Periodicals, Inc.

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Introduction

Second-order perturbation theory^[1] shows that the London dispersion interaction energy between two nonoverlapping 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 . Equation (1) can be pictured as in Figure 1, with dashed lines representing the intersystem Coulomb interaction, and the filled bubbles representing $\chi^{(i)}$, the density response function of system i with all intrasystem Coulomb interactions included.

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):

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

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

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

Equation (1), however, includes other multipolar terms.

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

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

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 calculations^[2] over the years, where noncontacting macroscopic objects interact. More recently,^[3] pairwise atom–atom theory as in (3) has been used for correction of the semilocal density functional interaction between molecular species right down to intimate contact. With carefully chosen short-ranged correction terms f and atom–atom coefficients C_6 (not the same as the gas-phase ones!), this approach has shown much semiquantitative 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 prechosen “centers” (usually atoms). We term these departures type-A, type-B, and type-C nonadditivity.

Type-A Nonadditivity

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_n coefficients) to describe the interaction between the

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same two atoms when they are bonded in molecules. See Figure 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 shows 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 semiempirically,^[3,4] for example, 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 be.^[3] The transferability of C_6 coefficients can be further improved by basing them on *ab initio* work plus, for example, the number of bonds in which an atom participates.^[6]

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 Scheffler^[5] exploited this 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 $\alpha_A^{(free)}$, 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 Nakai^[7] have also given a nonempirical density-based way to obtain C_6 coefficients for atoms in molecules.

The Becke–Johnson C_6 scheme^[8] 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–Grimme,^[4] Tkatchenko–Scheffler,^[5] Sato–Nakai,^[7] and Becke–Johnson^[8] approaches all still make the assumption of additivity of two-center interactions only (e.g., atom pairs). Ref. [6] also considers three-center interactions, and the next sections discuss these and higher effects.

Type-B Nonadditivity

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

Type-B nonadditivity 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 Figure 1 and thereby changing the correlation energy (see Fig. 3a).

The lowest-order term shown in Figure 3a leads, in the isotropic case, to an irreducible three-centre 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 approximation^[9] (dRPA), then^[10] the set of ring diagrams like Figure 3 constitute the part of the total dRPA correlation energy^[9–13] that depends on the subsystem separations R_{ij} . Thus, E_c^{dRPA} contains type-B nonadditive effects. So does the correlation energy from theories that go beyond dRPA, such as dRPA + second-order screened exchange, coupled-cluster theory, adiabatic connection, fluctuation dissipation, time-dependent density functional approaches,^[14,15] 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 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 Ref. [9]], a fact that helps in understanding some recent simplified models^[12,16,17] to be discussed below.

Note that here the type-B nonpairwise interaction is defined as an interaction between more than two centers. This

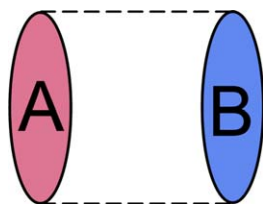


Figure 1. Feynman diagram for GCP interaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

definition does not correspond to the number of Coulomb lines^[11,13] but rather to the number of centers involved. For example, Figure 3b shows a fourth-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 Figure 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 Figure 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 three-center nonpairwise terms.^[6] Jones et al.^[12] have given a diagrammatic scheme explaining multipole, high-order Coulomb, and multi-center terms within an oscillator model.

An example of a pure type-B effect is the calculation^[17] by Kim et al. on chains of noncontacting 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 Figure 3a.

Grimme et al. in their recent work^[6] also included a lowest-order type-B term between three atoms, corresponding to Figure 3a, as did Schwerdtfeger and Hermann^[18] in their work on rare-gas crystals. Tkatchenko et al.^[16] 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 Figure 3b.

Sato and Nakai^[19] also refined their earlier work^[7] by including some three- and four-center terms, but it is not clear that



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. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

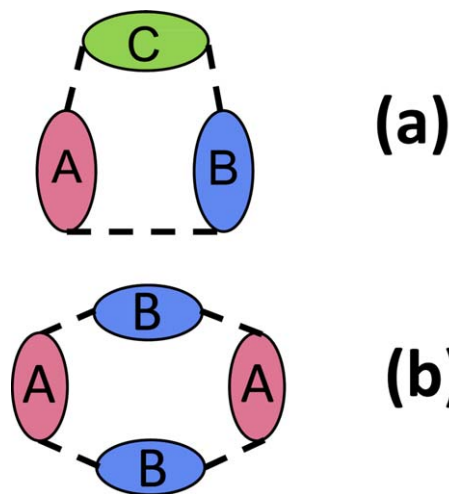


Figure 3. a) Lowest-order type-B nonadditive (beyond pairwise) energy: center C screens the Coulomb interaction between centers A and B and (b) A fourth-order dRPA term contributing to pairwise interaction beyond R^{-6} (not type B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the physical origin of these is the type-B electric screening process.

The “many-body” method of Tkatchenko et al.^[16] was used to show^[20] 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 reached^[21] 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 nonadditivity. Inclusion of the Axilrod–Teller three-center term is often insufficient^[17] to capture these N -dependences.

All these type-B effects are missed by pairwise-additive theories, even ones in the van der Waals Density Functional (vdW-DF) class that are quite sophisticated, seamless, and nonempirical in their treatment of the short-ranged part of the dispersion interaction.

Type-C Nonadditivity

The discrete atom-based approaches described above assume that each electron can be ascribed to a particular center (atom). Type-C nonadditivity is an intrinsically quantal phenomenon that occurs in cases of degeneracy. This causes zero energy denominators in perturbation theory, which favors large bare electronic response and large electron density

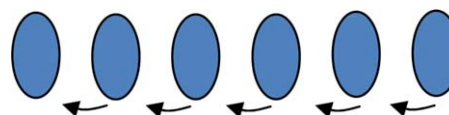


Figure 4. Long electron paths, type-C physics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

Method	Describes type A nonadditivity?	Describes type B nonadditivity?	Describes type C nonadditivity?	Comments
Wu–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 and Scheffler ^[5]	Y	N	N	Ref. [16] is RPA-related but lacks hopping.
Tkatchenko et al. ^[16]	Y	Y	(N?)	
vdW-DF	Y	N	N	Includes multipoles
Lifshitz (theory for parallel thick plates)	N/A (not atom-based)	N/A (but does include long-ranged screening)	N/A (but can deal with 3D metals)	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 <i>n</i> -centre interactions
DMC, high-order quantum-chemical approaches	Y	Y	Y	Right answers for right reasons. Convergence? Comp. time?

fluctuations related to hopping of electrons between neighboring atoms: see Figure 4.

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 three-dimensional (3D) metals, although 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,^[22,23] 2D metals,^[24] and 1D conductors such as metallic nanotubes.^[22,25] Type-C effects were also demonstrated^[26] 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 consequence^[22] 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 sheets^[22] compared with $-C_4 D^{-4}$ from Eq. (3); $E \sim -C_{5/2} D^{-5/2}$ for parallel 2D metal sheets^[24] 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,^[22,25,27] 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,^[20,27] 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 summarize, three distinct physical considerations (labeled type A, B, and 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 modeling 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 nonadditivity refers to the different dispersion C_n^{ij} coefficients for atoms in molecules, compared with their gas-phase values, a basically quantal orbital-compression effect.

Type-B nonadditivity 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 (e.g., bucky balls, some molecular crystals). Its most dramatic chemical effects found to date are in the N -dependence of the vdW interaction between two well-separated N -

atom molecules.^[20] However, it has distinct effects on other systems as well.^[17,18,20,28]

Type-C nonadditivity is a quantum mechanical effect arising from electronic degeneracy, with consequent high-polarizability and intercenter electronic hopping. Its most striking effects^[22–27] found to date are changes in the exponent p of the asymptotic decay with distance, D^{-p} , of the dispersion energy between extended low-dimensional gapless systems (e.g., metallic nanostructures, graphene). In such systems, it may also have consequences at shorter separations.^[26,27]

Table 1 summarizes the expected performance of some popular computational algorithms in treating type-A, B, and C nonadditivity, based on the physics that these methods contain.

A number of open questions remain. Two examples are as follows:

- 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?

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Keywords: London dispersion forces · DFT + D · direct random-phase approximation · nonpairwise interactions · van der Waal's forces · nonadditivity

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